# Synthesis of a Potential 10E4 Tetrasaccharide Antigen Involved in Scrapie Pathogenesis

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To test the hypothesis that tetrasaccharide **3** is involved in scrapie pathogenesis, tetrasaccharide derivative **32** functionalized with an amine linker at the reducing end was synthesized. A (2+2) glycosylation approach was chosen to furnish the target compound in fully protected form. To investigate its biological role, tetrasaccharide **32** was further functionalized to the corresponding thiol **33** using *Traut*'s reagent. During the course of the synthesis, the *N,N*-diacetyl protecting group proved surprisingly labile to radical and acidic conditions.

**Introduction.** – Heparin and heparan sulfate are the most complex glucosaminoglycans (GAGs), a class of protein-conjugated polysaccharides found in the extracellular matrix of all mammalian cells. GAGs are involved in important biological functions by binding to different growth factors, enzymes, morphogens, cell-adhesion molecules, and cytokines [1]. Many aspects of GAG chemistry [2], biology [1d][3], and structure-activity relationship (SAR) [4] have been reviewed recently.

The unbranched, highly sulfated polysaccharide heparin is composed of disaccharide units consisting of a uronic acid (UA) 1,4-linked to a D-glucosamine (GlcN) unit. L-Iduronic acid (IdoA, 90%) predominates its *C(5)*-epimer D-glucuronic acid (GlcA, 10%). Typically, a heparin disaccharide contains three sulfate groups: *O*-sulfation at the OH group at C(2) of the uronic acids, at the OH group at C(3) and/or C(6) of the amino sugar. Additionally, the glucosamine unit can be *N*-sulfated, *N*-acetylated, or, less frequently, remain unmodified. Heparan sulfate is more heterogeneous than heparin as it contains more *N*-acetyl D-glucosamines (GlcNAc) and glucuronic acids, and less *O*-sulfates [5].

Recent evidence points to the possible involvement of a specific heparan sulfate carbohydrate sequence in scrapie pathogenesis [6]. Scrapie is a transmissible neurodegenerative disease characterized by the deposition of $PrP^{Sc}$, a misfolded, abnormally protease-resistant isoform of the parent prion protein $PrP^{C}$ [7]. Considerable progress has been made toward understanding the molecular and cellular biology of prions; however, precise details of the conversion mechanism to the disease-associated form remain elusive [8]. It has been shown that the carbohydrate antigen on heparan sulfate recognized by the monoclonal antibody 10E4 is uniquely co-distributed with the abnormal prion protein $PrP^{Sc}$ already in the earliest detectable brain lesions of scrapie-infected mice [6]. To elucidate the role of the 10E4 antigen in scrapie pathogenesis, it is crucial to determine its exact structure. Since biological sources do not yield suffi-

cient amounts of clean material to establish the structure of the 10E4 antigen or to determine its interactions with $PrP^{Sc}$ on the molecular level, chemical synthesis serves as a last resort.

A tetrasaccharide recognized by antibody 10E4 has been isolated and was examined by electrospray mass spectrometry (ESI-MS) [9]. The tetrasaccharide sequence was found to contain a unique non-sulfated motif that includes a glucosamine with a free amine in the sequence, UA-(1 → 4)-GlcN-$\alpha$-(1 → 4)-UA-(1 → 4)-GlcNAc. Tetrasaccharides **1** (GlcA-$\beta$-(1 → 4)-GlcN-$\alpha$-(1 → 4)-IdoA-$\alpha$-(1 → 4)-GlcNAc) and **2** (GlcA-$\beta$-(1 → 4)-GlcN-$\alpha$-(1 → 4)-GlcA-$\beta$-(1 → 4)-GlcNAc) were postulated to be the most likely structures of the 10E4 antigen (*Fig. 1*).

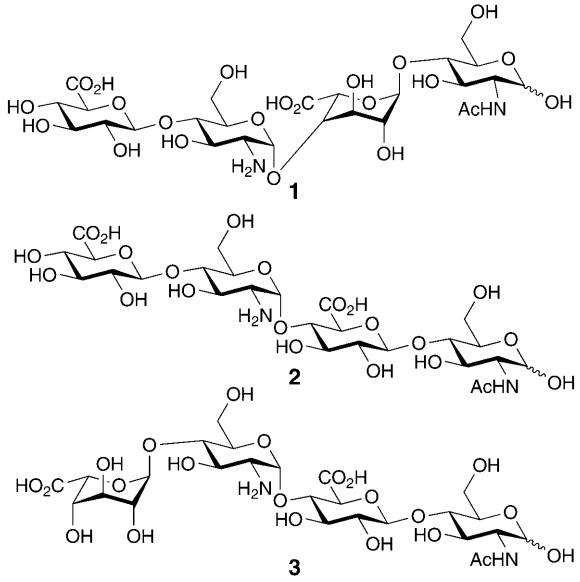


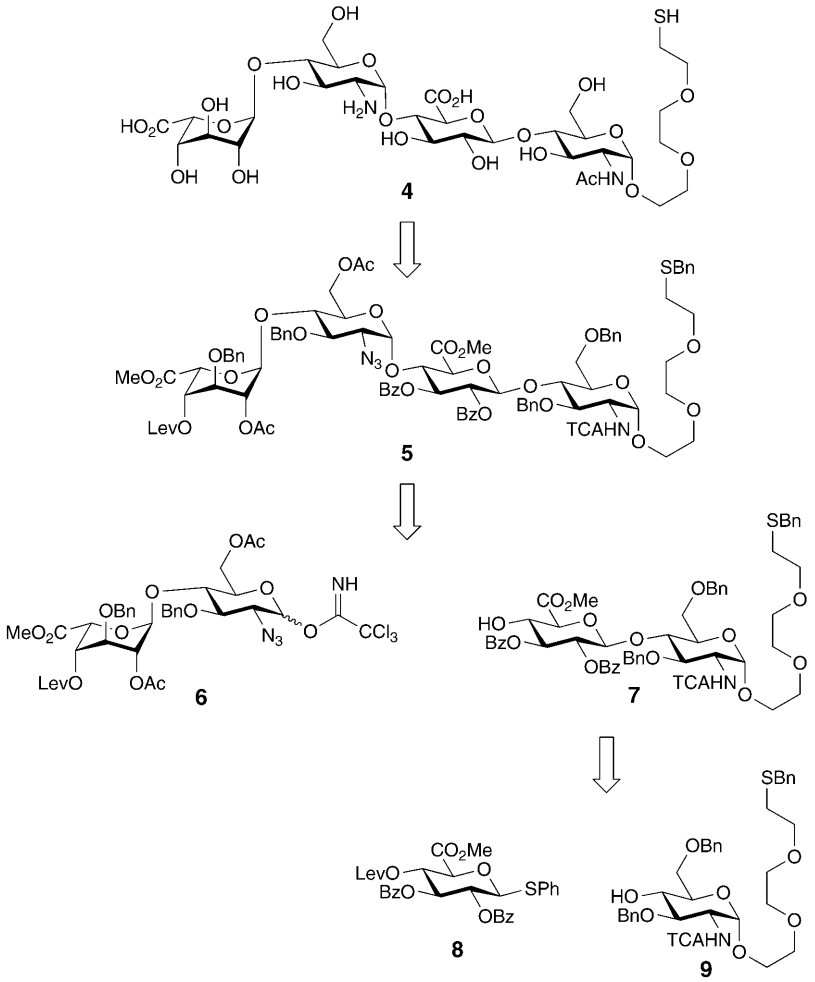

Fig. 1. *Structures of tetrasaccharides* **1**–**3**

Both, **1** and **2** were synthesized and tested by *Bonnaffé*, *Feizi*, and co-workers [10] using the neoglycolipid (NGL) technology for oligosaccharide presentation and ligand discovery [11]. 10E4 bound neither of the two structures. Therefore, tetrasaccharide **3** (IdoA-$\alpha$-(1 → 4)-GlcN-$\alpha$-(1 → 4)-GlcA-$\beta$-(1 → 4)-GlcNAc; *Fig. 1*) was identified as candidate antigen of 10E4 [9][12]. Herein, we describe the first total synthesis of a derivative of tetrasaccharide **3**.

**Results and Discussion.** – 1. *Synthesis of Tetrasaccharide* **4**. Handling oligosaccharides with a free reducing end can be problematic due to their aldehyde-like reactivity. Therefore, tetrasaccharide **4** (*Scheme 1*), with a functionalized linker [13] attached *via* an $\alpha$-linkage[1]) to the reducing end, was chosen as synthetic target. Attachment of **4** to

[1]) Tetrasaccharide **3** is $\alpha$-linked to the subsequent uronic acid.

Scheme 1. *Retrosynthetic Analysis of Tetrasaccharide* **4**

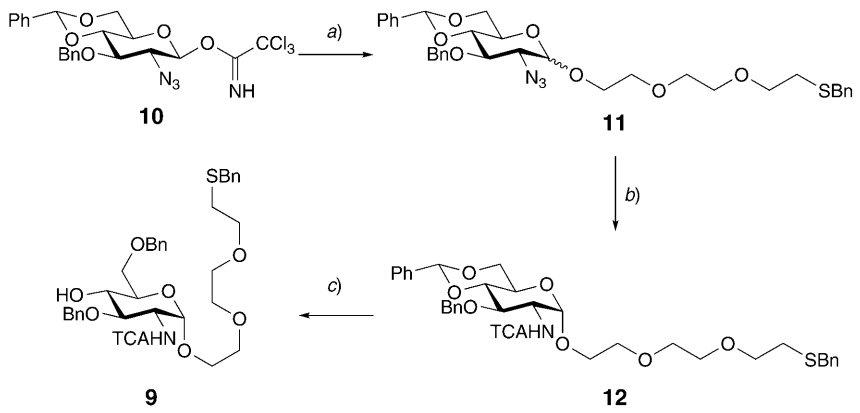



microarrays can be accomplished *via* the free sulfanyl function of the linker by conjugation to maleimide-derivatized structures [14].

Retrosynthetic analysis of tetrasaccharide **4** reveals a convergent (2+2) approach to provide the fully protected precursor **5** (*Scheme 1*). Tetrasaccharide **5** would be converted to **4** by radical-transformation of the trichloroacetyl (TCA) group to an acetate group using $Bu_3SnH$ and catalytic amounts of 2,2′-azobis[isobutyronitrile] (AIBN), followed by global deprotection. Disaccharide **6** had previously been prepared in our laboratory [15]. Thus, initial efforts focused on the synthesis of reducing end disaccharide **7** and two monosaccharides, thioglycoside **8** and the TCA-protected glucosamine derivative **9** (*Scheme 1*).

Placement of the sulfanyl-linker *via* an $\alpha$-linkage to the reducing-end monosaccharide necessitated azido-glucose trichloroacetimidate **10** [16] as starting point for cou-

*Scheme 2*

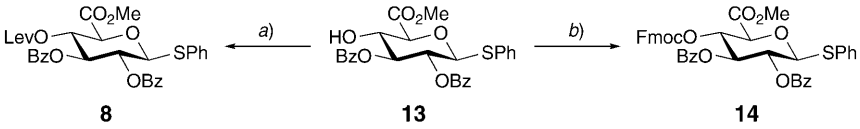



*a*) H–$(OCH_2CH_2)_3$–SBn, TMSOTf, $CH_2Cl_2$, r.t.; 83% ($\alpha/\beta$ 0.57:0.43). *b*) 1. $Me_3P$, THF, $H_2O$, r.t.; 2. TCA-Cl, $Et_3N$, $CH_2Cl_2$, 0° to r.t.; 89% (**12**$\alpha$: 50%, **12**$\beta$: 39%). *c*) TES, TFAA, TFA, $CH_2Cl_2$, 0° to 15°; 67%.

pling to 2-{2-[2-(benzylsulfanyl)ethoxy]ethoxy}ethanol [13][17] (*Scheme 2*). The trimethylsilyl triflate (TMSOTf)-catalyzed glycosylation furnished **11** in 83% yield. However, the 0.57:0.43 mixture of $\alpha/\beta$-isomers (determined by $^1$H-NMR) were inseparable by flash chromatography (FC). Azido-glucose **11** was converted to the TCA-protected glucosamine **12** (89%) by reduction of the azido derivative with $Me_3P$ to the amine, followed by acylation with TCA-Cl. At this stage, the two anomers were readily separated by FC. The desired $\alpha$-isomer was converted to **9** (67%) by regioselective opening of the benzylidine group, using trifluoroacetic acid (TFA), trifluoroacetic anhydride (TFAA), and triethylsilane ($Et_3SiH$, TES).

The OH group at C(4) of glucuronic acid **13** [18] was reacted with levulinic acid (LevOH), diisopropylcarbodiimide (DIPC), and 4-(dimethylamino)pyridine (DMAP) to yield 89% of fully protected thioglycoside **8** (*Scheme 3*). Alternatively, **13** was treated with [(9*H*-fluoren-9-yl)methoxy]carbonyl chloride (Fmoc-Cl) in pyridine to yield building block **14** (80%) that is potentially useful for the automated synthesis of oligosaccharides [19].

*Scheme 3*




*a*) LevOH, DIPC, DMAP, $CH_2Cl_2$, r.t.; 89%. *b*) Fmoc-Cl, pyridine, 0° to r.t.; 80%.

Crystal structures of **8** and **14** (*Fig. 2*) confirmed the absolute configuration of these compounds and offered insights into the conformational constraints of such systems. These are two of the rare X-ray crystal structures of thioglycoside building blocks [20].

Union of glucosamine **9** and glucuronic acid **8** to obtain disaccharide **15** presented a challenge (*Scheme 4*). 1-(Phenylsulfinyl)piperidine (BSP, 'benzenesulfinyl piperidine')

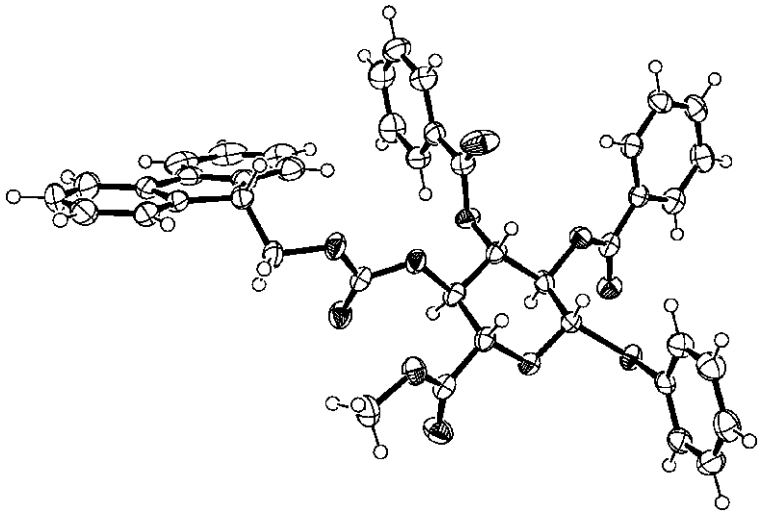


Fig. 2. *ORTEP* [21] *Representation of the crystal structure of Fmoc-protected thioglycoside building block* **14**

and triflic anhydride ($Tf_2O$) were used to pre-activate thioglycoside **8** [22]. To avoid *ortho*-ester formation, no base was added to the reaction mixture[2]). The reaction did not proceed satisfactorily. Despite the participating BzO group at C(2) of **8**, the reaction did not selectively afford disaccharide **15**. The thioether moiety of **9** is believed to coordinate to the anomeric center and thereby diminish $\beta$-selectivity. A complex mixture of products had to be purified by FC and recycling preparative HPLC to afford **15** in 31% yield. Removal of the Lev protecting group with *in situ* generated hydrazine acetate proceeded in 97% yield to give **7** (*Scheme 4*). With compound **7** in hand, assembly of the fully protected tetrasaccharide **5** was attempted by reaction of **7** with trichloroacetimidate **6**. Unfortunately, the formation of the tetrasaccharide **5** was never achieved in acceptable yield or purity (*Scheme 4*).

Rearranged disaccharide **16** and silylated building block **17** were obtained as main products (*Fig. 3*), presumably due to the highly disarmed[3]) nature of building block **7** and complications caused by the thioether. Unreacted **7** was also isolated.

Due to these major difficulties in both coupling steps, we decided to modify our strategy and introduce the thiol at the tetrasaccharide stage – following the two crucial coupling steps.

2. *Synthesis of Tetrasaccharide* **32** *Using a Pentenyl Linker.* Monosaccharide **18** (*Scheme 5*) was chosen to replace **9** at the reducing end of the tetrasaccharide. The *N*,*N*-diacetyl protecting group [24] was selected for evaluation as amine-protecting group. The diacetyl derivative can be readily converted to the *N*-monoacetate by hydrolysis at the end of a synthesis. Masking of GlcNAc as $GlcNAc_2$ or GlcN(TCA)

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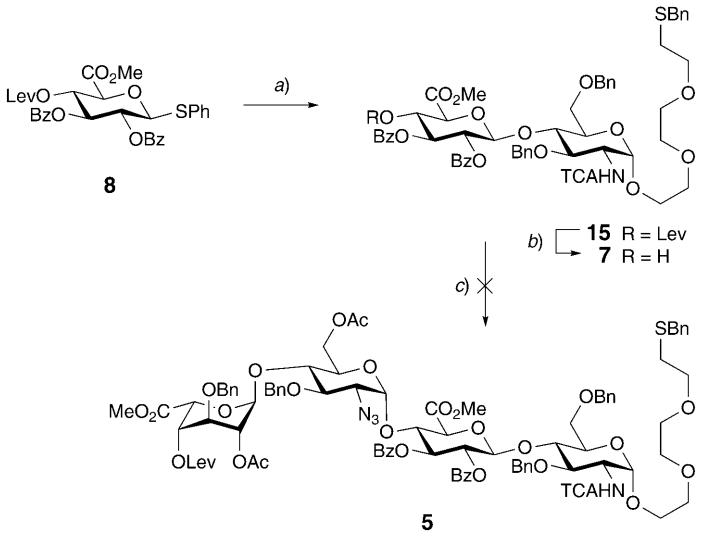
[2]) Usually, a base such as 2,4,6-tri-(*tert*-butyl)pyrimidine (TTBP) is used with $Tf_2O$-activation systems to quench TfOH that is generated in the course of the reaction [22].

[3]) For *Fraser-Reid*'s armed–disarmed approach, see [23].

*Scheme 4*




*a*) BSP, $Tf_2O$, $CH_2Cl_2$, $-60°$ to $-40°$, then **9**, $-40°$ to r.t.; 31%. *b*) Pyridine, AcOH, $N_2H_4{\cdot}H_2O$, $CH_2Cl_2$, r.t.; 97%. *c*) **6**, TMSOTf, $CH_2Cl_2$, $-25°$ to r.t.

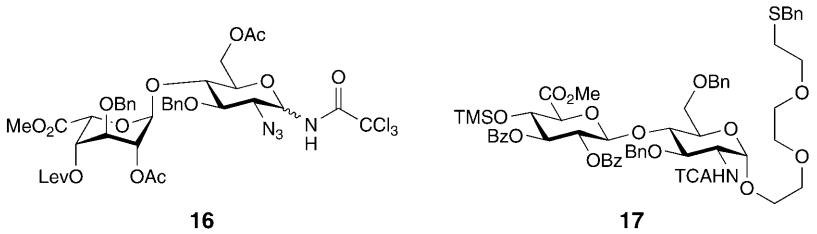


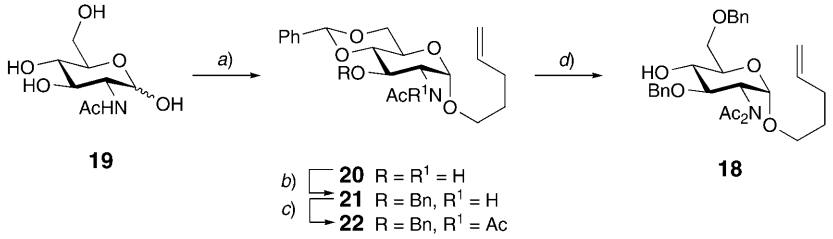

Fig. 3. *Structures of rearranged glycosyl trichloroacetimidate* **16** *and silylated building block* **17**

is generally recommended, since GlcNAc derivatives are poor nucleophiles in glycosylation reactions [24d] [25][4]); even an inhibitory effect of a remote *N*-Ac group upon trichlororoacetimidate-mediated coupling was observed when the GlcNAc was present at the reducing end of a disaccharide [27]. The synthesis of **18** started with a *Fischer* glycosylation [28] of *N*-acetyl-D-glucosamine **19** in pent-4-en-1-ol, followed by installation of the 4,6-benzylidene acetal, and furnished selectively the desired $\alpha$-glucosamine derivative **20** (65%). *O*-Benzylation of the remaining free OH group to afford **21** was achieved in 92% yield using BnBr, BaOH, and BaO [29][5]). Microwave irradiation at 85° using AcCl and diisopropylethylamine (DIPEA) in $MeCN/CH_2Cl_2$ 3 : 2 (*v*/*v*) was used to form the *N*,*N*-diacetyl derivative **22** in 93% yield. Regioselective opening of the benzylidene group, using TFA, TFAA, and TES, afforded **18** (67%). The reaction con-

[4]) However, there were also numerous successful glycosylation reactions performed on *N*-Ac-containing acceptors, see, *e.g.*, [26].

[5]) Other methods such as BnBr/NaH or $BnBr/Ag_2O$ did not give satisfactory results.

*Scheme 5*

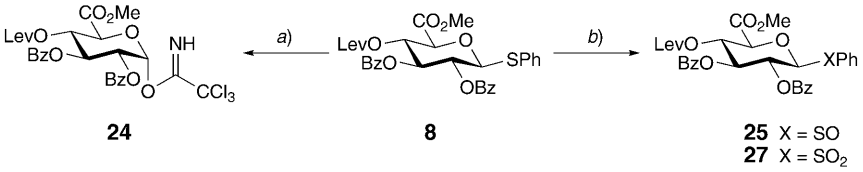



*a*) 1. Pent-4-en-1-ol, $TsOH \cdot H_2O$, 90°; 2. $PhCH(OMe)_2$, $TsOH \cdot H_2O$, MeCN, r.t.; 65%. *b*) BaO, $BaOH \cdot 8H_2O$, BnBr, DMF, r.t.; 92%. *c*) AcCl, DIPEA, $CH_2Cl_2$/MeCN 3:2 (*v*/*v*), 85° (microwave, 80 W); 93%. *d*) TES, TFAA, TFA, $CH_2Cl_2$, 0° to 14°; 67%.

ditions had to be carefully adjusted, as longer reaction times and especially higher temperature (>15°) led to a dramatic decrease in yield due to partial cleavage of one of the *N*-acetates.

Since the BSP/$Tf_2O$ system that was used for the condensation of **8** and **9** to form disaccharide **15** is incompatible with the pent-4-enyl moiety of **18**, we evaluated MeOTf as an activator for **8**. Coupling reactions with differently activatable building blocks were also tested for their ability to furnish the desired disaccharide **23**. We first converted thioglycoside **8** to the corresponding trichloroacetimidate **24**, sulfoxide **25**, and phosphate **26**[6]) by reacting **8** with *N*-iodosuccinimide (NIS) and $Tf_2O$, followed by $CCl_3CN$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (for **24**; 57%), 3-chloroperoxybenzoic acid (*m*-CPBA) (for **25**; 90%)[7]), or NIS and dibutylphosphoric acid (for **26**), respectively. Sulfoxide **25** was obtained as a mixture of epimers (*Scheme 6*). The molecular structure of the (*S*)-epimer that crystallized selectively was elucidated (*Fig. 4*). It is one of the rare X-ray crystal structures of monosaccharides building blocks containing a sulfoxide leaving group [30].

*Scheme 6*




*a*) 1. NIS, $Tf_2O$, $CH_2Cl_2/H_2O$ 100:1 (*v*/*v*), r.t.; 2. $CCl_3CN$, DBU, $CH_2Cl_2$, 0° to r.t.; 57%. *b*) *m*-CPBA, $CH_2Cl_2$, −78° to 0°; 90% (**25**), 8% (**27**).

Disaccharide **23** was obtained in poor yield (28%), following activation of **8** with MeOTf and reaction with **18**, and could not be purified from the by-products (*Table 1*). Partial cleavage of one of the two *N*-acetyl groups and methylation of the OH

[6]) Synthesis and coupling of **26** are not shown.

[7]) Sulfone **27** (8%) was obtained as a side-product.

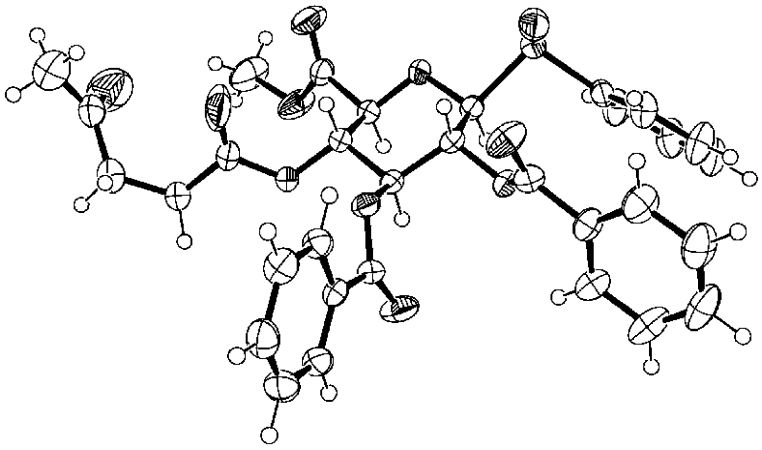
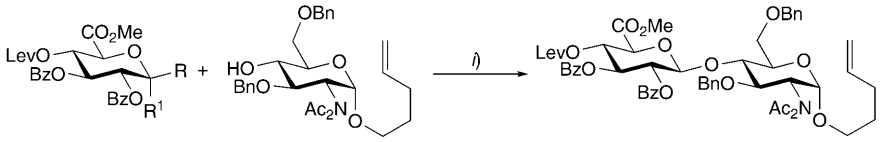


Fig. 4. *ORTEP* [21] *Representation of the crystal structure of Lev-protected sulfoxide building block* **25** ((*S*)-epimer)

Table 1. *Coupling Reactions of* **8**, **24**, **26**, *or* **25** *with* **18** *to form Disaccharide* **23**




**X** **18** **23**

| **X** | **18** [equiv.] | *i*) | Yield [%] |
|---|---|---|---|
| **8** (R = SPh, $R^1$ = H) | 0.5 | MeOTf (5 equiv.), r.t. | 28[a]) |
| **24** (R = H, $R^1$ = $OC(NH)CCl_3$) | 0.8 | TMSOTf (0.2 equiv.), 0° | 19 |
| **26** (R = H, $R^1$ = $OP(O)(OBn)_2$) | 0.8 | TMSOTf (1 equiv.), −50° to r.t. | traces |
| **25** (R = S(O)Ph, $R^1$ = H) | 0.8 | $Tf_2O$ (0.6 equiv.), −78° to −35° to 3° | 32 |

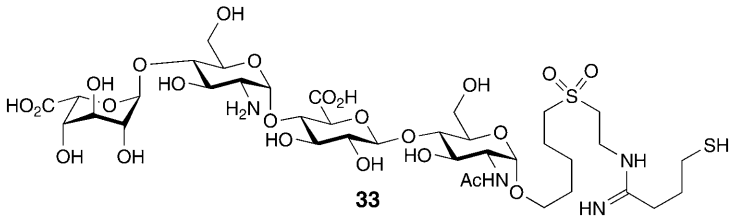
[a]) Contains traces of impurities (by $^1$H-NMR).

group at C(4) of **18** occurred. The use of trichloroacetimidate building block **24** and catalytic amounts of TMSOTf afforded **23** in 19% yield. The reaction of phosphate **26** with stoichiometric amounts of TMSOTf was very slow, and only traces of disaccharide **23** were isolated. Finally, coupling of sulfoxide **25** with building block **18**, using again $Tf_2O$ but no base[3]), furnished disaccharide **23** in mediocre yield (32%) (*Table 1*). Cleavage of one of the two *N*-acetyl groups of **18** as well as of disaccharide **23** was the major side reaction.

Removal of the Lev group using *in situ* generated hydrazine acetate yielded **28** (69%; *Scheme 7*). Again, partial loss of an *N*-acetyl group was observed. The TMSOTf-catalyzed coupling of **28** with disaccharide **6** to give tetrasaccharide **29** was achieved in 26% yield. The poor reactivity of the highly disarmed building block **28** most likely resulted in rearranged disaccharide **16** (*Fig. 3*) and the silylation of **28**. In addition, starting material **28** (35%) was re-isolated. Pentenyl functionalization was

achieved by transforming the pentenyl moiety of tetrasaccharide **29** *via* a radical reaction with $HS(CH_2)_2NHCbz$ [31] and catalytic amounts of AIBN [32] in benzene[8]) to the Cbz-protected amine **30** (62%). An additional 27% of the mono-*N*-acetylated tetrasaccharide was also obtained and used to proceed with the synthesis. To avoid elimination of levulinate at the iduronic acid moiety, the Lev group was cleaved prior to global hydrolysis. The free alcohol is less prone to elimination than the corresponding Lev ester. Therefore, **30** was reacted with *in situ* generated hydrazine acetate. The crude product, a mixture of mono- and di-*N*-acetate, due to partial cleavage of one of the two *N*-acetates, was subsequently treated in a one-pot reaction with $LiOH/H_2O_2$ to simultaneously oxidize the sulfine to the sulfone, and KOH/MeOH to furnish **31** (49%). The yield was diminished by inadvertent conversion of the Cbz-group to the corresponding methyl carbamate and partial cleavage to the free amine. Hydrogenation of **31** using $H_2$ and Pd/C afforded **32**.

3. *Functionalization with* Traut*'s Reagent*. To install the terminal thiol, **32** was reacted with *Traut*'s reagent [14][33]. The thiol **33** (*Fig. 5*) can be used for conjugation to maleimide-derivatized structures including chip surfaces and carrier proteins [14].




**33**

Fig. 5. *Structure of the tetrasaccharide* **33** (after functionalization of **32** with *Traut*'s reagent)

**Conclusions.** – We described the first total synthesis of the potential 10E4 tetrasaccharide antigen **32**. The use of 2-{2-[2-(benzylsulfanyl)ethoxy]ethoxy}ethyl as a linker at the reducing end did not produce satisfying results as it complicated subsequent coupling steps, including loss of selectivity for a glycosylation involving a participating group. Employing the well-established pentenyl-linker and subsequent functionalization steps on the tetrasaccharide stage helped us to overcome these challenges.

In the course of the synthesis of fully protected tetrasaccharide **30**, it became evident that the *N*,*N*-diacetyl moiety is labile not only to basic but also to acidic conditions (*e.g.*, TFA, TfOH), even if the acid is used only at low temperature (*e.g.*, 0°) and/or in catalytic amounts (*e.g.*, TMSOTf). This finding confirmed observations by *Crich* and *Dudkin* [24d]. In addition, the *N*,*N*-diacetyl was found to be neither fully compatible with the conditions used for Lev deprotection ($N_2H_4$), nor with the radical conditions used for linker functionalization to afford **30**. These findings override the advantages of the *N*,*N*-diacetyl moiety such as smooth installation and deprotection. *N*,*N*-Diacetyl derivatives should be used with great care as a protecting group in oligosaccharide synthesis. Biological investigations involving tetrasaccharide **33** are currently ongoing.

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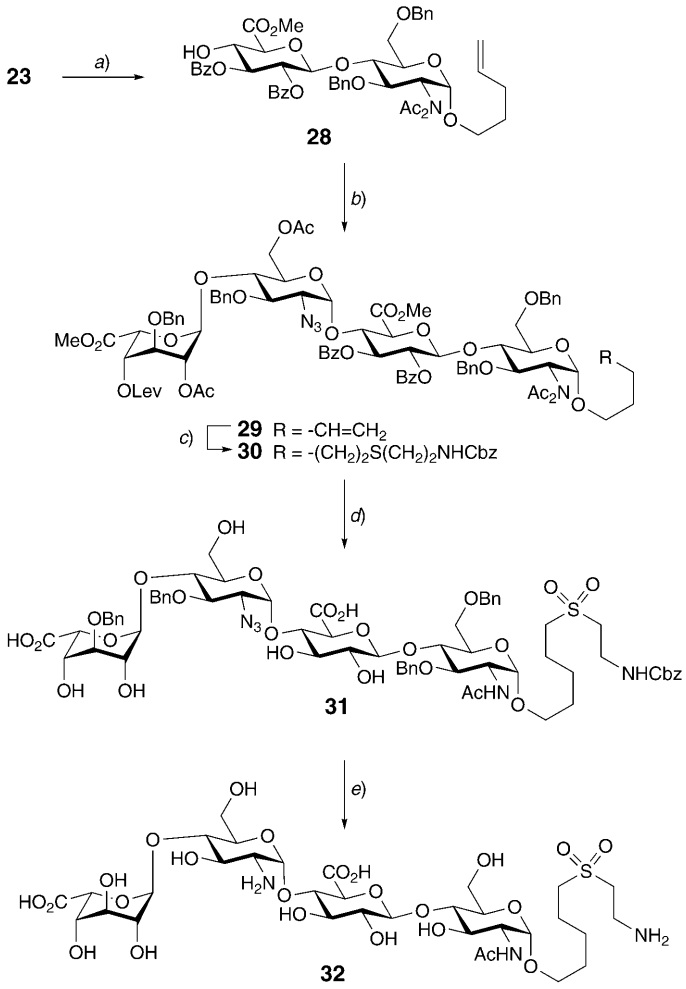
[8]) Benzene gave a significantly higher yield than THF.

*Scheme 7*




*a*) Pyridine, AcOH, $N_2H_4{\cdot}H_2O$, r.t.; 69%. *b*) **6**, TMSOTf, $CH_2Cl_2$, $-25°$ to $-10°$; 26%. *c*) $HS(CH_2)_2$-NHCbz, AIBN, PhH, 80°; 62%. *d*) 1. Pyridine, AcOH, $N_2H_4{\cdot}H_2O$, $CH_2Cl_2$, r.t.; 2. $H_2O_2$, 1M LiOH, THF, $-5°$ to r.t., then 3M KOH, MeOH, r.t.; 49%. *e*) $H_2$, Pd/C, MeOH/$H_2O$ 2:1 (*v*/*v*), r.t.; 73%.

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## Experimental Part

1. *General*. All chemicals used were reagent grade and used as supplied except where noted. $CH_2Cl_2$, THF and toluene were purified by a *Cycle-Trainer Solvent Delivery System*. Pyridine and $Et_3N$ were freshly distilled over $CaH_2$ under $N_2$ before use. $CCl_3CN$ was distilled over $P_2O_5$ under Ar and stored

at 0°. $Tf_2O$ was distilled under Ar. Solvents for chromatography and workup procedures were distilled. Reactions were performed under an Ar atmosphere except where noted. *Abbreviations:* AIBN: 2,2′-Azoisobis[butyronitrile], BSP: (phenylsulfinyl)piperidine, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene, Cbz: $PhCH_2OC(O)$, DIPC: 1,3-diisopropylcarbodiimide, DIPEA: diisopropylethylamine ($EtN(i\text{-}Pr)_2$), DMAP: 4-(dimethylamino)pyridine, Fmoc-Cl: [(9H-fluoren-9-yl)methoxy]carbonyl chloride, h.v.: high vacuum (0.01–0.1 Torr), LevOH: levulinic acid, *m*-CPBA: 3-chloroperoxybenzoic acid, NIS: *N*-iodosuccinimide, TCA-Cl: trichloroacetyl chloride, TES: triethylsilane ($Et_3SiH$), $Tf_2O$: trifluoromethanesulfonic anhydride, TFA: trifluoroacetic acid, TFAA: trifluoroacetic anhydride, TMSOTf: trimethylsilyl trifluoromethanesulfonate, TsOH: *p*-toluenesulfonic acid. TLC: *Merck* silica gel *60* $F_{254}$ plates; detection under UV light at 254 nm and monitoring by solns. of ninhydrine (300 mg of ninhydrine, 3 ml of AcOH, and 100 ml of BuOH), anisaldehyde (23 ml of anisaldehyde, 9.4 ml of AcOH, 32 ml of conc. $H_2SO_4$, 880 ml of EtOH) or 'Mo-stain' (25 g of phosphomolybdic acid, 10 g of $Ce(SO_4)_2 \cdot H_2O$, 60 ml of conc. $H_2SO_4$, 940 ml of $H_2O$), followed by heating with a heat gun. FC: *Fluka* silica gel *60* (230–400 mesh). Gel-filtration chromatography: *Sephadex G-25* from *Amersham Biosciences*. Prep. RP-HPLC: *Waters* HPLC system (*Waters*, binary HPLC pump 1525, ELS detector 2420, dual $\lambda$ absorbance detector 2487) with *SunFire* $C_8$ column (*SunFire* 5 μm prep. column, $C_8$ (150 × 10 mm)). Recycling prep. HPLC (*LC-9101*, *Japan Analytical Industry Co., Ltd.*); flow rate: 3.5 ml/min; solvent: $CHCl_3$. Optical rotations $[\alpha]_D^{r.t.}$: *Perkin-Elmer 241* polarimeter (10 cm, 1 ml cell); the solvents and concentrations (in g/100 ml) are indicated. Microwave irradiation: *CEM Discover* microwave. IR Spectra: as 1–2% $CHCl_3$ soln. on a *Perkin-Elmer-782* spectrophotometer; in $cm^{-1}$. NMR Spectra: $^1$H-NMR Spectra: *Bruker AV600* (600 MHz), *Bruker DRX500* (500 MHz), *Bruker DRX400* (400 MHz), or *Varian VXR300* (300 MHz) spectrometers. $^{13}$C-NMR Spectra: *Bruker AV600* (150 MHz), *Bruker DRX500* (125 MHz), *Bruker DRX400* (100 MHz), or *Varian VXR300* (75 MHz) spectrometers. Chemical shifts $\delta$ are given in ppm relative to resonances of solvent, coupling constants *J* are given in Hertz (Hz). In ambiguous cases, $^1$H-assignment is based on selective homonuclear decoupling experiments and 2D experiments. High-resolution mass spectra were performed by the MS service at the Laboratory for Organic Chemistry, ETH Zürich (HR-MALDI-MS) and by the MS service of the UNI-Fribourg (HR-ESI-MS) and are given in *m*/*z*.

*2-{2-[2-(Benzylsulfanyl)ethoxy]ethoxy}ethyl 2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*D*-glucopyranoside* (**11**). *2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*D*-glucopyranosyl trichloroacetimidate* (**10** [16]; 1.27 g, 2.4 mmol) and 2-{2-[2-(benzylsulfanyl)ethoxy]ethoxy}ethanol [17] (0.92 g, 3.6 mmol) were co-evaporated with toluene (2×) and dissolved in $CH_2Cl_2$ (48 ml). TMSOTf (46 μl, 0.24 mmol) was added, and the pale yellow soln. was stirred for 1 h at r.t. The reaction was quenched with $Et_3N$ (1 ml), and the solvents were evaporated. FC (toluene/acetone 24:1) afforded **11** (1.24 g, 83%) as a mixture of $\alpha$- and $\beta$-anomer ($\alpha/\beta$ 0.57:0.43). Colorless oil. $R_f$ (toluene/acetone 12:1) 0.36. IR ($CHCl_3$): 3008*w*, 2924*w*, 2871*w*, 2112*s*, 1602*w*, 1496*w*, 1454*w*, 1369*w*, 1094*s*, 999*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 2.59–2.65 (*m*, 2 H); 3.34–3.89 (*m*, 15.43 H); 3.91–4.03 (*m*, 1 H); 4.09 (*t*, *J* = 9.5, 0.57 H); 4.25–4.35 (*m*, 1 H); 4.45 (*d*, *J* = 7.8, 0.43 H); 4.79 (*m*, 1 H); 4.91 (*m*, 1 H); 4.96 (*d*, *J* = 3.7, 0.57 H); 5.57 (*s*, 0.43 H); 5.58 (*s*, 0.57 H); 7.20–7.43 (*m*, 13 H); 7.46–7.51 (*m*, 2 H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 30.7; 36.7; 62.7; 63.0; 66.2; 66.2; 67.6; 68.6; 69.0; 69.6; 70.2; 70.4; 70.4; 70.8; 70.9; 74.9; 75.0; 76.1; 77.3; 79.0; 81.6; 82.9; 98.7; 101.4; 101.4; 102.8; 126.0; 127.0; 127.9; 128.2; 128.3; 128.4; 128.4; 128.5; 129.0; 129.0; 137.2; 137.3; 137.9; 137.9; 138.5. HR-MALDI-MS: 644.2392 ($[M+Na]^+$, $C_{33}H_{39}N_3NaO_7S^+$; calc. 644.2401).

*2-{2-[2-(Benzylsulfanyl)ethoxy]ethoxy}ethyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-(trichloroacetamido)-*D*-glucopyranoside* (**12**). A soln. of **11** (1.18 g, 1.90 mmol) in THF (19 ml) and $H_2O$ (2 ml) at 0° was treated with a 1M soln. of $Me_3P$ in THF (3.8 ml, 3.8 mmol). After stirring for 2 h at r.t., additional $H_2O$ (2 ml) was added, and stirring was continued for 19 h at r.t. Then, the mixture was concentrated, co-evaporated with toluene (3×) and $CH_2Cl_2$ (3×), and dried for 2 h under h.v. The residue was dissolved in $CH_2Cl_2$ (27 ml), and $Et_3N$ (0.66 ml, 4.8 mmol) and TCA-Cl (0.30 ml, 2.7 mmol) were added at 0°. The mixture was stirred for 1.5 h at r.t., diluted with $CH_2Cl_2$ (250 ml), washed with $H_2O$ (75 ml), sat. $NaHCO_3$ soln. (75 ml) and again $H_2O$ (75 ml), dried ($MgSO_4$) and concentrated. FC (toluene/AcOEt 9:1 → 4:1) afforded **12*α*** (0.71 g, 50%) and **12*β*** (0.55 g, 39%).

*Data of* **12*α***. Colorless, highly viscous oil. $R_f$ (toluene/AcOEt 85:15) 0.33. $[\alpha]_D^{r.t.} = +45.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3415*w*, 2995*w*, 2871*w*, 1718*m*, 1514*m*, 1454*w*, 1375*w*, 1087*s*, 1045*m*, 1003*m*. $^1$H-

NMR ($CDCl_3$, 300 MHz): 2.60 (*t*, *J* = 6.7, 2 H); 3.53–3.94 (*m*, 16 H); 4.22 (*dd*, *J* = 9.3, 4.1, 1 H); 4.29 (*dd*, *J* = 10.3, 4.4, 1 H); 4.70 (*d*, *J* = 11.5, 1 H); 4.90 (*d*, *J* = 11.8, 1 H); 4.97 (*d*, *J* = 3.7, 1 H); 5.60 (*s*, 1 H); 6.92 (*d*, *J* = 9.0, 1 H); 7.21–7.31 (*m*, 10 H); 7.38–7.41 (*m*, 3 H); 7.47–7.51 (*m*, 2 H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 30.7; 36.7; 54.7; 62.9; 67.4; 68.9; 70.2; 70.3; 70.6; 70.8; 74.5; 76.1; 82.6; 92.6; 97.6; 101.3; 125.9; 127.0; 127.6; 127.7; 128.2; 128.3; 128.4; 128.9; 129.0; 137.2; 137.9; 138.3; 161.6. HR-MALDI-MS: 762.1418 ($[M+Na]^+$, $C_{35}H_{40}Cl_3NNaO_8S^+$; calc. 762.1432).

*Data of* **12*β***. Colorless, highly viscous oil. $R_f$ (toluene/AcOEt 85:15) 0.16. $[\alpha]_D^{r.t.} = -8.8$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3429*w*, 3008*w*, 2876*w*, 1717*m*, 1522*m*, 1454*w*, 1370*w*, 1175*w*, 1097*s*, 1029*m*, 1005*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 2.59 (*td*, *J* = 6.7, 1.2, 2 H); 3.52–3.81 (*m*, 15 H); 3.84–3.89 (*m*, 1 H); 4.19 (*dd*, *J* = 10.1, 8.9, 1 H); 4.36 (*dd*, *J* = 10.6, 5.0, 1 H); 4.69 (*d*, *J* = 11.5, 1 H); 4.89 (*d*, *J* = 11.5, 1 H); 5.04 (*d*, *J* = 8.4, 1 H); 5.59 (*s*, 1 H); 7.06 (*d*, *J* = 7.8, 1 H); 7.22–7.30 (*m*, 10 H); 7.36–7.39 (*m*, 3 H); 7.48–7.51 (*m*, 2 H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 30.7; 36.7; 58.4; 66.1; 68.7; 68.8; 70.2; 70.5; 70.6; 70.8; 74.6; 76.5; 82.6; 92.6; 100.4; 101.2; 126.0; 127.0; 127.8; 128.1; 128.2; 128.4; 128.5; 128.9; 129.0; 137.2; 137.8; 138.2; 161.9. HR-MALDI-MS: 762.1418 ($[M+Na]^+$, $C_{35}H_{40}Cl_3NNaO_8S^+$; calc. 762.1432).

*2-{2-[2-(Benzylsulfanyl)ethoxy]ethoxy}ethyl 3,6-Di*-O-*benzyl-2-deoxy-2-(trichloroacetamido)*-α-D-*glucopyranoside* (**9**). Compound **12*α*** (0.108 g, 0.126 mmol) was co-evaporated with toluene (3×), dried under h.v. overnight. Then, compound **12*α*** was dissolved in $CH_2Cl_2$ (1 ml) and cooled to 0°. The soln. was treated with TES (0.14 ml, 0.87 mmol) and TFAA (21 µl, 0.15 mmol), and stirred at 0° for 10 min. Then, TFA (56 µl, 0.73 mmol) was added dropwise. The mixture was stirred at 0° for 3 h, warmed to 15° in 2.5 h, and the reaction was quenched with ice-cold sat. $NaHCO_3$ soln. The aq. phase was extracted with $CH_2Cl_2$ (3×), and the combined org. phases were washed with sat. $NaHCO_3$ soln., dried ($MgSO_4$), and concentrated. FC (hexane/AcOEt 4:1 → 3:2) afforded **9** (72.5 mg, 67%). Colorless, highly viscous oil. $R_f$ (hexane/AcOEt 1:1) 0.50. $[\alpha]_D^{r.t.} = +47.3$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3419*w*, 3008*w*, 2919*w*, 2872*w*, 1718*s*, 1514*m*, 1454*w*, 1363*w*, 1303*w*, 1108*s*, 1056*s*. $^1$H-NMR ($CDCl_3$, 300 MHz): 1.96 (br. *s*, 1 H); 2.62 (*t*, *J* = 6.9, 2 H); 3.53–3.86 (*m*, 17 H); 4.21 (*td*, *J* = 9.6, 3.6, 1 H); 4.55 (*d*, *J* = 12.1, 1 H); 4.62 (*d*, *J* = 11.8, 1 H); 4.72 (*d*, *J* = 11.5, 1 H); 4.80 (*d*, *J* = 11.5, 1 H); 4.93 (*d*, *J* = 3.6, 1 H); 7.12 (*d*, *J* = 9.3, 1 H); 7.22–7.38 (*m*, 15 H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 30.7; 36.7; 54.4; 67.2; 69.9; 70.1; 70.3; 70.4; 70.5; 70.8; 71.8; 73.7; 74.6; 80.0; 92.6; 97.3; 127.0; 127.6; 127.7; 127.8; 128.4; 128.4; 128.5; 128.8; 137.6; 137.9; 138.2; 161.5. HR-MALDI-MS: 764.1574 ($[M+Na]^+$, $C_{35}H_{42}Cl_3NNaO_8S^+$; calc. 764.1589).

*Methyl 2,3-Di*-O-*benzoyl-1-deoxy-4*-O-*levulinoyl-1-(phenylsulfanyl)*-β-D-*glucopyranosyluronate* (**8**). A soln. of **13** [18] (1.12 g, 2.35 mmol) in $CH_2Cl_2$ (15 ml) at 0° was subsequently treated with DMAP (0.46 g, 3.8 mmol), DIPC (0.55 ml, 3.5 mmol), and LevOH (0.39 ml, 3.8 mmol). The mixture was stirred for 3 h at r.t., diluted with AcOEt/hexane 3:2 (*v*/*v*; 200 ml), filtered through a plug of silica, and concentrated. FC (hexane/AcOEt 7:3 → 1:1) afforded **8** (1.27 g, 89%). White solid. $R_f$ (hexane/AcOEt 3:2) 0.20. $[\alpha]_D^{r.t.} = +70.1$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 2957*w*, 1735*s*, 1602*w*, 1455*w*, 1440*w*, 1364*w*, 1155*m*, 1091*m*, 1070*m*, 1026*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 2.03 (*s*, MeC); 2.33–2.64 (*m*, $CH_2CH_2$); 3.80 (*s*, MeO); 4.23 (*d*, *J* = 9.9, H–C(5)); 4.98 (*d*, *J* = 10.0, H–C(1)); 5.39 (*t*, *J* = 9.7, H–C(2) or H–C(3) or H–C(4)); 5.42 (*t*, *J* = 9.8, H–C(2) or H–C(3) or H–C(4)); 5.71 (*t*, *J* = 9.5, H–C(2) or H–C(3) or H–C(4)); 7.25–7.55 (*m*, 7 arom. H); 7.46–7.55 (*m*, 4 arom. H); 7.85–7.96 (*m*, 4 arom. H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 27.8 ($CH_2C(O)O$); 29.6 (*Me*C); 37.7 ($CC(O)CH_2$); 53.1 (MeO); 69.6, 69.9, 73.5, 76.3 (C(2), C(3), C(4), C(5)); 86.6 (C(1)); 128.3, 128.5, 128.6, 128.9, 129.7, 131.2, 133.3 (arom. CH, arom. C); 164.7, 165.4, 166.7, 171.0 (C(O)); 205.3 ($MeC(O)CH_2$). HR-MALDI-MS: 629.1441 ($[M+Na]^+$, $C_{32}H_{30}NaO_{10}S^+$; calc. 629.1452).

*Methyl 2,3-Di*-O-*benzoyl-1-deoxy-4*-O-*{[(9*H*-fluoren-9-yl)methoxy]carbonyl}-1-(phenylsulfanyl)*-β-D-*glucopyranosyluronate* (**14**). A soln. of **13** [18] (0.149 g, 0.293 mmol) in pyridine (2 ml) at r.t. was treated with Fmoc-Cl (0.151 g, 0.585 mmol). The mixture was stirred for 45 min at r.t., diluted with AcOEt (40 ml), and washed with a soln. of $H_2O$/conc. HCl 95:5 (*v*/*v*; 3×20 ml), sat. aq. $Na_2CO_3$ (2×20 ml) and $H_2O$ (20 ml), dried ($MgSO_4$), and concentrated. FC (toluene/AcOEt 1:0 → 9:1) afforded **14** (0.172 g, 80%). White solid. $R_f$ (toluene/AcOEt 9:1) 0.50. $[\alpha]_D^{r.t.} = +48.0$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3067*w*, 3007*w*, 2957*w*, 1759*s*, 1736*s*, 1602*w*, 1451*m*, 1386*w*, 1092*m*, 1070*m*, 1025*m*, 968*w*. $^1$H-NMR ($CDCl_3$, 300 MHz): 3.76 (*s*, Me); 4.07 (*t*, *J* = 7.5, $CHCH_2$); 4.24 (*d*, *J* = 7.5, $CH_2CH$); 4.36 (*d*, *J* = 9.9, H–C(5)); 5.02 (*d*, *J* = 9.9, H–C(1)); 5.33 (*t*, *J* = 9.7, H–C(2) or H–C(3) or H–C(4)); 5.45 (*t*, *J* = 9.6, H–C(2) or H–C(3) or H–C(4)); 5.84 (*t*, *J* = 9.4, H–C(2) or H–C(3) or H–C(4)); 7.14–7.56 (*m*, 17 arom. H); 7.69–7.72 (*m*, 2

arom. H); 7.87–7.89 (*m*, 2 arom. H); 7.95–7.98 (*m*, 2 arom. H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 46.3 (*C*$HCH_2$); 53.1 (Me); 69.9, 70.7, 73.1, 73.4, 76.0 (CH*C*$H_2$, C(2), C(3), C(4), C(5)); 86.7 (C(1)); 119.8, 125.1, 127.0, 127.7, 128.3, 128.5, 128.9, 129.8, 131.2, 133.3, 141.0, 142.8, 142.9 (arom. CH, arom. C); 153.7 (OC(O)O); 164.7, 165.3, 166.6 (C(O)). HR-MALDI-MS: 753.1752 ($[M+Na]^+$, $C_{42}H_{34}NaO_{10}S^+$; calc. 753.1765).

*2-{2-[2-(Benzylsulfanyl)ethoxy]ethoxy}ethyl (Methyl 2,3-Di*-O*-benzoyl-4*-O*-levulinoyl-β-*D*-glucopyranosyluronate)-(1 → 4)-3,6-di*-O*-benzyl-2-deoxy-2-(trichloroacetamido)-α-*D*-glucopyranoside* (**15**). Compound **8** (81 mg, 134 μmol) and BSP (30.8 mg, 147 μmol) were co-evaporated with toluene (2×), dried for 2 h under h.v., and dissolved in $CH_2Cl_2$ (2.7 ml). Freshly activated powdered 4-Å molecular sieves were added, and the mixture was stirred for 30 min at r.t., cooled to −60°, treated with $Tf_2O$ (24.7 μl, 147 μmol) and warmed to −40°. Then, a soln. of **9** (101 mg, 136 μmol) in $CH_2Cl_2$ (1.7 ml) was added dropwise, and the soln. was allowed to warm to 5° in 80 min, stirred for 15 min at r.t., and the reaction was quenched with $Et_3N$ (0.19 ml, 1.34 mmol). The mixture was diluted with $CH_2Cl_2$, then washed with 10% $Na_2S_2O_3$ soln. (10 ml), sat. $NaHCO_3$ soln., and $H_2O$, dried ($MgSO_4$), and concentrated. 2×FC (*i*) hexane/acetone 4:1 → 7:3 and *ii*) toluene/AcOEt 4:1 → 3:2) afforded **15** (52 mg, 31%). Pale yellow, highly viscous oil. $R_f$ (toluene/AcOEt 3:2) 0.50. $[\alpha]_D^{r.t.} = +39.7$ ($c = 0.35$, $CHCl_3$). IR ($CHCl_3$): 3415*w*, 3005*w*, 2923*w*, 2862*w*, 1723*s*, 1600*w*, 1513*w*, 1451*w*, 1364*w*, 1313*w*, 1149*m*, 1093*s*, 1067*m*, 1036*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 2.04 (*s*, Me (Lev)); 2.40–2.62 (*m*, $CH_2CH_2$ (Lev), S*C*$H_2$CH$_2$); 3.38–3.77 (*m*, $OCH_2CH_2OCH_2CH_2OCH_2$, S*C*$H_2$Ph, H–C(3) or H–C(4), H–C(5), $CH_2$(6)); 3.52 (*s*, $CO_2$Me); 3.88 (*d*, *J* = 9.6, H–C(5′)); 4.08–4.18 (*m*, H–C(2) and H–C(3) or H–C(4)); 4.35 (*d*, *J* = 12.2, 1 H, PhC*H*); 4.63 (*d*, *J* = 11.8, PhC*H*); 4.76 (*d*, *J* = 7.4, H–C(1′)); 4.77 (*d*, *J* = 12.2, PhC*H*); 4.94 (*d*, *J* = 3.8, 1 H, H–C(1)); 5.12 (*d*, *J* = 11.8, PhC*H*); 5.34–5.51 (*m*, H–C(2′), H–C(3′), H–C(4′)); 6.75 (*d*, *J* = 8.5, NH); 7.21–7.57 (*m*, 21 arom. H); 7.83–7.90 (*m*, 4 arom. H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 27.8; 29.7; 30.7; 36.7; 37.8; 52.8; 54.5; 67.2; 67.4; 69.8; 70.1; 70.2; 70.3; 70.5; 70.8; 71.7; 72.4; 72.6; 73.7; 74.8; 77.3; 77.7; 92.5; 96.9; 100.2; 127.0; 127.2; 127.7; 128.2; 128.3; 128.4; 128.8; 128.8; 129.7; 129.7; 133.3; 133.4; 137.6; 138.3; 138.5; 161.4; 164.5; 165.4; 166.6; 171.0; 205.4. HR-MALDI-MS: 1260.2933 ($[M+Na]^+$, $C_{61}H_{66}Cl_3NNaO_{18}S^+$; calc. 1260.2958).

*2-{2-[2-(Benzylsulfanyl)ethoxy]ethoxy}ethyl (Methyl 2,3-Di*-O*-benzoyl-β-*D*-glucopyranosyluronate)-(1 → 4)-3,6-di*-O*-benzyl-2-deoxy-2-(trichloroacetamido)-α-*D*-glucopyranoside* (**7**). A soln. of **15** (43 mg, 34.7 μmol) in $CH_2Cl_2$ (0.35 ml) at r.t. was subsequently treated with pyridine (83 μl), AcOH (55 μl), and $N_2H_4 \cdot H_2O$ (2.4 μl, 69.4 μmol). The mixture was stirred for 1 h at r.t., and the reaction was quenched with acetone (1 ml) and concentrated. FC (hexane/AcOEt 3:2 → 1:1) afforded **7** (38.4 mg, 97%). Pale yellow, highly viscous oil. $R_f$ (hexane/AcOEt 3:2) 0.20. $[\alpha]_D^{r.t.} = +36.5$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3600*w*, 3422*w*, 3008*w*, 2892*w*, 1731*s*, 1600*w*, 1515*w*, 1452*w*, 1364*w*, 1313*w*, 1093*s*, 1070*m*, 1041*m*, 909*w*. $^1$H-NMR ($CDCl_3$, 300 MHz): 2.58 (*t*, *J* = 6.7, S*C*$H_2$CH$_2$); 3.28 (*d*, *J* = 2.8, OH); 3.40–3.79 (*m*, $OCH_2CH_2OCH_2CH_2OCH_2$, S*C*$H_2$Ph, H–C(3) or H–C(4), H–C(5), $CH_2$(6), H–C(5′)); 3.51 (*s*, $CO_2$Me); 4.05–4.23 (*m*, H–C(2), H–C(3) or H–C(4), H–C(4′)); 4.36 (*d*, *J* = 12.1, PhC*H*); 4.62 (*d*, *J* = 11.5, PhC*H*); 4.74 (*d*, *J* = 7.9, H–C(1′)); 4.79 (*d*, *J* = 12.1, PhC*H*); 4.94 (*d*, *J* = 3.7, H–C(1)); 5.05 (*d*, *J* = 11.5, PhC*H*); 5.31 (*t*, *J* = 9.1, H–C(3′)); 5.39 (*dd*, *J* = 9.8, 7.9, H–C(2′)); 6.79 (*d*, *J* = 8.7, NH); 7.21–7.55 (*m*, 21 arom. H); 7.85–7.87 (*m*, 2 arom. H); 7.93–7.96 (*m*, 2 arom. H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 30.5; 36.5; 52.6; 54.2; 67.1; 67.3; 69.9; 70.1; 70.2; 70.3; 70.6; 71.4; 73.6; 74.1; 74.4; 74.8; 76.7; 77.7; 92.4; 96.9; 100.2; 126.9; 127.1; 127.5; 128.1; 128.3; 128.4; 128.5; 128.8; 128.9; 129.6; 129.8; 133.3; 133.4; 137.5; 138.3; 138.6; 161.5; 164.8; 166.3; 168.9. HR-MALDI-MS: 1162.2572 ($[M+Na]^+$, $C_{56}H_{60}Cl_3NNaO_{16}S^+$; calc. 1162.2591).

*Pent-4-enyl* N*-Acetyl-2-amino-4,6-*O*-benzylidene-2-deoxy-α-*D*-glucopyranoside* (**20**). To a soln. of N*-acetyl-*D*-glucosamine* (**19**; 10 g, 45.2 mmol) in pent-4-en-1-ol (70 ml) was added $TsOH \cdot H_2O$ (0.86 g, 4.5 mmol), and the mixture was stirred at 90° for 24 h. The reaction was quenched with $Et_3N$ (10 ml), and the solvents were evaporated. The residue was filtered through a plug of silica (MeOH/$CH_2Cl_2$ 1:17), co-evaporated with toluene (2×), dried under h.v. overnight, and suspended in MeCN (410 ml). The mixture was treated with benzaldehyde dimethyl acetal (13.7 ml, 90.8 mmol) at r.t., its pH was adjusted to 3–4 by the addition of $TsOH \cdot H_2O$ (2.7 g, 14.2 mmol), and stirred for 15 h at r.t. The reaction was quenched with $Et_3N$ (30 ml), and the solvents were evaporated. FC (hexane/AcOEt 1:2 → 0:1) afforded **20** (11.1 g, 65%). Pale yellow solid. $R_f$ (AcOEt) 0.23. $[\alpha]_D^{r.t.} = +35.5$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3590*w*,

3440*w*, 3007*w*, 2936*w*, 2871*w*, 1673*s*, 1509*m*, 1456*w*, 1376*m*, 1311*w*, 1126*m*, 1086*s*, 1033*s*, 997*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 1.67–1.76 (*m*, 2 H); 2.02 (*s*, 3 H); 2.10–2.18 (*m*, 2 H); 3.36–3.44 (*m*, 2 H); 3.56 (*t*, *J* = 9.2, 1 H); 3.67–3.84 (*m*, 3 H); 3.89 (*td*, *J* = 9.5, 3.1, 1 H); 4.16–4.20 (*m*, 1 H); 4.24 (*dd*, *J* = 9.5, 3.9, 1 H); 4.80 (*d*, *J* = 3.8, 1 H); 4.98–5.08 (*m*, 2 H); 5.54 (*s*, 1 H); 5.74–5.88 (*m*, 1 H); 5.95 (*d*, *J* = 8.7, 1 H); 7.32–7.37 (*m*, 3 H); 7.47–7.51 (*m*, 2 H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 23.4; 28.5; 30.4; 54.1; 62.6; 67.5; 68.8; 70.4; 82.0; 97.7; 101.8; 115.2; 126.2; 128.1; 129.0; 137.0; 137.7; 171.2. HR-MALDI-MS: 400.1720 ($[M+Na]^+$, $C_{20}H_{27}NNaO_6^+$; calc. 400.1731).

*Pent-4-enyl* N-*Acetyl-2-amino-3*-O-*benzyl-4,6*-O-*benzylidene-2-deoxy-α*-D-*glucopyranoside* (**21**). To a suspension of **20** (0.50 g, 1.32 mmol), BaO (0.81 g, 5.28 mmol), and $BaOH \cdot 8\,H_2O$ (0.21 g, 0.66 mmol) in DMF (2.2 ml) was added BnBr (0.32 ml, 2.65 mmol), and the mixture was stirred for 20 h at r.t., diluted with $CH_2Cl_2$ (40 ml), and cooled to 0°. At 0°, 50% aq. AcOH (20 ml) was added to dissolve the solids. The two phases were separated, and the org. phase was washed with ice-cold $H_2O$, sat. $NaHCO_3$ soln., and again ice-cold $H_2O$, dried ($MgSO_4$), and concentrated. FC (toluene/AcOEt 10:3 → 5:2) afforded **21** (0.57 g, 92%). White solid. $R_f$ (hexane/AcOEt 1:1) 0.25. $[\alpha]_D^{r.t.} = +101.9$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3443*w*, 3008*w*, 2936*w*, 2874*w*, 1676*s*, 1513*m*, 1453*w*, 1375*w*, 1131*m*, 1088*s*, 1047*s*, 1001*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 1.64–1.75 (*m*, 2 H); 1.92 (*s*, 3 H); 2.06–2.14 (*m*, 2 H); 3.38 (*dt*, *J* = 9.7, 6.5, 1 H); 3.64–3.88 (*m*, 5 H); 4.24–4.31 (*m*, 2 H); 4.65 (*d*, *J* = 12.1, 1 H); 4.79 (*d*, *J* = 3.7, 1 H); 4.93 (*d*, *J* = 12.1, 1 H); 4.96–5.05 (*m*, 2 H); 5.34 (*d*, *J* = 9.3, 1 H); 5.60 (*s*, 1 H); 5.72–5.85 (*m*, 1 H); 7.27–7.43 (*m*, 8 H); 7.48–7.53 (*m*, 2 H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 23.3; 28.4; 30.3; 52.4; 62.7; 67.4; 68.9; 73.9; 76.0; 82.7; 98.0; 101.1; 115.0; 125.9; 127.6; 127.9; 128.2; 128.3; 128.9; 137.3; 137.8; 138.5; 169.6. HR-MALDI-MS: 490.2199 ($[M+Na]^+$, $C_{27}H_{33}NNaO_6^+$; calc. 490.2200).

*Pent-4-enyl* N,N-*Diacetyl-2-amino-3*-O-*benzyl-4,6*-O-*benzylidene-2-deoxy-α*-D-*glucopyranoside* (**22**). To a soln. of **21** (0.415 g, 0.89 mmol) in $CH_2Cl_2$ (3 ml) and MeCN (2 ml), AcCl (0.32 ml, 4.5 mmol) and DIPEA (0.31 ml, 1.8 mmol) were added, and the mixture was heated in a microwave at 85° (80 W) for 3 h, diluted with $CH_2Cl_2$, and washed with sat. $NaHCO_3$ soln. The aq. phase was extracted once with $CH_2Cl_2$. The combined org. phases were dried ($MgSO_4$) and concentrated. FC (hexane/AcOEt 7:3) afforded **22** (0.45 g, 93%). Colorless oil. $R_f$ (hexane/AcOEt 6:4) 0.45. $[\alpha]_D^{r.t.} = +132.1$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2937*w*, 2871*w*, 1697*m*, 1678*m*, 1454*w*, 1368*w*, 1123*m*, 1092*s*, 1041*m*, 998*m*, 914*w*. $^1$H-NMR ($CDCl_3$, 300 MHz): 1.63–1.73 (*m*, 2 H); 2.05–2.15 (*m*, 2 H); 2.28 (*s*, 6 H); 3.37 (*dt*, *J* = 9.7, 6.4, 1 H); 3.66–3.82 (*m*, 3 H); 3.93 (*td*, *J* = 9.7, 4.5, 1 H); 4.30 (*dd*, *J* = 10.1, 4.5, 1 H); 4.60 (*dd*, *J* = 10.9, 3.4, 1 H); 4.68 (*dd*, *J* = 10.9, 8.1, 1 H); 4.72 (*d*, *J* = 11.5, 1 H); 4.83 (*d*, *J* = 3.7, 1 H); 4.94 (*d*, *J* = 11.5, 1 H); 4.98–5.07 (*m*, 2 H); 5.61 (*s*, 1 H); 5.72–5.86 (*m*, 1 H); 7.23–7.33 (*m*, 5 H); 7.38–7.44 (*m*, 3 H); 7.49–7.53 (*m*, 2 H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 26.7; 28.6; 30.3; 58.8; 62.8; 68.0; 68.9; 73.8; 75.1; 84.0; 98.9; 101.2; 115.3; 125.9; 127.6; 127.7; 128.2; 129.0; 137.1; 137.5; 138.4; 175.2. HR-MALDI-MS: 532.2297 ($[M+Na]^+$, $C_{29}H_{35}NNaO_7^+$; calc. 532.2306).

*Pent-4-enyl* N,N-*Diacetyl-2-amino-3,6*-O-*dibenzyl-2-deoxy-α*-D-*glucopyranoside* (**18**). After co-evaporating with toluene (2×), **22** (0.386 g, 0.757 mmol) was dissolved in $CH_2Cl_2$ (5 ml), cooled to 0°, and treated with TES (0.73 ml, 4.5 mmol) and TFAA (0.11 ml, 0.76 mmol). The mixture was stirred at 0° for 10 min, and TFA (0.29 ml, 3.8 mmol) was added dropwise. After the soln. was stirred at 0° for 2.5 h, it was warmed to 14° in 2.5 h, and, after stirring at 14° for 1 h, the reaction was quenched with $Et_3N$ (3.5 ml), diluted with $CH_2Cl_2$, and washed with sat. $NaHCO_3$ soln. The aq. phase was extracted once with $CH_2Cl_2$. The combined org. phases were dried ($MgSO_4$) and concentrated. FC (toluene/AcOEt 9:1 → 7:3) afforded **18** (259 mg, 67%). Colorless oil. $R_f$ (toluene/AcOEt 7:3) 0.33. $[\alpha]_D^{r.t.} = +139.4$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3497*w* 3008*m*, 2916*w*, 2862*w*, 1744*w*, 1676*s*, 1496*w*, 1454*w*, 1400*w*, 1365*s*, 1123*m*, 1046*s*, 916*w*. $^1$H-NMR ($CDCl_3$, 300 MHz): 1.62–1.72 (*m*, 2 H); 2.06–2.13 (*m*, 2 H); 2.31 (*s*, 6 H); 2.53 (*d*, *J* = 2.5, 1 H); 3.37 (*dt*, *J* = 9.7, 6.4, 1 H); 3.64–3.82 (*m*, 5 H); 4.32 (*dd*, *J* = 11.1, 3.6, 1 H); 4.51 (*dd*, *J* = 10.9, 7.8, 1 H); 4.55 (*d*, *J* = 12.1, 1 H); 4.63 (*d*, *J* = 12.1, 1 H); 4.74 (*d*, *J* = 11.8, 1 H); 4.80 (*d*, *J* = 11.5, 1 H); 4.82 (*d*, *J* = 3.7, 1 H); 4.95–5.06 (*m*, 2 H); 5.71–5.85 (*m*, 1 H); 7.25–7.38 (*m*, 10 H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 26.7; 28.6; 30.3; 59.3; 67.7; 69.7; 70.1; 73.2; 73.3; 73.7; 78.6; 98.4; 115.2; 127.6; 127.7; 127.8; 128.4; 128.5; 137.6; 138.6; 175.5. HR-MALDI-MS: 534.2463 ($[M+Na]^+$, $C_{29}H_{37}NNaO_7^+$; calc. 534.2462).

*(Methyl 2,3-Di*-O-*benzoyl-4*-O-*levulinoyl-β*-D-*glucopyranosyluronate) Trichloroacetimidate* (**24**). A soln. of **8** (0.20 g, 0.33 mmol) in $CH_2Cl_2/H_2O$ 100:1 (*v*/*v*; 3.3 ml) was treated at r.t. with a soln. of NIS

(103 mg, 0.46 mmol) and $Tf_2O$ (8 µl, 48 µmol) in $CH_2Cl_2$ (4.5 ml). After 15 h, 10% $Na_2S_2O_3$ soln. (10 ml) was added, and the layers were separated. The org. layer was washed with 10% $NaHCO_3$ soln., dried ($MgSO_4$), and concentrated. FC (toluene/AcOEt 4:1 → 3:2) afforded the hemiacetal (0.12 g, 0.23 mmol) that was dissolved in $CH_2Cl_2$ (0.6 ml), and, at 0°, $CCl_3CN$ (0.6 ml) and DBU (2.3 µl, 23 µmol) were added. The soln. was stirred at 0° for 45 min, subsequently for 1.5 h at r.t. and concentrated. FC (toluene/AcOEt 9:1 → 4:1) afforded **24** (123 mg, 57%). White foam. $R_f$ (toluene/AcOEt 4:1) 0.33. $[\alpha]_D^{r.t.} = +113.3$ ($c = 0.53$, $CHCl_3$). IR ($CHCl_3$): 3344*w*, 3032*w*, 2954*w*, 1732*s*, 1678*m*, 1602*w*, 1585*w*, 1452*w*, 1354*w*, 1148*m*, 1108*s*, 1069*m*, 1029*s*, 972*w*. $^1$H-NMR ($CDCl_3$, 300 MHz): 2.04 (*s*, CMe); 2.41–2.65 (*m*, $CH_2CH_2$); 3.79 (*s*, MeO); 4.64 (*d*, $J = 10.3$, H–C(5)); 4.84 (*d*, $J = 3.3$, H–C(1)); 5.53 (*dd*, $J = 10.6$, 3.3, H–C(2)); 5.54 (*t*, $J = 10.1$, H–C(3) or H–C(4)); 6.10 (*t*, $J = 10.0$, H–C(3) or H–C(4)); 7.32–7.41 (*m*, 4 arom. H); 7.47–7.55 (*m*, 2 arom. H); 7.91–7.96 (*m*, 4 arom. H); 8.66 (*s*, NH). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 27.8 ($CH_2C(O)O$); 29.7 (C*Me*); 37.7 ($CC(O)CH_2$); 53.3 (MeO); 69.1, 69.4, 70.2, 70.8 (C(2), C(3), C(4), C(5)); 90.5 ($CCl_3$); 92.8 (C(1)); 128.4, 128.7, 129.8, 129.8 (arom. CH); 133.4, 133.5 (arom. C); 160.1 ($CCCl_3$); 165.1, 165.4, 167.0, 171.1 (C(O)); 205.3 (Me*C*(O)Me). HR-MALDI-MS: 680.0453 ($[M+Na]^+$, $C_{28}H_{26}Cl_3NNaO_{11}^+$; calc. 680.0464).

*Methyl 2,3-Di*-O-*benzoyl-1-deoxy-4*-O-*levulinoyl-1-phenylsulfinyl)-β*-D-*glucopyranosyluronate* (**25**) *and Methyl 2,3-Di*-O-*benzoyl-1-deoxy-4*-O-*levulinoyl-1-(phenylsulfonyl)-β*-D-*glucopyranosyluronate* (**27**). A soln. of **8** (1.59 g, 2.55 mmol) in $CH_2Cl_2$ (20 ml) at −78° was treated with a soln. of *m*-CPBA (70–75%, 0.73 g, 2.9–3.2 mmol) in $CH_2Cl_2$ (5 ml). The mixture was warmed to 0° in 1.5 h and stirred at 0° for 30 min, the reaction was quenched with sat. $NaHCO_3$ soln., and the soln. was diluted with $CH_2Cl_2$. The aq. phase was extracted with $CH_2Cl_2$ (2×). The combined org. phases were washed with brine, dried ($MgSO_4$), and concentrated. FC (toluene/AcOEt 8:2 → 3:2) afforded **25** (1.43 g, 90%; 3:1 mixture of epimers) and **27** (0.13 g, 8%).

*Data of* **25**. White solid. $R_f$ (toluene/AcOEt 3:2) 0.16. $[\alpha]_D^{r.t.} = +54.0$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 1739*s*, 1602*w*, 1452*w*, 1365*w*, 1152*m*, 1093*m*, 1070*m*, 1046*w*, 1027*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 2.01 (*s*, 0.75 H, CMe); 2.02 (*s*, 2.25 H, CMe); 2.32–2.60 (*m*, $CH_2CH_2$); 3.72 (*s*, 2.25 H, MeO); 3.73 (*s*, 0.75 H, MeO); 4.15 (*d*, $J = 9.7$, 0.25 H, H–C(5)); 4.29 (*d*, $J = 9.0$, 0.75 H, H–C(5)); 4.58 (*d*, $J = 9.3$, 0.25 H, H–C(1)); 4.80 (*d*, $J = 8.7$, 0.75 H, H–C(1)); 5.33 (*t*, $J = 8.9$, 0.75 H, H–C(4)); 5.38–5.45 (*m*, 0.25 H, H–C(4)); 5.64–5.76 (*m*, H–C(2), H–C(3)); 7.30–7.53 (*m*, 10 arom. H); 7.67–7.78 (*m*, 3 arom. H); 7.85–7.91 (*m*, 2 arom. H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 27.7 ($CH_2C(O)O$); 29.6 (C*Me*); 37.6 ($CC(O)CH_2$); 53.0, 53.5 (MeO); 66.9, 67.6, 68.6, 68.9, 72.4, 73.1, 76.0, 76.4 (C(2), C(3), C(4), C(5)); 90.5, 92.9 (C(1)); 125.6, 125.8, 128.2, 128.3, 128.4, 128.5, 128.8, 128.9, 129.7, 129.8, 131.5, 131.8, 133.4, 138.5 (CH, arom.; C, arom.); 164.4, 165.2, 165.4, 166.0, 166.3, 170.9, 170.9 (C(O)); 205.3 (Me*C*(O)Me). HR-MALDI-MS: 645.1413 ($[M+Na]^+$, $C_{32}H_{30}NaO_{11}S^+$; calc. 645.1401).

*Data of* **27**. White solid. $R_f$ (toluene/AcOEt 3:2) 0.31. $[\alpha]_D^{r.t.} = +21.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3032*w*, 2956*w*, 1741*s*, 1602*w*, 1585*w*, 1450*w*, 1331*m*, 1315*w*, 1150*s*, 1105*m*, 1094*m*, 1070*m*, 1026*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 2.03 (*s*, CMe); 2.33–2.60 (*m*, $CH_2CH_2$); 3.74 (*s*, MeO); 4.24 (*d*, $J = 9.7$, H–C(5)); 4.79 (*d*, $J = 9.7$, H–C(1)); 5.21 (*t*, $J = 9.3$, H–C(4)); 5.60 (*t*, $J = 9.3$, H–C(2) or H–C(3)); 5.70 (*t*, $J = 9.0$, H–C(2) or H–C(3)); 7.33–7.41 (*m*, 4 arom. H); 7.48–7.55 (*m*, 2 arom. H); 7.58–7.63 (*m*, 2 arom. H); 7.70–7.75 (*m*, 1 arom. H); 7.82–7.86 (*m*, 2 arom. H); 7.93–7.97 (*m*, 2 arom. H); 7.99–8.03 (*m*, 2 arom. H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 27.7 ($CH_2C(O)O$); 29.6 (C*Me*); 37.6 ($CC(O)CH_2$); 53.2 (MeO); 67.3, 68.8, 72.8, 76.0 (C(2), C(3), C(4), C(5)); 88.8 (C(1)); 128.3, 128.7, 128.9, 129.8, 129.9, 130.7, 133.4, 133.5, 134.1, 134.8 (arom. CH, arom. C); 164.7, 165.2, 165.8, 170.9 (C(O)); 205.3 (Me*C*(O)Me). HR-MALDI-MS: 661.1355 ($[M+Na]^+$, $C_{32}H_{30}NaO_{12}S^+$; calc. 661.1350).

*Pent-4-enyl (Methyl 2,3-Di*-O-*benzoyl-4*-O-*levulinoyl-β*-D-*glucopyranosyluronate)-(1 → 4)*-N,N-*diacetyl-2-amino-3,6-di*-O-*benzyl-2-deoxy-α*-D-*glucopyranoside* (**23**). Compound **25** (0.91 g, 1.45 mmol) was co-evaporated with toluene (2×), dried for 1 h under h.v., and dissolved in $CH_2Cl_2$ (29 ml). Freshly activated, powdered 4-Å molecular sieves (1.86 g) were added, and the mixture was stirred for 30 min at r.t. and cooled to −78°. At −78°, $Tf_2O$ (0.15 ml, 0.87 mmol) was added, and the mixture was allowed to warm to −35° in 1 h and stirred at −35° for 20 min. Then, a soln. of **18** (0.57 g, 1.12 mmol) in $CH_2Cl_2$ (3 ml) was added, the mixture was allowed to warm to 3° in 3 h, and the reaction was quenched with $Et_3N$ (0.6 ml). The mixture was diluted with $CH_2Cl_2$, filtered through *Celite*, and washed with sat. $NaHCO_3$ soln. The aq. layer was extracted with $CH_2Cl_2$ (2×), and the combined org. phases were washed with

brine, dried ($MgSO_4$), and concentrated. FC (toluene/AcOEt 4:1 → 3:2) and subsequent purification by recycling prep. HPLC afforded **23** (382 mg, 32%). White foam. $R_f$ (toluene/AcOEt 1:1) 0.38. $[\alpha]_D^{r.t.} = +86.5$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2944*w*, 1736*s*, 1677*w*, 1602*w*, 1452*w*, 1365*m*, 1149*m*, 1093*s*, 1070*m*, 1028*m*. $^1$H-NMR ($CDCl_3$, 400 MHz): 1.49–1.62 (*m*, $OCH_2CH_2$); 1.91–2.01 (*m*, $OCH_2CH_2CH_2$); 2.05 (*s*, Me (Lev)); 2.19 (*s*, $NAc_2$); 2.39–2.66 (*m*, $CH_2CH_2$ (Lev)); 3.25 (*dt*, $J = 9.7$, 6.3, 1 H, $OCH_2CH_2$); 3.38 (*dd*, $J = 10.9$, 1.7, H–C(6)); 3.46–3.52 (*m*, H–C(5), 1 H of $OCH_2CH_2$); 3.52 (*s*, $CO_2Me$); 3.70 (*dd*, $J = 10.9$, 2.6, H–C(6)); 3.88 (*d*, $J = 9.6$, H–C(5′)); 4.05 (*dd*, $J = 10.0$, 8.1, H–C(4)); 4.38 (*d*, $J = 12.1$, PhC*H*); 4.43 (*dd*, $J = 11.2$, 3.6, H–C(2)); 4.50 (*dd*, $J = 11.2$, 8.1, H–C(3)); 4.61 (*d*, $J = 11.6$, PhC*H*); 4.75 (*d*, $J = 3.6$, H–C(1)); 4.77–4.87 (*m*, $CH_2$=CH); 4.81 (*d*, $J = 10.3$, H–C(1′)); 4.82 (*d*, $J = 12.1$, PhC*H*); 5.14 (*d*, $J = 11.6$, PhC*H*); 5.36–5.48 (*m*, H–C(2′), H–C(3′), H–C(4′)); 5.64 (*ddt*, $J = 17.1$, 10.2, 6.6, $CH_2$=C*H*); 7.19–7.57 (*m*, 16 arom. H); 7.84–7.90 (*m*, 4 arom. H). $^{13}$C-NMR ($CDCl_3$, 100 MHz): 26.6 (Me ($NAc_2$)); 27.8 ($CH_2C(O)O$); 28.2 ($OCH_2CH_2$); 29.5 (Me (Lev)); 30.0 ($OCH_2CH_2CH_2$); 37.7 ($MeC(O)CH_2$); 52.7 (MeO); 58.9 (C(2)); 67.4 (C(6)); 67.6 ($OCH_2CH_2$); 69.9 (C(4′)); 70.1 (C(5)); 71.7, 72.5 (C(2′), C(3′)); 72.8 (C(5′)); 73.5, 73.8 ($PhCH_2$); 77.2 (C(3)); 78.2 (C(4)); 98.3 (C(1)); 100.1 (C(1′)); 115.1 ($CH_2$=CH); 127.1, 127.6, 128.1, 128.4, 128.4, 128.5, 128.6, 128.9, 129.0, 129.7, 129.9 (arom. CH); 133.4, 133.4, 137.5 (arom. C); 137.7 (CH=$CH_2$); 139.5 (arom. C); 164.6, 165.6, 166.8, 171.1, 175.4 (C(O)); 205.6 (Me*C*(O)Me). HR-MALDI-MS: 1030.3853 ($[M+Na]^+$, $C_{55}H_{61}NNaO_{17}^+$; calc. 1030.3832).

*Pent-4-enyl (Methyl 2,3-Di-*O*-benzoyl-β-*D*-glucopyranosyluronate)-(1 → 4)-*N,N*-diacetyl-2-amino-3,6-di-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (**28**). A soln. of **23** (98.5 mg, 97.7 μmol) in $CH_2Cl_2$ (3 ml) at 0° was subsequently treated with pyridine (0.23 ml), AcOH (0.16 ml), and $N_2H_4 \cdot H_2O$ (4.4 μl, 127 μmol). The mixture was stirred for 1.25 h at r.t. Then, additional $N_2H_4 \cdot H_2O$ (2.4 μl, 69 μmol) was added, and the resulting mixture was stirred for 45 min at r.t., subsequently the reaction was quenched with acetone (1 ml), and the soln. was concentrated. Co-evaporation with toluene (2×), followed by FC (toluene/AcOEt 7:3 → 3:2), afforded **28** (61.4 mg, 69%). White foam. $R_f$ (toluene/AcOEt 1:1) 0.45. $[\alpha]_D^{r.t.} = +83.5$ ($c = 0.67$, $CHCl_3$). IR ($CHCl_3$): 3600*w*, 3008*w*, 2954*w*, 1733*s*, 1600*w*, 1452*w*, 1365*w*, 1094*s*, 1069*m*, 1028*m*. $^1$H-NMR ($CDCl_3$, 300 MHz): 1.53–1.60 (*m*, $OCH_2CH_2$); 1.93–2.19 (*m*, $OCH_2CH_2CH_2$); 2.22 (*s*, $NAc_2$); 3.22–3.29 (*m*, 1 H of $OCH_2CH_2$, OH); 3.39 (*dd*, $J = 10.7$, 1.7, H–C(6)); 3.47–3.55 (*m*, H–C(5), 1 H of $OCH_2CH_2$); 3.52 (*s*, MeO); 3.71 (*dd*, $J = 10.7$, 2.3, H–C(6)); 3.77 (*d*, $J = 9.7$, H–C(5′)); 4.06–4.13 (*m*, H–C(4), H–C(4′)); 4.38 (*d*, $J = 12.1$, PhC*H*); 4.45 (*dd*, $J = 11.1$, 3.3, H–C(2′)); 4.51 (*dd*, $J = 11.2$, 7.8, H–C(3′)); 4.62 (*d*, $J = 11.2$, PhC*H*); 4.74–4.87 (*m*, H–C(1), H–C(1′), $CH_2$=CH, PhC*H*); 5.03 (*d*, $J = 11.2$, PhC*H*); 5.28 (*t*, $J = 9.5$, H–C(3′)); 5.41 (*dd*, $J = 9.8$, 8.0, H–C(2′)); 5.64 (*ddt*, $J = 17.1$, 10.3, 6.7, $CH_2$=C*H*); 7.18–7.57 (*m*, 16 arom. H); 7.84–7.87 (*m*, 2 arom. H); 7.94–7.96 (*m*, 2 arom. H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 26.5; 28.1; 29.9; 52.5; 58.7; 67.2; 67.5; 70.0; 70.6; 71.3; 72.9; 73.7; 74.2; 74.9; 76.6; 77.6; 98.2; 100.1; 115.0; 127.0; 127.4; 128.0; 128.3; 128.3; 128.6; 128.9; 129.6; 129.8; 133.3; 137.4; 137.5; 139.3; 164.7; 166.4; 168.9; 175.4. HR-MALDI-MS: 932.3482 ($[M+Na]^+$, $C_{50}H_{55}NNaO_{15}^+$; calc. 932.3464).

*Pent-4-enyl (Methyl 2-*O*-Acetyl-3-*O*-benzyl-4-*O*-levulinoyl-α-*L*-idopyranosyluronate)-(1 → 4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside)-(1 → 4)-(methyl 2,3-Di-*O*-benzoyl-β-*D*-glucopyranosyluronate)-(1 → 4)-*N,N*-diacetyl-2-amino-3,6-di-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (**29**). Compounds **28** (185 mg, 0.203 μmol) and **6** [15] (220 mg, 244 μmol) were co-evaporated with toluene (2×), dried under h.v. overnight and dissolved in $CH_2Cl_2$ (4 ml). Freshly activated, powdered 4-Å molecular sieves (337 mg) were added, and the mixture was stirred for 30 min at r.t. and cooled to −25°. At −25°, TMSOTf (4.7 μl, 24 μmol) was added, and the soln. was warmed to −10° in 1 h and stirred at −10° for 2.75 h. The reaction was quenched with $Et_3N$ (74 μl), and the soln. was diluted with $CH_2Cl_2$, filtered through *Celite*, concentrated, and co-evaporated with toluene (2×). FC (toluene/AcOEt 3:1 → 2:3), and subsequent purification by recycling prep. HPLC afforded **29** (88.5 mg, 26%). White foam. $R_f$ (toluene/AcOEt 2:3) 0.30. $[\alpha]_D^{r.t.} = +15.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2928*w*, 2112*m*, 1741*s*, 1453*w*, 1358*w*, 1153*m*, 1090*m*, 1028*s*. $^1$H-NMR ($CDCl_3$, 600 MHz): 1.49–1.59 (*m*, $OCH_2CH_2$); 1.93–1.99 (*m*, $OCH_2CH_2CH_2$); 2.07 (*s*, AcO); 2.08 (*s*, AcO); 2.16 (*s*, Me (Lev)); 2.20 (*s*, $NAc_2$); 2.46 (*ddd*, $J = 17.4$, 6.8, 5.4, 1 H, $CH_2CH_2$ (Lev)); 2.53 (*ddd*, $J = 17.4$, 8.0, 5.2, 1 H, $CH_2CH_2$ (Lev)); 2.64 (*ddd*, $J = 18.3$, 6.8, 5.2, 1 H, $CH_2CH_2$ (Lev)); 2.74 (*ddd*, $J = 18.3$, 8.0, 5.4, 1 H, $CH_2CH_2$ (Lev)); 3.22 (*dd*, $J = 10.2$, 3.6, H–C(2″)); 3.25 (*dt*, $J = 11.2$, 4.1, 1 H, $OCH_2CH_2$); 3.40 (*dd*, $J = 10.9$, 1.6, H–C(6));

3.43–3.52 (*m*, H–C(5), 1 H of OC$H_2$CH$_2$); 3.45 (*s*, $CO_2$Me (IdoA)); 3.50 (*s*, $CO_2$Me (GlcA)); 3.66 (*dd*, *J* = 10.2, 9.3, H–C(3″)); 3.69–3.71 (*m*, H–C(6), H–C(5″)); 3.77 (*d*, *J* = 9.6, H–C(5′)); 3.79 (*t*, *J* = 3.3, H–C(3‴)); 3.84 (*t*, *J* = 9.6, H–C(4″)); 4.04 (*dd*, *J* = 10.0, 8.4, H–C(4)); 4.20 (*dd*, *J* = 12.7, 2.5, H–C(6″)); 4.27 (*t*, *J* = 9.4, H–C(4′)); 4.41 (*dd*, *J* = 11.1, 3.8, H–C(2)); 4.42–4.44 (*m*, PhC$H$, H–C(6″)); 4.48 (*dd*, *J* = 11.1, 8.4, H–C(3)); 4.53 (*d*, *J* = 10.8, PhC$H$); 4.56 (*d*, *J* = 11.3, PhC$H$); 4.70 (*d*, *J* = 11.4, PhC$H$); 4.73 (*d*, *J* = 10.8, PhC$H$); 4.75 (*d*, *J* = 3.8, H–C(1)); 4.76 (*d*, *J* = 11.4, PhC$H$); 4.80–4.82 (*m*, 1 H, C$H_2$=CH); 4.80 (*d*, *J* = 8.0, H–C(1′)); 4.81 (*d*, *J* = 11.9, PhC$H$); 4.85 (*ddd*, *J* = 17.1, 3.5, 1.6, 1 H, C$H_2$=CH); 4.87–4.88 (*m*, H–C(2‴), H–C(5‴)); 4.96 (*d*, *J* = 3.6, H–C(1″)); 5.05 (*d*, *J* = 11.3, PhC$H$); 5.07 (*t*, *J* = 3.4, H–C(4‴)); 5.12 (*d*, *J* = 2.3, H–C(1‴)); 5.39 (*dd*, *J* = 9.9, 8.0, H–C(2′)); 5.57 (*dd*, *J* = 9.9, 9.2, H–C(3′)); 5.64 (*ddt*, *J* = 17.1, 10.3, 6.7, CH$_2$=C$H$); 7.15–7.56 (*m*, 26 arom. H); 7.88–7.93 (*m*, 4 arom. H). $^{13}$C-NMR ($CDCl_3$, 150 MHz): 20.8, 20.9 (Me (OAc)); 26.6 (Me ($NAc_2$)); 27.8 (C$H_2$C(O)O); 28.2 (OCH$_2$C$H_2$); 29.7 (Me (Lev)); 30.0 (OCH$_2$CH$_2$C$H_2$); 37.5 (MeC(O)C$H_2$); 52.1 (MeO (IdoA)); 52.8 (MeO (GlcA)); 59.0 (C(2)); 61.5 (C(6″)); 63.8 (C(2″)); 67.1, 67.8 (C(2‴), C(5‴)); 67.5 (C(6)); 67.6 (OC$H_2$CH$_2$); 68.1 (C(4‴)); 70.2 (C(5)); 70.5 (C(5″)); 71.9 (C(2′)); 73.0 (PhC$H_2$); 73.1 (C(3‴)); 73.4 (PhC$H_2$); 73.6 (C(3′)); 73.8 (PhC$H_2$); 74.4 (C(4″)); 74.8 (C(5′)); 75.0 (PhC$H_2$); 76.9 (C(3)); 77.8 (C(4′)); 78.3 (C(4)); 78.4 (C(3″)); 97.7 (C(1‴)); 98.3 (C(1)); 99.1 (C(1″)); 100.4 (C(1′)); 115.1 (C$H_2$=CH); 127.1, 127.4, 127.6, 127.6, 128.0, 128.1, 128.1, 128.1, 128.2, 128.3, 128.4, 128.5, 128.5, 128.6, 129.0, 129.0, 129.1, 129.5, 129.6, 129.8, 133.0, 133.3 (arom. CH); 137.3 (arom. C); 137.5 (C$H$=CH$_2$); 137.6, 137.7, 139.3 (C, arom.); 164.8, 165.4, 167.3, 168.6, 169.8, 170.6, 171.7, 175.4 (C(O)); 205.8 (Me*C*(O)Me). HR-MALDI-MS: 1611.5768 ([*M* – HOAc + Na]$^+$, $C_{84}H_{92}N_4NaO_{27}^+$; calc. 1611.5841).

*5-[2-[(Benzyloxycarbonyl)amino]ethylsulfanyl]pentyl (Methyl 2-*O*-Acetyl-3-*O*-benzyl-4-*O*-levulinoyl-α-*L*-idopyranosyluronate)-(1 → 4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside)-(1 → 4)-(methyl 2,3-Di-*O*-benzoyl-β-*D*-glucopyranosyluronate)-(1 → 4)-*N,N*-diacetyl-2-amino-3,6-di-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (**30**). To a degased soln. of **29** (60.9 mg, 36.9 μmol) and HS(CH$_2$)$_2$-NHZ [31] (117 mg, 0.55 mmol) in benzene (3 ml) at r.t., a soln. of AIBN (0.6 mg, 3.7 μmol) in benzene (0.6 ml) was added, and the soln. was instantly heated to reflux. After 2.25 h at reflux, the reaction was quenched with hexene (0.4 ml), and the soln. was stirred for 15 min at r.t. and concentrated. FC (toluene/acetone 4 : 1 → 2 : 1) afforded **30** (42.5 mg, 62%). Colorless, highly viscous oil. $R_f$ (toluene/AcOEt 2 : 3) 0.28. $[\alpha]_D^{r.t.} = +31.8$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3456*w*, 3008*w*, 2928*w*, 2112*m*, 1740*s*, 1513*w*, 1453*w*, 1367*m*, 1155*m*, 1090*m*, 1028*s*, 909*w*. $^1$H-NMR ($CDCl_3$, 500 MHz): 1.20–1.25 (*m*, CH$_2$C$H_2$CH$_2$); 1.36–1.44 (*m*, 2 CH$_2$C$H_2$CH$_2$); 2.01 (*s*, AcO); 2.02 (*s*, AcO); 2.10 (*s*, Me (Lev)); 2.14 (*s*, $NAc_2$); 2.35–2.49 (*m*, CH$_2$ (Lev), $SCH_2$); 2.54–2.61 (*m*, 1 H of C$H_2$CH$_2$ (Lev), $SCH_2$); 2.68 (*ddd*, *J* = 18.4, 7.9, 5.5, 1 H, C$H_2$CH$_2$ (Lev)); 3.14–3.19 (*m*, H–C(2″), 1 H of OC$H_2$CH$_2$); 3.30–3.46 (*m*, H–C(5), H–C(6), 1 H of OC$H_2$CH$_2$, $NCH_2$); 3.40 (*s*, MeO (IdoA)); 3.44 (*s*, MeO (GlcA)); 3.59–3.66 (*m*, H–C(6), H–C(3″), H–C(5″)); 3.72 (*d*, *J* = 9.7, H–C(5′)); 3.74 (*t*, *J* = 3.8, H–C(3‴)); 3.78 (*t*, *J* = 9.6, H–C(4″)); 3.98 (*dd*, *J* = 9.9, 8.3, H–C(4)); 4.14 (*dd*, *J* = 12.7, 2.5, H–C(6″)); 4.20 (*t*, *J* = 9.4, H–C(4′)); 4.34–4.39 (*m*, H–C(2), H–C(6″), PhC$H$); 4.42 (*dd*, *J* = 11.1, 8.3, H–C(3)); 4.47 (*d*, *J* = 10.5, PhC$H$); 4.49 (*d*, *J* = 10.0, PhC$H$); 4.64 (*d*, *J* = 11.4, PhC$H$); 4.67 (*d*, *J* = 11.5, PhC$H$); 4.69 (*d*, *J* = 4.3, H–C(1)); 4.70 (*d*, *J* = 11.4, PhC$H$); 4.74 (*d*, *J* = 13.2, PhC$H$); 4.76 (*d*, *J* = 8.1, H–C(1′)); 4.82–4.83 (*m*, H–C(2‴), H–C(5‴)); 4.90 (*d*, *J* = 3.6, H–C(1″)); 4.99 (*d*, *J* = 11.4, PhC$H$); 5.01 (*t*, *J* = 3.5, H–C(4‴)); 5.04 (*s*, C(O)OC$H_2$Ph); 5.12 (*d*, *J* = 2.1, H–C(1‴)); 5.13 (br. *s*, NH); 5.32 (*dd*, *J* = 9.9, 8.1, H–C(2′)); 5.51 (*t*, *J* = 9.5, H–C(3′)); 7.09–7.48 (*m*, 31 arom. H); 7.82–7.87 (*m*, 4 arom. H). $^{13}$C-NMR ($CDCl_3$, 125 MHz): 21.0; 21.1; 25.4; 26.8; 28.0; 29.0; 29.4; 29.9; 31.8; 32.4; 37.7; 40.4; 52.3; 53.0; 59.2; 61.7; 64.0; 67.0; 67.3; 67.9; 68.0; 68.3; 68.4; 70.5; 70.7; 72.1; 73.2; 73.3; 73.6; 73.8; 74.0; 74.5; 75.0; 75.2; 77.1; 77.5; 78.0; 78.6; 78.6; 97.9; 98.5; 99.3; 100.6; 127.3; 127.6; 127.7; 127.8; 128.2; 128.3; 128.3; 128.3; 128.4; 128.5; 128.5; 128.6; 128.7; 128.7; 128.8; 129.2; 129.2; 129.3; 129.7; 129.7; 130.0; 133.2; 133.6; 136.7; 137.5; 137.8; 137.9; 139.5; 156.5; 165.1; 165.6; 167.5; 168.8; 170.0; 170.8; 171.9; 175.6; 206.1. HR-MALDI-MS: 1882.6708 ([*M* + Na]$^+$, $C_{96}H_{109}N_5NaO_{31}S^+$; calc. 1882.6719).

*5-[2-[(Benzyloxycarbonyl)amino]ethylsulfonyl]pentyl (3-*O*-Benzyl-α-*L*-idopyranosyluronate)-(1 → 4)-(2-azido-3-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside)-(1 → 4)-(β-*D*-glucopyranosyluronate)-(1 → 4)-*N*-acetyl-2-amino-3,6-di-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (**31**). A soln. of **30** (42.3 mg, 22.7 μmol) in $CH_2Cl_2$ at 0° was subsequently treated with pyridine (0.22 ml), AcOH (0.15 ml), and a soln. of $N_2H_4 \cdot H_2O$ in $CH_2Cl_2$ (1 : 4 (*v*/*v*), 8 μl, 45.5 μmol). The mixture was stirred for 2.25 h at r.t., the reaction

Table 2. *Crystallographic Data for the Building Blocks* **8**, **14**, *and* **25**

| | **8** | **14** | **25** |
|---|---|---|---|
| Crystallized from | AcOEt/hexane | AcOEt/hexane | AcOEt/hexane |
| Empirical formula | $C_{32}H_{30}O_{10}S$ | $C_{42}H_{34}O_{10}S$ | $C_{32}H_{30}O_{11}S$ |
| Crystal temp. [K] | 203(2) | 180(2) | 200(2) |
| Crystal dimensions [mm] | $0.13\times0.10\times0.09$ | $0.14\times0.11\times0.08$ | $0.22\times0.18\times0.16$ |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Lattice parameters: | | | |
| $\theta$ Range [°] | $2.03<\theta<25.04$ | $2.84<\theta<25.02$ | $3.56<\theta<25.05$ |
| $a$ [Å] | 10.0739(7) | 5.7218(1) | 5.7329(2) |
| $b$ [Å] | 5.9307(4) | 29.4717(6) | 15.8855(4) |
| $c$ [Å] | 24.8830(19) | 10.5331(3) | 16.4909(5) |
| $\alpha$ [°] | 90 | 90 | 90 |
| $\beta$ [°] | 94.682(2) | 95.924(1) | 90.575(1) |
| $\gamma$ [°] | 90 | 90 | 90 |
| $V$ [Å$^3$] | 1481.68(18) | 1766.72(7) | 1501.75(8) |
| Space group | $P2_1$ | $P2_1$ | $P2_1$ |
| $Z$ | 2 | 2 | 2 |
| $\rho_{calc}$ [g cm$^{-3}$] | 1.360 | 1.374 | 1.377 |
| $\mu$ [mm$^{-1}$] | 0.168 | 0.154 | 0.170 |
| Total reflections measured | 3939 | 4879 | 4779 |
| Independent reflections | 3939 | 4879 | 4779 |
| Reflections observed | 3354 | 4178 | 4497 |
| Criterion | $I>2\sigma(I)$ | $I>2\sigma(I)$ | $I>2\sigma(I)$ |
| Parameters | 421 | 480 | 400 |
| Final $R$ | 0.0591 | 0.0408 | 0.0459 |
| $wR_2$ | 0.1485 | 0.0967 | 0.1200 |
| Goodness-of-fit | 1.104 | 0.908 | 1.034 |
| $\Delta\rho_{(max,min)}$ [eÅ$^{-3}$] | 0.24, −0.23 | 0.17, −0.17 | 0.59, −0.26 |

was quenched with acetone (1 ml), and the soln. was concentrated. The residue was co-evaporated with toluene (2×), filtered through a plug of silica gel ($CH_2Cl_2$/acetone 7:3), dried under h.v. for 12 h, and dissolved in THF (3.2 ml). At −5°, $H_2O_2$ (30%, 1.1 ml) and 1M aq. LiOH (1.8 ml) were added, and the mixture was stirred for 24 h at r.t. Then, MeOH (1.7 ml) and 3M aq. KOH (3.2 ml) were added, and stirring was continued for 17.5 h at r.t. Then, the mixture was neutralized with *IR-120$^+$ Amberlite* resin, filtered, co-evaporated with MeOH (2×), and concentrated. Purification by RP-HPLC ($H_2O$ (20% i-PrOH, 0.1% TFA)/MeCN (20% i-PrOH, 0.1% TFA) 9:1 for 2 min, 9:1 → 0:1 in 20 min, flow rate 4.7 ml/min) afforded **31** (16.0 mg, 49%). White, fluffy solid. $t_R$ 12.4–14.1 min. $[\alpha]_D^{r.t.}=+51.1$ ($c=1.0$, MeOH). $^1$H-NMR ($CD_3OD$, 500 MHz): 1.47–1.51 (*m*, $OCH_2CH_2CH_2$); 1.56–1.60 (*m*, $OCH_2CH_2$); 1.75–1.80 (*m*, $SCH_2CH_2CH_2$); 1.82 (*s*, Me); 3.03–3.06 (*m*, $SCH_2CH_2CH_2$); 3.34–3.38 (*m*, H−C(2″), $NCH_2CH_2$, 1 H of $OCH_2CH_2$); 3.52 (*t*, $J=6.7$, $NCH_2$); 3.56 (*t*, $J=9.1$, CH); 3.61–3.95 (*m*, H−C(6), $CH_2$(6″), 1 H of $OCH_2CH_2$, 12 CH); 4.00–4.05 (*m*, H−C(2), H−C(6)); 4.31 (*d*, $J=11.4$, PhC*H*); 4.44 (*d*, $J=8.2$, H−C(1′)); 4.44 (*d*, $J=10.1$, PhC*H*); 4.48 (*d*, $J=11.8$, PhC*H*); 4.57–4.63 (*m*, 3 PhC*H*); 4.66–4.69 (*m*, H−C(1), PhC*H*, CH); 4.98 (*d*, $J=11.0$, PhC*H*); 5.03 (*s*, $C(O)OCH_2Ph$); 5.15 (br. *s*, H−C(1‴)); 5.58 (*d*, $J=3.7$, H−C(1″)); 7.10–7.40 (*m*, 25 arom. H). $^{13}$C-NMR ($CD_3OD$, 125 MHz): 21.3 ($SO_2CH_2CH_2CH_2$); 21.5 (Me); 25.1 ($OCH_2CH_2CH_2$); 28.5 ($OCH_2CH_2$); 34.6 ($NCH_2$); 51.9 ($NCH_2CH_2$); 52.8, 52.9 (C(2), $NCH_2CH_2$); 60.0 (C(6″)); 64.0 (C(2″)); 66.5 ($C(O)OCH_2Ph$); 66.9 (CH); 67.6 ($OCH_2CH_2$); 68.3 (C(6)); 68.8, 69.0, 70.9 (CH); 72.0 ($PhCH_2$); 72.5 (CH); 73.2 ($PhCH_2$); 73.9 (CH); 74.2 ($PhCH_2$, CH); 74.5 ($PhCH_2$); 74.9, 76.5, 76.9, 77.0, 77.5, 78.4, 78.9 (CH); 97.5 (C(1)); 98.3 (C(1″)); 100.6 (C(1‴));

103.1 (C(1′)); 127.1, 127.2, 127.4, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.6 (CH, arom.); 137.0, 138.3, 138.4, 139.3 (arom. C); 157.4 (NC(O)O); 170.4 (N*C*(O)Me); 172.1, 172.2 (C*C*(O)O). HR-MALDI-MS: 1454.5121 ($[M+Na]^+$, $C_{69}H_{85}N_5NaO_{26}S^+$; calc. 1454.5096).

*5-(2-Aminoethylsulfonyl)pentyl (α-*L*-Idopyranosyluronate)-(1 → 4)-(2-amino-2-deoxy-α-*D*-glucopyranoside)-(1 → 4)-(β-*D*-glucopyranosyluronate)-(1 → 4)*-N*-acetyl-2-amino-2-deoxy-α-*D*-glucopyranoside* (**32**). Compound **31** (15.9 mg, 11.1 μmol) was dissolved in MeOH (2 ml) and $H_2O$ (1 ml). Under an Ar atmosphere, 100% Pd/C (15.9 mg) was added, and the Ar atmosphere exchanged for $H_2$. The mixture was stirred for 18 h at r.t., filtered through *Celite*, co-evaporated with MeOH (2×), and concentrated. The residue was purified by *Sephadex G-25* chromatography ($H_2O$/MeOH 9 : 1) and lyophilized to afford **32** (7.4 mg, 73%). White, fluffy solid. $[\alpha]_D^{r.t.} = +139.9$ ($c = 0.57$, $H_2O$). $^1$H-NMR ($D_2O$, 600 MHz): 1.52–1.60 (*m*, 2 H); 1.61–1.67 (*m*, 2 H); 1.83–1.88 (*m*, 2 H); 2.02 (*s*, 3 H); 3.32–3.36 (*m*, 3 H); 3.37 (*dd*, $J = 9.3$, 8.0, 1 H); 3.48 (*dd*, $J = 10.2$, 6.0, 1 H); 3.49 (*dd*, $J = 8.3$, 5.8, 1 H); 3.53 (*t*, $J = 6.7$, 2 H); 3.61 (*t*, $J = 6.7$, 2 H); 3.64–3.67 (*m*, 1 H); 3.65 (*dd*, $J = 8.2$, 7.0, 1 H); 3.69–3.92 (*m*, 13 H); 4.52 (*d*, $J = 4.5$, H–C(1)); 4.45 (*d*, $J = 7.9$, H–C(1′)); 4.87 (*d*, $J = 2.8$, H–C(1‴)); 5.65 (*d*, $J = 3.8$, H–C(1″)). $^{13}$C-NMR ($D_2O$, 150 MHz): 23.3 ($CH_2$); 24.6 (Me); 26.9, 30.5, 35.5, 51.8, 55.2 ($CH_2$); 56.2, 57.0 (CH); 61.9, 62.7, 66.3 ($CH_2$); 70.4, 71.0, 72.0, 73.2, 74.1, 74.2, 74.2, 74.4, 75.3, 76.0, 78.7, 79.3, 82.0 (CH); 98.0, 99.1, 104.1, 104.9 (C(1), C(1′), C(1″), C(1‴)); 177.0, 177.3, 178.6 (C(O)). HR-ESI-MS: 912.3123 ($[M+H]^+$, $C_{33}H_{58}N_3O_{24}S^+$; calc. 912.3125).

*X-Ray Crystal-Structure Determination of* **8**, **14**, *and* **25** (see the *Table 2*, and *Figs. 2* and *4*). The intensities were collected on a *Bruker-Nonius Kappa-CCD*, Mo$K_\alpha$ radiation, $\lambda = 0.7107$ Å. The structure was solved by direct methods [34] and refined by full-matrix least-squares analysis [35] including an isotropic extinction correction. All non-H-atoms were refined anisotropically (H-atoms isotropic, wherby H-positions are based on stereochemical considerations). *Table 2* shows the crystal data and details of the refinement procedure.

CCDC-614522 (**8**), CCDC-614523 (**14**), and CCDC-614524 (**25**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* www.ccdc.cam.ac.uk/data_request/cif.

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