Supporting Information for

Folding Control of Non-natural Glycopeptide Using Saccharide-coded Structural Information for Polypeptide

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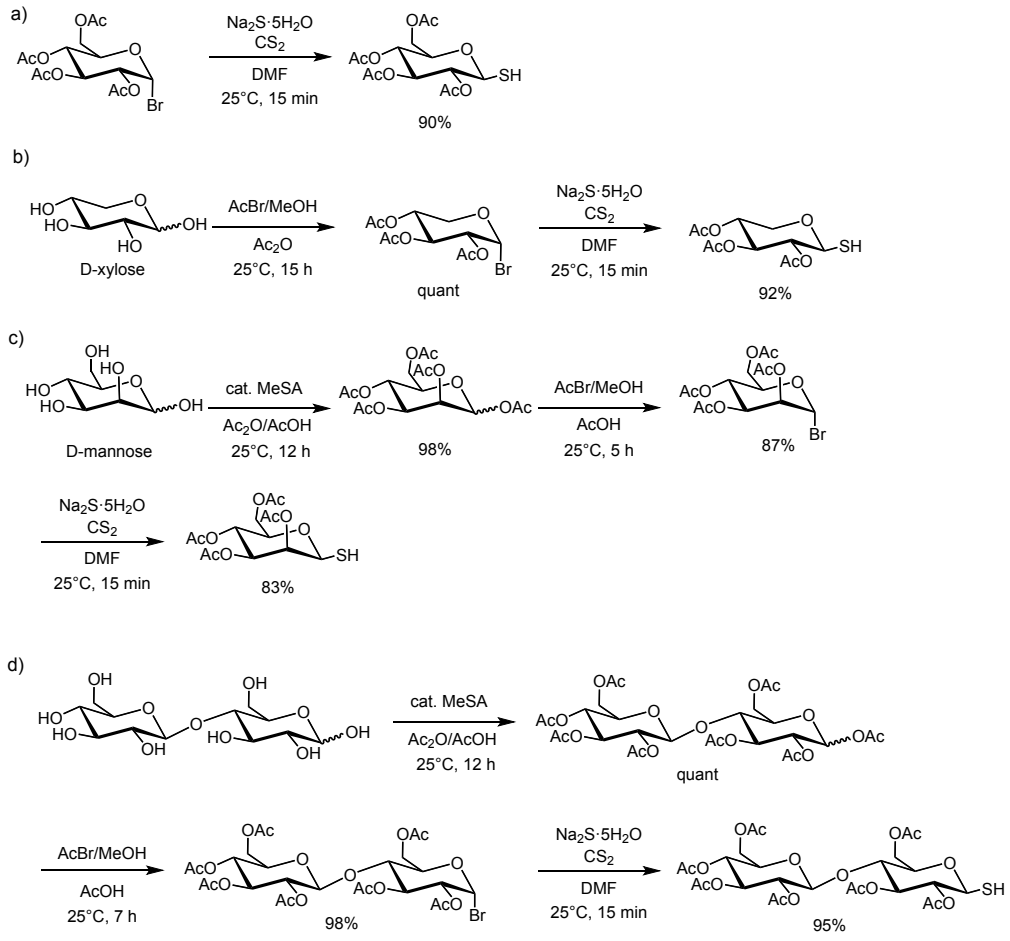
1.1 General. Unless otherwise indicated, all reactions were carried out under an Ar atmosphere, whereas the workup was performed in air. ^{1}H NMR spectra were recorded in $CDCl_3$, DMSO-d_6, methanol-d_4 and D_2O on JEOL JNM-ECS400 or JEOL JNM-ECA500 spectrometers using $SiMe_4$ as an internal standard. IR spectra were recorded on a SHIMADZU IR Prestige-21 spectrometer using KBr tablet. HR-MS measurement was carried out on a Thermo Fisher Scientific LTQ-Orbitrap XL spectrometer. Retention time of polymers were measured by size exclusion chromatography (SEC) analyses using a SHIMAZU LC-10AS, SPD-10A UV-vis detector, and CTO-10A column oven equipped with two SEC columns TOSOH TSKgel GMH_{HR}-M carried out at 40 °C and a flow rate of 0.7 mL min^{-1} with $CHCl_3$ as the eluent. The enantiomeric excess was determined by HPLC analysis using SHIMAZU LC-10 and SPD-10AV equipped with DAICEL Chiralcel OD-H column. CD spectra were obtained by JASCO J-720WO with cryostat at –80 to 50 °C. UV-vis spectra were obtained by a SHIMAZU UV 3100PC.

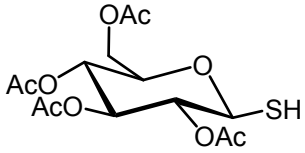
1.2 Materials All solvents used for reactions were passed through purification columns just before use and tetrahydrofuran was dried by sodium-benzophenone and distilled under argon. Planar-chiral Cp′Ru complexes were prepared as reported previously.[1]

1-3. Synthesis of thiols [2]

Scheme S1. Synthetic pathway of saccharide-SH

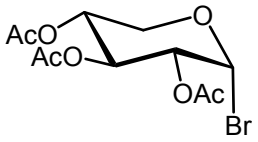


2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranose



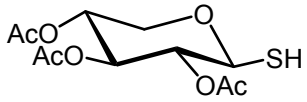
To a white suspension of $Na_2S·5H_2O$ (1.40 g, 5.8 mmol) in DMF (10 mL) was dropwise added carbon disulfide (0.33 mL, 4.4 mmol) at room temperature. On addition of the 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (1.24 g, 2.9 mmol) to the resulting red-colored solution, the color of the reaction became yellow and the reaction mixture was stirred at 25 °C for 15 min. The reaction mixture was diluted with 0.5 M HCl and extracted with ethyl acetate (3×50 mL), dried (Na_2SO_4), and concentrated to furnish the yellow solid. The solid was purified by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate = 4/1 then *n*-hexane/ethyl acetate = 1/1) to give white solid (0.84 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz):) δ 5.19 (t, *J* = 9.4 Hz, 1H, H-3), 5.10 (t, *J* = 9.4 Hz, 1H, H-4), 4.97 (t, *J* = 9.4 Hz, 1H, H-2), 4.57 (t, *J* = 9.4 Hz, 1H, H-1), 4.25 (dd, *J* = 12.5, 4.8 Hz, 1H, H-6a), 4.12 (dd, *J* = 12.5, 2.2 Hz, 1H, H-6b), 3.75 (ddd, J = 10.0, 4.9, 2.2 Hz, 1H, H-5), 2.34 (d, *J* = 9.9 Hz, 1H, SH), 2.09 (s, 3H, C(O)CH_3), 2.08 (s, 3H, C(O)CH_3), 2.02 (s, 3H, C(O)CH_3), 2.01 (s, 3H, C(O)CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.5, 170.0, 169.5, 169.3, 78.6, 76.3, 73.5, 68.1, 62.0, 20.7, 20.6, 20.5, 20.5. HRMS (ESI+): Calcd for $C_{14}H_{20}NaO_9S$ ($[M+Na]^+$): *m*/*z* 387.0726, Found: *m*/*z* 387.0725.

2,3,4-Tri-*O*-acetyl-α-D-xylopyranosyl bromide [3]



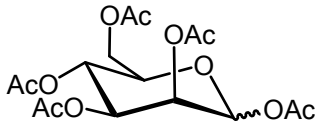
Acetyl bromide (3.93 mL, 53.2 mmol) and CH_3OH (2.15 mL,53.2 mmol) were added to AcOH (20 mL) and stirred at 25 °C (protected from light) for 15 min, followed by addition of D-xylose (2.0 g, 13.3 mmol) and Ac_2O (15 mL). The reaction mixture was further stirred 15 h at 25 °C. The solution was diluted with dichloromethane, washed with saturated solution of sodium bicarbonate and dried with sodium sulfate. The solvent was removed, and ether was added to give pale yellow solid (4.51 g, quant). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.58 (d, *J* = 3.9 Hz, 1H, H-1), 5.56 (t, *J* = 9.9 Hz, 1H, H-3), 5.49 (td, *J* = 9.9, 6.0 Hz, 1H, H-4), 4.77 (dd, *J* = 9.9, 3.9 Hz, 1H, H-2). 4.05 (dd, *J* = 11.1, 6.0 Hz, 1H, H-5), 3.88 (t, *J* = 11.1 Hz, 1H, H-5), 2.10 (s, 3H, C(O)CH_3), 2.06 (s, 3H, C(O)CH_3), 2.05 (s, 3H, C(O)CH_3).

1,2,3,4-Tetra-*O*-acetyl-1-thio-β-D-xylopyranose



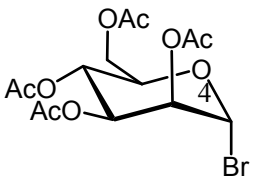
To a white suspension of $Na_2S·5H_2O$ (1.60 g, 7.2 mmol) in DMF (10 mL) was dropwise added carbon disulfide (5.31 mmol) at room temperature. On addition of the 1,2,3,4-tetra-*O*-acetyl-α-D-xylopyranosyl bromide (1.20 g, 3.5 mmol) to the resulting red-colored solution, the color of the reaction became pale red and the reaction mixture was stirred at 25 °C for 15 min. The reaction mixture was diluted with 0.5 M HCl and extracted with ethyl acetate (3×50 mL), dried (Na_2SO_4), and concentrated to produce white solid (0.94 g, 92%).^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.16 (t, *J* = 9.4 Hz, 1H, H-3), 4.96 (ddd, *J* = 9.4, 8.8, 5.3 Hz, 1H, H-4), 4.89 (t, *J* = 8.8 Hz, 1H, H-2), 4.57 (t, 8.8 Hz, 1H, H-1), 4.21 (dd, *J* = 11.9, 5.3 Hz, 1H, H-5), 3.38 (dd, *J* = 11.9, 9.5 Hz, 1H, H-5), 2.28 (d, *J* = 8.8 Hz, 1H, SH);, 2.08 (s, 3H, C(O)CH_3), 2.05 (s, 3H, C(O)CH_3), 2.04 (s, 3H, C(O)CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.1, 169.9, 169.8, 79.1, 73.5, 72.6, 68.7, 66.4, 20.9, 20.8, 20.8. HRMS (ESI+): Calcd for $C_{11}H_{16}NaO_7S$ ($[M+Na]^+$): *m*/*z* 315.0514, Found: *m*/*z* 315.0512.

D-Mannopyranose pentaacetate



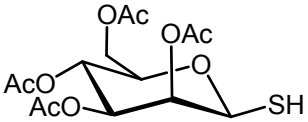
To anhydrous D-mannose (5.0 g, 27.7 mmol) in AcOH (20 mL) were added Ac_2O (17.0 mL, 171.9 mmol) and methanesulfonic acid (4 drops), and the reaction mixture was stirred at 25 °C for 12 h. The solution was diluted with ethyl acetate, washed with saturated solution of sodium bicarbonate and dried with sodium sulfate. The solvent was removed to give colorless oil (10.6 g, 98%), as mixture of anomer (1.25/1 α:β). ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.09 (d, *J* = 1.9 Hz, 1H, H-1α), 5.87 (d, *J* = 1.2 Hz, 1H, H-1β), 5.49 (dd, *J* = 3.3, 1.3 Hz, 1H, H-2β), 5.38 – 5.34 (m, 2H, H-3α and H-4α), 5.32 – 5.29 (m, 1H, H-4β), 5.27 (d, *J* = 2.2 Hz, 1H, H2α), 5.14 (dd, *J* = 10.0, 3.3 Hz, 1H, H-4β), 4.32 (d, *J* = 5.4 Hz, 1H, H-6aβ), 4.29 (dd, *J* = 12.4, 4.9 Hz, 1H, H-6aα), 4.15 (d, *J* = 2.3 Hz, 1H, H-6bβ), 4.10 (dd, *J* = 12.4, 2.4 Hz, 1H, H-6bα), 4.07 – 4.03 (m, 1H, H-5α), 3.81 (ddd, *J* = 9.9, 5.5, 2.4 Hz, 1H, H-5β), 2.21 (s, 3H, O(CO)CH_3), 2.17 (s, 6H, 2 x O(CO)CH_3), 2.17 (s, 3H, O(CO)CH_3), 2.11 (s, 3H, O(CO)CH_3), 2.10 (s, 3H, O(CO)CH_3), 2.06 (s, 6H, 2 x O(CO)CH_3), 2.01 (s, 6H, 2 x O(CO)CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 170.7, 170.3, 170.1, 169.9, 169.8, 169.6, 169.6, 168.4, 168.1, 90.7, 90.6, 73.3, 70.7, 70.6, 68.8, 68.4, 68.2, 65.6, 65.5, 62.2, 62.1, 21.5, 20.9, 20.8, 20.8, 20.7, 20.8, 20.7, 20.7, 20.6, 20.5.

1,2,3,4-Tetra-*O*-acetyl-α-D-mannopyranosyl bromide



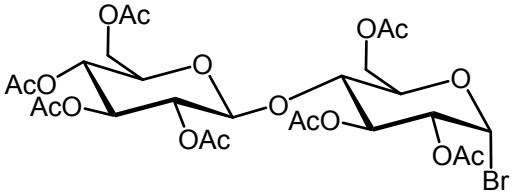
Acetyl bromide (5.91 mL, 80.0 mmol) and CH_3OH (3.23 mL, 80.0 mmol) were added to AcOH (50 mL) and stirred at 25 °C (protected from light) for 20 min, followed by addition of resulting colorless oil (7.8 g, 20.0 mmol) and Ac_2O (50 mL). The reaction mixture was further stirred 5 h at 25°C. The solution was diluted with dichloromethane, washed with saturated solution of sodium bicarbonate and dried with sodium sulfate. The solvent was removed to give pale yellow oil (7.15 g, 87%), as mixture of anomer (162/1 α:β). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.29 (d, *J* = 1.5 Hz, 1H, H-1), 5.71 (dd, *J* = 10.3, 3.4 Hz, 1H, H-3), 5.44 (dd, *J* = 3.4, 1.7 Hz, 1H, H-2), 5.37 (t, *J* = 10.3 Hz, 1H, H-4), 4.32 (dd, *J* = 12.4, 5.0 Hz, 1H, H-6a), 4.21 (ddd, *J* = 10.3, 5.0, 2.2 Hz, 1H, H-5), 4.13 (dd, *J* = 12.4, 2.2 Hz, 1H, H-6b), 2.17 (s, 3H, O(CO)C*H*$_3$), 2.11 (s, 3H, O(CO)C*H*$_3$), 2.07 (s, 3H, O(CO)C*H*$_3$), 2.00 (s, 3H, O(CO)C*H*$_3$).

2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-mannopyranose



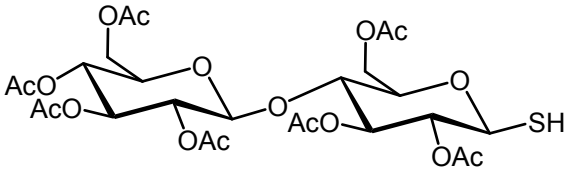
To a white suspension of $Na_2S{\cdot}5H_2O$ (2.80 g, 10.6 mmol) in DMF (15 mL) was dropwise added carbon disulfide (0.66 mL, 8.8 mmol) at room temperature. On addition of the 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (2.48 g, 5.8 mmol) to the resulting red-colored solution, the color of the reaction became yellow and the reaction mixture was stirred at 25 °C for 15 min. The reaction mixture was diluted with 0.5 M HCl and extracted with EtOAc (4×50 mL), dried (Na_2SO_4), and concentrated to furnish the yellow solid. The solid was purified by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate = 4/1 then *n*-hexane/ethyl acetate = 1/1) to give white solid (1.75 g, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.44 (dd, *J* = 3.5, 1.2 Hz, 1H, H-2), 5.23 (t, *J* = 10.2 Hz, 1H, H-4), 5.07 (dd, *J* = 10.1, 3.4 Hz, 1H, H-3), 4.89 (dd, *J* = 9.7, 1.2 Hz, 1H, H-1), 4.26 (dd, *J* = 12.1, 5.6 Hz, 1H, H-6), 4.13 (dd, *J* = 12.1, 2.5 Hz, 1H, H-6), 3.70 (ddd, *J* = 9.7, 5.6, 2.5 Hz, 1H, H-5), 2.54 (d, *J* = 9.7 Hz, 1H, SH), 2.23 (s, 3H, C(O)C*H*$_3$), 2.10 (s, 3H, C(O)C*H*$_3$), 2.04 (s, 3H, C(O)C*H*$_3$), 1.95 (s, 3H, C(O)C*H*$_3$). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.8, 170.3, 170.2, 169.7, 77.1, 76.5, 72.2, 71.7, 65.4, 62.7, 20.9, 20.8, 20.7, 20.6. HRMS (ESI+): Calcd for $C_{14}H_{20}NaO_9S$ ([M+Na]$^+$): *m*/*z* 387.0726, Found: *m*/*z* 387.0725.

2,3,4,6-Tetra-*O*-Acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide



To anhydrous D-cellobiose (1.46 g, 4.27 mmol) in AcOH (10 mL) were added Ac_2O (8.5 mL) and methanesulfonic acid (4 drops), and the reaction mixture was stirred at 25 °C for 12 h. the suspension of the reaction became homogeneous solution. The solution was diluted with ethyl acetate, washed with saturated solution of sodium bicarbonate and dried with sodium sulfate. The solvent was removed to give white solid (2.9 g, quant), as mixture of amoner (1.25/1 α:β). Acetyl bromide (1.0 mL, 13.36 mmol) and CH_3OH (0.2 mL, 4.35 mmol) were added to AcOH (20 mL) and stirred at 25 °C (protected from light) for 20 min, followed by addition of resulting white solid (2.90 g, 4.27 mmol). The reaction mixture was further stirred 7 h at 25 °C. The solution was diluted with dichloromethane, washed with saturated solution of sodium bicarbonate and dried with sodium sulfate. The solvent was removed, and ether was added to give white solid (2.98 g, 98%), as mixture of amoner (93/1 α:β). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.52 (d, *J* = 4.2 Hz, 1H, H-1), 5.53 (t, *J* = 9.7 Hz, 1H, H-3), 5.20 – 5.04 (m, 2H, H-2', H-4'), 4.94 (dd, *J* = 9.9, 9.0 Hz, 1H, H-3'), 4.77 (dd, *J* = 10.0, 4.1 Hz, 1H, H-2), 4.55 (d, *J* = 7.8 Hz, 1H, H-1'), 4.56–4.50 (m, 2H, H-6a, H-6b), 4.43 (dd, *J* = 9.9, 2.6 Hz, 1H, H-5), 4.37 (dd, *J* = 12.5, 4.5 Hz, 1H, H-4), 4.25–4.15 (m, 1H, H-5'), 4.06 (dd, *J* = 12.5, 2.3 Hz, 1H, H-6a'), 3.75 (dd, *J* = 12.5, 7.0 Hz, 1H, H6b'), 2.14 (s, 3H, C(O)CH_3), 2.10 (s, 6H, C(O)CH_3), 2.05 (s, 6H, C(O)CH_3), 2.01 (s, 3H, C(O)CH_3), 1.99 (s, 3H, C(O)CH_3).

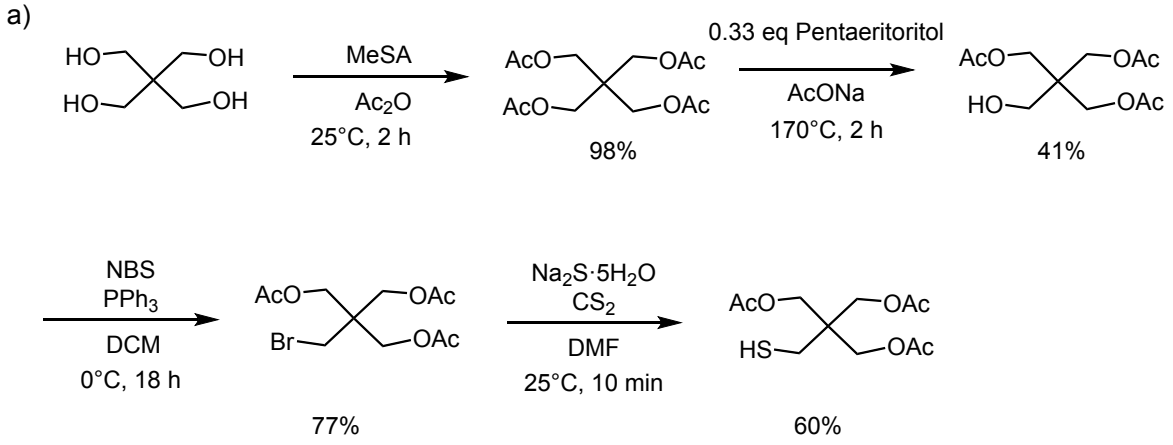
2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1-4)-2,3,6-tri-*O*-acetyl-1-thio--β-D-glucopyranose



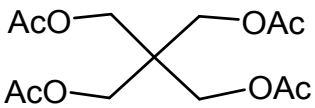
To a white suspension of $Na_2S{\cdot}5H_2O$ (1.6 g, 7.0 mmol) in DMF (15 mL) was dropwise added carbon disulfide (0.43 mL, 5.25 mmol) at room temperature. On addition of the 2,3,4,6-Tetra-*O*-Acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide (2.0 g, 3.5 mmol) to the resulting red-colored solution, the color of the reaction became yellow and the reaction mixture was stirred at 25 °C for 15 min. The reaction mixture was diluted with 0.5 M HCl and extracted with EtOAc (4×50 mL), dried (Na_2SO_4), and concentrated to furnish the yellow solid. The solid was washed with ether to give white solid (2.36 g, 95%). ^{1}H NMR ($CDCl_3$, 500 MHz): 5.22–5.05 (m, 3H, H-3, H-2', H-4'), 4.94 (dd, *J* = 9.9, 9.0 Hz, 1H, H-3'), 4.96–4.85 (m, *J* = 10.0, 4.1 Hz, 1H, H-2), 4.55 (d, *J* = 7.8 Hz, 1H, H-1'), 4.56–4.43 (m, 2H, H-1, H-6a, H-6b), 4.43 (m, 2H, H-2, H-5), 4.36 (dd, *J* = 12.5, 4.5 Hz, 1H, H-4), 4.14–4.01 (m, 2H, H-5', H-6a'), 3.78 (t, *J* = 9.3 Hz, 1H, H6b'), 2.25 (d, *J* = 9.3 Hz, 1H, SH), 2.14 (s, 3H, C(O)CH_3), 2.09 (s, 3H, C(O)CH_3), 2.07 (s, 3H, C(O)CH_3), 2.03 (s, 3H, C(O)CH_3), 2.02 (s, 3H, C(O)CH_3), 2.00 (s, 3H, C(O)CH_3), 1.98 (s, 3H, C(O)CH_3). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.6, 170.4, 170.3, 169.9, 169.7, 169.4, 169.2, 100.95, 78.6, 77.3, 76.4, 73.9, 73.3, 73.0, 72.1, 71.7, 67.9, 62.2, 61.7, 20.9, 20.8, 20.7, 20.6, 20.6. two carbon peaks were missing due to overlap. HRMS (ESI+): Calcd for $C_{26}H_{36}NaO_{17}S$ ($[M+Na]^+$): *m/z*

675.1571, Found: *m/z* 675.1569.

Scheme S3. Synthetic pathway of pentaeritoritol-SH

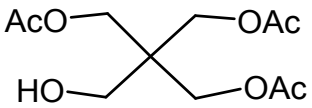


Pentaerythritol tetraacetate



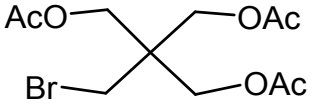
To a pentaerythritol (2.00 g, 14.6 mmol) was added methanesulfonic acid (4 drops) and 20 mL of Ac_2O. The reaction mixture was stirred for 2 h at 25 °C. Block of ice (8 blocks) and ethyl acetate (60 mL) were added to the reaction mixture. The organic layer was carefully washed with $NaHCO_3$ and brine, and dried over Na_2SO_4. After removal of the solvent to give white solid (4.35 g, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.02 (s, 8H, CH_2), 2.07 (s, 12H, COCH_3).

Pentaerythritol triacetate



To a mixture of pentaerythritol tetraacetate (4.35 g, 14.3 mmol) and pentaerythotitol (0.33 eq) was added Sodium acetate (2 mg). The reaction mixture was stirred at 170 ºC. After 2 h, the reaction mixture was cooled to room temperature. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 5/1) to give white solid (1.58 g, 41%). ^{1}H NMR (acetone-d_6, 400 MHz): δ 4.10 (s, 6H, CH_2), 3.61 (s, 2H, CH_2OH), 2.01 (s, 9H, COCH_3).

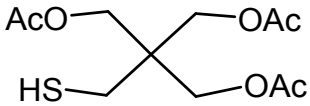
2-(Acetoxymethyl)-2-(bromomethyl)propane-1,3-diyl diacetate



To a dichloromethane solution (20 mL) of pentaerythritol triacetate (1.80 g, 6.80 mmol) and

triphenylphosphine (2.49 g, 9.52 mmol) was a dichloromethane solution (15 mL) of *N*-bromosuccinimide (NBS) (1.53 g, 8.58 mmol) at 0 °C, and the reaction mixture was stirred at 0 ºC. After 18 h, the organic layer was cwashed with brine, and dried over Na_2SO_4. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 2/1) to give colorless oil (1.70 g, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.14 (s, 6H, CH_2), 3.47 (s, 2H, CH_2Br), 2.07 (s, 9H, COCH_3).

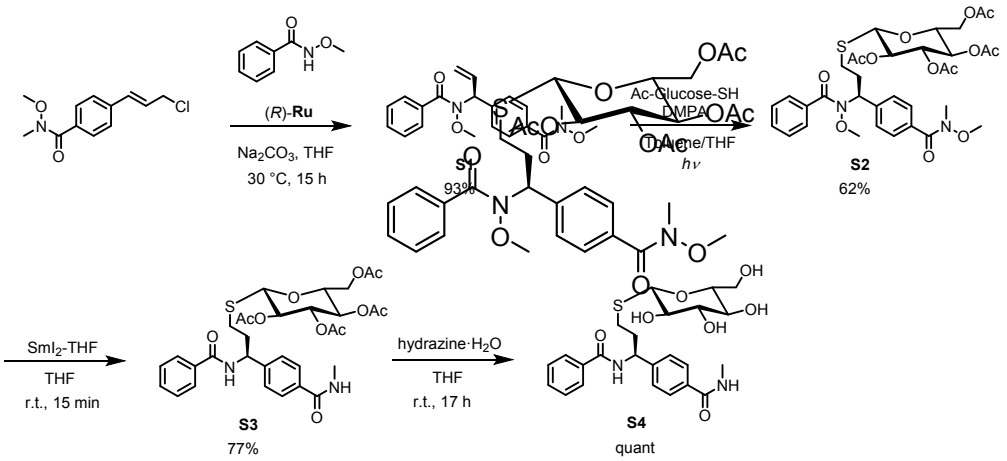
2-(Acetoxymethyl)-2-(mercaptomethyl)propane-1,3-diyl diacetate



To a white suspension of $Na_2S·5H_2O$ (0.86 g, 3.62 mmol) in DMF (10 mL) was dropwise added carbon disulfide (0.21 mL, 2.71 mmol) at room temperature. On addition of the 2-(acetoxymethyl)-2-(bromomethyl)propane-1,3-diyl diacetate (0.589 g, 1.81 mmol) to the resulting red-colored solution, and the reaction mixture was stirred at 25 °C for 10 min. The reaction mixture was diluted with 0.5 M HCl and extracted with EtOAc (4×50 mL), dried (Na_2SO_4), and concentrated to furnish the yellow oil. The oil was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 8/1) to give colorless oil (0.30 g, 60%). Although the peaks that cannot be assigned were included in ^{1}H NMR, the unknown compounds were separated after post-polymerization modification. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.14 (s, 6H, CH_2), 3.48 (s, 2H, CH_2SH), 2.65 (d, J = 9.3 Hz, 1H, SH), 2.08 (s, 9H, COCH_3). HRMS (ESI+): Calcd for $C_{11}H_{18}NaO_6S$ ([M+Na]$^+$): m/z 301.0722, Found: m/z 301.0729.

1-5 Oligomer synthesis

Scheme S4. Synthesis of oligomer (*n* = 1)

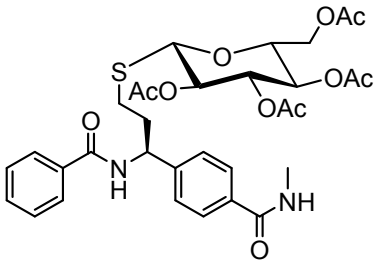


Synthesis of S2

To a toluene/THF (1/2 v/v%) solution (4.0 mL) of **S1** (96.0 mg, 0.27 mmol)[4] and 2,2-dimethoxy-2-phenylacetophenone (DMPA) (69 mg, 0.29 mmol) was added 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (0.52 g, 1.62 mmol), and the reaction mixture was irradiated with an LED lamp (365 nm) for 3 h. The reaction mixture was concentrated under reduced pressure. The residue was purified

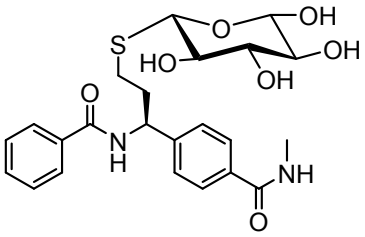
by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate = 2/1 then dichloromethane/ethyl acetate = 2/1) to give a white solid of **S2** (120 mg, 62%).^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 8.3 Hz, 2H, Ar), 7.61 (dd, *J* = 8.4, 1.5 Hz, 2H, Ar), 7.53–7.36 (m, 5H, Ar), 5.82 (t, *J* = 6.6 Hz, 1H, –C*H*CH_2CH_2S–), 5.19 (t, *J* = 9.4 Hz, 1H, H-3), 5.06 (t, *J* = 9.4 Hz, 1H, H-4), 4.49 (d, *J* = 9.8 Hz, 1H, H-1), 4.20 (dd, *J* = 12.0, 4.8 Hz, 1H, H-6a), 4.14–4.05 (m, 2H, H-2, H-6b), 3.69 (ddd, *J* = 10.0, 4.8, 2.2 Hz, 1H, H-5), 3.57 (s, 3H, NCH_3), 3.43 (s, 3H, N–OCH_3), 3.31 (s, 3H, N–OCH_3), 2.85–2.80 (m, 1H, –CHC$H_2$$CH_2S$), 2.74–2.61 (m, 2H, –$CHCH_2CH_2$S), 2.37–2.30 (m, 1H, –CHC$H_2$$CH_2S$), 2.03 (s, 3H, C(O)C$H_3$), 2.08 (s, 3H, C(O)C$H_3$), 2.00 (s, 3H, C(O)C$H_3$), 1.99 (s, 3H, C(O)C$H_3$). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.2, 170.7, 170.3, 169.5, 169.5, 169.4, 141.4, 134.5, 134.0, 130.9, 128.7, 128.7, 128.3, 128.1, 127.8, 83.9, 76.1, 73.9, 69.85, 68.28, 64.4, 62.1, 61.1, 60.4, 20.7, 20.7, 20.7, 20.6, 20.6. one carbon peak was missing due to overlap. HRMS (ESI): Calcd for $C_{34}H_{42}N_2NaO_{13}S$ ([M+Na]$^+$): *m*/*z* 741.2305, Found: *m*/*z* 741.2305.

Synthesis of S3



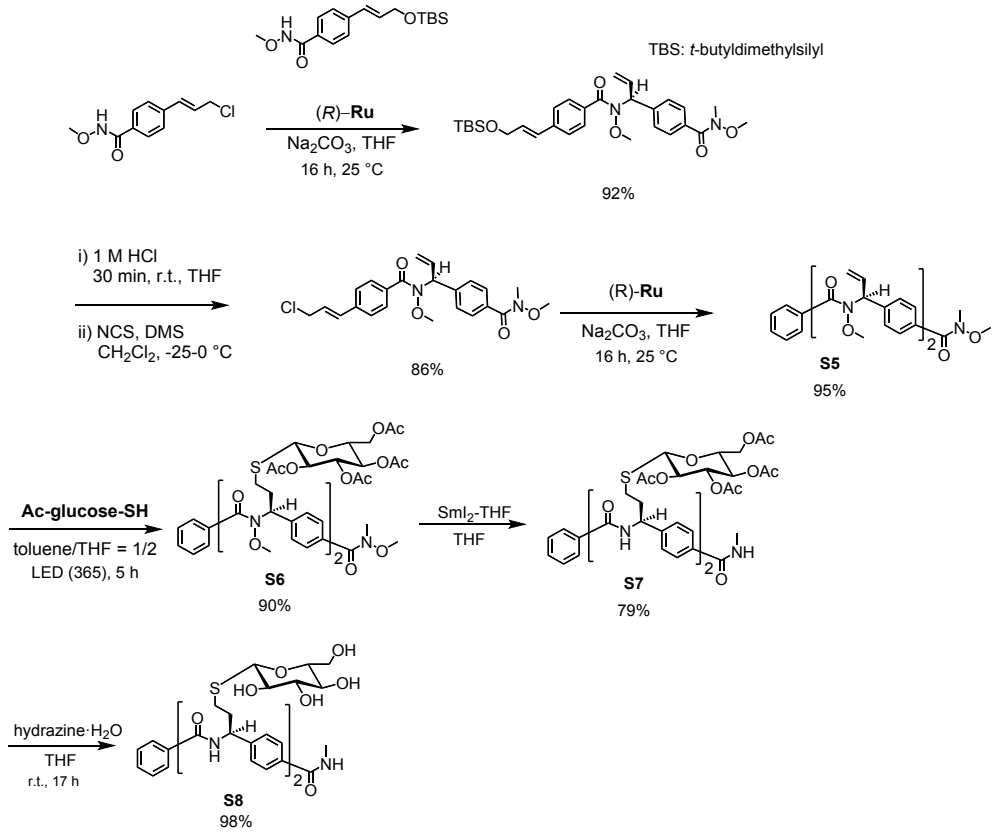
To a stirring solution of **S2** (115 mg, 0.16 mmol) in 0.5 mL of THF was added at 25 °C a solution of SmI_2-THF complex (7.4 mL, 0.1 M in THF), dropwise via syringe. After stirring for 15 min at 25 °C, the reaction was quickly quenched with a 10% aqueous solution of $Na_2S_2O_3·H_2O$ (10 mL) then diluted with CH_2Cl_2 (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×5 ml). The combined organic layers were dried over Na_2SO_4 and then filtered. The filtrate was concentrated *in vacuo* to give pale yellow solid. The solid was washed with *n*-hexane to give a white solid (81 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 8.1 Hz, 2H, Ar), 7.71 (d, *J* = 8.4 Hz, 2H, Ar), 7.53–7.36 (m, 5H, Ar), 6.97 (d, *J* = 7.44 Hz, 1H, NH), 6.42 (q, *J* = 4.8 Hz, 1H, NH), 5.32 (q, *J* = 6.9 Hz, 1H, –C*H*CH_2CH_2S–), 5.20 (t, *J* = 9.3 Hz, 1H, H-3), 5.01 (t, *J* = 9.3 Hz, 1H, H-4), 4.49 (d, *J* = 9.9 Hz, 1H, H-1), 4.18 (dd, *J* = 12.1, 4.8 Hz, 1H, H-6a), 4.17–4.01 (m, 2H, H-2, H-6b), 3.71 (ddd, *J* = 10.1, 4.8, 2.2 Hz, 1H, H-5), 2.98 (d, *J* = 4.8 Hz, 3H, NCH_3), 2.85–2.75 (m, 2H, –CHC$H_2$$CH_2S$), 2.70–2.61 (m, 2H, –$CHCH_2CH_2$S), 2.03 (s, 3H, C(O)C$H_3$), 2.02 (s, 3H, C(O)C$H_3$), 2.00 (s, 3H, C(O)C$H_3$), 1.94 (s, 3H, C(O)C$H_3$). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.9, 170.3, 170.2, 169.6, 168.0, 167.1, 145.2, 134..2, 134.1, 131.8, 128.7, 127.5, 127.2, 126.8, 83.7, 76.1, 73.8, 69.7, 68.4, 68.1, 62.1, 53.2, 26.9, 25.7, 20.8, 20.7, 20.7, 20.7. HRMS (ESI): Calcd for $C_{32}H_{38}N_2NaO_{11}S$ ([M+Na]$^+$): *m*/*z* 681.2094, Found: *m*/*z* 681.2090.

Synthesis of S4

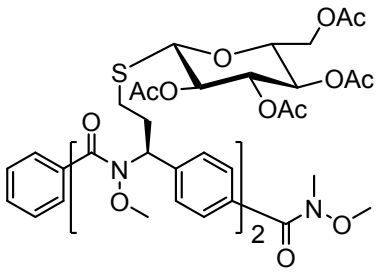


To a THF solution (2.0 mL) of **S3** (62 mg, 0.09 mmol) was hydrazine·H_2O (20.0 eq) at 0°C, and the reaction mixture was stirred at room temperature. After 17 h, the reaction was quenched with acetone. After the solvent was removed under reduced pressure, the residue was purified by washing the DCM and ethyl acetate to give white solid (43 mg, quant). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.88 (d, J = 8.4 Hz, 1H, NH), 8.43 (q, J = 4.8 Hz, 1H, NH), 7.94 (d, J = 8.2 Hz, 2H, Ar), 7.84 (d, J = 8.3 Hz, 2H, Ar), 7.64–7.50 (m, 5H, Ar), 5.26 (q, J = 6.9 Hz, 1H, –C*H*CH_2CH_2S–), 5.17 (d, J = 6.2 Hz, 1H, OH-H2), 5.06 (d, J = 4.8 Hz, 1H, OH-H3), 4.98 (d, J = 4.8 Hz, 1H, OH-H4), 4.52 (t, J = 5.8 Hz, 1H, OH-H6), 4.36 (d, J = 9.5 Hz, 1H, H-1), 3.58(s, 1H, H-6), 3.42 (s, 1H, H-6), 3.26–3.07 (m,, 4H, H-2, H-3, H-4, H-5), 2.83 (d, J = 4.8 Hz, 3H, NCH_3), 2.85–2.75 (m, 1H, –$CHCH_2CH_2$S), 2.30–2.20 (m, 1H, –$CHCH_2CH_2$S), 2.18–2.11 (m, 1H, –$CHCH_2CH_2$S). One proton peak (–$CHCH_2CH_2$S) was missing due to overlap with solvent. IR (KBr): 3333, 1652, 1547 cm^{-1}. HRMS (ESI): Calcd for $C_{23}H_{28}N_2NaO_7S$ ([M+Na]$^+$): *m*/*z* 499.1515, Found: *m*/*z* 499.1516.

Scheme S5. Synthesis of oligomer (*n* = 2)

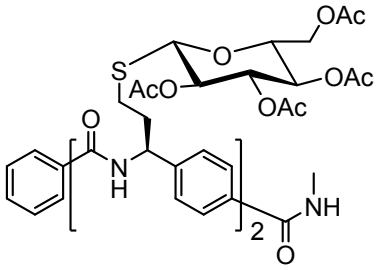


Synthesis of S6



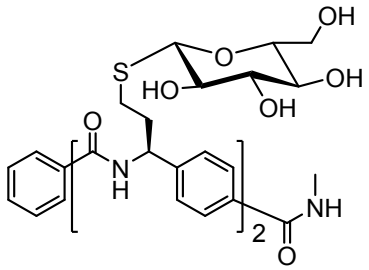
To a toluene/THF (1/2 v/v%) solution (4.0 mL) of **S5** (113 mg, 0.23 mmol)[4] and DMPA (64 mg, 0.27 mmol) was added 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (0.48 g, 1.50 mmol), and the reaction mixture was irradiated with an LED lamp (365 nm) for 5 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: dichloromethane/ethyl acetate = 4/1) to give a white solid of **S6** (260 mg, 90%).^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.23–7.16 (m, 6H, Ar), 7.23–7.16 (m, 6H, Ar), 7.09–7.05 (m, 7H, Ar), 5.52 (bs, 2H, –C*H*CH_2CH_2S–), 5.12 (t, *J* = 9.6 Hz, 2H, H-3), 5.03 (t, *J* = 9.6 Hz, 2H, H-4), 4.49 (d, *J* = 9.9 Hz, 2H, H-1), 4.25 (m, 2H, H-2), 4.18 (dd, *J* = 12.0, 4.8 Hz, 2H, H-6a), 4.04 (dd, *J* = 12.4, 2.1 Hz,2H, H-6b), 3.65 (ddd, *J* = 10.0, 4.8, 2.1 Hz, 2H, H-5), 3.57 (s, 3H, NCH_3), 3.43 (s, 3H, N–OCH_3), 3.36 (s, 6H, N–OCH_3), 2.85–2.80 (m, 2H, –$CHCH_2CH_2S$), 2.74–2.61 (m, 4H, –$CHCH_2CH_2S$), 2.37–2.30 (m, 2H, –$CHCH_2CH_2S$), 2.03 (s, 6H, C(O)CH_3), 2.08 (s, 6H, C(O)CH_3), 2.00 (s, 6H, C(O)CH_3), 1.99 (s, 6H, C(O)CH_3).

Synthesis of S7



To a stirring solution of **S6** (110 mg, 0.087 mmol) in 0.5 mL of THF was added at 25 °C a solution of SmI_2-THF complex (6.0 mL, 0.1 M in THF), dropwise via syringe. After stirring for 15 min at 25 °C, the reaction was quickly quenched with a 10% aqueous solution of $Na_2S_2O_3 \cdot H_2O$ (10 mL) then diluted with CH_2Cl_2 (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×5 ml). The combined organic layers were dried over Na_2SO_4 and then filtered. The filtrate was concentrated *in vacuo* to give pale yellow solid. The solid was washed with *n*-hexane to give a white solid (81 mg, 77%). (78.3 mg, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81–7.71 (m, 6H, Ar), 7.52–7.42 (m, 6H, Ar), 6.84 (d, J = 8.3 Hz, NH), 6.77 (d, J = 8.0 Hz, NH), 6.2 (q, J = 4.1 Hz, N*H*CH_3), 5.33 (q, J = 7.2 Hz, –C*H*CH_2CH_2S–), 5.25–5.15 (m, 2H, H-3), 5.10–4.95 (m, 2H, H-4), 4.56–4.41 (m, 2H, H-1), 4.23–3.97 (m, 4H, H-2, H-6a, H-6b), 3.72–3.64 (m, 2H, H-5), 3.00 (d, J = 4.7 Hz, 3H, NHC*H*$_3$) 2.80–2.65 (m, 4H, –$CHCH_2$C*H*$_2$S), 2.31–2.21 (m, 4H, –CHC*H*$_2CH_2S$), 2.37–2.30 (m, 2H, –CHC*H*$_2CH_2S$), 2.03–1.97 (m, 24H, C(O)C*H*$_3$). HRMS (ESI): Calcd for $C_{55}H_{65}N_3NaO_{21}S_{21}$ ([M+Na]$^+$): *m*/*z* 1204.3606, Found: *m*/*z* 1204.3606.

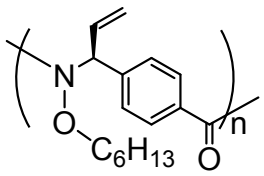
Synthesis of S8



To a THF solution (2.0 mL) of **S7** (97 mg, 0.083 mmol) was hydrazine·H_2O (30.0 eq) at 0°C, and the reaction mixture was stirred at room temperature. After 17 h, the reaction was quenched with acetone. After the solvent was removed under reduced pressure, the residue was purified by washing the DCM and ethyl acetate to give white solid (67.6 mg, 98%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.91 (d, J = 7.8 Hz, 1H, NH), 8.83 (d, J = 8.02 Hz, 1H, NH), 8.43 (q, J = 4.8 Hz, 1H, NH), 7.97–7.82 (m, 6H, Ar), 7.60–7.50 (m, 7H, Ar), 5.25 (q, J = 3.9 Hz, 2H, –C*H*CH_2CH_2S–), 5.29–4.83 (br, 6H, OH-H2, OH-H3, OH-H4), 4.52 (br, 2H, OH-H6), 4.36 (m, 2H, H-1), 3.58 (s, 1H, H-6), 3.68 (m, 2H, H-6a), 3.25–3.05 (m,, 8H, H-2, H-3, H-4, H-5), 2.83 (d, J = 4.8 Hz, 3H, NC*H*$_3$), 2.85–2.60 (m, 4H, –$CHCH_2$C*H*$_2$S), 2.30–2.21 (m, 2H, –CHC*H*$_2CH_2S$), 2.20–2.11 (m, 2H, –CHC*H*$_2CH_2S$). One proton peak (H-6b) was missing due to overlap with H_2O. IR (KBr): 3328, 1653, 1548 cm^{-1}HRMS (ESI): Calcd for $C_{40}H_{51}N_3NaO_{13}S_2$ ([M+Na]$^+$): *m*/*z* 868.2761, Found: *m*/*z* 868.9661.

1-6. Synthesis of Polymers

Asymmetric polymerization;

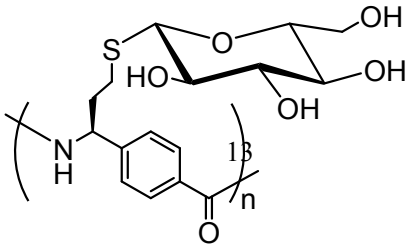


To a mixture of molecular sieve 3A, Na_2CO_3 (1.2 eq), a monomer (1.0 eq) and (*R*) or (*S*)-Cp′Ru (2 mol%) were added THF (0.5 mmol/1 mL), which was stirred at 30 °C. After 3 days, dichloromethane was added to the reaction mixture. The insoluble part was filtered through Celite. The combined organic layer was washed with water. After drying over Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography with CH_2Cl_2 and dried under vacuum to give a pale-yellow solid (69%, M_n = 19 000, M_w/M_n = 1.6). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, 2H, *J* = 8.0 Hz, Ar), 7.49 (d, 2H, *J* = 8.0 Hz, Ar), 7.69 (ddd, 1H, *J* = 17.3, 10.2, 7.2 Hz, CHC*H*═CH_2), 6.11 (br, 1H, C*H*CH═CH_2), 5.40 (d, 1H, *J* = 10.2 Hz, CHCH═CH_2), 5.37(d, 1H, *J* = 17.3 Hz, CHCH═CH_2), 3.56 (br, 1H, OCH_2), 3.28 (br, 1H, OCH_2), 1.30–0.98 (m, 8H, CH_2), 0.79 (t, 3H, *J* = 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.8, 141.1, 134.0, 133.8, 128.3, 127.9, 119.4, 77.2, 63.7, 31.4, 27.8, 25.4, 22.4, 13.9.

Standard method of post-polymerization modification

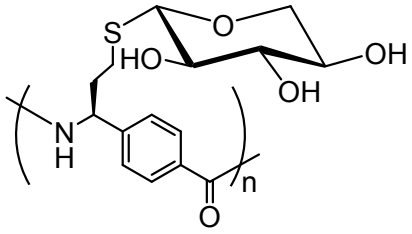
To a toluene/THF (1/2 v/v%) solution (5 mL) of the polymer (0.15 mmol of C=C groups) and DMPA (38.4 mg, 0.15 mmol) was added thiol (0.90 mmol), and the reaction mixture was irradiated at 365 nm with an lamp for 5 h. The crude product was purified by using an SEC column (Shodex; KF 2003 × 2; flow rate 3.0 mL min^{-1}) to give the pale brown solid (1st step). To a THF solution (0.10 M) of the resulting polymer was added THF solution of SmI_2–THF complex (2.3 equiv) at 25 °C, dropwise via syringe. After stirring for 1.5 h at 25 °C, the reaction was rapidly quenched with a 10% solution of $Na_2S_2O_3·H_2O$ and then diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were concentrated *in vacuo*. The crude product was purified by using an SEC column (Shodex; KF 2003 × 2; flow rate 3.0 mL min^{-1}), and washed with *n*-hexane to give white powder (2nd step). To a THF solution (2.0 mL) of resulting powder was added hydrazine·H_2O (20.0 eq/ unit) at 0°C, and the reaction mixture was stirred at 25 °C. After 17 h, the reaction was quenched with acetone. After the solvent was removed under reduced pressure, ether was added to give white solid. The solid was purified by washing with DCM to give target compounds **poly-1a–1d** (3rd step). The acetylation of OH groups were carried out by acetic anhydride in AcOH.

Synthesis of poly-1a.



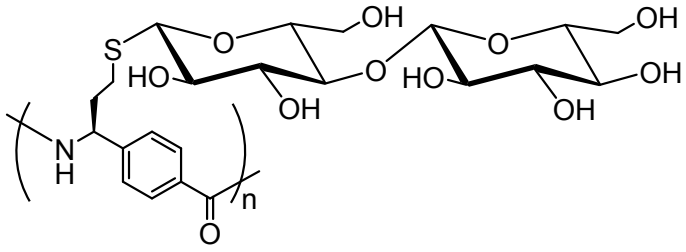
According to the standard method of asymmetric polymerization and post-polymerization modification, **poly-1a** was obtained as a white powder (1st step; 100% conv., 93%, 2nd step; 95% (M_w = 29,000, M_w/M_n = 2.1), 3rd step; quant). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.91 (bs, 1H, NH), 7.90 (d, J = 8.4 Hz, 2H, Ar), 7.90 (d, J = 7.5 Hz, 2H, Ar), 5.26 (bs, 1H, –C*H*CH_2CH_2S–), 5.19 (d, J = 5.8 Hz, 1H, OH-H2), 5.08 (d, J = 4.5 Hz, 1H, OH-H3), 4.99 (d, J = 4.5 Hz, 1H, OH-H4), 4.59 (t, J = 5.7 Hz, 1H, OH-H6), 4.36 (d, J = 9.3 Hz, 1H, H-1), 3.70 (m, 1H, H-6a), 3.49 (m, 1H, H-6b), 3.22–3.19 (m,, 2H, H-3, H-5), 3.16–3.13 (m, 1H, H-4), 3.09–3.06 (m, 1H, H-2), 2.85–2.78 (m, 1H, –$CHCH_2C$*H*$_2$S), 2.70–2.62 (m, 1H, –$CHCH_2C$*H*$_2$S), 2.30–2.19 (m, 1H, –CHC*H*$_2CH_2$S), 2.18–2.20 (m, 1H, –CHC*H*$_2CH_2$S). IR (KBr): 3387, 1652, 1548 cm^{-1}.

Synthesis of poly-1b.



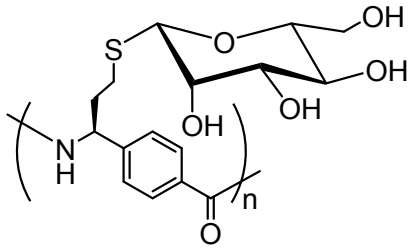
According to the standard method of reductive cleavage using SmI_2-THF complex, **poly-1b** was obtained as a white solid (1st step; 100% conv., 92%, 2nd step; 87% (M_w = 33,000, M_w/M_n = 2.4), 3rd step; 77%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.89 (bs, 1H, NH), 7.88 (d, J = 8.4 Hz, 2H, Ar), 7.53 (d, J = 7.5 Hz, 2H, Ar), 5.26–5.20 (br, 2H, –C*H*CH_2CH_2S– and OH-H2), 5.12 (br, 1H, OH-H3), 5.05 (br, 1H, OH-H4), 4.34 (d, J = 8.9 Hz, 1H, H-1), 4.27–4.25 (br, 1H, H-5a), 4.42–4.14 (br, 1H, H-5b), 3.72, 3.21–3.02 (m, 3H, H-2, H-3, H-4), 2.74–2.69 (m, 2H, –$CHCH_2C$*H*$_2$S), 2.22(br, 1H, –CHC*H*$_2CH_2$S), 2.15 (br, 1H, –CHC*H*$_2CH_2$S). IR (KBr): 3350, 1640, 1549 cm^{-1}.

Synthesis of poly-1b.



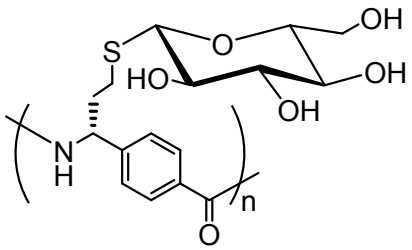
According to the standard method of asymmetric polymerization and post-polymerization modification, **poly-1d** was obtained as a white powder (1st step; 100% conv., 97%, 2nd step; 90% (M_w = 29,000, M_w/M_n = 2.7), 3rd step; quant). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.98 (bs, 1H, NH), 7.89 (br, 2H, Ar), 7.55 (br, 2H, Ar), 5.37 (bs, 1H, –C*H*CH_2CH_2S–), 5.29–4.32 (7H, OH), 5.29–4.32 (14H, CH and CH_2), 2.85–2.78 (m, 1H, –$CHCH_2C$*H*$_2$S), 2.70–2.62 (m, 1H, –$CHCH_2C$*H*$_2$S), 2.30–2.19 (m, 1H, –CHC*H*$_2CH_2$S), 2.18–2.20 (m, 1H, –CHC*H*$_2CH_2$S). IR (KBr): 3372, 1642, 1549 cm^{-1}.

Synthesis of poly-1d.



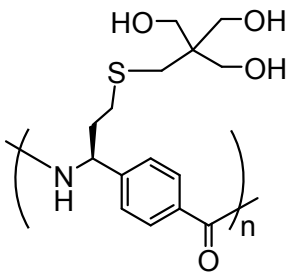
According to the standard method of reductive cleavage using SmI_2-THF complex, **poly-1b** was obtained as a white solid (1st step; 100% conv., 91%, 2nd step; 81% (M_w = 31,000, M_w/M_n = 2.3), 3rd step; quant). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.99 (brs, 1H, NH), 7.90 (br, 2H, Ar), 7.54 (br, 2H, Ar), 5.21 (br, 1H, –C*H*CH_2CH_2S–), 5.19 (m, 3H, OH-H2, OH-H3, OH-H4), 4.47 (br, 1H, OH-H6), 4.17 (bs, 1H, H-1), 3.80–3.68 (br, 2H, H-2, H-6a), 3.54 (br, 1H, H-6b), 3.18–3.13 (br, 1H, H-4), 2.81–2.70 (m, 2H, –CHCH$_2$C*H*$_2$S), 2.31–2.20 (m, 1H, –CHC*H*$_2$CH$_2$S), 2.15–2.07 (m, 1H, –CHC*H*$_2$CH$_2$S). Two peaks was missing to overlap with water. IR (KBr): 3373, 1642, 1548 cm^{-1}.

Synthesis of poly-1a (stereochemistry on main chain is (*R*)).



According to the standard method of asymmetric polymerization and post-polymerization modification, **poly-1a** was obtained as a white powder (1st step; 100% conv., 90%, 2nd step; 88% (M_w = 29,000, M_w/M_n = 2.4), 3rd step; quant). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.91 (bs, 1H, NH), 7.90 (d, J = 8.4 Hz, 2H, Ar), 7.90 (d, J = 7.5 Hz, 2H, Ar), 5.26 (bs, 1H, –C*H*CH_2CH_2S–), 5.19 (d, J = 5.8 Hz, 1H, OH-H2), 5.08 (d, J = 4.5 Hz, 1H, OH-H3), 4.99 (d, J = 4.5 Hz, 1H, OH-H4), 4.59 (t, J = 5.7 Hz, 1H, OH-H6), 4.41 (d, J = 9.3 Hz, 1H, H-1), 3.70 (m, 1H, H-6a), 3.49 (m, 1H, H-6b), 3.22–3.19 (m,, 2H, H-3, H-5), 3.16–3.13 (m, 1H, H-4), 3.09–3.06 (m, 1H, H-2), 2.85–2.78 (m, 1H, –CHCH$_2$C*H*$_2$S), 2.70–2.62 (m, 1H, –CHCH$_2$C*H*$_2$S), 2.30–2.19 (m, 1H, –CHC*H*$_2$CH$_2$S), 2.18–2.20 (m, 1H, –CHC*H*$_2$CH$_2$S).

Synthesis of poly-S9.



According to the standard method of asymmetric polymerization and post-polymerization modification, **poly-S1** was obtained as a pale brown powder (1st step; 100% conv., 78%, 2nd step; 92% (M_w = 29,000, M_w/M_n = 2.1), 3rd step; 98%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.99 (bs, 1H, NH), 7.89 (br, 2H, Ar), 7.53 (br, 2H, Ar), 5.23 (bs, 1H, –C*H*CH_2CH_2S–), 4.32 (br, 6H, –C*H*$_2$OH), 4.18 (br, *2*H, –C*H*$_2$S–), 4.42–4.10 (br, 3H, OH), 3.22 (m, 2H, –CHCH_2C*H*$_2$S), 2.16–2.12 (m, 1H, –CHC*H*$_2$CH_2S), 2.02–1.91 (m, 1H, –CHC*H*$_2$CH_2S). IR (KBr): 3394, 1648, 1547 cm^{-1}.

2. NMR Analysis

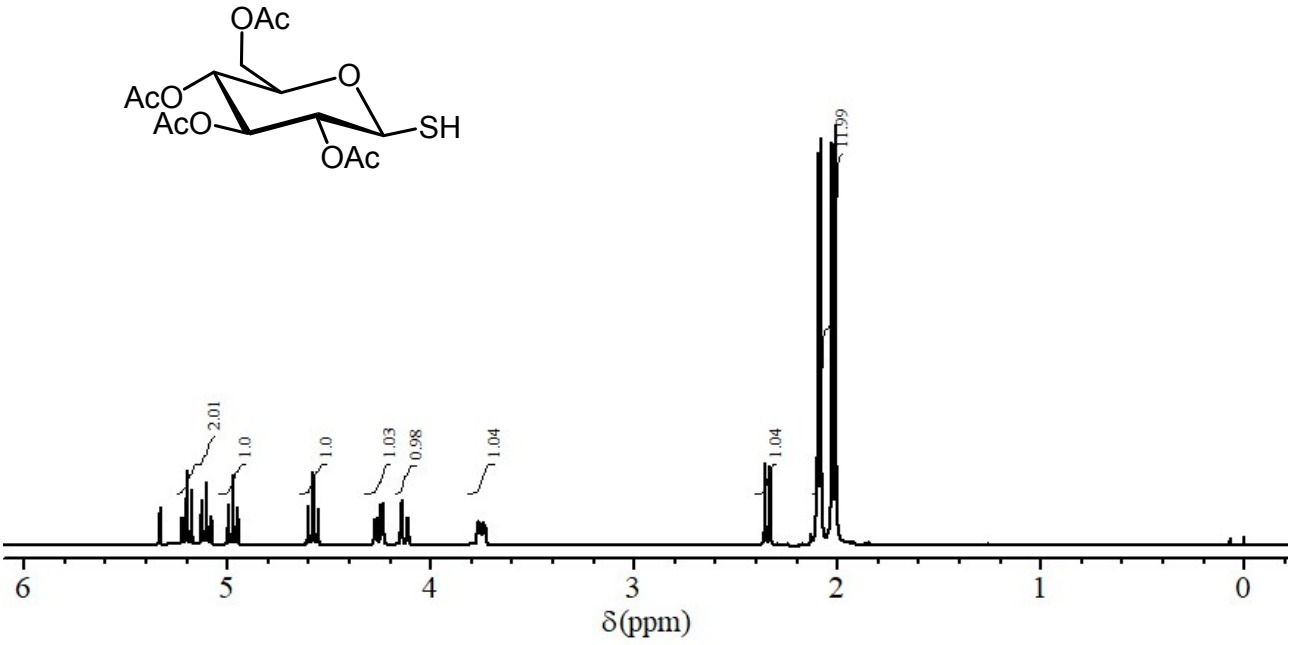


Figure S1. [1]H NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose.

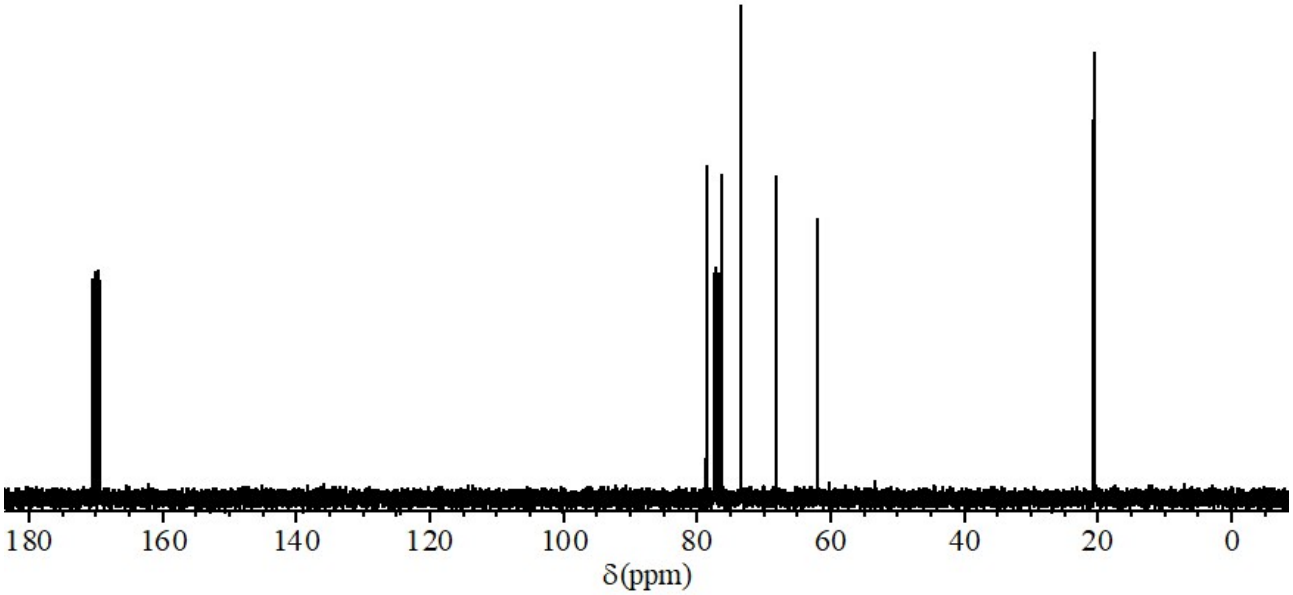


Figure S2. [13]C NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose.

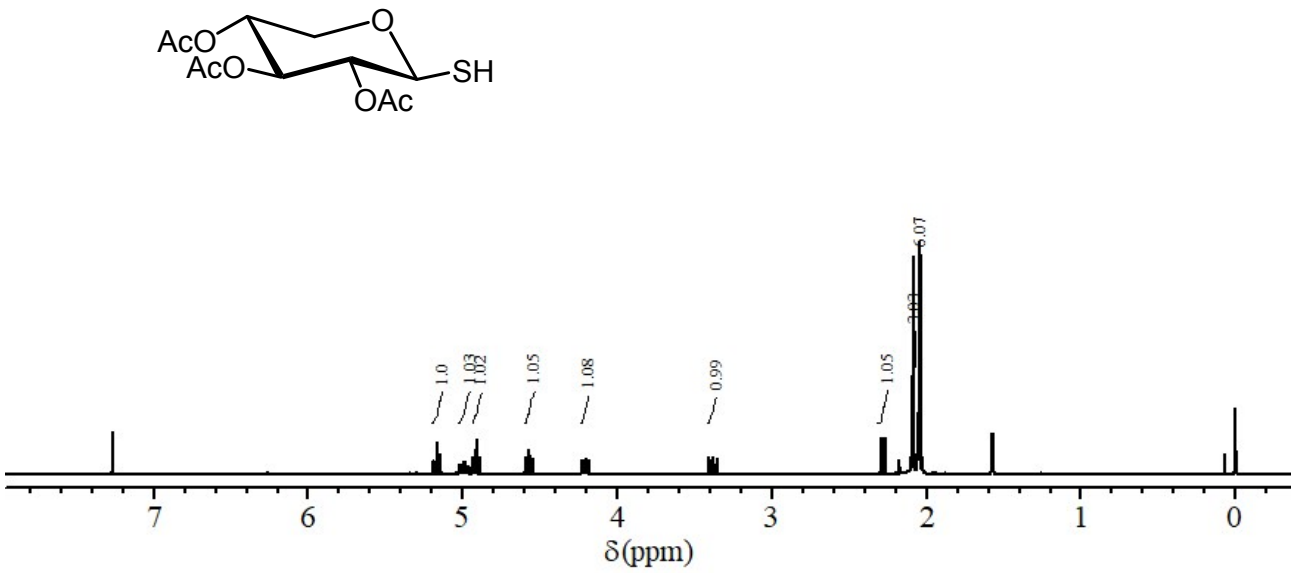


Figure S3. [1]H NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-1-thio-β-D-xylopyranose

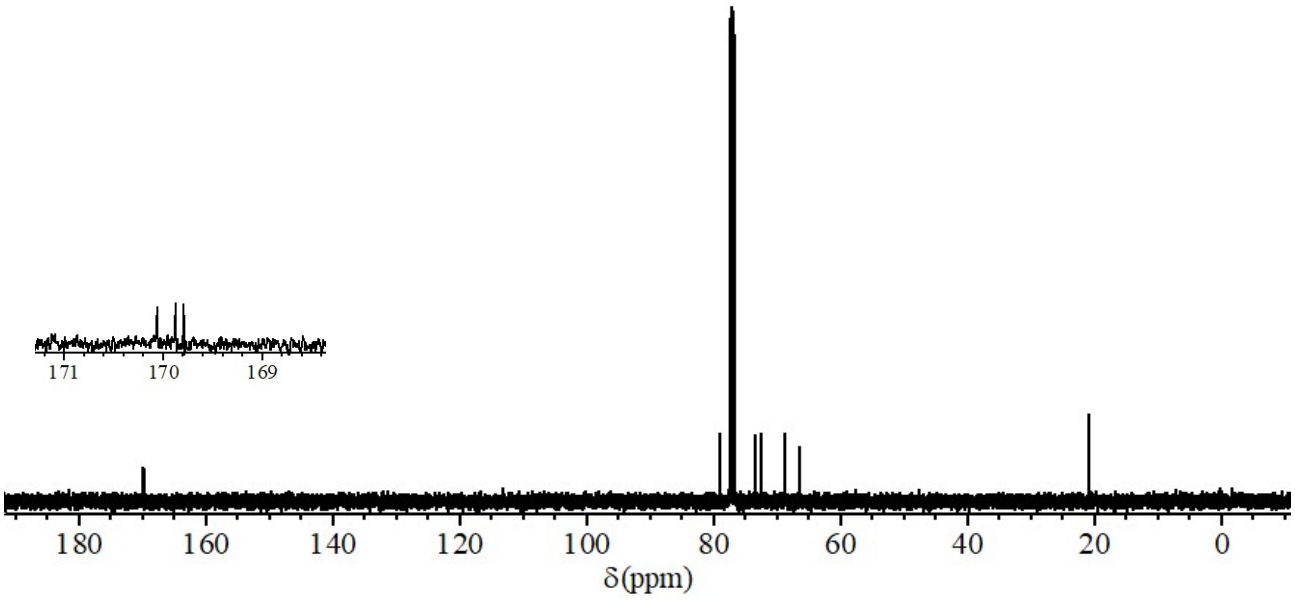


Figure S4. [13]C NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-1-thio-β-D-xylopyranose

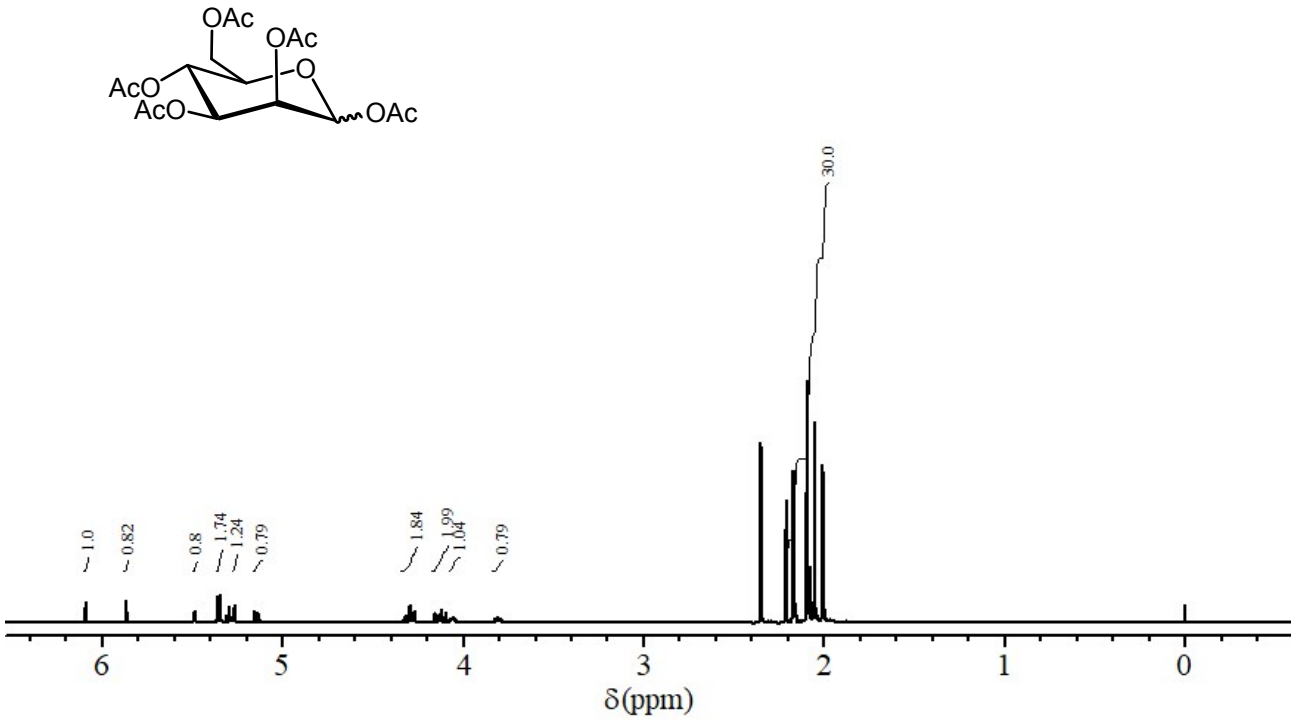


Figure S5. [1]H NMR spectrum of D-mannopyranose pentaacetate

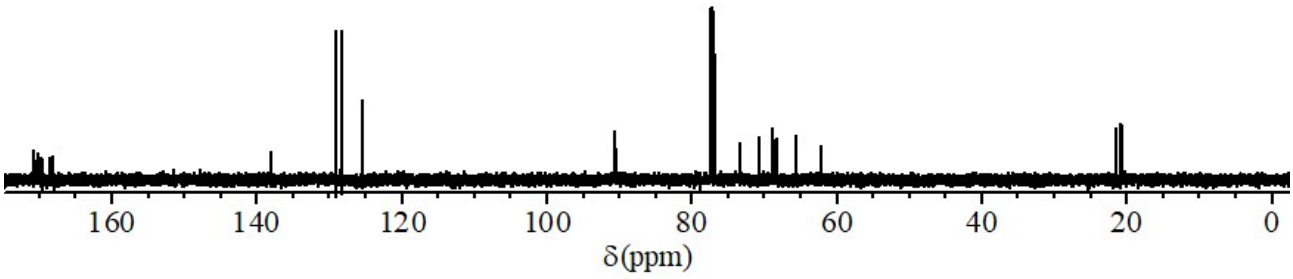


Figure S6. [13]C NMR spectrum of D-mannopyranose pentaacetate

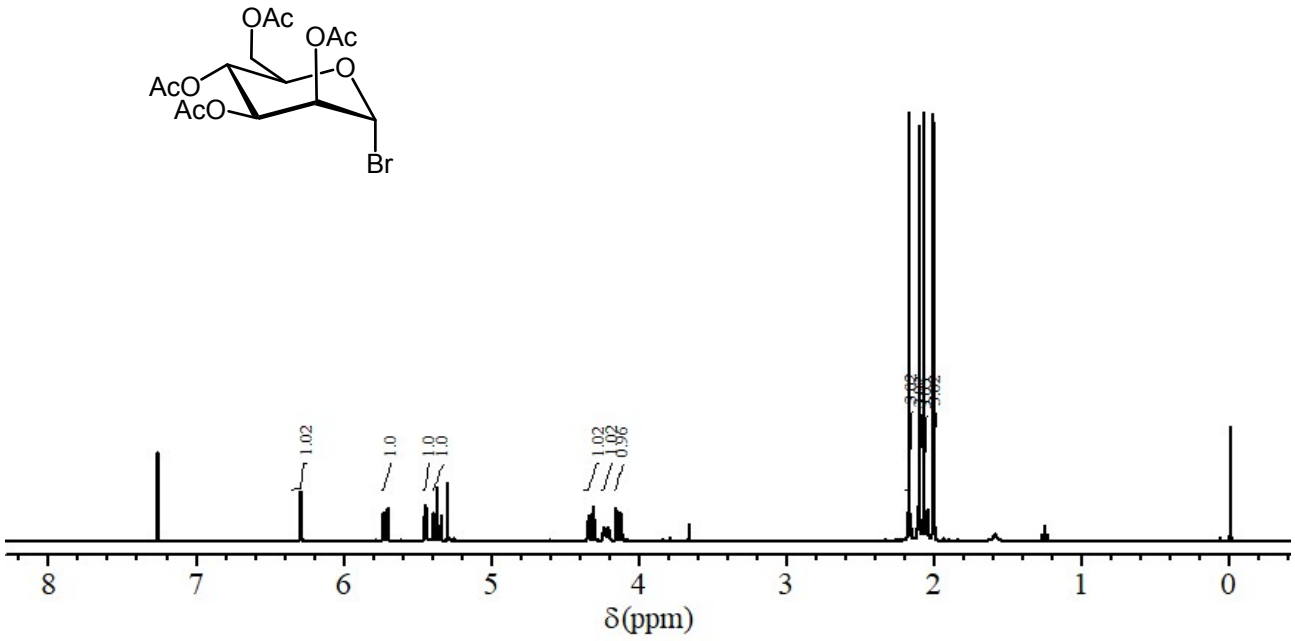


Figure S7. [1]H NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-α-D-mannopyranosyl bromide.

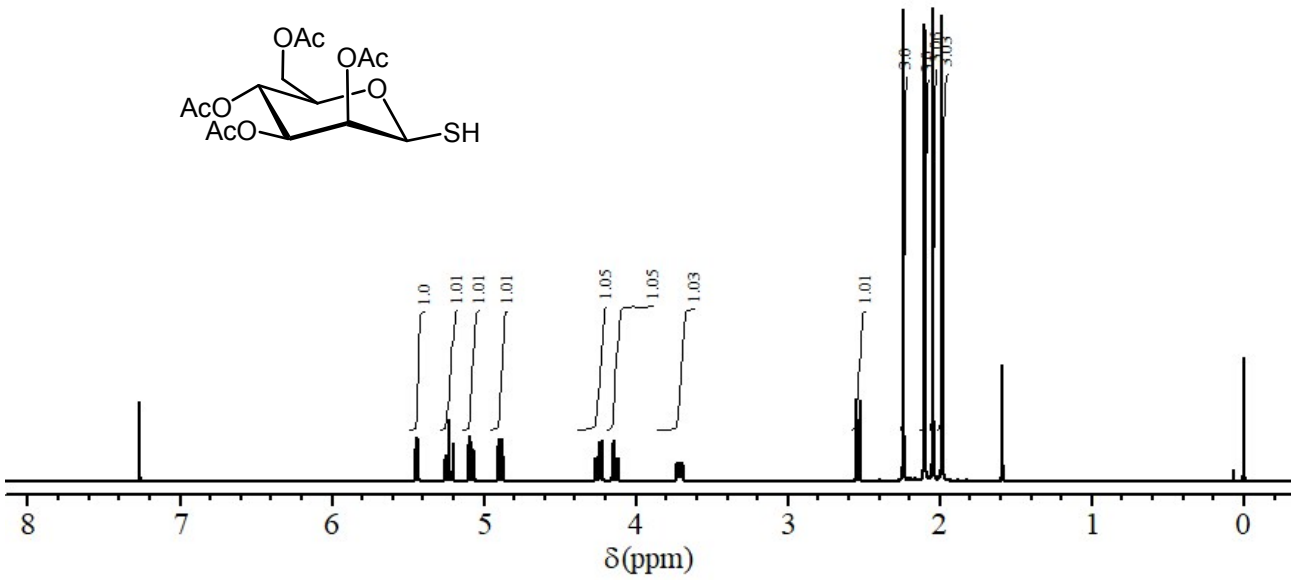


Figure S8. [1]H NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-mannopyranose.

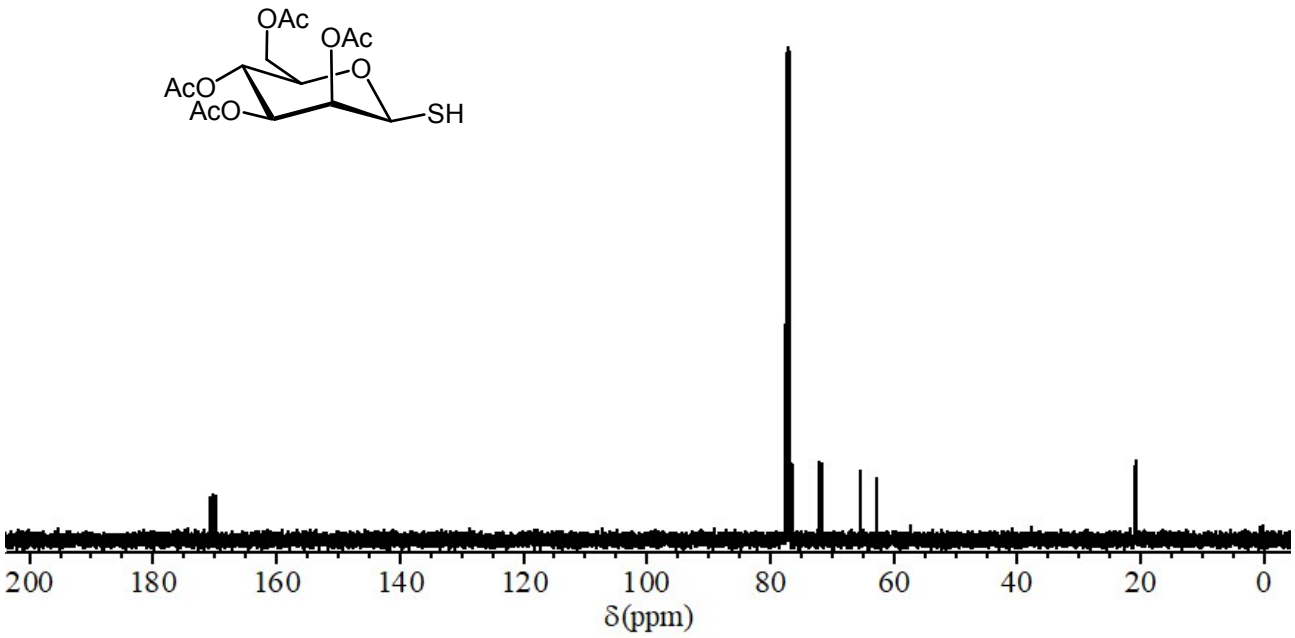


Figure S9. ^{13}C NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-mannopyranose

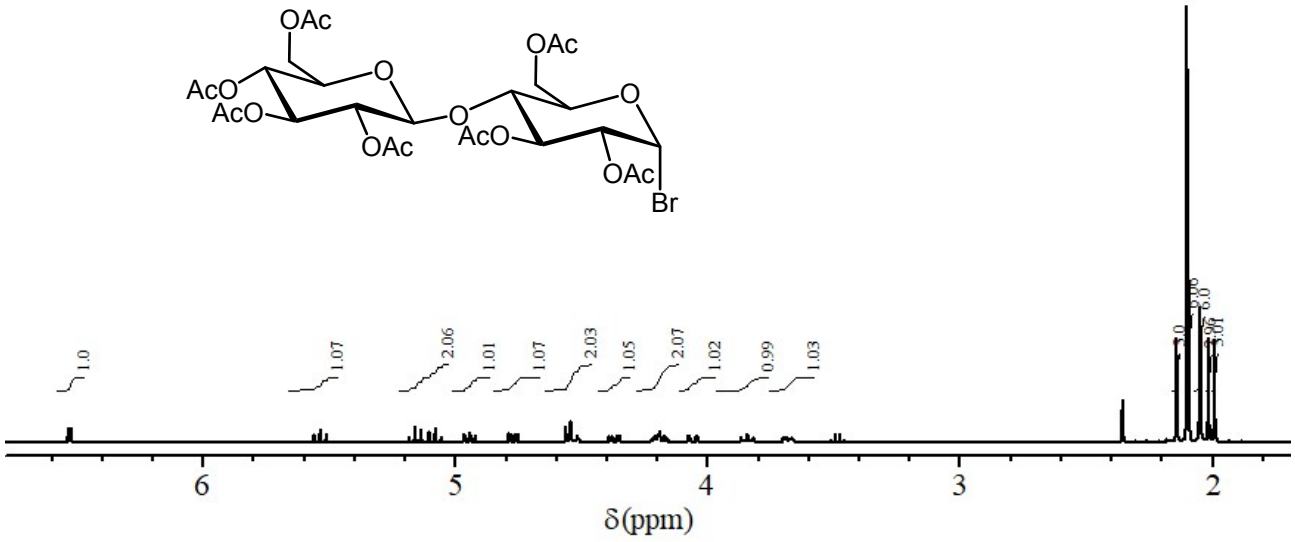


Figure S10. ^{1}H NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide

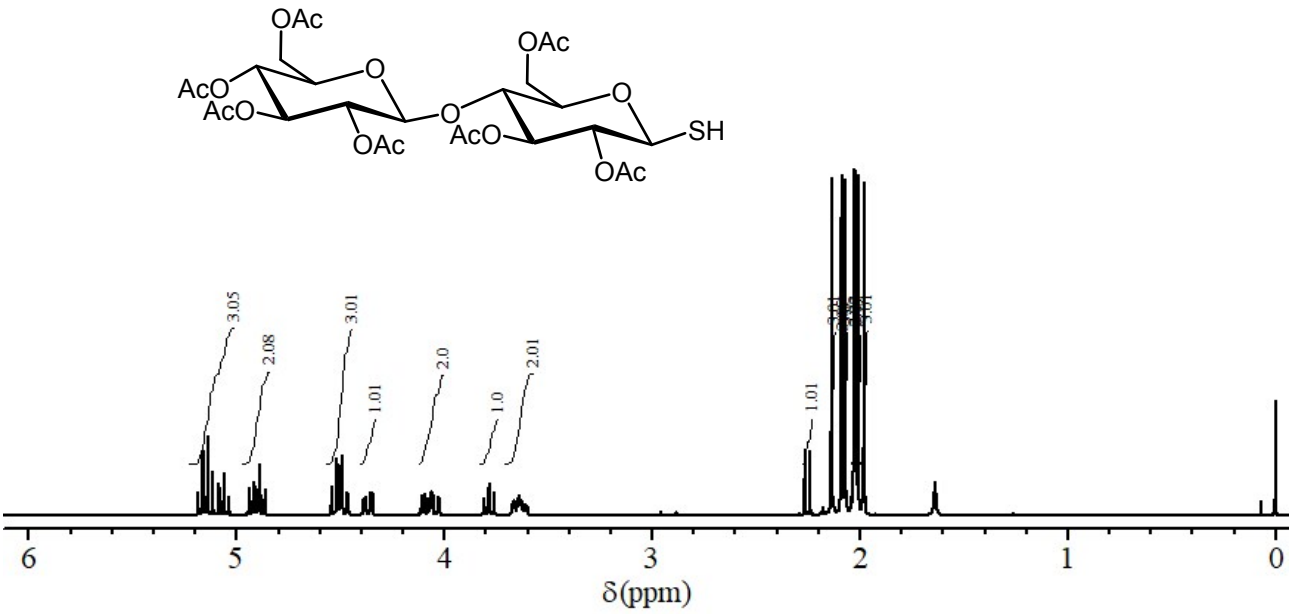


Figure S11. ^{1}H NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-cellobiopyranose

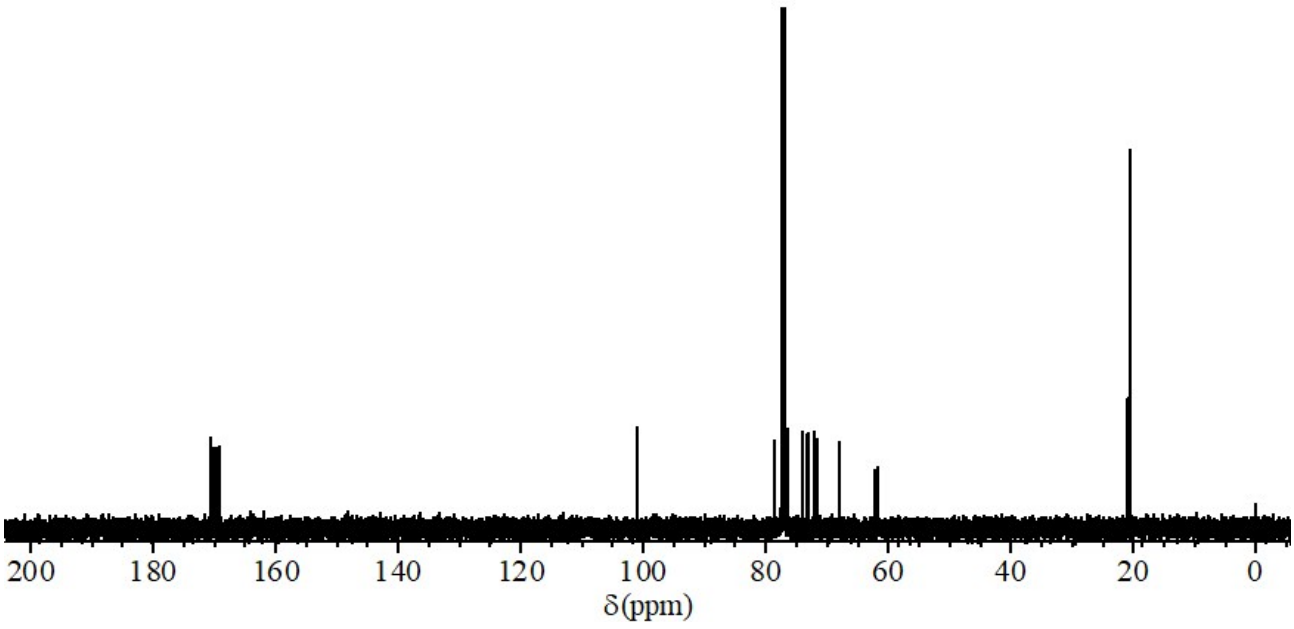


Figure S12. ^{13}C NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-cellobiopyranose

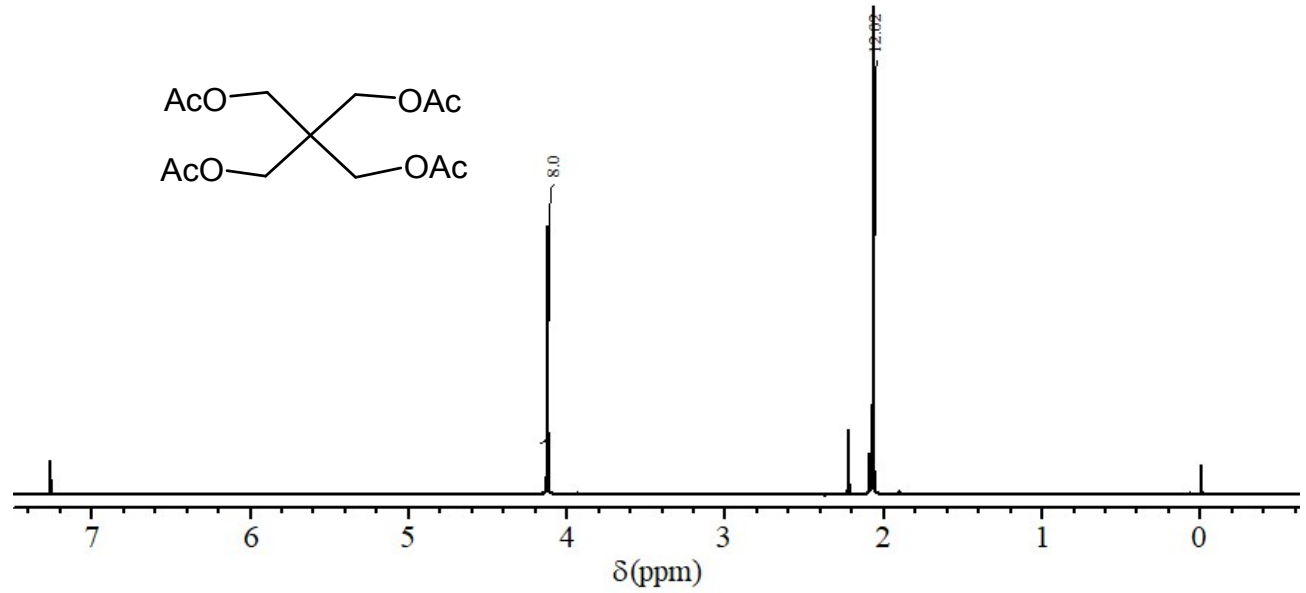


Figure S13. ^{1}H NMR spectrum of pentaerythritol tetraacetate.

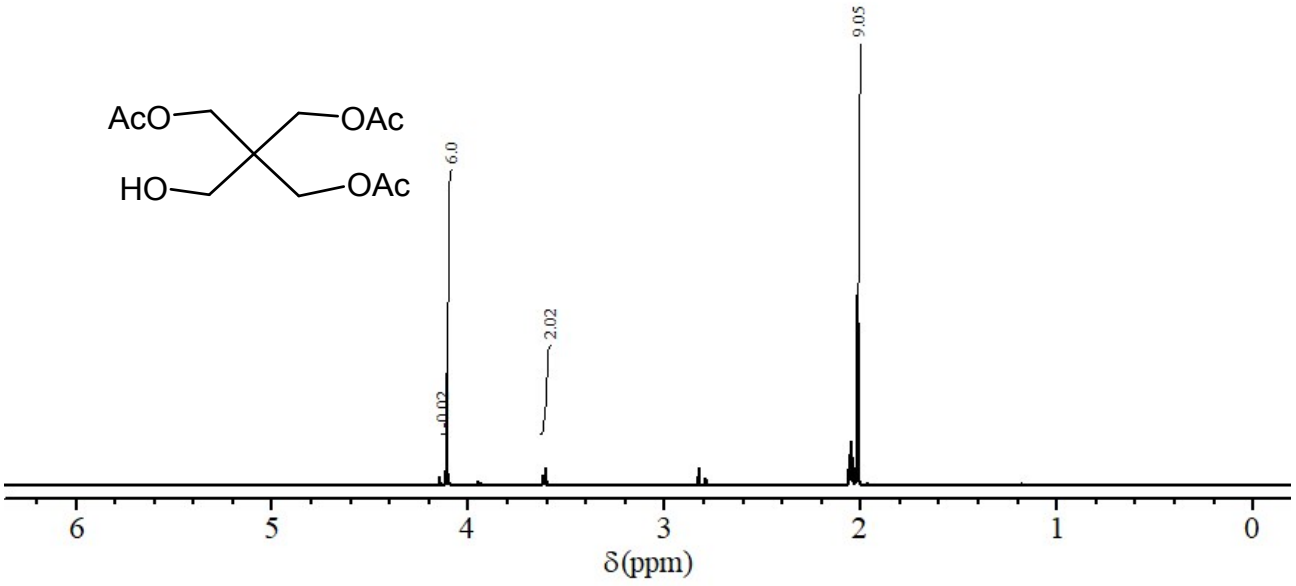


Figure S14. ^{1}H NMR spectrum of pentaerythritol tetraacetate.

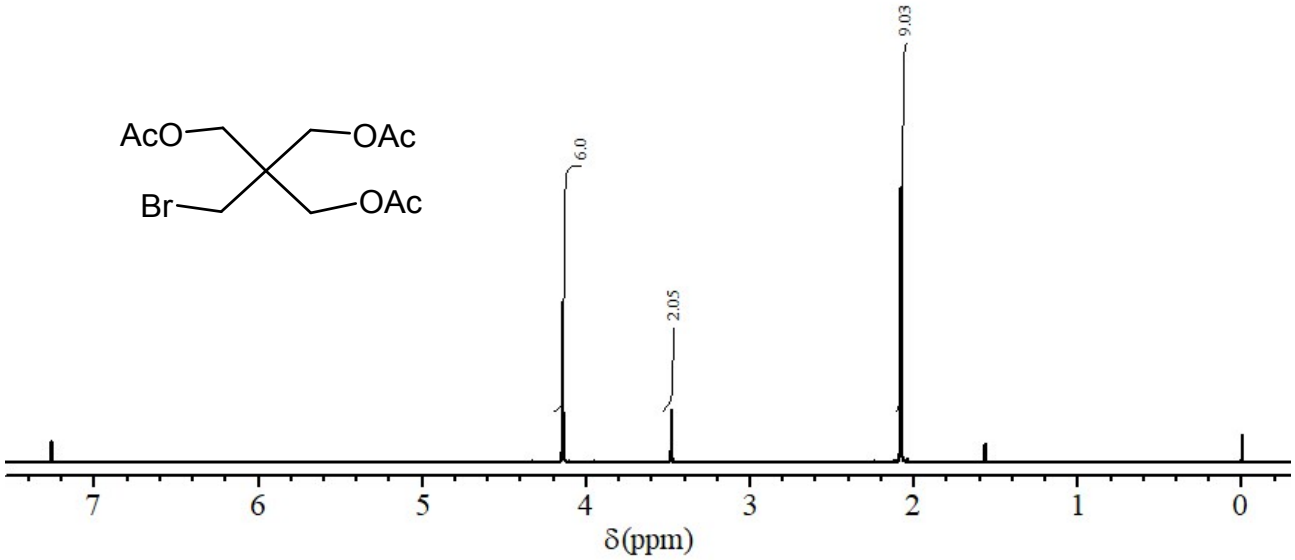


Figure S15. [1]H NMR spectrum of 2-(acetoxymethyl)-2-(bromomethyl)propane-1,3-diyl diacetate.

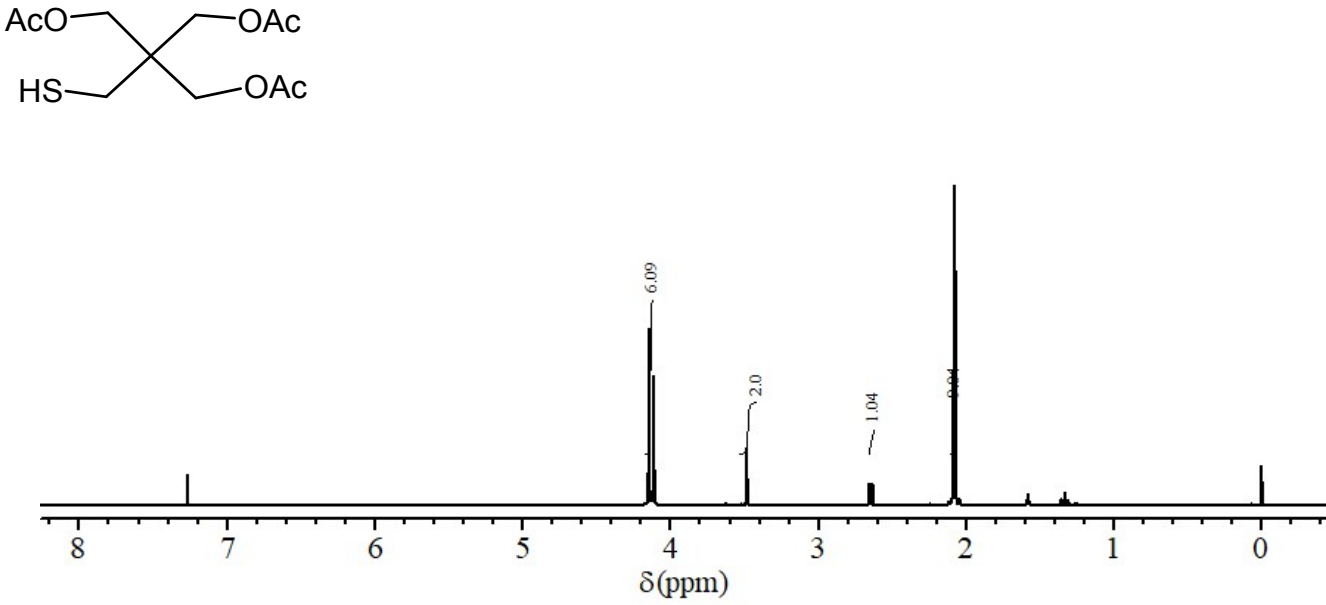


Figure S16. [1]H NMR spectrum of 2-(acetoxymethyl)-2-(mercaptomethyl)propane-1,3-diyl diacetate.

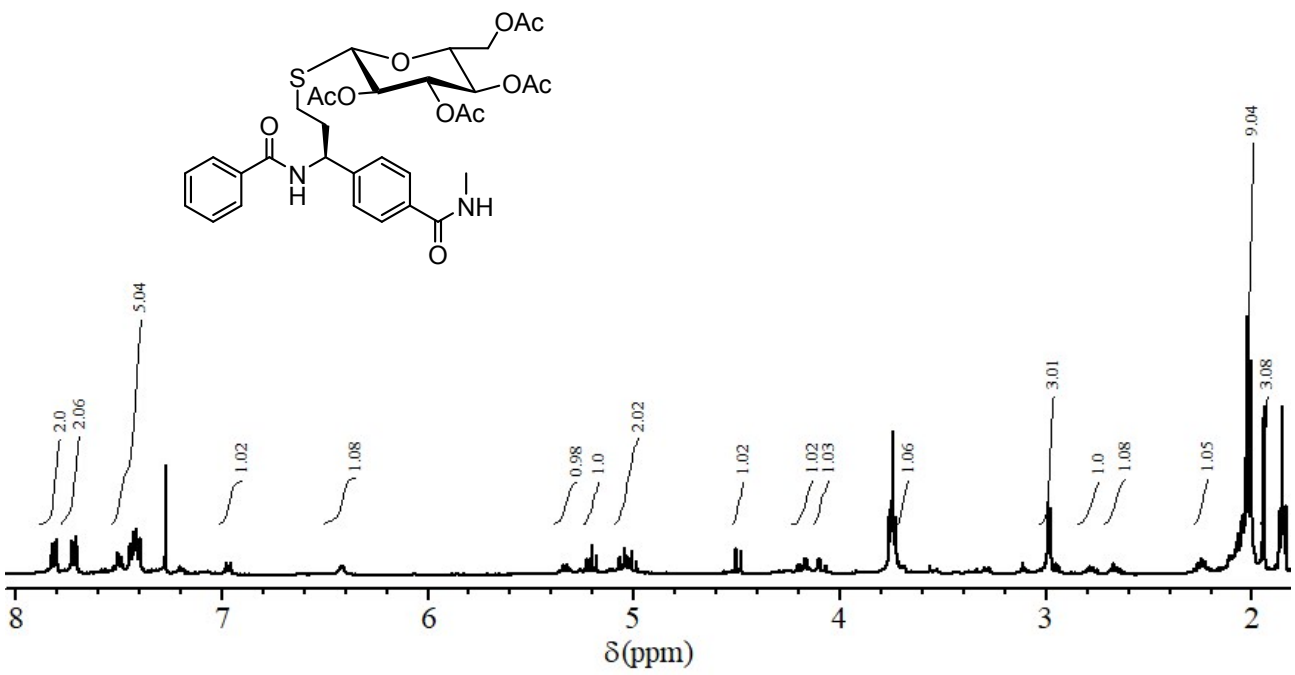


Figure S17. ^{1}H NMR spectrum of **S3**

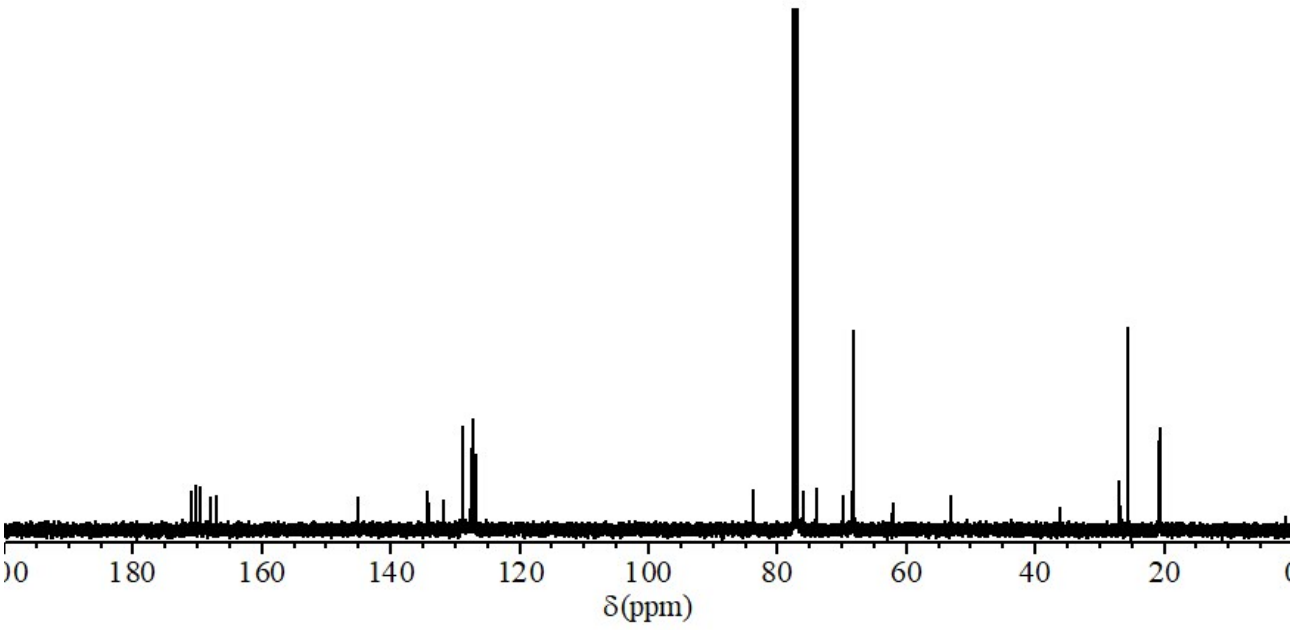


Figure S18. ^{13}C NMR spectrum of **S3**

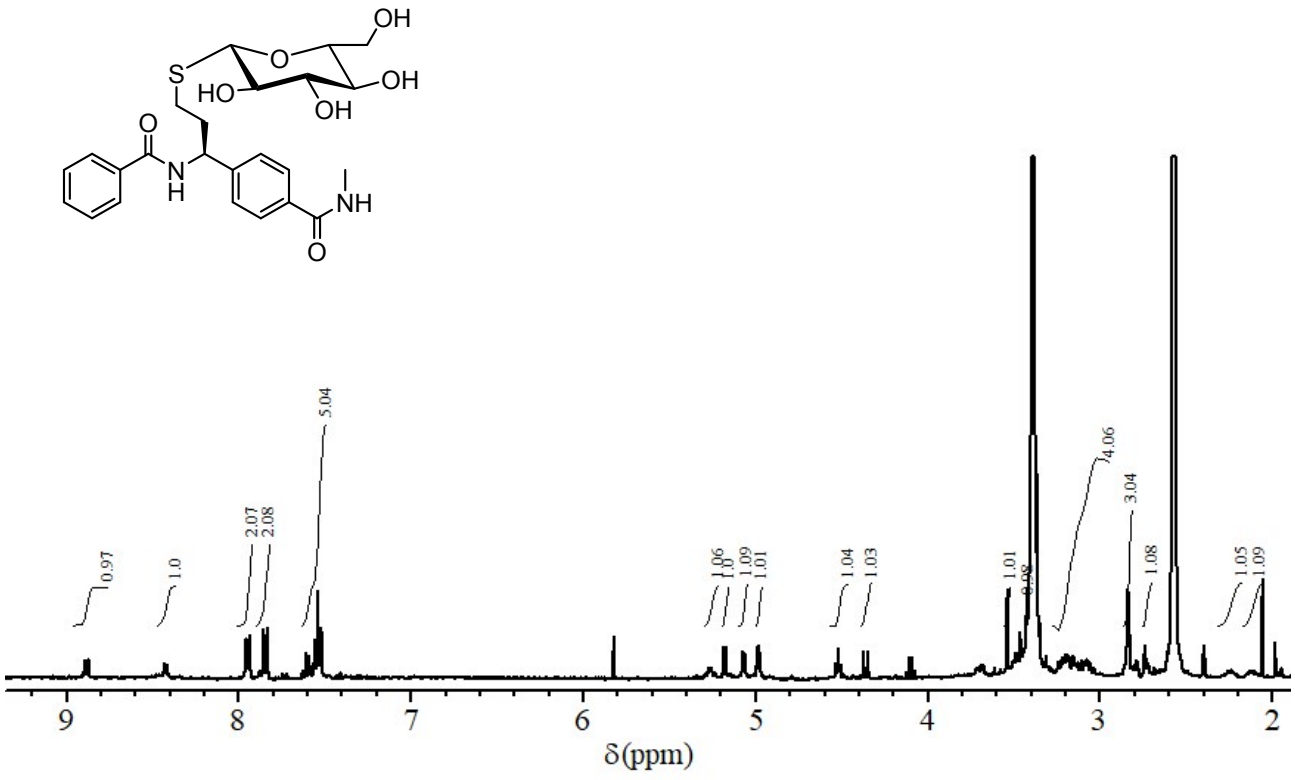


Figure S19. [1]H NMR spectrum of **S4**

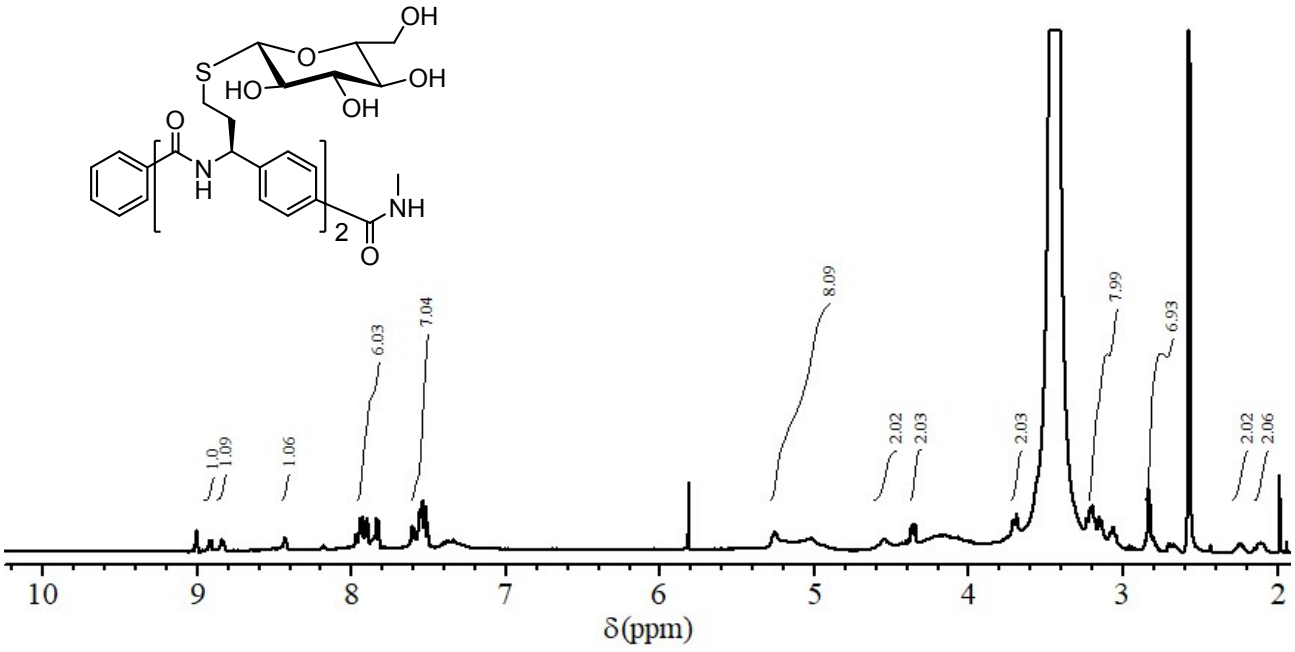


Figure S20. [1]H NMR spectrum of **S8**

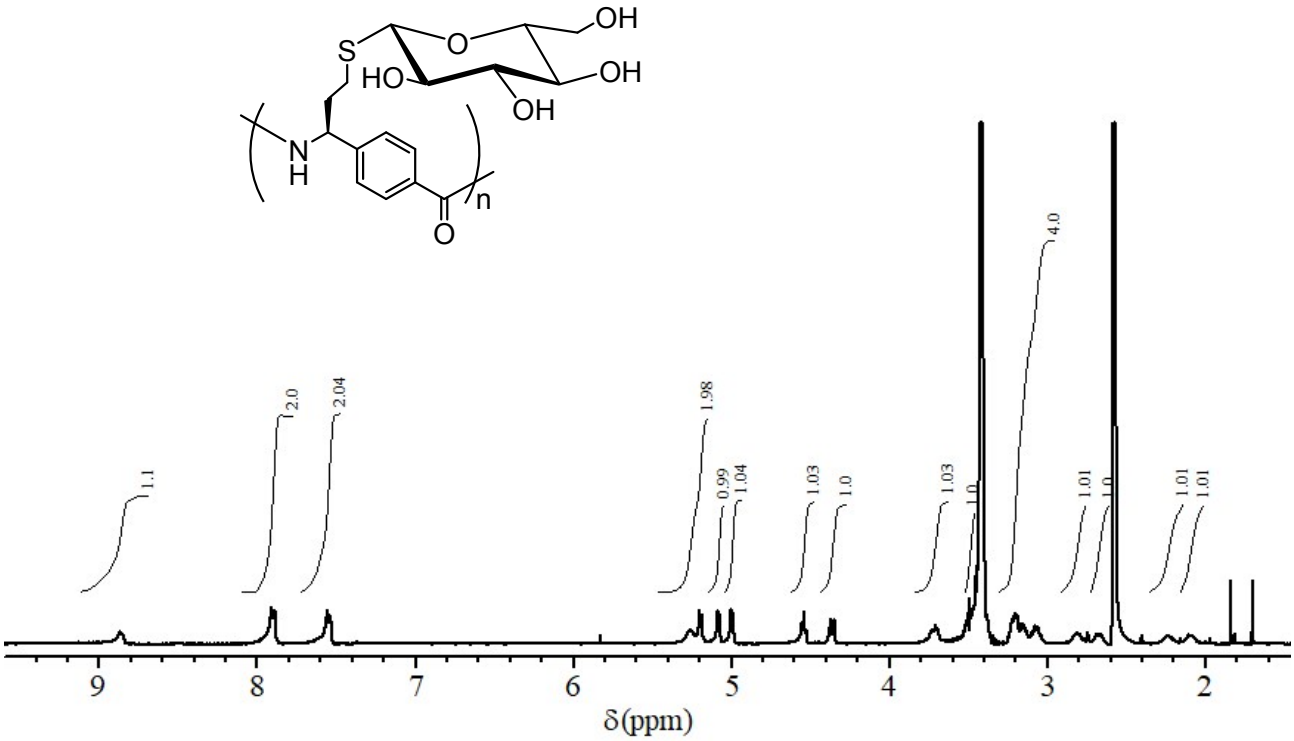


Figure S21. [1]H NMR spectrum of **poly-1a**

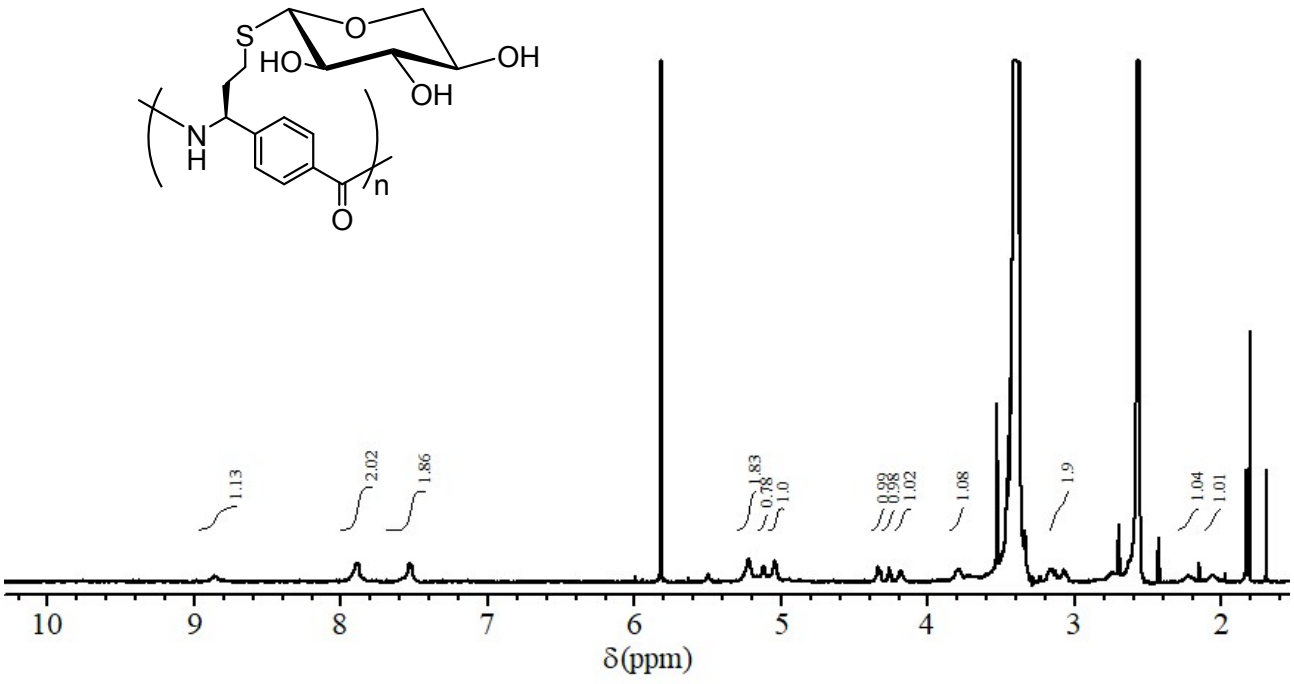


Figure S22. [1]H NMR spectrum of **poly-1b**

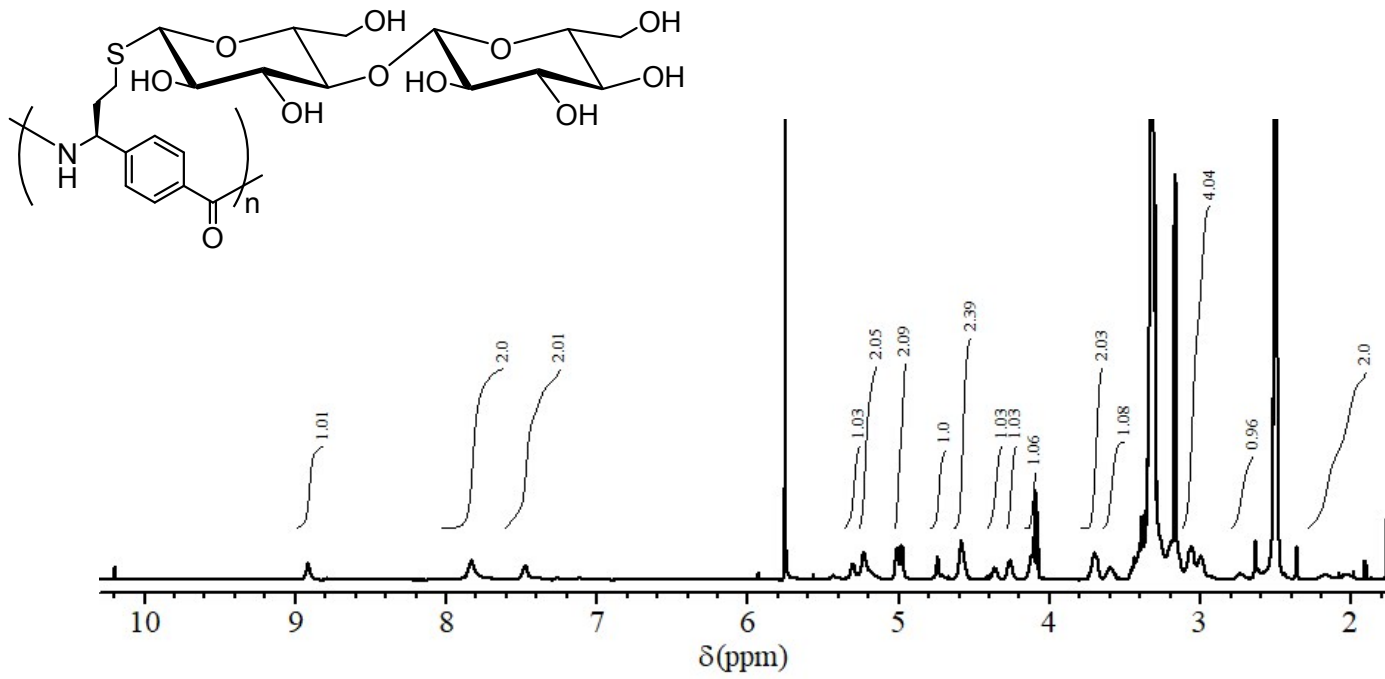


Figure S23. ^{1}H NMR spectrum of **poly-1c**

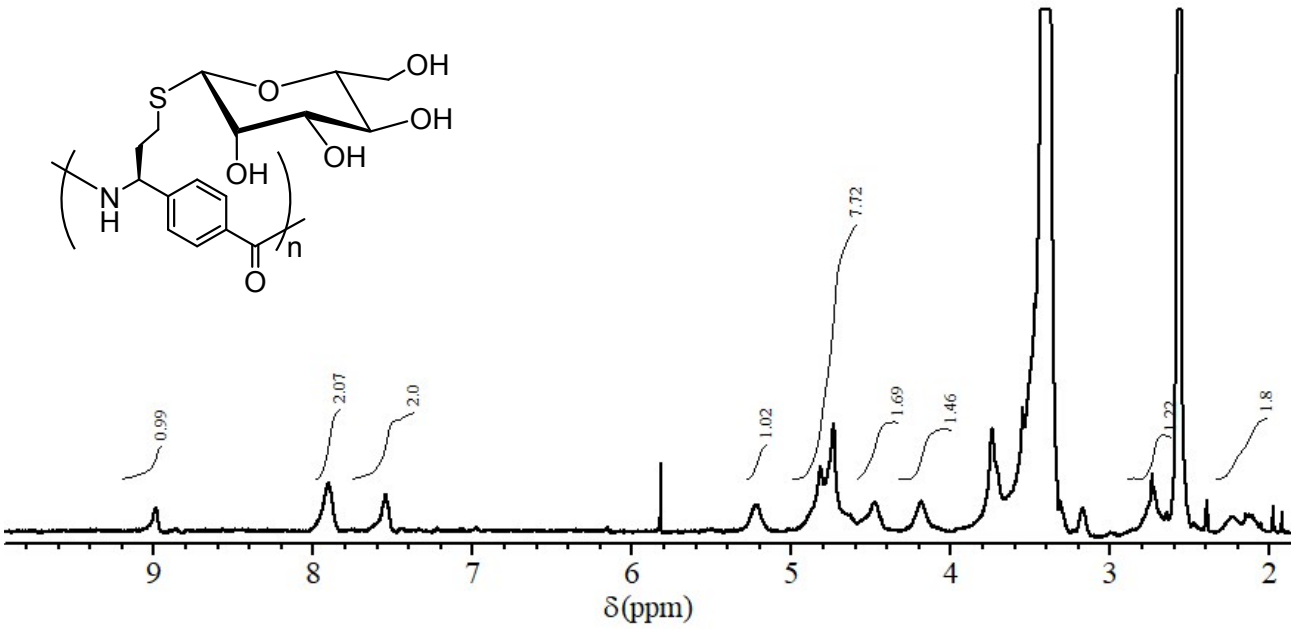


Figure S24. ^{1}H NMR spectrum of **poly-1d**

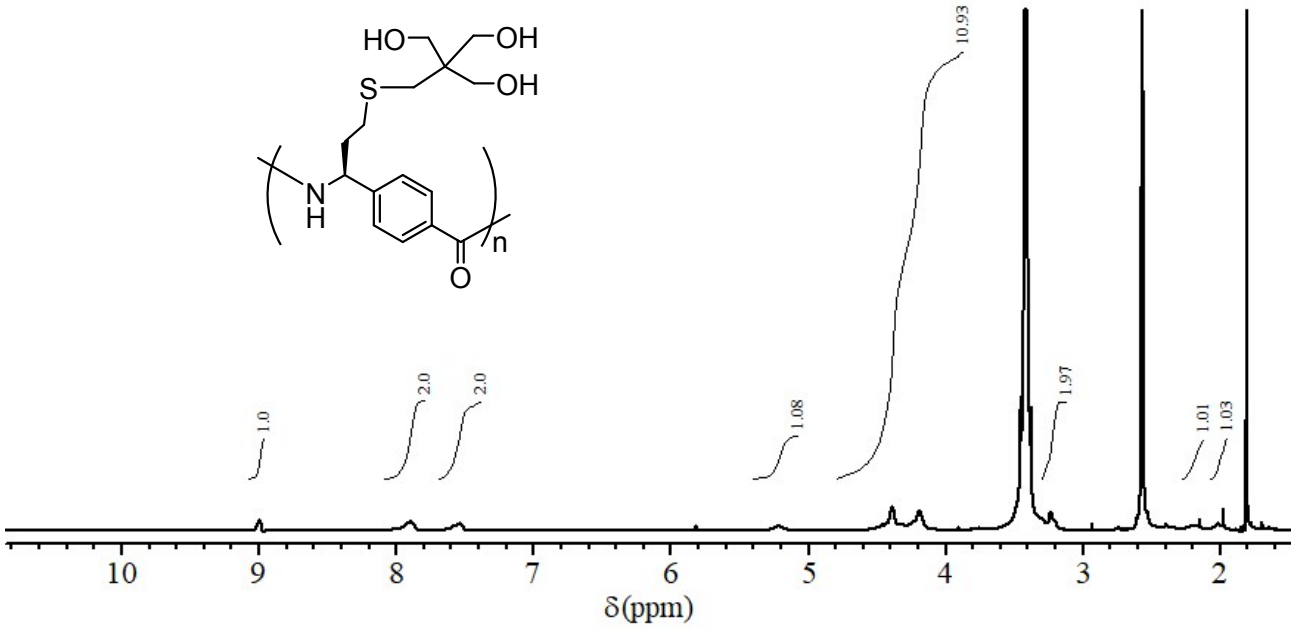


Figure S25. ^{1}H NMR spectrum of **poly-S9**.

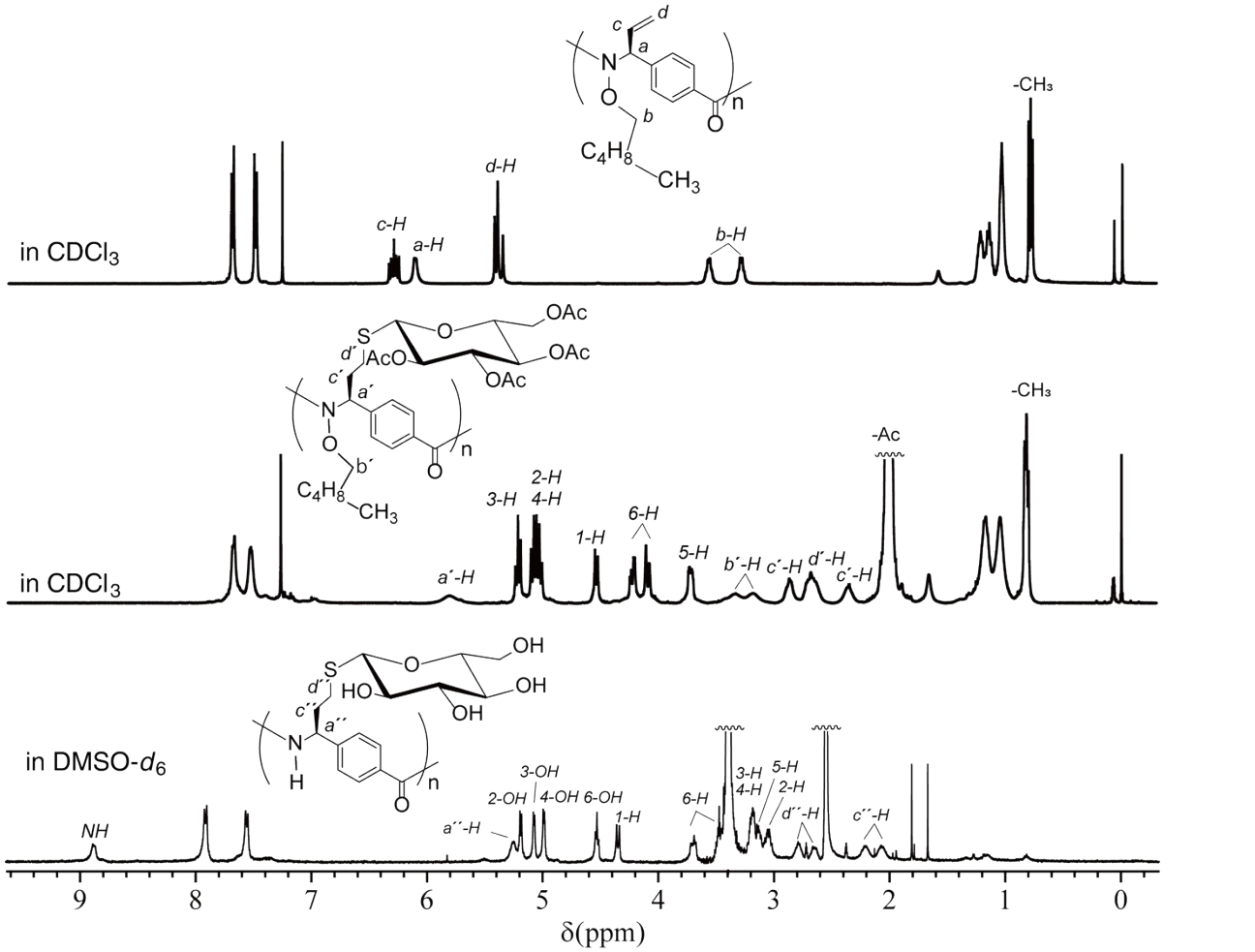


Figure S26. Overlay of ^{1}H NMR spectra of precursors and **poly-1a** (500 MHz, $CDCl_3$ and DMSO-d_6, 298 K).

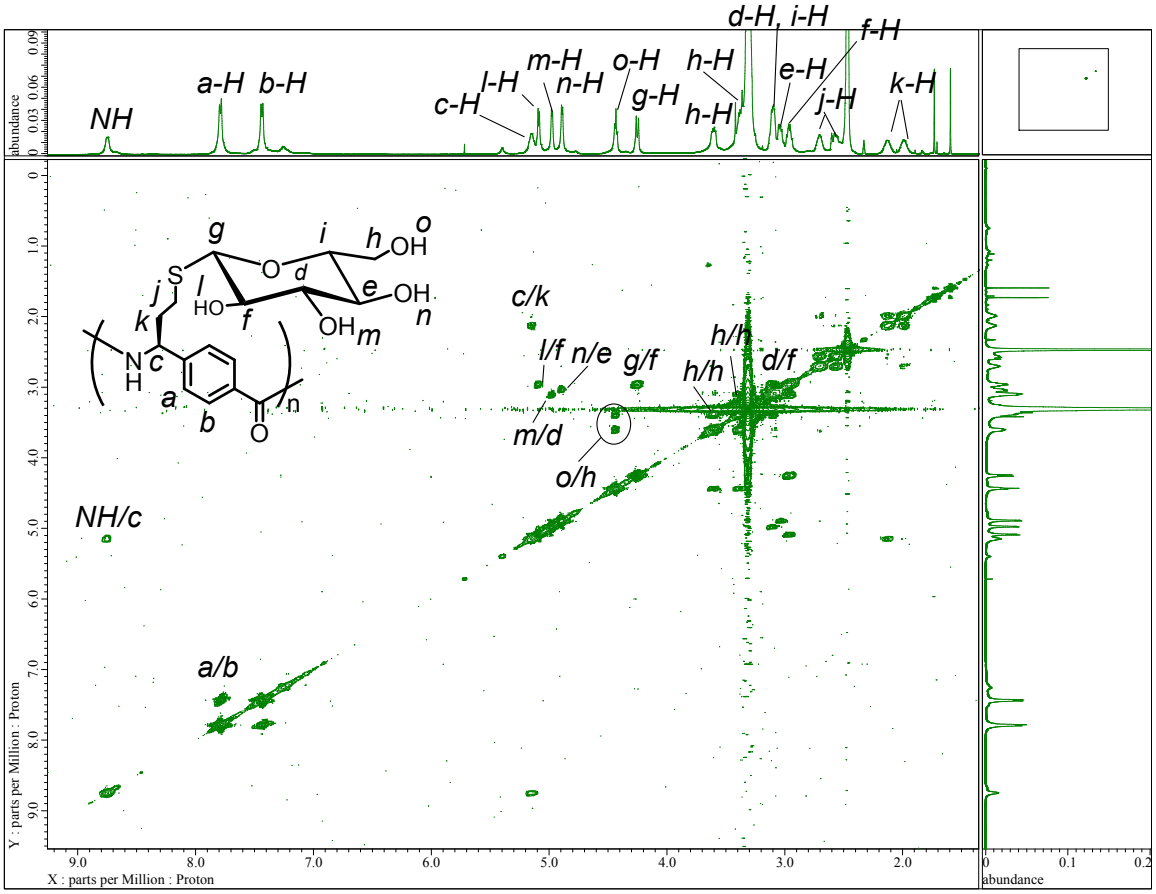


Figure S27. ^{1}H-^{1}H COSY of **poly-1a** (500 MHz, DMSO-d_6, 298 K)

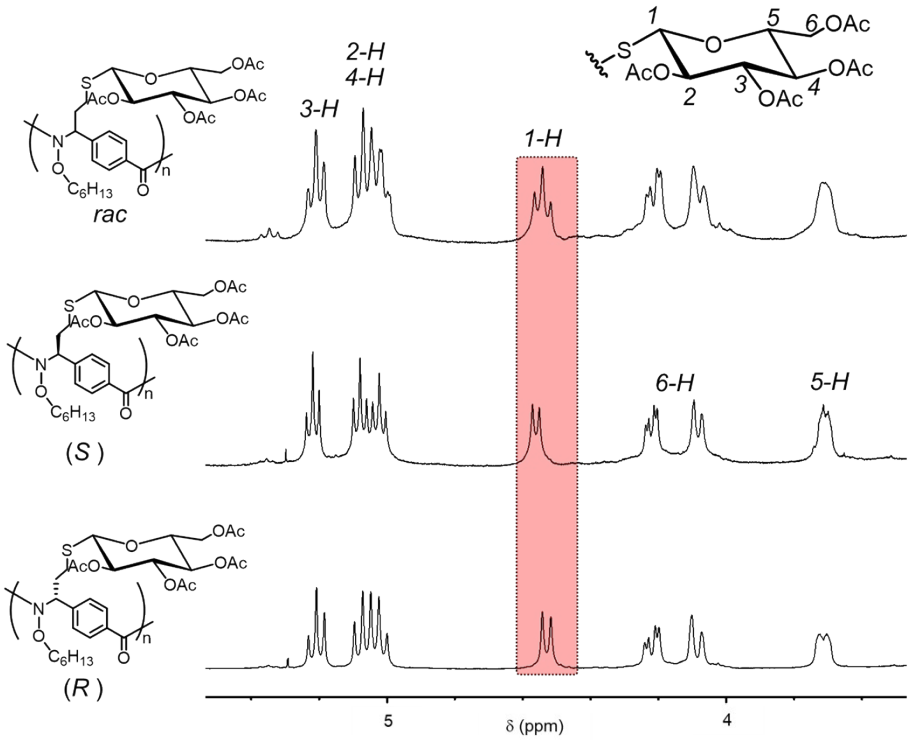


Figure S28. ^{1}H NMR spectra of (*S/R*) or (*rac*)-**precursor** ($CDCl_3$, 298 K). Diastereomeric protons were separated depending on the chirality of the main chain, indicating that enentio-selectivity of polymer is strictly controlled. (*rac*)- **precursor** was synthesized by (*rac*)-Cp′Ru.

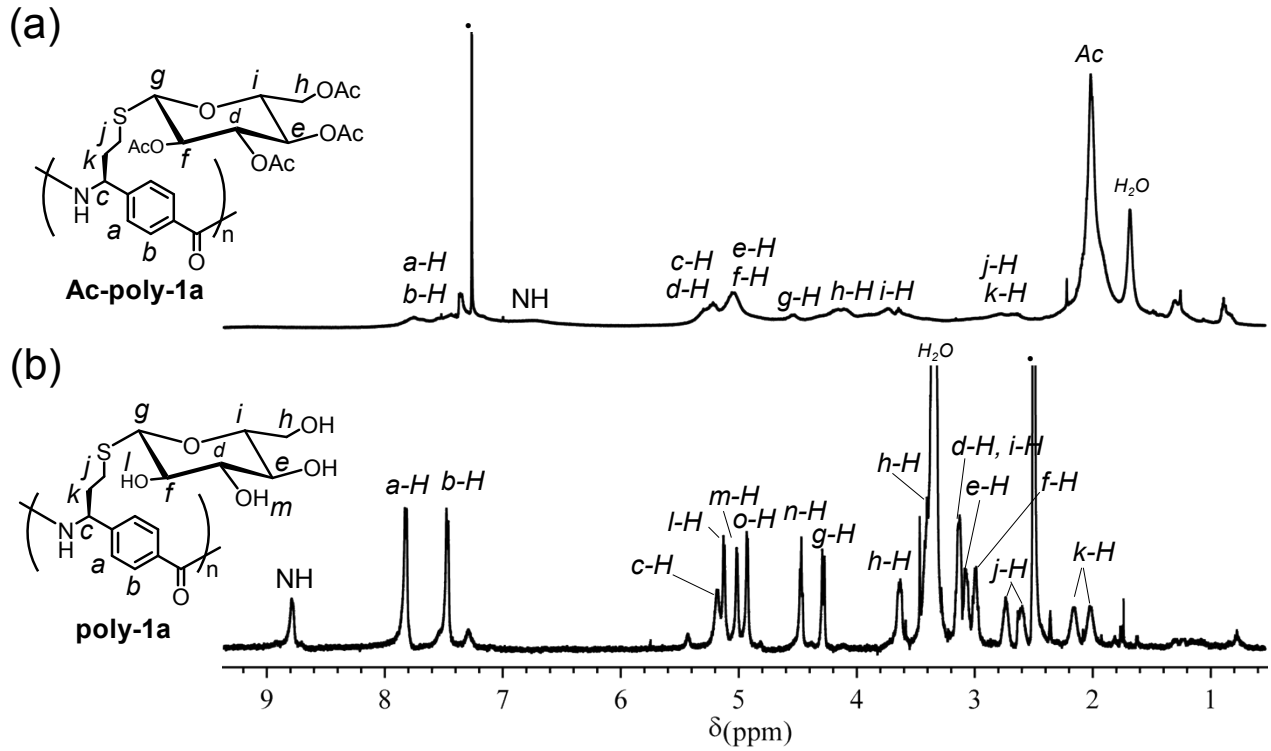


Figure S29. ^{1}H NMR spectra of (a) **Ac-poly-1a** and (b) **poly-1a** (500 MHz, (a) $CDCl_3$ and (b) DMSO-d_6, 298 K).

3. IR Analysis

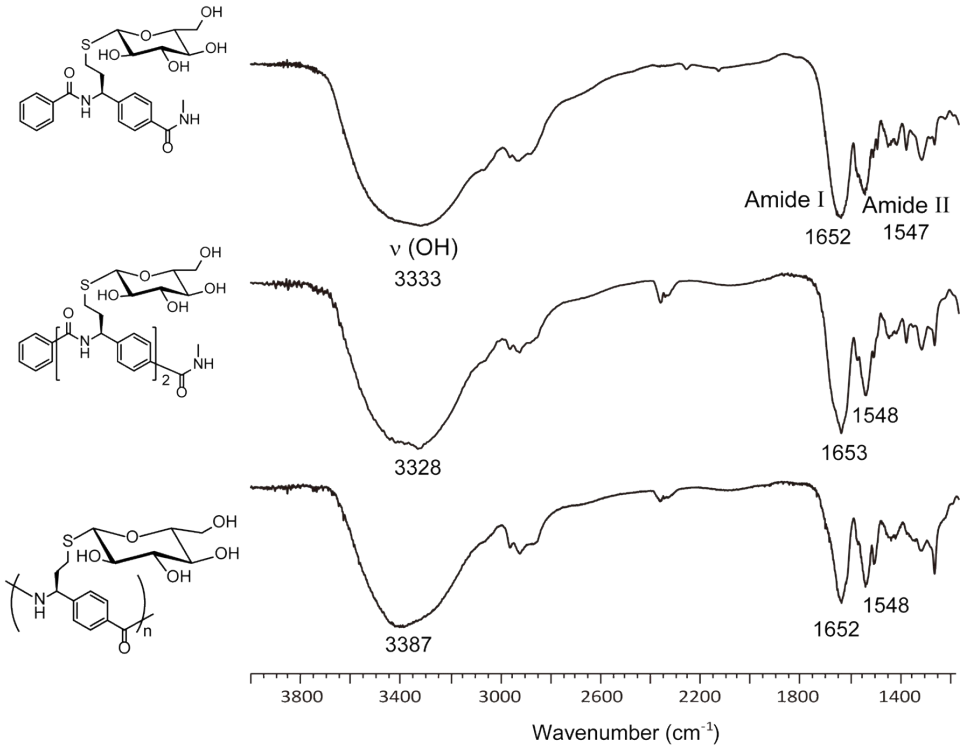


Figure S30. FI-IR spectra of oligomers and **poly-1a**.

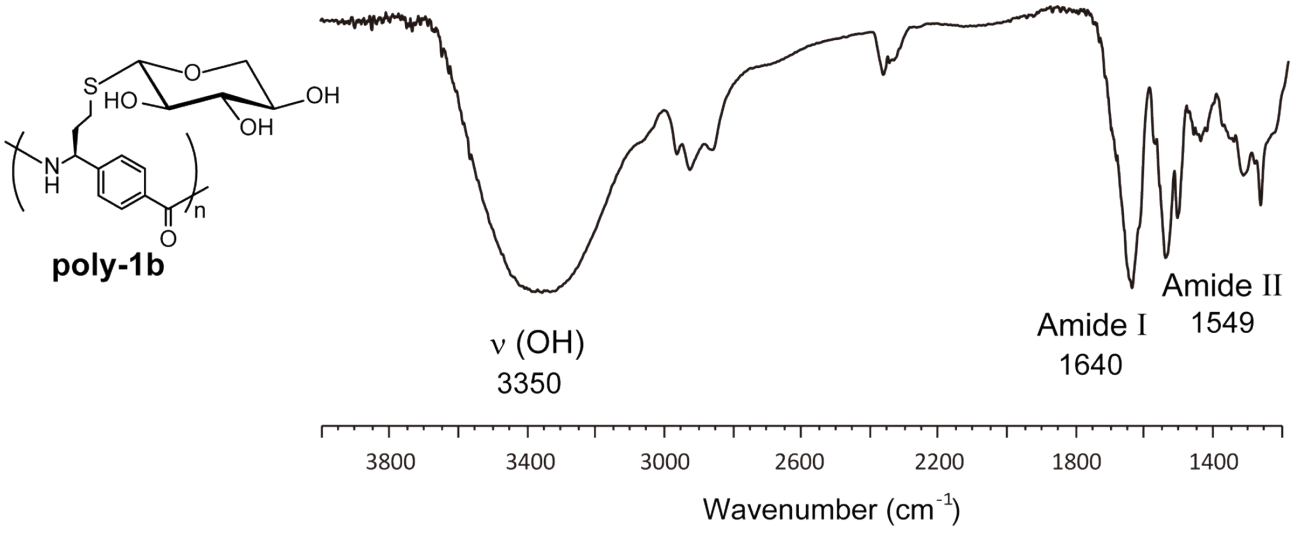


Figure S31. FI-IR spectrum of **poly-1b** (KBr tablet).

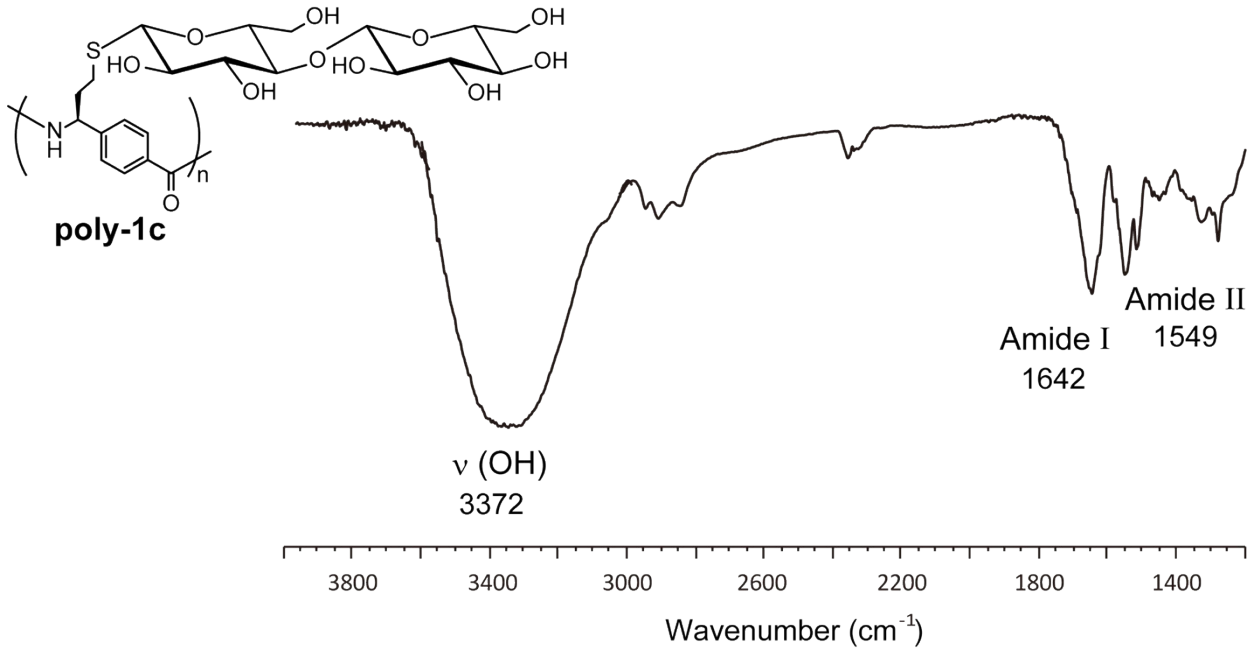


Figure S32. FI-IR spectrum of **poly-1c** (KBr tablet).

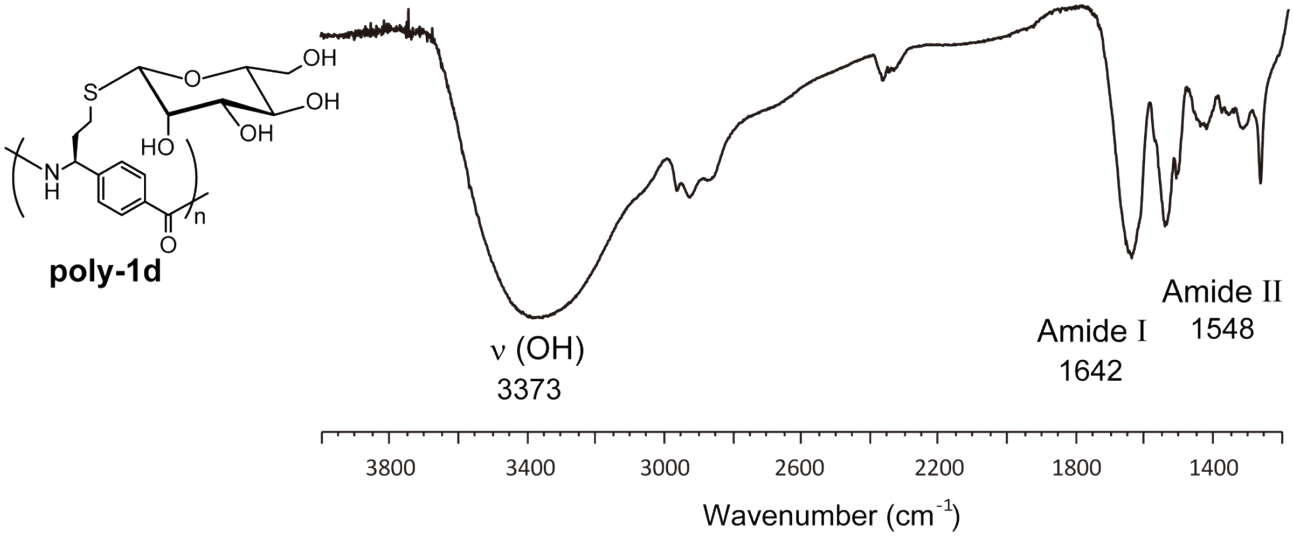


Figure S33. FI-IR spectrum of **poly-1d** (KBr tablet).

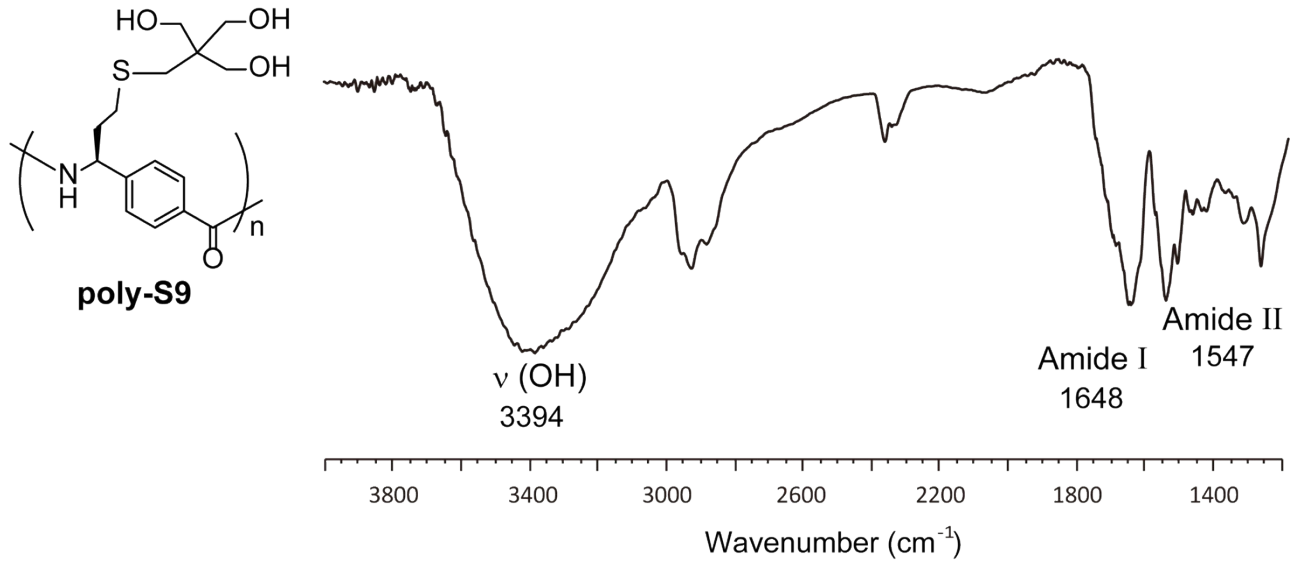


Figure S34. FI-IR spectrum of **poly-S9** (KBr tablet).

4. SEC Analysis

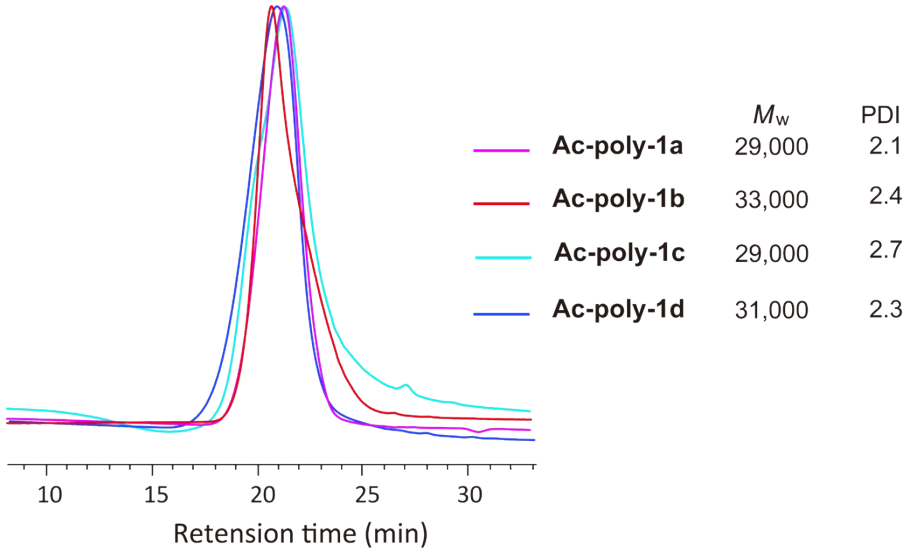


Figure S35. SEC chromatograms of **Ac-poly-1** in $CHCl_3$ at 40 °C.

5. AFM Analysis

A solution of **poly-1a** in 1% (v/v) pyridine/THF (10 μM) and 1% (v/v) pyridine/H_2O (10 μM) was prepared. Samples for the AFM measurements of **poly-1a** were prepared by drop casting (ca. 20 μL) of dispersions onto freshly cleaved mica substrates at room temperature (about 25 °C), and the substrates were then dried under vacuum for 1 h. The AFM images were obtained in air by tapping mode on an Agilent Technology Agilent PicoPlus 5100.

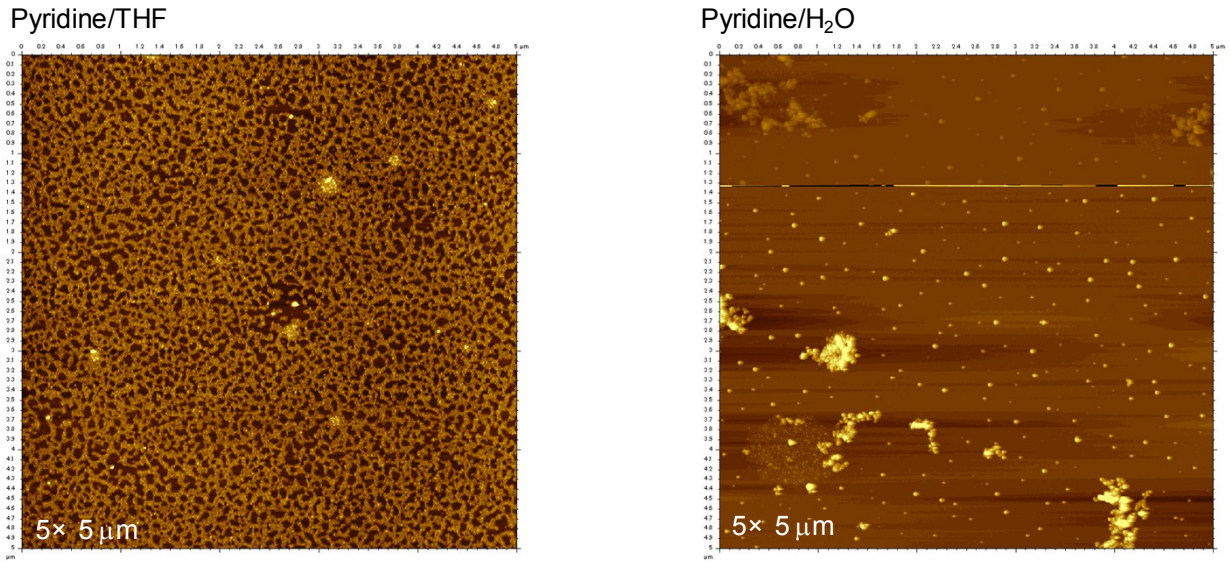


Figure S36. AFM images of **poly-1a** by casting 1% pyridine/THF or H_2O solution.

6. UV and CD spectra

Unless otherwise indicated, all circular dichroism (CD) spectra were measured using 1 mm path length quartz cuvettes. Concentration-dependence experiment on the CD signal was measured using 10, 1 and 0.1 mm path length quartz cuvettes, additive experiment of bronic acid measured using 1 mm path length quartz cuvettes. 20 scans were averaged for each sample. Δε (mol.L^{-1}.cm^{-1}) was calculated using the equation: $\Delta\varepsilon = (4\pi\log e \times \theta_{obs} \times M_0) / (180l \times 1000c)$. Where θ_{obs} is the measured ellipticity in millidegrees, while M_0 is the molecular weight or molecular weight per unit in the polymer, l is path length in centimeter (0.1 cm), and c is the concentration of the sample.

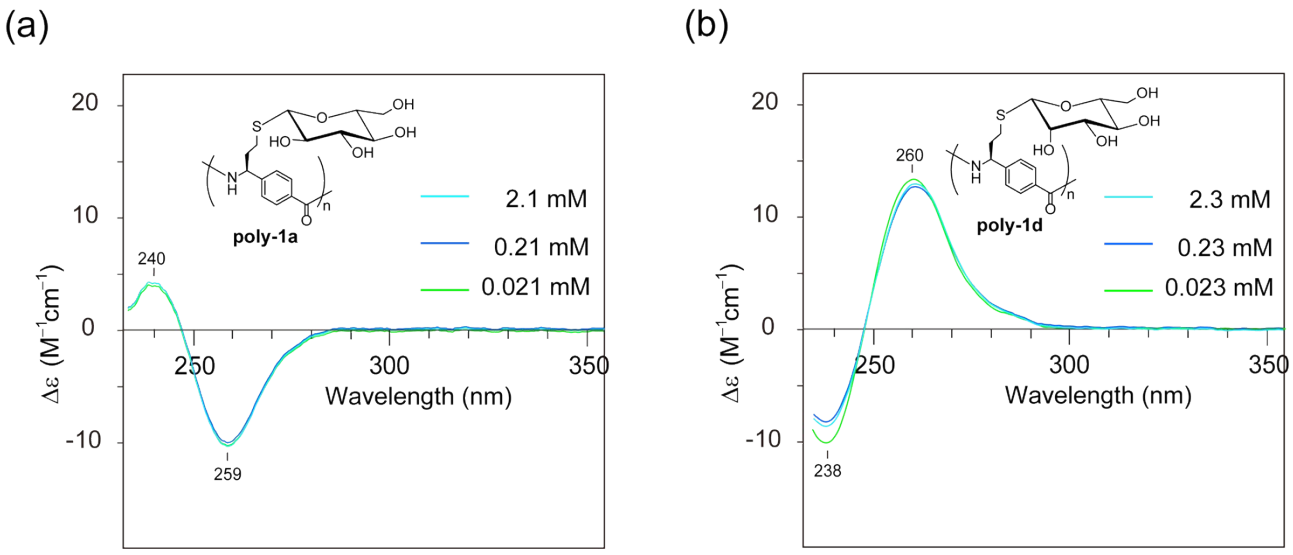


Figure S37. CD spectra of (a) **poly-1a** (2.1–0.021 mM) and (b) **poly-1b** (2.3–0.023 mM) in 1%DMSO/H_2O solution at 25 °C.

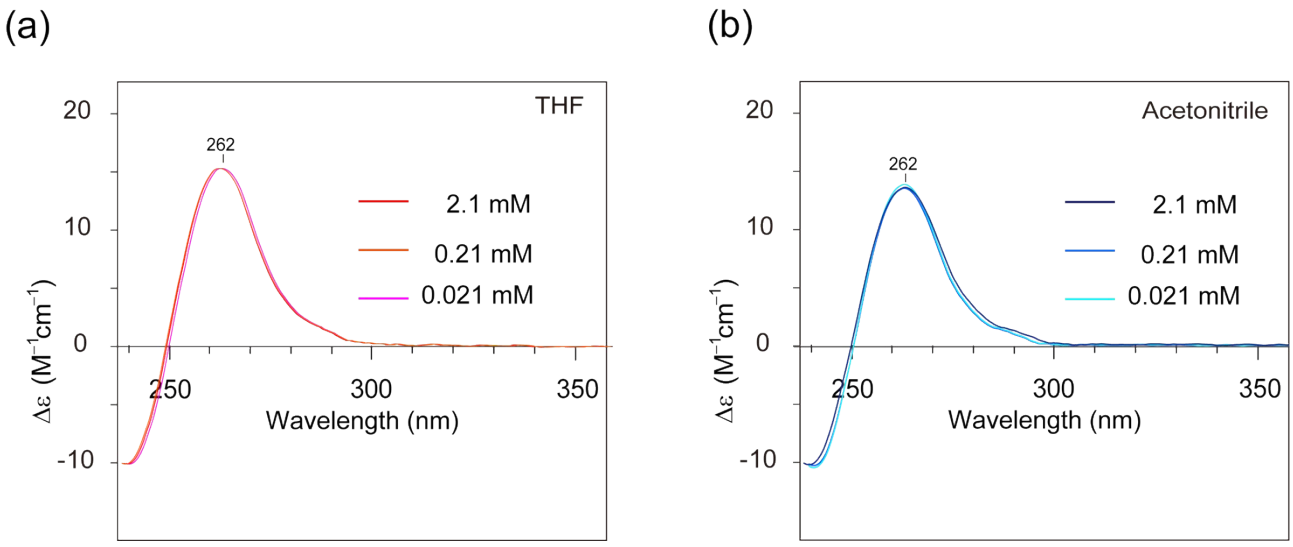


Figure S38. CD spectra of **poly-1a** (2.1–0.021 mM) in (a) 1%DMSO/THF and (b) 1%DMSO/MeCN solution at 25 °C.

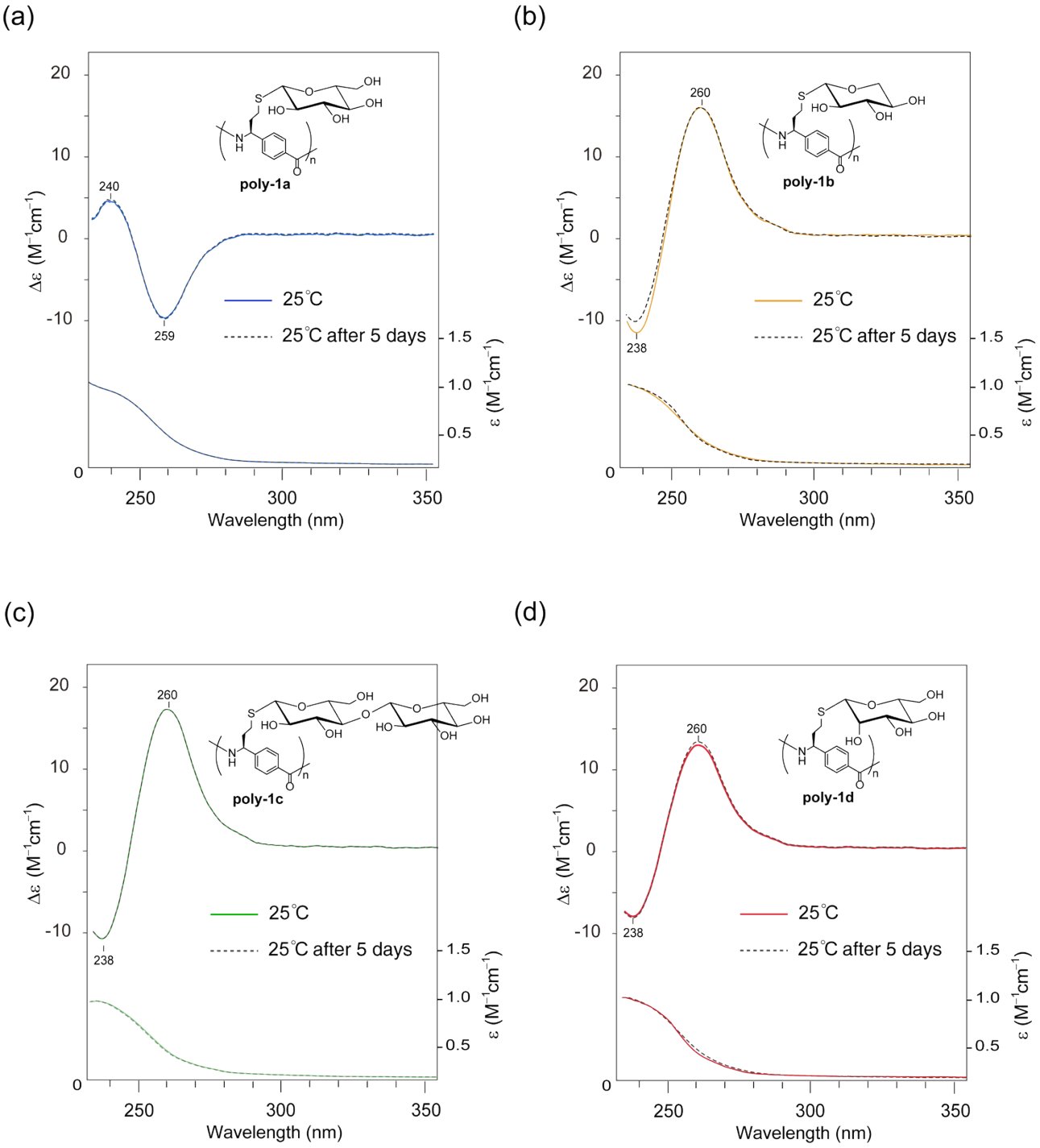


Figure S39. Time-dependent CD and UV spectra of (a) **poly-1a** (0.21 mM), (b) **poly-1b** (0.21 mM), (c) **poly-1c** (0.21 mM) and (d) **poly-1d** (0.23 mM) in %DMSO/H_2O solution at 25 °C. Dash curves indicate the CD and UV spectra after 5 days, indicating that both state are under thermodynamic control. The sample solution was left in a thermostatic bath (25 °C) for 5 days.

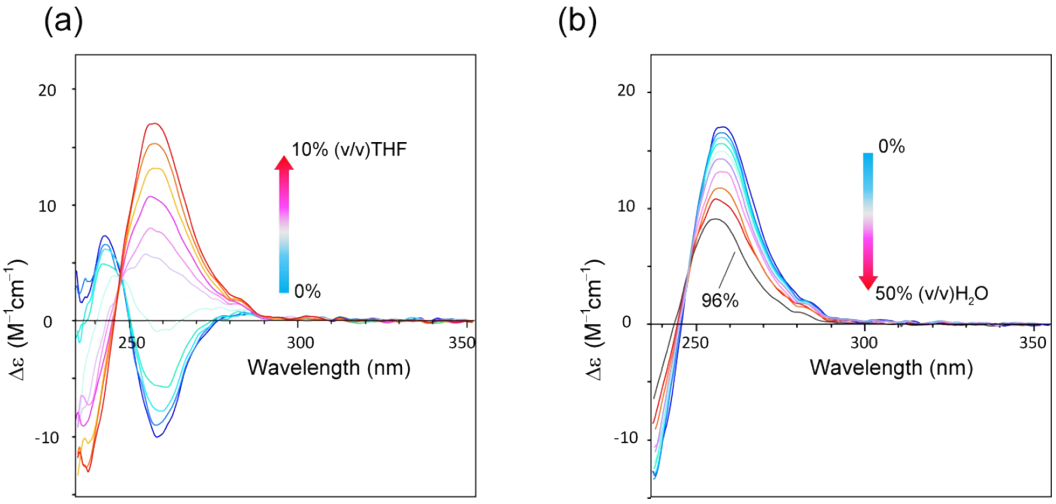


Figure S40. Results of CD titration experiment of **poly-1a** in THF or H_2O at 25 °C in the presence of 0–10% THF and (b) 0–96% H_2O. Initial concentration: [**poly-1a**] = 0.30 mM. Helix-to-helix transition by adding solvents only occurred from (*M*)-helix to (*P*)-helix.

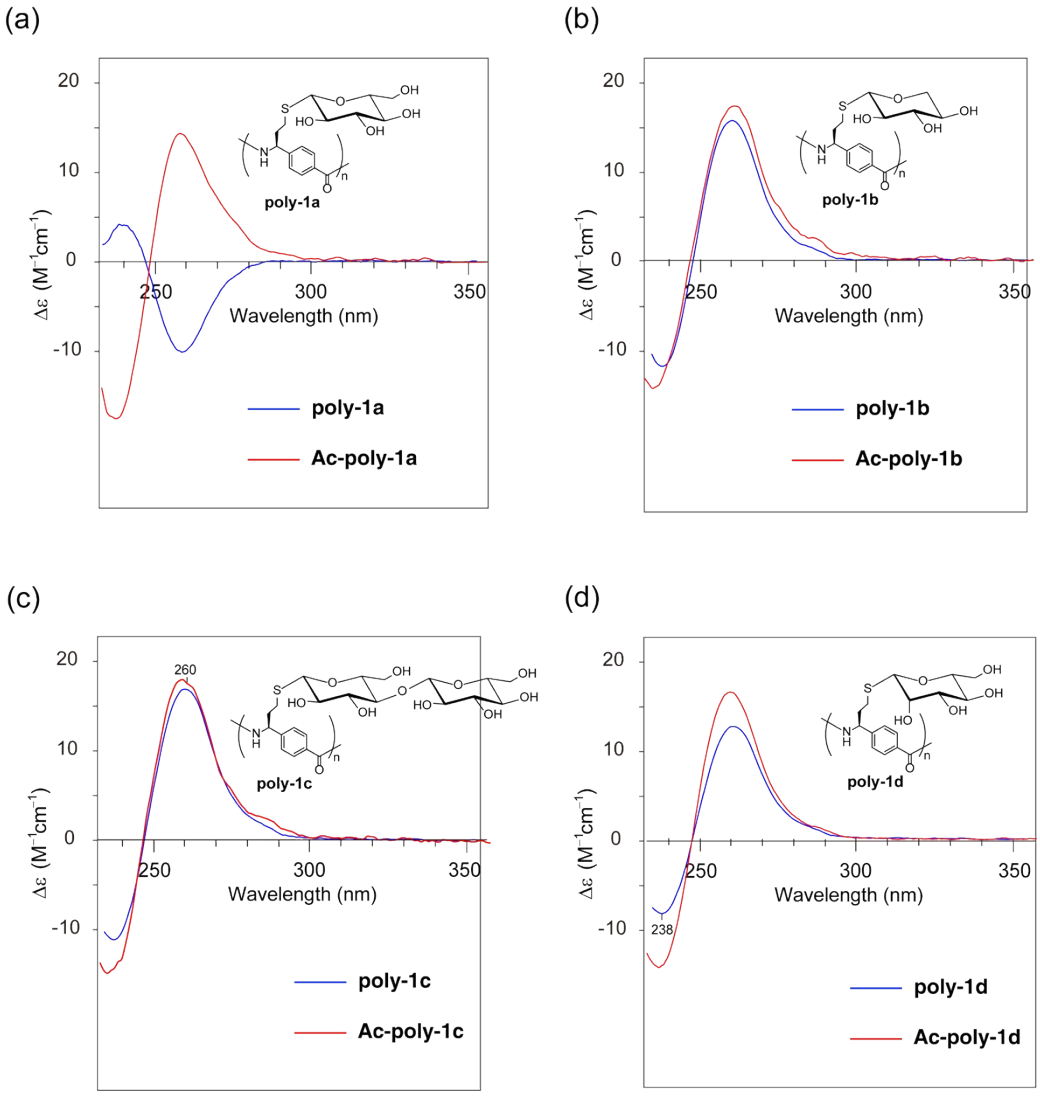


Figure S41. CD/UV spectra of **poly-1a–d** and **Ac-poly-1a–d** in 1%DMSO/H_2O solution at 25 °C.

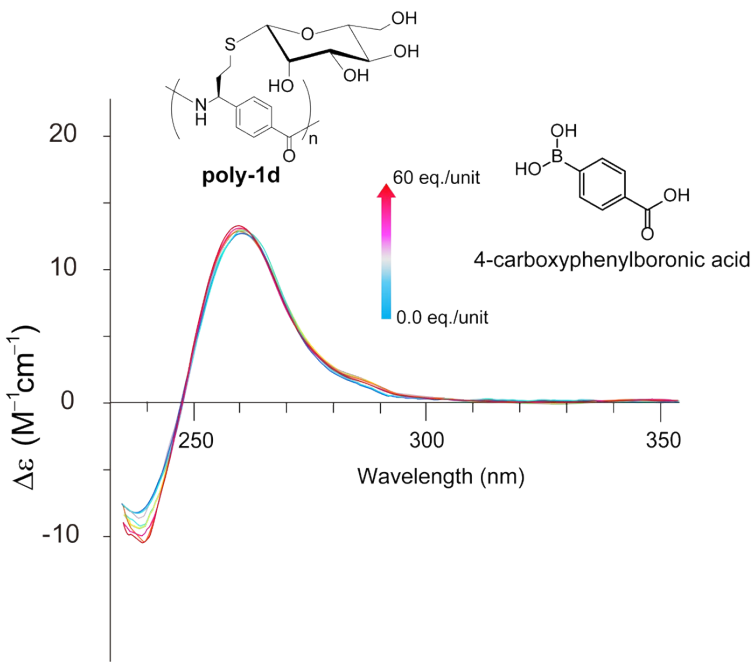


Figure S42. Addition experiment of 4-carboxyphenylboronic acid into **poly-1d** (0-60 equivalent). Initial concentration: [**poly-1d**] = 0.22 mM.

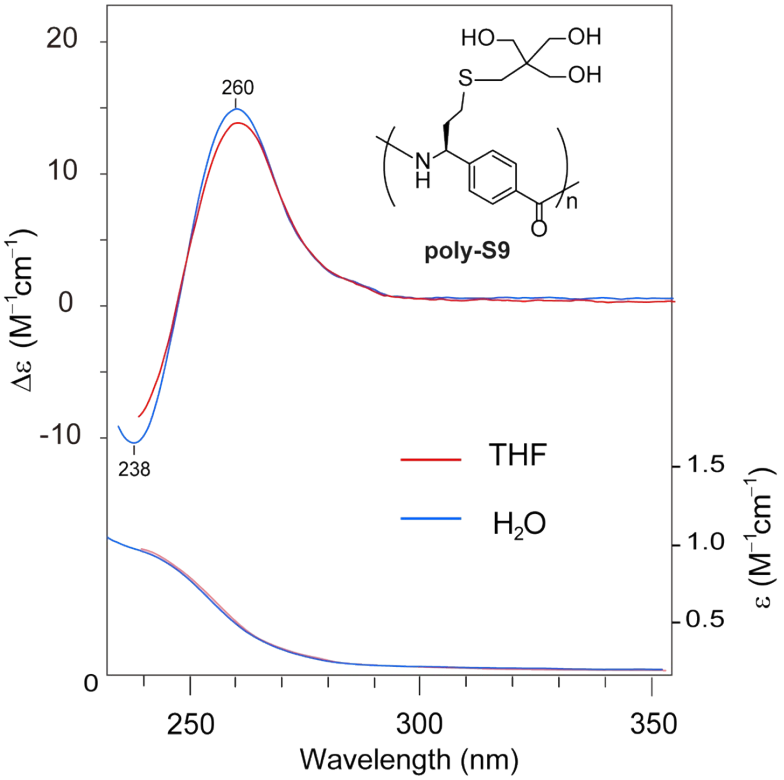


Figure S43. CD/UV spectra of **poly-S9** and **Ac-poly-S9** in 1%DMSO/H_2O solution at 25 °C. This result indicate that (*M*)-helical conformation was not induced by polyhydric alcohol.

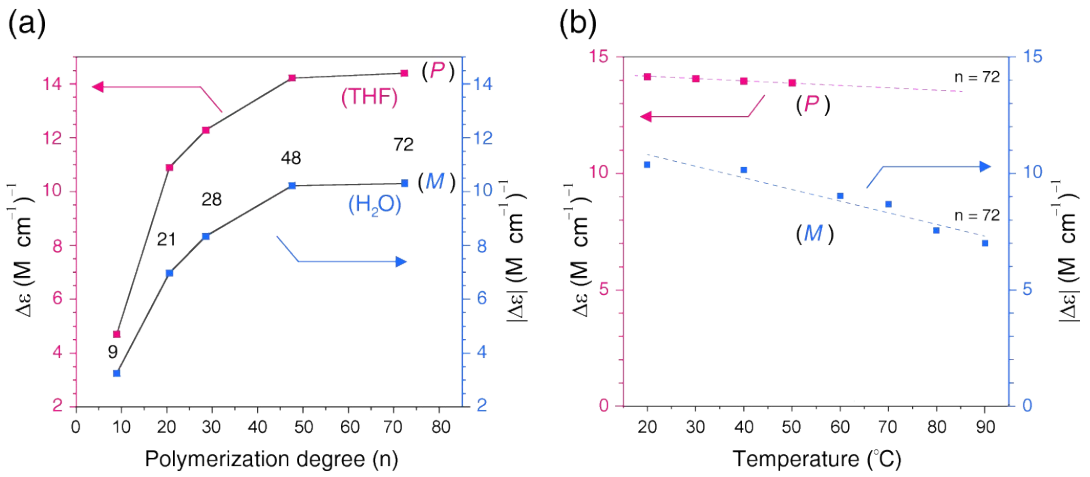


Figure S44. (a) CD intensity of **poly-1a** at 260 nm in THF (pink plots, left vertical axis) and at 259 nm in H_2O (blue plots, right vertical axis) as a function of polymerization degree *n*. (b) Temperature dependence (20 to 90 °C) of the CD intensity of **poly-1a** at 260 nm in THF (pink plots, left vertical axis) and at 259 nm in H_2O (blue plots, right vertical axis).

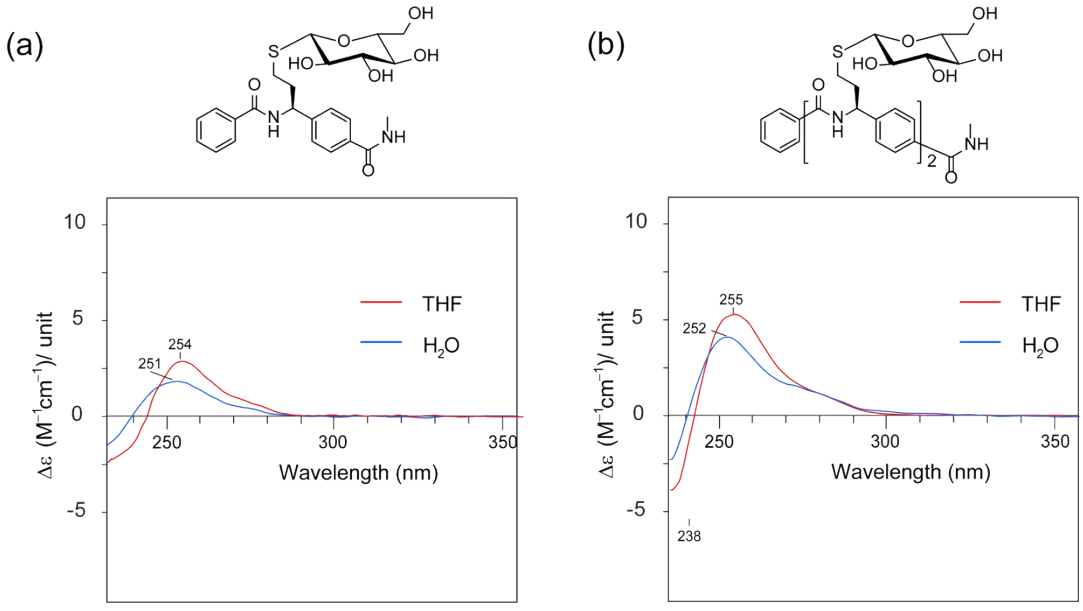


Figure S45 CD/UV spectra of oligomers in 1%DMSO/THF and 1%DMSO/H_2O solution at 25 °C. (a) oligomer (*n* = **1**) (b) oligomer (*n* = **2**)

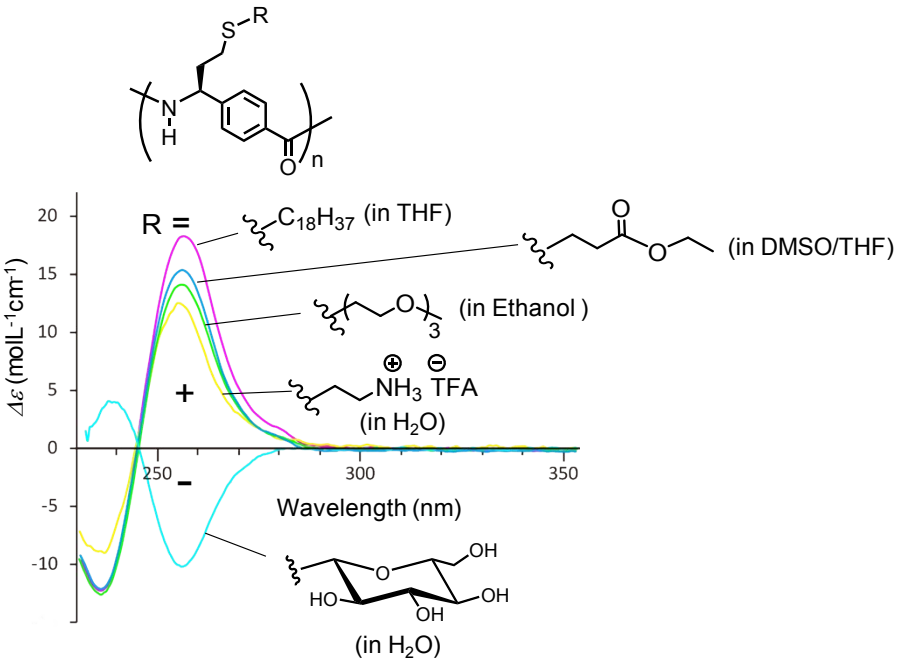


Figure S46. CD/UV spectra of various arylopeptides in various solvents at 25 °C.

7. Computational Study

Conformational search was carried out using a MacroModel (Schrödinger Inc, Maestro 11.9), and geometry optimization and frequency calculation were performed using Becke's three parameter hybrid functionals (B3LYP) in Gaussian 09[5] program packages. 6-31G** basis set was employed. The optimized geometry was analyzed by MolStudio R4.0 (NEC Corp., Japan) and GaussView 5.0 (Gaussian, Inc.). The CD and UV spectra of oligomers were simulated by time-dependent (TD-DFT) calculations after the geometrical optimization in tetrahydrofuran and water using the polarizable continuum model (PCM) as self-consistent reaction field (SCRF) method.

7-1. Structual optimization of S4 (oligomer, *n* = 1)

The crystal structure (CCDC 1554046) was used for the initial structures, **S4** (oligomer *n* = 1) was made by adding $CONHCH_3$ group with *anti* geometry and *β*-D-glucose as side chain. And then

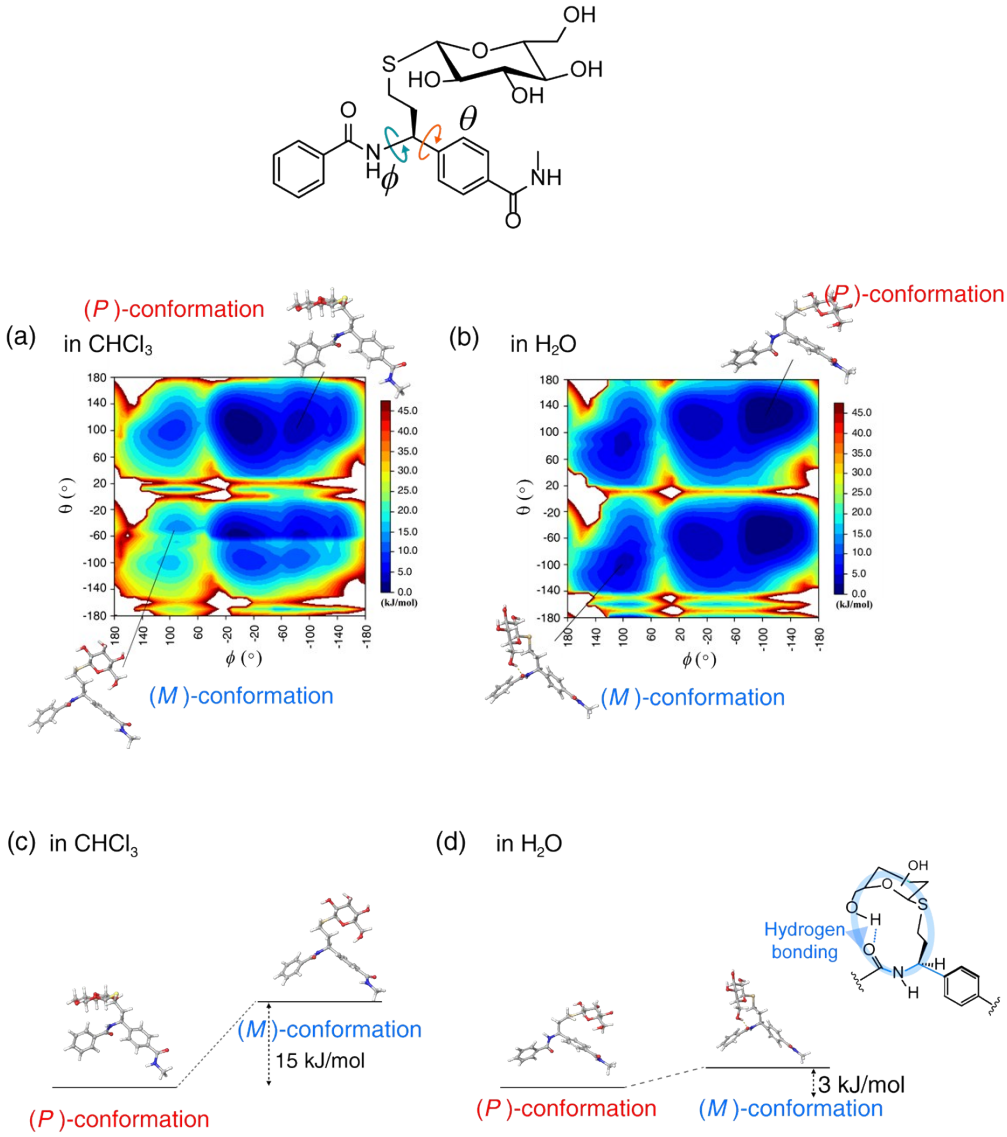


Figure S47. Energy diagrams for dihedral angle change around asymmetric carbon on the main chain in (a) $CHCl_3$ and (b) H_2O (*n* = 1). (c) The energy gap between (*P*)- and (*M*)-conformation of optimized structures in $CHCl_3$ and (d) H_2O.

geometry optimization and frequency calculation of the resulting model of **S4** were performed in THF by DFT. As shown in Figure S47a-b, the energy diagrams for dihedral angle change around the asymmetric carbon on the main chain of **S4** in $CHCl_3$ and H_2O were examined using coordination scan program by MacroModel (force field; OPLS3e, Schrödinger Inc, Maestro 11.9). The energy gap between (*P*) and (*M*)-conformation in each solvent is much smaller than that of in organic solvent, indicating that (*M*)-helix would be formed easily by H_2O (Figure S47c-d).

Based on the experimental results, CD/UV simulations of (*P*)-conformation in THF and (*M*)-conformation in H_2O were conducted by TD-DFT theory (Figure S48). Their results is similar to experimental results of oligomer (*n* = 1, Figure S45).

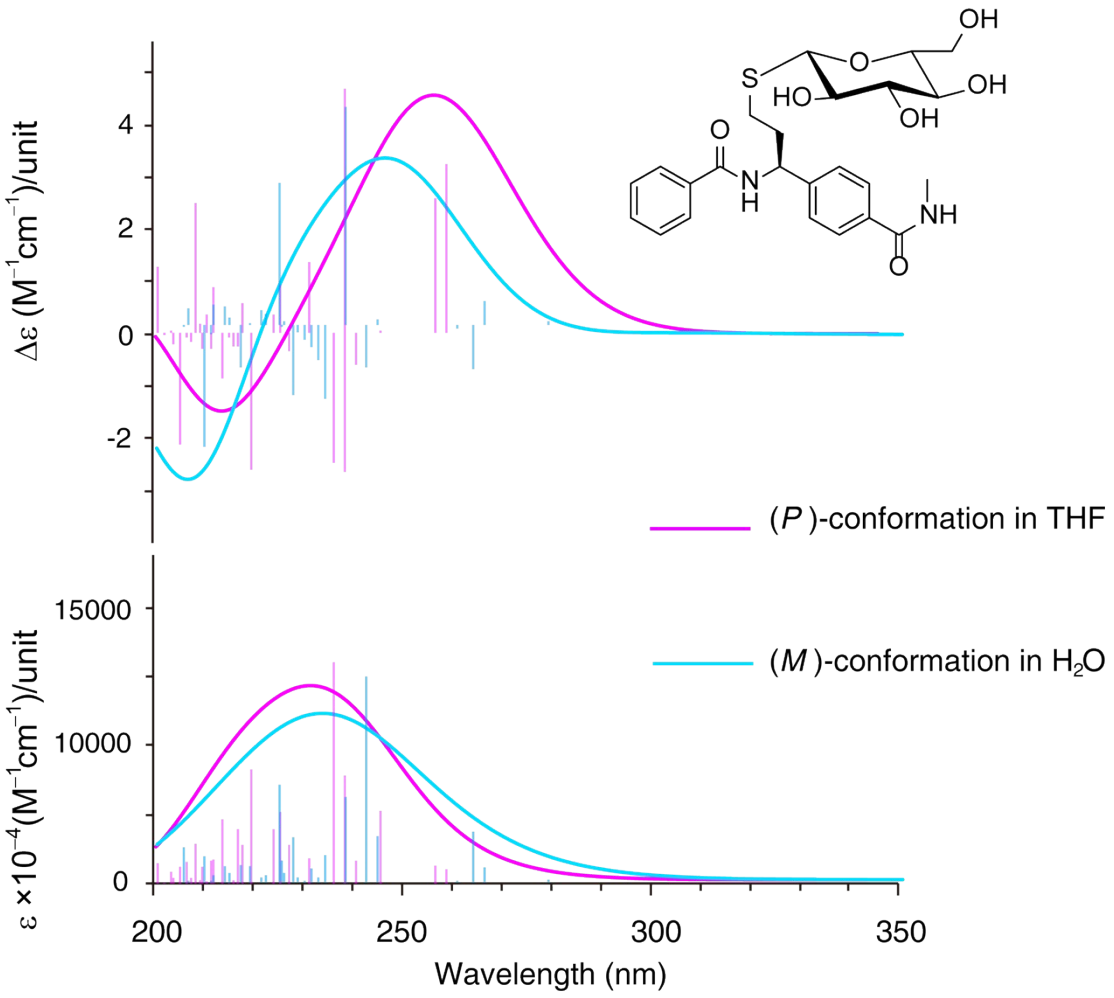


Figure S48. The simulated CD/UV spectra of **S4** (oligomer (*n* = 1)) calculated by TD-DFT (B3LYP/6-31G (d, p)) in THF and H_2O.

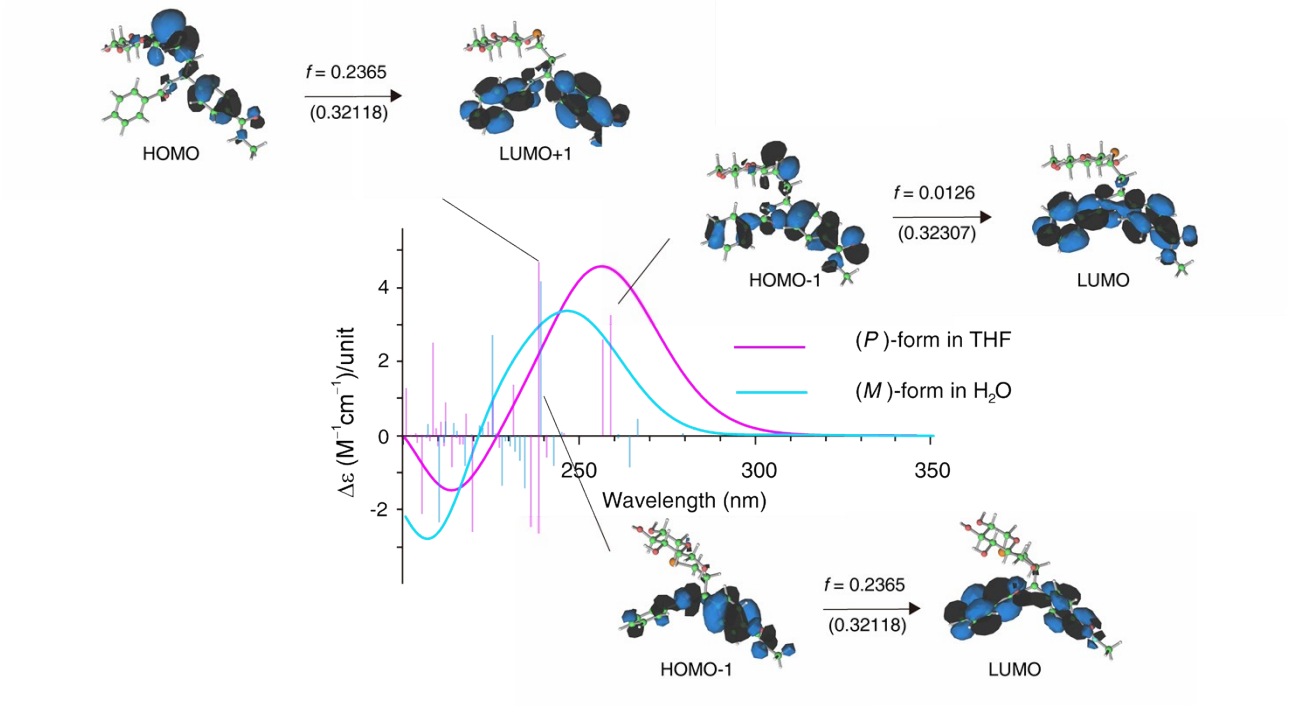


Figure S49. Calculated CD/UV spectra of **S4** (oligomer (n = 1)), the calculated predominant transitions for the absorption bands (nm), oscillator strength (f) and the molecular orbitals (MOs). The coefficients indicating their contributions to the excitation are shown in the parentheses under arrows.

7-2. Structual optimization of S8 (oligomer, n = 2)

Oligomers (n = 2) were made from above (*P*)-conformation in THF and (*M*)-conformation in H_2O by fusing the arylene rings. Conformational searches of the oligomer using a MacroModel produce mainly two type of conformers, which is Zig-zag type and Twist type. The seven conformers from the most stable order based on the conformational search are showed on Figure S50.

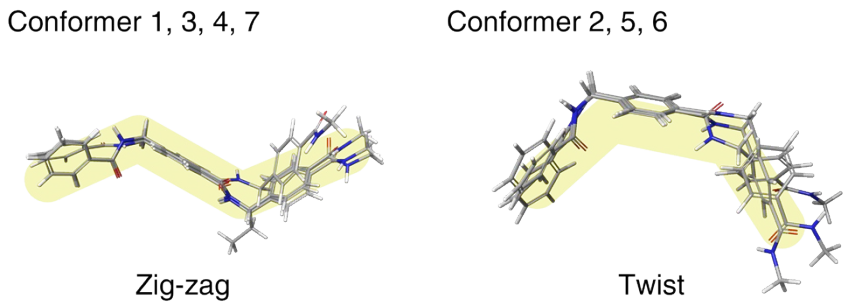


Figure S50. Conformational search of oligomer (n = 2) calculated by a MacroModel program (force field; OPLS3e, in H_2O, 298 K). Side chains are omitted for clarity.

Calculated CD and UV spectra of the zig-zag conformers in THF and H_2O calculations were obtained by TD-DFT (Figure S51), and this is not match to experimental result of polymers. Conversely, the simulated spectra of twist conformers is very similar to experimental result (Figure 1a-b in the text).

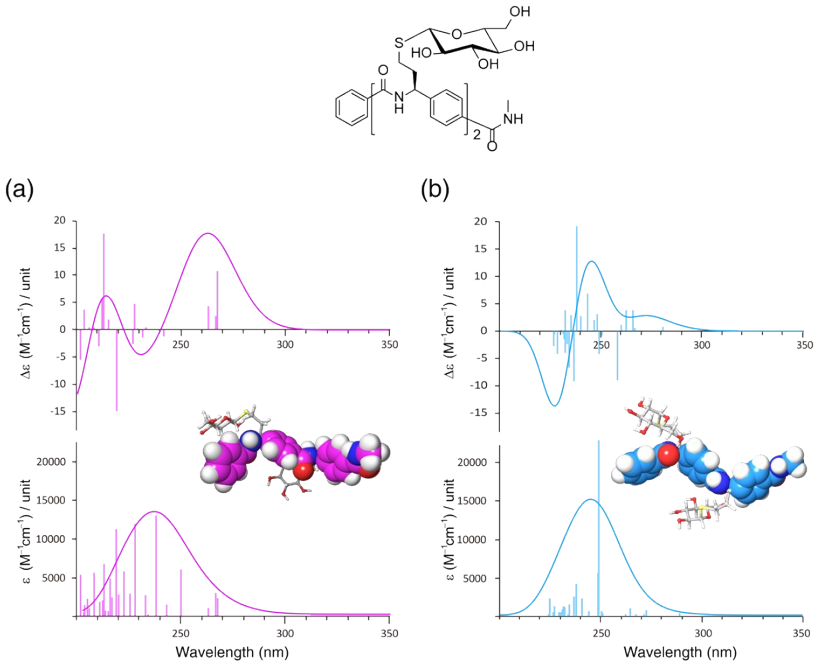


Figure S51. The simulated CD/UV spectra of zig-zag type in (a) THF and (b) H_2O calculated by TD-DFT calculation (B3LYP/6-31G (d, p)) in THF and H_2O.

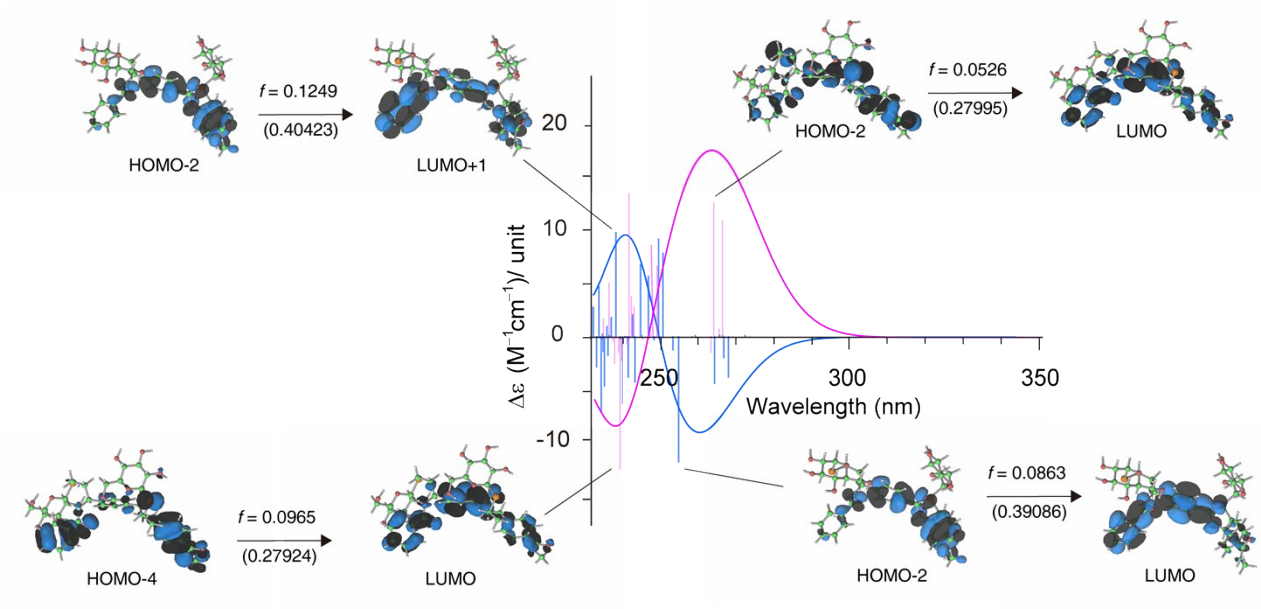


Figure S52. The calculated predominant transitions for the absorption bands (wavelength, nm), oscillator strength (*f*) and the molecular orbitals (MOs) for oligomer (n = 2) of twist type. The coefficients indicating their contributions to the excitation are shown in the parentheses under arrows.

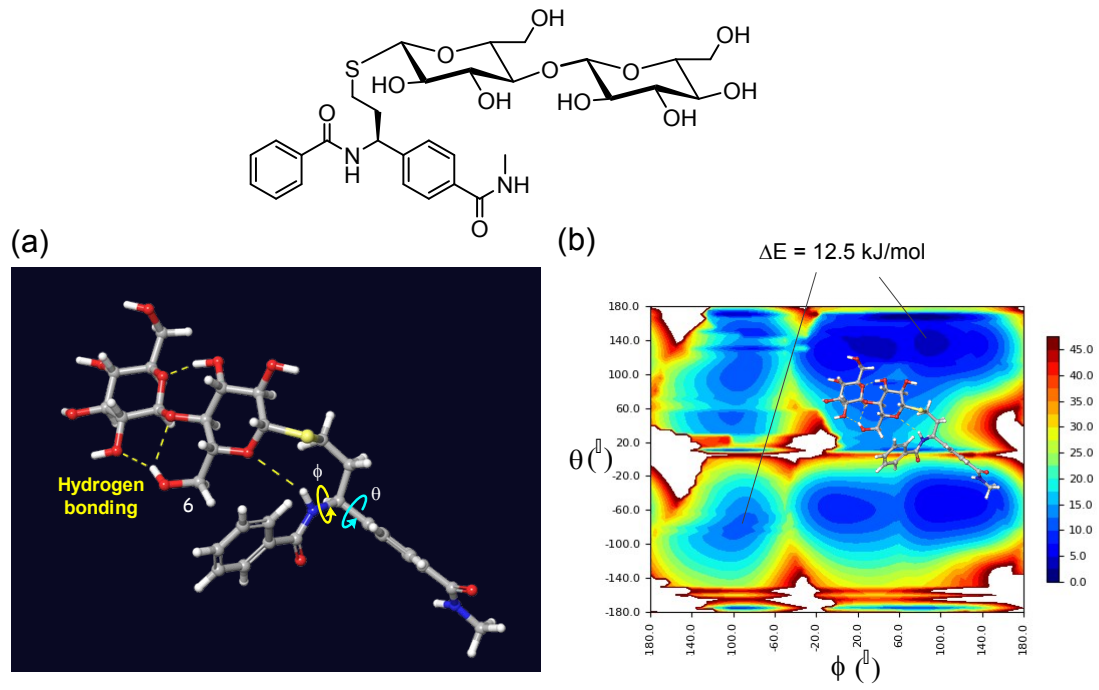


Figure S53. Optimized structure and Energy diagrams for dihedral angle change around asymmetric carbon on the main chain in H_2O. Oligomer; n = 1, side chain; cellobiose derivative.

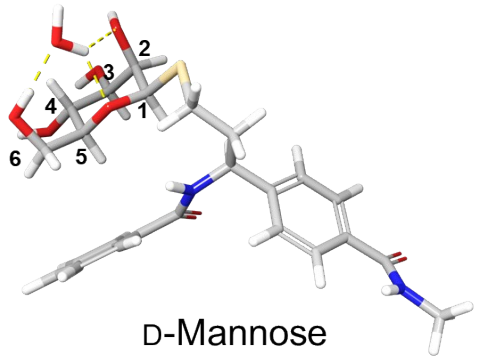


Figure S54. Optimized structure of oligomer (n = 1, side chain; D-mannose) including a H_2O molecule. This form of hydration structure appears to be a valid form.[6]

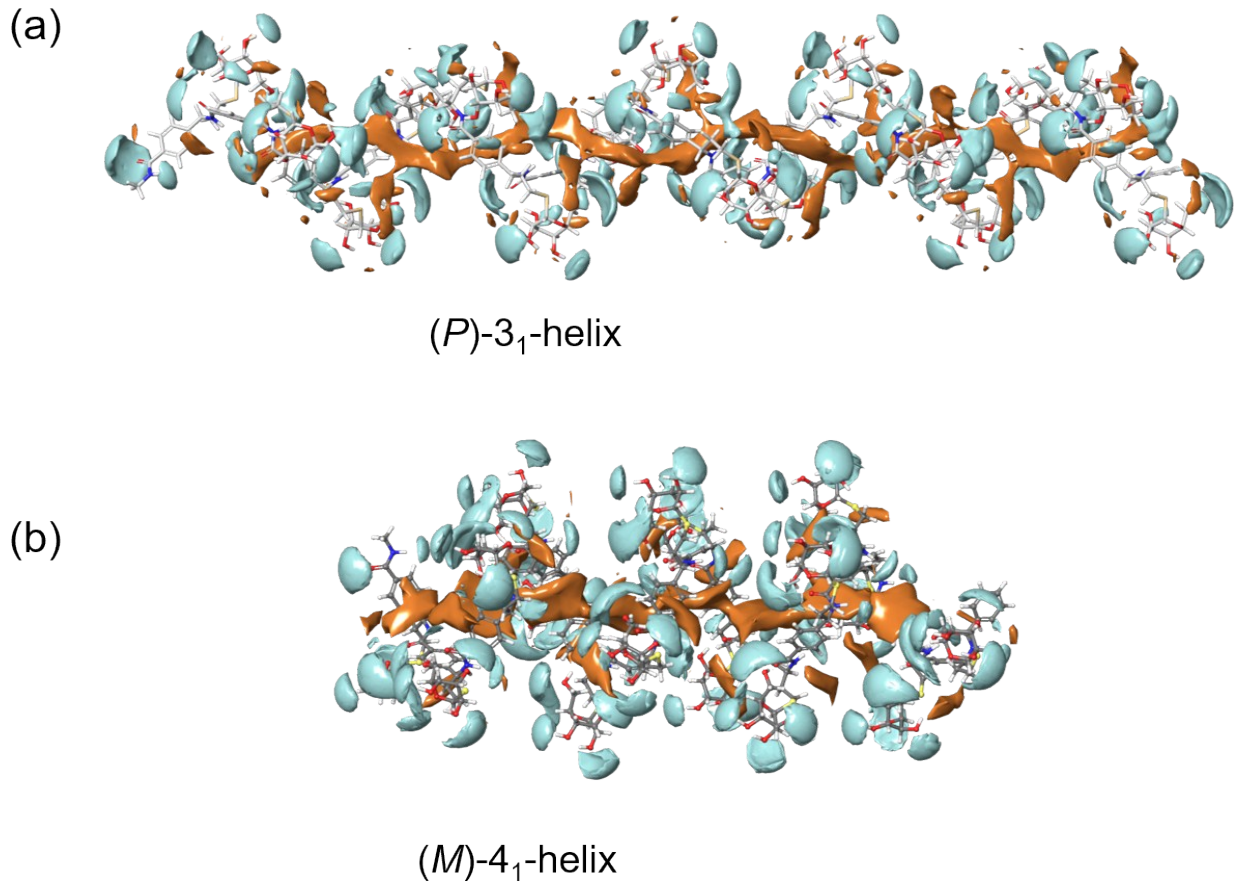


Figure S55. Hydrophobic/hydrophilic map of **poly-1a**. (a) (*P*)-helix, (b) (*M*)-helix (hydrophobic; brown, hydrophilic; pale blue). The hydrophobic part of the (*M*)-helix is effectively covered by hydrophilic saccharide substituents.

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