Supplementary Information

Systematic synthesis of low-molecular weight fucoidan derivatives and their effect on cancer cells

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General methods for synthesis.

NMR spectra were recorded on a JEOL ECA-500 (500 MHz for $^1$H, 125 MHz for $^{13}$C) spectrometer. $^1$H NMR data are reported as follows; chemical shift in parts per million (ppm) downfield or upfield from tetramethylsilane ($\delta$ 0.00), CD$_3$OD ($\delta$ 3.31) or CDCl$_3$ ($\delta$ 7.26), integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constants (Hz). $^{13}$C chemical shifts are reported in ppm downfield or upfield from CDCl$_3$ ($\delta$ 77.1), CD$_3$OD ($\delta$ 49.0) or acetone-$d_6$ ($\delta$ 29.8). ESI-TOF Mass spectra were measured on a Waters LCT premier XE. Melting points were determined on a micro hot-stage (Yanako MP-S3) and were uncorrected. Optical rotations were measured on a JASCO P-2200 polarimeter. Silica gel TLC and column chromatography were performed using Merck TLC 60F-254 (0.25 mm) and Silica Gel 60 N (spherical, neutral, 63-210 µm) (Kanto Chemical Co., Inc.), respectively. Gel filtration chromatography separations were performed using Sephadex LH-20 (GE Healthcare). Air- and/or moisture-sensitive reactions were carried out under an argon atmosphere using oven-dried glassware. In general, organic solvents were purified and dried using appropriate procedures, and evaporation and concentration were carried out under reduced pressure below 30 °C, unless otherwise noted.

Synthesis of the common key intermediate 13.

2,6-Dimethylphenyl 4’-O-benzoyl-2’-O-benzyl-3’-O-chloroacetyl-$\alpha$-L-fucopyranosyl-(1’→4)-2-O-benzyl-3-O-(p-methoxy)benzyl-$\beta$-L-fucopyranoside (23)

To a solution of 22$^{1}$ (121 mg, 0.209 mmol) and 14$^{2}$ (51.2 mg, 0.104 mmol) in Et$_2$O (3.60 mL) was added MS 5A (121 mg, 100 wt% to 22) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was cooled to −60 °C, and then Yb(OTf)$_3$ (53.1 mg, 85.6 µmol) was added to the reaction mixture. After the reaction mixture was stirred for 4 h at the same temperature, the reaction was quenched with triethylamine (0.100 mL, 0.717 mmol). The resultant mixture was filtered through Celite. And then, water was added to the filtrate. The resultant mixture was extracted with EtOAc (10 mL × 3), and then the extracts were washed with brine (30 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (2/1 n-hexane/EtOAc) to give 23 (94.0 mg, 0.103...
To a solution of 23 (94.8 mg, 0.104 mmol) in MeCN (2.06 mL) and H₂O (18.6 μL) were added NIS (46.4 mg, 0.206 mmol) and Sc(OTf)₃ (5.10 mg, 10.3 μmol) at −40 °C. After being stirred for 2 h, the reaction mixture was stirred for 1 h at −20 °C. And then, the reaction mixture was poured into a solution of saturated aq. NaHCO₃ (50 mL) and saturated aq. Na₂S₂O₃ (50 mL) at 0 °C. The resultant mixture was extracted with EtOAc (100 mL×3), and then the extracts were washed with brine (100 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (1/1 n-hexane/EtOAc) to give S7 (66.9 mg, 84.5 μmol, 82% yield, α/β = 1/1). White foam; Rf 0.36 (1/1 n-hexane/EtOAc); [α]²⁷D −119.9° (c 3.0, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 8.02-7.99 (2H, m, Ar-H), 7.64-7.26 (15H, m, Ar-H), 6.86-6.81 (2H, m, Ar-H), 5.32 (1/2H, dd, J = 2.0 Hz, J = 3.5 Hz), 5.01 (1/2H, d, J = 3.7 Hz), 4.97 (1/2H, ABq, J = 11.2 Hz), 4.87 (1/2H, ABq, J = 11.2 Hz), 4.96 (1/2H, d, J = 3.5 Hz), 4.82 and 4.76 (1H, ABq, J = 11.5 Hz, ArCH₂), 4.71-4.57 (11/2H, m), 4.10-4.01 (2H, m), 3.95-3.85 (3H, m), 3.78 (3H, s, OMe), 3.74 (1/2H, d, J = 2.9 Hz), 3.63 (1/2H, dd, J = 7.5 Hz, J = 9.8 Hz), 3.55 (1/2H, q, J = 6.3 Hz), 3.42 (1/2H, dd, J = 9.8 Hz, J = 2.9 Hz), 1.37 (3H, d, J = 6.6 Hz), 1.32 (3H, d, J = 6.6 Hz), 0.91 (3H, d, J = 6.6 Hz), 0.87 (3H, d, J = 6.6 Hz); ¹³C-NMR (125 MHz, CDCl₃) δ 166.6, 166.4, 159.3, 138.0, 138.7, 132.6, 130.5, 129.9, 129.7, 129.2, 128.8, 128.7, 128.5, 128.4, 128.0, 128.0, 127.8, 127.7, 113.8×2, 99.9, 90.3, 82.3, 78.2, 78.0, 75.7, 74.6, 73.6, 72.8, 72.7, 74.5, 72.4, 65.2, 55.4, 40.9, 22.9×2, 17.1, 16.0; HRMS (ESI-TOF) m/z 911.3189 (911.3232 calcd. for C₅₁H₅₆O₁₁SCl, [M+H]+).
128.5, 128.5, 128.2, 128.1, 113.9, 100.0, 99.8, 98.0, 91.7, 79.7, 79.1, 78.0, 76.2, 75.9, 74.8, 73.8, 73.4, 72.9, 72.8, 72.7, 72.4, 71.3, 67.1, 65.2, 55.4, 40.8, 31.7, 17.0, 16.6, 15.9, 14.3; HRMS (ESI-TOF) m/z 813.2639 (813.2654 calcd. for C_{43}H_{47}O_{12}NaCl, [M+Na]^+).

4’-O-Benzoyl-2’-O-benzyl-3’-O-chloroacetyl-α-L-fucopyranosyl-(1’→4)-2-O-benzyl-3-O-(p-methoxy)benzyl-L-fucopyranosyl trichloroacetimidate (24)

To a solution of S7 (0.120 g, 0.152 mmol) in CH_{2}Cl_{2} (1.80 mL) were added CCl_{3}CN (45.7 μL, 0.456 mmol) and DBU (6.80 μL, 45.5 μmol) at room temperature. After being stirred for 15 h, the reaction mixture was concentrated in vacuo. The residue was subjected to silica gel column chromatography (2/1 n-hexane/EtOAc, 1% NEt\textsubscript{3}) to give 24 (0.108 g, 0.116 mmol, 76% yield, α/β = 6/1). White foam; R\textsubscript{f} 0.57, 0.27 (2/1 n-hexane/EtOAc, 1% NEt\textsubscript{3}); \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) δ 8.61 (1/7H, s, OC(N\textsubscript{H})CCl\textsubscript{3}), 8.51 (6/7H, s, OC(N\textsubscript{H})CCl\textsubscript{3}), 8.01 (2H, m, Ar-H), 7.64-7.22 (15H, m, Ar-H), 6.80 (2H, m, Ar-H), 6.60 (6/7H, d, J = 3.2 Hz, Ar-H), 5.72 (1/7H, d, J = 7.7 Hz), 5.60-5.48 (2H, m), 4.08 (1/7H, br-q, J = 6.6 Hz), 5.00-4.58 (54/7H, m), 4.13 (6/7H, dd, J = 3.2, 10.3 Hz), 4.05 (12/7H, m), 3.95-3.85 (18/7H, m), 3.83 (6/7H, br-d, J = 2.6 Hz), 3.79 (3H, s), 3.66 (1/7H, br-q, J = 6.3 Hz), 3.52 (1/7H, dd, J = 2.6, 10.1 Hz), 1.39 (3/7H, d, J = 6.6 Hz), 1.32 (18/7H, d, J = 6.6 Hz), 0.92 (3/7H, d, J = 6.3 Hz), 0.92 (18/7H, d, J = 6.6 Hz); \textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{3}) α isomer : δ 166.6, 166.3, 161.2, 159.2, 138.3, 137.6, 133.5, 130.5, 129.9, 129.7, 129.6, 128.6, 128.6, 128.5, 128.4, 128.1, 127.9, 127.7, 113.7, 99.8, 95.1, 91.6, 78.8, 75.1, 75.0, 73.9, 73.1, 72.9, 72.8, 72.6, 72.3, 69.9, 65.2, 55.3, 40.8, 16.5, 15.9; LRMS (ESI-TOF) m/z 934.18 (934.19 calcd. for C_{45}H_{48}NO_{12}Cl_{4}, [M+H]^+).

Octyl 4’-O-benzoyl-2’-O-benzyl-3’-O-chloroacetyl-α-L-fucopyranosyl-(1’→4)-2-O-benzyl-3-O-(p-methoxy)benzyl-L-fucopyranoside (S8)

To a solution of 24 (0.831 g, 0.888 mmol) in CH_{2}Cl_{2} (12.5 mL) were added octanol (0.418 mL, 2.66 mmol) and MS 5A (0.831 g, 100 wt% to 24) at room temperature. After being stirred...
at the same temperature for 1 h, the reaction mixture was cooled to −40 °C, and then Yb(OTf)$_3$ (0.220 g, 0.355 mmol) was added to the reaction mixture. After the reaction mixture was stirred for 4.5 h at the same temperature, the reaction was quenched with triethylamine (1.00 mL, 7.17 mmol). The resultant mixture was filtered through Celite. And then, water was added to the filtrate. The resultant mixture was extracted with CDCl$_3$ (20 mL×3), and then the extracts were washed with brine (50 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (12/1 PhMe/EtOAc) to give S8 (0.714 mg, 0.790 mmol, 89% yield). Yellow syrup; R$_f$ 0.48 (12/1 PhMe/EtOAc); [α]$^2$D$^-153.0^\circ$ (c 0.12, CHCl$_3$); 1H-NMR (500 MHz, CDCl$_3$) δ 8.02 (2H, m, Ar-H), 7.60-7.25 (15H, m, Ar-H), 6.81 (2H, m, Ar-H), 5.54 (1H, dd, J$_{2',3'}$ = 10.9 Hz, J$_{3',4'}$ = 3.2 Hz, H-3’), 5.48 (1H, br-d, J$_{3',4'}$ = 3.2 Hz, H-4’), 5.03 (1H, d, J$_{1',2'}$ = 3.8 Hz, H-1’), 4.97 and 4.80 (2H, ABq, J = 11.2 Hz, ArCH$_2$), 4.73 and 4.61 (2H, ABq, J = 10.9 Hz, ArCH$_2$), 4.67 (2H, s, ArCH$_2$), 4.59 (1H, br-q, J$_{5,6}$ = 6.6 Hz, H-5), 4.29 (1H, d, J$_{1,2}$ = 7.8 Hz, H-1), 4.04 (1H, dd, J$_{1',2'}$ = 3.8 Hz, J$_{2',3'}$ = 10.9 Hz, H-2’), 3.95-3.86 (3H, m, ClAc, H-h), 3.79 (3H, s, OMe), 3.68-3.65 (2H, m, H-2, 4), 3.49-3.42 (2H, m, H-5’, h), 3.37 (1H, dd, J$_{2,3}$ = 9.8 Hz, J$_{3,a}$ = 2.9 Hz, H-3), 1.68-1.63 (2H, m, H-g), 1.48-1.20 (13H, m, H-6', b, c, d, e, f), 0.90-0.86 (6H, m, H-6, a); 13C-NMR (125 MHz, CDCl$_3$) δ 166.6, 166.4, 159.2, 138.8, 138.0, 133.4, 130.8, 129.9, 129.3, 128.6, 128.4, 127.9, 127.7, 113.8, 104.2, 100.1, 79.9, 78.8, 78.6, 74.9, 73.3, 73.1, 72.9, 72.7, 72.4, 70.7, 70.1, 65.2, 55.4, 40.8, 32.0, 29.9, 29.6, 29.4, 26.4, 22.8, 16.8, 16.0, 14.3; HRMS (ESI-TOF) m/z 903.4084 (903.4086 calcd. for C$_{51}$H$_{64}$O$_{12}$Cl, [M+H]$^+$).

Octyl 4’-O-benzyol-2’-O-benzyl-α-L-fucopyranosyl-(1’→4)-2-O-benzyl-3-O-(p-methoxy)benzyl-β-L-fucopyranoside (25)

To a solution of S8 (0.697 g, 0.772 mmol) in DMF (20.9 mL) were added 2,6-lutidine (0.358 mL, 3.09 mmol) and thiourea (0.235 g, 3.09 mmol) at room temperature, and then the reaction mixture was stirred for 16.5 h at 70 °C. After cooling to room temperature, the reaction mixture was poured into water at room temperature. The resultant mixture was extracted with a mixed solvent of hexane/AcOEt (1/1, v/v, 20 mL×3), and then the extracts were washed with brine (50 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (6/1 PhMe/EtOAc) to give 25 (0.600 mg, 0.726 mmol, 94% yield) as a single isomer. White foam; R$_f$ 0.49 (6/1 PhMe/EtOAc); [α]$^2$D$^-73.3^\circ$ (c 3.0, CHCl$_3$);
H-NMR (500 MHz, CDCl₃) δ 8.02 (2H, m, Ar-H), 7.60-7.25 (15H, m, Ar-H), 6.81 (2H, m, Ar-H), 5.40 (1H, dd, J₃',₄' = 3.2 Hz, J₄',₅' = 1.2 Hz, H-4’), 5.03 (1H, d, J₁',₂' = 3.4 Hz, H-1’), 4.93 and 4.79 (2H, ABq, J = 10.9 Hz, ArCH₂), 4.77 (1H, ABq, J = 12.9 Hz, ArCH₂), 4.68 (3H, m, ArCH₂×2), 4.55 (1H, dq, J₄,₅ = 0.9 Hz, J₅,₆ = 6.6 Hz, H-5), 4.39 (1H, d, J₁,₂ = 7.8 Hz, H-1), 3.97-3.92 (1H, m, H-h), 3.88 (1H, dd, J₁',₂' = 3.4 Hz, J₂',₃' = 10.1 Hz, H-2’), 3.78 (3H, s, OMe), 3.70 (1H, d, J₃,₄ = 2.9 Hz, H-4), 3.61 (1H, dd, J₁,₂ = 7.8 Hz, J₂,₃ = 10.0 Hz, H-2), 3.51-3.43 (2H, m, H-5’, h), 3.38 (1H, dd, J₂,₃ = 10.0 Hz, J₃,₄ = 2.9 Hz, H-3), 2.21 (1H, d, J₃',OHi = 3.2 Hz, C₃'-OH), 1.72-1.59 (2H, m, H-g), 1.45-1.20 (13H, m, H-6’, b, c, d, e, f), 0.92 (3H, d, J₅,₆ = 6.6 Hz, H-6), 0.88 (3H, t, J = 6.9 Hz, H-a); ¹³C-NMR (125 MHz, CDCl₃) δ 166.6, 159.0, 138.7, 138.0, 133.0, 130.6, 130.0, 129.8, 129.1, 128.3, 128.2, 128.7, 127.5, 113.6×2, 103.9, 99.5, 79.9, 78.4, 78.1, 76.5, 74.7, 74.6, 72.5, 72.5, 70.5, 69.9, 67.8, 65.6, 55.2, 31.8, 29.8, 29.4, 29.2, 26.2, 22.6, 16.8, 16.1, 14.1; HRMS (ESI-TOF) m/z 827.4396 (827.4370 calcd. for C₄₉H₆₃O₁₁, [M+H]+).

Octyl 4'''-O-benzoyl-2'''-O-benzyl-α-L-fucopyranosyl-(1'''→4'')-2''-O-benzyl-3'''-O-(p-methoxy)benzyl-α-L-fucopyranosyl-(1''→3')-4'-O-benzoyl-2'-O-benzyl-α-L-fucopyranosyl-(1'→4)-2-O-benzyl-3-O-(p-methoxy)benzyl-β-L-fucopyranoside (13)

To a solution of 24 (1.15 g, 1.23 mmol) and 25 (0.500 g, 0.605 mmol) in Et₂O (17.0 mL) was added MS 5A (1.15 g, 100 wt% to 24) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was cooled to −80 °C, and then TMSOTf (11.7 μL, 64.6 μmol) was added to the reaction mixture. After the reaction mixture was stirred for 3.5 h at the same temperature, the reaction was quenched with triethylamine (1.00 mL, 7.17 mmol). The resultant mixture was filtered through Celite. And then, water was added to the filtrate. The resultant mixture was extracted with AcOEt (20 mL×3), and then the extracts were washed with brine (50 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was passed through silica gel column chromatography (6/1 PhMe/EtOAc) to give the crude product S9.

To a solution of the above crude product S9 in DMF (29.0 mL) were added 2,6-lutidine
(0.280 mL, 2.42 mmol) and thiourea (0.184 g, 2.42 mmol) at room temperature, and then the reaction mixture was stirred for 16 h at 70 °C. After cooling to room temperature, the reaction mixture was poured into water at room temperature. The resultant mixture was extracted with a mixed solvent of hexane/AcOEt (1/1, v/v, 30 mL×3), and then the extracts were washed with brine (50 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (10/1 PhMe/acetone) to give 13 (0.746 g, 0.490 mmol, 81% yield in 2 steps). White foam; Rᶠ 0.42 (10/1 PhMe/acetone); [α]²⁷D −152.0° (c 0.56, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.98 (4H, m, Ar-H), 7.56-7.15 (30H, m, Ar-H), 6.80 (2H, m, Ar-H), 6.65 (2H, m, Ar-H), 5.57 (1H, br-d, J₃',₄' = 1.7 Hz, H-4'), 5.39 (1H, d, J₁''',₂''' = 3.5 Hz, H-1'''), 5.32 (1H, br-d, J₃'',₄'' = 2.3 Hz, H-4'''), 4.99 (1H, dd, J₁',₂' = 3.2 Hz, H-1'), 4.95 (1H, d, J₁,₂' = 3.5 Hz, H-1'), 4.91 (2H, ABq, J = 10.9 Hz, ArCH₂), 4.79-4.73 (2H, m, ArCH₂), 4.65 (2H, s, ArCH₂), 4.61 (1H, ABq, J = 11.8 Hz, ArCH₂), 4.56-4.41 (9H, m, H-5 or H-5' or H-5'' or H-5'''×2, H-3', ArCH₂×3), 4.30 (1H, d, J₁₂ = 7.8 Hz, H-1), 4.19 (1H, ddd, J₂'',₃'' = 10.1 Hz, J₃'',₄'' = 3.2 Hz, J₃'',OH = 3.2 Hz, H-3'''), 4.55 (1H, br-q, J = 6.6 Hz, H-5 or 5' or 5'' or 5'''×2), 3.98-3.91 (2H, m, H-2', h), 3.86 (1H, dd, J₁'',₂'' = 3.5 Hz, J₂'',₃'' = 10.1 Hz, H-2'''), 3.81 (1H, dd, J₁',₂' = 3.2 Hz, J₂',₃' = 10.3 Hz, H-2'''), 3.77-3.73 (4H, m, H-3'', OMe), 3.67 (1H, br-d, J₃,₄ = 3.0 Hz, H-4), 3.63-3.57 (5H, m, H-2, 4'', OMe), 3.50 (1H, m, H-h), 3.43 (1H, br-q, J = 6.3 Hz, H-5 or 5' or 5'' or 5'''×2), 3.36 (1H, dd, J₁',₃' = 10.0 Hz, J₃',₄' = 2.6 Hz, H-3'), 2.09 (1H, d, J₃'',OH = 3.2 Hz, C₃''-OH), 1.70-1.59 (2H, m, H-g), 1.45-1.20 (16H, m, H-6 or 6' or 6'' or 6'''×2, H-b, c, d, e, f), 0.90-0.82 (9H, m, H-6 or 6' or 6'' or 6'''×2, H-a); ¹³C-NMR (125 MHz, CDCl₃) δ 166.7, 166.4, 159.2, 159.0, 138.8, 138.7, 138.5, 137.8, 133.1×2, 133.1×2, 130.9, 130.8, 130.1, 130.0, 129.2, 128.6, 128.6, 128.6, 128.4, 128.4, 128.4, 128.1, 128.1, 128.0, 127.7, 127.7, 127.3, 113.8, 113.7, 104.0, 99.9, 99.1, 92.0, 80.1, 79.1, 78.8, 77.6, 76.5, 75.7, 75.0, 74.5, 74.4, 74.1, 73.4, 73.1, 72.6, 72.1, 71.5, 70.7, 70.5, 70.0, 69.9, 67.9, 66.7, 65.9, 65.6, 55.4, 55.1, 32.0, 30.0, 29.6, 29.5, 26.3, 22.8, 17.0, 16.3×2, 16.1, 14.3; HRMS (ESI-TOF) m/z 1523.7236 (1523.7305 calcd. for C₉₀H₁₀₇O₂₁, [M+H]+).
Synthesis of the type II fucoidan derivatives 7-11.

Octyl 4'''-O-benzyl-α-L-fucopyranosyl-(1'''→4'')-α-L-fucopyranosyl-(1''→3')-4''-O-benzyl-α-L-fucopyranosyl-(1'→4)-β-L-fucopyranoside (S10)

To a solution of 13 (20.4 mg, 13.4 μmol) in MeOH/AcOEt (4.00 mL, 1/1) was added Pd(OH)$_2$/C (20.4 mg, 100 wt% to 13) under H$_2$ atmosphere at room temperature. After being stirred for 4 h, the reaction mixture was filtered through Celite, and then filtrate was concentrated in vacuo. The residue was subjected to reverse phase silica gel column chromatography (8/1 CHCl$_3$/MeOH) to give S10 (11.0 mg, 11.9 μmol, 88% yield). White solid; R$_f$ 0.45 (8/1 CHCl$_3$/MeOH); m.p. 126-127 °C; [α]$^2_0$ $-$154.2° (c 0.62, MeOH); $^1$H-NMR (500 MHz, CD$_3$OD) δ 8.02 (4H, m, Ar-H), 7.57 (2H, m, Ar-H), 7.45 (4H, m, Ar-H), 5.55 (1H, br-d, J = 2.9 Hz, H-4’ or 4''''), 5.37 (1H, br-d, J = 3.5 Hz, H-4’ or 4''''), 5.12 (1H, d, J$_{1''',2'''}$ = 3.9 Hz, H-1'''), 4.99 (1H, d, J = 3.7 Hz, H-1’ or 1'''), 4.93 (1H, d, J = 4.2 Hz, H-1’ or 1'''), 4.88-4.73 (2H, m, H-5 or 5’ or 5'' or 5'''×2), 4.26-4.19 (2H, m, H-1, H-5 or 5’ or 5'' or 5''''), 4.15 (1H, dd, J = 3.2, 10.3 Hz, H-3’ or 3'''), 4.06 (1H, dd, J = 3.5, 10.6 Hz, H-3’ or 3'''), 3.95 (1H, dd, J = 3.7, 10.6 Hz, H-2’ or 2'''''), 3.90-3.83 (2H, m, H-4'', H-h), 3.80-3.67 (5H, m, H-2'', H-2’ or 2''''', H-3'', H-4, H-5 or 5’ or 5'' or 5'''''), 3.59-3.52 (2H, m, H-3, h), 3.45 (1H, dd, J$_{1,2}$ = 7.5 Hz, J$_{2,3}$ = 10.0 Hz, H-2), 1.65-1.59 (2H, m, H-g), 1.40-1.20 (16H, m, H-6 or 6’ or 6'' or 6'''’’×2, H-b, c, d, e, f), 1.08 (3H, d, J = 6.6 Hz, H-6 or 6’ or 6'' or 6'''’’), 0.87 (3H, t, J = 6.9 Hz, H-a); $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 167.9, 167.0, 133.9, 133.4, 130.1, 130.0, 129.9, 129.5, 128.8, 128.6, 103.5, 101.3, 101.0, 100.8, 80.2, 79.7, 79.5, 74.4, 73.8, 73.5, 72.0, 71.2, 70.8, 70.5, 70.3, 69.6, 69.5, 68.8, 68.0, 66.4, 66.1, 32.0, 29.6, 29.6, 29.4, 26.0, 22.8, 17.0, 16.7, 16.3, 16.2, 14.2; HRMS (ESI-TOF) m/z 945.4093 (945.4096 calcd. for C$_{46}$H$_{66}$O$_{19}$Na, [M+Na$^+$]).

Octyl α-L-fucopyranosyl-(1'''→4'')-α-L-fucopyranosyl-(1''→3')-α-L-fucopyranosyl-(1’→4)-β-L-fucopyranoside (11)
To a solution of S10 (20.2 mg, 21.9 μmol) in MeOH (1.01 mL) was added 28% NaOMe in MeOH (12.8 μL, 87.6 μmol), and then the resultant mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the reaction was quenched with Amberlite® IR 120 H⁺ form. The resultant suspension was filtered, the filtrate was concentrated in vacuo. The residue was subjected to silica gel column chromatography (3/1 CHCl₃/MeOH) to give 11 (15.2 mg, 21.3 μmol, 97% yield). White solid; Rf 0.16 (3/1 CHCl₃/MeOH); m.p. 132-133 °C; [α]D −179.6° (c 1.0, MeOH); ¹H-NMR (500 MHz, CD₃OD) δ 5.01 (1H, d, J = 4.1 Hz, H-1’ or 1” or 1’’), 4.95-4.85 (2H, m, H-1’ or 1’’ or 1’’’ ×2), 4.62-4.49 (2H, m, H-5 or 5’ or 5’’ or 5’’’×2), 4.40 (1H, br-q, J = 6.6 Hz, H-5 or 5’ or 5’’ or 5’’’), 4.25 (1H, d, J₁₂ = 7.8 Hz, H-1), 3.94 (1H, dd, J = 2.9, 10.3 Hz, H-3’ or 3’’ or 3’’’), 3.90-3.68 (11H, m, H-2’, 2’’, 2’’’, H-3’ or 3’’ or 3’’’ ×2, H-4, 4’, 4’’, 4’’’, H-5 or 5’ or 5’’ or 5’’’), 1.70-1.61 (2H, m, H-g), 1.44-1.24 (16H, m, H-6 or 6’ or 6’’ or 6’’’×2, H-b, c, d, e, f), 0.90 (3H, t, J = 6.9 Hz, H-a); ¹³C-NMR (125 MHz, CD₃OD) δ 105.1, 102.7, 102.6, 98.1, 82.5, 80.5, 78.0, 74.4, 73.8, 72.4, 72.3, 71.5, 71.4, 71.0, 70.6, 70.4, 70.3, 69.2, 68.8, 68.2, 67.4, 33.0, 30.9, 30.6, 30.4, 27.1, 23.7, 16.8, 16.7, 16.5×2, 14.4; HRMS (ESI-TOF) m/z 737.3550 (737.3572 calcd. for C₃₂H₅₈O₁₇Na, [M+Na]+).

Octyl 2’’’,3’’’,4’’’-tri-O-sulfo-α-L-fucopyranosyl-(1’’’→4’’’)-2’’,3’’’-di-O-sulfo-α-L-fucopyranosyl-(1’’→3’’)-2’,4’-di-O-sulfo-α-L-fucopyranosyl-(1’→4)-2,3-di-O-sulfo-β-L-fucopyranoside (7)

To a solution of 11 (6.20 mg, 8.67 μmol) in DMF (0.310 mL) was added SO₃•NEt₃ (212 mg, 1.17 mmol) at room temperature. After the reaction mixture was stirred for 1 d, 3 M NaOH aq.
[(0.850 mL, 2.55 mmol)] was added to the reaction mixture and the mixture was stirred for 30 min. And then, the resultant mixture was subjected to reverse phase silica gel column chromatography (100/0 to 0/50 H₂O/MeOH) and gel filtration chromatography to give 7 (11.5 mg, 7.04 μmol, 81% yield). White solid; \(\rho_r\) 0.25 (10/10/3 CHCl₃/MeOH/H₂O); m.p. >300 °C; [α]D²⁻⁰.85₋₄¹.₉ (c 0.26, H₂O); \(^1\)H-NMR (500 MHz, D₂O) \(\delta\) 5.31 (1H, d, \(J = 3.5\) Hz, H-1’ or 1’’) or 1’’’), 5.27 (1H, d, \(J = 3.5\) Hz, H-1’ or 1’’ or 1’’’), 4.88-4.85 (2H, m, H-4’ or 4’’ or 4’’’×2), 4.80-4.61 (2H, m, H-3’ or 3’’ or 3’’’×2), 4.56 (1H, dd, \(J = 3.5\) Hz, \(J = 10.9\) Hz, H-2’ or 2’’ or 2’’’), 4.50-4.35 (6H, m, H-2’ or 2’’ or 2’’’×2, H-2, 3, H-5 or 5’ or 5’’ or 5’’’), 3.78-3.66 (2H, m, H-5 or 5’ or 5’’ or 5’’’), 1.52-1.43 (2H, m, H-g), 1.32-1.10 (22H, m, H-6, 6’, 6’’’, b, c, d, e, f), 0.72 (3H, t, \(J = 6.9\) Hz, H-a); \(^13\)C-NMR (125 MHz, D₂O, acetone-\(d_6\)) \(\delta\) 101.4, 99.0, 98.9, 96.9, 80.3, 80.2, 80.1, 79.2, 78.3, 76.2, 74.4, 73.8, 73.0, 72.8, 72.6, 71.2, 70.7, 68.3, 67.9, 67.3, 31.5, 29.1, 28.9 25.3, 22.4, 16.4×2, 16.2, 16.0, 13.8; HRMS (ESI-TOF) \(m/z\) 1654.8116 (1654.8060 calcd. for C₃₂H₄₉O₄₄Na₁₀S₉, [M+Na]+).

Octyl 2’’’-3’’’-di-O-sulfo-\(\alpha\)-L-fucopyranosyl-(1’’’→4’’’)-2’’’,3’’’-di-O-sulfo-\(\alpha\)-L-fucopyranosyl-(1’’’→3’’’)-2’-O-sulfo-\(\alpha\)-L-fucopyranosyl-(1’′→4)-2,3-di-O-sulfo-\(\beta\)-L-fucopyranoside (8)

To a solution of S10 (18.0 mg, 19.5 μmol) in DMF (0.900 mL) was added SO₃•NEt₃ (371 mg, 2.05 mmol) at room temperature. After the reaction mixture was stirred for 1 d, 3 M NaOH aq. (0.680 mL, 2.05 mmol) was added to the reaction mixture and the mixture was stirred for 30 min. And then, the resultant mixture was subjected to reverse phase silica gel column chromatography (100/0 to 0/50 H₂O/MeOH) and gel filtration chromatography to give 8 (25.9 mg, 18.1 μmol, 93% yield). White solid; \(\rho_r\) 0.34 (10/10/3 CHCl₃/MeOH/H₂O); m.p. >300 °C; [α]D²⁻₀.₃₂₋₅ (c 0.30, H₂O); \(^1\)H-NMR (500 MHz, D₂O) \(\delta\) 5.28 (1H, d, \(J = 3.7\) Hz, H-1’’’ or 1’’’), 5.18 (2H, m, H-1’, H-1’’ or 1’’’), 4.62 (2H, m, H-3’’, 3’’’), 4.54 (1H, dd, \(J = 4.0, 10.9\) Hz, H-2’’ or 2’’’), 4.50-4.40 (4H, m, H-2’, H-2’’ or 2’’’), 4.35 (1H, br-q, \(J = 6.3\) Hz, H-5 or 5’ or 5’’ or 5’’’), 4.28-4.21 (3H, m, H-1, 2, H-5 or 5’ or 5’’ or 5’’’), 4.15--
Octyl 2'''-O-benzyl-α-L-fucopyranosyl-(1'''→4'')-2''-O-benzyl-3'''-O-(p-methoxy)benzyl-α-L-fucopyranosyl-(1''→3')-2'-O-benzyl-3-O-(p-methoxy)benzyl-β-L-fucopyranoside (S11)

To a solution of 13 (70.9 mg, 47.0 μmol) in MeOH (3.50 mL) was added 28% NaOMe in MeOH (27.5 μL, 188 μmol), and then the resultant mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the reaction was quenched with Amberlite® IR 120 H+ form. The resultant suspension was filtered, the filtrate was concentrated in vacuo. The residue was subjected to silica gel column chromatography (4/1 PhMe/acetone) to give S11 (49.1 mg, 37.4 μmol, 80% yield). White foam; Rf 0.32 (4/1 PhMe/acetone); [α]27D −130.2° (c 0.43, CHCl3); 1H-NMR (500 MHz, CDCl3) δ 7.39-7.21 (24H, m, Ar-H), 6.85-6.80 (4H, m, Ar-H), 4.96-4.83 (5H, m, H-1, 1', 1'', ArCH2), 4.77-4.45 (10H, m, ArCH2×5), 4.40 (1H, br-q, J = 6.1 Hz, H-5 or 5' or 5'' or 5''''), 4.31 (1H, br-q, J = 6.3 Hz, H-5 or 5' or 5'' or 5'''), 4.27 (1H, d, J1,2 = 7.8 Hz, H-1), 4.13 (1H, dd, J = 3.2 Hz, J = 10.1 Hz, H-2', 2''), 3.70 (1H, dd, J = 3.5 Hz, J2,3'' = 10.1 Hz, H-2'''), 3.68 (1H, m, H-4•'), 3.66 (1H, d, J3,4 = 2.9 Hz, H-4), 3.62 (1H, br-s, H-4'''), 3.59 (1H, dd, J1,2 = 7.8 Hz, J2,3 = 10.0 Hz, H-2), 3.48 (1H, m, H-3'''), 3.40 (1H, br-q, J = 6.6 Hz, H-5 or 5' or 5'' or 5'''), 3.34 (1H, dd, J2,3 = 10.0 Hz, J3,4 = 2.9 Hz, H-3), 1.70-1.60 (2H, m, H-g), 1.45-1.20 (13H, m, H-6 or 6' or 6'' or 6'''), 1.13-1.07 (9H, m, H-6 or 6' or 6'' or 6'''), 0.90 (3H, t, J = 6.9 Hz, H-a); 13C-NMR (125 MHz, CDCl3) δ 159.2, 159.1, 139.0, 138.7, 137.9, 137.7, 133.5, 130.9, 130.6, 130.2, 129.3, 129.2, 128.8, 128.6, 128.5, 128.3, 128.3, 128.2, 128.2, 127.8, 127.6, 127.4, 113.9×2, 113.7×2, 104.1, 100.0, 98.8, 94.4, 80.2, 78.7×2, 77.8, 75.3, 75.0, 74.8, 74.6, 74.2, 73.2, 72.7, 72.4, 71.9, 70.8, 70.2, 69.0,
68.6, 67.5, 66.2, 65.6, 55.4, 55.3, 32.0, 29.9, 29.6, 29.4, 26.3, 22.8, 16.9, 16.5, 16.3, 16.2, 14.2; HRMS (ESI-TOF) m/z 1315.6774 (1315.6781 calcd. for C_{76}H_{99}O_{19}, [M+H]^+).

**Octyl 2''''-O-benzyl-3''''',4'''''-di-O-sulfo-α-L-fucopyranosyl-(1''''→4'')-2''-O-benzyl-3''''-O-(p-methoxy)benzyl-α-L-fucopyranosyl-(1''→3'')-2'′-O-benzyl-3''′,4''′-di-O-sulfo-α-L-fucopyranosyl-(1→4)-2-O-benzyl-3-O-(p-methoxy)benzyl-β-L-fucopyranoside (S12)**

To a solution of S11 (48.0 mg, 36.5 μmol) in DMF (2.40 mL) was added SO₃•NEt₃ (280 mg, 1.54 mmol) at room temperature. After the reaction mixture was stirred for 1 d, 3 M NaOH aq. (1.40 mL, 4.20 mmol) was added to the reaction mixture and the mixture was stirred for 1 h. And then, the resultant mixture was subjected to reverse phase silica gel column chromatography (100/0 to 0/100 H₂O/MeOH) to give S12 (59.0 mg, 36.4 μmol, quant.). White solid; Rf 0.10 (3/1 CHCl₃/MeOH); m.p. 148-149 °C; [α]^{27}_D −83.4° (c 0.78, MeOH); ¹H-NMR (500 MHz, CD₃OD) δ 7.42-7.06 (24H, m, Ar-H), 6.72 (2H, m, Ar-H), 6.62 (2H, m, Ar-H), 5.41 (1H, d, J_{1'',2''} = 3.2 Hz, H-1''), 4.91-4.85 (2H, m, ArCH₂), 4.82 (1H, d, J_{1''''′,2''''′} = 3.4 Hz, H-1''''′), 4.80-4.68 (3H, m, H-1′, 3''′, 4''′′), 4.64 (1H, br-d, J_{3',4'} = 1.7 Hz, H-4′), 4.60-4.45 (8H, m, ArCH₂×4), 4.37 and 4.33 (2H, ABq, J = 11.2 Hz, ArCH₂), 4.25-4.17 (4H, m, H-5 or 5′ or 5'' or 5''′ or 5''′′, H-h), 4.05 (1H, br-q, J = 6.6 Hz, H-5 or 5′ or 5'' or 5''′ or 5''''), 3.85 (1H, dd, J_{1'',2''} = 2.9 Hz, J_{2'',3''} = 10.2 Hz, H-2''′), 3.82-3.74 (4H, m, H-2''′, 2''′′, 3''′, h), 3.66 (4H, m, H-4′′, OMe), 3.55 (4H, m, H-4''′, OMe), 3.46 (1H, dd, J_{1,2} = 7.8 Hz, J_{2,3} = 10.0 Hz, H-2), 3.42-3.36 (2H, m, H-5 or 5′ or 5'' or 5''′, H-h), 3.30 (1H, dd, J_{2,3} = 10.0 Hz, J_{3,4} = 4.1 Hz, H-3), 1.55-1.46 (2H, m, H-g), 1.35-1.10 (16H, m, H-6 or 6′ or 6'' or 6''′×2, H-b, c, d, e, f), 0.97 (3H, d, J = 6.3 Hz, H-6 or 6′ or 6'' or 6''′), 0.85-0.74 (6H, m, H-6 or 6′ or 6'' or 6''′ or 6''''), H-a); ¹³C-NMR (125 MHz, CD₃OD) δ 160.6, 160.3, 140.5, 140.4, 140.3, 140.1, 132.7, 132.1, 130.3, 130.1, 129.9, 129.5×2, 129.3×2, 129.2×2, 129.1, 128.9, 128.6, 128.3×2, 128.2, 114.6×2, 114.5×2, 105.0, 101.3, 100.6, 95.0, 81.7, 80.4, 80.2, 80.1, 78.4, 78.1, 77.5, 76.6, 76.5, 76.2, 76.0, 74.8, 74.5, 73.6, 73.3, 73.3, 72.2, 72.1, 70.6, 68.6, 68.2, 67.4, 55.7, 55.5, 33.0, 31.1, 30.8, 30.6, 30.5, 27.4, 23.8, 17.7, 17.5, 17.4, 17.3, 14.5; HRMS (ESI-TOF) m/z 1621.5000 (1621.4943 calcd. for C_{76}H_{96}O_{25}Na_{3}S_{3}, [M+H]^+).
Octyl 3'''',4'''-di-O-sulfo-α-L-fucopyranosyl-(1'''→4'')-α-L-fucopyranosyl-(1''→3')-4''-O-sulfo-α-L-fucopyranosyl-(1'→4)-β-L-fucopyranoside (10)

To a solution of S12 (50.5 mg, 31.1 μmol) in MeOH/H₂O (10.0 mL, 1/1) was added Pd(OH)₂/C (50.5 mg, 100 wt% to S12) under H₂ atmosphere at room temperature. After being stirred for 6 h, the reaction mixture was filtered through Celite, and then filtrate was concentrated in vacuo. The residue was subjected to reverse phase silica gel column chromatography (100/0 to 0/100 H₂O/MeOH) to give 10 (26.7 mg, 26.2 μmol, 84% yield). White solid; Rᶠ 0.32 (10/10/3 CHCl₃/MeOH/H₂O); m.p. >300 °C; [α]D 27 −113.4° (c 0.10, H₂O); ¹H-NMR (500 MHz, D₂O) δ 5.02 (1H, d, J1'',2'' = 4.0 Hz, H-1''), 4/93 (1H, d, J1''',2'''' = 4.0 Hz, H-1'''), 4.88 (1H, d, J1,2' = 4.3 Hz, H-1'), 4.79 (1H, d, J3''',4''' = 2.9 Hz, H-4'''), 4.67 (1H, m, H-4'), 4.60 (1H, br-q, J5''',6'''' = 6.3 Hz, H-5'''), 4.58-4.51 (2H, m, H-3'''', 5'), 4.30 (1H, d, J1,2 = 8.0 Hz, H-1), 4.25 (1H, br-q, J5''',6'''' = 6.6 Hz, H-5'''), 3.93 (1H, dd, J2,3' = 10.6 Hz, J3',4' = 2.9 Hz, H-3'), 3.90-3.85 (2H, m, H-2''', 3'''), 3.81-3.76 (6H, m, H-2', 2'', 4, 4'', 5, h), 3.62 (1H, dd, J2,3 = 10.3 Hz, J3,4 = 3.4 Hz, H-3), 3.55 (1H, m, H-h), 3.40 (1H, dd, J1,2 = 8.0 Hz, J2,3 = 10.3 Hz, H-2), 1.52-1.47 (2H, m, H-g), 1.30-1.10 (22H, m, H-6, 6', 6'', 6''', b, c, d, e, f), 0.75 (3H, t, J = 7.2 Hz, H-a); ¹³C-NMR (125 MHz, D₂O, acetone-d₆) δ 102.3, 100.7, 100.3, 99.7, 80.3, 80.3, 79.4, 79.2, 77.2, 75.3, 72.5, 71.0, 70.7, 70.6, 69.5, 68.5, 68.6, 67.8, 67.8, 67.0, 66.7, 66.4, 31.3, 29.0, 28.6, 28.6, 25.3, 22.2, 15.9, 15.8, 15.5×2, 13.6, 15.3; HRMS (ESI-TOF) m/z 1021.1868 (1021.1915 calcd. for C₃₂H₆₀O₃₅Na₃S₃, [M+H]+).

Octyl 2'''-O-benzyl-α-L-fucopyranosyl-(1'''→4'')-2'''-O-benzyl-α-L-fucopyranosyl-(1''→3')-2'O-benzyl-α-L-fucopyranosyl-(1'→4)-2-O-benzyl-β-L-fucopyranoside (S13)
To a solution of S11 (26.1 mg, 19.8 μmol) in CH₂Cl₂/PBS buffer (pH 7.2, v/v, 30 mM) (3.00 mL, 1/1) was added DDQ (13.4 mg, 59.0 μmol) at room temperature. The mixture was stirred for 21 h at the same temperature. The reaction mixture was quenched with saturated aq. NaHCO₃ (10 mL). The resultant mixture was extracted with CHCl₃ (10 mL×3), and then the extracts were washed with brine (30 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (3/1 PhMe/acetone) to give S13 (17.1 mg, 15.8 μmol, 80% yield). White solid; Rₚ 0.29 (3/1 PhMe/acetone); m.p. 77-78 °C; [α]₂₇D −81.4° (c 0.35, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.43-7.23 (20H, m, Ar-H), 4.93 (1H, d, J = 3.8 Hz, H-1’ or 1’’ or 1’’’), 4.91-4.87 (3H, m, H-1’ or 1’’ or 1’’’, ArCH₂), 4.81 (1H, m, H-1’ or 1’’ or 1’’’), 4.81 and 4.65 (2H, ABq, J = 11.7 Hz, ArCH₂), 4.65 and 4.49 (2H, ABq, J = 12.0 Hz, ArCH₂), 4.58 (2H, s, ArCH₂), 4.31 (1H, d, J₁,₂ = 7.8 Hz, H-1), 4.13-3.90 (7H, m, H-3’, 3’’, 4, H-5 or 5’ or 5’’ or 5’’’×3), 3.85-3.83 (2H, m, H-2’ or 2’’ or 2’’’, H-4’ or 4’’ or 4’’’), 3.75 (1H, dd, J = 3.5 Hz, J = 10.0 Hz, H-2’ or 2’’ or 2’’’), 3.71-3.46 (9H, m, H-2’ or 2’’ or 2’’’, H-3, H-4’ or, 4’ or 4’’’×2, H-5 or 5’ or 5’’ or 5’’’×2, OH×2, H-h), 3.36 (1H, s, OH), 3.22 (1H, dd, J₁,₁₂ = 7.8 Hz, J₂,₃ = 9.5 Hz, H-2), 2.49 (1H, s, OH), 2.38 (1H, s, OH), 1.73-1.63 (2H, m, H-g), 1.45-1.18 (19H, m, H-6 or 6’ or 6’’ or 6’’’×3, H-b, c, d, e, f), 1.08 (3H, d, J = 6.6 Hz, H-6 or 6’ or 6’’ or 6’’’), 0.88 (3H, t, J = 6.9 Hz, H-a); ¹³C-NMR (125 MHz, CDCl₃) δ 138.8, 138.4, 137.8, 137.6, 128.8, 128.4, 128.4, 128.2, 128.1, 127.7, 127.4, 104.1, 100.3, 99.9, 94.4, 85.1, 84.1, 80.0, 76.8, 76.6, 75.3, 74.8, 74.4, 74.4, 74.1, 73.4, 73.0, 71.4, 70.7×2, 70.5, 68.8, 68.3, 67.2, 67.0, 66.7, 32.0, 29.9, 29.6, 29.4, 26.3, 22.8, 16.8, 16.4, 16.3, 16.2, 14.3; HRMS (ESI-TOF) m/z 1075.5585 (1075.5630 calcd. for C₆₀H₈₃O₁₇Na₂ [M+H]+).

Octyl 2''-O-benzyl-3'',4''-di-O-sulfo-α-L-fucopyranosyl-(1'''→4'')-2''-O-benzyl-3''-O-sulfo-α-L-fucopyranosyl-(1''→3'')-2'-O-benzyl-3',4'-di-O-sulfo-α-L-fucopyranosyl-(1'→4)-2-O-benzyl-3-O-sulfo-β-L-fucopyranoside (S14)

To a solution of S13 (17.7 mg, 16.4 μmol) in DMF (0.885 mL) was added SO₃•NET₃ (224 mg, 1.23 mmol) at room temperature. After the reaction mixture was stirred for 1 d, 3 M NaOH aq. (0.500 mL, 1.50 mmol) was added to the reaction mixture and the mixture was stirred for 30 min. And then, the resultant mixture was subjected to reverse phase silica gel column
chromatography (100/0 to 0/100 H$_2$O/MeOH) and gel filtration chromatography to give S14 (22.7 mg, 14.3 μmol, 87% yield). White solid; $R_f$ 0.55 (10/10/3 CHCl$_3$/MeOH/H$_2$O); m.p. >300 °C; [α]$^{22}_D$-118.0° (c 0.31, H$_2$O); $^1$H-NMR (500 MHz, D$_2$O) δ 7.50-6.90 (20H, m, Ar-H), 5.36 (1H, d, $J_{1''\',2'''}=$ 3.4 Hz, H-1''), 4.80-4.76 (3H, m, H-1', 1''', ArCH$_2$), 4.73-4.55 (6H, m, H-3'', 4'', ArCH$_2$), 4.51-4.31 (6H, m, H-1, 3''', 4', ArCH$_2$), 4.03 (1H, dd, $J_{2,3}=$ 9.6 Hz, $J_{3,4}=$ 2.3 Hz, H-3), 3.79-3.70 (4H, m, H-2', 2''', 4, 4'''), 3.61-3.50 (2H, m, H-5 or 5' or 5'' or 5''', H-h), 3.42 (1H, m, H-h), 3.33-3.20 (3H, m, H-2, H-5 or 5' or 5'' or 5'''×2), 1.47-1.41 (2H, m, H-g), 0.68 (3H, t, $J=$ 6.9 Hz, H-a); $^{13}$C-NMR (125 MHz,D$_2$O, acetone-d$_6$) δ 137.9, 137.5, 137.3, 130.8, 130.6, 129.5, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 103.0, 99.5, 98.8, 91.8, 80.3, 80.0, 78.2, 77.9, 76.9, 75.2, 74.9, 74.8, 73.8, 72.9, 72.4, 70.8, 70.2, 69.9, 69.1, 67.7, 66.6, 66.4, 31.5, 28.9, 25.9, 22.4, 16.4, 16.0×2, 15.9, 13.7; HRMS (ESI-TOF) m/z 1585.2606 (1585.2568 calcd. for C$_60$H$_{78}$O$_{32}$Na$_5$S$_5$, [M+H]$^+$).

Octyl 3''',4'''-di-O-sulfo-α-L-fucopyranosyl-(1'''→4'')-3''-O-sulfo-α-L-fucopyranosyl-(1''→3')-4'-O-sulfo-α-L-fucopyranosyl-(1'→4)-3-O-sulfo-β-L-fucopyranoside (9)

To a solution of S14 (19.6 mg, 12.4 μmol) in MeOH/H$_2$O (7.84 mL, 1/1) was added Pd(OH)$_2$/C (39.2 mg, 200 wt% to S14) under H$_2$ atmosphere at room temperature. After being stirred for 16 h, the reaction mixture was filtered through Celite, and then filtrate was concentrated in vacuo. The residue was subjected to reverse phase silica gel column chromatography (100/0 to 0/100 H$_2$O/MeOH) to give 9 (15.0 mg, 12.2 μmol, 99% yield). White solid; $R_f$ 0.55 (10/10/3 CHCl$_3$/MeOH/H$_2$O); m.p. >300 °C; [α]$^{22}_D$-135.6° (c 0.31, H$_2$O); $^1$H-NMR (500 MHz, D$_2$O) δ 5.05 (1H, d, $J_{1''',2'''}=$ 4.0 Hz, H-1'''), 4.96 (1H, d, $J_{1''\',2''}=$ 3.8 Hz, H-1''), 4.91 (1H, d, $J_{1',2'}=$ 4.3 Hz, H-1'), 4.77 (1H, br-d, $J_{3''',4'''}=$ 2.9 Hz, H-4'''), 4.68 (1H, m, H-4'), 4.54-4.46 (3H, m, H-3''', 3''', H-5 or 5' or 5'' or 5'''), 4.44-4.37 (2H, m, H-1, H-5 or 5' or 5'' or 5'''), 4.27 (1H, br-q, $J=$ 6.9 Hz, H-5 or 5' or 5'' or 5'''), 4.20 (1H, dd, $J_{2,3}=$ 10.3 Hz, $J_{3,4}=$ 2.9 Hz, H-3), 4.08 (1H, br-d, $J_{3',4'}=$ 3.2 Hz, H-4''), 4.02 (1H, br-d, $J_{3,4}=$ 2.9 Hz, H-4),

S15
3.95 (1H, dd, \(J_{2',3'} = 10.0\) Hz, \(J_{3',4'} = 2.3\) Hz, H-3’), 3.90-3.80 (3H, m, H-2’, 2″’, 2’’’), 3.79-3.73 (2H, m, H-5 or 5’ or 5’’ or 5’’’), H-h), 3.58-3.49 (2H, m, H-2, h), 1.47-1.45 (2H, m, H-g), 1.25-1.10 (22H, m, H-6, 6’, 6’’, 6’’’, b, c, d, e, f), 0.72 (3H, t, \(J = 6.9\) Hz, H-a);

\[\text{13C-NMR (125 MHz, D}_2\text{O, acetone-}d_6) \delta 102.5, 100.5, 100.1, 99.0, 80.1, 79.6, 79.3, 78.0, 76.9, 76.7, 76.3, 75.2, 71.2, 70.8, 69.1, 68.0, 67.5, 67.0, 66.9 \times 2, 66.8, 31.4, 29.1, 28.8, 25.4, 22.4, 16.3, 15.8, 15.6, 13.8; HRMS (ESI-TOF) \text{m/z 589.0416 (589.0408 calcd. for C}_{32}\text{H}_{53}\text{O}_{32}\text{Na}_{3}\text{S}_5, [M-2Na]^{2-}).}\]

**Synthesis of the oligofucosides 26 and 27.**

Octyl 2’-O-benzyl-α-L-fucopyranosyl-(1’→4)-2-O-benzyl-3-O-(p-methoxy)benzyl-β-L-fucopyranoside (S15)

To a solution of 25 (26.0 mg, 31.4 \(\mu\)mol) in MeOH (2.60 mL) was added 28% NaOMe in MeOH (303 \(\mu\)L, 2.07 mmol), and then the resultant mixture was stirred at 50 °C for 6 h. After cooling to room temperature, the reaction was quenched with Amberlite® IR 120 H⁺ form. The resultant suspension was filtered, the filtrate was concentrated in vacuo. The residue was subjected to silica gel column chromatography (1/1 PhMe/AcOEt) to give S15 (14.8 mg, 20.5 \(\mu\)mol, 65% yield). Colorless syrup; \(R_f 0.50\) (1/1 PhMe/EtOAc); \([\alpha]_23^D = -92.4°\) (c 0.41, CHCl₃);

\[\text{1H-NMR (500 MHz, CDCl}_3) \delta 7.40-7.23 (12H, m, Ar-H), 6.81 (2H, m, Ar-H), 5.03 (1H, d, \(J_{1',2'} = 3.5\) Hz, H-1’), 4.93 (1H, ABq, \(J = 10.9\) Hz, ArCH₂), 4.77-4.73 (2H, m, ArCH₂), 4.69 and 4.64 (2H, ABq, \(J = 12.3 \text{ Hz, ArCH}_2\)), 4.56 (1H, ABq, \(J = 11.5 \text{ Hz, ArCH}_2\)), 4.36 (1H, br-q, \(J_{5,6} = 6.3\) Hz, H-5), 4.29 (1H, d, \(J_{1,2} = 7.8\) Hz, H-1), 4.12 (1H, dd, \(J_{1',2'} = 3.5\) Hz, \(J_{2',3'} = 10.0\) Hz, H-2’), 3.93 (1H, m, H-h), 3.79 (3H, s, OMe), 3.77-3.72 (2H, m, H-3’, 4), 3.66 (1H, d, \(J_{3',4'} = 2.9\) Hz, H-4’), 3.58 (1H, dd, \(J_{1,2} = 7.8\) Hz, \(J_{2',3'} = 9.8\) Hz, H-2), 3.50-3.41 (2H, m, H-5’, h), 3.37 (1H, dd, \(J_{2',3'} = 9.8\) Hz, \(J_{3',4'} = 2.9\) Hz, H-3’), 1.64 (2H, m, H-g), 1.43-1.20 (13H, m, H-6’, b, c, d, e, f), 1.08 (3H, d, \(J_{5,6} = 6.6\) Hz, H-6), 0.87 (3H, t, \(J = 6.6\) Hz, H-a); \[\text{13C-NMR (125 MHz, CDCl}_3) \delta 159.2, 138.9, 138.1, 130.8, 129.3, 128.7, 128.4, 128.3, 128.1, 127.6, 113.8, 104.1, 99.1, 80.3, 78.6, 78.2, 74.9, 72.7, 72.5, 72.1, 70.6, 70.2, 69.0, 66.1, 55.4, 32.0, 29.9, 29.6, 29.4, 26.3, 22.8, 16.9, 16.2, 14.2; HRMS (ESI-TOF) \text{m/z 745.3926 (745.3928 calcd. for C}_{42}\text{H}_{58}\text{O}_{10}\text{Na, [M+Na]^{+}).}\]

Octyl 2’-O-benzyl-α-L-fucopyranosyl-(1’→4)-2-O-benzyl-β-L-fucopyranoside (28)
To a solution of S15 (14.8 mg, 20.5 μmol) in CH₂Cl₂/PBS buffer (pH 7.2, v/v, 30 mM) (3.00 mL, 1/1) was added DDQ (21.2 mg, 93.4 μmol) at room temperature. The mixture was stirred for 20 h at the same temperature. The reaction mixture was quenched with saturated aq. NaHCO₃ (6 mL). The resultant mixture was extracted with CHCl₃ (6 mL×3), and then the extracts were washed with brine (15 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (1/1 PhMe/AcOEt) to give 28 (11.4 mg, 18.9 μmol, 93% yield). Colorless syrup; Rᵣ 0.32 (1/1 PhMe/EtOAc); [α]ᵥ²⁵D −86.6° (c 1.0, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.42-7.22 (10H, m, Ar-H), 4.98 (1H, d, J₁',₂' = 3.7 Hz, H-1’), 4.90 and 4.79 (2H, ABq, J = 11.5 Hz, ArCH₂), 4.68 and 4.53 (2H, ABq, J = 11.8 Hz, ArCH₂), 4.31 (1H, ABq, J₁₂ = 7.5 Hz, H-1), 4.14-4.08 (2H, m, H-4, 5), 3.95 (1H, m, H-h), 3.79-3.73 (3H, m, H-2', 4', OH), 3.49 (1H, m, H-h), 3.25 (1H, dd, J₁₂ = 7.5 Hz, J₂₃ = 9.5 Hz, H-2), 2.47 (1H, s, OH), 2.35 (1H, s, OH), 1.64 (2H, m, H-g, 1.43-1.20 (13H, m, H-6’, b, c, d, e, f), 1.17 (3H, d, J₅₆ = 6.6 Hz, H-6), 0.87 (3H, t, J = 6.9 Hz, H-a); ¹³C-NMR (125 MHz, CDCl₃) δ 138.7, 137.8, 128.8, 128.5, 128.3, 128.3, 128.0, 127.8, 127.8, 104.1, 99.5, 83.7, 79.5, 74.6, 73.9, 72.9, 71.5, 70.6, 70.5, 68.9, 67.1, 32.0, 29.9, 29.6, 29.4, 26.3, 22.8, 16.7, 16.2, 14.2; HRMS (ESI-TOF) m/z 603.3539 (603.3533 calcd. for C₃₄H₅₁O₉, [M+H]+).

Octyl 2’-O-benzyl-3’,4’-di-O-sulfo-α-L-fucopyranosyl-(1’→4)-2-O-benzyl-3-O-sulfo-β-L-fucopyranoside (S16)

To a solution of 28 (11.4 mg, 18.9 μmol) in DMF (0.342 mL) was added SO₃•NEt₃ (103 mg, 0.568 mmol) at room temperature. After the reaction mixture was stirred for 1 d, 3 M NaOH aq. (0.377 mL, 1.13 mmol) was added to the reaction mixture and the mixture was stirred for 30 min. And then, the resultant mixture was subjected to reverse phase silica gel column chromatography (100/0 to 0/100 H₂O/MeOH) and gel filtration chromatography to give S16 (15.0 mg, 16.5 μmol, 86% yield). White solid; Rᵣ 0.55 (10/10/3 CHCl₃/MeOH/H₂O); m.p. >300 °C; [α]ᵥ³⁰D −75.8° (c 1.0, MeOH); ¹H-NMR (500 MHz, CD₃OD) δ 7.57-7.20 (10H, m, Ar-H), 5.21 (1H, d, J₁',₂' = 3.4 Hz, H-1’), 5.02-4.80 (4H, m, H-3’, 4’, ArCH₂), 4.77-4.71 (2H, m,
ArCH$_2$), 4.45 (1H, br-q, $J_{5',6'} = 6.3$ Hz, H-5'), 4.40-4.36 (2H, m, H-1, 3), 4.21 (1H, d, $J_{3,4} = 2.6$ Hz, H-4), 3.90 (1H, dd, $J_{1',2'} = 3.4$ Hz, H$_{2,3'} = 10.3$ Hz, H-2'), 3.85 (1H, m, H-h), 3.65-3.56 (2H, m, H-2, 5), 3.48 (1H, m, H-g), 1.63-1.54 (2H, m, H-6'), 1.37 (3H, d, $J_{5,6} = 6.3$ Hz, H-6), 1.33-1.21 (13H, m, H-6', b, c, d, e, f), 0.89 (3H, t, $J = 6.9$ Hz, H-a); $^{13}$C-NMR (125 MHz, D$_2$O, acetone-d$_6$) $\delta$ 140.2, 129.4, 129.3, 129.0, 128.3, 104.6, 100.9, 80.8, 80.4, 79.1, 78.2, 76.5, 76.0, 75.7, 74.1, 72.0, 70.9, 67.8, 33.0, 30.9, 30.6, 30.4, 27.3, 17.6, 17.3, 14.4; HRMS (ESI-TOF) $m/z$ 931.1483 (931.1515 calcd. for C$_{34}$H$_{47}$O$_{18}$Na$_4$S$_3$, [M+Na]$^+$).

Octyl 3',4'-di-O-sulfo-α-L-fucopyranosyl-(1'→4)-3-O-sulfo-β-L-fucopyranoside (26)

To a solution of S16 (82.6 mg, 90.9 μmol) in MeOH/H$_2$O (16.5 mL, 1/1) was added Pd(OH)$_2$/C (165 mg, 200 wt% to S16) under H$_2$ atmosphere at room temperature. After being stirred for 4 h, the reaction mixture was filtered through Celite, and then filtrate was concentrated in vacuo. The residue was subjected to reverse phase silica gel column chromatography (100/0 to 0/100 H$_2$O/MeOH) to give 26 (64.2 mg, 88.1 μmol, 97% yield). White solid; $R_f$ 0.54 (10/10/3 CHCl$_3$/MeOH/H$_2$O); m.p. >300 °C; [$\alpha$]$_{27}D$ −85.9° ($c$ 1.0, H$_2$O); $^{1}$H-NMR (500 MHz, D$_2$O) $\delta$ 5.02 (1H, d, $J_{1',2'} = 3.6$ Hz, H-1'), 4.85 (1H, br-d, $J_{3',4'} = 2.9$ Hz, H-4'), 4.60 (1H, dd, $J_{2',3'} = 10.9$ Hz, $J_{3',4'} = 2.9$ Hz, H-3'), 4.55 (1H, br-q, $J_{5',6'} = 6.6$ Hz, H-5'), 4.46 (1H, d, $J_{1,2} = 7.8$ Hz, H-1), 4.29 (1H, dd, $J_{2,3} = 10.0$ Hz, $J_{2,3'} = 2.9$ Hz, H-2), 3.92 (1H, dd, $J_{1,2'} = 3.6$ Hz, $J_{2,3'} = 10.9$ Hz, H-2'), 3.87-3.80 (2H, m, H-5, h), 3.70-3.60 (2H, m, H-2, h), 1.60-1.53 (2H, m, H-g), 1.35-1.17 (16H, m, H-6, 6', b, c, d, e, f), 0.80 (3H, t, $J = 6.9$ Hz, H-a); $^{13}$C-NMR (125 MHz, D$_2$O, acetone-d$_6$) $\delta$ 103.1, 100.9, 80.4, 80.1, 77.7, 75.8, 71.7, 71.6, 69.6, 67.6×2, 32.0, 29.6, 29.3, 29.2, 25.9, 22.9, 16.8, 16.4, 14.3; HRMS (ESI-TOF) $m/z$ 729.0783 (729.0757 calcd. for C$_{20}$H$_{36}$O$_{18}$Na$_{3}$S$_{3}$, [M+H]$^+$).

Octyl 4''''-O-benzoyl-2''''-O-benzyl-3''''-O-chloroacetyl-α-L-fucopyranosyl-(1''''→4'')-2''-O-benzyl-α-L-fucopyranosyl-(1''→3')-4''-O-benzoyl-2''-O-benzyl-α-L-fucopyranosyl-(1''→4'')-2''-O-benzyl-α-L-fucopyranosyl-(1''→3')-4''-O-benzoyl-2''-O-benzyl-α-L-fucopyranosyl-(1''→4)','-2''-O-benzyl-3-O-(p-methoxy)benzyl-β-L-fucopyranoside (29)

S18
To a solution of 24 (61.6 mg, 65.8 \textmu mol) and 13 (54.5 mg, 36.1 \textmu mol) in Et$_2$O (1.00 mL) was added MS 5A (61.6 mg, 100 wt\% to 24) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was cooled to $-80^\circ$C, and then TMSOTf (0.700 \textmu L, 3.62 \textmu mol) was added to the reaction mixture. After the reaction mixture was stirred for 5.5 h at the same temperature, the reaction was quenched with triethylamine (0.100 mL, 0.717 mmol). The resultant mixture was filtered through Celite. And then, water was added to the filtrate. The resultant mixture was extracted with AcOEt (5 mL$\times$3), and then the extracts were washed with brine (10 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was passed through silica gel column chromatography (6/1 PhMe/EtOAc) to give 29 (78.4 mg, 34.1 \textmu mol, 94\% yield). Colorless syrup; $R_f$ 0.42 (10/1 PhMe/acetone); [$\alpha$]$^D_{24}$ $-145.7^\circ$ (c 1.0, CHCl$_3$);

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 8.01 (2H, m, Ar-H), 7.92 (4H, m, Ar-H), 7.65-7.05 (45H, m, Ar-H), 6.81 (2H, m, Ar-H), 6.60 (4H, m, Ar-H), 5.61 (1H, br-d, $J = 1.8$ Hz, H-4' or 4'' or 4''' or 4'''' or 4''''' or 4'''''), 5.51 (1H, br-d, $J = 2.3$ Hz, H-4' or 4'' or 4''' or 4'''' or 4''''' or 4'''''), 5.45-5.43 (4H, m, H-1' or 1'' or 1''' or 1'''' or 1''''''×4), 4.97-4.92 (3H, m, H-3' or 3'' or 3''' or 3'''' or 3''''''×3), 4.78-4.66 (7H, m), 4.56-4.28 (16H, m), 4.10-3.82 (10H, m), 3.81 (7H, m), 3.65-3.59 (3H, m), 3.55-3.47 (7H, m, OMe×2, H-h), 3.44 (1H, br-q, $J = 6.6$ Hz, H-5 or 5' or 5'' or 5''' or 5'''' or 5''''''), 3.38 (1H, dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 2.9$ Hz, H-3), 1.70-1.59 (2H, m, H-g), 1.45-1.20 (19H, m, H-6 or 6' or 6'' or 6''' or 6'''' or 6'''''' or 6''''''×3), H-b, c, d, e, f), 0.90-0.78 (12H, m, H-6 or 6' or 6'' or 6''' or 6'''' or 6'''''' or 6''''''×3, H-a); $^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta$ 166.5, 166.4, 166.2, 163.3, 159.2, 158.9, 158.9, 138.9, 138.6, 138.6, 138.5, 138.4, 137.8, 133.4, 133.1, 133.0, 130.8, 130.1, 129.9, 129.2, 129.2, 128.8, 128.6, 128.5, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 127.8, 127.7, 127.6, 127.3, 127.2, 113.8×2, 113.6×2, 104.0, 100.1, 100.0×2, 92.0, 91.8, 80.1, 79.3, 79.0, 78.4, 77.8, 76.6, 75.5, 75.4, 75.3, 75.0, 74.9, 73.8, 73.6, 73.3, 73.0, 72.9, 72.6, 72.5, 72.2, 71.9, 71.7, 71.1, 70.7, 70.5, 70.4, 70.0, 69.9, 69.8, 68.1, 66.9, 66.6, 65.9, 65.7, 65.0, 55.4, 55.1, 55.0, 40.8, 32.0, 30.0, 29.6, 29.5, 26.3, 22.8, 17.0, 16.5, 16.4, 16.3, 16.2, 15.9, 14.3; HRMS (ESI-TOF) $m/z$ 2296.0049 (2295.9955 calcd. for C$_{133}$H$_{152}$O$_{32}$Cl, [M+H]$^+$).
To a solution of 29 (15.2 mg, 6.61 μmol) in MeOH (1.50 mL) was added 28% NaOMe in MeOH (0.136 mL, 926 μmol), and then the resultant mixture was stirred at 50 °C for 24 h. After cooling to room temperature, the reaction was quenched with Amberlite® IR 120 H⁺ form. The resultant suspension was filtered, the filtrate was concentrated in vacuo. The residue was subjected to silica gel column chromatography (2/1 PhMe/AcOEt) to give S17 (10.9 mg, 5.42 μmol, 82% yield). White foam; \( R_f \) 0.32 (2/1 PhMe/AcOEt); \( [\alpha]_{25}^D \) −80.1° (c 0.16, CHCl₃); \(^1\)H-NMR (500 MHz, CDCl₃) \( \delta \) 7.45-7.15 (36H, m, Ar-H), 6.83 (6H, m, Ar-H), 4.90-4.80 (9H, m, H-1' or 1'' or 1''' or 1'''' or 1'''''), 4.80-4.44 (14H, m), 4.40 (1H, br-q, \( J = 7.4 \) Hz, H-5 or 5' or 5'' or 5''' or 5'''' or 5'''''), 4.31 (2H, m, H-5 or 5' or 5'' or 5''' or 5'''' or 5'''''×2), 4.26 (1H, d, \( J_{1,2} = 7.7 \) Hz, H-1), 4.13 (1H, dd, \( J = 2.3, 10.0 \) Hz, H-3' or 3'' or 3''' or 3'''' or 3'''''), 4.05-3.95 (2H, m, H-6 or 6' or 6'' or 6''' or 6'''' or 6'''''×2), 3.93-3.55 (26H, m), 3.47 (1H, m, H-6 or 6' or 6'' or 6''' or 6'''' or 6'''''×5), 0.85 (3H, t, \( J = 7.2 \) Hz, H-a); \(^{13}\)C-NMR (125 MHz, CDCl₃) \( \delta \) 159.3, 159.2, 159.1, 139.0, 138.8, 138.6, 137.9, 137.8, 130.9, 130.7, 130.5, 129.3, 129.2, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 127.8, 127.9, 127.6, 127.5, 127.4, 113.9×2, 113.8×2, 113.7×2, 104.1, 100.1, 99.8, 98.9, 94.4, 94.3, 80.3, 78.8×2, 78.5, 77.8, 75.4, 75.2×2, 75.0, 74.7×2, 74.4, 74.2, 73.5, 73.3, 72.6, 72.4, 72.0×2, 71.9, 70.8, 70.1, 69.0, 68.6, 67.7, 67.5, 66.2, 65.6, 55.4, 55.3, 32.0, 29.9, 29.6, 29.4, 26.3, 22.8, 17.0, 16.9, 16.5×2, 16.4×2, 16.2, 14.2; HRMS (ESI-TOF) m/z 1907.9492 (1907.9453 calcd. for \( \text{C}_{110}\text{H}_{139}\text{O}_{28}, [\text{M+H}]^+ \)).
Octyl 2'''''-O-benzyl-α-L-fucopyranosyl-(1'''''→4''''')-2''''-O-benzyl-α-L-fucopyranosyl-
(1''''→3''')-2''-O-benzyl-α-L-fucopyranosyl-(1''→4'')-2''-O-benzyl-α-L-fucopyranosyl-
(1''→3')-2'-O-benzyl-α-L-fucopyranosyl-(1'→4)-2-O-benzyl-β-L-fucopyranoside (30)

To a solution of S17 (21.6 mg, 12.8 μmol) in CH₂Cl₂/PBS buffer (pH 7.2, 30 mM) (4.20 mL, v/v, 1/1) was added DDQ (21.7 mg, 95.7 μmol) at room temperature. The mixture was stirred for 39 h at the same temperature. The reaction mixture was quenched with saturated aq. NaHCO₃ (10 mL). The resultant mixture was extracted with CHCl₃ (15 mL×3), and then the extracts were washed with brine (30 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (3/1 PhMe/AcOEt) to give 30 (13.0 mg, 8.40 μmol, 65% yield). White solid; Rₚ 0.21 (1/2 PhMe/AcOEt); m.p. 85-86 °C; [α]²⁷D −157.6° (c 0.11, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.45-7.20 (30H, m, Ar-H), 4.94-4.88 (5H, m), 4.85-4.78 (4H, m), 4.66-4.61 (3H, m), 4.56 (4H, m), 4.50 (1H, ABq, J = 11.8 Hz, ArCH₂), 4.31 (1H, d, J₁,₂ = 7.5 Hz, H-1), 4.16-4.01 (8H, m, H-3' or 3'' or 3''' or 3'''' or 3'''''×3, H-5 or 5' or 5'' or 5''' or 5'''' or 5'''''×5), 3.97-3.92 (4H, m, H-3' or 3'' or 3''' or 3'''' or 3''''' or 3''''''×2, H-4), 3.85-3.80 (4H, m), 3.76 (1H, dd, J = 3.4, 10.0 Hz, H-2' or 2'' or 2'''' or 2''''''), 3.71-3.69 (3H, m, H-4' or 4'' or 4''' or 4'''' or 4'''''×3), 3.66-3.46 (10H, m), 3.22 (1H, dd, J₁,₂ = 7.5 Hz, J₃,₄ = 9.5 Hz, H-2), 2.46 (1H, s, OH), 2.37 (1H, s, OH), 2.04 (1H, s, OH), 1.72-1.61 (2H, m, H-g), 1.40-1.20 (19H, m, H-6 or 6' or 6'' or 6''' or 6'''' or 6''''''×3, H-b, c, d, e, f), 1.19 (3H, d, J = 6.6 Hz, H-6 or 6' or 6'' or 6''' or 6'''' or 6''''''), 1.09 (3H, d, J = 6.6 Hz, H-6 or 6' or 6'' or 6''' or 6'''' or 6''''''), 0.87 (3H, t, J = 7.2 Hz, H-a); ¹³C-NMR (125 MHz, CDCl₃) δ 138.8, 138.4, 138.3, 137.9, 137.9, 137.6, 128.8, 128.8, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 127.8, 127.7, 127.5, 127.5, 104.2, 100.8, 100.4, 99.9, 94.6, 94.4, 85.5, 85.0, 84.1, 80.0, 75.3, 75.1, 74.8, 74.6, 74.5, 74.4, 74.2, 74.1, 73.6, 73.4, 73.0, 71.4, 70.7, 70.7, 70.6, 70.6, 68.8, 68.2, 68.2, 67.2, 67.1, 67.0, 66.9, 66.7, 32.0, 29.9, 29.6, 29.4, 26.3, 22.8; HRMS (ESI-TOF) m/z 1569.7594 (1569.7547 calcd. for C₈₆H₁₁₄O₂₅Na, [M+Na]⁺).
Octyl 2'''''-O-benzyl-3'''',4'''''-di-O-sulfo-α-L-fucopyranosyl-(1'''''→4'''')-2'''''-O-benzyl-3''''-O-sulfo-α-L-fucopyranosyl-
(1'''''→4'''')-2''''-O-benzyl-3''''-O-sulfo-α-L-fucopyranosyl-(1''''→3''')-2''-O-benzyl-4''-O-sulfo-α-L-
fucopyranosyl-(1'→4)-2-O-benzyl-3-O-sulfo-β-L-fucopyranoside (S18)

To a solution of 30 (13.7 mg, 8.85 μmol) in DMF (0.665 mL) was added SO₃•NEt₃ (164 mg, 0.905 mmol) at room temperature. After the reaction mixture was stirred for 1 d, 3 M NaOH aq. (0.450 mL, 1.35 mmol) was added to the reaction mixture and the mixture was stirred for 30 min. And then, the resultant mixture was subjected to reverse phase silica gel column chromatography (100/0 to 0/100 H₂O/MeOH) and gel filtration chromatography to give S18 (20.0 mg, 8.84 μmol, 99% yield). White solid; [α]²₅₀⁻135.4° (c 0.26, H₂O); ¹H-NMR (500 MHz, D₂O) δ 7.49-7.02 (30H, m, Ar-H), 5.34 (1H, d, J = 3.2 Hz, H-1' or 1'' or 1''' or 1'''' or 1''''' or 1''''''), 5.22 (1H, d, J = 3.2 Hz, H-1' or 1'' or 1''' or 1'''' or 1''''' or 1''''''), 4.90-4.84 (2H, m, H-1' or 1'' or 1''' or 1'''' or 1'''''×2), 4.80-4.50 (17H, m, H-1' or 1'' or 1''' or 1'''' or 1''''' or 1'''''' or 3'''' or 3'''''' or 3'''''''' or 3'''''''' or 3''''''''' or 3''''''''''), 4.48-4.35 (6H, m), 4.11-4.03 (2H, m, H-3, H-5 or 5' or 5'' or 5''' or 5'''' or 5'''''' or 5''''''''), 3.80 (1H, br-q, J = 6.3 Hz, H-5 or 5' or 5'' or 5''' or 5'''' or 5'''''' or 5''''''''), 3.70-3.74 (5H, m), 3.73-3.56 (6H, m), 3.55-3.47 (2H, m, H-4', H-4'' or 4''' or 4'''' or 4'''''' or 4'''''''' or 4''''''''' or 4'''''''''' or 4''''''''''' or 4'''''''''''', H-5 or 5' or 5'' or 5''' or 5'''' or 5'''''' or 5'''''''' or 5''''''''''), 3.43 (1H, m, H-h), 3.36 (1H, dd, J₁₂ = 7.8 Hz, J₂₃ = 10.6 Hz, H-2), 3.30 (1H, br-q, J = 6.3 Hz, H-5 or 5' or 5'' or 5''' or 5'''' or 5'''''' or 5'''''''' or 5''''''''''), 3.21 (1H, br-q, J = 6.3 Hz, H-5 or 5' or 5'' or 5''' or 5'''' or 5'''''' or 5'''''''' or 5''''''''''), 1.42-1.35 (2H, m, H-g), 1.22-1.00 (25H, m, H-6 or 6' or 6'' or 6''' or 6'''' or 6''''' or 6''''''''×5, H-b, c, d, e, f), 0.79 (3H, d, J = 6.6 Hz, H-6 or 6' or 6'' or 6''' or 6'''' or 6''''' or 6''''''''), 0.68 (3H, t, J = 7.2 Hz, H-a); ¹³C-NMR (125 MHz, D₂O, acetone-d₆) δ 137.9, 137.7, 137.6, 137.3, 137.1, 136.6, 130.7, 130.0, 130.3, 129.4, 129.3, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.9, 102.8, 99.3, 99.1, 98.5, 92.0, 91.6, 80.6, 80.2, 79.9, 78.2, 77.4×2, 75.4, 75.2, 75.1, 74.9×2, 74.6, 74.2, 73.9, 73.0, 72.3, 72.0, 70.7, 70.3, 70.2, 69.8,
Octyl 3''''''-di-O-sulfo-α-L-fucopyranosyl-(1'''''''→4'''''''')-3'''''''-O-sulfo-α-L-
fucopyranosyl-(1'''''''→3'''')-4''''-O-sulfo-α-L-fucopyranosyl-(1''''→4'')-3'''-O-sulfo-α-L-
fucopyranosyl-(1''→3'')-4''-O-sulfo-α-L-fucopyranosyl-(1→4)-3'-O-sulfo-β-L-
fucopyranoside (27)

To a solution of S18 (20.0 mg, 8.84 μmol) in MeOH/H2O (8.00 mL, 1/1) was added Pd(OH)2/C (40.0 mg, 200 wt% to S18) under H2 atmosphere at room temperature. After being stirred for 17 h, the reaction mixture was filtered through Celite, and then filtrate was concentrated in vacuo. The residue was subjected to reverse phase silica gel column chromatography (100/0 to 0/100 H2O/MeOH) to give 27 (10.3 mg, 5.98 μmol, 68% yield). White solid; Rf 0.59 (10/10/3 CHCl3/MeOH/H2O); m.p. >300 °C; [α]24D = −133.2° (c 0.33, H2O); 1H-NMR (500 MHz, D2O) δ 5.13 (2H, m, H-1’ or 1”’ or 1’’’’ or 1’’’’’’×2), 5.03 (1H, d, J = 4.0 Hz, H-1’ or 1”’ or 1’’’’ or 1’’’’’’), 5.00 (1H, d, J = 4.0 Hz, H-1’ or 1”’ or 1’’’’ or 1’’’’’’), 4.98 (1H, d, J = 4.0 Hz, H-1’ or 1”’ or 1’’’’ or 1’’’’’’), 4.84 (1H, d, J = 2.9 Hz, H-4’ or 4” or 4’’’’ or 4’’’’’’ or 4’’’’’’), 4.80-3.60 (5H, m), 4.55 (3H, m, H-3’ or 3’’’’ or 3’’’’’’ or 3’’’’’’’’×2, H-5 or 5’’ or 5’’’’ or 5’’’’’’ or 5’’’’’’’’), 4.50-4.43 (2H, m, H-1, H-5 or 5’ or 5’’ or 5’’’’ or 5’’’’’’ or 5’’’’’’’’), 4.36 (1H, br-q, J = 6.5 Hz, H-5 or 5’ or 5’’ or 5’’’’ or 5’’’’’’ or 5’’’’’’’’), 4.28 (1H, dd, J2,3 = 10.3 Hz, J3,4 = 2.9 Hz, H-3), 4.16 (2H, m, H-4’ or 4” or 4’’ or 4’’’’ or 4’’’’’’ or 4’’’’’’’’×2), 4.08 (1H, d, J3,4 = 2.9 Hz, H-4), 4.06-4.01 (2H, m, H-3’ or 3’’ or 3’’’’ or 3’’’’’’ or 3’’’’’’’’), H-5 or 5’ or 5’’ or 5’’’’ or 5’’’’’’ or 5’’’’’’’’), 3.98-3.86 (5H, m, H-2’’, 2’’, 2’’, 2’’’’’, 2’’’’’’), 3.84-3.78 (2H, m, H-5 or 5’ or 5’’ or 5’’’’ or 5’’’’’’ or 5’’’’’’’’), H-h), 3.65-3.56 (2H, m, H-2, h), 1.58-1.52 (2H, m, H-g), 1.32-1.20 (28H, m, H-6, 6’, 6”’, 6’’’, 6’’’’, 6’’’’’, b, c, d, e, f), 0.79 (3H, t, J = 7.2 Hz, H-a); 13C-NMR (125 MHz, D2O, acetone-d6) δ 102.4, 100.7, 100.5, 100.1, 99.3×2, 80.2, 79.8, 79.4, 78.1, 78.0, 77.1, 76.8, 76.7, 76.6, 76.5, 75.2, 71.2, 70.8, 69.0, 68.7, 68.2, 68.1, 67.6, 67.0×2, 66.9×2, 66.8, 62.7, 31.3, 30.2, 29.1, 28.6×2, 25.4, 22.2, 16.3, 16.2×2, 15.6, 15.5, 15.4, 13.7; HRMS (ESI-TOF) m/z 837.0242 (837.0250 calcd. for C44H100O46Na5S7, [M−2Na]2−).
References.


$^1$H and $^{13}$C NMR spectra
Figure S1 $^1$H-NMR spectrum of 15

Figure S2 $^{13}$C-NMR spectrum of 15
Figure S3 $^1$H-NMR spectrum of 16

Figure S4 $^{13}$C-NMR spectrum of 16
Figure S5 $^1$H-NMR spectrum of 17

Figure S6 $^{13}$C-NMR spectrum of 17
Figure S7 $^1$H-NMR spectrum of S1

Figure S8 $^{13}$C-NMR spectrum of S1
Figure S9 $^1$H-NMR spectrum of 18

Figure S10 $^{13}$C-NMR spectrum of 18
Figure S11 $^1$H-NMR spectrum of S2

Figure S12 $^{13}$C NMR spectrum of S2
Figure S13 $^1$H-NMR spectrum of 19

Figure S14 $^{13}$C-NMR spectrum of 19

S32
Figure S15 $^1$H-NMR spectrum of 20α
Figure S16 $^{13}$C-NMR spectrum of 20α

Figure S17 $^1$H-NMR spectrum of 20β
Figure S18 $^{13}$C-NMR spectrum of 20$\beta$

Figure S19 $^1$H-NMR spectrum of 21
Figure S20 $^{13}$C-NMR spectrum of 21

Figure S21 $^1$H-NMR spectrum of 12
Figure S22 $^{13}$C-NMR spectrum of 12

Figure S23 $^1$H-NMR spectrum of S3
Figure S24 $^1$C-NMR spectrum of S3

Figure S25 $^1$H-NMR spectrum of 6

Figure S26 $^1$C-NMR spectrum of 6
Figure S27 $^1$H-NMR spectrum of 3
Figure S28 $^{13}$C-NMR spectrum of 3

Figure S29 $^1$H-NMR spectrum of 5
Figure S30 $^1$C-NMR spectrum of 5

Figure S31 $^1$H-NMR spectrum of S4
Figure S32 $^{13}$C-NMR spectrum of S4

Figure S33 $^1$H-NMR spectrum of S5
Figure S34 $^{13}$C-NMR spectrum of S5

Figure S35 $^1$H-NMR spectrum of S6
Figure S36 $^{13}$C-NMR spectrum of S6

Figure S37 $^1$H-NMR spectrum of 4
Figure S38 $^{13}$C-NMR spectrum of 4

Figure S39 $^1$H-NMR spectrum of 23
Figure S40 $^{13}$C-NMR spectrum of 23

Figure S41 $^1$H-NMR spectrum of S7
Figure S42 $^{13}$C-NMR spectrum of S7

Figure S43 $^1$H-NMR spectrum of 24
Figure S44 $^{13}$C-NMR spectrum of 24

Figure S45 $^1$H-NMR spectrum of S8
**Figure S46** $^1$C-NMR spectrum of S8

**Figure S47** $^1$H-NMR spectrum of 25
Figure S48 $^{13}$C-NMR spectrum of 25

Figure S49 $^1$H-NMR spectrum of 13
Figure S50 $^{13}$C-NMR spectrum of 13

Figure S51 $^1$H-NMR spectrum of S10
Figure S52 $^1$C-NMR spectrum of S10

Figure S53 $^1$H-NMR spectrum of 11
Figure S54 $^{13}$C-NMR spectrum of 11

Figure S55 $^1$H-NMR spectrum of 7
Figure S56 $^{13}$C-NMR spectrum of 7

Figure S57 $^1$H-NMR spectrum of 8
Figure S58 $^{13}$C-NMR spectrum of 8

Figure S59 $^1$H-NMR spectrum of S11
Figure S60 $^{13}$C-NMR spectrum of S11

Figure S61 $^1$H-NMR spectrum of S12
Figure S62 $^{13}$C-NMR spectrum of S12

Figure S63 $^1$H-NMR spectrum of 10
Figure S64 $^{13}$C-NMR spectrum of 10

Figure S65 $^1$H-NMR spectrum of S13
Figure S66 $^{13}$C-NMR spectrum of S13

Figure S67 $^1$H-NMR spectrum of S14
Figure S68 $^{13}$C-NMR spectrum of S14

Figure S69 $^1$H-NMR spectrum of 9
Figure S70 $^{13}$C-NMR spectrum of 9

Figure S71 $^1$H-NMR spectrum of S15
Figure S72 $^{13}$C-NMR spectrum of S15

Figure S73 $^1$H-NMR spectrum of 28
Figure S74 $^{13}$C-NMR spectrum of 28

Figure S75 $^1$H-NMR spectrum of S16
Figure S76 $^{13}$C-NMR spectrum of S16

Figure S77 $^1$H-NMR spectrum of 26
Figure S78 $^{13}$C-NMR spectrum of 26

Figure S79 $^1$H-NMR spectrum of 29
Figure S80 $^{13}$C-NMR spectrum of 29

Figure S81 $^1$H-NMR spectrum of S17
**Figure S82** $^{13}$C-NMR spectrum of S17

**Figure S83** $^1$H-NMR spectrum of 30
Figure S84 $^{13}$C-NMR spectrum of 30

Figure S85 $^1$H-NMR spectrum of S18
Figure S86 $^{13}$C-NMR spectrum of S18

Figure S87 $^1$H-NMR spectrum of 27
Figure S88 $^{13}$C-NMR spectrum of 27