Experimental Section

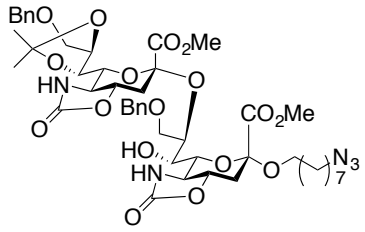
General Techniques

NMR spectra were recorded on a JEOL Model ECP-400 (400 MHz for 1H, 100 MHz for 13C) instrument in the indicated solvent. Chemical shifts are reported in units per million (ppm) relative to the signal for internal tetramethylsilane (δ 0 ppm for 1H) for solutions in $CDCl_3$. NMR spectral data are reported as follows: chloroform-d (7.26 ppm for 1H), D_2O (HOD (4.8654 ppm at 285 K, 4.7015 ppm at 303 K, 4.6201 ppm at 311 K, 4.3560 ppm at 339 K as internal standard using 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as external standard)) or $(CD_3)_2CO$ (215.9 ppm for ^{13}C) as internal standard for D_2O. Multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; sep, septet; m, multiplet; br, broad; and , J, coupling constants in Hertz. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer. Only the strongest and/or structurally important absorption is reported as the IR data in cm-1. All reactions were monitored by thin- layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light, visualized by p-anisaldehyde solution, ceric sulfate or 0.5% ninhydrin n-butanol solution. Merck silica gel 60 (0.063 – 0.200 mm) was used for column chromatography. ESI TOF Mass spectra were measured with Waters LCT PremierTM XE. HRMS (ESI-TOF) were calibrated with leucine enkephalin (SIGMA) as an internal standard. Gel permeation chromatography (GPC) for quantitative analysis were performed on a Japan Analytical Industry Model LC 605 (recycling preparative HPLC), with a Japan Analytical Industry Model RI-5 refractive index detector and a Japan Analytical Industry Model 310 ultra violet detector with polystylene gel column (JAIGEL- 1H, 20mm x 600mm) using chloroform as a solvent (3.5mL/min). Dry THF, dry CH_2Cl_2, dry MeCN, and dry toluene were obtained using a GlassContour solvent purification system.

Methyl (8-azidooctyl 5-amino-*5-N,4-O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-amino-9-*O*-benzyl-5*N*,4*O*-carbonyl-3,5-dideoxy-7,8-*O*-isopropylidene-D-glycero-α-D-galacto-2-nonulopyranosylonate)-D-glycero-α-D-galacto-2-nonulopyranosid)onate (8)

A mixture of methyl (phenyl 5-amino-9-*O*-benzyl-*5-N,*4-*O*-carbonyl-7,8-*O*-isopropylidene -3,5-dideoxy-2-thio-D-glycero-β-D-galacto-2-nonulopyranosid)onate (**8**) (210 mg, 0.396 mmol,) and methyl (8-azidooctyl 5-amino-9-*O*-benzyl-5-*N,*4-*O*-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosid) onate (**7**) (109 mg, 0.198 mmol), and pulverized activated MS-3A (200 mg) in dry CH_2Cl_2 (4.00 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 ˚C. *N*-iodosuccinimide (93.7 mg, 0.416 mmol) and a catalytic amount of trifluoromethanesulfonic acid (3.50 mL, 0.0397 mmol) was added to reaction mixture at -78 ˚C. After being stirred for 1.5 h with being allowed to -60 ˚C, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was chromatographed on silica gel with 98:2 chloroform-methanol and further purified by gel permeation chromatography (GPC) to give **8** (163 mg, 0.168 mmol, 84%, α only). The α/β ratios were determined by ^{1}H NMR analysis.

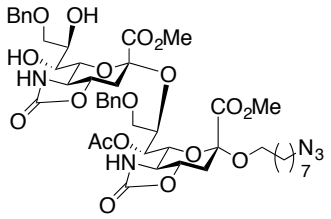
$[\alpha]_D^{23}$ -43.7 (c 1.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.35 (m, 10H, aromatic), 5.53 (br-s, 1H, N*H*), 5.36 (br-s, 1H, N*H*), 4.65 (d, 1H, Bn, *J* = 12.1 Hz), 4.60 (d, 1H, Bn, *J* = 12.1 Hz), 4.46-4.53 (m, 3H), 4.16-4.20 (m, 1H), 4.11 (dd, 1H, *J* = 2.4, 6.8 Hz), 3.94-4.04 (m, 3H), 3.79-3.94 (m, 9H), 3.77 (s, 3H), 3.65 (m, 1H), 3.57 (dd, 1H, *J* = 10.6, 11.1 Hz), 3.49 (dd, 1H, *J* = 10.1, 10.6 Hz), 3.19-3.26 (m, 4H), 3.03 (d, 1H, *J* = 6.3 Hz), 2.96 (dd, 1H, *J* = 3.4, 12.1 Hz), 2.91 (dd, 1H, *J* = 3.9, 12.1 Hz), 2.19 (dd, 1H, *J* = 12.1, 12.6 Hz), 2.02 (dd, 1H, *J* = 12.1, 12.6 Hz), 1.38 (s 3H), 1.63 (s 3H), 1.55-1.60 (m, 4H), 1.29 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 168.0, 159.8, 159.8, 137.9, 137.6, 128.6, 128.5, 128.0, 127.8, 127.7, 109.3, (101.8, 100.3, anomeric), 76.6, 76.3, 76.0, 75.4, 75.2, 73.6, 73.6, 7.09, 70.4, 68.5, 65.1, 58.4, 58.2, 53.6, 52.8, 51.5, 37.4, 29.6, 29.3, 29.1, 28.8, 26.8, 26.7, 25.9, 24.9; IR (KBr) 3302, 2937, 2097, 1771, 1371, 1146, 1086, 754 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{47}H_{64}N_5O_{17}$ $[M+H]^+$ 970.4297, found 970.4298.



Methyl (8-azidooctyl 5-amino-5-*N*,4-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-amino-9-*O*-benzyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-D-glycero-α-D-galacto-2-nonulopyranosid)onate (9)

To a stirred solution **8** (70.4 mg, 0.0726 mmol) in THF (725 mL) and H_2O (150 mL) was added trifluoroacetic acid (580 mL) at room temperature. After being stirred at 40 ˚C for 1.5 h, the reaction mixture was poured into saturated aq. $NaHCO_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$, and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo.* The residue was chromatographed on silica gel with 97:3 chloroform-methanol to give **9** (42.8 mg, 0.0462 mmol, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.34 (m, 10H), 6.13 (br-s, 1H), 5.92 (br-s, 1H), 4.56 (s, 2H), 4.51 (s, 2H), 4.30-4.31 (m, 1H), 3.94-4.05 (m, 3H), 3.59-3.90 (m, 16H), 3.53 (dd, 1H, *J* = 9.2, 10.6 Hz), 3.48 (dd, 1H, *J* = 9.2, 9.7 Hz), 3.42 (d, 1H, *J* = 4.8 Hz), 3.19-3.26 (m, 4H), 2.96 (dd, 1H, *J* = 3.4, 12.1 Hz), 2.89 (dd, 1H, *J* = 3.9, 12.1 Hz), 2.21 (dd, 1H, *J*= 12.1, 12.6 Hz), 2.03 (dd, 1H, *J* = 12.1 Hz, 12.6 Hz), 1.50-1.61 (m, 4H), 1.23-1.34 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 168.6, 160.5, 160.2, 137.8, 137.6, 128.6, 128.0, 127.9, 127.8, 127.8, (100.5, 100.4, anomeric) 77.9, 77.8, 77.7, 76.2, 73.7, 71.9, 71.7, 71.4, 71.2, 70.2, 69.9, 65.3, 58.7, 57.5, 53.7, 53.6, 53.0, 51.5, 37.4, 29.8, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 28.9, 26.7, 26.1, 26.1, 25.9; IR (KBr) 3398, 2930, 2097, 1749, 1366, 1074, 737 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{44}H_{60}N_5O_{17}$ $[M+H]^+$ 930.3984, found 930.3991.

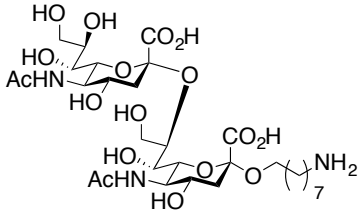


8-aminooctyl 5-acetamido-8-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid (11)

To a stirred solution of **9** (21.7 mg, 0.0234 mmol) in 1,4-dioxane (1.00 mL) and H_2O (1.00 mL) was added LiOH•H_2O (30.0 mg) at room temperature. After being stirred at 80 ˚C for 40 h, the reaction mixture was evaporated *in vacuo*. The residue was purified by reverse–phase column chromatography (Bond Elut-C18). The residue was used for the next reaction. To a stirred solution of above residue in H_2O (2.00 mL) was add $NaHCO_3$ (50.0 mg) acetic anhydride (20.0 mL) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was evaporated *in vacuo*. The residue was used for the next reaction without further purification. To a stirred solution of the residue in methanol (2.00 mL) was add NaOMe (20.0 mg) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was evaporated *in vacuo*. The residue was purified by revese–phase column chromatography (Bond Elut-C18). The residue was used for the next reaction. To a stirred solution of above residue in methanol (1.00 mL) and H_2O (1.00 mL) was added

$Pd(OH)_2$ (40.0 mg). The reaction mixture was hydrogenolyzed for 3 h under H_2 gas atmosphere. The reaction mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was purified by reverse–phase column chromatography (Bond Elut-C18) to **11** (12.1 mg, 0.0166 mmol, 4 steps 71%).

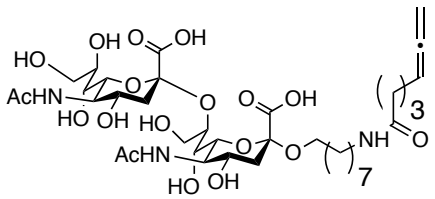
$[\alpha]_D^{26}$ +9.31 (c 1.41, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.09-4.17 (m, 2H), 3.49-3.70 (m,13H), 3.40 (dt, 1H, *J* = 6.8, 9.2 Hz), 2.97 (t, 2H, *J* = 7.7 Hz), 2.74 (dd, 1H, *J* = 4.8, 12.6 Hz), 2.62 (dd, 1H, *J* = 4.3, 12.6 Hz), 2.01 (s, H), 2.04 (s, H), 1.71 (dd, 1H, *J* = 12.6, 12.1 Hz), 1.51-1.65 (m, 5H), 1.31 (m, 8H); ^{13}C NMR (100 MHz, D_2O, Acetone-d_6) δ 175.7, 175.7, 174.1, 174.1, (102.0, 101.2, anomeric), 79.5, 74.9, 73.6, 73.5, 72.5, 70.5, 69.2, 68.7, 65.6, 63.6, 63.5, 62.5, 62.5, 53.3, 52.7, 52.7, 41.4, 40.3, 29.5, 28.7, 27.4, 26.1, 25.7, 23.1, 22.9; IR (KBr) 3436, 2930, 1603, 1437, 1038, 667 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{30}H_{54}N_3O_{17}$ $[M+H]^+$ 728.3453, found 728.3455.



***N*-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonicacid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonicacid (3-12)**

To a stirred solution of 8-aminooctyl 5-acetamido-8-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid (**3-10**) (5.73 mg, 7.58 μmol, 1.00 eq.) in H_2O (500 μL) was added 2,5-dioxo pyrrolidin-1-yl 5,6-heptadienoate (**3-11**) (3.38 mg, 15.2 μmol, 2.00 eq.) in 1,4-dioxane (500 μL) at room temperature. After being stirred at the same temperature for 17 h, the reaction mixture was evaporated *in vacuo*. The residue was purified by reverse-phase column chromatography (Bond Elut-C18) to give *N*-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid (**3-12**) (5.00mg, 5.98 μmol, 79%).

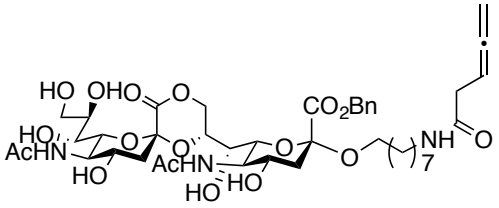
$[\alpha]_D^{21}$ +0.206 (*c* 0.225, MeOH); ^{1}H NMR (400 MHz, D_2O) δ 5.12 (tt, 1H, *J* = 6.6 Hz), 4.69 (dt, 2H, *J* = 6.6 Hz), 4.09-4.16 (m, 2H), 3.53-3.88 (m, 13H), 3.38 (dt, 1H, *J* = 7.2, 8.7 Hz), 3.07 (m, 2H,), 3.12 (m, 2H), 2.73 (dd, 1H, *J* = 4.4, 12.1 Hz), 2.60 (dd, 1H, $J_{3eq.,4}$ = 4.4, 12.1 Hz), 2.23 (m, 2H), 1.99 (s, 6H), 2.02 (s, 6H), 1.84-1.92 (m, 2H), 1.71 (t, 1H, *J* = 12.1 Hz), 1.50-1.58 (m, 3H), 1.10-1.26 (m, 10H); ^{13}C NMR (100 MHz, D_2O) δ 215.5, 208.4, 176.0, 175.1, 175.1, 173.4, 101.4, 100.6, 89.4, 78.7, 75.2, 774.2, 72.8, 71.8, 70.0, 68.5, 68.4, 68.0, 65.2, 62.8, 61.8, 52.6, 52.0, 40.6, 39.5, 35.3, 29.2, 28.9, 28.7, 28.6, 28.6, 27.2, 26.3, 25.5, 25.4, 25.0, 22.6, 22.5, 22.3; HRMS (ESI-TOF) Calcd. for $C_{37}H_{62}N_3O_{18}$ $[M+H]^+$ 836.4028, found 836.3994.



diSia-Bn ester monomer 16

To a stirred solution of **5** (137 mg, 0.164 mmol) in DMF (1.64 mL) was added BnBr (58.5 μL, 0.492 mmol), Cs_2CO_3 (214 mg, 0.656 mmol) and a catalytic amount of TBAI at room temperature. After being stirred at 60 ˚C for 24 h, the reaction mixture was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 90:10 chloroform:methanol to give diSia-Bn monomer **6** (93.8 mg, 0.103 mmol, 61%).

$[\alpha]_D^{21}$ -20.3 (*c* 1.61, $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD) δ 7.30-7.50 (m, 5H), 5.29 (d, 1H, *J* = 12.2 Hz), 5.19 (d, 1H, *J* = 12.2 Hz), 5.09 (dt, 1H, *J* = 6.8, 13.5 Hz), 4.87 (dd, 1H, *J* = 14.2 Hz), 4.63-4.68 (m, 2H), 4.59 (dd, 1H, *J* = 4.9, 12.2 Hz), 4.34 (dt, 1H, *J* = 5.4, 10.8 Hz), 4.23 (dt, 1H, *J* = 5.4, 11.7 Hz), 4.07 (dd, 1H, *J* = 7.3, 14.6 Hz), 3.45-3.89 (m, 13H), 3.14 (dd, 2H, *J* = 6.8, 7.3 Hz), 2.67 (dd, 1H, $J_{3,4}$ = 4.9, 12.7 Hz), 2.38 (dd, 1H, $J_{3,4}$ = 5.4, 13.2 Hz), 2.21 (dd, 2H, *J* = 7.4, 7.8 Hz), 1.90-2.15 (m, 8H), 1.55-1.76 (m, 4H), 1.37-1.55 (m, 4H), 1.27-1.35 (m, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ 210.9, 176.6, 176.3, 175.8, 170.4, 168.6, 137.7, 135.1, 132.8, 131.2, 130.6, 130.5x2, 130.4x2, (101.5, 98.3, anomeric), 90.7, 75.8, 75.3, 75.2, 73.3, 72.9, 72.5, 70.6, 70.4, 69.5, 69.4, 69.1x2, 66.3, 65.9, 54.6, 54.3, 42.9, 42.6, 41.3, 41.2, 37.2, 31.5, 31.2, 31.1, 29.6, 28.7, 27.8, 27.7, 27.3, 23.7, 23.4; IR (KBr) 3272, 2931, 1742, 1638, 1557, 1456, 1375, 1297, 1182, 1125, 1040, 700, 613 (cm^{-1}); HRMS (ESI-TOF) Calcd. for $C_{44}H_{66}N_3O_{17}$ $[M+H]^+$ 908.4392, found 908.4419.



Polymrization of the lactone monomer 16 to 17a and 17b

Bis(1,5-cyclooctadiene)nickel (0.1 M solution of toluene), 10-azido-3-trifluoroacetyl-1- decene (**14**) (0.1 M solution of toluene) and **Monomer** (1.00 eq.) in **solvent** were placed under a nitrogen atmosphere in a test tube equipped with a three way tap and a magnetic stirrer bar. The mixture was stirred at room temperature for **reaction time**. After complete conversion of the monomer (monitored by TLC analysis), the solution was precipitated with **solvent** and concentrated *in vacuo* to give **Polymer**.

20 mer 17a

According to the general procedure 2 with the following amounts: Bis(1,5-cyclooctadiene) nickel (41.2 μL, 4.12 μmol, 0.0500 eq.), 10-azido-3-trifluoroacetyl-1-decene (**14**) (41.2 μL, 4.96 μmol, 0.0600 eq.) was added a solution of diSia-Bn monomer (**16**) (75.0 mg, 82.6 μmol, 1.00 eq.) in MeOH (500 μL) at room temperature for 3 days to give

azido-poly-disia-Bn ester 20 mer **17a** (73.1 mg, 97%).

^{1}H NMR (400 MHz, CD_3OD) δ 7.20-7.45 (m, 5H), 5.10-5.40 (m, 2H), 4.50-4.67 (br-m), 4.20-4.40 (br-m, 1H), 4.00-4.12 (dt, 1H, *J* = 5.4, 11.7 Hz), 3.40-3.95 (br-m, 11H), 3.00-3.40 (br-m, 4H), 2.47-2.79 (br-m, 2H, H-3eq., H-3'eq.), 1.80-2.46 (br-m, 10H), 1.03-1.80 (br-m, aliphatic).; IR (KBr) 3442, 2095, 1640, 611 (cm^{-1}).

50 mer 17b

According to the general procedure 2 with the following amounts: Bis(1,5-cyclooctadiene) nickel (13.0 μL, 1.30 μmol, 0.0200 eq.), 10-azido-3-trifluoroacetyl-1-decene (**14**) (13.0 μL, 1.56 μmol, 0.0240 eq.) was added a solution of diSia-Bn monomer **16** (59.0 mg, 65.0 μmol, 1.00 eq.) in MeOH (500 μL) at room temperature for 3 days to give azido-poly-disia-Bn ester 50 mer **17b** (52.3 mg, 89%).

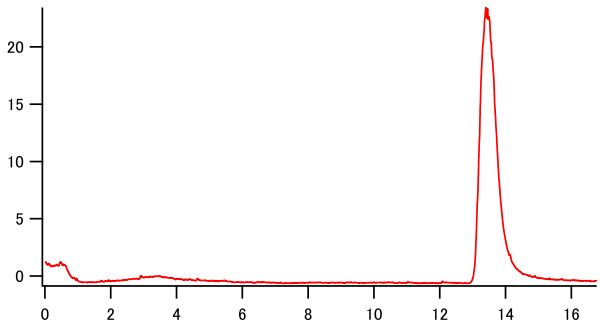
^{1}H NMR (400 MHz, CD_3OD) δ 7.15-7.42 (m, 5H, aromatic), 5.10-5.40 (m, 2H), 4.45-4.70 (br-m), 4.18-4.40 (br-m, 1H), 4.00-4.15 (br-m, 1H), 3.42-3.97 (br-m, 11H), 3.00-3.40 (br-m, 4H), 2.47-2.79 (br-m, 2H,), 1.03-2.46 (br-m, H-3ax., H-3'ax., Acx2, NHC(O)CH_2, aliphatic); IR (KBr) 3291, 2108, 1743m 1641, 1559, 1126, 1072, 1038 (cm^{-1}).

Hirololysis of the Glycopolymers 17a and 17b

20 mer 3a

To a stirred solution of azido-poly-disia-Bn ester 20 mer **17a** (24.3 mg, 1.34 μmol, 1.00 eq.) in H_2O (500 μL) and 1,4-dioxane (500 μL) was added LiOH・H_2O (0.561 mg, 13.4 mmol, 10.0 eq.) at room temperature. After being stirred at 60 ˚C for 1 day, the reaction mixture was evaporated *in vacuo*. The residue was purified with PD-10 to give 20mer **3a** (22.0 mg, quant.). DP and PDI of the purified polymer **17a** were estimated by a size-exclusion chromatography (SEC: TSKgel-α2500 and TSKgel-α3000) eluted with 0.1% CHOOH in H_2O solution to be 26 and 1.09, respectively. Mn was determiend relative to a PEG standard samples

^{1}H NMR (400 MHz, D_2O) δ 5.00-5.30 (br-s, 0.7 H), 3.88-4.20 (br-m, 2H, H-8, H-9a), 3.40-3.90 (br-m, 14H, H-4, H-5, H-6, H-7, H-9b, H-4', H-5', H-6', H-7', H-8', H-9'x2, OCH_2x2), 3.30 (br-s, 1H, OCH_2CH_2), 2.90-3.10 (br-s, 1H, OCH_2CH_2), 2.44-2.70 (br-m, H-3eq., H-3'eq.), 1.70-2.20 (br-m, 10H, H-3ax., H-3'ax., Acx2, NHC(O)CH_2), 0.95-1.70 (br-m, aliphatic)

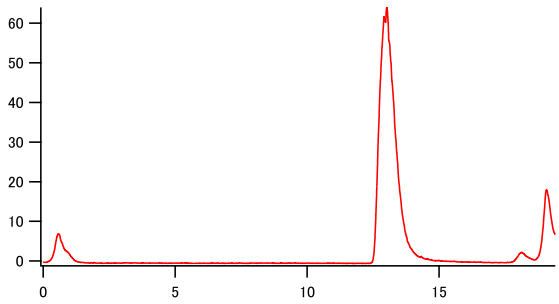


GPC-HPLC chart of **3a**

50 mer 3-29c

To a stirred solution of azido-poly-disia-Bn ester 50 mer **17b** (17.3 mg, 0.381 μmol, 1.00 eq.) in H_2O (500 μL) and 1,4-dioxane (500 μL) was added LiOH・H_2O (0.160 mg, 3.81 μmol, 10.0 eq.) at room temperature. After being stirred at 60 ˚C for 1 day, the reaction mixture was evaporated *in vacuo*. The residue was purified with PD-10 to give azido-poly-*N*-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid 50mer **3b** (16.5 mg, quant.). DP and PDI of the purified polymer **17b** were estimated by a size-exclusion chromatography (SEC: TSKgel-α2500 and TSKgel-α3000) eluted with 0.1% CHOOH in H_2O solution to be 42 and 1.14, respectively. Mn was determiend relative to a PEG standard samples

^{1}H NMR (400 MHz, D_2O) δ 5.00-5.40 (br-s, 0.5 H), 3.90-4.20 (br-m, H-8, H-9a), 3.20-3.90 (br-m, 15H, H-4, H-5, H-6, H-7, H-9b, H-4', H-5', H-6', H-7', H-8', H-9'x2, OCH_2x2, OCH_2CH_2), 3.01 (br-s, OCH_2CH_2), 2.40-2.75 (br-m, 2H, H-3eq., H-3'eq.), 1.70-2.30 (br-m, 10H, H-3ax., H-3'ax., Acx2, $NHC(O)CH_2$), 0.90-1.70 (br-m, aliphatic).



GPC-HPLC chart of **3b**

Fluorescent labeling of the glycolymer 3

20 mer 1a

To a stirred solution of azido-poly-*N*-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid 20 mer **3-29b** (10.2 mg, 5.62 μmol, 1.00 eq.) and TAMRA-alkyne (0.627 mg, 1.12 μmol, 2.00 eq.) in saturated aq. $NaHCO_3$ (500 μL) was added a catalytic amount of 0.5 M aqueous $CuSO_4$ and 0.5 M aqueous Na ascorbate at room temperature. After being stirred at the same temperature for 1 day, the reaction mixture was evaporated *in vacuo*. The residue was purified with PD-10 to give TAMRA-poly-*N*-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonicacid)-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid 20 mer **3-30b** (10.3 mg, quant.).

^{1}H NMR (400 MHz, D_2O) δ 8.34 (s, aromatic), 4.90-5.10 (br-s), 3.90-4.10 (br-m, 2H, H-8, H-9a), 2.80-3.83 (br-m, 19H, H-4, H-5, H-6, H-7, H-9b, H-3', H-4', H-5', H-6', H-7', H-8', H-9'x2, OCH_2, OCH_2CH_2, $NHCH_2$), 2.40-2.70 (br-m, 2H, H-3eq., H-3'eq.), 0.80-2.20 (br-m, H-3ax., H-3'ax., Acx2, aliphatic); IR (KBr) 3437, 1634, 1361, 1121, 837, 769, 669, 620 (cm^{-1}); HRMS

50 mer 1b

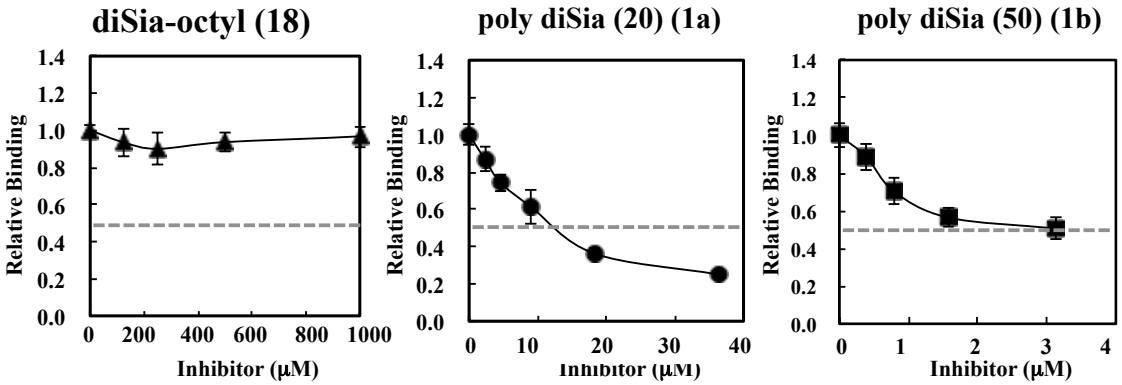
To a stirred solution of azido-poly-*N*-5,6-heptadienylcarbonylaminooctyl 5-acetamido-8-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D-galacto-2-

nonulopyranosylonic acid 50 mer **3-29c** (9.7 mg, 0.214 μmol, 1.00 eq.) and TAMRA-alkyne (0.239 mg, 4.27 μmol, 2.00 eq.) in saturated aq. $NaHCO_3$ (500 μL) was added a catalytic amount of 0.5 M aqueous $CuSO_4$ and 0.5 M aqueous Na ascorbate at room temperature. After being stirred at the same temperature for 1 day, the reaction mixture was evaporated *in vacuo*. The residue was purified with PD-10 to give TAMRA-poly-*N*-5,6-heptadienylcarbonyl-aminooctyl 5-acetamido-8-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-3,5-dideoxy-D-glycero-α-D- galacto-2-nonulopyranosylonic acid 50 mer **3-30c** (10.0 mg, quant.).

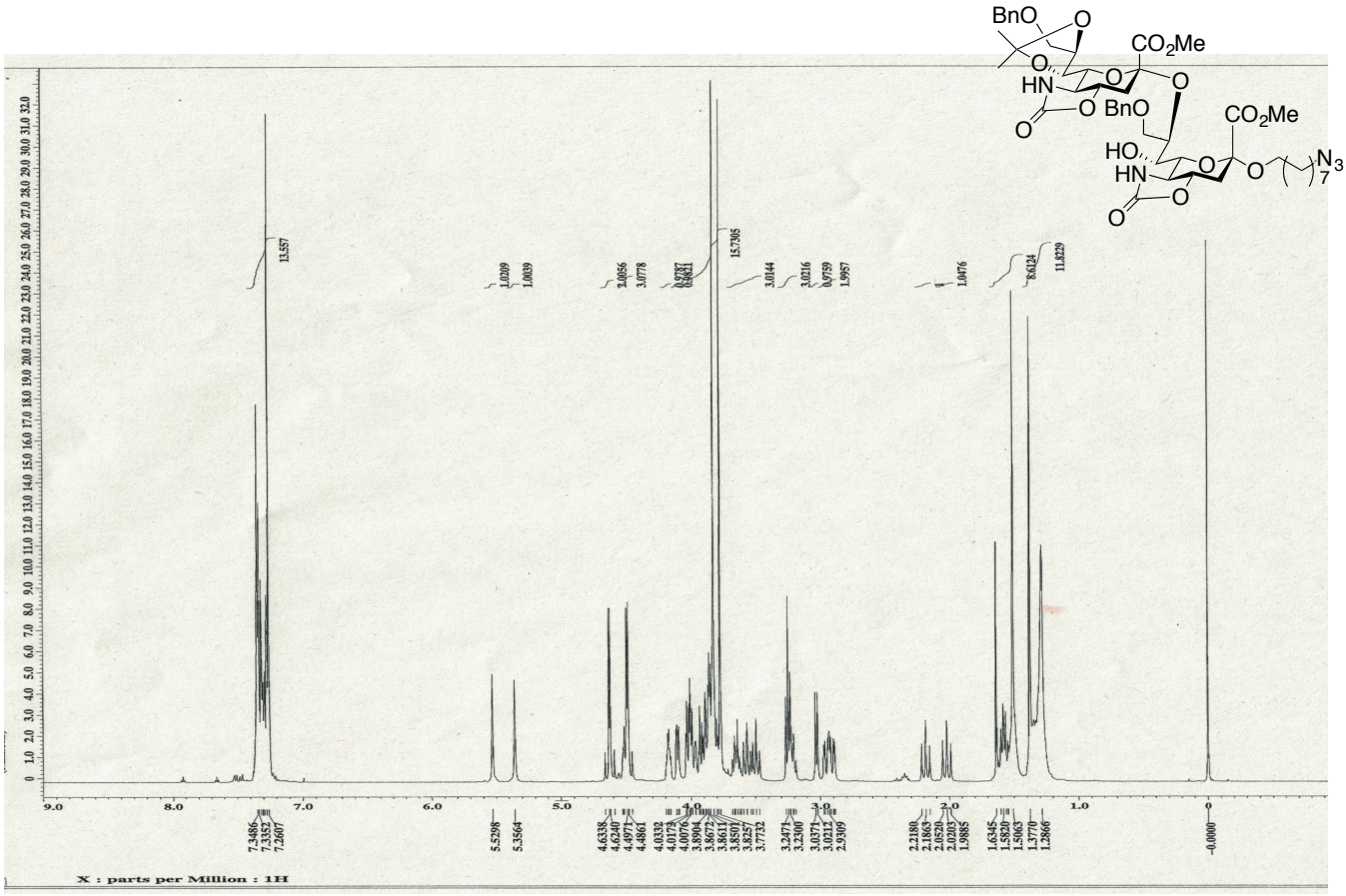
^{1}H NMR (400 MHz, D_2O) δ 8.32 (br-s, 0.1 H, aromatic), 3.95-4.10 (br-m, 2H, H-8, H-9a), 3.20-3.90 (br-m, 17H, H-4, H-5, H-6, H-7, H-9b, H-3', H-4', H-5', H-6', H-7', H-8', H-9'x2, OCH_2, OCH_2CH_2), 2.90-3.10 (br-s, 2H, $NHCH_2$), 2.63 (br-dd, 1H, H-3eq. or H-3' eq., $J_{3,4}$ = 2.9 Hz, J_{gem} = 11.2 Hz), 1.70-2.20 (br-m, 10H, H-3ax., H-3'ax., Acx2, $NHC(O)CH_2$), 1.00-1.70 (br-m, aliphatic).

Dissociating effect of the fluorescent-labelled diSia polymers 1a and 1b and the diSia 18 on the Siglec-7-GD3 interaction

Fc chimaera containing the three N-terminal domains of siglec-7 were purified with Protein A–agarose from tissue culture supernatants of stably transfected CHO cells. 996 well plastic plates were incubated with GD3 in ethanol (30 pmol/well) and solution was dried up for incubation at 37°C for 2h. The immobilized GD3 was a target molecule for Siglec7. Prior to the binding assay, the Fc-chimaeras were complexed with an anti-human IgG+M+A antibody coupled to peroxidase (1:1000 dilution) in 0.1% BSA containing PBS (10 mM phosphate buffer, 150 mM NaCl (pH 7.2)) for 30 min at room temperature. A 50 µl aliquot of this mixture was added per well and incubated for 4 h at room temperature. After five washes with PBS containing 0.05% tween-20 (PBST), the diSia polymer (1a and 1b) or diSia (18) containing PBS or PBS was added to the plate and incubated for 1 h at room temperature. After washing with PBST, 100 µl of the substrate solution was added to the well (100 mM Tris-HCl (pH 6.8), 0.05% *o*-phenylenediamine, 0.006% H_2O_2) and the reaction was stopped by adding 100µl of 2N H_2SO_4. The amount of bound peroxidase was quantified by the measurement of absorbance 490 nm using a microplate reader.



Supplemental figure. Inhibition of the GD3-Siglec7 interaction in the presence or absence of inhibitors. The GD3-Siglec7 interaction was measured by the ELISA based method. The absorbance in the absence of inhibitors were set to 1.0. Disia-octyl (18), monoSia-octyl, polydiSia (20) (1a) and polydiSia (50) (1b) were used as inhibitors as indicated concentrations.The concentration that lead to 50% inhibition was defined as IC50.


BnO
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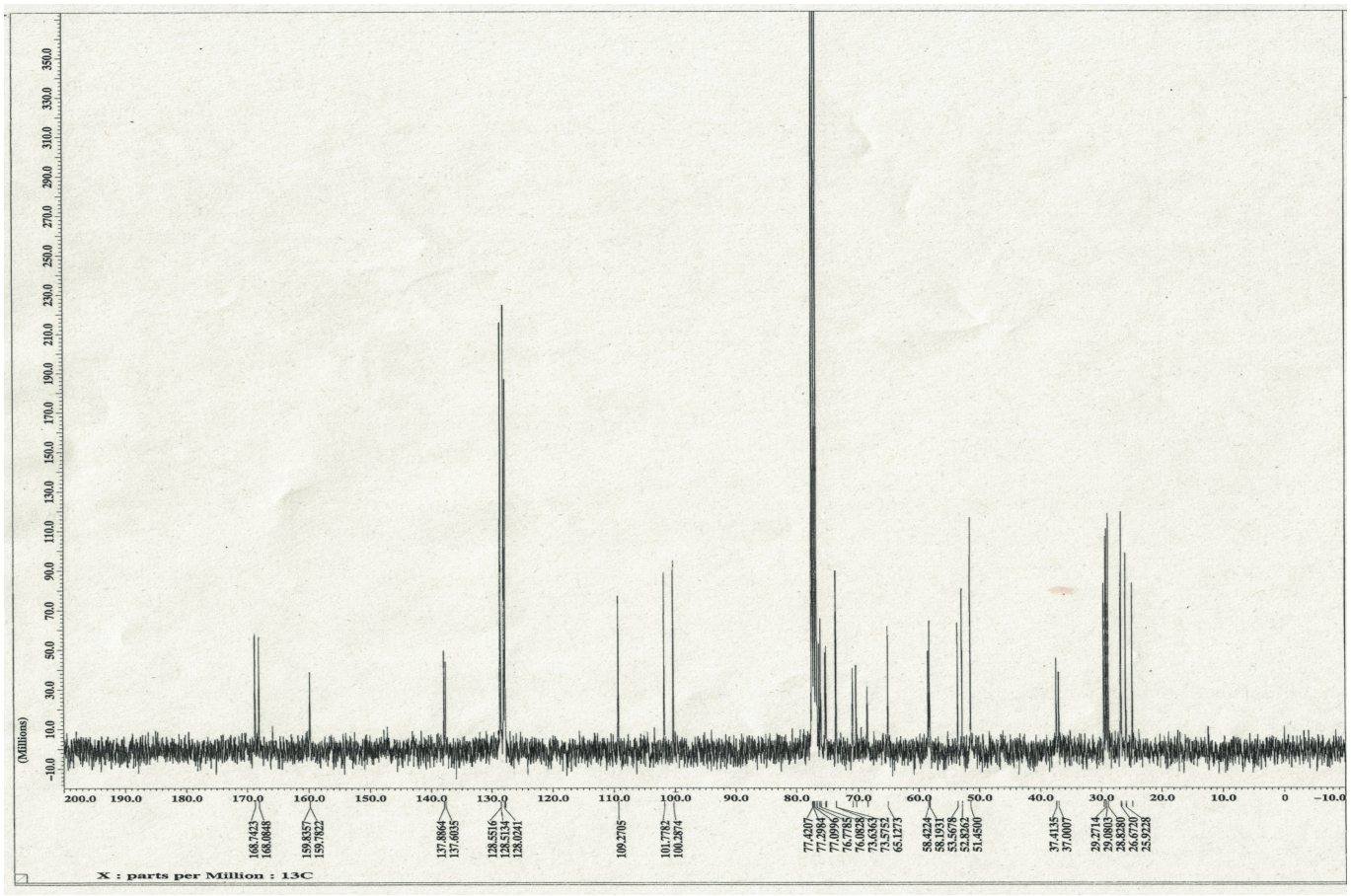
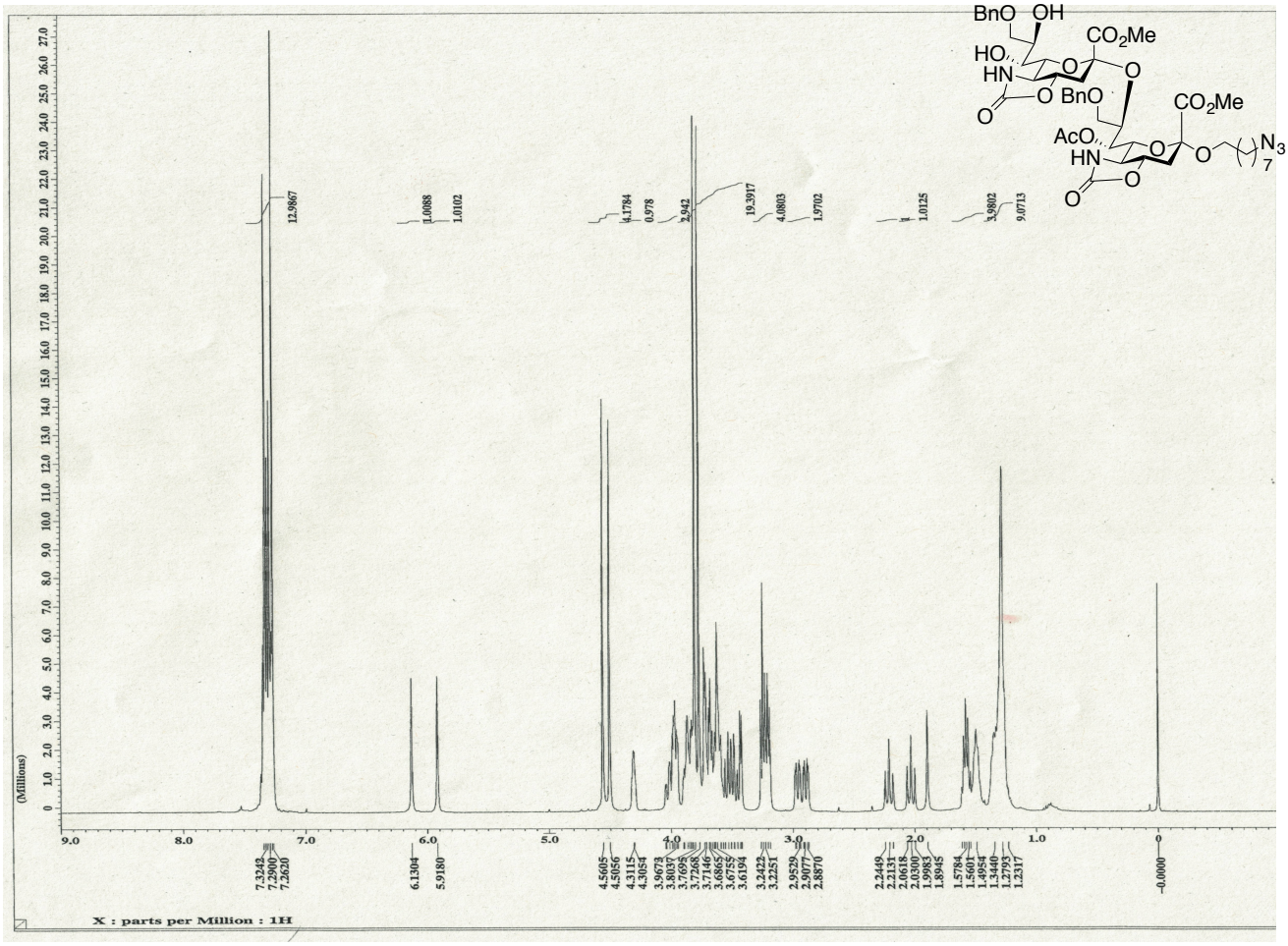
CO2Me
O
HN
O
O
BnO
CO2Me
HO
HN
O
O
N3
7
X : parts per Million : 1H


(Millions)
X : parts per Million : 13C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HO
HN
O
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CO2Me
AcO
HN
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1.0102
4.1784
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1.9702
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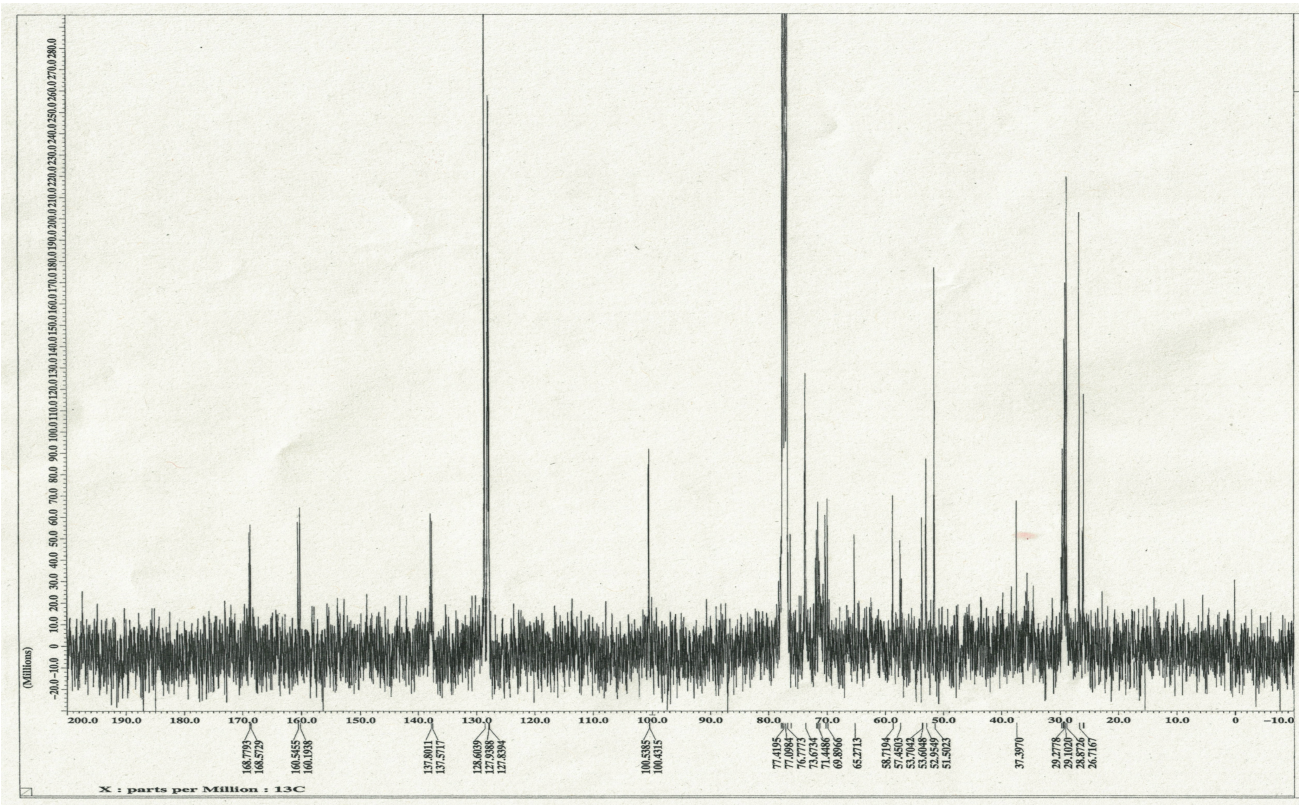
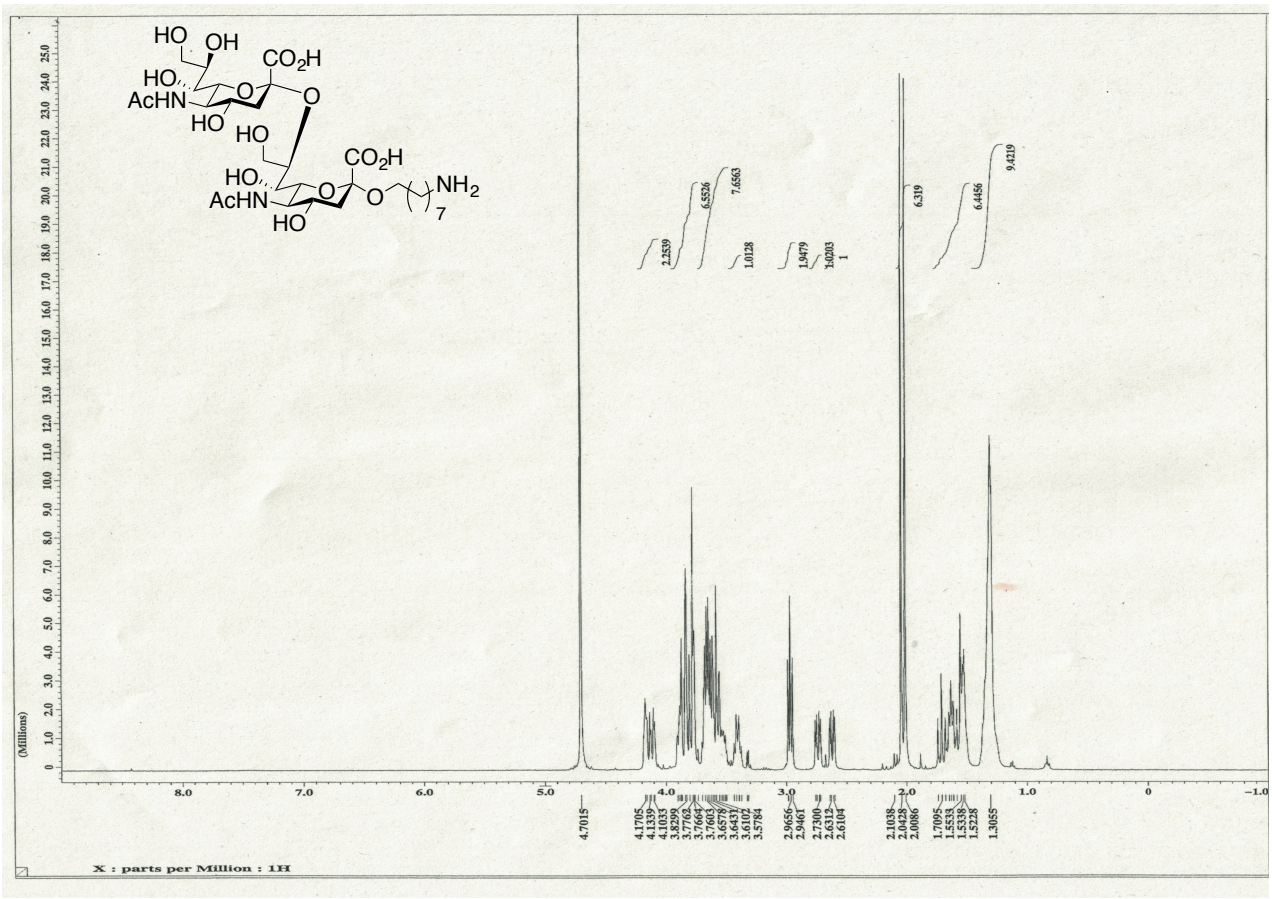
9.0713
(Millions)
X : parts per Million : 1H


(Millions)
X : parts per Million : 13C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CO2H
HO
AcHN
O
HO
HO
CO2H
HO
AcHN
O
O
NH2
7
HO
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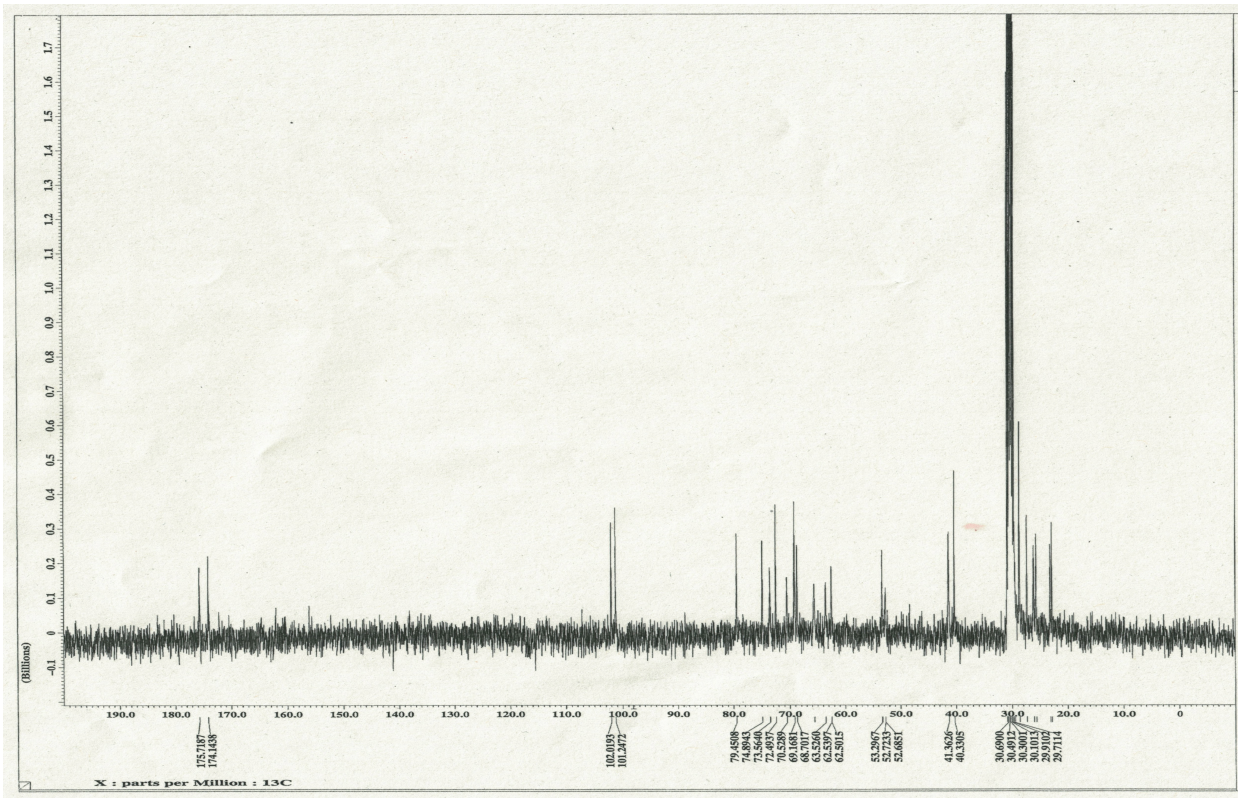
6.5526
7.6563
1.0128
1.9479
3.0203
1
6.319
6.4456
9.4219
(Millions)
X : parts per Million : 1H


(Billions)
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174.1438
102.0193
101.2472
79.4508
74.8943
73.5640
72.4937
70.5289
69.1483
68.7017
63.5260
62.5397
62.5015
53.2967
52.7233
52.6851
41.3626
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30.6900
30.4912
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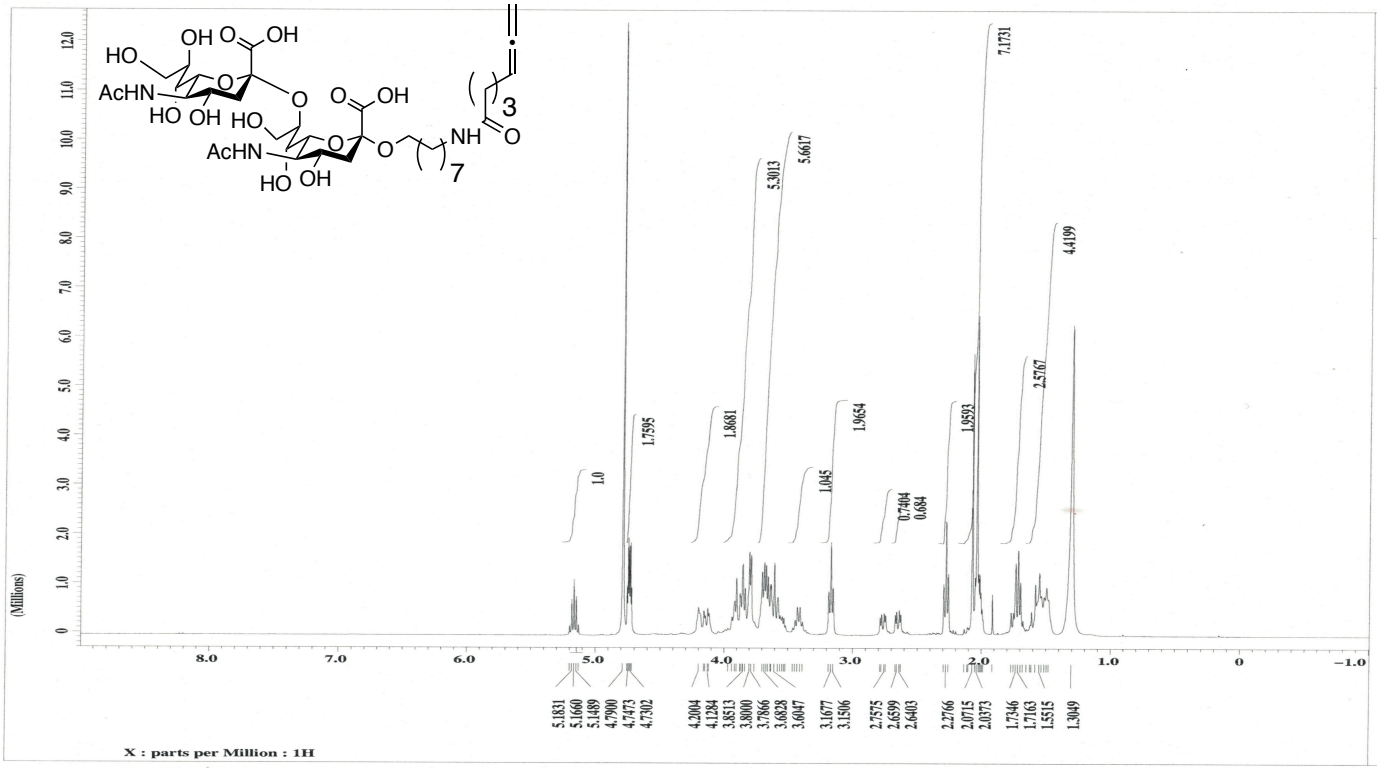
30.1011
29.9107
29.7114
X : parts per Million : 13C


(Millions)
X : parts per Million : 1H
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5.6617
4.4199
2.5767
1.8681
1.9654
1.9593
1.7595
1.045
0.7404
0.684
1.0
5.1831
5.1660
5.1489
4.7900
4.7473
4.7302
4.2004
4.1284
3.8513
3.8000
3.7866
3.6828
3.6047
3.1677
3.1506
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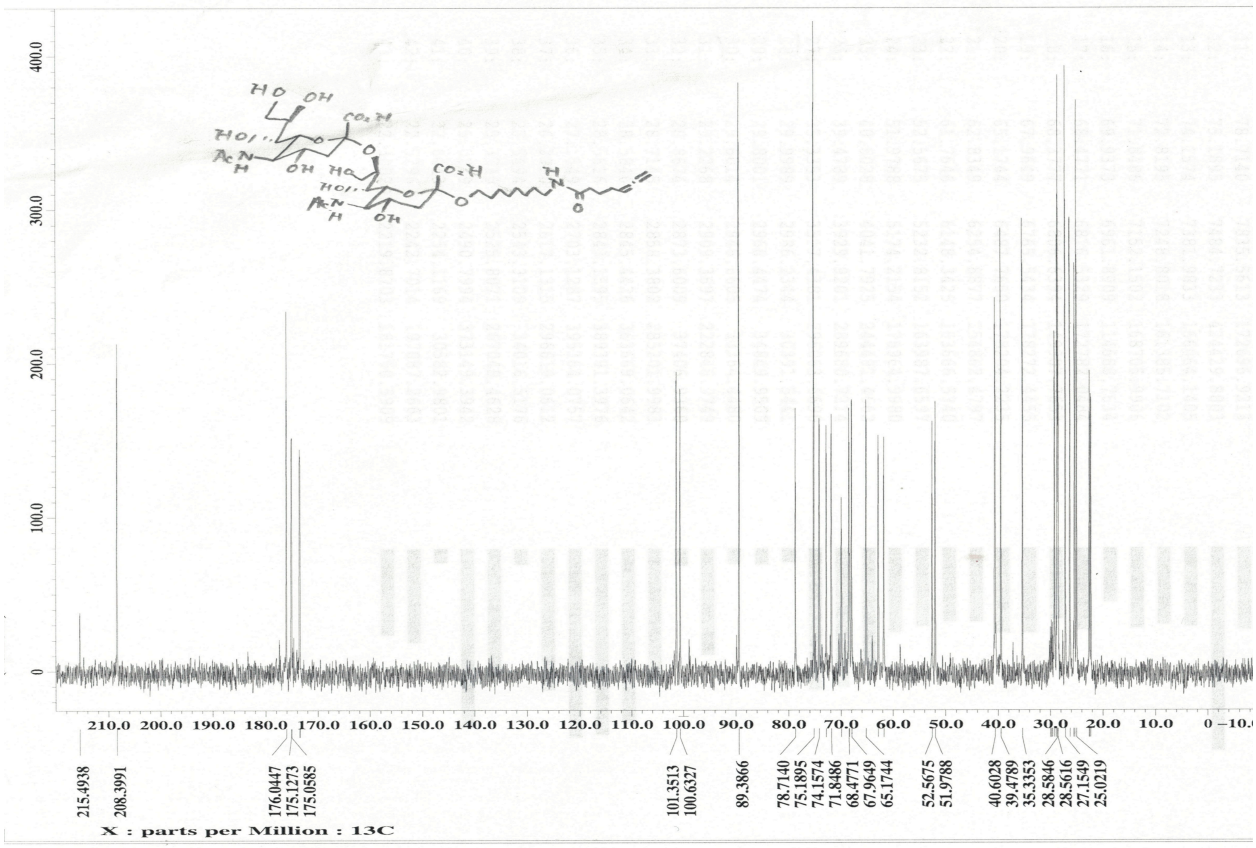
1.5515
1.3049


X : parts per Million : 13C
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175.1273
175.0585
101.3513
100.6327
89.3866
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75.1895
74.1574
71.8486
68.4771
67.9649
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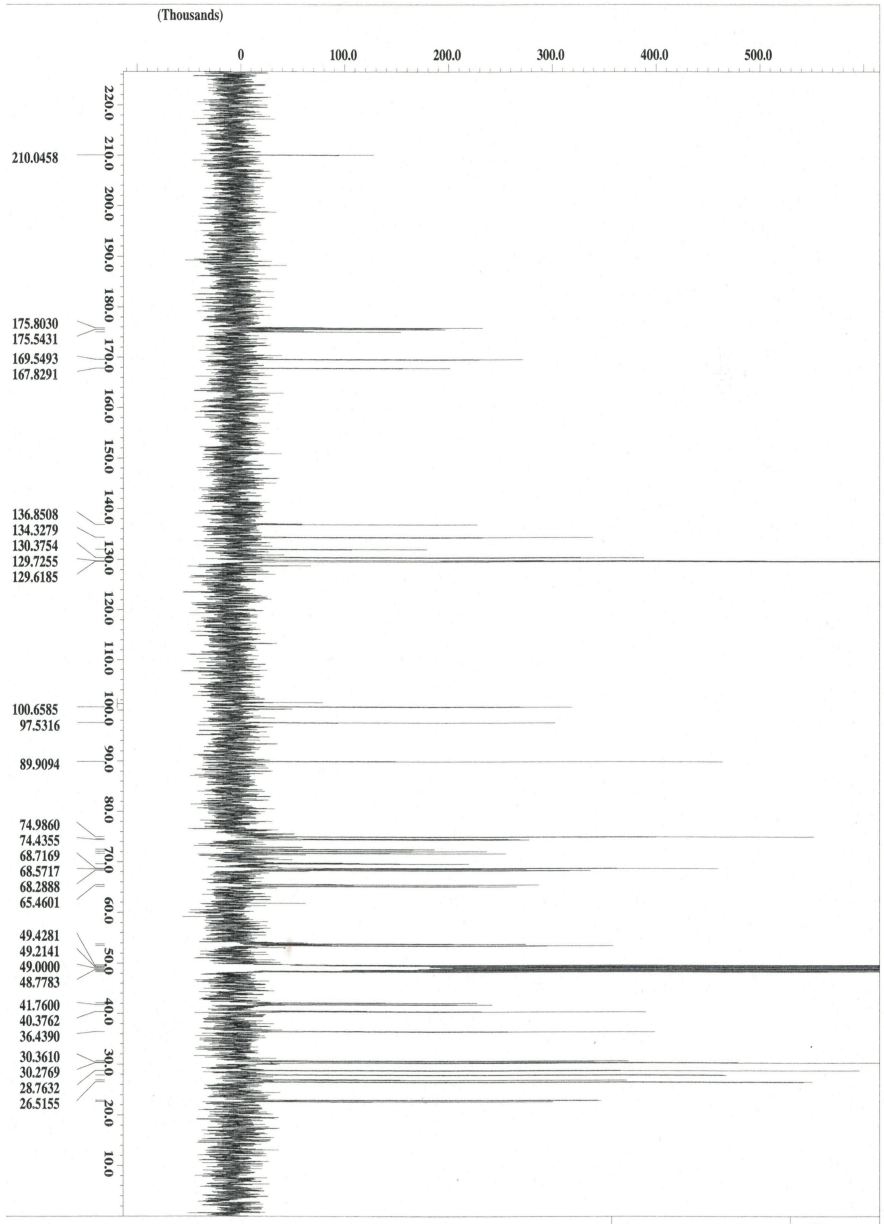
27.1549
25.0219


(Thousands)
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300.0
400.0
500.0
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175.5431
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136.8508
134.3279
130.3754
129.7255
129.6185
100.6585
97.5316
89.9094
74.9860
74.4355
68.7169
68.5717
68.2888
65.4601
49.4281
49.2141
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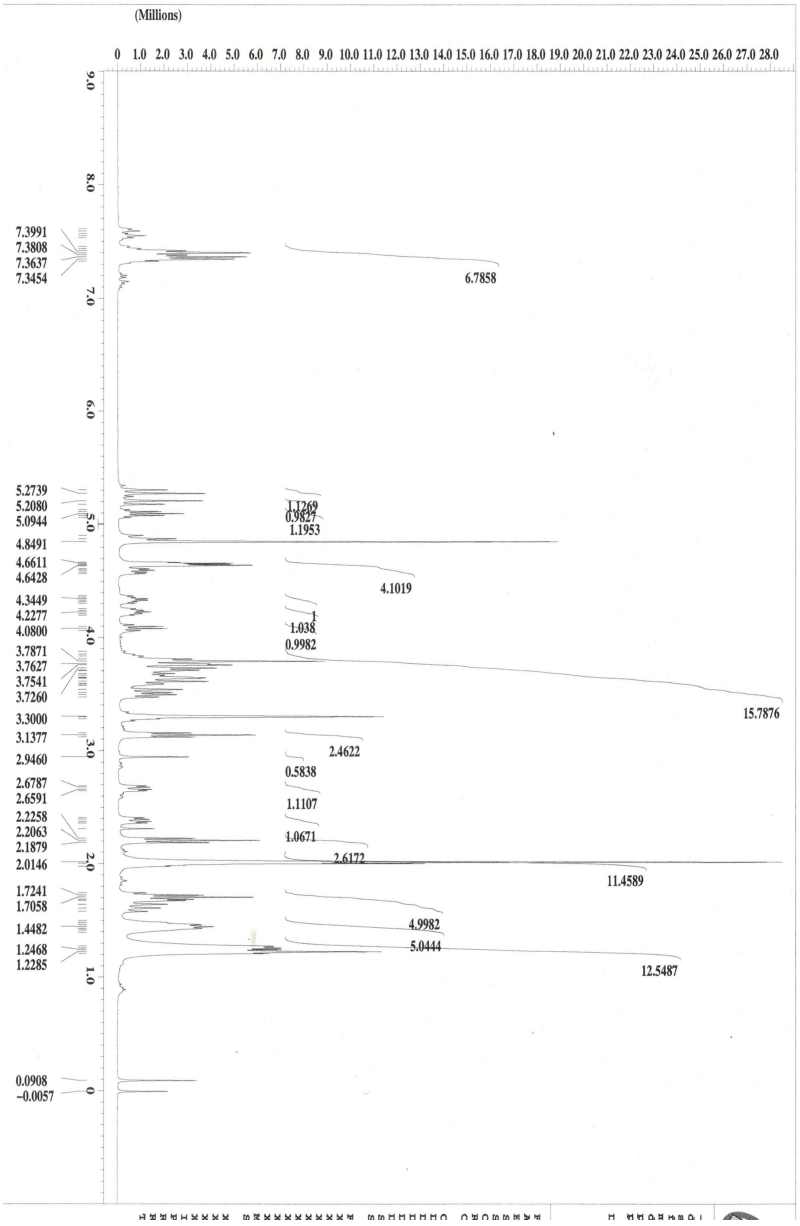
28.7632
26.5155


(Millions)
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7.3991
7.3808
7.3637
7.3454
6.7858
5.2739
5.2080
5.0944
1.1269
0.9827
1.1953
4.8491
4.6611
4.6428
4.1019
4.3449
4.2277
4.0800
1.038
0.9982
3.7871
3.7627
3.7541
3.7260
15.7876
3.3000
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1.7241
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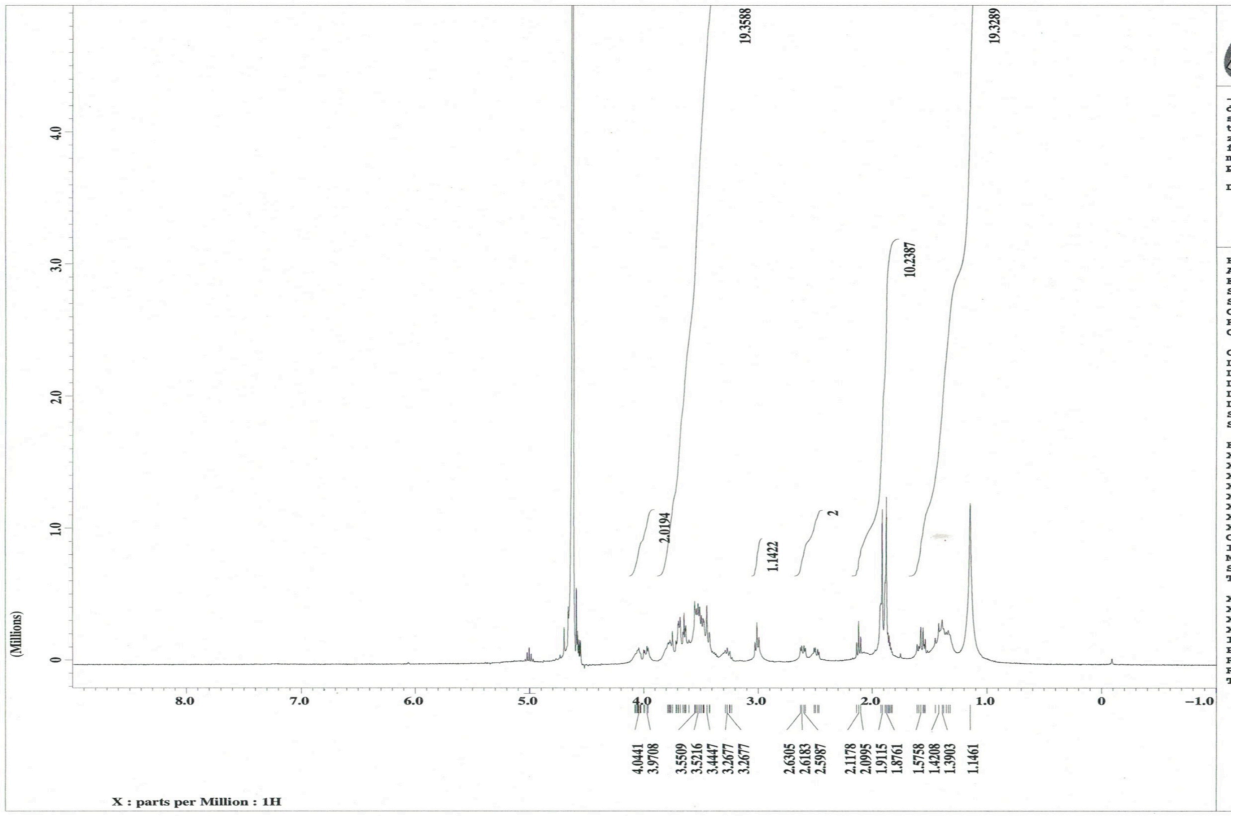
20 mer **3a**



50mer **3b**