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Synthesis of new sulfonic acid-containing oligosaccharide mimetics of sialyl Lewis A

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Dedicated to Professor Károly Lempert on the occasion of his 85th birthday

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ABSTRACT

Two trisaccharides as new sulfonic acid mimetics of the sialyl Lewis A tetrasaccharide were synthesized. The natural sialic acid residue is replaced by a C-sulfonic acid moiety attached to position C-3′ of the lactosamine unit of the mimetics. The L-fucose unit was also replaced by a D-arabinose ring in one of the analogues. Formation of the sulfonic acid moiety on the trisaccharide level could be successfully achieved by means of introduction of an acetylthio moiety into the galactose skeleton and subsequent oxidation. The equatorial arrangement of the acetylthio group linked to C-3 of the galactose ring could be achieved by double nucleophilic substitution; efficient formation of the *gulo*-triflate derivatives required low-power microwave activation. Oxidation of the acetylthio group was carried out using Oxone in acetic acid.

1. Introduction

Selectins are members of the family of adhesive molecules. This name comes from their selective property and collective lectin domain.[1,2] Three different calcium ion-dependent carbohydrate-binding proteins were identified: L-selectin is expressed on neutrophils, monocytes and lymphocyte subsets of leucocytes, whereas, E-selectin and P-selectin are expressed on endothelial cells and on thrombocytes (platelets).[3,4] These proteins are responsible for the initial steps of extravasation of leucocytes during an inflammatory response and cancer metastasis by the recognition of their specific carbohydrate ligands. Asthma, psoriasis, rheumatoid arthritis, ARDS, lupus, cancer metastasis, septic shock or reperfusion syndrome diseases are all based on lymphocyta-endothel connection.[5]

Sialyl Lewis A tetrasaccharide **1** (sLe^a) and its positional isomer sialyl Lewis X tetrasaccharide **2** (sLe^x) are the natural ligands of selectins (Fig. 1). They are expressed on cell surfaces. Sialyl Le^a is related to the Lewis blood group system, while sLe^x was originally described as the X-hapten, which was later designated Le^x. These carbohydrate epitopes have been identified as lead compounds for binding to P- and E-selectins and also bind to L-selectin.[6–8]

To prevent the above-mentioned pathological processes, development of various sLe^a and sLe^x mimetics, which can inhibit the binding events of selectins with their natural ligands would be an effective tool.

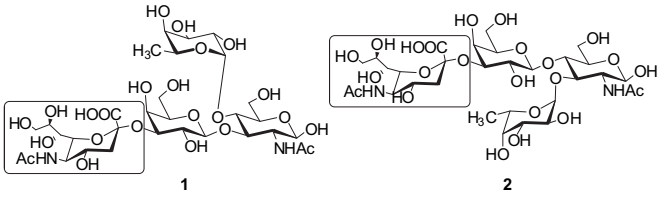

Figure 1. Sialyl Le^a (**1**) and sialyl Le^x (**2**).

On the other hand, sLe^a and sLe^x are tumour markers, since they are highly expressed on many malignant cells, and they have been demonstrated to be a prognostic indicator of metastatic diseases. The CA19-9 antibody, used in one of the top cancer diagnostic assays, binds sLe^a and indicates the presence of this antigen in pancreatic and gastrointestinal cancer patient's sera.[9]

A mixture of sulfated Le^a and Le^x was isolated by Yuen et al.[10] These natural oligosaccharides were even more potent inhibitors than the sialylated Lewis antigens.[11] The present paper describes the synthesis of the new sLe^a mimetics **3** and **4**, in which the sialic

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acid unit is replaced by a sulfonic acid group (Fig. 2). This group has a stronger ionic character and we expect higher stability against sulfatases and esterases. The L-fucosyl unit was also replaced by a D-arabinosyl moiety in compound **4** because such a structure is more stable towards enzymatic degradation[12] than the highly acid sensitive α-L-fucosyl interglycosidic linkage.[13]

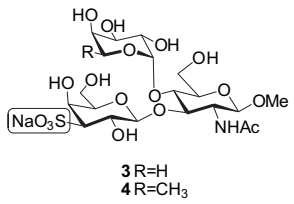


Figure 2. New synthetic analogues of the sLe[a].

2. Results and discussion

For the preparation of the planned oligosaccharide sulfonic acids, introduction of the easily oxidizable thioacetyl group into the carbohydrate skeleton seemed to be the best approach.[14–17] The synthesis of the target molecules may be accomplished by two synthetic paths; introduction of the thioacetyl group either at the monosaccharide or at oligosaccharide level.

Our plan was to prepare a sulfonic acid ester-containing monosaccharide through formation of a thioacetyl function by nucleophilic substitution, followed by oxidation and subsequent conversion of the sulfonic acid salt into the appropriate methyl ester. Then the synthesis of the trisaccharides **3** and **4** were planned using the monosaccharide precursors **5**–**8** as depicted in Figure 3. D-Arabinopyranosyl bromide **6** and L-fucosyl bromide **7**[18] were used as the donors, and allyl *N*-acetyl-glucosamine **8**[19] was selected as the acceptor in the glycosylation reactions. The anomeric allyl group was chosen because of its capability of conjugation to proteins.[20] It is known from the literature[21–23] that 3-acetylthio-galactoside can be prepared via two subsequent nucleophilic substitution reactions, and a strict substitution pattern of the galactose is required for the successful synthesis: OH-2 has to be protected by an ester group, and OH-4 and OH-6 have to be protected in the form of a benzylidene acetal.[23]

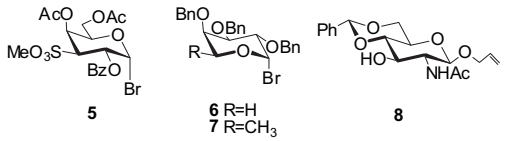
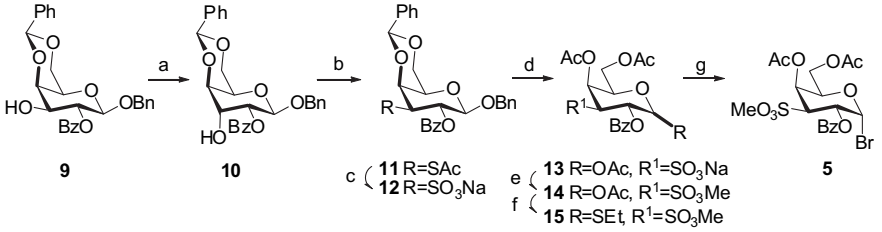


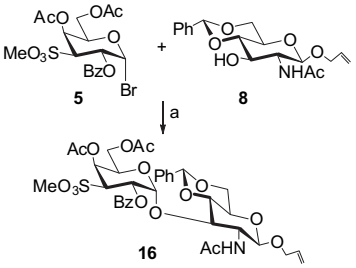
Figure 3. The anticipated sugar building blocks.

Therefore, compound **9**[24] was prepared as starting material for the synthesis of donor **5**. Inversion of the configuration at C-3′ via formation of a triflate and subsequent displacement with tetrabutylammonium nitrite ($TBANO_2$) afforded the *gulo*-derivative **10** in good yield. Formation of the C-3 triflate derivative of **10** and treatment with potassium thioacetate (KSAc) gave the desired 3-acetylthio-galactosyl derivative **11** in two steps with a 87% overall yield. Oxidation of the SAc moiety was achieved with Oxone[25] to give the sulfonic acid sodium salt **12** in a yield of 68%. Then compound **12** was converted to the donor molecule **5**: debenzylation and debenzylidenation of **12** and subsequent acetylation afforded the triacetyl derivative **13**, as a mixture of α/β anomers, in 60% yield. To transform the sulfonic acid salt group of **13** into an ester (**14**), first, the sulfonic acid was liberated by Amberlite IR-120 cationic exchange resin, and then methylation with diazo-methane in ether afforded compound **14** in a moderate yield, also as a mixture of α/β anomers. Thioglycoside formation of **14** using $BF_3 \cdot OEt_2$ as a promoter and thioethanol as a reagent gave the anomeric mixture **15** only in a moderate yield. The α-bromide derivative **5** was freshly prepared using bromine immediately before the coupling reaction (Scheme 1).



Scheme 1. Reagents and conditions: (a) Tf_2O, pyridine, dry CH_2Cl_2, −20 °C to rt, 1 h, then $TBANO_2$, dry CH_3CN, rt, one day, 78%; (b) Tf_2O, pyridine, dry CH_2Cl_2, −30 °C to 0 °C, 1 h, then KSAc, dry DMF, one day, 87%; (c) Oxone, KOAc, glacial acetic acid, two days, rt, 68%; (d) Pd(C), H_2, four days, then Ac_2O, pyridine, rt, 60%; (e) Amberlite IR-120H$^+$, MeOH, then CH_2N_2, dry Et_2O, 0 °C, 1 h, 44%; (f) $BF_3 \cdot OEt_2$, dry CH_2Cl_2, HSEt, 0 °C, 1 h, 48%; (g) Br_2, dry CH_2Cl_2.

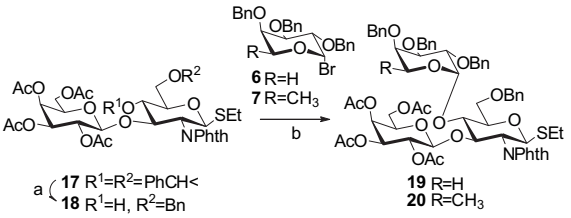
Surprisingly, coupling of acceptor **8** with the methylsulfonic acid group-containing galactosyl bromide **5** under Helferich conditions afforded exclusively the disaccharide **17**[26,27] in 40% yield (Scheme 2) whose interglycosidic linkage was assigned to be α on the basis of the NMR data (for C-1′: 105.49 ppm, $J_{C1'-H1'}$=179 Hz). Some unusual α-galactosylations have been known in the literature.[28,29] The methylsulfonic acid group may decrease the π-donor ability of the carbonyl oxygen of the benzoyl group by a strong dipole–dipole interaction, therefore the glycosylium ion cannot be stabilized in form of an acyloxonium cation intermediate despite the possibility of neighbouring group participation.



Scheme 2. Reagents and conditions: (a) $Hg(CN)_2$, dry CH_3NO_2, dry toluene, rt, 1 1/2 h, 40%.

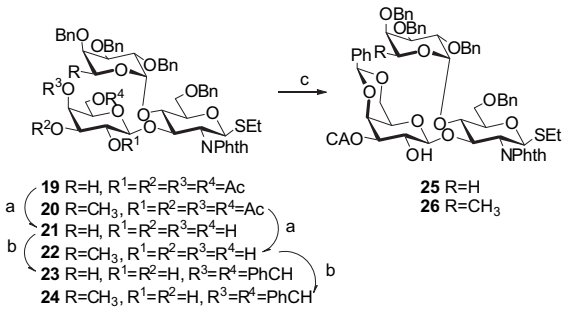
To eliminate this problem we changed our synthetic strategy and tried to create the sulfonic acid moiety at the oligosaccharide level, therefore the known disaccharide **17** was used for the preparation of the desired trisaccharides. The glucosamine acceptor was

also changed to the *N*-phthaloylated thioglucoside.[18] According to our expectation the phthaloyl group ensured better solubility and higher yields. The ethylthio aglycone was expected to make the synthesis of higher oligosaccharides possible for further synthetic studies. The reductive ring opening method[30] of the known β-linked disaccharide **17**[31,32] was used for the formation of the 6-*O*-benzyl derivative **18**. Treatment of **18** with the donors **6** and **7** by means of the in situ anomerization procedure[18] furnished the trisaccharide derivatives **20** and **21** in 52% and 56% yields, respectively (Scheme 3).



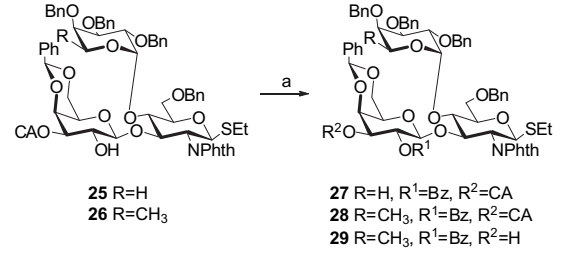
Scheme 3. Reagents and conditions: (a) $BF_3{\cdot}OEt_2$, Et_3SiH, dry CH_2Cl_2, 0 °C, 3 h, 77%; (b) TBABr, dry DMF, rt, one day, 52% for **19**, 56% for **20**.

To avoid cleavage of the phthalimido ring, deacetylation of compounds **19** and **20** was carried out carefully in dry THF and MeOH in the presence of 1–2 drops of 30% NaOMe in MeOH to afford **21** and **22** in good yields. The hydroxyl groups at C-4 and C-6 of the galactose units of **21** and **22** were protected in form of benzylidene acetals, then dibutylstannylidene-mediated acylation with chloroacetyl chloride[33,34] was applied to selectively protect the position C-3′ of **23** and **24** to give **25** and **26** in 70% and 79% yields (Scheme 4).



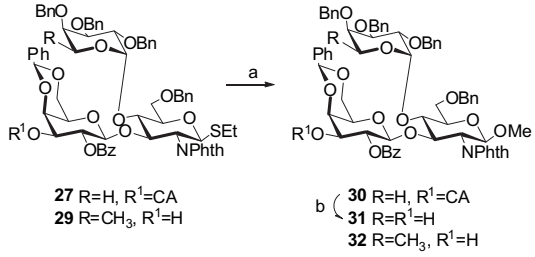
Scheme 4. Reagents and conditions: (a) 1–2 drops of 30% NaOMe in MeOH, dry THF–MeOH (1:1), rt, 1 h, 90% for **21**, 88% for **22**; (b) $PhCH(OMe)_2$, cat. CSA, dry CH_3CN, rt, 4 h, 82% for **23**, 78% for **24**; (c) Bu_2SnO, dry toluene, then ClAcCl, dry DMF, toluene, 4 Å MS, 0 °C, 1 h, 70% for **25**, 79% for **26**.

Benzoylation of the hydroxyl group of **25** could be achieved by using BzCl in pyridine and 1 equiv of 4-dimethylaminopyridine (DMAP) to afford **27** in 80% yield. In the case of the fucosylated derivative **26** under similar condition only 44% yield of compound **28** was formed since the longer reaction times resulted also in the dechloroacetyl derivative **29** (34%) (Scheme 5).



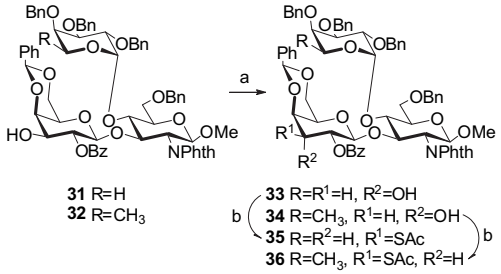
Scheme 5. Reagents and conditions: (a) BzCl, dry CH_2Cl_2, pyridine, DMAP, rt, 2–4 h, from **25**: 80% for **27**, from **26**: 44% for **28**, 34% for **29**.

Before introduction and oxidation of the acetylthio moiety the ethylthio aglycon, which is also oxidizable, had to be changed into a non-oxidizable function. Therefore compounds **27** and **29** were converted into the appropriate methyl glycosides with dry MeOH in the presence of the NIS-TMSOTf promoter system to afford **30** and **32** in high yields. Dechloroacetylation of **30** with thiourea[35] gave the C-3′ hydroxyl derivative **31** in 73% yield (Scheme 6).



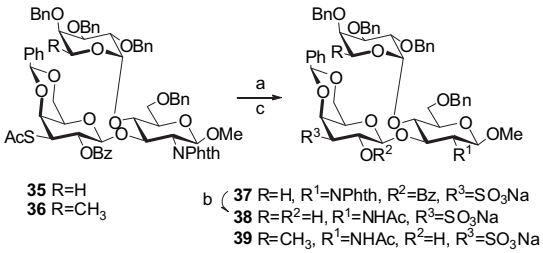
Scheme 6. Reagents and conditions: (a) NIS, TMSOTf, dry MeOH, CH_2Cl_2, −70 °C to rt, overnight, 85% for **30**, 84% for **32**; (b) thiourea, pyridine, CH_2Cl_2, MeOH, overnight, 73%.

Formation of the C-3′ triflate derivatives of **31** and **32** and subsequent treatment with $TBANO_2$ afforded the *gulo*-compounds **33** and **34** in good yields. The critical step was the formation of the *gulo*-triflates, which was carried out using Tf_2O in pyridine in the presence of a catalytic amount of DMAP. TLC monitoring of this reaction showed only 40% conversion of the starting material at rt after three days. We assume that there might be a strong hydrogen bonding between the OH-3′group and the C-2′ benzoyl carbonyl oxygen, and the phthalimido group may cause sterical hindrance as well, giving rise to the low reactivity of this hydroxyl group. To reach complete formation of the *gulo*-triflate, low-power activation microwave (CEM Discover Microwave machine) was employed. After 1 h TLC indicated >90% conversion of the starting compounds. Treatment of the triflates with KSAc afforded the desired, fully protected C-3′ thioacetylated Le[a] mimetics **35** and **36** in 70% and 78% overall yields for the two steps (Scheme 7).



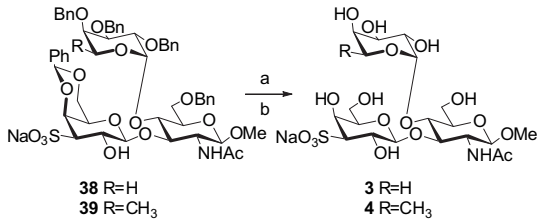
Scheme 7. Reagents and conditions: (a) Tf_2O, pyridine, dry CH_2Cl_2, −20 °C to rt, 1 h, then $TBANO_2$, dry CH_3CN, rt, one day, 70% for **33**, 67% for **34**; (b) Tf_2O, pyridine, dry CH_2Cl_2, 0 °C, 1/2 h, then MW, 35 °C, 1 h, then KSAc, dry DMF, overnight, 70% for **35**, 78% for **36**.

Oxidation of the arabinose-containing thioacetyl derivative **35** with Oxone gave **37** in 56% yield. Salt **37** was then treated with ethylenediamine (EDA) in ethanol at reflux to remove the acyl protecting groups followed by N-acetylation with Ac_2O in MeOH[36] to develop the acetamido group of **38** (64%). To achieve higher yields in the case of the fucose-containing trisaccharide **36** the opposite sequence of the reactions was applied. First, compound **36** was deacylated with EDA followed by selective acetylation of the amino group with Ac_2O in MeOH, then the liberated thiol was oxidized with Oxone to afford **39** with 62% overall yield for the three steps (Scheme 8).



Scheme 8. Reagents and conditions: (a) from **35**, Oxone, glacial AcOH, KOAc, rt, two days, 56% for **37**; (b) EDA, dry EtOH, reflux, one day, then Ac_2O, MeOH, rt, 2 h, 64% for **38**; (c) from **36**, EDA, dry EtOH, reflux, one day, then Ac_2O, MeOH, then Oxone, cc. AcOH, KOAc, rt, 4 h, 62% for **39** over three steps.

The benzyl ethers and the benzylidene acetal of **38** were removed in two steps. Acid hydrolysis and hydrogenolysis in the presence of Pd/C catalyst gave the target compound **3** in high yield. In the case of **39**, removal of these protecting groups was achieved only by hydrogenolysis to furnish compound **4** as the second new sulfonic acid trisaccharide mimetic of the sLe^a tetrasaccharide **1** (Scheme 9).



Scheme 9. Reagents and conditions: (a) from **38**, 80% AcOH, 50 °C, 1 h, then Pd(C), H_2 (10 bar), EtOH, one day, 93% for **3**; (b) from **39**, Pd(C), H_2 (10 bar), 96% EtOH, four days, 92% for **4**.

3. Conclusion

In conclusion, two trisaccharides (**3**, **4**) as new sulfonic acid analogues of the sialyl Lewis A were synthesized. These compounds contain a sulfonic acid sodium salt moiety attached equatorially to C-3 of the galactose ring substituting the natural sialic acid residue. The trisaccharides were synthesized from monosaccharide building blocks, the natural L-fucose unit of sLe^a was replaced by D-arabinose in mimetic **3**. Formation of the sulfonic acid function was carried out, first, on the monosaccharide level by means of introduction of an acetylthio moiety to position C-3 and subsequent oxidation, however the desired β-galactosylation attempted with the 3-sodiumsulfonato-galactosyl donor failed. Introduction of the sulfonic acid moiety on the trisaccharide level proved to be the successful method. The equatorial arrangement of the acetylthio group linked to C-3 of the galactose ring could be achieved by double nucleophilic substitution; while synthesis of the *galacto*-triflates took place smoothly, for the efficient formation of the *gulo*-triflate derivatives low-power microwave activation was required. Oxone in the presence of acetic acid was used as the reagent for the oxidation of the masked thiol group.

4. Experimental section

4.1. General

Optical rotations were measured at rt with a Perkin–Elmer 241 automatic polarimeter. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. All reactions were performed under anhydrous conditions (using argon) and monitored by TLC on Kieselgel 60 F_{254} (Merck) visualized under UV light and charred with 5% sulfuric acid in ethanol. Column chromatography was performed on Silica Gel 60 (Merck 0.062–0.200 nm). Chemicals were purchased from Aldrich and Fluka and used without further purification. Molecular sieves were activated by heating to 360 °C overnight and were cooled over P_2O_5 in vacuo. The organic solutions were dried over $MgSO_4$, and concentrated in vacuum. The ^1H (200.13, 360.13, 400.13 and 500.13 MHz) and ^{13}C NMR (50.3, 90.54, 100.62 and 125.76 MHz) spectra were recorded with Bruker WP-200SY, Bruker AM-360, Bruker DRX-400 and Bruker DRX-500 spectrometers for solutions in $CDCl_3$. The use of a different solvent is indicated therein. The ^1H–^{13}C HSQC and ^1H–^1H COSY experiments were performed on Bruker DRX-400 and Bruker DRX-500 spectrometers at 298 K. Chemical shifts are referenced to Me_4Si (0.00 ppm for ^1H) or to the residual solvent signals (77.00 ppm for ^{13}C). IR spectra were recorded on a Perkin–Elmer 16 PC FTIR spectrometer. Microwave-assisted procedures were taken place in a CEM-Discover Focused Microwave Synthesis System (2450 MHz) with a built-in infrared temperature sensor and a CEM-Explorer computer controlled robotic sampler attaching system. Samples were measured in 10 mL crimp-sealed, thick-walled reaction tubes equipped with a magnetic stirrer. MALDI-TOF MS spectra were recorded on a Bruker Biflex III spectrometer in the positive, linear mode using satd 2,4,6-trihydroxyacetophenone in water as matrix.

4.2. General method I for the synthesis of the benzylidene acetal derivatives

To a solution of the starting material (15.5 mmol) in dry acetonitrile (80 mL) was added benzaldehyde dimethylacetal (3.5 mL, 1.5 equiv) and a catalytic amount of (±)10-camphorsulfonic acid (CSA) (90 mg) and the mixture was stirred at rt until the complete conversion of the starting material (detected by TLC). The mixture was neutralized with triethylamine (TEA) and the solvent was evaporated. The crude product was purified by crystallization or by column chromatography using 1% of TEA in the eluent.

4.3. General method II for the reductive ring opening of the benzylidene acetal derivatives with $BF_3{\cdot}OEt_2/Et_3SiH$

To a cold (0 °C) solution of the starting material (0.34 mmol) in dry CH_2Cl_2 was added Et_3SiH (272 μL, 5 equiv) and $BF_3{\cdot}OEt_2$ (86 μL, 2 equiv). The mixture was allowed to reach rt and was stirred for 4 h, then it was diluted with CH_2Cl_2, washed with satd aq $NaHCO_3$, washed again with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography.

4.4. General method III for the in situ anomerisation reactions with TBABr

The appropriate bromide donor was freshly prepared from the corresponding ethyl 1-thioglycoside derivative (1.1 equiv) in dry CH_2Cl_2 (3 mL) by adding Br_2 (193 μL, 1.1 equiv) at rt. After half an hour the mixture was concentrated under reduced pressure and coevaporated twice with dry toluene. To a mixture of the acceptor (1 equiv) and 3 Å MS in dry DMF was added TBABr (1.2 equiv) and stirred for 2 h at rt, then the solution of the bromide derivative in CH_2Cl_2 was added. After one day the mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed twice with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography.

4.5. General method IV for the preparation of the *gulo*-configured derivatives

To a solution of the starting compound (1.2 mmol) in dry CH_2Cl_2 (5 mL) and pyridine (1 mL) was added dropwise Tf_2O (1.9 mmol, 1.6 equiv) at −30 °C and the mixture was stirred for 1 h. After dilution with CH_2Cl_2, it was washed with satd aq $NaHCO_3$, and with water, dried ($MgSO_4$) and concentrated. The crude triflate was dried under high vacuum for 3 h. To a solution of the crude triflate in dry acetonitrile (10 mL) was added $TBANO_2$ (3 equiv) and stirred overnight. When TLC indicated the complete conversion of the triflate the mixture was concentrated. The residue was diluted with EtOAc, washed three times with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography.

4.6. Benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-gulopyranoside (10)

Prepared from **9** (548 mg, 1.2 mmol) according to general method **IV** and purified by column chromatography (1:1 EtOAc–hexane, R_f 0.49) to give compound **10** (411 mg, 75%) as a colourless syrup: $[\alpha]_D^{23}$ −57.9 (*c* 0.13, $CHCl_3$). ^{1}H NMR (360 MHz) δ=7.96 (dd, 2H, *J*=8.3 Hz, *J*=1.2 Hz, arom.), 7.55–7.45 (m, 3H, arom.), 7.42–7.10 (m, 10H, arom.), 5.48 (s, 1H, PhC*H*), 5.38 (dd, 1H, *J*=8.4, 3.1 Hz, H-2), 5.10 (d, 1H, *J*=8.4 Hz, H-1), 4.89 (d, 1H, *J*=12.7 Hz, PhCH_2), 4.65 (d, 1H, *J*=12.7 Hz, PhCH_2), 4.34–4.25 (m, 2H), 4.02–3.95 (m, 2H), 3.8–3.7 (m, 1H), 2.93 (br s, 1H, OH) ppm ^{13}C NMR (90 MHz) δ=165.3 (PhC=O), 137.7, 137.66, 133.34, 129.91, 129.81, 129.14, 128.73, 128.47, 128.31, 127.73, 127.61, 126.48 (arom. *C*), 101.18 (PhCH), 96.85 (C-1), 76.4, 71.34, 71.2, 68.92, 65.66 (skeleton *C*s), 70.15 (PhCH_2), 69.31 (C-6) ppm. Anal. Calcd for $C_{27}H_{26}O_7$ (462.49): C, 70.12; H, 5.67. Found: C, 70.01; H, 5.78.

4.7. Benzyl 3-*S*-acetyl-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside (11)

To a solution of compound **10** (1.64 g, mmol) in dry CH_2Cl_2 (30 mL) and pyridine (2 mL) was added dropwise Tf_2O (955 μL, 3.55 mmol, 1.6 equiv) at −50 °C and the mixture was allowed to reach 0 °C and stirred for 1 h. The mixture was diluted with CH_2Cl_2, washed with satd aq $NaHCO_3$, washed again with water, dried ($MgSO_4$) and concentrated. The crude triflate was dried under high vacuum for 3 h. To a solution of the crude triflate in dry DMF (15 mL) was added KSAc (1.21 g, 10.6 mmol, 3 equiv) and the reaction stirred overnight at rt. The residue was diluted with CH_2Cl_2, washed three times with water, dried ($MgSO_4$) and concentrated. Column chromatography (1:1 EtOAc–hexane) of the residue gave compound **11** (1.64 g, 87%) as a syrup. Crystallization from ethanol gave pale yellow crystals: mp 141–142 °C; $[\alpha]_D^{23}$ +48.1 (*c* 0.12, $CHCl_3$). ^{1}H NMR (360 MHz) δ=8.00–7.93 (m, 2H, arom.), 7.60–7.51 (m, 3H, arom.), 7.47–7.32 (m, 5H, arom.), 7.20–7.10 (m, 5H, arom.), 5.55 (s, 1H, PhC*H*), 5.52 (dd, 1H, *J*=8.4, 3.1 Hz, H-2), 4.88 (d, 1H, *J*=12.7 Hz, PhCH_2), 4.71 (d, 1H, *J*=7.8 Hz, H-1), 4.67 (d, 1H, *J*=12.7 Hz, PhCH_2), 4.38 (d, 1H, *J*=12.4 Hz, H-6a), 4.18 (dd, 1H, *J*=11.4, 3.2 Hz, H-3), 4.14–4.05 (m, 2H, H-4, H-6b), 3.69 (s, 1H, H-5), 2.23 (s, 3H, SCOCH_3) ppm. ^{13}C NMR (90 MHz) δ=195.29 (SCOCH$_3$), 165.67 (PhC=O), 137.83, 137.55, 133.54, 130.35, 130.09, 129.47, 128.77, 128.67, 128.61, 128.13, 128.05, 126.70 (arom. *C*s), 101.67 (PhCH), 101.06 (C-1), 76.25 (C-4), 70.19 (PhCH_2), 69.49 (C-2), 69.43 (C-6), 68.93 (C-5), 47.28 (C-3), 30.90 (SCOCH$_3$) ppm. Anal. Calcd for $C_{29}H_{28}O_9S$ (520.59): C, 66.91; H, 5.42; S, 6.16. Found: C, 66.75; H, 5.52; S, 6.22. MALDI-TOF *m*/*z* calcd for $[M+Na]^+$ 543.145. Found: 543.204.

4.8. Benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-deoxy-3-sodiumsulfonato-β-D-galactopyranoside (12)

To a suspension of compound **11** (1.37 g, 2.6 mmol) in glacial acetic acid (50 mL) was added KOAc (5.15 g, 20 equiv) and Oxone (4.02 g, 2.5 equiv) and the reaction stirred vigorously for two days. TLC analysis indicated the completion of the reaction. The reaction mixture was neutralized by adding satd aq and solid $NaHCO_3$ and washed three times with EtOAc. The collected organic phase was washed with water, dried ($MgSO_4$) and concentrated. Column chromatography (95:5→9:1 CH_2Cl_2–MeOH, R_f 0.46) of the residue gave compound **12** (0.926 g, 68%) as a syrup and **11** (0.158 g, 12%) was also recovered. Compound **12**: $[\alpha]_D^{23}$ −25.8 (*c* 0.10, $CHCl_3$). ^{1}H NMR (360 MHz, CD_3OD) δ=8.04 (dd, 2H, *J*=8.3, 1.2 Hz, arom.), 7.65–7.55 (m, 3H, arom.), 7.45 (t, 2H, *J*=7.7 Hz, arom.), 7.38–7.28 (m, 3H, arom.), 7.18–7.03 (m, 5H, arom.), 5.87 (dd, 1H, *J*=11.3, 7.9 Hz, H-2), 5.69 (s, 1H, PhC*H*), 4.86 (d, 1H, *J*=12.6 Hz, PhCH_2), 4.79 (d, 1H, *J*=7.9 Hz, H-1), 4.67 (d, 1H, *J*=2.5 Hz, H-4), 4.63 (d, 1H, *J*=12.4 Hz, PhCH_2), 4.27 (dq, 2H, *J*=12.5, 1.5 Hz, H-6a,b), 3.71–3.68 (m, 1H, H-5), 3.51 (dd, 1H, *J*=11.4, 2.9 Hz, H-3) ppm. ^{13}C NMR (90 MHz, CD_3OD) δ=167.20 (PhC=O), 137.17, 136.67, 133.27, 130.01, 129.37, 128.79, 128.10, 127.93, 127.61, 125.98 (arom. *C*s), 100.83, 100.06 (PhCH or C-1), 74.11, 68.70, 68.46 (C-2, C-4, C-5), 70.27 (PhCH_2), 68.96 (C-6), 61.21 (C-3) ppm. Anal. Calcd for $C_{27}H_{25}NaO_9S$ (548.54): C, 59.12; H, 4.59; Na, 4.19; S, 5.85. Found: C, 59.02; H, 4.62; S, 5.89. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 571.101. Found: 570.792.

4.9. 1,4,6-Tri-*O*-acetyl-2-*O*-benzoyl-3-deoxy-3-sodiumsulfonato-α,β-D-galactopyranose (13)

To a solution of compound **12** in ethanol (5 mL) and acetic acid (96%, 1 mL) was added 10% Pd/C (50 mg) and the reaction stirred under H_2 overnight. The mixture was diluted with ethanol and filtered through Celite. The filtrate was concentrated under diminished pressure. The residue was treated with Ac_2O (0.75 mL) and pyridine (1 mL) for 2 h. Then the mixture was concentrated and coevaporated twice with toluene. Column chromatography (9:1 CH_2Cl_2–MeOH) of the residue gave an unseparable mixture of the α and β anomers of **13** in a 4:1 ratio (109 mg, 57%) as a syrup. Anal. Calcd for $C_{19}H_{21}NaO_{12}S$ (496.42): C, 45.97; H, 4.26; S, 6.46. Found: C, 45.89; H, 4.29; S, 6.50. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 519.055. Found: 519.204.

4.10. 1,4,6-Tri-*O*-acetyl-2-*O*-benzoyl-3-deoxy-3-methylsulfonato-α,β-D-galactopyranose (14)

To a solution of compound **13** (0.896 g, 1.8 mmol) in MeOH (5 mL) was added Amberlite IR-120H$^+$ cation exchange resin until pH ~ 1. The mixture was filtered and cooled to 0 °C and freshly prepared diazo-methane in ether was added until a pale yellow colour was sustained. The mixture was concentrated under diminished pressure and was purified by column chromatography (98:2 CH_2Cl_2–acetone, R_f 0.50) to give an unseparable mixture of the α and β anomers of **14** in a 4:1 ratio (0.39 g, 44%) as a syrup. Anal. Calcd for $C_{20}H_{24}O_{12}S$ (488.46): C, 49.18; H, 4.95; S, 6.56. Found: C, 49.01; H, 5.01; S, 6.51. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 511.089. Found: 511.258.

4.11. Ethyl 4,6-di-*O*-acetyl-2-*O*-benzoyl-3-deoxy-3-methylsulfonato-1-thio-α,β-D-galactopyranose (15)

To a solution of compound **14** (201 mg, 0.58 mmol) in dry CH_2Cl_2 was added EtSH (128 μL, 3 equiv). The mixture was cooled to 0 °C and $BF_3 \cdot OEt_2$ (143 μL, 2 equiv) was added. The mixture was stirred for 1 h, then diluted with CH_2Cl_2, washed three times with water, dried ($MgSO_4$) and concentrated. Column chromatography

(98:2 CH_2Cl_2–acetone, R_f 0.66) of the residue gave an unseparable mixture of the α and β anomers of **15** in a 5:1 ratio (135 mg, 48%) as a syrup. Anal. Calcd for $C_{20}H_{26}O_{10}S$ (490.54): C, 48.97; H, 5.34; S, 13.07. Found: C, 48.88; H, 5.36; S, 13.10.

4.12. Allyl 2-acetamido-3-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-3-deoxy-3-methylsulfonato-α-D-galactopyranosyl)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (16)

Bromo sugar **5** was freshly prepared from **15** (70 mg, 0.14 mmol) according to general method **IV**. To a stirred suspension of acceptor **8** (100 mg, 0.29 mmol, 2 equiv) in dry CH_3NO_2 (1 mL) and dry toluene (2 mL) containing activated 3 Å molecular sieves (powdered, 0.5 g) was added $Hg(CN)_2$ (150 mg, 2 equiv) and the mixture cooled to 0 °C. The bromo sugar in dry CH_3NO_2 (1 mL) was added via syringe and the mixture was stirred for 2 h when TLC showed disappearance of the donor. The mixture was diluted with CH_2Cl_2 and filtered through a layer of Celite and the filtrate was washed twice with aq KI (5%) and water, dried ($MgSO_4$) and concentrated. Column chromatography (96:4, CH_2Cl_2–MeOH) of the residue gave compound **16** (44 mg, 40%) as a syrup: $[\alpha]_D^{23}$ +20.5 (*c* 0.12, $CHCl_3$). ^{1}H NMR (500 MHz) δ=7.94 (d, 2H, *J*=7.2 Hz, arom.), 7.60 (t, 1H, *J*=7.5 Hz, arom.), 7.51 (d, 2H, *J*=6.6 Hz, arom.), 7.44 (t. 2H, *J*=7.8 Hz, arom.), 7.37–7.29 (m, 3H, arom.), 6.10 (d, 1H, *J*=7.1 Hz, NH*A*c), 5.93–5.84 (m, 1H, OCH_2CHCH_2), 5.58 (d, 1H, *J*=2.5 Hz, H-2′), 5.53 (s, 1H, PhC*H*), 5.32–5.18 (m, 4H, H-1, H-1′, OCH_2CHCH_2), 5.16–5.12 (m, 1H, H-5′), 4.76 (dd, 1H, *J*=7.8, 1.6 Hz, H-4′), 4.57 (t, 1H, *J*=9.4 Hz, H-3), 4.37 (dd, 1H, *J*=10.5, 4.7 Hz, H-6a), 4.36–4.31 (m, 1H, OCH_2CHCH_2), 4.13–4.08 (m, 1H, OCH_2CHCH_2), 4.01–3.96 (m, 4H, H-6′a, OCH_3), 3.76 (t, 1H, *J*=10 Hz, H-6b), 3.67 (dd, 1H, *J*=7.8 Hz, *J*=2.5 Hz, H-3′), 3.62–3.56 (m, 1H, H-5), 3.54 (t, 1H, *J*=9.1 Hz, H-4), 3.18 (td, 1H, *J*=9.5, 7.9 Hz, H-2), 3.08 (dd, 1H, *J*=12.2, 2.5 Hz, H-6′b), 2.06 (s, 3H, $OCOCH_3$), 1.94, 1.91 (2 s, 6H, $OCOCH_3$, $NHCOCH_3$) ppm. ^{13}C NMR (125 MHz) δ=171.07, 170.47, 170.02 (2×$OCOCH_3$, $NHCOCH_3$), 165.59 (*O*COPh), 137.28, 133.99, 129.65, 129.10, 128.66, 128.52, 128.32, 126.39 (arom. *C*s), 133.71 (OCH_2CHCH_2), 117.81 (OCH_2CHCH_2), 105.49 (C-1′, *J*=179 Hz), 101.94 (PhCH, *J*=163 Hz), 98.93 (C-1, *J*=167 Hz), 80.60 (C-4), 79.43 (C-2), 77.19 (C-4′), 73.16 (C-3), 70.57 (OCH_2CHCH_2), 69.76 (C-5′), 68.83 (C-6), 66.02 (C-5), 63.78 (C-3′), 63.38 (C-6), 59.23 (C-2), 56.75 (OCH_3), 23.44 ($NHCOCH_3$), 20.70, 20.60 (2×$OCOCH_3$) ppm. Anal. Calcd for $C_{36}H_{43}O_{16}NS$ (777.79): C, 55.59; H, 5.57; N, 1.80; S, 4.12. Found: C, 55.50; H, 5.62; N, 1.85; S, 4.05. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 800.22. Found: 800.41.

4.13. Ethyl 3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (18)

Prepared from **17** (2.05 g, 2.66 mmol) according to general method **II** and purified by column chromatography (95:5 CH_2Cl_2–acetone) to give compound **18** (1.58 g, 77%) as a syrup: $[\alpha]_D^{23}$ −10.3 (*c* 0.18, $CHCl_3$). IR ν_{max} (KBr) 3477, 2930, 2871, 1752, 1715, 1468, 1453, 1428, 1386, 1219, 1172, 1136, 1078, 969, 736, 722, cm^{-1}; ^{1}H NMR (360 MHz) δ=7.94–7.72 (m, 4H, arom.), 7.40–7.22 (m, 5H, arom.), 5.29 (d, 1H, *J*=3.0 Hz, H-4′), 5.16 (d, 1H, *J*=10.5 Hz, H-1), 5.14 (dd, 1H, *J*=10.6 Hz, *J*=8 Hz, H-2′), 4.80 (dd, 1H, *J*=10.5 Hz, *J*=3.4 Hz, H-3′), 4.67–4.59 (m, 2H, PhC*H*$_2$), 4.55–4.47 (m, 1H, H-3), 4.40 (d, 1H, *J*=8 Hz, H-1′), 4.33 (t, 1H, *J*=10.4 Hz, H-2), 4.14–4.07 (m, 2H, H-6′a,b), 3.99–3.88 (m, 3H, H-5′, H-6a, OH), 3.77–3.71 (m, 1H, H-6b), 3.70–3.62 (m, 2H, H-5, H-4), 2.76–2.56 (m, 2H, SCH_2CH_3), 2.13, 2.04, 1.88, 1.53 (4×s, 12H, 4×$OCOCH_3$), 1.18 (t, 3H, *J*=7.4 Hz, SCH_2CH_3) ppm. ^{13}C NMR (90 MHz) δ=170.28, 169.98, 169.85, 168.75 (4×$OCOCH_3$), 168.42, 167.14 (2×C=O, NPhth), 138.29, 134.43, 131.43, 131.34, 128.22, 127.46, 123.71, 123.58 (arom. *C*s), 100.89 (C-1′, *J*=162.4 Hz), 82.84 (C-3), 80.95 (C-1, *J*=157.6 Hz), 79.79 (C-4), 73.37 (PhCH_2), 71.06 (C-5′), 70.70 (C-3′), 69.62 (C-5), 69.57 (C-6), 68.39 (C-2′), 66.70 (C-4′), 61.36 (C-6′), 53.80 (C-2), 23.92 (SCH_2CH_3), 20.48, 20.44, 20.30, 19.78 (4×$OCOCH_3$), 14.82 (SCH_2CH_3) ppm. Anal. Calcd for $C_{37}H_{43}O_{15}NS$ (773.80): C, 57.43; H, 5.60; N, 1.81; S, 4.14. Found: C, 57.39; H, 5.62; N, 1.83; S, 4.13. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 796.23. Found: 796.21.

4.14. Ethyl 3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (19)

Bromo sugar **6** was prepared from thioglycoside donor (1.39 g, 3.0 mmol, 1.05 equiv) and coupled with acceptor **18** (2.21 g, 2.86 mmol) according to general method **III**. Column chromatography of the residue (1:1 hexane–EtOAc) gave compound **19** (1.33 g, 52%) as a syrup and **18** (1.10 g, 33%) was also recovered. Compound **19**: $[\alpha]_D^{23}$ −45 (*c* 0.13, $CHCl_3$). ^{1}H NMR (360 MHz) δ=7.90–7.73 (m, 4H, arom.), 7.48–7.17 (m, 20H, arom.), 5.25 (br d, 1H, *J*=2.6 Hz), 5.18 (s, 1H), 5.08 (d, 1H, *J*=10.4 Hz), 5.02 (t, 1H, *J*=9.2 Hz), 4.95–4.63 (m, 7H), 4.59–4.44 (m, 3H), 4.43–4.32 (m, 2H), 4.26 (d, 1H, *J*=8.4 Hz), 4.22–4.12 (m, 2H), 4.07–3.94 (m, 4H), 3.91 (s, 1H), 3.82 (d, 1H, *J*=12.8 Hz), 3.72–3.58 (m, 3H), 2.75–2.50 (m, 2H, SCH_2CH_3), 2.03, 1.97, 1.84, 1.60 (4×s, 12H, 4×$OCOCH_3$), 1.15 (t, 3H, *J*=7.4 Hz, SCH_2CH_3) ppm. ^{13}C NMR (90 MHz) δ=170.04, 169.98, 169.78, 169.43 (4×$OCOCH_3$), 138.86, 138.67, 138.46, 138.29, 134.84, 128.59, 128.44, 128.38, 127.80, 127.64, 127.58, 127.40, 127.24, 123.76 (arom. *C*s), 100.24 (C-1′, *J*=161.8 Hz), 98.23 (C-1″, *J*=172.4 Hz), 80.89 (C-1, *J*=158.3 Hz), 80.08, 78.82, 75.94, 75.16, 74.02, 73.16, 70.38, 68.12, 66.39 (skeleton *C*s), 74.98, 73.22, 72.09, 71.05 (overlap) (4×PhCH_2), 67.66 (C-6), 60.53, 59.92 (C-6′, C-5″), 55.31 (C-2), 23.46 (SCH_2CH_3), 20.63, 20.57, 20.50, 20.20 (4×$OCOCH_3$), 15.00 (SCH_2CH_3) ppm. Anal. Calcd for $C_{63}H_{69}O_{19}NS$ (1176.28): C, 64.33; H, 5.91; N, 1.19; S, 2.73. Found: C, 64.20; H, 6.01; N, 1.17; S, 2.69. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1198.41. Found: 1198.41.

4.15. Ethyl 3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (20)

Bromo sugar **7** was prepared from thioglycoside donor (4.78 g, 3.0 mmol, 1.5 equiv) and coupled with acceptor **18** (7.2 g, 9.3 mmol) according to general method **III**. Column chromatography of the residue (92:8 CH_2Cl_2–EtOAc) gave compound **20** (6.21 g, 56%) as a syrup and **18** was also recovered (3.26 g, 27%). Compound **20** has $[\alpha]_D^{23}$ −11.3 (*c* 0.20, $CHCl_3$). IR ν_{max} (KBr) 3434, 2932, 2872, 1755, 1715, 1611, 1427, 1388, 1315, 1031, 952, 912, 736, 721, 698, 600 cm^{-1}; ^{1}H NMR (360 MHz) δ=7.92–7.76 (m, 4H, arom.), 7.47 (d, 2H, *J*=7.8 Hz, arom.), 7.40–7.20 (m, 18H, arom.), 5.25–5.19 (m, 2H), 5.06 (d, 1H, *J*=10.5 Hz, H-1), 5.07–4.97 (m, 2H, H-2′, PhCH_2), 4.94–4.71 (m, 7H, H-3, H-5″, PhCH_2), 4.48–4.41 (m, 3H, H-3′, PhCH_2), 4.37 (t, 1H, *J*=10.3 Hz, H-2), 4.30–4.17 (m, 3H, H-1′, H-2′, H-6′a), 4.07–3.95 (m, 4H, H-3″, H-4, H-6a, H-6′b), 3.79 (s, 1H, H-4″), 3.74–3.59 (m, 3H, H-5, H-5′, H-6b,), 2.76–2.50 (m, 2H, SCH_2CH_3), 2.02, 2.00, 1.84, 1.73 (4×s, 12H, 4×$OCOCH_3$), 1.33 (d, 3H, *J*=6.3 Hz, C*H*$_3$-6″), 1.17 (t, 3H, *J*=7.4 Hz, SCH_2CH_3) ppm. ^{13}C NMR (90 MHz) δ=169.85, 169.72, 169.57, 169.07 (4×$OCOCH_3$), 138.58, 138.48, 138.10, 134.59, 128.56, 128.23, 128.10, 127.63, 127.46, 127.28, 127.17, 126.79, 123.50 (arom. *C*s), 100.34 (C-1′, *J*=161.7 Hz), 97.51 (C-1″, *J*=170.9 Hz), 80.68 (C-3), 80.57 (C-1, *J*=153.1 Hz), 79.91 (C-5), 76.15 (C-4″), 75.53 (C-2″), 75.30 (C-3″), 72.50 (C-4), 70.86 (C-3′), 70.06 (C-5′), 67.64 (C-2′), 66.13 (double int., C-4′, C-5″), 74.72, 73.72, 72.90, 72.05 (4×PhCH_2), 67.23 (C-6), 59.54 (C-6′), 55.05 (C-2), 23.25 (SCH_2CH_3), 20.40, 20.27 (double int.), 20.23 (4×$OCOCH_3$), 16.80 (C-6″), 14.77 (SCH_2CH_3) ppm. Anal. Calcd for $C_{64}H_{71}O_{19}NS$ (1190.31): C, 64.58; H, 6.01; N, 1.18; S, 2.69. Found: C, 64.50; H, 6.05; N, 1.19; S, 2.71. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1212.42. Found: 1212.55.

4.16. Ethyl 6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-2-deoxy-3-*O*-(β-D-galactopyranosyl)-2-phthalimido-1-thio-β-D-glucopyranoside (21)

To a solution of compound **19** (880 mg, 0.75 mmol) in dry THF (10 mL) and dry CH_2Cl_2 (10 mL) was added three drops of $NaOCH_3$ (30% in MeOH) and the reaction stirred for 1 h. The mixture was neutralized with Amberlite IR-120H$^+$ cation exchange resin, filtered and concentrated. Column chromatography of the residue (94:6 CH_2Cl_2–MeOH) gave compound **21** (679 mg, 90%) as a syrup: $[\alpha]_D^{23}$ −45.1 (*c* 0.13, $CHCl_3$). ^{1}H NMR (360 MHz) δ=7.88–7.66 (m, 4H, arom.), 7.36–7.19 (m, 20H, arom.), 5.24–5.15 (m, 2H), 4.82 (t, 1H, *J*=9.7 Hz), 4.76 (d, 1H, *J*=10.7 Hz), 4.68–4.53 (m, 6H), 4.36 (s, 2H), 4.38 (t, 1H, *J*=10.4 Hz), 4.19–4.10 (m, 2H), 4.02 (t, 1H, *J*=9.4 Hz), 3.93–3.46 (m, 13H), 3.30–3.07 (m, 3H), 2.73–2.52 (m, 2H, SC*H*$_2$CH$_3$), 1.17 (t, 3H, *J*=7.4 Hz, SCH$_2$C*H*$_3$) ppm. ^{13}C NMR (90 MHz) δ=138.58, 138.34, 138.11, 134.32, 128.35, 128.28, 127.78, 127.71, 127.54 (arom. *C*s), 101.69 (C-1′), 97.88 (C-1″), 80.97 (C-1), 79.51, 76.11, 75.35, 74.61, 74.05, 73.62, 73.16, 70.36, 69.50 (skeleton *C*s), 74.46, 73.04, 72.08, 71.61 (4×PhC*H*$_2$), 68.26 (C-6), 62.99, 61.37 (C-6′, C-5″), 54.95 (C-2), 23.76 (SC*H*$_2$CH$_3$), 14.93 (SCH$_2$C*H*$_3$) ppm. Anal. Calcd for $C_{55}H_{61}O_{15}NS$ (1008.14): C, 65.53; H, 6.10; N, 1.39; S, 3.18. Found: C, 65.48; H, 6.13; N, 1.41; S, 3.15. MALDI-TOF: *m*/*z* calcd for [M+Na]$^+$ 1030.37. Found: 1030.72.

4.17. Ethyl 6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-3-*O*-(β-D-galactopyranosyl)-2-phthalimido-1-thio-β-D-glucopyranoside (22)

Prepared from **20** (6.19 g, 5.21 mmol) in a similar manner as described in Section 4.16. Column chromatography of the residue (neat EtOAc) gave compound **22** (4.69 g, 88%) as a syrup: $[\alpha]_D^{23}$ −43.8 (*c* 0.19, $CHCl_3$). ^{1}H NMR (360 MHz) δ=7.83–7.58 (m, 4H, arom.), 7.42–7.15 (m, 20H, arom.), 5.20 (bd, 1H, *J*=2.3 Hz), 5.11 (d, 1H, *J*=10.3 Hz, H-1), 4.93 (d, 1H, *J*=11.2 Hz), 4.86–4.50 (m, 7H), 4.44 (s, 2H), 4.39 (t, 1H, *J*=10.4 Hz), 4.10–3.58 (m, 11H), 3.42–2.98 (m, 7H), 2.73–2.50 (m, 2H, SC*H*$_2$CH$_3$), 1.16 (t, 3H, *J*=7.2 Hz, SCH$_2$C*H*$_3$), 1.09 (d, 3H, *J*=5.8 Hz, C*H*$_3$-6″) ppm. ^{13}C NMR (90 MHz) δ=138.86, 138.80, 138.17, 138.04, 128.50, 128.32, 128.25, 128.06, 127.74, 127.51, 127.42, 127.35, 127.24 (arom. *C*s), 101.96 (C-1′, *J*=158.2 Hz), 97.16 (C-1″, *J*=168.7 Hz), 80.87 (C-1, *J*=159.9 Hz), 79.62 (double int.), 77.92, 76.27, 75.91, 74.12, 73.44, 72.92, 70.74, 69.02, 66.74 (skeleton *C*s), 74.90, 74.59, 73.00, 72.08 (4×PhC*H*$_2$), 67.89 (C-6), 62.65 (C-6′), 55.08 (C-2), 23.63 (SC*H*$_2$CH$_3$), 16.60 (C-6″), 14.92 (SCH$_2$C*H*$_3$) ppm. Anal. Calcd for $C_{56}H_{63}O_{15}NS$ (1022.16): C, 65.80; H, 6.21; N, 1.37; S, 3.14. Found: C, 65.69; H, 6.28; N, 1.35; S, 3.12. MALDI-TOF: *m*/*z* calcd for [M+Na]$^+$ 1044.38. Found: 1044.57.

4.18. Ethyl 6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-3-*O*-(4,6-*O*-benzylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (23)

Prepared from **21** (1.216 g, 1.21 mmol) according to general method **I**. Column chromatography of the residue (96:4 CH_2Cl_2–MeOH) gave compound **23** (1.12 g, 85%) as a syrup: $[\alpha]_D^{23}$ −59 (*c* 0.19, $CHCl_3$). ^{1}H NMR (360 MHz) δ=7.90–7.65 (m, 4H, arom.), 7.44–7.14 (m, 25H, arom.), 5.45 (s, 1H, PhC*H*), 5.20 (d, 1H, *J*=10.4 Hz, H-1), 5.16 (d, 1H, *J*=3.4 Hz), 4.85 (d, 1H, *J*=11.5 Hz), 4.76 (t, 1H, *J*=9.7 Hz), 4.68–4.35 (m, 7H), 4.12 (d, 1H, *J*=12.1 Hz), 4.03–3.82 (m, 9H), 3.71–3.42 (m, 5H), 3.18 (s, 1H), 3.10 (dd, 1H, *J*=9.3, 2.8 Hz), 2.89 (br s, 1H, OH), 2.80–2.50 (m, 3H, OH, SC*H*$_2$CH$_3$), 1.17 (t, 3H, *J*=7.4 Hz, SCH$_2$C*H*$_3$) ppm. ^{13}C NMR (90 MHz) δ=168.82, 168.01 (2×C=O, NPhth), 139.15, 138.89, 138.37, 138.09, 137.57, 128.40, 128.09, 127.82, 127.38, 127.56, 126.95, 125.70 (arom. *C*s), 102.83 (PhC*H*, *J*=157.4 Hz), 100.09 (C-1′, *J*=162.3 Hz), 98.26 (C-1″, *J*=170.9 Hz), 80.75 (C-1, *J*=158.6 Hz), 79.96, 77.89, 76.81, 75.40, 75.07, 74.78, 73.53, 72.03, 70.53, 66.39 (skeleton *C*s), 74.73, 72.90, 71.56, 70.48 (4×PhC*H*$_2$), 68.94, 67.37 (C-6, C-6′), 60.92 (C-5″), 55.13 (C-2), 23.49 (SC*H*$_2$CH$_3$), 14.85 (SCH$_2$C*H*$_3$) ppm. Anal. Calcd for $C_{62}H_{65}O_{15}NS$ (1096.24): C, 67.93; H, 5.98; N, 1.28; S, 2.92. Found: C, 67.78; H, 6.02; N, 1.30; S, 2.96. MALDI-TOF: *m*/*z* calcd for [M+2Na]$^+$ 1141.39. Found: 1142.71.

4.19. Ethyl 6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-(4,6-*O*-benzylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (24)

Prepared from **22** (3.68 g, 3.6 mmol) according to general method **I**. Column chromatography of the residue (7:3 EtOAc–hexane) gave compound **24** (3.79 g, 78%) as a syrup: $[\alpha]_D^{23}$ −47 (*c* 0.13, $CHCl_3$). ^{1}H NMR (360 MHz) δ=7.93–7.64 (m, 4H, arom.), 7.51 (d, 2H, *J*=7.7 Hz, arom.), 7.36–7.13 (m, 23H, arom.), 5.55 (s, 1H, PhC*H*), 5.21 (dd, 1H, *J*=10.4, 2.3 Hz), 5.08 (s, 1H), 4.88–4.52 (m, 6H), 4.42–4.36 (m, 3H), 4.27 (dd, 2H, *J*=22.7 Hz, *J*=11.7 Hz), 4.04–3.89 (m, 7H), 3.73–3.54 (m, 4H), 3.31 (s, 1H), 3.26 (s, 1H), 3.13 (dd, 1H, *J*=9.3, 2.9 Hz), 2.75–2.51 (m, 4H, 2×OH, SC*H*$_2$CH$_3$), 1.17 (t, 3H, *J*=7.4 Hz, SCH$_2$C*H*$_3$), 1.04 (d, 3H, *J*=6.3 Hz, C*H*$_3$-6″) ppm. ^{13}C NMR (90 MHz) δ=168.85, 168.16 (2×C=O, NPhth), 139.24, 139.01, 138.30, 138.17, 137.47, 134.56, 134.03, 131.78, 130.86, 128.78, 128.63, 128.10, 127.77, 127.49, 127.37, 127.27, 127.20, 127.08, 126.84, 125.57, 124.09, 123.03 (arom. *C*s), 103.50 (PhC*H*, *J*=157.6 Hz), 99.75 (C-1′, *J*=168.3 Hz), 97.80 (C-1″, *J*=173.6 Hz), 80.60 (C-1, *J*=159.2 Hz), 80.01, 79.49, 78.43, 76.88, 75.00, 74.91, 72.92, 72.12, 70.68, 66.55, 66.08 (skeleton *C*s), 74.77, 74.61, 72.81, 71.03 (4×PhC*H*$_2$), 69.06, 67.30 (C-6, C-6′), 55.29 (C-2), 23.35 (SC*H*$_2$CH$_3$), 16.30 (C-6″), 14.92 (SCH$_2$C*H*$_3$) ppm. Anal. Calcd for $C_{63}H_{67}O_{15}NS$ (1110.27): C, 68.15; H, 6.08; N, 1.26; S, 2.89. Found: C, 68.03; H, 6.12; N, 1.28; S, 2.87. MALDI-TOF: *m*/*z* calcd for [M+Na]$^+$ 1132.41. Found: 1132.59.

4.20. Ethyl 6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-3-*O*-(4,6-*O*-benzylidene-3-*O*-chloroacetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (25)

A solution of compound **23** (569 mg, 0.52 mmol) and Bu_2SnO (168 mg, 1.3 equiv) in dry toluene (15 mL) was stirred using a Dean–Stark apparatus containing activated 4 Å molecular sieves at reflux for 3 h. The mixture was concentrated and dried under high vacuum for 3 h. To a solution of the crude acetal in dry DMF (3 mL) and dry toluene (2 mL) containing activated 4 Å molecular sieves was added chloroacetyl chloride (50 μL, 1.05 equiv) at 0 °C. After stirring for 1 h the mixture was filtered through Celite, concentrated and coevaporated twice with toluene. Column chromatography of the residue (96:4 CH_2Cl_2–acetone) gave compound **25** (475 mg, 78%) as a syrup: $[\alpha]_D^{23}$ −18.3 (*c* 0.12, $CHCl_3$). IR ν_{max} (KBr) 3014, 2969, 2358, 2341, 1736, 1364, 1228, 1216, 1107, 903, 527, 516 cm^{-1}; ^{1}H NMR (360 MHz) δ=7.88–7.79 (m, 2H), 7.72–7.65 (m, 2H), 7.47–7.40 (m, 2H), 7.35–7.14 (m, 23H), 5.43 (s, 1H, PhC*H*), 5.21 (d, 1H, *J*=7.4 Hz), 5.16 (d, 1H, *J*=3.2 Hz), 4.88–4.77 (m, 2H), 4.69–4.33 (m, 8H), 4.27–3.78 (m, 13H), 3.65 (dd, 2H, *J*=20.6, 10.3 Hz), 3.51–3.42 (m, 2H), 3.28 (s, 1H), 2.82 (br s, 1H, OH), 2.73–2.50 (m, 2H, SC*H*$_2$CH$_3$), 1.16 (t, 3H, *J*=7.4 Hz, SCH$_2$C*H*$_3$) ppm. ^{13}C NMR (90 MHz) δ=168.70, 168.07 (2×C=O, NPhth), 166.81 (*C*OCH$_2$Cl), 139.10, 138.84, 138.30, 138.03, 137.40, 134.53, 134.21, 128.76, 128.35, 128.06, 127.79, 127.40, 127.33, 127.26, 127.20, 127.05, 126.88, 126.79, 125.50, 123.89, 123.19 (arom. *C*s), 102.55 (PhC*H*, *J*=156.2 Hz), 99.77 (C-1′, *J*=158.3 Hz), 98.27 (C-1″, *J*=173.7 Hz), 80.65 (C-1, *J*=153.6 Hz), 79.84, 77.76, 76.56, 75.34, 75.07, 74.86, 73.56, 72.35, 67.41, 66.00 (skeleton *C*s), 74.69, 72.85, 71.52, 70.57 (4×PhC*H*$_2$), 68.74, 67.28 (C-6, C-6′), 60.89 (C-5″), 55.06 (C-2), 40.58 (COC*H*$_2$Cl), 23.45 (SC*H*$_2$CH$_3$), 14.83 (SCH$_2$C*H*$_3$) ppm. Anal. Calcd for $C_{64}H_{66}O_{16}NSCl$

(1172.72): C, 65.55; H, 5.67; N, 1.19; S, 2.73; Cl, 3.02. Found: C, 65.42; H, 5.73; N, 1.20; S, 2.69. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1194.37. Found: 1194.46.

4.21. Ethyl 6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-(4,6-*O*-benzylidene-3-*O*-chloroacetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (26)

Prepared from **24** (3.78 g, 3.40 mmol) in a similar manner as described in Section 4.20. Column chromatography of the residue (9:1 CH_2Cl_2–EtOAc) gave compound **26** (3.20 g, 79%) as a syrup: $[\alpha]_D^{23}$ −10.6 (*c* 0.21, $CHCl_3$). ^1H NMR (360 MHz) δ=7.86 (dd, 2H, *J*=15.8 Hz, *J*=6.0 Hz, arom.), 7.75–7.65 (m, 2H, arom.), 7.49 (d, 2H, *J*=7.1 Hz, arom.), 7.37–7.12 (m, 23H), 5.50 (s, 1H, PhC*H*), 5.22 (d, 1H, *J*=10.4 Hz), 5.11 (d, 1H, *J*=3.1 Hz), 4.88–4.74 (m, 3H), 4.71–4.57 (m, 3H), 4.48–4.25 (m, 6H), 4.22 (d, 1H, *J*=11.2 Hz), 4.14–3.89 (m, 8H), 3.85 (t, 1H, *J*=8.8 Hz), 3.65 (dd, 2H, *J*=20.5, 10.3 Hz), 3.52 (d, 1H, *J*=11.3 Hz), 3.32 (s, 1H), 3.25 (s, 1H), 2.75–2.51 (m, 3H, OH, SC*H*$_2$CH$_3$), 1.17 (t, 3H, *J*=7.4 Hz, SCH$_2$C*H*$_3$), 1.06 (d, 3H, *J*=6.3 Hz, C*H*$_3$-6″) ppm. ^{13}C NMR (90 MHz) δ=168.82, 168.30 (2×C=O, NPhth), 166.87 (*C*OCH$_2$Cl), 139.21, 138.99, 138.26, 138.13, 137.40, 134.70, 134.28, 131.57, 130.76, 128.75, 128.61, 128.09, 127.77, 127.49, 127.34, 127.27, 127.21, 127.14, 126.84, 125.46, 124.04, 123.24 (arom. *C*s), 102.91 (PhCH, *J*=158.6 Hz), 99.50 (C-1′, *J*=160.5 Hz), 97.84 (C-1″, *J*=169.9 Hz), 80.52 (C-1, *J*=155.7 Hz), 79.94, 79.43, 78.42, 76.90, 74.97 (double int.), 72.96, 72.37, 67.51, 66.10, 66.05 (skeleton *C*s), 74.74, 74.60, 72.84, 71.06 (4×PhC*H*$_2$), 68.89, 67.22 (C-6, C-6′), 55.27 (C-2), 40.65 (COC*H*$_2$Cl), 23.32 (S*C*H$_2$CH$_3$), 16.28 (C-6″), 14.93 (SCH$_2$*C*H$_3$) ppm. Anal. Calcd for $C_{65}H_{68}O_{16}NSCl$ (1186.75): C, 65.78; H, 5.78; N, 1.18; S, 2.70; Cl, 2.99. Found: C, 65.70; H, 5.80; N, 1.16; S, 2.72. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1208.38. Found: 1208.57.

4.22. Ethyl 6-*O*-benzyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-chloroacetyl-β-D-galactopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (27)

To a solution of compound **25** (218 mg, 0.19 mmol) in dry CH_2Cl_2 (4 mL) and in dry pyridine (0.5 mL) was added BzCl (30 μL, 1.1 equiv) at 0 °C. The reaction only started when DMAP (1 equiv) was added to the mixture. After half an hour the mixture was diluted with CH_2Cl_2, washed with 1 M HCl, water, satd aq $NaHCO_3$ and water again, dried ($MgSO_4$) and concentrated. Column chromatography of the residue (1:1 EtOAc–hexane) gave compound **27** (191 mg, 80%) as a syrup: $[\alpha]_D^{23}$ −1.5 (*c* 0.13, $CHCl_3$). IR ν_{max} (KBr) 2867, 1774, 1715, 1452, 1383, 1366, 1264, 1139, 1092, 737, 720, 697 cm^{-1}; ^1H NMR (360 MHz) δ=7.82–7.73 (m, 4H, arom.), 7.46 (t, 4H, *J*=7.2 Hz, arom.), 7.36–7.16 (m, 26H), 5.59 (t, 1H, *J*=9.2 Hz), 5.51 (s, 1H, PhC*H*), 5.17 (d, 1H, *J*=2.8 Hz), 5.03–4.91 (m, 2H), 4.88–4.78 (m, 2H), 4.71 (d, 1H, *J*=12.6 Hz), 4.61–4.40 (m, 6H), 4.38–4.26 (m, 3H), 4.11–3.56 (m, 12H), 3.44–3.37 (m, 2H), 2.67–2.38 (m, 2H, SC*H*$_2$CH$_3$), 1.07 (t, 3H, *J*=7.4 Hz, SCH$_2$C*H*$_3$) ppm. ^{13}C NMR (90 MHz) δ=166.95 (*C*OCH$_2$Cl), 164.94 (PhC=O), 139.37, 139.20, 138.41, 138.22, 137.15, 134.37, 133.15, 131.31, 129.83, 129.30, 128.92, 128.61, 128.20, 128.11, 128.06, 127.84, 127.41, 127.27, 126.96, 126.75, 125.56 (arom. *C*s), 100.07 (PhCH, *J*=153.4 Hz), 99.82 (C-1′, *J*=161.6 Hz), 98.38 (C-1″, *J*=170.8 Hz), 80.69 (C-1, *J*=153.4 Hz), 80.17, 78.13, 75.60 (double int.), 75.23, 73.54, 73.35, 72.95, 68.65, 66.26 (skeleton *C*s), 74.86, 72.91, 71.64, 70.57 (4×PhC*H*$_2$), 68.93, 67.33 (C-6, C-6′), 60.72 (C-5″), 55.13 (C-2), 40.24 (COC*H*$_2$Cl), 23.11 (S*C*H$_2$CH$_3$), 14.77 (SCH$_2$*C*H$_3$) ppm. Anal. Calcd for $C_{71}H_{70}O_{17}NSCl$ (1276.83): C, 66.79; H, 5.53; N, 1.10; S, 2.51; Cl, 2.78. Found: C, 66.68; H, 5.54; N, 1.12; S, 2.50. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1298.40. Found: 1298.51.

4.23. Ethyl 6-*O*-benzyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-chloroacetyl-β-D-galactopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (28) and ethyl 6-*O*-benzyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (29)

Prepared from **26** (3.146 g, 2.65 mmol) in a similar manner as described in Section 4.22, but the mixture was stirred for 3 h. Column chromatography of the residue (98:2 CH_2Cl_2–acetone) gave compound **28** (1.494 g, 44%) as a syrup and dechloroacetylated derivative **29** (1.148 g, 34%) as a syrup. Compound **28**: $[\alpha]_D^{23}$ +1.5 (*c* 0.14, $CHCl_3$). IR ν_{max} (KBr) 2929, 2868, 1776, 1737, 1715, 1495, 1452, 1383, 1365, 1314, 1263, 1167, 1136, 1092, 1059, 1002, 952, 737, 712, 697 cm^{-1}; ^1H NMR (360 MHz) δ=7.91–7.69 (m, 5H, arom.), 7.64 (t, 1H, *J*=7.4 Hz, arom.), 7.58–7.42 (m, 5H, arom.), 7.37–7.16 (m, 23H), 5.60 (dd, 1H, *J*=10.6, 8.7 Hz), 5.58 (s, 1H, PhC*H*), 5.10 (d, 1H, *J*=3.3 Hz), 5.01–4.79 (m, 5H), 4.65 (d, 1H, *J*=11.6 Hz), 4.62 (s, 2H), 4.53–4.44 (m, 2H), 4.41–4.34 (m, 3H), 4.31 (t, 1H, *J*=10.5 Hz), 4.18–4.10 (m, 2H), 4.04–3.89 (m, 5H), 3.79 (d, 1H, *J*=15.2 Hz), 3.67–3.52 (m, 3H), 3.46 (s, 1H), 3.20 (s, 1H), 2.66–2.37 (m, 2H, SC*H*$_2$CH$_3$), 1.37 (d, 3H, *J*=6.4 Hz, C*H*$_3$-6″), 1.07 (t, 3H, *J*=7.4 Hz, SCH$_2$C*H*$_3$) ppm. ^{13}C NMR (90 MHz) δ=167.02 (O=*C*CH$_2$Cl), 164.88 (PhC=O), 139.44, 139.22, 138.33, 137.18, 134.33, 133.12, 131.30, 129.81, 129.33, 128.98, 128.78, 128.16, 128.08, 127.79, 127.53, 127.47, 127.30, 127.19, 127.07, 126.85, 125.67 (arom. *C*s), 100.34 (PhCH, *J*=159.1 Hz), 99.70 (C-1′, *J*=157.3 Hz), 97.94 (C-1″, *J*=170 Hz), 80.61 (C-1, *J*=156.8 Hz), 80.23, 79.65, 78.93, 75.75, 75.17, 73.73, 73.00, 72.93, 68.65, 66.33, 66.28 (skeleton *C*s), 74.89, 74.71, 72.83, 71.19 (4×PhC*H*$_2$), 69.00, 67.26 (C-6, C-6′), 55.10 (C-2), 40.27 (COC*H*$_2$Cl), 22.96 (SC*H*$_2$CH$_3$), 16.27 (C-6″), 14.82 (SCH$_2$*C*H$_3$) ppm. Anal. Calcd for $C_{72}H_{72}O_{17}NSCl$ (1290.86): C, 66.99; H, 5.62; N, 1.09; S, 2.48; Cl, 2.75. Found: C, 66.89; H, 5.66; N, 1.11; S, 2.46. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1312.41. Found: 1312.79.

Compound **29**: $[\alpha]_D^{23}$ −6.6 (*c* 0.12, $CHCl_3$). IR ν_{max} (KBr) 3454, 2969, 2918, 1736, 1434, 1364, 1227, 1216, 528 cm^{-1}; ^1H NMR (360 MHz) δ=7.90–7.66 (m, 6H, arom.), 7.62 (t, 1H, *J*=7.4 Hz, arom.), 7.54 (d, 2H, *J*=7.6 Hz, arom.), 7.47 (t, 2H, *J*=7.6 Hz, arom.), 7.36–7.15 (m, 23H), 5.61 (s, 1H, PhC*H*), 5.35 (t, 1H, *J*=9.0 Hz), 5.08 (br d, 1H, *J*=2.3 Hz), 4.97 (t, 2H, *J*=10.9 Hz), 4.87 (d, 1H, *J*=6.6 Hz), 4.83 (d, 1H, *J*=11.5 Hz), 4.65 (d, 1H, *J*=11.6 Hz), 4.60 (s, 2H), 4.46 (d, 1H, *J*=12.4 Hz), 4.41–4.32 (m, 4H), 4.20 (d, 1H, *J*=11.2 Hz), 4.12–4.06 (m, 2H), 4.03–3.92 (m, 4H), 3.66–3.57 (m, 3H), 3.43 (dt, 1H, *J*=10.4, 3.5 Hz), 3.37 (s, 1H), 3.25 (s, 1H), 2.69–2.42 (m, 3H, OH, SC*H*$_2$CH$_3$), 1.31 (d, 3H, *J*=6.3 Hz, C*H*$_3$-6″), 1.09 (t, 3H, *J*=7.4 Hz, SCH$_2$C*H*$_3$) ppm. ^{13}C NMR (90 MHz) δ=166.39 (PhC=O), 139.40, 139.20, 138.31, 137.23, 134.32, 132.99, 131.42, 129.97, 129.67, 129.00, 128.76, 128.16, 128.11, 128.06, 127.80, 127.53, 127.47, 127.27, 127.22, 127.06, 126.87, 125.62 (arom. *C*s), 100.03 (PhCH, *J*=159.9 Hz), 99.93 (C-1′, *J*=165.2 Hz), 97.91 (C-1″, *J*=169.8 Hz), 80.70 (C-1, *J*=156.5 Hz), 80.24, 79.64, 78.89, 75.58, 75.09 (triple int.), 72.91, 72.10, 71.97, 66.61, 66.30 (skeleton *C*s), 74.90, 74.69, 72.81, 71.21 (4×PhC*H*$_2$), 69.08, 67.29 (C-6, C-6′), 55.15 (C-2), 22.98 (SC*H*$_2$CH$_3$), 16.52 (C-6″), 14.82 (SCH$_2$*C*H$_3$) ppm. Anal. Calcd for $C_{70}H_{71}O_{16}NS$ (1214.37): C, 69.23; H, 5.89; N, 1.15; S, 2.64. Found: C, 69.18; H, 5.92; N, 1.13; S, 2.66. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1236.44. Found: 1236.74.

4.24. Methyl 6-*O*-benzyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-chloroacetyl-β-D-galactopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (30)

A solution of compound **27** (253 mg, 0.2 mmol) in dry CH_2Cl_2 (3 mL) containing activated 3 Å molecular sieves was added dry MeOH (34 μL, 4 equiv) and the reaction stirred at −70 °C for 2 h.

A mixture of NIS (44 mg, 1.3 equiv) and TMSOTf (8 μL, 0.25 equiv) in dry THF (0.5 mL) was added via syringe, stirred for overnight and allowed to reach rt. Pyridine (100 μL) was added to the reaction and the mixture was diluted with CH_2Cl_2, filtered through Celite. The filtrate was washed with satd aq $Na_2S_2O_3$, water, satd aq $NaHCO_3$, again with water, dried ($MgSO_4$) and concentrated. Column chromatography of the residue (98:2 CH_2Cl_2–acetone) gave compound **30** (228 mg, 90%) as a syrup: $[\alpha]_D^{23}$ −5.9 (*c* 0.10, $CHCl_3$). IR ν_{max} (KBr) 3747, 3062, 3030, 2865, 1775, 1715, 1633, 1496, 1467, 1220, 1139, 1091, 1052, 1027, 1000, 908, 787, 738, 712, 698, 639, 530 cm^{-1}; ^1H NMR (360 MHz) δ=7.79–7.58 (m, 7H, arom.), 7.50–7.18 (m, 27H), 5.58 (t, 1H, *J*=9.5 Hz, *J*=8.9 Hz), 5.51 (s, 1H, PhC*H*), 5.16 (d, 1H, *J*=2.7 Hz), 4.95 (t, 1H, *J*=9.9 Hz), 4.88–4.77 (m, 3H), 4.70 (d, 1H, *J*=12.5 Hz), 4.57–4.29 (m, 8H), 4.21 (t, 1H, *J*=10.2 Hz, *J*=8.9 Hz), 4.10–3.78 (m, 8H), 3.78–3.52 (m, 4H), 3.40 (s, 2H), 3.25 (s, 3H, OCH_3) ppm. ^{13}C NMR (90 MHz) δ=166.89 (*C*OCH_2Cl), 164.95 (PhC=O), 139.36, 139.16, 138.42, 138.12, 137.15, 134.25, 133.04, 131.28, 129.76, 129.27, 128.87, 128.52, 128.10, 127.80, 127.47, 127.39, 127.25, 126.98, 126.90, 126.71, 125.53, 123.51 (arom. *C*s), 99.95, 99.75, 98.61, 98.27 (Ph*C*H, C-1, C-1′, C-1″), 78.06, 75.65, 75.57, 75.47, 73.84, 73.46 (double int.), 68.88, 66.18 (skeleton *C*s), 74.83, 72.91, 71.48, 70.49 (4×Ph*C*H_2), 68.88, 67.03 (C-6, C-6′), 60.57 (C-5″), 56.01, 55.15 (OCH_3, C-2), 40.21 ($COCH_2Cl$) ppm. Anal. Calcd for $C_{70}H_{68}O_{18}NCl$ (1246.74): C, 67.44; H, 5.50; N, 1.12; Cl, 2.84. Found: C, 67.32; H, 5.56; N, 1.14. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1268.40. Found: 1268.59.

4.25. Methyl 6-*O*-benzyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (31)

To a solution of compound **30** (355 mg, 0.28 mmol) in CH_2Cl_2 (2 mL), MeOH (8 mL) and pyridine (2 mL) was added thiourea (77 mg, 5 equiv) and the reaction stirred overnight. The mixture was diluted with CH_2Cl_2, washed twice with water, dried ($MgSO_4$) and concentrated. Column chromatography of the residue (92:8 CH_2Cl_2–EtOAc) gave compound **31** (248 mg, 73%) as a syrup: $[\alpha]_D^{23}$ −21.4 (*c* 0.13, $CHCl_3$). IR ν_{max} (KBr) 3452, 3027, 2969, 2923, 1736, 1717, 1452, 1364, 1266, 1227, 1216, 1092, 1052, 1027, 997, 737, 713, 697, 528 cm^{-1}; ^1H NMR (360 MHz) δ=7.86 (d, 2H, *J*=7.8 Hz, arom.), 7.80–7.68 (m, 4H, arom.), 7.57 (t, 1H, *J*=7.2 Hz, arom.), 7.48–7.40 (m, 4H, arom.), 7.36–7.14 (m, 23H, arom.), 5.49 (s, 1H, PhC*H*), 5.31 (t, 1H, *J*=9 Hz), 5.15 (s, 1H), 4.99 (t, 1H, *J*=9.9 Hz), 4.85 (d, 1H, *J*=11.4 Hz), 4.80 (d, 1H, *J*=8.5 Hz), 4.71 (d, 1H, *J*=12.6 Hz), 4.57–4.30 (m, 7H), 4.56 (t, 1H, *J*=9.6 Hz), 4.05–3.88 (m, 8H), 3.73–3.53 (m, 3H), 3.48–3.38 (m, 2H), 3.25 (s, 4H), 2.64 (br s, 1H, OH) ppm. ^{13}C NMR (90 MHz) δ=166.33 (Ph*C*=O), 139.25, 139.04, 138.34, 138.02, 137.19, 134.22, 132.84, 131.25, 129.81, 129.55, 128.82, 128.39, 128.09, 128.01, 127.95, 127.75, 127.37, 127.19, 126.93, 126.84, 126.69, 125.47, 123.38 (arom. *C*s), 99.92, 99.63, 98.66, 98.20 (Ph*C*H, C-1, C-1′, C-1″), 78.03, 75.65, 75.50, 75.36 (double int.), 73.47, 73.30, 72.14, 71.55, 66.46 (skeleton Cs), 74.71, 72.82, 71.46, 70.50 (4×Ph*C*H_2), 68.87, 67.02 (C-6, C-6′), 60.61 (C-5″), 56.00, 55.93 (OCH_3, C-2) ppm. Anal. Calcd for $C_{68}H_{67}O_{17}N$ (1170.26): C, 69.79; H, 5.77; N, 1.20. Found: C, 69.68; H, 5.84; N, 1.18. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1192.43. Found: 1192.67.

4.26. Methyl 6-*O*-benzyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (32)

Prepared from **29** (104 mg, 0.08 mmol) in a similar manner as described in Section 4.24. Column chromatography of the residue (1:1 EtOAc–hexane) gave compound **32** (87 mg, 84%) as a syrup: $[\alpha]_D^{23}$ −6.6 (*c* 0.12, $CHCl_3$). IR ν_{max} (KBr) 3443, 2916, 2864, 1777, 1715, 1602, 1495, 1467, 1452, 1387, 1363, 1316, 1266, 1214, 1171, 1097, 1055, 1027, 1000, 903, 873, 821, 735, 722, 697 cm^{-1}; ^1H NMR (360 MHz) δ=7.94–7.16 (m, 34H), 5.60 (s, 1H, PhC*H*), 5.34 (t, 1H, *J*=8.9 Hz), 5.08 (s, 1H), 4.97 (t, 1H, *J*=9.9 Hz), 4.90–4.77 (m, 3H), 4.67–4.58 (m, 3H), 4.50–4.35 (m, 5H), 4.30–3.90 (m, 7H), 3.68–3.53 (m, 3H), 3.47–3.19 (m, 6H), 2.62 (br s, 1H, OH), 1.30 (d, 3H, *J*=5.9 Hz, *C*H_3-6″) ppm. ^{13}C NMR (90 MHz) δ=166.51 (Ph*C*=O), 139.42, 139.20, 138.36, 138.25, 137.29, 134.25, 132.95, 131.44, 129.96, 129.63, 128.98, 128.72, 128.14, 127.80, 127.43, 127.35, 127.22, 127.07, 126.85, 125.63, 123.52 (arom. *C*s), 99.95 (double int.), 98.73 (Ph*C*H, C-1, C-1′), 97.85 (C-1″, *J* 170.9 Hz), 79.62, 78.83, 75.66 (double int.), 75.29, 73.70, 73.06, 72.13, 72.00, 66.60, 66.30 (skeleton *C*s), 74.85, 74.72, 72.84, 71.19 (4×Ph*C*H_2), 69.09, 67.03 (C-6, C-6′), 55.99 (double int.)(OCH_3, C-2), 16.51 (C-6″) ppm. Anal. Calcd for $C_{69}H_{69}O_{17}N$ (1184.28): C, 69.98; H 5.87, N 1.18. Found: C 69.87, H 5.94, N 1.15. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1206.45. Found: 1206.41.

4.27. Methyl 6-*O*-benzyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-gulopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (33)

Prepared from **31** (245 mg, 0.21 mmol) according to general method **IV**. Column chromatography of the residue (1:1 EtOAc–hexane) gave compound **33** (170 mg, 70%) as a syrup: $[\alpha]_D^{23}$ −21.9 (*c* 0.15, $CHCl_3$). ^1H NMR (360 MHz) δ=7.97 (d, 2H, *J*=7.3 Hz, arom.), 7.80 (dd, 2H, *J*=5.2, 3.0 Hz, arom.), 7.68 (dd, 2H, *J*=5.3, 3.0 Hz, arom.), 7.60 (t, 1H, *J*=7.3 Hz, arom.), 7.49 (dd, 4H, *J*=14.6, 7.3 Hz, arom.), 7.33–7.16 (m, 23H, arom.), 5.49 (s, 1H, PhC*H*), 5.21 (dd, 1H, *J*=8.5, 2.5 Hz), 5.07 (s, 1H), 5.03 (dd, 1H, *J*=10.3, 9.4 Hz), 4.92 (d, 1H, *J*=8.5 Hz), 4.85 (d, 1H, *J*=6.6 Hz), 4.82 (d, 1H, *J*=9.4 Hz), 4.73 (d, 1H, *J*=12.5 Hz), 4.53–4.25 (m, 7H), 4.20 (s, 1H), 4.03–3.82 (m, 9H), 3.64–3.54 (m, 4H), 3.42 (s, 1H), 3.31 (s, 3H, OCH_3) ppm. ^{13}C NMR (90 MHz) δ=165.46 (Ph*C*=O), 139.36, 139.17, 138.48, 138.08, 137.71, 134.21, 133.21, 131.49, 129.97, 129.41, 128.69, 128.49, 128.19, 128.10, 128.03, 127.83, 127.50, 127.36, 126.98, 126.75, 125.60, 123.29 (arom. *C*s), 99.62, 98.93 (Ph*C*H, C-1), 98.26 (C-1″, *J*=170.9 Hz), 96.21 (C-1′, *J*=164.4 Hz), 78.14, 76.12, 75.73, 75.50, 75.44, 73.47, 72.38, 71.14, 68.88, 65.90 (skeleton *C*s), 74.80, 73.47, 71.54, 70.56 (4×Ph*C*H_2), 69.25, 67.09 (C-6, C-6′), 60.77 (C-5″), 56.25, 56.16 (OCH_3, C-2) ppm. Anal. Calcd for $C_{68}H_{67}O_{17}N$ (1170.26): C, 69.79; H, 5.77; N, 1.20. Found: C, 69.62; H, 5.83; N, 1.17. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1192.43. Found: 1192.66.

4.28. Methyl 6-*O*-benzyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-gulopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (34)

Prepared from **32** (936 mg, 0.79 mmol) according to general method **IV**. Column chromatography of the residue (1:1 EtOAc–hexane) gave compound **34** (625 mg, 64%) as a syrup: $[\alpha]_D^{23}$ −11 (*c* 0.25, $CHCl_3$). IR ν_{max} (KBr) 3410, 3062, 3030, 2922, 2853, 2357, 1777, 1715, 1496, 1452, 1386, 1361, 1316, 1270, 1220, 1135, 1097, 1044, 1027, 1015, 995, 754, 737, 722, 699 cm^{-1}; ^1H NMR (360 MHz) δ=7.95 (d, 2H, *J*=7.9 Hz, arom.), 7.83–7.76 (m, 2H, arom.), 7.69 (dd, 2H, *J*=5.3 Hz, *J*=3.1 Hz, arom.), 7.63–7.46 (m, 5H, arom.), 7.35–7.14 (m, 23H, arom.), 5.56 (s, 1H, PhC*H*), 5.26 (dd, 1H, *J*=8.4, 2.1 Hz), 5.06–4.98 (m, 2H), 4.93–4.78 (m, 4H), 4.61–4.55 (m, 3H), 4.44–4.25 (m, 4H), 4.21 (s, 1H), 4.16 (d, 1H, *J*=11.3 Hz), 4.06 (d, 1H, *J*=11.3 Hz), 3.99–3.88 (m, 5H), 3.66–3.51 (m, 4H), 3.30 (s, 3H, OCH_3), 3.22 (s, 1H), 1.88–1.70 (br s, 1H, OH), 1.23 (d, 3H, *J*=6.9 Hz, *C*H_3-6″) ppm. ^{13}C NMR (90 MHz) δ=165.32 (Ph*C*=O), 139.46, 139.24, 138.40, 138.18, 137.73, 134.18, 133.23, 131.50, 129.98, 129.37, 128.68, 128.20,

128.09, 127.78, 127.44, 127.38, 127.26, 127.03, 126.83, 125.71, 123.32 (arom. *C*s), 99.52, 98.90 (PhCH, C-1), 97.81 (C-1″, *J*=169.1 Hz), 96.39 (C-1′, *J*=161.3 Hz), 79.57, 78.81, 76.16, 75.56, 75.32, 72.98, 72.73, 71.07, 69.01, 66.29, 65.91 (skeleton *C*s), 74.83, 74.67, 72.81, 71.14 (4×PhCH$_2$), 69.33, 67.04 (C-6, C-6′), 56.15 (double int.)(OCH$_3$, C-2), 16.49 (C-6″) ppm. Anal. Calcd for $C_{69}H_{69}O_{17}N$ (1184.28): C, 69.98; H, 5.87; N, 1.18. Found: C, 69.90; H, 5.91; N, 1.16. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1206.45. Found: 1206.76.

4.29. Methyl 3-*O*-(3-*S*-acetyl-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (35)

To a solution of compound **33** (205 mg, 0.18 mmol) in dry CH_2Cl_2 (2 mL) and pyridine (0.5 mL) in a CEM equipped vessel was added dropwise Tf_2O (67 μL, 1.6 equiv) at 0 °C and the mixture was allowed to reach rt and stirred for half an hour. The mixture was activated under MW conditions (*t*=1 h, *T*=35 °C, power=10 kW, pressure=20 PSI), then diluted with CH_2Cl_2, washed twice with water, dried ($MgSO_4$) and concentrated. The crude triflate was left under high vacuum for 3 h. To a solution of the crude triflate in dry DMF (6 mL) was added KSAc (62 mg, 3 equiv) and the reaction stirred at 70 °C for 2 h. The residue was diluted with EtOAc, washed three times with water, dried ($MgSO_4$) and concentrated. Column chromatography (1:1 EtOAc–hexane) of the residue gave compound **35** (150 mg, 70%) as a syrup: $[\alpha]_D^{23}$ −4.2 (*c* 0.02, $CHCl_3$). IR ν_{max} (KBr) 3457, 2969, 1736, 1453, 1365, 1228, 1216, 1091, 696, 527 cm^{-1}; ^{1}H NMR (360 MHz) δ=7.82–7.69 (m, 5H, arom.), 7.60 (t, 1H, *J*=7.3 Hz, arom.), 7.49–7.39 (m, 4H, arom.), 7.36–7.17 (m, 24H, arom.), 5.52 (s, 1H, PhC*H*), 5.34 (dd, 1H, *J*=10.5, 8.1 Hz, H-2′), 5.14 (d, 1H, *J*=2.5 Hz, H-1″), 4.93 (t, 1H, *J*=9.9 Hz, H-3), 4.84 (d, 1H, *J*=11.9 Hz, PhC*H*$_2$), 4.81 (d, 1H, *J*=9.1 Hz, H-1), 4.69 (d, 1H, *J*=12.7 Hz, C-5″a), 4.57–4.37 (m, 7H, H-1′, H-6′a, PhC*H*$_2$), 4.18 (dd, 1H, *J*=10.3, 8.8 Hz, H-2), 4.03–3.88 (m, 7H, H-2″, H-3″, H-4′, H-4, H-6a, H-6′b, PhC*H*$_2$), 3.85–3.77 (m, 2H, H-3′, PhC*H*$_2$), 3.70–3.49 (m, 4H, H-5″b, H-6b, H-5, H-5′), 3.40 (s, 1H, H-4″), 3.25 (s, 3H, OCH$_3$), 2.05 (s, 3H, SCOC*H*$_3$) ppm. ^{13}C NMR (90 MHz) δ=194.48 (S*C*OCH$_3$), 165.14 (PhC=O), 139.42, 139.27, 138.49, 138.20, 137.29, 134.17, 132.83, 131.39, 129.90, 129.60, 128.84, 128.58, 128.18, 128.10, 128.05, 127.83, 127.50, 127.42, 127.29, 126.98, 126.73, 125.56, 123.58 (arom. *C*s), 101.51 (C-1′, *J*=160.4 Hz), 100.09 (C-1, *J*=161 Hz), 98.65 (PhCH, *J*=162.6 Hz), 98.27 (C-1″, *J*=173.1 Hz), 78.09, 75.74, 75.62, 75.59 (double int.), 75.53, 68.38 (skeleton *C*s), 74.86, 72.93, 71.51, 70.55 (4×PhCH$_2$), 69.01 (C-6′), 67.11 (C-1), 60.55 (C-5″), 56.00, 55.90 (C-2, OCH$_3$), 46.95 (C-3′), 30.28 (SCOCH$_3$) ppm. Anal. Calcd for $C_{70}H_{69}O_{17}NS$ (1228.36): C, 68.44; H, 5.66; N, 1.14; S, 2.61. Found: C, 68.32; H, 5.70; N, 1.15; S, 2.59. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1250.42. Found: 1250.62.

4.30. Methyl 3-*O*-(3-*S*-acetyl-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (36)

Prepared from **34** (623 mg, 0.53 mmol) in a similar manner as described in Section 4.29. Column chromatography of the residue (1:1 EtOAc–hexane) gave compound **36** (507 mg, 78%) as a syrup: $[\alpha]_D^{23}$ +3.1 (*c* 0.16, $CHCl_3$). IR ν_{max} (KBr) 3477, 3061, 3029, 2902, 2864, 2358, 1778, 1715, 1602, 1584, 1495, 1467, 1452, 1386, 1362, 1318, 1261, 1213, 1163, 1135, 1095, 1055, 1027, 1000, 952, 932, 910, 793, 734, 722, 711, 697, 630, 530 cm^{-1}; ^{1}H NMR (360 MHz) δ=7.77–7.66 (m, 5H, arom.), 7.60–7.52 (m, 4H, arom.), 7.43–7.15 (m, 25H, arom.), 5.54 (s, 1H, PhC*H*), 5.36 (dd, 1H, *J*=10.1 Hz, *J*=8.2 Hz, H-2′), 5.10 (s, 1H, H-1″), 4.97–4.79 (m, 4H, H-3, H-5″, H-1, PhC*H*$_2$), 4.71–4.59 (m, 3H, PhC*H*$_2$), 4.50 (d, 1H, *J*=7.1 Hz, H-1′), 4.46–4.36 (m, 3H, H-6′a, PhC*H*$_2$), 4.24–4.12 (m, 2H, H-2, PhC*H*$_2$), 4.08–3.92 (m, 6H, H-6′b, H-2″, H-4′, H-4, H-3″, H-6a), 3.83 (d, 1H, *J*=10.7 Hz, H-3′), 3.68–3.44 (m, 4H, H-6b, H-5, PhC*H*$_2$, H-5′), 3.22 (s, 4H, H-4″, OCH$_3$), 1.99 (s, 3H, SCOC*H*$_3$), 1.34 (d, 3H, *J*=6 Hz, C*H*$_3$-6″) ppm. ^{13}C NMR (90 MHz) δ=194.00 (S*C*OCH$_3$), 164.92 (PhC=O), 139.34, 139.08, 138.23, 138.10, 137.20, 134.05, 132.64, 131.13, 129.70, 129.45, 128.68, 128.50, 127.96, 127.61, 127.31, 127.24, 127.20, 127.02, 126.91, 126.65, 125.50, 123.39 (arom. *C*s), 101.52 (C-1′, *J*=160 Hz), 99.74 (PhCH, *J*=161 Hz), 98.47 (C-1, *J*=161.2 Hz), 97.72 (C-1″, *J*=170.8 Hz), 79.41 75.51, 75.37, 75.20, 73.03 (C-2″, C-3″, C-4, C-5, C-4′), 78.79 (C-4″), 74.66, 74.50, 72.66, 70.98 (4×PhCH$_2$), 73.97 (C-3), 68.87 (C-6′), 68.71 (C-2′), 68.14 (C-5′), 66.90 (C-6), 66.14 (C-5″), 55.72 (double int.)(C-2, OCH$_3$), 46.82 (C-3′), 30.05 (SCOCH$_3$), 16.04 (C-6″) ppm. Anal. Calcd for $C_{71}H_{71}O_{17}NS$ (1242.38): C, 68.64; H, 5.76; N, 1.13; S, 2.58. Found: C, 68.50; H, 5.80; N, 1.15; S, 2.60. MALDI-TOF: *m*/*z* calcd for $[M+Na]^+$ 1264.43. Found: 1264.71.

4.31. Methyl 3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-deoxy-3-sodiumsulfonato-β-D-galactopyranosyl)-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (37)

Prepared from **35** (117 mg, 0.10 mmol) in a similar manner as described in Section 4.8. Column chromatography of the residue (92:8 CH_2Cl_2–MeOH) gave compound **37** (67 mg, 56%) as a syrup and **35** (22 mg, 18%) was also recovered. Compound **37**: $[\alpha]_D^{23}$ −15.1 (*c* 0.11, $CHCl_3$, one drop of MeOH). IR ν_{max} (KBr) 3452, 2969, 1734, 1716, 1452, 1365, 1228, 1216, 1091, 689, 527 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, CD_3OD) δ=7.90–7.15 (m, 34H), 5.64 (s, 1H, PhC*H*), 5.09 (s, 1H), 4.94 (t, 1H, *J*=9.3 Hz), 4.88–4.74 (m, 3H), 4.63–4.29 (m, 11H), 4.18 (d, 1H, *J*=12.2 Hz), 4.10–4.00 (m, 2H), 3.96–3.81 (m, 3H), 3.71 (d, 1H, *J*=11.6 Hz), 3.68–3.54 (m, 3H), 3.43–3.33 (m, 2H), 3.27 (s, 3H, OCH$_3$) ppm. ^{13}C NMR (90 MHz) δ=166.68 (PhC=O), 138.72, 138.55, 137.82, 137.59, 134.07, 132.39, 130.88, 129.90, 129.27, 128.17, 127.83, 127.62, 127.54, 127.29, 127.14, 127.01, 126.83, 126.67, 125.64, 123.33 (arom. *C*s), 99.65, 98.56, 98.31 (C-1, C-1′, C-1″), 77.75, 75.21, 75.10, 74.96, 74.16, 73.52, 72.84, 68.37 (skeleton *C*s), 74.43, 72.72, 71.50, 70.60 (4×PhCH$_2$), 68.87 (C-6′), 66.93 (C-6), 60.92 (C-5″), 56.00, 55.80 (C-2, OCH$_3$) ppm. MALDI-TOF *m*/*z* calcd for $C_{68}H_{66}O_{19}NSNa$ (1256.30), $[M+Na]^+$ 1278.37. Found: 1278.59.

4.32. Methyl 2-acetamido-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-arabinopyranosyl)-3-*O*-(4,6-*O*-benzylidene-3-deoxy-3-sodiumsulfonato-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranoside (38)

To a solution of compound **37** (43 mg, 0.03 mmol) in anhyd ethanol (5 mL) was added EDA (300 μL) and the reaction heated at reflux for two days. The amine was detected by ninhydrin and the mixture was concentrated and coevaporated twice with toluene. The residue was dissolved in MeOH (3 mL) and treated with Ac_2O (1 mL). After 1 h the mixture was concentrated and coevaporated twice with toluene. Column chromatography of the residue (85:15 CH_2Cl_2–MeOH) gave compound **38** (39 mg, 64%) as a syrup: $[\alpha]_D^{23}$ −67.2 (*c* 0.1, MeOH). IR ν_{max} (KBr) 3415, 2922, 1649, 1555, 1496, 1452, 1365, 1188, 1138, 1091, 1054, 1028, 1000, 736, 696, 645, 573, 523 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, CD_3OD) δ=7.64 (d, 2H, *J*=7.6 Hz, arom.), 7.40–7.11 (m, 23H, arom.), 5.67 (s, 1H, PhC*H*), 5.03 (s, 1H), 4.65–4.40 (m, 6H), 4.38–4.11 (m, 6H), 4.04–3.25 (m, 19H), 3.17 (d, 1H, *J*=9.4 Hz), 2.03 (s, 3H, NHCOC*H*$_3$) ppm. ^{13}C NMR (90 MHz) δ=172.64 (NHCOCH$_3$), 138.50, 138.28, 137.84, 137.59, 137.28, 127.76, 127.56, 127.48, 127.33, 127.19, 127.05, 126.96, 126.74, 126.46, 126.30, 125.39 (arom. *C*s), 103.17, 100.84, 99.15, 97.72 (PhCH, C-1, C-1′, C-1″), 77.11, 76.38, 74.97, 74.85, 74.40, 72.78 (double int.), 68.06, 66.42, 62.03 (skeleton Cs), 74.20, 72.48, 71.03, 69.96 (4×PhCH$_2$), 68.66 (C-6′), 66.77 (C-6), 60.35 (C-5″), 55.62, 55.18

(OCH_3, C-2), 21.81 ($NHCOCH_3$) ppm. MALDI-TOF *m*/*z* calcd for $C_{55}H_{62}O_{17}NSNa$ (1064.13), $[M+Na]^+$ 1086.35. Found: 1086.50.

4.33. Methyl 2-acetamido-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-(4,6-*O*-benzylidene-3-deoxy-3-sodiumsulfonato-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranoside (39)

To a solution of compound **36** (157 mg, 0.13 mmol) in anhyd ethanol (5 mL) was added EDA (1 mL) and the reaction heated at reflux for one day. The amine was detected by ninhydrin and the mixture was concentrated and coevaporated twice with toluene. The residue was dissolved in MeOH (3 mL) and treated with Ac_2O (1 mL). After 1 h the mixture was concentrated, coevaporated twice with toluene and dried. The residue was oxidized in a similar manner as described in Section 4.8. Column chromatography of the residue (8:2 CH_2Cl_2–MeOH) gave compound **39** (93 mg, 62% over three steps) as a syrup: $[\alpha]_D^{23}$ −57.7 (*c* 0.15, MeOH). ^1H NMR (360 MHz, $CDCl_3$, CD_3OD) δ=7.71 (d, 2H, *J*=7.3 Hz, arom.), 7.40–7.13 (m, 23H, arom.), 5.70 (s, 1H, PhC*H*), 4.98 (d, 1H, *J*=2.3 Hz), 4.90 (dd, 1H, *J*=12.8, 6.5 Hz), 4.82–4.50 (m, 10H), 4.45 (d, 1H, *J*=12.2 Hz), 4.37–4.06 (m, 5H), 4.01–3.75 (m, 5H), 3.63 (d, 1H, *J*=10.4 Hz), 3.50 (s, 1H), 3.49–3.39 (m, 4H), 3.36–3.32 (m, 1H), 3.22 (s, 1H), 3.15 (dd, 1H, *J*=10.8, 2.4 Hz), 2.03 (s, 3H, $NHCOCH_3$), 1.11 (d, 3H, *J*=6.3 Hz, CH_3-6″) ppm. ^{13}C NMR (90 MHz) δ=174.07 ($NHCOCH_3$), 139.89, 139.77, 139.09, 138.85, 138.58, 129.24, 128.87, 128.52, 128.31, 128.15, 127.91, 127.68, 126.88 (arom. *C*s), 104.65, 102.27, 100.45 (PhCH, C-1, C-1′), 98.64 (C-1″, *J*=170.7 Hz), 79.88, 79.30, 76.04, 75.80, 74.19, 73.57, 69.42, 67.63, 67.40, 63.43 (skeleton *C*s), 75.68, 75.47, 73.86, 71.90 (4×$PhCH_2$), 70.01 (C-6′), 68.08 (C-6), 57.04, 56.28 (OCH_3, C-2), 23.15 ($NHCOCH_3$), 16.47 (C-6″) ppm. MALDI-TOF *m*/*z* calcd for $C_{56}H_{64}O_{17}NSNa$ (1078.16), $[M+Na]^+$ 1100.37. Found: 1100.36.

4.34. Methyl 2-acetamido-4-*O*-(β-D-arabinopyranosyl)-3-*O*-(3-deoxy-3-sodiumsulfonato-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranoside (3)

Compound **38** (40 mg, 0.04 mmol) was dissolved in aq AcOH (80%) and stirred at 60 °C for 1 h. The mixture was concentrated, coevaporated twice with toluene and dried. To the residue in ethanol (5 mL) was added 10% Pd/C (20 mg) and the reaction stirred under H_2 (10 bar) for one day. The mixture was filtered through Celite and the filtrate was concentrated. Column chromatography of the residue in LH-20 (1:1 MeOH–water) gave **3** (20 mg, 87%) as an amorphous powder: $[\alpha]_D^{23}$ −58.1 (*c* 0.04, water). IR ν_{max} (KBr) 3415, 2925, 1650, 1562, 1377, 1322, 1217, 1138, 1058, 840, 790, 632, 506 cm^{-1}; ^1H NMR (360 MHz, CD_3OD) δ=5.07 (d, 1H, *J*=2.9 Hz, H-1″), 4.73 (d, 1H, *J*=12.7 Hz, H-5″a), 4.59 (d, 1H, *J*=7.5 Hz, H-1′), 4.47 (d, 1H, *J*=8.5 Hz, H-1), 4.25 (s, 1H), 4.14 (t, 1H, *J*=9.5 Hz), 4.02–3.81 (m, 6H), 3.77–3.69 (m, 3H), 3.61 (t, 1H, *J*=6.0 Hz), 3.58–3.47 (m, 4H), 3.34–3.28 (m, 2H), 3.05 (dd, 1H, *J*=11 Hz *J*=1.8 Hz, H-3′), 2.03 (s, 3H, $NHCOCH_3$) ppm. ^{13}C NMR (90 MHz, CD_3OD) δ=104.52, 102.82, 99.85 (C-1, C-1′, C-1″), 78.26, 76.94, 76.56, 73.99, 70.31, 69.55, 69.26, 67.91, 67.15, 64.98 (skeleton *C*s), 64.80, 62.40, 60.86 (C-6, C-6′, C-5″), 57.91, 56.62 (OCH_3, C-2), 23.32 ($NHCOCH_3$) ppm. MALDI-TOF *m*/*z* calcd for $C_{20}H_{34}O_{17}NSNa$ (615.54), $[M+Na]^+$ 638.13. Found: 638.86.

4.35. Methyl 2-acetamido-3-*O*-(3-deoxy-3-sodiumsulfonato-β-D-galactopyranosyl)-4-*O*-(α-L-fucopyranosyl)-2-deoxy-β-D-glucopyranoside (4)

To a solution of compound **39** (66 mg, 0.06 mmol) in ethanol (5 mL) was added 10% Pd/C (30 mg) and the reaction stirred under H_2 (10 bar) for four days. The mixture was filtered through Celite and the filtrate was concentrated. Column chromatography of the residue (5:4:1 CH_2Cl_2–MeOH–water) gave **4** (36 mg, 92%) as an amorphous powder: $[\alpha]_D^{23}$ −58.4 (*c* 0.11, MeOH). IR ν_{max} (KBr) 3420, 2932, 1651, 1557, 1377, 1318, 1168, 1037, 965, 809, 772, 635, 523 cm^{-1}; ^1H NMR (360 MHz, CD_3OD) δ=5.04 (d, 1H, *J*=3.8 Hz, H-1″), 4.89–4.82 (m, 1H, H-5″), 4.54 (d, 1H, *J*=7.4 Hz, H-1′), 4.37 (d, 1H, *J*=8.2 Hz, H-1), 4.22 (d, 1H, *J*=1.8 Hz, H-4′), 4.02–3.68 (m, 11H, H-2, H-2′, H-2″, H-3, H-3″, H-4, H-4″, H-6a, H-6b, H-6′a, H-6′b), 3.54–3.48 (m, 1H, H-5′), 3.46 (s, 3H, OCH_3), 3.44–3.37 (m, 1H, H-5), 2.85 (dd, 1H, *J*=10.8, 2.3 Hz, H-3′), 1.98 (s, 3H, $NHCOCH_3$), 1.17 (d, 3H, *J*=6.5 Hz, CH_3-6″) ppm. ^{13}C NMR (90 MHz, CD_3OD) δ=174.18 ($NHCOCH_3$), 105.21 (C-1″), 103.34 (C-1′), 99.73 (C-1), 78.90, 78.27, 77.39, 73.72 (double int.), 71.69, 70.20, 68.22, 67.71, 66.93 (skeleton *C*s), 64.86 (C-3′), 62.45 (C-6′), 61.25 (C-6), 57.15, 57.03 (OCH_3, C-2), 23.24 ($NHCOCH_3$), 16.74 (C-6″) ppm. MALDI-TOF *m*/*z* calcd for $C_{21}H_{36}O_{17}NSNa$ (629.56), $[M+Na]^+$ 652.15. Found: 652.21.

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