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Supporting Information

Directed one-pot syntheses of crown ether wheel-containing main chain-type polyrotaxanes with controlled rotaxanation ratios

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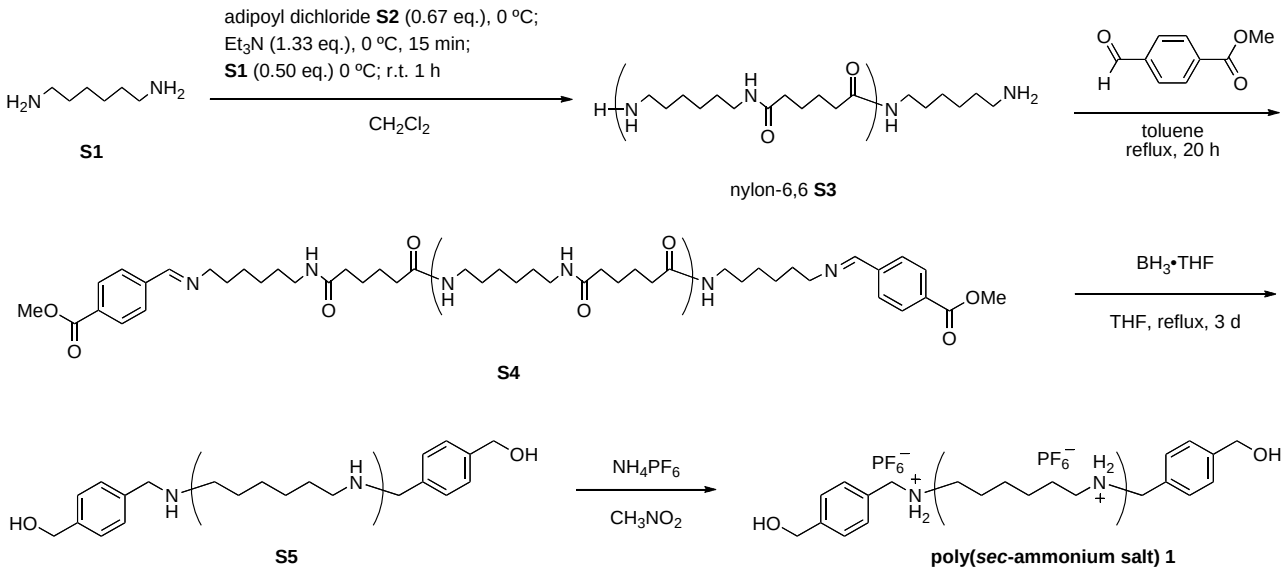
1. General Procedure

Melting points were measured on a MELTING POINT APPARATUS SMP3 (Stuart Scientific) instrument. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL-400 NMR spectrometer operating at 400 MHz and 100 MHz, respectively, and tetramethylsilane (in $CDCl_3$) and solvent peak (CD_3OD: 3.31 ppm, DMSO-d_6: 2.50 ppm, acetone-d_6: 2.05 ppm) were used as the internal standard. IR spectra were obtained with a JASCO FT/IR-460 plus spectrometer. Molecular weight and its distribution were measured by size exclusion chromatography, which was performed on a JASCO HSS-1500 system equipped with consecutive TOHSO TSK gel G2000HXL and GMHXL eluted with chloroform at a flow rate of 0.85 mL/min calibrated using polystyrene standards. Mass Spectra were recorded on a JEOL JMS-700 with 3-nitrobenzylalcohol (NBA) as the matrix. All solvents were distilled or dried before use according to the general purification procedure. Commercially available reagents were used without further purification unless otherwise noted. All reactions were carried out under inert atmosphere of argon. Silica gel liquid column chromatography was performed using Wakogel C-400HG (Wako Pure Chemical Industries Ltd.) GPC (Gel permeation liquid column chromatography) was performed by LC-9204 system with JAIGEL 1H-40 (Japan Analytical Industry) with chloroform eluent.

2. Chemical Syntheses

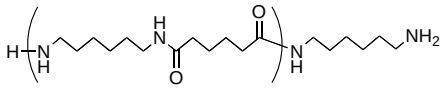
2-1. Synthesis of Polyrotaxane by *Method A*

Preparation of poly(*sec*-ammonium salt) 1[S1)].



Scheme S1

Preparation of nylon-6,6 amine terminated (S3)

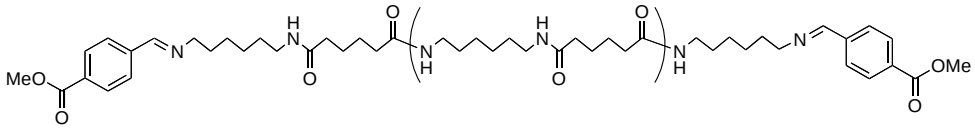


nylon-6,6 **S3**

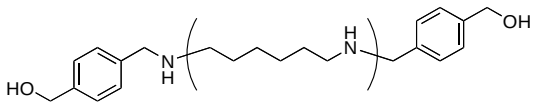
To a solution of hexamethylenediamine **S1** (3.5 g, 30 mmol) in dichloromethane (35 mL) was added a solution of adipoyl dichloride **S2** (2.9 mL, 20 mmol) in dropwise at 0 ºC. After that triethylamine (5.6 mL, 40 mmol) in dichloromethane (10 mL) was dropwise added to the mixture. After stirring for 15 min at 0 ºC, additional hexamethylene diamine (1.7 g, 15 mmol) in dichloromethane (20 mL) was added. Then the mixture was warmed to ambient temperature. After 1h stirring, $NaHCO_3$ aq. (100 mL) was added to the mixture and the formed precipitates were collected by filtration. The obtained colorless solid was washed with methanol (20 mL) and chloroform (20 mL). The titled nylon-6,6 amine terminated **S3** was obtained as a colorless solid (2.0 g) in 45% yield.

IR (KBr) ν 3304, 3073, 2934, 2860, 1638, 1539, 1474, 1371, 1276, 1199, 935, 690, 581 cm^{-1}.

Preparation of nylon-6,6 methylester terminated (S4) and polyamine hydroxy terminated (S5)



S4



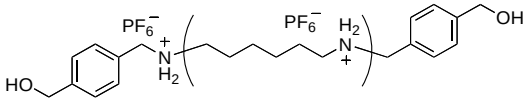
S5

S3 (1.0 g) and methyl 4-formyl benzoate (3.3 g, 20 mmol) were suspended in toluene (30 mL), then refluxed with a Dean-Stark trap. After 20 h, the solution was poured into a large excess of methanol and the formed precipitates were collected by filtration. After drying *in vacuo*, **S4** was obtained as a brown solid (1.0 g) in quantitative yield.

A suspension of the obtained **S4** (1.0 g) and 1.0 M BH_3•THF (36 mL, 36 mmol) in THF (4 mL) was refluxed for 3 days. The solvent was removed under reduced pressure. And 6 M HCl aq. (30 mL) was added to the residue, then the mixture was refluxed for 3 h. After cooling to 0 ºC, the solution was neutralized with 10% NaOH aq. in an ice bath, and the formed precipitates were collected by filtration. After drying *in vacuo*, the precipitates were extracted with chloroform and the soluble part was purified by reprecipitation from hexane followed by diethyl ether. The corresponding hydroxy terminated polyamine **S5** was obtained as a colorless solid (0.76 g) in 71% yield.

^{1}H NMR ($CDCl_3$) δ 7.32-7.26 (m, 8H), 4.66 (s, 4H), 3.78 (s, 4H), 2.58 (t, *J* = 7.2 Hz, 104H), 1.59 (br, 85H), 1.48 (br, 115H), 1.32 (br, 117H) ppm; IR (KBr) ν 3260, 2926, 2852, 2815, 1638, 1542, 1478, 1375, 1312, 1126, 728 cm^{-1}.

Preparation of Poly(*sec*-ammonium salt) 1

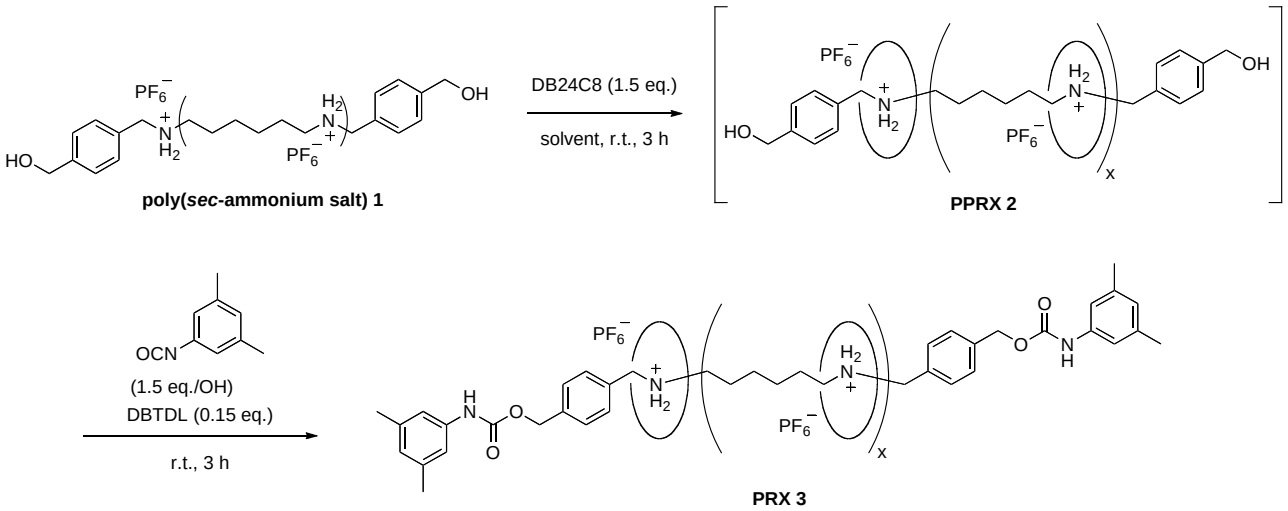


poly(*sec*-ammonium salt) 1

S5 (99 mg, 1.0 mmol $C_6H_{12}NH$ unit) and NH_4PF_6 (0.25 g, 1.5 mmol) were suspended in nitromethane (1.0 mL) and stirred to dissolve the polymer with bubbling argon gas. The clear solution was poured into a large excess of ethyl acetate and the precipitate was purified by reprecipitation from ethyl acetate. The titled **1** was obtained as a colorless solid (0.16 g) in 66% yield.

^{1}H NMR (DMSO-d_6) δ8.17 (br, 71H), 7.40 (s, 8H), 5.25 (s, 2H), 4.51 (d, *J* = 4.4 Hz, 4H), 4.11 (s, 4H), 2.85 (br, 160H), 1.54 (br, 170H), 1.30 (br, 181H) ppm; IR (KBr) ν 3268, 2946, 2871, 1594, 1476, 1426, 844, 763, 740, 558 cm^{-1}.

General procedure for synthesis of polyrotaxane PRX 3 (Method A)



poly(*sec*-ammonium salt) 1 **PPRX 2** **PRX 3**

Scheme S2

A suspension of poly(*sec*-ammonium salt) **1** (25 mg, 0.10 mmol: $C_6H_{12}NH$ unit) and dibenzo-24-crown-8 ether (DB24C8, 67 mg, 0.15 mmol) in solvent (0.10 mL) was stirred vigorous for 3 h at r.t. to form **PPRX 2**. Then to the solution was added 3,5-dimethylphenylisocyanate (21 mL, 0.15 mmol) and dibutyltin dilaurate (DBTDL, 9.0 μL, 15 μmol), and the mixture was stirred

for 3 h. The reaction mixture was poured into ethyl acetate and the precipitates were collected by filtration. The precipitates were dissolved in a small amount of acetonitrile and the solution was poured into water, then the precipitates were collected by filtration and dried *in vacuo* to give **PRX 3** as a pale yellowish solid.

Table 1 entry 4 **PRX 3 (*RR* = 98)**

^{1}H NMR (DMSO-d_6) δ 7.38 (d, J = 7.56 Hz, 4H, phenyl of axis), 7.29 (d, J = 7.56 Hz, 4H, phenyl of axis), 6.94 (br, 126H, phenyl of DB24C8), 6.88 (br, 126H, phenyl of DB24C8), 6.57 (br, 52H, NH_2), 5.06 (s, 4H, O side benzyl), 4.51 (s, 4H, NH_2 side benzyl), 4.06 (b, 253H, methylene), 3.76 (b, 252H, methylene), 3.61 (br, 246H, methylene), 3.01 (br, 130H, methylene), 1.43-1.10 (m, 179H, methylene), 0.68 (b, 99H, methylene) ppm; IR (KBr, Run 3) 3448, 2932, 159, 1506, 1458, 1254, 1214, 1125, 1057, 954, 842, 750, 558, 694 cm^{-1}; T_{d5} 248.7 ºC, T_g 90.6 ºC.

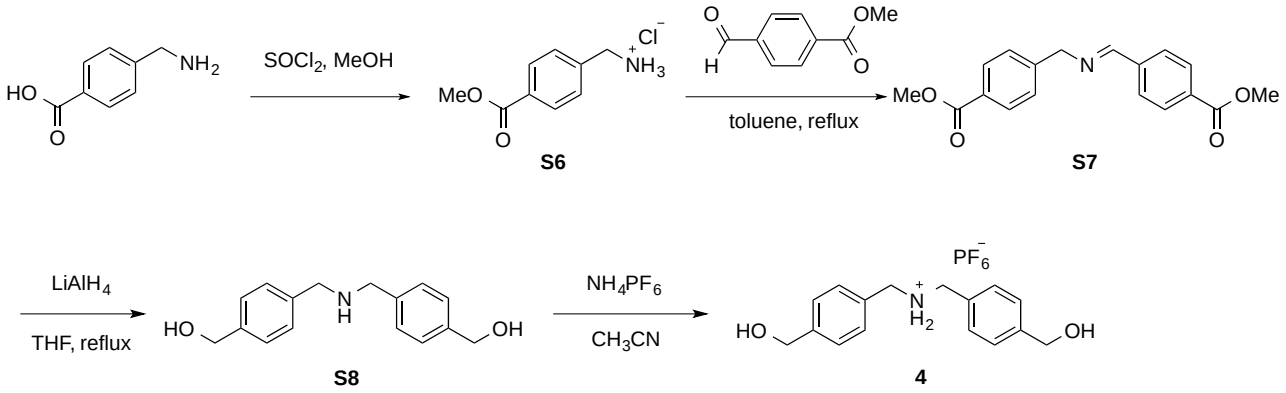
Neutralization of **PRX 3 (*RR* = 98)** by N-acetylation

PRX 3 (*RR* = 98) (50 mg, 79 μmol ($C_6H_{12}NH$ unit) was dissolved in DMF (1 mL), then triethylamine (0.80 mL, 5.7 mmol) and acetic anhydride (0.30 mL, 3.2 mmol) were added at r.t. After 24 h vigorous stirring at 50 ºC, water (10 mL) was added to quench the reaction. The mixture was neutralized with Na_2CO_3 and the precipitates were collected by filtration. The precipitates were purified by preparative GPC to give partially *N*-acetylated **PRX 3 (*RR* = 98)** was obtained in 98% yield. The degree of *N*-acetylation of **PRX 3 (*RR* = 98)** was estimated by IR as 89%.

^{1}H NMR (DMSO-d_6) δ 7.10-6.40 (m), 4.15-0.95 (m) ppm; IR (KBr) 2925, 1618, 1507, 1458, 1253, 1215, 1125, 1057, 954, 843, 742, 556, 476, cm^{-1}; SEC ($CHCl_3$, PSt standards, 303 K, RI): M_n 1530, PDI 1.38; T_{d5} 260 °C, T_g 152 °C.

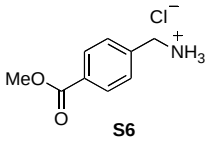
2-2. Synthesis of Polyrotaxane by *Method B*

Synthesis of axle precursor 4[S2)]



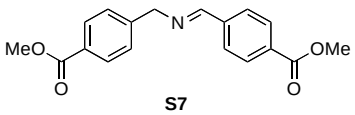
Scheme S3

Preparation of S6



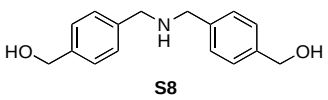
To a suspension of 4-(aminomethyl)benzoic acid (20 g, 0.13 mol) in MeOH (600 mL) was slowly added $SOCl_2$ (31 g, 0.26 mol), then the mixture was stirred at r.t. for 12 h. The solvent was removed under reduced pressure, then the residue (**S6**) was used to the next reaction without further purification.

Preparation of S7



S6 (6.5 g, 32 mmol) was suspended in toluene (300 mL) and methyl 4-formylbenzoate (5.8 g, 35 mmol) was added. The mixture was refluxed with removal of water by Dean-Stark trap. After overnight refluxing, toluene was distilled off under reduced pressure. The titled **S7** was obtained as the residue and it was used without further purification.

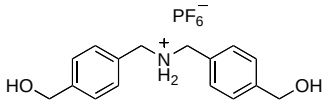
Preparation of S8



To a suspension of $LiAlH_4$ (4.9 g, 0.13 mmol) in THF (200 mL) was added a suspension of **S7** (10 g, 32 mmol) in hot THF (200 mL) with cooling by an ice bath. Then the suspension was

heated to reflux overnight. After cooling to 0 ºC, sat. Na_2SO_4 aq. was added carefully to the mixture until stop the generation of hydrogen, and the slurry was stirred for 1 h. The slurry was extracted by suction filtration and the precipitates were extracted with ethyl acetate. The combined filtrate was washed with water and brine. The organic layer was dried over $MgSO_4$, filtred, and the solvent was removed under reduced pressure. The residual pale yellowish oil was used as **S8** (7.5 g, 2.9 mmol, 91%) without further purification.

Preparation of 4[S2)]



4

To a solution of **S8** (1.5 g, 5.8 mmol) in acetonitrile (55 mL) was added NH_4PF_6 (1.1 g, 7.0 mmol), and the solution was stirred vigorously with Ar bubbling to remove the generated ammonia gas. After 1 h, the solvent was removed under reduced pressure, and then the residue was purified by recrystallization from acetonitrile and chloroform. The titled dihydroxy dibenzyl ammonium **4** (2.3 g, 5.7 mmol) was obtained in 99% yield as a white solid.

m.p.153.2-153.6 °C (decomp.)

^{1}H NMR (CD_3CN) δ 7.45-7.40 (m, 8H), 4.63 (s, 4H), 4.21 (s, 4H), 3.30 (brs, 2H) ppm; IR (KBr) ν 3252, 2989, 2943, 2789, 2709, 2584, 1559, 1519, 1464, 1415, 1280, 1218, 1040, 1021, 971, 843, 770, 557, 514 cm^{-1}.

Lit. 160 °C (decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ=7.42 (d, *J* = 8.0 Hz, 4H), 7.39 (d, *J* = 8.0 Hz, 4H), 5.12 (brs, 2H), 4.59 (s, 4H), 4.21 (s, 4H); ^{13}C NMR (100 MHz, CD_3CN) δ= 144.8, 131.0, 130.1, 128.1, 128.0, 64.2, 52.4 ppm; IR (KBr) 3393(br), 3249, 3227, 2989, 2942, 2892, 2789, 2710, 1581, 1415, 1040, 1021, 836 cm^{-1}.

General procedure for PRX 6 and PRX 6Ac syntheses

The hydroxy terminated ammonium PF_6 salt **4** (1.0 g, 2.5 mmol) and DB24C8 were dissolved in dichloromethane (12.5 mL) and stirred at 20 ºC for 30 min under light shielding. To the pseudo[2]rotaxane solution, previously purified 4,4'-diphenylmethane diisocyanate **5** (0.63 g, 2.5 mmol) and DBTDL (50 μL, 83 μmol) were added and the solution was stirred at 20 ºC for 15 h. After addition of 3,5-dimethylphenylisocyanate **2** (0.71 mL, 5.0 mmol) the reaction mixture was stirred for an additional 10 h, followed by addition of 3,5-dimethylphenol (1.2 g, 9.9 mmol) and another 10 h stirring. The reaction mixture was poured into diethyl ether, and the precipitates were collected by decantation. The obtained precipitates were dissolved in a small amount of acetone and poured into diethyl ether again. The precipitates were collected by decantation and

dried in vacuo to give titled **PRX 6** as a colorless powder.

PRX 6 (0.50 g, 0.50 mol), triethylamine (0.35 mL, 2.5 mmol), and acetic anhydride (0.14 mL, 1.5 mmol) were dissolved in DMF (5 mL) and the mixture was stirred for 3 d at r.t. After cooling to r.t., the solution was poured into excess water and the precipitates were collected by filtration and washed with water. The precipitates were dissolved in a small amount of THF and poured into methanol and the precipitates were collected by filtration and dried *in vacuo* to give **PRX 6Ac** as a colorless powder.

Table 2, entry 1: **PRX 6 (*RR* = 95)**

According to the general procedure, DB24C8 (2.24 g, 5.00 mmol) was used. After reprecipitation, **PRX 6** with 95% *C* value (2.5 g) was obtained in 93% yield as a colorless powder.

^{1}H NMR (CD_3COCD_3) δ 8.66 (s, 2H), 7.66 (br, 1.6H), 7.44 (d, *J* = 8.3 Hz, 4H), 7.42 (d, *J* = 8.1 Hz, 4H), 7.25 (d, *J* = 8.1 Hz, 4H), 7.14 (d, *J* = 8.3 Hz, 4H), 6.86 (br, 8H), 5.17-5.12 (m, 0.30H), 5.05 (s, 3.7H), 4.78 (br, 3.7H), 4.66 (br, 0.30H), 4.16-4.14 (m, 8H), 3.89-3.85 (m, 10H), 3.62-3.58 (m, 8H), 2.28-2.23 (m, 0.50H) ppm; ^{13}C NMR (, DMSO-d_6) δ 153.3, 153.2, 146.9, 137.7, 137.4, 136.9, 135.6, 131.3, 130.1, 129.1, 128.9, 128.1, 127.7, 121.0, 118.3, 112.4, 70.2, 69.7, 67.5, 65.1, 64.9, 51.6, 49.8 ppm; IR (KBr) ν 3396, 3143, 3060, 2921, 2877, 1733, 1596, 1524, 1506, 1456, 1413, 1354, 1317, 1217, 1125, 1054, 1018, 953, 915, 848, 739, 558 cm^{-1}; T_{d5} 224 °C, T_g 161 ºC.

PRX 6Ac (*RR* = 95)

According to the general N-acetylation procedure, **PRX 6Ac (*RR* = 95)** (0.45 g) was obtained in 92% yield and 100% conversion yield as a colorless powder.

^{1}H NMR (DMSO-d_6) δ 9.64 (br, 1H), 9.12 (br, 0.9H), 7.34-7.00 (m, 8H), 6.92 (br, *3.5*H), 6.84 (br, 3.5H), 5.43 (br, 0.40H), 5.27 (br, 1.6H), 5.08 (br, 2H), 4.46-4.36 (m, 4H), 4.01 (br, 7H), 3.76 (br, 1.2H), 3.58 (m, 8H), 2.28-2.23 (m, 0.50H) ppm; ^{13}C NMR (DMSO-d_6) δ 153.3, 153.2, 146.9, 137.7, 137.4, 136.9, 135.6, 131.3, 130.1, 129.1, 128.9, 128.1, 127.7, 121.0, 118.3, 112.4, 70.2, 69.7, 67.5, 65.1, 64.9, 51.6, 49.8 ppm; IR (KBr) ν 3396, 3143, 3060, 2921, 2877, 1733, 1596, 1524, 1506, 1456, 1413, 1354, 1317, 1217, 1125, 1054, 1018, 953, 915, 848, 739, 558 cm^{-1}; SEC (DMF, PSt standards, 303 K, RI) M_n 28000, PDI 3.6; T_{d5} 293 °C, T_g 115 ºC.

Table 2, entry 2: **PRX 6 (*RR* = 90)**

According to the general procedure for **PRX 6**, DB24C8 (1.12 g, 2.50 mmol) was used. After reprecipitation, **PRX 6** with 90% *C* value (2.2 g) was obtained in 84% yield as a pale yellow solid. T_{d5} 254 °C. T_g 147 ºC

The N-acetylation of **PRX 6 (*RR* = 90)** (0.50 g) afforded **PRX 6Ac (*RR* = 90)** (0.45 g) in 92% yield

with 100% conversion. SEC (DMF, PSt standards, 303 K, RI) M_n 42000, PDI 2.2; T_{d5} 291 °C, T_g 116 ºC.

Table 2, entry 3: **PRX 6 (*RR* = 55)**

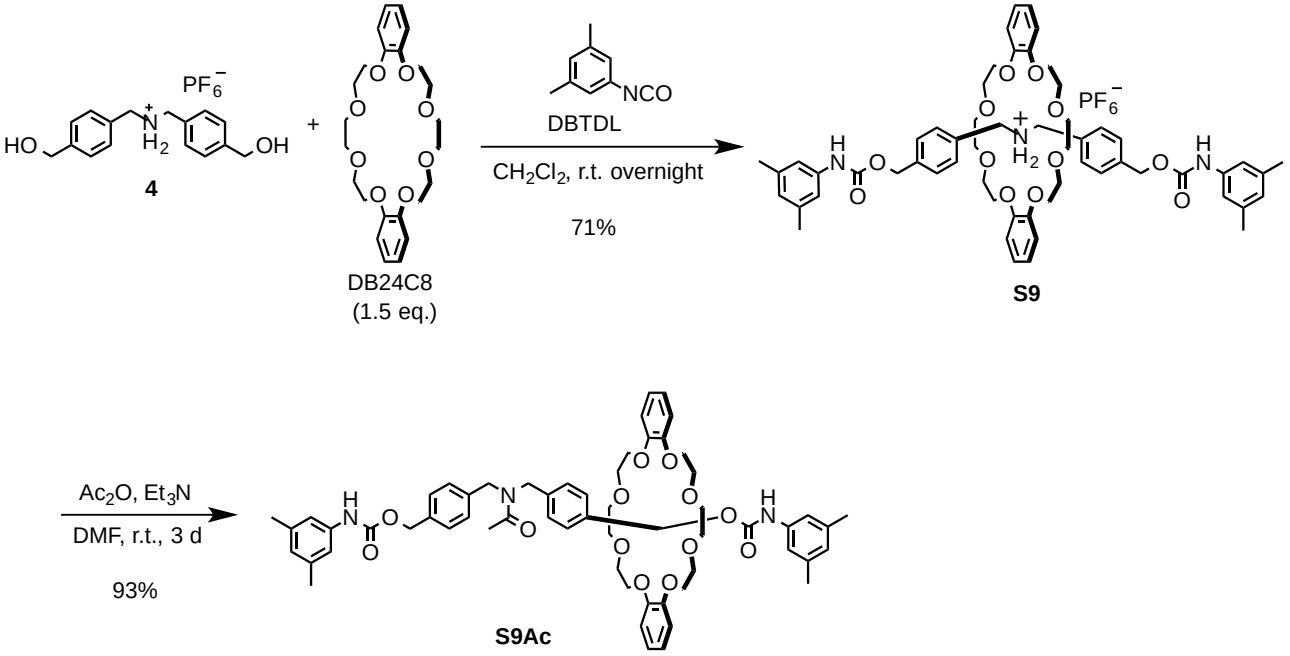
According to the general procedure, DB24C8 (0.561 g, 1.25 mmol) was used. After reprecipitation, **PRX 6** with 55% *C* value 1.8 g was obtained in 84% yield as a pale yellow solid.

^{1}H NMR (CD_3COCD_3) δ 8.67 (br, 2H), 7.68 (br, 2H), 7.48-7.43 (m, 8H), 7.25 (d, *J* = 8.3 Hz, 4H), 7.15 (d, *J* = 8.3 Hz, 4H), 6.91-6.87 (m, 8H), 5.19 (s, 1.8H), 5.06 (s, 2.2H), 4.80 (br, 2.2H), 4.66 (s, 1.8H), 4.16-4.14 (m, 5H), 3.89-3.85 (m, 7H), 3.62-3.58 (m, 5H), 2.28-2.19 (m, 0.79H) ppm; T_{d5} 231 °C, T_g 154 ºC.

The N-acetylation of **PRX 6 (*RR* = 55)** (0.50 g) affodrded **PRX 6Ac (*RR* = 55)** (0.33 g) in 78% yiled with 100% conversion.

SEC (DMF, PSt standards, 303 K, RI) M_n 33000, PDI 2.2; T_{d5} 287 °C. T_g 108 ºC.

2-3. Synthesis of model [2]rotaxane S9 and S9Ac



Scheme S4

Preparation of S9

4 (0.20 g, 0.50 mmol) and DB24C8 (0.33 g, 0.74 mmol) were dissolved in dichloromethane (5.0 mL), and then the mixture was stirred for 30 min at rt. To a solution, 3,5-dimethylphenylisocyanate (0.21 mL, 1.5 mmol) and DBTDL (10 μL, 0.08 mmol) were added. After overnight stirring at rt, the solvent was removed under reduced pressure. The residue was

purified by silica gel column chromatography (EtOAc / Hexane = 3 / 1, R_f = 0.20) to give **S9** (0.41 g, 0.36 mmol) in 72% as a white solid.

m.p. 97.5–103.0 °C; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.60 (br, 2H), 7.28–7.23 (m, 8H), 7.08 (s, 4H), 7.98 (br, 2H), 6.87–6.84 (m, 4H), 6.77–6.74 (m, 4H), 6.68 (s, 2H), 5.07 (s, 4H), 4.57–4.55 (m, 4H), 4.07–4.05 (m, 8H), 3.73–3.72 (m, 8H), 3.41 (s, 8H), 2.26 (s, 12H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 153.3, 147.4, 138.7, 137.7, 129.3, 128.0, 125.1, 121.7, 116.4, 112.8, 70.6, 70.5, 70.1, 68.2, 65.7, 52.3, 21.3 ppm; FT-IR (KBr) ν 3395, 3151, 3067, 2919, 2877, 1734, 1615,1544, 1505, 1458, 1354, 1326, 1253, 1217, 1123, 1095, 1057, 1016, 954, 843, 744, 689, 602, 557 cm^{-1}; HR-MS FAB Calcd for $C_{58}H_{70}N_3O_{12}$ $[M\text{-}PF_6^-]^+$, *m/z* = 1000.4954; Found, *m/z* = 1000.4951.

Preparation of S9Ac

S9 (0.10 g, 87 μmol), acetic anhydride (41 μL, 0.44 mmol), and triethylamine (61 μL, 0.44 mmol) were dissolved in DMF (0.87 mL), and then the mixture was stirred for 3 days at rt. The mixture was dilluted with water to generate precipitates. The precipitates were collected by filtration and purified by recycle GPC to give **S9Ac** (84 mg, 81 μmol) in 93% yield as a white solid.

m.p. 190.2–190.8 ºC; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 8.38–8.34 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 5.9 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.01–6.84 (m, 14H), 6.71 (s, 1H), 5.72–5.70 (m, 2H), 5.18–5.10 (m, 2H), 4.50–4.48 (m, 2H), 4.36–4.29 (m, 2H), 4.20–4.07 (m, 8H), 3.94–3.90 (m, 4H), 3.77–3.72 (m, 4H), 3.54–3.51 (m, 4H), 3.40–3.37 (m, 4H), 2.28 (s, 6H), 2.16–2.11 (m, 9H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 171.0, 153.8, 148.41, 148.36, 139.5, 138.8, 138.6, 138.2, 138.1, 137.6, 136.7, 135.6, 135.2, 134.7, 133.7, 128.8, 128.5, 127.6, 127.2, 126.6, 125.8, 125.3, 123.4, 123.3, 120.74, 120.70, 116.3, 115.52, 115.48, 111.9, 69.8, 69.7, 68.0, 66.6, 66.4, 65.9, 65.7, 50.6, 50.3, 47.7, 47.4, 21.7, 21.4, 21.31, 21.29 ppm; FT-IR (KBr) ν 3364, 2919, 2830, 1726, 1615, 1558, 1505, 1454, 1327, 1272, 1254, 1226, 1125, 1051, 936, 841, 741 cm^{-1}; R-MS FAB Calcd for $C_{60}H_{71}N_3O_{13}Na$ $[M+Na]^+$, *m/z* = 1064.4885; Found, *m/z* = 1064.4894.

3. Solubility of PRXs[a]

	DMF	CH_3CN	acetone	MeOH	CH_2Cl_2	$CHCl_3$
PRX 3 (*RR* = 98)	++	+	–	–	–	–
PRX 6 (*RR* = 90)	++	++	++	–	++	–
PRX 6Ac (*RR* = 90)	++	++	++	–	++	–

[a] 2 mg/1 mL at r.t., ++: soluble, +: partially soluble, –; insoluble.

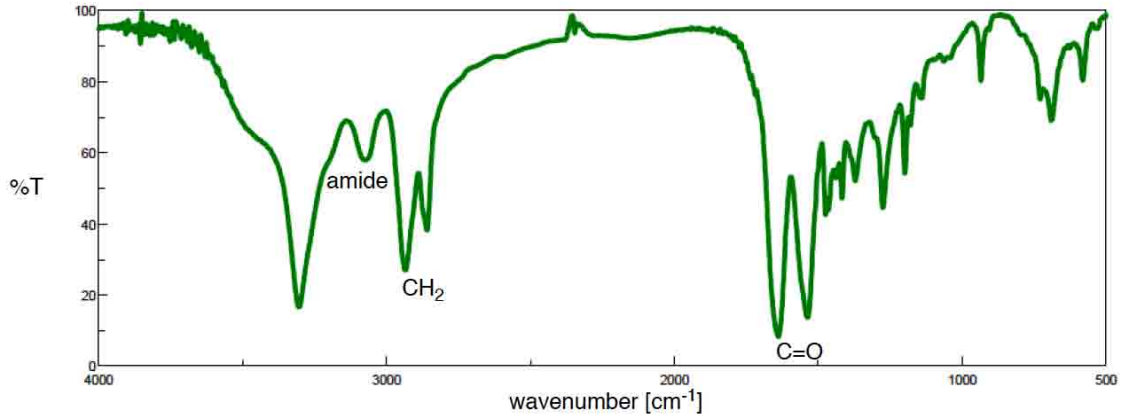
4. References

S1) (a) T. Perner, R. C. Shultz, *Br. Polym. J.*, **1987**, *19*, 181. (b) D. Saeki, N. Kihara, T. Takata, *Polym. Prepr. Jpn.*, **2003**, *52*, 347.

S2) (a) P. R. Ashton, M. C. Fyfe, S. K. Hickingbottom, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1998**, *4*, 577. (b) K. Hirose, K. Ishibashi, Y. Shiba, Y. Doi, Y. Tobe, *Chem. Lett.* **2007**, *36*, 810.

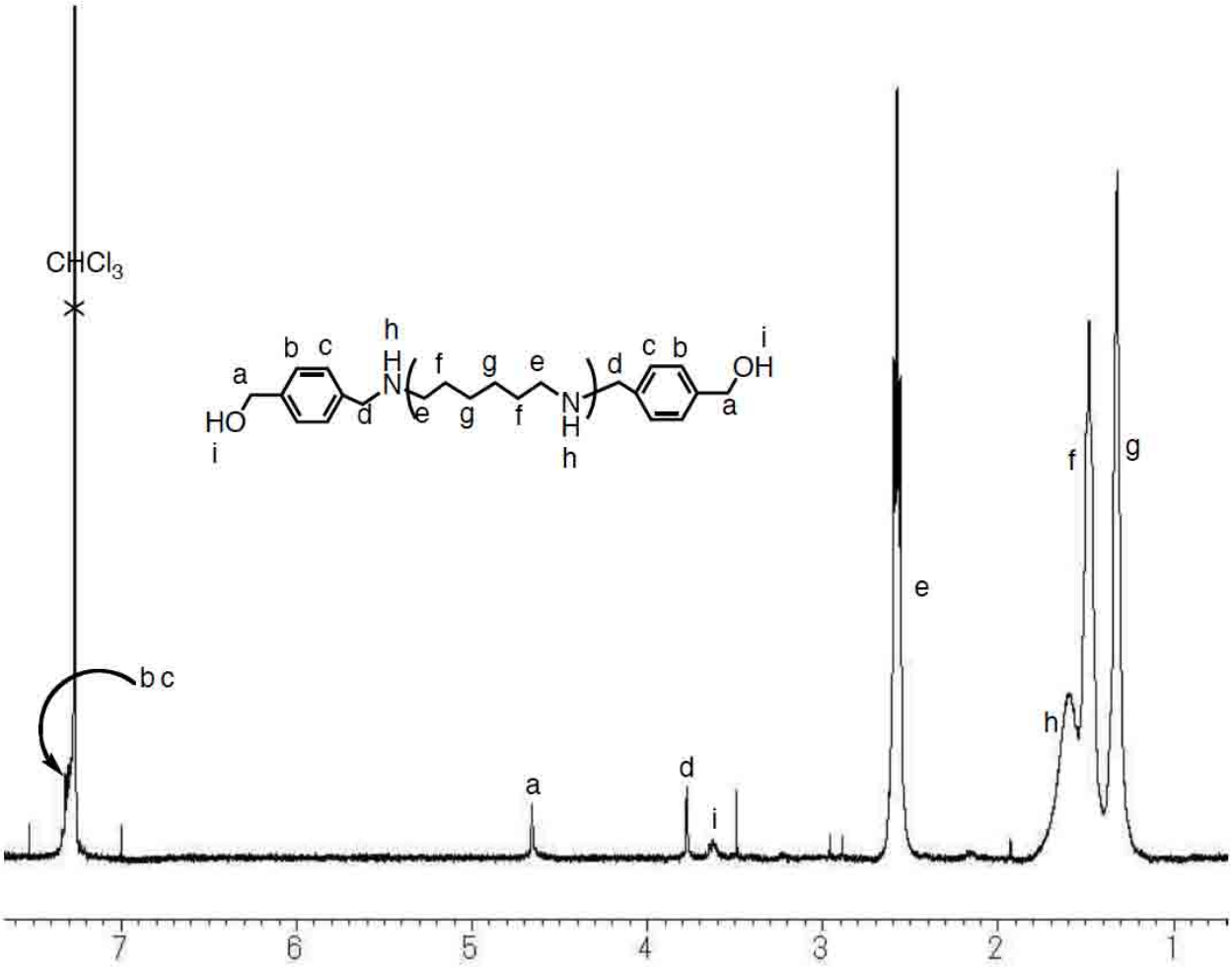
5. Spectra data of synthesized compounds

nylon-6,6 methylester terminated **S4**

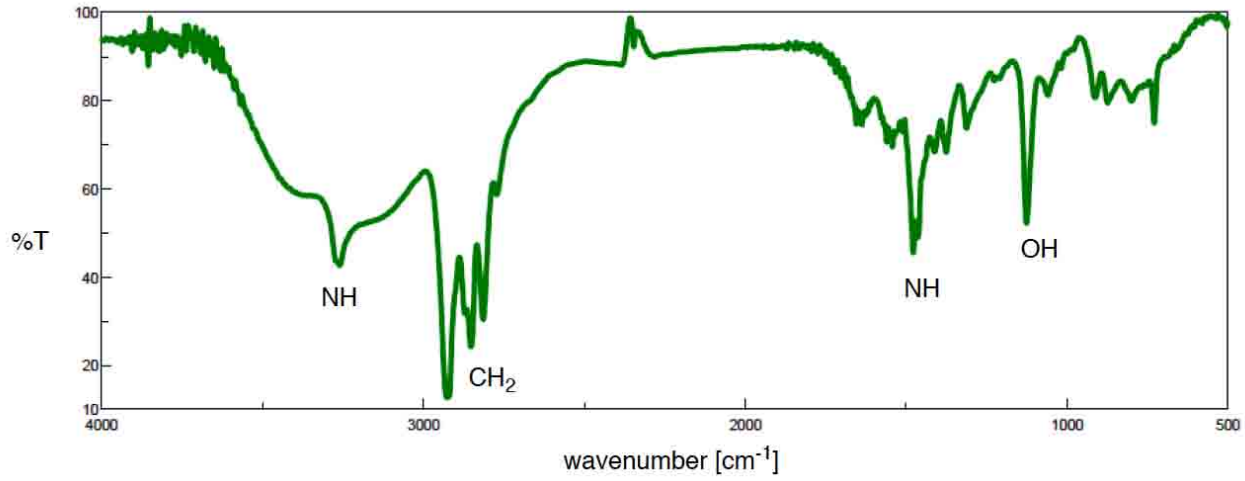


IR Spectrum of **S4** (KBr)

Polyamine hydroxy terminated **S5**

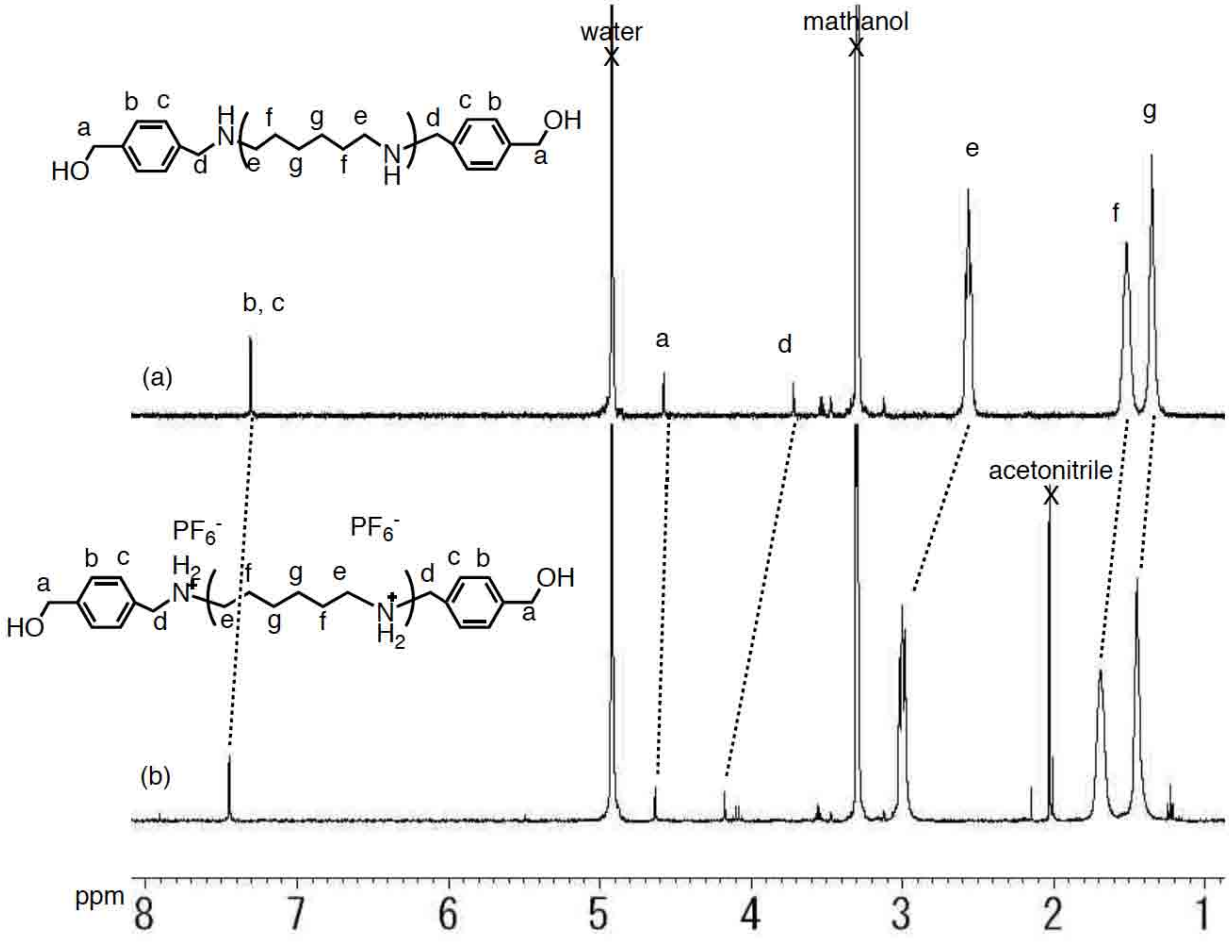


^{1}H NMR spectrum of **S5** (400 MHz, $CDCl_3$)

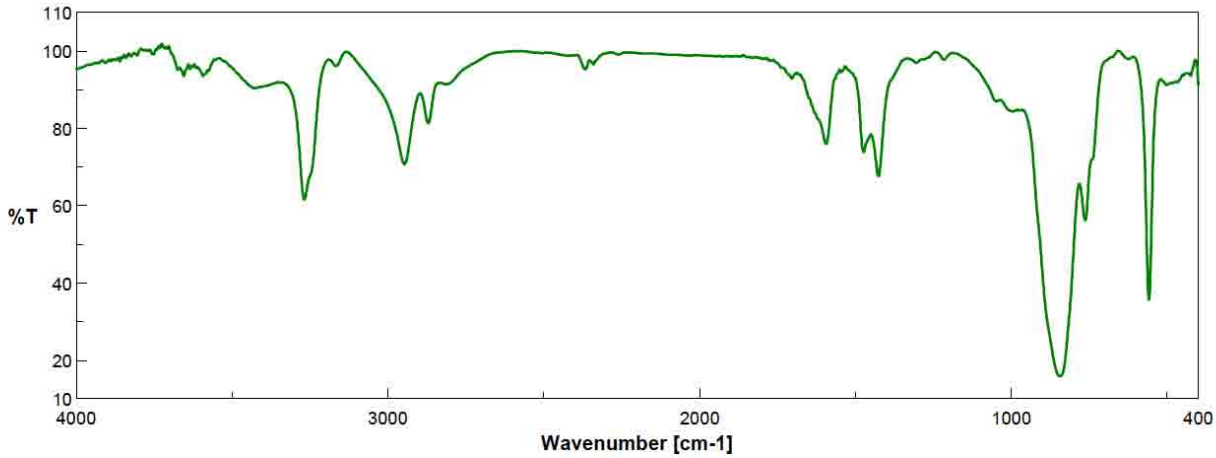


IR spectrum of **S5** (KBr)

Poly(*sec*-ammonium PF_6 salt) **1**

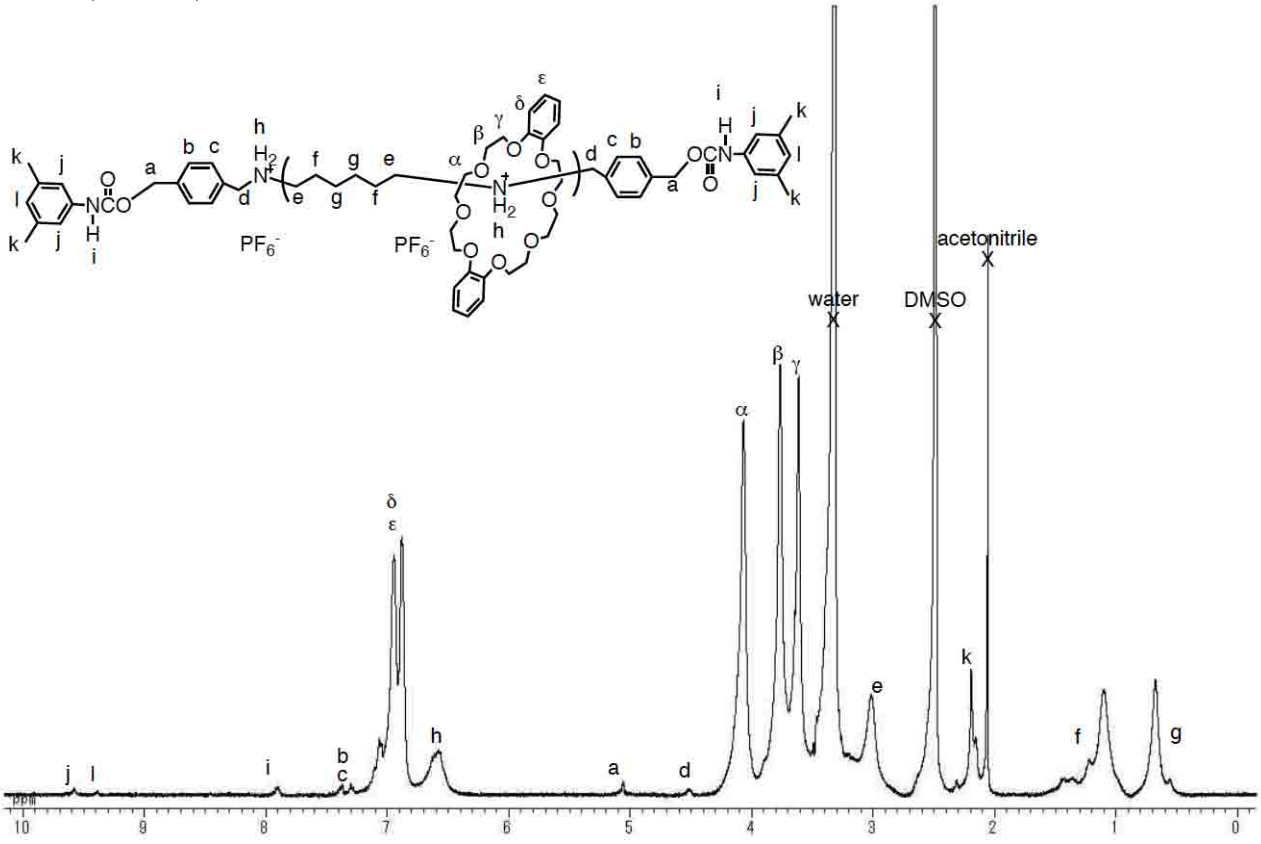


^{1}H NMR Spectra of (a) **S5** and (b) **1** (400 MHz, CD_3OD)

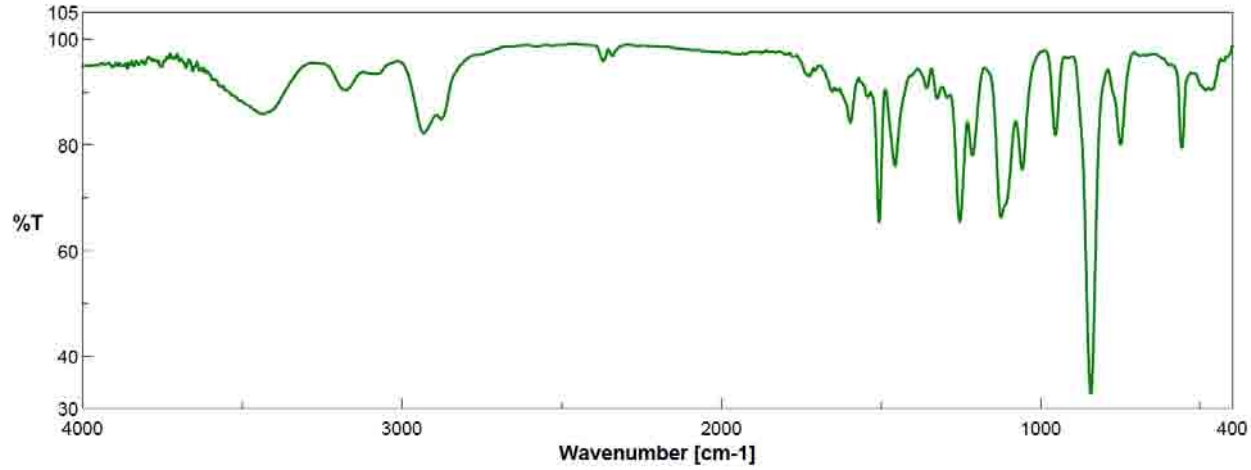


IR spectrum of **1** (KBr)

PRX 3 (*RR* =98)

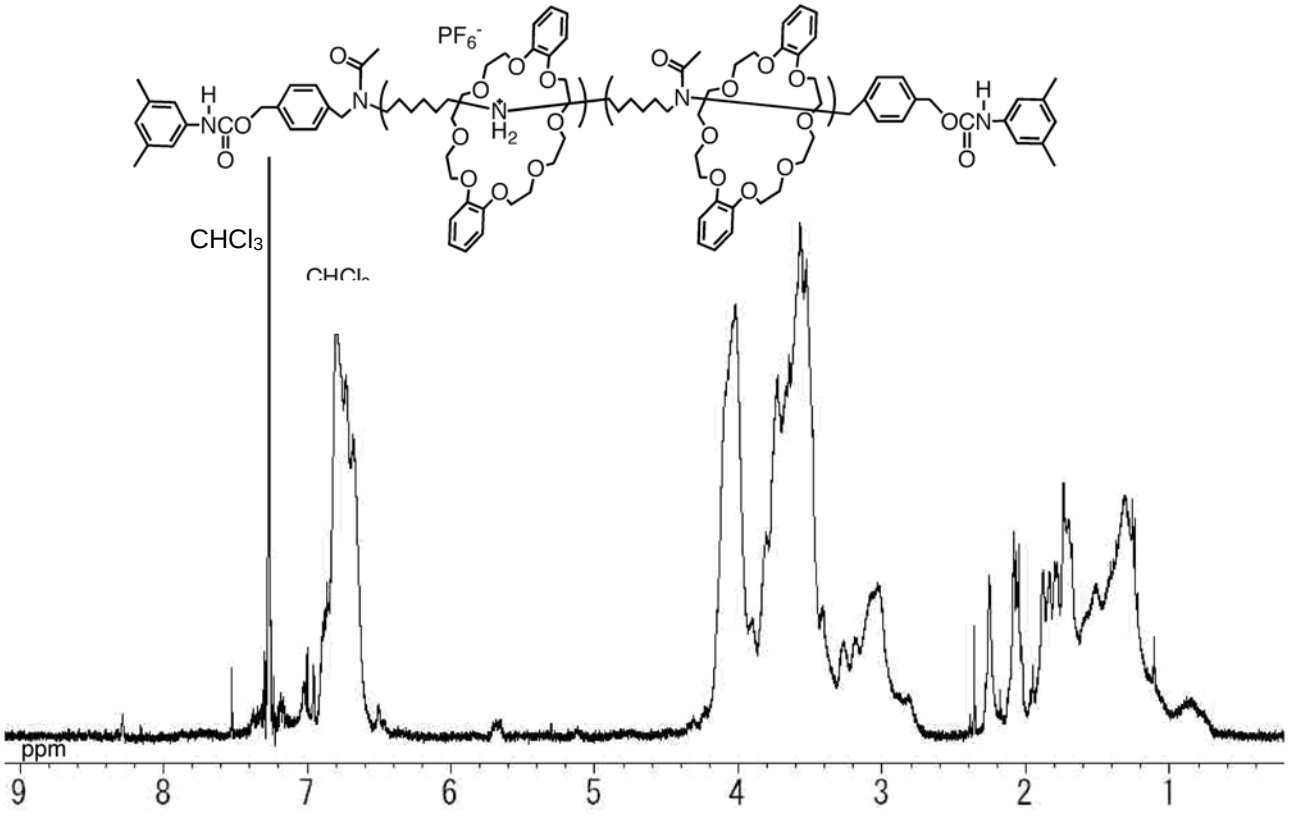


^{1}H NMR spectrum of **PRX 3 (*RR* =98)** (400 MHz, DMSO-d_6)

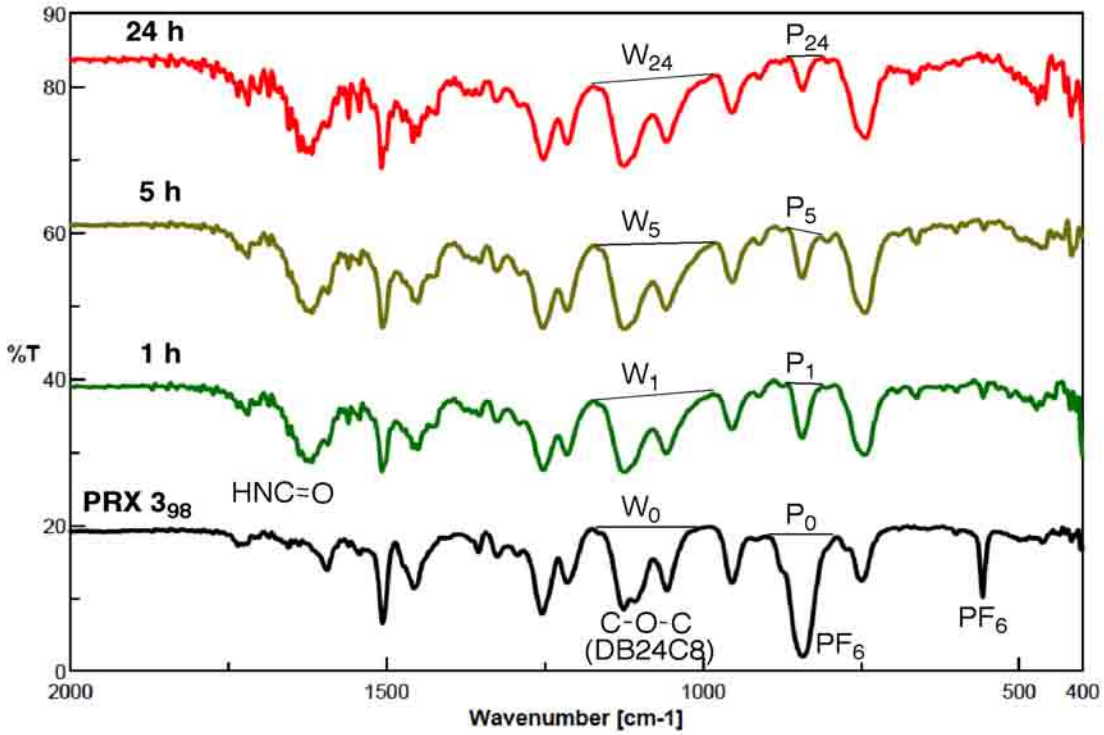


IR spectrum of **PRX 3 (*RR* =98)** (KBr)

N-acetylated **PRX 3 (*RR* =98)**

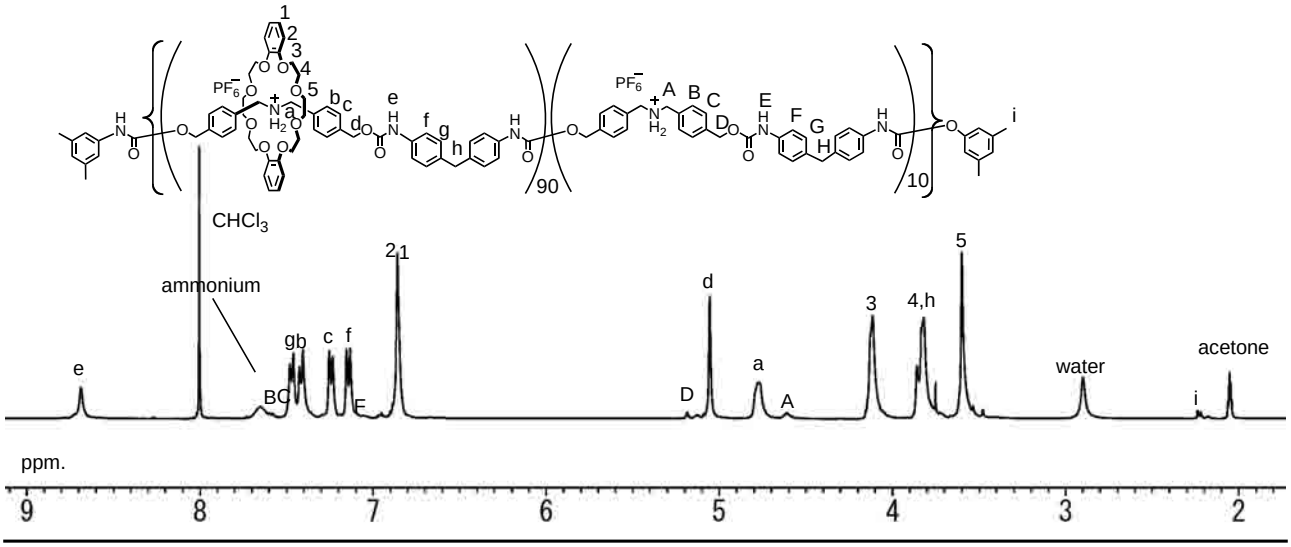


^{1}H NMR spectrum of *N*-acetylated **PRX 3Ac (*RR* =98)**(400 MHz, DMSO-d_6)

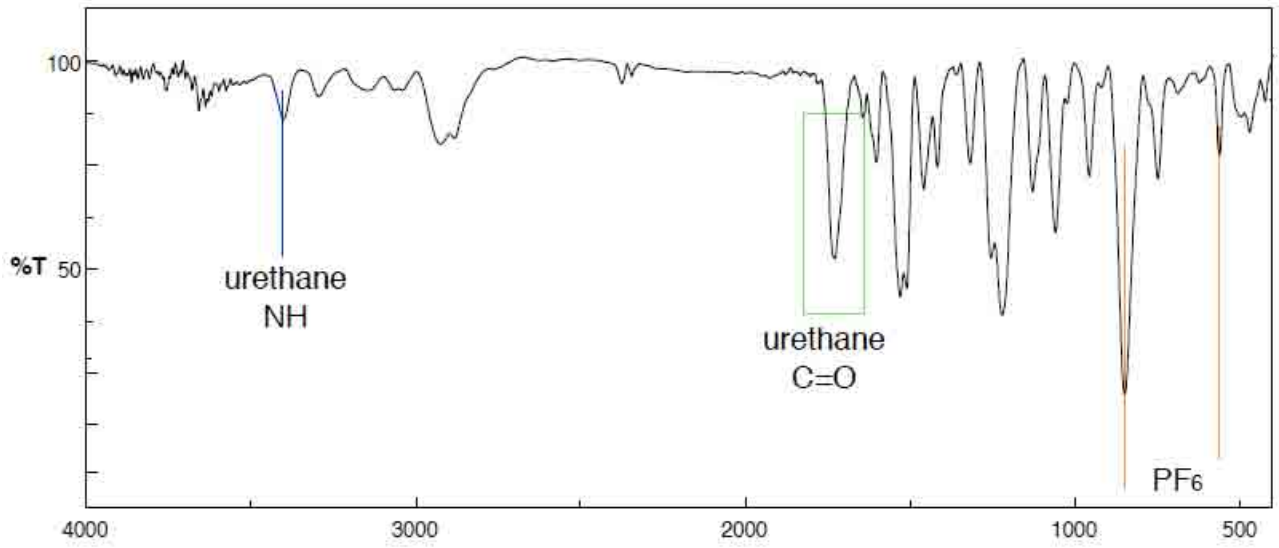


Time-dependent IR spectra of *N*-acetylation of **PRX 3 (*RR* =98)** (KBr)

PRX 6 (*RR* =95)

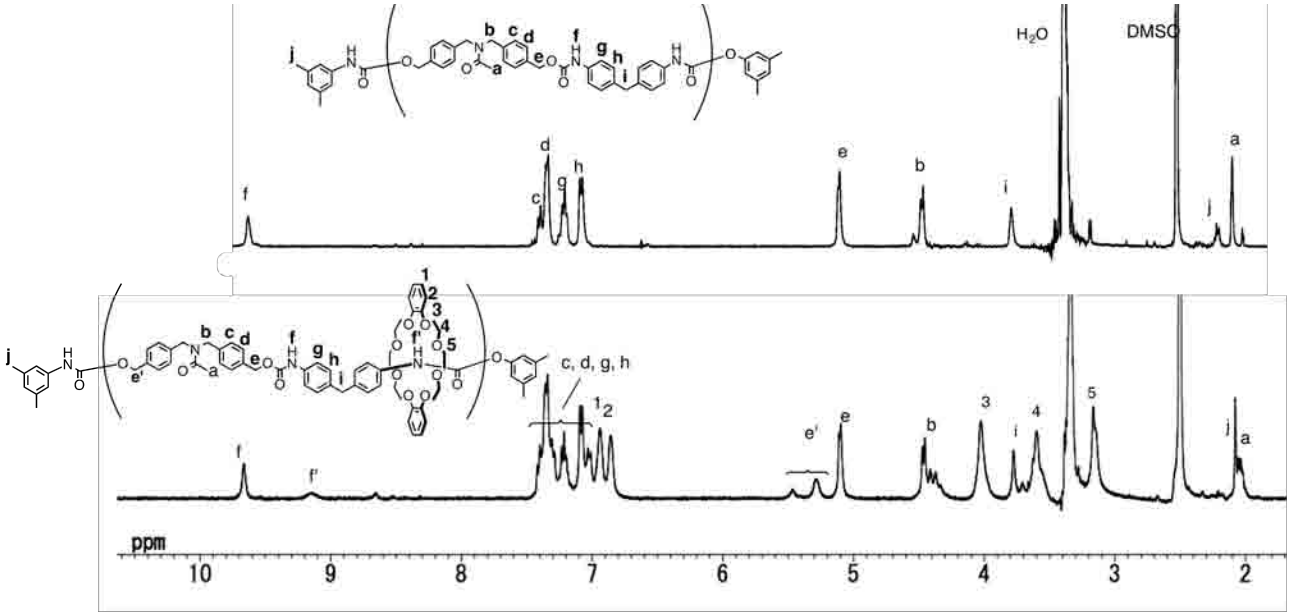


^{1}H NMR spectrum of **PRX 6 (*RR* =95)** (400 MHz, acetone-d_6)

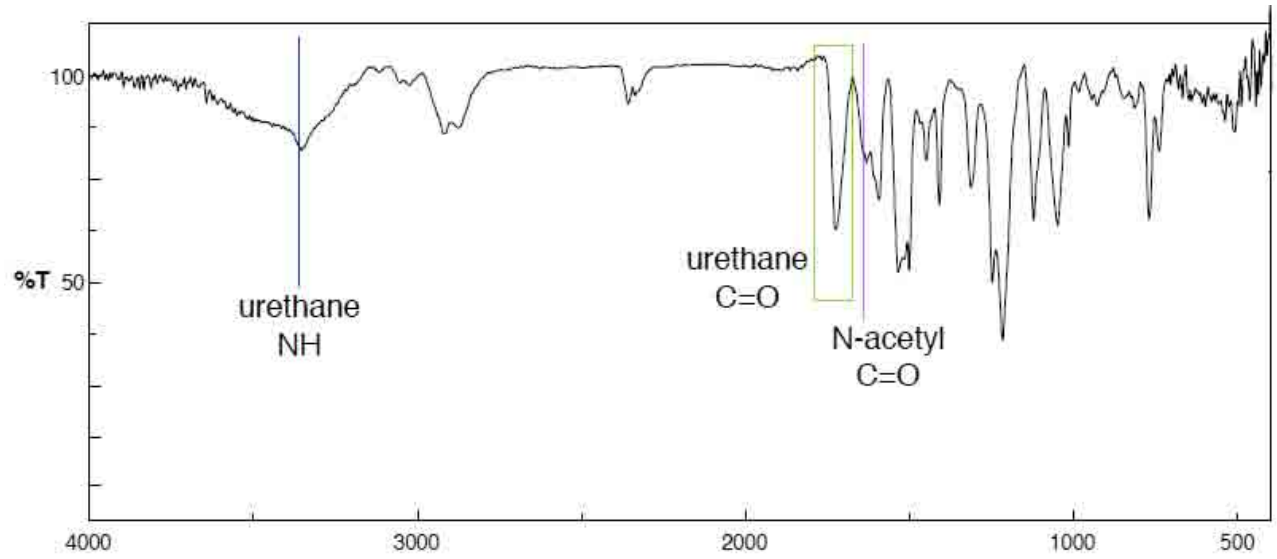


IR spectrum of **PRX 6a (*RR* =95)** (KBr)

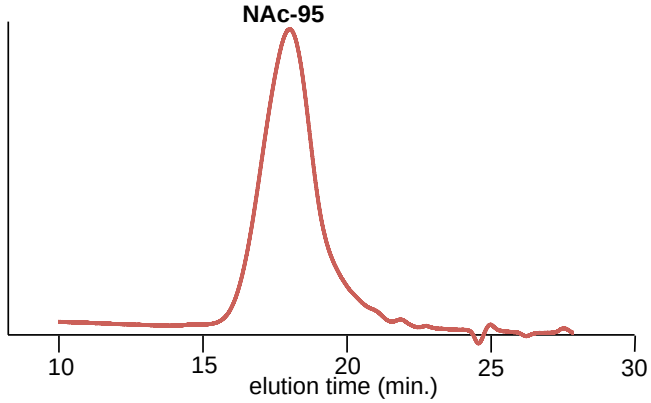
PRX 6Ac (*RR* =95)



^{1}H NMR spectrum of **PRX 6Ac (*RR* = 0 and 95)** (400 MHz, DMSO-d_6)

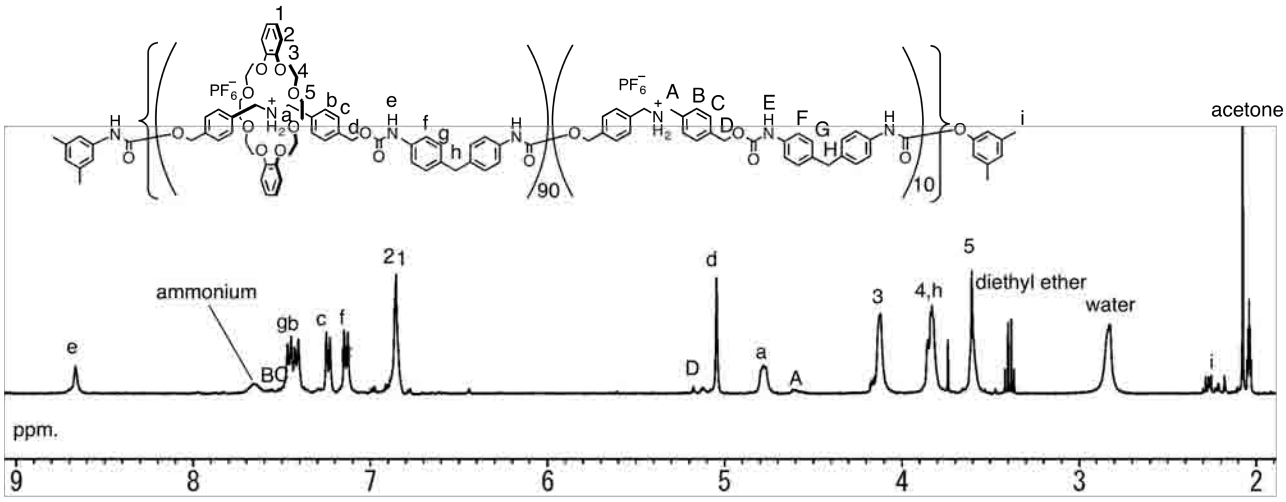


IR spectrum of **PRX 6Ac (*RR* = 95)** (KBr)

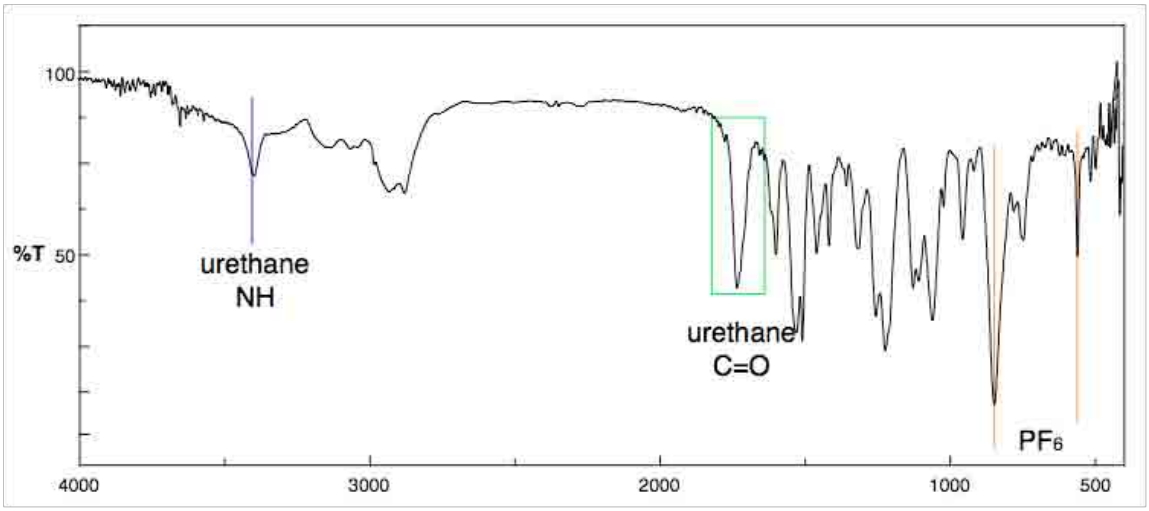


SEC chart of **PRX 6Ac (*RR* = 95)**

PRX 6 (*RR* =90)

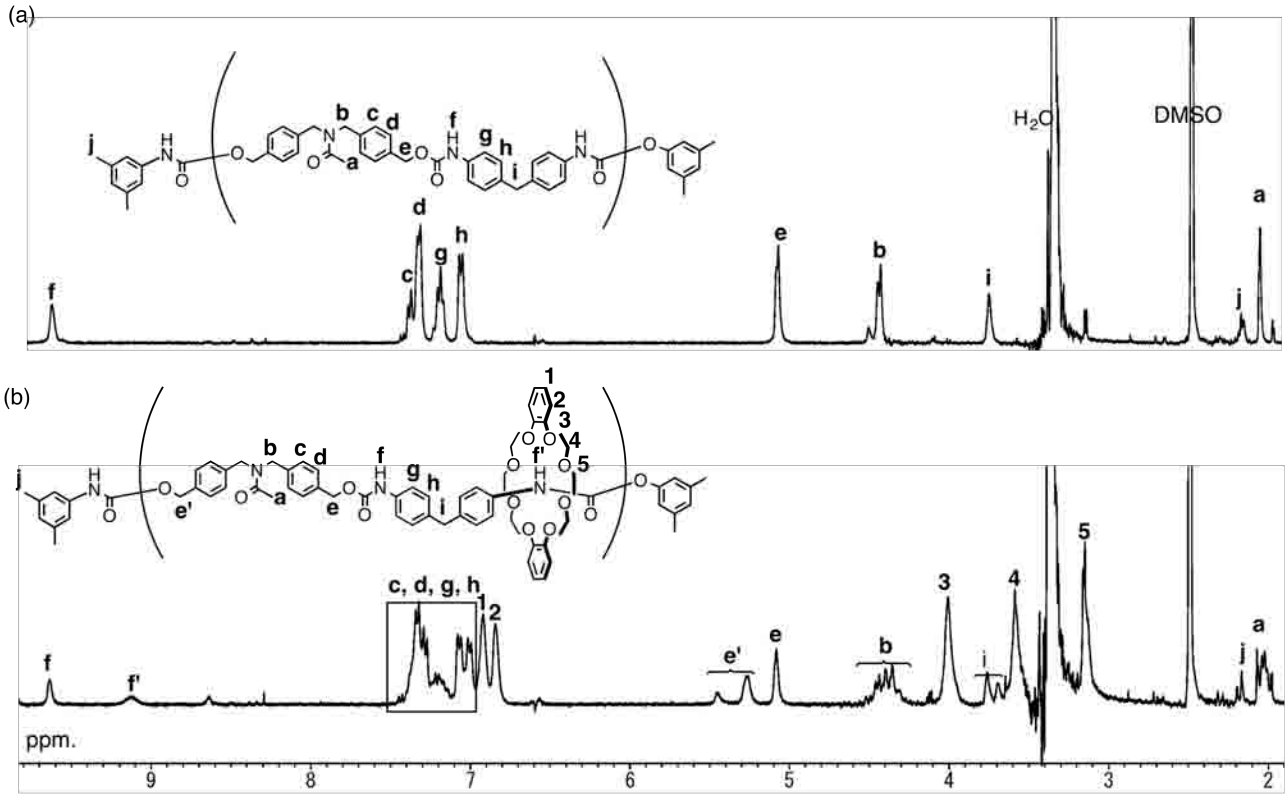


^{1}H NMR spectrum of **PRX 6 (*RR* = 90)** (400 MHz, acetone-d_6)

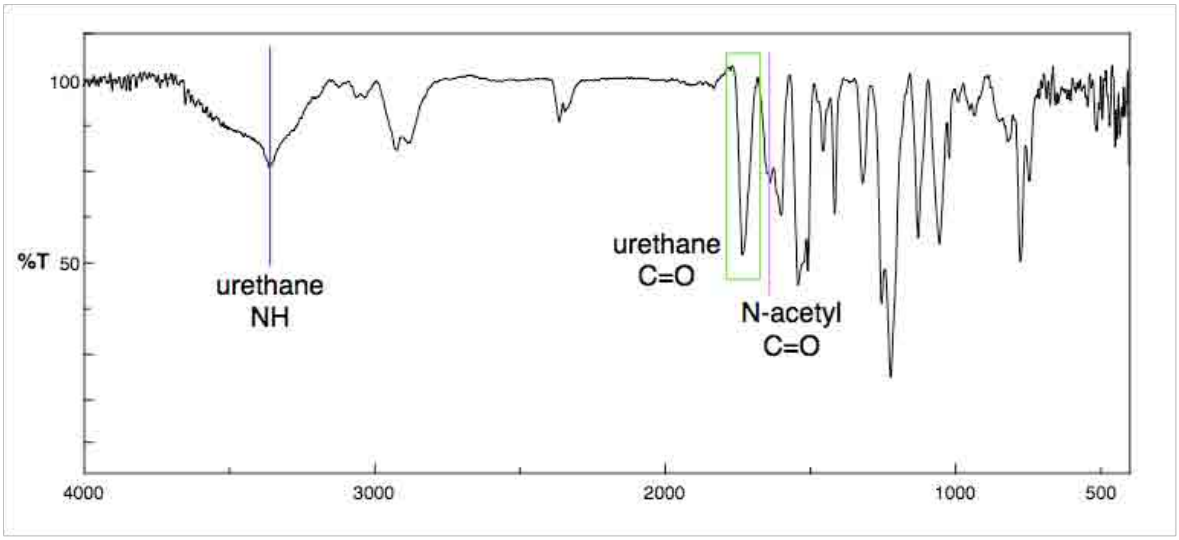


IR spectrum of **PRX 6 (*RR* = 90)** (KBr)

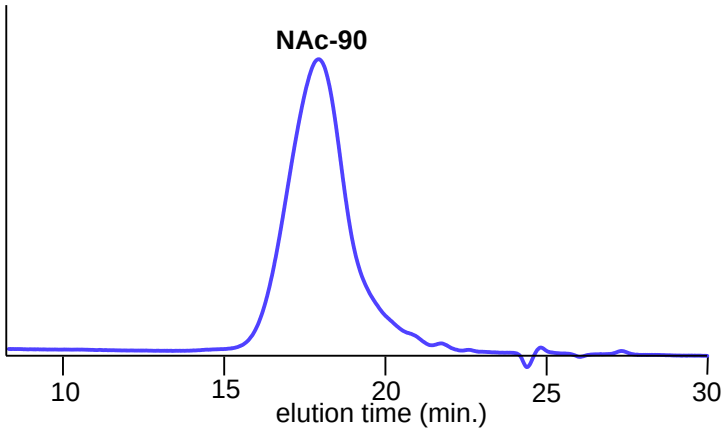
PRX 6Ac (*RR* =90)



^{1}H NMR spectrum of **PRX 6Ac (*RR* = 0 and 90)** (400 MHz, DMSO-d_6)

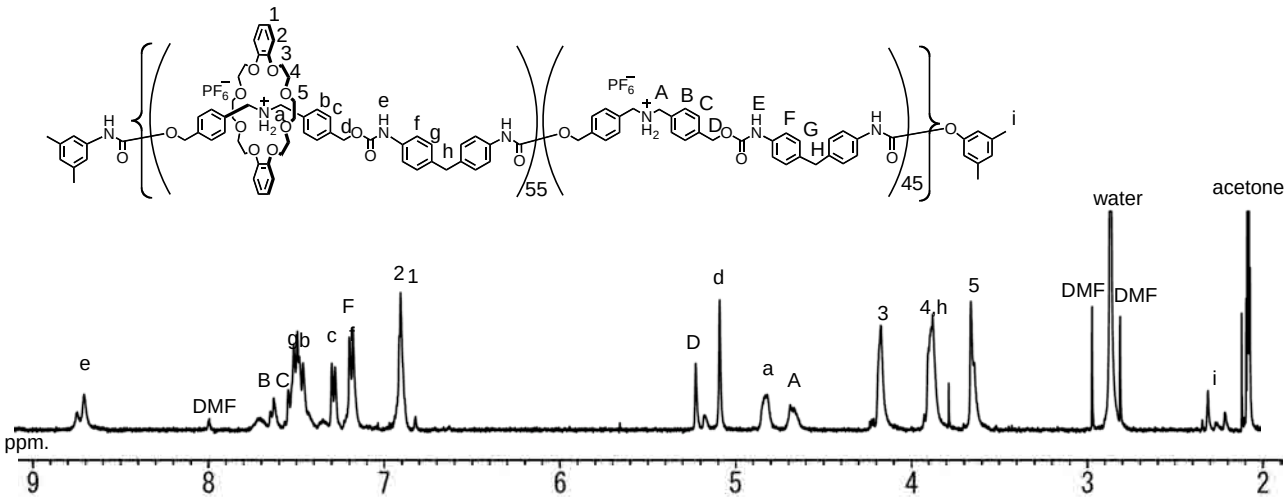


IR spectrum of **PRX 6Ac (*RR* =90)**(KBr)

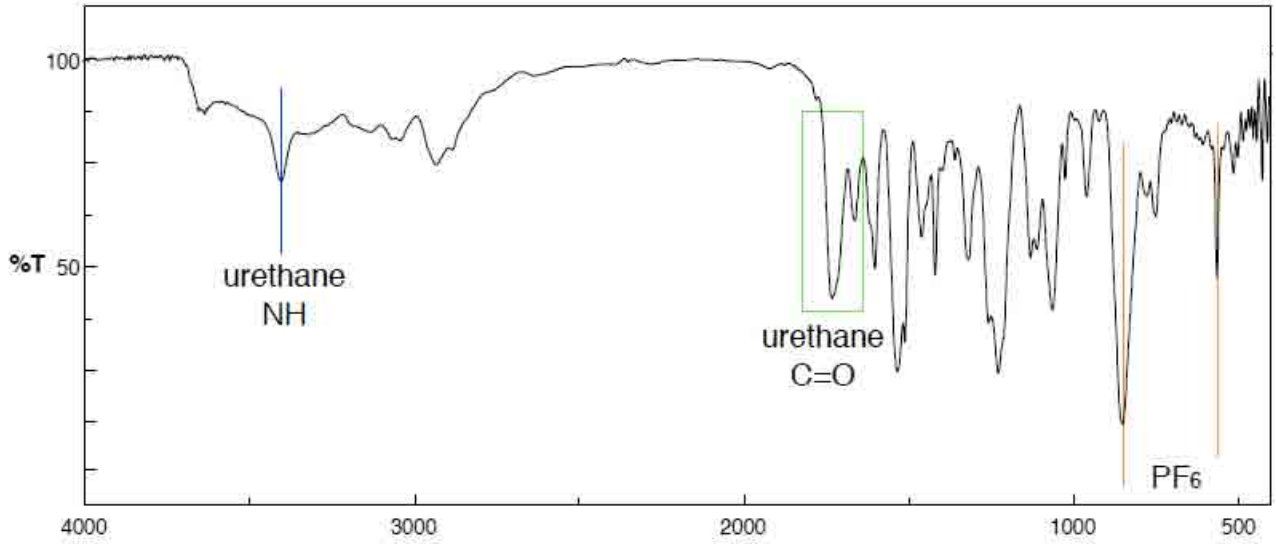


SEC chart of **PRX 6Ac (*RR* =90)**

PRX 6 (*RR* =55)

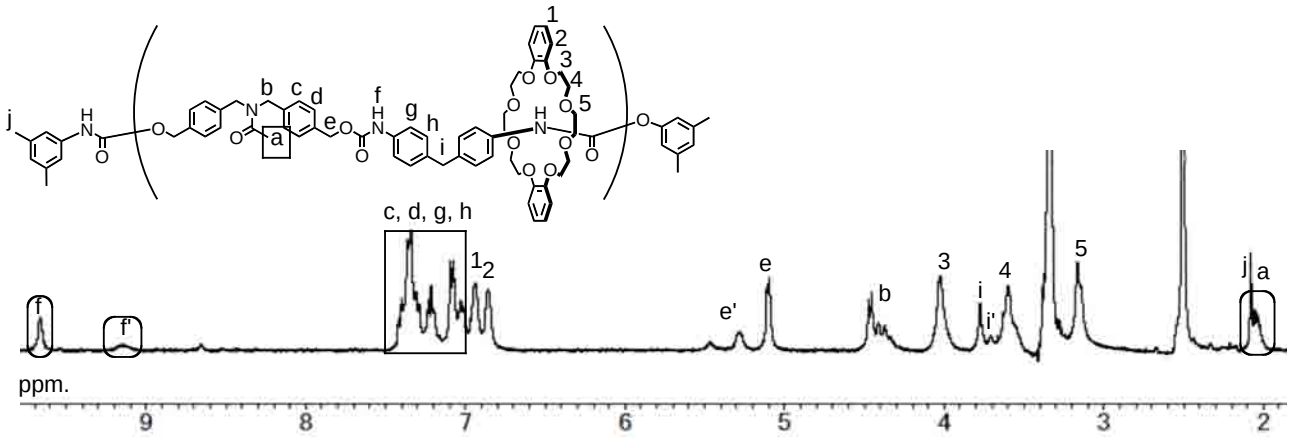


^{1}H NMR spectrum of **PRX 6 (*RR* =55)** (400 MHz, CD_3COCD_3)

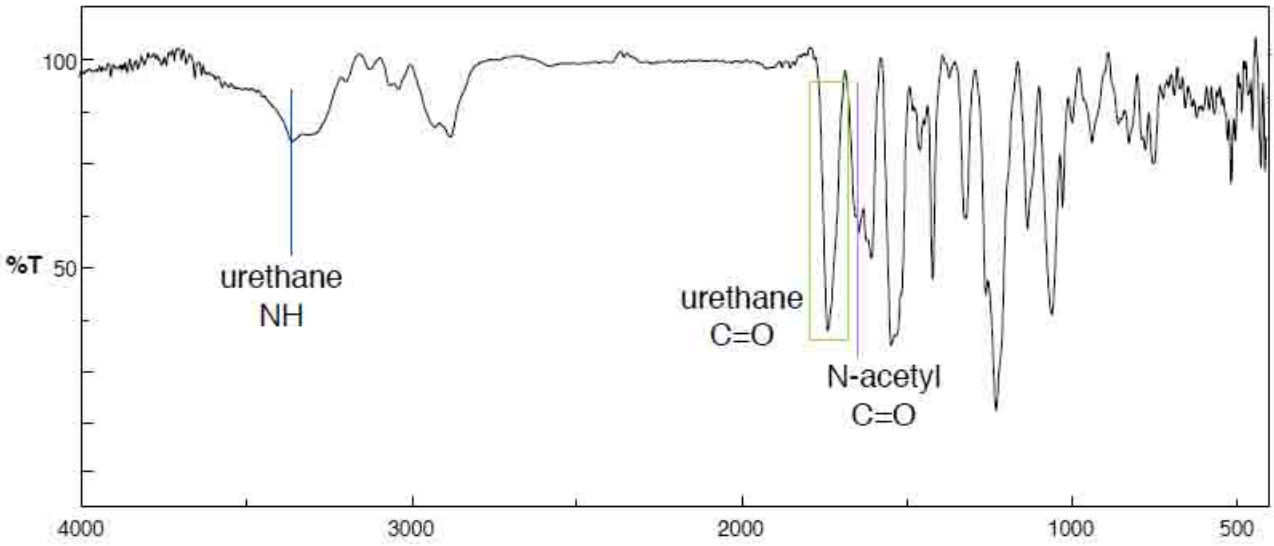


IR spectrum of **PRX 6 (*RR* =55)** (KBr)

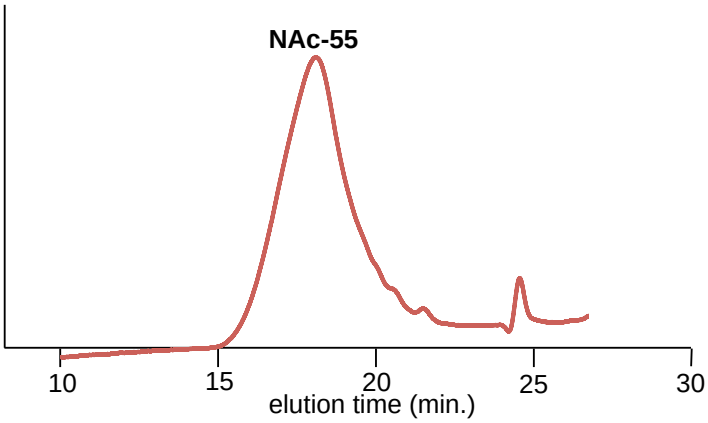
PRX 6Ac (*RR* =55)



^{1}H NMR spectrum of **PRX 6Ac (*RR* =55)** (400 MHz, DMSO-d_6)

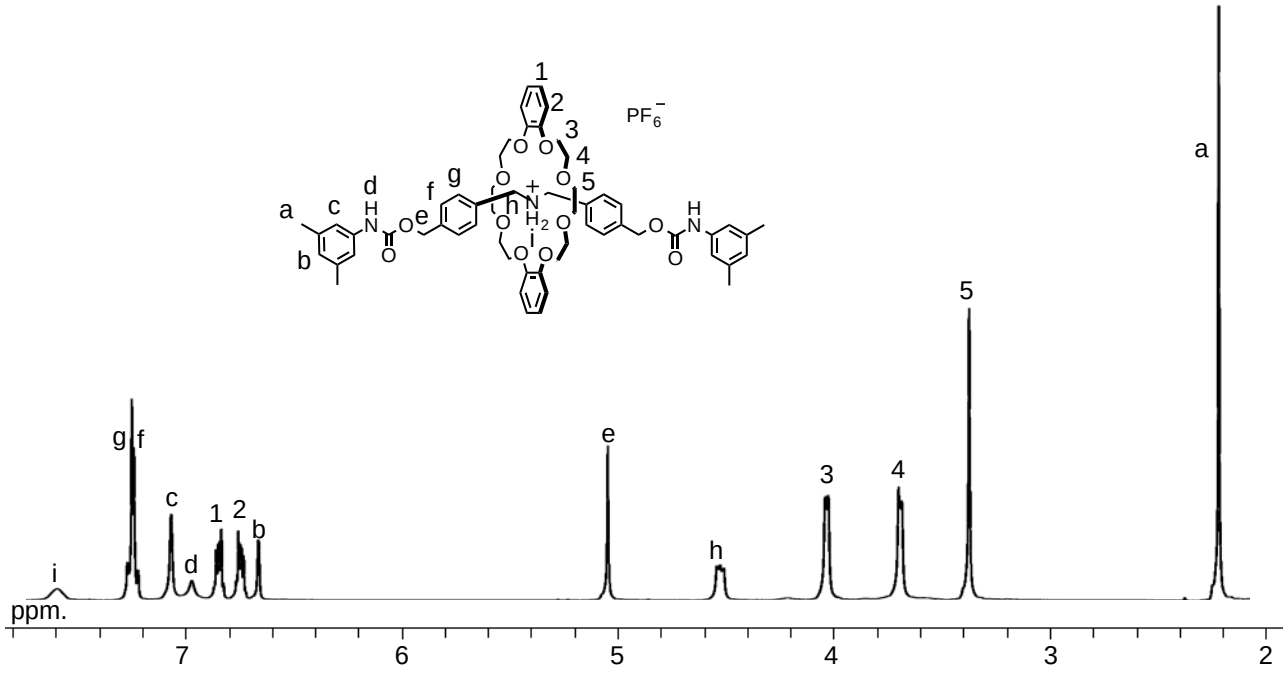


IR spectrum of **PRX 6Ac (*RR* =55)** (KBr)

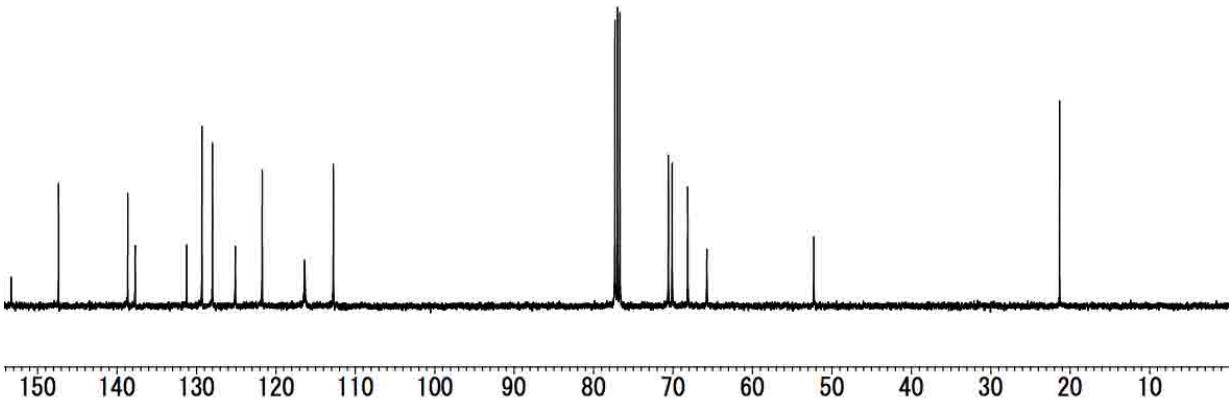


SEC chart of **PRX 6Ac (*RR* =55)**

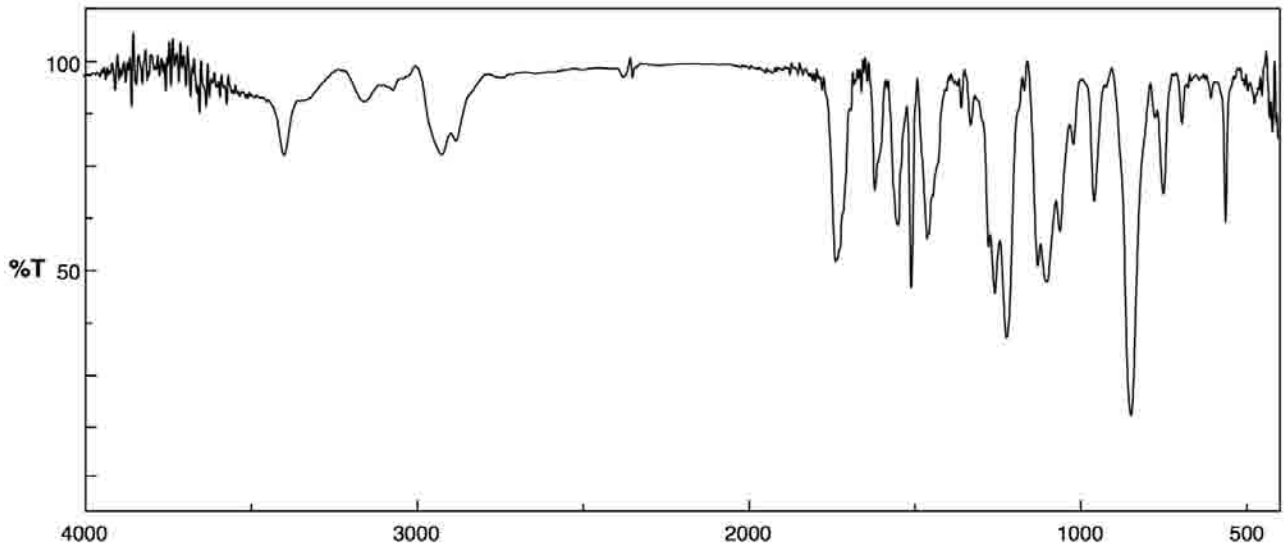
Model [2]Rotaxane S9



^{1}H NMR spectrum of **S9**(400 MHz, $CDCl_3$)

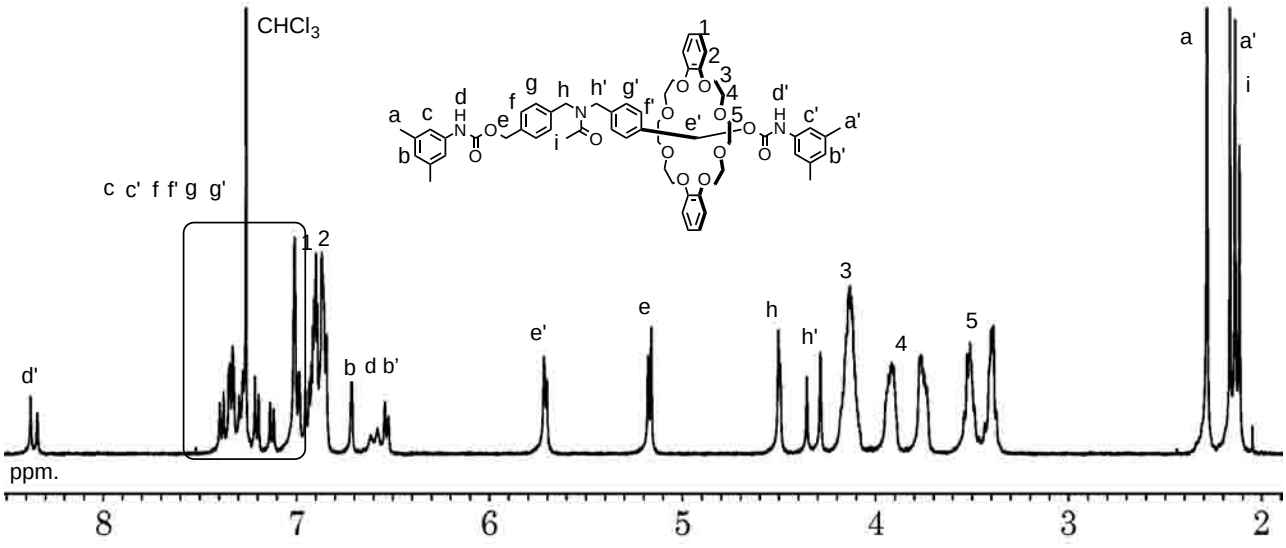


^{13}C NMR spectrum of **S9** (100 MHz, $CDCl_3$)

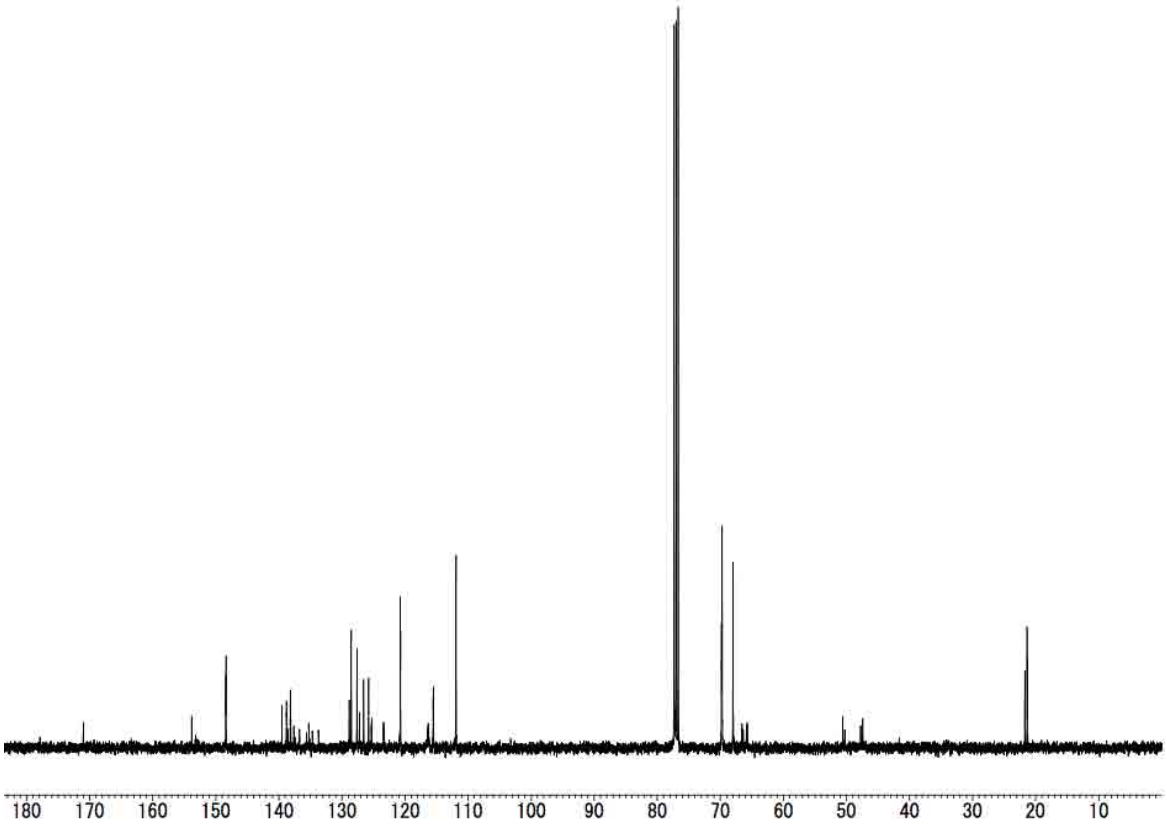


IR spectrum of **S9** (KBr)

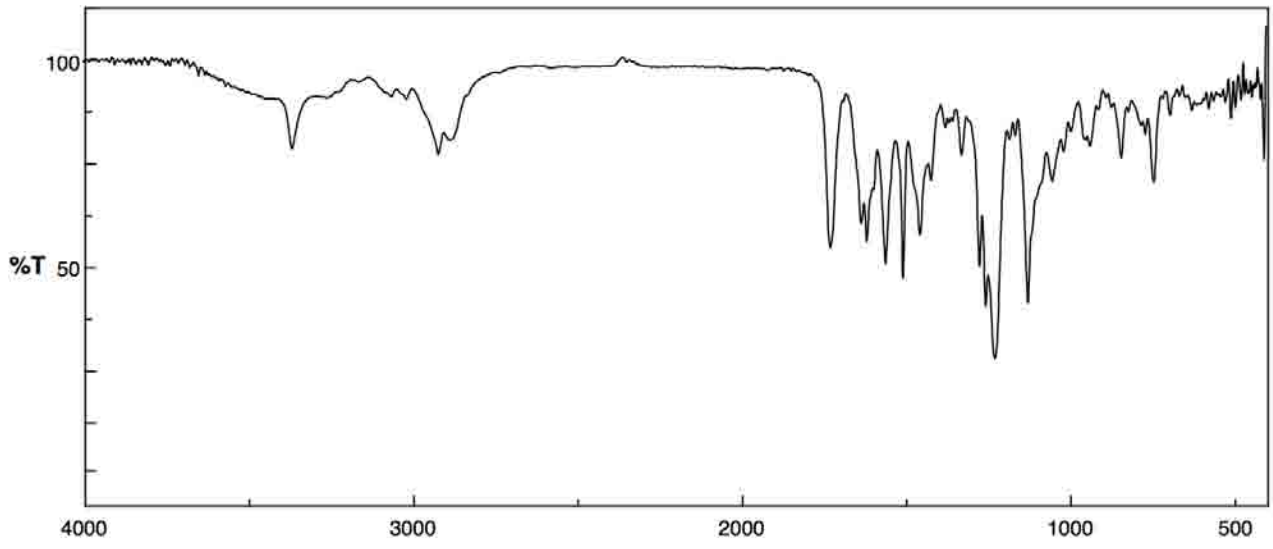
Model [2]Rotaxane S9Ac



^{1}H NMR spectrum of **S9Ac** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **S9Ac** (100 MHz, $CDCl_3$)



IR spectrum of **S9Ac** (KBr)

6. Table of thermal properties of PRXs

	T_{d5}	T_g
PRX 6 (*RR* = 55)	231	154
PRX 6Ac (*RR* = 55)	287	108
PRX 6 (*RR* = 90)	254	147
PRX 6Ac (*RR* = 90)	291	116
PRX 6 (*RR* = 0) (Axle polymer)	195	172
PRX 6Ac (*RR* = 0) (Axle polymer)	274	135
model [2]rotaxane **S9**	262	–
model [2]rotaxane **S9Ac**	286	–