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Supplementary Information

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

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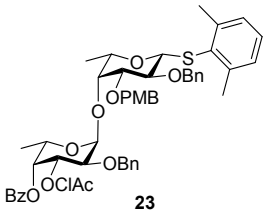
General methods for synthesis.

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 (δ 0.00), CD_3OD (δ 3.31) or $CDCl_3$ (δ 7.26), integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, d = quartet, and m = multiplet) and coupling constants (Hz). ^{13}C chemical shifts are reported in ppm downfield or upfield from $CDCl_3$ (δ 77.1), CD_3OD (δ 49.0) or acetone-d_6 (δ 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-α-L-fucopyranosyl-(1'→4)-2-*O*-benzyl-3-*O*-(*p*-methoxy)benzyl-1-thio-β-L-fucopyranoside (23)

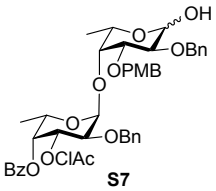


23

To a solution of **22**[1] (121 mg, 0.209 mmol) and **14**[2] (51.2 mg, 0.104 mmol) in Et_2O (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_2SO_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

mmol, 99% yield). White foam; R_f 0.61 (2/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ −119.9° (*c* 3.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.04 (2H, m, Ar-H), 7.63-7.08 (18H, m, Ar-H), 6.80 (2H, m, Ar-H), 5.62 (1H, dd, $J_{2',3'}$ = 10.6 Hz, $J_{3',4'}$ = 3.1 Hz, H-3'), 5.55 (1H, br-d, $J_{3',4'}$ = 2.3 Hz, H-4'), 5.10 (1H, d, $J_{1',2'}$ = 3.5 Hz, H-1'), 5.04 and 4.94 (2H, ABq, J = 10.6 Hz, ArCH_2), 4.81-4.66 (5H, m, ArCH_2×2, H-5), 4.29 (1H, d, $J_{1,2}$ = 9.8 Hz, H-1), 4.09 (1H, dd, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 10.6 Hz, H-2'), 3.91 and 3.88 (2H, ABq, J = 14.9 Hz, ClAc), 3.77 (5H, m, H-2, 4, OMe), 3.40 (1H, dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 2.9 Hz, H-3), 3.28 (1H, br-q, $J_{5',6'}$ = 6.6 Hz, H-5'), 2.56 (6H, s, SPhMe_2), 1.25 (3H, d, $J_{5',6'}$ = 6.6 Hz, H-6'), 0.93 (3H, d, $J_{5,6}$ = 6.6 Hz, H-6); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.8, 166.4, 159.2, 144.7, 138.6, 138.2, 133.5, 132.6, 130.5, 129.9, 129.7, 129.2, 128.8, 128.7, 128.5, 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, 74.4, 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 $C_{51}H_{56}O_{11}SCl$, $[M+H]^+$).

4'-*O*-Benzoyl-2'-*O*-benzyl-3'-*O*-chloroacetyl-α-L-fucopyranosyl-(1'→4)-2-*O*-benzyl-3-*O*-(*p*-methoxy)benzyl-L-fucopyranose (S7)

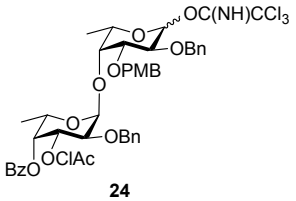


S7

To a solution of **23** (94.8 mg, 0.104 mmol) in MeCN (2.06 mL) and H_2O (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. $NaHCO_3$ (50 mL) and saturated aq. $Na_2S_2O_3$ (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 Na_2SO_4, 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; R_f 0.36 (1/1 *n*-hexane/EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) 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), 5.54-5.45 (2H, m), 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, ArCH_2), 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); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 166.4, 159.3, 138.0, 137.7, 133.5, 130.7, 129.9, 129.7, 129.3, 128.7, 128.6,

128.5, 128.5, 128.2, 128.1, 113.9, 100.0, 99.8, 98.0, 91.7, 80.1, 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 $C_{43}H_{47}O_{12}NaCl$, $[M+Na]^+$).

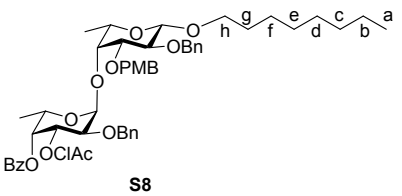
4'-*O*-Benzoyl-2'-*O*-benzyl-3'-*O*-chloroacetyl-α-L-fucopyranosyl-(1'→4)-2-*O*-benzyl-3-*O*-(*p*-methoxy)benzyl-L-fucopyranosyl trichloroacetimidate (24)



24

To a solution of **S7** (0.120 g, 0.152 mmol) in CH_2Cl_2 (1.80 mL) were added CCl_3CN (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_3) to give **24** (0.108 g, 0.116 mmol, 76% yield, α/β = 6/1). White foam; R_f 0.57, 0.27 (2/1 *n*-hexane/EtOAc, 1% NEt_3); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.61 (1/7H, s, OC(N*H*)CCl_3), 8.51 (6/7H, s, OC(N*H*)CCl_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); ^{13}C-NMR (125 MHz, $CDCl_3$) 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-β-L-fucopyranoside (S8)

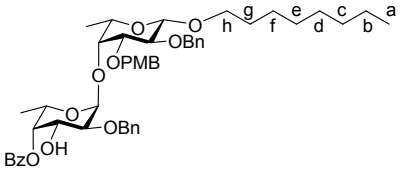


S8

To a solution of **24** (0.831 g, 0.888 mmol) in CH_2Cl_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_2SO_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); $[\alpha]^{27}_D$ −153.0° (*c* 0.12, $CHCl_3$); ^{1}H-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, $J_{3,4}$ = 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); ^{13}C-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*-benzoyl-2'-*O*-benzyl-α-L-fucopyranosyl-(1'→4)-2-*O*-benzyl-3-*O*-(*p*-methoxy)benzyl-β-L-fucopyranoside (25)

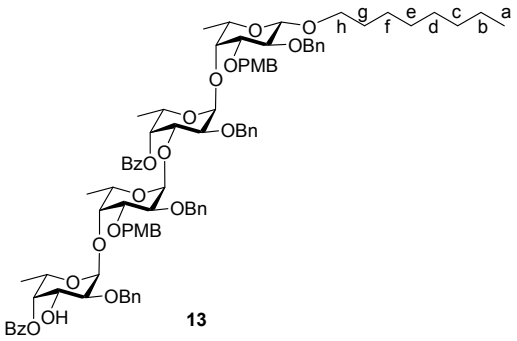


25

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_2SO_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); $[\alpha]^{27}_D$ −73.3° (*c* 3.0, $CHCl_3$);

^{1}H-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), 5.40 (1H, dd, $J_{3',4'}$ = 3.2 Hz, $J_{4',5'}$ = 1.2 Hz, H-4'), 5.03 (1H, d, $J_{1',2'}$ = 3.4 Hz, H-1'), 4.93 and 4.79 (2H, ABq, J = 10.9 Hz, ArCH_2), 4.77 (1H, ABq, J = 12.9 Hz, ArCH_2), 4.68 (3H, m, ArCH_2×2), 4.55 (1H, dq, $J_{4,5}$ = 0.9 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.39 (1H, ddd, $J_{2',3'}$ = 10.1 Hz, $J_{3',4'}$ = 3.2 Hz, $J_{3',OH}$ = 3.2 Hz, H-3'), 4.30 (1H, d, $J_{1,2}$ = 7.8 Hz, H-1), 3.97-3.92 (1H, m, H-h), 3.88 (1H, dd, $J_{1',2'}$ = 3.4 Hz, $J_{2',3'}$ = 10.1 Hz, H-2'), 3.78 (3H, s, OMe), 3.70 (1H, d, $J_{3,4}$ = 2.9 Hz, H-4), 3.61 (1H, dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.0 Hz, H-2), 3.51-3.43 (2H, m, H-5', h), 3.38 (1H, dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 2.9 Hz, H-3), 2.21 (1H, d, $J_{3',OH}$ = 3.2 Hz, $C_{3'}$-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, $J_{5,6}$ = 6.6 Hz, H-6), 0.88 (3H, t, J = 6.9 Hz, H-a); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 159.0, 138.7, 138.0, 133.0, 130.6, 130.0, 129.8, 129.1, 128.3, 128.3, 128.2, 127.8, 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 $C_{49}H_{63}O_{11}$, $[M+H]^+$).

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)



13

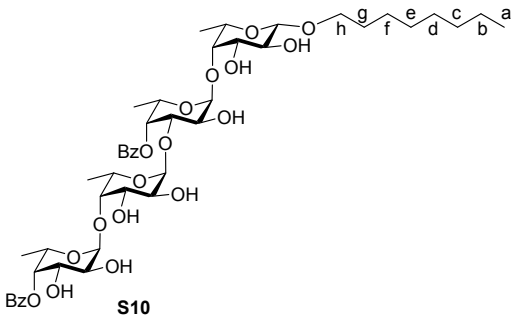
To a solution of **24** (1.15 g, 1.23 mmol) and **25** (0.500 g, 0.605 mmol) in Et_2O (17.0 mL) was added MS 5A (1.15 g, 100 wt% to **24**) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was cooled to −80 °C, and then TMSOTf (11.7 μL, 64.6 μmol) was added 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 Na_2SO_4, 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 Na_2SO_4, 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; R_f 0.42 (10/1 PhMe/acetone); $[\alpha]^{27}_D$ −152.0° (*c* 0.56, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) 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, $J_{3',4'}$ = 1.7 Hz, H-4'), 5.39 (1H, d, $J_{1''',2'''}$ = 3.5 Hz, H-1'''), 5.32 (1H, br-d, $J_{3''',4'''}$ = 2.3 Hz, H-4'''), 4.99 (1H, dd, $J_{1'',2''}$ = 3.2 Hz, H-1''), 4.95 (1H, d, $J_{1',2'}$ = 3.5 Hz, H-1'), 4.91 (2H, ABq, J = 10.9 Hz, ArCH_2), 4.79-4.73 (2H, m, ArCH_2), 4.65 (2H, s, ArCH_2), 4.61 (1H, ABq, J = 11.8 Hz, ArCH_2), 4.56-4.41 (9H, m, H-5 or H-5' or H-5'' or H-5'''×2, H-3', ArCH_2×3), 4.30 (1H, d, $J_{1,2}$ = 7.8 Hz, H-1), 4.19 (1H, ddd, $J_{2''',3'''}$ = 10.1 Hz, $J_{3''',4'''}$ = 3.2 Hz, $J_{3''',OH}$ = 3.2 Hz, H-3'''), 4.55 (1H, br-q, J = 6.6 Hz, H-5 or 5' or 5'' or 5'''), 3.98-3.91 (2H, m, H-2', h), 3.86 (1H, dd, $J_{1''',2'''}$ = 3.5 Hz, $J_{2''',3'''}$ = 10.1 Hz, H-2'''), 3.81 (1H, dd, $J_{1'',2''}$ = 3.2 Hz, $J_{2'',3''}$ = 10.3 Hz, H-2''), 3.77-3.73 (4H, m, H-3'', OMe), 3.67 (1H, br-d, $J_{3,4}$ = 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'''), 3.36 (1H, dd, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 2.6 Hz, H-3'), 2.09 (1H, d, $J_{3''',OH}$ = 3.2 Hz, $C_{3'''}$-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); ^{13}C-NMR (125 MHz, $CDCl_3$) 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, 130.1, 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 $C_{90}H_{107}O_{21}$, $[M+H]^+$).

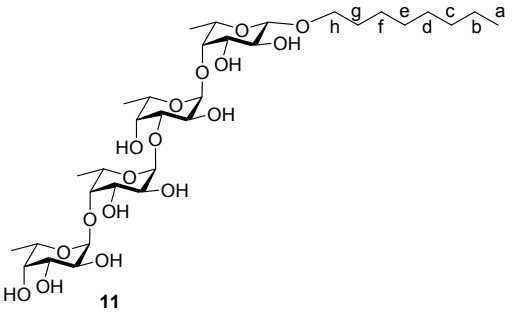
Synthesis of the type II fucoidan derivatives 7-11.

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; $[\alpha]^{27}_D$ −154.2° (*c* 0.62, MeOH); ^{1}H-NMR (500 MHz, CD_3OD) 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'', 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'''), 1.01 (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 $C_{46}H_{66}O_{19}Na$, $[M+Na]^+$).

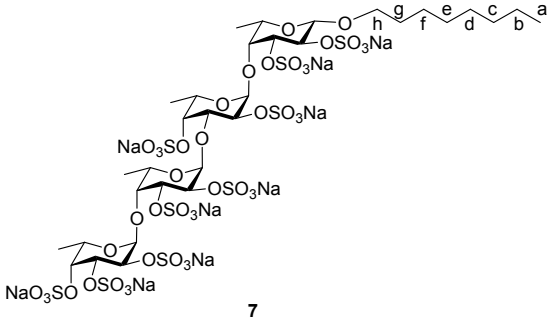
Octyl α-L-fucopyranosyl-(1'''→4'')-α-L-fucopyranosyl-(1''→3')-α-L-fucopyranosyl-(1'→4)-β-L-fucopyranoside (11)



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 $CHCl_3$/MeOH) to give **11** (15.2 mg, 21.3 μmol, 97% yield). White solid; R_f 0.16 (3/1 $CHCl_3$/MeOH); m.p. 132-133 °C; $[\alpha]^{27}_D$ −179.6° (*c* 1.0, MeOH); ^{1}H-NMR (500 MHz, CD_3OD) 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, $J_{1,2}$ = 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''', h), 3.57 (2H, m, H-3, h), 3.43 (1H, dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 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), 1.20 (6H, m, H-6 or 6' or 6'' or 6'''×2), 0.90 (3H, t, J = 6.9 Hz, H-a); ^{13}C-NMR (125 MHz, CD_3OD) 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 $C_{32}H_{58}O_{17}Na$, $[M+Na]^+$).

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)

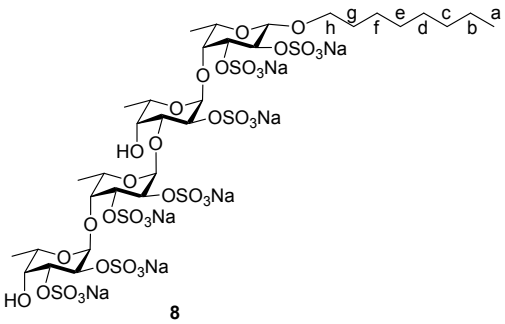


7

To a solution of **11** (6.20 mg, 8.67 μmol) in DMF (0.310 mL) was added SO_3•NEt_3 (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 H_2O/MeOH) and gel filtration chromatography to give **7** (11.5 mg, 7.04 μmol, 81% yield). White solid; R_f 0.25 (10/10/3 $CHCl_3$/MeOH/H_2O); m.p. >300 °C; $[\alpha]^{27}_D$ −41.9° (*c* 0.26, H_2O); ^{1}H-NMR (500 MHz, D_2O) δ 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'''), 5.19 (1H, d, *J* = 3.7 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'''×2), 4.34-4.22 (3H, m, H-1, H-3' or 3'' or 3''', H-5 or 5' or 5'' or 5'''), 4.19-4.13 (2H, m, H-4, H-4' or 4'' or 4'''), 3.78-3.66 (2H, m, H-5 or 5' or 5'' or 5''', h), 3.53 (1H, m, H-h), 1.52-1.43 (2H, m, H-g), 1.32-1.10 (22H, m, H-6, 6', 6'', 6''', b, c, d, e, f), 0.72 (3H, t, *J* = 6.9 Hz, H-a); ^{13}C-NMR (125 MHz, D_2O, acetone-d_6) δ 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 28.8, 25.3, 22.4, 16.4×2, 16.2, 16.0, 13.8; HRMS (ESI-TOF) *m/z* 1654.8116 (1654.8060 calcd. for $C_{32}H_{49}O_{44}Na_{10}S_9$, $[M+Na]^+$).

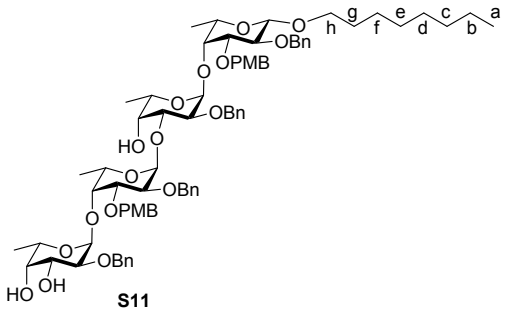
Octyl 2''',3'''-di-*O*-sulfo-α-L-fucopyranosyl-(1'''→4'')-2'',3''-di-*O*-sulfo-α-L-fucopyranosyl-(1''→3')-2'-*O*-sulfo-α-L-fucopyranosyl-(1'→4)-2,3-di-*O*-sulfo-β-L-fucopyranoside (8)



To a solution of **S10** (18.0 mg, 19.5 μmol) in DMF (0.900 mL) was added SO_3•NEt_3 (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 H_2O/MeOH) and gel filtration chromatography to give **8** (25.9 mg, 18.1 μmol, 93% yield). White solid; R_f 0.34 (10/10/3 $CHCl_3$/MeOH/H_2O); m.p. >300 °C; $[\alpha]^{27}_D$ −32.5° (*c* 0.30, H_2O); ^{1}H-NMR (500 MHz, D_2O) δ 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''', H-3, H-5 or 5' or 5'' or 5'''), 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-

4.06 (4H, m, H-3', 4, 4'', 4'''), 3.99 (1H, br-d, $J_{3',4'}$ = 2.6 Hz, H-4'), 3.74 (2H, m, H-5 or 5' or 5'' or 5''', H-h), 3.52 (1H, m, H-h), 1.54-1.43 (2H, m, H-g), 1.30-1.10 (22H, m, H-6, 6', 6'', 6''', b, c, d, e, f), 0.72 (3H, t, J = 6.9 Hz, H-a); ^{13}C-NMR (125 MHz, D_2O, acetone-d_6) δ 101.4, 99.1, 98.9, 95.3, 80.0, 78.8, 78.1, 76.2, 75.3, 74.2, 74.0, 73.0, 72.8, 71.2, 71.2, 70.8, 69.9, 68.1, 67.4×3, 31.5, 29.4, 29.1, 28.8, 25.3, 22.4, 16.3, 15.9, 15.7, 15.6, 13.8; HRMS (ESI-TOF) *m/z* 1428.9403 (1428.9465 calcd. for $C_{32}H_{52}O_{38}Na_7S_7$, $[M+H]^+$).

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-α-L-fucopyranosyl-(1'→4)-2-*O*-benzyl-3-*O*-(*p*-methoxy)benzyl-β-L-fucopyranoside (S11)

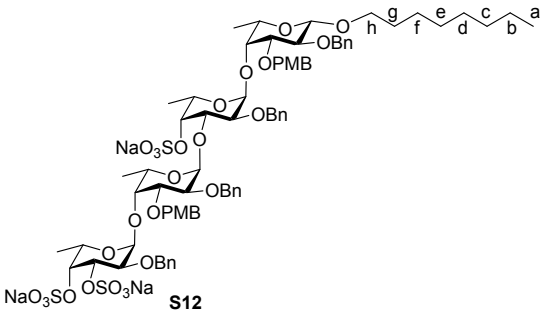


S11

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; R_f 0.32 (4/1 PhMe/acetone); $[\alpha]^{27}_D$ −130.2° (*c* 0.43, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) 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'', ArCH_2), 4.77-4.45 (10H, m, ArCH_2×5), 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, $J_{1,2}$ = 7.8 Hz, H-1), 4.13 (1H, dd, J = 3.2 Hz, J = 10.1 Hz, H-3' or 3''), 3.99 (1H, m, H-3'''), 3.95-3.75 (12H, m, H-2', 2'', 4, OMe×2, H-h, H-3' or 3'', H-5 or 5' or 5'' or 5'''), 3.70 (1H, dd, $J_{1''',2'''}$ = 3.5 Hz, $J_{2''',3'''}$ = 10.1 Hz, H-2'''), 3.68 (1H, m, H-4' or 4''), 3.66 (1H, d, $J_{3,4}$ = 2.9 Hz, H-4), 3.62 (1H, br-s, H-4'''), 3.59 (1H, dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.0 Hz, H-2), 3.48 (1H, m, H-h), 3.40 (1H, br-q, J = 6.6 Hz, H-5 or 5' or 5'' or 5'''), 3.34 (1H, dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 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''', H-b, c, d, e, f), 1.13-1.07 (9H, m, H-6 or 6' or 6'' or 6'''×3), 0.90 (3H, t, J = 6.9 Hz, H-a); ^{13}C-NMR (125 MHz, $CDCl_3$) 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, 128.3, 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 $C_{76}H_{99}O_{19}$, $[M+H]^+$).

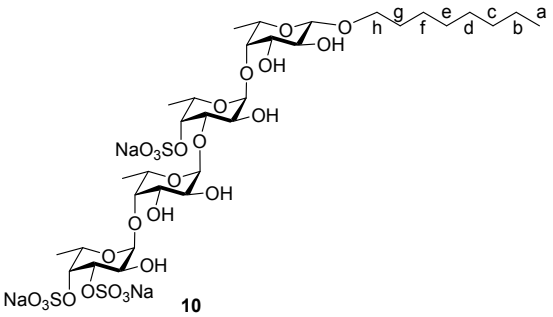
Octyl 2'''-*O*-benzyl-3''',4'''-di-*O*-sulfo-α-L-fucopyranosyl-(1'''→4'')-2''-*O*-benzyl-3''-*O*-(*p*-methoxy)benzyl-α-L-fucopyranosyl-(1''→3')-2'-*O*-benzyl-3',4'-di-*O*-sulfo-α-L-fucopyranosyl-(1'→4)-2-*O*-benzyl-3-*O*-(*p*-methoxy)benzyl-β-L-fucopyranoside (S12)



S12

To a solution of **S11** (48.0 mg, 36.5 μmol) in DMF (2.40 mL) was added SO_3•NEt_3 (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 H_2O/MeOH) to give **S12** (59.0 mg, 36.4 μmol, quant.). White solid; R_f 0.10 (3/1 $CHCl_3$/MeOH); m.p. 148-149 °C; $[\alpha]^{27}_D$ −83.4° (*c* 0.78, MeOH); ^{1}H-NMR (500 MHz, CD_3OD) 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, ArCH_2), 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, ArCH_2×4), 4.37 and 4.33 (2H, ABq, J = 11.2 Hz, ArCH_2), 4.25-4.17 (4H, m, H-1, 3', H-5 or 5' or 5'' or 5'''×2), 4.05 (1H, br-q, J = 6.6 Hz, H-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''', H-a); ^{13}C-NMR (125 MHz, CD_3OD) 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 $C_{76}H_{96}O_{28}Na_3S_3$, $[M+H]^+$).

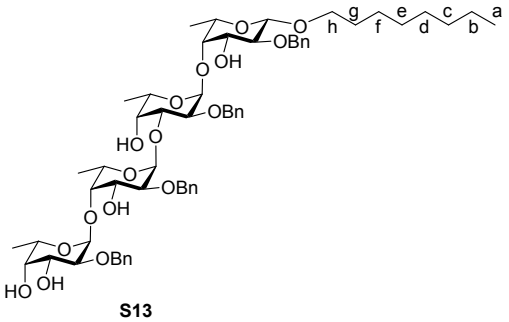
Octyl 3’’’,4’’’-di-*O*-sulfo-α-L-fucopyranosyl-(1’’’→4’’)-α-L-fucopyranosyl-(1’’→3’)-4’-*O*-sulfo-α-L-fucopyranosyl-(1’→4)-β-L-fucopyranoside (10)



10

To a solution of **S12** (50.5 mg, 31.1 μmol) in MeOH/H_2O (10.0 mL, 1/1) was added $Pd(OH)_2$/C (50.5 mg, 100 wt% to **S12**) under H_2 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 H_2O/MeOH) to give **10** (26.7 mg, 26.2 μmol, 84% yield). White solid; R_f 0.32 (10/10/3 $CHCl_3$/MeOH/H_2O); m.p. >300 °C; $[\alpha]^{27}_D$ −113.4° (*c* 0.10, H_2O); ^{1}H-NMR (500 MHz, D_2O) δ 5.02 (1H, d, $J_{1'',2''}$ = 4.0 Hz, H-1’’), 4/93 (1H, d, $J_{1''',2'''}$ = 4.0 Hz, H-1’’’), 4.88 (1H, d, $J_{1',2'}$ = 4.3 Hz, H-1’), 4.79 (1H, d, $J_{3''',4'''}$ = 2.9 Hz, H-4’’’), 4.67 (1H, m, H-4’), 4.60 (1H, br-q, $J_{5''',6'''}$ = 6.3 Hz, H-5’’’), 4.58-4.51 (2H, m, H-3’’’, 5’), 4.30 (1H, d, $J_{1,2}$ = 8.0 Hz, H-1), 4.25 (1H, br-q, $J_{5'',6''}$ = 6.6 Hz, H-5’’), 3.93 (1H, dd, $J_{2',3'}$ = 10.6 Hz, $J_{3',4'}$ = 2.9 Hz, H-3’), 3.90-3.85 (2H, m, H-2’’’, 3’’), 3.81-3.67 (6H, m, H-2’, 2’’, 4, 4’’, 5, h), 3.62 (1H, dd, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 3.4 Hz, H-3), 3.55 (1H, m, H-h), 3.40 (1H, dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 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); ^{13}C-NMR (125 MHz, D_2O, acetone-d_6) 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, 68.6, 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 $C_{32}H_{56}O_{26}Na_3S_3$, $[M+H]^+$).

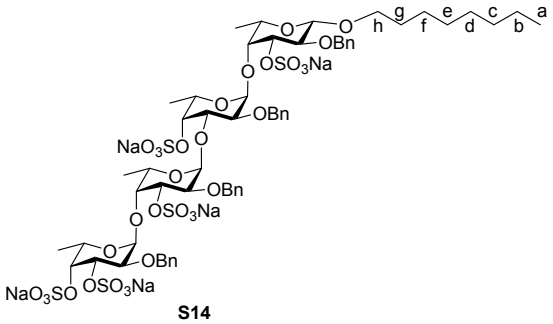
Octyl 2’’’-*O*-benzyl-α-L-fucopyranosyl-(1’’’→4’’)-2’’-*O*-benzyl-α-L-fucopyranosyl-(1’’→3’)-2’-*O*-benzyl-α-L-fucopyranosyl-(1’→4)-2-*O*-benzyl-β-L-fucopyranoside (S13)



S13

To a solution of **S11** (26.1 mg, 19.8 μmol) in CH_2Cl_2/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. $NaHCO_3$ (10 mL). The resultant mixture was extracted with $CHCl_3$ (10 mL×3), and then the extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4, 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; R_f 0.29 (3/1 PhMe/acetone); m.p. 77-78 °C; $[\alpha]^{27}_D$ −81.4° (*c* 0.35, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) 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''', ArCH_2), 4.81 (1H, m, H-1' or 1'' or 1'''), 4.81 and 4.65 (2H, ABq, J = 11.7 Hz, ArCH_2), 4.65 and 4.49 (2H, ABq, J = 12.0 Hz, ArCH_2), 4.58 (2H, s, ArCH_2), 4.31 (1H, d, $J_{1,2}$ = 7.8 Hz, H-1), 4.13-3.90 (7H, m, H-3', 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''', OH×2, H-h), 3.36 (1H, s, OH), 3.22 (1H, dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 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); ^{13}C-NMR (125 MHz, $CDCl_3$) 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 $C_{60}H_{83}O_{17}$, $[M+H]^+$).

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)

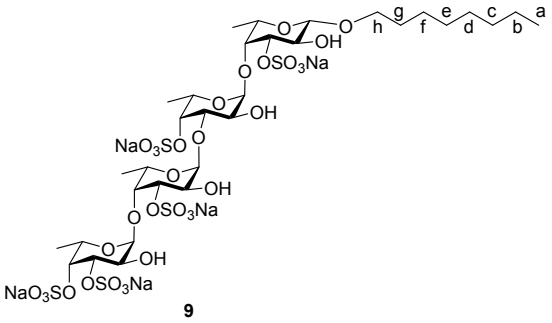


S14

To a solution of **S13** (17.7 mg, 16.4 μmol) in DMF (0.885 mL) was added SO_3•NEt_3 (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_2O/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_2O); m.p. >300 °C; $[\alpha]^{27}_D$ −118.0° (*c* 0.31, H_2O); ^{1}H-NMR (500 MHz, D_2O) 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), 3.92 (1H, br-q, *J* = 6.3 Hz, H-5 or 5' or 5'' or 5'''), 3.81 (1H, dd, $J_{1'',2''}$ = 3.4 Hz, $J_{2'',3''}$ = 10.9 Hz, H-2''), 3.79-3.70 (4H, m, H-2', 2''', 4, 4''), 3.66 (1H, dd, $J_{2',3'}$ = 10.9 Hz, $J_{3',4'}$ = 2.9 Hz, H-3'), 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), 1.29-0.93 (22H, m, H-6, 6', 6'', 6''', b, c, d, e, f), 0.68 (3H, t, *J* = 6.9 Hz, H-a); ^{13}C-NMR (125 MHz,D_2O, acetone-d_6) δ 137.9, 137.5, 137.3, 136.3, 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 $C_{60}H_{78}O_{32}Na_5S_5$, $[M+H]^+$).

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)

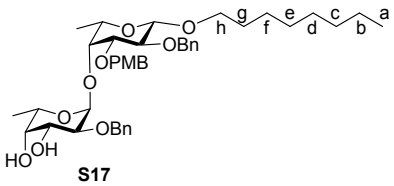


To a solution of **S14** (19.6 mg, 12.4 μmol) in MeOH/H_2O (7.84 mL, 1/1) was added $Pd(OH)_2$/C (39.2 mg, 200 wt% to **S14**) under H_2 atmosphere at room temperature. After being stirred for 16 h, the reaction mixture was filtered through Celite, and then filtrate was concentrated in *vacuo*. The residue was subjected to reverse phase silica gel column chromatography (100/0 to 0/100 H_2O/MeOH) to give **9** (15.0 mg, 12.2 μmol, 99% yield). White solid; R_f 0.54 (10/10/3 $CHCl_3$/MeOH/H_2O); m.p. >300 °C; $[\alpha]^{27}_D$ −135.6° (*c* 0.31, H_2O); ^{1}H-NMR (500 MHz, D_2O) 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),

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); ^{13}C-NMR (125 MHz, D_2O, acetone-d_6) δ 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, 66.9×2, 66.8, 31.4, 29.1, 28.8, 25.4, 22.4, 16.3, 15.8, 15.6, 13.8; HRMS (ESI-TOF) *m/z* 589.0416 (589.0408 calcd. for $C_{32}H_{53}O_{32}Na_3S_5$, $[M-2Na]^{2-}$).

Synthesis of the oligofucosides 26 and 27.

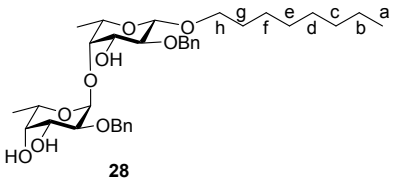
Octyl 2'-*O*-benzyl-α-L-fucopyranosyl-(1'→4)-2-*O*-benzyl-3-*O*-(*p*-methoxy)benzyl-β-L-fucopyranoside (S15)



S17

To a solution of **25** (26.0 mg, 31.4 μmol) in MeOH (2.60 mL) was added 28% NaOMe in MeOH (303 μL, 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 μmol, 65% yield). Colorless syrup; R_f 0.50 (1/1 PhMe/EtOAc); $[\alpha]^{23}_D$ −92.4° (*c* 0.41, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 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, ArCH_2), 4.77-4.73 (2H, m, ArCH_2), 4.69 and 4.64 (2H, ABq, J = 12.3 Hz, ArCH_2), 4.56 (1H, ABq, J = 11.5 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); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 159.2, 138.9, 138.1, 130.8, 129.3, 128.7, 128.4, 128.3, 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) *m/z* 745.3926 (745.3928 calcd. for $C_{42}H_{58}O_{10}Na$, $[M+Na]^+$).

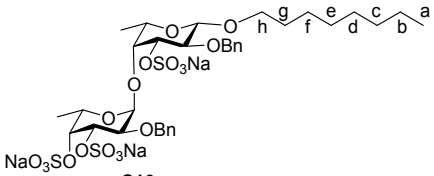
Octyl 2'-*O*-benzyl-α-L-fucopyranosyl-(1'→4)-2-*O*-benzyl-β-L-fucopyranoside (28)



28

To a solution of **S15** (14.8 mg, 20.5 μmol) in CH_2Cl_2/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. $NaHCO_3$ (6 mL). The resultant mixture was extracted with $CHCl_3$ (6 mL×3), and then the extracts were washed with brine (15 mL), dried over anhydrous Na_2SO_4, 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; R_f 0.32 (1/1 PhMe/EtOAc); $[\alpha]^{23}_D$ −86.6° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.42-7.22 (10H, m, Ar-H), 4.98 (1H, d, $J_{1',2'}$ = 3.7 Hz, H-1'), 4.90 and 4.79 (2H, ABq, J = 11.5 Hz, ArCH_2), 4.68 and 4.53 (2H, ABq, J = 11.8 Hz, ArCH_2), 4.31 (1H, ABq, $J_{1,2}$ = 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, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 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, $J_{5,6}$ = 6.6 Hz, H-6), 0.87 (3H, t, J = 6.9 Hz, H-a); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.7, 137.8, 128.8, 128.5, 128.3, 128.3, 128.0, 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 $C_{34}H_{51}O_9$, $[M+H]^+$).

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

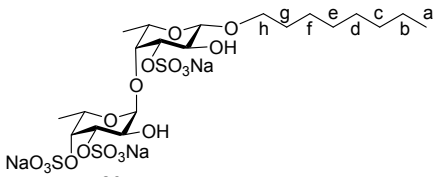


S16

To a solution of **28** (11.4 mg, 18.9 μmol) in DMF (0.342 mL) was added SO_3•NEt_3 (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 H_2O/MeOH) and gel filtration chromatography to give **S16** (15.0 mg, 16.5 μmol, 86% yield). White solid; R_f 0.55 (10/10/3 $CHCl_3$/MeOH/H_2O); m.p. >300 °C; $[\alpha]^{26}_D$ −75.8° (*c* 1.0, MeOH); ^{1}H-NMR (500 MHz, CD_3OD) δ 7.57-7.20 (10H, m, Ar-H), 5.21 (1H, d, $J_{1',2'}$ = 3.4 Hz, H-1'), 5.02-4.80 (4H, m, H-3', 4', ArCH_2), 4.77-4.71 (2H, m,

Ar*CH*$_2$), 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, $J_{2',3'}$ = 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-h), 1.63-1.54 (2H, m, H-g), 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_2O, acetone-d_6) δ 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, 23.7, 17.6, 17.3, 14.4; HRMS (ESI-TOF) *m/z* 931.1483 (931.1515 calcd. for $C_{34}H_{47}O_{18}Na_4S_3$, $[M+Na]^+$).

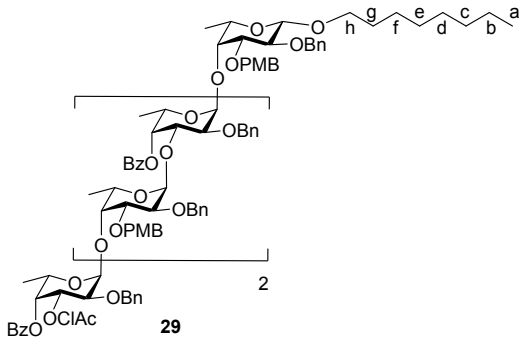
Octyl 3',4'-di-*O*-sulfo-α-L-fucopyranosyl-(1'→4)-3-*O*-sulfo-β-L-fucopyranoside (26)



26

To a solution of **S16** (82.6 mg, 90.9 μmol) in MeOH/H_2O (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_2O/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_2O); m.p. >300 °C; $[\alpha]^{27}_D$ −85.9° (*c* 1.0, H_2O); ^{1}H-NMR (500 MHz, D_2O) δ 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, $J_{3,4}$ = 2.9 Hz, H-3), 4.11 (1H, br-d, $J_{3,4}$ = 2.9 Hz, H-4), 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_2O, acetone-d_6) δ 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 $C_{20}H_{36}O_{18}Na_3S_3$, $[M+H]^+$).

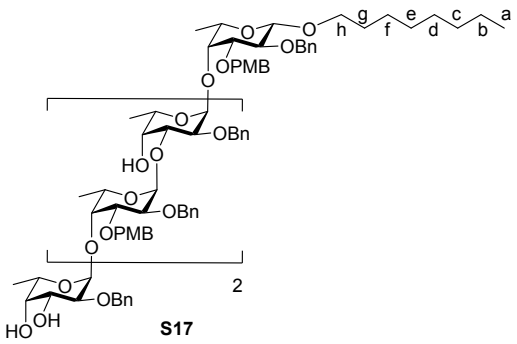
Octyl 4'''''-*O*-benzoyl-2'''''-*O*-benzyl-3'''''-*O*-chloroacetyl-α-L-fucopyranosyl-(1'''''→4'''')-2''''-*O*-benzyl-3''''-*O*-(*p*-methoxy)benzyl-α-L-fucopyranosyl-(1''''→3''')-4'''-*O*-benzoyl-2'''-*O*-benzyl-α-L-fucopyranosyl-(1'''→4'')-2''-*O*-benzyl-3''-*O*-(*p*-methoxy)benzyl-α-L-fucopyranosyl-(1''→3')-4'-*O*-benzoyl-2'-*O*-benzyl-α-L-fucopyranosyl-(1'→4)-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



29

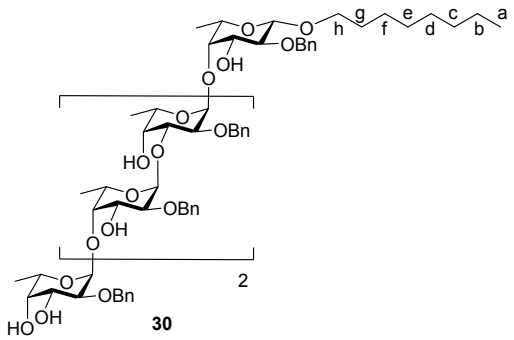
To a solution of **24** (61.6 mg, 65.8 μmol) and **13** (54.5 mg, 36.1 μmol) in Et_2O (1.00 mL) was added MS 5A (61.6 mg, 100 wt% to **24**) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was cooled to −80 °C, and then TMSOTf (0.700 μL, 3.62 μmol) was added 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×3), and then the extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_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 μmol, 94% yield). Colorless syrup; R_f 0.42 (10/1 PhMe/acetone); $[\alpha]^{24}_D$ −145.7° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 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’’’’’), 5.51 (1H, br-d, J = 2.3 Hz, H-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’’’’’×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’’’’’×3, H-a); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.5, 166.4, 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, 130.8, 130.1, 129.9, 129.2, 129.2, 128.8, 128.6, 128.5, 128.4, 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 $C_{133}H_{152}O_{32}Cl$, $[M+H]^+$).

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-α-L-fucopyranosyl-(1’’’→4’’)-2’’-*O*-benzyl-3’’-*O*-(*p*-methoxy)benzyl-α-L-fucopyranosyl-(1’’→3’)-2’-*O*-benzyl-α-L-fucopyranosyl-(1’→4)-2-*O*-benzyl-3-*O*-(*p*-methoxy)benzyl-β-L-fucopyranoside (S17)



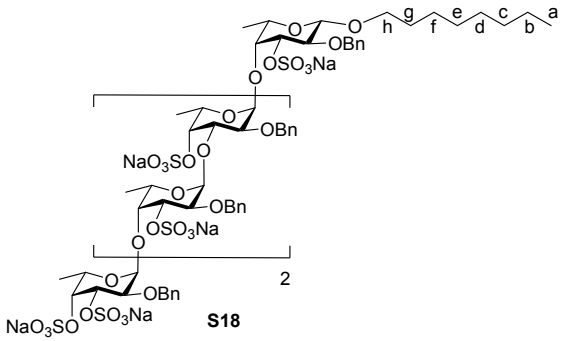
To a solution of **29** (15.2 mg, 6.61 μmol) in MeOH (1.50 mL) was added 28% NaOMe in MeOH (0.136 mL, 926 μmol), and then the resultant mixture was stirred at 50 °C for 24 h. After cooling to room temperature, the reaction was quenched with Amberlite® IR 120 H^+ form. The resultant suspension was filtered, 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, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 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-3’ or 3’’ or 3’’’ or 3’’’’ or 3’’’’’×2), 3.93-3.55 (26H, m), 3.47 (1H, m, H-h), 3.39 (1H, br-q, J = 6.3 Hz, H-5 or 5’ or 5’’ or 5’’’ or 5’’’’ or 5’’’’’), 3.33 (1H, dd, J = 3.2, 9.7 Hz, H-3), 2.58 (1H, s, OH), 2.36-2.25 (3H, m, OH×3), 1.75-1.58 (2H, m, H-g), 1.50-1.20 (13H, m, H-6 or 6’ or 6’’ or 6’’’ or 6’’’’ or 6’’’’’, H-b, c, d, e, f), 1.20-1.04 (15H, 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, $CDCl_3$) δ 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, 128.3, 128.2, 128.1, 127.8, 127.8, 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 $C_{110}H_{139}O_{28}$, $[M+H]^+$).

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 CH_2Cl_2/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. $NaHCO_3$ (10 mL). The resultant mixture was extracted with $CHCl_3$ (15 mL×3), and then the extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4, 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; R_f 0.21 (1/2 PhMe/AcOEt); m.p. 85-86 °C; $[\alpha]^{27}_D$ −157.6° (*c* 0.11, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) 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, Ar*CH*$_2$), 4.31 (1H, d, $J_{1,2}$ = 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’’’’’×2, H-4, h), 3.85-3.80 (4H, m), 3.76 (1H, dd, J = 3.4, 10.0 Hz, H-2’ or 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, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 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’’’’’), 1.06 (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); ^{13}C-NMR (125 MHz, $CDCl_3$) 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, 70.4, 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 $C_{86}H_{114}O_{25}Na$, $[M+Na]^+$).

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

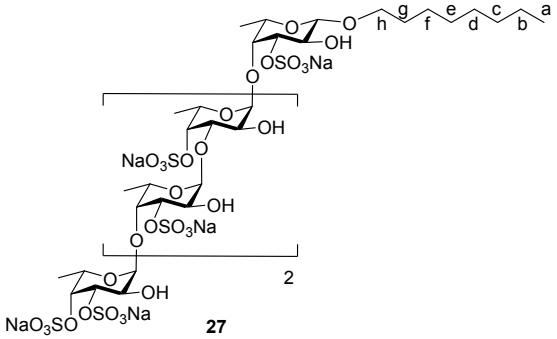


S18

To a solution of **30** (13.7 mg, 8.85 μmol) in DMF (0.665 mL) was added SO_3•NEt_3 (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 H_2O/MeOH) and gel filtration chromatography to give **S18** (20.0 mg, 8.84 μmol, 99% yield). White solid; R_f 0.54 (10/10/3 $CHCl_3$/MeOH/H_2O); m.p. >300 °C; $[\alpha]^{28}_D$ −135.4° (*c* 0.26, H_2O); ^{1}H-NMR (500 MHz, D_2O) 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’’’’’) , 5.22 (1H, d, *J* = 3.2 Hz, H-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’’’’’, H-3’ or 3’’ or 3’’’ or 3’’’’ or 3’’’’’×3, H-4’ or 4’’ or 4’’’ or 4’’’’ or 4’’’’’, ArCH_2×6), 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’’’’’), 3.80 (1H, br-q, *J* = 6.3 Hz, H-5 or 5’ or 5’’ or 5’’’ or 5’’’’ or 5’’’’’), 3.87-3.74 (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’’’’’, H-5 or 5’ or 5’’ or 5’’’ or 5’’’’ or 5’’’’’), 3.43 (1H, m, H-h), 3.36 (1H, dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 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’’’’’), 3.21 (1H, br-q, *J* = 6.3 Hz, H-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’’’’’×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’’’’’), 0.68 (3H, t, *J* = 7.2 Hz, H-a); ^{13}C-NMR (125 MHz, D_2O, acetone-d_6) δ 137.9, 137.7, 137.6, 137.3, 137.1, 136.6, 130.7, 130.6, 130.3, 129.4, 129.3, 128.9, 128.7, 128.6, 128.5, 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,

69.1, 68.8, 67.5, 67.0, 66.7, 66.5, 66.3, 31.4, 29.3, 28.7, 25.7, 22.3, 16.4×2, 16.3, 16.0, 15.9, 15.4, 13.7; LRMS (ESI-TOF) *m/z* 2261.37 (2261.34 calcd. for $C_{86}H_{108}O_{46}Na_7S_7$, $[M+H]^+$).

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-α-L-fucopyranosyl-(1’’→3’)-4’-*O*-sulfo-α-L-fucopyranosyl-(1’→4)-3-*O*-sulfo-β-L-fucopyranoside (27)



27

To a solution of **S18** (20.0 mg, 8.84 μmol) in MeOH/H_2O (8.00 mL, 1/1) was added $Pd(OH)_2$/C (40.0 mg, 200 wt% to **S18**) under H_2 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 H_2O/MeOH) to give **27** (10.3 mg, 5.98 μmol, 68% yield). White solid; R_f 0.59 (10/10/3 $CHCl_3$/MeOH/H_2O); m.p. >300 °C; $[\alpha]^{24}_D$ −133.2° (*c* 0.33, H_2O); ^{1}H-NMR (500 MHz, D_2O) δ 5.13 (2H, m, H-1’ or 1’’ or 1’’’ or 1’’’’ or 1’’’’’×2), 5.03 (1H, d, J = 4.0 Hz, H-1’ or 1’’ or 1’’’ or 1’’’’ or 1’’’’’), 5.00 (1H, d, J = 4.0 Hz, H-1’ or 1’’ or 1’’’ or 1’’’’ or 1’’’’’), 4.98 (1H, d, J = 4.0 Hz, H-1’ or 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’’’’ or 3’’’’’×2, H-5 or 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, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 2.9 Hz, H-3), 4.16 (2H, m, H-4’ or 4’’ or 4’’’ or 4’’’’ or 4’’’’’×2), 4.08 (1H, d, $J_{3,4}$ = 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); ^{13}C-NMR (125 MHz, D_2O, acetone-d_6) 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 $C_{44}H_{71}O_{46}Na_5S_7$, $[M-2Na]^{2-}$).

References.

1) Gildersleeve, J.; Pascal, R. A.; Kahne, D. *J. Am. Chem. Soc.* **1998**, *120*, 5961.
2) Krylov, V. B.; Kaskova, Z. M.; Vinnitskiy, D. Z.; Ustyuzhanina, N. E.; Grachev, A. A.; Chizhov, A. O.; Nifantiev, N. E. *Carbohydr. Res.* **2011**, *346*, 540.

^{1}H and ^{13}C NMR spectra

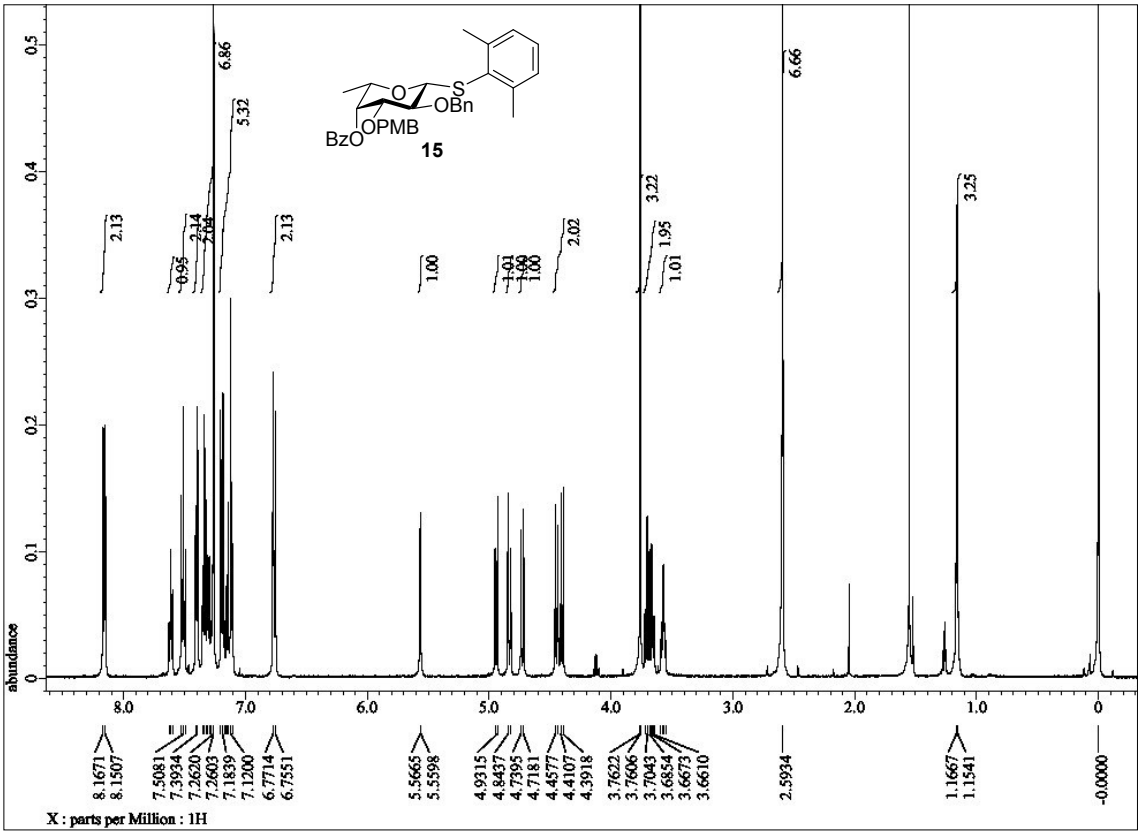


Figure S1 ^{1}H-NMR spectrum of **15**

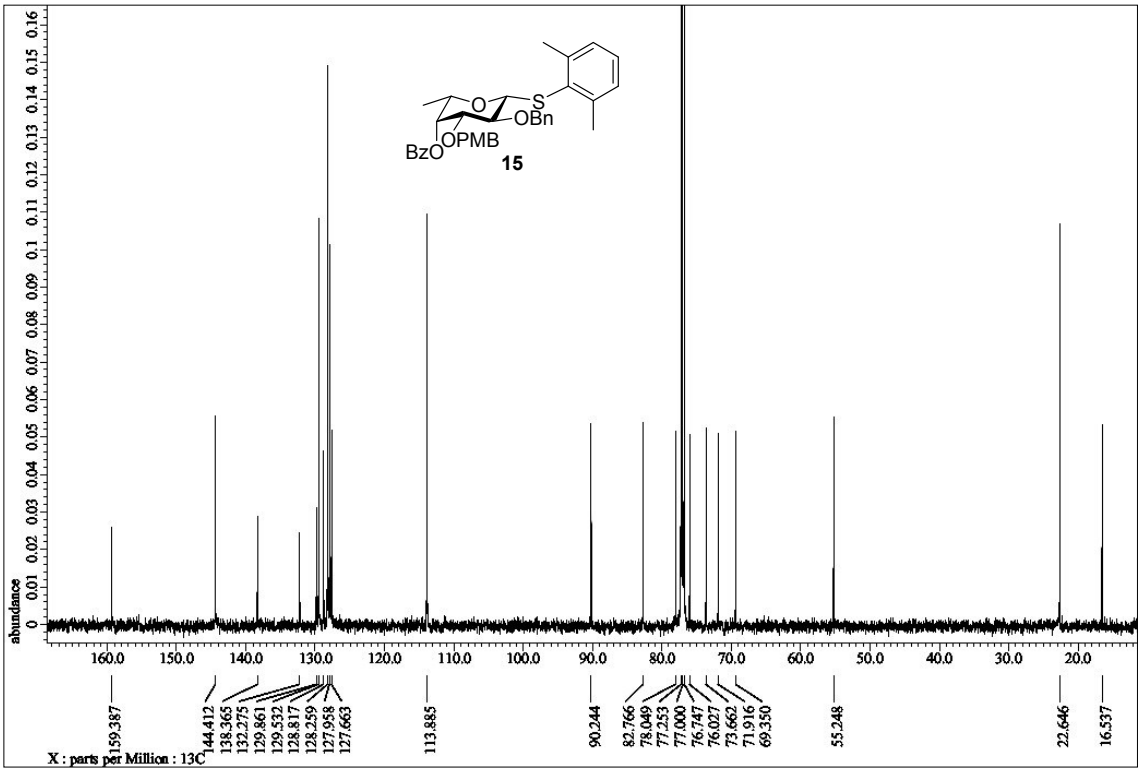


Figure S2 ^{13}C-NMR spectrum of **15**

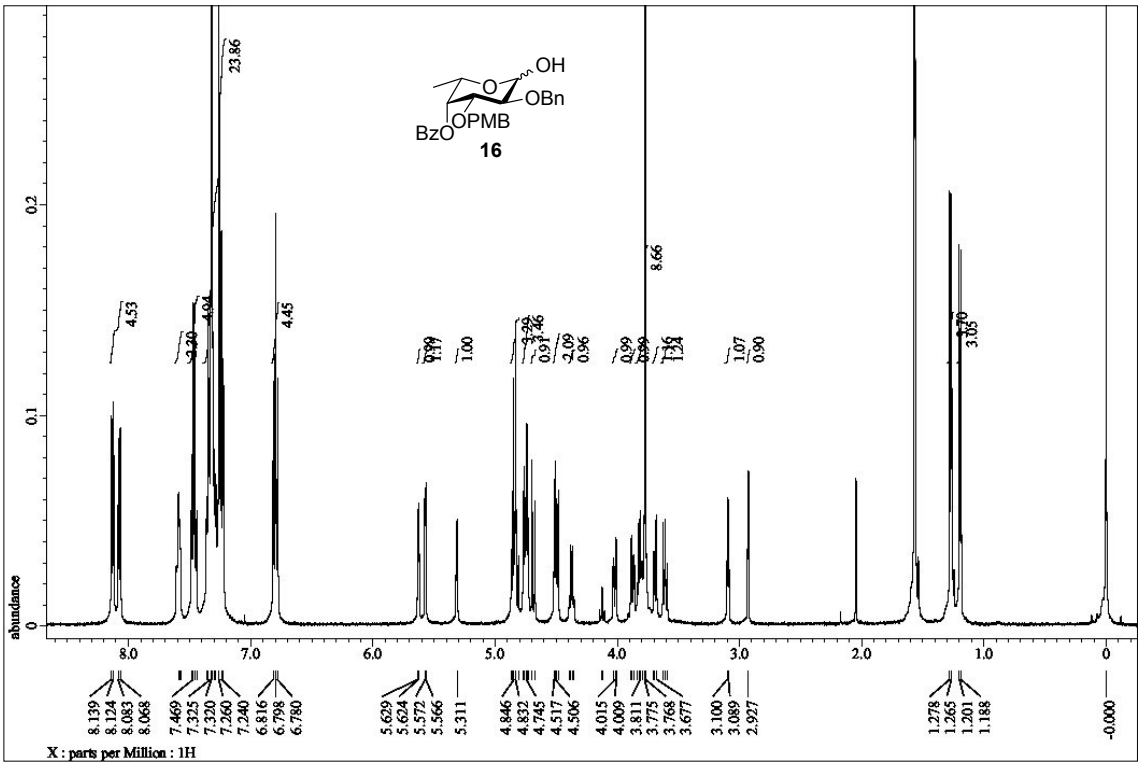


Figure S3 ^{1}H-NMR spectrum of **16**

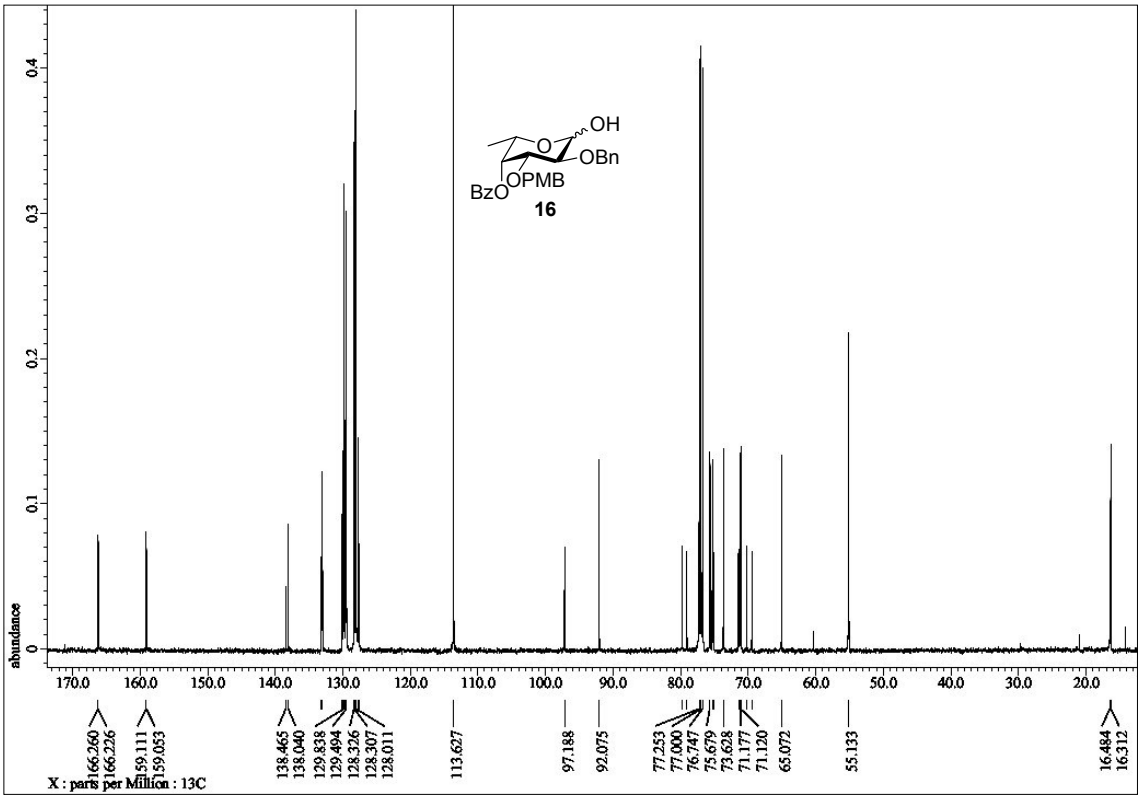


Figure S4 ^{13}C-NMR spectrum of **16**

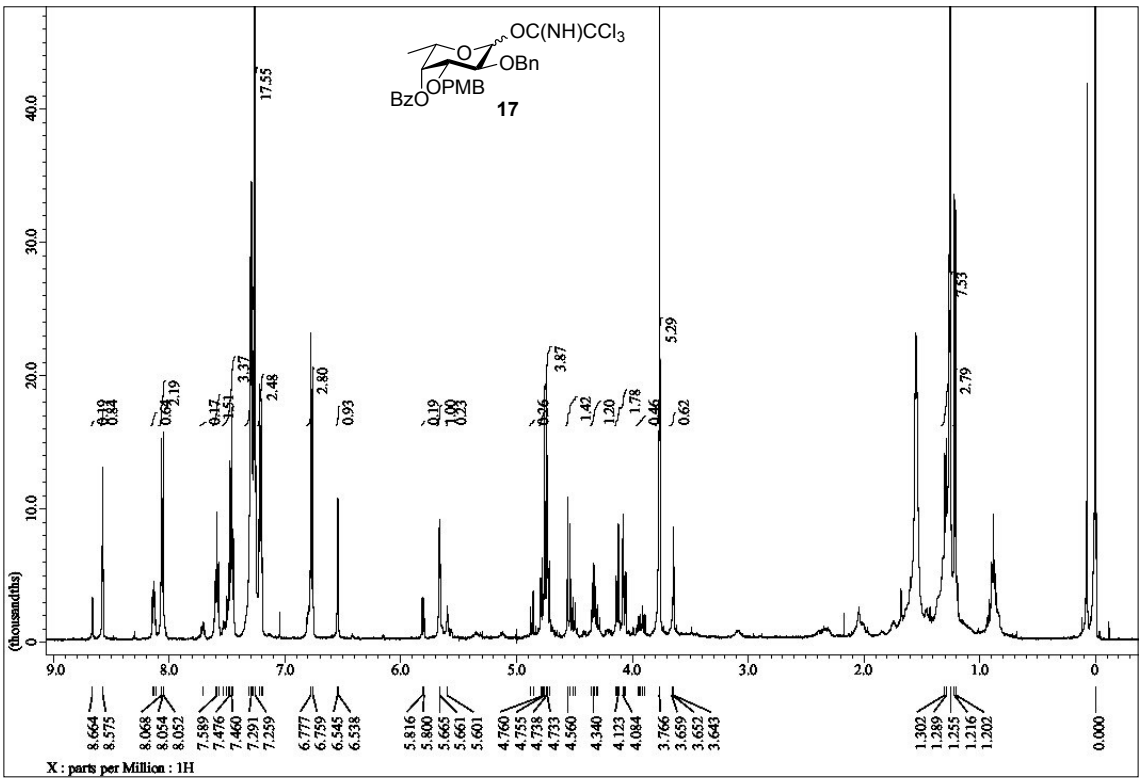


Figure S5 ^{1}H-NMR spectrum of **17**

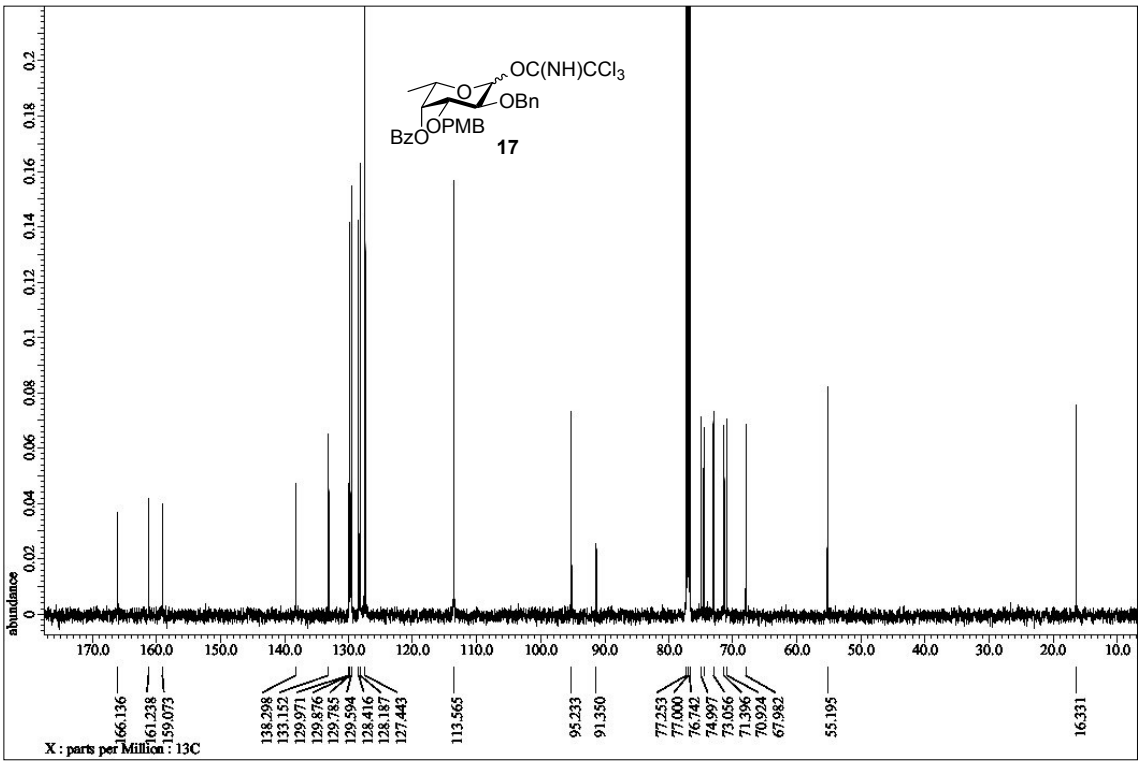


Figure S6 ^{13}C-NMR spectrum of **17**

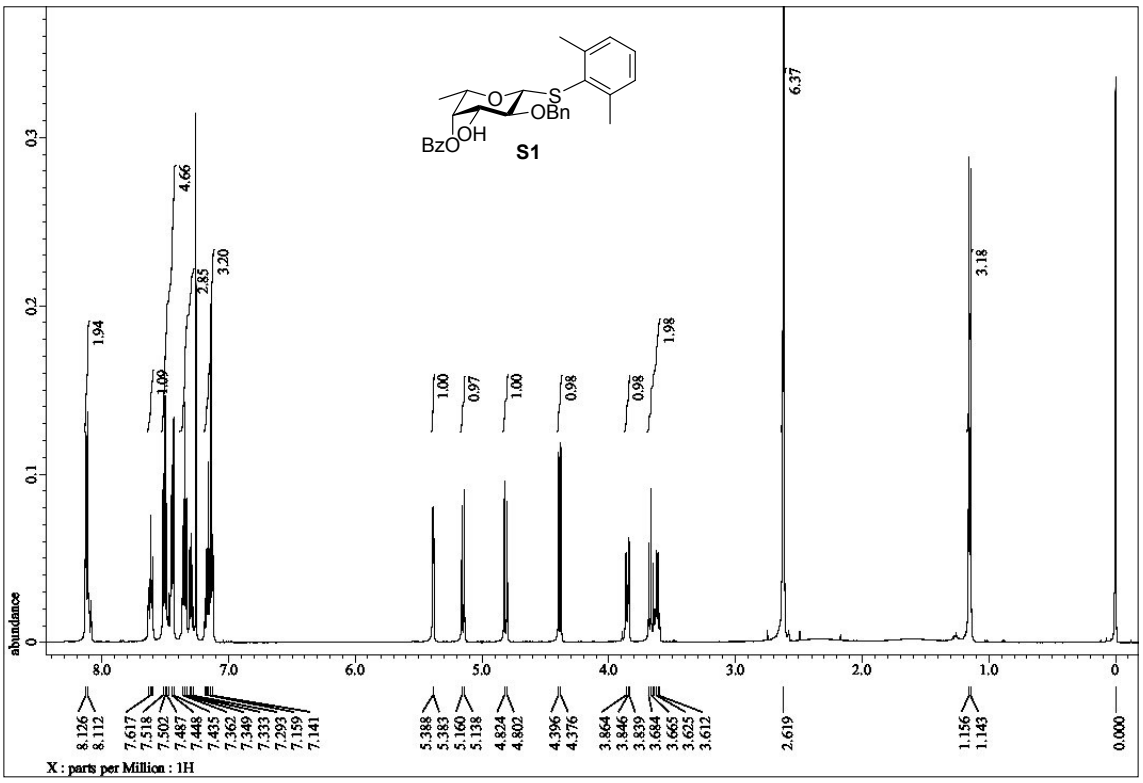


Figure S7 ^{1}H-NMR spectrum of **S1**

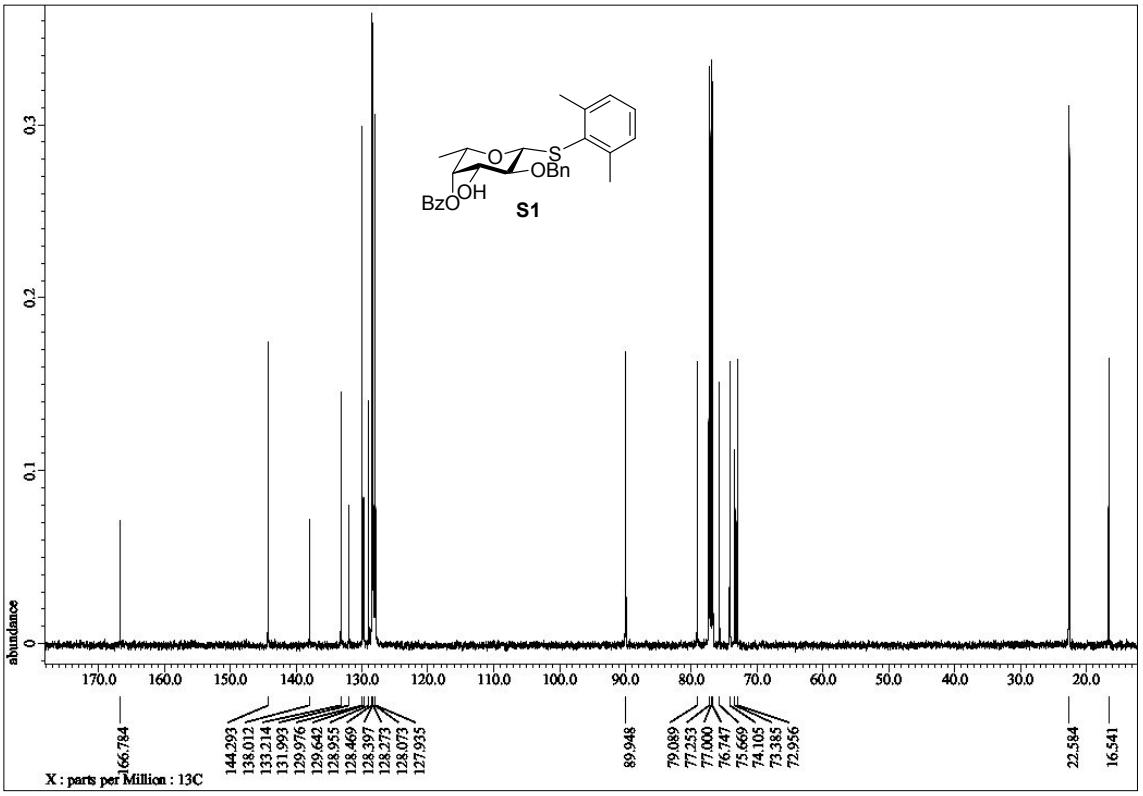


Figure S8 ^{13}C-NMR spectrum of **S1**

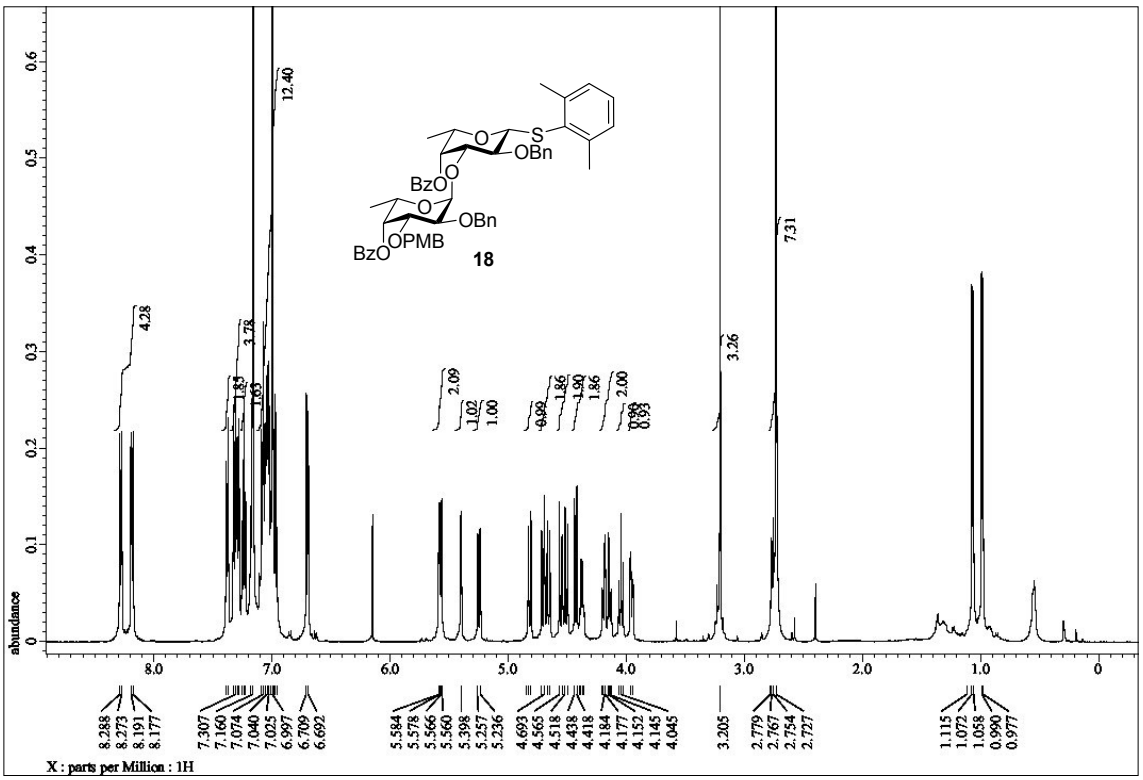


Figure S9 ^{1}H-NMR spectrum of **18**

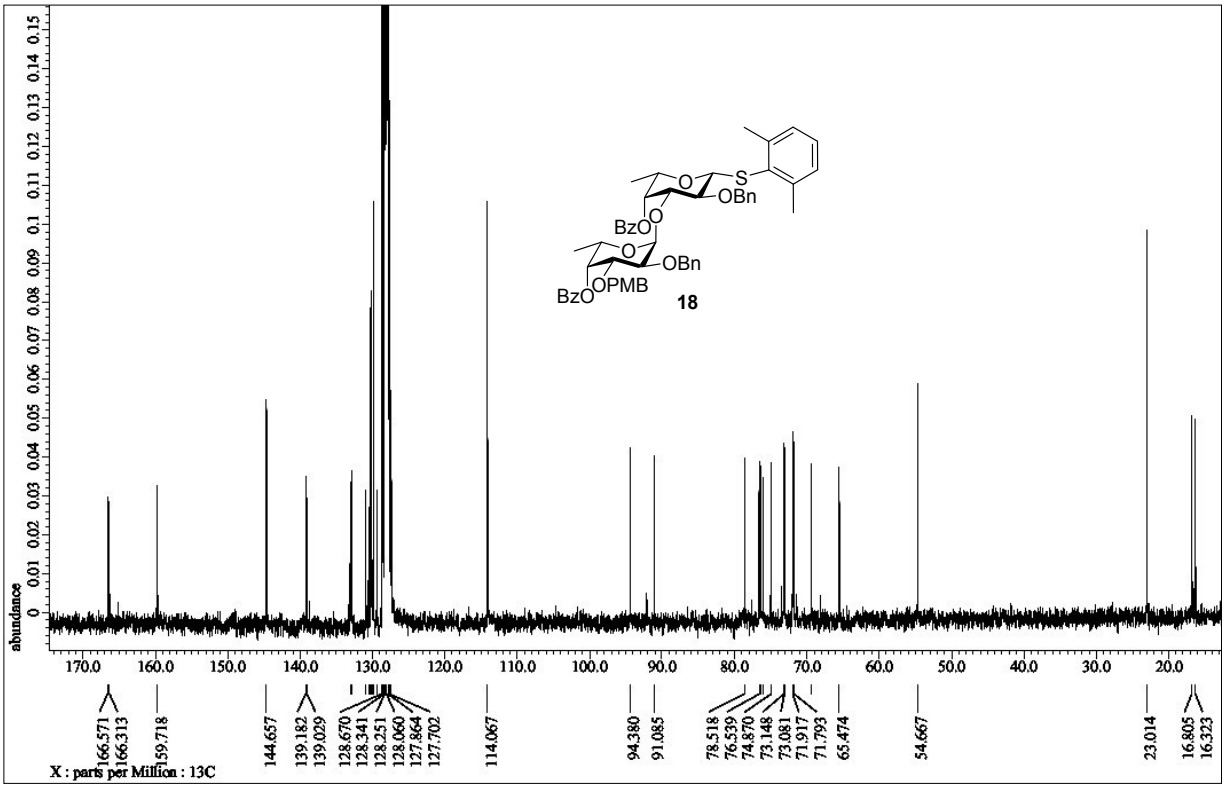


Figure S10 ^{13}C-NMR spectrum of **18**

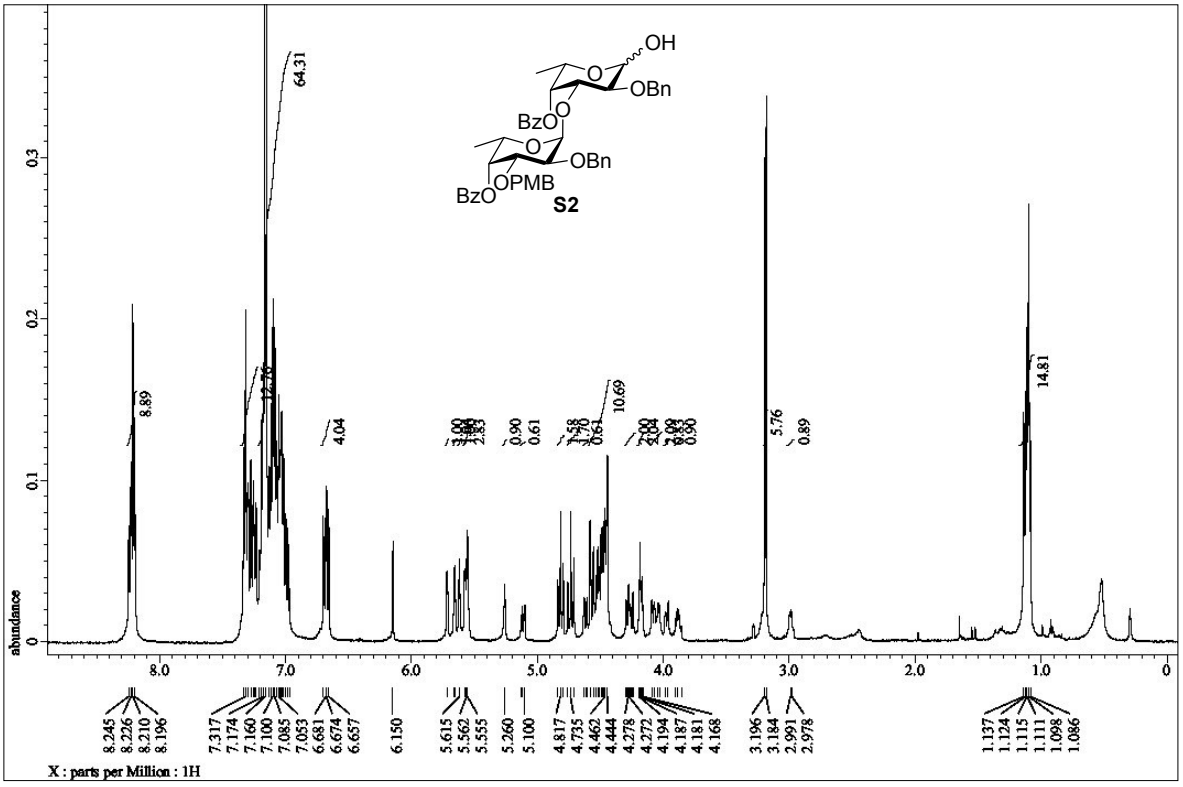


Figure S11 ^{1}H-NMR spectrum of **S2**

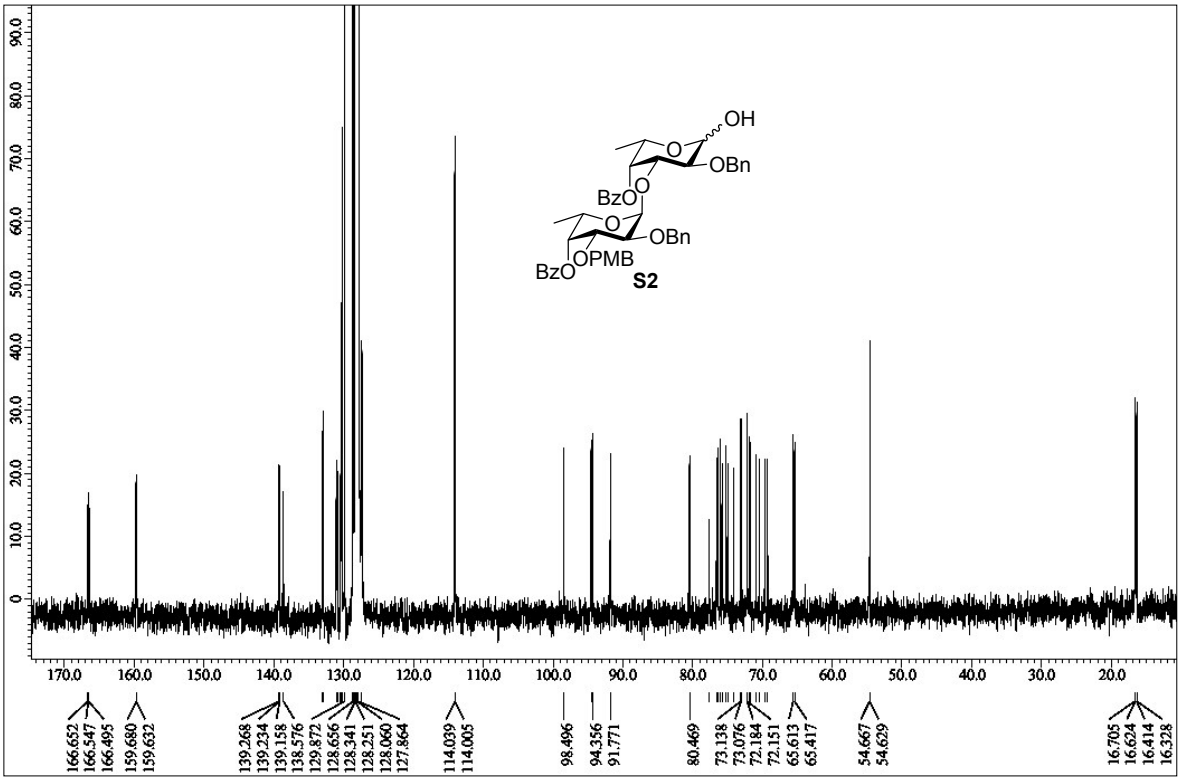


Figure S12 ^{13}C NMR spectrum of **S2**

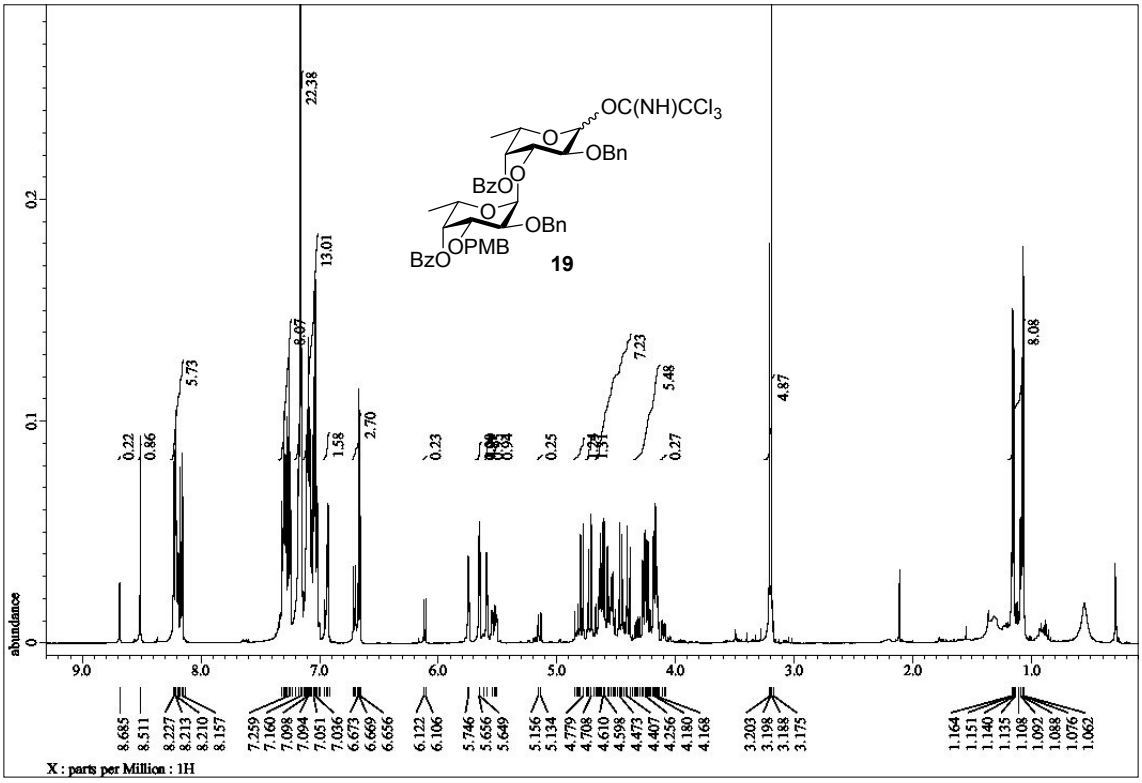


Figure S13 ^{1}H-NMR spectrum of **19**

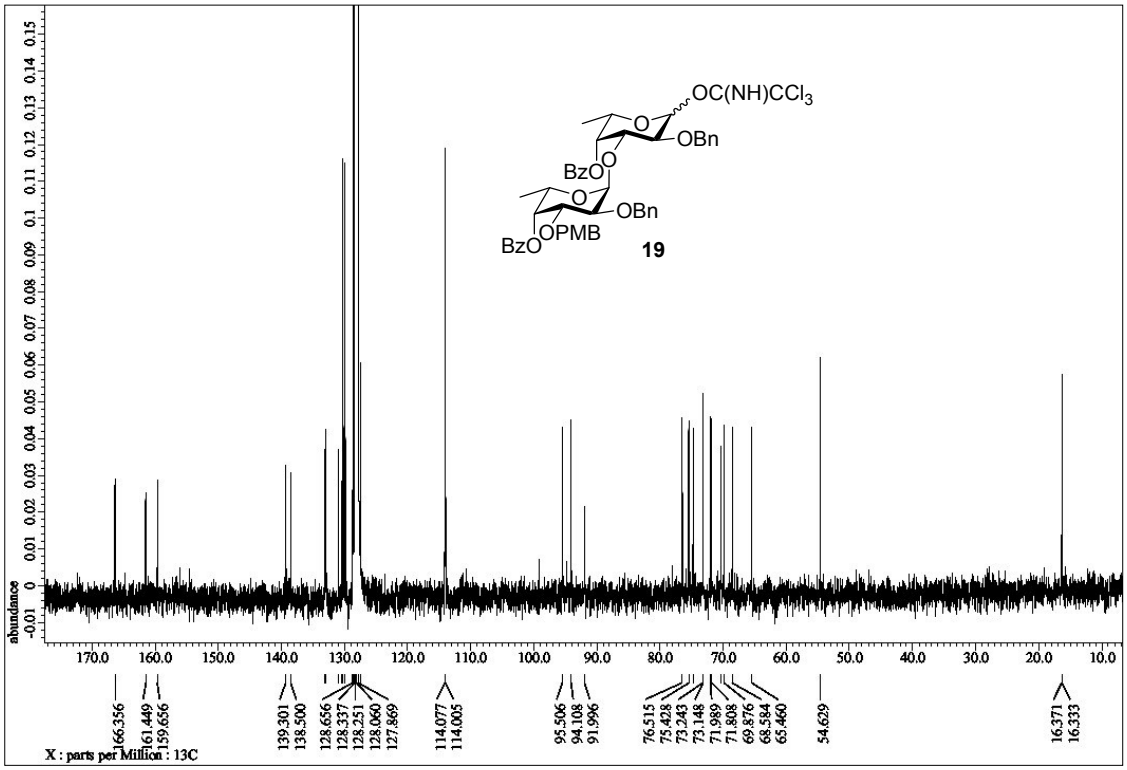


Figure S14 ^{13}C-NMR spectrum of **19**

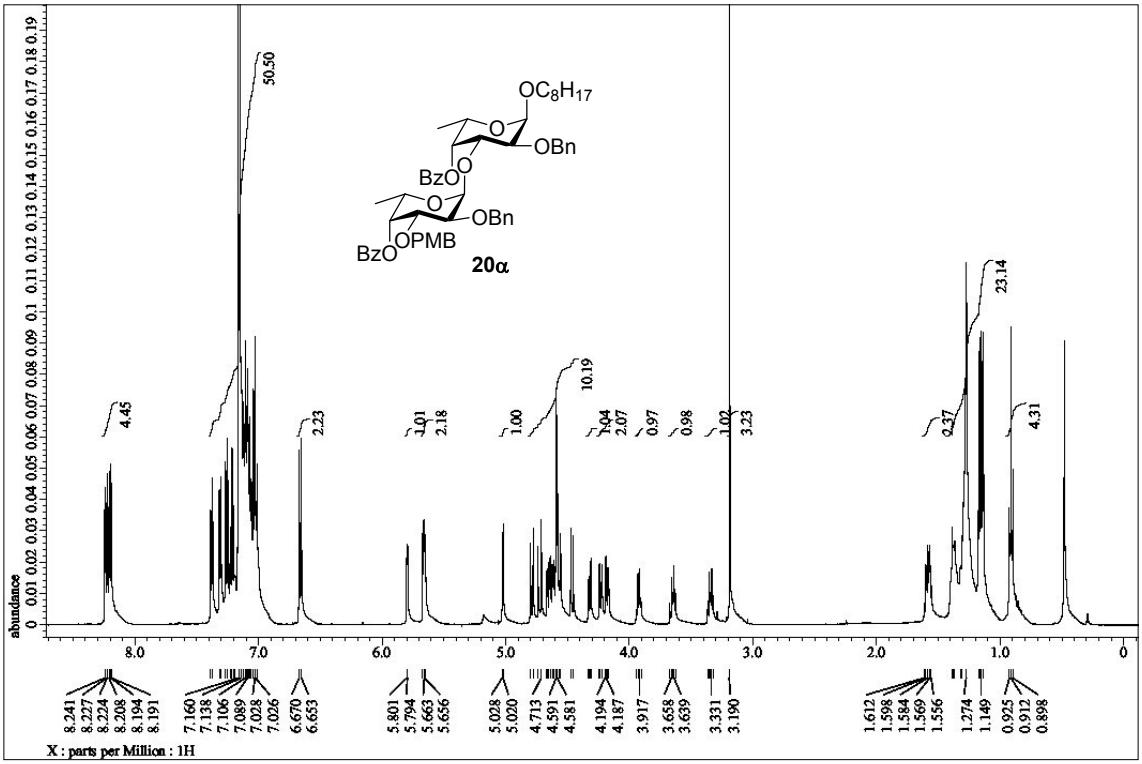


Figure S15 ^{1}H-NMR spectrum of **20α**

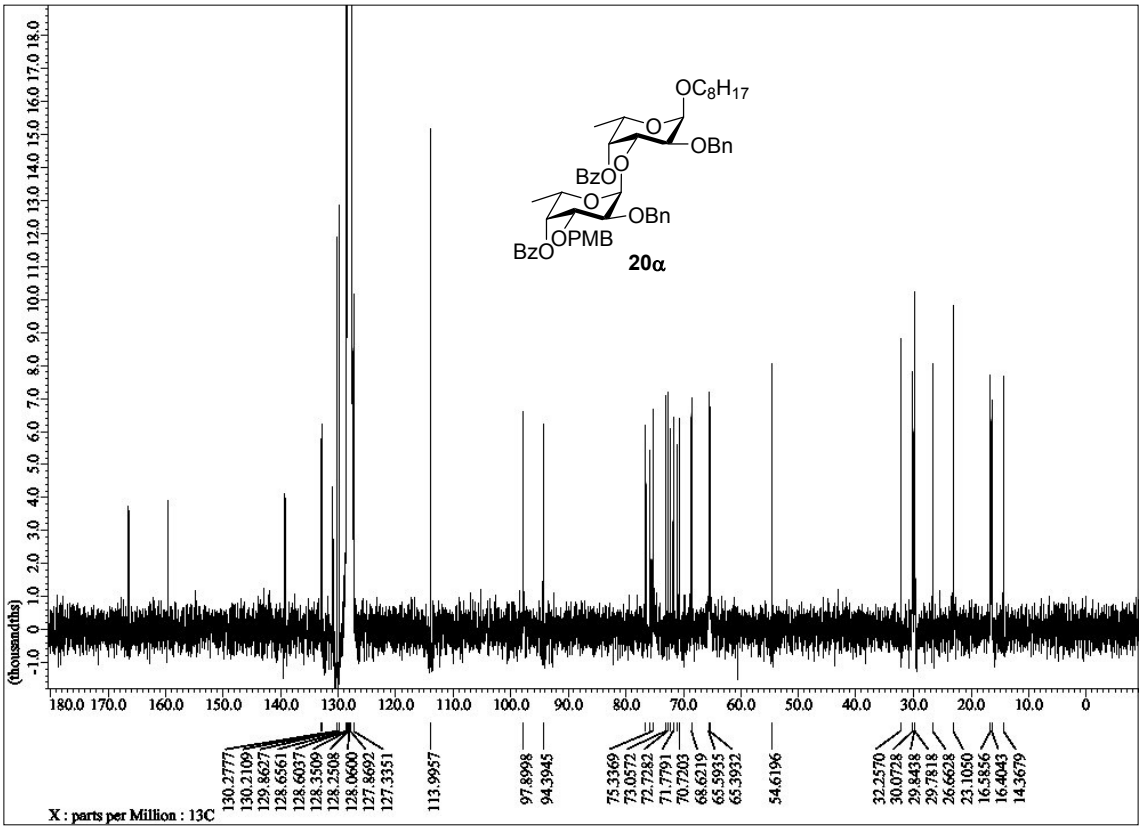


Figure S16 ^{13}C-NMR spectrum of **20α**

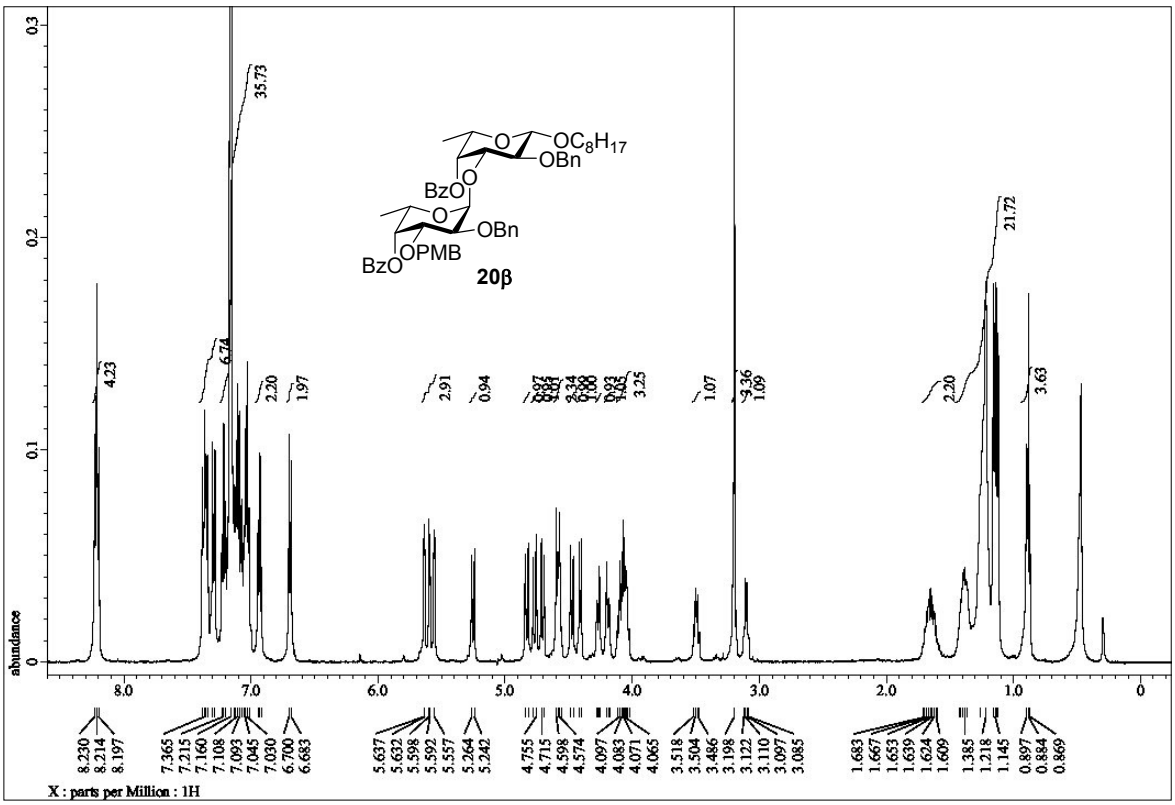


Figure S17 ^{1}H-NMR spectrum of **20β**

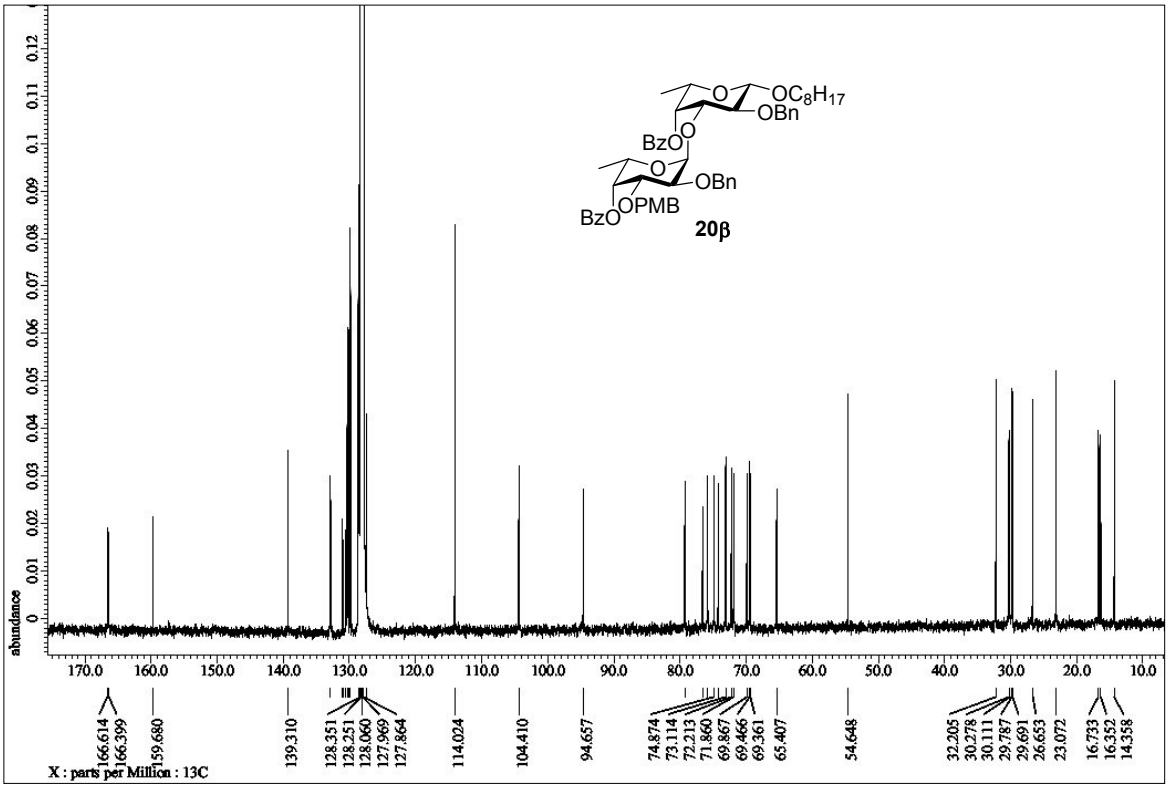


Figure S18 ^{13}C-NMR spectrum of **20β**

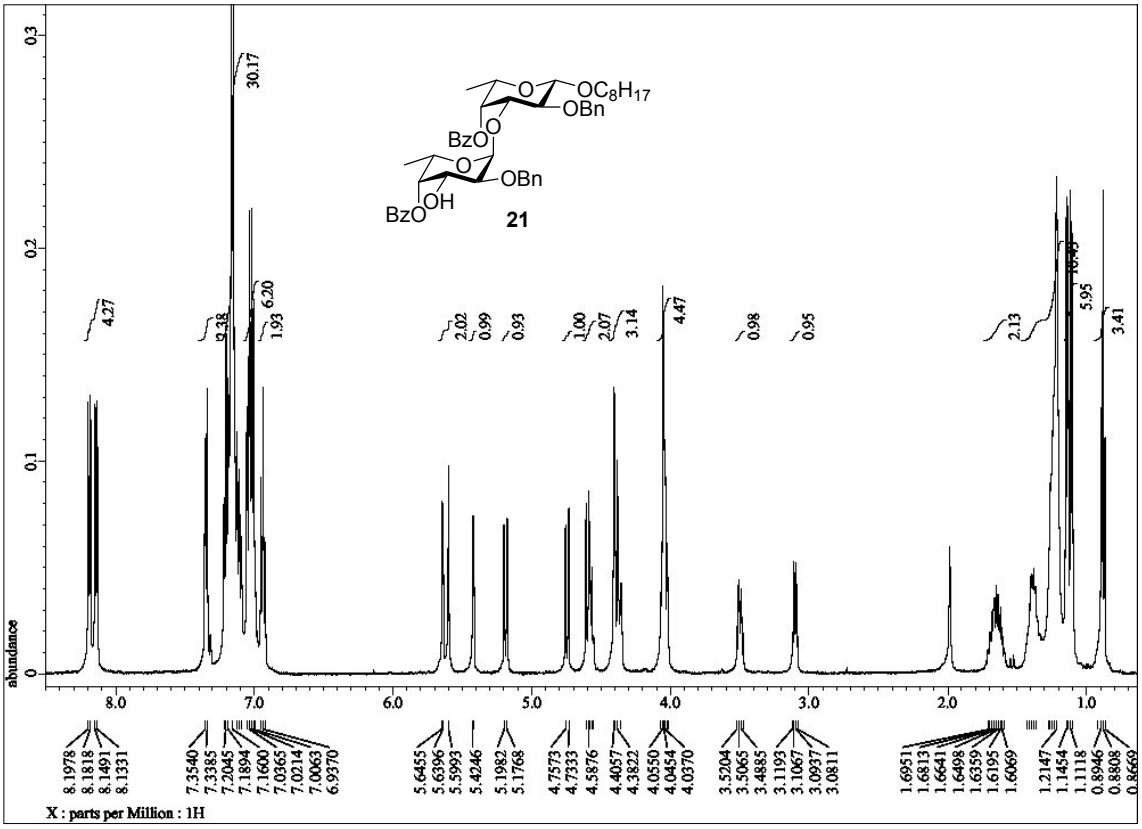


Figure S19 ^{1}H-NMR spectrum of **21**

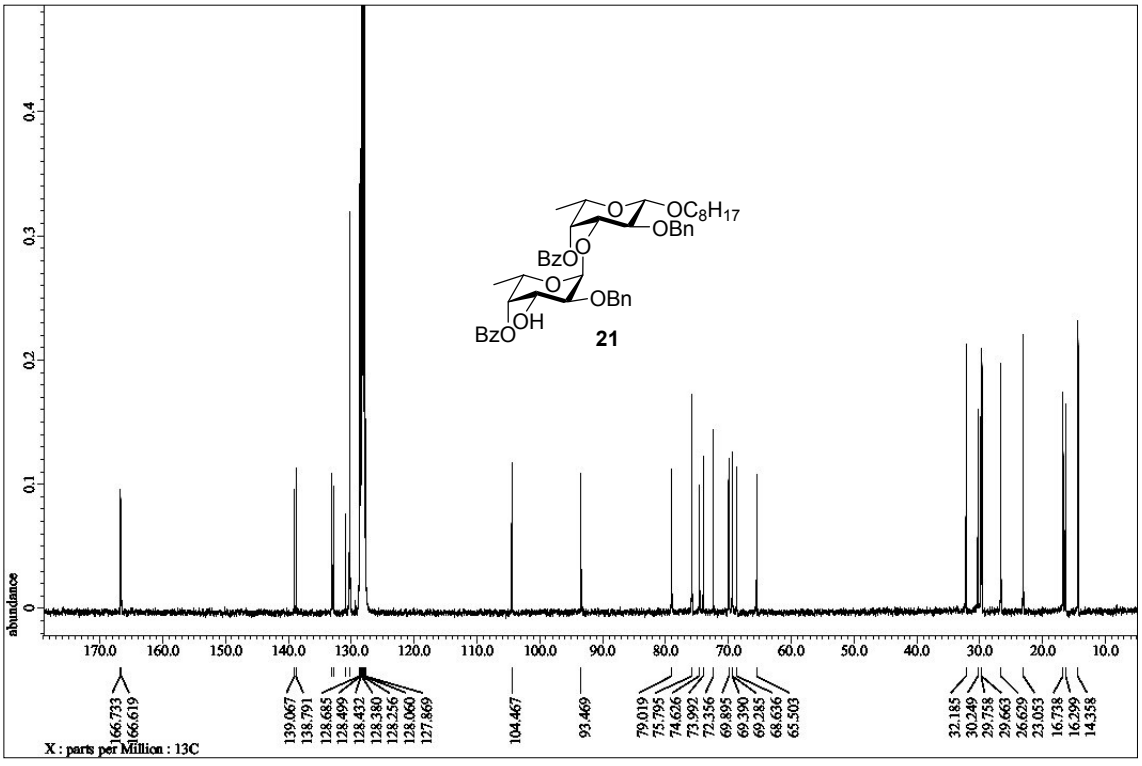


Figure S20 ^{13}C-NMR spectrum of **21**

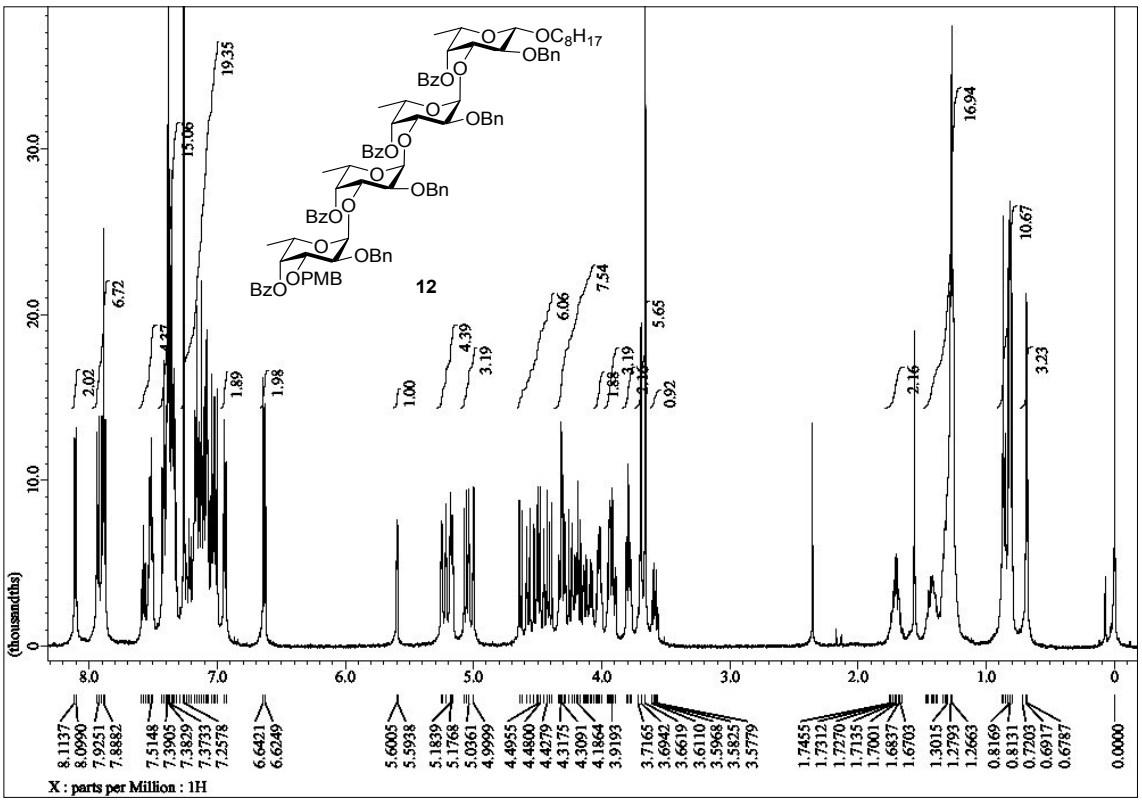


Figure S21 ^{1}H-NMR spectrum of **12**

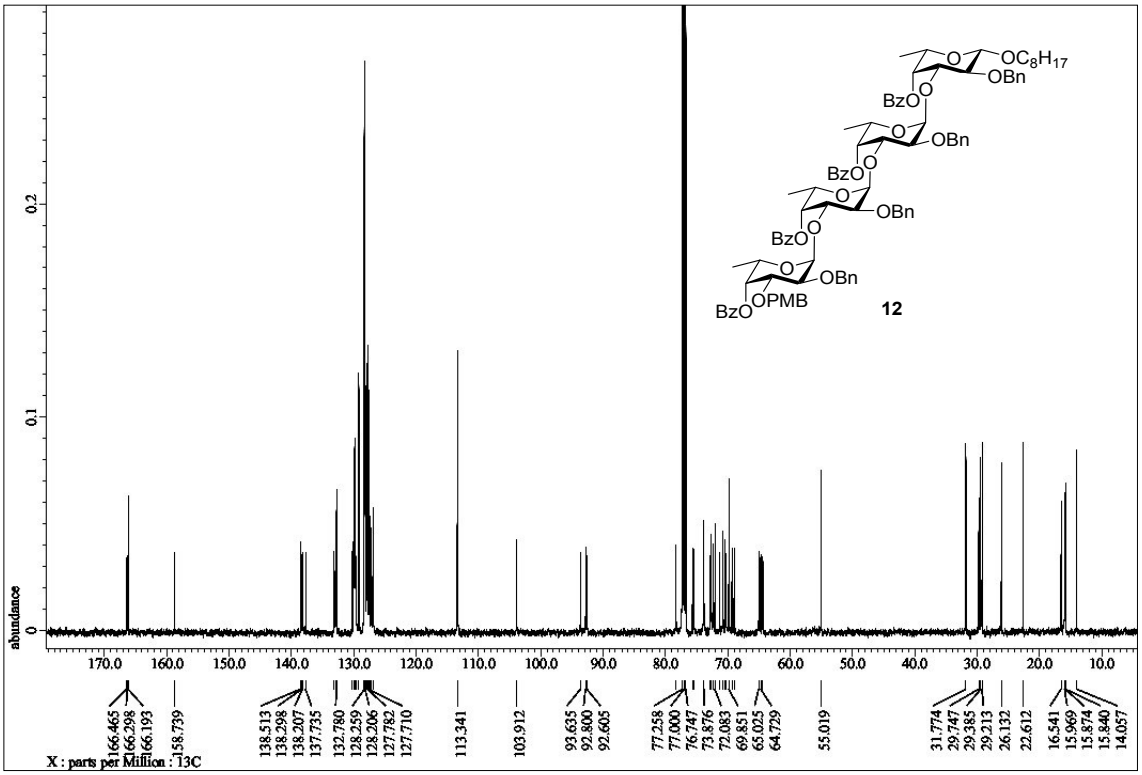


Figure S22 ^{13}C-NMR spectrum of **12**

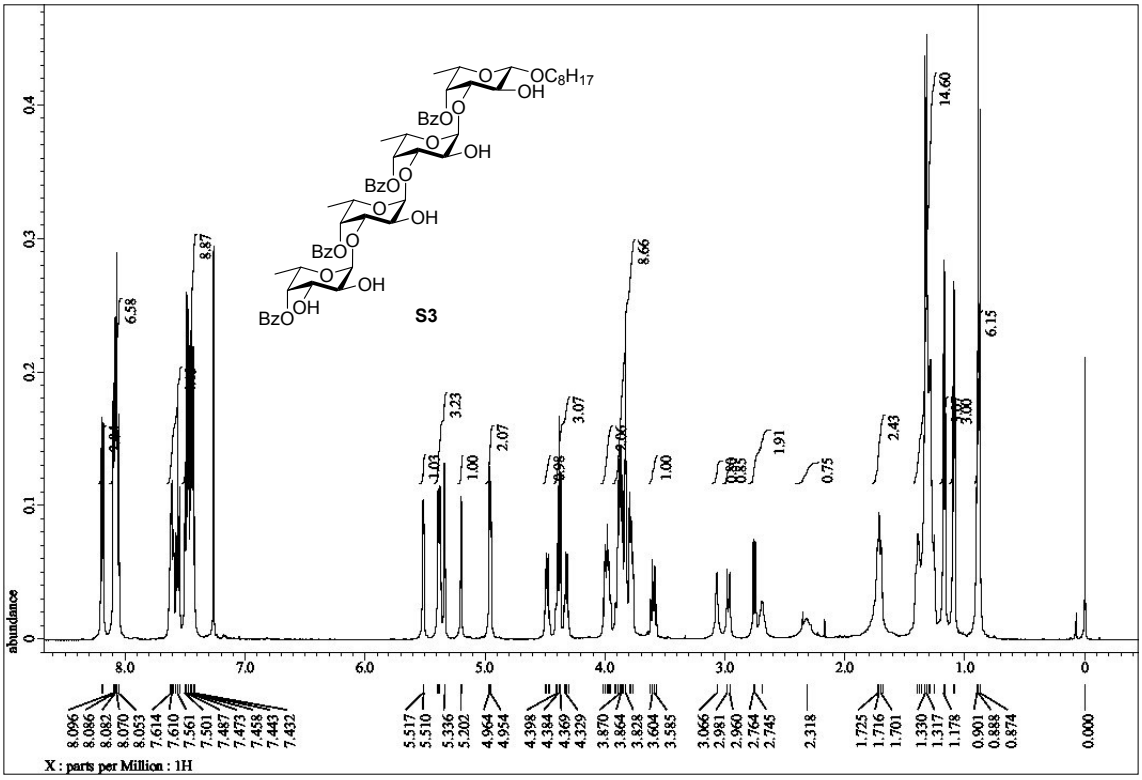


Figure S23 ^{1}H-NMR spectrum of **S3**

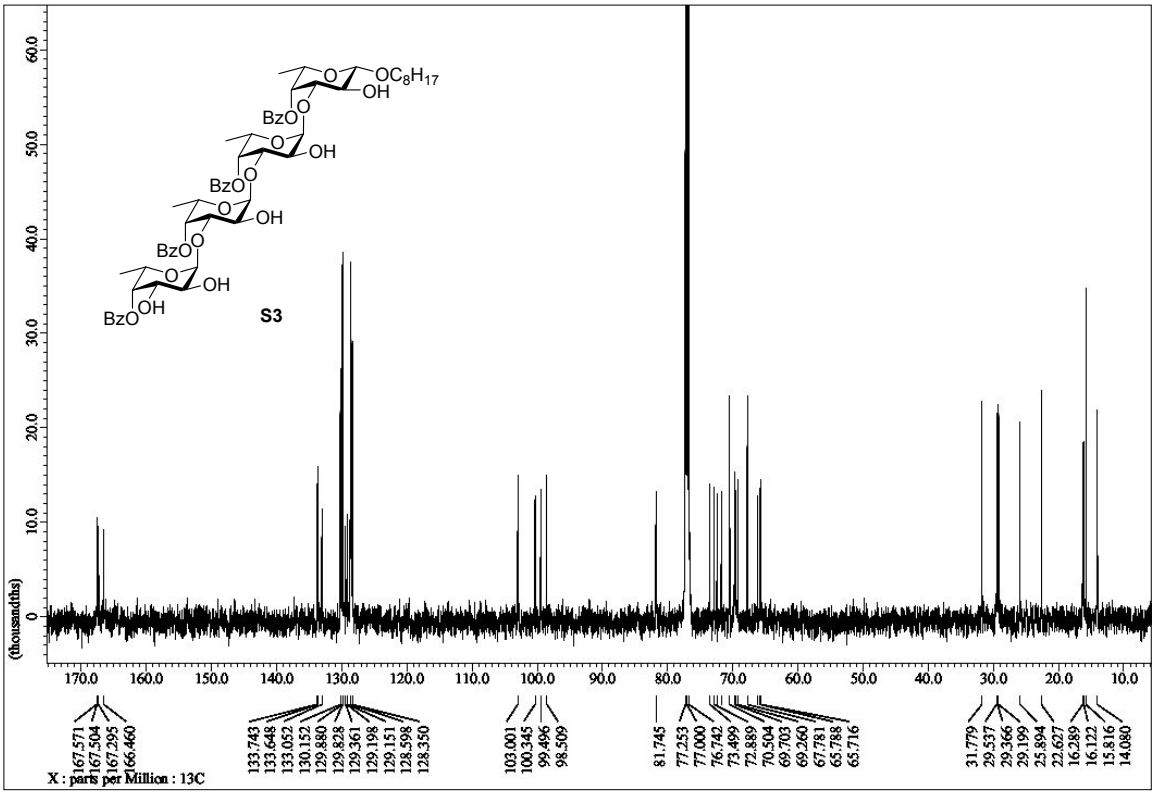


Figure S24 ^{13}C-NMR spectrum of **S3**

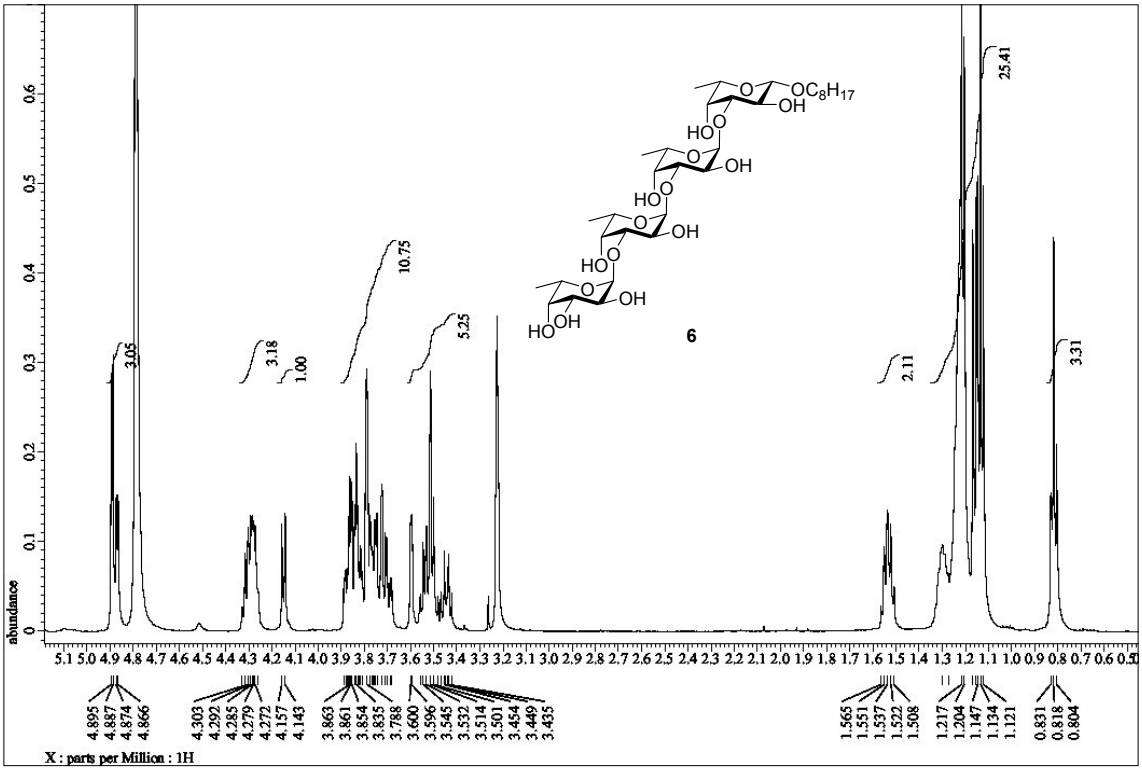


Figure S25 ^{1}H-NMR spectrum of **6**

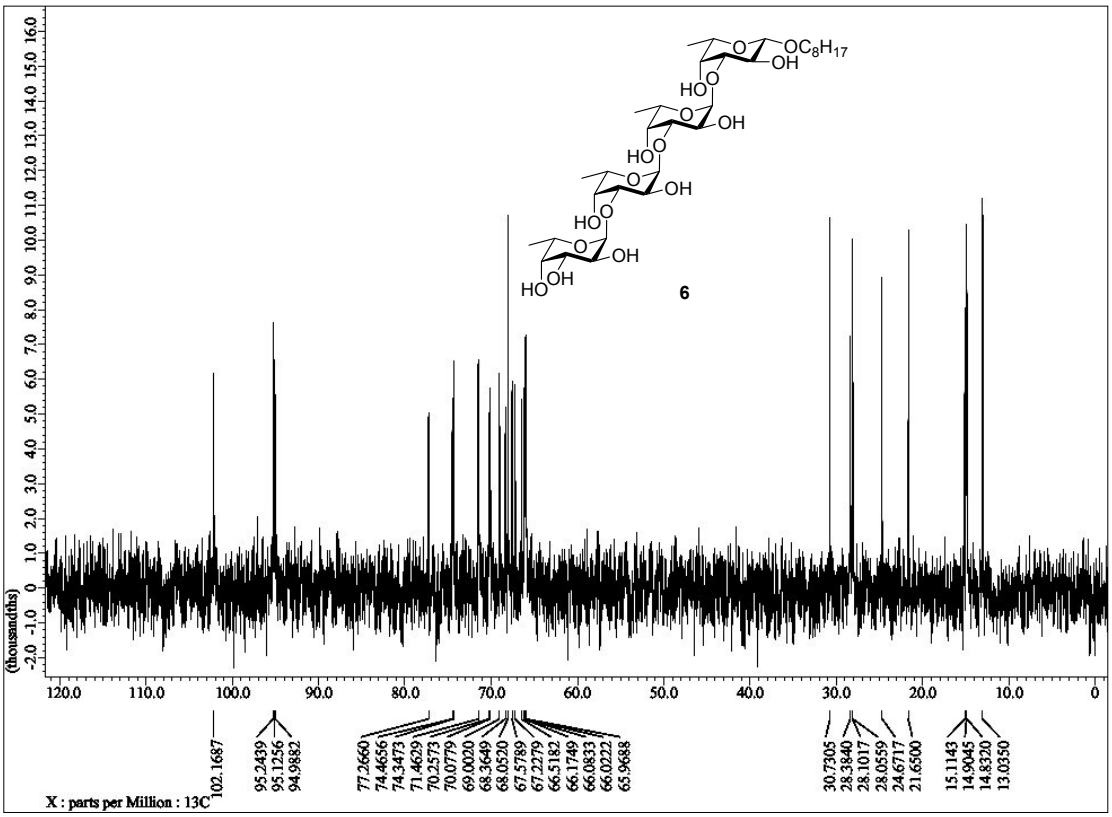


Figure S26 ^{13}C-NMR spectrum of **6**

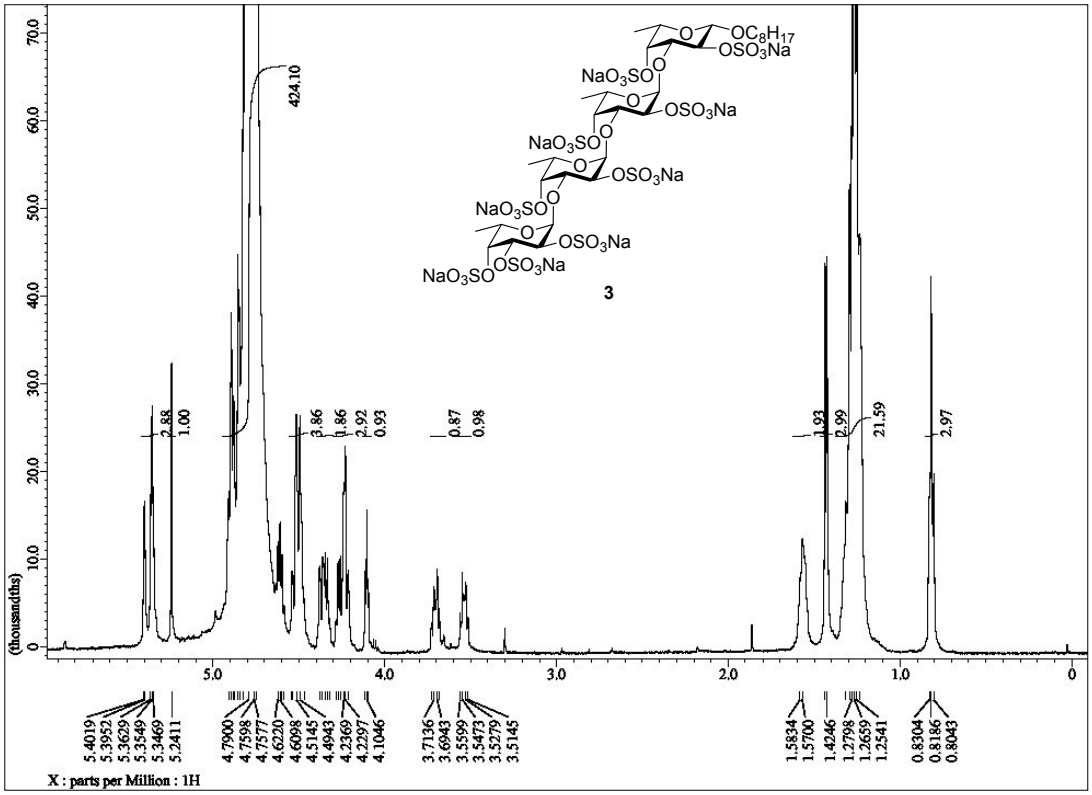


Figure S27 ^{1}H-NMR spectrum of **3**

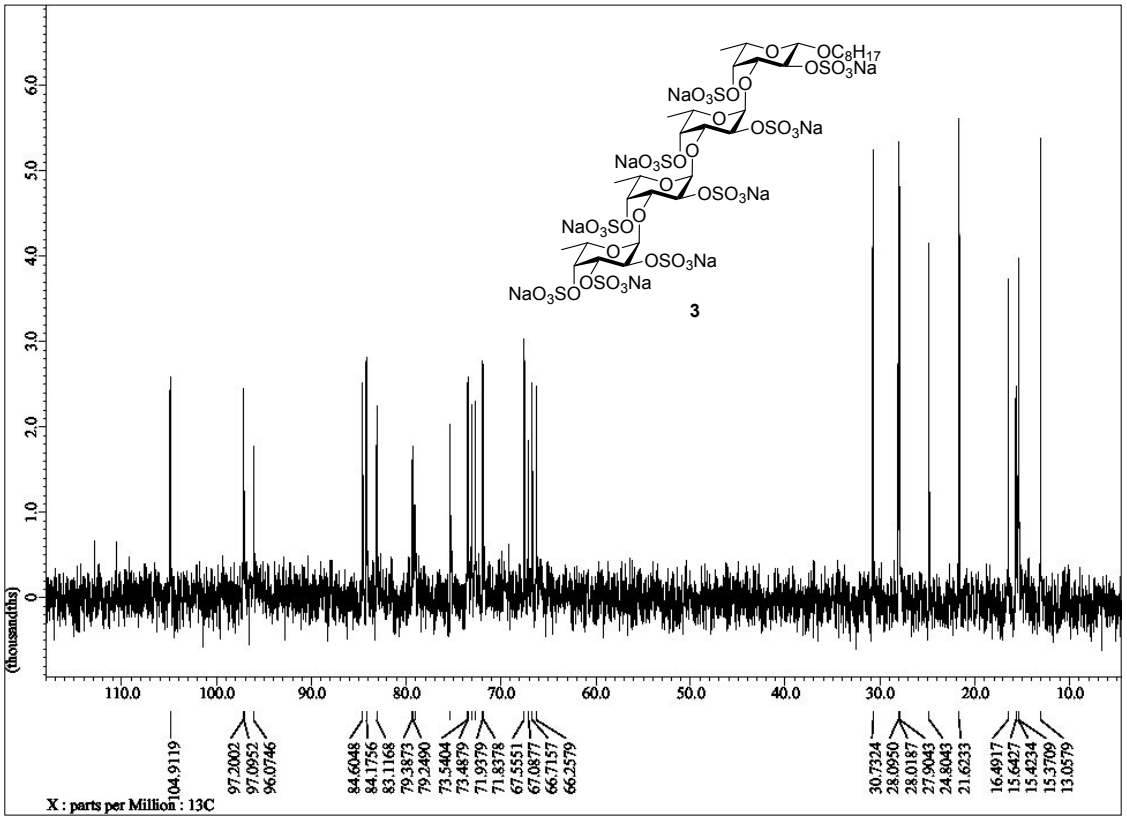


Figure S28 ^{13}C-NMR spectrum of **3**

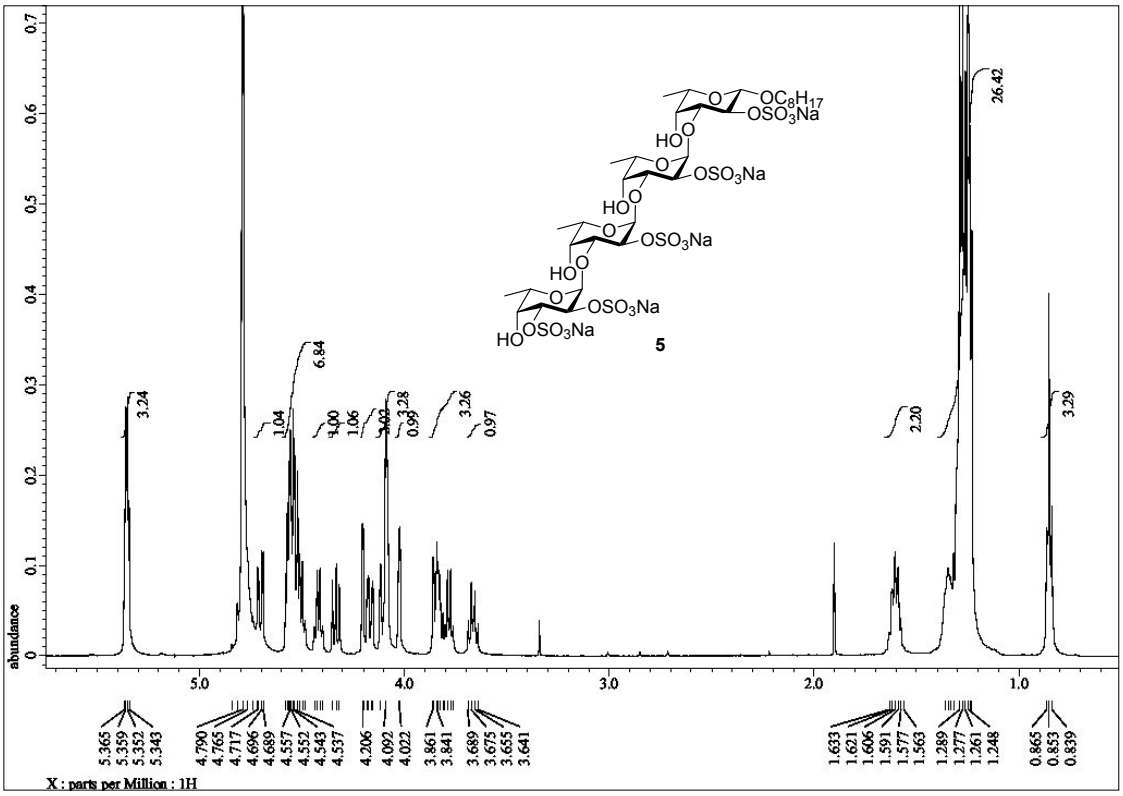


Figure S29 ^{1}H-NMR spectrum of **5**

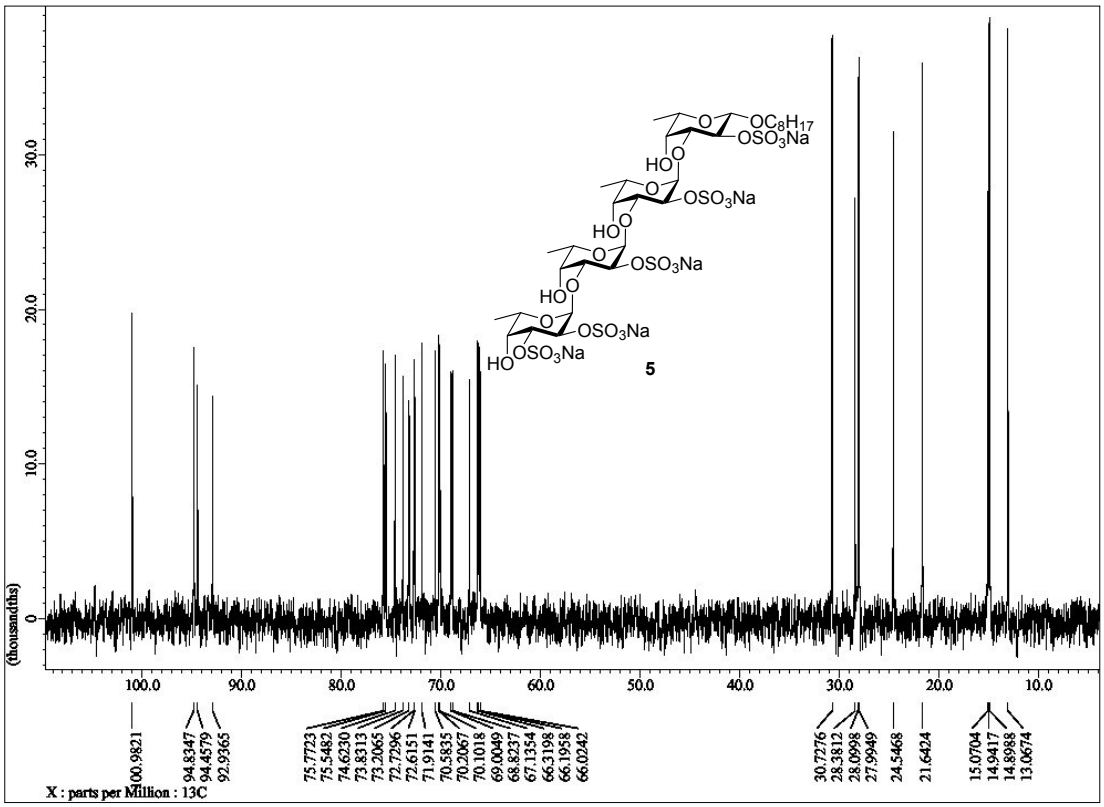


Figure S30 ^{13}C-NMR spectrum of **5**

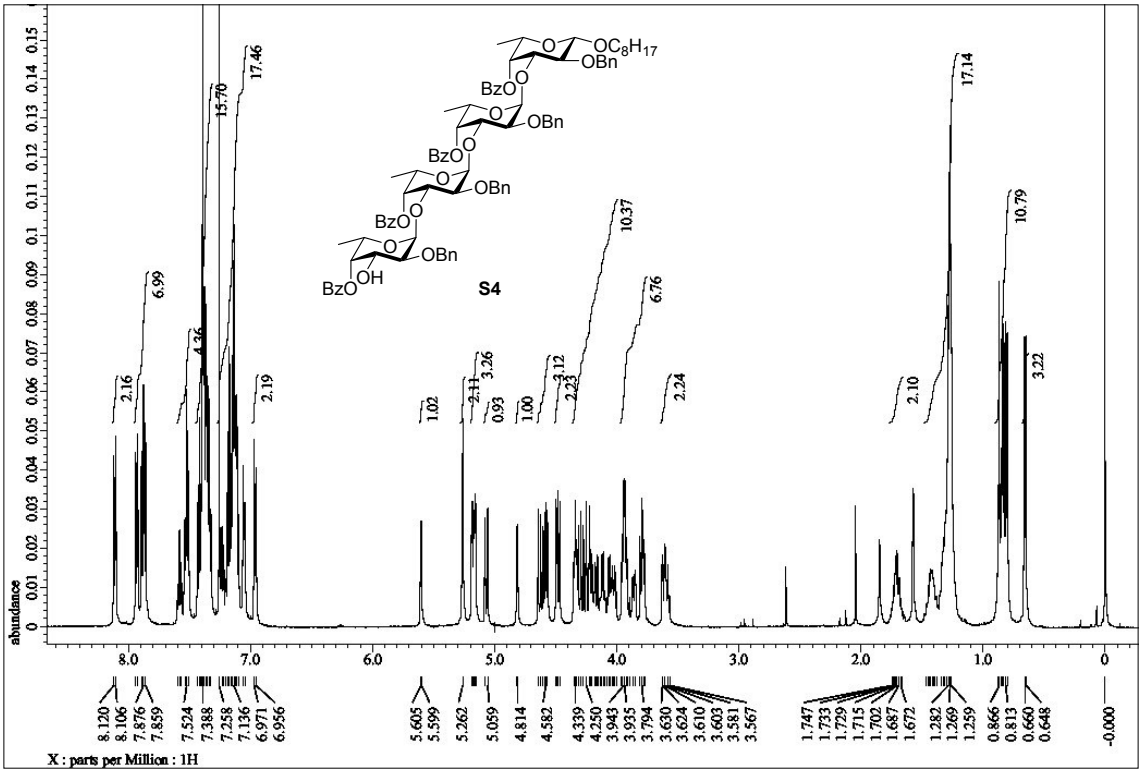


Figure S31 ^{1}H-NMR spectrum of **S4**

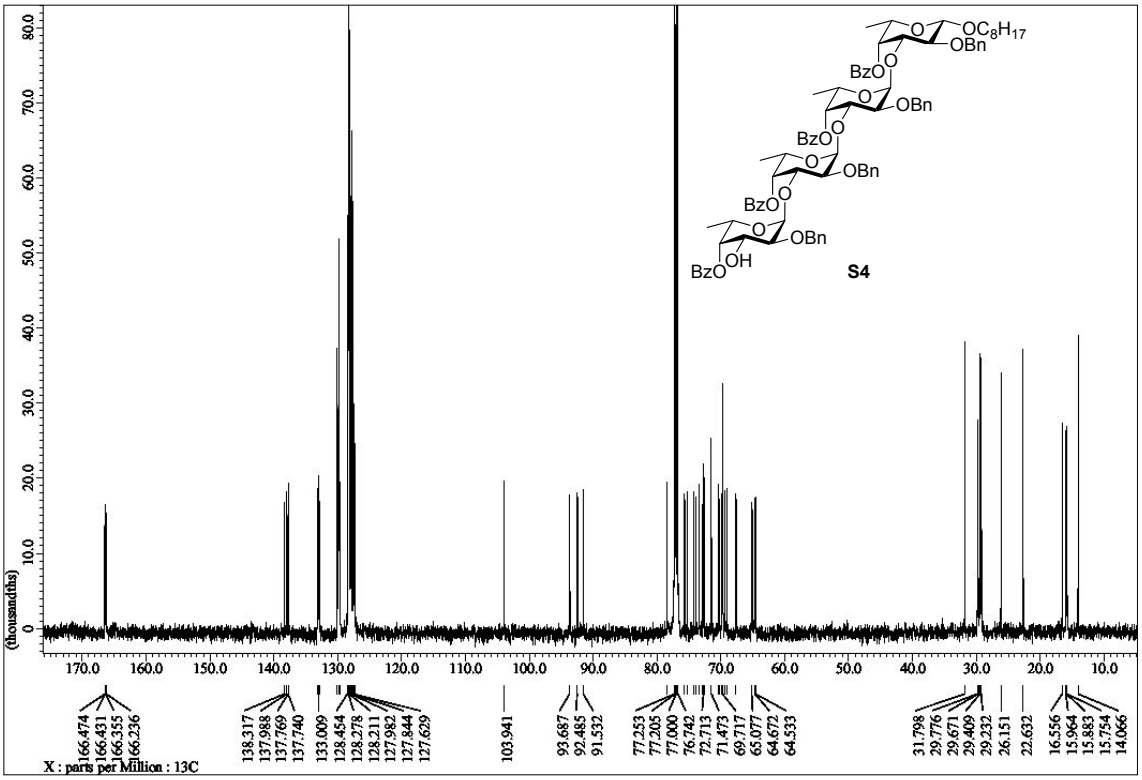


Figure S32 ^{13}C-NMR spectrum of **S4**

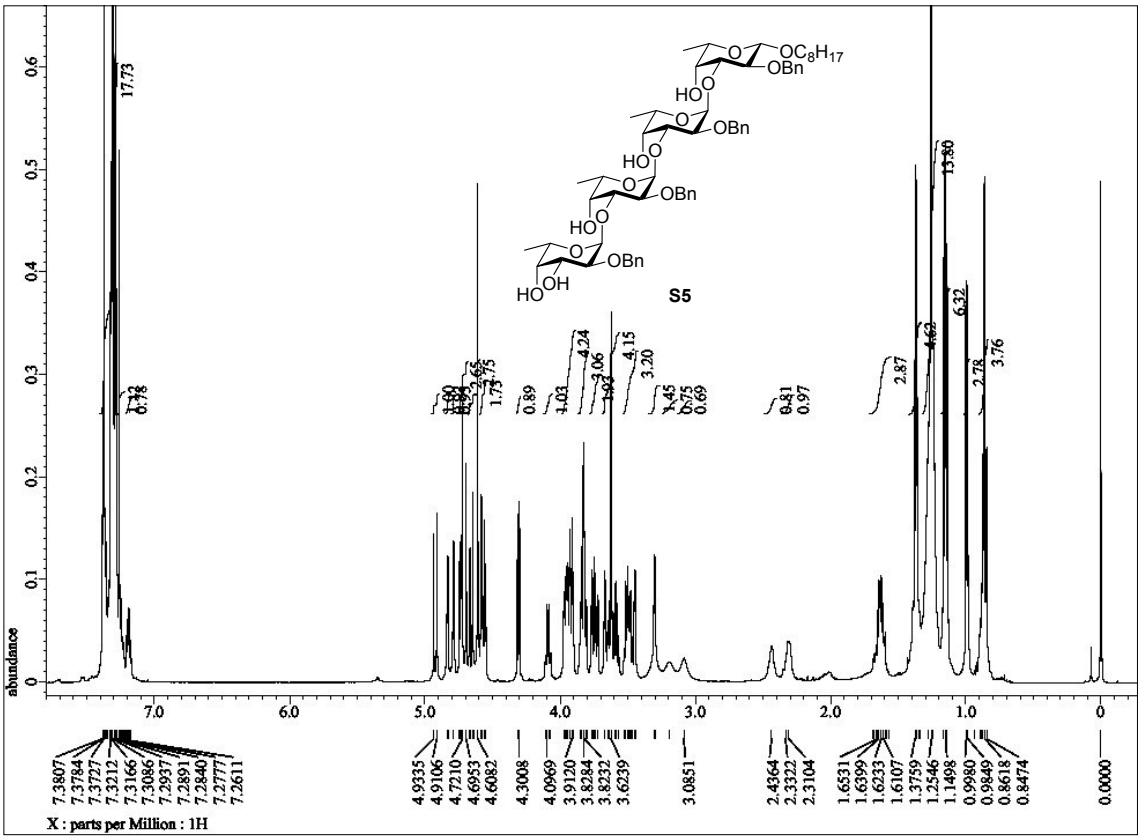


Figure S33 ^{1}H-NMR spectrum of **S5**

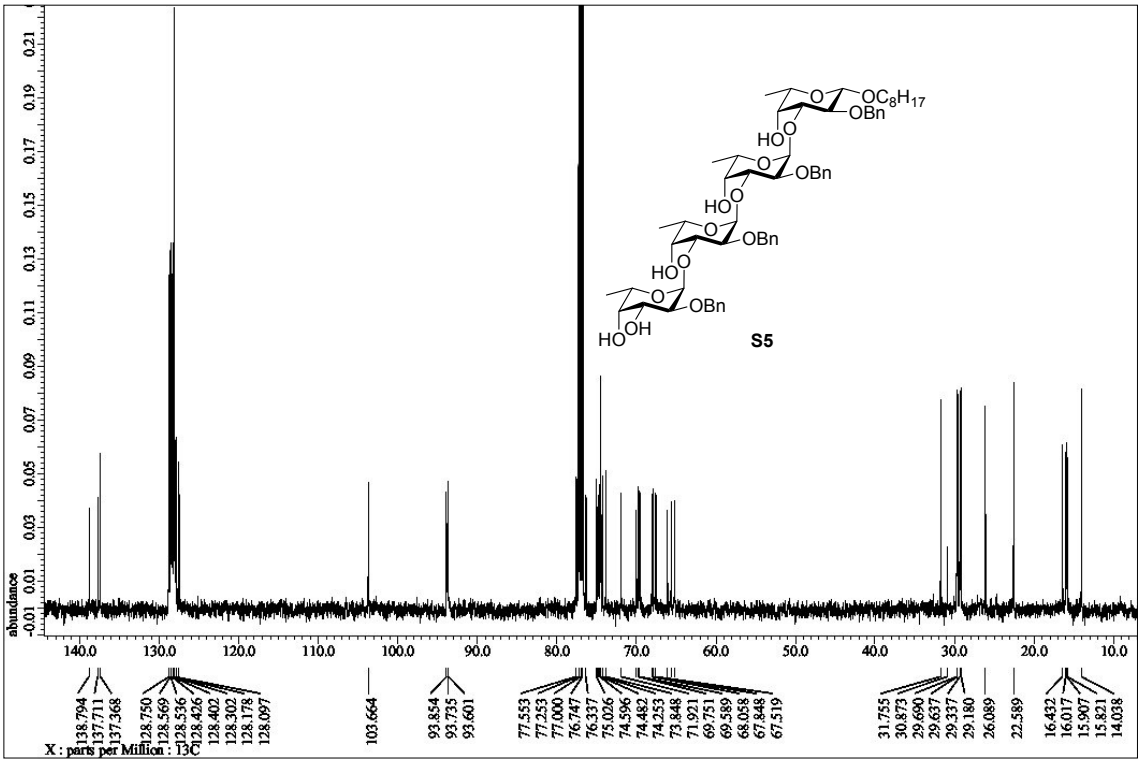


Figure S34 ^{13}C-NMR spectrum of **S5**

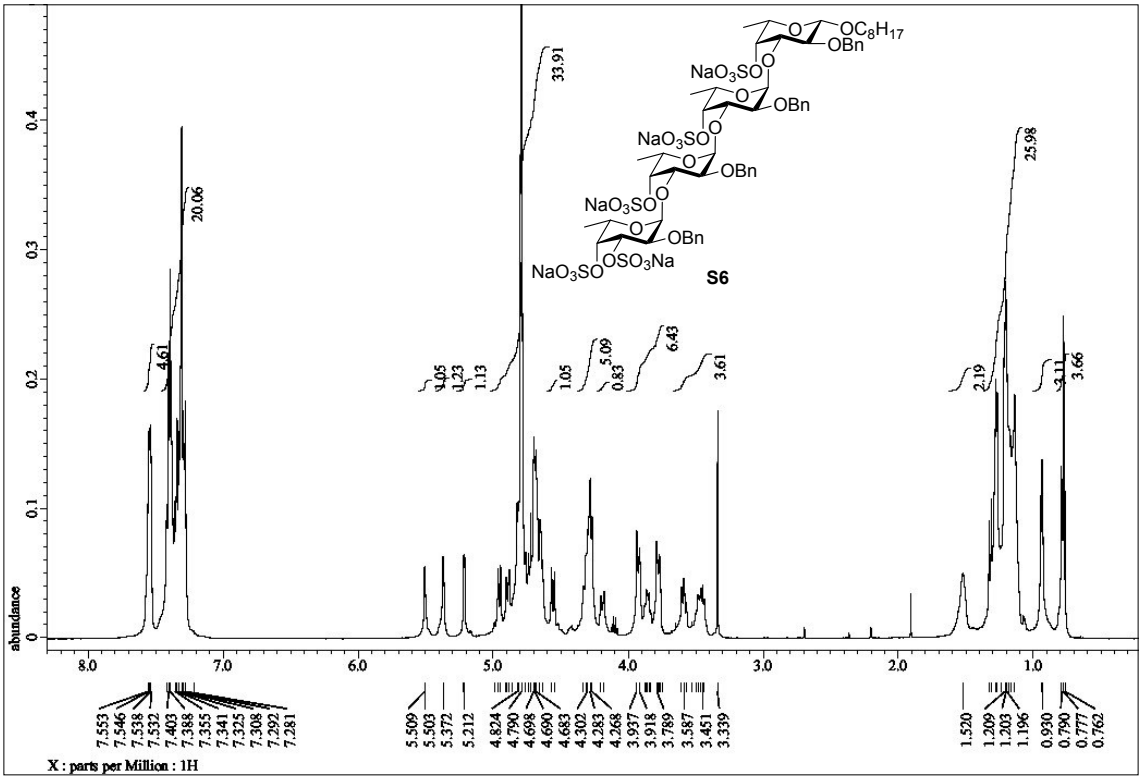


Figure S35 ^{1}H-NMR spectrum of **S6**

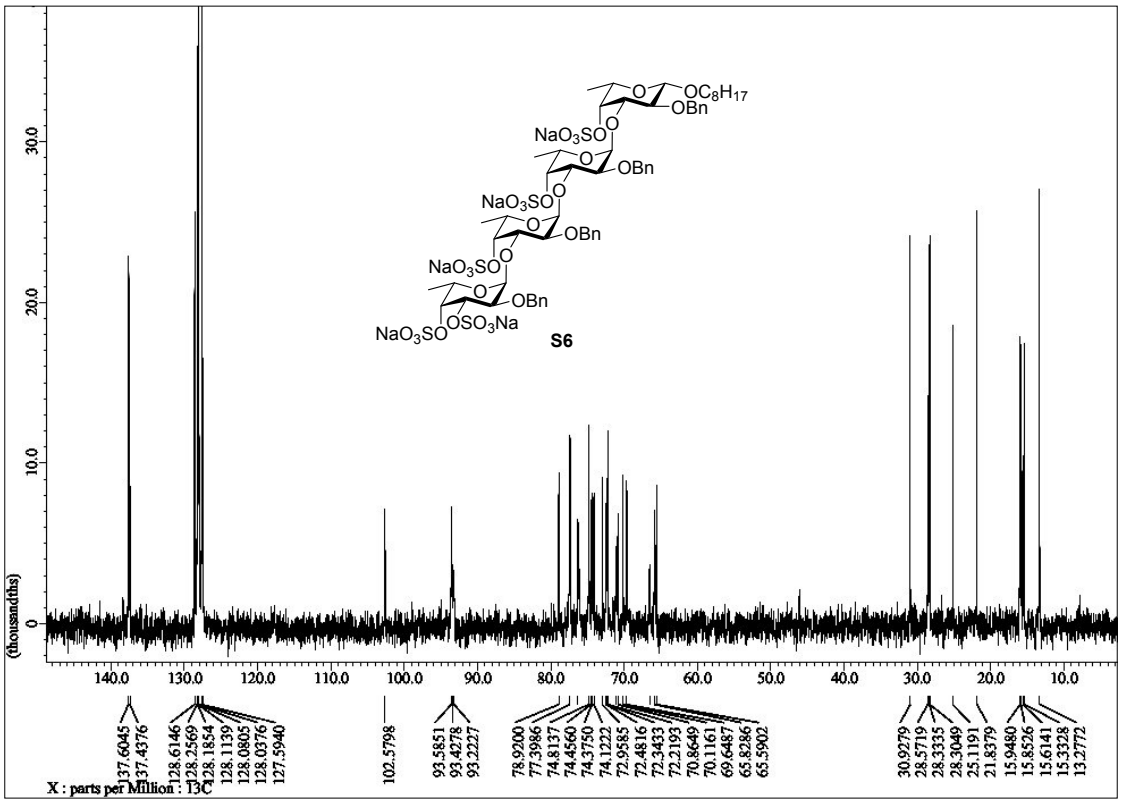


Figure S36 ^{13}C-NMR spectrum of **S6**

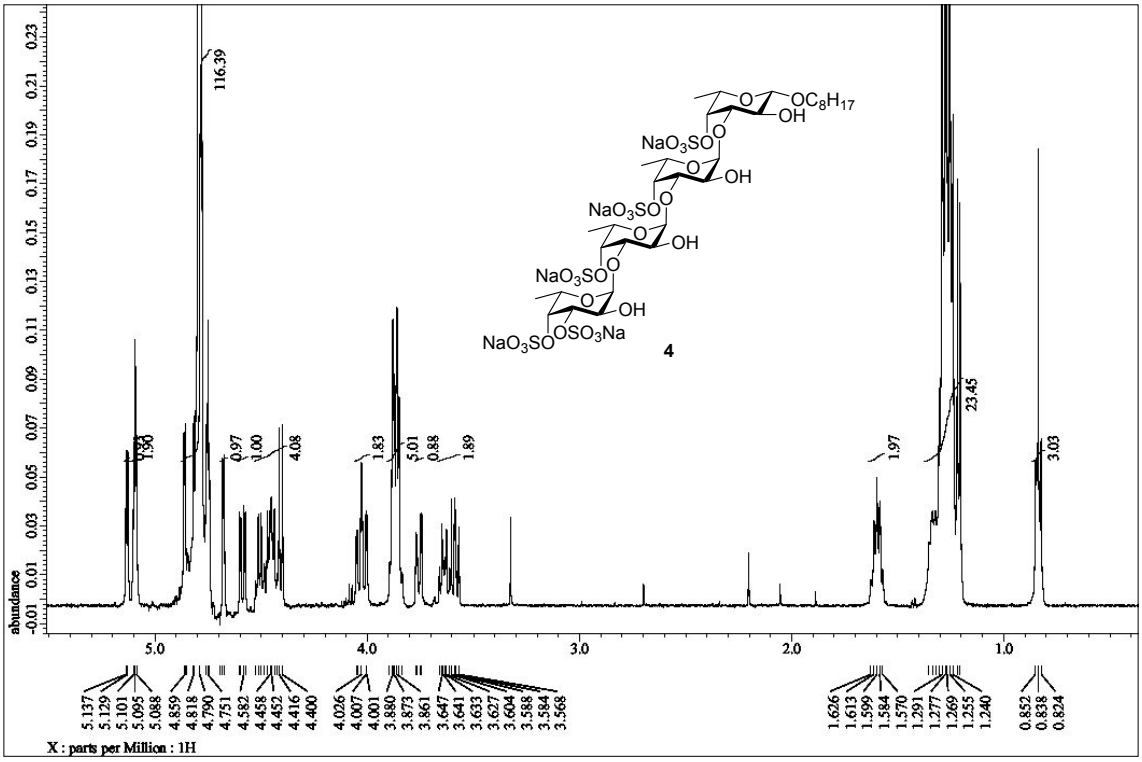


Figure S37 ^{1}H-NMR spectrum of **4**

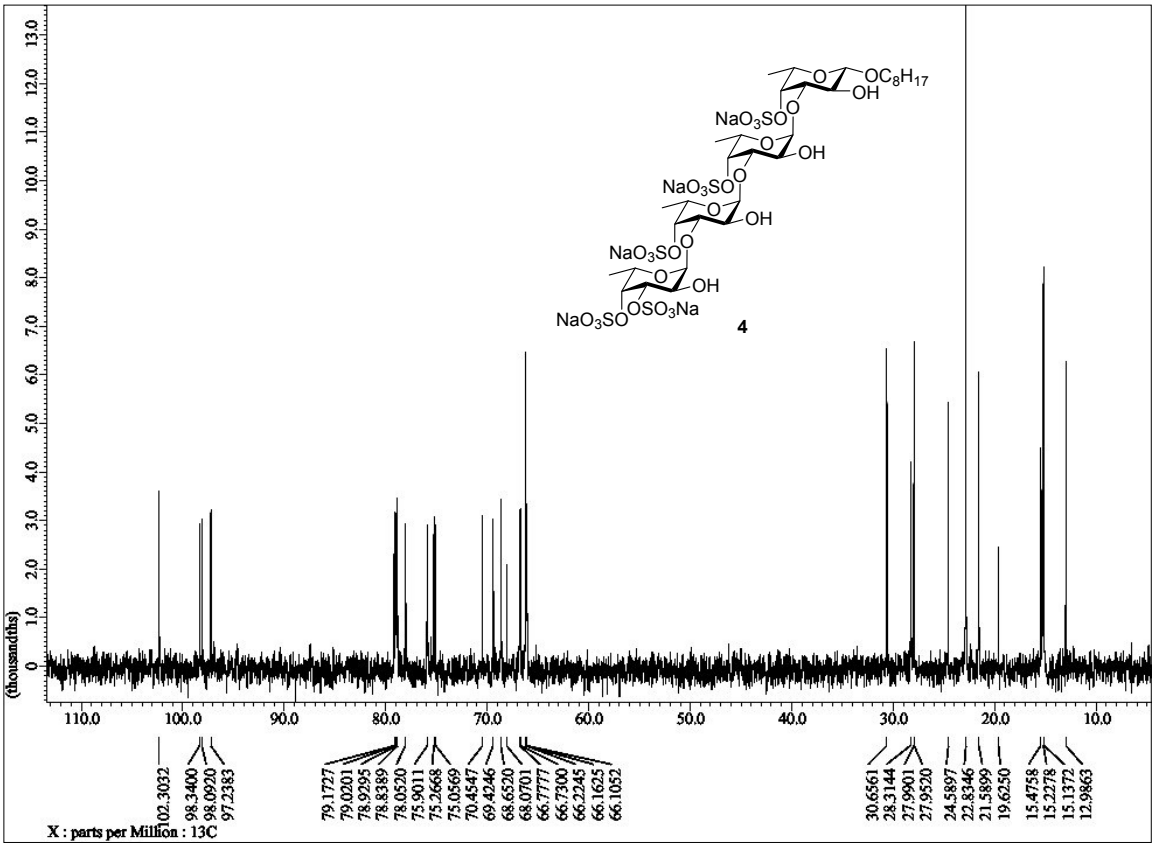


Figure S38 ^{13}C-NMR spectrum of **4**

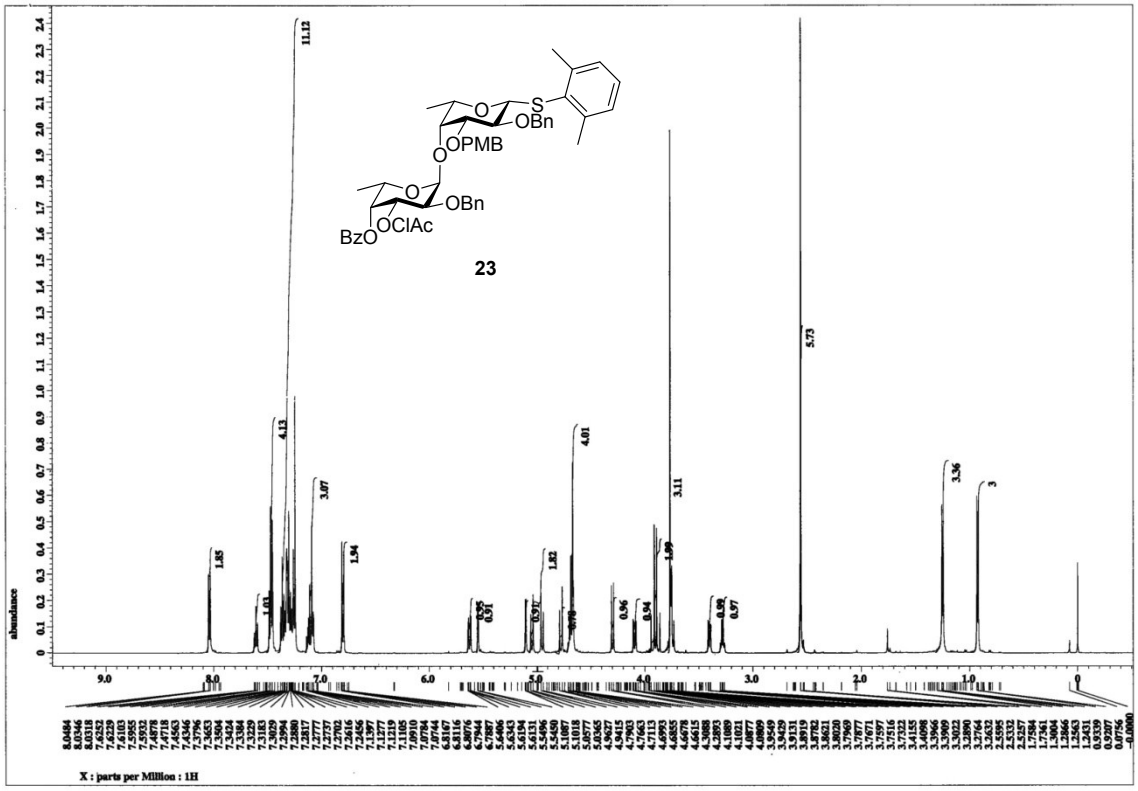


Figure S39 ^{1}H-NMR spectrum of **23**

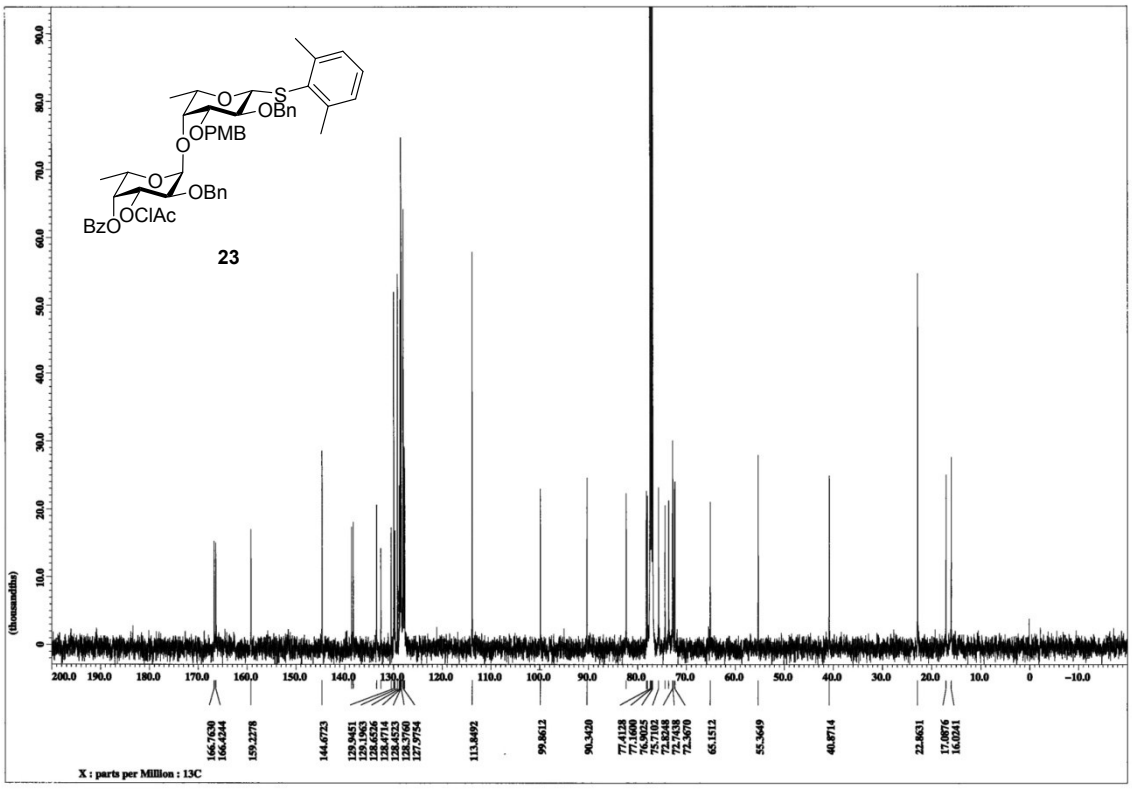


Figure S40 ^{13}C-NMR spectrum of **23**

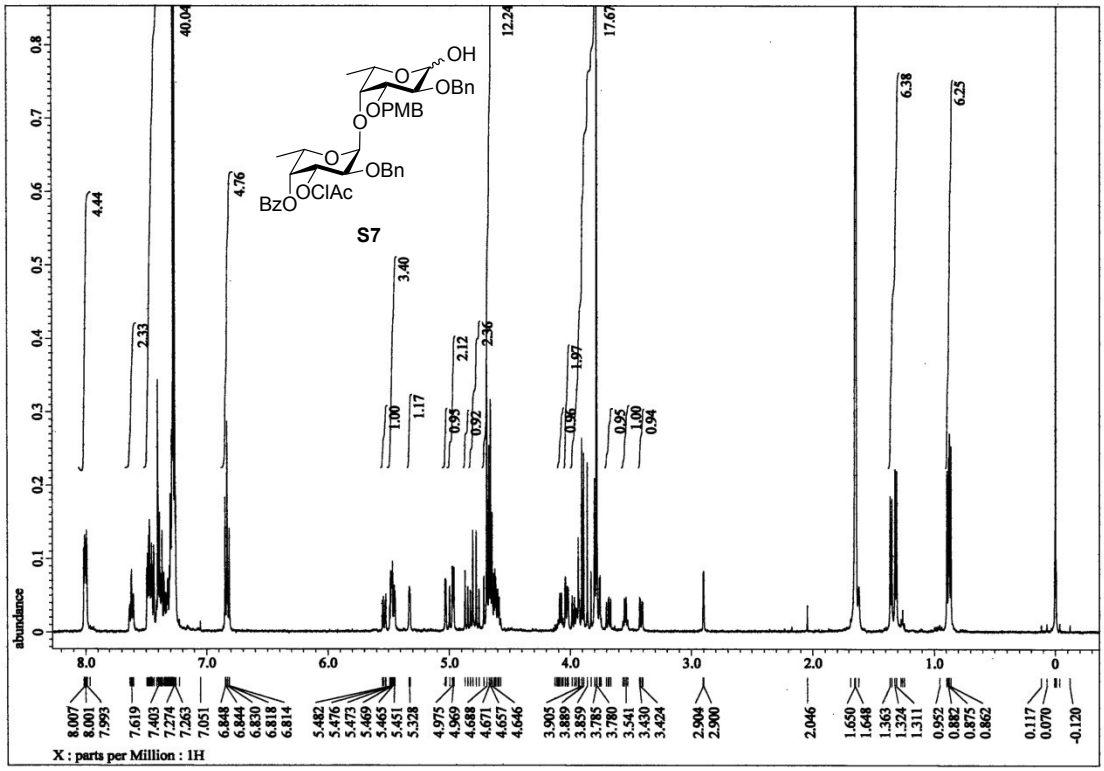


Figure S41 ^{1}H-NMR spectrum of **S7**

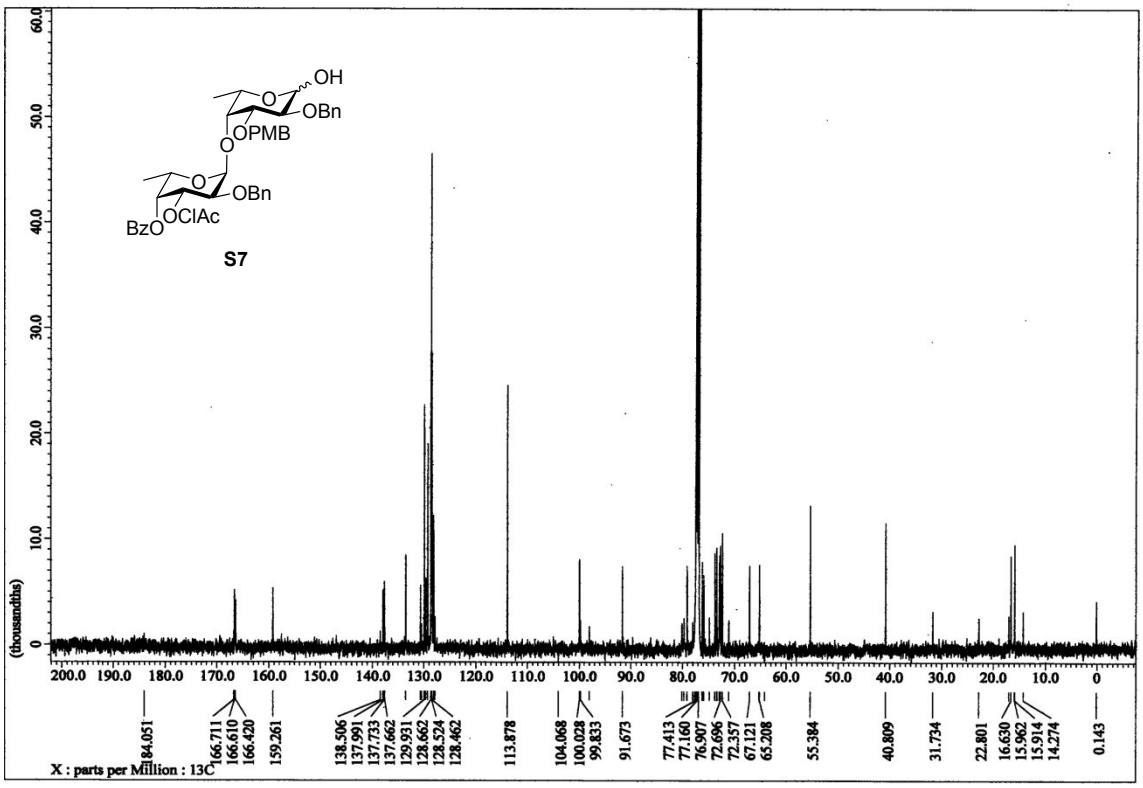


Figure S42 ^{13}C-NMR spectrum of **S7**

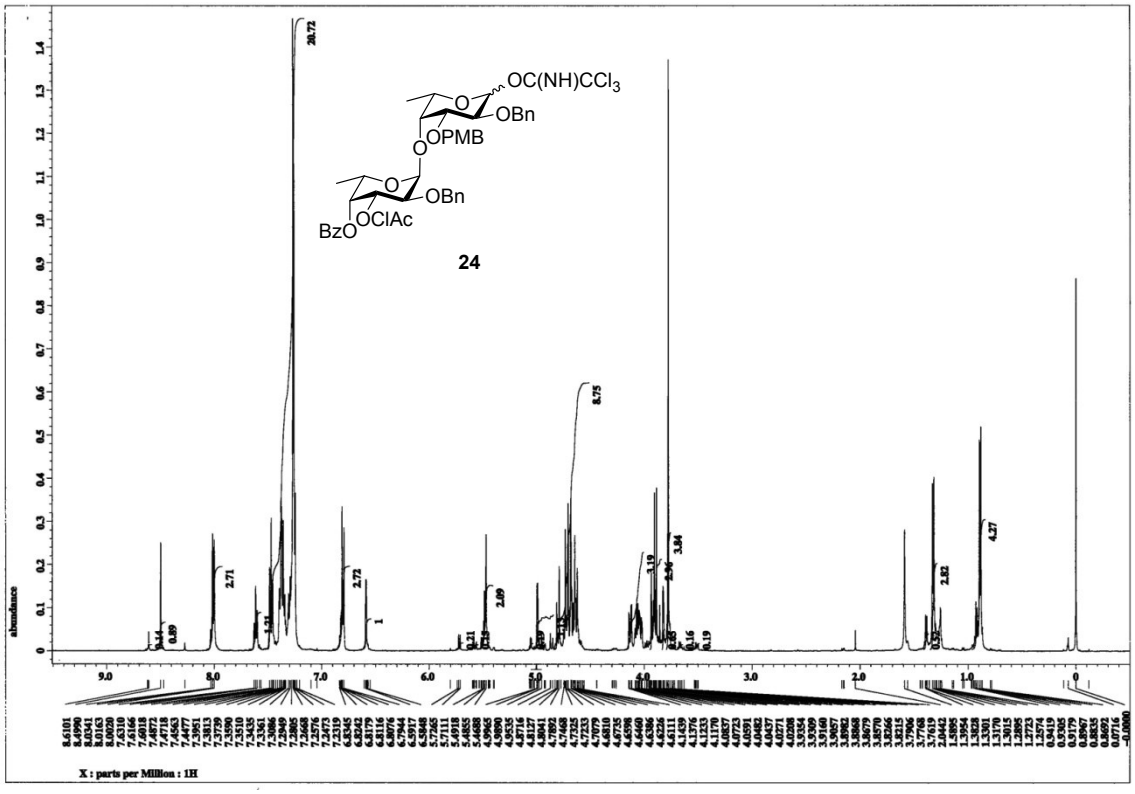


Figure S43 ^{1}H-NMR spectrum of **24**

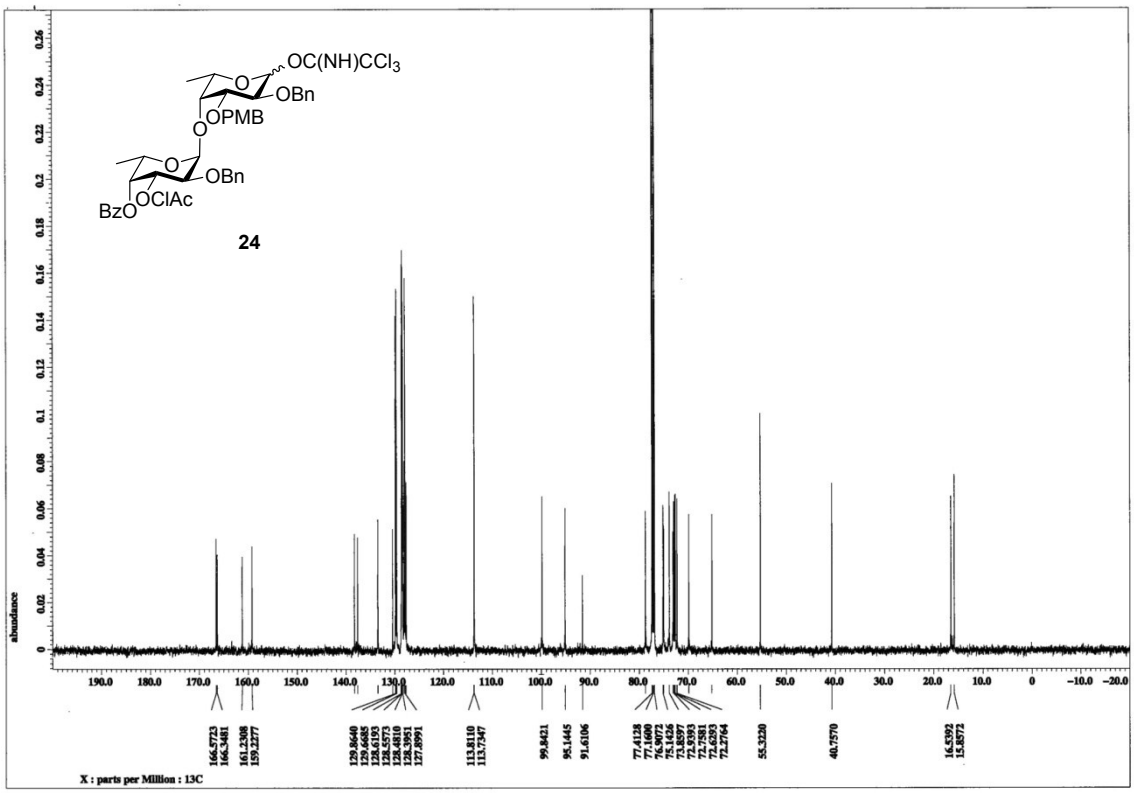


Figure S44 ^{13}C-NMR spectrum of **24**

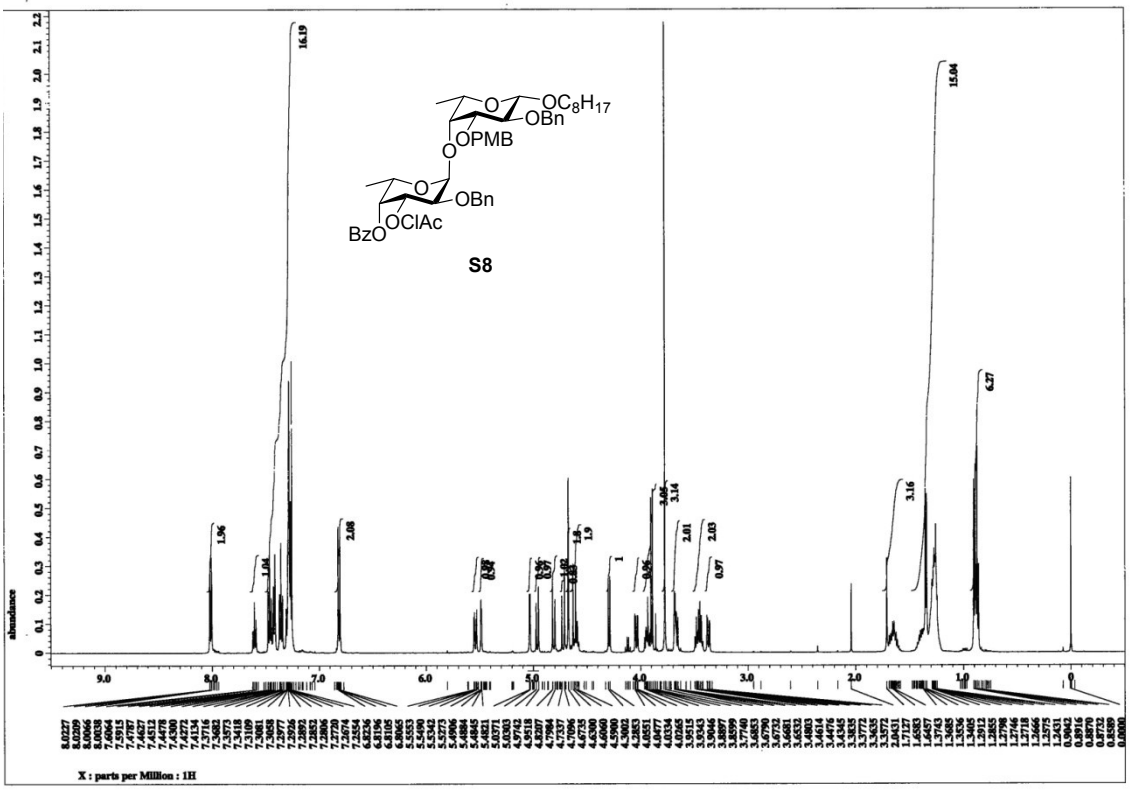


Figure S45 ^{1}H-NMR spectrum of **S8**

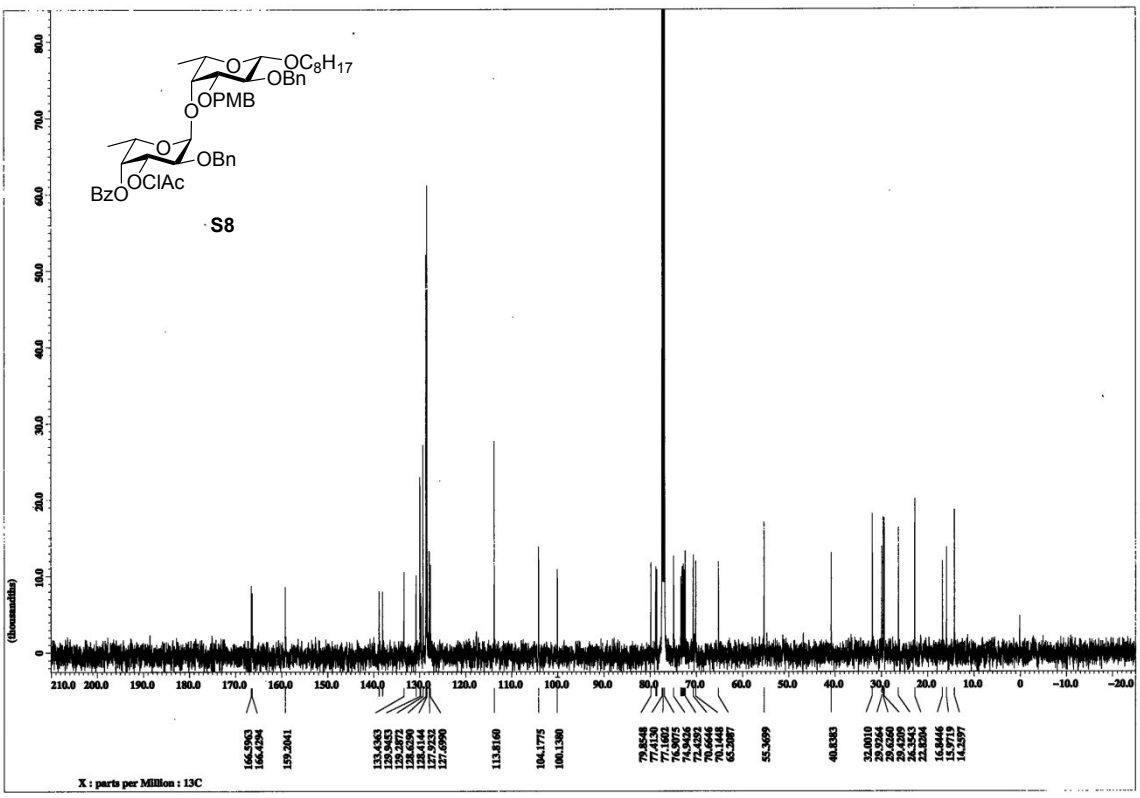


Figure S46 ^{13}C-NMR spectrum of **S8**

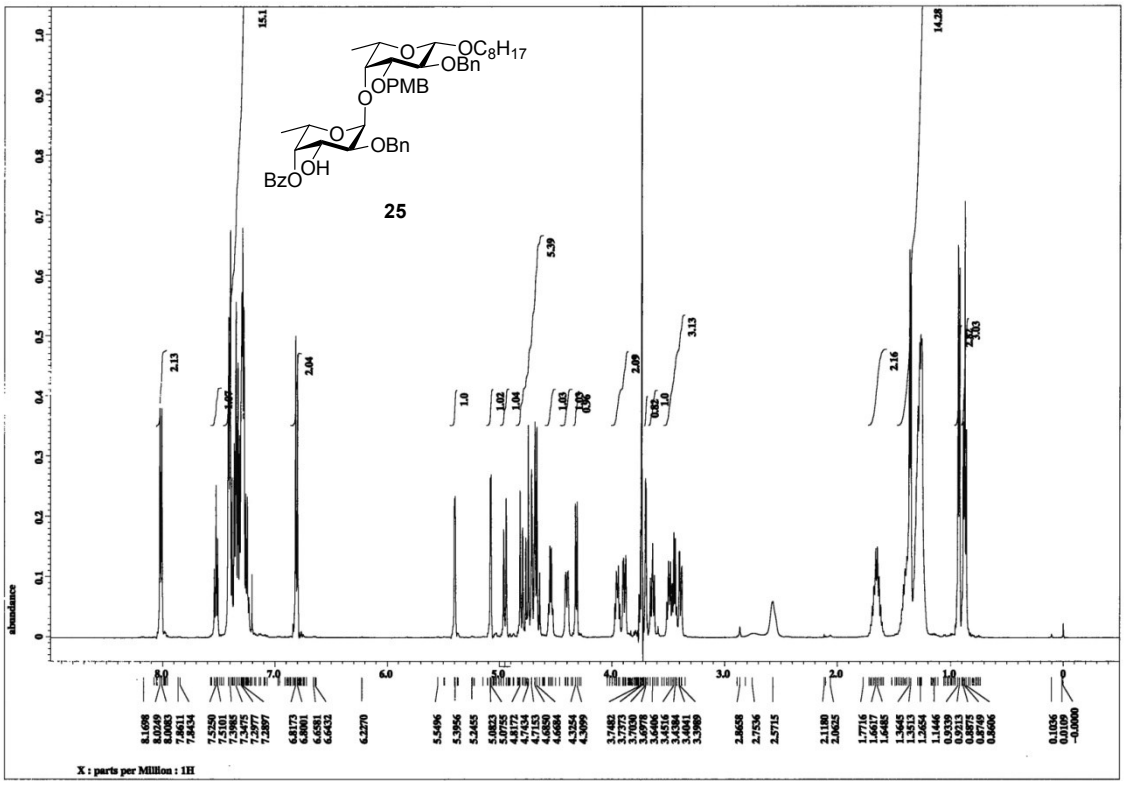


Figure S47 ^{1}H-NMR spectrum of **25**

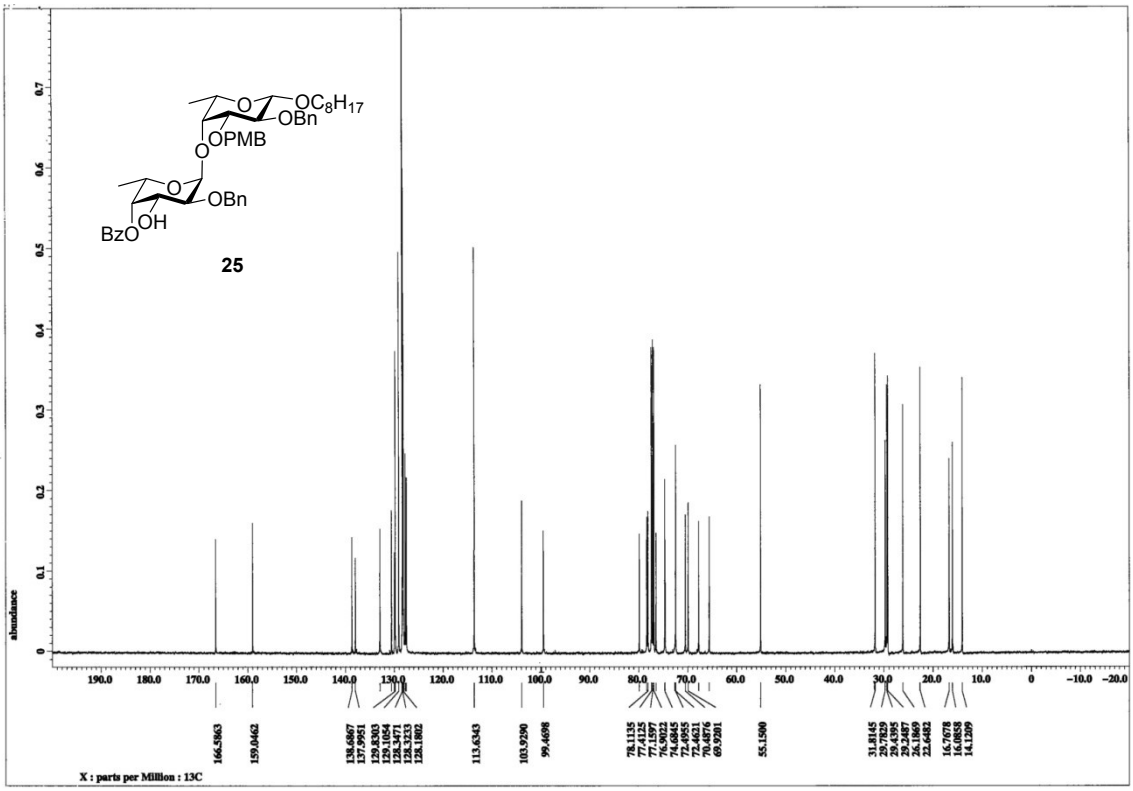


Figure S48 ^{13}C-NMR spectrum of **25**

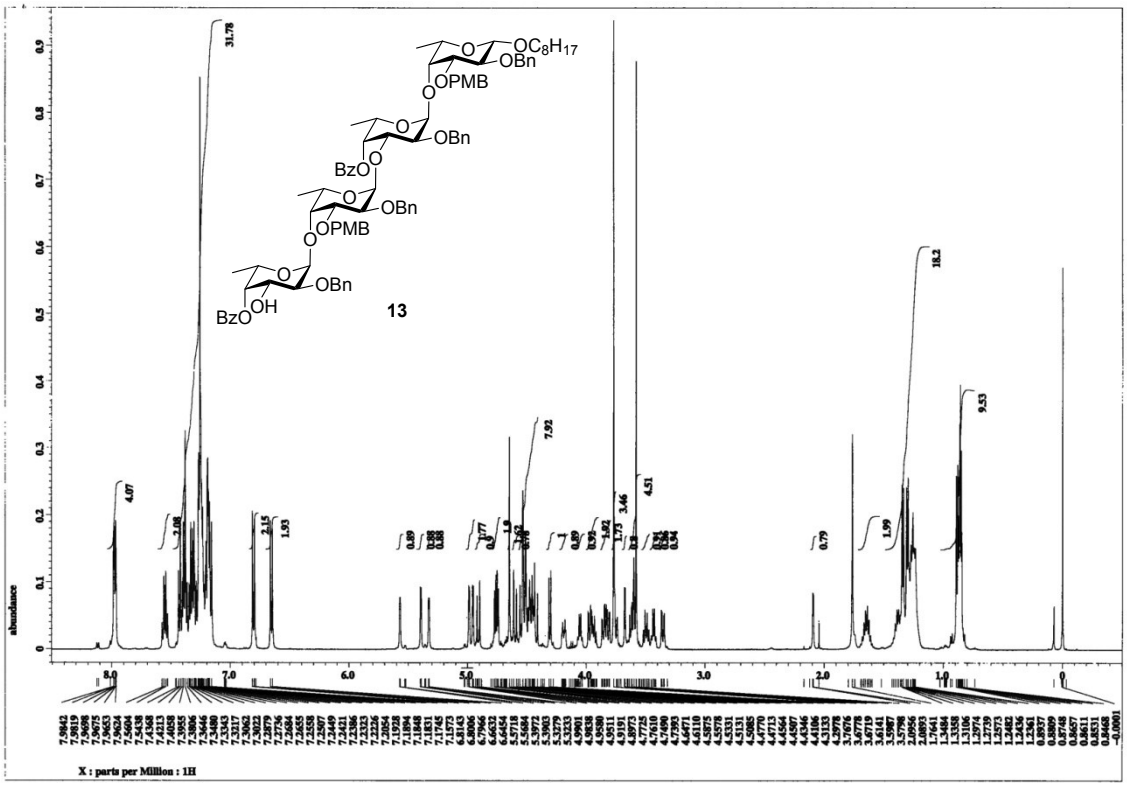


Figure S49 ^{1}H-NMR spectrum of **13**

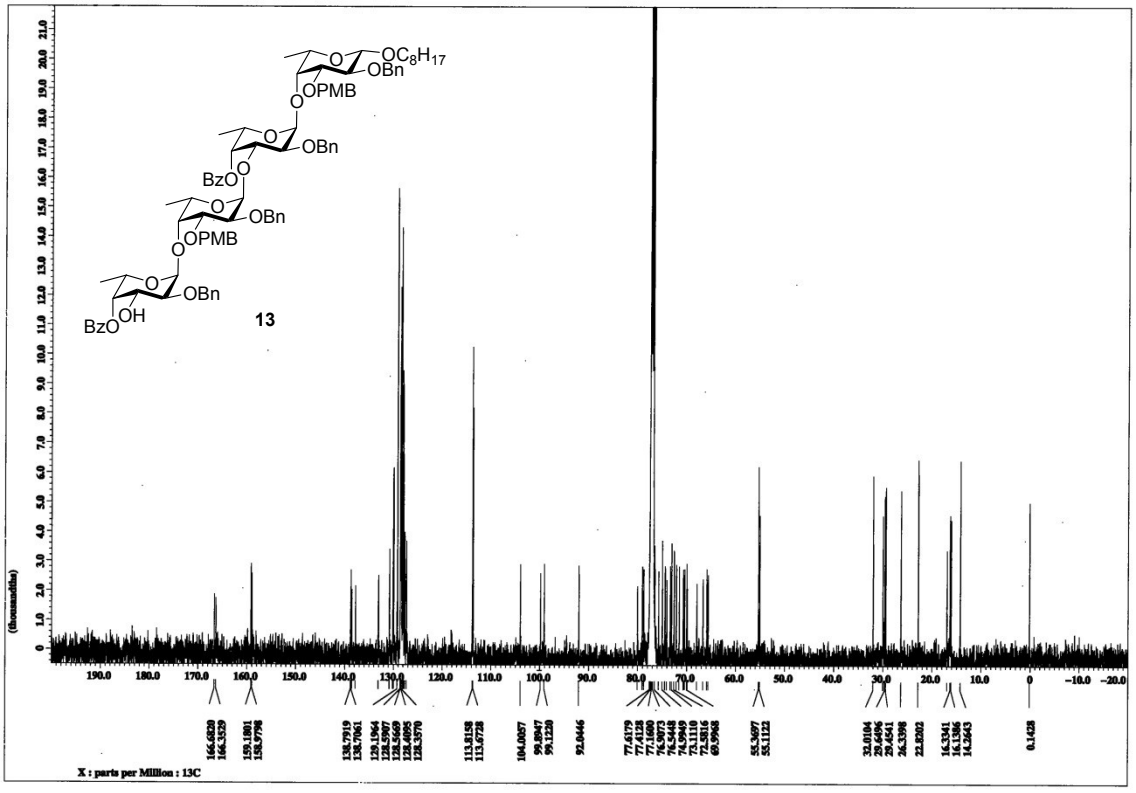


Figure S50 ^{13}C-NMR spectrum of **13**

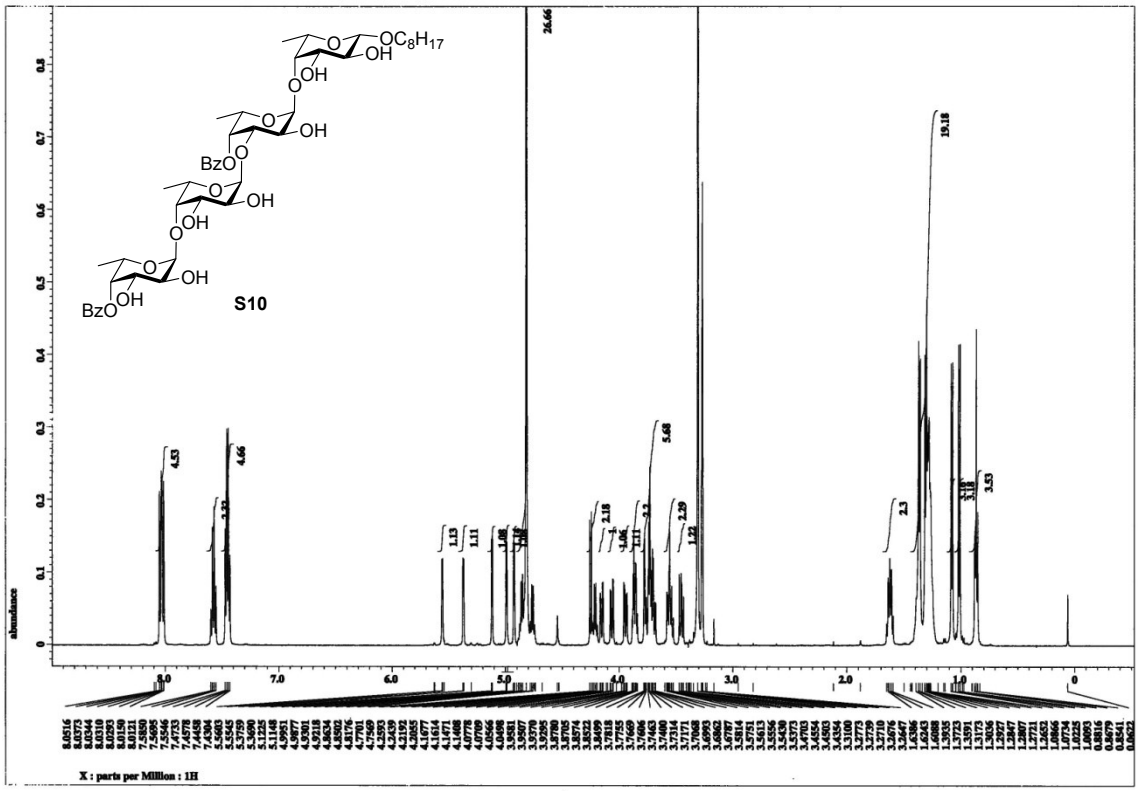


Figure S51 ^{1}H-NMR spectrum of **S10**

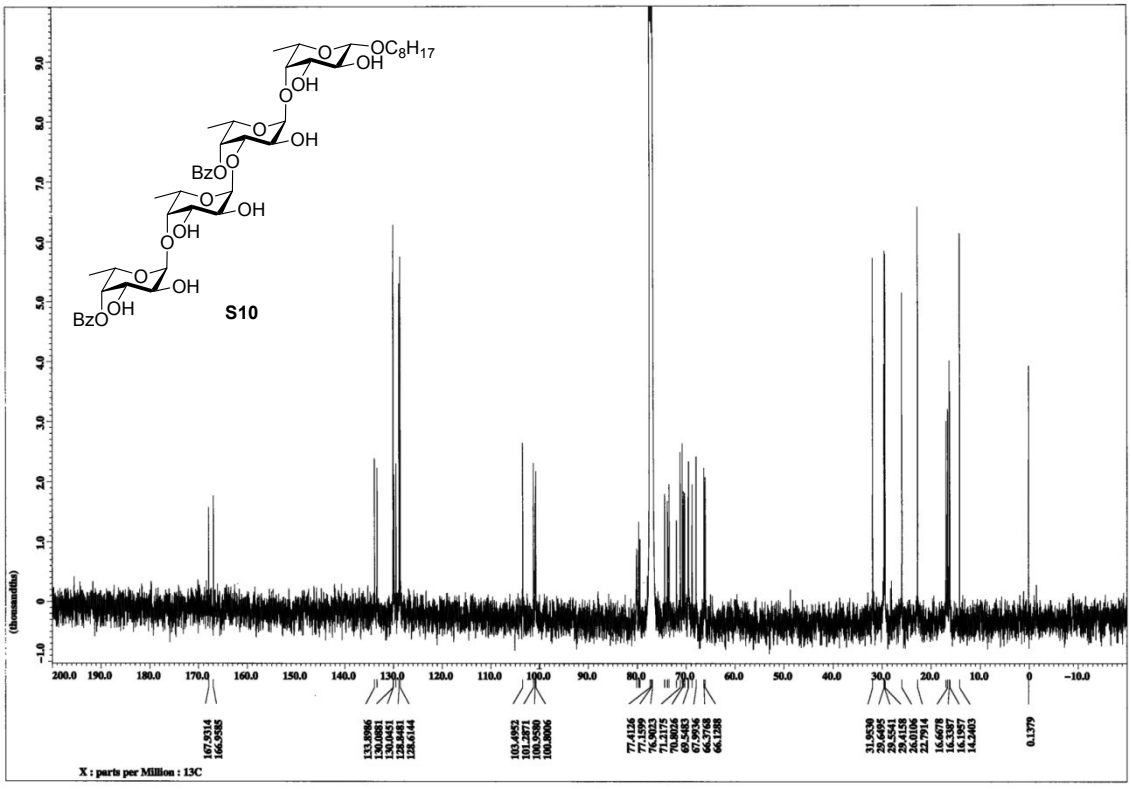


Figure S52 ^{13}C-NMR spectrum of **S10**

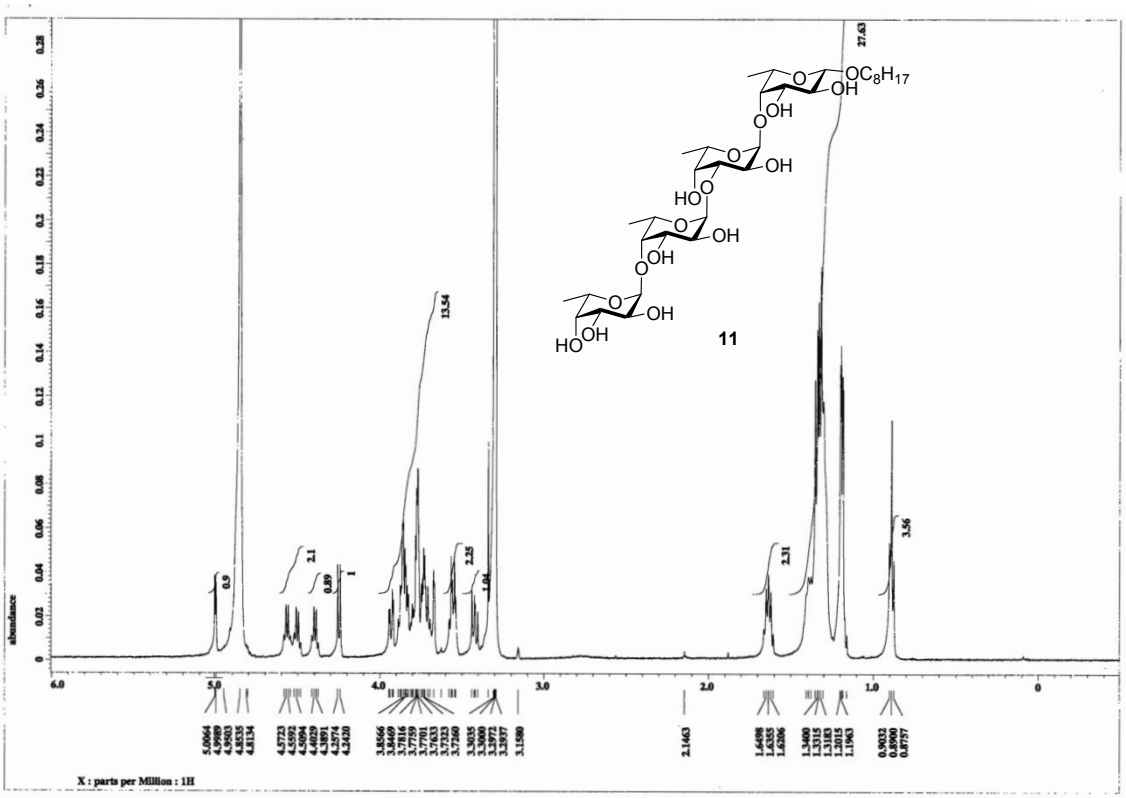


Figure S53 ^{1}H-NMR spectrum of **11**

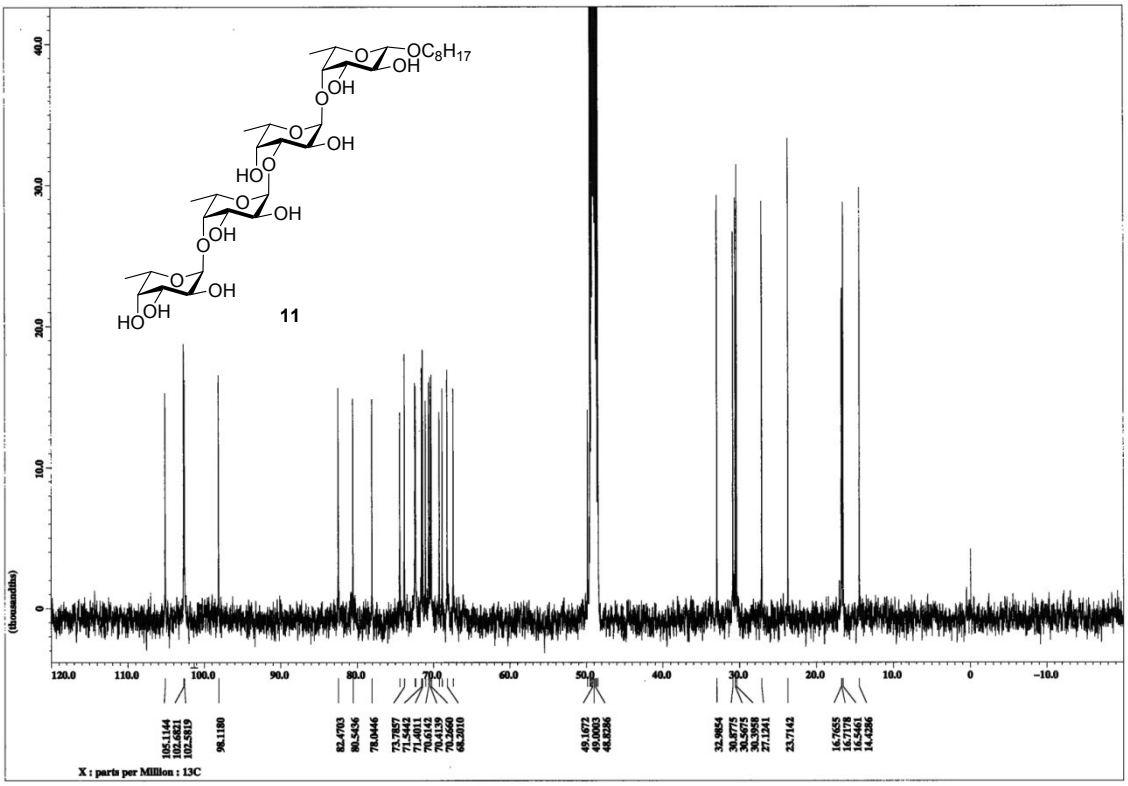


Figure S54 ^{13}C-NMR spectrum of **11**

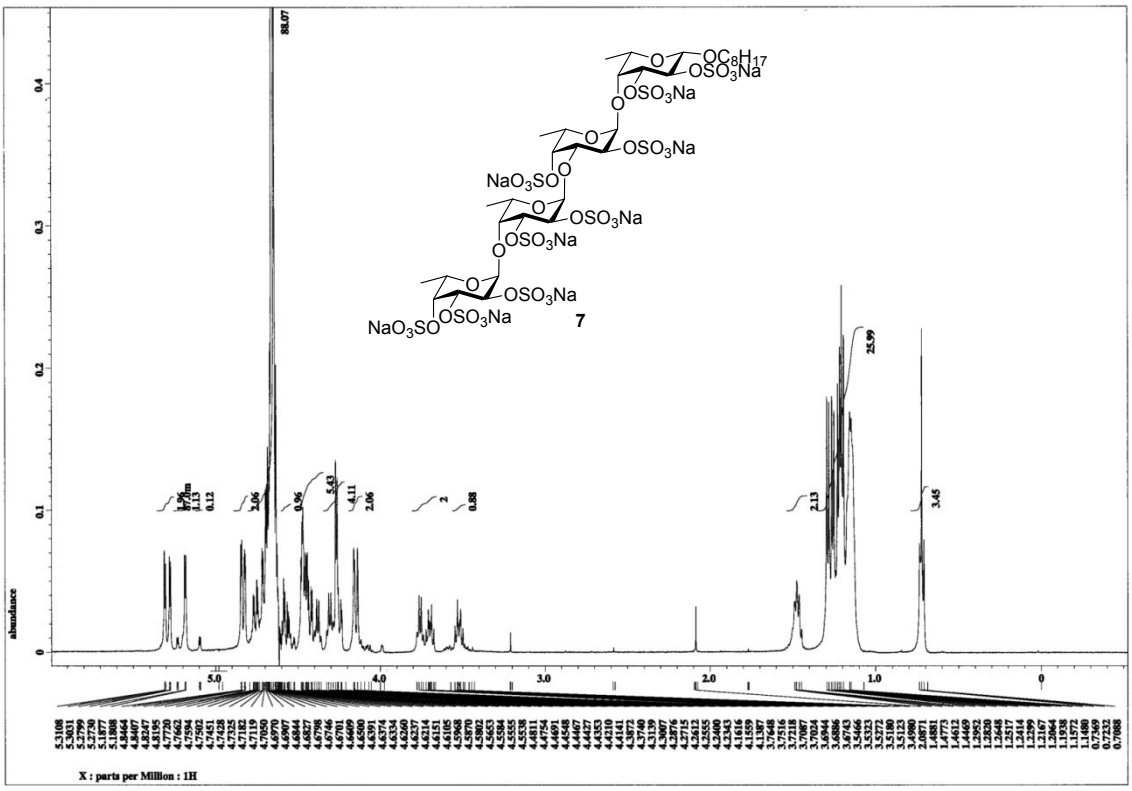


Figure S55 ^{1}H-NMR spectrum of **7**

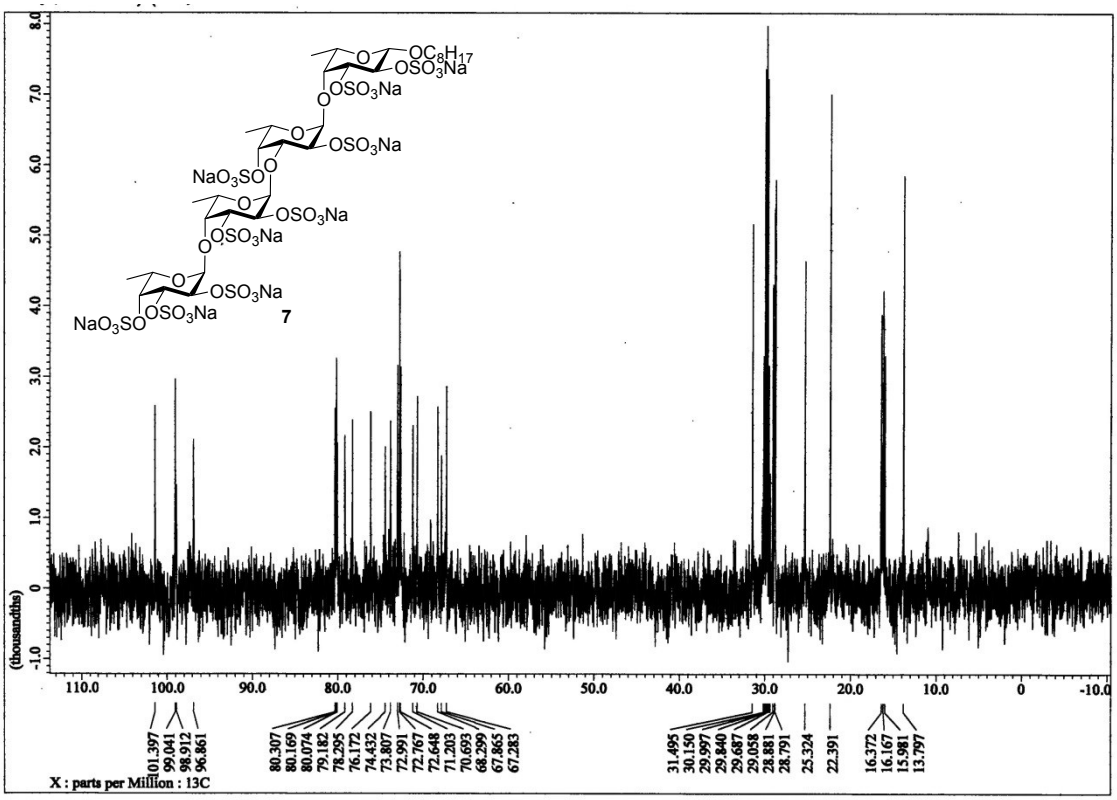


Figure S56 ^{13}C-NMR spectrum of **7**

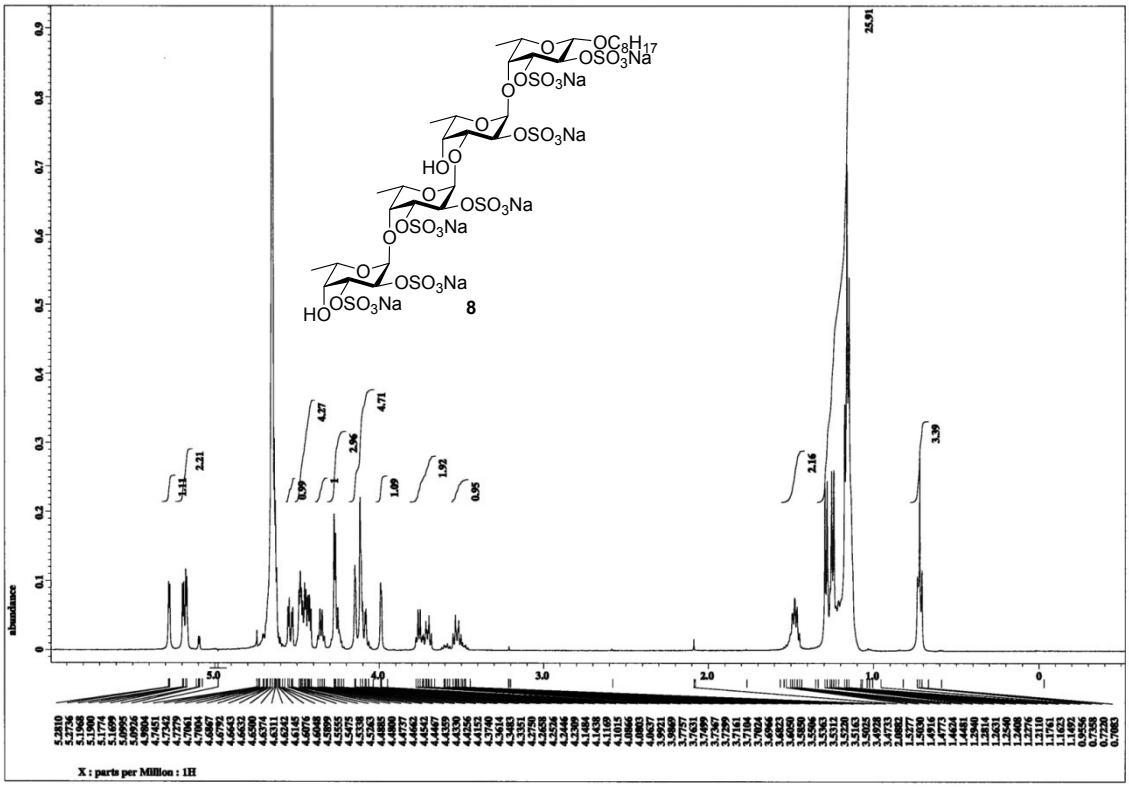


Figure S57 ^{1}H-NMR spectrum of **8**

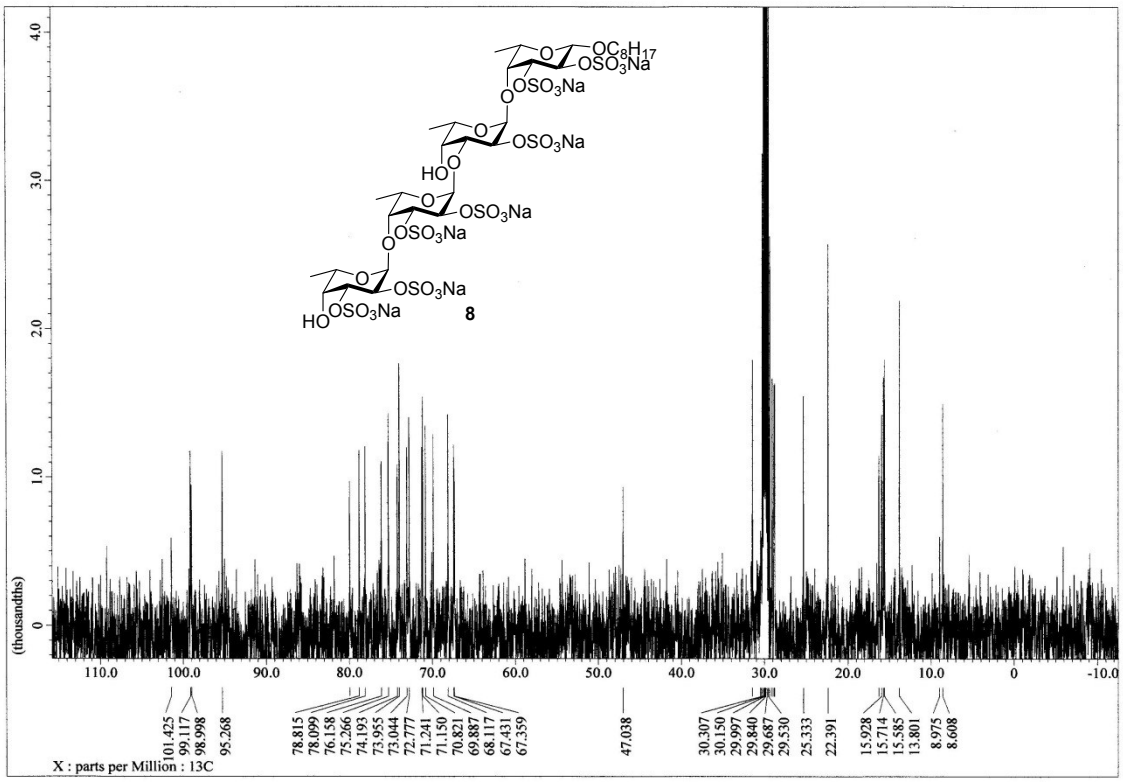


Figure S58 ^{13}C-NMR spectrum of **8**

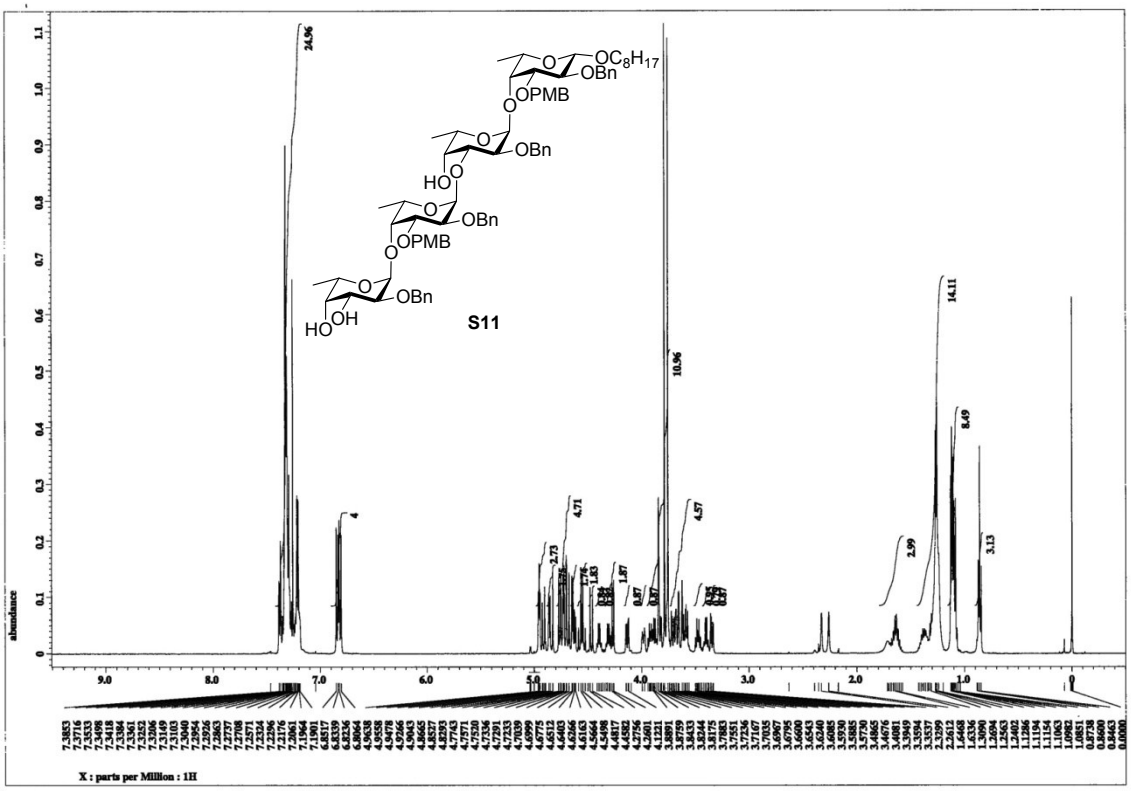


Figure S59 ^{1}H-NMR spectrum of **S11**

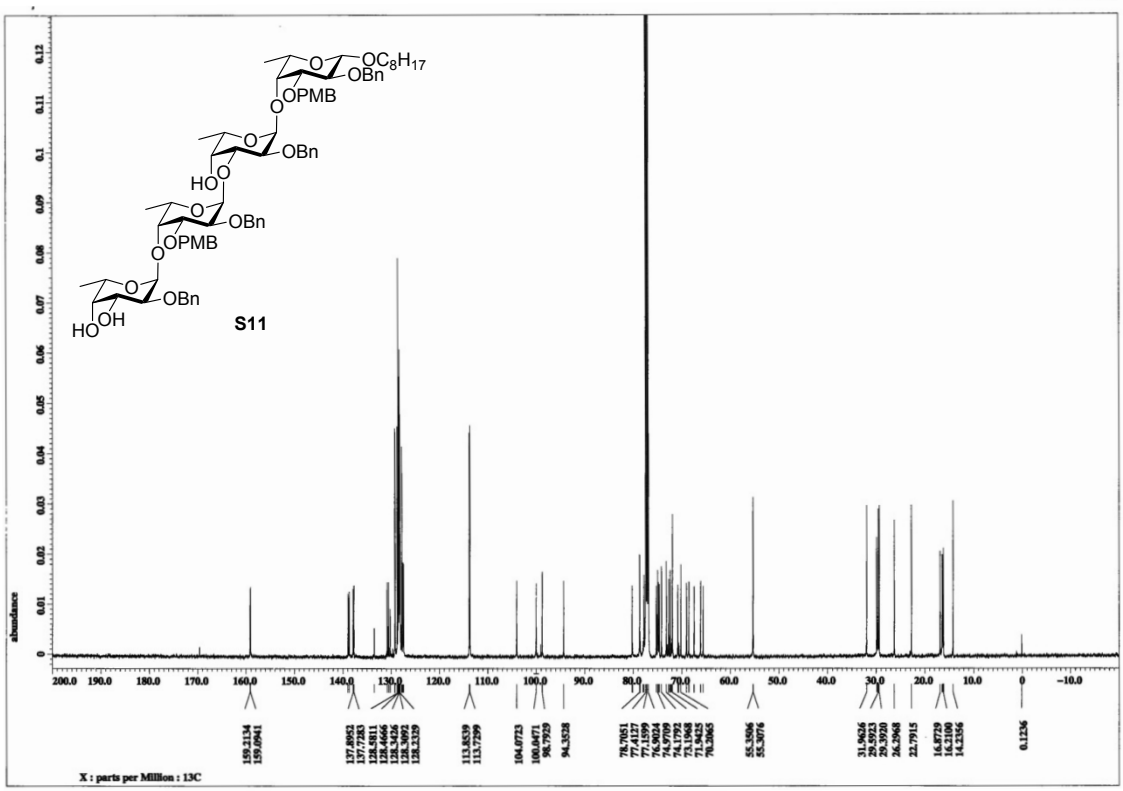


Figure S60 ^{13}C-NMR spectrum of **S11**

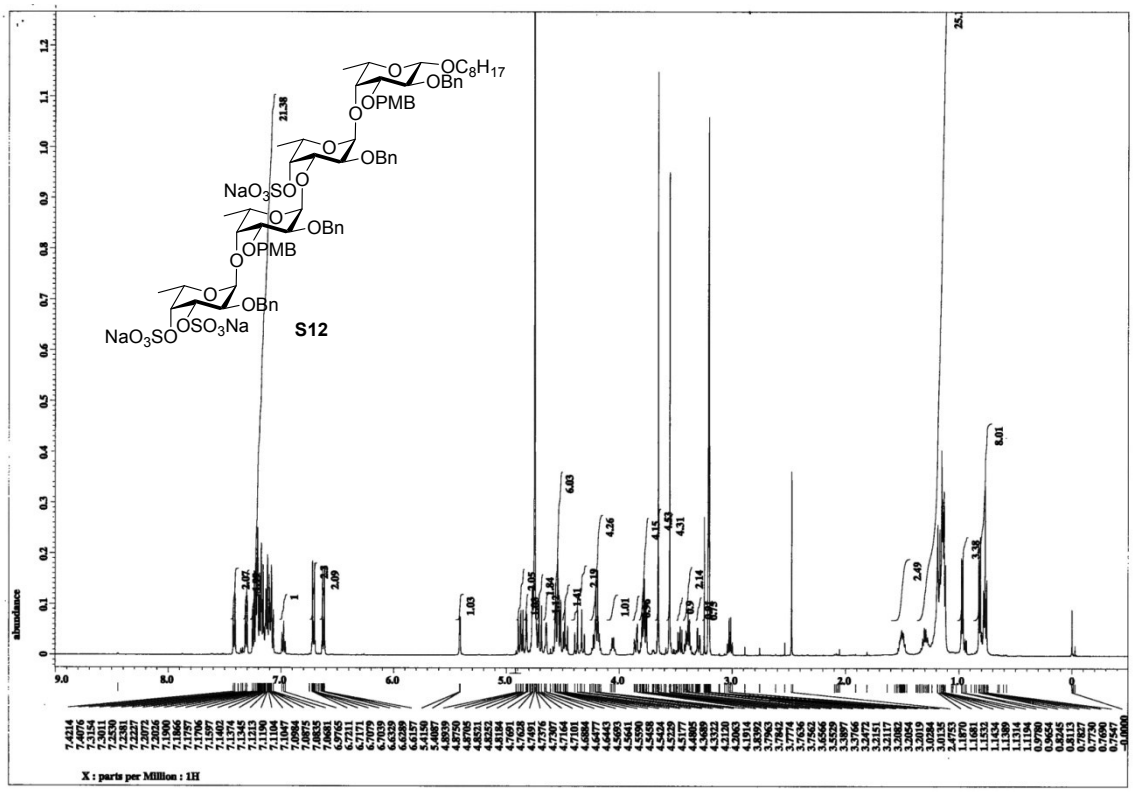


Figure S61 ^{1}H-NMR spectrum of **S12**

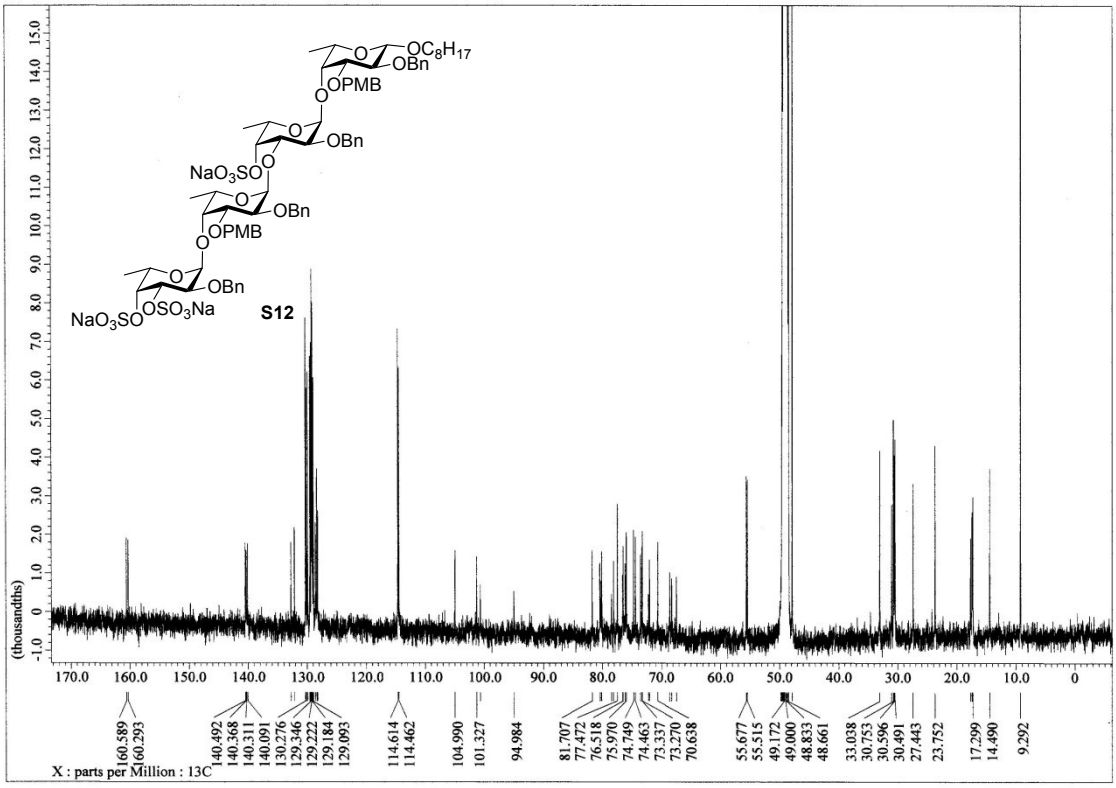


Figure S62 ^{13}C-NMR spectrum of **S12**

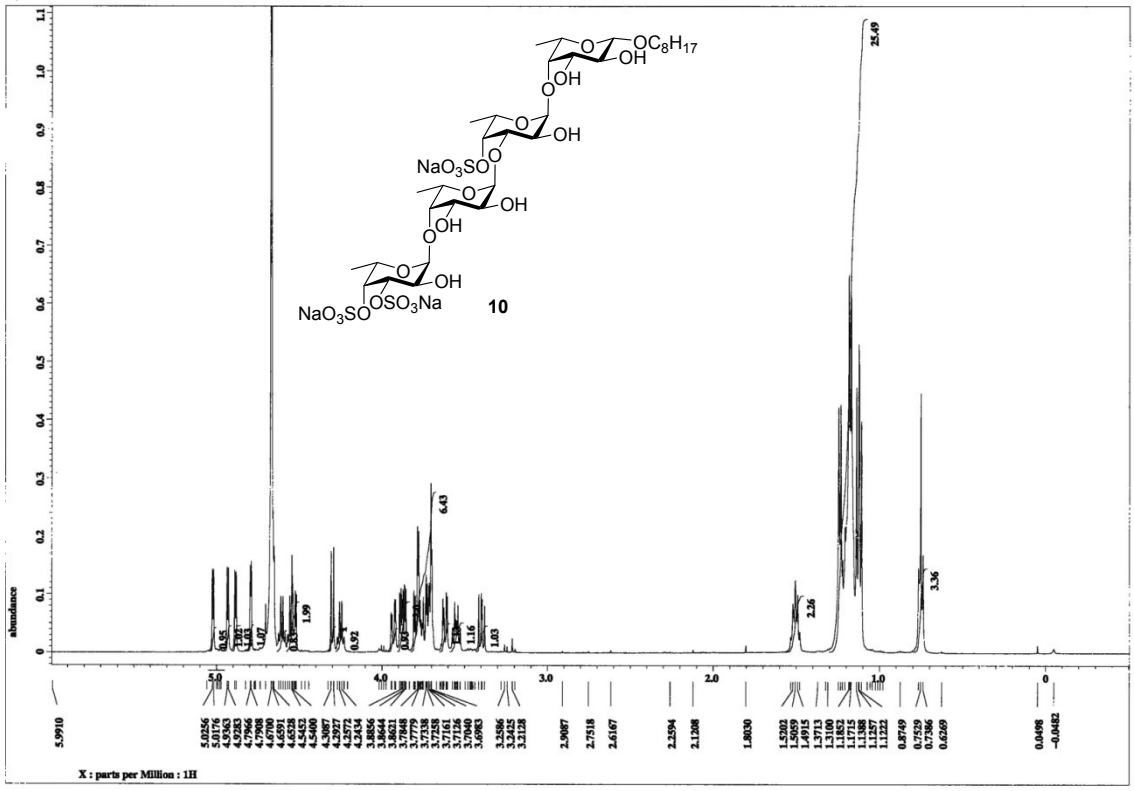


Figure S63 ^{1}H-NMR spectrum of **10**

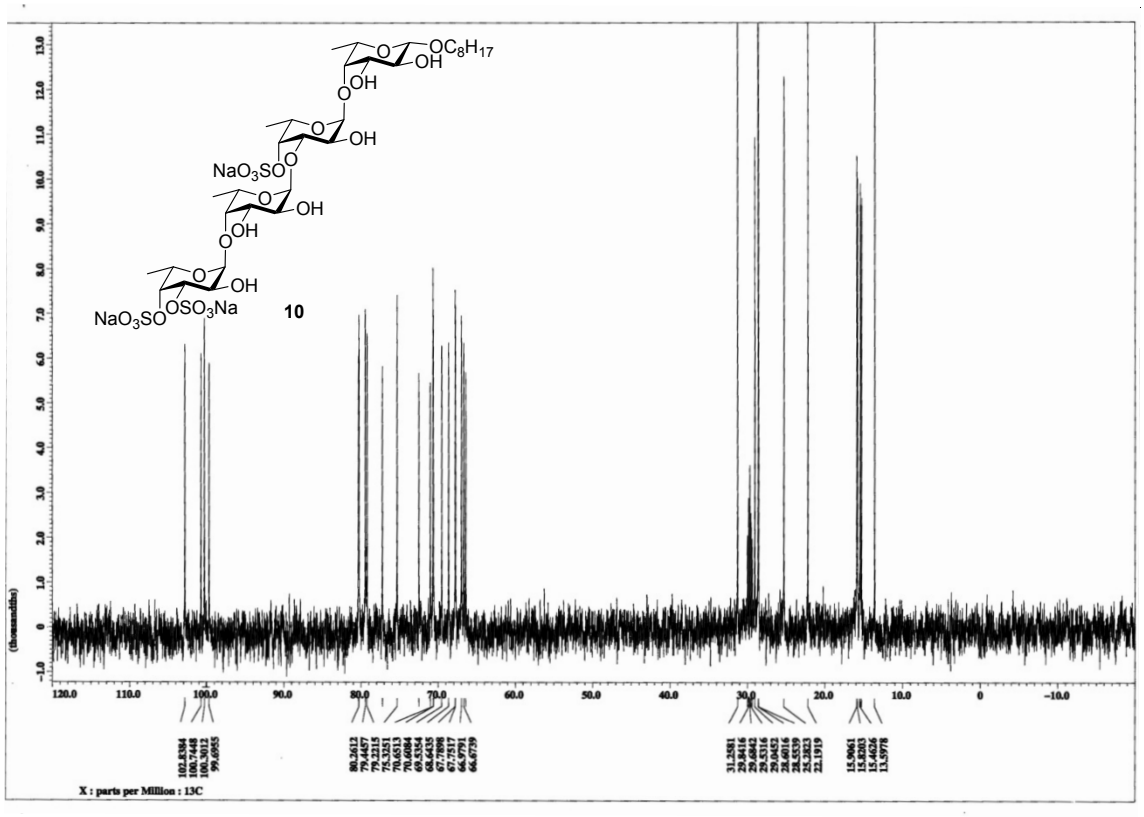


Figure S64 ^{13}C-NMR spectrum of **10**

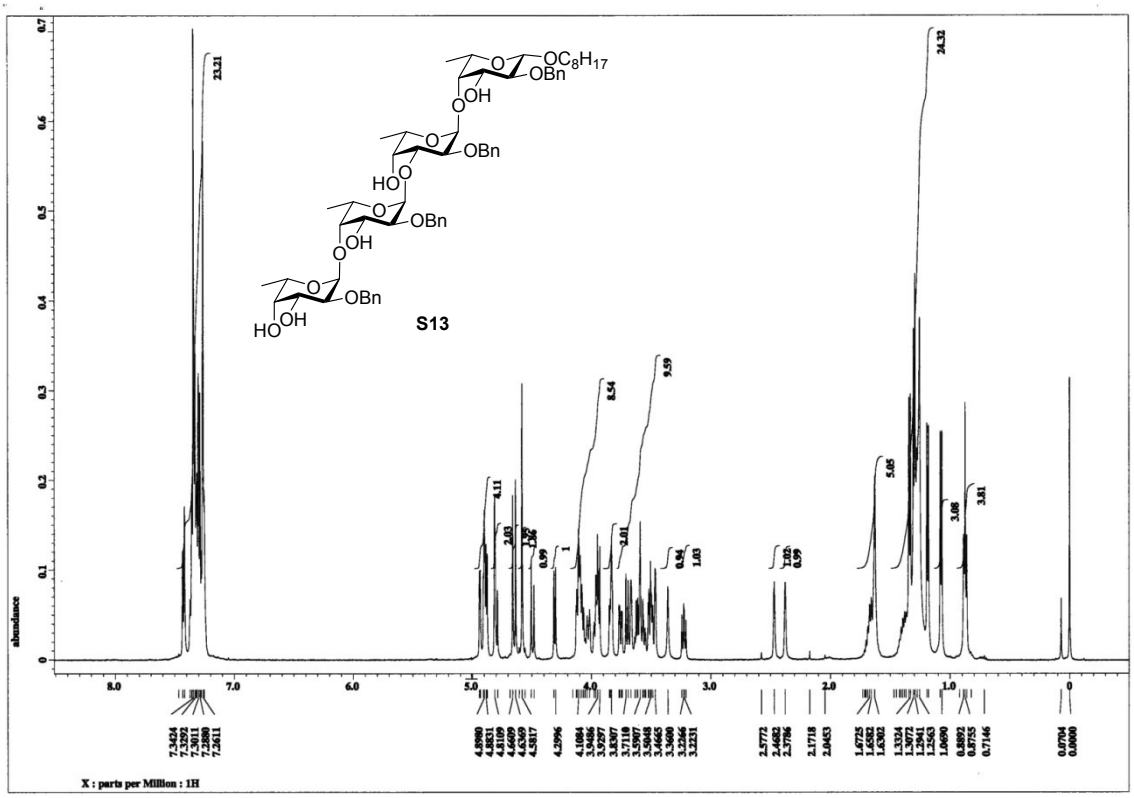


Figure S65 ^{1}H-NMR spectrum of **S13**

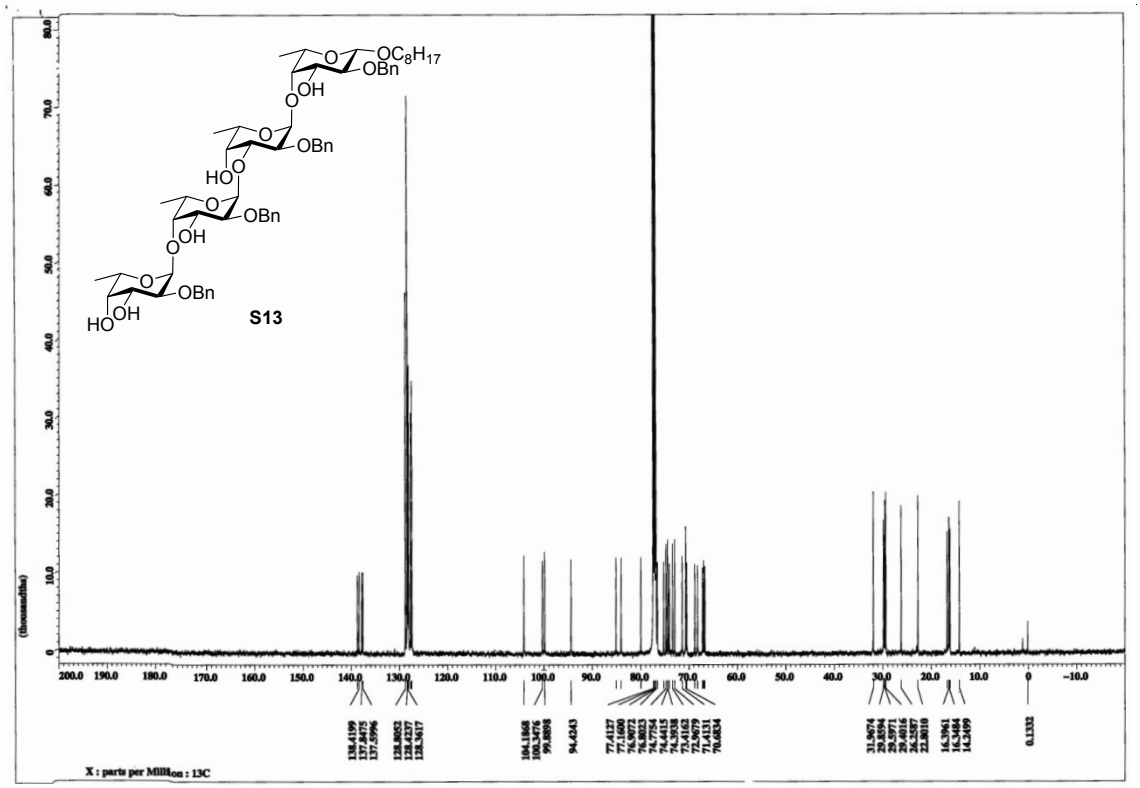


Figure S66 ^{13}C-NMR spectrum of **S13**

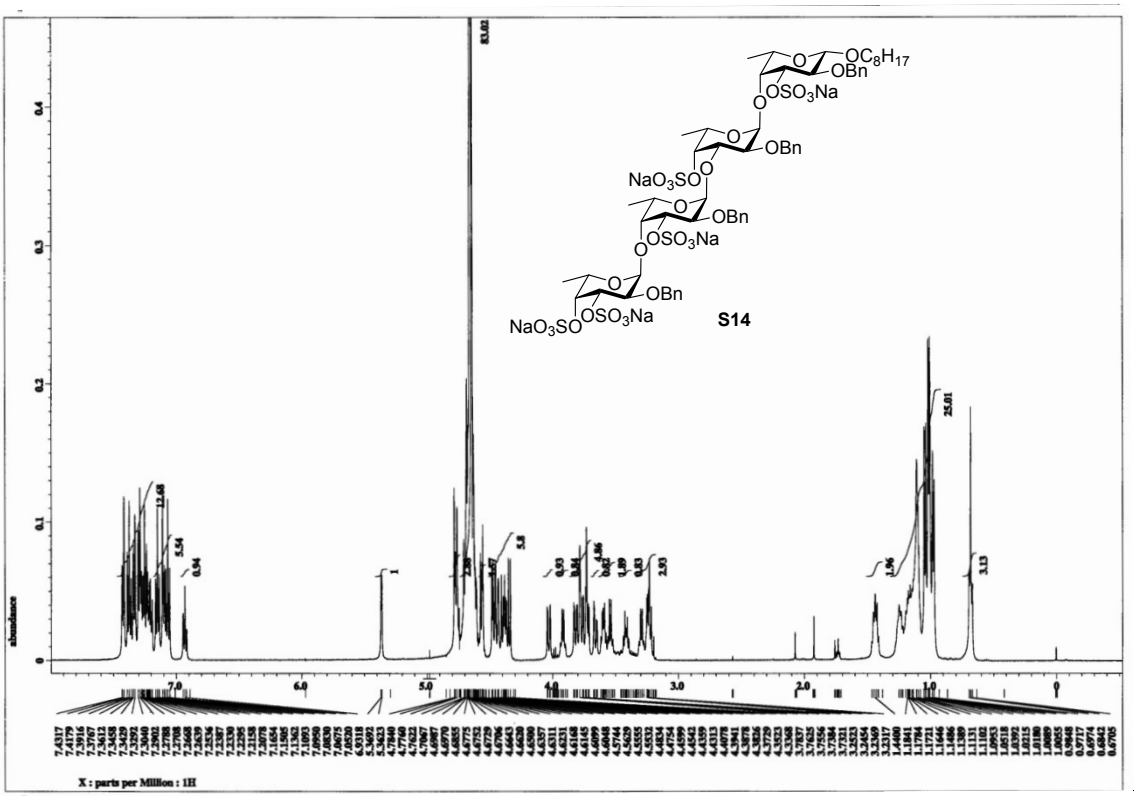


Figure S67 ^{1}H-NMR spectrum of **S14**

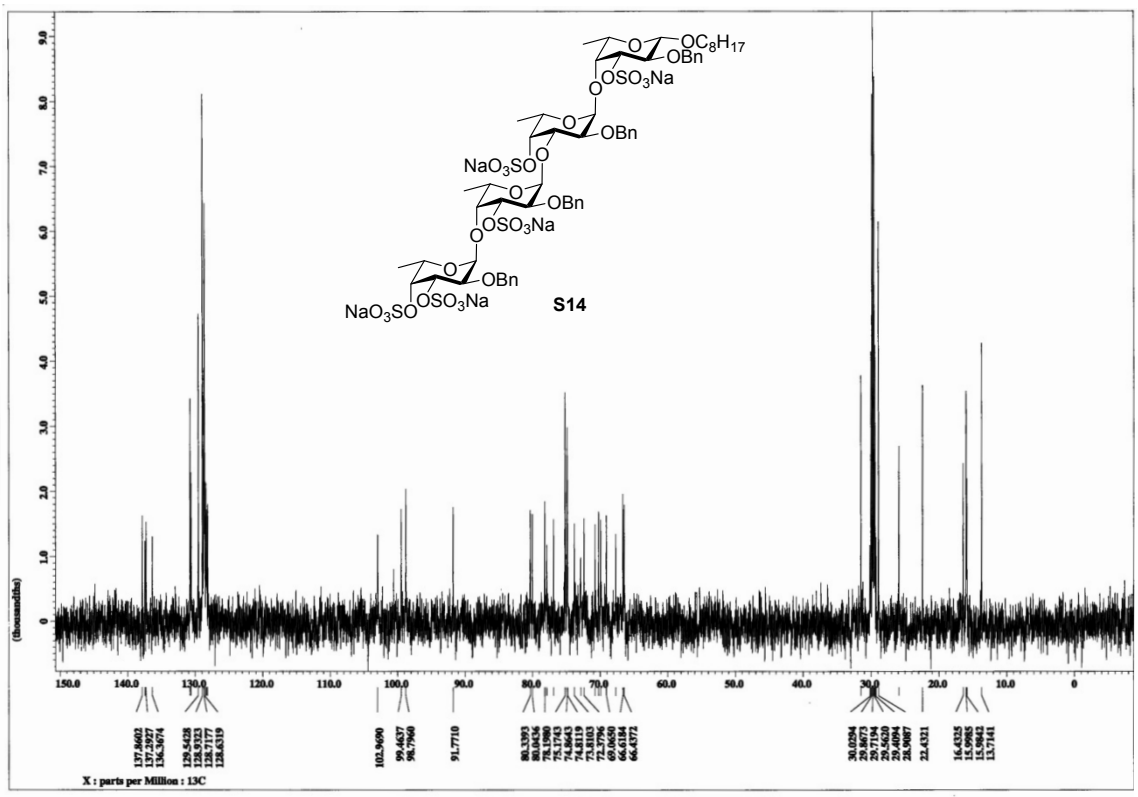


Figure S68 ^{13}C-NMR spectrum of **S14**

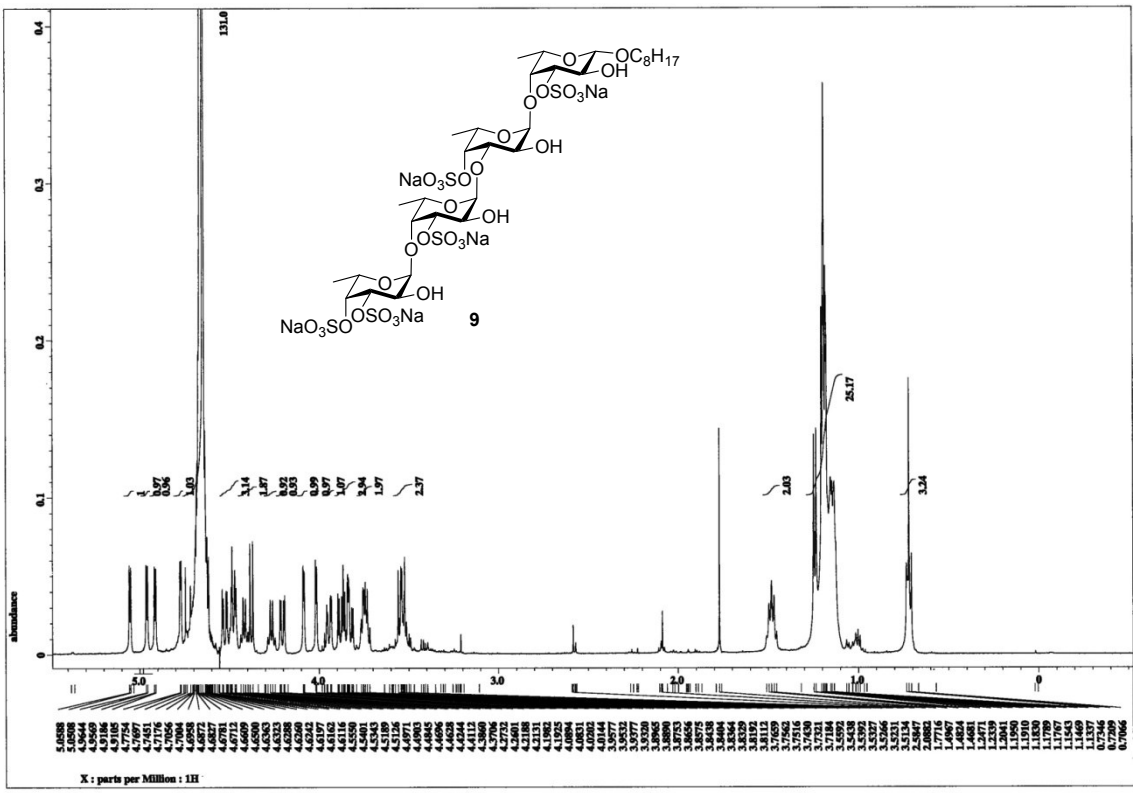


Figure S69 ^{1}H-NMR spectrum of **9**

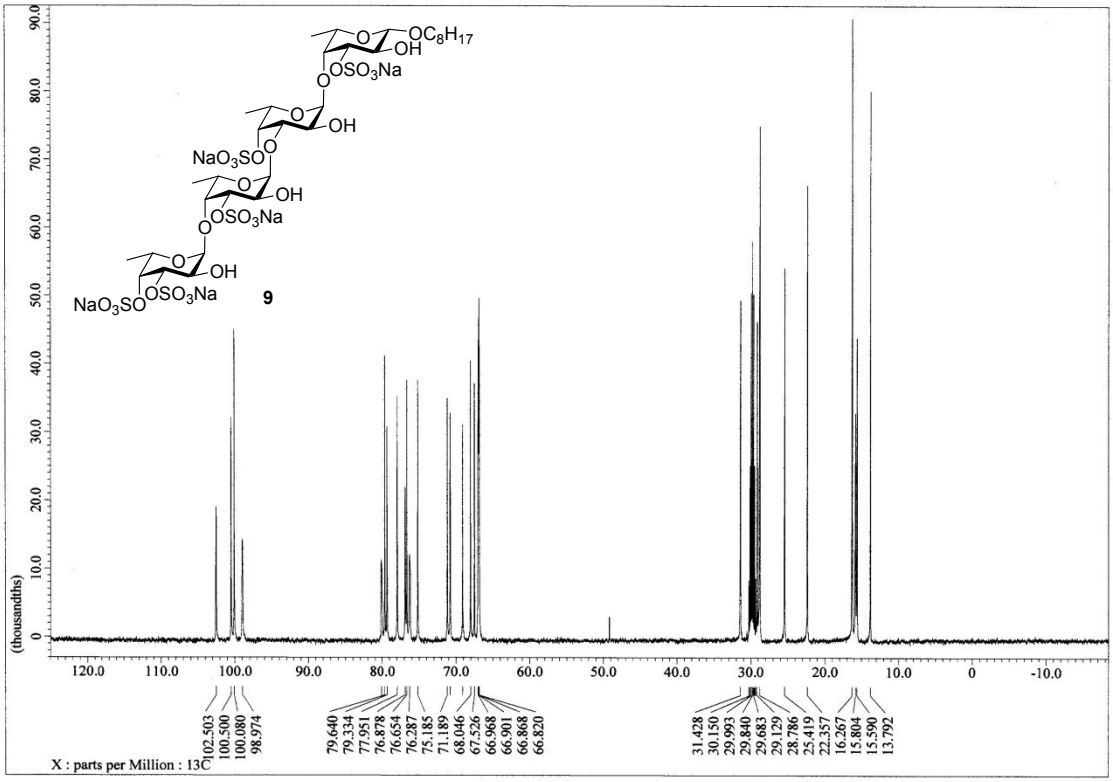


Figure S70 ^{13}C-NMR spectrum of **9**

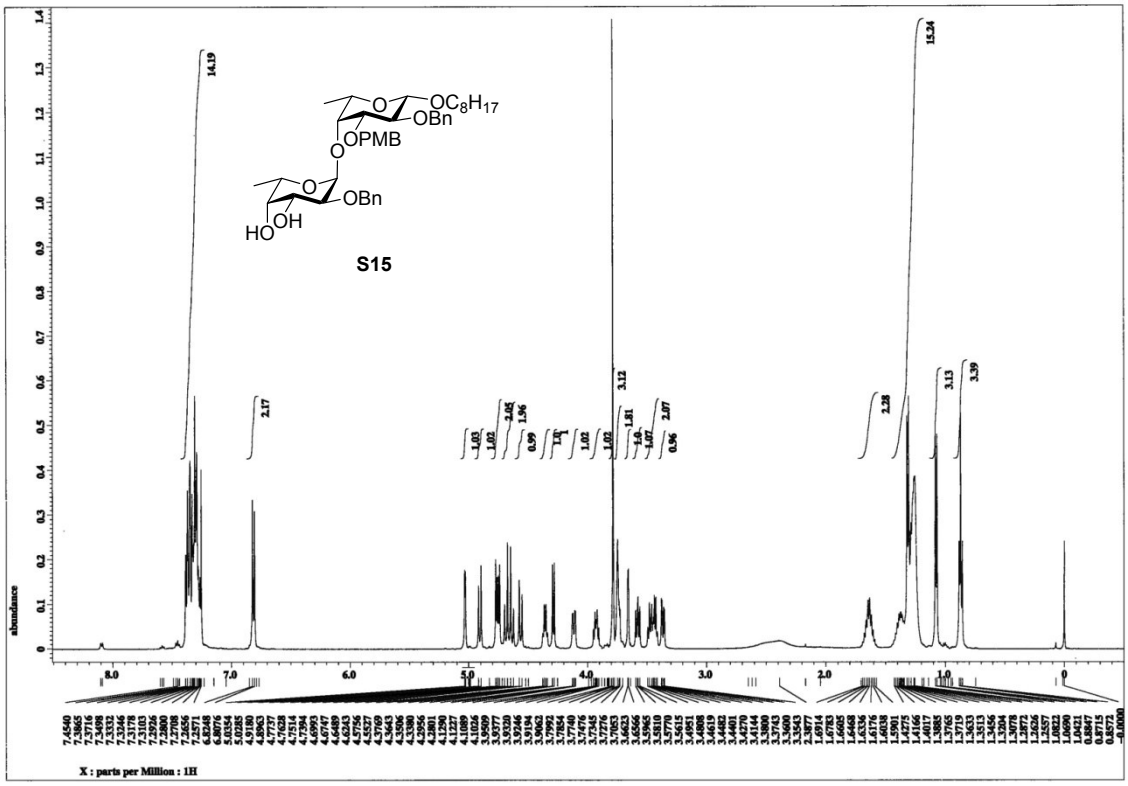


Figure S71 ^{1}H-NMR spectrum of **S15**

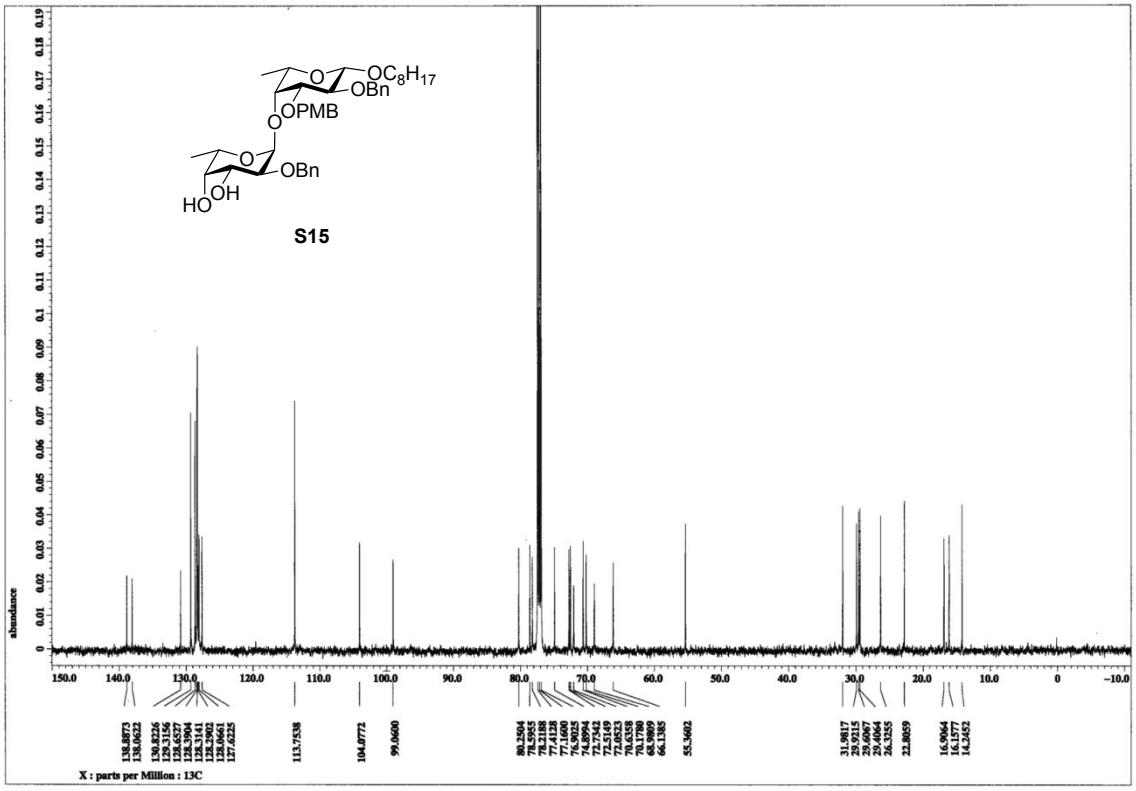


Figure S72 ^{13}C-NMR spectrum of **S15**

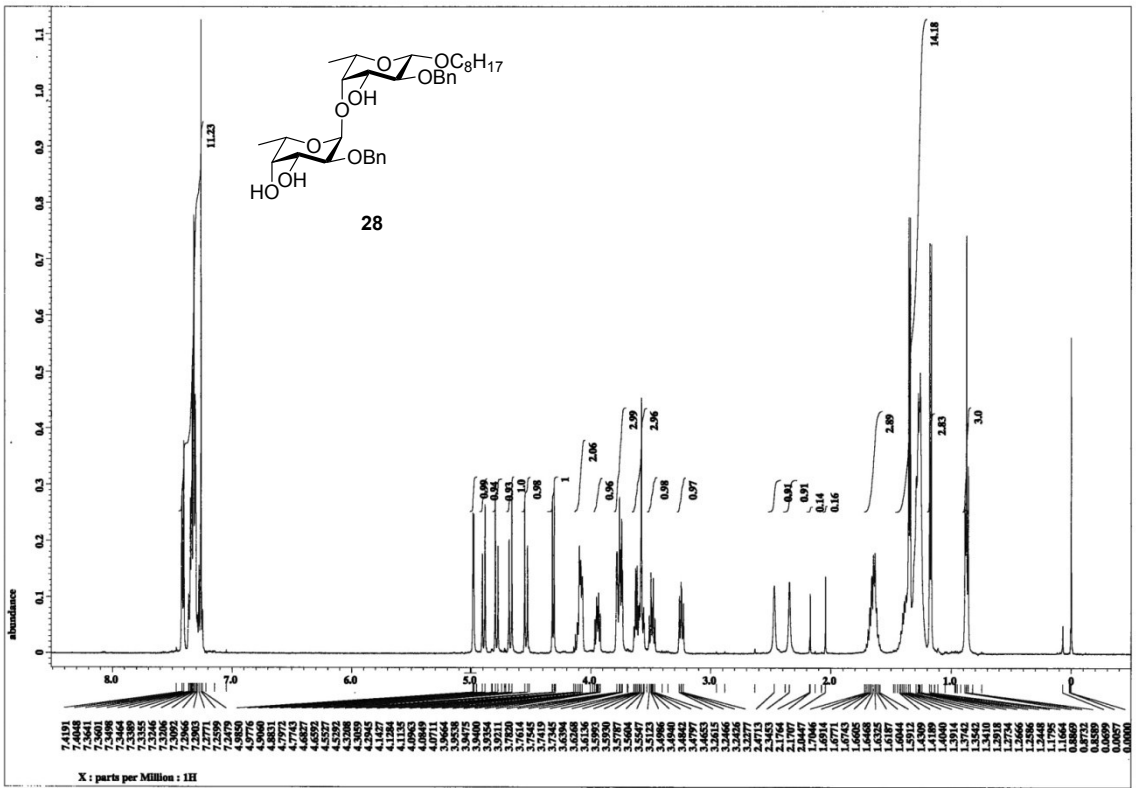


Figure S73 ^{1}H-NMR spectrum of **28**

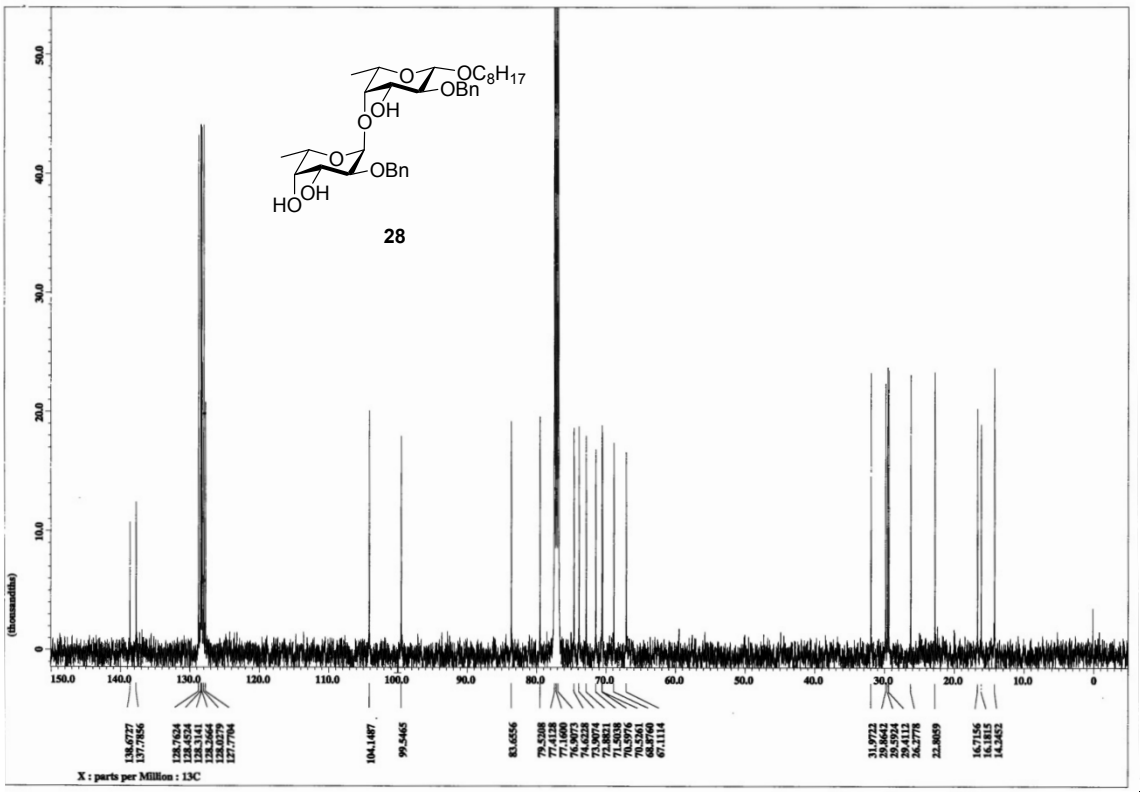
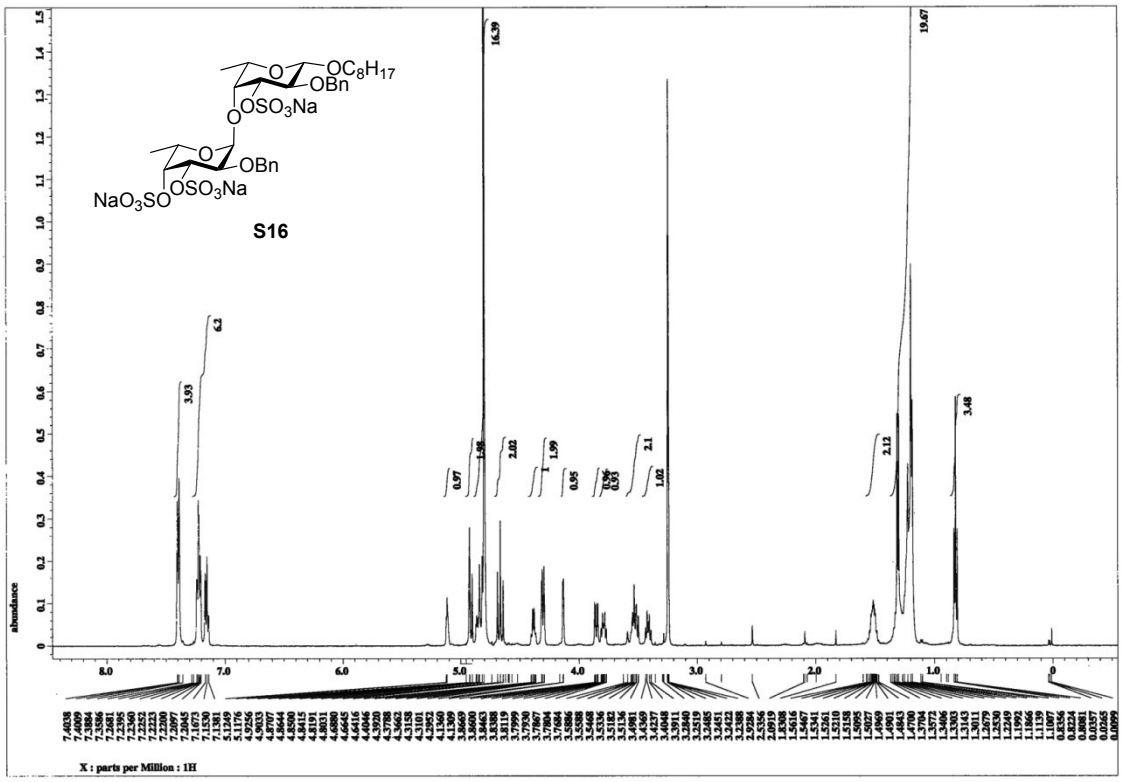


Figure S74 ^{13}C-NMR spectrum of **28**



Figreu S75 ^{1}H-NMR spectrum of **S16**

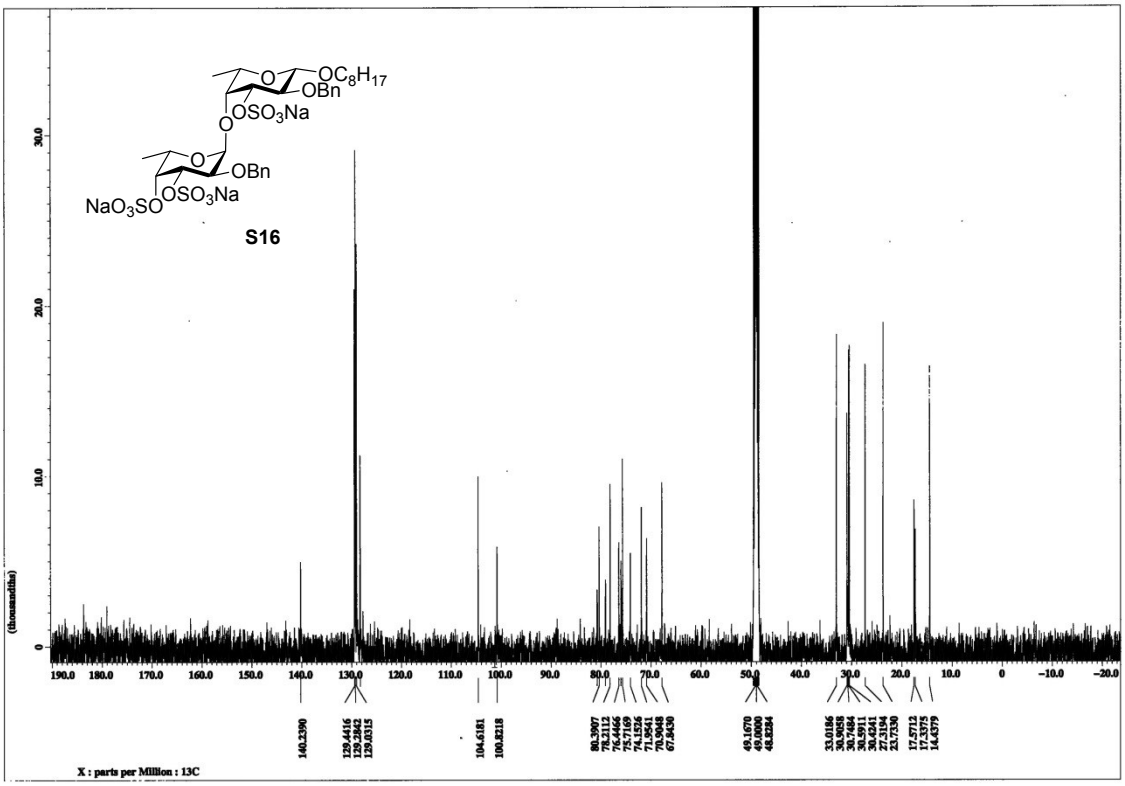


Figure S76 ^{13}C-NMR spectrum of **S16**

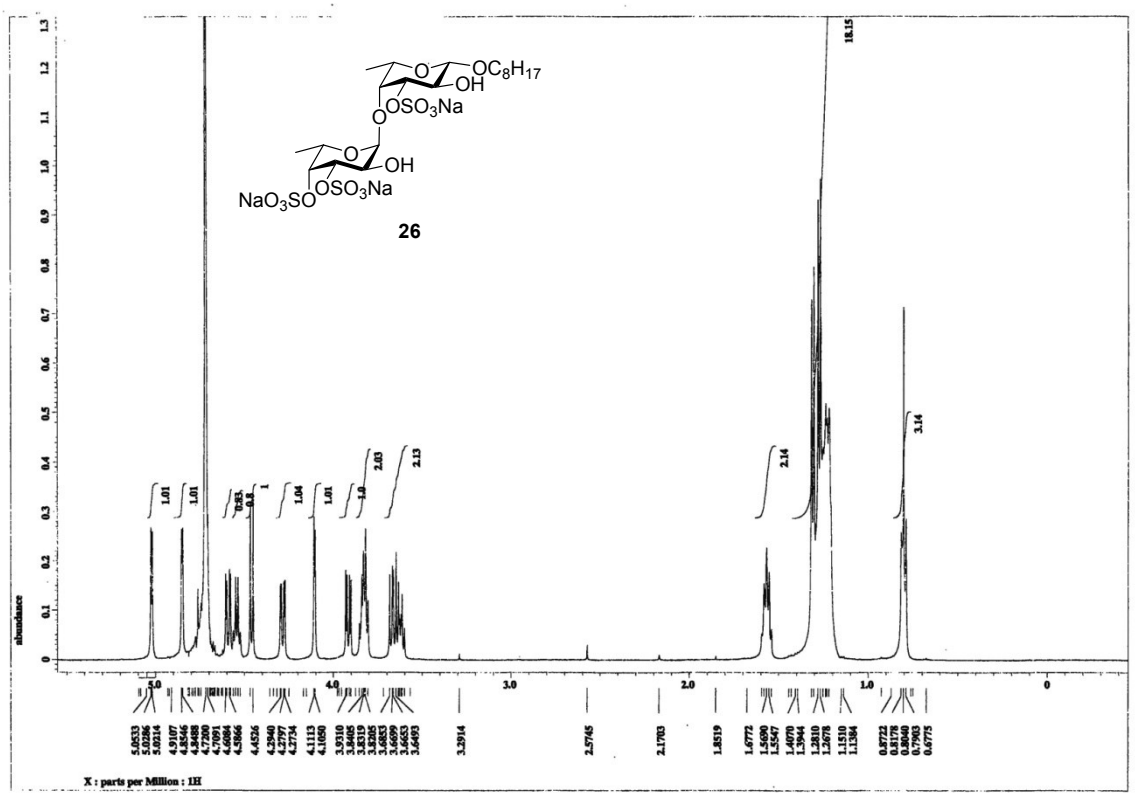


Figure S77 ^{1}H-NMR spectrum of **26**

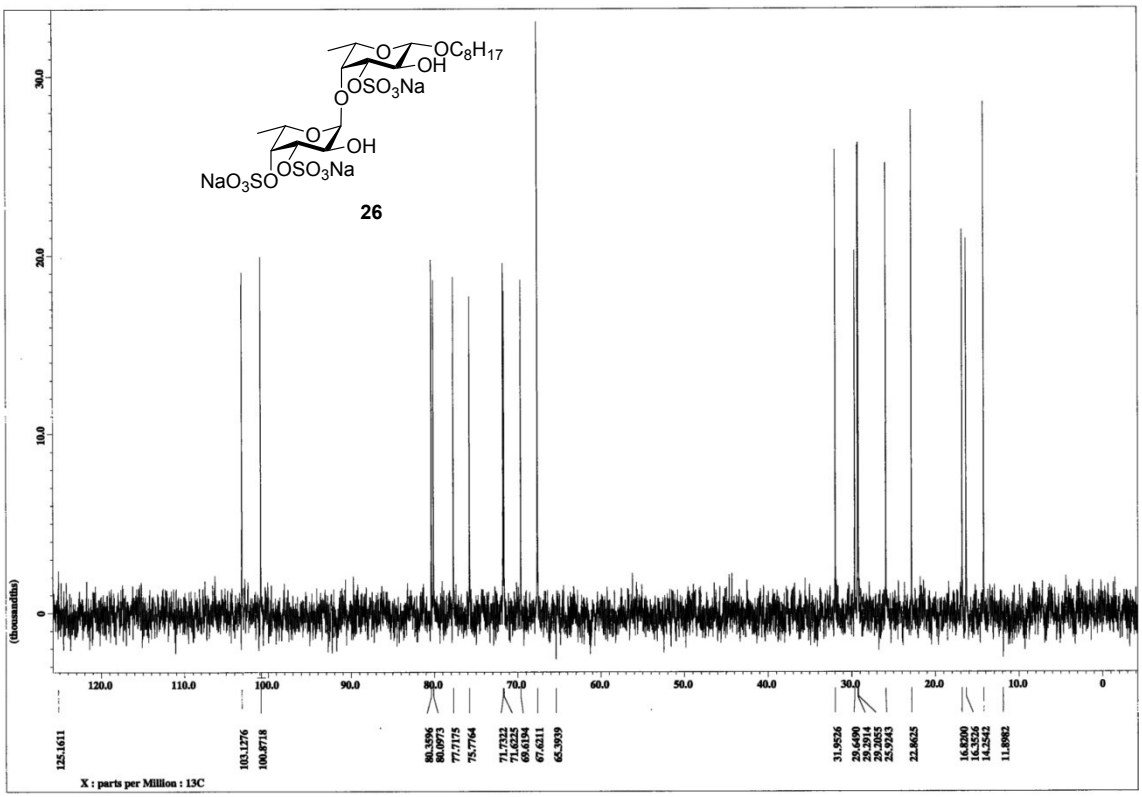


Figure S78 ^{13}C-NMR spectrum of **26**

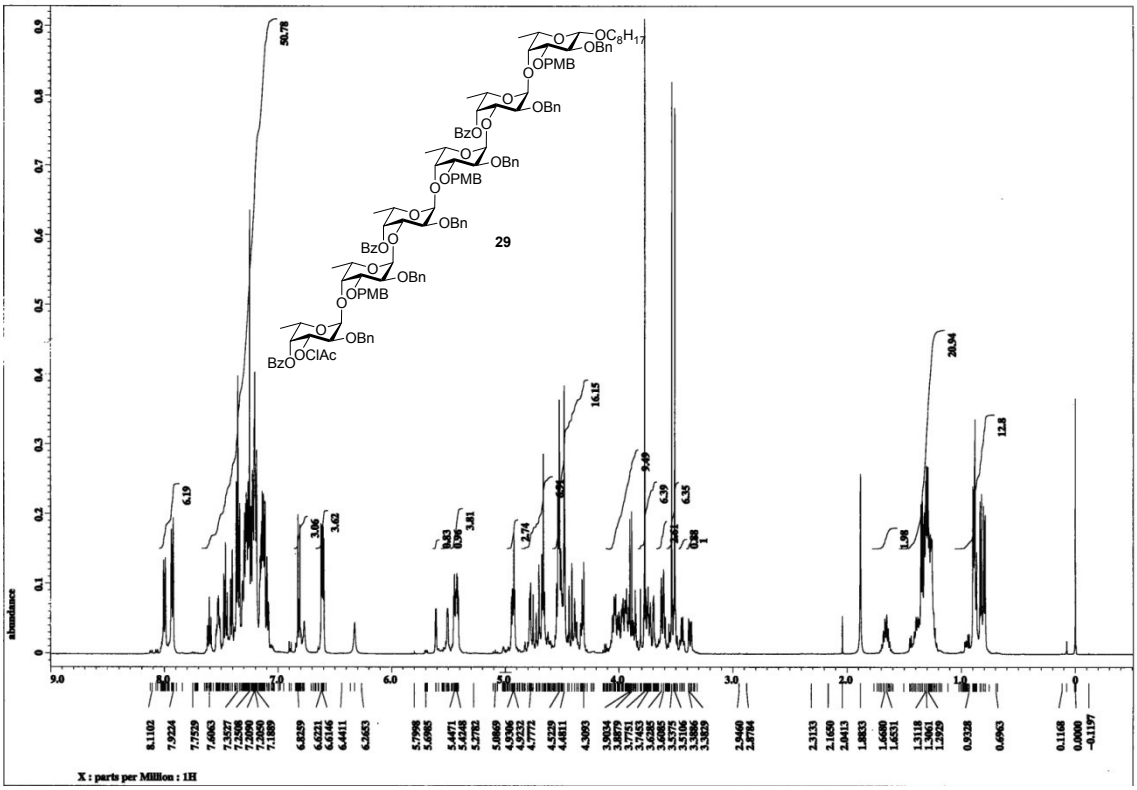


Figure S79 ^{1}H-NMR spectrum of **29**

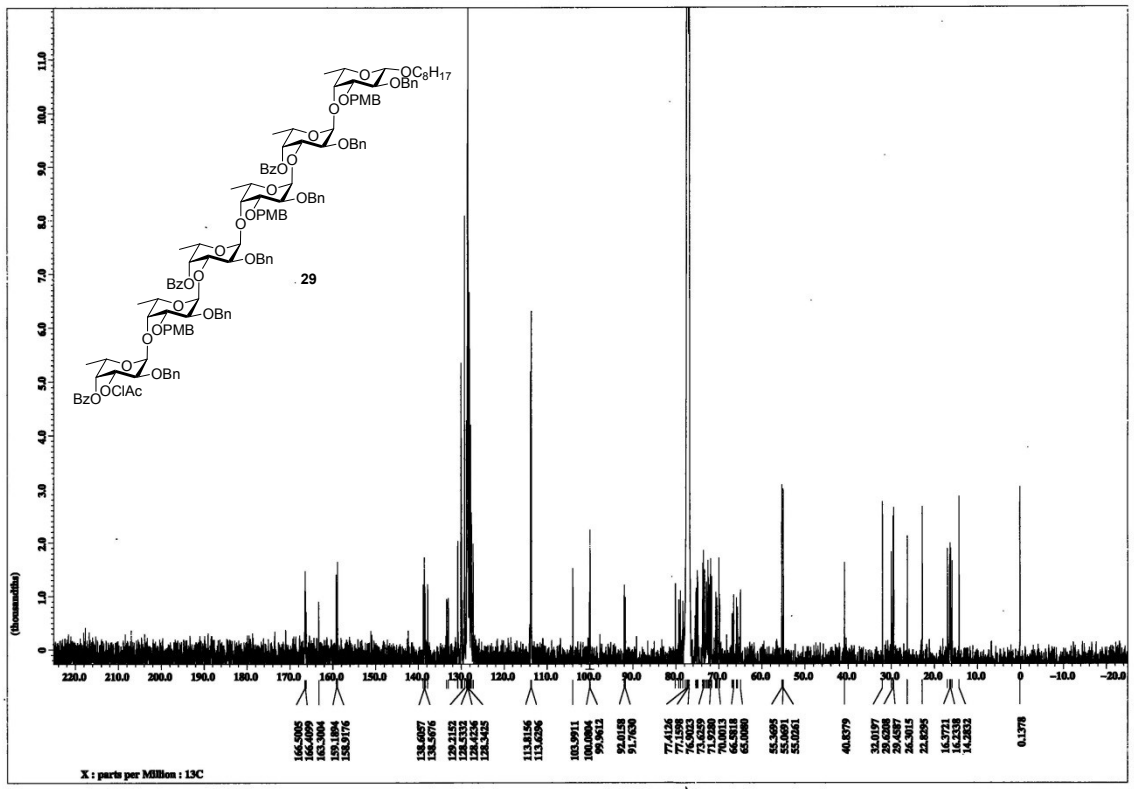


Figure S80 ^{13}C-NMR spectrum of **29**

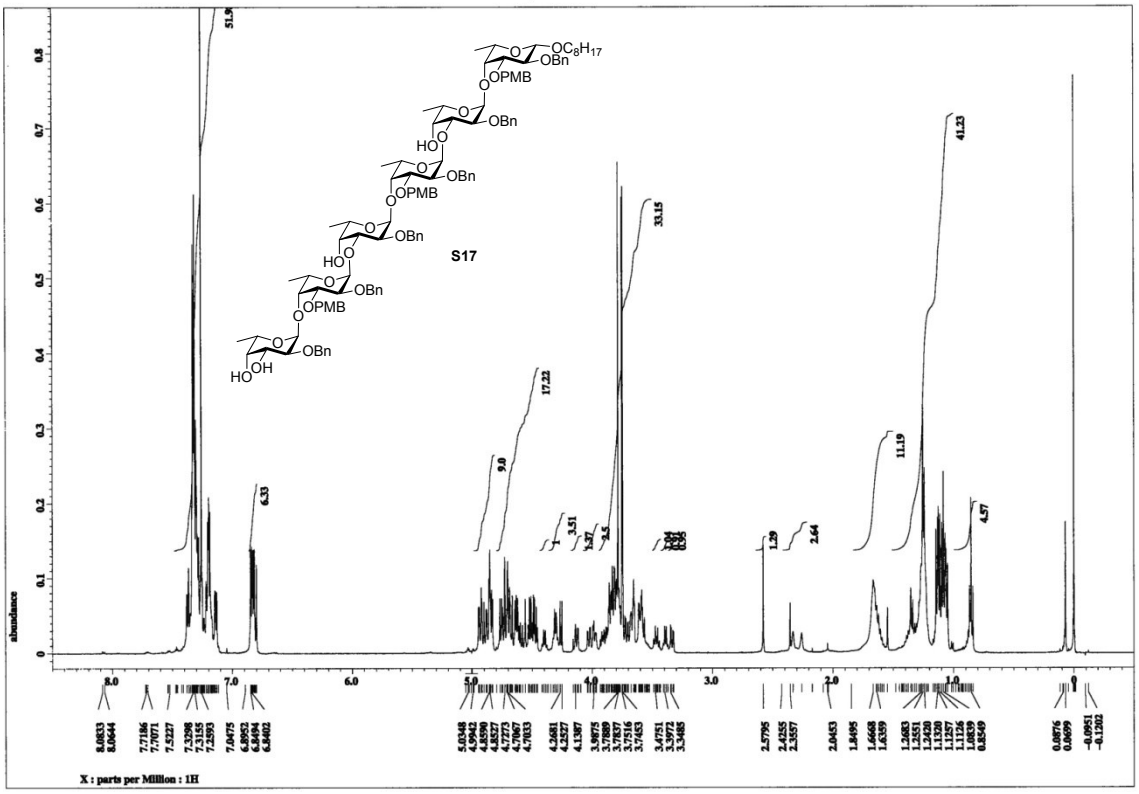


Figure S81 ^{1}H-NMR spectrum of **S17**

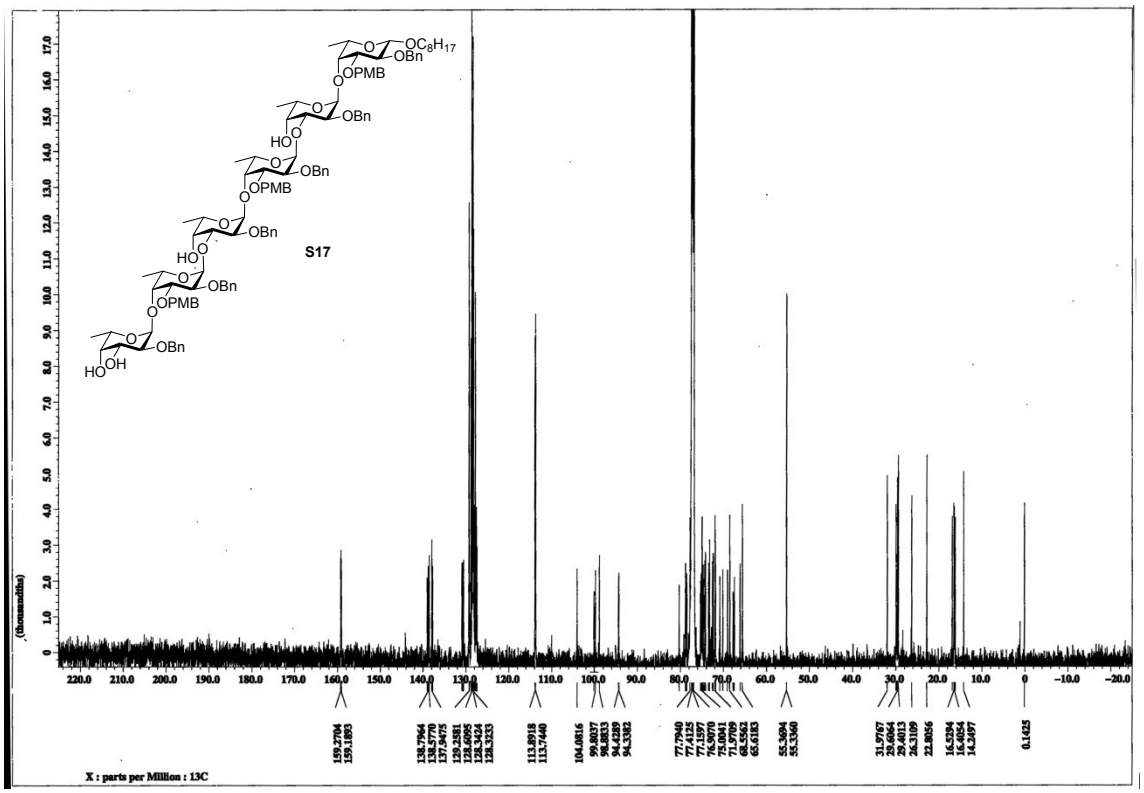


Figure S82 ^{13}C-NMR spectrum of **S17**

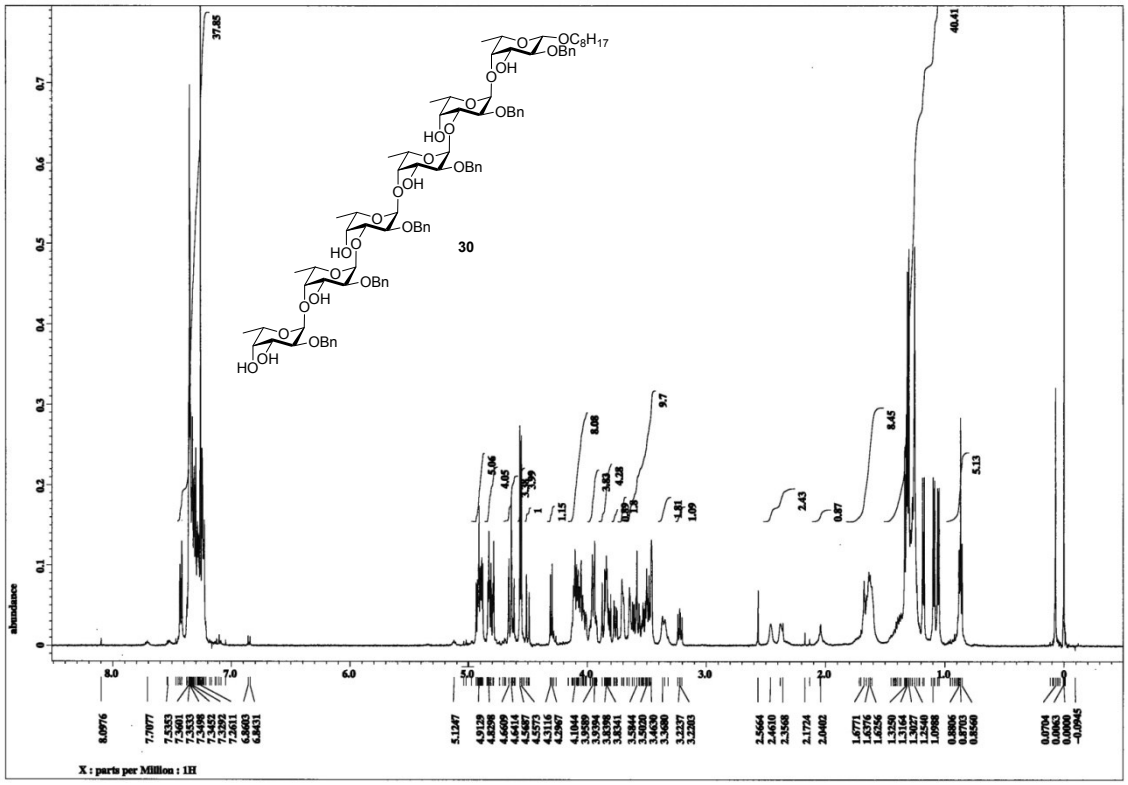


Figure S83 ^{1}H-NMR spectrum of **30**

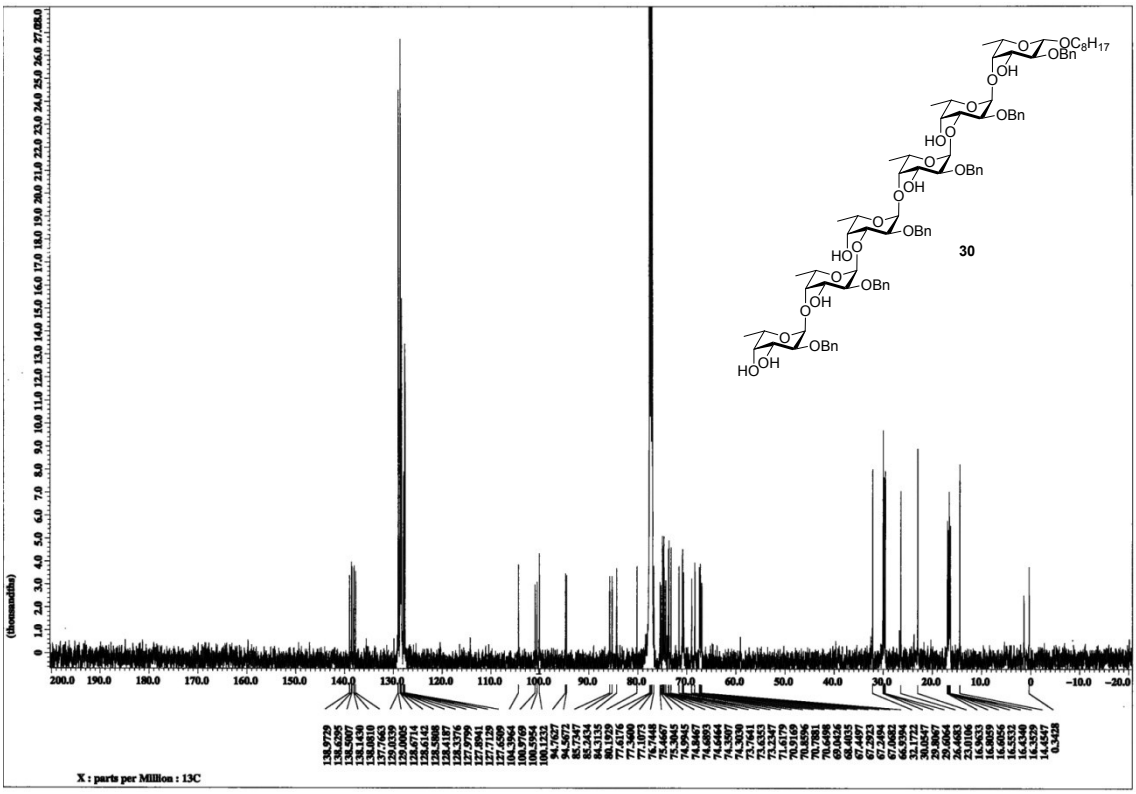


Figure S84 ^{13}C-NMR spectrum of **30**

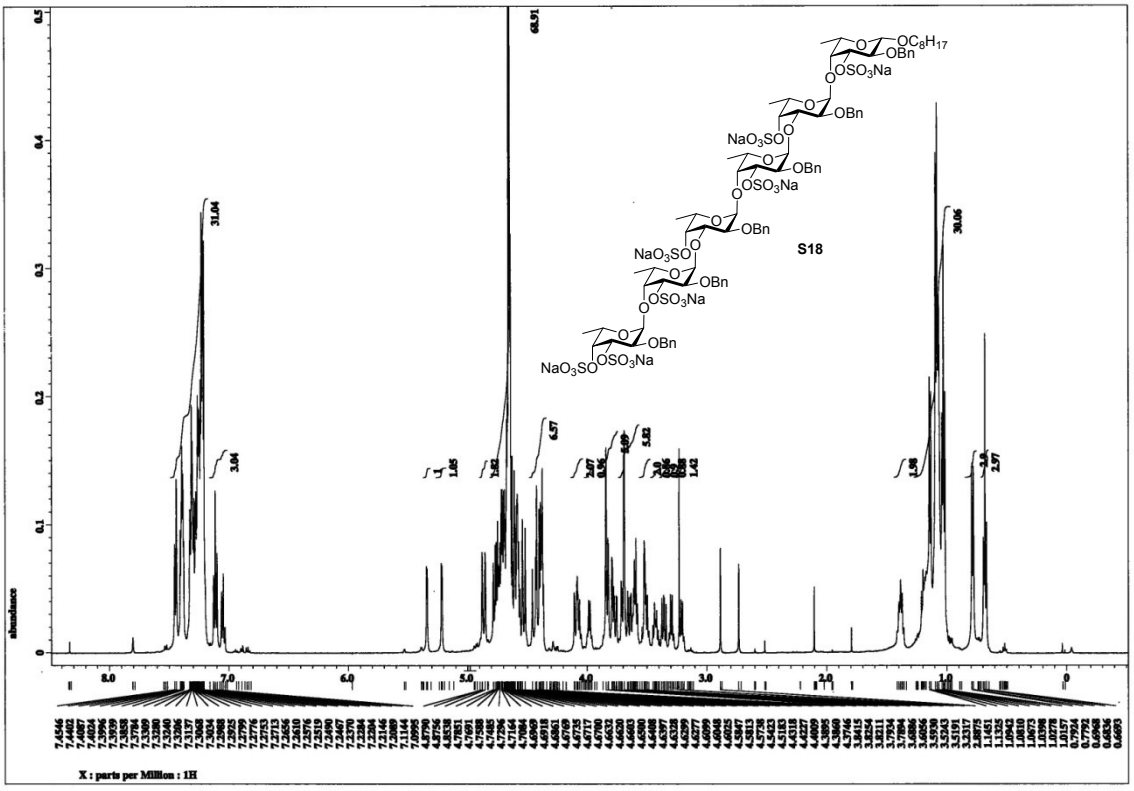


Figure S85 ^{1}H-NMR spectrum of **S18**

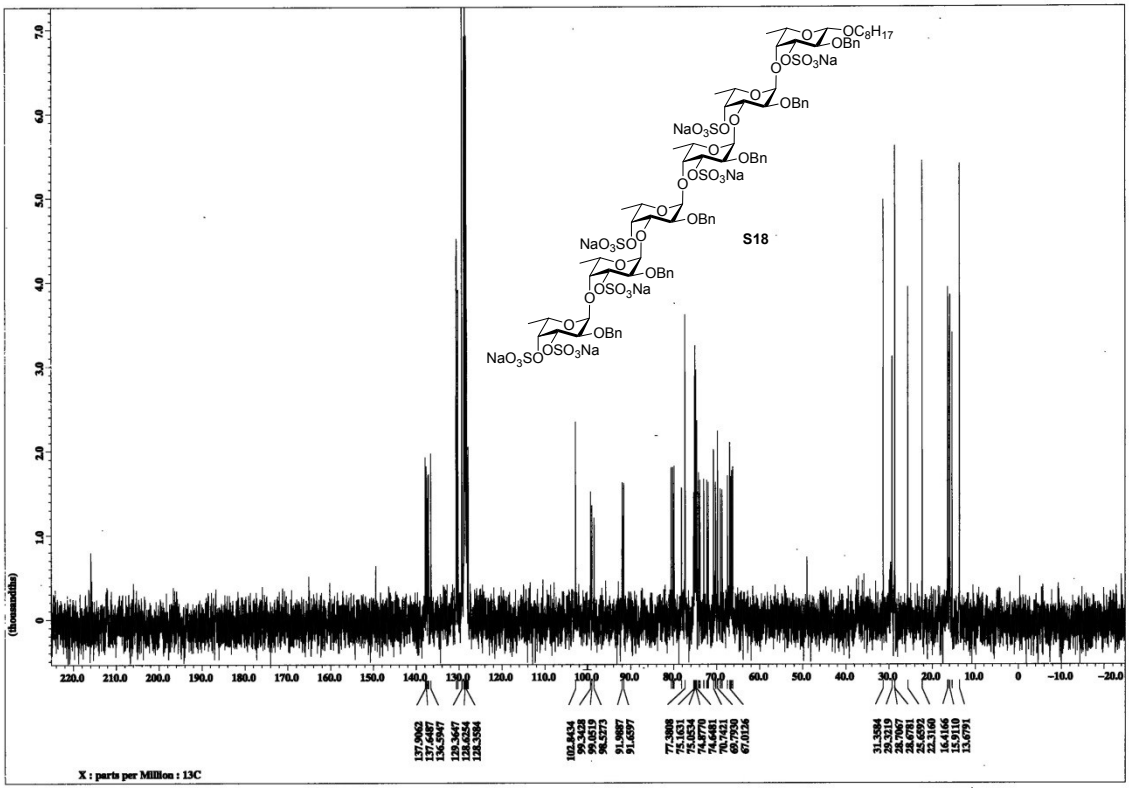


Figure S86 ^{13}C-NMR spectrum of **S18**

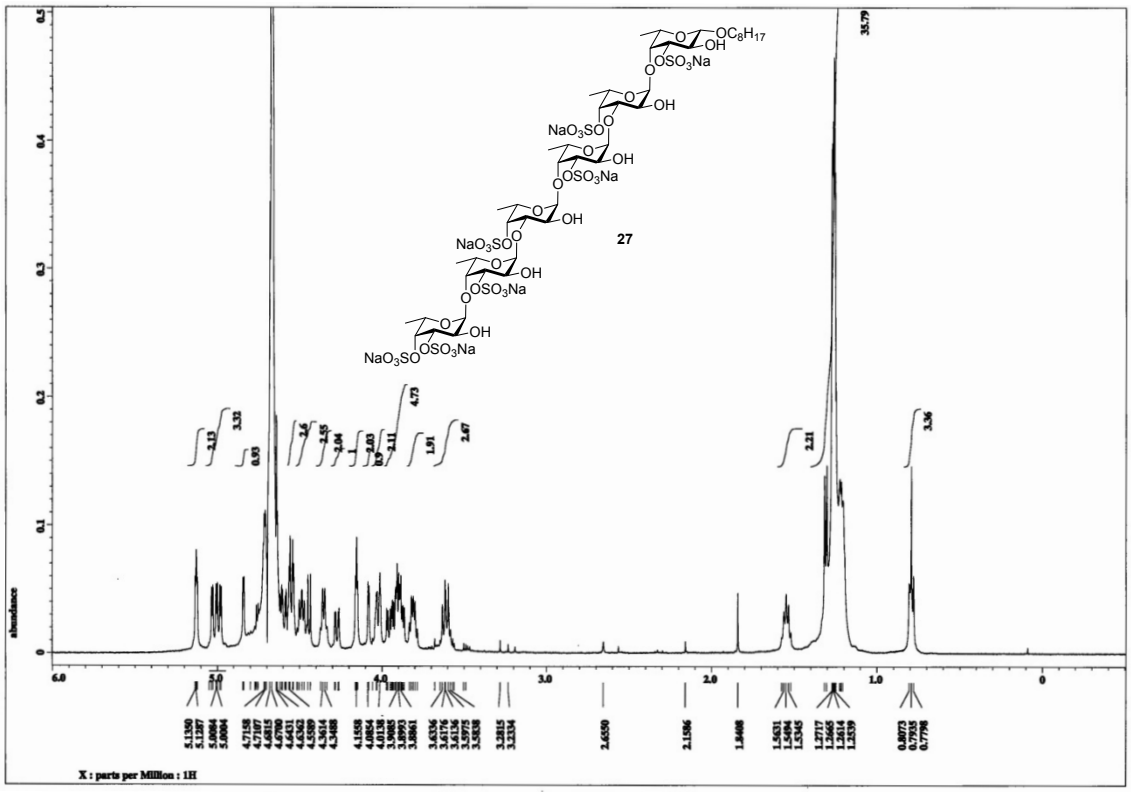


Figure S87 ^{1}H-NMR spectrum of **27**

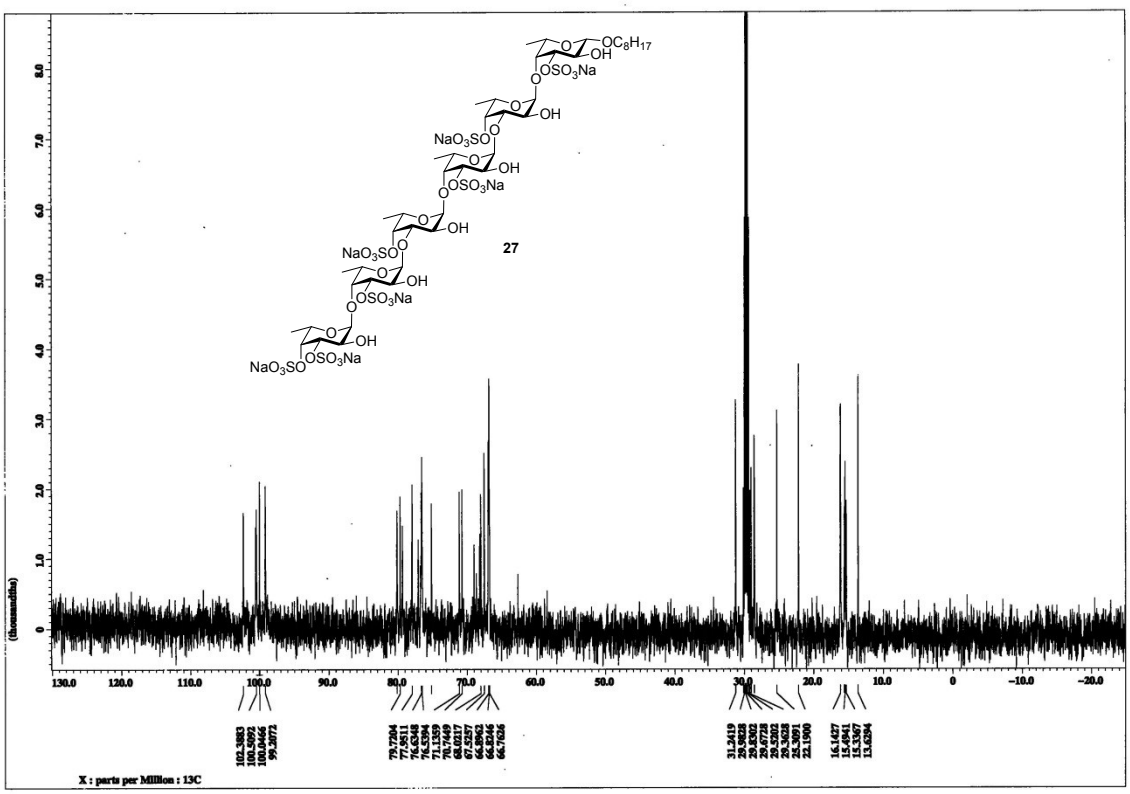


Figure S88 ^{13}C-NMR spectrum of **27**