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Supporting infomation

Convergent Stereoselective Synthesis of Multiple Sulfated Heparosan Dodecasaccahrides.

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Heptadecafluoro-undecyl 3-(3,4-dihydro-2H-pyran-2-yl)propanamide (3)

To a stirred solution of (3,4-dihydro-2H-pyran-2-yl)propanoic acid (27.1 mg, 174 μmol) in CH_2Cl_2 (3.48 mL) was added heptadecafluoro-undecylamine (124 mg, 261 μmol) and DCC (53.8 mg, 261 μmol, 1.50 eq.) at room temperature. After being stirred at the same temperature for 5 h, the reaction mixture was poured into saturated aq. NH_4Cl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with water and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatographed on silica gel (elution with toluene:acetone = 87:13) to give **3** (78.1 mg, 127 μmol, 73 %).: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (d, 1H, J = 5.8 Hz), 5.79 (br-s, 1H), 4.66-4.70 (m, 1H), 3.75-3.82 (m, 1H), 3.35 (q, 2H, J = 6.3 Hz), 2.28-2.42 (m, 2H), 1.52-2.20 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 143.4, 100.9, 74.2, 38.6, 32.5, 31.0, 28.5, 28.0, 21.0, 19.8; ^{19}F NMR (373 MHz, $CDCl_3$) δ -112.3, -119.9, -120.1, -120.9, -121.6, -124.3; IR (KBr) 3319, 2925, 1648, 1545, 1204, 1149, 1070, 658 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{19}H_{19}NO_2F_{17}$ $[M+H]^+$ 616.1144, found 616.1139.

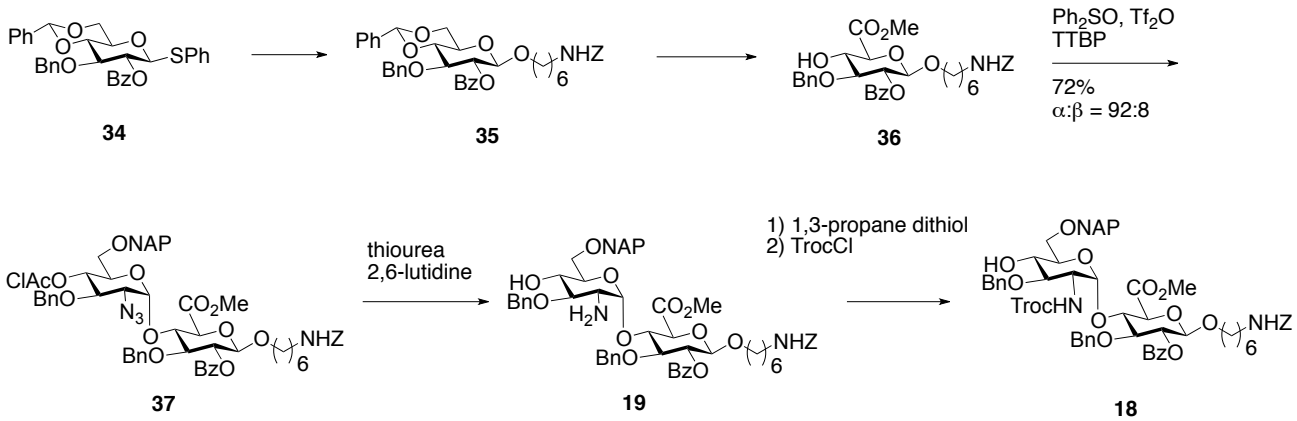
***N*-Hydroxysuccinimidyl (4-methoxyphenylcarbonylthio)acetate (4)**

To a stirred solution of mercaptoacetic acid (3.48 mL, 50.0 mmol, 1.00 eq.) in H_2O (50.0 mL) was added $NaHCO_3$ (6.30 g, 75.0 mmol, 1.50 eq.) at 0 ˚C. After being stirred at the same temperature for 10 min, the reaction mixture was added *p*-methoxy benzoic chloride (6.89 mL, 50.0 mmol) dropwise at 0 ˚C. After being stirred at same temperature for 10 min, the reaction mixture was added $NaHCO_3$ (6.30 g, 75.0 mmol) at 0 ˚C. After being stirred at room temperature, the reaction mixture was poured into ice-cooled 6 M HCl and filtered. The filtrate mixture was recrystalized from CH_2Cl_2-hexane. The residue was used for the next reaction without further purification. To a stirred solution of the residue (50.0 mmol, 1.00 eq.) in dry THF (500 mL) was added SuOH (6.90 g, 60.0 mmol, 1.20 eq.) and DIC (9.28 mL, 60.0 mmol, 1.20 eq.) at room temperature. After being stirred at the same temperature for 3 h, the reaction mixture was poured into saturated aq. NH_4Cl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with water and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was precipitated from ethyl acetate-hexane to give **4** (2.22 g, 6.50 mmol, 2 steps 13 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 2H, C, $J_{B,C}$ = 8.7 Hz), 6.95 (d, 2H, B, $J_{B,C}$ = 8.7 Hz), 4.16 (s, 2H,-D), 3.88 (s, 3H, A), 2.84 (s, 4H, E); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 168.7, 165.1, 164.5, 130.0, 128.5, 114.1, 55.7, 28.2, 25.7; IR (KBr) 2951, 1819, 1657, 1372, 1050, 816, 647 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{14}H_{13}NO_6S$ $[M+NH_4]^+$ 341.0807, found 341.0809.

Phenylthio (methyl 2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate (9)

To a stirred solution of phenylthio 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-gluco pyranoside (6.71 g, 12.1 mmol) in dry CH_2Cl_2 (120 mL) was added TFA (30.0 mL) and MeOH (12.0 mL) at 0 ˚C. After being stirred at the room temperature for 6 h, the reaction mixture was poured into ice-cooled saturated aq. $NaHCO_3$. 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 Na_2SO_4, filtered and evaporated *in vacuo*. The residue was used for the next reaction without further purification. To a stirred solution of the residue in CH_2Cl_2 (80.0 mL) and H_2O (40.0 mL) was added catalytic amount of TEMPO (476 mg, 3.02 mmol) and BAIB (8.77 g, 27.2 mmol) at 0 ˚C. After being stirred at room temperature for 6 h, the reaction 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 10% aq. $Na_2S_2O_3$ and brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was used for the next reaction without further purification. To a stirred solution of the residue in DMF (60.0 mL) was added MeI (1.89 mL, 30.4 mmol,) and K_2CO_3 (6.00 g, 100 mg/mL) at 0 ˚C. After being stirred at room temperature for 10 h, the reaction mixture was neutralized with MeOH and poured into ice-cooled 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$, and brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was precipitated from ethyl acetate-hexane to give **9** (4.25 g, 8.59 mmol, 3 steps 71%): $[\alpha]_D^{27}$ +18.8 (*c* 0.90, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-8.04 (m, 15H, aromatic), 5.25 (dd, 1H, *J* = 9.2, 9.7 Hz), 4.82 (d, 1H, *J* = 9.7 Hz), 4.76 (d, 1H, *J* = 11.6 Hz), 4.71 (d, 1H, *J* = 11.6 Hz), 4.03 (dd, 1H, *J* = 9.2, 9.7 Hz), 3.95 (d, 1H, *J* = 9.7 Hz), 3.86 (s, 3H), 3.73 (dd, 1H, *J* = 9.2, 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 165.1, 137.7, 133.4, 132.8, 132.6, 130.0, 129.8, 129.0, 128.5, 128.4, 128.2, 128.1, 127.8, (87.3 anomeric), 82.3, 77.7, 74.8, 72.0, 71.5, 53.0; IR (KBr) 3508, 2953, 2913, 1717, 1449, 1301, 1093, 740, 709 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{27}H_{27}O_7S$ $[M+H]^+$ 495.1476, found 495.1478.



***N*-Benzyloxycarbonyl-6-aminohexyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (35)**. A mixture of phenylthio 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**34**) (521 mg, 0.741 mmol), *N*-benzyloxycarbonyl-6-aminohexanol (280 mg, 1.11 mmol) and pulverized activated MS-4A (741 mg) in dry CH_2Cl_2 (7.41 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 -10 ˚C. NIS (249 mg, 1.11 mmol) and a catalytic amount of TfOH (20.5 μL, 0.222 mmol) was added to the reaction mixture at -10 ˚C. After being stirred at the same temperature for 5 h, the reaction mixture was neutralized with NEt_3 and filtered through a pad of Celite®. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and 10% 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 10% aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (elution with toluene:acetone = 98:2) to give **35** (465 mg, 0.652 mmol, 88%): $[\alpha]_D^{26}$ +11.7 (*c* 0.92, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-8.03 (m, 20H, aromatic), 5.60 (s, 1H), 5.28 (dd, 1H, *J* = 7.7, 8.2 Hz), 5.05 (s, 2H), 4.83 (d, 1H, *J* = 12.1 Hz), 4.70 (d, 1H, *J* = 12.1 Hz), 4.60 (br-s, 1H), 4.57 (d, 1H, *J* = 7.7 Hz), 4.38 (dd, 1H, *J* = 4.8, 10.6 Hz), 3.82-3.89 (m, 4H), 3.39-3.52 (m, 2H), 2.99 (t, 2H, *J* = 6.3 Hz), 1.11-1.50 (m, 8H, aliphatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 138.0, 137.3, 133.2, 130.0, 129.9, 129.1, 128.6, 128.4x2, 128.2x3, 128.1, 127.6, 126.1, (102.0 anomeric), 81.8, 78.0, 74.0, 73.6, 70.1, 68.8, 66.6, 66.4, 29.8, 29.7, 29.3, 26.3, 25.5; IR (KBr) 2921, 2855, 1720, 1696, 1528, 1452, 1317, 1030, 740, 710 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{41}H_{49}N_2O_9$ $[M+NH_4]^+$ 713.3438, found 713.3447.

***N*-benzyloxycarbonyl-6-aminohexyl (methyl 2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate (36)**. To a stirred solution of **35** (6.28 g, 9.03 mmol) in dry CH_2Cl_2 (18.0 mL) was added TFA (9.03 mL) and MeOH (4.50 mL) at 0 ˚C. After being stirred at the same temperature for 30 min, the reaction mixture was poured into ice-cooled saturated aq. $NaHCO_3$. 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 evaporated *in vacuo*. The residue was used for the next reaction without further purification. To a stirred solution of the residue (9.03 mmol) in CH_2Cl_2 (9.03 mL) and H_2O (3.01 mL) was added catalytic amount of TEMPO and BAIB (7.27 g, 22.6 mmol, 2.50 eq.) at 0 ˚C. After being stirred at the same temperature for 6 h, the reaction mixture was poured into a mixture of saturated aq. $NaHCO_3$ and 10% 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 10% aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was used for the next reaction without further purification. To a stirred solution of the residue (9.03 mmol, 1.00 eq.) in DMF (45.2 mL) was added MeI (1.40 mL, 22.6 mmol) and K_2CO_3 (4.52 g, 100 mg/mL) at 0 ˚C. After being stirred at room temperature for 10 h, the reaction mixture was neutralized with MeOH and poured into ice-cooled 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$, and brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was precipitated from ethyl acetate-hexane to give **36** (4.02 g, 6.32 mmol, 3 steps 70%): $[\alpha]_D^{26}$ +5.25 (*c* 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-8.00 (m, 15H, aromatic), 5.23 (dd, 1H, *J* = 7.7, 8.7 Hz), 5.08 (s, 2H), 4.77 (d, 1H, *J* = 11.6 Hz), 4.73 (d, 1H, *J* = 11.6 Hz), 4.62 (br-s, 1H), 4.55 (d, 1H, *J* = 7.7 Hz), 4.09 (dd, 1H, *J* = 8.7, 9.7 Hz), 3.91 (d, 1H, *J* = 9.7 Hz), 3.86 (dt, 1H, *J* = 6.3, 9.7 Hz), 3.83 (s, 3H), 3.71 (dd, 1H, *J* = 8.7, 8.7 Hz), 3.42 (dt, 1H, *J* = 6.3, 9.7 Hz), 2.99 (t, 2H, *J* = 6.3 Hz), 1.11-1.47 (m, 8H, aliphatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 165.1, 162.6, 156.4, 156.3, 137.9, 136.8, 133.2, 129.9, 129.8, 128.6, 128.4x2, 128.2, 128.1x2, 127.7, (101.6 anomeric), 80.9, 77.4, 77.3, 77.1, 76.8, 74.4, 73.1, 72.1, 70.1, 66.6, 60.4, 52.8, 40.9x2, 36.5, 31.5, 29.7, 29.2, 26.2, 25.5; IR (KBr) 3394, 2931, 1735, 1533, 1454, 1266, 1094, 756, 712 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{35}H_{41}NO_{10}$ $[M+H]^+$ 636.2809, found 636.2813.

_N_-benzyloxycarbonyl-6-aminohexyl 2-azido-3-_O_-benzyl-4-_O_-chloroacetyl-2-deoxy-6-_O_-naphthylmethyl-α-D-glucopyranosyl-(1→4)-(methyl 2-_O_-benzoyl-3-_O_-benzyl-β-D-glucopyranosyluronate) (37): A mixture of **10** (1.00 g, 1.95 mmol), Ph_2SO (1.10 g, 5.47 mmol), TTBP (1.45 g, 5.87 mmol) and pulverized activated MS-4A (2.5 g) in dry CH_2Cl_2 (30.0 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 -60 ˚C. Tf_2O (114 μL, 0.820 mmol) was added to the reaction mixture at the same temperature. After being stirred at -40 ˚C for 30 min, a solution of **36** (1.49 g, 2.34 mmol) in dry CH_2Cl_2 (10.0 mL) was added at -60 ˚C and the reaction mixture was allowed to warm slowly to room temperature. After being stirred at the same temperature for 5 h, the reaction mixture was neutralized with NEt_3 and filtered through a pad of Celite®. The filtrate mixture was poured into brine. 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 Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (elution with $CHCl_3$:MeOH 98:2) and by gel permeation chromatography (GPC) to give **37** (1.54 g, 1.37 mmol, 70%, α/β = >95/5): $[\alpha]_D^{20}$ +28.5 (*c* 1.63, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-8.05 (m, 27H, aromatic), 5.58 (d, 1H, H-1', $J_{1',2'}$ = 3.9 Hz), 5.34 (dd, 1H, H-2, $J_{1,2}$ = 7.6 Hz, $J_{2,3}$ = 8.7 Hz), 5.23 (dd, 1H, *J* = 9.7, 9.7 Hz), 5.08 (s, 2H), 4.93 (d, 1H, *J* = 11.2 Hz), 4.77 (d, 1H, *J* = 10.2 Hz), 4.72 (d, 1H, *J* = 10.2 Hz), 4.67 (d, 1H, *J* = 11.7 Hz), 4.64 (d, 1H, *J* = 7.6 Hz), 4.60 (d, 1H, *J* = 11.2 Hz), 4.55 (d, 1H, *J* = 11.7 Hz), 4.31 (dd, 1H, *J* = 8.7, 9.2 Hz), 4.10 (d, 1H, *J* = 9.2 Hz), 4.02 (dd, 1H, *J* = 8.7, 8.7 Hz), 3.89 (dd, 1H, *J* = 9.7, 10.1 Hz), 3.85 (m, 1H, 3.71 (s, 3H), 3.63 (ddd, 1H, *J* = 3.4, 4.8, 9.7 Hz), 3.57 (m, 1H), 3.56 (d, 1H, *J* = 14.5 Hz), 3.49 (d, 1H, *J* = 14.5 Hz), 3.46 (dd, 1H, *J* = 3.4 Hz, *J* = 10.1 Hz), 3.42 (m, 1H), 3.37 (dd, 1H, *J* = 3.9, 10.1 Hz), 3.01 (t, 2H, *J* = 6.3 Hz), 1.10-1.52 (m, 8H, aliphatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.9, 165.0, 156.4, 146.6, 137.6, 137.2, 136.8, 135.0, 133.4, 133.3, 133.1, 129.8, 129.7, 128.6, 128.4, 128.2, 128.1x3, 128.0, 127.9x2, 127.7, 127.0, 126.2, 126.1, 126.0, (101.4, 97.4 anomeric), 82.5, 77.3, 74.8, 74.7, 74.6, 74.5, 73.9, 73.8, 72.7, 70.0, 69.0, 68.6, 66.6, 62.9, 52.8, 40.9, 40.5, 29.7, 29.2, 28.1, 26.3, 25.5; IR (KBr) 2934, 2109, 1726, 1265, 1079, 1028, 754, 699 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{61}H_{69}N_5O_{15}Cl$ $[M+NH_4]^+$ 1146.4479, found 1146.4485.

Methyl (_N_-benzyloxycarbonyl-6-aminohexyl 4-_O_-(2-azido-3-_O_-benzyl-2-deoxy-6-_O_-naphthylmethyl-_N_-benzyloxycarbonyl-6-aminohexyl 2-azido-3-_O_-benzyl-2-deoxy-6-_O_-naphthylmethyl-α-D-glucopyranosyl-(1→4)-(methyl 2-_O_-benzoyl-3-_O_-benzyl-β-D-glucopyranosyluronate) (19). To a stirred solution of **37** (1.50 g, 1.33 mmol, 1.00 eq.) in DMF (26.6 mL) was added thiourea (10.0 g, 13.3 mmol) and 2,6-lutidine (238 μL, 1.60 mmol) at room temperature. After being stirred at 50 ˚C for 12 h, the reaction mixture was poured into ice-cooled 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$, and brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (elution with toluene:ethyl acetate = 84:16) to give **19** (1.21 g, 1.23 mmol, 93%): $[\alpha]_D^{27}$ +52.8 (*c* 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-8.04 (m, 27H, aromatic), 5.50 (d, 1H, *J* = 3.9 Hz), 5.33 (dd, 1H, *J* = 7.6, 8.2 Hz), 5.08 (s, 2H), 4.82 (br-s, 2H), 4.77

(d, 1H, *J* = 10.1 Hz), 4.76 (d, 1H, *J* = 12.1 Hz), 4.70 (d, 1H, *J* = 10.1 Hz), 4.67 (d, 1H, *J* = 12.1 Hz), 4.60 (d, 1H, *J* = 7.6 Hz), 4.29 (dd, 1H, *J* = 8.7, 9.7 Hz), 4.08 (d, 1H, *J* = 9.7 Hz), 3.99 (dd, 1H, *J* = 8.2, 8.7 Hz), 3.85 (m, 1H,), 3.72-3.80 (m, 3H), 3.70 (s, 3H), 3.62 (dd, 1H, *J* = 5.3, 9.7 Hz), 3.50 (ddd, 1H, *J* = 4.8, 5.3, 9.7 Hz), 3.41 (m, 1H), 3.25 (dd, 1H, *J* = 3.9, 9.7 Hz), 3.01 (t, 2H, *J* = 6.3 Hz), 1.14-1.48 (m, 8H, aliphatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.0, 156.4, 155.4x2, 138.2, 137.4, 136.8, 135.1, 133.4, 133.3, 133.1, 129.8x2, 128.6x2, 128.4x2, 128.2, 128.0x2, 127.9, 127.8x2, 126.8, 126.3, 126.1, 125.7, (101.3, 97.8 anomeric), 82.6, 79.4, 75.1, 74.7, 74.6, 74.5, 74.0, 73.8, 72.9, 70.2, 69.9, 66.6, 62.7, 52.7, 40.9, 29.7, 29.2, 26.3, 25.5; IR (KBr) 3417, 2931, 2109, 1727, 1454, 1266, 1071, 1027, 755 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{59}H_{68}N_5O_{14}$ $[M+NH_4]^+$ 1070.4772, found 1070.4763.

***N*-benzyloxycarbonyl-6-aminohexyl 3-*O*-benzyl-2-deoxy-6-*O*-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)- α-D-glucopyranosyl-(1→4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate) (18)**. To a stirred solution of **19** (4.00 g, 4.14 mmol) in MeOH (40.0 mL) and THF (5.0 mL) was added 1,3-propanedithiol (2.0 mL) and NEt_3 (1.0 mL) at room temperature. After being stirred at the same temperature for 24 h, the reaction mixture was added 1,3-propanedithiol (2.0 mL) and NEt_3 (1.0 mL) at same temperature. After being stirred at the same temperature for another 24 h, the reaction mixture was evaporated *in vacuo*. The residue was briefly purified by column chromatographed on a small amount of silica gel (elution with with $CHCl_3$:MeOH 98:2). To a stirred solution of the residue in THF (60.0 mL) and H_2O (20.0 mL) was added $NaHCO_3$ (3.48 g, 41.4 mmol) and TrocCl (610 μL, 4.55 mmol) at 0 ˚C. After being stirred at the same temperature for 10 min, the reaction mixture was poured into brine. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by column chromatographed on silica gel (elution with toluene:ethyl acetate = 86:14) to give **18** (4.03 g, 3.35 mmol, 2 steps 81%): $[\alpha]_D^{27}$ +37.0 (*c* 0.71, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-7.99 (m, 27H, aromatic), 5.45 (d, 1H, *J* = 9.7 Hz), 5.29-5.33 (m, 2H), 5.08 (s, 2H), 4.59-4.79 (m, 7H), 4.56 (d, 1H, *J* = 6.8 Hz), 4.48 (d, 1H, *J* = 12.1 Hz), 4.27 (dd, 1H, *J* = 9.2, 9.7 Hz), 4.00 (d, 1H, *J* = 9.7 Hz), 3.95-4.00 (m, 1H), 3.91 (dd, 1H, *J* = 8.7, 9.2 Hz), 3.78-3.86 (m, 3H), 3.69 (s, 3H), 3.65 (dd, 1H, *J* = 4.9, 10.2 Hz), 3.57-3.62 (m, 1H), 3.46 (dd, 1H, *J* = 10.1, 10.1 Hz), 3.38 (dt, 1H, *J* = 6.7, 9.7 Hz), 3.00 (t, 2H, *J* = 6.3 Hz), 2.86 (s, 1H), 1.12-1.45 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 164.9, 156.4, 154.2, 138.4, 136.8, 135.1, 133.4, 133.3, 133.1, 129.8, 129.6, 128.6, 128.5x2, 128.4, 128.1x2, 128.0x2, 127.8, 127.7, 126.3, 126.1, 125.7, (101.3, 99.0 anomeric), 95.4, 81.2, 79.6, 77.3, 75.8, 75.1, 74.7, 74.2, 74.0, 73.8, 72.4, 70.9, 70.0, 69.9, 66.6, 54.6, 52.8, 40.9, 29.7, 29.1, 26.2, 25.5; IR (KBr) 3431, 2939, 1736, 1513, 1266, 1071, 758, 712 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{62}H_{71\ M2}O_{16}Cl_3$ $[M+NH_4]^+$ 1218.3900, found 1218.3896.

***N*-benzyloxycarbonyl-6-aminohexyl 2-azido-3-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-6-*O*- naphthylmethyl α-D-glucopyranosyl-(1→4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-naphthylmethyl-α-D-glucopyranosyl-(1→4)-(methyl**

2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate) (21). A mixture of **14** (97.0 mg, 98.1 μmol) and **19** (68.9 mg, 65.4 μmol) and pulverized activated MS-4A (250 mg) in dry CH_2Cl_2 (1.30 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 -40 ˚C. NIS (22.1 mg, 98.1 μmol) and TfOH (1.75 μL, 19.6 μmol) was added to the reaction mixture at same temperature. After being stirred at -10 ˚C for 6 h, the reaction mixture was neutralized with NEt_3 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 Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (elution with $CHCl_3$:MeOH = 98:2) and by gel permeation chromatography (GPC) to give **21** (29.7 mg, 15.3 μmol, 25%, β/α = >95/5): $[\alpha]_D^{28}$ +34.0 (*c* 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-8.08 (m, 49H, aromatic), 5.53 (d, 1H, *J* = 3.9 Hz), 5.45 (d, 1H, *J* = 3.4 Hz), 5.24-5.30 (m, 2H), 5.20 (dd, 1H, *J* = 7.6, 8.2 Hz), 5.09-5.12 (m, 2H), 5.09 (s, 2H), 4.89 (d, 1H, *J* = 11.6 Hz), 4.55-4.71 (m, 8H,), 4.52 (d, 1H, *J* = 7.3 Hz), 4.49 (d, 1H, *J* = 12.4 Hz), 4.40 (d, 1H, *J* = 10.6 Hz), 4.15 (dd, 1H, *J* = 8.7, 9.7 Hz), 4.15 (dd, 1H, *J* = 8.7, 9.7 Hz), 3.88-4.03 (m, 6H), 3.79 (dt, 1H, *J* = 5.8, 9.7 Hz), 3.41-3.70 (m, 9H), 3.31-3.39 (m, 2H), 3.21 (dd, 1H, *J* = 3.9, 10.7 Hz), 3.13 (m, 1H), 2.99-3.05 (m, 5H), 2.99 (s, 3H), 1.12-1.44 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 168.0, 165.9, 165.0, 164.4, 138.3, 137.5, 137.3, 137.2, 136.8, 135.1, 135.0, 133.6, 133.4x2, 133.3x2, 133.1, 129.8, 129.7, 129.5, 129.2, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3x2, 128.2x2, 128.1, 128.0x2, 127.9, 127.8, 127.7, 127.5, 127.2, 127.1, 127.0, 126.9, 126.7, 126.2, 126.1x2, (101.3, 97,4 anomeric), 82.9, 82.6, 77.7, 77.6, 77.3, 76.3, 75.6, 75.4, 75.0, 74.9x3, 74.7, 74.4, 74.0x2, 73.9, 72.9, 70.4, 69.9, 69.0, 68.6, 66.6, 66.5, 63.3, 62.5, 52.7, 51.8, 40.9, 40.6, 29.7, 29.1, 26.3, 25.5; IR (KBr) 2929, 2109, 1736, 1453, 1264, 1070, 756, 711 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{106}H_{109}N_7O_{26}Cl$ $[M+H]^+$ 1930.7111, found 1930.7087.

***N*-benzyloxycarbonyl-6-aminohexyl 3-*O*-Benzyl-4-*O*-chloroacetyl-2-deoxy-6-*O*-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-3-*O*-Benzyl-2-deoxy-6-*O*-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-3-*O*-benzyl-2-deoxy-6-*O*-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate) (23)**. A mixture of **16** (699 mg, 614 μmol), **6** (1.33 g, 614 μmol) and pulverized activated MS-4A (2.4 g) in dry CH_2Cl_2 (12.3 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 -40 ˚C. NIS (148 mg, 656 μmol, 1.70 eq.) and TfOH (11.0 μL, 123 μmol, 0.30 eq.) was added to the reaction mixture at same temperature. After being stirred at -20 ˚C for 2 h, the reaction mixture was neutralized with NEt_3 and filtered through a pad of Celite®. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and 10% 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 10% aq. $Na_2S_2O_3$ and brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by MPLC (elution with toluene:ethyl acetate = 90:10 to 80:20) and by gel permeation chromatography (GPC) to give **23** (890 mg, 280 μmol, 68%, β/α = >95/5): $[\alpha]_D^{28}$ +54.6 (*c* 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.81-8.05 (m, 71H, aromatic), 5.26-5.44 (m, 6H), 5.09-5.19 (m, 4H), 5.07 (s, 2H), 4.99-5.05 (m, 2H), 4.98 (d, 1H, *J* = 12.6 Hz), 4.90 (d, 1H, *J* = 11.6 Hz), 4.76 (d, 1H, *J* = 12.1 Hz), 4.50-4.70 (m, 16H), 4.45 (d, 1H, *J* = 12.1 Hz), 4.32 (m, 2H), 4.23-4.25 (m, 2H), 3.96-4.15 (m, 6H), 3.67-3.94 (m, 13H), 3.65 (s, 3H), 3.56-3.64 (m, 2H), 3.44-3.52 (m, 3H), 3.30-3.41 (m, 3H), 3.25-3.27 (m, 1H), 3.23 (s, 3H), 3.16-3.19 (m, 2H), 3.14 (s, 3H), 2.92-2.99 (m, 3H), 1.05-1.48 (m, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 168.8, 168.4, 168.3, 166.2, 165.2, 164.7, 156.5, 154.5, 154.4, 139.1, 139.0, 138.3, 137.2, 137.0, 136.4, 136.2, 135.8, 134.2, 134.1, 134.0x2, 133.8, 133.7x2, 133.6, 133.5x2, 133.4, 130.0, 129.9x2, 129.3, 129.2, 129.1, 129.0, 128.9x2, 128.8, 128.7, 128.6x2, 128.5, 128.4x2, 128.3, 128.2, 128.1, 128.0x2, 127.9, 127.8x2, 127.7, 127.1x2, 127.0, 126.9, 126.8, 126.5, 126.3x2, (101.5, 100.4, 100.3, 100.2, 98.2, 97.9 anomeric), 95.8, 82.8, 82.6, 77.9x2, 77.7, 77.6, 77.5, 76.9, 76.6, 75.6, 75.3, 75.2, 75.0, 74.8, 74.7, 74.6, 74.5, 74.4, 74.1, 74.0, 73.9x3, 72.9x2, 71.5x2, 70.4, 67.0, 66.6, 53.1, 52.4, 41.2, 30.1, 30.0, 29.5, 26.6, 25.8; IR (KBr) 3030, 2927, 1736, 1512, 1264, 1070, 1042, 755, 711 (cm^{-1}).

_N_-benzyloxycarbonyl-6-aminohexyl 3-_O_-Benzyl-2-deoxy-6-_O_-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-_O_-benzoyl-3-_O_-benzyl-β-D-glucopyranosyluronate)-(1→4)-3-_O_-Benzyl-2-deoxy-6-_O_-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-_O_-benzoyl-3-_O_-benzyl-β-D-glucopyranosyluronate)-(1→4)-3-_O_-benzyl-2-deoxy-6-_O_-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-_O_-benzoyl-3-_O_-benzyl-β-D-glucopyranosyluronate) (23). To a stirred solution of **22** (1.78 g, 559 μmol) in DMF (11.2 mL) was added thiourea (128 mg, 1.68 mmol) and 2,6-lutidine (77.2 μL, 671 μmol) at room temperature. After being stirred at 50 °C for 12 h, the reaction mixture was poured into ice-cooled 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$, and brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by MPLC (elution with toluene:ethyl acetate = 88:12 to 78:22) to give **23** (1.61 g, 520 μmol, 93%): $[\alpha]_D^{28}$ +45.3 (*c* 0.11, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.81-8.04 (m, 71H,), 5.38 (d, 1H, *J* = 3.4 Hz), 5.25-5.34 (m, 4H), 5.09-5.19 (m, 3H), 5.07 (s, 2H), 4.99-5.05 (m, 3H), 4.98 (d, 1H, *J* = 11.6 Hz), 4.90 (d, 1H, *J* = 11.6 Hz), 4.82 (d, 1H, *J* = 11.6 Hz), 4.71-4.78 (m, 2H), 4.64 (d, 1H, *J* = 12.1 Hz), 4.49-4.59 (m, 13H), 4.45 (d, 1H, *J* = 11.1 Hz), 4.31-4.37 (m, 2H), 4.23 (d, 1H, *J* = 10.6 Hz), 4.17 (d, 1H, *J* = 10.6 Hz), 4.07-4.11 (m, 3H), 3.96-4.03 (m, 2H), 3.66-3.95 (m, 13H), 3.65 (s, 3H), 3.55-3.59 (m, 1H), 3.44-3.50 (m, 4H), 3.30-3.40 (m, 3H), 3.22 (s, 3H), 3.16-3.20 (m, 3H), 3.14 (s, 3H), 2.91-3.03 (m, 4H), 1.03-1.47 (m, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 168.8, 168.4, 168.3, 165.2, 164.7, 156.6, 156.5, 154.5, 154.4, 139.1, 139.0, 138.9, 137.5, 137.2, 137.1, 137.0, 136.3, 136.2, 135.8, 134.1, 134.0, 133.8, 133.7x2,

133.6, 133.5x2, 133.4, 130.0, 129.9x2, 129.3, 129.2, 129.0, 128.9x2, 128.8x2, 128.7x2, 128.6x3, 128.5, 128.4, 128.3x2, 128.2, 128.1, 128.0, 127.9, 127.8x2, 127.7, 127.5, 127.2, 127.1x2, 127.0, 126.9, 126.5, 126.3, 126.1, (101.5, 100.9, 100.4, 100.2, 98.2, 98.0 anomeric), 95.9, 95.8x2, 82.8, 82.7, 82.6, 79.8, 77.9, 77.6, 77.5, 76.9, 76.6, 75.6, 75.3, 75.2x2, 75.0, 74.9, 74.8x2, 74.7x2, 74.6, 74.5, 74.4, 74.2, 74.1, 74.0x2, 73.9, 73.8, 73.0, 71.5, 71.4, 71.1, 70.6, 70.4, 67.0, 66.6, 54.8, 53.0, 52.5, 52.4, 41.2, 30.1, 30.0, 29.5, 26.6, 25.8; IR (KBr) 3029, 2927, 1736, 1510, 1264, 1070, 756, 711 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{158}H_{160}N_4O_{42}Cl_9$ $[M+H]^+$ 3099.7704, found 3099.7690.

_N_-benzyloxycarbonyl-6-aminohexyl 3-_O_-Benzyl-4-_O_-chloroacetyl-2-deoxy-6-_O_-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-_O_-benzoyl-3-_O_-benzyl-β-D-glucopyranosyluronate)-(1→4)-3-_O_-benzyl-2-deoxy-6-_O_-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-_O_-benzoyl-3-_O_-benzyl-β-D-glucopyranosyluronate)-(1→4)-3-_O_-Benzyl-2-deoxy-6-_O_-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-_O_-benzoyl-3-_O_-benzyl-β-D-glucopyranosyluronate)-(1→4)-3-_O_-benzyl-2-deoxy-6-_O_-naphthylmethyl-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl-(1→4)-(methyl 2-_O_-benzoyl-3-_O_-benzyl-β-D-glucopyranosyluronate) (24).

A mixture of **16** (786 mg, 691 μmol, 1.50 eq.), **23** (1.43 g, 461 μmol, 1.00 eq.) and pulverized activated MS-4A (1.8 g) in dry CH_2Cl_2 (9.2 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 -40 ˚C. NIS (166 mg, 738 μmol) and TfOH (8.21 μL, 92.2 μmol) was added to the reaction mixture at same temperature. After being stirred at -20 ˚C for 2 h, the reaction mixture was neutralized with NEt_3 and filtered through a pad of Celite®. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and 10% 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 10% aq. $Na_2S_2O_3$ and brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by MPLC (elution with toluene:ethyl acetate = 90:10 to 80:20) and by gel permeation chromatography (GPC) to give **24** (1.11 g, 267 μmol, 58%, α/β = >95/5). (Spectra were shown in text.)

Synthesis of _N_-sulfated dodecasaccharide 2.

Hexaaminododecasaccharide 31. To a stirred solution of **28** (290 mg, 44.1 μmol) in CH_2Cl_2 (1.00 mL) and AcOH (50.0 μL) was added Zn dust (150 mg) at room temperature. After being stirred at the same temperature for 1 h or 12 h, the raction mixture was poured into ice-cooled saturated aq. $NaHCO_3$ and filtered through a pad of Celite®. The filtrate was evaporated *in vacuo.* The residue was purified by MPLC (elution with toluene:acetone:NEt_3 93.75:6:0.25 to 79.75:20:0.25) to give **31** (97.5 mg, 17.7 μmol, 40%): ^1H NMR

(400 MHz, $CDCl_3$) δ 6.75-8.05 (m, 548H, aromatic), 5.20-5.50 (m, 34H), 4.92-5.17 (m, 58H), 4.70-4.92 (m, 17H), 4.05-4.69 (m, 102H), 3.30-4.02 (m, 192H), 2.90-3.29 (m, 106H), 2.61-2.85 (m, 106H), 1.02-2.40 (m, 88H); ^{19}F NMR (373 MHz, $CDCl_3$) δ -112.4, -120.0, -120.2, -121.0, -121.6, -124.4; IR (KBr) 3383, 2926, 1753, 1453, 1265, 1038, 755, 710 (cm^{-1}).

Sulfonamide dodecasaccharide 32. To a stirred solution of **31** (78.3 mg, 14.2 μmol) in dry DMF (1.0 mL) was added $SO_3 \cdot NEt_3$ (181 mg) and NEt_3 (50 μL) at room temperature. After being stirred at r.t. for 24 h, the reaction mixture was neutralized with 5% aq. $NaHCO_3$ and evaporated *in vacuo*. The residue was purified by fluorous column chromatography (Fluoro *Flash*® SPE) to give **32** (40.0 mg, 6.52 μmol, 46%): ^1H NMR (400 MHz, CD_3OD) δ 6.70-8.05 (m, 548H, aromatic), 5.52-5.85 (m, 13H), 5.13-5.50 (m, 17H), 4.57-5.11 (m, 110H), 4.35-4.55 (m, 52H), 2.90-4.55 (m, 352H), 0.90-2.50 (m, 88H); ^{19}F NMR (373 MHz, CD_3OD) δ -112.3, -120.0, -120.2, -121.0, -121.6, -124.3; IR (KBr) 3449, 2956, 1735, 1453, 1264, 1071, 760, 710 (cm^{-1}).

Carboxylate-dodecasaccharide 33. To a stirred solution of **32** (19.8 mg, 3.23 μmol,) in 1,4-dioxane (0.60 mL) and H_2O (0.30 mL) was added NaOMe (10.0 mg) at room temperature. After being stirred at 35 ˚C for 24 h, the reaction mixture was evaporated *in vacuo*. The residue was purified by size exclusion column chromatography on Sephadex PD-10 to give **33**. (17.5 mg, 3.23 μmol): H NMR (400 MHz, CD_3OD) δ 7.05-7.90 (m, 428H, aromatic), 4.90-5.70 (m, 53H), 4.40-4.82 (m, 88H), 3.39-4.38 (m, 235H), 2.60-3.27 (m, 96H), 0.85-2.40 (m, 88H); ^{19}F NMR (373 MHz, CD_3OD) δ -111.8, -114.3, -119.6, 120.4, -121.0, -121.2, -123.9; IR (KBr) 3419, 2929, 1634, 1454, 1206, 1040, 753, 699 (cm^{-1}).

***N*-sulfated dodecasaccharide 2.**

To a solution of **33** (19.1 mg, 3.24 μmol) dry THF (0.500 mL), liq. NH_3 (4.5 mL) and Na (20.0 mg) were added at –78 °C. After being stirred at the same temperature for 30 min, the reaction mixture was quenched with NH_4Cl. The residue was evaporated *in vacuo* and purified by size exclusion column chromatography on Sephadex PD-10 to give glucopyranoside-linking-fluorous tag. To a stirred solution of the residue in 1,4-dioxane (0.60 mL) and H_2O (0.30 mL) was added **4** (8.0 mg, 20.2 μmol, 10.0 eq.) and $NaHCO_3$ (10.0 mg) at room temperature. After being stirred at the same temperature for 6 h, the reaction mixture was immediately used in next step. To a stirred solution of the residue in 1,4-dioxane (0.60 mL) and H_2O (0.30 mL) was added TFA (0.050 mL) at 0 °C. After being stirred at same temperature for 20 min, the reaction mixture was added ethyl acetate (10.0 mL) and H_2O (5.0 mL). After being stirred at room temperature for 5 min, the aqueous layer was quenched with $NaHCO_3$ aq. and evaporated *in vacuo* . To a stirred solution of the residue in H_2O (1.00 mL) was added DOWEX cation exchange resin Na form (10.0 mg) at room temperature. After being stirred at the same temperature for 5 min, the reaction mixture was filtered and purified by size exclusion column cromatography on Sephadex PD-10. (5.50 mg, 1.94 μmol, 60%).
$[\alpha]_D^{26}$ +57.5 (*c* 0.24, H_2O); ^1H NMR (400 MHz, D_2O) δ 7.99 (d, 2H, C, *J* = 9.2 Hz), 7.10 (d, 2H, *J* = 9.2 Hz), 5.62 (d, 1H, *J* = 3.4 Hz), 5.57-5.60 (m, 5H), 4.47-4.51 (d, 5H), 4.33 (d, 1H, *J* = 7.7 Hz), 3.91 (s, 3H), 3.63-3.87 (m, 49H), 3.59 (dd, 1H, *J* = 9.2 Hz, *J* = 9.7 Hz), 3.48-3.51 (m, 1H), 3.45 (dd, 1H, *J* = 9.2, 9.7 Hz),

3.36-3.40 (m, 5H), 3.18-3.30 (m, 9H), 1.44-1.51 (m, 4H), 1.20-1.29 (m, 4H); ^{13}C NMR (100 MHz, D_2O) δ 172.4x3, 172.3, 171.3, 164.5, 135.2, 130.1, 129.0, 128.5, 114.7, (102.6x2, 102.5, 102.4, 102.3x2, 98.2x3, 98.0), 78.2, 78.1, 77.3, 77.1, 76.9, 76.8, 76.0, 75.8x2, 74.4, 74.3x3, 74.2, 74.1, 73.0, 72.8, 72.4, 71.4, 71.2x3, 70.8, 69.6, 69.5, 67.9, 61.9, 60.2, 59.5, 58.2, 58.1, 56.1, 54.3, 54.2, 39.8, 32.9, 30.5, 28.8, 28.3, 25.7, 25.6, 25.5, 24.7x2, 24.6, 22.2; IR (KBr) 3294, 2942, 1726, 1651, 1219, 1017, 915, 644 (cm^{-1}); HRMS (ESI-TOF) Calcd for $C_{88}H_{137}N_7O_{82}S_7Na$ $[M+Na]^+$ 2850.4708, found 2850.4587.