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Electronic supplementary information

Nuclear Transport facilitated by the Interaction Between Nuclear Pores and Carbohydrates

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1 Synthesis of CdTe/ZnS QDs

MPA stabilized CdTe QDs

The synthesis of 3-mercaptopropanoic acid (MPA) stabilized CdTe QDs was carried out according to the literature.[1] MPA stabilized CdTe QDs were prepared by the addition of a NaHTe solution (1M, 1.23 ml) to a nitogen-saturated $CdCl_2$ solution (12.5 mM, 200 ml; pH 9.0) in the presence of MPA (29.5 mM) as a stabilizer. The molar ratio of Cd^{2+}/MPA/HTe^- was fixed at 2/4.8/1. The solution was refluxed for 4 h at 130 °C, then cooled to room temperature.

Dodecanthiol coated CdTe QDs

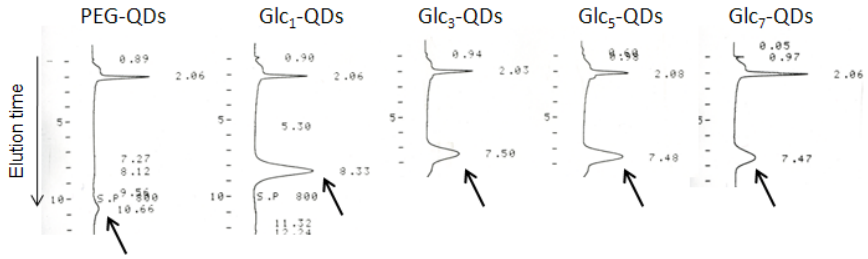
Dodecanthiol coating of MPA-stabilized CdTe QDs was performed according to the previous literature.[2] MPA-CdTe core solution (100 ml) was mixed with dodecanthiol (50 ml), and acetone (20 ml) was then added to the mixture and the solution was stirred vigorously at 60 °C overnight. After evaporation, the organic layer containing CdTe QDs was extracted and diluted with toluene. The mixture was refluxed at 120 °C for 1 h then cooled to room temperature, and purification of dodecanthiol-coated CdTe QDs were performed by reprecipitation twice with methanol. After evaporation, the dodecanthiol-coated CdTe QDs were stored in the dark.

TOPO/TBP stabilized CdTe/ZnS QDs

The synthesis of TOPO/TBP-stabilized CdTe/ZnS QDs was carried out according to the literature.[2] Dodecanthiol-coated CdTe QDs (40 mg) were dissolved in 0.5 ml toluene. A solution containing tributylphosphine (TBP; 8.3 g), 1 M diethylzinc in heptane (1.3 g) and hexamethyldisilithiane (0.30 g) was prepared in a glove box and stored under nitrogen at -20°C, which is referred as a shell solution. A solution of trioctylphosphine oxide (TOPO; 4 g) was heated to 100 °C and purged for 1 h under a vacuum. TBP (0.5 ml) was injected into the TOPO solution, and the dodecanthiol-coated QDs solution (0.5 ml) was also injected into the solution at 160 °C and purged in order to evaporate the chloroform and toluene. The flask was filled with nitrogen gas and refluxed at 160 °C. The shell solution (1 ml) was then added dropwise at 100 µl/min. After cooling to 60 °C, 3 ml butanol was added. The resultant TOPO/TBP-stabilized CdTe/ZnS QDs were stored in the dark.

2 HPLC analysis of maltooligo-QDs

The maltooligo-QDs were dissolved in water (10 nM). Reverse phase chromatography was performed on a TSKgel Phenyl-5PW RP (TOSOH) with a linear gradient of 0 to 80 % acetonitrile solution over a period of 2-12 min. Acetonitrile were run over a period of 12-17 min. Detection wavelength was 350 nm. The flow rate was 0.5 ml/min.



FigureS1. The HPLC profiles of PEG-, Glc_1-, Glc_3-, Glc_5- and Glc_7-QDs loaded on hydrophobic column.

3 Wide view of digitonin-permeabilized HeLa cells incubated with Glc_3–QDs

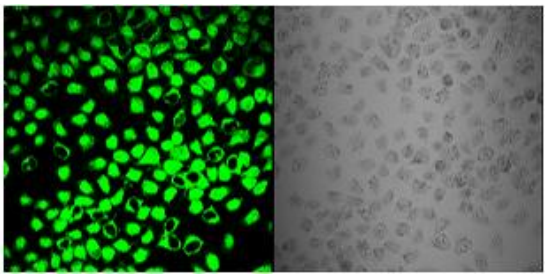


Figure S2. Confocal fluorescence and DIC images of digitonin-permeabilized HeLa cells incubated with Glc_3–QDs(100nM).

4 The double staining of digitonin-permeabilized Hela cells with NLS-BSA and Gl_3-QDs

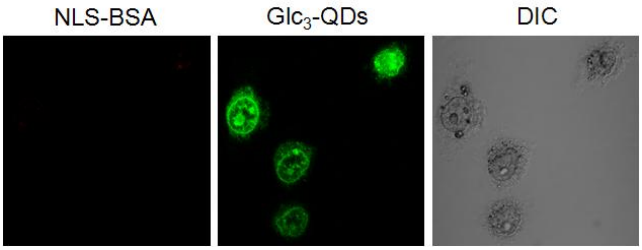


Figure S3. Confocal fluorescence and DIC images of digitonin-permeabilized HeLa cells incubated with NLS labeled Texas Red-BSA (NLS–BSA; 0.3mg/ml) and Glc3–QDs(100nM) in the absence of cytosolic factors .

5 SPR sensorgrams of the bindings between Nup62N and dextran 60000

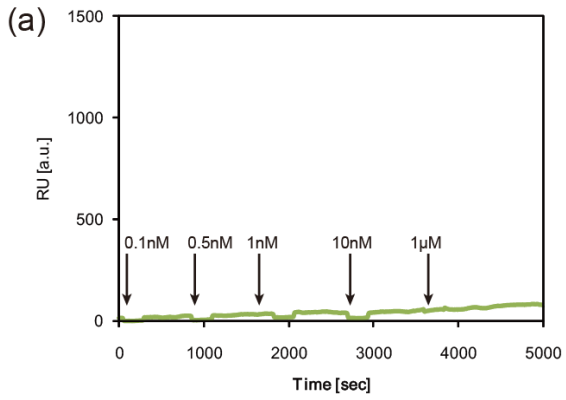
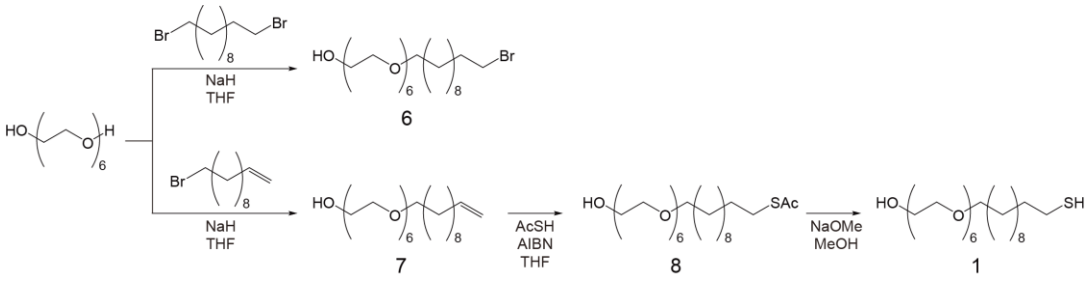


Figure S4. SPR sensorgrams of the bindings between Nup62N and dextran 60000.

6 Synthesis of maltooligosaaccharide derivatives

PEG and oligosaccharide derivatives were synthesized according to our previous report. [3] The identification of NMR spectra was carried out by using Laignel's report as a reference.[4]



Scheme S1. Chemical synthesis of PEG derivatives **1**.

29-bromo-3,6,9,12,15,18-hexaoxanonacosan-1-ol, ***6***.

Hexaethylene glycol (10 g, 36 mmol) was dissolved in dry THF (20 ml). The solution was cooled on ice and added the 60% NaH in oil (0.28 g, 7.0 mmol) and 1,11-dibromoundecane (3.0 ml, 13 mmol). The reaction was allowed to warm to room temperature and stirred for 12 h. The solvent was removed, the residue was dissolved in $CHCl_3$ and washed three times with H_2O. The organic layer was dried over Na_2SO_4 and evaporated under vacuum. The residue was chromatographed on a silica-gel column using EtOAc/MeOH (9:1) to yield a clear syrup (1.7 g, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57- 3.74 (m, 24H), 3.44 (t, J = 6.8

Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.85 (qn, *J*= 6.9 Hz, 2H), 1.57 (qn, *J* = 6.9 Hz, 2H), 1.42 (qn, *J* = 7.0 Hz, 2H), 1.28 (br-s, 12H). MS (MALDI-TOF): calcd for $C_{37}H_{47}BrO_7Na$ $[M+Na]^+$ 537.24, found 537.06, 539.11.

3,6,9,12,15,18-hexaoxanonacos-28-en-1-ol, ***7***.

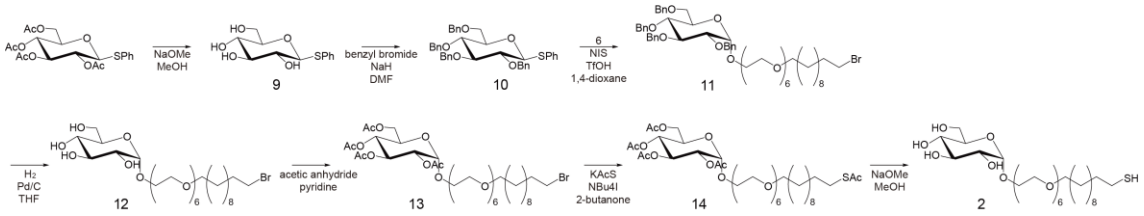
Hexaethylene glycol (15 g, 53 mmol) was dissolved in dry THF (55 ml). The solution was cooled on ice and added the 60% NaH in oil (1.6 g, 40 mmol) and 1,11-bromo-1-undecene (6.2 g, 27 mmol). The reaction was allowed to warm to room temperature and stirred for 12 h. After removing the solvent, the residue was dissolved in $CHCl_3$, washed three times with H_2O. The organic layer was dried over Na_2SO_4 and evaporated under vacuum. The residue was chromatographed on a silica-gel column using EtOAc/MeOH (80: 20 to 97: 3) to yield a yellow syrup (5.8 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76- 5.86 (m, 1H), 4.92- 5.02 (m, 2H), 3.57- 3.74 (m, 24H), 3.44 (t, *J* = 6.8 Hz, 2H), 2.04 (q, *J* = 6.8 Hz, 2H), 1.57 (qn, *J* = 6.9 Hz, 2H), 1.37 (qn, *J* = 6.9 Hz, 2H), 1.28 (br-s, 10H). MS (MALDI-TOF): calcd for $C_{23}H_{46}O_7Na$ $[M+Na]^+$ 457.31, found 457.46.

S-1-hydroxy-3,6,9,12,15,18-hexaoxanonacosan-29-yl ethanethioate, ***8***.

Compound **7** was (1.1 g, 2.6 mmol) was dissolved in dry THF (15 ml). The solution was added the AcSH (1.0 ml, 13 mmol) and AIBN (0.42 g, 2.6 mmol) and refluxed for 3 h. The solvent was removed, the residue was dissolved in $CHCl_3$ and washed three times with H_2O. The organic layer was dried over Na_2SO_4 and evaporated under vacuum. The residue was chromatographed on a silica-gel column using MeOH/ $CHCl_3$ (1: 9) to yield a clear syrup (0.17 g, 13 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72- 3.74 (m, 2H), 3.56- 3.70 (m, 22H), 3.44 (t, *J* = 6.9 Hz, 2H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.32 (s, 3H), 1.52- 1.59 (m, 4H), 1.26 (br-s, 14H). MS (MALDI-TOF): calcd for $C_{25}H_{50}O_8SNa$ $[M+Na]^+$ 533.31, found 533.59.

29-mercapto-3,6,9,12,15,18-hexaoxanonacosan-1-ol, ***1****, mixture of disulfide form.*

Compound **8** was (80 mg, 0.16 mmol) was dissolved in MeOH (3 ml). After the addition of 28% NaOMe in MeOH (3.0 mg, 0.016 mmol), the solution was stirred for 4 h at room temperature. The neutralization was carried out the addition of DOWEX50WX8-200. After the filtration through the filter paper, the solvent was removed under vacuum to give 69 mg of clear syrup including the 26% of disulfide form (95 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.45- 3.57 (m, 29.7 H), 3.45- 3.48 (m, 2.7 H), 3.37 (t, *J* = 6.61 Hz, 2.7 H), 2.59 (t, *J* = 7.27 Hz, 2 H), 2.39 (tt, J = 7.20, 1 Hz, 0.7H), 1.55- 1.62 (m, 1.4 H), 1.44- 1.51 (m, 4 H), 1.22 (br-s, 18.9 H). HRMS (ESI): calcd for $C_{46}H_{94}O_{14}S_2Na_2$ (disulfide form) $[M+Na]^{2+}$ 490.293, found 490.296.



Scheme S2. Chemical synthesis of Glc_1 derivative.

Compound 9 and 10. Phenyl-2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (3.0 g, 4.79 mmol) was dissolved in MeOH (20 ml). The solution was added the 28% NaOMe (260 µl, 0.96 mmol) and stirred for 12 h at room temperature. The neutralization was carried out by the addition of DOWEX50WX8-200. After the filtration through the filter paper, the solvent was removed under vacuum to give crude **9** (1.3 g of orange syrup, 98 %). The syrup was dissolved in dry DMF. The solution was cooled at -20 °C, added the NaH (3.3 g, 47 mmol) and benzyl bromide (8.3 ml, 47 mmol). The reaction was allowed to warm to room temperature and stirred for 12 h. The solvent was removed, the residue was dissolved in $CHCl_3$ and washed three times with H_2O. The organic layer was dried over Na_2SO_4 and evaporated under vacuum. The residue was chromatographed on a silica-gel column using Hexane/ EtOAc (6: 1) to yield a yellow syrup (2.4 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56- 7.60 (m, 2H), 7.19- 7.40 (m, 23H), 4.81- 4.91 (m, 4H), 4.52- 4.74 (m, 5H), 3.62- 3.80 (m, 4H), 3.49- 3.53 (m, 2H). MS (MALDI-TOF): calcd for $C_{40}H_{40}O_5SNa$ $[M+Na]^+$ 655.22, found 655.07.

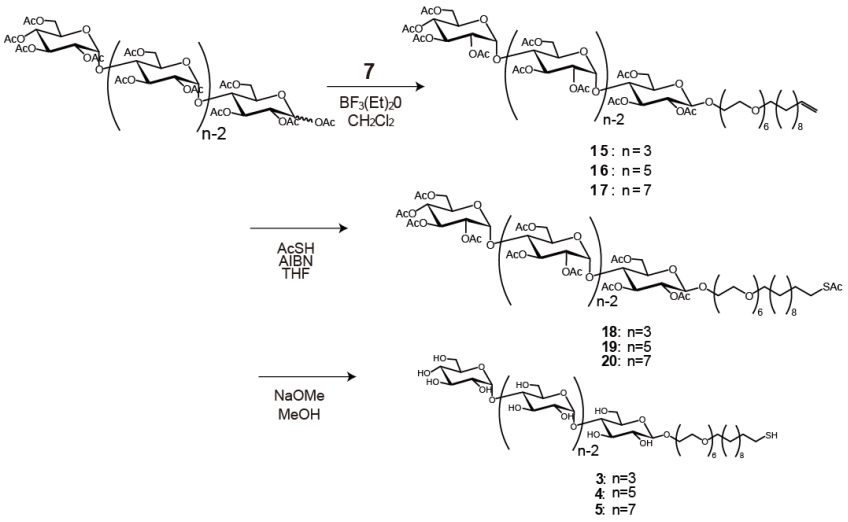
Compound 11. Compound **6** (0.61 g, 1.2 mmol) and **10** (1.3 g, 2.1 mmol) were dissolved in 1,4-Dioxane (20 ml) and added molecular seives and N-Iodosuccinimide (1.3 g, 5.9 mmol). The reaction mixture was added the trifluoromethanesulfonic acid (34 mg, 0.23 mmol) under a nitrogen atmosphere and stirred overnight. After filtration through the celite, the solvent was removed. The residue was dissolved in $CHCl_3$ and washed with $Na_2S_2O_3$ and two times with brine. The organic layer was dried over Na_2SO_4 and evaporated under vacuum. The residue was chromatographed on a silica-gel column using EtOAc/ $CHCl_3$ (3: 7) to give **11** as a syrup (0.33 g, 27%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25- 7.56 (m, 20H), 4.99- 4.42 (m, 9H), 3.98 (t, *J* = 9.4 Hz, 1H), 3.54- 3.69 (m, 27H), 3.44 (t, *J* = 6.8 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.85 (qn, *J* = 6.8 Hz, 2H), 1.57 (t, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.4 Hz, 2H), 1.27 (br-s, 12H). MS (MALDI-TOF) calcd for $C_{57}H_{81}BrO_{12}Na$ $[M+Na]^+$ 1059.48, found 1058.84, 1060.90.

Compound 12 and 13, *mixture of anomers*. Compound **11** (0.33 g, 0.32 mmol) and

Palladium 10 %wt. on activated carbon were added THF (10ml) and stirred for 4 h under a hydrogen atmosphere. After filtration through the celite, the solvent was removed. The residue was dissolved in pyridine (15 ml) and acetic anhydride (15 ml) and stirred overnight. After evaporation, The residue was chromatographed on a silica-gel column using EtOAc/ $CHCl_3$ (6: 4) to give **11** as a syrup (0.18 g, 67%, α/β＝77: 23). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.49 (t, *J* = 9.5 Hz, 0.77H), 5.20 (t, *J* = 9.4 Hz, 0.23H), 5.12 (d, *J* = 3.7 Hz, 0.77H, α1H), 5.09 (t, *J* = 10 Hz, 0.23H), 5.06 (t, *J* = 9.3 Hz, 0.77H), 4.99 (dd, *J* = 9.6, 7.9 Hz, 0.23H), 4.87 (dd, *J* = 10, 3.7 Hz, 0.77H), 4.60 (d, *J* = 8.0 Hz, 0.23H, β1H), 4.24- 4.29 (m, 0.77H), 4.06- 4.15 (m, 2H), 3.92- 3.97 (m, 0.23H), 3.56- 3.82 (m, 24H), 3.44 (t, *J* = 6.8 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 2.10 (s, 2.3H), 2.09 (s, 0.69H), 2.07 (s, 2.3H), 2.05 (s, 0.69H), 2.03 (s, 2.3H), 2.02 (s, 0.69H), 2.01 (s, 2.3H), 2.01 (s, 0.69H), 1.82- 1.89 (m, 2H), 1.58 (m, 2H), 1.42 (m, 2H), 1.27 (br-s, 12H). MS (MALDI-TOF): calcd for $C_{37}H_{65}BrO_{16}Na$ $[M+Na]^+$ 867.34, found 866.89, 868.93.

Compound 14. Compound **13** (0.18 g, 0.21 mmol) was dissolved in 2-butnanone (7.5 ml). After addition of potassium thioacetate (75 mg, 0.64 mmol) and tetrabutylammonium iodide (8 mg, 0.021 mmol), reaction mixture was refluxed for 4 h. The solvent was removed, the residue was dissolved in $CHCl_3$ and washed with $Na_2S_2O_3$ and two times with H_2O. The organic layer was dried over Na_2SO_4 and evaporated under vacuum. The residue was chromatographed on a silica-gel column using EtOAc/ $CHCl_3$ (gradient from 0: 10 to 10: 0) to give a syrup (0.18 g, 94 %, α/β＝97: 3). ^{1}H NMR (400 MHz, $CDCl_3$) 5.49 (t, *J* = 9.7 Hz, 1H), 5.13 (d, *J* =3.6 Hz, 1H, α1H), 5.07 (t, *J* = 9.8 Hz, 1H), 4.87 (dd, *J* = 10, 3.7 Hz, 1H), 4.61 (d, *J* =7.84 Hz, 0.03H, β1H), 4.26- 4.29 (m, 1H), 4.06- 4.13 (m, 2H), 3.57- 3.65 (m, 24H), 3.44 (t, *J* = 6.8 Hz, 2H), 2.86 (t, *J* =7.35 Hz, 2H), 2.32 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.54- 1.57 (m, 4H), 1.28 (br-s, 14H). MS (MALDI-TOF): calcd for $C_{39}H_{68}O_{17}SK$ $[M+K]^+$ 879.42, found 878.77.

Compound 2. Compound **14** (39 mg, 0.047 mmol) was dissolved in MeOH (1 ml). After the addition of 28% NaOMe in MeOH (1.4 mg, 0.0072 mmol), the solution was stirred for 3 h at room temperature. The neutralization was carried out by the addition of DOWEX50WX8-200. After the filtration through the filter paper, the solvent was removed under vacuum to give 30 mg of clear syrup (100 %, α/β＝97: 3). ^{1}H NMR (400MHz, CD_3OD): δ 4.82 (d, *J* = 3.6 Hz, 0.97 H, α1H), 4.29 (d, *J* = 7.7 Hz, 0.03 H, β1H), 3.78- 3.88 (m, 2 H), 3.55- 3.72 (m, 30 H), 3.46 (t, *J* = 6.6 Hz, 2 H), 3.25- 3.38 (m, 2 H), 2.68 (t, *J* = 7.3 Hz, 2 H), 1.70 (qn, *J* = 7.0 Hz, 2 H), 1.57 (qn, *J* = 6.6 Hz, 2 H), 1.32 (br-s, 14 H). HRMS (ESI^+): calcd for $C_{58}H_{114}O_{24}S_2Na_2$ (disulfide form) $[M+Na]^{2+}$ 652.347, found 652.347.



Scheme S3. Chemical synthesis of maltooligosaccharides derivatives.

Compound 15. Acetylated maltotriose (2.0 g, 2.1 mmol) and compound **7** (1.38 g, 3.18 mmol) were dissolved in dry CH_2Cl_2 (13 ml) under a nitrogen atmosphere. The reaction mixture was added boron trifluoride-ethyl ether complex (500 µl, 3.52 µmol) and stirred overnight at room temperature. The neutralization was carried out by the addition of $NaHCO_3$. Organic layer was washed with brine and dried over Na_2SO_4. After evaporation, the residue was chromatographed on a silica-gel column using EtOAc/ $CHCl_3$ (4: 6 to 7: 3) to give **15** as a yellow syrup (1.26 g, 54 %). ^{1}H NMR (400MHz, $CDCl_3$): δ 5.80- 5.90 (m, 1H), 5.45 (d, *J* = 4.3 Hz, 1H), 5.44 (t, *J* = 8.4 Hz, 1H), 5.40 (t, *J* = 10 Hz, 1H), 5.32 (d, *J* = 3.8 Hz, 1H), 5.30 (t, *J* = 9.2 Hz, 1H), 5.11 (t, *J* = 9.8 Hz, 1H), 4.92- 5.05 (m, 2H), 4.90 (dd, *J* = 3.9, 11 Hz, 1H), 4.85 (dd, *J* = 9.3, 8.1, 1H), 4.78 (dd, *J* = 11, 4.1, 1H), 4.65 (d, *J* = 7.9 Hz, 1H), 4.51 (dd, *J* = 12, 3.2 Hz, 1H), 4.50 (dd, *J* = 12, 2.8 Hz, 1H), 4.35 (dd, *J* = 12, 4.2 Hz, 1H), 4.29 (dd, *J* = 13, 3.6 Hz, 1H), 4.23 (dd, *J* = 12, 3.4 Hz, 1H), 4.09 (dd, *J* = 13, 2.1 Hz, 1H), 3.95- 4.03 (m, 5H), 3.60- 3.80 (m, 24H), 3.48 (t, *J* = 6.8 Hz, 2H), 2.22 (s, 3H), 2.20 (s, 3H), 2.14 (s, 3H), 2.02- 2.10 (m, 23H), 1.61 (qn, *J* = 6.9 Hz, 2H), 1.32 (br-s, 12H). MS (MALDI-TOF): calcd for $C_{61}H_{96}O_{32}SNa$ $[M+Na]^+$ 1364.40 found 1363.27.

Compound 18. Compound **15** (1.2 g, 0.91 mmol) was dissolved in dry THF (16 ml). AcSH (0.40 ml, 5.3 mmol) and AIBN (80 mg, 0.49 mmol) were added to the solution and refluxed for 12 hr. After the solvent was removed, the residue was dissolved in $CHCl_3$ and washed three times with H_2O. The organic layer was dried over Na_2SO_4 and evaporated under vacuum. The residue was chromatographed on a silica-gel column using EtOAc/ $CHCl_3$ (0:

10 to 7: 3) to yield **18** as a clear syrup (0.94 g, 73 %). ^{1}H NMR (400MHz, $CDCl_3$): δ 5.57 (d, *J* = 4.3 Hz, 1H), 5.55 (t, *J* = 8.1 Hz, 1H), 5.50 (t, *J* = 10 Hz, 1H), 5.42 (d, *J* = 3.8 Hz, 1H), 5.40 (t, *J* = 9.1 Hz, 1H), 5.22 (t, *J* = 9.9 Hz, 1H), 5.01 (dd, *J* = 11, 4.1 Hz, 1H), 4.96 (dd, *J* = 9.3, 8.0 Hz, 1H), 4.89 (dd, *J* = 10, 4.0 Hz, 1H), 4.76 (d, *J* = 7.8 Hz, 1H), 4.61 (dd, *J* = 12, 3.0 Hz, 1H), 4.61 (dd, *J* = 12, 2.4 Hz, 1H), 4.46 (dd, *J* = 12, 4.1 Hz, 1H), 4.40 (dd, *J* = 12, 3.5 Hz, 1H), 4.33 (dd, *J* = 12, 3.3 Hz, 1H), 4.20 (dd, *J* = 13, 2.4 Hz, 1H), 4.07- 4.14 (m, 5H), 3.71- 3.90 (m, 24H), 3.59 (t, *J* = 6.8 Hz, 2H), 3.01 (t, *J* = 7.3, 2H), 2.47 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H), 2.02- 2.10 (m, 21H), 1.71 (qn, *J* = 7.5 Hz, 4H), 1.41 (br-s, 14H). MS (MALDI-TOF): calcd for $C_{63}H_{100}O_{33}SNa$ $[M+Na]^+$ 1439.58, found 1438.50.

Compound 3. Compound **18** (0.30 g, 0.21 mmol) was dissolved in MeOH (10 ml). After the addition of 28% NaOMe in MeOH (4.5 mg, 0.30 mmol), the solution was stirred for 1.5 h at room temperature. The neutralization was carried out the addition of DOWEX50WX8-200. After the filtration through the filter paper, the solvent was removed under vacuum to give white solid (quant). ^{1}H NMR (400 MHz,CD_3OD): δ 5.16 (d, *J* = 4.1 Hz, 1H), 5.14 (d, *J* = 5.0 Hz, 1 H), 4.33 (d, *J* =7.76 Hz, 1 H), 3.98-4.03 (m,1 H), 3.22-3.87 (m, 53 H), 2.68 (t, *J* =7.2 Hz, 2 H), 1.57 (qn, *J* = 6.9 Hz, 4H), 1.31 (br-s, 14 H). HRMS (ESI^+): calcd for $C_{41}H_{78}O_{22}SNa$: 977.46, found 976.99; HRMS (m/z, ESI^+) calcd for $C_{41}H_{78}O_{22}SNa$ $[M+Na]^+$ 977.460, found 977.464.

Compound 19. Compound **19** was synthesized according to the same procedure of compound **15** or **18**. The identification of the compound **19** by NMR and mass spectrometry were as follows; ^{1}H NMR (400MHz, $CDCl_3$): δ 5.33- 5.43 (m, 5H), 5.29 (d, *J* = 4.1 Hz, 2H), 5.28 (d, *J* = 3.6 Hz, 1H), 5.08 (t, *J* = 10 Hz, 1H), 4.86 (dd, *J* = 11, 4.0 Hz, 1H), 4.81 (dd, *J* = 9.4, 7.9 Hz, 1H), 4.71- 4.76 (m, 3H), 4.61 (d, *J* = 7.9 Hz, 1H), 4.46- 4.52 (m, 4H), 4.37 (dd, *J* = 12, 3.7 Hz, 1H), 4.30 (dd, *J* = 12, 3.5 Hz, 1H), 4.26 (dd, *J* = 13, 3.6 Hz, 1H), 4.22 (dd, *J* = 14, 2.7 Hz, 1H), 4.16 (dd, *J* = 13, 2.2 Hz, 1H), 3.91- 4.06(m, 10H), 3.42- 3.74 (m, 24H), 3.44 (t, *J* = 6.8 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.52- 1.61 (m, 4H), 1.26 (br-s, 14H). MS (MALDI-TOF): calcd for $C_{87}H_{132}O_{49}SNa$ $[M+Na]^+$ 2015.76, found 2015.40.

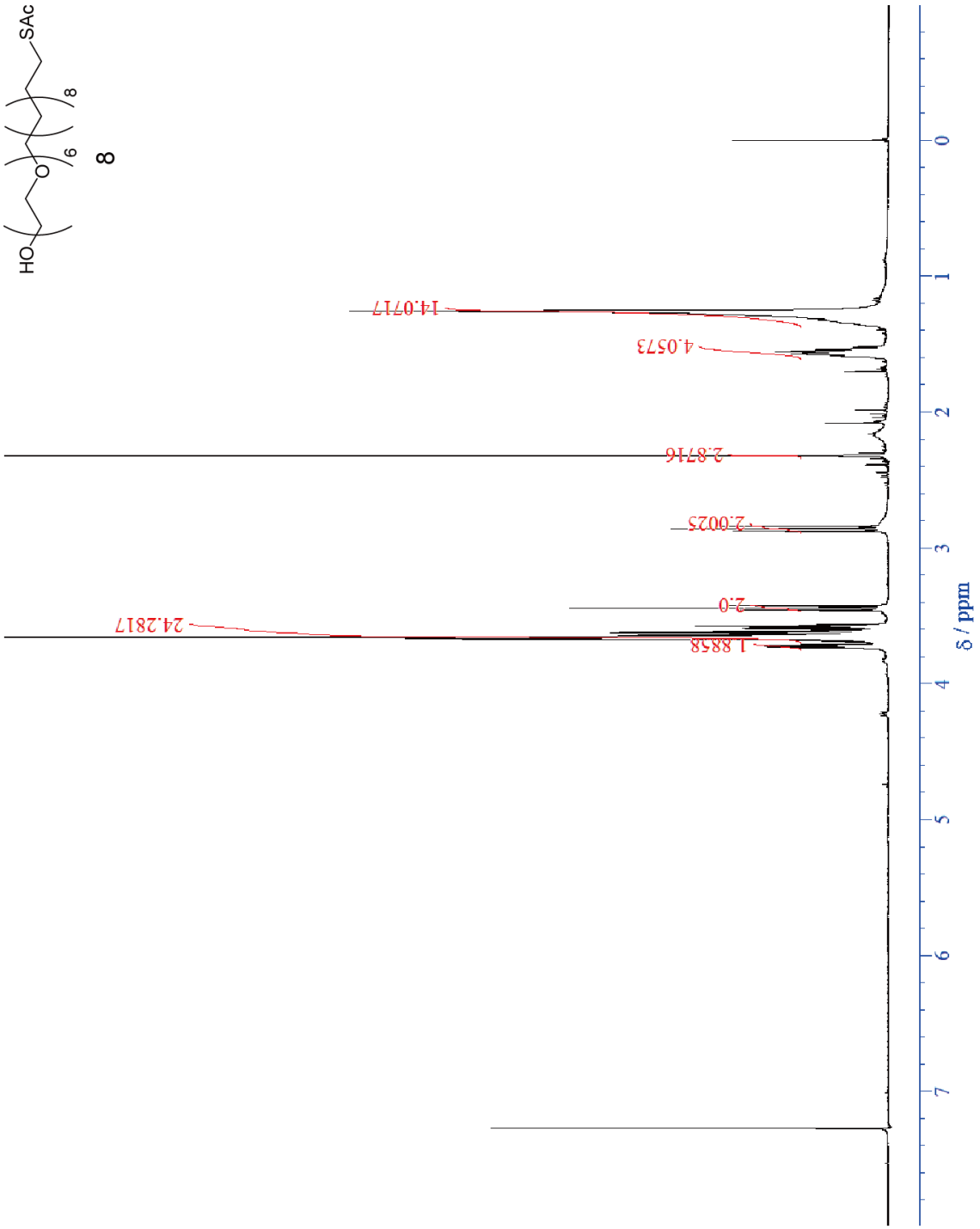
Compound 4. Compound **19** (0.50 g, 0.25 mmol) was dissolved in MeOH (10 ml). After the addition of 28% NaOMe in MeOH (24 mg, 1.6 mmol), the solution was stirred for 1.5 h at 40 °C. The neutralization was carried out the addition of DOWEX50WX8-200. After the

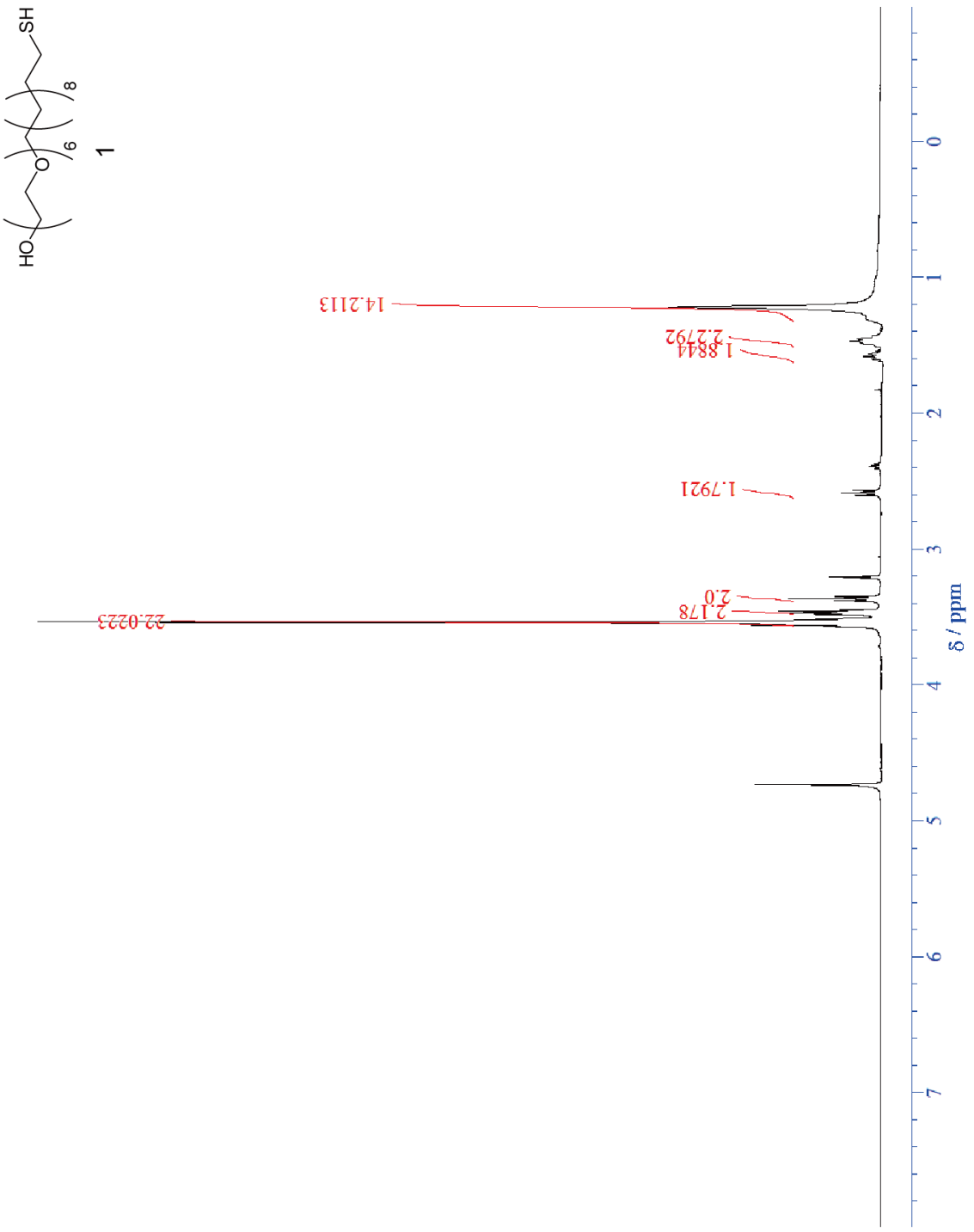
filtration through the filter paper, the solvent was removed under vacuum to give white solid (quant). ^{1}H NMR (400MHz, D_2O) δ 5.31 (d, *J* = 4.0 Hz, 1H), 5.28 (d, *J* = 3.9 Hz, 2H), 5.26 (d, *J* = 4.1 Hz, 1H), 4.37 (d, *J* =7.92 Hz, 1 H), 3.95-3.98 (m,1 H), 3.46-3.86 (m, 51 H), 3.37 (t, *J* = 6.3 Hz, 2 H), 3.30 (t, *J* = 9.3 Hz, 1 H), 3.23 (t, *J* = 8.9 Hz, 1 H), 2.39 (t, *J* = 7.0 Hz, 2 H), 1.48 (qn, *J* = 6.2 Hz, 4 H), 1.31 (br-s, 14 H); HRMS (FAB): calcd for $C_{53}H_{98}O_{32}S$ 1278.58, found 1278.61.

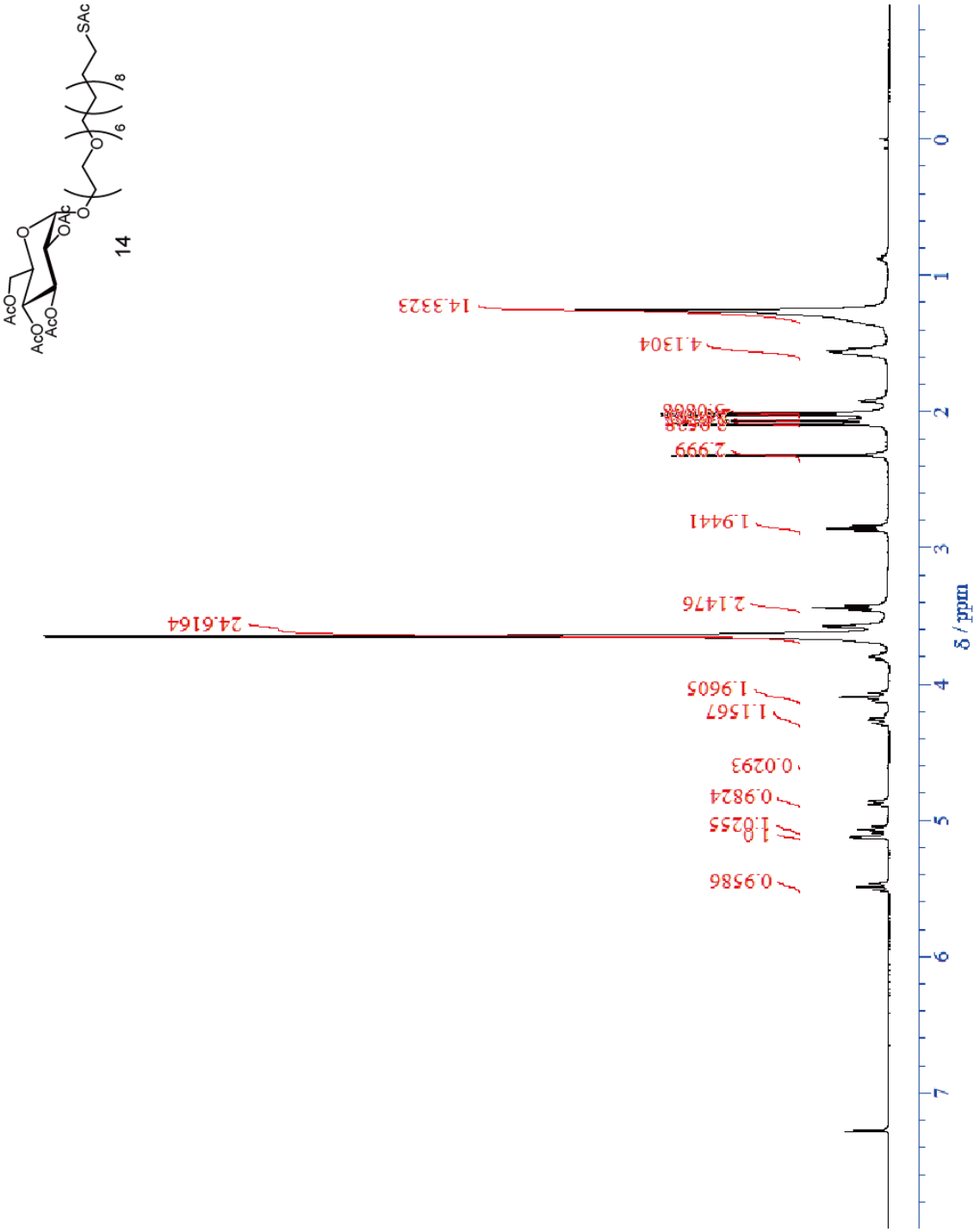
Compound 20. Compound **20** was synthesized according to the same procedure of compound **15** or **18**. The identification of **20** by NMR and mass spectrometry were as follows; ^{1}H NMR (600MHz, $CDCl_3$): δ 5.40- 5.45 (m, 6H), 5.38 (t, *J* = 9.7 Hz, 1H), 5.31- 5.34 (m, 5H), 5.28 (t, *J* = 9.0 Hz, 1H), 5.10 (t, *J* = 9.7 Hz, 1H), 4.88 (dd, *J* = 4.1, 11 Hz, 1H), 4.83 (dd, *J* = 8.0, 9.4 Hz, 1H), 4.73- 4.78 (m, 5H), 4.63 (d, *J* = 7.8 Hz, 1H), 4.51- 4.57 (m, 6H), 4.39 (dd, *J* = 3.7, 12 Hz, 1H), 4.27- 4.34 (m, 4H), 4.24 (dd, *J* = 1.9, 12 Hz, 1H), 4.19 (dd, *J* = 2.4, 13 Hz, 1H), 4.07 (dd, *J* = 1.7, 12 Hz, 1H), 3.94- 4.05 (m, 11H), 3.59- 3.75 (m, 24H), 3.47 (t, *J* = 6.8 Hz, 2H), 2.88 (t, *J* = 7.44 Hz, 2H), 2.35 (s, 3H), 2.00- 2.23 (m, 63H), 1.58 (qn, *J* = 7.1 Hz, 4H), 1.28 (br-s, 14H). MS (MALDI-TOF): calcd for $C_{111}H_{164}O_{65}SNa$ $[M+Na]^+$ 2591.93, found 2591.72.

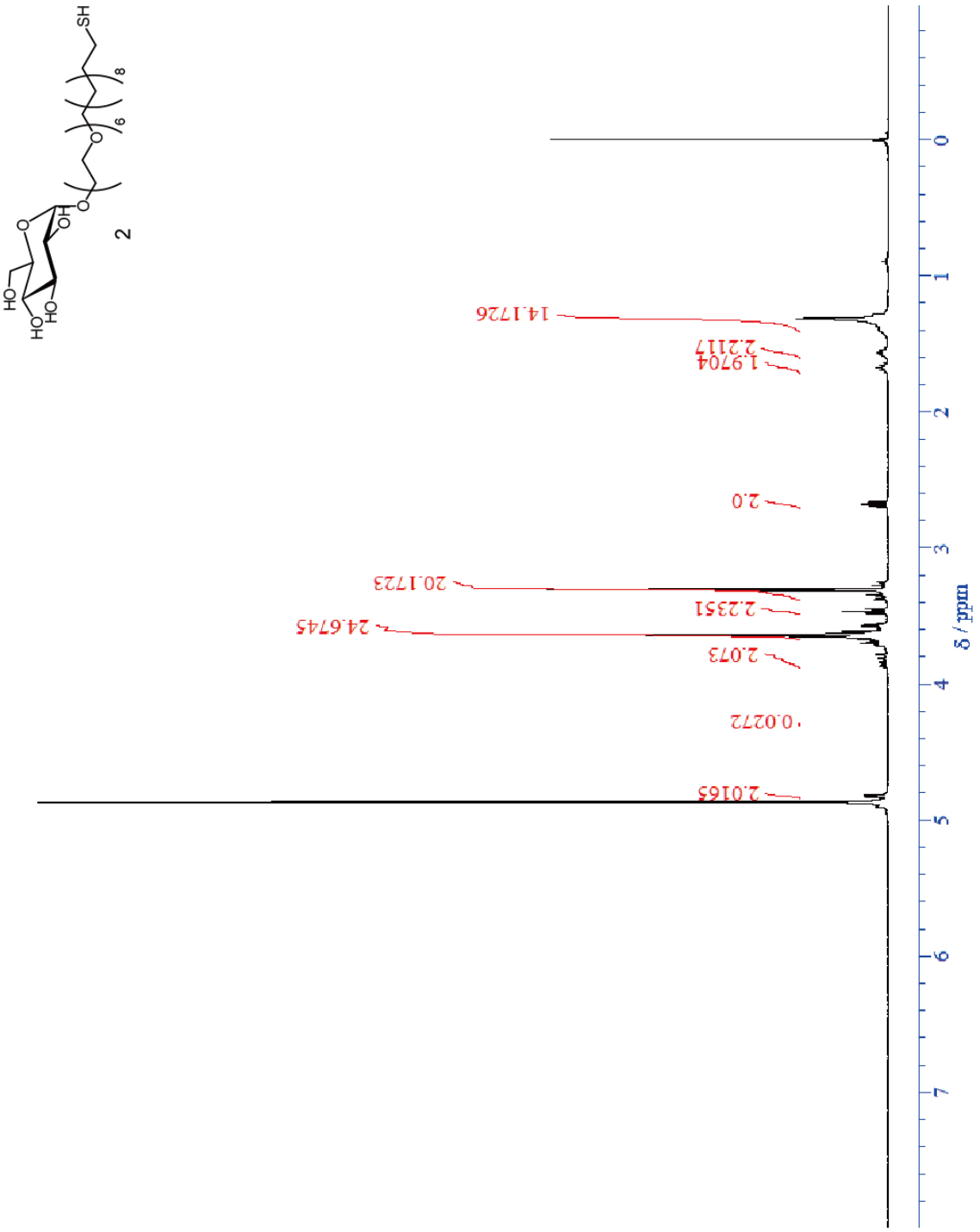
Compound 5. Compound **20** (17.1 mg, 6.7 mmol) was dissolved in MeOH (5 ml). After the addition of 28% NaOMe in MeOH (0.89 mg, 4.7 mmol), the solution was stirred for 1.5 h at 40 °C. The neutralization was carried out by the addition of DOWEX50WX8-200. After the filtration through the filter paper, the solvent was removed under vacuum to give **5** as a white solid (quant). ^{1}H NMR (600MHz, D_2O) δ 5.39- 5.44 (m, 6 H), 4.53 (d, *J* =7.3 Hz, 1 H), 4.09-4.11 (m,1 H), 3.60- 3.98 (m, 63 H), 3.54 (t, *J* = 5.6 Hz, 2 H), 3.45 (t, *J* = 9.2 Hz, 1 H), 3.37 (t, *J* = 8.5 Hz, 1 H), 2.55 (t, *J* = 7.2 Hz, 2 H), 1.62-1.68 (m, 4 H), 1.35 (br-s, 14 H). HRMS (FAB): calcd for $C_{65}H_{118}O_{42}S$ 1602.68, found 1602.73.

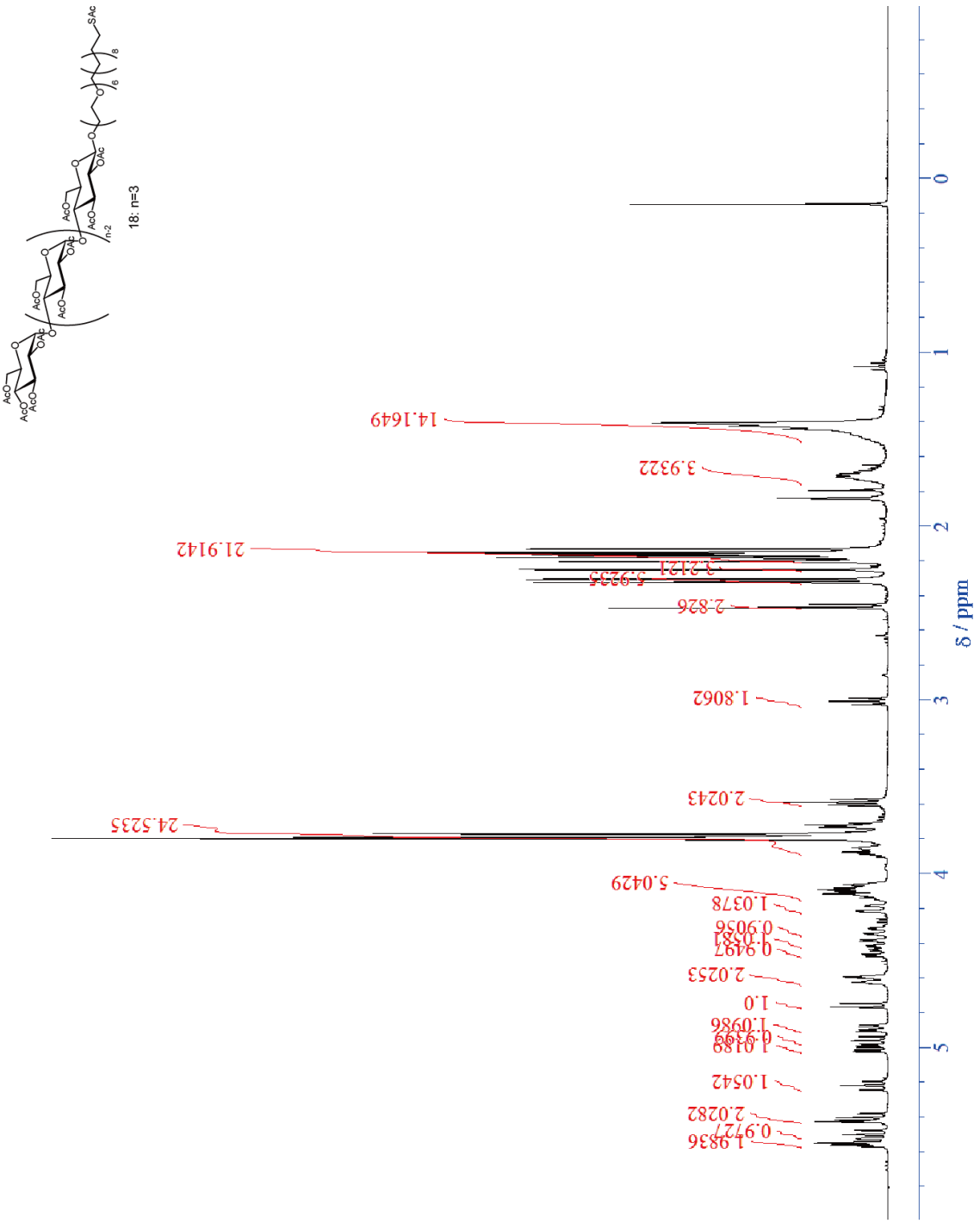
7 ^{1}H-NMR spectra of synthesized compounds

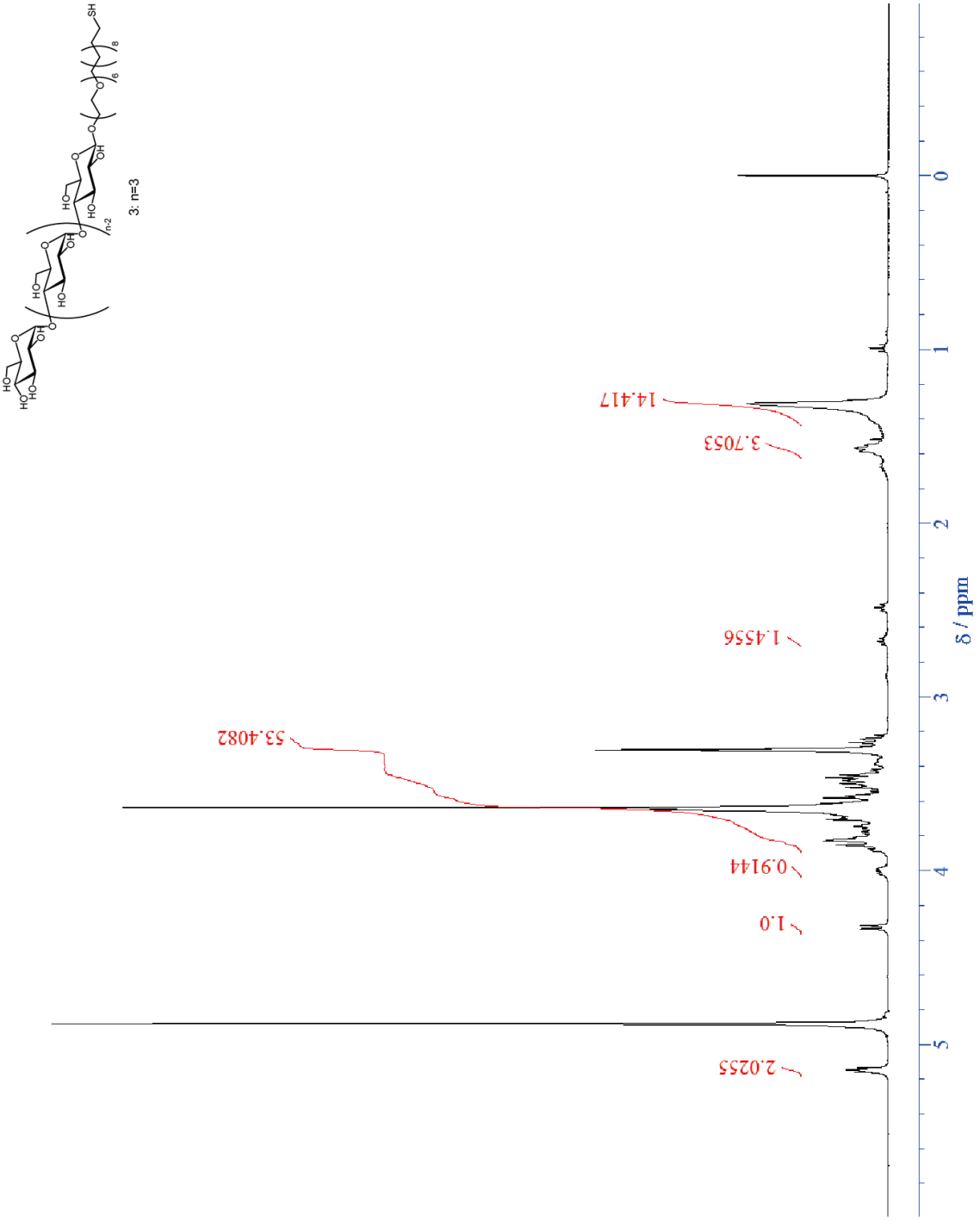








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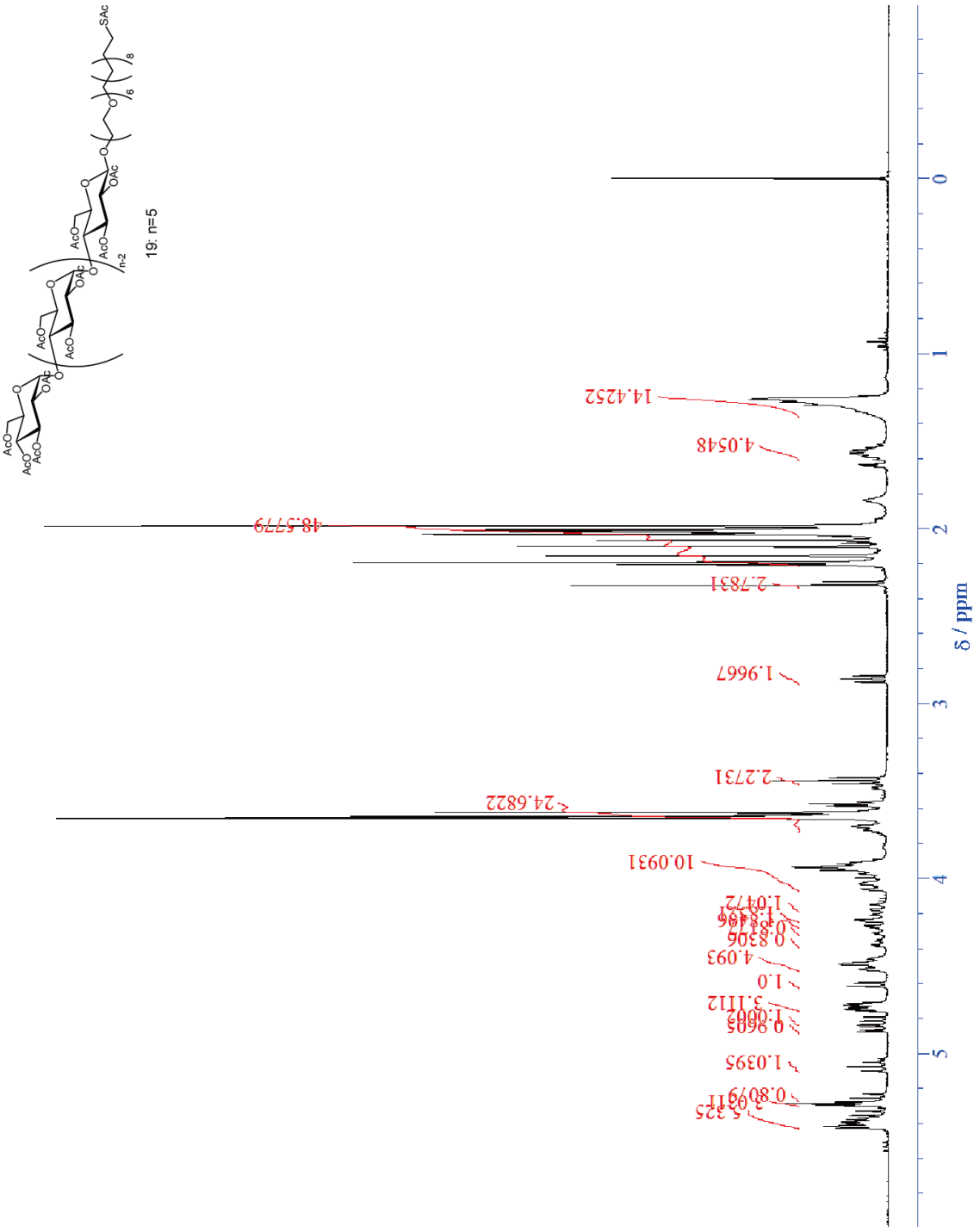

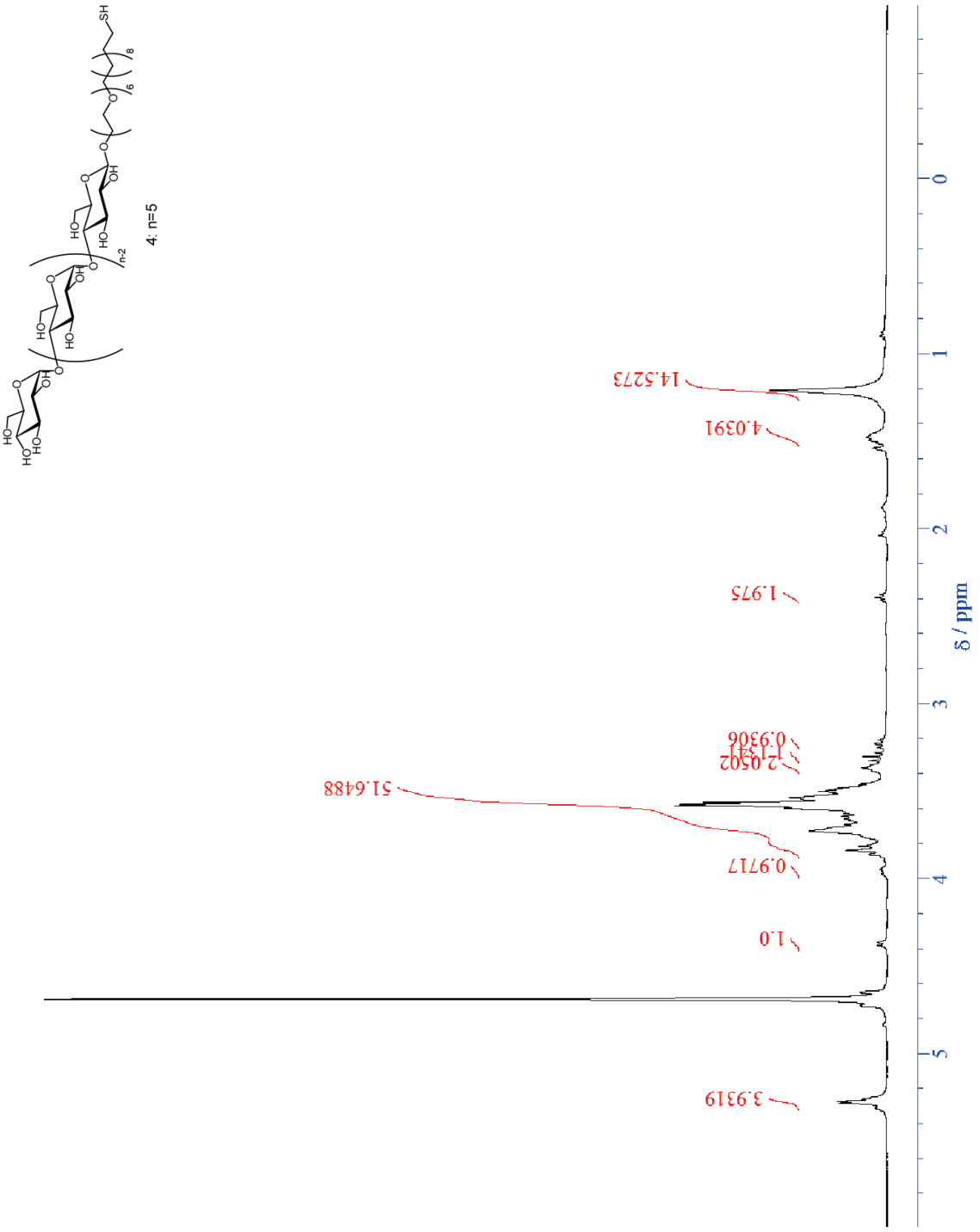

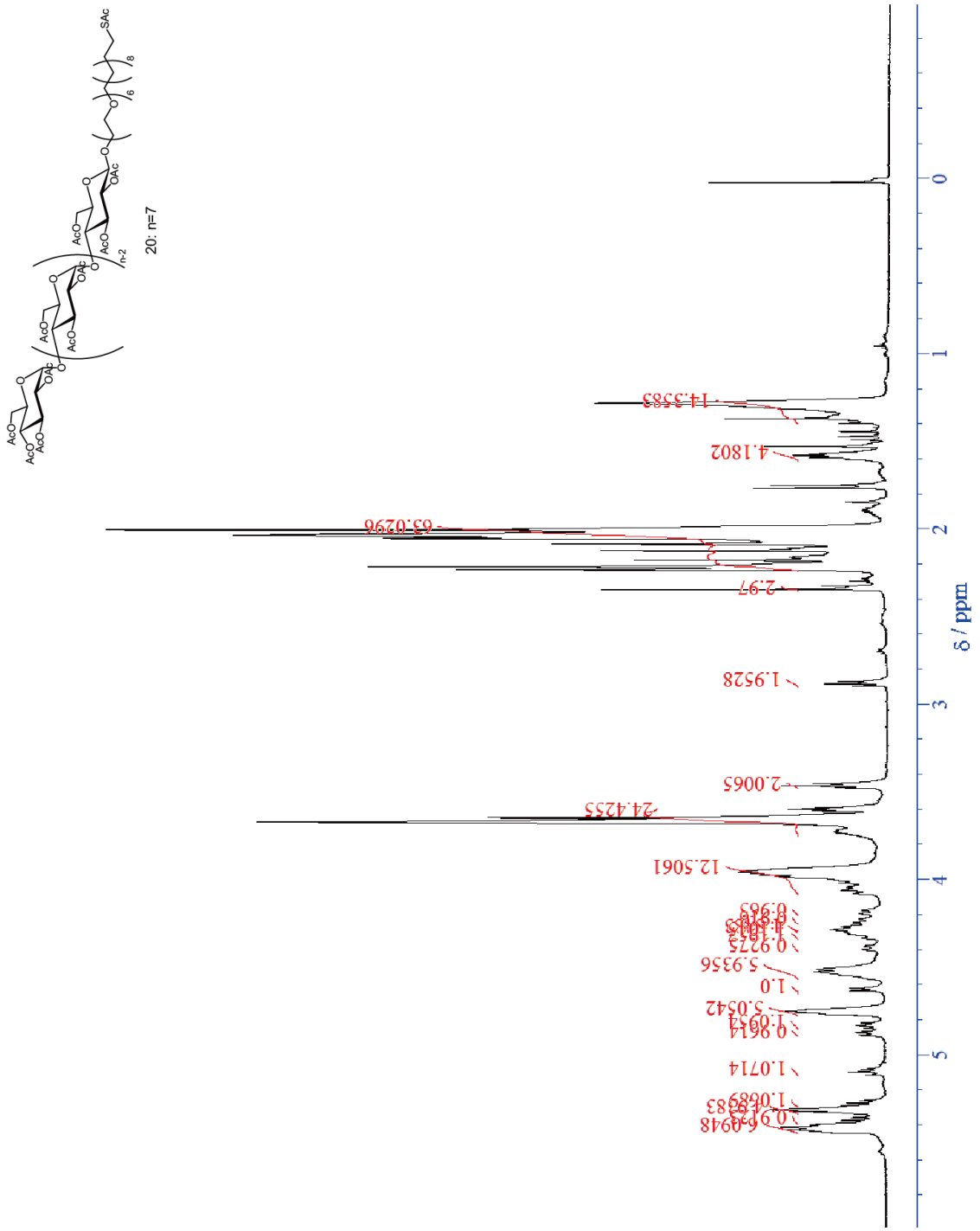

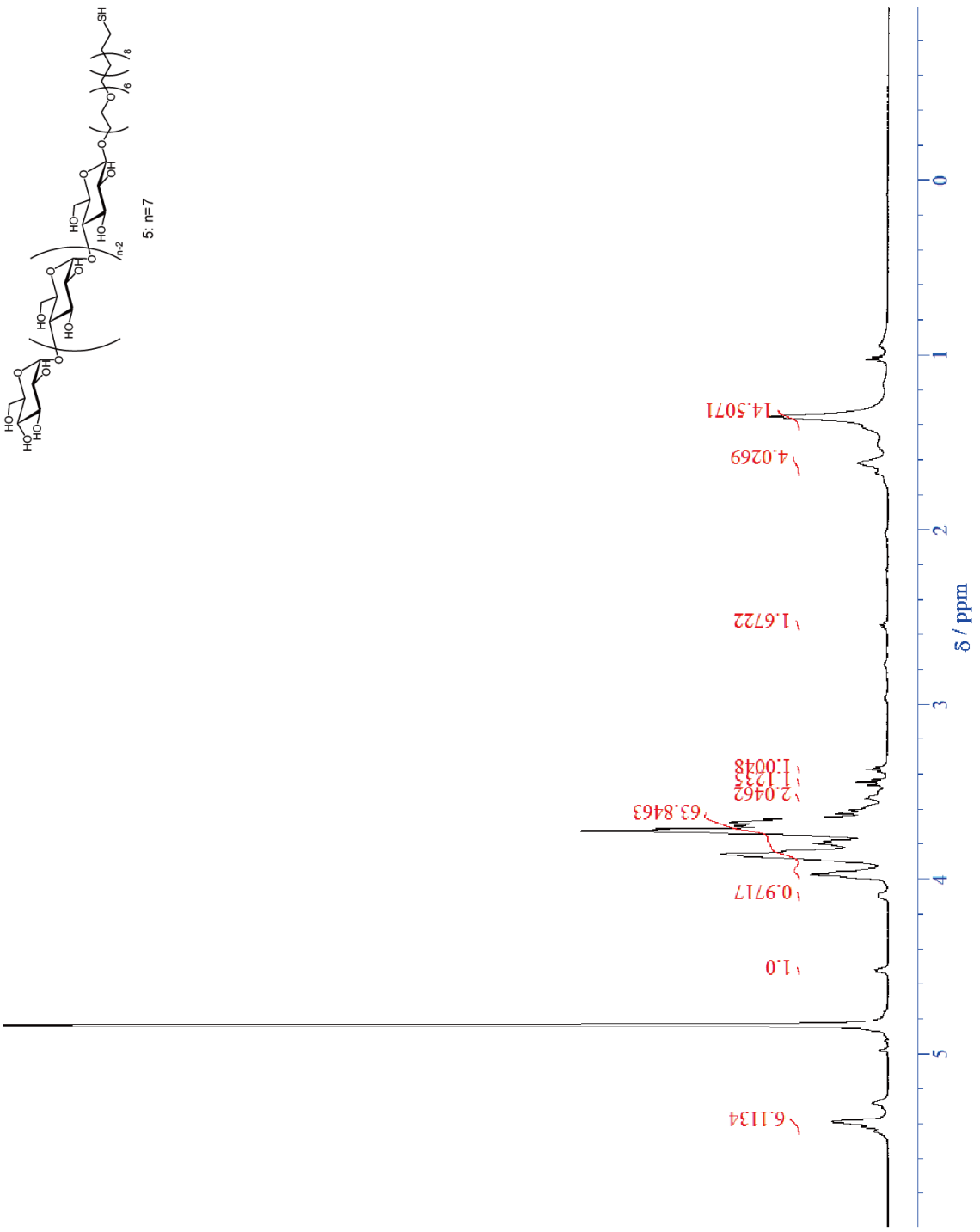

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