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Acid-promoted synthesis of per-O-sulfated fucooligosaccharides related to fucoidan fragments ☆

Vadim B. Krylov [a], Zinaida M. Kaskova [c], Dmitry Z. Vinnitskiy [c], Nadezhda E. Ustyuzhanina [a], Alexey A. Grachev [a], Alexander O. Chizhov [b], Nikolay E. Nifantiev [a,*]

[a] Laboratory of Glycoconjugate Chemistry, N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, 119991 Moscow, Russia
[b] Laboratory of NMR spectroscopy, N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, 119991 Moscow, Russia
[c] Higher Chemical College, Russian Academy of Sciences, Miusskaya sq. 9, 125047 Moscow, Russia

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ABSTRACT

The synthesis of per-O-sulfated derivatives of di-, tetra-, hexa-, octa-, dodeca-, and hexadecafucosides related to natural fucoidans of different types has been performed with the use of previously reported acid-promoted protocol for per-O-sulfation of polyols by SO_3 complexes.[2] During the treatment of (1→3)-linked oligofucosides under these conditions with the promotion by TfOH, the unusual rearrangement of the reducing pyranose residue into furanose one was observed. To avoid the formation of rearrangement by-products, the use of a series of strong acids as promoters of sulfation of large oligofucosides was studied and the improved protocol was developed based on the use of TFA instead of TfOH. The efficiency of the new method was demonstrated by the syntheses of per-O-sulfated derivatives of dodeca- and hexadecafucosides. The described method of O-sulfation opens access to the preparation of the oligosaccharides related to fucoidan fragments and their per-O-sulfated derivatives interesting for elucidation of the relationship between their structure and biological activity.

1. Introduction

Natural O-sulfated polysaccharides fucoidans from brown seaweeds and marine invertebrates exhibit a wide range of biological activities, including anticoagulant, antiangiogenic, and antimicrobial, as well as the ability to inhibit P- and L-Selectin mediated inflammation.[3–6] To determine the structure of pharmacophore fragments within the fucoidan chains, we carried out the systematic synthesis[1,7–12] (see Ref. 13 for review), conformational analysis,[8,10–12,14–16] and studies of biological activities of various oligofucosides related to natural fucoidans.

Highly sulfated oligofucosides represent special interest for biomedical investigations because of previous observations that chemically O-sulfated fucoidans exhibit enhanced anticoagulant activity and could be considered as a possible alternative to most widely used anticoagulant heparin.[6,17] The synthesis of highly and per-O-sulfated derivatives of large oligosaccharides still needs the development of preparative protocols. The known typical procedures (see Ref. 2 and papers cited therein) often result in the formation of complex mixtures of target products together with partly sulfated ones, which are difficult for preparative separation.

Recently we have described[2] the acid-promoted protocol to transform the oligosaccharides into their per-O-sulfated derivatives by the treatment with the SO_3 complexes in the presence of triflic acid (TfOH). In this communication we report the further optimization of the developed method and its application to the first synthesis of a series of per-O-sulfated derivatives of oligofucosides related to the main types of natural fucoidan chains (Scheme 1). The first series of the compounds consists of di-, tetra-, hexa-, octa-, dodeca-, and hexadecasaccharides **1b**–**6b** built up of (1→3)-linked α-L-fucopyranose residues, which correspond to polysaccharides isolated from seaweeds *Laminaria saccharina*[18,19] (new name *Saccharina latissima*[20]), *Chorda filum*,[21] and *Cladosiphon okamuranus*.[22] The second series of the compounds is presented by di-, tetra-, and hexasaccharides **7b**–**9b** built up of alternating (1→3)- and (1→4)-linked α-L-fucopyranose residues related to fucoidans from *F. evanescens*,[23] *F. distihus*,[24] and *Ascophyllum nodosum*.[25] In addition, the synthesis of per-O-sulfated trisaccharide **10b** consisted only from (1→4)-linked α-L-fucopyranose residues like in the fucoidan from *L. cichorioides* seaweed was reported and turned out to be highly sulfated and containing ca. 2 sulfo groups per fucose unit.[26] Similar fucan was also isolated from *Arabacia lixula* sea urchin.[27] Finally, disaccharides **11b** and **12b**, bearing (1→2)-linked α-L-fucopyranosyl and α-D-glucuronyl units and representing the branch points of fucoidans from

☆ Synthesis, NMR, and conformational studies of fucoidan fragments. Part 11. For Part 10, see Ref. 1.

* Corresponding author. Tel./fax: +7 499 135 8784.
E-mail address: nen@ioc.ac.ru (N.E. Nifantiev).

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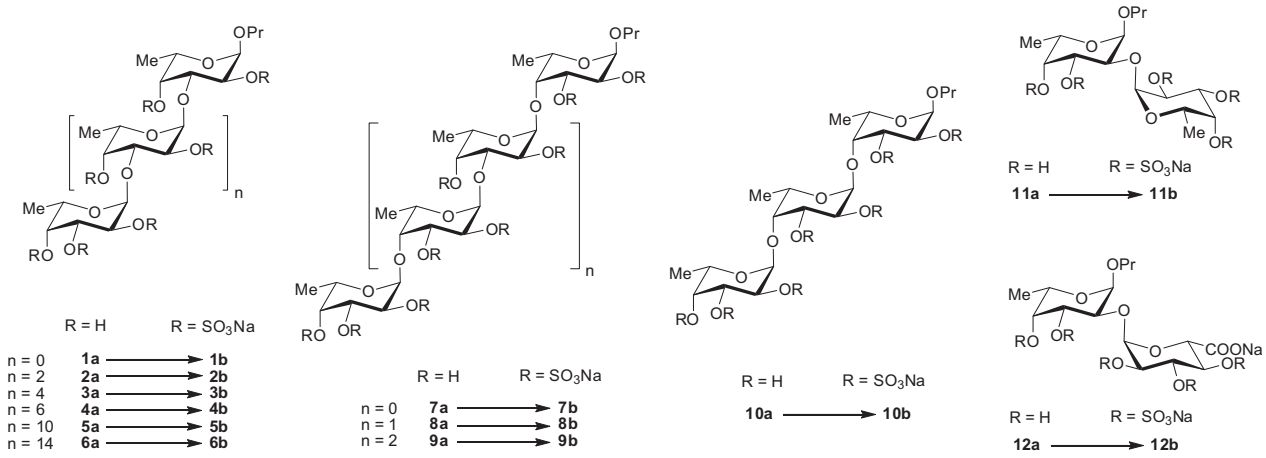


Scheme 1. Target per-O-sulfated oligosaccharides **1b**–**12b** and their precursors **1a**–**12a**.

L. saccharina[18,19] and *C. okamuranus*,[22] respectively, have also been reported.

2. Results and discussion

2.1. Synthesis of oligosaccharide substrates for per-O-sulfation studies

The synthesis of target oligosaccharides **1b**–**12b** was performed from the corresponding parent non-sulfated compounds **1a**–**12a**. Highly stereoselective syntheses of disaccharides **1a**, **7a**, **11a**, and **12a**, tetrasaccharides **2a** and **8a**, hexasaccharides **3a** and **9a**, and octasaccharide **4a** were reported in our previous communications.[1,7,24]

The synthesis of dodeca- and hexadecasaccharides **5a** and **6a** was performed from the protected precursors **13**,[28] **17**,[7] and **19**[7] (Scheme 2) according to the main procedures, which were previously used by us for the synthesis of oligofucosides.[7] Thus, monosaccharide **13**[28] was subjected to 3-O-chloroacetylation followed by bromination with *N*-bromosuccinimide (NBS) and hydrolysis in aq acetone[29] followed by the subsequent treatment with CCl_3CN to give trichloroacetimidate **14** in a overall yield of 72% (Scheme 3). The TMSOTf-catalyzed glycosylation of **13** with **14** was performed at −90 °C and gave disaccharide **15** in a moderate yield of 66%. Low temperature allowed us to increase the selectivity of the reaction and to minimize the formation of the by-product resulted from the undesirable SEt-transfer (not shown). The obtained product **15** was then transformed into acceptor **16** by the selective removal of the chloroacetyl group with NH_2CSNH_2 and 2,4,6-collidine in methanol at 60 °C with an almost quantitative yield. Coupling of disaccharides **16** and **17** was performed as described for the synthesis of compound **15** and afforded tetrasaccharide donor **18** in a yield of 55%.

The acidic methanolysis of previously obtained **19**[7] afforded octasaccharide acceptor **20**, which was further glycosylated by donor **18** to give dodecasaccharide **21** in a yield of 69%. This product was subjected to the catalytic hydrogenolysis and reduction of the allyl group into the propyl one followed by the saponification of the benzoyl and acetyl groups. Additional hydrogenolysis of the obtained product was performed to remove the residual benzyl groups, which remained in a low extent as the result of low solubility of partly debenzylated intermediates under the hydrogenolysis conditions. Finally, deprotected dodecasaccharide **5a** was obtained in a total yield of 61%.

For the synthesis of hexadecasaccharide **6a**, the O-acetyl group in dodecasaccharide **21** was selectively removed by acidic methanolysis to form acceptor **22** (72%). Its glycosylation by donor **18** in the presence of NIS-TMSOTf gave the substituted hexadecasaccharide **23** in a yield of 74%. The removal of all protective groups in **23** together with the reduction of the allyl group into the propyl one was performed as described for the preparation of dodecasaccharide **5a** to give hexadecasaccharide **6a** in a total yield of 54%.

The synthesis of trisaccharide **10a** was performed from previously reported monosaccharide acceptor **24** and disaccharide donor **25** (Scheme 3).[7] Coupling of **24** and **25** in the presence of TMSOTf yielded trisaccharide **26**, which was then subjected to hydrogenolysis and subsequent saponification to give trifucoside **10a**.

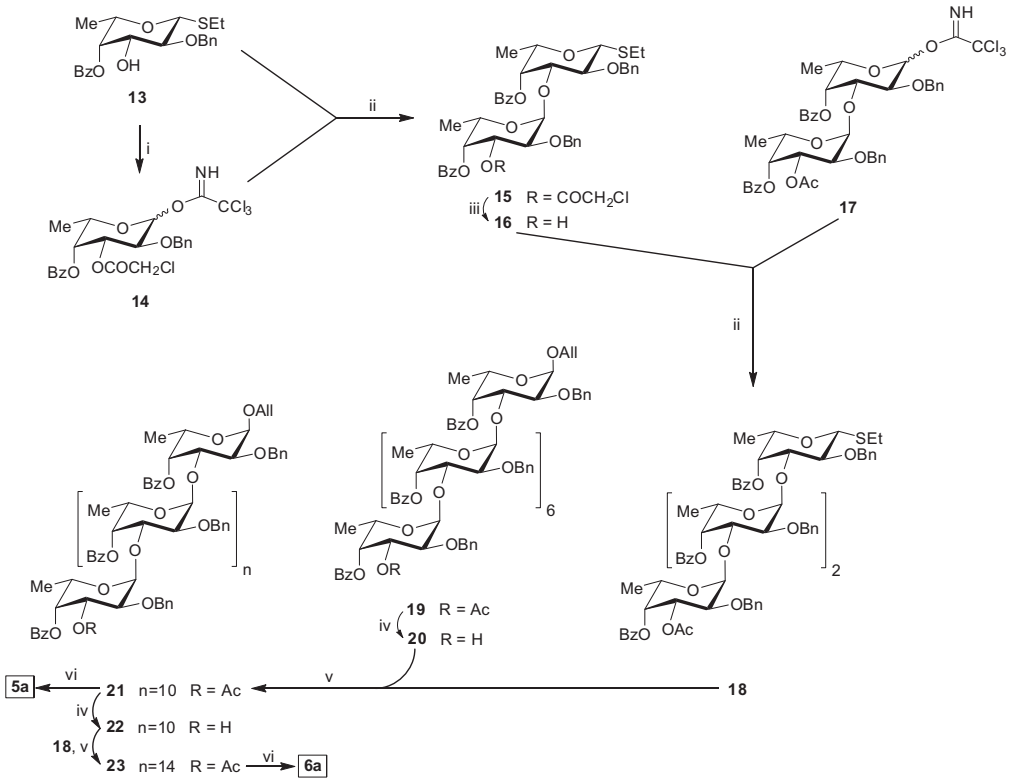
2.2. Synthesis of per-O-sulfated oligosaccharides 1b–12b

Preparation of per-O-sulfated disaccharides **1b** and **11b** from the corresponding unprotected compounds **1a** and **11a** was reported to be efficient under the treatment with the $Py{\cdot}SO_3$ complex in DMF at room temperature.[14] The same conditions were shown to be inapplicable for per-O-sulfation of tetrasaccharide **2a** and resulted in the formation only of a mixture of partially sulfated derivatives.[2] The temperature increase and the variation of the solvents and sulfation reagents afforded no per-O-sulfated tetrasaccharide **2b**.[2]

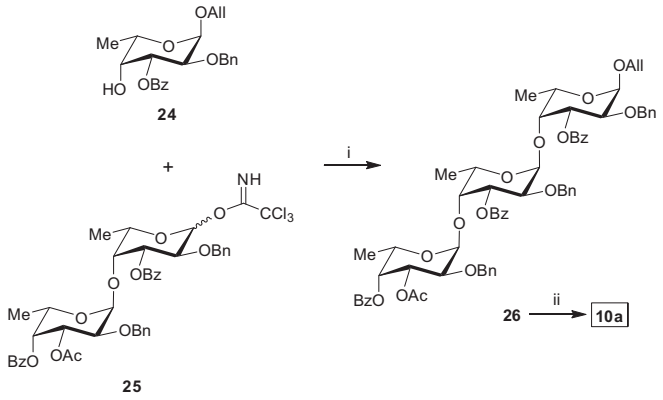
Recently, we reported a new protocol for the per-O-sulfation of polyols of different types with the use of the complex $Et_3N{\cdot}SO_3$ (5.0 equiv per OH group) in DMF at 0 °C in the presence of TfOH (1.0–1.6 equiv per OH group).[2] The addition of strong acid to the reaction mixture was assumed to deliberate unbound SO_3 and facilitate the per-O-sulfation of polyols. In particular, we demonstrated that linear tetrafucoside **2a** can be transformed into per-O-sulfated derivative **2b** in a good yield.[2] In continuation of this work, we studied the acid-promoted per-O-sulfation of larger oligosaccharides (**3a–6a**).

Contrary to the result of the per-O-sulfation of disaccharide **1a** (Table 1, entry 1, see also Fig. 1) and tetrasaccharide **2a**,[2] a similar reaction with hexa- and octasaccharides resulted in the formation of a mixture of partly O-sulfated products. Our attempts to use a larger amount of an acidic promoter gave rise to the formation of an unexpected product with the unusual set of signals in ^1H and ^{13}C NMR spectra. To assess its structure, the sulfation of di-(**1a**) and tetrasaccharide **2a** in the presence of a larger amount of TfOH were studied further.

Thus, the treatment of **1a** in the presence of TfOH in an amount of 2 equiv per OH group resulted in the formation of a 3.2:1 mixture of two disaccharide products **1b** and **27** (Scheme 4 and



Scheme 2. Synthesis of dodeca- and hexadecasaccharides **5a** and **6a**. Reagents and conditions: (i) (1) $CH_2ClCOCl$, Py, CH_2Cl_2; (2) NBS, acetone–water; (3) CCl_3CN, DBU, CH_2Cl_2, −40 °C, 2 h, 72%; (ii) TMSOTf, −90 °C, 1 h, 66% for **15** and 55% for **18**; (iii) NH_2CSNH_2, 2,4,6-collidine, MeOH, 60 °C, 24 h, 94%, (iv) HCl, MeOH, 20 °C, 6 h, 76% for **20**, 72% for **22**; (v) NIS, TfOH, CH_2Cl_2, −40 °C, 2 h, 69% for **21** and 74% for **23**; (vi) (1) H_2, Pd/C, THF–EtOH–AcOH, 20 °C, 5 h, (2) NaOH, CH_2Cl_2–EtOH–H_2O, 60 °C, 12 h; (3) H_2, Pd/C, MeOH–AcOH, 20 °C, 5 h, 61% for **5a** and 54% for **6a**.



Scheme 3. Synthesis of trifucoside **10a**. Reagents and conditions: (i) TMSOTf, −40 °C, 3 h, 77%; (ii) (1) H_2, Pd/C, MeOH–EtOAc, 20 °C, 5 h, (2) NaOH, MeOH–H_2O, 20 °C, 24 h, 75%.

Table 1
Acid-promoted sulfation of disaccharide **1a** by $Et_3N{\cdot}SO_3$ (5 equiv per OH group) in DMF at 0 °C and formation of side product **27**

Entry	Amount of acid (equiv per OH group)	Time (h)	Products	Yield (%)
1	1.0	24	**1b**	77
2	2.0	24	**1b**:**27** = 3.1:1	82
3	2.0	186	**1b**:**27** = 1:2.3 + decomposition	

Table 1, entry 2). Increasing in the reaction time to 168 h (1 week) favored to accumulate side product **27** (entry 3, ratio **1**:**27** = 1:2.3) (Fig. 1) and was accompanied by the formation of decomposition products.

The formation of similar side product **28** was more intensive in the case of homologous tetrasaccharide **2a**. Thus, the acid-promoted sulfation of **2a** by the $Et_3N{\cdot}SO_3$ complex (5 equiv per OH group) in the presence of TfOH (2 equiv per OH group) during 48 h resulted in the formation of product **28** only, which was confirmed by mass spectrometry and NMR spectroscopy. Very surprisingly, their data show that compound **28** has the terminal 2,5-di-O-sulfated α-L-fucofuranose unit in the 'reducing end'. Its structure was confirmed by characteristic resonances for fucofuranose of H-4 (4.02 ppm, t) and C-4 (83.9 ppm) in the ^1H and ^{13}C NMR spectra (see Fig. 2 and Table 2).[30,31] Moreover, the presence of the five-membered ring was evidenced by a correlation of H-1–C-4 as well as C-1–H-4 in HMBC NMR experiments. Spatial proximity of H-4 with H-2 was observed from NOE NMR experiments. Signals of molecular ion in ESI-MS also confirmed that products **2b** and **28** are the isomers.

Similarly to the transformation **2a**→**28**, the treatment of hexasaccharide **3a** and octasaccharide **4a** by the $Et_3N{\cdot}SO_3$ complex (5 equiv per OH group) in the presence of TfOH (2 equiv per OH group) during 48 h at 0 °C resulted to their complete conversion into the corresponding rearranged derivatives **29** and **30** in yields of ~70%. The observed unusual rearrangement of the fucopyranoside residue into the fucofuranoside one with the cleavage of the cyclic C(1)–O(5) bond followed by the recyclization and formation of a new O(4)–C(1) bond but without affecting propyl aglycon belongs to a rare type of reactions in carbohydrate chemistry.[32–34] This transformation is contrary to the usual situation when the cleavage of the acyclic C(1)–O(1) glycoside bond proceeds more intensely than that of the cyclic C(1)–O(5) bond. It is noticeable that the described transformation proceeds selectively only with the fucopyranoside unit at the reducing end but not with other ones

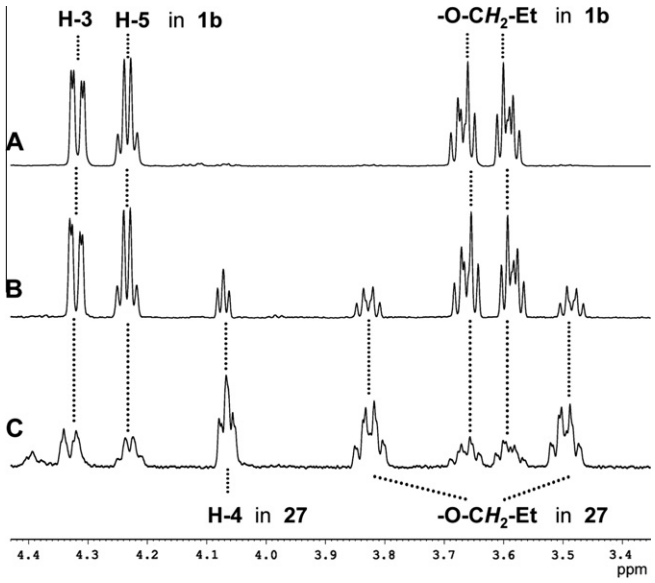
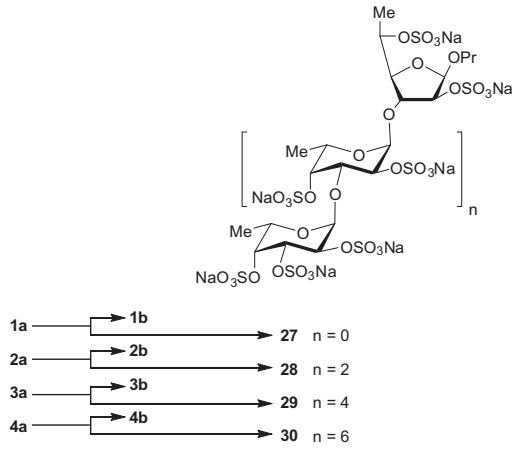


Figure 1. Parts of ^{1}H NMR spectra of the products of TfOH-promoted per-O-sulfation of disaccharide **1a** described in Table 1: (A) entry 1 (only product **1a** is formed), (B) entry 2 and (C) entry 3.



Scheme 4. Products of the TfOH-promoted per-O-sulfation of oligofucosides **1a**–**4a**.

presented in the oligosaccharide chains under investigation. The discussed process does not have direct analogy among chemical reactions, only enzymatic transformation 'fucopyranoside→fucofuranoside' without cleavage of aglycon is known.[35] Detailed investigation of the mechanism and scopes of the observed rearrangement is in progress and will be reported elsewhere.

It could be expected that the optimization of an acidic promoter used for the activation of the sulfating reagent can improve the yield of the target non-rearranged per-O-sulfated products. Using of chlorosulfonic acid (1.0 equiv per OH group) as a promoter also gave compound **29** in a yield of 83% without any significant amounts of product **3b** (Table 3, entry 1). Sulfation promoting activities of both H_2SO_4 and $BF_3{\cdot}Et_2O$ in an amount of 1.0 equiv per OH group were insufficient to perform per-O-sulfation and produced a complex mixture of partly sulfated products (Table 3, entries 2 and 3). Fortunately, the use of weaker trifluoroacetic acid (TFA) led to desired product **3b**. Thus, its use in an amount of 1.0 equiv per OH group formed a 5:1 mixture (^{1}H NMR monitoring) of **3b** and **29** (Table 3, entry 4), while a decrease in the amount of TFA down to 0.5 equiv per OH group gave 76% of desired **3b** as the only formed product (Table 3, entry 5).

Promotion with TFA, which was used in the synthesis of hexasaccharide **3b** (Table 3, entry 5), was successfully applied to the synthesis of per-O-sulfated octasaccharide **4b** (yield 78%), dodecasaccharide **5b** (yield 72%), and hexadecasaccharide **6b** (yield 75%) from parent unsubstituted oligofucosides **4a**–**6a**. Compounds **4b**, **5b**, and **6b** had one product in the ^{1}H NMR spectra with the signal groups presented in the spectra of previously synthesized α-(1→3)-linked oligofucosides **2b** and **3b**. The ratio of integral intensities of H-1 signals for 'reducing' unit (δ 5.21, d) and non-reducing units (δ 5.40, br s) corresponded well to a number of fucopyranose residues in oligosaccharides **4b**–**6b** (Fig. 3).

Per-O-sulfation of oligosaccharides **8a** and **9a** related to the second type of fucoidan backbone consisted of alternating α-(1→4)- and α-(1→3)-linked fucopyranose residues and only of α-(1→4)-linked compounds **7a** and **10a** were studied further starting first from disaccharide **7a**. Both TFA and TfOH acids were tested as promoters to give desired pentasulfate **7b** in a yield of 80% and 83%, respectively (Table 4, entries 1 and 2). No rearrangement of the terminal fucopyranose residue (at the 'reducing' end) into the fucofuranose one is possible for compounds **7a**–**10a** because of the 4-O-substitution of this unit in these compounds. Therefore, for these examples TfOH was used as the promoter of sulfation in an amount of 1 equiv per OH group to give per-O-sulfated tetra- and

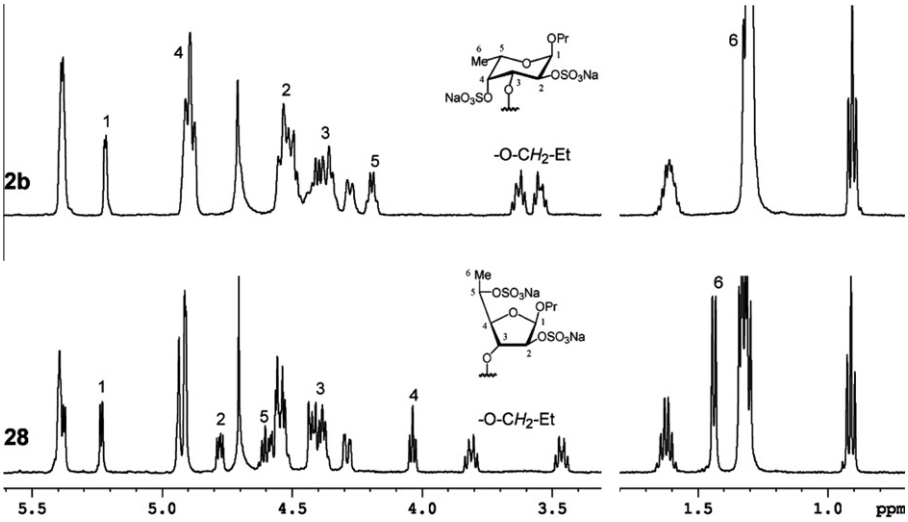


Figure 2. Comparison of ^{1}H NMR spectra of isomeric tetrasaccharides **2b** and **28**.

Table 2
Selected spectral characteristics of **2b** and **28**

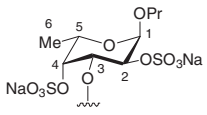
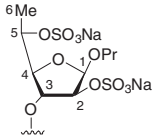
Structure	Selected NMR data						
 **2b**	H-1	H-2	H-3	H-4	H-5	H-6	O–CH_2–Et
	5.21	4.52	4.28	4.90	4.22	1.30	3.55; 3.63
	C-1	C-2	C-3	C-3	C-5	C-6	O–CH_2–Et
	97.4	76.2	76.1	81.3	68.3	17.0	71.9
	$J_{H-1,H-2}$	$J_{H-4,H-5}$	$J_{C-4,H-1}$	$J_{C-1,H-4}$	$J_{C-5,H-1}$	$J_{C-1,H-5}$	
	3.4 Hz	~1 Hz	—	—	6.9 Hz	—	
 **28**	H-1	H-2	H-3	H-4	H-5	H-6	O–CH_2–Et
	5.23	4.77	4.43	4.02	4.61	1.45	3.47; 3.82
	C-1	C-2	C-3	C-3	C-5	C-6	O–CH_2–Et
	101.2	81.6	81.2	83.9	78.6	18.0	71.8
	$J_{H-1,H-2}$	$J_{H-4,H-5}$	$J_{C-4,H-1}$	$J_{C-1,H-4}$	$J_{C-5,H-1}$	$J_{C-1,H-5}$	
	4.4 Hz	6.0 Hz	7.0 Hz	3.2 Hz	—	—	

Table 3
Sulfation of hexasaccharide **3a** with $Et_3N{\cdot}SO_3$ (5 equiv per OH group) in DMF at 0 °C promoted by different acids

Entry	Acid	Amount of acid (equiv per OH group)	Products	Yield (%)
1	$ClSO_3H$	1.0	**29**	83
2	H_2SO_4	1.0	Mixture of partially sulfated products	
3	$BF_3{\cdot}Et_2O$	1.0	Mixture of partially sulfated products	
4	TFA	1.0	**3b**:**29** ~ 5:1	73
5	TFA	0.5	**3b**	76

hexasaccharides **8b**, **9b**, and **10b** in 84%, 83%, and 75% yields, respectively (Table 4, entries 3–5). Comparable results were obtained also in the preparation of per-O-sulfated disaccharides **11b** and **12b** (Table 4, entries 6 and 7).

3. Conclusion

The synthesis of per-O-sulfated oligosaccharides **1b**–**12b** related to various types of fucoidans is described. Preparation of target products is achieved by using acid-promoted sulfation suitable for oligosaccharides of different types. The described acid-promoted sulfation protocol appeared to be a powerful method for the per-O-sulfation of large oligosaccharides, which is not accessible in the preparative scale by previously known methods. The unknown rearrangement of the fucopyranose unit at the reducing end into the fucofuranose one was observed and the efficiency of this process depended on the type of the used acid promoter. The variation of the type and amount of the acidic promoter allows the direct formation of per-O-sulfated rearranged **28**–**30** or non-rearranged **1b**–**6b** oligosaccharides to access. The sulfation of oligosaccharides **7a**–**12a** with 4-O- or 2-O-substituted terminal residues was free from any side processes and gave per-O-sulfated derivatives **7b**–**12b** in a good yield. The results of conformational and biological studies of synthetic fucoidan fragments **1b**–**12b** will be published elsewhere.

4. Experimental

4.1. General methods

TLC was performed on Silica Gel 60 F_{254} (Merck) with toluene-EtOAc and with detection by charring with H_3PO_4. Liquid chromatography was performed on Silicagel 60–200 μm (Fluka) by gradient elution with toluene-EtOAc. Gel chromatography was performed on a BioBeads SX-3 (Bio Rad) column (2 × 70 cm) by elution with toluene at a flow rate of 1 mL/min and on a Sephadex G-15 column (3.5 × 50 cm) by elution with water at a flow rate of 1 mL/min. Optical rotations were determined with a Jasco DIP-360 digital polarimeter at 26–30 °C. All solvents used for the syntheses were purified according to conventional procedures.[36] NMR spectra for substituted compounds were recorded on AM-300, DRX-500, and Avance 600 Bruker spectrometers at 303 K. NMR spectra for non-protected oligosaccharides **5a** and **10a** were recorded in D_2O, for **6a** in CD_3OD on a DRX-500 Bruker spectrometer. NMR spectra for sulfated oligosaccharides **1b–12b**, **27–30** were recorded in D_2O on DRX-500 and Avance 600 Bruker spectrometers. Gradient enhanced 2D gCOSY, gNOESY, and gHSQC experiments, as well as TOCSY experiments, were used for resonance assignment. High resolution mass spectra (HR MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI).[37] The measurements were done 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 done 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. All reactions involving air- or moisture-sensitive reagents were carried out using dry solvents under dry argon.

4.2. Preparation of protected oligosaccharides

4.2.1. 4-*O*-Benzoyl-2-*O*-benzyl-3-*O*-chloroacetyl-L-fucopyranosyl trichloroacetimidate (14)

To a soln of monosaccharide **13** (400 mg, 1.00 mmol) in anhydrous CH_2Cl_2 (10 mL), Py (320 μL, 4.0 mmol) and chloroacetylchloride (160 μL, 2.0 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 (10:1 toluene–EtOAc) to give the chloroacetylated derivative as a yellowish foam. Then it was dissolved in (1:9) H_2O–acetone CH_3COCH_3 (20 mL) and *N*-bromosuccinimide (535 mg, 3.00 mmol) was added at 0 °C. The mixture was vigorously stirred for 10 min, then diluted with CH_2Cl_2 and washed with aq $NaHCO_3$ (3 × 100 mL). The organic phase was dried over anhyd Na_2SO_4 and concentrated under diminished pressure giving a white residue. To a soln of the above residue in anhyd CH_2Cl_2 (5 mL) CCl_3CN (1 mL, 10.0 mmol) and DBU (75 μL, 0.50 mmol)

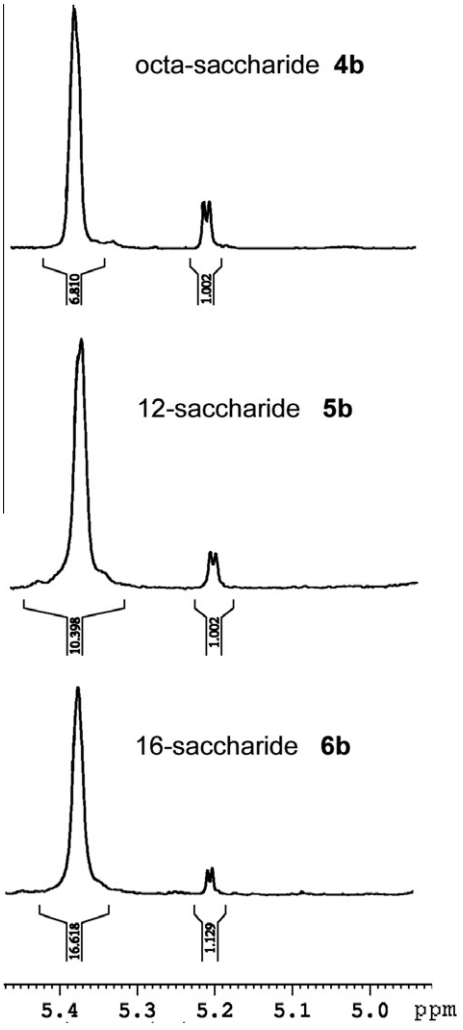


Figure 3. Parts of ^{1}H NMR spectra of per-O-sulfated octa-, dodeca-, and hexadecasaccharides **4b**–**6b** with the integration of anomeric signals of reducing and non-reducing residues.

Table 4
Acid-promoted sulfation of oligosaccharides **7a**–**12a** by the treatment with 5 equiv per OH group $Et_3N{\cdot}SO_3$ in DMF

Entry	Saccharide	Acid	Amount of acid (equiv per OH group)	Product	Yield (%)
1	**7a**	TFA	0.5	**7b**	80
2	**7a**	TfOH	1.0	**7b**	83
3	**8a**	TfOH	1.0	**8b**	84
4	**9a**	TfOH	1.0	**9b**	83
5	**10a**	TfOH	1.0	**10b**	75
6	**11a**	TfOH	1.0	**11b**	72
7	**12a**	TfOH	1.0	**12b**	85

were added 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 column chromatography (5:1 petroleum ether–EtOAc) gave **14** (415 mg, 72% over three steps, α/β = 1.4:1) as a syrup; ^{1}H NMR (300 MHz, $CDCl_3$): α-isomer—δ 1.24 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6), 3.91–3.97 (m, 2H, CH_2Cl), 4.18 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 7.9 Hz, H-2), 4.48 (q, 1H, $J_{5,6}$ 6.3 Hz, H-5), 4.63–4.76 (m, 2H, CH_2Ph), 5.55 (dd, 1H, $J_{2,3}$ 7.9 Hz, $J_{3,4}$ 3.2 Hz, H-3), 5.63 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 6.61 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 7.20–8.10 (m, 10H, 2Ph), 8.66 (s, 1H, =N*H*); β-isomer—δ 1.32 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6), 3.75–3.90 (m, 2H, CH_2Cl), 4.02 (t, 1H, $J_{1,2}$, $J_{2,3}$ 8.1 Hz, H-2), 4.10 (q, 1H, $J_{5,6}$ 6.4 Hz, H-5), 4.65, 4.91 (2d, 2H, *J* 11.3 Hz, CH_2Ph), 5.25 (dd, 1H, $J_{2,3}$ 8.1 Hz, $J_{3,4}$ 3.3 Hz, H-3), 5.51 (d, 1H, $J_{3,4}$ 3.3 Hz, H-4), 5.91 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 7.20–8.10 (m, 10H, 2Ph), 8.77 (s, 1H, =N*H*). Anal. Calcd for $C_{24}H_{23}Cl_4NO_7$: C, 49.76; H, 4.00; N, 2.42. Found: C, 49.52; H, 4.07; N, 2.64.

4.2.2. Ethyl 4-*O*-benzoyl-2-*O*-benzyl-3-*O*-chloroacetyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-1-thio-β-L-fucopyranoside (15)

A mixture of MS 4 Å (500 mg), thioglycoside acceptor **13** (300 mg, 0.75 mmol), and donor **14** (400 mg, 0.69 mmol) in CH_2Cl_2 (8 mL) was stirred for 30 min at room temperature, cooled to −90 °C, and then TMSOTf (50 μL, 0.26 mmol) was added dropwise. The resulting mixture was stirred at −90 to −80 °C until the disappearance of starting **14** (TLC monitoring), quenched with Et_3N, diluted with $CHCl_3$, and filtered through a Celite layer. Column chromatography of the residue (5:1 petroleum ether–EtOAc) afforded **15** (373 mg, 66%) as a colorless foam; $[\alpha]_D$ −214 (*c* 1.0, EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (d, 3H, $J_{5,6}$ 6.5 Hz, H-6^{II}), 1.28 (d, 3H, $J_{5,6}$ 6.8 Hz, H-6^{I}), 1.42 (t, 3H, *J* 7.4 Hz, CH_2CH_3), 2.82–2.98 (m, 2H, CH_2CH$_3$), 3.66–3.79 (m, 2H, CH_2Cl), 3.80–3.96 (m, 3H, H-2^{I}, H-5^{I}, H-2^{II}), 4.04 (dd, 1H, $J_{2,3}$ 9.4 Hz, $J_{3,4}$ 3.2 Hz, H-3^{I}), 4.27 (q, 1H, $J_{5,6}$ 6.5, H-5^{II}), 4.32, 4.50 (2d, 2H, *J* 12.5 Hz, CH_2Ph), 4.60 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1^{I}), 4.71, 5.14 (2d, 2H, *J* 9.7 Hz, CH_2Ph), 5.18 (d, 1H, $J_{4,3}$ 3.4 Hz, H-4^{II}), 5.39 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1^{II}), 5.48 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.4 Hz, H-3^{II}), 5.69 (d, 1H, $J_{3,4}$ 3.2, H-4^{I}), 7.05–8.10 (m, 20H, 4Ph). Anal. Calcd for $C_{44}H_{47}ClO_{11}S$: C, 64.50; H, 5.78. Found: C, 64.70; H, 5.90.

4.2.3. Ethyl 4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-1-thio–L-fucopyranoside (16)

A mixture of disaccharide **15** (170 mg, 0.21 mmol), 2,4,6-collidine (30 μL, 0.22 mmol), and thiourea (77 mg, 1.01 mmol) in MeOH (6 mL) and $CHCl_3$ (1 mL) was boiled under reflux for 24 h, cooled, and evaporated to dryness. A soln of the residue in $CHCl_3$ was washed with 1 M HCl and satd $NaHCO_3$ and concentrated. The residue was purified by column chromatography (5:1 toluene–EtOAc) to give **16** (145 mg, 94%) as a white foam; $[\alpha]_D$ −174 (*c* 1.0, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (d, 3H, $J_{5,6}$ 6.5 Hz, H-6^{II}), 1,25 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.38 (t, 3H, *J* 7.5 Hz, CH_2CH_3), 2.00 (s br, 1H, O*H*), 2.78–2.91 (m, 2H, CH_2CH$_3$), 3.75 (dd, 1H, $J_{1,2}$ 3.1 Hz, $J_{2,3}$ 10 Hz, H-2^{II}), 3.78–3.84 (m, 2H, H-2^{I}, H-5^{I}), 4.03 (dd, 1H, $J_{2,3}$ 9.4, $J_{3,4}$ 3.0 Hz, H-3^{I}), 4.09–4.14 (m br, 1H, H-3^{II}), 4.21 (q, 1H, $J_{5,6}$ 6.5 Hz, H-5^{II}), 4.35, 4.54 (2d, 2H, *J* 12.0 Hz, CH_2Ph), 4.57 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1^{I}), 4.66, 5.07 (2d, 2H, *J* 10.3 Hz, CH_2Ph), 5.04 (d, 1H, $J_{3,4}$ 3.7 Hz, H-4^{II}), 5.43 (d, 1H, $J_{1,2}$ 3.1 Hz, H-1^{II}), 5.69 (d, 1H, $J_{3,4}$ 3.0 Hz, H-4^{I}), 7.10–8.10 (m, 20H, 4Ph). Anal. Calcd for $C_{42}H_{46}O_{10}S$: C, 67.91; H, 6.24. Found: C, 68.04; H, 6.49.

4.2.4. Ethyl 3-*O*-acetyl-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-1-thio–L-fucopyranoside (18)

Glycosylation of difucoside **16** (130 mg, 0.175 mmol) with trichloroacetimidate **17** (170 mg, 0.192 mmol) as described for the preparation of **15** gave tetrasaccharide **18** (141 mg, 55%) as a yellowish syrup; $[\alpha]_D$ −235 (*c* 1.0, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.55 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6^{IV}), 0.85 (d, 6H, $J_{5,6}$ 6.5 Hz, H-6$^{II–III}$), 1.24 (d, 3H, $J_{5,6}$ 6.5 Hz, H-6^{I}), 1.37 (t, 3H, *J* 7.4 Hz, CH_2CH_3), 2.02 (s, 3H, COCH_3), 2.75–2.90 (m, 2H, CH_2CH$_3$), 3.76 (dd, 1H, $J_{1,2}$ 3.4 Hz, $J_{2,3}$ 10.5, H-2^{IV}), 3.78–3.84 (m, 2H, H-2^{I}, H-5^{I}), 3.92–4.00 (m, 2H, H-2$^{II–III}$), 4.01 (dd, 1H, $J_{2,3}$ 9.4 Hz, $J_{3,4}$ 3.0 Hz, H-3^{I}), 4.12–4.21 (m, 5H, H-5$^{II–IV}$, H-3^{III}, PhC*H*H′), 4.32–4.42 (m, 4H, 3 × PhC*H*H′, H-3^{II}), 4.53–4.68 (m, 4H, 3 × PhC*H*H′, H-1^{I}), 5.00 (d, 1H, $J_{3,4}$ 3.1 Hz,

H-4[IV]), 5.07–5.11 (m, 2H, H-1[IV], PhC*H*H′), 5.16 (d, 1H, $J_{3,4}$ 2.6 Hz, H-4[III]), 5.24 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.1 Hz, H-3[IV]), 5.28–5.31 (m, 3H, H-1[II–III], H-4[II]), 5.67 (d, 1H, $J_{4,5}$ 3.0 Hz, H-4[I]), 7.00–8.12 (m, 40H, 8Ph). Anal. Calcd for $C_{84}H_{88}O_{21}S$: C, 68.84; H, 6.05. Found: C, 68.61; H, 5.91.

4.2.5. Allyl 4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranoside (20)

Anhyd HCl in MeOH (0.5 M, 5.2 mL), obtained by adding AcCl (200 μL, 2.8 mmol) to chilled MeOH (5 mL), was added to a soln of **19** (245 mg, 0.087 mmol) in anhyd CH_2Cl_2 (2 mL). The resulting mixture was kept for 6 h at ambient temperature, diluted with $CHCl_3$, washed with satd $NaHCO_3$ and water, and concentrated. Column chromatography of the residue (10:1 toluene–EtOAc) gave **20** (184 mg, 76%) as a colorless foam; $[\alpha]_D$ −287 (*c* 1.0, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.52–0.65 (m, 12H, 4 × H-6), 0.68, 0,99, 1.11, 1.20 (4d, 12H, $J_{5,6}$ 6.5 Hz, 4 × H-6), 3.55–4.52 (m, 42H, 8 × H-2, 8 × H3, 8 × H-5, 8 × PhC*H*$_2$, CH$_2$=CH–C*H*$_2$), 4.70–5.35 (m, 16H, 8 × H-1, 6 × H-4, C*H*$_2$=CH–CH$_2$), 5.42 (s br, 1H, H-4), 5.63 (s br, 1H, H-4), 5.87–6.00 (m, 1H, CH$_2$=C*H*–CH$_2$), 6.90–8.00 (80H, 16 × Ph). Selected ^{13}C NMR data (125 MHz, $CDCl_3$): δ 15.6–16.0 (8 × C-6), 91.9–93.2 (7 × C-1), 96.3 (C-1), 117.7 (*C*H$_2$=CH–CH$_2$). Anal. Calcd for $C_{163}H_{166}O_{41}$: C, 70.40; H, 6.02. Found: C, 70.23; H, 6.09.

4.2.6. Allyl 3-*O*-acetyl-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranoside (21)

To a soln of **21** (172 mg, 0.062 mmol) and **18** (91 mg, 0.062 mmol) in CH_2Cl_2 (3 mL), MS 4 Å (300 mg) was added, and the resulting mixture was stirred for 30 min at rt. After cooling to −15 °C NIS (21 mg, 0.093 mmol) was added, and the mixture was stirred for 10 min. Then the temperature of the reaction mixture was decreased to −40 °C, and TfOH (2.7 μL, 0.03 mmol) was added. After the stirring for 2 h the reaction was quenched with a drop of pyridine, the mixture was diluted with $CHCl_3$ and filtered through a Celite layer. The filtrate was washed with 1 M aq $Na_2S_2O_3$ and water, concentrated, and was twice coevaporated with toluene. Chromatographic purification of the residue (15:1 toluene–EtOAc) produced **21** (179 mg, 69%) as a colorless syrup; $[\alpha]_D$ −288 (*c* 1.0, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.56 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6), 0.60–0.70 (m, 24H, 8 × H-6), 0.75, 1.07, 1.17, (3d, 9H, $J_{5,6}$ 6.5 Hz, 3 × H-6), 1.74 (s, 3H, COC*H*$_3$), 3.74–4.83 (m, 61H, 12 × H-2, 11 × H3, 12 × H-5, 12 × PhC*H*$_2$, CH$_2$=CH–C*H*$_2$), 4.96–5.40 (m, 25H, 12 × H-1, 10 × H-4, H-3, C*H*$_2$=CH–CH$_2$), 5.50 (s br, 1H, H-4), 5.70 (s br, 1H, H-4), 5.95–6.04 (m, 1H, CH$_2$=C*H*–CH$_2$), 6.96–8.06 (120H, 24 × Ph). Selected ^{13}C NMR data (125 MHz, $CDCl_3$): δ 15.5–16.3 (12 × C-6), 92.5–93.3 (11 × C-1), 96.5 (C-1), 117.8 (*C*H$_2$=CH–CH$_2$). Anal. Calcd for $C_{245}H_{248}O_{62}$: C, 70.32; H, 5.97. Found: C, 70.31; H, 6.03.

4.2.7. Allyl 4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranoside (22)

O-Deacetylation of **21** (108 mg, 0.026 mmol) was performed as described for the preparation of **20** to give dodecasaccharide **22** (77 mg, 72%); $[\alpha]_D$ −288 (*c* 1.0, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.63–0.73 (m, 27H, 8 × H-6), 0.78, 1.09, 1.20, (3d, 9H, $J_{5,6}$ 6.5 Hz, 3 × H-6), 3.63–4.88 (m, 62H, 12 × H-2, 12 × H3, 12 × H-5, 12 × PhC*H*$_2$, CH$_2$=CH–C*H*$_2$), 4.98–5.44 (m, 24H, 12 × H-1, 10 × H-4, C*H*$_2$=CH–CH$_2$), 5.51 (s br, 1H, H-4), 5.72 (s br, 1H, H-4), 5.96–6.04 (m, 1H, CH$_2$=C*H*–CH$_2$), 6.98–8.10 (120H, 24 × Ph). Selected ^{13}C NMR data (150 MHz, $CDCl_3$): δ 15.8–16.3 (12 × C-6), 91.6–93.3 (11 × C-1), 96.6 (C-1), 117.7 (*C*H$_2$=CH–CH$_2$). Anal. Calcd for $C_{243}H_{246}O_{61}$: C, 70.45; H, 5.99. Found: C, 70.35; H, 6.13.

4.2.8. Allyl 3-*O*-acetyl-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranoside (23)

Glycosylation of dodecasaccharide **22** (70 mg, 0.0169 mmol) with tetrasaccharide **18** (27 mg, 0.182 mmol) was performed as described for the preparation of **21** and gave hexadecasaccharide **23** (69 mg, 74%) as a yellowish syrup; $[\alpha]_D$ −277 (*c* 1.0, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.58 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6), 0.62–0.73 (m, 36H, 12 × H-6), 0.78, 1.08, 1.20, (3d, 9H, $J_{5,6}$ 6.5 Hz, 3 × H-6), 1.75 (s, 3H, COC*H*$_3$), 3.74–4.85 (m, 81H, 16 × H-2, 15 × H3, 16 × H-5, 16 × PhC*H*$_2$, CH$_2$=CH–C*H*$_2$), 4.98–5.43 (m, 33H, 16 × H-1, 14 × H-4, H-3, C*H*$_2$=CH–CH$_2$), 5.51 (s br, 1H, H-4), 5.71 (s br, 1H, H-4), 5.97–6.05 (m, 1H, CH$_2$=C*H*–CH$_2$), 7.00–8.10 (160H, 32 × Ph). Selected ^{13}C NMR data (150 MHz, $CDCl_3$): δ 15.5–16.3 (16 × C-6), 92.6–93.3 (15 × C-1), 96.6 (C-1), 117.6 (*C*H$_2$=CH–CH$_2$). Anal. Calcd for $C_{325}H_{328}O_{82}$: C, 70.38; H, 5.96. Found: C, 70.49; H, 5.91.

4.2.9. Allyl 3-*O*-acetyl-4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→4)-3-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→4)-3-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranoside (26)

A mixture of MS 4 Å (150 mg), acceptor **24** (40 mg, 0.101 mmol), and donor **25** (97 mg, 0.110 mmol) in CH_2Cl_2 (2 mL) was stirred for 30 min at room temperature, cooled to −40 °C, and then TMSOTf (4.6 μL, 0.024 mmol) was added. The resulting mixture was stirred at −40 to −30 °C until the disappearance of

starting **25** (TLC monitoring), quenched with Et_3N, diluted with $CHCl_3$, and filtered through a Celite layer. Column chromatography of the residue (5:1 petroleum ether–EtOAc) gave **26** (87 mg, 77%) as a colorless foam; $[\alpha]_D$ −168 (*c* 1.0, EtOAc). ^1H NMR (600 MHz, $CDCl_3$): δ 0.47 (d, 3H, $J_{5,6}$ 6.3, H-6^{III}), 0.77 (d, 3H, $J_{5,6}$ 6.6 Hz, H-6^{II}), 1.33 (d, 3H, $J_{5,6}$ 6.6 Hz, H-6^{I}), 1.91 (s, 3H, $COCH_3$), 3.94 (dd, 1H, $J_{1,2}$ 3.3 Hz, $J_{2,3}$ = 10.6 Hz), 4.04–4.26 (m, 7H, H-$2^{I–II}$, –$CH_2CH{=}CH_2$, H-5^{I}, H-$4^{I–II}$), 4.28 (q, 2H, $J_{5,6}$ 6.4 Hz, H-$5^{II–III}$), 4.53–4.75 (m, 6H, 3 × $PhCH_2$), 4.88 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1^{I}), 5.03 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1^{II}), 5.10 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1^{III}), 5.23, 5.36 (2d, 2H, *J* 10.5 Hz, *J* 16.8 Hz,, $–CH_2CH{=}CH_2$), 5.43 (s br, 1H, H-4^{III}), 5.46 (dd, 1H, $J_{2,3}$ 10.8 Hz, $J_{3,4}$ 2.9 Hz, H-3^{III}), 5.55–5.61 (m, 2H, H-$3^{I–II}$), 5.92–6.00 (m, 1H, $–CH_2CH{=}CH_2$), 7.15–8.10 (m, 30H, 6Ph). Anal. Calcd for $C_{65}H_{68}O_{17}$: C, 69.63; H, 6.11. Found: C, 69.41; H, 5.97.

4.3. Preparation of unprotected oligofucosides 5a, 6a, and 10a

4.3.1. Propyl α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranoside (5a)

To a soln of oligofucoside **21** (66 mg, 0.016 mmol) in (1:3:0.1) THF–EtOH–AcOH (3 mL) Pd/C (10%, 40 mg) was added. The mixture was stirred under H_2 (1 atm) at rt for 5 h and then filtered through a Celite layer. The catalyst was carefully washed with MeOH–CH_2Cl_2, and the combined filtrates were concentrated. The residue was dissolved in a mixture CH_2Cl_2–EtOH (1:5) (1.5 mL) and treated with 2 M aq NaOH (0.7 mL) for 12 h at 60 °C. The oligosaccharide products were isolated from the reaction mixture by column chromatography on a gel Sephadex G-15 (60 × 3 cm) with water elution. Freeze-drying of the oligosaccharide fraction, dissolution of the residue in MeOH–AcOH (20:1), and stirring of the mixture under H_2 (1 atm) in the presence of 10% Pd/C (10 mg) for 5 h led to the complete deprotection of **21**. Separation of the mixture from Pd/C by filtration, concentration of the solution, column chromatography of the residue on a gel Sephadex G-15 (60 × 3 cm) with water elution, and further lyophilization gave **5a** (18 mg, 61%) as a white amorphous powder; $[\alpha]_D$ −143 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.93 (t, 3H, *J* 7.3 Hz, $CH_2CH_2CH_3$), 1,24 (d, 36H, $J_{5,6}$ 6.2 Hz, H-$6^{I–XII}$), 1.60–1.69 (m, 2H, $CH_2CH_2CH_3$), 3.50–3.56, 3.59–3.65 (2 × m, 2H, $CH_2CH_2CH_3$), 3.79–3.85 (m, 2H, H-2^{XII}, H-4^{XII}), 3.91–4.14 (m, 35H, H-$2^{I–XI}$, H-$3^{I–XII}$, H-$4^{I–XI}$, H-5^{I}), 4.30–4.42 (m, 11H, H-$5^{II–XII}$), 4.93 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 5.08 (d, 1H, $J_{1,2}$ 3.8, H-1^{XII}), 5.12 (br s, 10H, H-$1^{II–XI}$). ^{13}C NMR (150 MHz, D_2O): δ 11.3 ($CH_2CH_2CH_3$), 16.8 (C-$6^{I–XII}$), 23.6 ($CH_2CH_2CH_3$), 67.9 (C-$2^{I–XI}$), 68.1 (C-$5^{I–XI}$), 68.4 (C-5^{XII}), 69.5 (C-2^{XII}), 70.0 (C-$4^{I–XI}$), 71.0 (C-3^{XII}), 71.7 ($CH_2CH_2CH_3$), 73.4 (C-4^{XII}), 75.9 (C-3^{I}), 76.4 (C-$3^{II–XI}$), 96.5 (C-1^{I}), 97.0 (C-$1^{II–XI}$), 99.7 (C-1^{XII}). HRESIMS: found *m/z* 929.3672; calcd for $C_{75}H_{128}O_{49}$ $[M+2Na]^{2+}$ 929.3654.

4.3.2. Propyl α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranosyl-(1→3)-α-L-fucopyranoside (6a)

Deprotection of hexadecasaccharide **23** (62 mg, 0.011 mmol) as described for the preparation of compound **5a** gave hexadecasaccharide **6a** (14 mg, 54%); $[\alpha]_D$ −157 (*c* 1.0, H_2O).

^1H NMR (600 MHz, CD_3OD): δ 0.91 (t, 3H, *J* 7.6 Hz, $CH_2CH_2CH_3$), 1.22 (d, 48H, *J* 6.3 Hz, H-$6^{I–XVI}$), 1.60–1.68 (m, 2H, $CH_2CH_2CH_3$), 3.48–3.55, 3.57–3.64 (2 × m, 2H, $CH_2CH_2CH_3$), 3.78–3.83 (m, 2H, H-2^{XVI}, H-4^{XVI}), 3.88–4.09 (m, 47H, H-$2^{I–XV}$, H-$3^{I–XVI}$, H-$4^{I–XV}$, H-5^{I}), 4.28–4.39 (m, 15H, H-$5^{II–XVI}$), 4.90 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1^{I}), 5.06 (d, 1H, $J_{1,2}$ 3.2, H-1^{XVI}), 5.10 (br s, 14H, H-$1^{II–XV}$). Selected ^{13}C NMR data (150 MHz, D_2O): δ 16.8 (C-$6^{I–XII}$), 67.8 (C-$2^{I–XI}$), 68.1 (C-$5^{I–XI}$), 69.9 (C-$4^{I–XI}$), 76.2 (C-$3^{II–XI}$), 97.0 (C-$1^{II–XI}$). HRESIMS: found *m/z* 1221.4794; calcd for $C_{99}H_{168}O_{65}$ $[M+2Na]^{2+}$ 1221.4812.

4.3.3. Propyl α-L-fucopyranosyl-(1→4)-α-L-fucopyranosyl-(1→4)-α-L-fucopyranoside (10a)

A mixture of trifucoside **26** (75 mg, 0.067 mmol) and the catalyst 10% Pd/C (37 mg) in MeOH–EtOAc (3:1) (4 mL) was stirred under H_2 (1 atm) at rt for 5 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 1 M aq NaOH (1 mL) for 24 h. Deprotected trisaccharide was isolated from the reaction mixture by column chromatography on a gel Sephadex G-15 (60 × 3 cm) with water elution followed by lyophilization to give **10a** (25 mg, 75%) as a white amorphous powder; $[\alpha]_D$ −131 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.93 (t, 3H, J 7.4 Hz, $CH_2CH_2CH_3$), 1.19 (d, 3H, $J_{5,6}$ 6.6 Hz, H-6^{III}), 1.27 (d, 3H, $J_{5,6}$ 6.7 Hz, H-6^{II}), 1.32 (d, 3H, $J_{5,6}$ 6.7 Hz, H-6^{I}), 1.60–1.67 (m, 2H, $CH_2CH_2CH_3$), 3.49–3.53, 3.63–3.68 (2 m, 2H, $CH_2CH_2CH_3$), 3.80–3.88 (m, 6H, H-$2^{I–III}$, H-$4^{I–III}$), 3.92–3.98 (m, 2H, H-$3^{I,III}$), 4.03 (dd, 1H, $J_{2,3}$ 10.3 Hz, $J_{3,4}$ 3.2 Hz, H-3^{II}), 4.14 (q, 1H, $J_{5,6}$ 6.6 Hz, H-5^{I}), 4.51–4.58 (m, 2H, H-$5^{II–III}$), 4.94 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{I}), 4.97 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{II}), 5.00 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{III}). ^{13}C NMR (150 MHz, D_2O): δ 11.3 ($CH_2CH_2CH_3$), 16.7 (C-$6^{I–III}$), 23.6 ($CH_2CH_2CH_3$), 68.4, 68.5, 69.1 (C-$5^{I–III}$), 69.6 (H-2^{II}), 70.2, 70.4, 70.6, 70.9 (C-$3^{I–III}$, H-$2^{I,III}$), 71.8 ($CH_2CH_2CH_3$), 73.45 (C-4^{III}), 81.6, 81.7 (C-$4^{I–II}$), 99.83 (C-1^{I}), 101.9, 102.0 (C-$1^{II–III}$). HRESIMS: found *m/z* 521.2186; calcd for $C_{21}H_{38}O_{13}$ $[M+Na]^+$ 521.2205.

4.4. Preparation of per-*O*-sulfated oligofucosides 1b–12b and 28–30

4.4.1. General procedure of acid-promoted O-sulfation

To a vigorously stirred soln of oligosaccharide (10 mg) in anhyd DMF (1 mL) the complex $Et_3N{\cdot}SO_3$ (5 equiv per OH group) was added followed by the introduction of an appropriate promoting acid (0.5–2 equiv per OH group) at 0 °C. The mixture was stirred until the reaction was completed (TLC monitoring), and then an excess of 1 M aq NaOH was added. The aqueous phase was washed with CH_2Cl_2 (2 × 1 mL), then loaded onto a Sephadex G-15 column (60 × 3 cm), and eluted with water; the fraction containing the product was collected and freeze-dried to give the per-O-sulfated oligosaccharide as an amorphous substance.

4.4.2. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranoside pentasodium salt (1b)

Per-O-sulfation of **1a** (10 mg, 0.028 mmol) promoted with TfOH (12 μL, 0.14 mmol, 1.0 equiv per OH group) during 24 h gave **1b** (18.8 mg, 77%); $[\alpha]_D$ −106 (*c* 0.5, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.92 (3H, t, *J* 7.5 Hz, CH_2CH_3), 1.26–1.31 (m, 6H, H-$6^{I–II}$), 1.58–1.67 (m, 2H, CH_2CH_3), 3.53–3.59 (m, 1H, O–CH*H′*-Et), 3.60–3.67 (m, 1H, O–*CH*H′-Et), 4.20 (q, 1H, $J_{5,6}$ 6.6 Hz, H-5^{I}), 4.29 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 2.6 Hz, H-3^{I}), 4.46 (q, 1H, $J_{5,6}$ 6.4 Hz, H-5^{II}), 4.57 (m, 2H, H-$2^{I–II}$), 4.91–4.96 (m, 3H, H-$4^{I–II}$, H-3^{II}), 5.23 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1^{I}), 5.39 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1^{II}). ^{13}C NMR (150 MHz, D_2O): δ 11.3 (CH_2CH_3) 17.2 (C-6^{II}), 17.3 (C-6^{I}), 23.3 (CH_2CH_3), 68.0 (C-5^{I}), 68,6 (C-5^{II}), 71.8 (O–CH_2–Et), 73.8 (C-3^{II}),

74.8 (C-2^{II}), 75.5 (C-3^{I}), 76.0 (C-2^{I}), 80.9 (C-4^{II}), 81.4 (C-4^{I}), 97.6 (C-1^{I}), 99.1 (C-1^{II}). HRESIMS: found *m/z* 884.8561; calcd for $C_{15}H_{23}Na_5O_{24}S_5$ $[M+Na]^+$ 884.8563.

4.4.3. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranoside nonasodium salt (2b)

Per-O-sulfation of **2a** (10 mg, 0.016 mmol) promoted with TFA (5.3 μL, 0.072 mmol, 0.5 equiv per OH group) during 24 h gave **2b** (17.6 mg, 75%); $[\alpha]_D$ −107 (*c* 1.0, H_2O). ^1H NMR (500 MHz, D_2O): 0.94 (t, 3H, *J* 7.4 Hz, $CH_2CH_2CH_3$), 1.29–1.35 (m, 12H, 12 H-6), 1.57–1.66 (m, 2H, $CH_2CH_2CH_3$), 3.52–3.58 (m, 1H, OCHH′), 3.60–3.67 (m, 1H, OCHH′), 4,22 (q, 1H, H-5^{I}, $J_{5,6}$ 6.7 Hz), 4.30–4.47 (m, 5H, H-$3^{I–III}$, H-$5^{II–III}$), 4.51–4.61 (m, 5H, H-$2^{I–IV}$, H-5^{IV}), 4.89–4.97 (m, 5H, H-$4^{I–IV}$, H-3^{IV}), 5.21 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1^{I}), 5.42 (s br, 3H, H-$1^{II–IV}$). ^{13}C NMR (125 MHz, D_2O): δ 11.3 (CH_2CH_3), 17.0, 17.3 (C-$6^{I–IV}$), 23.3 (CH_2CH_3), 68,2, 68.3, 68.8 (C-$5^{I–IV}$), 71.9 (O–CH_2–Et), 73.8, 74.0, 75.2, 76.1, 76.2 (C-$3^{I–IV}$, C-$2^{I–IV}$), 81.2, 81.5 (C-$4^{I–IV}$), 97.4 (C-1^{I}), 98.7, 99.6 (C-$1^{II–IV}$). HRESIMS: found *m/z* 757.8796; calcd for $C_{27}H_{39}Na_9O_{44}S_9$ $[M-2Na]^{2-}$ 757.8798.

4.4.4. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranoside tridecasodium salt (3b)

Per-O-sulfation of **3a** (10 mg, 0.011 mmol) promoted with TFA (5.3 μL, 0.72 mmol, 0.5 equiv per OH group) during 24 h gave **3b** (18.3 mg, 76%); $[\alpha]_D$ −89 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.93 (t, 3H, *J* 7.5 Hz, CH_2CH_3), 1.29–1.38 (m, 18H, H-$6^{I–VI}$), 1.60–1.70 (m, 2H, CH_2CH_3), 3.52–3.59 (m, 1H, O–CHH′-Et), 3.60–3.67 (m, 1H, O–CHH′-Et), 4.22 (q, 1H, $J_{5,6}$ 6.7 Hz, H-5^{I}), 4.29–4.46 (m, 9H, H-$3^{I–V}$, H-$5^{II–V}$), 4.47–4.57 (m, 7H, H-$2^{I–VI}$, H-5^{VI}), 4.89–4.96 (m, 7H, H-$4^{I–VI}$, H-3^{VI}), 5.21 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1^{I}), 5.41 (s br, 5H, H-$1^{II–VI}$). ^{13}C NMR (150 MHz, D_2O): δ 11.3 (CH_2CH_3), 17.1, 17.3 (C-$6^{I–VI}$), 23.3 (CH_2CH_3), 68,2, 68.3, 68.9 (C-$5^{I–VI}$), 71.9 (O–CH_2–Et), 73.8 (C-3^{VI}), 74.1 (C-2^{VI}), 75.2, 75.5, 76.1, 76.2 (C-$3^{I–V}$, C-$2^{I–V}$), 81.3, 81.5 (C-$4^{I–VI}$), 97.4 (C-1^{I}), 98.8, 100.1 (C-$1^{II–VI}$). HRESIMS: found *m/z* 1153.7926; calcd for $C_{39}H_{55}Na_{13}O_{64}S_{13}$ $[M+2Na]^{2+}$ 1153.7936.

4.4.5. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranoside heptadecasodium salt (4b)

Per-O-sulfation of **4a** (10 mg, 0.0081 mmol) promoted with TFA (5.1 μL, 0.069 mmol, 0.5 equiv per OH group) during 24 h gave **4b** (18.8 mg, 78%). $[\alpha]_D$ −84 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.96 (t, 3H, *J* 7.6 Hz, CH_2CH_3), 1.32–1.40 (m, 24H, H-$6^{I–VI}$), 1.61–1.71 (m, 2H, CH_2CH_3), 3.54–3.61 (m, 1H, O–CHH′-Et), 3.62–3.69 (m, 1H, O–CHH′-Et), 4.25 (q, 1H, $J_{5,6}$ 6.7 Hz, H-5^{I}), 4.32–4.48 (m, 13H, H-$3^{I–VII}$, H-$5^{II–VII}$), 4.50–4.60 (m, 9H, H-$2^{I–VIII}$, H-5^{VIII}), 4.92–4.99 (m, 9H, H-$4^{I–VIII}$, H-3^{VIII}), 5.25 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1^{I}), 5.44 (s br, 7H, H-$1^{II–VIII}$). ^{13}C NMR (150 MHz, D_2O): δ 11.4 (CH_2CH_3). 17.1, 17.3 (C-$6^{I–VIII}$), 23.4 (CH_2CH_3), 68.2, 68.4, 69.1 (C-$5^{I–VIII}$), 71.9 (O–CH_2–Et), 73.8 (C-3^{VIII}), 74.1 (C-2^{VIII}), 75.2, 75.7, 76.1, 76.3 (C-$3^{I–VII}$, C-$2^{I–VII}$), 81.3, 82.1 (C-$4^{I–VIII}$), 97.4 (C-1^{I}), 98.8, 100.2 (C-$1^{II–VIII}$). HRESIMS: found *m/z* 964.1730; calcd for $C_{51}H_{71}Na_{17}O_{84}S_{17}$ $[M-3Na]^{3-}$ 964.1707.

4.4.6. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranoside sodium salt (5b)

Per-O-sulfation of **5a** (10 mg, 0.0055 mmol) promoted with TFA (5.1 μL, 0.069 mmol, 0.5 equiv per OH group) during 24 h gave **5b** (17.3 mg, 72%); $[\alpha]_D$ −116 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.93 (t, 3H, *J* 7.4 Hz, CH_2CH_3), 1.27–1.44 (m, 36H, H-$6^{I–XII}$), 1.60–1.69 (m, 2H, CH_2CH_3), 3.54–3.59 (m, 1H, O-CHH′-Et), 3.61–3.67 (m, 1H, O–CHH′-Et), 4.22 (q, 1H, $J_{5,6}$ 6.7, H-5^{I}), 4.28–4.45 (m, 21H, H-$3^{I–XI}$, H-$5^{II–XI}$), 4.47–4.56 (m, 13H, H-$2^{I–XII}$, H-5^{XII}), 4.88–4.96 (m, 13H, H-$4^{I–XII}$, H-3^{XII}), 5.24 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1^{I}), 5.41 (s br, 11H, H-$1^{II–XII}$). Selected ^{13}C NMR data (150 MHz, CDC_{l3}): 17.2 (C-$6^{I–XVI}$), 68.3, (C-$5^{I–XVI}$), 75.5 76.3, (C-$3^{I–XV}$, C-$2^{I–XVI}$), 81.2, 82.1 (C-$4^{I–XVI}$), 97.4 (C-1^{I}), 100.0, 98.8 (C-$1^{II–XVI}$).

4.4.7. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranoside sodium salt (6b)

Per-O-sulfation of **6a** (10 mg, 0.0042 mmol) promoted with TFA (5.1 μL, 0.069 mmol, 0.5 equiv per OH group) during 24 h gave **6b** (18.0 mg, 75%); $[\alpha]_D$ −108 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.95 (t, 3H, *J* 7.6 Hz, CH_2CH_3), 1.37 (d, 48H, $J_{5,6}$ 6.1 Hz, H-$6^{I–XVI}$), 1.63–1.70 (m, 2H, CH_2CH_3), 3.55–3.61 (m, 1H, O–CHH′-Et), 3.62–3.68 (m, 1H, O–CHH′-Et), 4.24 (m, 1H, H-5^{I}), 4.32–4.48 (m, 29H, H-$3^{I–XV}$, H-$5^{II–XV}$), 4.49–4.59 (m, 17H, H-$2^{I–XVI}$, H-5^{XVI}), 4.90–4.97 (m, 17H, H-$4^{I–XVI}$, H-3^{XVI}), 5.26 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1^{I}), 5.43 (s br, 15H, H-$1^{II–XVI}$). Selected ^{13}C NMR data (150 MHz, D_2O): 17.1 (C-$6^{I–XVI}$), 68.3, (C-$5^{I–XVI}$), 75.5 76.2, (C-$3^{I–XV}$, C-$2^{I–XVI}$), 81.3, 82.1 (C-$4^{I–XVI}$), 97.4 (C-1^{I}), 100.2, 98.8 (C-$1^{II–XVI}$).

4.4.8. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→4)-2,3-di-*O*-sulfonato-α-L-fucopyranoside pentasodium salt (7b)

Per-O-sulfation of **7a** (10 mg, 0.028 mmol) promoted with TfOH (12.4 μL, 0.14 mmol 1.0 equiv per OH group) during 24 h gave **7b** (20.3 mg, 83%); $[\alpha]_D$ −96 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.97 (t, 3H, *J* 7.5 Hz, –$CH_2CH_2CH_3$), 1.35 (d, 3H, $J_{5,6}$ 6.5 Hz, H-6^{II}), 1.42 (d, 3H, $J_{5,6}$ 6.6 Hz, H-6^{I}), 1.63–1.71 (m, 2H, $CH_2CH_2CH_3$), 3.58–3.64, 3.68–3.73 (2 × m, 2H, $CH_2CH_2CH_3$), 4.24 (q, 1H, $J_{5,6}$ 6.6 Hz, H-5^{I}), 4.32 (br s, 1H, H-5^{I}), 4.57–4.62 (m, 2H, H-2^{II}, H-5^{II}), 4.67 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.8 Hz, H-2^{I}), 4.72 (dd, 1H, $J_{3,4}$ 2.3 Hz, $J_{2,3}$ 10.8 Hz, H-3^{I}), 4.86 (dd, 1H,, $J_{3,4}$ 2.6 Hz, $J_{2,3}$ 10.7 Hz, H-3^{II}), 5.01 (d, 1H, $J_{3,4}$ 2.6 Hz, H-4^{II}), 5.28 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 5.35 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1^{II}). ^{13}C NMR (150 MHz, D_2O): δ 11.4 (–$CH_2CH_2CH_3$), 17.0 (C-6^{I}), 17.3 (C-6^{II}), 23.4 (–$CH_2CH_2CH_3$), 68.5 (C-5^{II}), 68.7 (C-5^{I}), 71.9 (–$CH_2CH_2CH_3$), 73.8 (C-3^{II}), 74.0 (C-2^{I}), 74.2 (C-2^{II}), 75.5 (C-3^{I}), 81.2 (C-$4^{I–II}$), 97.9 (C-1^{I}), 100.3 (C-1^{II}). HRESIMS: found *m/z* 884.8569; calcd for $C_{15}H_{23}Na_5O_{24}S_5$ $[M+Na]^+$ 884.8563; found *m/z* 838.8760; calcd for $[M-Na]^-$ 838.8779.

4.4.9. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→4)-2,3-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→4)-2,3-di-*O*-sulfonato-α-L-fucopyranoside nonasodium salt (8b)

Per-O-sulfation of **8a** (10 mg, 0.016 mmol) promoted with TfOH (12.8 μL, 0.14 mmol, 1.0 equiv per OH group) during 24 h gave **8b** (19.7 mg, 84%); $[\alpha]_D$ −107 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): 0.95 (t, 3H, *J* 7.4 Hz, $CH_2CH_2CH_3$), 1.34–1.42 (m, 12H, H-6$^{I–IV}$), 1.61–1.70 (m, 2H, $CH_2CH_2CH_3$), 3.57–3.61, 3.66–3.71 (2 × m, 2H, $CH_2CH_2CH_3$), 4.23 (q, 1H, $J_{5,6}$ 6.7 Hz, H-5^{I}), 4.31 (br s, 2H, H-4^{I,III}), 4.40 (dd, 1H, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 2.2 Hz, H-3^{II}), 4.44 (q, 1H, $J_{5,6}$ 6.4 Hz, H-5), 4.53 (q, 1H, $J_{5,6}$ 6.5 Hz, H-5), 4.56–4.64 (m, 4H, H-2$^{I–II,\ IV}$, H-5), 4.68 (dd, 1H, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 2.2 Hz, H-3^{I}), 4.72 (dd, 1H, $J_{1,2}$ 3.4 Hz, $J_{2,3}$ 10.8 Hz, H-2^{III}), 4.85 (dd, 1H, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 2.8 Hz, H-3^{IV}), 4.92 (dd, 1H, $J_{2,3}$ 2.4 Hz, $J_{3,4}$ 10.7 Hz, H-3^{III}), 4.96 (d, 1H, $J_{3,4}$ 2.2 Hz, H-4^{II}), 4.99 (d, 1H, $J_{3,4}$ 2.4 Hz, H-4^{IV}), 5.25 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1^{I}), 5.32 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1^{IV}), 5.38 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1^{II}), 5.46 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1^{III}). ^{13}C NMR (150 MHz, D_2O): δ 11.4 (–$CH_2CH_2CH_3$), 17.0, 17.2, 17.3, 17.5 (C-6$^{I–IV}$), 23.4 (–$CH_2CH_2CH_3$), 68.4, 68.8, 69.0, 69.4 (C-5$^{I–IV}$), 71.9 (–$CH_2CH_2CH_3$), 73.2 (C-3^{II}), 73.9 (C-3^{IV}, C-2^{III}), 74.1, 74.2 (C-2^{I,IV}), 74.9 (C-3^{III}), 75.3 (C-2^{II}), 75.8 (C-3^{I}), 80.9 (C-4^{II}), 81.3, 81.4 (C-4$^{I,III–IV}$), 97.5 (C-1^{III}), 97.9 (C-1^{I}), 100.2 (C-1^{IV}), 100.4 (C-1^{II}). HRESIMS: found *m/z* 757.8817; calcd for $C_{27}H_{39}Na_9O_{44}S_9$ $[M-2Na]^{2-}$ 757.8798.

4.4.10. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→4)-2,3-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl–(1→4)-2,3-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→4)-2,3-di-*O*-sulfonato-α-L-fucopyranoside tridecasodium salt (9b)

Per-O-sulfation of **9a** (10 mg, 0.011 mmol) promoted with TfOH (12.7 μL, 0.14 mmol, 1.0 equiv per OH group) during 24 h gave **9b** (20.0 mg, 83%); $[\alpha]_D$ −115 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): 0.96 (t, 3H, *J* 7.5 Hz, $CH_2CH_2CH_3$), 1.35–1.44 (m, 18H, H-6$^{I–VI}$), 1.63–1.70 (m, 2H, $CH_2CH_2CH_3$), 3.57–3.63, 3.67–3.73 (2 × m, 2H, $CH_2CH_2CH_3$), 4.24 (q, 1H, $J_{5,6}$ 6.7 Hz, H-5^{I}), 4.31–4.34 (m, 3H, H-4^{I,III,V}), 4.38–4.41 (m, 2H, H-3^{II,IV}), 4.44 (q, 1H, $J_{5,6}$ 6.6 Hz, H-5), 4.49–4.56 (m, 3H, 3 × H-5), 4.58–4.66 (m, 5H, H-2^{I,II,IV,VI}, H-5), 4.67–4.71 (m, 2H, H-3^{I}, H-2^{III}), 4.72–4.75 (m, 1H, H-2^{V}), 4.86 (dd, 1H, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 3.0 Hz, H-3^{VI}), 4.91–4.95 (m, 2H, H-3^{III,V}), 4.97–5.01 (3 × d, 3H, $J_{3,4}$ 2.5 Hz, H-4^{II,IV,VI}), 5.27 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1^{I}), 5.34 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1^{VI}), 5.39, 5.43 (2 × d, 2H, $J_{1,2}$ 3.6 Hz, H-1^{II,IV}), 5.46, 5.48 (2 × d, 2H, $J_{1,2}$ 3.4 Hz, H-1^{III,V}). ^{13}C NMR (150 MHz, D_2O): δ 11.4 (–$CH_2CH_2CH_3$), 17.0, 17.3, 17.5 (C-6$^{I–VI}$), 23.4 (–$CH_2CH_2CH_3$), 68.4, 68.8, 68.9, 69.0, 69.5 (C-5$^{I–VI}$), 71.9 (–$CH_2CH_2CH_3$), 73.2 (C-3^{II}), 73.9, 74.0, 74.1 (C-2^{I,III,V,VI}, C-3^{IV,VI}) 74.9, 75.1 (C-3^{III,V}), 75.4, 75.5 (C-2^{II,IV}), 75.9 (C-3^{I}), 80.9 (C-4^{II}), 81.4, 81.5 (C-4$^{I,III–VI}$), 97.5 (C-1^{III}), 97.9 (C-1^{I}), 98.2 (C-1^{V}), 100.1 (C-1^{VI}), 100.2, 100.3 (C-1^{II,IV}). HRESIMS: found *m/z* 730.8823; calcd for $C_{39}H_{55}Na_{13}O_{64}S_{13}$ $[M-3Na]^{3-}$ 730.8804.

4.4.11. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→4)-2,3-di-*O*-sulfonato-α-L-fucopyranosyl-(1→4)-2,3-di-*O*-sulfonato-α-L-fucopyranoside heptasodium salt (10b)

Per-O-sulfation of **10a** (10 mg, 0.020 mmol) promoted with TfOH (12.4 μL, 0.14 mmol, 1.0 equiv per OH group) during 24 h gave **10b** (17.9 mg, 75%); $[\alpha]_D$ −102 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.97 (t, 3H, *J* 7.5 Hz, $CH_2CH_2CH_3$), 1.37 (d, 3H, $J_{5,6}$ 6.5 Hz, H-6), 1.42 (d, 3H, $J_{5,6}$ 6.6 Hz, H-6), 1.46 (d, 3H, $J_{5,6}$ 6.7 Hz, H-6), 1.64–1.71 (m, 2H, $CH_2CH_2CH_3$), 3.58–3.63, 3.67–3.73 (2 × m, 2H, $CH_2CH_2CH_3$), 4.23 (q, 1H, $J_{5,6}$ 6.7 Hz, H-5), 4.32 (d, 1H, $J_{3,4}$ 2.4 Hz, H-4^{I}), 4.34 (d, 1H, $J_{3,4}$ 2.5 Hz, H-4^{II}), 4.54 (q, 1H, $J_{5,6}$ 6.6 Hz, H-5), 4.58–4.63 (m, 2H, H-5, H-2^{III}), 4.66–4.72 (m, 3H, H-2$^{I–II}$, H-3^{I}), 4.83–4.87 (m, 2H, H-3$^{II–III}$), 5.00 (d, 1H, $J_{3,4}$ 3.0 Hz, H-4^{III}), 5.28 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1^{I}), 5.33 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1^{III}), 5.37 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1^{II}). ^{13}C NMR (150 MHz, D_2O): δ 11.3 ($CH_2CH_2CH_3$), 17.0, 17.3 (C-6$^{I–III}$), 23.4 ($CH_2CH_2CH_3$), 68.5, 68.8, 69.8 (C-5$^{I–III}$), 71.9 ($CH_2CH_2CH_3$), 73.8 (C-3^{III}), 74.0, 74.2, 74.3 (C-2$^{I–III}$), 75.1 (C-3^{II}), 75.5 (C-3^{I}), 80.6 (C-4^{I}), 81.4 (C-4^{III}), 81.7 (C-4^{II}), 97.9 (C-1^{I}), 100.3 (C-1$^{II–III}$). HRESIMS: found *m/z* 582.9116; calcd for $C_{21}H_{31}Na_7O_{34}S_7$ $[M-2Na]^{2-}$ 582.9116.

4.4.12. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-sulfonato-α-L-fucopyranoside pentasodium salt (11b)

Per-O-sulfation of **11a** (8 mg, 0.022 mmol) promoted with TfOH (9.8 μL, 0.11 mmol, 1.0 equiv per OH group) during 24 h gave **11b** (14.1 mg, 72%); $[\alpha]_D$ −104 (*c* 1.0, H_2O). ^1H and ^{13}C NMR spectra coincided with the previously reported ones.[12] HRESIMS: found *m/z* 407.9443; calcd for $C_{15}H_{23}Na_5O_{24}S_5$ $[M-2Na]^{2-}$ 407.9443.

4.4.13. Propyl 2,3,4-tri-*O*-sulfonato-α-D-glucopyranosyl uronic acid-(1→2)-2,3-di-*O*-sulfonato-α-L-fucopyranoside hexasodium salt (12b)

Per-O-sulfation of **12a** (7.3 mg, 0.018 mmol) promoted with TfOH (8.0 μL, 0.09 mmol, 1.0 equiv per OH group) during 24 h gave **12b** (14.0 mg, 85%); $[\alpha]_D$ −14 (*c* 1.0, H_2O). ^1H NMR (600 MHz, D_2O): δ 0.96 (t, 3H, *J* 7.5 Hz, –$CH_2CH_2CH_3$), 1.30 (d, 3H, $J_{5,6}$ 6.5 Hz, H-6^{I}), 1.65–1.72 (m, 2H, –$CH_2CH_2CH_3$), 3.60–3.68 (m, 2H, –$CH_2CH_2CH_3$), 3.21 (dd, 1H, $J_{1,2}$ 3.8 Hz, $J_{2,3}$ 10.6 Hz, H-2^{I}), 4.25 (q, 1H, $J_{5,6}$ 6.5 Hz, H-5^{I}), 4.41 (d, 1H, $J_{4,5}$ 5.5 Hz, H-5^{II}), 4.54 (dd, 1H, $J_{1,2}$ 2.3 Hz, $J_{2,3}$ 6.5 Hz, H-2^{II}), 4.73–4.78 (m, 2H, H-3^{I}, H-4^{II}), 4.94–4.98 (m, 2H, H-3^{II}, H-4^{I}), 5.09 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1^{I}), 5.45 (d, 1H, $J_{1,2}$ 2.3 Hz, H-1^{II}). ^{13}C NMR (150 MHz, D_2O): δ 11.3 (–$CH_2CH_2CH_3$), 17.1 (C-6^{I}), 23.4 (–$CH_2CH_2CH_3$), 67.2 (C-5^{I}), 71.9 ($CH_2CH_2CH_3$), 74.17 (C-2^{II}), 75.3 (C-3^{II}, C-2^{I}), 75.7 (C-3^{I}, C-4^{II}), 76.2 (C-5^{II}), 80.5 (C-4^{I}), 97.8 (C-1^{II}), 99.3 (C-1^{I}). HRESIMS: found *m/z* 936.8141; calcd for $C_{15}H_{20}Na_6O_{26}S_5$ $[M+Na]^{+}$ 936.8125.

4.4.14. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,5-di-*O*-sulfonato-α-L-fucofuranoside nonasodium salt (28)

Per-O-sulfation of **2a** (10 mg, 0.016 mmol) promoted with TfOH (25.6 μL, 0.29 mmol, 2.0 equiv per OH group) during 48 h gave **28** (16.7 mg, 71%); $[\alpha]_D$ −126 (*c* 1.0, H_2O). ^1H NMR (500 MHz, D_2O): δ 0.91 (t, 3H, *J* 7.5 Hz, CH_2CH_3), 1.32–1.40 (m, 9H, H-6$^{II–IV}$), 1.45 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6^{I}), 1.58–1.67 (m, 2H, CH_2CH_3), 3.43–3.50 (m, 1H, O–CH′-Et), 3.77–3.85 (m, 1H, O–CH′-Et), 4.02 (t, 1H, $J_{3,4}$ $J_{4,5}$ 6.0 Hz, H-4^{I}), 4.28 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 2.5 Hz, H-3^{II}), 4.34–4.42 (m, 4H, H-3^{I,III}, H-5^{II,III}), 4.50–4.61 (m, 4H, H-2$^{II–IV}$, H-5^{IV}), 4.61–4.65(m, 1H, H-5^{I}), 4.77 (dd, 1H, $J_{1,2}$ 4.4 Hz, $J_{2,3}$ 7.3 Hz, H-2^{I}), 4.87–4.95 (m, 6H, H-4$^{II–IV}$, H-3^{IV}), 5.23 (d, 1H, $J_{1,2}$ 4.4 Hz, H-1^{I}), 5.39–5.44 (m, 3H, H-1$^{II–IV}$). ^{13}C NMR (125 MHz, D_2O): δ11.2 (CH_2CH_3); 17.2, 17.5 (C-6$^{II–IV}$), 18.0 (C-6^{I}), 23.3 (CH_2CH_3), 68.1 (C-5^{II}), 68.7, 69.1 (C-5$^{III–IV}$), 71.8 (O–CH_2–Et), 73.8 (C-3^{IV}), 73.9 (C-2^{IV}), 75,2, 75.5, 75.6, 75,7 (C-2^{II,III}, C-3^{II,III}), 78.6 (H-5^{I}), 81.2 (C-3^{I}), 81.3, 81.5, 81.6 (C-4$^{II–VI}$), 83.9 (C-4^{I}), 98.4, 99.5 (C-1$^{II–IV}$), 101.2 (C-1^{I}). HRESIMS: found *m/z* 757.8783; calcd for $C_{27}H_{39}Na_9O_{44}S_9$ $[M-2Na]^{2-}$ 757.8798.

4.4.15. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-αα-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,5-di-*O*-sulfonato-α-L-fucofuranoside tridecasodium salt (29)

Per-O-sulfation of **3a** (10 mg, 0.011 mmol) promoted with TfOH (25.4 μL, 0.29 mmol, 2.0 equiv per OH group) during 48 h gave **29**

(17.8 mg, 74%); $[\alpha]_D$ −138 (*c* 0.5, H_2O). ^1H NMR (500 MHz, D_2O): δ 0.93 (t, 3H, *J* 7.4 Hz, CH_2CH_3), 1.30–1.38 (m, 15H, H-$6^{II–VI}$), 1.45 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6^I), 1.58–1.67 (m, 2H, CH_2CH_3), 3.44–3.51 (m, 1H, O–CH*H*′-Et), 3.77–3.86 (m, 1H, O–C*H*H′-Et), 4.02 (t, 1H, $J_{3,4}$ $J_{4,5}$ 6.0 Hz, H-4^I), 4.26 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 2.5 Hz, H-3^{II}), 4.34–4.46 (m, 8H, H-$3^{I,III–V}$, H-$5^{II–V}$), 4.48–4.58 (m, 6H, H-$2^{II–VI}$, H-5^{VI}), 4.58–4.65 (m, 1H, H-5^I), 4.77 (dd, 1H, $J_{1,2}$ 4.4 Hz, $J_{2,3}$ 7.3 Hz, H-2^I), 4.90–4.97 (m, 6H, H-$4^{II–VI}$, H-3^{VI}), 5.23 (d, 1H, $J_{1,2}$ 4.4 Hz, H-1^I), 5.39–5.44 (m, 5H, H-$1^{II–VI}$). ^{13}C NMR (125 MHz, D_2O): δ 11.2 (CH_2CH_3); 17.3 (C-$6^{II–VI}$), 18.0 (C-6^I), 23.3 (CH_2CH_3), 68.2 (C-5^{II}), 68.8, 69.0, 69.3 (C-$5^{III–VI}$), 71.8 (O–CH_2–Et), 73.8 (C-3^{VI}), 74.0 (C-2^{VI}), 75.5, 75.7, 75.9 (C-$3^{III–V}$, C-$2^{II–V}$), 76.6 (H-3^{II}), 78.6 (H-5^I), 81.2 (C-3^I), 81.9, 81.5, 81.3 (C-$4^{II–VI}$), 83.9 (C-4^I), 100.3, 98.8, 98.4 (C-$1^{II–VI}$), 101.3 (C-1^I). HRESIMS: found *m/z* 1107.8149; calcd for $C_{39}H_{55}Na_{13}O_{64}S_{13}$ $[M-2Na]^{2-}$ 1107.8152.

4.4.16. Propyl 2,3,4-tri-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-2,5-di-*O*-sulfonato-α-L-fucofuranoside heptadecasodium salt (30)

Per-O-sulfation of **4a** (10 mg, 0.0081 mmol) promoted with TfOH (24.4 μL, 0.28 mmol, 2.0 equiv per OH group) during 48 h gave **30** (16.6 mg, 69%); $[\alpha]_D$ −121 (*c* 1.0, H_2O). ^1H NMR (500 MHz, D_2O): δ 0.93 (t, 3H, *J* 7.4 Hz, CH_2CH_3), 1.30–1.40 (m, 21H, H-$6^{II–VIII}$), 1.45 (d, 3H, $J_{5,6}$ 6.5 Hz, H-6^I), 1.58–1.66 (m, 2H, CH_2CH_3), 3.43–3.51 (m, 1H, O–CH*H*′-Et), 3.77–3.87 (m, 1H, O–C*H*H′-Et), 4.04 (t, 1H, $J_{3,4}$ $J_{4,5}$ 5.9 Hz, H-4^I), 4.25 (dd, 1H, $J_{2,3}$ 10.3 Hz, $J_{3,4}$ 2.3 Hz, H-3^{II}), 4.30–4.45 (m, 12H, H-$3^{I,III–VII}$, H-$5^{II–VII}$), 4.48–4.57 (m, 8H, H-$2^{II–VIII}$, H-5^{VIII}), 4.57–4.67 (m, 1H, H-5^I), 4.78 (dd, 1H, $J_{1,2}$ 4.4 Hz, $J_{2,3}$ 7.3 Hz, H-2^I), 4.89–4.96 (m, 8H, H-$4^{II–VIII}$, H-3^{VIII}), 5.23 (d, 1H, $J_{1,2}$ = 4.4 Hz, H-1^I), 5.37–5.43 (m, 7H, H-$1^{II–VIII}$). ^{13}C NMR (125 MHz, D_2O): δ 11.2 (CH_2CH_3), 17.3 (C-$6^{II–VIII}$), 18.1 (C-6^I), 23.3 (CH_2CH_3), 68.2 (C-5^{II}), 68.8, 68.9, 69.3 (C-$5^{III–VIII}$), 71.8 (O–CH_2–Et), 73.8 (C-3^{VIII}), 74.1 (C-2^{VIII}), 75.5, 75.6, 75.9 (C-$3^{III–VII}$, C-$2^{II–VII}$), 76.5 (H-3^{II}), 78.5 (H-5^I), 81.1 (C-3^I), 81.3, 81.5, 82.0 (C-$4^{II–VI}$), 83.9 (C-4^I), 98.4, 98.6, 100.2 (C-$1^{II–VIII}$), 101.2 (C-1^I). HRESIMS: found *m/z* 1503.7348; calcd for $C_{51}H_{71}Na_{17}O_{84}S_{17}$ $[M+2Na]^{2+}$ 1503.7291.

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Supplementary data

Supplementary data (high resolution mass spectra of non-protected and sulfated oligofucosides) associated with this article can be found, in the online version, at doi:10.1016/j.carres.2011.01.005.

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