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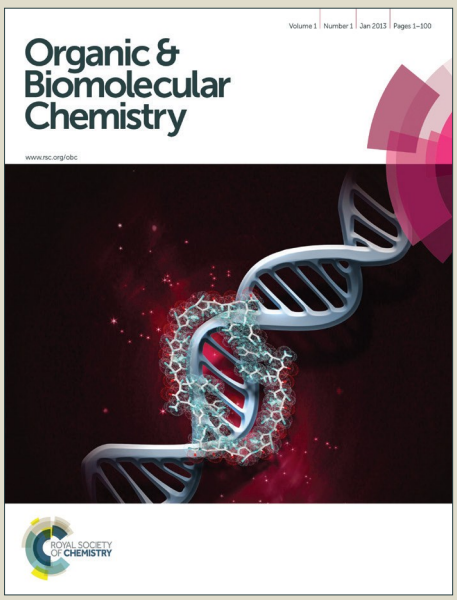

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ARTICLE

The synthesis of heterosaccharides related to the fucoidan from *Chordaria flagelliformis* bearing α-L-fucofuranosyl unit

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Sulfated polysaccharides fucoidans from brown algae are build up mainly of α-L-fucopyranosyl units and form a group of natural biopolymers with a wide spectrum of biological activities. Systematic synthesis of oligosaccharides representing fucoidans fragments gives molecular probes for detecting pharmacophores within fucoidan polysaccharide chains. Recently, it was discovered that fucoidan from brown seaweed *Chordaria flagelliformis* contains not only α-L-fucopyranosyl units but also α-L-fucofuranosyl ones. To establish the influence of the unusual α-L-fucofuranose residue on the biological activity and conformational properties of fucoidans, the synthesis of selectively *O*-sulfated pentasaccharide, which represent the main repeating unit of the fucoidan from *C. flagelliformis*, was performed. Features of the synthesis were the use of the pyranoside-*into*-furanoside rearrangement to prepare the fucofuranoside precursor and remote stereocontrolling participation of *O*-acyl groups to manage stereoselective α-bond formation in glycosylation reactions.

Introduction

Sulfated polysaccharides fucoidans from brown seaweeds possess different types of biological activities including anticoagulant, antithrombotic, anti-inflammatory, antiangiogenic.[1-6] Fucoidan chains are built up mainly of sulfated α-L-fucopyranoside residues, but the fine structure of these biopolymers varies depending on parent seaweed species.[2,4,5] Types of glycoside bonds between monosaccharide units, the degree and pattern of *O*-sulfation, presence of branches and non-fucose components were shown to influence the biological effects of fucoidans.[2,6,7]

To establish the structure-activity relationship within the fucoidans, we perform the systematic synthesis of oligosaccharides related to these biopolymers originated from different brown seaweed species. In addition to a variety of unsulfated[8] as well as selectively[9-11] and per-*O*-sulfated[12] homofucooligosaccharides, di- and trisaccharides bearing α-D-glucuronic acid residue[13] were also prepared.

Recently, it was discovered that the fucoidan from brown seaweed *Chordaria flagelliformis* contains not only α-L-fucopyranosyl units but also α-L-fucofuranosyl ones.[14] This fucoidan contains an α-(1→3)-linked polyfucopyranoside backbone where one third of fucopyranosyl residues bears (1→2)-linked α-D-glucuronic acid substituents and a half of them holds a (1→4)-linked α-L-fucofuranosyl residue (Figure 1, A). The pattern of anti-inflammatory and anticoagulant activities[15] of this fucoidan dramatically differs from the activities of structurally related fucoidans (*e.g.* the fucoidans from the seaweed *Cladosiphon okamuranus*) but not containing fucofuranosyl side unit. This difference may be attributed to the presence of the fucofuranosyl residue.

The biological role of specific fucoidan fragments cannot be established by using of these biopolymers due to their structural irregularity, whereas the synthetic oligosaccharides with strictly defined structure could be considered as appropriate tools for this purpose. Herewith we report the synthesis of tetra- (**1**,**2**) and pentasaccharides **3**,**4** related to the branch points of the fucoidan from the seaweed *C. flagelliformis*[14] as the models for further biological, NMR and conformational studies of the fucoidan from *C. flagelliformis*.

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† Electronic Supplementary Information (ESI) available: characterization data, NMR and HRMS spectra. See DOI: 10.1039/b000000x/

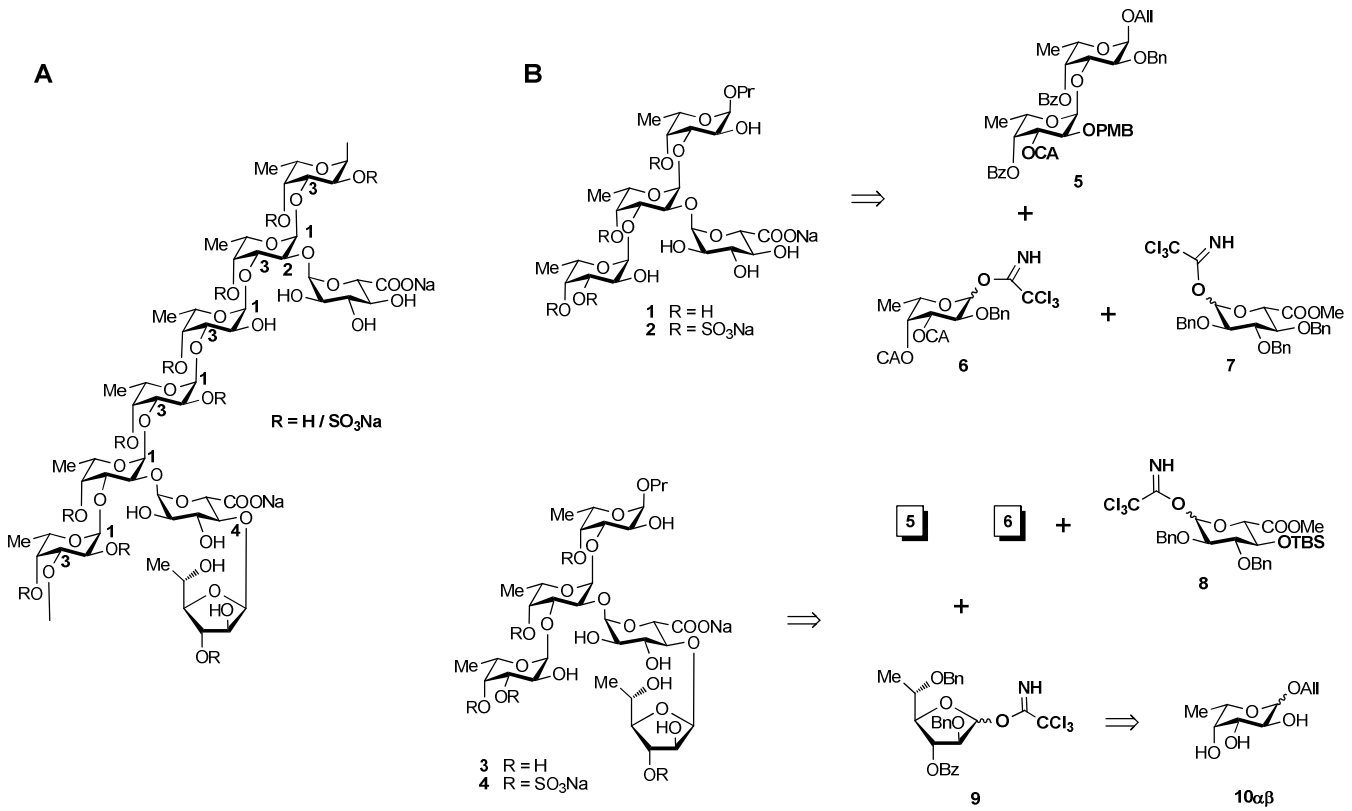
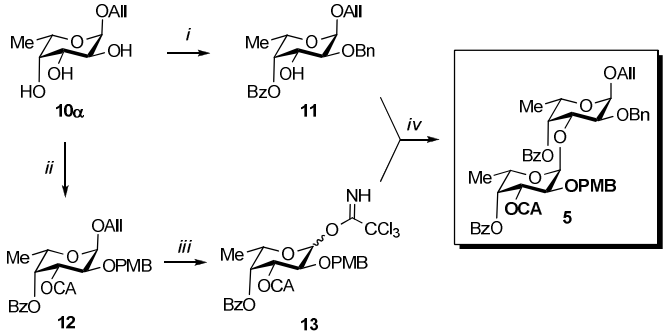


Figure 1. (A): tentative structure of fucoidan from the seaweed *C. flagelliformis*[14]; (B): target oligosaccharides **1-4** related to branched fragments of this fucoidan and retrosynthetic analysis of their structures which revealed synthetic blocks **5-9**.

Results and discussion

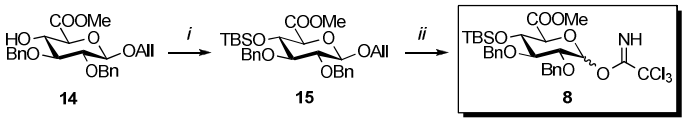
The starting blocks **5-9** for the preparation of target oligosaccharides **1-4** were selected based on the results of the retrosynthetic analyses shown in Figure 1B. It suggests the use of the pyranoside-*into*-furanoside rearrangement[16-18] as a way to fucofuranosyl donor **9**. The blocks **6**[19] and **7**[20] were prepared according to described synthetic protocols.



Scheme 1 Synthesis of disaccharide block **5**. Reagents and conditions: (i): 1) $PhC(OMe)_3$, CSA, DMF, rt, 2 h; 2) NaH (60%), BnBr, 0 °C, 2 h; 3) AcOH (80% aq.), rt, 20 min, 85%; (ii): 1) $PhC(OMe)_3$, CSA, DMF, rt, 2 h; 2) NaH (60%), PMBCl, Bu_4NI, 0 °C, 2 h; 3) AcOH (80% aq.), rt, 20 min; 4) CACl, Py, rt, 2 h; 79%; (iii): 1) $PdCl_2$, MeOH, rt, 1 h; 2) CCl_3CN, Cs_2CO_3, rt, 3 h, 76%; (iv): TMSOTf, CH_2Cl_2, -30 °C, 15 min, 95%.

The synthesis of the disaccharide glycosyl acceptor **5** was performed starting from allyl α-L-fucopyranoside **10α** which was first transformed into acceptor **11** using a one pot three-step process according to published procedure.[10] A similar one pot reaction sequence followed by chloroacetylation was applied for the preparation of selectively protected allyl fucoside **12**. Its deallylation followed by imidate formation gave the donor **13**. TMSOTf-promoted coupling of **13** with acceptor **11** gave stereospecifically α-(1→3)-linked disaccharide **5** in an excellent yield of 95% (Scheme 1). Configuration of formed bond was confirmed by the characteristic $J_{1,2}$ coupling constant value (3.5 Hz).

The synthesis of glucuronosyl donor **8** (Scheme 2) was performed starting from monosaccharide **14**[16] by its silylation (**14**→**15**), deallylation and imidate formation (**15**→**8**).

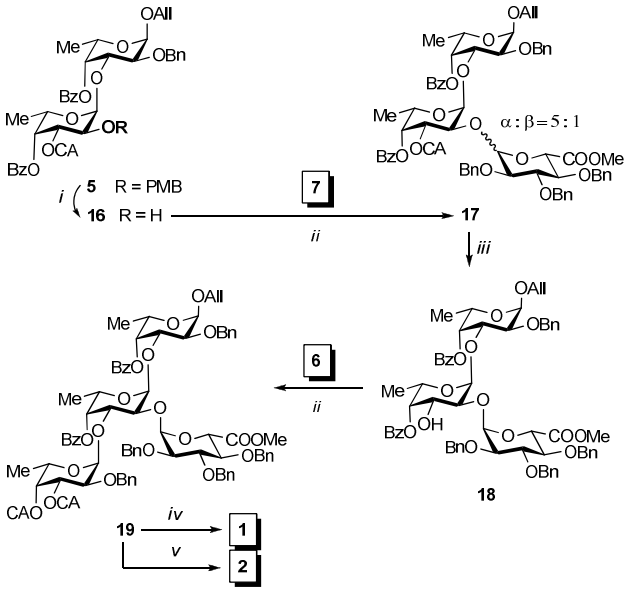


Scheme 2. Synthesis of synthetic block **8**. Reagents and conditions: (i): TBSCl, imidazole, rt, overnight, 94%; (ii): 1) $PdCl_2$, MeOH, rt, 1 h; 2) CCl_3CN, Cs_2CO_3, rt, 3 h, 72%.

To assemble the target tetrasaccharides **1** and **2** the *p*-methoxybenzyl group in difucoside **5** was removed by acidic hydrolysis (transformation **5**→**16** on Scheme 3) and thus

liberated OH-group at C-2 was glycosylated by glucuronosyl donor **7** to give the trisaccharide product **17** as 5:1 mixture of corresponding α- and β-isomers that was assessed by integration of H-6' signals in ^{1}H NMR spectra. Anomeric configurations of GlcA units were confirmed by the characteristic $J_{1,2}$ coupling constant values (3.9 Hz for α- and 7.6 Hz for β-isomer). Individual α-isomer was obtained as compound **18** after dechloroacetylation of **17**.

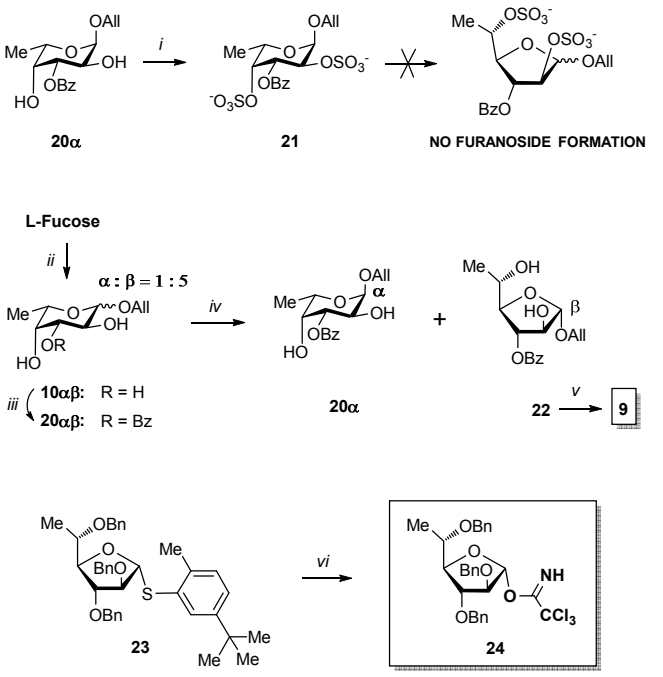
Fucosylation of the acceptor **18** by the donor **6** in the presence of TMSOTf proceeded smoothly and gave the α-linked tetrasaccharide **19** as an only formed product. Configuration of formed bond was confirmed by the characteristic $J_{1,2}$ coupling constant value (3.7 Hz). Its debenzylation by catalytic hydrogenolysis was accompanied by reduction of the allyl group into propyl one; following saponification gave the target tetrasaccharide **1**. For the synthesis of selectively sulfated tetrasaccharide **2**, the acyl protections in precursor **19** were removed and thus liberated OH-groups were sulfated by complex Py·SO_3 in DMF. Following debenzylation and reduction of the allyl group into propyl one gave the target tetrasaccharide **2**.



Scheme 3. Synthesis of the target tetrasaccharides **1** and **2**. Reagents and conditions: (i): TFA (90% aq.), CH_2Cl_2, rt, 10 min, 96%; (ii): TMSOTf, CH_2Cl_2, -30 ºC, 15 min, 78% for **17**, 68% for **19**; (iii): $NH_2C(S)NH_2$, 2,4,6-Collidine, MeOH, 65 ºC, 24 h, 80%; (iv): 1) H_2, Pd/C, rt, 1h; 2) NaOH 2N(aq.), MeOH, rt, 24 h, 91%; (v): 1) NaOH 2N(aq.), THF, MeOH, 65 ºC, 10 h; 2) Py·SO_3, DMF, 40 ºC, 3 h; 3) H_2, Pd/C, rt, 12 h, 81%.

The synthetic methods for preparation of selectively protected furanosides in general are more complicated than those for pyranosides. However, different innovative and facile approaches intensively evolve nowadays.[21-25] Previously we developed a method for synthesis of furanoside **9** employing the novel pyranoside-into-furanoside rearrangement.[16] The reported[16] synthesis of donor **9** was started from the β-isomer of fucopyranoside **10**, however its preparation is multistep and laborious due to the necessity of difficult chromatographic separations. To optimize the synthesis of the block **9**, we tried to prepare it from easily available α-fucopyranoside **20α** (Scheme 4)[26] by its pyranoside-*into*-furanoside rearrangement.[16-18] But this reaction led only to per-*O*-sulfated pyranoside **21** but not to the desired furanoside product. Even elongation of the reaction time from 24 h up to 144 h did not allow us to detect any traces of furanoside. Thus, only β-isomer **10β** is applicable for the preparation of fucofuranosyl donor **9**.

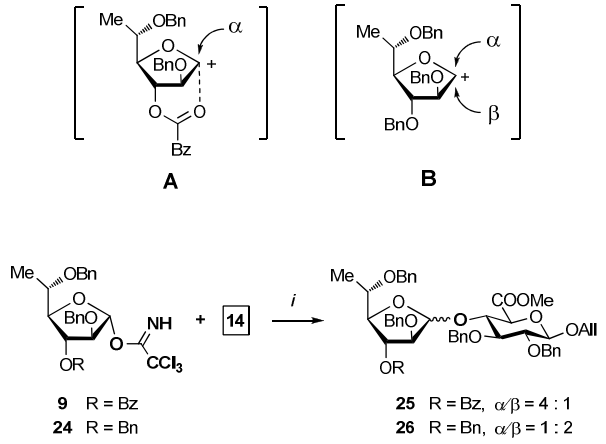
To synthesize the required **10β**, allylation of L-fucose with allyl bromide in the presence of NaOH was studied. It gave an anomeric mixture of allyl fucopyranosides **10αβ** (Scheme 4) with domination of the target β-isomer (α:β = 1:5). This mixture was subjected to regioselective 3-*O*-benzoylation,[27] pyranoside-*into*-furanoside rearrangement and solvolytic de-*O*-sulfation to give non-rearranged α-pyranoside **20α** and β-furanoside **22**, which were easily separated by column chromatography. The formation of the furanoside ring was confirmed by ^{1}H and ^{13}C NMR spectra which corresponded to previously reported data for monosaccharide **22**[16]. Further dibenzylation of diol **22** followed by deallylation and imidate formation gave the fucofuranosyl donor **9**. Fucofuranosyl donor **24** was synthesized from thioglycoside **23**[28] by bromination with NBS followed by hydrolysis and imidate formation (Scheme 4).



Scheme 4. Synthesis of block **9**. Reagents and conditions: (i): 1) Py·SO_3, HSO_3Cl, DMF, rt, 48 h; 2) $NaHCO_3$(aq), rt, 15 min; (ii): AllBr, NaOH, H_2O, rt, 24 h, 91%; (iii): BzCl, (*i*-Pr)$_2$NEt, 2-APB, rt, 1 h, 95% (iv): 1) Py·SO_3, HSO_3Cl, DMF, rt, 48 h; 2) $NaHCO_3$(aq), rt, 15 min; 3) IR-120(H^+), DMF-dioxane, 60 ºC, 30 min, 66% for **22,** 13% for **20α**; (v): 1) BnBr, Ag_2O, rt, overnight; 2) $PdCl_2$, MeOH, rt, 1 h; 3) CCl_3CN, DBU, CH_2Cl_2, -30 ºC, 2 h; (vi): 1) NBS, H_2O-acetone, 0 ºC, 10 min; 2) CCl_3CN, DBU, CH_2Cl_2, -30 ºC, 2 h, 72%.

In spite of the recent progress in selective 1,2-*cis* furanosylation,[29-31] those methods are still unsufficiently developed, while stereoselective α-L-fucofuranosylation has not been reported at all. To assess the possibility of the use of stereodirecting effect of a remote *O*-acyl group to manage selective α-L-fucofuranosylation in the synthesis of target pentasaccharides **3** and **4**, we studied model fucofuranosylations of acceptor **14** by tri-O-benzylated donor **24** and selectively protected donor **9**[14] bearing an *O*-benzoyl group at O-3. Following to the concept of stereodirecting participation of remote *O*-acyl groups in glycosylation reactions,[31-33,11] it was possible to expect the formation from donor **9** of stabilized cation **A** (Scheme 5) that would be attacked by a nucleophile predominantly from the α-side and of non-stabilized cation **B** from per-O-benzylated donor **21** whose nucleophile attack is possible from both α- and β-sides.

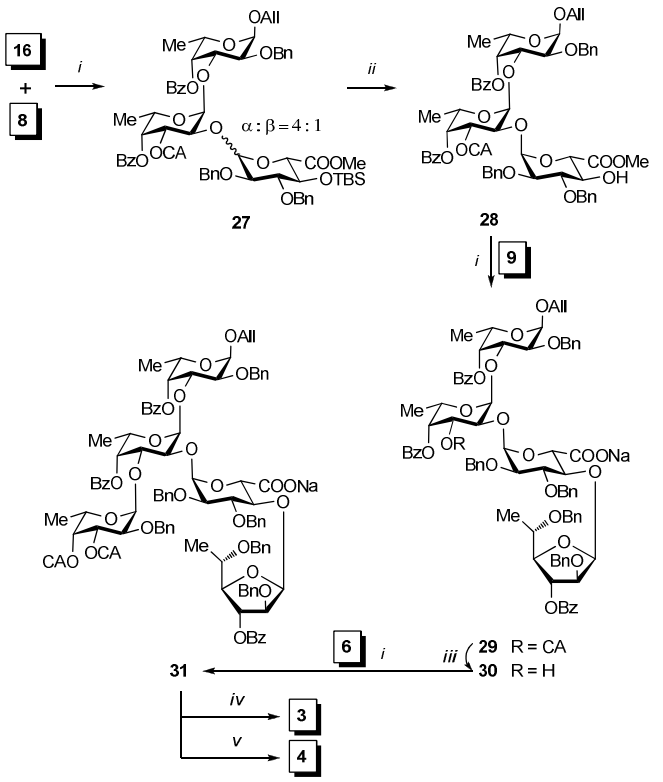
As expected, glycosylation of acceptor **14** by donor **9** with the stereodirecting 3-*O*-benzoyl group resulted in the formation of a mixture of disaccharides **25** with domination of the α-isomer (α:β = 4:1), while glycosylation with tri-*O*-benzylated donor **24** gave a mixture of α- and β-isomers **26** in a ratio of 1:2 as it was assessed by integration of H-6' signals in their ^{1}H NMR spectra. Anomeric configurations were confirmed by characteristic chemical shifts of C-1' in ^{13}C NMR spectra (δ 99.8 for α- and 107.1 for β-isomer). This result proved the possibility of stereodirecting participation of the remote 3-O-benzoyl group and allows us to consider donor **9** as a promising building block for α-fucofuranosylation in the synthesis of target pentasaccharides **3** and **4**.



Scheme 5. Model glycosylations by fucofuranosyl donors **9** and **24**. Reagents and conditions: (i): TMSOTf, CH_2Cl_2, -30 ºC, 15 min, 52% for **25**, 60% for **26**.

To prepare the pentasaccharides **3** and **4**, the coupling of the disaccharide **16** and the monosaccharide **8** was performed first and gave a mixture **27** of isomeric α- and β-linked trisaccharides in a ratio of 4:1 (Scheme 6) that was confirmed by integration of OMe signals in ^{1}H NMR spectra. Individual α-isomer was isolated in the form of monohydroxy derivative **28** after removal of the silyl group with aq. HF. The acceptor **28** was glycosylated by fucofuranosyl donor **9** to give a mixture of α- and β-linked tetrasaccharides in a ratio of 10:1. This result was even better than that of model glycosylation **9**+**14** (see Scheme 5). Individual α-isomer **29** was isolated in a yield of 79% and then subjected to de-O-chloroacetylation (**29**→**30**) followed by 3'-O-fucopyranosylation by donor **6** to give pentasaccharide **31**. Removal of all protecting groups and reduction of the allyl group into propyl one gave the pentasaccharide **3**. Alternatively, saponification of **31** by LiOH and Bu_4NOH in THF followed by *O*-sulfation and hydrogenolysis afforded the required selectively *O*-sulfated pentasaccharide **4**.

The structures of thus synthesized oligosaccharides **1**-**4** were assessed based on NMR spectroscopy and mass-spectrometry data. Complete assignment of ^{1}H and ^{13}C NMR spectra was performed using the combination of 2D experiments, including COSY, HSQC, HMBC, TOCSY, and ROESY (see Experimental and Table 1). The chemical shifts of central residues of non-sulfated oligosaccharides **1** and **3** were in a good agreement with published[14] data for de-O-sulfated fucoidan from *C. flageliformis*.



Scheme 6. Preparation of the target pentasaccharides **3**-**4**. Reagents and conditions: (i): TMSOTf, CH_2Cl_2, -30 ºC, 15 min, 87% for **27**, 79% for **29**, 86% for **31**; (ii): HF (40% $_{aq.}$), CH_3CN, 40 ºC, 2 h, 77%; (iii): $NH_2C(S)NH_2$, 2,4,6-Collidine, MeOH, 65 ºC, 24 h, 80%; (iv): 1) H_2, Pd/C, rt, 1 h; 2) NaOH 2N(aq.), MeOH, rt, 24 h, 82%; (v): 1) LiOH 2N (aq.), THF, rt, 20 h; 2) Bu_4NOH, THF, rt, 48 h; 3) Py·SO_3, DMF, 40 ºC, 3 h; 4) H_2, Pd/C, rt, 12 h, 76%.

Conclusions

The stereoselective synthesis of the oligosaccharides related to the branch points of the fucoidan from the seaweed *C. flageliformis* has been performed by stepwise attachment of corresponding monosaccharide residues to the starting disaccharide acceptor. The pyranoside-*into*-furanoside rearrangement was applied to the preparation of the fucofuranosyl donor. Stereodirecting participation of the remote *O*-acyl group was used to manage α-stereoselectivity of both fucopyranosylation and fucofuranosylation. Selectively *O*-sulfated oligosaccharides **2** and **4** represent useful models for investigation of structure-activity relationships within fucoidan-related substances. The results of their biological and conformational studies will be published elsewhere.

Table 1. ^{1}H and ^{13}C NMR chemical shifts for oligosaccharides **1**, **3** and desulfated fucoidan from *C. flagelliformis* (DSF).

N	Residue	NMR chemical shift (δ)					
		C-1/ H-1	C-2/ H-2	C-3/ H-3	C-4/ H-4	C-5/ H-5	C-6/ H-6
1	→2,3)-α-L-Fuc*p*-(1→3[a]	95.32/ 5.15	71.61/ 4.19	74.10/ 4.29	68.28/ 4.12	67.62/ 4.29	16.52/ 1.24
3	→2,3)-α-L-Fuc*p*-(1→3[b]	95.47/ 5.21	72.35/ 4.22	73.91/ 4.34	68.30/ 4.18	68.22/ 4.49	16.53/ 1.28
DSF	→2,3)-α-L-Fuc*p*-(1→3[c]	95.9/ 5.15	71.8/ 4.19	73.9/ 4.29	68.2/ 4.14	67.8/ 4.34	16.7/ 1.20
1	α-D-GlcA*p*-(1→2[a]	100.55/ 5.29	72.30/ 3.59	74.10/ 3.73	73.05/ 3.52	74.02/ 3.97	176.3/ n/a
DSF	α-D-GlcA*p*-(1→2[c]	100.8/ 5.31	72.2/ 3.62	74.1/ 3.71	72.7/ 3.54	73.5/ 4.00	176.0/ -
3	→4)-α-D-GlcA*p*-(1→2[b]	100.66/ 5.32	72.03/ 3.71	72.99/ 3.86	81.69/ 3.63	73.24/ 4.14	176.89/ -
DSF	→4)-α-D-GlcA*p*-(1→2[c]	100.8/ 5.29	72.7/ 3.70	73.1/ 3.80	81.4/ 3.60	72.9/ 4.10	176.0/ -
3	α-L-Fuc*f*-(1→4[b]	103.38/ 5.10	77.59/ 4.14	75.80/ 4.18	86.21/ 3.71	68.36/ 3.99	19.74/ 1.30
DSF	α-L-Fuc*f*-(1→4[c]	103.5/ 5.02	77.7/ 4.08	75.9/ 4.08	86.2/ 3.63	68.2/ 3.91	19.8/ 1.22

Experimental

General methods

Commercial chemicals were used without purification unless noted. All solvents were distilled and dried if necessary according to standard procedures[34] or purchased as dry (DMF, THF, CH_3CN, Acrus). All reactions involving air- or moisture-sensitive reagents were carried out using dry solvents under Ar atmosphere. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck). Analysis TLC plates were inspected by UV light (λ = 254 nm) and developed by treatment with a mixture of 15% H_3PO_4 and orcinol (1.8 g/l) in EtOH/H_2O (95:5, v/v) followed by heating. Silica gel column chromatography was performed with Silica Gel 60 (40-63 μm, E. Merck). Solvents for column chromatography and thin layer chromatography (TLC) are listed in volume to volume ratios. Gel-filtration was performed on a Sephadex G-15 column (400 × 17 mm) by elution with water at a flow rate of 1.5 mL/min.

NMR spectra were recorded on Bruker AMX400 (400 MHz), Bruker DRX-500 (500 MHz), or Bruker AV600 (600 MHz) spectrometers equipped with 5-mm pulsed-field-gradient (PFG) probes at temperatures denoted in the spectra in supplementary. Microtubes (Shigemi, Inc.) were used for sensitivity enhancement of small concentration probes. The resonance assignment in ^{1}H and ^{13}C NMR spectra was performed using various 2D-experiments (e.g., COSY, NOESY, HSQC, HMBC, TOCSY, HSQC-TOCSY, and ROESY). Chemical shifts are reported in ppm referenced to the solvent residual peaks as standard (δ 7.27 for chloroform or δ 3.31 methanol for ^{1}H NMR and δ 77.0 and δ 49.0 for ^{13}C NMR).

Optical rotations were measured using a JASCO P-2000 polarimeter at ambient temperature (22-25 °C).

High-resolution mass spectra (HR MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI).[35] The measurements were performed in a positive ion mode (interface capillary voltage –4500 V) or in a negative ion mode (3200 V); mass range from *m/z* 50 to *m/z* 3000 Da; external or internal calibration was made with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in a mixture of acetonitrile and water (50:50 v/v, flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

Allyl 2-*O*-*p*-methoxybenzyl-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranoside (12). Trimethyl orthobenzoate (1.3 mL, 7.35 mmol) and CSA (110 mg, 0.47 mmol) were added to a solution of allyl α-L-fucoside **10α** (1.00 g, 4.9 mmol) in DMF (10 mL). After 2h the starting material disappeared (TLC control) and then the solution was cooled to 0 °C and 60% NaH (600 mg, 14.7 mmol) was added. The mixture was stirred at rt for 1 h, then cooled to 0 °C and *p*-methoxybenzyl chloride (2.00 mL, 14.7 mmol) and Bu_4NI (300 mg, 0.82 mmol) were added. After 1 h, ice-cold water (100 mL) was added to the reaction mixture and the suspension was extracted with CH_2Cl_2 (3×100 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. The resulting residue was dissolved in CH_2Cl_2 (5 mL) and 80% aq AcOH (2 mL) was added. The mixture was kept at rt for 20 min, then H_2O (100 mL) was added and the mixture was extracted with CH_2Cl_2 (3×100 mL). The organic layers were concentrated and purified by flash column chromatography (silica gel, toluene – EtOAc, 2:1). The

intermediate was dissolved in anhydrous CH_2Cl_2 (15 mL) and Py (1.2 mL, 14.7 mmol) and chloroacetyl chloride (0.6 mL, 7.35 mmol) were added. After 1 h, the mixture was diluted with $CHCl_3$ and washed successively with 1 M HCl, satd $NaHCO_3$, and water. The solvent was evaporated and the residue was chromatographed (silica gel, hexane – EtOAc, 6:1 →3:1) to give the monosaccharide **12** (1.95 g, 79%) as a yellowish foam. R_f=0.41 (hexane-EtOAc 3:1). $[\alpha]_D$=-122° (c=1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10-6.80 (m, 9H, 2xAr), 5.93-5.60 (m, 1H, CH_2CH=CH_2), 5.54-5.50 (m, 2H, H-3, H-4), 5.40-5.35 (m, 1H, CH_2CH=CH*H*'), 5.27-5.25 (m, 1H, CH_2CH=C*H*H'), 4.93 (d, $J_{1,2}$=3.6 Hz, 1H, H-1), 4.64 (d, 1H, *J*=12.0 Hz, CH*H*'Ar), 4.56 (d, *J*=12.0 Hz, 1H, C*H*H'Ar), 4.28 (q, *J*=6.6 Hz, 1H, H-5), 4.22 (dd, *J*=6.3 Hz, *J*=13 Hz, 1H, OCH*H*'CH), 4.08 (dd, *J*=6.3 Hz, *J*=13 Hz, 1H, OC*H*H'CH), 3.98 (dd, $J_{1,2}$=3.7 Hz, $J_{2,3}$=10.3 Hz, 1H, H-2), 3.93 (m, 2H, C(O)CH_2Cl), 3.80 (s, 3H, OMe), 1.18 (d, $J_{5,6}$=6.6 Hz, 3H, H-6). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.5 (*C*(O)Ph), 166.2 (*C*(O)CH_2Cl), 133.7 (CH_2CH=*C*H_2), 133.3 (Ar), 129.8 (Ar), 129.6 (Ar), 128.5 (Ar), 118.0 (CH_2*C*H=CH_2), 113.8 (Ar), 96.4 (C-1), 72.6 (*C*H_2Ar), 72.5 (C-2), 72.3 (C-3), 71.9 (C-4), 68.7 (O*C*H_2CH), 64.3 (C-5), 55.2 (OMe), 40.6 (C(O)*C*H_2Cl), 15.9 (C-6). HRMS(ESI): Calcd *m/z* for $[M+Na]^+$ $C_{26}H_{29}ClO_8$ 527.1443, found 527.1444.

General procedure A, allyl cleavage and preparation of trichloroacetimidates. To a stirred solution of a starting allyl glycoside(1 mmol) in anhydrous MeOH (5 mL) $PdCl_2$ (71 mg, 0.4 mmol) was added and the mixture was vigorously stirred for 1 h. Then the mixture was filtered through a celite layer, washed with MeOH. The filtrate was neutralized with Et_3N and evaporated *in vacuo*. The residue was purified by chromatography (silica gel, eluent: toluene/EtOAc = 5:1→2:1). The resulting hemiacetal was dissolved in CH_2Cl_2 (8 mL), trichloroacetonitrile (0.5 mL, 5 mmol) and Cs_2CO_3 (977 mg, 3 mmol) were added and the mixture was vigorously stirred at 20 °C for 3 h. Then the mixture was filtered through a celite layer, washed with EtOAc and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel passivated by Et_3N (eluent: toluene/EtOAc = 20:1→10:1) to give a trichloroacetimidate as a white foam.

2-*O*-*p*-Methoxybenzyl-3-*O*-chloroacetyl-4-*O*-benzoyl-α,β-L-fucopyranoside trichloroacetimidates (13). Allyl fucoside **12** (1.44 g, 2.85 mmol) was treated according to general procedure A to give trichloroacetimidates **13** (1,32 g, 76%, α:β = 1:2). For analytical purpose, the anomers were separated and characterized individually. For further glycosylation donor **13** was used as a mixture of α- and β-isomers.

For α-isomer: R_f=0.73 (hexane-EtOAc 2:1). ^{1}H NMR (600 MHz, $CDCl_3$): 8.57 (s, 1H, N*H*), 8.0-6.7 (9H, 2×Ar), 6.47 (d, $J_{1,2}$=3.6 Hz, 1H, H-1), 5.55-5.51 (m, 1H, H-4), 5.44 (dd, $J_{2,3}$=10.5 Hz, $J_{3,4}$=3.3 Hz, 1H, H-3), 4.52 (m, 2H, CH_2Ar), 4.37 (q, *J*=6.2 Hz, 1H, H-5), 4.08-4.04 (m, 1H, H-2), 3.85 (m, 2H, C(O)CH_2Cl), 3.69 (s, 3H, OMe), 1.14 (d, $J_{5,6}$=6.5 Hz, 3H, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (*C*(O)Ph), 166.2 (*C*(O)CH_2Cl), 133.6 (Ar), 129.9 (Ar), 129.5 (Ar), 128.7 (Ar), 114.0 (Ar), 94.7 (C-1), 72.7 (*C*H_2Ar), 72.1 (C-3), 71.9 (C-2), 71.3 (C-4), 67.6 (C-5), 55.3 (OMe), 40.7 (C(O)*C*H_2Cl), 16.2 (C-6). Calcd *m/z* for $[M+Na]^+$ $C_{25}H_{25}Cl_4NO_8$ 630.0226, found 630.0233.

For β-isomer: R_f=0.55 (hexane-EtOAc 2:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.68 (s, 1H, N*H*), 8.0-6.7 (m, 9H, 2xAr), 5.80 (d, $J_{1,2}$=8.1 Hz, 1H, H-1), 5.40 (dd, $J_{3,4}$=3.5 Hz, $J_{4,5}$=0.9 Hz, 1H, H-4), 5.12 (dd, $J_{2,3}$=10.1 Hz, $J_{3,4}$=3.5 Hz, 1H, H-3), 4.74 (d, *J*=10.9 Hz, 1H, CH*H*'Ar), 4.51 (1H, d, *J*=10.9 Hz, C*H*H'Ar), 4.02-3.97 (m, 1H, H-5), 3.91 (dd, $J_{1,2}$=8.1 Hz, $J_{2,3}$=10.1 Hz, 1H, H-2), 3.76 (m, 2H, *C*(O)CH_2Cl), 3.67 (s, 3H, OMe), 1.27 (d, $J_{5,6}$=6.4 Hz, 3H, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (*C*(O)Ph), 166.3 (*C*(O)CH_2Cl), 133.6 (Ar), 130.0 (Ar), 129.7 (Ar), 128.7 (Ar), 113.9 (Ar), 98.4 (C-1), 75.0 (C-2), 74.8 (C-3, *C*H_2Ar), 70.9 (C-4), 70.3 (C-5), 55.3 (OMe), 40.5 (C(O)*C*H_2Cl), 16.2 (C-6). Calcd *m/z* for $[M+Na]^+$ $C_{25}H_{25}Cl_4NO_8$ 630.0226, found 630.0230.

General procedure B, glycosylation. To a mixture of a glycosyl donor (1.1 mmol), a glycosyl acceptor (1.0 mmol) and molecular sieves 4 Å (1.00 g) in anhydrous CH_2Cl_2 (10 mL) 0.1 M TMSOTf in CH_2Cl_2 (50 μL) was added at -30 °C under argon protection. The mixture was stirred for 15 min, then neutralized with Et_3N and evaporated. The resulting material was purified by chromatography (silica gel, eluent: toluene/EtOAc = 15:1→5:1) to give a glycosylation product.

Allyl 2-*O*-*p*-methoxybenzyl-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (5). Glycosylation of acceptor **11** (250 mg, 0.628 mmol) with donor **13** (420 mg, 0.692 mmol) as described in the general procedure B gave disaccharide **5** (505 mg, 95%) as a colorless syrup. R_f=0.50 (hexane-EtOAc 3:1). $[\alpha]_D$=-229° (c=1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): 8.04 (d, *J*=7.1 Hz, 2H, *o*-Bz), 7.97 (d, *J*=7.1 Hz, 2H, *o*-Bz), 7.62 (t, *J*=7.5 Hz, 1H, *p*-Bz), 7.57 (t, *J*=7.4 Hz, 1H, *p*-Bz), 7.50-7.32 (m, 9H, 2xBz, Bn), 7.04 (2H, d, *J*=8.6 Hz, *o*-MBn), 6.71 (2H, d, *J*=8.6 Hz, *m*-MBn), 5.97-6.05 (1H, m, CH_2CH=CH_2), 5.68 (d, $J_{3,4}$=3.3 Hz, 1H, H-4 (Fuc)), 5.50 (dd, $J_{2,3}$=10.5 Hz, $J_{3,4}$=3.3 Hz, 1H, H-3 (Fuc')), 5.41 (dd, *J*=1.6 Hz, *J*=17.2 Hz, 1H, CH_2CH=CH*H*'), 5.34 (d, $J_{1,2}$=3.5 Hz, 1H, H-1 (Fuc')), 5.32 (1H, d, $J_{3,4}$=3.3 Hz, H-4 (Fuc')), 5.28 (1H, dd, *J*=1.3 Hz, *J*=10.4 Hz, CH_2CH=C*H*H'), 5.06 (d, $J_{1,2}$=3.7 Hz, 1H, H-1 (Fuc)), 4.78 (m, 2H, CH_2Ph), 4.48 (q, *J*=6.5 Hz, 1H, H-5 (Fuc')) 4.44-4.39 (m, 2H, H-3 (Fuc), CH*H*'PhOMe), 4.28-4.23 (m, 2H, OCH*H*'CH, C*H*H'PhOMe), 4.21 (q, *J*=6.5 Hz, 1H, H-5 (Fuc)), 4.13 (dd, *J*=6.3 Hz, *J*=13.1 Hz, 1H, OC*H*H'CH), 4.08 (dd, $J_{1,2}$=3.7 Hz, $J_{2,3}$=10.2 Hz, 1H, H-2 (Fuc)), 3.93 (dd, $J_{1,2}$=3.5 Hz, $J_{2,3}$=10.5 Hz, 1H, H-2 (Fuc')), 3.79 (m, 2H, CH_2Cl), 3.77 (s, 3H, OMe), 1.20 (d, $J_{5,6}$=6.6 Hz, 3H, H-6 (Fuc)), 1.01 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc')). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.5 (*C*(O)Ph), 166.4 (*C*(O)Ph), 166.2 (*C*(O)CH_2Cl), 159.1 (*p*-MBn), 138.0 (Bn), 134.0 (CH_2*C*H=CH_2), 133.2 (*p*-Bz), 133.0 (*p*-Bz), 127.9-130.0 (Ar), 117.7 (CH_2CH=*C*H_2), 113.5 (*m*-MBn), 96.2 (C-1 (Fuc)), 93.0 (C-1 (Fuc')), 74.6 (C-2 (Fuc)), 72.3 (C-3 (Fuc')), 72.0 (C-4 (Fuc')), 71.9 (*C*H_2PhOMe), 71.7 (C-2 (Fuc')), 70.5 (C-3 (Fuc)),

69.7 (C-4 (Fuc)), 68.5 (O*C*H$_2$CH), 65.0 (C-5 (Fuc)), 64.6 (C-5 (Fuc')), 55.2 (OMe), 40.6 (*C*H$_2$Cl), 16.3 (C-6 (Fuc)), 15.9 (C-6 (Fuc')). HRMS(ESI): Calcd *m/z* for [M+Na]$^+$ $C_{46}H_{49}ClO_{13}$ 867.2754, found 867.2745.

Methyl (allyl 2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl β-D-glucopyranoside)uronate (15). Imidazole (350 mg, 5.15 mmol) and TBSCl (680 mg, 4.48 mmol) were added to a solution of methyl (allyl 2,3-di-*O*-benzyl-β-D-glucopyranoside)uronate **14** (0.96 g, 2.24 mmol) in dry DMF (10 mL) and the resulting mixture was stirred overnight. Then the reaction mixture was diluted with EtOAc (100 mL) and washed with aqueous $NaHCO_3$ (5%, 100 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, eluent: hexane/EtOAc = 20:1) to give product **15** (1.14 g, 94%) as a colorless oil. R_f=0.90 (hexane-EtOAc 3:1). $[\alpha]_D$ = 12° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34-7.20 (m, 10H, 2×Ph), 5.89-5.96 (m, 1H, CH_2CH=CH_2), 5.33 (d, *J*=17.2 Hz, 1H, CH_2CH=CH*H*'), 5.21 (d, *J*=11.1 Hz, 1H, CH_2CH=C*H*H'), 5.02 (d, *J*=11.4 Hz, 1H, CH*H*'Ph), 4.93 (d, *J*=10.7 Hz, 1H, CH*H*'Ph), 4.71 (d, *J*=11.5 Hz, 1H, C*H*H'Ph), 4.62 (d, *J*=10.8 Hz, 1H, C*H*H'Ph), 4.53 (d, $J_{1,2}$=7.7 Hz, 1H, H-1), 4.42 (dd, *J*=5.0 Hz, *J*=12.7 Hz, 1H, OCH*H*'CH), 4.12 (dd, *J*=6.2 Hz, *J*=12.9 Hz, 1H, OC*H*H'CH), 3.94 (t, *J*=9.0 Hz, 1H, , H-4), 3.85 (d, *J*=9.3 Hz, 1H, H-5), 3.79 (s, 3H, OMe), 3.54 (t, *J*=8.7 Hz, 1H, H-2), 3.47 (t, *J*=8.7 Hz, 1H, H-3), 0.86 (s, 9H, $Si(CH_3)_2C(CH_3)_3$), 0.01 (6H, s, $Si(CH_3)_2C(CH_3)_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0 (C-6), 138.8 (Bn),. 138.3 (Bn), 133.8 (CH_2CH=CH_2), 127.0-129.8 (2xAr), 117.6 (CH_2CH=CH_2), 102.9 (C-1), 84.0 (C-3), 82.2 (C-2), 76.7 (C-5), 75.0 (*C*H$_2$Ph), 74.7 (*C*H$_2$Ph), 72.3 (C-4), 70.5 (O*C*H$_2$CH), 52.3 (OMe), 25.8 (SiC(*C*H$_3$)$_3$), 18.0 (Si*C*(CH$_3$)$_3$), -3.9 (Si(CH$_3$)(*C*H$_3$)^{t}Bu), -5.2 (Si(*C*H$_3$)(CH$_3$)^{t}Bu). HRMS(ESI): Calcd *m/z* for [M+Na]$^+$ $C_{30}H_{42}O_7Si$ 565.2592, found 565.2587.

Methyl (2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl α,β-D-glucopyranosyl)uronate trichloroacetimidates (8). Allyl glycoside **15** (1.14 g, 2.1 mmol) was treated according to general procedure A to give trichloroacetimidates **8** (977 mg, 72%, α:β = 2:1). R_f=0.55 (hexane-EtOAc 5:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.65 (s, 1H, N*H*, β), 8.56 (s, 1H, N*H*, α), 7.09-7.28 (m, 20H, 2xAr α, 2xAr β), 6.43 (d, $J_{1,2}$=2.9 Hz, 1H, H-1 α), 5.87 (d, $J_{1,2}$=7.4 Hz, 1H, H-1 β), 4.79-5.00 (m, 3H, CH*H*'Ph α, C*H*$_2$Ph β), 4.46-4.71 (m, 5H, C*H*$_2$Ph α, C*H*H'Ph α, C*H*$_2$Ph β), 4.24 (d, 1H, $J_{4,5}$=9.5 Hz, H-5 α), 3.99-4.10 (m, 2H, H-4 β, H-5 β), 3.88 (t, *J*=8.8 Hz, 1H, H-4 α), 3.63-3.80 (m, 9H, H-2 β, H-2 α, H-3 α, OMe α, OMe β), 3.81 (t, *J*=8.1 Hz, 1H, H-3 β), 0.77 (s, 9H, $Si(CH_3)_2C(CH_3)_3$ α), 0.76 (s, 9H, $Si(CH_3)_2C(CH_3)_3$ β), -0.06 (s, 6H, $Si(CH_3)_2C(CH_3)_3$ β), -0.08 (s, 6H, $Si(CH_3)_2C(CH_3)_3$ α). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2 (C-6 α), 168.7 (C-6 β), 138.7 (Bn α), 138.5 (Bn β), 137.7 (Bn β), 137.6 (Bn α), 128.5-127.0 (2xAr α, 2xAr β), 97.9 (C-1 β), 93.9 (C-1 α), 84.0 (C-3 β), 80.6 (C-3 α), 80.4 (C-2 β), 79.4 (C-2 α), 76.8 (C-5 β), 75.1 (*C*H$_2$Ph α), 74.6 (C-5 α, *C*H$_2$Ph β), 74.4 (*C*H$_2$Ph β), 73.0 (*C*H$_2$Ph α), 71.9 (C-4, α), 71.8 (C-4 β), 52.5 (OMe, α), 52.4 (OMe β), 25.8 (SiC(*C*H$_3$)$_3$ β), 25.8 (SiC(*C*H$_3$)$_3$ α), 18.0 (Si*C*(CH$_3$)$_3$ α), 18.0 (Si*C*(CH$_3$)$_3$ β), -3.9 (Si(CH$_3$)(*C*H$_3$)^{t}Bu α), -4.0 (Si(CH$_3$)(*C*H$_3$)^{t}Bu β), -5.2 (Si(*C*H$_3$)(CH$_3$)^{t}Bu β), -5.2 (Si(*C*H$_3$)(CH$_3$)^{t}Bu α). HRMS(ESI): Calcd *m/z* for [M+Na]$^+$ $C_{29}H_{38}Cl_3NO_7Si$ 668.1375, found 668.1371.

Allyl 3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (16). Aqueous TFA (90%, 0.8 mL) was added dropwise to a solution of disaccharide **5** (580 mg, 0.69 mmol) in CH_2Cl_2 (8 mL). The reaction mixture was stirred for 10 min, then diluted with toluene (30 mL) and concentrated. The residue was purified by chromatography (silica gel, eluent: hexane/EtOAc = 7:1→4:1) to give product **16** (480 mg, 96%) as a colorless oil. R_f=0.55 (toluene-EtOAc 6:1). $[\alpha]_D$=-210° (c=1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J*=7.5 Hz, 2H, Bz), 8.05 (d, *J*=7.5 Hz, 2H, Bz), 7.65-7.26 (m, 10H, 3xAr), 6.88 (d, *J*=8.6 Hz, 1H, Bn), 6.02-5.94 (m, 1H, CH_2C*H*=CH_2), 5.54 (d, $J_{3,4}$=5.5 Hz, 1H, H-4 (Fuc)), 5.42-5.37 (m, 1H, CH_2CH=CH*H*'), 5.31-5.21 (m, 4H, H-1 (Fuc'), H-3 (Fuc'), H-4 (Fuc'), CH_2CH=C*H*H'), 5.08 (d, $J_{1,2}$=3.5 Hz, 1H, H-1 (Fuc)), 4.70-4.63 (m, 2H, C*H*$_2$Ph), 4.46-4.38 (m, 2H, H-3 (Fuc), H-5 (Fuc)), 4.27-4.18 (m, 2H, H-5 (Fuc'), OCH*H*'CH), 4.14-4.05 (m, 2H, H-2 (Fuc'), OC*H*H'CH), 4.02-3.93 (m, 3H, H-2 (Fuc), C(O)C*H*$_2$Cl), 2.56 (br s, 1H, 2-O*H*), 1.22 (d, 3H, $J_{5,6}$=6.5 Hz, H-6 (Fuc)), 0.91 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc')). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3 (*C*(O)CH$_2$Cl), 167.0 (*C*(O)Ph), 166.2 (*C*(O)Ph), 137.8 (Bn), 133.8 (CH_2CH=CH_2), 133.7 (*p*-Bz), 133.3 (*p*-Bz), 130.9-128.0 (3xAr), 117.8 (CH_2CH=*C*H$_2$), 96.6 (C-1 (Fuc')), 96.0 (C-1 (Fuc)), 74.8 (C-2 (Fuc)), 73.2 (C-3 (Fuc')), 73.1 (C-3 (Fuc)), 72.8 (*C*H$_2$Ph), 71.6 (C-4 (Fuc')), 71.5 (C-4 (Fuc)), 68.6 (O*C*H$_2$CH), 66.8 (C-2 (Fuc')), 65.3 (C-5 (Fuc)), 64.9 (C-5 (Fuc')), 40.6 (C(O)*C*H$_2$Cl), 16.3 (C-6 (Fuc')), 15.7 (C-6 (Fuc)). Calcd *m/z* for [M+Na]$^+$ $C_{38}H_{41}ClO_{12}$ 747.2184, found 747.2179.

Allyl methyl 2,3,4-tri-*O*-benzyl-α,β-D-glucopyranosyluronate-(1→2)-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranosides (17). Glycosylation of acceptor **16** (133 mg, 0.185 mmol) with donor **7** (127 mg, 0.204 mmol) as described in the general procedure B gave trisaccharide **17** (171 mg, 78%, α:β=5:1) as a colorless syrup. R_f=0.40 (toluene-EtOAc 10:1). For α-isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15 (d, *J*=7.4 Hz, 2H, *p*-Bz), 8.08 (d, *J*=7.4 Hz, 2H, *p*-Bz), 7.51-7.15 (m, 26H, 6xAr), 5.92-6.01 (m, 1H, CH_2C*H*=CH_2), 5.72 (d, $J_{3,4}$=3.0 Hz, 1H, H-4 (Fuc)), 5.68 (dd, $J_{2,3}$=10.5 Hz, $J_{3,4}$=3.3 Hz, 1H, H-3 (Fuc')), 5.52 (d, $J_{1,2}$=3.2 Hz, 1H, H-1 (Fuc')), 5.40-5.34 (m, 2H, H-4 (Fuc), OCH_2CH=CH*H*'), 5.30 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (GlcA)), 5.22 (d, *J*=10.4 Hz, 1H, CH_2CH=C*H*H'), 5.02 (d, $J_{1,2}$=3.4 Hz, 1H, H-1 (Fuc)), 4.86 (d, *J*=11.4 Hz, 1H, CH*H*'Ph), 4.80 (d, *J*=11.1 Hz, 1H, CH*H*'Ph), 4.73 (d, *J*=11.6 Hz, 1H, C*H*H'Ph), 4.66 (d, *J*=10.9 Hz, 1H, C*H*H'Ph), 4.60-4.58 (m, 2H, C*H*$_2$Ph), 4.57-4.53 (m, 2H, H-5 (Fuc'), H-5 (GlcA)), 4.50-4.44 (m, 2H, H-3 (Fuc), CH*H*'Ph), 4.40 (dd, $J_{1,2}$=3.2 Hz, $J_{2,3}$=10.4 Hz, 1H, H-2 (Fuc')), 4.25 (d, *J*=10.9 Hz, 1H, C*H*H'Ph), 4.23-4.16 (m, 2H, H-5 (Fuc),

OCH*H*'CH), 4.10 (dd, $J_{1,2}$=3.5 Hz, $J_{2,3}$=10.3 Hz, 1H, H-2 (Fuc)), 4.07-4.03 (m, 1H, OC*H*H'CH), 3.81 (s, 3H, OMe), 3.75-3.67 (m, 3H, H-3 (GlcA), H-4 (GlcA), C(O)CH*H*'Cl), 3.60-3.55 (m, 2H, H-2 (GlcA), C(O)C*H*H'Cl), 1.10 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc)), 1.06 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc')). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.3 (C-6 (GlcA)), 166.4 (*C*(O)CH_2Cl), 166.1 (*C*(O)Ph), 166.0 (*C*(O)Ph), 138.6 (Bn), 138.2 (Bn), 138.1 (Bn), 137.9 (Bn), 133.9 (CH_2*C*H=CH_2), 133.4 (*p*-Bz), 132.9 (*p*-Bz), 130.5 (Bz), 129.8 (Bz), 129-127 (6xAr), 117.6 (CH_2CH=*C*H_2), 98.2 (C-1 (GlcA)), 96.2 (C-1 (Fuc)), 95.9 (C-1 (Fuc')), 80.6 (GlcA)), 79.9 (C-4 (GlcA)), 79.3 (C-2 (GlcA)), 75.1 (*C*H_2Ph), 75.0 (*C*H_2Ph), 74.8 (C-2 (Fuc)), 73.0 (C-3 (Fuc')), 72.9 (*C*H_2Ph), 72.8 (*C*H_2Ph), 72.1 (C-3 (Fuc)), 71.7 (C-4 (Fuc')), 71.3 (C-2 (Fuc')), 71.2 (C-4 (Fuc)), 70.7 (C-5 (GlcA)), 68.4 (O*C*H_2CH), 65.4 (C-5 (Fuc)), 64.8 (C-5 (Fuc')), 52.7 (OMe), 40.5 (C(O)*C*H_2Cl), 16.2 (C-6 (Fuc)), 15.8 (C-6 (Fuc')). Selected NMR signals for minor β-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.44-4.47 (m, 3H, H-1 (GlcA), C*H*$_2$Ph), 3.85 (1H, d, $J_{4,5}$=9.8 Hz, H-5 (GlcA)), 3.52 (1H, t, *J*=9.4 Hz, H-4 (GlcA)), 3.19 (1H, t, *J*=9.1 Hz, H-3 (GlcA)), 3.01 (1H, dd, $J_{1,2}$=7.6 Hz, $J_{2,3}$=9.1 Hz, H-2 (GlcA)). ^{13}C NMR (100 MHz, $CDCl_3$): 100.0 (C-1 (GlcA)), 96.3 (C-1 (Fuc)), 91.9 (C-1 (Fuc')), 83.6 (C-3 (GlcA)), 81.0 (C-2 (GlcA)), 78.8 (C-4 (GlcA)), 74.0 (C-5 (GlcA)). Calcd *m/z* for $[M+Na]^+$ $C_{66}H_{69}ClO_{18}$ 1207.4065, found 1207.4059.

Allyl methyl 2,3,4-tri-O-benzyl-α-D-glucopyranosyluronate-(1→2)-4-O-benzoyl-α-L-fucopyranosyl-(1→3)-2-O-benzyl-4-O-benzoyl-α-L-fucopyranoside (18). A mixture of trisaccharide **17** (150 mg, 0.114 mmol), 2,4,6-collidine (22.5 μL, 0.171 mmol), and thiourea (165 mg, 0.573 mmol) in MeOH (5 mL) and $CHCl_3$ (1 mL) was boiled under reflux for 24 h, cooled, and taken to dryness. A solution of the residue in $CHCl_3$ (50 mL) was washed with 1 M HCl (50 mL) and water (50 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, eluent: toluene/EtOAc = 20:1→10:1) to give **18** (101 mg, 80%) as a white foam. R_f=0.30 (toluene-EtOAc 10:1), $[\alpha]_D$=-104° (c=1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J*=7.0 Hz, 2H, Bz), 8.10 (*J*=7.0 Hz, 2H, d, Bz), 7.62-7.07 (m, 26H, 6xAr), 5.98-5.90 (m, 1H, CH_2C*H*=CH_2), 5.69 (d, $J_{3,4}$=3.2 Hz, 1H, H-4 (Fuc)), 5.37-5.33 (m, 2H, H-1 (Fuc'), CH_2CH=CH*H*'), 5.22-5.19 (m, 2H, H-4 (Fuc'), CH_2CH=CH*H*'), 5.07 (d, $J_{1,2}$=3.7 Hz, 1H, H-1 (GlcA)), 4.97 (d, $J_{1,2}$=3.7 Hz, 1H, H-1 (Fuc)), 4.79-4.62 (m, 7H, 3xC*H*$_2$Ph, CH*H*'Ph), 4.57 (d, $J_{4,5}$=6.9 Hz, 1H, H-5 (GlcA)), 4.56 (d, *J*=5.7 Hz, 1H, C*H*H'Ph), 4.42 (dd, $J_{2,3}$=10.1 Hz, $J_{3,4}$=3.2 Hz, 1H, H-3 (Fuc)), 4.38 (q, *J*=6.4 Hz, 1H, H-5 (Fuc')), 4.28 (dt, J_t=2.9 Hz, $J_{2,3}$=10.1 Hz, 1H, H-3 (Fuc')), 4.20-4.15 (m, 2H, H-5 (Fuc), OCH*H*'CH), 4.04-4.00 (m, 2H, H-2 (Fuc), OC*H*H'CH), 3.98 (dd, $J_{1,2}$=3.2 Hz, $J_{2,3}$=10.1 Hz, 1H, H-2 (Fuc')), 3.91 (t, *J*=9.4 Hz, 1H, H-3 (GlcA)), 3.79 (s, 3H, OMe), 3.68 (t, *J*=9.6 Hz, 1H, H-4 (GlcA)), 3.51 (dd, $J_{1,2}$=3.9 Hz, $J_{2,3}$=9.9 Hz, 1H, H-2 (GlcA)), 3.48 (d, *J*=2.5 Hz, 1H, 3-O*H*), 1.06 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc)), 1.04 (3H, d, $J_{5,6}$=6.4 Hz, H-6 (Fuc')). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.3 (C-6 (GlcA)), 166.6 (Bz), 165.8 (Bz), 138.7 (Bn), 138.3 (Bn), 138.2 (Bn), 137.1 (Bn), 134.0 (CH_2CH=*C*H_2), 133.1 (Bz), 132.9 (Bz), 130.2 (Bz), 129.9 (Bz), 127.5-128.5 (6×Ar), 117.4 (CH_2*C*H=CH_2), 100.8 (C-1 (GlcA)), 97.5 (C-1 (Fuc')), 96.3 (C-1 (Fuc)), 81.3 (C-3 (GlcA)), 80.1 (C-4 (GlcA)), 79.3 (C-2 (Fuc')), 78.5 (C-2 (GlcA)), 75.7 (C-2 (Fuc)), 75.4 (*C*H_2Ph), 75.2 (*C*H_2Ph), 74.1 (C-4 (Fuc')), 73.9 (*C*H_2Ph), 73.4 (C-3 (Fuc)), 72.9 (*C*H_2Ph), 72.1 (C-4 (Fuc)), 70.9 (C-5 (GlcA)), 68.5 (O*C*H_2CH), 68.4 (C-3 (Fuc')), 65.7 (C-5 (Fuc')), 65.4 (C-5 (Fuc)), 52.6 (OMe), 16.1 (C-6 (Fuc)), 16.0 (C-6 (Fuc')). Calcd *m/z* for $[M+Na]^+$ $C_{64}H_{68}O_{17}$ 1131.4349, found 1131.4344.

Allyl 2-*O*-benzyl-3,4-di-*O*-chloroacetyl-α-L-fucopyranosyl-(1→3)-{methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)}-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (19). Glycosylation of acceptor **18** (122 mg, 0.11 mmol) with donor **6** (93 mg, 0.17 mmol) as described in the general procedure B gave tetrasaccharide **19** (112 mg, 68%) as a colorless syrup. R_f=0.61 (toluene-EtOAc 10:1), $[\alpha]_D$=-119° (c=1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J*=7.2 Hz, 2H, *o*-Bz), 8.00 (d, *J*=7.2 Hz, 2H, *o*-Bz), 7.54 (t, *J*=7.4 Hz, 1H, *p*-Bz), 7.49 (t, *J*=7.4 Hz, 1H, *p*-Bz), 7.40-6.95 (m, 29H, 5xBn, 2xBz), 5.90-5.83 (m, 1H, CH_2C*H*=CH_2), 5.76 (d, $J_{3,4}$=3.1 Hz, 1H, H-4 (Fuc)), 5.50 (d, $J_{1,2}$=3.3 Hz, 1H, H-1 (Fuc')), 5.36 (d, $J_{3,4}$=3.1 Hz, 1H, H-4 (Fuc')), 5.32 (dd, $J_{2,3}$=10.4 Hz, $J_{3,4}$=3.3 Hz, 1H, H-3 (Fuc'')), 5.30-5.26 (m, 2H, H-1 (GlcA), CH_2CH=CH*H*'), 5.24 (d, $J_{1,2}$=3.7 Hz, 1H, H-1 (Fuc'')), 5.12 (dd, *J*=1.2 Hz, *J*=10.4 Hz, 1H, CH_2CH=C*H*H'), 5.05 (d, *J*=12.5 Hz, 1H, CH*H*'Ph), 4.96 (d, $J_{3,4}$=3.3 Hz, 1H, H-4 (Fuc'')), 4.86 (d, $J_{1,2}$=3.6 Hz, 1H, H-1 (Fuc)), 4.80-4.74 (m, 3H, C*H*H'Ph, 2xCH*H*'Ph), 4.69-4.57 (m, 4H, C*H*$_2$Ph, 2xC*H*H'Ph), 4.44-4.39 (m, 3H, H-3 (Fuc), H-3 (Fuc'), H-5 (GlcA)), 4.34 (q, *J*=6.5 Hz, 1H, H-5 (Fuc'')), 4.30-4.25 (m, 2H, H-2 (Fuc'), CH*H*'Ph), 4.18 (q, *J*=6.6 Hz, 1H, H-5 (Fuc)), 4.14-4.06 (m, 3H, H-5 (Fuc'), OCH*H*'CH, C*H*H'Ph), 4.00-3.90 (m, 4H, H-2 (Fuc), OC*H*H'CH, C(O)C*H*$_2$Cl), 3.85 (t, *J*=9.1 Hz, 1H, H-3 (GlcA)), 3.77 (t, *J*=9.2 Hz, 1H, H-4 (GlcA)), 3.73 (s, 3H, OMe), 3.70-3.65 (m, 4H, H-2 (GlcA), H-2 (Fuc''), C(O)C*H*$_2$Cl), 1.10 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc)), 0.99 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc')), 0.84 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc'')). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.2 (C-6 (GlcA)), 167.2 (*C*(O)CH_2Cl), 166.6 (*C*(O)CH_2Cl), 166.1 (*C*(O)Ph), 166.0 (*C*(O)Ph), 138.9 (Bn), 138.6 (Bn), 138.6 (Bn), 138.4 (Bn), 138.0 (Bn), 134.2 (CH_2*C*H=CH_2), 133.3 (*p*-Bz), 133.2 (*p*-Bz), 130.2 (*o*-Bz), 130.1 (*o*-Bz), 129.8-127.4 (5xBn, 2xBz), 117.7 (CH_2CH=*C*H_2), 99.3 (C-1 (GlcA)), 97.1 (C-1 (Fuc')), 96.5 (C-1 (Fuc)), 92.4 (C-1 (Fuc'')), 81.8 (C-3 (GlcA)), 80.0 (C-4 (GlcA)), 79.2 (C-2 (GlcA)), 75.6 (C-2 (Fuc)), 75.3 (*C*H_2Ph), 75.0 (*C*H_2Ph), 74.5 (C-2 (Fuc')), 74.0 (*C*H_2Ph), 73.9 (C-3 (Fuc)), 73.6 (C-4 (Fuc'')), 73.0 (*C*H_2Ph), 72.8 (C-4 (Fuc)), 72.4 (C-2 (Fuc'')), 72.2 (*C*H_2Ph), 72.0 (C-3 (Fuc'')), 71.3 (C-5 (GlcA)), 70.7 (C-3 (Fuc')), 69.7 (C-4 (Fuc')), 68.8 (O*C*H_2CH), 65.6 (C-5 (Fuc')), 65.4 (C-5 (Fuc)), 64.5 (C-5 (Fuc'')), 52.7 (OMe), 40.6 (C(O)*C*H_2Cl), 40.6 (C(O)*C*H_2Cl), 16.3 (C-6 (Fuc')), 16.2 (C-6 (Fuc)), 15.5 (C-6 (Fuc'')). Calcd *m/z* for $[M+Na]^+$ $C_{81}H_{86}Cl_2O_{23}$ 1519.4829, found 1519.4859.

Sodium salt propyl α-L-fucopyranosyl-(1→3)-{α-D-glucopyranosyluronate-(1→2)}-α-L-fucopyranosyl-(1→3)-α-L-fucopyranoside (1). A mixture of tetrasaccharide **19** (25 mg, 0.0177 mmol) and the catalyst 10% Pd/C (20 mg) in MeOH–EtOAc (1:1) (2 mL) was stirred under H_2 (1 atm) at rt for 1 h and then filtered through a celite layer. The catalyst was carefully washed with MeOH and the combined filtrates were concentrated. The residue was dissolved in MeOH (1 mL) and treated with 2 M aq NaOH (0.2 mL) for 24 h. Deprotected trisaccharide was isolated from the reaction mixture by gel-chromatography on a gel Sephadex G-15 with water elution followed by lyophilization to give **1** (11.3 mg, 91%) as a white amorphous powder; $[\alpha]_D$=-140° (c=1, H_2O). ^{1}H NMR (600 MHz, D_2O): δ 5.29 (d, $J_{1,2}$=4.8 Hz, 1H, H-1 (GlcA)), 5.17 (d, $J_{1,2}$=3.7 Hz, 1H, H-1 (Fuc'')), 5.15 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (Fuc')), 4.93 (d, $J_{1,2}$=3.5 Hz, 1H, H-1 (Fuc)), 4.41 (q, J=6.6 Hz, 1H, H-5 (Fuc'')), 4.32-4.26 (m, 2H, H-3 (Fuc'), H-5 (Fuc')), 4.19 (dd, $J_{1,2}$=3.9 Hz, $J_{2,3}$=10.4 1H, Hz, H-2 (Fuc')), 4.12 (d, $J_{3,4}$=2.9 Hz, 1H, H-4 (Fuc')), 4.00-3.94 (m, 3H, H-5 (GlcA), H-2 (Fuc), H-3 (Fuc)), 4.10-4.05 (m, 2H, H-4 (Fuc), H-5 (Fuc)), 3.92 (dd, $J_{2,3}$=10.5 Hz, $J_{3,4}$=3.5 Hz, 1H, H-3 (Fuc'')), 3.84-3.80 (m, 2H, H-2 (Fuc''), H-4 (Fuc'')), 3.73 (t, J=9.5 Hz, 1H, H-3 (GlcA)), 3.68 (q, J=7.2 Hz, 1H, OCH*H*'CH_2), 3.59 (dd, $J_{1,2}$=4.8 Hz, $J_{2,3}$=9.9 Hz, 1H, H-2 (GlcA)), 3.54-3.49 (m, 2H, H-4 (GlcA), OC*H*H'CH_2), 1.68-1.61 (m, 2H, $CH_2CH_2CH_3$), 1.24 (m, 6H, H-6 (Fuc), H-6 (Fuc')), 1.21 (d, $J_{5,6}$=6.6 Hz, 3H, H-6 (Fuc'')), 0.93 (t, J=7.3 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C NMR (150 MHz, D_2O): δ 100.6 (C-1 (GlcA)), 99.5 (C-1 (Fuc)), 95.3 (C-1 (Fuc')), 94.5 (C-1 (Fuc'')), 75.0 (C-3 (Fuc)), 74.1 (C-3 (Fuc'), C-3 (GlcA)), 74.0 (C-5 (GlcA)), 73.1 (C-4 (Fuc'')), 73.1 (C-4 (GlcA)), 72.3 (C-2 (GlcA)), 71.6 (C-2 (Fuc')), 71.3 ($CH_2CH_2CH_3$), 70.9 (C-3 (Fuc'')), 69.1 (C-2 (Fuc'')), 69.0 (C-4 (Fuc)), 68.4 (C-5 (Fuc'')), 68.3 (C-4 (Fuc')), 67.8 (C-5 (Fuc)), 67.6 (C-5 (Fuc')), 67.5 (C-2 (Fuc)), 23.3 ($CH_2CH_2CH_3$), C-6 (Fuc'')), C-6 (Fuc'), 16.5 (C-6 (Fuc), 11.1 ($CH_2CH_2CH_3$). Calcd *m/z* for $[M+Na]^+$ $C_{27}H_{45}NaO_{19}$ 719.2345, found 719.2335.

Sodium salt propyl 3,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-{α-D-glucopyranosyluronate-(1→2)}-4-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-4-*O*-sulfonato-α-L-fucopyranoside (2). To a solution of tetrasaccharide **19** (32 mg, 0.021 mmol) in THF–MeOH (3:1) (2.5 mL) 2 M aq NaOH (0.4 mL) was added and the mixture was kept at 65 ºC for 10 h. The solution was neutralized with Amberlite IR-120 (H^+), the resin was filtered off and the filtrate was concentrated. The residue was purified by chromatography (silica gel, eluent: CH_2Cl_2/MeOH = 25:1→10:1). The resulting tetraol was dissolved in DMF (2 mL) and Py·SO_3 (140 mg, 0.88 mmol) was added. The reaction mixture was kept at 40 ºC for 3 h, then quenched with 1 M aq. $NaHCO_3$ up to pH 8-9 and concentrated *in vacuo*. The residue was dissolved in a minimal amount of water (0.4 mL) and then MeOH (5 mL) was added to precipitate inorganic salts. The solids were filtered off, washed with MeOH and the filtrate was concentrated. The residue was purified by chromatography (silica gel, eluent: CH_2Cl_2/MeOH = 10:1→1:1). A mixture of the resulting product and the catalyst 10% Pd/C (50 mg) in THF–EtOAc–EtOH (4:1:1) (3 mL) was stirred under H_2 (1 atm) at rt for 12 h and then filtered through a nylon membrane syringe filter (0.45 μm). The filtrate was concentrated and the residue was purified by gel-chromatography on a gel Sephadex G-15 with water elution followed by lyophilization to give **2** (19.5 mg, 81%) as a white amorphous powder; $[\alpha]_D$=-103.00º (c=1, H_2O). ^{1}H NMR (600 MHz, D_2O): δ 5.44 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (Fuc'')), 5.37 (d, $J_{1,2}$=4.1 Hz, 1H, H-1 (GlcA)), 5.30 (d, $J_{1,2}$=3.6 Hz, 1H, H-1 (Fuc')), 4.92 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (Fuc)), 4.90 (d, $J_{3,4}$=2.8 Hz, 1H, H-4 (Fuc')), 4.86 (d, $J_{3,4}$=3.0 Hz, 1H, H-4 (Fuc'')), 4.79 (d, $J_{3,4}$=2.8 Hz, 1H, H-4 (Fuc)), 4.73 (dd, $J_{2,3}$=10.5 Hz, $J_{3,4}$=3.0 Hz, 1H, H-3 (Fuc'')), 4.55-4.50 (2H, m, H-3 (Fuc'), H-5 (Fuc'')), 4.45 (q, J=6.6 Hz, 1H, H-5 (Fuc')), 4.24 (dd, $J_{1,2}$=3.6 Hz, $J_{2,3}$=10.4 Hz, 1H, H-2 (Fuc')), 4.20 (q, J=6.7 Hz, 1H, H-5 (Fuc)), 4.05-3.99 (m, 3H, H-2 (Fuc''), H-3 (Fuc), H-5 (GlcA)), 3.96 (dd, $J_{1,2}$=3.9 Hz, $J_{2,3}$=10.2 Hz, 1H, H-2 (Fuc)), 3.87 (t, J=9.5 Hz, 1H, H-3 (GlcA)), 3.65-3.60 (m, 2H, H-2 (GlcA), OCH*H*'CH_2), 3.53-3.48 (m, 1H, OC*H*H'CH_2), 3.47 (t, J=9.7 Hz, 1H, H-4 (GlcA)), 1.67-1.60 (m, 2H, $CH_2CH_2CH_3$), 1.32 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc'')), 1.31-1.29 (m, 6H, H-6 (Fuc), H-6 (Fuc')), 0.92 (t, J=7.4 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C NMR (150 MHz, D_2O): δ 177.6 (C-6 (GlcA)), 100.4 (C-1 (GlcA)), 99.3 (C-1 (Fuc)), 98.5 (C-1 (Fuc')), 94.4 (C-1 (Fuc'')), 80.6 (C-4 (Fuc'')), 80.2 (C-4 (Fuc)), 77.8 (C-4 (Fuc')), 77.1 (C-3 (Fuc)), 76.8 (C-3 (Fuc'')), 74.2 (C-3 (GlcA)), 73.8 (C-5 (GlcA)), 73.3 (C-4 (GlcA)), 72.6 (C-2 (GlcA)), 72.5 (C-2 (Fuc')), 71.9 (C-3 (Fuc')), 71.4 (OCH_2CH_2), 68.6 (C-2 (Fuc)), 67.9 (C-5 (Fuc'')), 67.9 (C-5 (Fuc')), 67.4 (C-5 (Fuc)), 67.4 (C-2 (Fuc'')), 23.3 ($CH_2CH_2CH_3$), C-6 (Fuc'')), 17.3-17.1 (C-6 (Fuc), C-6 (Fuc'), 11.2 ($CH_2CH_2CH_3$). Calcd *m/z* for $[M+H]^+$ $C_{27}H_{41}O_{31}S_4Na_5$ 1105.0076, found 1105.0060.

General procedure C, pyranoside-*into*-furanoside rearrangement. HSO_3Cl (26 μL, 0.39 mmol) was added dropwise to a stirred solution of a pyranoside derivative (0.10 mmol) and Py·SO_3 complex (159 mg, 1.00 mmol) in DMF (1.2 mL). The reaction mixture was kept for 48 h at 20 °C and then quenched with aqueous $NaHCO_3$ (266 mg in 3 mL H_2O, 3.17 mmol) and evaporated twice with water. The residue was dissolved in a minimal amount of water and then MeOH was added to precipitate inorganic salts. The solids were filtered off, washed with MeOH, and the filtrate was concentrated and used for the *O*-desulfation and NMR analysis without additional purification.

Sodium salt allyl 2,4-di-*O*-sulfonato-3-*O*-benzyl-α-L-fucopyranoside (21). Treatment of allyl 3-*O*-benzyl-α-L-fucopyranoside (**20α**) as described in the general procedure C gave totally *O*-sulfated derivative **21**. ^{1}H NMR (600 MHz, D_2O) δ 8.17 (d, J = 7.5 Hz, 2H, *o*-Bz), 7.75 (t, J = 7.5 Hz, 1H, *p*-Bz), 7.60 (t, J = 7.8 Hz, 2H, *m*-Bz), 6.09 (m, 1H, CH_2CH=CH_2), 5.50 (m, 2H, H-3, CH_2CH=CH*H*'), 5.39 (m, 2H, CH_2CH=C*H*H', H-1), 4.98 (d, $J_{3,4}$ = 3.4 Hz, 1H, H-4), 4.90 (dd, $J_{2,3}$=10.7 Hz, $J_{2,1}$=3.8 Hz, 1H, H-2), 4.46 (q, $J_{5,6}$=6.6 Hz, 1H, H-5), 4.36 (m, 1H, OC*H*H'CH), 4.26 (m, 1H, OCH*H*'CH), 1.39 (d, $J_{6,5}$=6.6 Hz, 3H, H-6). ^{13}C NMR (150 MHz, D_2O) δ 168.1

(*C*(O)Ph), 134.0 ($CH_2CH=CH_2$), 129.9 (Ph), 128.8 (Ph), 118.8 ($CH_2CH=CH_2$), 95.8 (C-1), 77.5 (C-4), 72.3 (C-2), 69.5 (C-3), 69.1 (OCH_2CH), 65.8 (C-5), 15.8 (C-6).

Allyl α,β-L-fucopyranosides (10α,β). Allyl bromide (2.5 mL, 30 mmol) and NaOH (1.0 g, 25 mmol) was added to a stirred solution of L-fucose (2.0 g, 12 mmol) in water (20 mL). The mixture was vigorously stirred at 20 °C for 24 h and then diluted with water (100 mL), and washed with EtOAc (2×150 mL). The water layer was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, eluent: CH_2Cl_2/MeOH = 20:1→10:1) to give **10α,β** (2.22 g, 91%, α:β = 1:4) as amorphous solid. R_f=0.43 (EtOAc-MeOH 10:1). For β-isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.88 (m, 1H, $CH_2CH=CH_2$), 5.23 (d, *J*=17.1 Hz, 1H, $CH_2CH=CHH'$), 5.09 (d, *J*=10.6 Hz, 1H, $CH_2CH=CHH'$), 4.27 (m, 1H, $OCHH'CH$), 4.18 (d, $J_{1,2}$=7.7 Hz, 1H, H-1), 4.05 (m, 1H, $OCHH'CH$), 3.67-3.59 (m, 2H, H-2, H-4), 3.55-3.47 (m, 2H, H-3, H-5), 1.22 (d, $J_{5,6}$=6.7 Hz, 3H, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.14 ($CH_2CH=CH_2$), 117.32 ($CH_2CH=CH_2$), 101.83 (C-1), 73.82 (C-3), 71.39 (C-4), 70.66 (C-2), 70.35 (C-5), 69.84 (OCH_2CH), 16.10 (C-6). NMR signals of minor α-isomer corresponded to previously reported data.[36]

Allyl 3-*O*-benzoyl-α,β-L-fucopyranosides (20α,β). Allyl α,β-L-fucopyranoside **10α,β** (2.0 g, 9.8 mmol) and 2-aminoethyl diphenylborinate (220 mg, 0.98 mmol) were dissolved in dry acetonitrile (20 mL). *N*,*N*-Diisopropylethylamine (2.56 mL, 14.7 mmol) and benzoyl chloride (1.7 mL, 14.8 mmol) were added, and the resulting mixture was stirred at room temperature for 1 h. Then the mixture was diluted with ethyl acetate, washed with water, and the aqueous layer was extracted back several times with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude material was purified by chromatography (silica gel, eluent: hexane/EtOAc = 1.5:1) to give monosaccharides **13** (2.87, 95%, α:β = 1:4) as a colorless oil. Spectral data of **20α,β** corresponded to previously reported data for α-[26] and β-isomer.[16]

Allyl 3-*O*-benzoyl-β-L-fucofuranoside (22). Treatment of allyl 3-*O*-benzyl-α,β-L-fucopyranoside (**20α,β**) (1.0 g, 3.2 mmol) as described in the general procedure C (pyranoside-*into*-furanoside rearrangement) gave a crude mixture of totally *O*-sulfated monosaccharides. The products were dissolved in DMF-dioxane (2:5) (55 mL) and Amberlite IR-120(H^+) cation-exchange resin was added up to pH=3. The reaction mixture was vigorously stirred at 60 °C for 30 min, cooled and neutralized with aqueous $NaHCO_3$. Saturated aqueous NaCl (200 mL) was added to the reaction mixture and desulfated products were extracted by EtOAc (2×150 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The resulting residue was purified by chromatography (silica gel, eluent: hexane/EtOAc = 4:1→2:1) to give monosaccharides **22** (655 mg, 66%) and **20α** (128 mg, 13%). Spectral data of **22** corresponded to previously reported data.[16]

2,3,5-tri-O-benzyl-β-L-fucofuranoside trichloroacetoimidates (24). N-Bromosuccinimide (122 mg, 0.684 mmol) was added at 0 °C to a stirred solution of (2-Methyl-5-*tert*-butylphenyl) 2,3,5-tri-O-benzyl-1-thio-β-L-fucofuranoside **(23)** (102 mg, 0.171 mmol) in aqueous acetone (1:9) (4 mL). The mixture was vigorously stirred for 10 min, then diluted with CH_2Cl_2 and washed with aq. $NaHCO_3$ (2 × 100 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under diminished pressure to give a white residue. To a solution of the above residue in anhydrous CH_2Cl_2 (2 mL) CCl_3CN (0,17 mL, 1.71 mmol) and DBU (15 μL, 0.10 mmol) were added at -30 °C under an argon atmosphere, and the mixture was then stirred for 2 h. The concentration of the reaction mixture followed by purification of the residue by chromatography on silica gel passivated by Et_3N (eluent: toluene/EtOAc = 20:1→10:1) gave trichloroacetimidate **24** (71 mg, 72%) as a white foam. R_f=0.60 (hexane-EtOAc = 3:1). $[\alpha]_D$=22º (c=1, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H, N*H*), 7.28-7.11 (m, 15H, 3xAr), 6.30 (s, 1H, H-1), 4.62 (d, 1H, *J*=11.9 Hz, CHH'Ph), 4.49 (m, 3H, CH_2Ph, CHH'Ph), 4.36 (q, 2H, *J*=11.8 Hz, CH_2Ph), 4.25 (t, *J*=5.4 Hz, 1H, H-4), 4.15 (d, $J_{2,3}$=1.9 Hz, 1H, H-2), 3.96 (dd, $J_{2,3}$=1.8 Hz, $J_{3,4}$=5.9 Hz, 1H, H-3), 3.68 (dd, $J_{4,5}$=5.2 Hz, $J_{5,6}$=6.3 Hz, 1H, H-5), 1.14 (d, $J_{5,6}$=6.4 Hz, 3H, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1 (C(NH)CCl_3), 138.6 (Ph), 137.8 (Ph), 137.5 (Ph), 128.7-127.5 (5xAr), 104.4 (C-1), 91.4 (CCl_3), 87.1 (C-4), 86.7 (C-2), 83.3 (C-3), 73.6 (C-5), 72.0 (2xCH_2Ph), 71.3 (CH_2Ph), 15.7 (C-6). Calcd *m/z* for $[M+Na]^+$ $C_{29}H_{30}Cl_3NO_5$ 600.1082, found 600.1092.

Allyl 2,5-di-*O*-benzyl-3-*O*-benzoyl-α,β-L-fucofuranosyl-(1→4)-methyl-2,3-di-*O*-benzyl-β-D-glucopyranozyl uronate (25). Glycosylation of acceptor **14** (184 mg, 0.43 mmol) with donor **9** (277 mg, 0.47 mmol) as described in the general procedure B gave disaccharides **26**: α-isomer (203 mg, 55%), β-isomer (48 mg, 13%). Spectral data of **26** α-isomer corresponded to previously reported data.[16] Spectral data for β-isomer: $[\alpha]_D$=-27º (c=1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, *J*=7.2 Hz, 2H, Bz), 7.63 (t, *J*=7.4 Hz, 1H, Bz), 7.51 (t, *J*=7.8 Hz, 2H, Bz), 7.37-7.19 (m, 20H, 4×Bn), 6.00-5.92 (m, 1H, $CH_2CH=CH_2$), 5.61 (s, 1H, H-1 (Fuc)), 5.42 (d, $J_{3,4}$=4.3 Hz, 1H, H-3 (Fuc)), 5.37 (d, *J*=17.3 Hz, 1H, $CH_2CH=CHH'$), 5.25 (d, *J*=10.5 Hz, 1H, $CH_2CH=CHH'$), 4.95 (d, *J*=11.0 Hz, 1H, CHH'Ph), 4.87 (d, *J*=11.0 Hz, 1H, CHH'Ph), 4.73-4.65 (m, 5H, CH_2Ph, CHH'Ph, 2xCHH'Ph), 4.52 (d, $J_{1,2}$=7.4 Hz, 1H, H-1 (GlcA)), 4.49 (d, *J*=11.8 Hz, 1H, CHH'Ph), 4.47-4.43 (m, 1H, $OCHH'CH$), 4.27 (dd, $J_{3,4}$=4.4 Hz, $J_{4,5}$=5.7 Hz, 1H, H-4 (Fuc)), 4.15 (dd, *J*=13.5 Hz, *J*=7.0 Hz, 1H, $OCHH'CH$), 4.11 (d, $J_{4,5}$=9.0 Hz, 1H, H-4 (GlcA)), 4.04 (s, 1H, H-2 (Fuc)), 3.94 (d, $J_{4,5}$=9.7 Hz, 1H, H-5 (GlcA)), 3.85-3.78 (m, 1H, H-5 (Fuc)), 3.77 (s, 3H, OMe), 3.63-3.55 (m, 2H, H-2 (GlcA), H-3 (GlcA)), 1.26 (3H, d, $J_{5,6}$=6.4 Hz, H-6 (Fuc)). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 168.5 (C-6 (GlcA)), 165.9 (C(O)Ph), 138.8 (Bn),

138.2 (Bn), 138.1 (Bn), 137.6 (Bn), 133.7 ($CH_2CH=CH_2$), 133.4 (Bz), 130-127 (Ar), 117.8 ($CH_2CH=CH_2$), 107.7 (C-1 (Fuc)), 102.7 (C-1 (GlcA)), 87.2 (C-2 (Fuc)), 85.6 (C-4 (Fuc)), 83.7 (C-3 (GlcA)), 81.6 (C-2 (GlcA)), 77.1 (C-3 (Fuc)), 76.4 (C-4 (GlcA)), 75.6 (C-5 (GlcA), CH_2Ph), 74.9 (CH_2Ph), 74.5 (C-5 (Fuc)), 71.7 (CH_2Ph), 71.5 (CH_2Ph), 70.6 (OCH_2CH), 52.8 (OMe), 16.0 (C-6 (Fuc)). Calcd *m/z* for $[M+Na]^+$ $C_{51}H_{54}O_{12}$ 881.3507, found 881.3516.

Allyl 2,3,5-tri-*O*-benzyl-α,β-L-fucofuranosyl-(1→4)-methyl-2,3-di-*O*-benzyl-β-D-glucopyranozyl uronate (26). Glycosylation of acceptor **14** (74 mg, 0.173 mmol) with donor **24** (110 mg, 0.190 mmol) as described in the general procedure B gave disaccharides **26** (88 mg, 60%, α:β = 1:2) as a colorless syrup. R_f=0.50 (toluene-EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.20 (m, 75H, 5xAr α, 5xAr β). 5.99-5.88 (m, 3H, $CH_2CH=CH_2$ α, $CH_2CH=CH_2$ β), 5.49 (s, 2H, H-1 (Fuc β)), 5.38-5.30 (m, 3H, $CH_2CH=CHH'$ α, $CH_2CH=CHH'$ β), 5.22-5.19 (m, 4H, H-1 (Fuc α), $CH_2CH=CHH'$ α, $CH_2CH=CHH'$ β), 5.00-4.81 (m, 5H, CHH'Ph α, CHH'Ph β, CH_2Ph α), 4.78-4.59 (m, 6H, CHH'Ph α, CHH'Ph β, CHH'Ph α, CHH'Ph β), 4.59-4.46 (m, 11H, H-1 (GlcA α), H-1 (GlcA β), CHH'Ph α, CHH'Ph β, CHH'Ph α, CHH'Ph β, CH_2Ph α), 4.46-4.38 (m, 6H, $OCHH'CH$ α, $OCHH'CH$ β, CHH'Ph α, CHH'Ph β), 4.28 (m, 4H, CH_2Ph β), 4.17-4.07 (m, 6H, H-4 (GlcA α), H-4 (GlcA β), $OCHH'CH$ α, $OCHH'CH$ β), 4.04-3.95 (m, 8H, H-5 (GlcA β), H-2 (Fuc α), H-3 (Fuc α), H-2 (Fuc β), H-4 (Fuc β)), 3.94-3.89 (m, 3H, H-3 (Fuc β), H-5 (GlcA α)), 3.79 (t, 1H, *J*=6.5 Hz, H-4 (Fuc α)), 3.71 (s, 6H, OMe β), 3.70 (s, 3H, OMe α), 3.74-3.63 (m, 6H, H-5 (Fuc α), H-5 (Fuc β), H-3 (GlcA α), H-3 (GlcA β)), 3.60-3.48 (m, 3H, H-2 (GlcA α), H-2 (GlcA β)), 1.20 (d, $J_{5,6}$=6.4 Hz, 6H, H-6 (Fuc β)), 1.03 (d, $J_{5,6}$=6.3 Hz, 3H, H-6 (Fuc α)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.5 (C-6 (GlcA α)), 168.7 (C-6 (GlcA β)), 139.1-137.5 (m, 5xAr α, 5xBn β), 133.8 ($CH_2CH=CH_2$ α), 133.7 ($CH_2CH=CH_2$ β), 128.5-127.2 (5xAr α, 5xAr β), 117.7 ($CH_2CH=CH_2$ β), 117.6 ($CH_2CH=CH_2$ α), 107.1 (C-1 (Fuc β)), 102.7 (C-1 (GlcA β)), 102.6 (C-1 (GlcA α)), 99.8 (C-1 (Fuc α)), 88.2 (C-2 (Fuc β)), 85.3 (C-4 (Fuc β)), 84.1 (C-2 (Fuc α)), 83.6 (C-3 (GlcA β)), 83.3 (C-4 (Fuc α)), 83.1 (C-3 (Fuc β)), 82.7 (C-3 (GlcA α)), 81.8 (C-2 (GlcA α)), 81.6 (C-2 (GlcA β)), 80.8 (C-3 (Fuc α)), 76.5 (C-5 (Fuc α)), 76.1 (C-4 (GlcA α)), 76.0 (C-4 (GlcA β)), 75.2 (C-5 (GlcA β)), 75.1 (2x CH_2Ph α,β), 74.8 (CH_2Ph β), 74.7 (CH_2Ph α), 74.7 (C-5 (GlcA α), 74.0 (C-5 (Fuc β)), 72.4 (CH_2Ph α), 72.1 (CH_2Ph α), 71.9 (CH_2Ph β), 71.4 (CH_2Ph β), 71.3 (CH_2Ph β), 71.1 (CH_2Ph α), 70.5 (OCH_2CH β), 70.4 (OCH_2CH α), 52.6 (OMe β), 52.5 (OMe α), 15.7 (C-6 (Fuc β), 15.6 (C-6 (Fuc α). Calcd *m/z* for $[M+Na]^+$ $C_{51}H_{56}O_{11}$ 867.3715, found 867.3726.

Allyl methyl 2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α,β-D-glucopyranosyluronate-(1→2)-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranosides (27). Glycosylation of acceptor **16** (290 mg, 0.4 mmol) with donor **8** (284 mg, 0.44 mmol) as described in the general procedure B gave trisaccharides **27** (420 mg, 87%, α:β = 4:1) as a colorless syrup. R_f=0.55 (hexane-EtOAc = 3:1). For α-isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J*=7.4 Hz, 2H, Bz), 8.05 (d, *J*=7.4 Hz, 2H, Bz), 7.50-7.05 (m, 21H, 5xAr), 6.00-5.92 (m, 1H, $CH_2CH=CH_2$), 5.77 (d, $J_{3,4}$=3.2 Hz, 1H, H-4 (Fuc)), 5.52 (dd, $J_{2,3}$=10.7 Hz, $J_{3,4}$=3.4 Hz, 1H, H-3 (Fuc')), 5.40-5.35 (m, 2H, H-1 (Fuc'), $CH_2CH=CHH'$), 5.32 (d, $J_{3,4}$=3.4 Hz, 1H, H-4 (Fuc')), 5.25 (d, *J*=10 Hz, 1H, $CH_2CH=CHH'$), 5.19 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (GlcA)), 5.01 (d, $J_{1,2}$=3.7 Hz, 1H, H-1 (Fuc)), 4.84-4.75 (m, 2H, CH_2Ph), 4.70-4.50 (m, 4H, 2xCH_2Ph), 4.49-4.39 (m, 2H, H-3 (Fuc), H-5 (Fuc')), 4.35-4.31 (m, 1H, H-4 (GlcA)), 4.30-4.26 (m, 1H, H-2 (Fuc')), 4.25-4.18 (m, 2H, H-5 (Fuc), $OCHH'CH$), 4.08-4.01 (m, 2H, H-2 (Fuc), $OCHH'CH$), 3.86-3.82 (m, 2H, H-3 (GlcA), H-5 (GlcA)), 3.78 (s, 3H, OMe), 3.60-3.54 (m, 2H, H-2 (GlcA), $C(O)CHH'Cl$), 3.44 (d, *J*=15.4 Hz, 1H, $C(O)CHH'Cl$), 1.15 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc)), 0.92 (s, 9H, $C(CH_3)_3$), (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc')), 0.13 (s, 3H, $Si(CH_3)(CH_3)$), 0.11 (s, 3H, $Si(CH_3)(CH_3)$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.9 (C-6 (GlcA)), 166.3 ($C(O)Ph$), 166.1 ($C(O)Ph$), 165.7 ($C(O)CH_2Cl$), 139.0 (Bn), 138.1 (Bn), 137.8 (Bn), 133.4 ($CH_2CH=CH_2$), 126.7-130.4 (5xAr), 117.9 ($CH_2CH=CH_2$), 98.1 (C-1 (Fuc), C-1 (GlcA)), 95.9 (C-1 (Fuc)), 80.2 (C-3 (GlcA)), 80.0 (C-2 (GlcA)), 75.8 (C-2 (Fuc)), 74.9 (C-3 (Fuc)), 74.6 (CH_2Ph), 72.8-72.3 (C-2 (Fuc'), C-3 (Fuc'), C-4 (Fuc'), C-4 (Fuc), C-4 (GlcA), C-5 (GlcA), 2xCH_2Ph), 71.7 (C-4 (Fuc')), 68.5 (OCH_2CH), 65.5 (C-5 (Fuc)), 65.0 (C-5 (Fuc')), 52.4 (OMe), 40.4 ($C(O)CH_2Cl$), 25.8 ($C(CH_3)_3$), 16.2 (C-6 (Fuc)), 15.7 (C-6 (Fuc')), -3.9 ($Si(CH_3)(CH_3)$), -5.4 ($Si(CH_3)(CH_3)$). Selected NMR signals for minor β-isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.50-4.42 (m, 3H, H-1 (GlcA), H-5 (Fuc'), CHH'Ph), 3.78 (d, $J_{4,5}$=9.5 Hz, 1H, H-5 (GlcA)), 3.61 (t, *J*=8.7 Hz, 1H, H-4 (GlcA)), 3.00 (t, *J*=8.7 Hz, 1H, H-2 (GlcA)), 2.91 (1H, t, *J*=8.7 Hz, H-3 (GlcA)). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 99.8 (C-1 (GlcA)), 83.3 (C-3 (GlcA)), 81.4 (C-2 (GlcA)), 76.0 (C-5 (GlcA)), 71.7 (C-4 (GlcA)). Calcd *m/z* for $[M+Na]^+$ $C_{65}H_{77}ClO_{18}Si$ 1231.4460, found 1231.4455.

Allyl methyl 2,3-di-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (28). To a solution of protected trisaccharide **27** (388 mg, 0.32 mmol) in CH_3CN (7 mL) an aqueous solution of HF (40%, 1 mL) was added. The reaction mixture was stirred for 2 h at 40 °C and then diluted with $CHCl_3$ (30 mL) and washed twice with aqueous Na_2CO_3 (5%, 150 mL) and water (150 mL). The organic layer was concentrated and the residue was chromatographed (silica gel, eluent: toluene/acetone = 50:1 → 30:1) to give the desilylated derivative **27** (270 mg, 77%) as a colorless syrup. R_f=0.51 (toluene-acetone = 10:1). $[\alpha]_D$=-135.5º (c=1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, *J*=7.2 Hz, 2H, *o*-Ph (Bz)), 8.11 (d, *J*=7.3 Hz, 2H, *o*-Ph (Bz)), 7.63 (t, *J*=7.3 Hz, 1H, *p*-Ph (Bz)), 7.55-7.15 (m, 20H, 5xPh), 6.06-5.98 (m, 1H, $CH_2CH=CH_2$), 5.72 (d, $J_{3,4}$=2.7 Hz, 1H, H-4 (Fuc)), 5.65 (dd, $J_{2,3}$=10.7 Hz, $J_{3,4}$=3.3 Hz, 1H, H-3 (Fuc')), 5.46-5.41 (m, 2H, H-1 (Fuc'), $CH_2CH=CHH'$), 5.35 (d, $J_{3,4}$=2.3 Hz, 1H, H-4 (Fuc')), 5.29 (dd, *J*=1.2 Hz, *J*=10.5 Hz, 1H,

CH_2CH=C*H*H'), 5.18 (d, $J_{1,2}$=3.0 Hz, 1H, H-1 (GlcA)), 5.13 (d, $J_{1,2}$=3.5 Hz, 1H, H-1 (Fuc)), 4.82-4.77 (m, 2H, CH_2Ph), 4.69 (q, *J*=6.4 Hz, 1H, H-5 (Fuc)), 4.58 (dd, $J_{2,3}$=10.4 Hz, $J_{3,4}$=2.9 Hz, 1H, H-3 (Fuc)), 4.54-4.43 (m, 4H, H-5 (GlcA), CH_2Ph, CH*H*'Ph), 4.35 (dd, $J_{1,2}$=3.4 Hz, $J_{2,3}$=10.7 Hz, 1H, H-2 (Fuc')), 4.32 (d, *J*=11.4 Hz, 1H, C*H*H'Ph), 4.27 (dd, *J*=5.0 Hz, *J*=13.3 Hz, 1H, OCH*H*'CH), 4.23-4.17 (m, 2H, H-2 (Fuc), H-5 (Fuc)), 4.11 (dd, *J*=6.0 Hz, *J*=13.3 Hz, 1H, OC*H*H'CH), 3.94-3.88 (m, 1H, H-4 (GlcA)), 3.81 (s, 3H, OMe), 3.64 (dd, *J*=15.4 Hz, *J*=55.8 Hz, 2H, CH_2Cl), 3.54 (t, *J*=7.6 Hz, 1H, H-3 (GlcA)), 3.48 (dd, $J_{1,2}$=3.1 Hz, $J_{2,3}$=8.1 Hz, 1H, H-2 (GlcA)), 1.16 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc)), 0.96 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fuc')). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 170.0 (C-6 (GlcA)), 167.5 (*C*(O)CH_2Cl), 166.3 (*C*(O)Ph), 166.2 (*C*(O)Ph), 138.4 (Bn), 137.8 (Bn), 137.8 (Bn), 133.9 (CH_2CH=*C*H_2), 133.4 (Bz), 133.3 (Bz), 130-127 (Ar), 117.4 (CH_2*C*H=CH_2), 99.1 (C-1 (GlcA)), 91.1 (C-1 (Fuc)), 95.9 (C-1 (Fuc')), 79.7 (C-3 (GlcA)), 77.0 (C-2 (GlcA)), 74.9 (C-2 (Fuc)), 73.9 (*C*H_2Ph), 73.3 (C-2 (Fuc')), 73.1 (C-5 (GlcA)), 72.9 (*C*H_2Ph), 72.8 (*C*H_2Ph), 72.1 (C-4 (Fuc)), 72.0 (C-3 (Fuc')), 71.8 (C-4 (Fuc')), 71.4 (C-3 (Fuc)), 71.3 (C-4 (GlcA)), 68.5 (O*C*H_2CH), 65.9 (C-5 (Fuc)), 64.7 (C-5 (Fuc')), 52.4 (OMe), 40.4 (*C*H_2Cl), 16.4 (C-6 (Fuc)), 15.5 (C-6 (Fuc')). Calcd *m/z* for $[M+Na]^+$ $C_{59}H_{63}ClO_{18}$ 1117.3595, found 1117.3594.

Allyl methyl 2,5-di-*O*-benzyl-3-*O*-benzoyl-α-L-fucofuranosyl-(1→4)-2,3-di-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (29). Glycosylation of acceptor **28** (270 mg, 0.25 mmol) with donor **9** (165 mg, 0.28 mmol) as described in the general procedure B gave tetrasaccharide **29** (297 mg, 79%) as a colorless syrup. R_f=0.35 (hexane-EtOAc = 3:1). $[\alpha]_D$=-107.8º (c=1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 (d, *J*=7.3 Hz, 2H, *o*-Ph (Bz)), 8.09 (d, *J*=8.0 Hz, 2H, *o*-Ph (Bz)), 8.01 (d, *J*=8.0 Hz, 2H, Bz), 7.64-7.13 (m, 34H, 8xAr), 6.03-5.95 (m, 1H, CH_2C*H*=CH_2), 5.83 (t, *J*=7.0 Hz, 1H, H-3 (Fucf)), 5.73 (d, $J_{3,4}$=3.0 Hz, 1H, H-4 (Fucp)), 5.61 (dd, $J_{2,3}$=10.7 Hz, $J_{3,4}$=3.3 Hz, 1H, H-3 (Fucp')), 5.45 (d, $J_{1,2}$=3.2 Hz, 1H, H-1 (Fucp')), 5.40-5.38 (m, 2H, H-1 (Fucf), CH_2CH=CH*H*'), 5.34 (d, $J_{3,4}$=3.3 Hz, 1H, H-4 (Fucp')), 5.27 (dd, *J*=1.3 Hz, *J*=10.4 Hz, 1H, CH_2CH=C*H*H'), 5.24 (d, $J_{1,2}$=4.0 Hz, 1H, H-1 (GlcA)), 5.08 (d, $J_{1,2}$=3.6 Hz, 1H, H-1 (Fucp)), 4.83-4.77 (m, 3H, 3xCH*H*'Ph), 4.74-4.70 (m, 2H, H-5 (GlcA), CH*H*'Ph), 4.64 (d, *J*=11.9 Hz, 1H, CH*H*'Ph), 4.59-4.51 (m, 6H, H-5 (Fucp'), CH_2Ph, 3xC*H*H'Ph), 4.47 (dd, $J_{2,3}$=10.2 Hz, $J_{3,4}$=3.1 Hz, 1H, H-3 (Fucp)), 4.36 (dd, $J_{1,2}$=3.2 Hz, $J_{2,3}$=10.6 Hz, 1H, H-2 (Fucp')), 4.26-4.19 (m, 2H, H-5 (Fucp), OCH*H*'CH), 4.12 (dd, $J_{1,2}$=3.6 Hz, $J_{2,3}$=10.1 Hz, 1H, H-2 (Fucp)), 4.08-4.05 (m, 2H, H-2 (Fucf), OC*H*H'CH), 4.05-3.96 (m, 3H, H-3 (GlcA), H-4 (GlcA), H-4 (Fucf)), 3.90-3.86 (m, 4H, H-5 (Fucf), OMe), 3.68 (d, *J*=15.4 Hz, 1H, CH*H*'Cl), 3.57-3.53 (m, 2H, H-2 (GlcA), C*H*H'Cl), 1.16 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fucp)), 1.04 (d, $J_{5,6}$=6.4 Hz, 3H, H-6 (Fucf)), 0.99 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fucp')). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.3 (C-6 (GlcA)), 166.3 (*C*(O)CH_2Cl), 166.0 (*C*(O)Ph), 166.9 (*C*(O)Ph), 165.3 (*C*(O)Ph), 139.2 (Bn), 138.7 (Bn), 138.1 (Bn), 138.0 (Bn), 137.6 (Bn), 134.0 (CH_2CH=*C*H_2), 133.3 (Bz), 133.1 (Bz), 132.9 (Bz), 130-127 (Ar), 117.6 (CH_2*C*H=CH_2), 100.5 (C-1 (GlcA)), 98.5 (C-1 (Fucf)), 96.7 (C-1 (Fucp')), 96.0 (C-1 (Fucp)), 82.5 (C-4 (Fucf)), 81.9 (C-2 (Fucf)), 80.0 (C-3 (GlcA)), 79.3 (C-2 (GlcA)), 77.0 (C-5 (Fucf)), 76.7 (C-4 (GlcA)), 75.5 (C-2 (Fucp)), 75.0 (C-3 (Fucf), *C*H_2Ph), 73.1 (C-3 (Fucp)), 72.8 (*C*H_2Ph), 72.7 (*C*H_2Ph), 72.5 (C-2 (Fucp')), 72.3 (C-3 (Fucp')), 71.9 (C-4 (Fucp'), *C*H_2Ph), 71.6 (C-4 (Fucp)), 71.5 (*C*H_2Ph), 70.6 (C-5 (GlcA)), 68.5 (O*C*H_2CH), 65.4 (C-5 (Fucp)), 64.8 (C-5 (Fucp')), 52.7 (OMe), 40.5 (*C*H_2Cl), 16.2 (C-6 (Fucp)), 15.6 (C-6 (Fucp')), 15.2 (C-6 (Fucf)). Calcd *m/z* for $[M+Na]^+$ $C_{86}H_{89}ClO_{23}$ 1547.5375, found 1547.5370.

Allyl 2,5-di-*O*-benzyl-3-*O*-benzoyl-α-L-fucofuranosyl-(1→4)-methyl 2,3-di-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (30). *O*-Dechloroacetylation of **29** (273 mg, 0.018 mmol) was performed as described for the preparation of **18** to give tetrasaccharide **30** (207 mg, 80%) as a colorless oil. R_f=0.32 (Toluene-EtOAc = 10:1). $[\alpha]_D$=-96.4º (c=1, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J*=7.0 Hz, 2H, *o*-Ph (Bz)), 8.10 (d, *J*=7.1 Hz, 2H, *o*-Ph (Bz)), 7.97 (d, *J*=7.1 Hz, 2H, *o*-Ph (Bz)), 7.62-7.00 (m, 34H, 8xAr), 5.99-5.88 (m, 1H, CH_2C*H*=CH_2), 5.76 (t, *J*=6.9 Hz, 1H, H-3 (Fucf)), 5.72 (d, $J_{3,4}$=2.9 Hz, 1H, H-4 (Fucp)), 5.39-5.33 (m, 2H, H-1 (Fucp), CH_2CH=CH*H*'), 5.31 (d, $J_{1,2}$=3.2 Hz, 1H, H-1 (Fucp')), 5.25-5.19 (m, 2H, H-4 (Fucp'), CH_2CH=C*H*H'), 4.99-4.93 (m, 3H, H-1 (GlcA), H-1 (Fucf), CH*H*'Ph), 4.78-4.45 (m, 10H, H-5 (GlcA), 4xCH_2Ph, C*H*H'Ph), 4.38-4.30 (m, 2H, H-3 (Fucp), H-5 (Fucp')), 4.27-4.16 (m, 3H, H-3 (Fucp'), H-5 (Fucp), OCH*H*'CH), 4.08-3.96 (m, 5H, H-2 (Fucf), H-4 (Fucf), H-2 (Fucp), H-3 (GlcA), OC*H*H'CH), 3.94-3.87 (m, 2H, H-4 (GlcA), H-2 (Fucp')), 3.86-3.80 (m, 4H, H-5 (Fucf), OMe), 3.49 (dd, $J_{1,2}$=3.8 Hz, $J_{2,3}$=9.6 Hz, 1H, H-2 (GlcA)), 1.23 (d, $J_{5,6}$=6.4 Hz, 3H, H-6 (Fucp)), 1.03 (d, $J_{5,6}$=6.4 Hz, 3H, H-6 (Fucp')), 0.99 (d, $J_{5,6}$=6.3 Hz, 3H, H-6 (Fucf)). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3 (C-6 (GlcA)), 166.6 (*C*(O)Ph), 165.8 (*C*(O)Ph), 165.4 (*C*(O)Ph), 139.2 (Bn), 138.6 (Bn), 138.4 (Bn), 137.8 (Bn), 137.2 (Bn), 134.0 (CH_2CH=*C*H_2), 133.3 (Bz), 132.1 (2xBz), 130-127 (8xAr), 117.8 (CH_2*C*H=CH_2), 101.0 (C-1 (GlcA)), 100.8 (C-1 (Fucp)), 98.0 (C-1 (Fucp')), 95.2 (C-1 (Fucf)), 82.7 (C-2 (Fucf)), 82.0 (C-4 (Fucf)), 80.9 (C-3 (GlcA)), 80.1 (C-2 (Fucp')), 78.8 (C-2 (GlcA)), 77.4 (C-5 (Fucf)), 77.1 (C-4 (GlcA)), 76.4 (C-2 (Fucp)), 75.7 (*C*H_2Ph), 75.1 (C-3 (Fucf)), 74.4 (C-3 (Fucp)), 74.0 (*C*H_2Ph), 74.0 (C-4 (Fucp')), 73.0 (*C*H_2Ph), 72.4 (C-4 (Fucp)), 72.0 (*C*H_2Ph), 71.7 (*C*H_2Ph), 70.8 (C-5 (GlcA)), 68.7 (O*C*H_2CH), 68.1 (C-3 (Fucp')), 65.6 (C-5 (Fucp')), 65.3 (C-5 (Fucp)), 52.8 (OMe), 16.2 (C-6 (Fucp)), 16.1 (C-6 (Fucp')), 15.2 (C-6 (Fucf)). Calcd *m/z* for $[M+Na]^+$ $C_{84}H_{88}O_{22}$ 1471.5659, found 1471.5650.

Allyl 2-*O*-benzyl-3,4-di-*O*-chloroacetyl-α-L-fucopyranosyl-(1→3)-{2,5-di-*O*-benzyl-3-*O*-benzoyl-α-L-fucofuranosyl-(1→4)-methyl-2,3-di-*O*-benzyl-α-D-

glucopyranosyluronate-(1→2)}-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (31). Glycosylation of acceptor **30** (203 mg, 0.14 mmol) with donor **6** (115 mg, 0.21 mmol) as described in the general procedure B gave pentasaccharide **31** (297 mg, 79%) as a colorless syrup. R_f=0.69 (Toluene-EtOAc = 8:1). $[\alpha]_D$=-96.75º (c=1, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J*=7.1 Hz, 2H, *o*-Ph(Bz)), 7.98 (d, *J*=7.1 Hz, 2H, *o*-Ph(Bz)), 7.96 (d, *J*=7.1 Hz, 2H, *o*-Ph(Bz)), 7.58 (t, *J*=7.3 Hz, 1H, *p*-Ph(Bz)), 7.50-7.00 (m, 38H, 9xPh), 5.91-5.80 (m, 1H, CH_2CH=CH_2), 5.78 (t, *J*=6.8 Hz, 1H, H-3 (Fucf)), 5.70 (d, $J_{3,4}$=3.2 Hz, 1H, H-4 (Fucp)), 5.45 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (Fucp')), 5.44 (d, $J_{1,2}$=4.2 Hz, 1H, H-1 (Fucf)), 5.37 (dd, $J_{2,3}$=10.4 Hz, $J_{3,4}$=3.4 Hz, 1H, H-3 (Fucp'')), 5.30 (dd, *J*=1.6 Hz, *J*=17.2 Hz, 1H, CH_2CH=CH*H'*), 5.22 (d, $J_{3,4}$=3.0 Hz, 1H, H-4 (Fucp')), 5.20-5.15 (m, 2H, H-1 (Fucp''), CH_2CH=C*H*H'), 5.10 (d, $J_{3,4}$=3.3 Hz, 1H, H-4 (Fucp'')), 5.02 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (GlcA)), 5.00 (d, *J*=14.2 Hz, 1H, CH*H'*Ph), 4.90 (d, $J_{1,2}$=3.7 Hz, 1H, H-1 (Fucp)), 4.88 (d, *J*=10.2 Hz, 1H, CH*H'*Ph), 4.76-4.67 (m, 2xC*H*H'Ph, 2xCH*H'*Ph), 4.59-4.54 (m, 3H, H-5 (GlcA), CH_2Ph), 4.52-4.45 (m, 3H, H-5 (Fucp''), 2xC*H*H'Ph), 4.33 (d, *J*=12.5 Hz, 1H, CH*H'*Ph), 4.33 (m, 1H, H-3 (Fucp)), 4.30 (m, 1H, H-3 (Fucp')), H-5 (Fucp), OCH*H'*CH, C*H*H'Ph), 4.17-4.08 (m, 5H, H-2 (Fucp'), H-5 (Fucp'), 4.07-3.95 (m, 6H, H-3 (GlcA), H-4 (GlcA), H-2 (Fucf), H-4 (Fucf), C(O)CH_2Cl), 3.92-3.86 (m, 2H, H-2 (Fucp), OC*H*H'CH), 3.81 (t, *J*=6.5 Hz, 1H, H-5 (Fucf)), 3.79 (s, 3H, OMe), 3.72-3.60 (m, 4H, H-2 (GlcA), H-2 (Fucp''), C(O)CH_2Cl), 1.12-1.08 (m, 6H, H-6 (Fucp), H-6 (Fucf)), 0.98 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fucp'')), 0.93 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fucp')). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2 (C-6 (GlcA)), 167.1 (*C*(O)CH_2Cl), 166.5 (*C*(O)CH_2Cl), 165.8 (*C*(O)Ph), 165.3 (*C*(O)Ph), 139.0 (Bn), 138.7 (Bn), 138.5 (Bn), 138.4 (Bn), 138.0 (Bn), 137.8 (Bn), 133.9 (CH_2*C*H=CH_2), 133.1 (Bz), 133.1 (Bz), 133.0 (Bz), 130.3-127.0 (9xAr), 117.7 (CH_2CH=*C*H_2), 100.8 (C-1 (Fucf)), 99.5 (C-1 (GlcA)), 97.1 (C-1 (Fucp')), 95.9 (C-1 (Fucp)), 92.3 (C-1 (Fucp'')), 82.5 (C-4 (Fucf)), 82.0 (C-2 (Fucf)), 80.9 (C-3 (GlcA)), 78.7 (C-2 (GlcA)), 76.7 (C-5 (Fucf)), 76.6 (C-4 (GlcA)), 76.4 (C-2 (Fucp)), 76.0 (C-2 (Fucp')), 75.1 (*C*H_2Ph), 75.0 (C-3 (Fucf)), 74.0 (C-3 (Fucp)), 73.9 (*C*H_2Ph), 73.5 (C-4 (Fucp'')), 72.7 (C-4 (Fucp), *C*H_2Ph), 72.4 (C-2 (Fucp'')), 72.2 (*C*H_2Ph), 72.0 (C-3 (Fucp''), *C*H_2Ph), 71.7 (*C*H_2Ph), 71.0 (C-5 (GlcA)), 69.7 (C-3 (Fucp')), 69.5 (C-4 (Fucp')), 68.6 (O*C*H_2CH), 65.1 (C-5 (Fucp')), 64.9 (C-5 (Fucp)), 64.0 (C-5 (Fucp'')), 52.8 (OMe), 40.5 (C(O)*C*H_2Cl), 40.4 (C(O)*C*H_2Cl), C-6 (Fucp')), 16.0 (C-6 (Fucp), 15.3 (C-6 (Fucp'')), 15.3 (C-6 (Fucf)). Calcd *m/z* for $[M+Na]^+$ $C_{101}H_{106}Cl_2O_{28}$ 1859.6140, found 1859.6200.

Sodium salt proryl α-L-fucopyranosyl-(1→3)-{α-L-fucofuranosyl-(1→4)-α-D-glucopyranosyluronate-(1→2)}-α-L-fucopyranosyl-(1→3)-α-L-fucopyranoside (3). Deprotection of pentasaccharide **31** (27 mg, 0.014 mmol) as described for the preparation of compound **1** gave pentasaccharide **3** (9.7 mg, 82%) as a white amorphous powder. $[\alpha]_D$=-77.3º (c=1, H_2O). ^{1}H NMR (600 MHz, D_2O): δ 5.32 (d, $J_{1,2}$=4.0 Hz, 1H, H-1 (GlcA)), 5.23 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (Fucp'')), 5.21 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (Fucp')), 5.10 (d, $J_{1,2}$=4.7 Hz, 1H, H-1 (Fucf)), 4.99 (br s, 1H, H-1 (Fucp)), 4.49 (q, *J*=6.3 Hz, 1H, H-5 (Fucp')), 4.36 (q, *J*=6.5 Hz, 1H, H-5 (Fucp'')), 4.34 (dd, $J_{2,3}$=10.4 Hz, $J_{3,4}$=3.0 Hz, 1H, H-3 (Fucp')), 4.22 (dd, $J_{1,2}$=3.8 Hz, $J_{2,3}$=10.4 Hz, 1H, H-2 (Fucp')), 4.20-4.17 (m, 2H, H-3 (Fucf), H-4 (Fucp')), 4.16-4.12 (m, 4H, H-4 (Fucp), H-5 (Fucp), H-2 (Fucf), H-5 (GlcA)), 4.03 (m, 2H, H-2 (Fucp), H-3 (Fucp)), 4.01-3.96 (m, 2H, H-3 (Fucp''), H-5 (Fucf)), 3.90-3.83 (m, 3H, H-3 (GlcA), H-2 (Fucp''), H-4 (Fucp'')), 3.74-3.68 (m, 3H, H-2 (GlcA), H-4 (Fucf), OCH*H'*CH_2), 3.63 (t, *J*=9.5 Hz, 1H, H-4 (GlcA)), 3.61-3.56 (m, 1H, OC*H*H'CH_2), 1.75-1.67 (m, 2H, $CH_2CH_2CH_3$), 1.33 (d, $J_{5,6}$=6.6 Hz, 3H, H-6 (Fucp)), 1.31 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fucp'')), 1.30 (d, $J_{5,6}$=6.4 Hz, 3H, H-6 (Fucf)), 1.28 (d, $J_{5,6}$=6.6 Hz, 3H, H-6 (Fucp')), 1.00 (t, *J*=7.4 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C NMR (150 MHz, D_2O): δ 176.9 (C-6 (GlcA)), 103.4 (C-1 (Fucf)), 100.7 (C-1 (GlcA)), 99.5 (C-1 (Fucp)), 95.5 (C-1 (Fucp')), 94.5 (C-1 (Fucp'')), 86.2 (C-4 (Fucf)), 81.7 (C-4 (GlcA)), 77.6 (C-2 (Fucf)), 75.8 (C-3 (Fucf)), 75.3 (C-3 (Fucp)), 73.9 (C-3 (Fucp')), 73.2 (C-5 (GlcA)), 73.1 (C-4 (Fucp'')), 73.0 (C-3 (GlcA)), 72.4 (C-2 (Fucp')), 72.0 (C-2 (GlcA)), 71.3 (O*C*H_2CH_2), 70.8 (C-3 (Fucp'')), C-2 (Fucp'')), 69.1 (C-4 (Fucp), 68.4 (C-5 (Fucf)), 68.3 (C-4 (Fucp')), 68.2 (C-5 (Fucp')), 67.7 (C-5 (Fucp)), 67.6 (C-5 (Fucp'')), 67.5 (C-2 (Fucp)), 23.4 (CH_2*C*H_2CH_3), 19.7 (C-6 (Fucf)), 16.7 (C-6 (Fucp)), 16.5 (C-6 (Fucp'), C-6 (Fucp'')), 11.1 (CH_2CH_2*C*H_3). Calcd *m/z* for $[M+H]^+$ $C_{33}H_{55}NaO_{23}$ 843.3105, found 843.3108.

Sodium salt proryl 3,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-{3-*O*-sulfonato-α-L-fucofuranosyl-(1→4)-α-D-glucopyranosyluronate-(1→2)}-4-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-4-*O*-sulfonato-α-L-fucopyranoside (4). To a solution of pentasaccharide **31** (30 mg, 0.016 mmol) in THF (2 mL) 2 M aqueous NaOH (0.2 mL) was added and the mixture was kept at 20 ºC for 20 h. Then 40% aqueous Bu_4NOH (0.1 mL) was added and the mixture was kept at 20 ºC for another 48 h. The solution was neutralized with Amberlite IR-120 (H^+), cation-exchange resin was filtered off and the filtrate was concentrated. The residue was purified by chromatography (silica gel, eluent: CH_2Cl_2/MeOH = 25:1→6:1). The resulting pentaol was dissolved in DMF (2 mL) and Py·SO_3 (140 mg, 0.88 mmol) was added. The reaction mixture was kept at 40 ºC for 3 h, then quenched with 1 M aq. $NaHCO_3$ up to pH 8-9 and concentrated *in vacuo*. The solid residue was dissolved in a minimal amount of water (~0.4 mL) and then MeOH (5 mL) was added to precipitate inorganic salts. The solids were filtered off, washed with MeOH and the filtrate was concentrated. The residue was purified by chromatography (silica gel, eluent: CH_2Cl_2/MeOH = 10:1→1:1). The mixture of the product and the catalyst 10% Pd/C (50 mg) in THF–EtOAc–EtOH (4:1:1) (3 mL) was stirred under H_2 (1 atm) at rt for 12 h and then filtered through a nylon membrane syringe filter (0.45 μm). The filtrate was concentrated and the residue was purified by column chromatography on a gel Sephadex G-15 with water elution

followed by lyophilization to give **4** (16.8 mg, 76%) as a white amorphous powder. $[\alpha]_D$=-87.7º (c=1, H_2O). ^{1}H NMR (600 MHz, D_2O): δ 5.53 (d, $J_{1,2}$=3.8 Hz, 1H, H-1 (Fucp'')), 5.47 (br s, 1H, H-1 (GlcA)), 5.36 (d, $J_{1,2}$=3.0 Hz, 1H, H-1 (Fucp')), 5.25 (d, $J_{1,2}$=4.9 Hz, 1H, H-1 (Fucf)), 5.03 (d, $J_{1,2}$=3.9 Hz, 1H, H-1 (Fucp)), 4.99 (d, $J_{3,4}$=2.5 Hz, 1H, H-4 (Fucp')), 4.95 (d, $J_{3,4}$=2.7 Hz, 1H, H-4 (Fucp'')), 4.89 (d, $J_{3,4}$=2.7 Hz, 1H, H-4 (Fucp)), 4.85-4.81 (m, 2H, H-3 (Fucp''), H-3 (Fucf)), 4.66-4.60 (m, 2H, H-3 (Fucp'), H-5 (Fucp'')), 4.56 (q, $J_{5,6}$=6.6 Hz, 1H, H-5 (Fucp')), 4.42 (t, J=5.4 Hz, 1H, H-2 (Fucf)), 4.33-4.26 (m, 2H, H-2 (Fucp'), H-5 (Fucp)), 4.23 (d, $J_{4,5}$=9.2 Hz, 1H, H-5 (GlcA)), 4.18-4.15 (m, 1H, H-5 (Fucf)), 4.15-4.09 (m, 2H, H-2 (Fucp''), H-3 (Fucp)), 4.08-4.03 (m, 2H, H-2 (Fucp), H-3 (GlcA)), 4.00 (t, J=5.2 Hz, 1H, H-4 (Fucf)), 3.80 (dd, $J_{1,2}$=2.9 Hz, $J_{2,3}$=9.7 Hz, 1H, H-2 (GlcA)), 3.77-3.72 (m, 1H, OCH*H*'CH_2), 3.70 (t, J=9.6 Hz, 1H, H-4 (GlcA)), 3.63-3.58 (m, 1H, OC*H*H'CH_2), 1.78-1.71 (m, 2H, $CH_2CH_2CH_3$), 1.44-1.38 (m, 9H, H-6 (Fucp), H-6 (Fucp'), H-6 (Fucp'')), 1.34 (d, $J_{5,6}$=6.5 Hz, 3H, H-6 (Fucf)), 1.03 (t, J=7.4 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C NMR (150 MHz, D_2O): δ 177.0 (C-6 (GlcA)), 104.1 (C-1 (Fucf)), 100.3 (C-1 (GlcA)), 99.3 (C-1 (Fucp)), 99.1 (C-1 (Fucp')), 94.5 (C-1 (Fucp'')), 86.2 (C-4 (Fucf)), 84.0 (C-3 (Fucf)), 82.3 (C-4 (GlcA)), 80.6 (C-4 (Fucp'')), 80.5 (C-4 (Fucp)), 77.9 (C-3 (Fucp)), 77.9 (C-4 (Fucp')), 77.0 (C-2 (Fucf)), 76.8 (C-3 (Fucp'')), 73.0 (C-3 (GlcA), C-5 (GlcA)), 72.9 (C-2 (Fucp')), 72.4 (C-2 (GlcA)), 71.9 (C-3 (Fucp')), 71.4 (OCH_2CH_2), 68.7 (C-2 (Fucp)), 68.1 (C-5 (Fucp'')), 68.0 (C-5 (Fucf)), 67.9 (C-5 (Fucp')), 67.5 (C-5 (Fucp)), 67.4 (C-2 (Fucp'')), 23.2 ($CH_2CH_2CH_3$), 19.7 (C-6 (Fucf)), 17.3 (C-6 (Fucp')), 17.1 (C-6 (Fucp)), 17.1 (C-6 (Fucp'')), 11.1 ($CH_2CH_2CH_3$). Calcd *m/z* for $[M-3Na+H]^{2-}$ $C_{33}H_{51}Na_3O_{38}S_5$ 642.0183, found 642.0159.

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Graphical Abstract