Supporting Information for

Synthesis and Characterization of Supramolecular Cross-linkers Containing Cyclodextrin Dimer and Trimer

Keisuke IIJIMA, Daisuke AOKI, Hiromitsu SOGAWA, Shigeo ASAI, and Toshikazu TAKATA†

Department of Organic and Polymeric Materials, Tokyo Institute of Technology

2-12-1 (H-126), *O-okayama, Meguro, Tokyo 152-8552, Japan*

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EXPERIMENTAL SECTION

Materials

α-CD was purchased from Junsei Chemical Co. Ltd. and used after drying at 80 °C overnight under vacuum. Cosmosil 75C_{18}-PREP was obtained from Nacalai Tesque, inc. IRGACURE 500® was kindly donated from BASF Japan Ltd. A methacrylate-type-macromonomer with 3,5-dimethylphenyl group at the therminal (**TBM**) was prepared according to the literature[1]. Dialkyne **1** was prepared according to the literature[2]. 6-azido-6-deoxy-α-cyclodextrin **2** was prepared according to the literature[3]. α-CD dimer **4** and trimer **5** were synthesized based on previously reported method[4]. *N*,*N*-dimethylacrylamide (purchased from Wako Pure Chemical Industries, Ltd.) was purified by passing through the alminum oxide column (filled with alminum oxide 90 standardized, Merck Ltd.) to remove the inhibitor. Other reagents and solvents commercially available were used without further purification unless otherwise noted.

Characterization

^{1}H (400MHz, 300MHz) and ^{13}C (100MHz) NMR spectra were recorded on a JEOL AL-400 spectrometer and a BRUKER SPECTROSPIN 300 using $CDCl_3$, dimethyl sulfoxide-d_6 and D_2O as the solvents and calibrated using the residual undeuterated solvent or tetramethylsilane as the internal standard. DOSY (500 MHz) NMR spectra were recorded on Bruker biospin·AVANCE III HD500 using D_2O and NaOD as the solvent and calibrated using the residual undeuterated solvent as the internal standard. The infrared (IR) spectra were recorded on a JASCO FT/IR-230 spectrometer. The melting points were measured on a MELTING POINT APPARATUS SMP3 (Stuart Scientific, Staffordshire, UK) and Melting Point Meter RFS-10 (Round Science Inc. Japan) instruments. Electrospray-ionization (high-resolution mass spectrometry) spectra were obtained at the Center for Advanced Material Analysis, Tokyo Institute of Technology. Thermogravimetric analyses (TGA) were performed on a Shimadzu TGA-50 instrument under an N_2 atmosphere (flow rate of 50 ml min^{-1}) to determine the 5% weight decomposition temperature (T_{d5}) at which 5% weight loss was observed. Differential scanning calorimetry (DSC) analyses were performed with a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under a nitrogen (flow rate 50 mL/min) with liquid N_2 as a refrigerant to determine glass transition temperature (T_g). Tensile testing (stress-strain) was conducted in a Shimadzu EZ-L 500N by using (12.0 mm × 2.0 mm × 1.0 mm) specimens and a strain rate of 12 mm/min. The obtained data were analyzed with TRAPEZIUM LITE (Shimadzu corporation, Japan). The UV irradiation was carried out on a high pressure mercury lamp OPM2-250H (USHIO INC.).

Hydrodynamic radius (R_h) of VSCs were estimated by diffusion constants obtained by DOSY NMR and calculated using following Stokes–Einstein's equation (1),

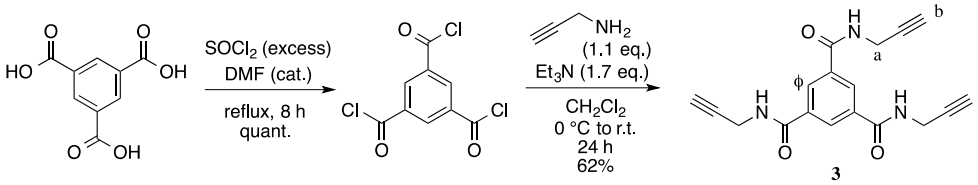
$$D = \frac{k_B T}{6\pi\eta r} \qquad (1)$$

where D, k_B, T, η, r are diffusion constant [m^2/s], Boltzmann constant, absolute temperature, viscosity of the solvent (H_2O: 0.890 mPa·s), hydrodynamic radius of the solute, respectively.

Swelling experiments were performed in distilled water, MeOH, DMF, and $CHCl_3$ at ambient temperature. The swelling ratio was defined as the difference of the weight of swollen gel ($W_{swollen}$) to the dried gel (W_{dry}), according to equation (2).

$$Swelling\ Ratio\ [\%] = \frac{W_{swollen} - W_{dry}}{W_{dry}} \times 100 \qquad (2)$$

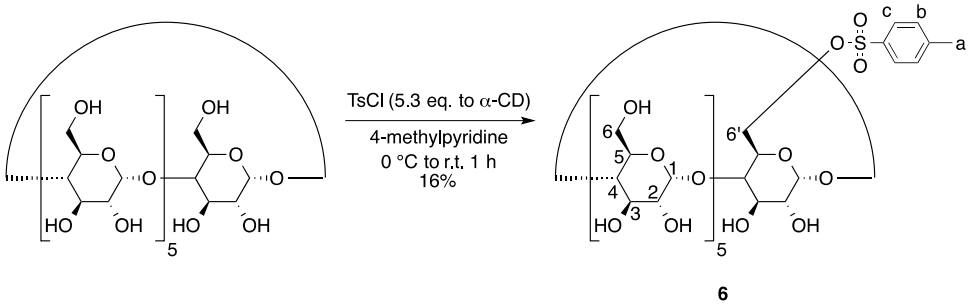
Synthesis of trialkyne 3.



Scheme S1. Synthesis of trialkyne **3**.

Trialkyne **3**[5] was synthesized as shown in **Scheme S1**. 1,3,5-benzenetricarboxylic acid (5.0 g, 24 mmol) was dissolved in thionyl chloride (15 mL, 0.21 mol) and droplet of DMF was added. After refluxing the reaction mixture for 8 h, excess thionyl chloride was removed by distillation to obtain benzene-1,3,5-tricarbonyl trichloride in quantitative yield. To a solution of the obtained trichloride (0.53 g, 2.0 mmol) in CH_2Cl_2 (100 mL) was added triethylamine (1.4 mL, 10 mmol) at 0 °C. Then the mixture was added dropwisely to the solution of propargylamine (0.4 mL, 6.3 mmol) in CH_2Cl_2 (50 mL) for 30 min. After stirring the reaction mixture for 24 h at ambient temperature, the mixture was concentrated and dissolved in ethyl acetate to wash with 2N H_2SO_4, water, and sat. $NaHCO_3$ aq. The organic layer was dried by Na_2SO_4, then filtrated and evaporated to give 0.40 g of trialkyne **3** (1.2 mmol, 62%) as a white solid; m.p. 205.5 – 207.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 9.27 (m, 3H, N–H), 8.50 (m, 3H, ϕ), 4.15 (m, 6H, a), 3.21 (m, 3H, b) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, 298 K): δ 165.17, 134.48, 129.05, 81.05, 73.13, 28.77 ppm; IR (KBr): ν 3292, 3278, 3245, 3061, 1636, 1547, 1295, 1060 cm^{-1}.

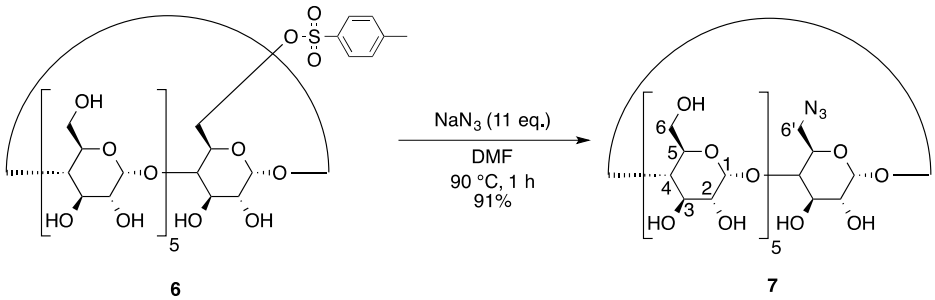
Synthesis of mono-6-tosyl-6-deoxy-α-CD 6.



Scheme S2. Synthesis of mono-6-tosyl-6-deoxy-α-CD **6**.

Mono-6-tosyl-6-deoxy-α-CD **6** was synthesized as shown in **Scheme S2**. To the solution of α-CD (10 g, 10 mmol) in 4-methylpyridine (100 mL) was added *p*-toluenesulfonyl chloride (10 g, 52 mmol) at 0 °C. Then the solution was stirred for 1 h at ambient temperature and then reprecipitated in 2 L of acetone. The precipitate was filtrated and dried to obtain the crude product (*ca*. 10 g). The crude product was purified by reverse-phase column chotomatography (column filler: Cosmosil 75C_{18}-PREP, eluent: water / MeOH = 5 / 1 to 3 / 1) to obtain 1.9 g of mono-6-tosyl-6-deoxy-α-CD **6** (1.7 mmol, 16%) as a white solid; m.p. > 180 °C (decomp.); ^{1}H NMR (400 MHz, 298 K, D_2O): δ 7.72–7.69 (d, J = 7.9 Hz, 4H, c), 7.39–7.37 (d, J = 7.9 Hz, 4H, b), 4.87–4.78 (m, 6H, H_1), 4.32–4.21 (m, 2H, H_6'), 3.84–3.61 (m, 22H, H_3, H_5, and H_6), 3.47–3.32 (m, 12H, H_2 and H_4), 2.32 (s, 3H, a) ppm.

Synthesis of mono-6-azido-6-deoxy-α-CD 7.

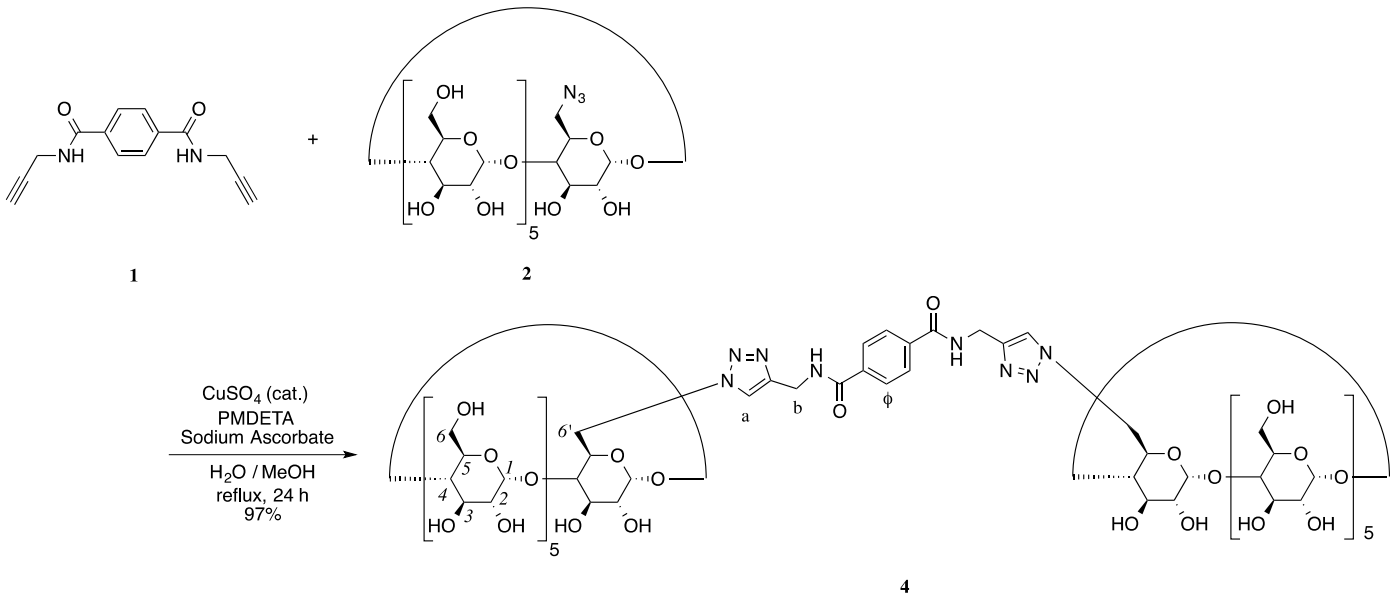


Scheme S3. Synthesis of mono-6-azido-6-deoxy-α-CD **7**.

Mono-6-azido-6-deoxy-α-CD **7** was synthesized as shown in **Scheme S3**. To the solution of mono-6-tosyl-6-deoxy-α-CD **6** (1.0 g, 0.89 mmol) in DMF (20 mL) was added sodium azide (0.63 g, 9.7 mmol) at ambient temperature. Then the solution was heated at 90 °C for 12 h. The reaction mixture was cooled to ambient temperature and reprecipitated in mixed solvent of acetone / water = 20 / 1. The precipitate was filtrated and dried to obtain 0.81 g of mono-6-azido-6-deoxy-α-CD **7** (0.81 mmol, 91%) as a white solid;

m.p. > 230 °C (decomp.); ^{1}H NMR (400 MHz, 298 K, D_2O): δ 4.90 (br, 6H, H_1), 3.84–3.68 (m, 24H, H_3, H_5, H_6, and H_6'), 3.52–3.43 (m, 12H, H_2 and H_4) ppm; IR (KBr): ν 3390, 2930, 2128, 2037, 1653, 1633, 1152, 1076, 1034, 638, 573 cm^{-1}.

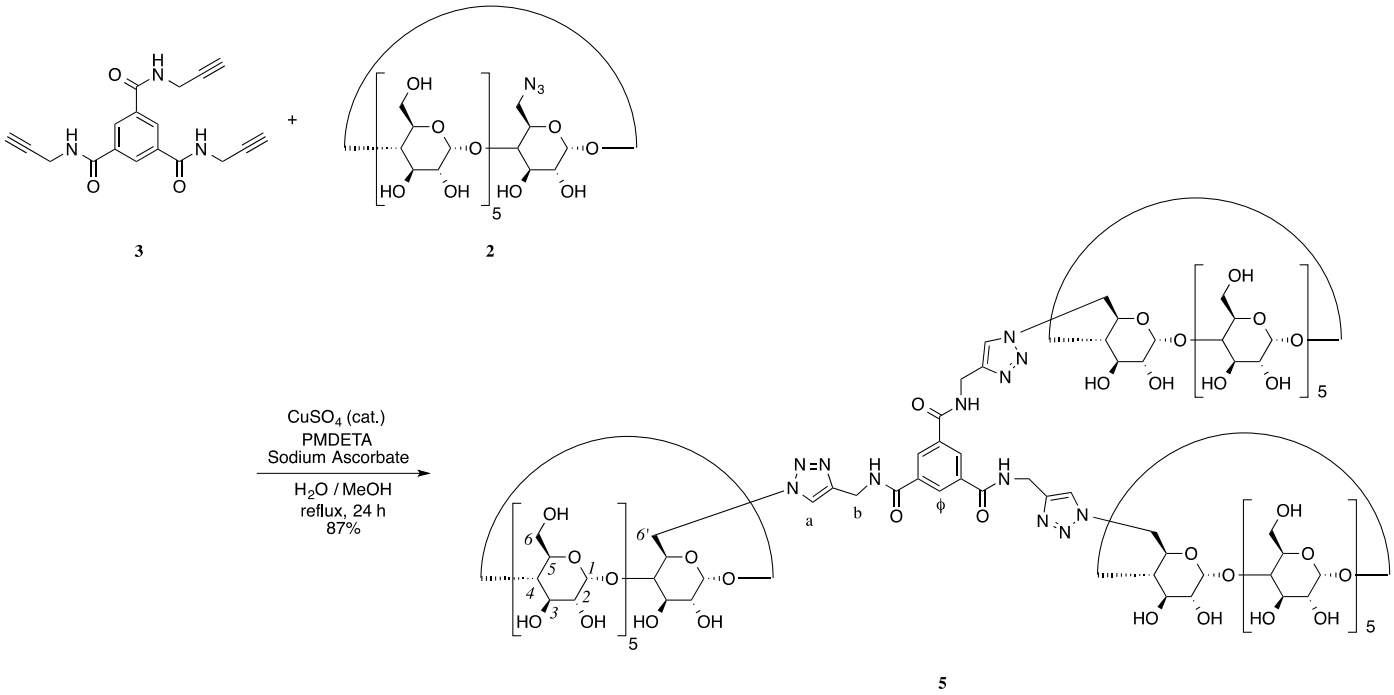
Synthesis of α-CD dimer 4.



Scheme S4. Synthesis of α-CD dimer **4**.

α-CD dimer **4** was synthesized as shown in **Scheme S4**. Dialkyne **1** (12 mg, 50 μmol) and mono-azido α-CD **2** (0.15 g, 0.15 mmol) were dissolved in mixed solvent of H_2O / MeOH = 1 / 1 (20 mL) and the flask was purged with Ar gas. Then to the solution were added *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA) (80 μL, 0.38 mmol), 0.06 M sodium ascorbate aq. (100 μL, 6.0 μmol), and 0.06 M $CuSO_4$ aq (100 μL, 6.0 μmol) in this order, and refluxed for 12 h. The reaction mixture was concentrated and reprecipitated in MeOH. The precipitate was filtrated and dried *in vacuo* to give 0.11 g of α-CD dimer **4** (49 μmol, 98%) as a white solid; m.p. >270 °C (decomp.); ^{1}H NMR (300 MHz, D_2O, 298 K): δ 7.94 (s, 2H, a), 7.80 (s, 4H, ϕ), 5.08–4.60 (m, 12H, H_1), 4.55–4.47 (m, 2H, b), 4.14–4.08 (m, 2H, b), 3.97–3.70 (m, 44H, H_3, H_5, and H_6), 3.62–3.40 (m, 24H, H_2 and H_4), 3.00–2.96 (d, *J* = 11 Hz, 2H, $H_{6'}$), 2.71–2.67 (d, *J* = 11 Hz, 2H, $H_{6'}$) ppm; ^{13}C NMR (100 MHz, D_2O, 298 K): 203.67, 178.62, 170.06, 161.79, 160.06, 135.68, 135.55, 135.13, 117.24, 115.46, 115.37, 114.79, 107.46, 107.19, 107.01, 106.34, 106.15, 105.85, 105.69, 104.91, 94.58, 93.29, 85.52, 69.01 ppm; ESI–TOF MS Calcd for $C_{86}H_{130}N_8O_{60}Na_2^{2+}$ $[M+2Na]^{2+}$, 1140.3576; found, 1140.3576; IR (KBr): ν 3393, 2932, 1638, 1155, 1080, 1035 cm^{-1}.

Synthesis of α-CD trimer 5.



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Scheme S5. Synthesis of α-CD trimer **5**.

α-CD trimer **5** was synthesized as shown in **Scheme S5**. Trialkyne **3** (10 mg, 31 μmol) and mono-azido α-CD **2** (0.15 g, 0.15 mmol) were dissolved in mixed solvent of H_2O / MeOH = 1 / 1 (12 mL) and the flask was purged with Ar gas. Then to the solution were added PMDETA (80 μL, 0.38 mmol), 0.06 M sodium ascorbate aq. (100 μL, 6.0 mmol), and 0.06 M $CuSO_4$ aq (100 μL, 6.0 mmol) in this order, and refluxed for 12 h. The reaction mixture was concentrated and reprecipitated in MeOH. The precipitate was filtrated and dried *in vacuo* to give 87 mg of α-CD trimer **5** (26 μmol, 84%) as a white solid; m.p. >270 °C (decomp.); ^{1}H NMR (300 MHz, D_2O, 298 K): δ 8.22 (s, 3H, a) 7.90 (s, 3H, ϕ), 5.00–4.75 (m, 18H, H_1), 4.49–4.43 (dd, J_1 = 11 Hz, J_2 = 11 Hz, 3H, b), 4.07–4.02 (dd, J_1 = 11 Hz, J_2 = 11 Hz, 3H, b), 3.89–3.30 (m, 102H, C(2)–C(6)H), 2.93–2.90 (d, J = 12 Hz, 3H, C(6')H), 2.66–2.63 (d, J = 12 Hz, 3H, C(6')H) ppm; ^{13}C NMR (100 MHz, D_2O, 298 K):δ 202.41, 178.59, 168.69, 163.47, 160.07, 135.66, 135.53, 135.14, 117.21, 115.45, 115.36, 114.84, 107.45, 107.19, 107.02, 106.34, 106.14, 105.84, 105.70, 104.89, 94.59, 93.33, 85.51, 69.15 ppm; ESI–TOF MS Calcd for $C_{126}H_{192}N_{12}O_{90}Na_2^{2+}$ $[M+2Na]^{2+}$, 1680.0317; found, 1680.0316, $C_{126}H_{192}N_{12}O_{90}Na_3^{3+}$ $[M+3Na]^{3+}$, 1127.6842; found, 1127.6840; IR (KBr): ν 3412, 2928, 1654, 1156, 1078, 1033 cm^{-1}.

Typical procedure for preparation of rotaxane cross-linked polymers.

To a solution of **TBM** (27 mg, 20 μmol) in 0.1 M NaOH (0.25 mL) was added α-CD dimer **4** (20 mg, 10 μmol) to form vinylic suprmolecular cross-linker (VSC). *N*,*N*-dimetylacrylamide (0.50 g, 5.0 mmol) and IRGACURE 500 (photo initiator, 1:1 wt% mixture of 1-hydroxycyclohexyl phenyl kenote and benzophenone) (40 μL) were added to the VSC solution, and degassed via freezing-thaw process for three times. Then the flask was purged with Ar gas, exposed under UV light for 5 min. and kept in the flask for 12 h to proceed the polymerization reaction. The obtained gel-like material was washed with H_2O, acetone, MeOH, THF for 1 d for each solvent in this order to remove unreacted materials, and dried at 80 °C *in vacuo* for 12 h to obtain **RCPα²-1** (0.36 g, 66%) as a white solid.

According to the same procedure, **RCPα²-2** (0.26 g, 71%) was obtained from **TBM** (27 mg, 20 μmol), α-CD dimer **4** (20 mg, 10 μmol), DMAAm (0.33 g, 3.3 mmol), and IRGACURE 500 (40 μL) in 0.1 M NaOH (0.17 mL). **RCPα²-3** (0.15 g, 64%) was obtained from **TBM** (27 mg, 20 μmol), α-CD dimer **4** (20 mg, 10 μmol), DMAAm (0.20 g, 2.0 mmol), and IRGACURE 500 (40 μL) in 0.1 M NaOH (0.10 mL). **RCPα³-1** (0.33 g, 62%) was also obtained from **TBM** (27 mg, 20 μmol), α-CD trimer **5** (22 mg, 6.7 μmol), DMAAm (0.50 g, 5.0 mmol), and IRGACURE 500 (40 μL) in 0.1 M NaOH (0.25 mL). **RCPα³-2** (0.24 g, 65%) was obtained from **TBM** (27 mg, 20 μmol), α-CD trimer **5** (22 mg, 6.7 μmol), DMAAm (0.33 g, 3.3 mmol), and IRGACURE 500 (40 μL) in 0.1 M NaOH (0.17 mL). **RCPα²-3** (0.10 g, 41%) was obtained from **TBM** (27 mg, 20 μmol), α-CD trimer **4** (22 mg, 6.7 μmol), DMAAm (0.20 g, 2.0 mmol), and IRGACURE 500 (40 μL) in 0.1 M NaOH (0.10 mL).

RCPα²-1; colorless solid; T_{d5} 352 °C; T_g 108 °C; IR (KBr): ν 3451, 2930, 2119, 1638, 1499, 1400, 1354, 1257, 1143, 1094, 1055, 734, 625, 553 cm^{-1}.

RCPα²-2; colorless solid; T_{d5} 364 °C; T_g 112 °C; IR (KBr): ν 3475, 2930, 2123, 1638, 1499, 1400, 1355, 1257, 1141, 1096, 1056, 735, 625 cm^{-1}.

RCPα²-3; colorless solid; T_{d5} 359 °C; T_g 87.4 °C; IR (KBr): ν 3475, 2931, 2131, 1638, 1499, 1400, 1355, 1257, 1141, 1095, 1056, 738, 625 cm^{-1}.

RCPα³-1; colorless solid; T_{d5} 346 °C; T_g 107 °C; IR (KBr): ν 3470, 2930, 2149, 1635, 1497, 1401, 1354, 1257, 1141, 1094, 1056, 742, 626 cm^{-1}.

RCPα³-2; colorless solid; T_{d5} 373 °C; T_g 110 °C; IR (KBr): ν 3479, 2932, 2135, 1635, 1497, 1404, 1354, 1257, 1141, 1094, 1057, 742, 627 cm^{-1}.

RCPα^3-3; colorless solid; T_{d5} 354 °C; T_g 93.9 °C; IR (KBr): ν 3478, 2932, 2123, 1634, 1497, 1404, 1354, 1257, 1142, 1094, 1056, 742, 627 cm^{-1}.

Typical procedure for the synthesis of chemically cross-linked poly(DMAAm) (CCP).

A mixture of photo-initiator (Irgacure500, 40 μL) and DMAAm (10 mmol) was added to a solution of *N*,*N*'-methylenebisacrylamide(BIS) (3.1 mg, 0.20 mmol) in 0.1 M NaOH (0.5 mL). The mixture was UV-irradiated at room temperature for 3 min to yield a solvent-insoluble gelled material. The gel was swollen in water, acetone, MeOH, and THF to remove unreacted materials, and gently dried *in vacuo* at 80 °C for 1 d to afford purified **CCP$_{BIS}$-1** as a white solid in 87% yield. According to the same procedure, **CCP$_{BIS}$-2** (0.86 g, 89%) was obtained from BIS (4.7 mg, 0.30 mmol) and **CCP$_{BIS}$-3** (0.87 g, 90%) was obtained from BIS (7.7 mg, 0.50 mmol).

CCP$_{BIS}$-1: colorless solid; T_{d5} 383 ºC, T_g 119 ºC; IR (KBr) υ 3449, 2937, 2931, 2123, 1638, 1509, 1458, 1397, 1255, 1142, 1096, 1058, 744, 629 cm^{-1}.

CCP$_{BIS}$-2: colorless solid; T_{d5} 354 ºC, T_g 120 ºC; IR (KBr) υ 3444, 2928, 2184, 1634, 1504, 1400, 1355, 1256, 1139, 1092, 1060, 905, 742, 617 cm^{-1}.

CCP$_{BIS}$-3: colorless solid; T_{d5} 397 ºC, T_g 120 ºC; IR (KBr) υ 3470, 2934, 2131, 1627, 1499, 1402, 1356, 1257, 1143, 1094, 1056, 739, 627 cm^{-1}.

Typical procedure for the preparation of film-type RCP / CCP

Synthesis of film-type **RCPα^2-1** is shown below as an example; to a solution of **TBM** (54 mg, 40 μmol) in 0.1 M NaOH (0.5 mL) was added α-CD dimer **4** (45 mg, 20 μmol) to form VSC. *N*,*N*-dimetylacrylamide (1.0 g, 10 mmol) and IRGACURE 500 (40 μL) were added to the VSC solution, and degassed via freezing-thaw process for three times. Then the flask was purged with Ar gas, and the precursor solution was poured into silicone template (**Figure S1**). The solution was exposed under UV light for 5 min. and kept in the flask for 12 h to proceed the polymerization reaction. The gel was purified by immersing in water, acetone, MeOH, and THF in this order to remove unreacted materials, and dried *in vacuo* at 80 °C for 1 d to afford the corresponding film-type RCP.

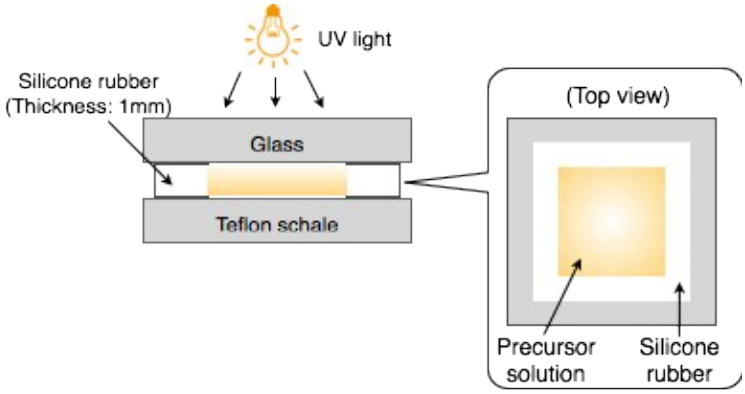


Figure S1. Template for film-type gel preparation.

Table S1. Diffusion constants and hydrodynamic radii of VSCs.

Entry	Material	Obtained VSC	Conc. of TBM [mmol/L]	Conc. of α-CD oligomer [mmol/L]	Diffusion Const. [m^2/s]	Hydrodynamic radius [nm]
1	α-CD dimer **4** **TBM**	**VSCα²-1**	0.028	0.014	1.60×10^{-10} 2.00×10^{-10}	1.40 1.13
2	α-CD dimer **4** **TBM**	**VSCα²-2**	0.042	0.028	1.41×10^{-10} 1.65×10^{-10}	1.60 1.36
3	α-CD dimer **4** **TBM**	**VSCα²-3**	0.069	0.035	0.969×10^{-10} 1.19×10^{-10}	2.32 1.89
4	α-CD trimer **5** **TBM**	**VSCα³-1**	0.028	0.093	1.34×10^{-10} 1.84×10^{-10}	1.68 1.22
5	α-CD trimer **5** **TBM**	**VSCα³-2**	0.042	0.014	1.13×10^{-10} 1.49×10^{-10}	1.99 1.50
6	α-CD trimer **5** **TBM**	**VSCα³-3**	0.069	0.023	0.881×10^{-10} 1.17×10^{-10}	2.55 1.93
7	α-CD dimer **4**	–	–	–	1.88×10^{-10}	1.31
8	α-CD trimer **5**	–	–	–	1.55×10^{-10}	1.58
9	**TBM**	–	–	–	2.21×10^{-10}	1.11

Table S2. Conversions of the VSC components to RCP estimated by ^{1}H NMR spectrum of the residual solution

Gel	Material	Conversion [%]
RCPα²-1	α-CD dimer **4**	70
	TBM	53
RCPα²-2	α-CD dimer **4**	42
	TBM	35
RCPα²-3	α-CD dimer **4**	54
	TBM	61
RCPα³-1	α-CD trimer **5**	51
	TBM	32
RCPα³-2	α-CD trimer **5**	60
	TBM	52
RCPα³-3	α-CD trimer **5**	56
	TBM	37

Table S3. Swelling ratio of **RCPα**s and **CCP$_{BIS}$**s.

Gel	Solvent	Swelling ratio [wt%]
RCPα^2-1	Water	4200
	MeOH	2700
	$CHCl_3$	5300
	DMF	2300
RCPα^2-2	Water	3000
	MeOH	2100
	$CHCl_3$	4200
	DMF	1700
RCPα^2-3	Water	2200
	MeOH	1700
	$CHCl_3$	3400
	DMF	1500
RCPα^3-1	Water	3800
	MeOH	2700
	$CHCl_3$	3600
	DMF	1700
RCPα^3-2	Water	3600
	MeOH	2000
	$CHCl_3$	4200
	DMF	1900
RCPα^3-3	Water	2000
	MeOH	1800
	$CHCl_3$	3300
	DMF	1400
CCP$_{BIS}$-1	Water	1200
	MeOH	860
	$CHCl_3$	1900
	DMF	730
CCP$_{BIS}$-2	Water	980
	MeOH	780
	$CHCl_3$	1600
	DMF	630
CCP$_{BIS}$-3	Water	770
	MeOH	650
	$CHCl_3$	1400
	DMF	550

Table S4. Fracture energy of **RCPα**s and **CCP$_{BIS}$**s.

Entry	Polymer	Fracture energy $\times 10^{-7}$ [N/m^3]	Young's modulus [MPa]
1	**RCPα^2-1**	1.4	0.006
2	**RCPα^2-2**	1.6	0.008
3	**RCPα^2-3**	1.0	0.003
4	**RCPα^3-1**	1.0	0.002
5	**RCPα^3-2**	0.93	0.0003
6	**RCPα^3-3**	1.0	0.0005
7	**CCP$_{BIS}$-1**	1.2	0.02

8	**CCP_{BIS}-2**	0.91	0.05
9	**CCP_{BIS}-3**	0.85	0.03

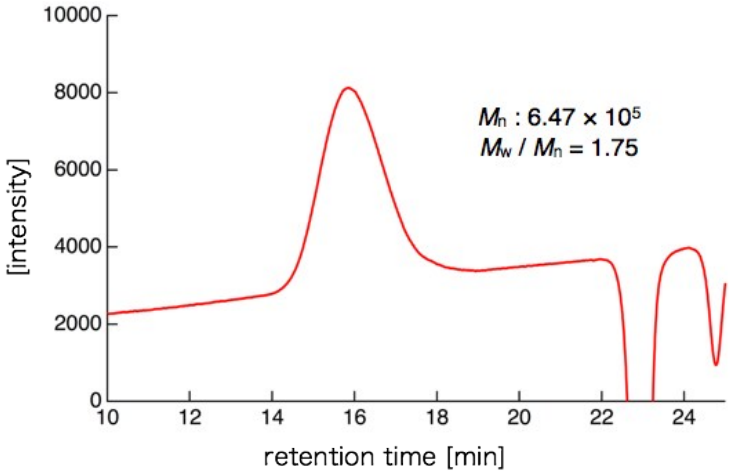


Figure S2. GPC curve of Poly (DMAAm) obtained under similar condition to **RCP□²-1** without **TBM** (Eluent: DMF, PSt standard, detected by RI).

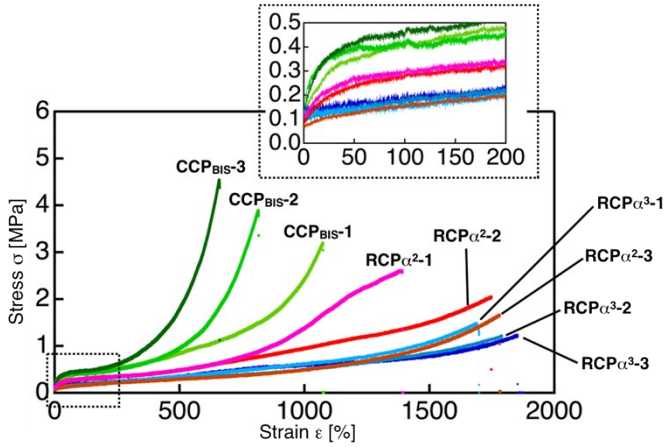
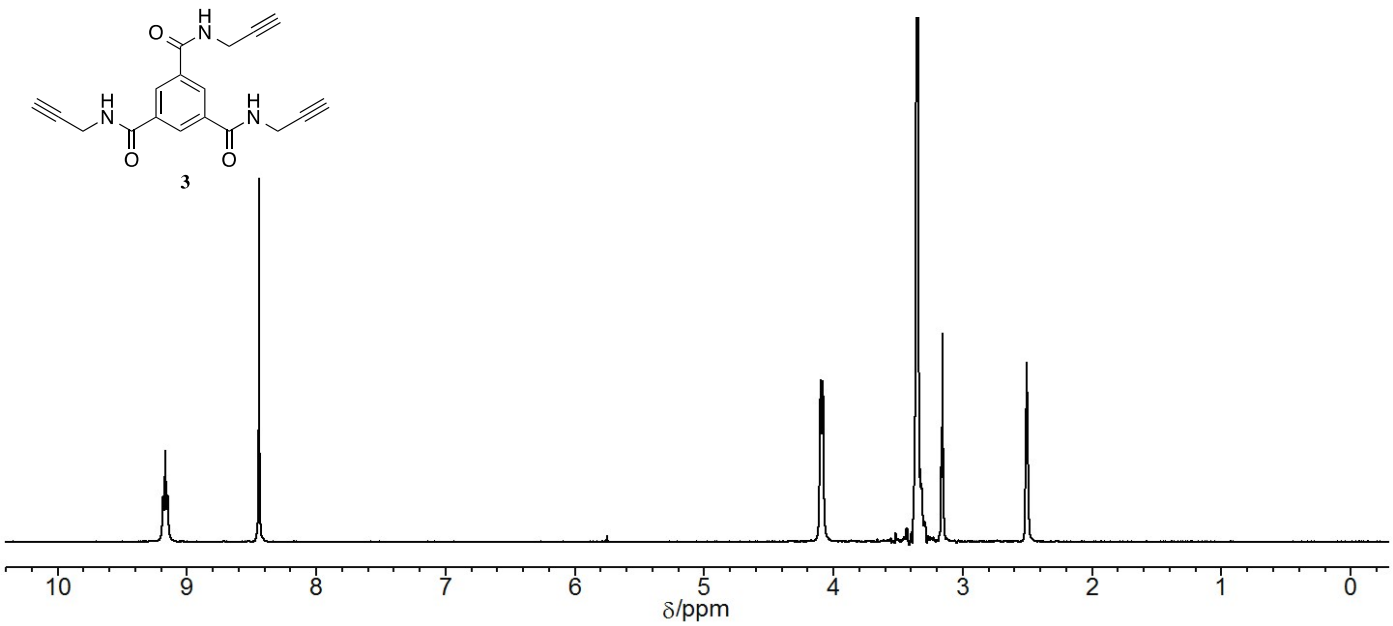


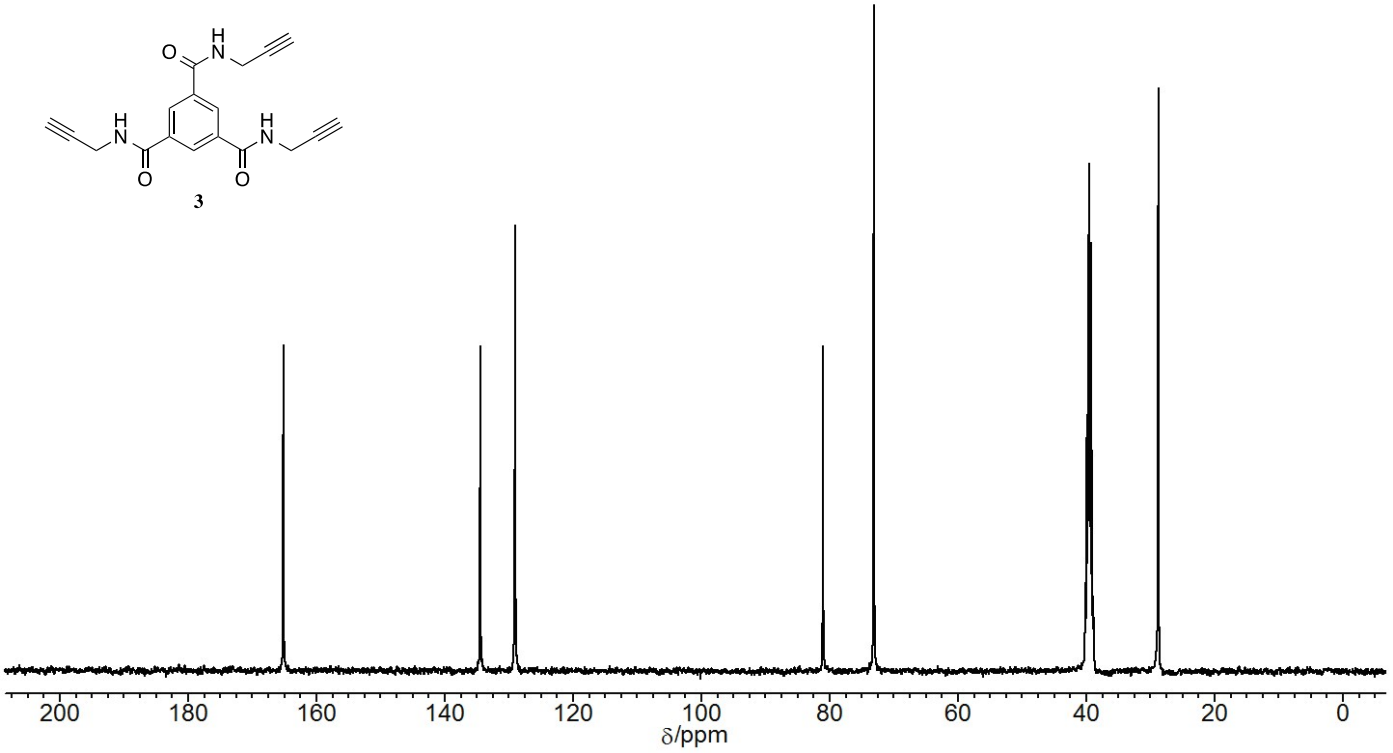
Figure S3. S–S curve of **RCPα** and **CCP_{BIS}** samples containing 20 wt% of water (sample size for tensile test: 12 mm × 5 mm × 1 mm; elongation rate: 12 mm/min, measured at 25 °C). Inserted figure (upper-right) shows the initial region of S-S curves. All RCPs showed higher elongation ability than CCPs.

Figure S4. Illustrated image of VSC composed of (left) α-CD dimer and **TBM** and (right) α-CD trimer and **TBM**.

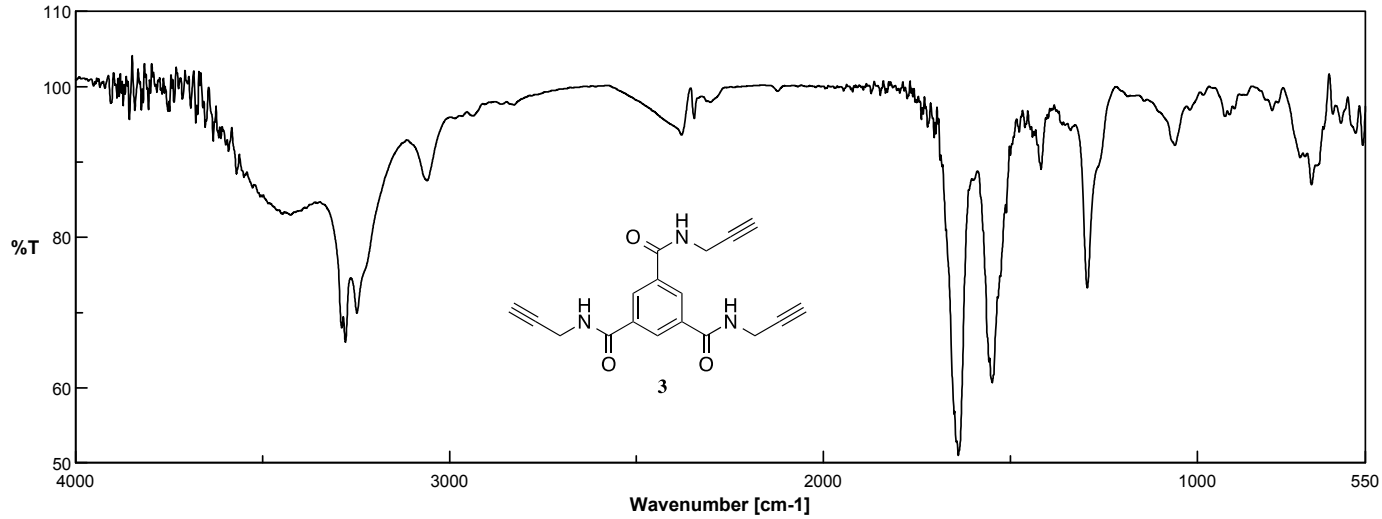
Spectral Charts



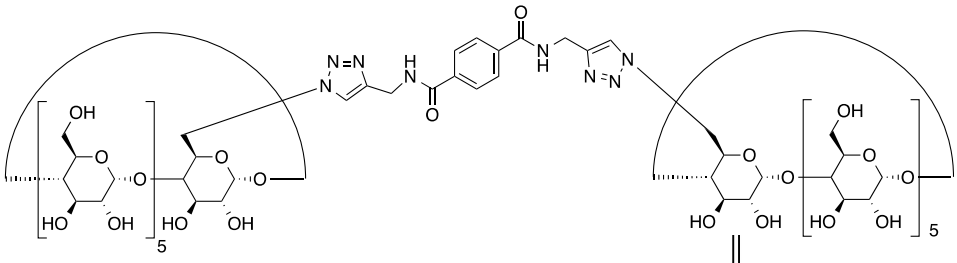
^{1}H NMR spectrum of **3** (300 MHz, DMSO-d_6, 298 K).

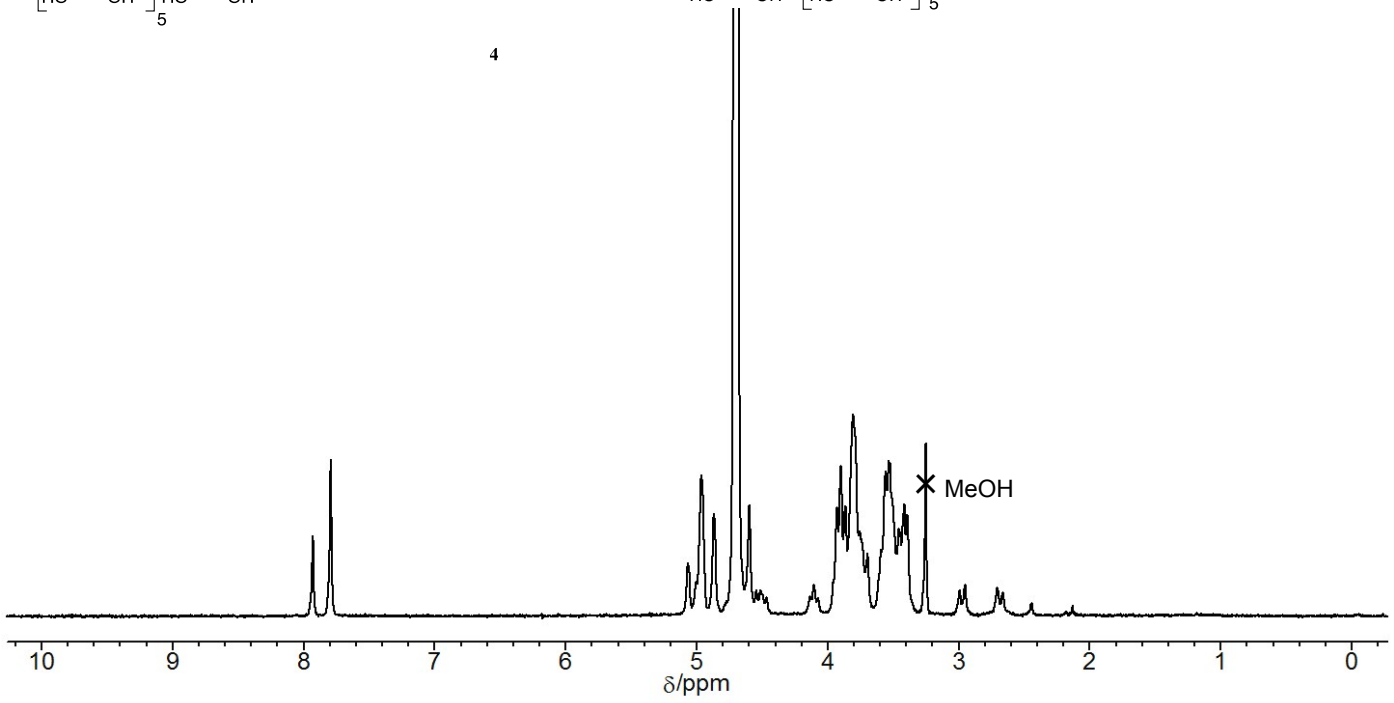


^{13}C NMR spectrum of **3** (75 MHz, DMSO-d_6, 298 K).

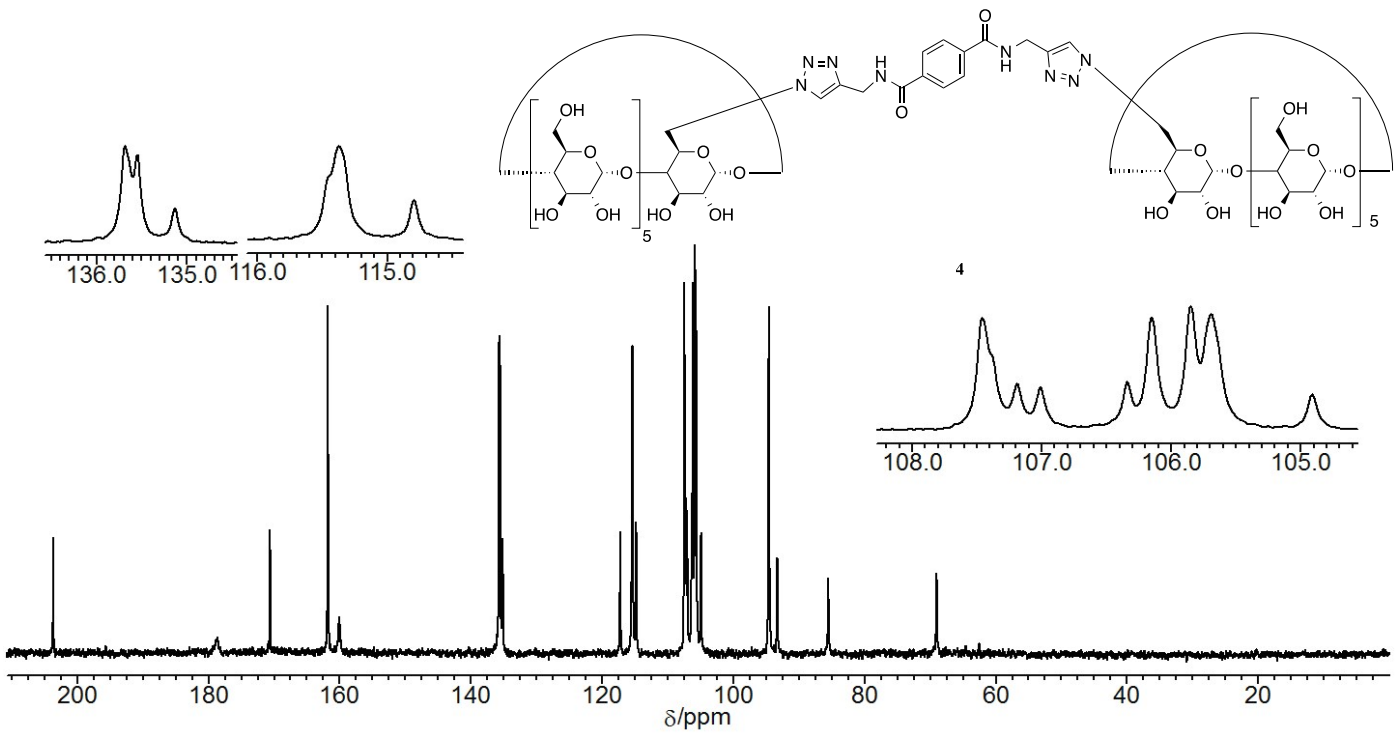


IR spectrum of **3** (KBr).

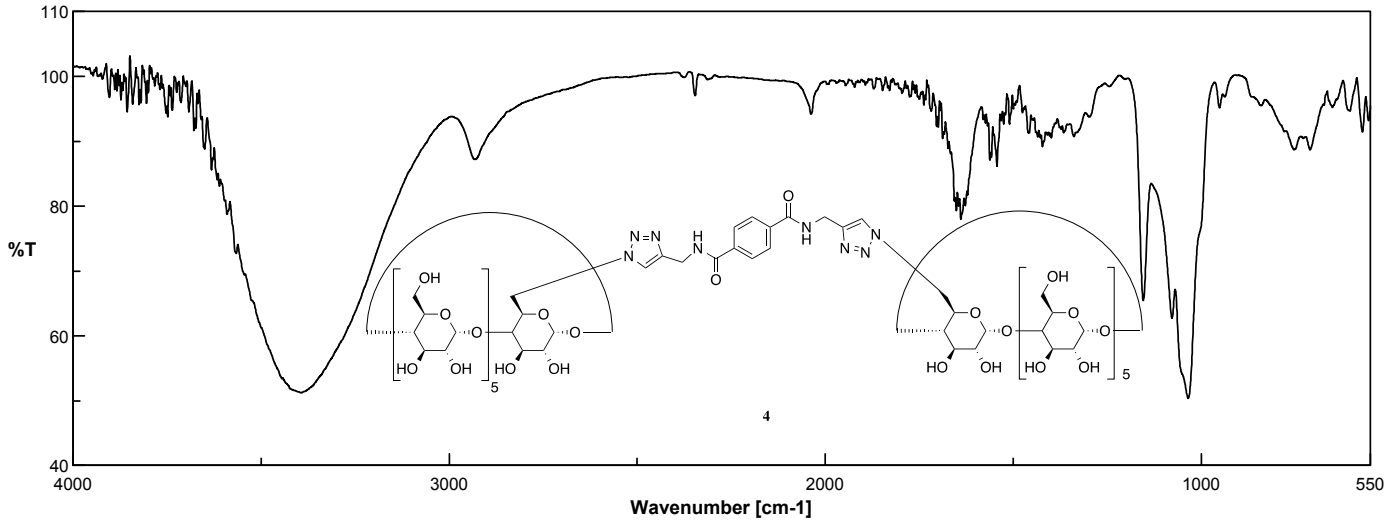




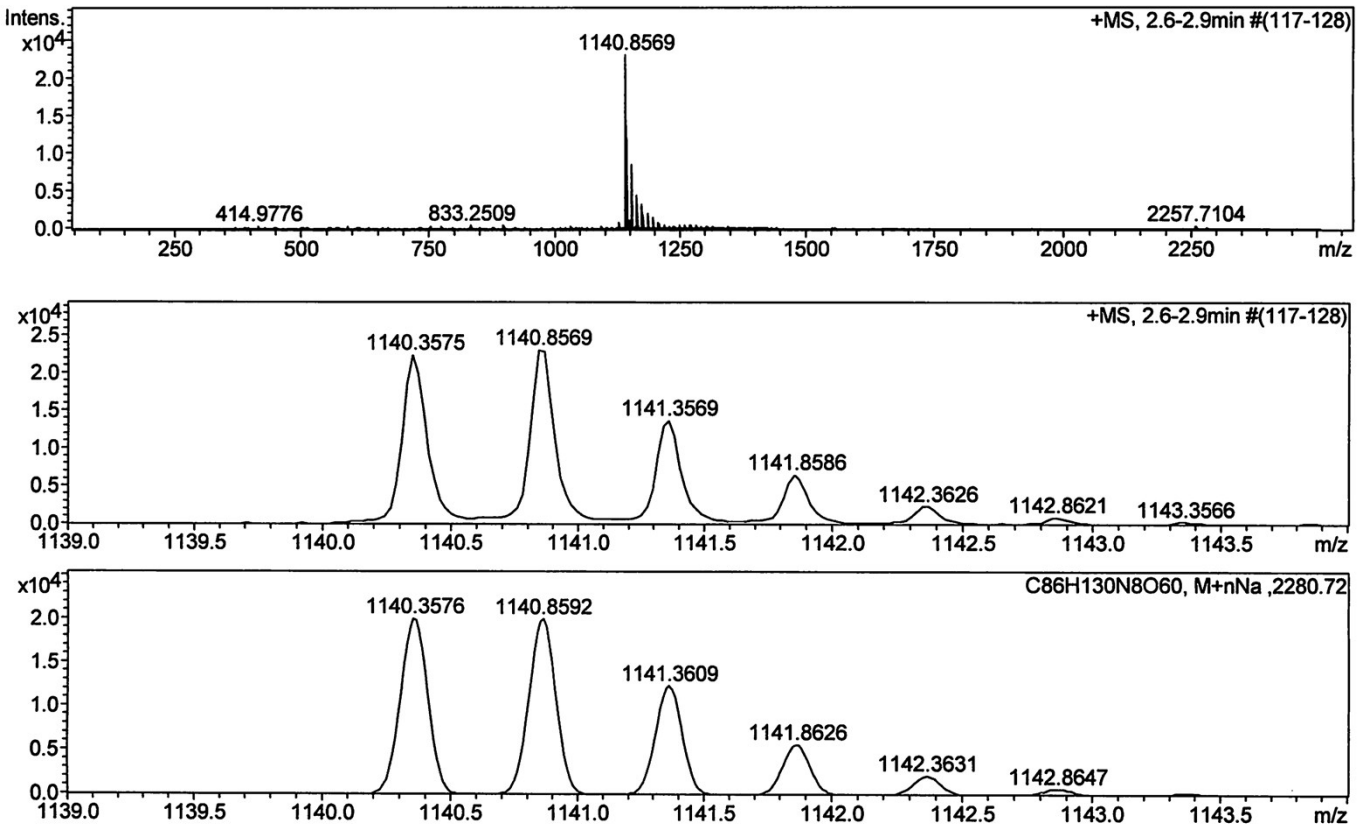
^{1}H NMR spectrum of **4** (300 MHz, D_2O, 298 K).



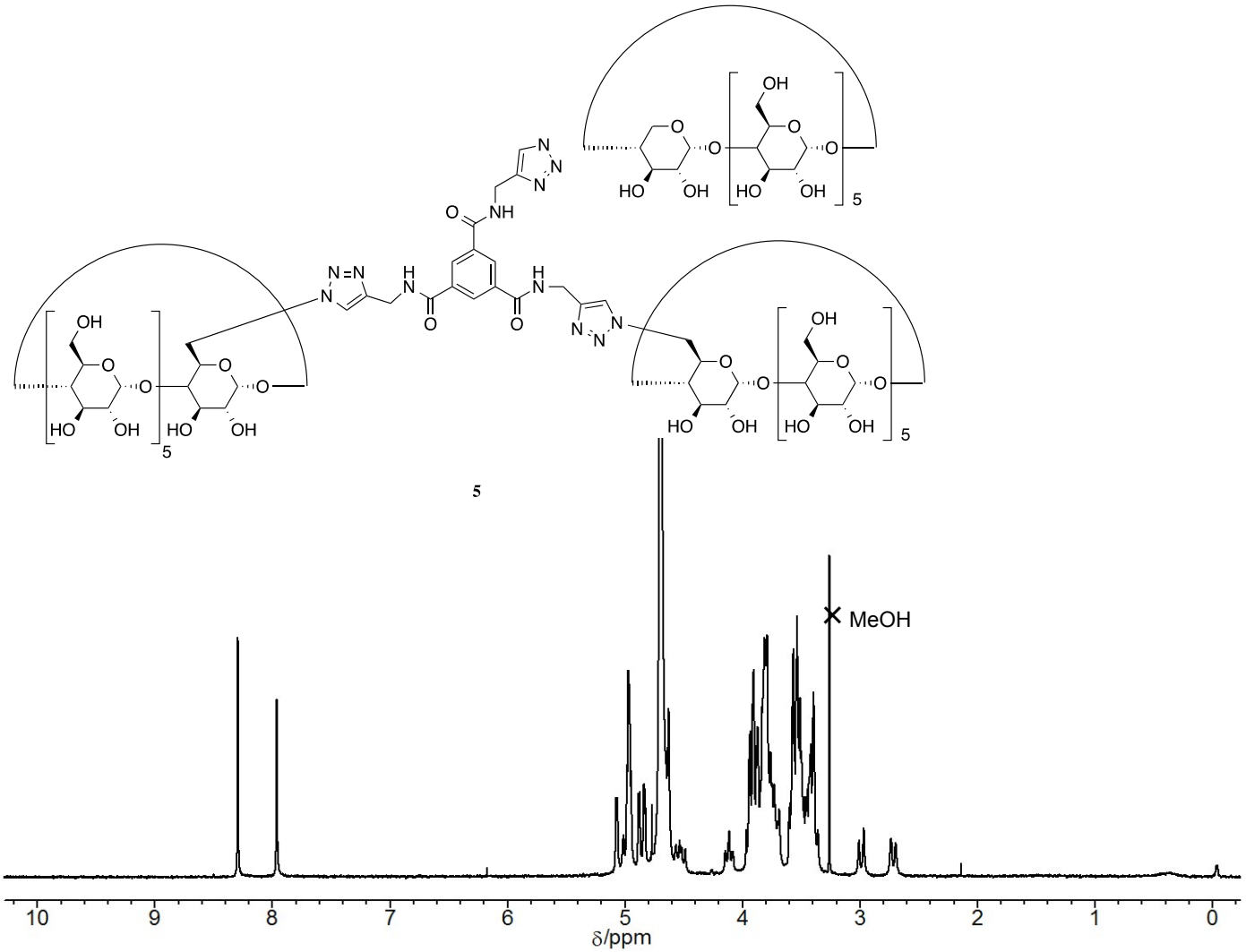
^{13}C NMR spectrum of **4** (100 MHz, D_2O, 298 K).



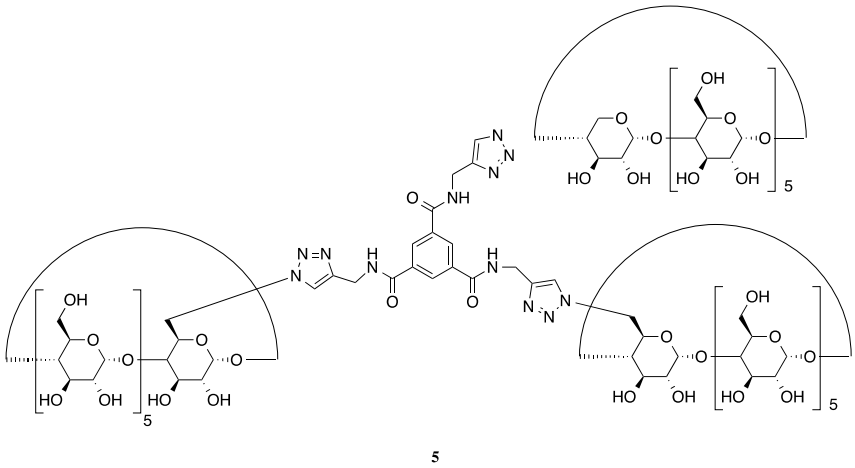
IR spectrum of **4** (KBr).



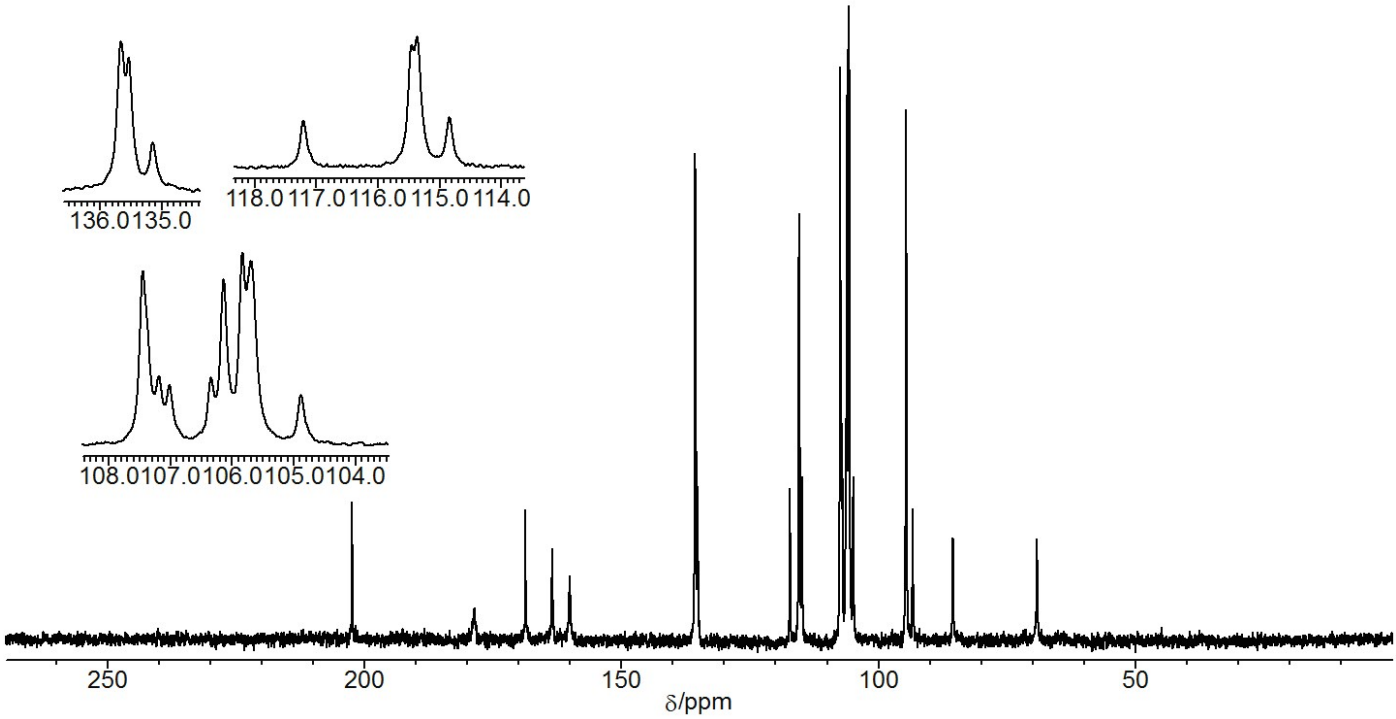
ESI–TOF MS spectra of **4** (upper: obtained spectrum (extended), middle: obtained (enlarged), and lower: expected (enlarged))



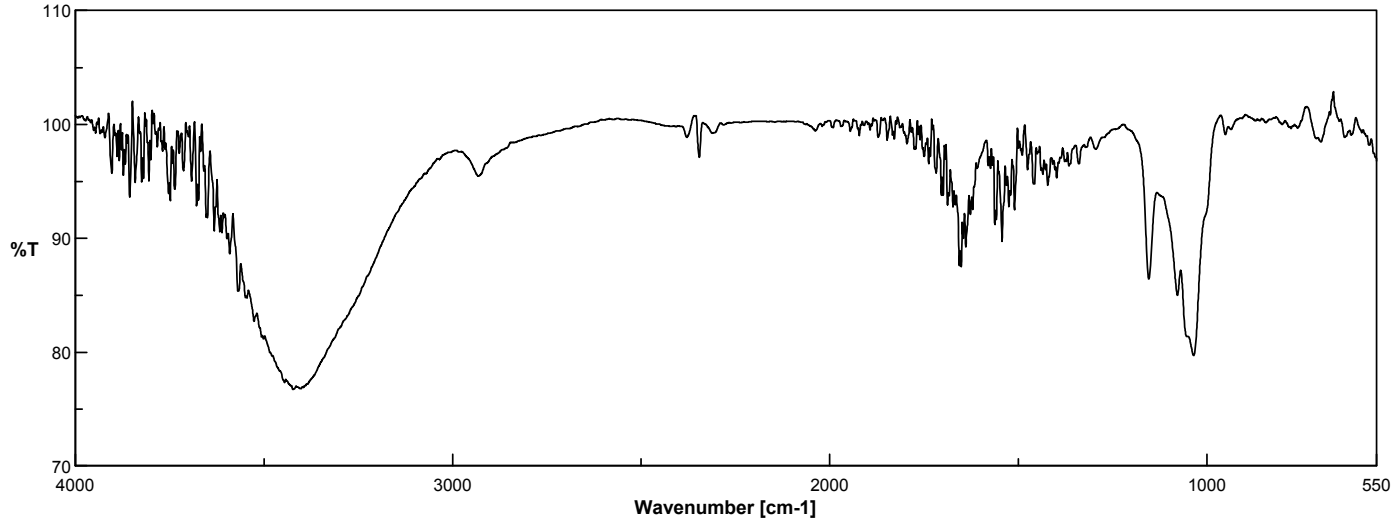
^{1}H NMR spectrum of **5** (300 MHz, D_2O, 298 K).



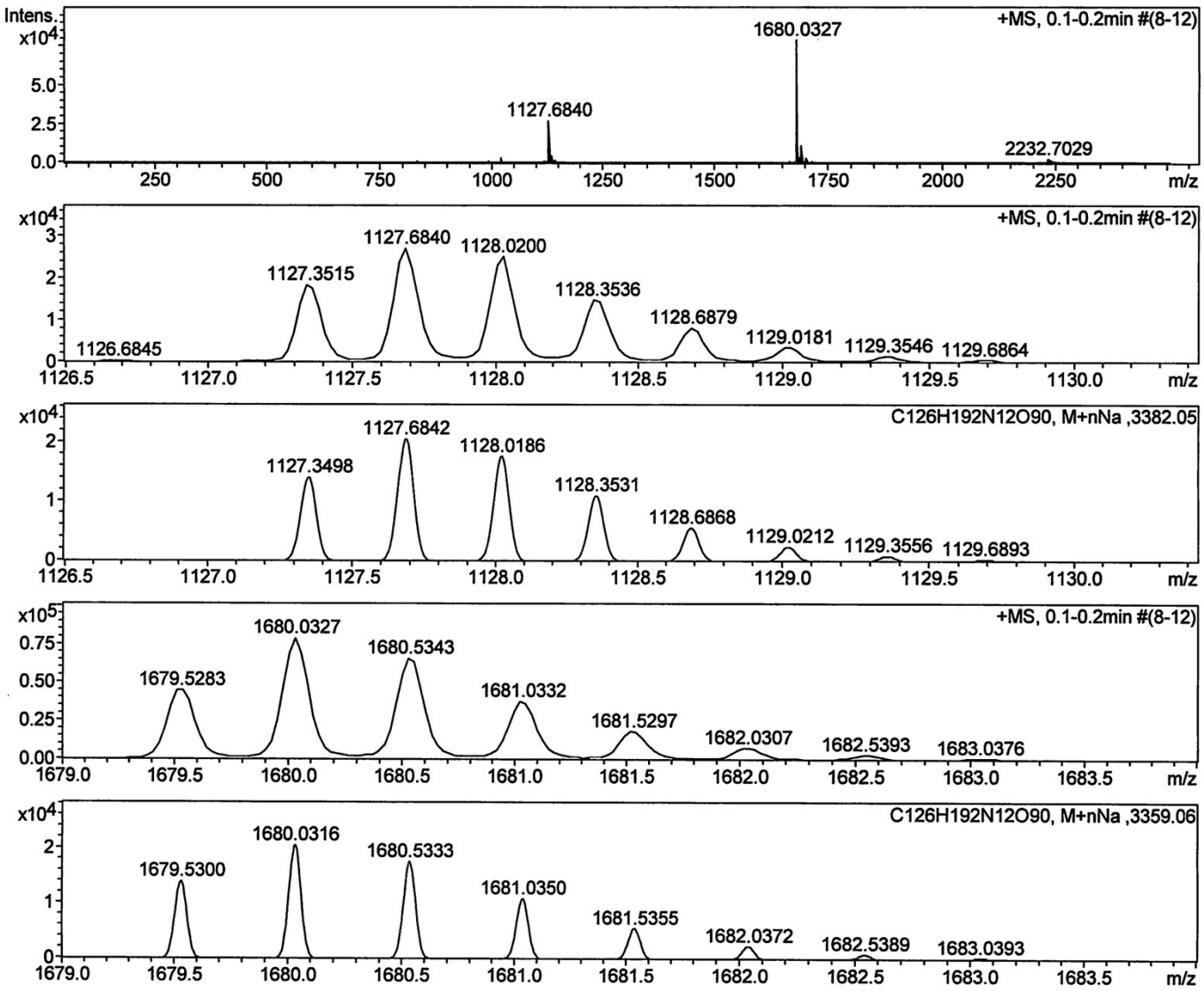
5



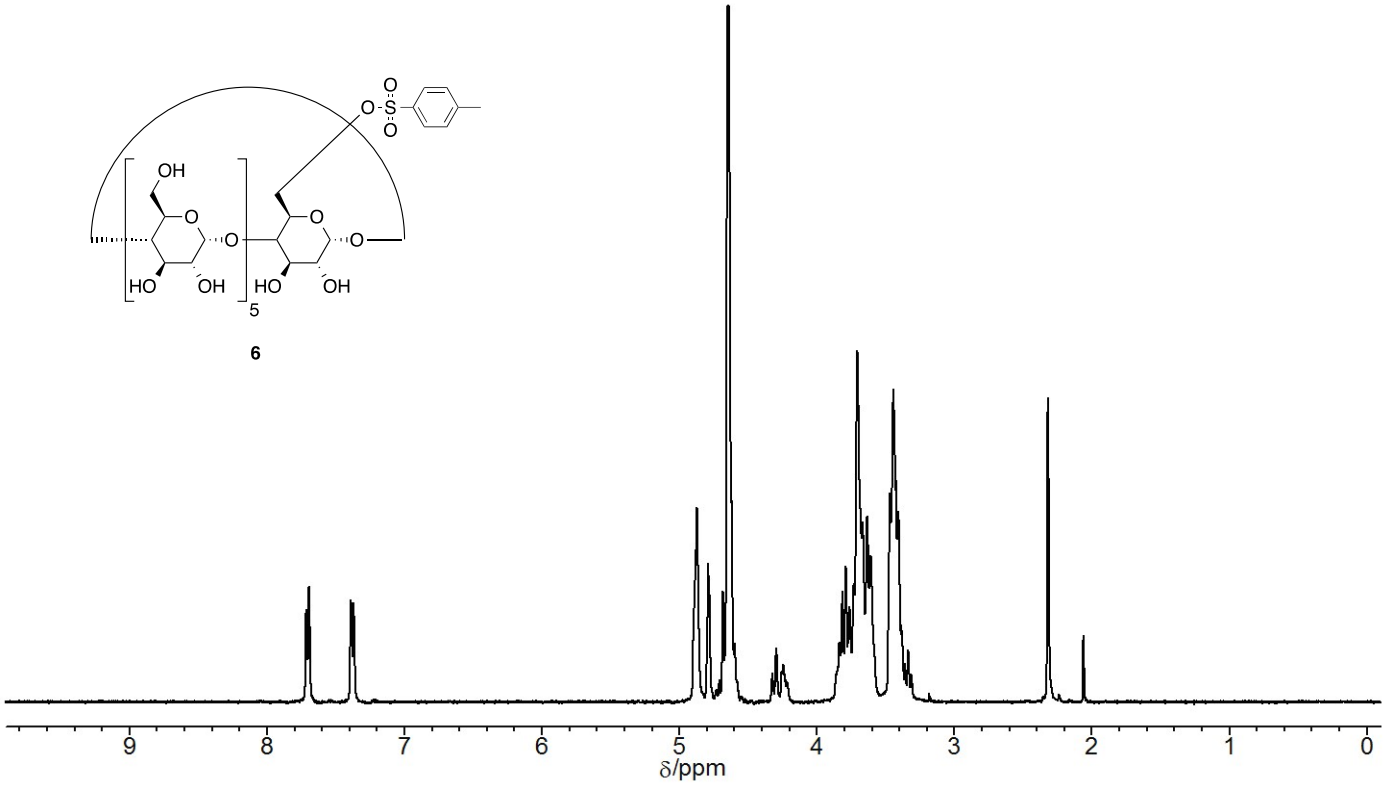
^{13}C NMR spectrum of **5** (100 MHz, D_2O, 298 K).



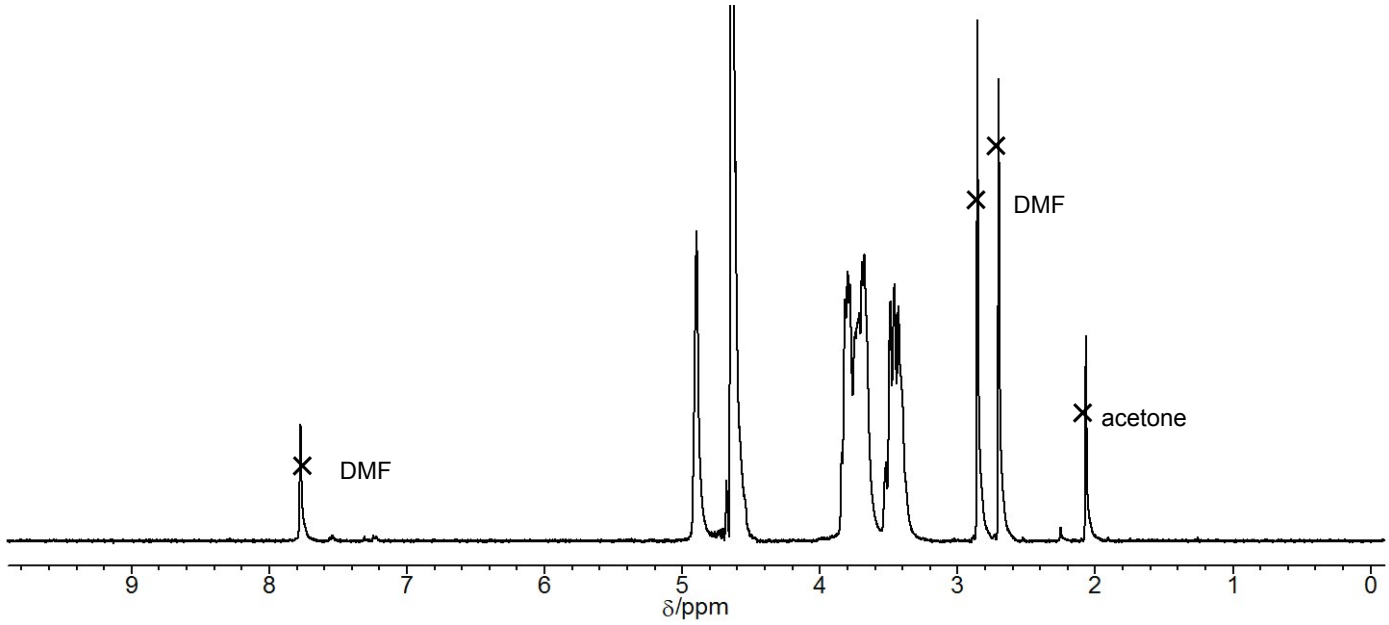
IR spectrum of **5** (KBr).



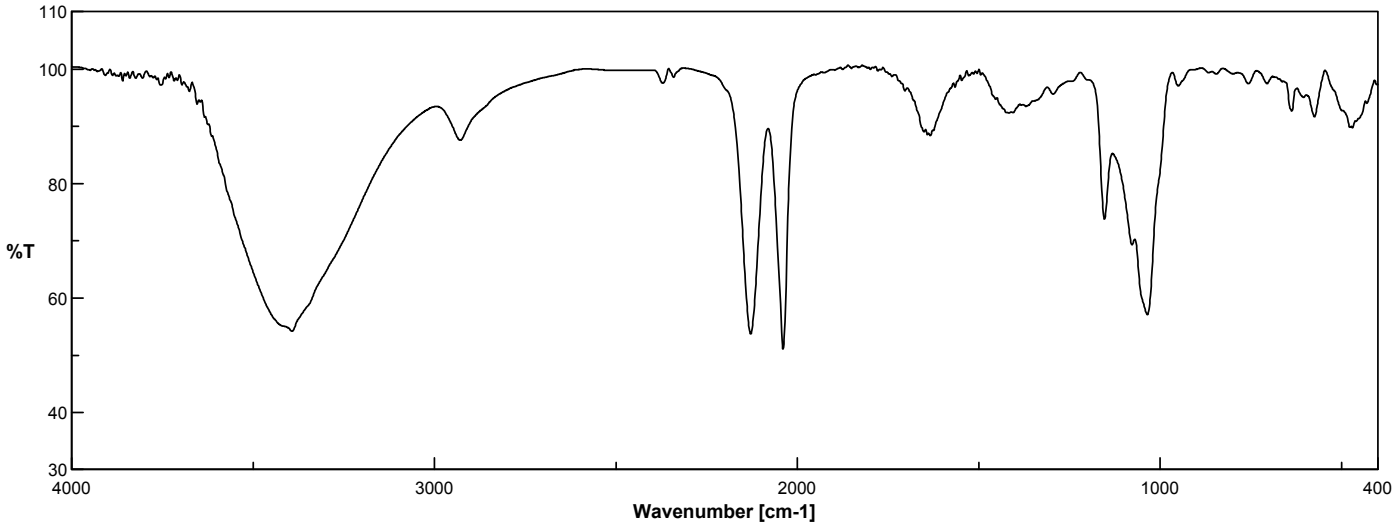
ESI–TOF MS spectrum of **5** (top: obtained spectrum (extended), second row from the top: obtained spectrum (enlarged from 1127 to 1130), middle: expected (enlarged from 1127 to 1130), second row from the bottom: obtained spectrum (enlarged from 1679 to 1684), bottom: expected (enlarged from 1679 to 1684)).



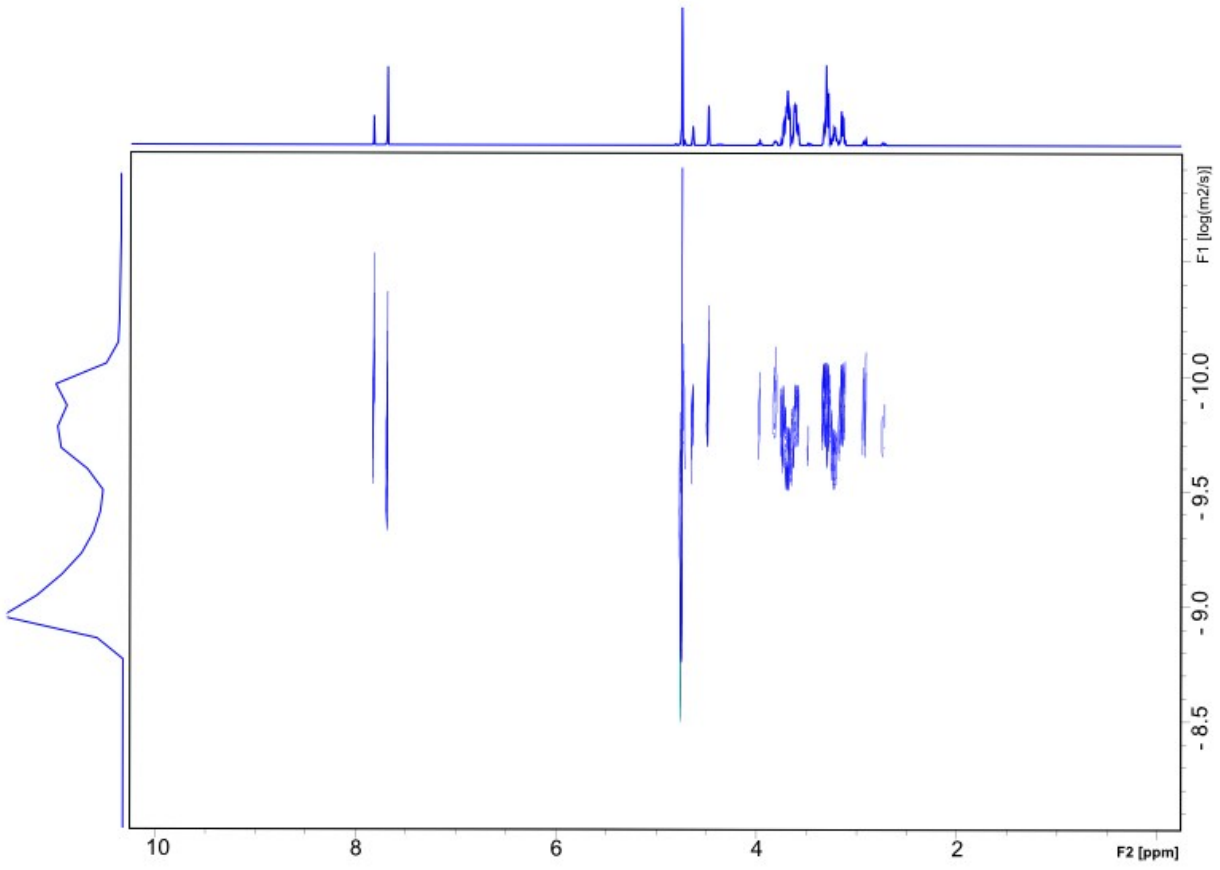
^{1}H NMR spectrum of **6** (400MHz, D_2O, 298 K).



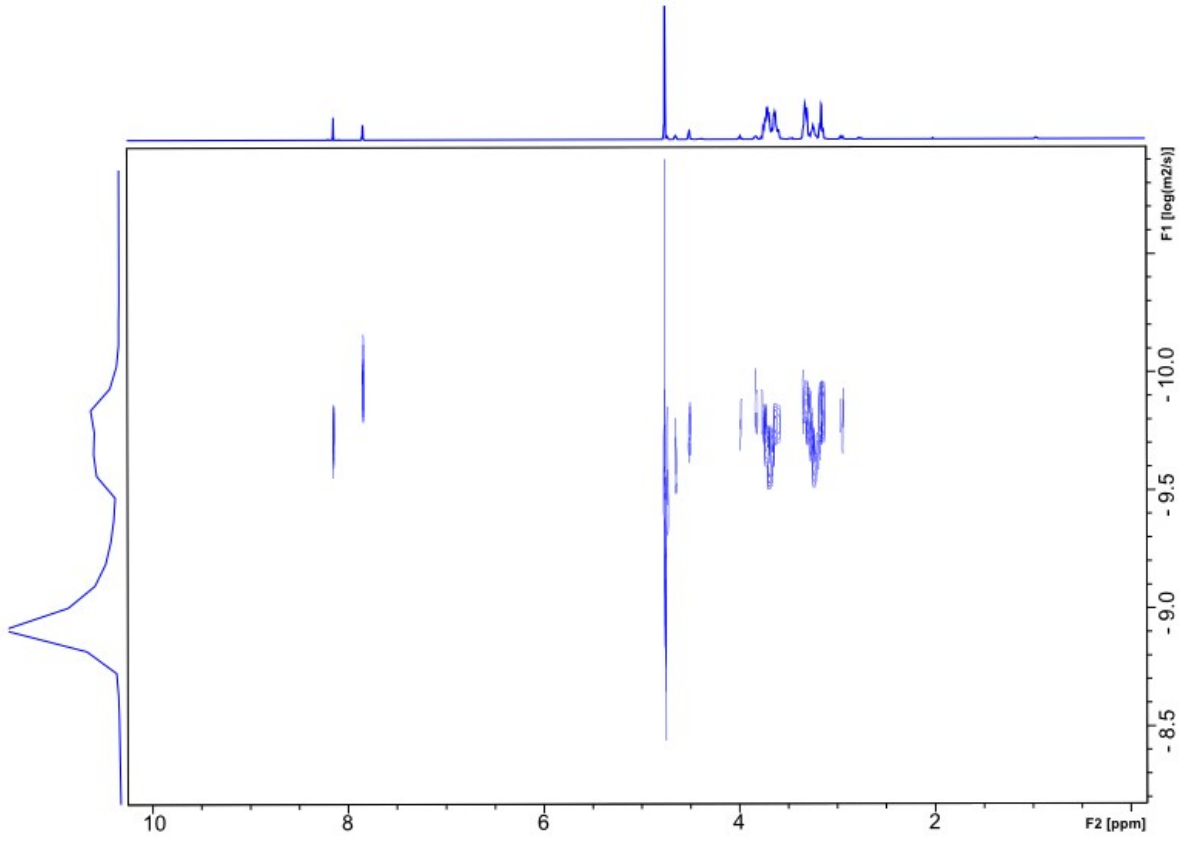
^{1}H NMR spectrum of **7** (400MHz, D_2O, 298 K).



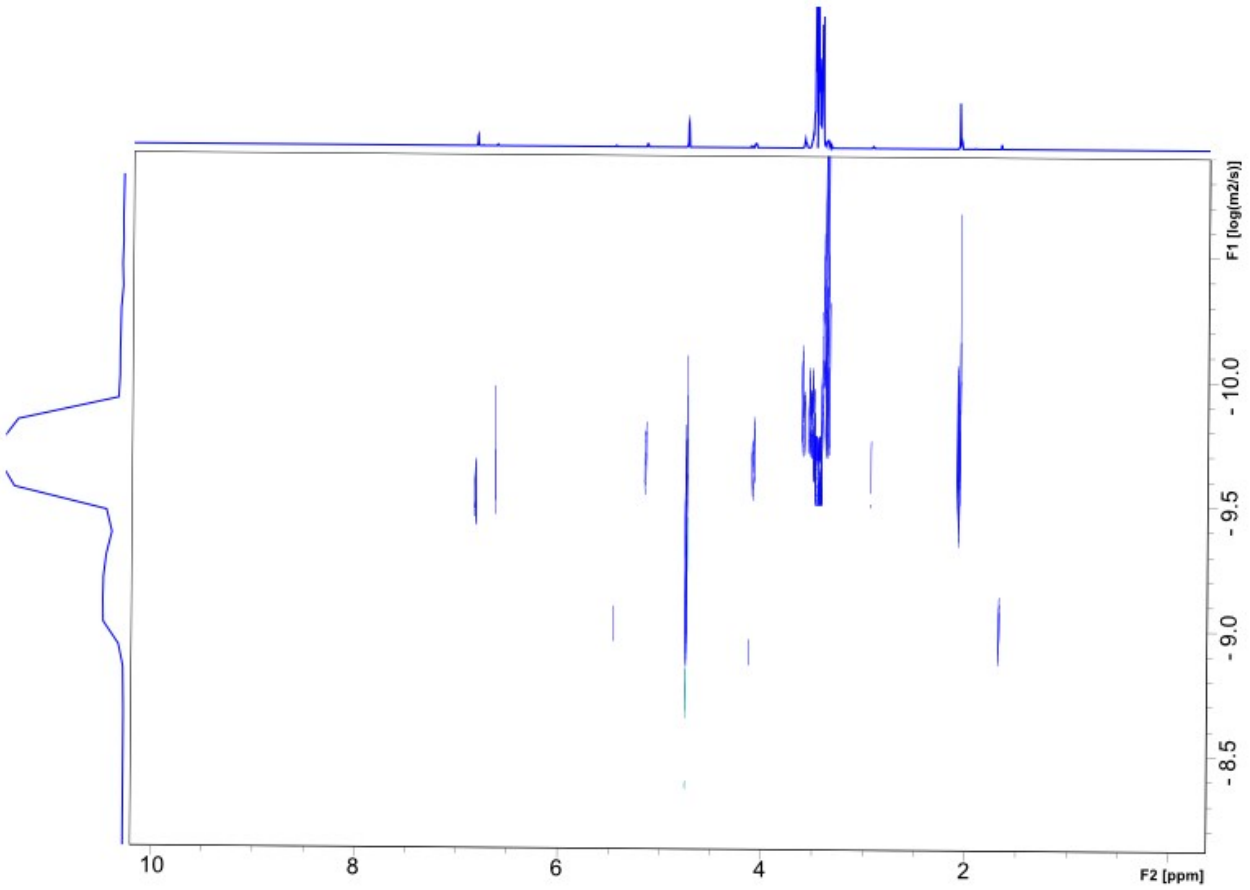
IR spectrum of **7** (KBr).



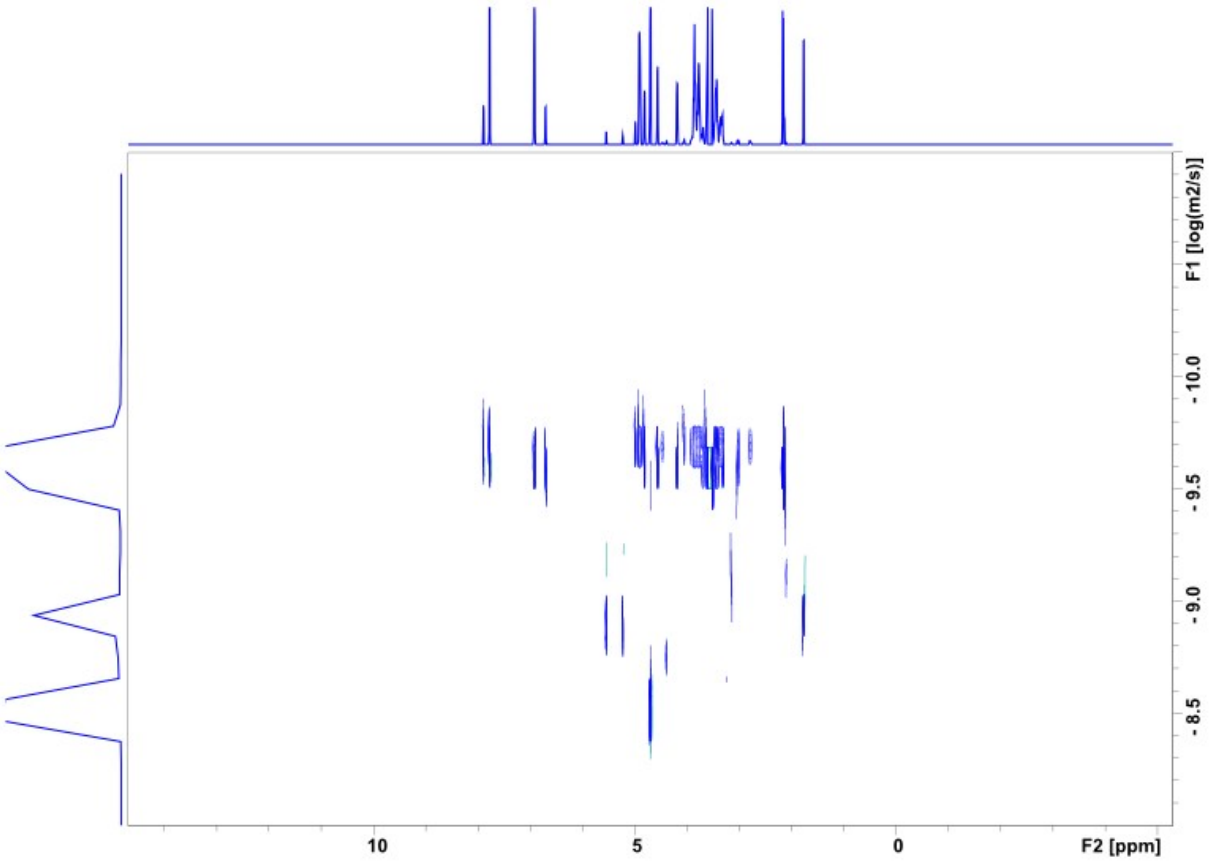
DOSY NMR spectrum of **4** (500 MHz, 0.1 M NaOD, 298 K).



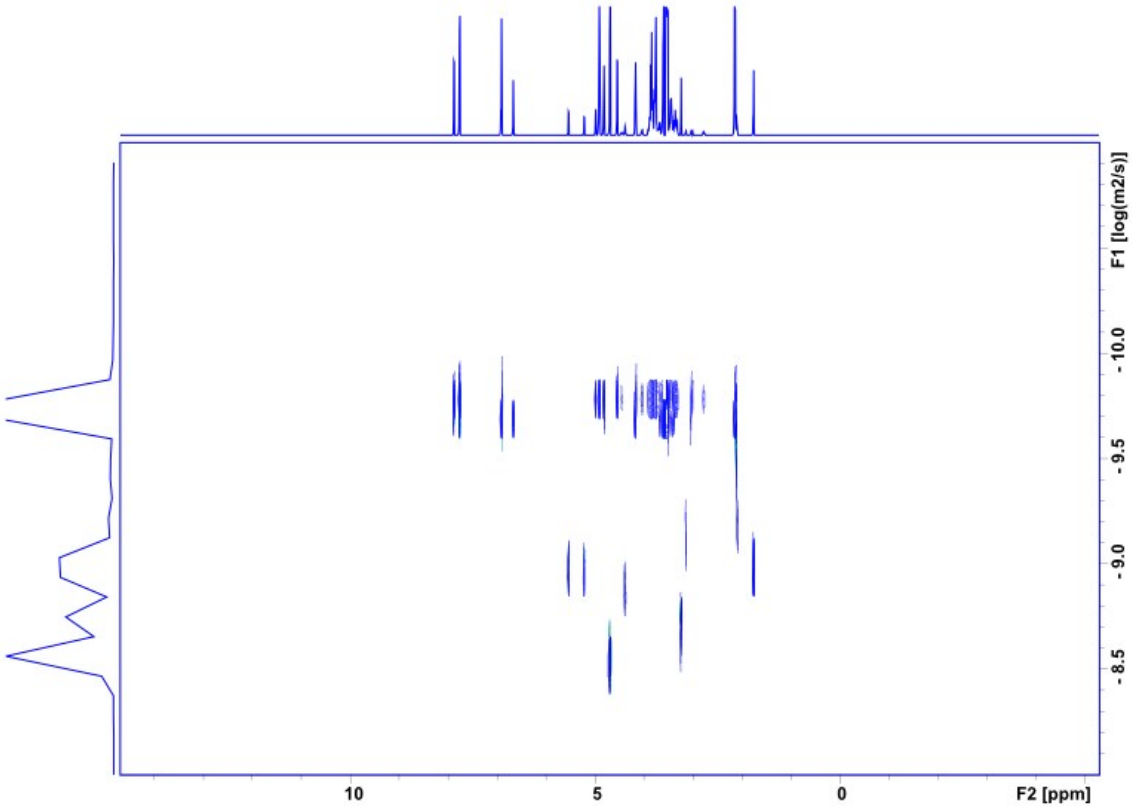
DOSY NMR spectrum of **5** (500 MHz, 0.1 M NaOD, 298 K).



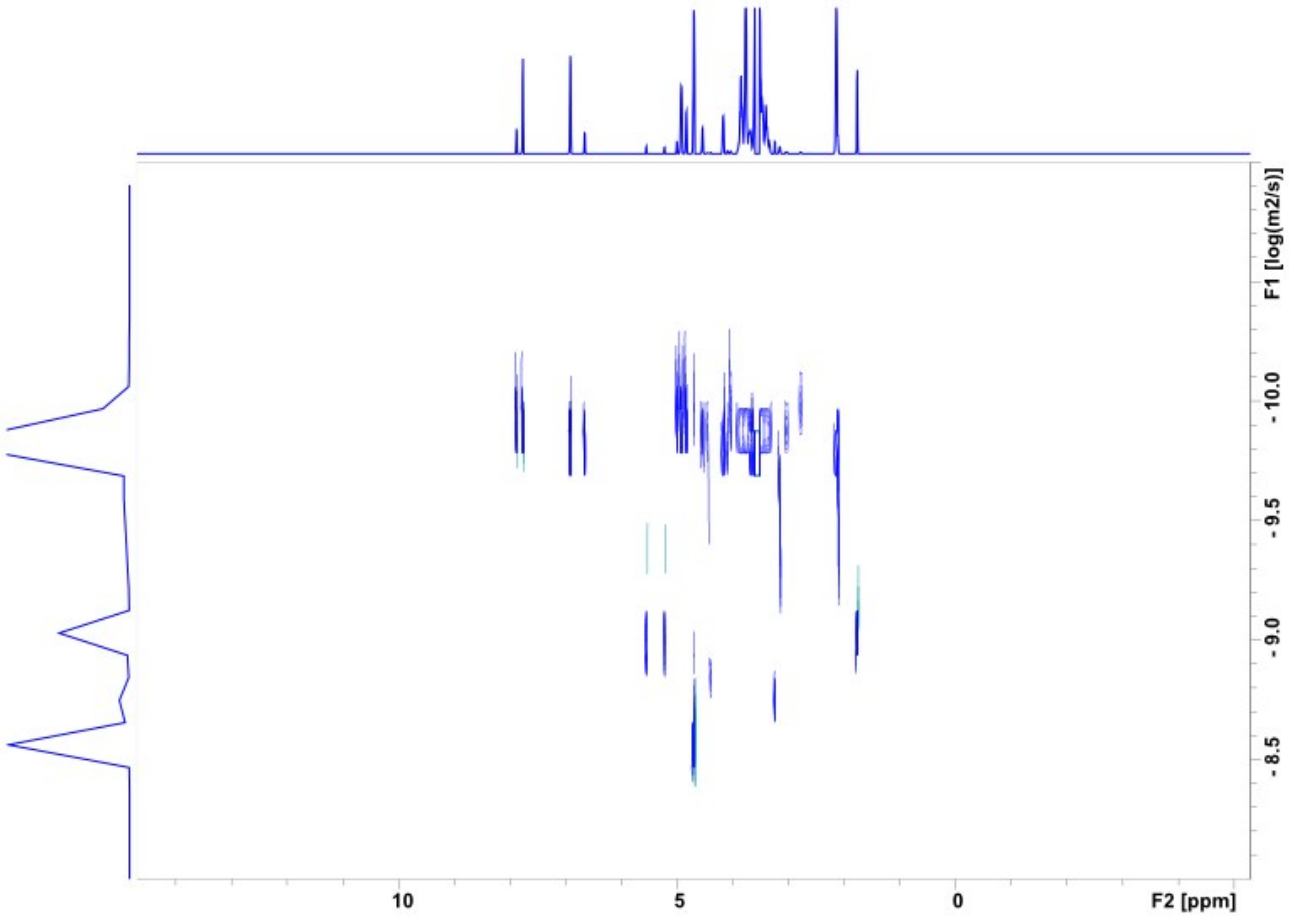
DOSY NMR spectrum of **TBM** (500 MHz, 0.1 M NaOD, 298 K).



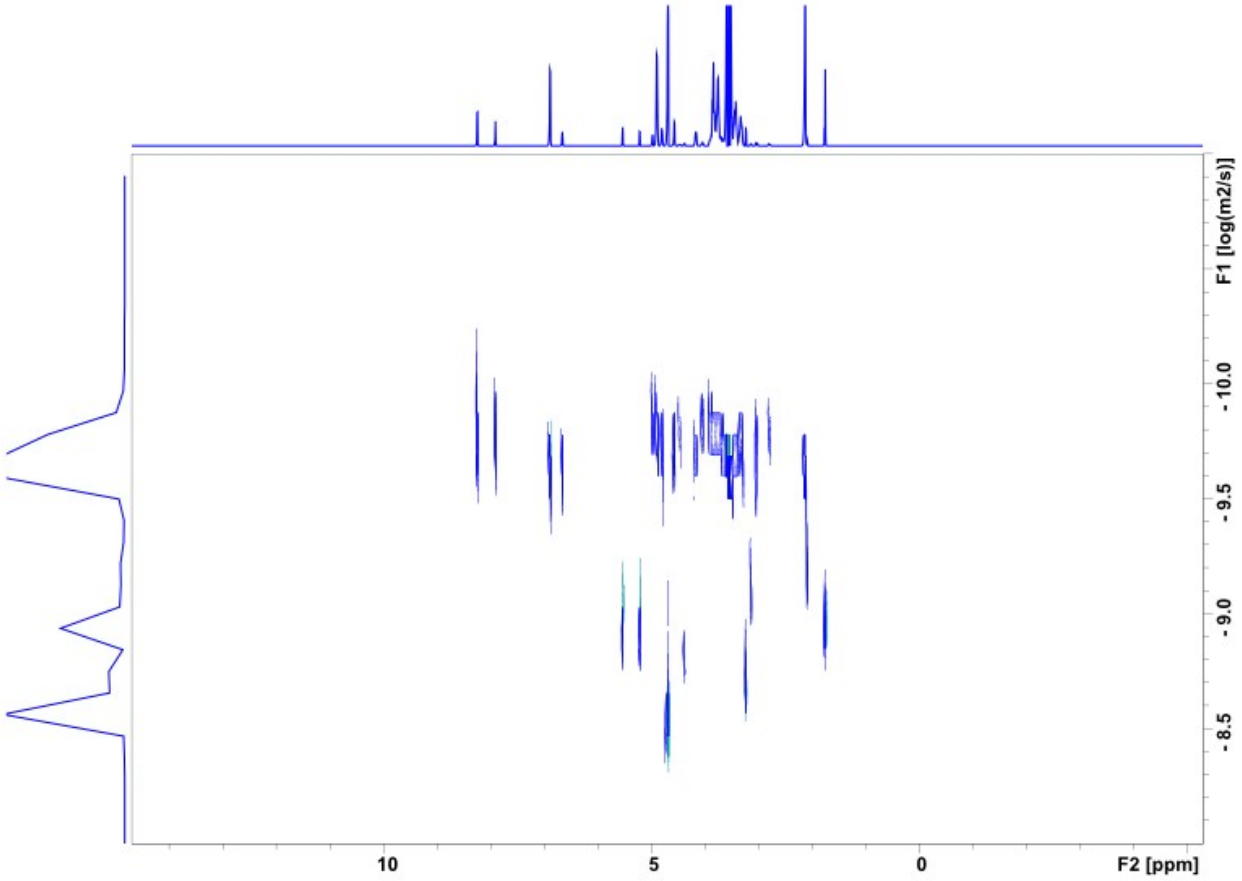
DOSY NMR spectrum of **VSCα²-1** (500 MHz, 0.1 M NaOD, 298 K).



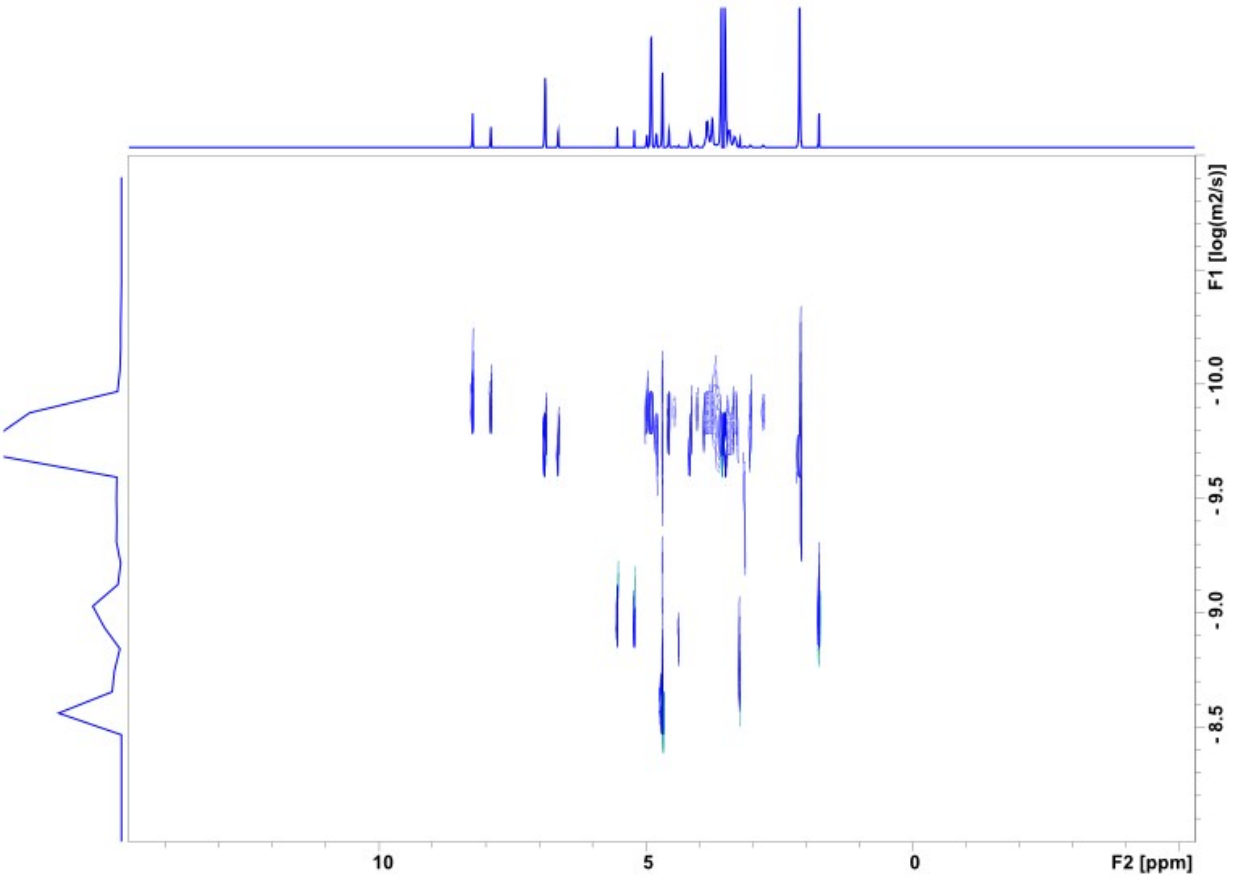
DOSY NMR spectrum of **VSCα²-2** (500 MHz, 0.1 M NaOD, 298 K).



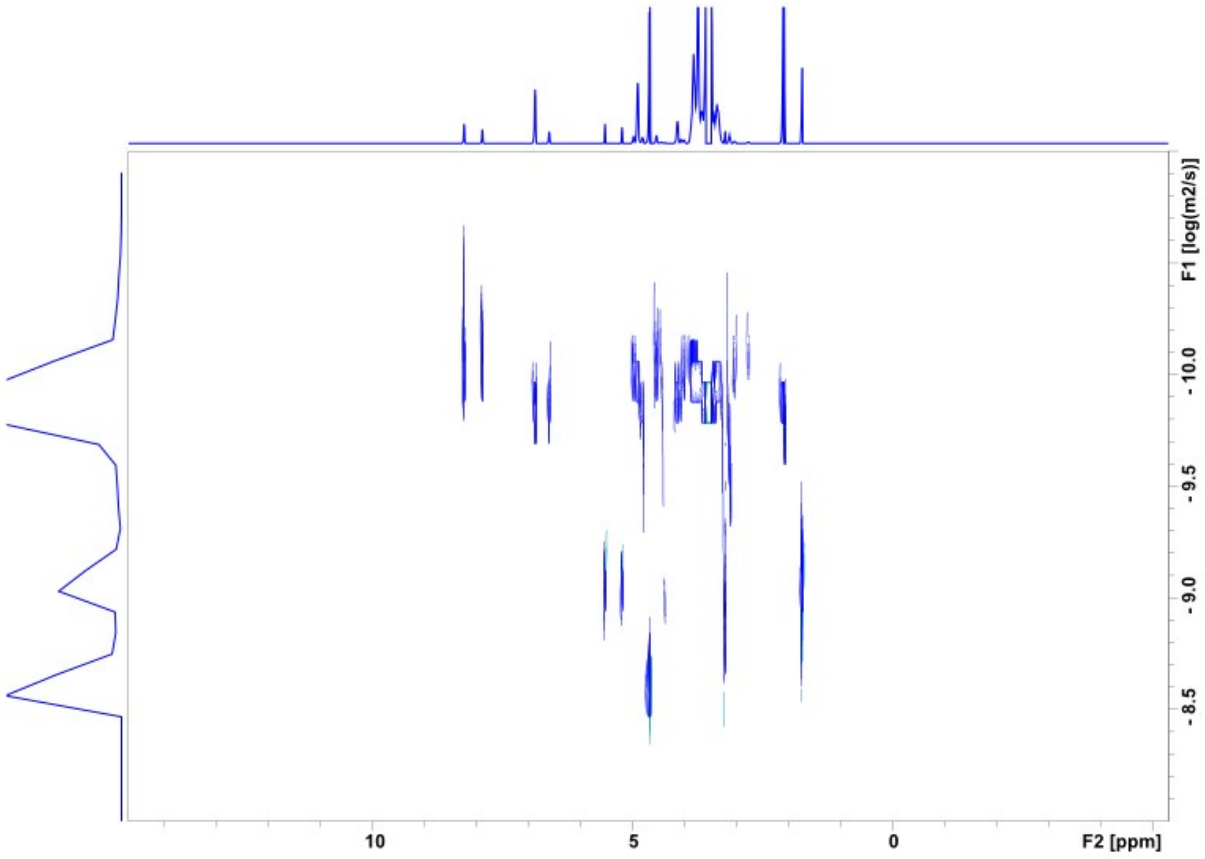
DOSY NMR spectrum of **VSCα²-3** (500 MHz, 0.1 M NaOD, 298 K).



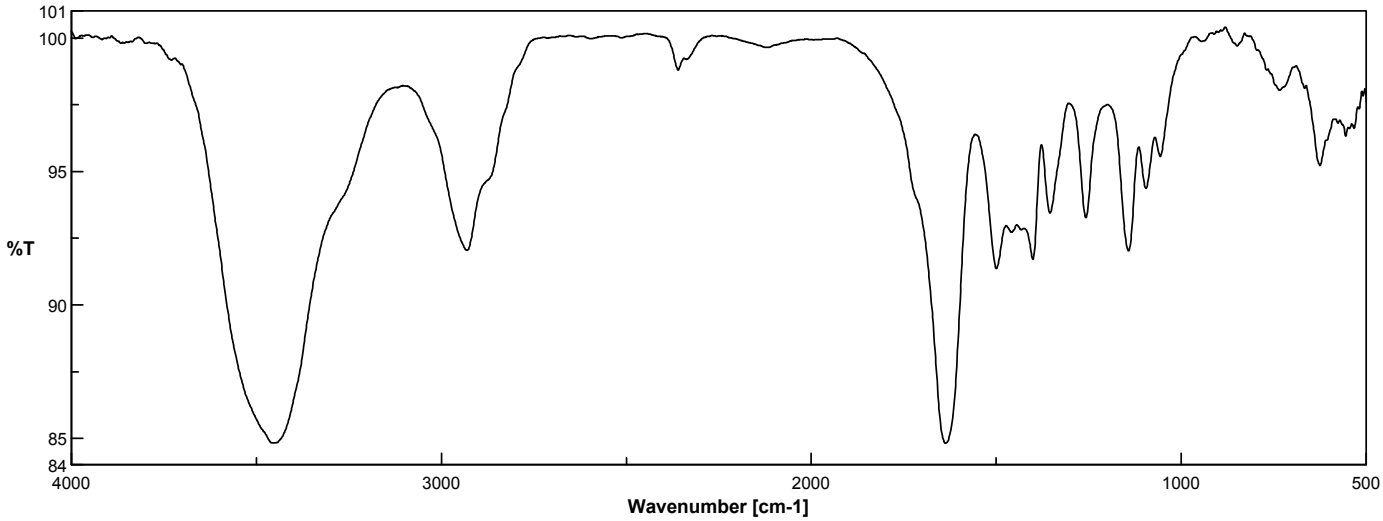
DOSY NMR spectrum of **VSCα³-1** (500 MHz, 0.1 M NaOD, 298 K).



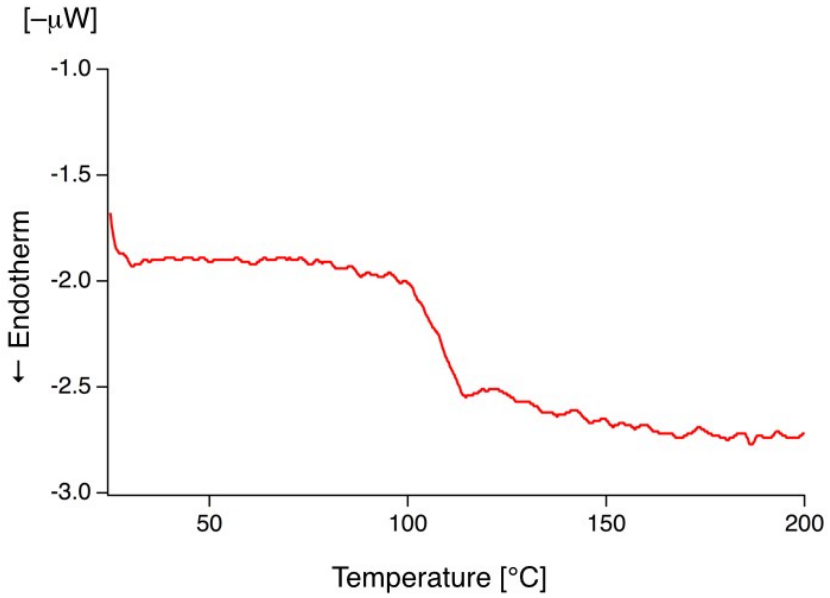
DOSY NMR spectrum of **VSCα³-2** (500 MHz, 0.1 M NaOD, 298 K).



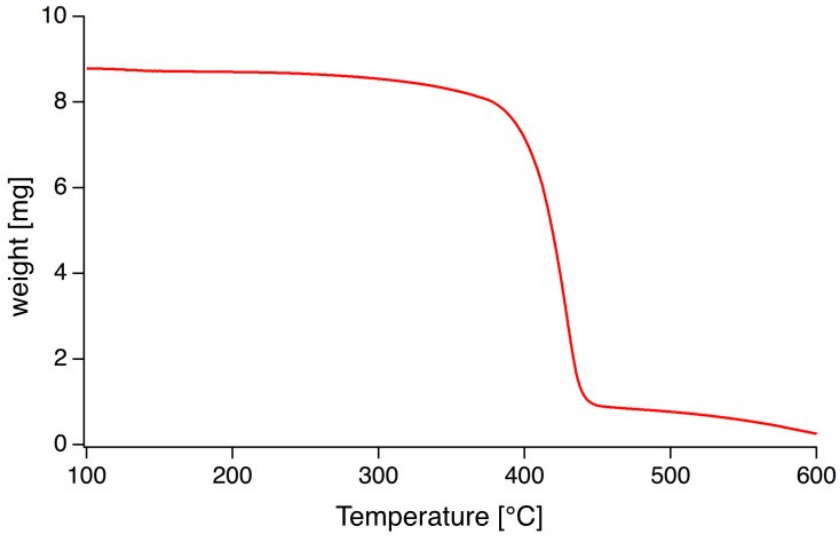
DOSY NMR spectrum of **VSCα³-3** (500 MHz, 0.1 M NaOD, 298 K).



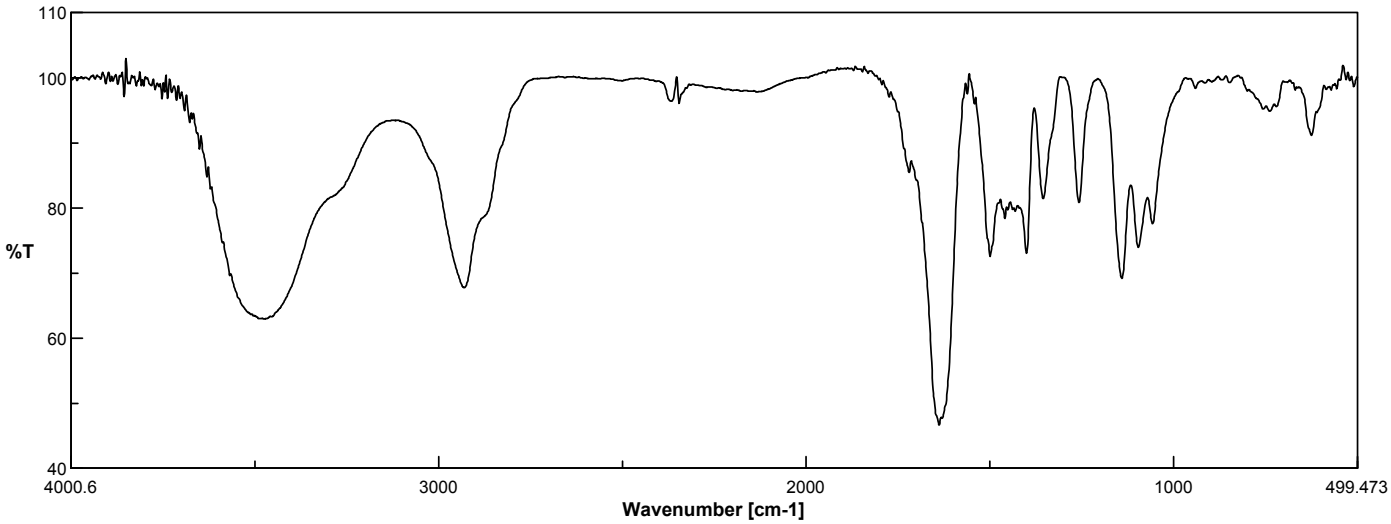
IR spectrum of **RCPα²-1** (KBr).



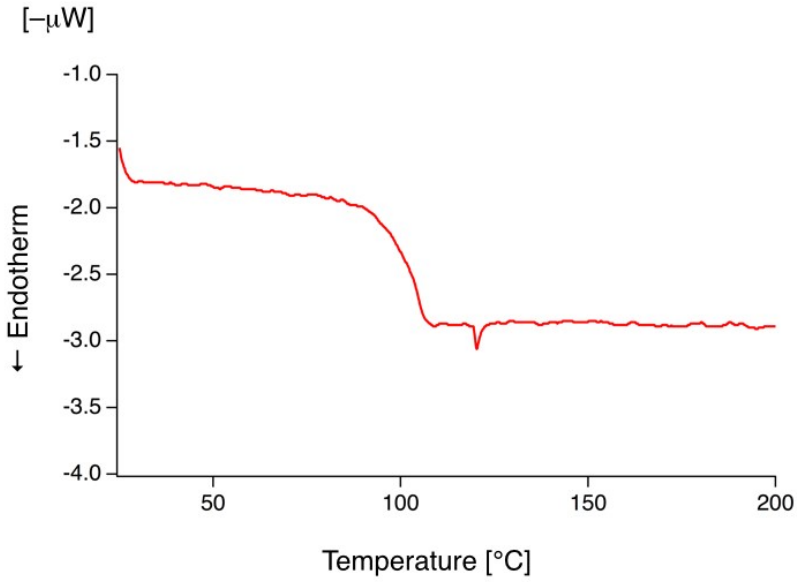
DSC thermogram of **RCPα²-1** (2nd heating, heating rate: 10 °C / min).



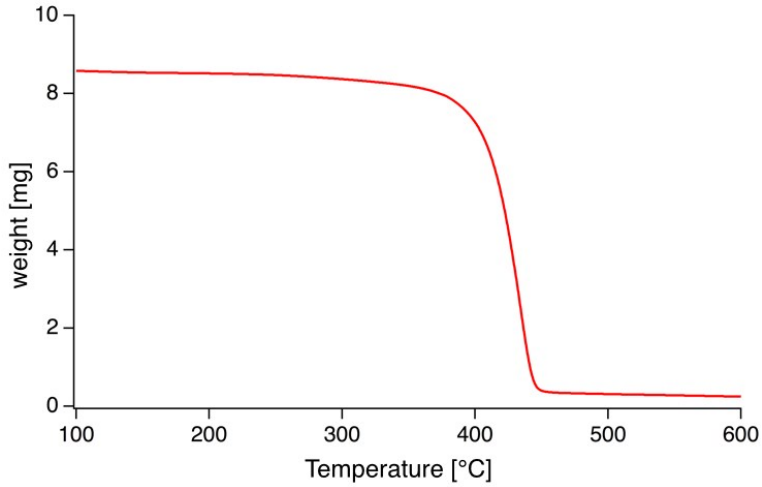
TGA result of **RCPα²-1** (heating rate: 10 °C / min).



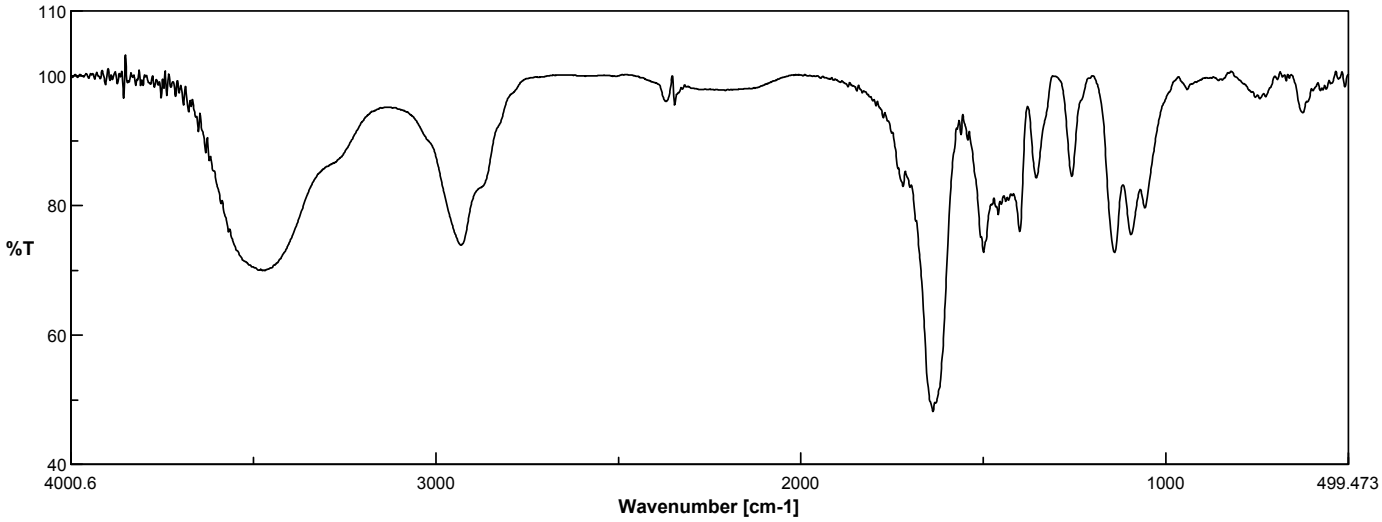
IR spectrum of **RCPα²-2** (KBr).



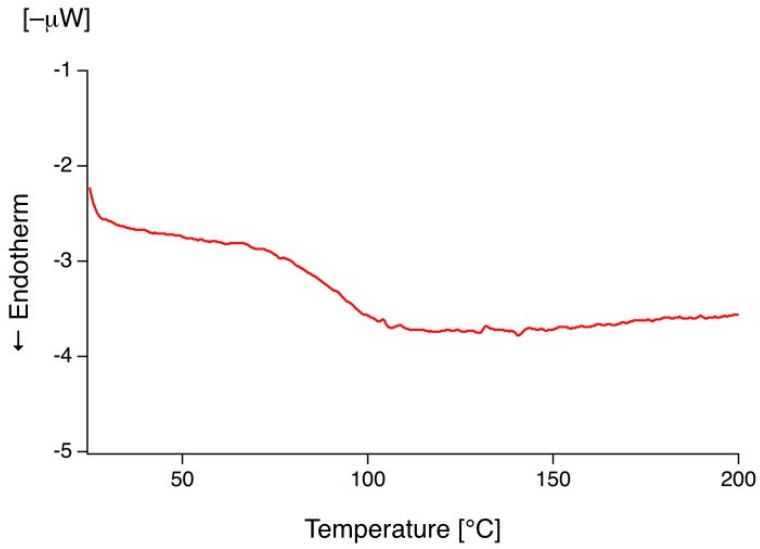
DSC thermogram of **RCPα²-2** (2nd heating, heating rate: 10 °C / min).



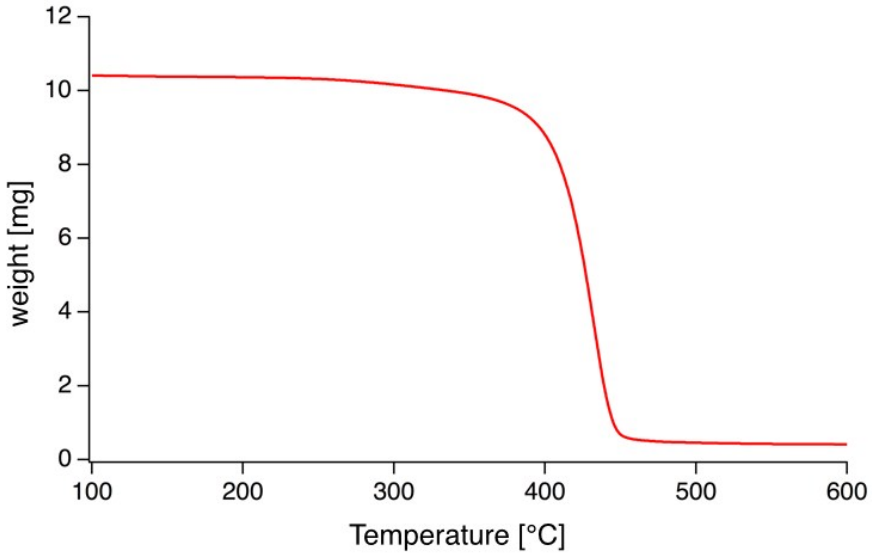
TGA result of **RCPα²-2** (heating rate: 10 °C / min).



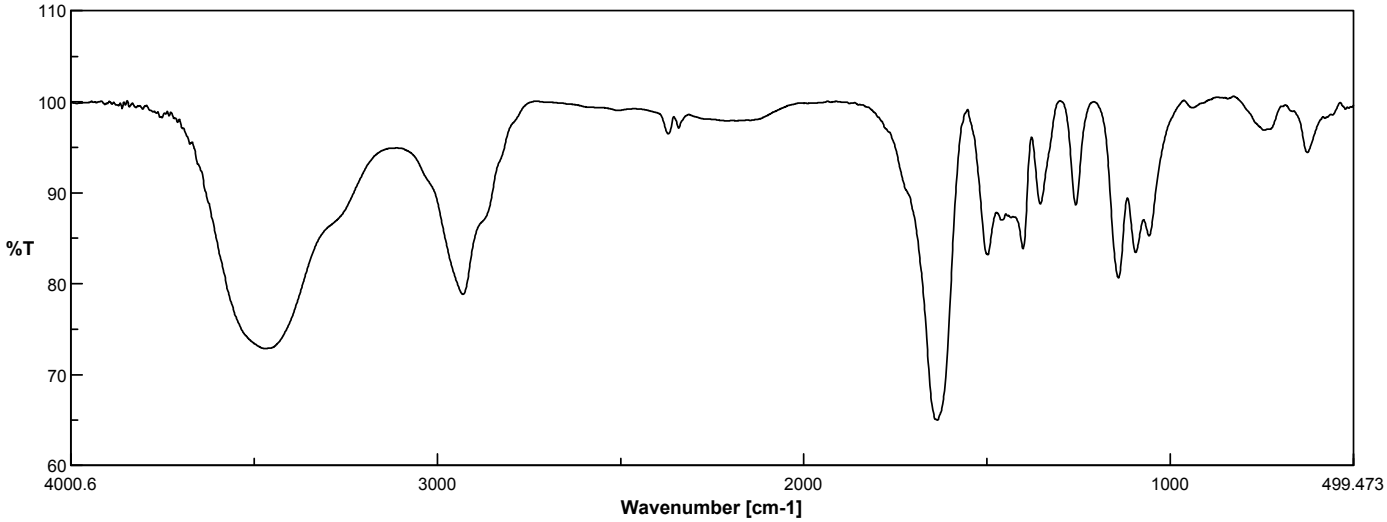
IR spectrum of **RCPα²-3** (KBr).



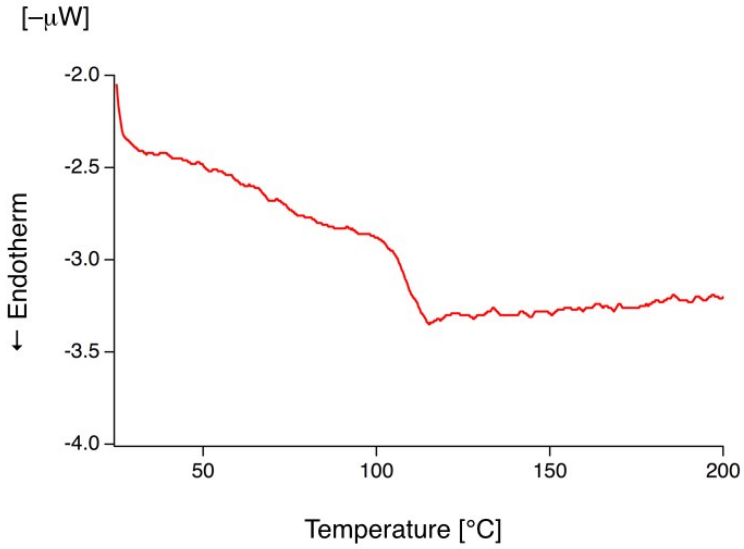
DSC thermogram of **RCPα²-3** (2nd heating, heating rate: 10 °C / min).



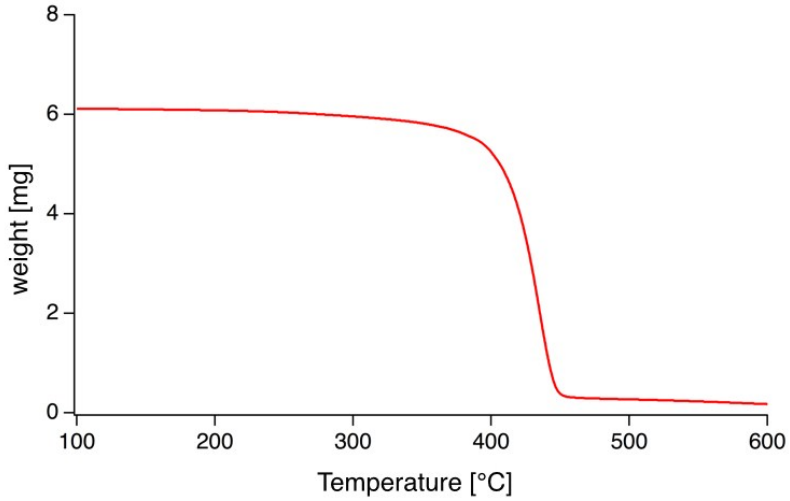
TGA result of **RCPα²-3** (heating rate: 10 °C / min).



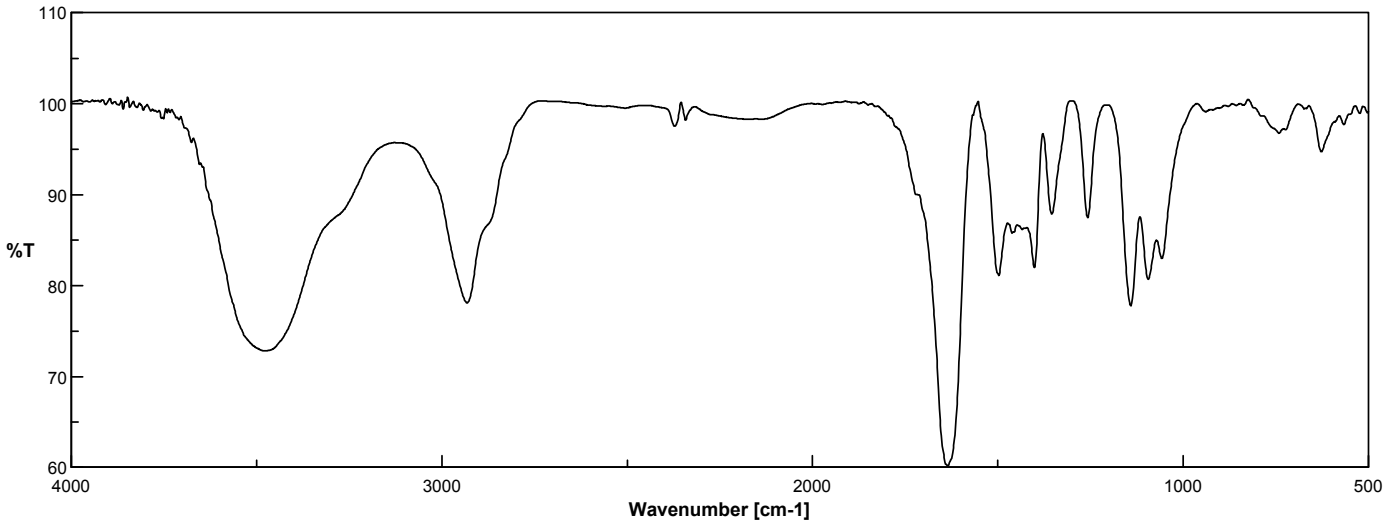
IR spectrum of **RCPα³-1** (KBr).



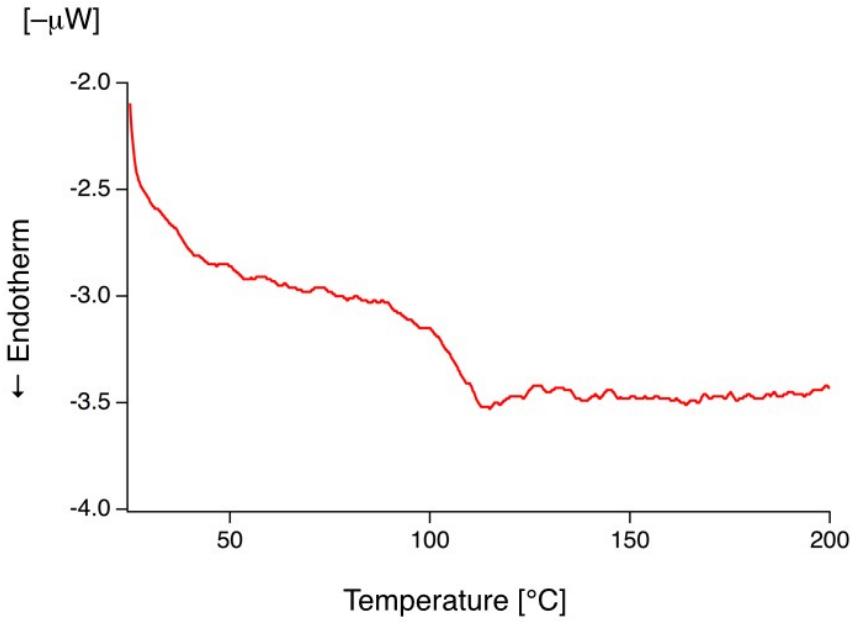
DSC thermogram of **RCPα³-1** (2nd heating, heating rate: 10 °C / min).



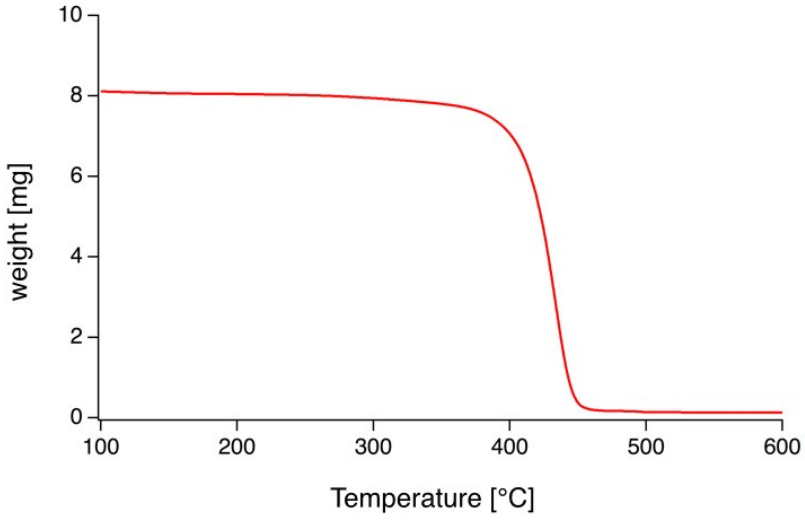
TGA result of **RCPα³-1** (heating rate: 10 °C / min).



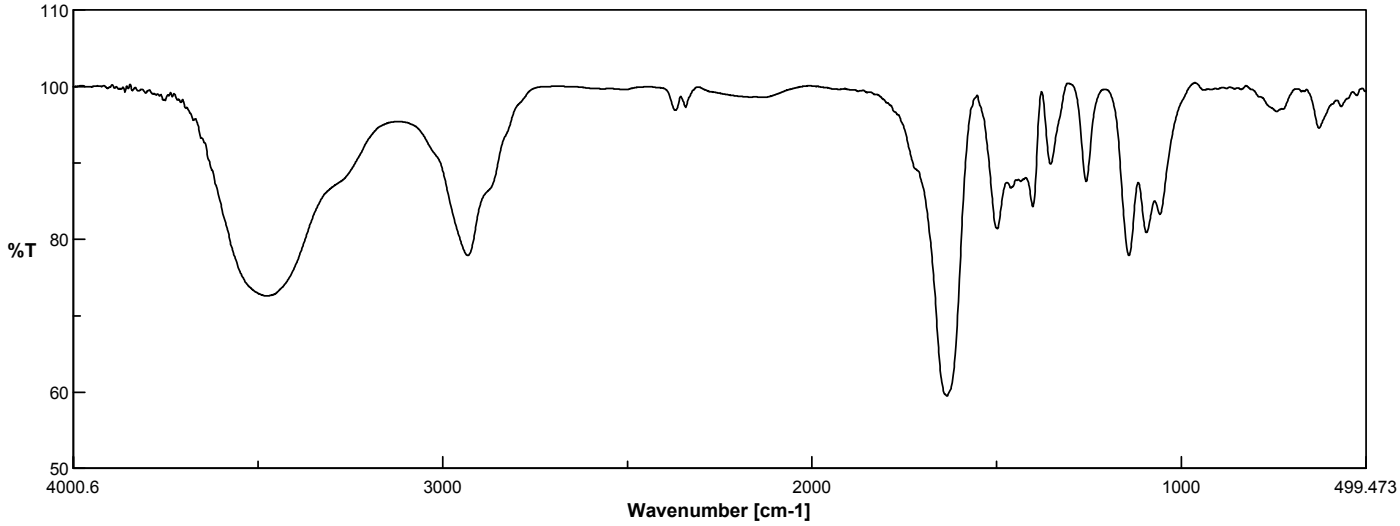
IR spectrum of **RCPα³-2** (KBr).



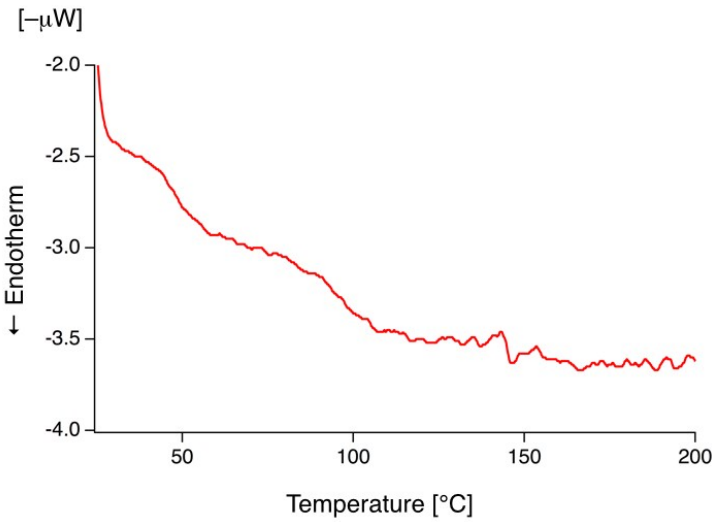
DSC thermogram of **RCPα³-2** (2nd heating, heating rate: 10 °C / min).



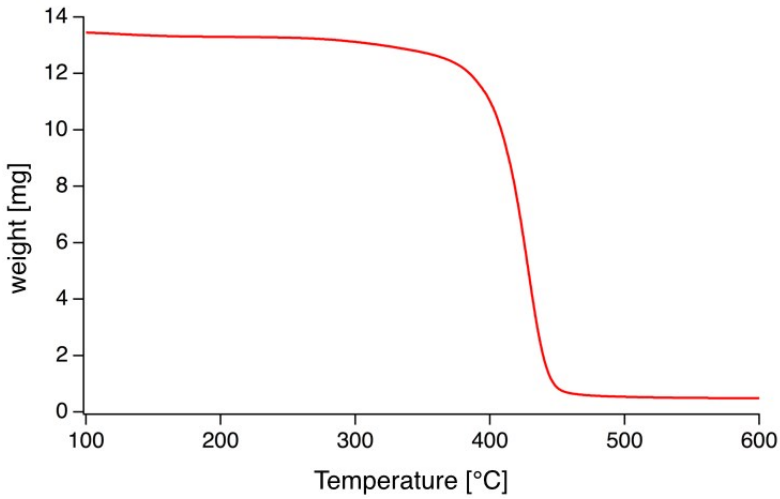
TGA result of **RCPα³-2** (heating rate: 10 °C / min).



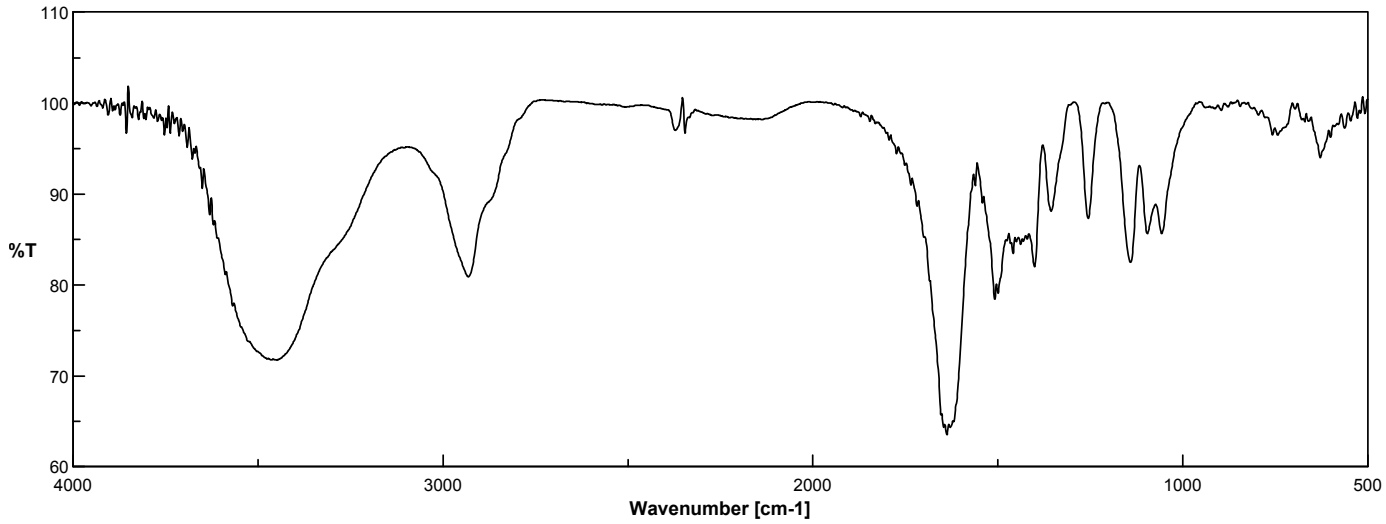
IR spectrum of **RCPα³-3** (KBr).



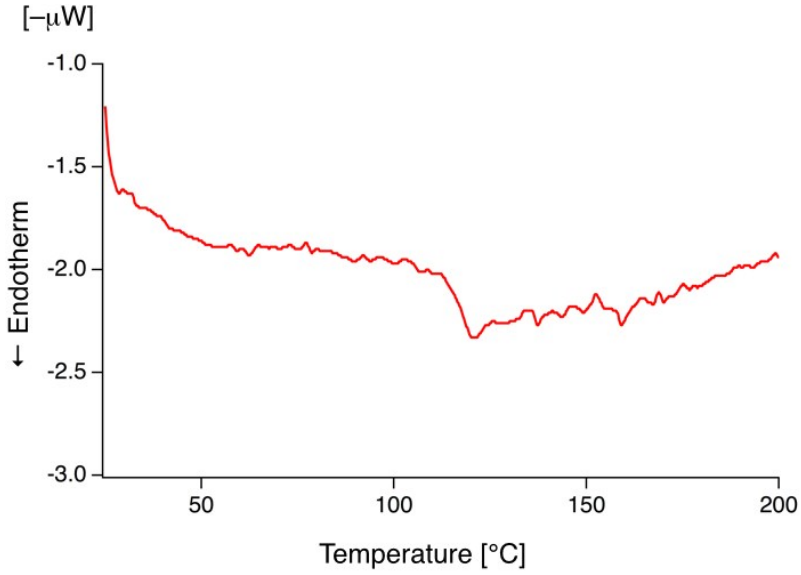
DSC thermogram of **RCPα³-3** (2nd heating, heating rate: 10 °C / min).



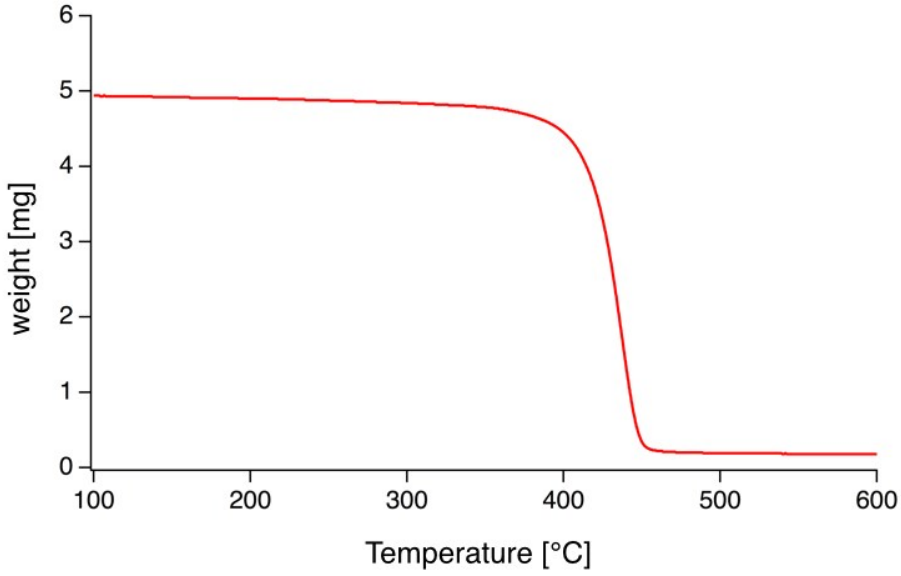
TGA result of **RCPα³-2** (heating rate: 10 °C / min).



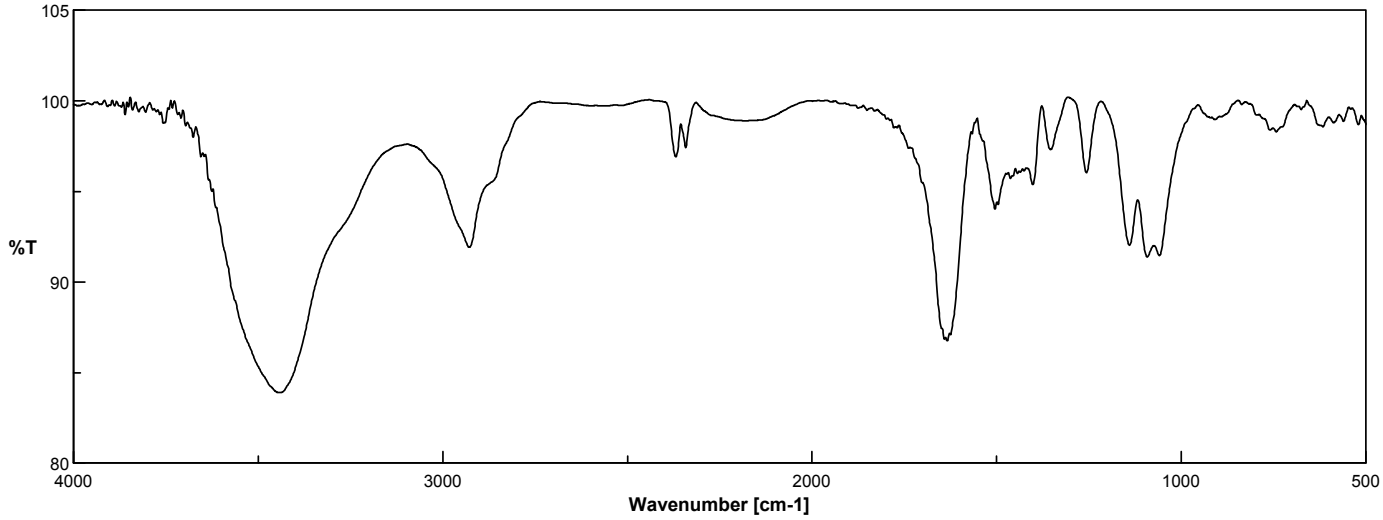
IR spectrum of **CCP_{BIS}-1** (KBr).



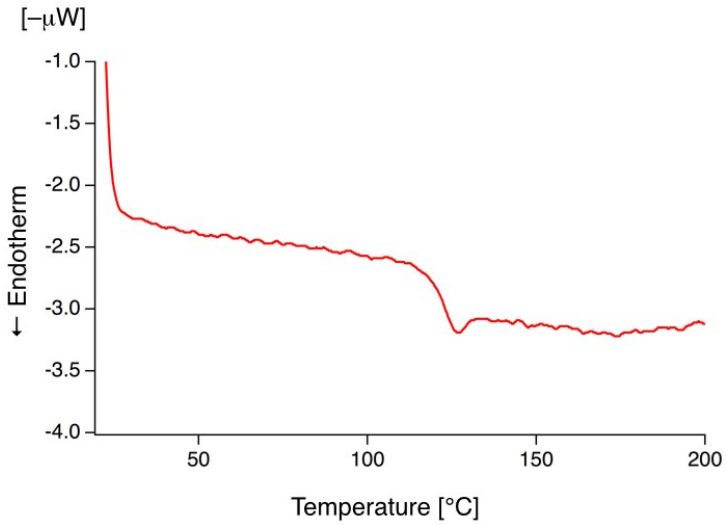
DSC thermogram of **CCP_{BIS}-1** (2^{nd} heating, heating rate: 10 °C / min).



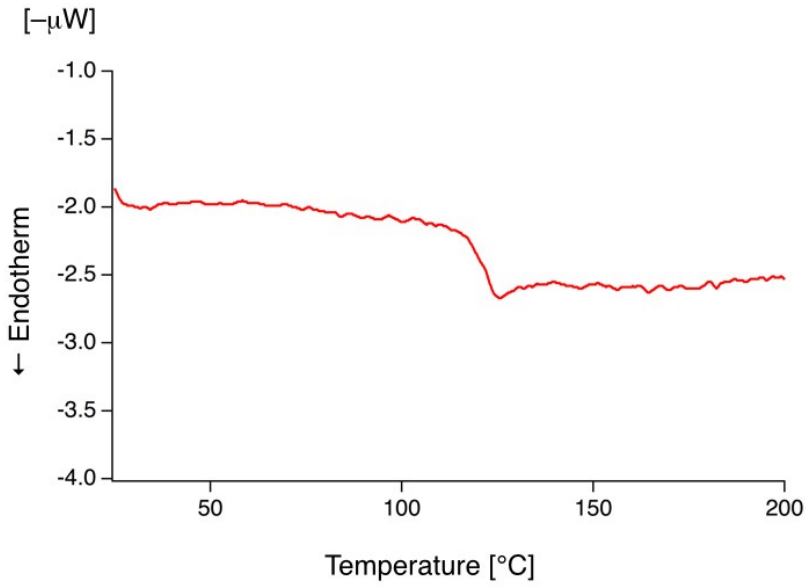
TGA result of **CCP_{BIS}-1** (heating rate: 10 °C / min).



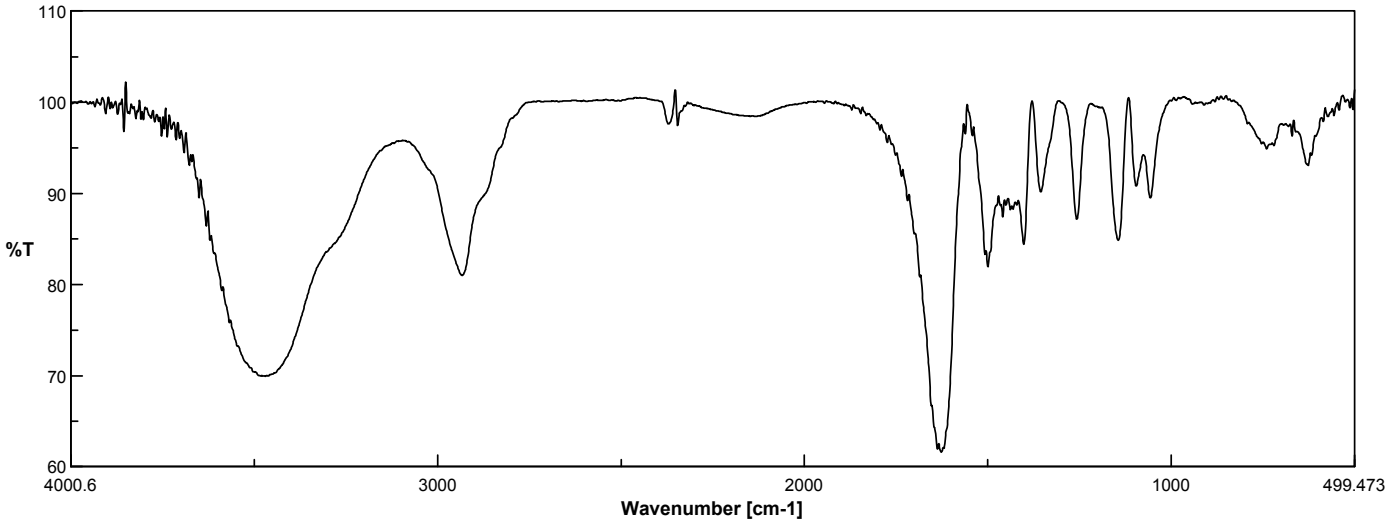
IR spectrum of **CCP_{BIS}-2** (KBr).



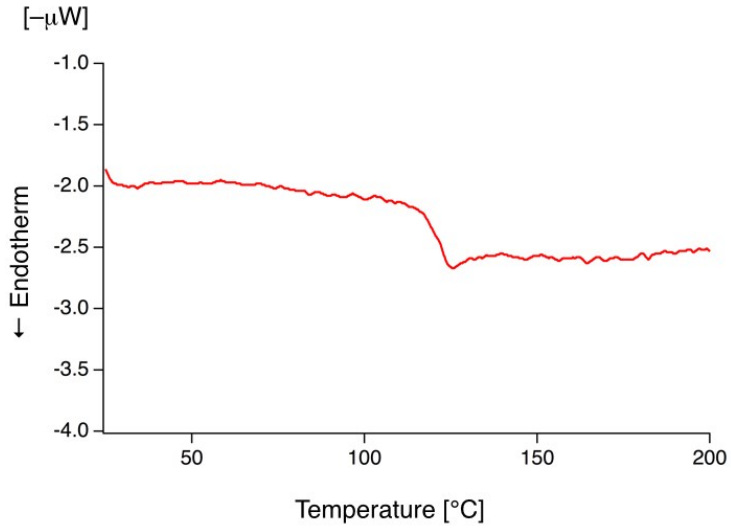
DSC thermogram of **CCP_{BIS}-2** (2^{nd} heating, heating rate: 10 °C / min).



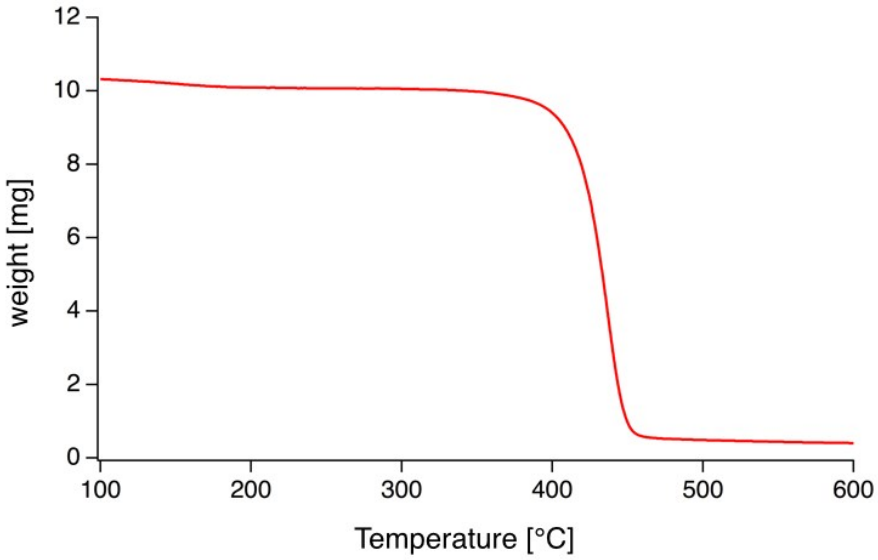
TGA result of **CCP_{BIS}-2** (heating rate: 10 °C / min).



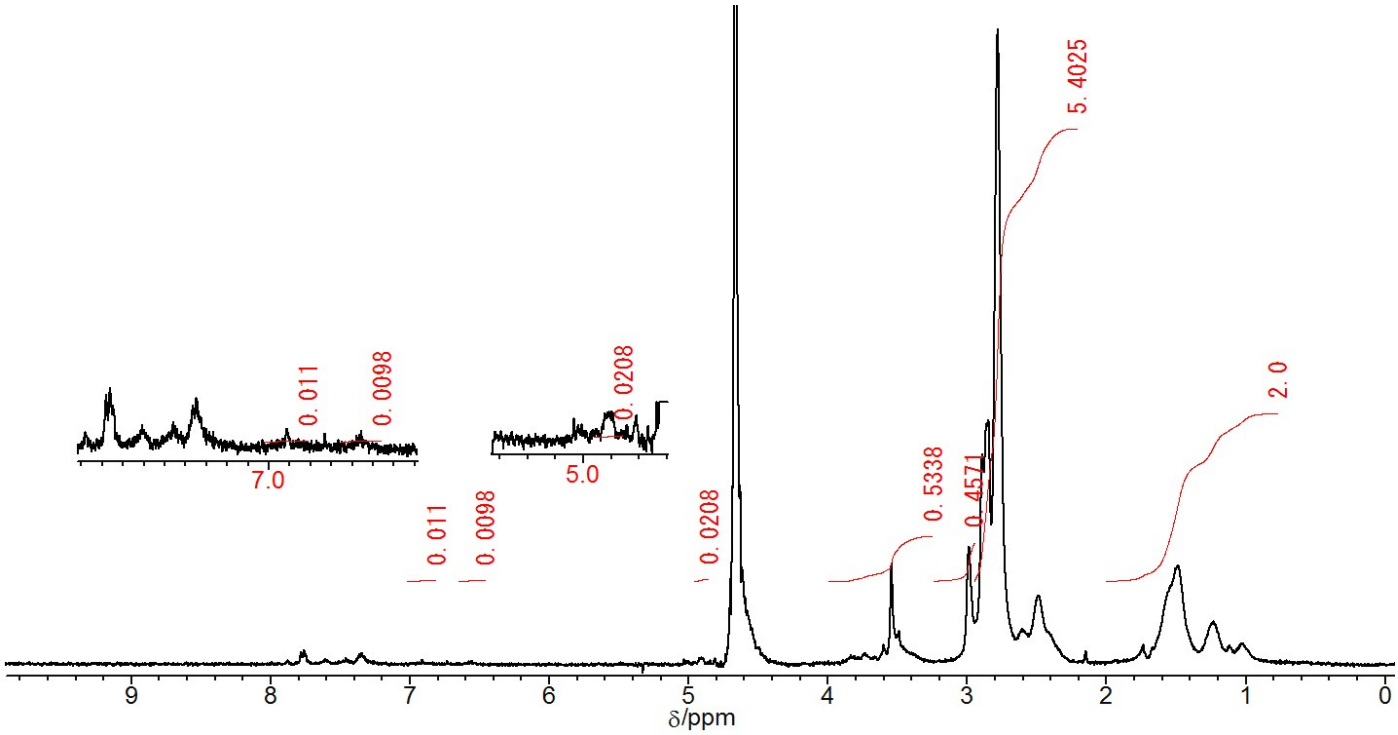
IR spectrum of **CCP_{BIS}-3** (KBr).



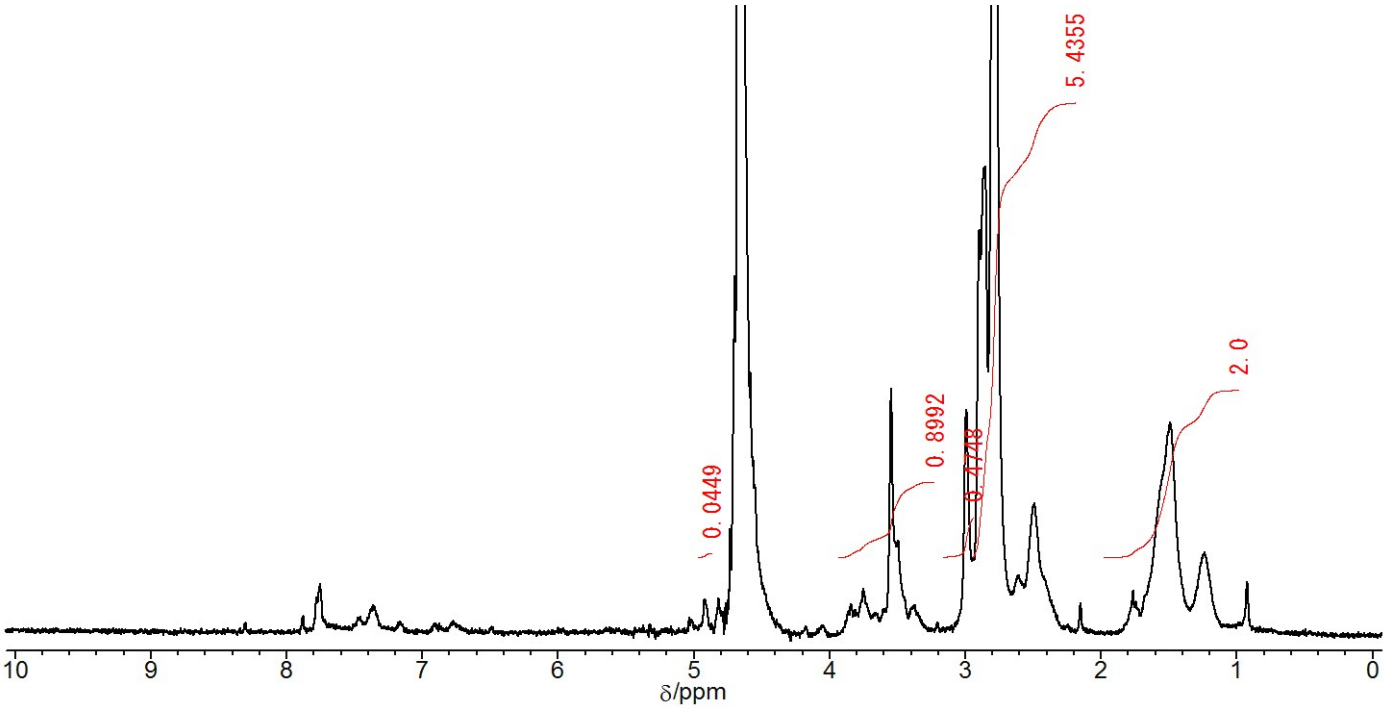
DSC thermogram of **CCP_{BIS}-3** (2^{nd} heating, heating rate: 10 °C / min).



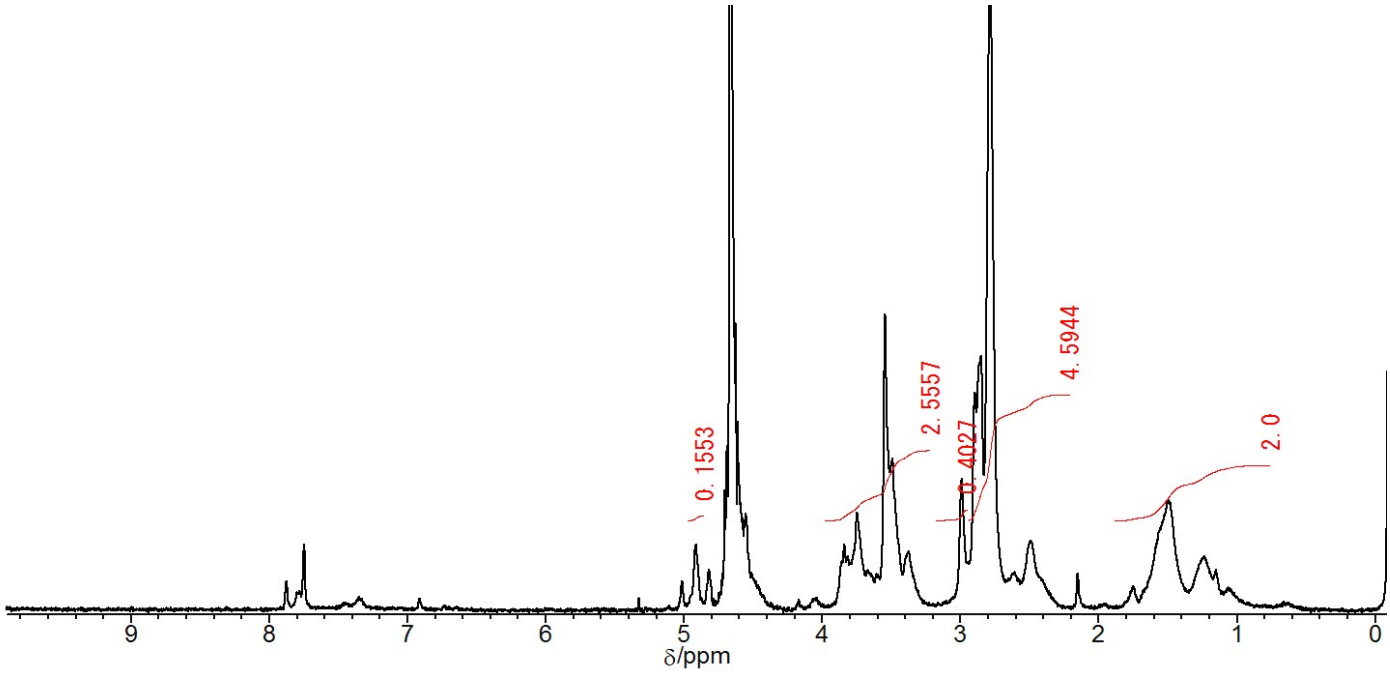
TGA result of **CCP_{BIS}-3** (heating rate: 10 °C / min).



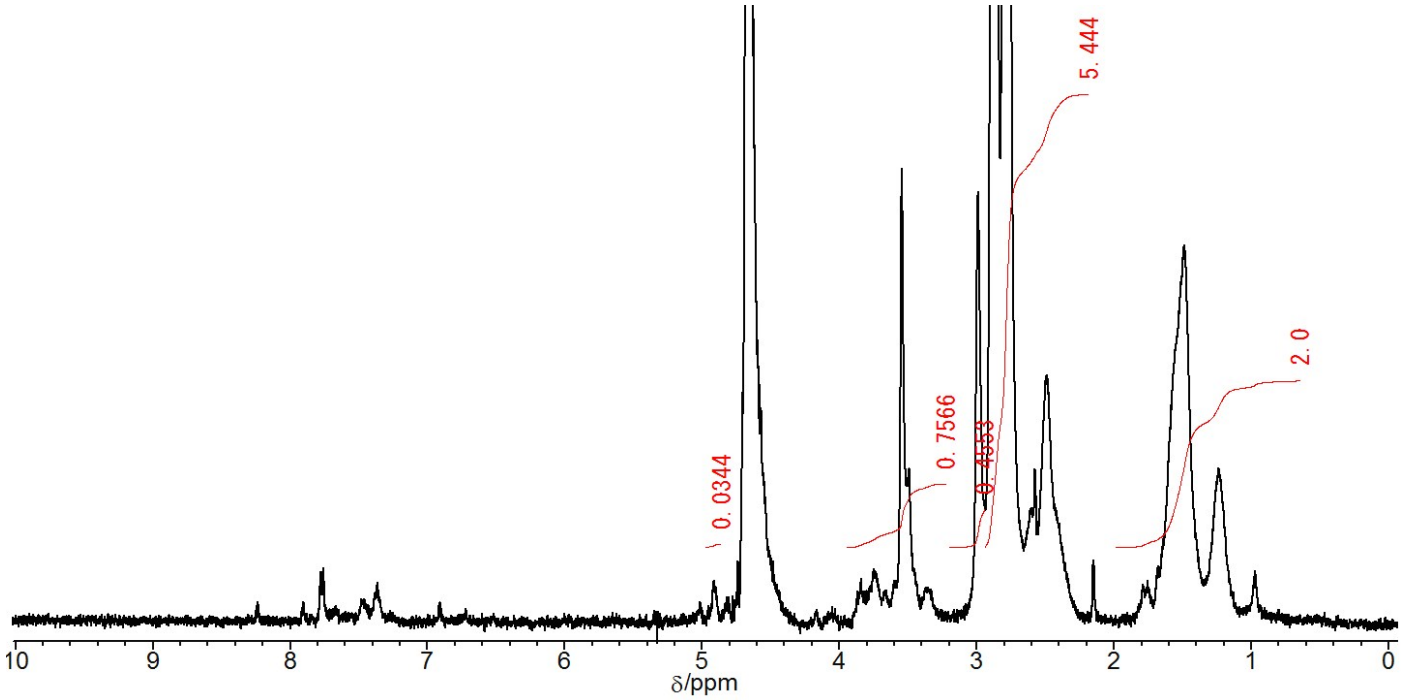
^{1}H NMR spectrum of the residual materials of **RCPα^2-1** (400 MHz, $CDCl_3$, 298 K).



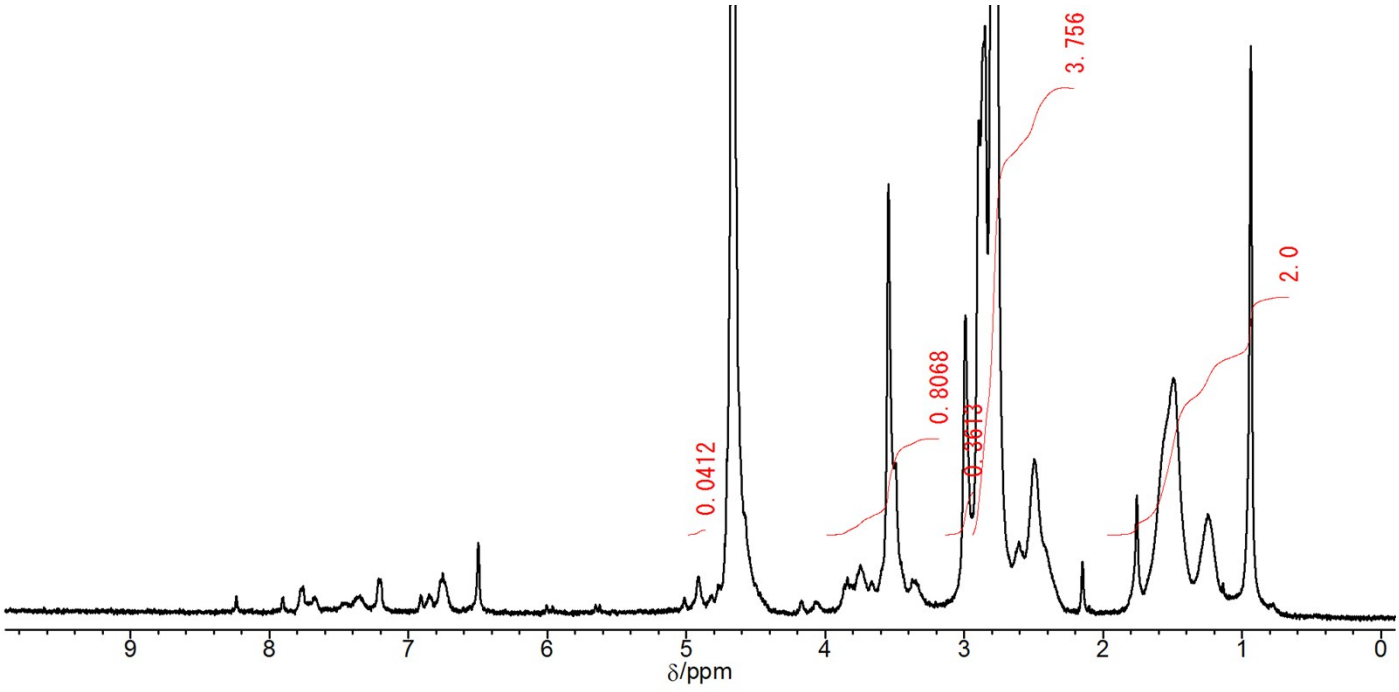
^{1}H NMR spectrum of the residual materials of **RCPα^{2}-2** (400 MHz, $CDCl_3$, 298 K).



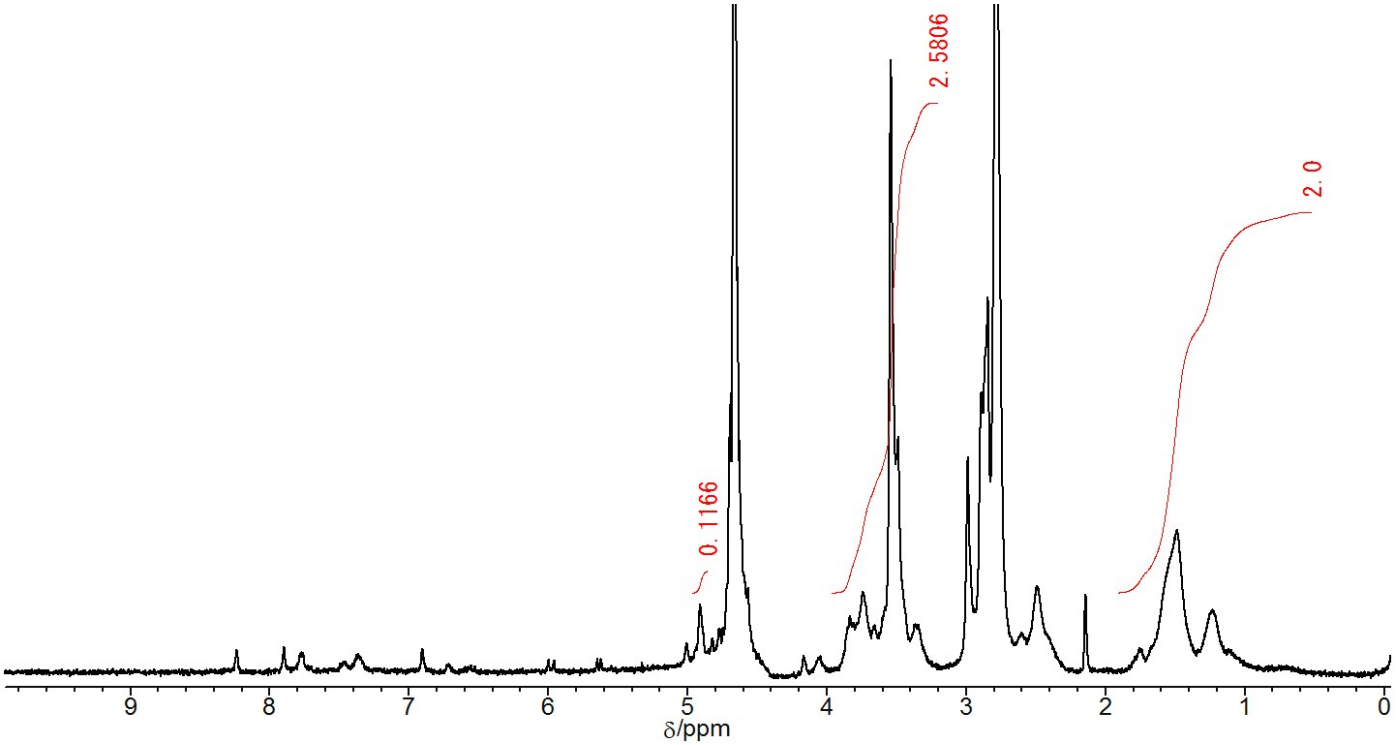
^{1}H NMR spectrum of the residual materials of **RCPα^{2}-3** (400 MHz, $CDCl_3$, 298 K).



^{1}H NMR spectrum of the residual materials of **RCPα^{3}-1** (400 MHz, $CDCl_3$, 298 K).



^{1}H NMR spectrum of the residual materials of **RCPα^{3}-2** (400 MHz, $CDCl_3$, 298 K).



^{1}H NMR spectrum of the residual materials of **RCPα^{3}-3** (400 MHz, $CDCl_3$, 298 K).

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