

Supporting information for

**Linear–Cyclic Polymer Structural Transformation  
and Its Reversible Control using a Rational Rotaxane Strategy**

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## Experimental Section

### 1. General Methods

$^1\text{H}$  (300 MHz) and  $^{13}\text{C}$  (75 MHz) NMR spectra were recorded on a Bruker Biospin AVANCE DPX-300 spectrometer using  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$  and  $(\text{CD}_3)_2\text{SO}$  as the solvent, and tetramethylsilane was used as the internal standard. DOSY spectra were recorded on a Bruker Biospin AVANCE HD-500 spectrometer using  $\text{CDCl}_3$  as the solvent, and tetramethylsilane was used as the internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Melting points were measured on a MELTING POINT APPARATUS SMP3 (Stuart Scientific) instrument. Differential scanning calorimetry (DSC) analysis was performed with a Shimadzu DSC-60 instrument under nitrogen (heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ ). The size exclusion chromatography (SEC) was performed in DMF (10 mM LiBr, 0.7 mL / min) using a JASCO HSS-1500 system equipped with consecutive linear polystyrene gel columns (TOSOH TSK gel G4000H<sub>HR</sub> and G2500H<sub>HR</sub>) at 30 °C. The number of average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity ( $M_w/M_n$ ) of the polymers were calculated on the basis of a polystyrene calibration. MALDI-TOF MS spectra were measured with a Shimadzu AXIMA-CFR mass spectrometer. High-resolution

mass (HR-MS) FAB and ESI data were measured by the National University Corporation, Tokyo Institute of Technology, Center for Advanced Materials Analysis, on request.

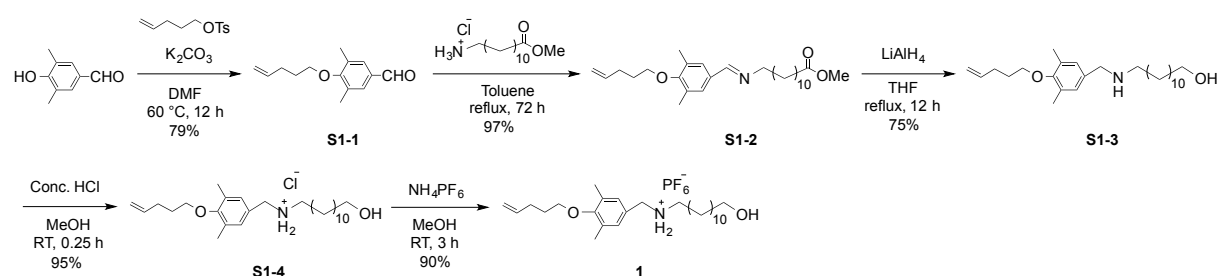
### ***Materials***

All solvents were distilled or dried before use according to the general purification procedure.<sup>[1]</sup> Commercially available reagents were used without further purification unless otherwise noted. All reactions were carried out under inert atmosphere of argon. Silica gel column chromatography was performed using silica gel N 60 (grain size 40–50  $\mu\text{m}$ ) (Kanto Chemical Co. Inc., Tokyo, Japan). GPC (Gel permeation liquid column chromatography) was performed by LC-9204 system with JAIGEL 1H-40 (Japan Analytical Industry) with  $\text{CHCl}_3$  eluent. All compounds given below bear the same formula numbers as used in the main text. Compounds **S2-1**, **S4-1**, and **S5-1** were prepared according to the literature.<sup>[2-4]</sup>

## 2. Chemical Synthesis

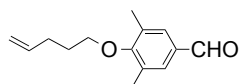
### 2.1 Synthesis of temporary stabilized [1]rotaxane end-cap agent

#### Synthesis of axle component



*Scheme S1. Synthesis of axle 1.*

#### Synthesis of aldehyde S1-1

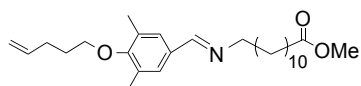


To a solution of 4-hydroxy-3,5-dimethylbenzaldehyde (8.3 g, 56 mmol) and 4-pentenyl 4-methylbenzenesulfonate (16 g, 67 mmol) in DMF (250 mL),  $K_2CO_3$  (46 g, 0.33 mol) was added at room temperature. The mixture was warmed to  $60\text{ }^\circ\text{C}$  and stirred for 12 h. The reaction mixture was cooled to room temperature and quenched by adding satd. aq.  $NaHCO_3$ . The solution was poured into a satd. aq.  $NaHCO_3$ , and the organic layer was washed with satd. aq.  $NaHCO_3$ , water, and brine. The organic layer was dried over  $MgSO_4$ , filtered, and concentrated. The crude product was purified by silica gel column

chromatography (*n*-hexane/EtOAc = 6/1,  $R_f$  = 0.5) to give aldehyde **S1-1** (9.5 g, 44 mmol, 79%) as a yellow oil.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  9.83 (s, 1H), 7.51 (s, 2H), 5.90 (m, 1H), 5.15 – 5.00 (m, 2H), 3.80 (t, 2H,  $J$  = 7 Hz), 2.31 (m, 8H), 1.93 (quint., 2H,  $J$  = 7 Hz) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  191.7, 161.8, 138.1, 132.5, 132.3, 131.0, 115.6, 71.9, 30.5, 29.9, 16.7 ppm; IR (NaCl)  $\nu$  3075, 2927, 2873, 2723, 1691, 1597, 1479, 1437, 1381, 1302, 1221, 1136, 999, 914, 737, 690  $\text{cm}^{-1}$ ; HR-MS FAB Calcd for  $\text{C}_{14}\text{H}_{19}\text{O}_2$   $[\text{M}+\text{H}]^+$ ,  $m/z$  = 219.1385; Found,  $m/z$  = 219.1385.

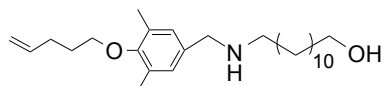
### Synthesis of imine S1-2



A mixture of **S1-1** (9.0 g, 41 mmol) and methyl 12-aminododecanoate hydrochloride (12 g, 45 mmol) in toluene (80 mL) was heated to reflux and stirred for 72 h. The reaction mixture was cooled to room temperature and evaporated. The residue was dissolved in dichloromethane and filtrated to remove the precipitates formed. The filtrate was washed with satd. aq.  $\text{NaHCO}_3$ , water, and brine, then dried over  $\text{MgSO}_4$ , filtered, and concentrated. The crude product was purified by reprecipitation from dichloromethane in *n*-hexane to give **S1-2** (17 g, 40 mmol, 96%) as a yellow oil.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  8.17 (s, 1H), 7.40 (s, 2H), 5.90 (m, 1H), 5.15 – 5.00 (m, 2H), 3.80 (t, 2H,  $J = 7$  Hz), 3.68 (s, 3H), 3.58 (dt, 2H,  $J = 7$  Hz), 2.31 (m, 10H), 1.93 (quint., 2H,  $J = 7$  Hz), 1.66 (m, 4H), 1.29 (m, 16H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  174.7, 160.8, 158.5, 138.4, 132.1, 131.7, 129.0, 115.5, 71.9, 62.2, 51.8, 34.5, 31.4, 30.6, 30.0, 29.8, 29.6, 29.5, 27.7, 25.3, 16.7 ppm; IR (NaCl)  $\nu$  3076, 2927, 2854, 1741, 1645, 1599, 1439, 1375, 1304, 1217, 1147, 1011, 914, 729, 685, 611, 548  $\text{cm}^{-1}$ .

### Synthesis of amine S1-3

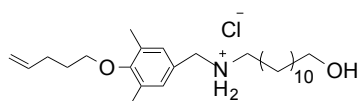


A solution of **S1-2** (17 g, 40 mmol) in dry THF (180 mL) was added dropwise to a suspension of lithium aluminum hydride (3.6 g, 96 mmol) in dry THF (200 mL) at 0 °C. The mixture was refluxed for 15 h. After addition of satd. aq.  $\text{Na}_2\text{SO}_4$  at 0 °C, the formed precipitates were filtered and extracted with THF. The combined filtrate was concentrated. The crude product was further purified by silica gel column chromatography ( $\text{CHCl}_3$  / MeOH = 10 / 1,  $R_f = 0.3$ ) to give amine **S1-3** (12 g, 30 mmol, 74%) as a white solid.

m.p. 46.5 – 47.7 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  6.97(s, 2H), 5.90 (m, 1H), 5.15 – 5.00 (m, 2H), 3.77 (t, 2H,  $J = 7$  Hz), 3.68 (s, 2H), 3.66 (t, 2H,  $J = 7$  Hz), 2.64 (t, 2H,  $J = 7$  Hz), 2.31 (m,

10H), 1.92 (quint., 2H,  $J = 7$  Hz), 1.56 (m, 4H), 1.29 (m, 16H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  155.3, 138.5, 135.8, 131.1, 129.0, 115.4, 71.9, 63.2, 54.0, 50.0, 33.2, 30.7, 30.4, 30.0, 29.8, 27.7, 26.2, 16.7 ppm; IR (NaCl)  $\nu$  3252, 3078, 3005, 2916, 2848, 1641, 1484, 1462, 1371, 1215, 1149, 1080, 1060, 993, 908, 866, 804, 723, 595  $\text{cm}^{-1}$ ; HR-MS FAB Calcd for  $\text{C}_{26}\text{H}_{46}\text{NO}_2$   $[\text{M}+\text{H}]^+$ ,  $m/z = 404.3523$ ; Found,  $m/z = 404.3529$ .

#### Synthesis of *sec*-ammonium chloride S1-4



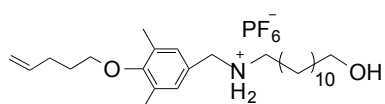
Conc. hydrochloric acid (0.60 mL, 7.20 mmol) was added to a solution of amine **S1-3** (10 g, 25 mmol) in methanol, then the reaction mixture was poured into a large amount of diethyl ether. The formed precipitates were collected by filtration and dried *in vacuo*, then a white solid **S1-4** (11 g, 24 mmol, 96%) was obtained.

m.p. 119.6 – 121.5 °C;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 298 K)  $\delta$  7.16 (s, 2H), 5.96 – 5.85 (m, 1H), 5.13 – 5.06 (m, 1H), 5.05 – 4.99 (m, 1H), 4.08 (s, 2H), 3.81 (t, 2H,  $J = 7$  Hz), 3.55 (t, 2H,  $J = 7$  Hz), 3.01 (t, 2H,  $J = 8$  Hz), 2.35 – 2.28 (m, 8H), 1.91 (quint., 2H,  $J = 8$  Hz), 1.71 (quint., 2H,  $J = 8$  Hz), 1.54 (quint., 2H,  $J = 7$  Hz), 1.42 – 1.17 (m, 16H) ppm;  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 298 K)  $\delta$  157.3, 138.3, 132.0, 130.6, 126.7, 114.6, 71.6, 62.0, 51.0, 32.7, 30.3, 29.76, 29.73, 29.69,



29.64, 29.62, 29.5, 29.2, 26.6, 26.1, 26.0, 15.5 ppm; IR (NaCl)  $\nu$  3401, 3244, 2919, 2849, 1668, 1471, 1306, 1220, 1160, 1059, 991, 908, 883, 723  $\text{cm}^{-1}$ ; ESI-TOF-MS Calcd for  $\text{C}_{26}\text{H}_{46}\text{NO}_2$   $[\text{M}-\text{Cl}]^+$ ,  $m/z = 404.3523$ ; Found,  $m/z = 404.3526$ .

### Synthesis of *sec*-ammonium hexafluorophosphate 1



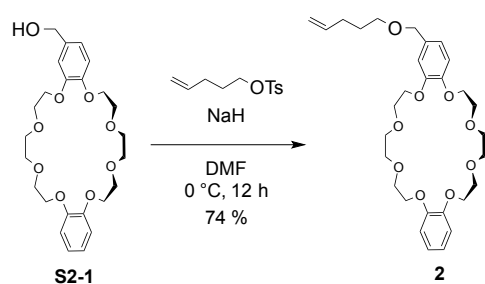
A satd. aq. ammonium hexafluorophosphate was added to the solution of **S1-4** (3.2 g, 7.20 mmol) in the least amount of methanol until the precipitates were formed. The precipitates were collected by filtration, washed with water, and dried *in vacuo* to give the ammonium hexafluorophosphate **S1-5** (2.7 g, 4.9 mmol, 68%) as a white solid.

m.p. 124.2 – 125.6  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 298 K)  $\delta$  7.15 (s, 2H), 5.96 – 5.85 (m, 1H), 5.13 – 5.06 (m, 1H), 5.05 – 4.99 (m, 1H), 4.07 (s, 2H), 3.81 (t, 2H,  $J = 6$  Hz), 3.55 (t, 2H,  $J = 7$  Hz), 3.00 (t, 2H,  $J = 8$  Hz), 2.35 – 2.28 (m, 8H), 1.91 (quint., 2H,  $J = 7$  Hz), 1.69 (quint., 2H,  $J = 7$  Hz), 1.54 (quint., 2H,  $J = 7$  Hz), 1.42 – 1.25 (m, 16H) ppm;  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 298 K)  $\delta$  157.3, 138.3, 132.1, 130.5, 126.7, 114.5, 71.6, 62.0, 51.0, 32.7, 30.3, 29.74, 29.72, 29.67, 29.60, 29.5, 29.2, 26.5, 26.1, 25.9, 15.5 ppm; IR (NaCl)  $\nu$  3403, 3262, 2918, 2852, 1642,

1585, 1473, 1420, 1306, 1224, 1161, 1057, 885, 847, 559  $\text{cm}^{-1}$ ; ESI-TOF-MS Calcd for

$\text{C}_{26}\text{H}_{46}\text{NO}_2$   $[\text{M}-\text{PF}_6]^+$ ,  $m/z = 404.3523$ ; Found,  $m/z = 404.3529$ .

### Synthesis of wheel component



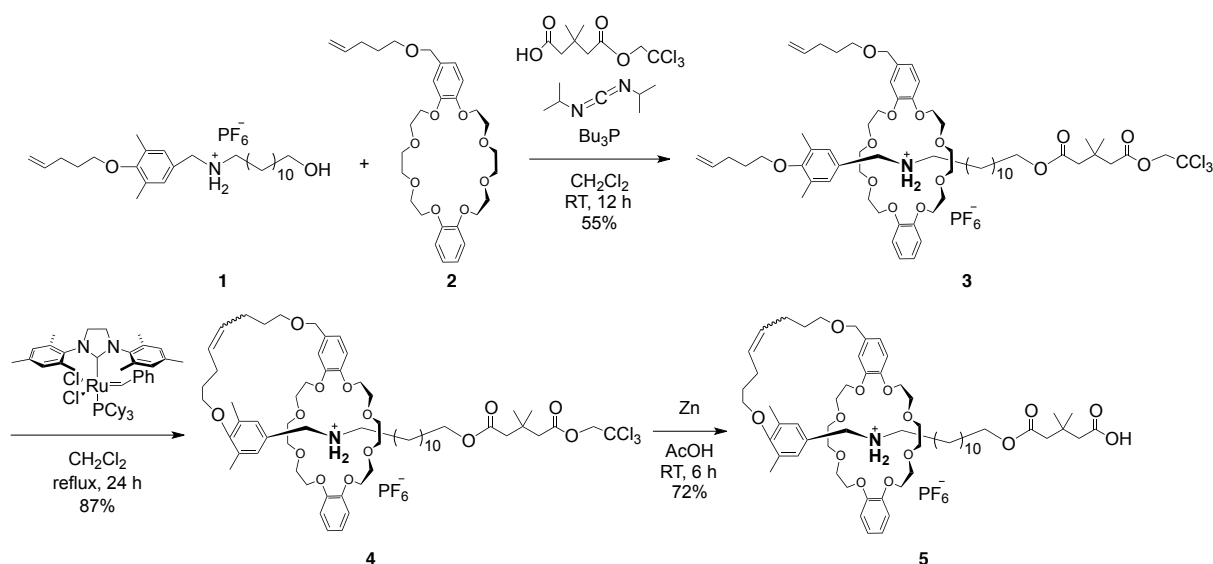
### *Scheme S2. Synthesis of 2.*

A solution of monohydroxymethyl dibenzo-24-crown-8-ether **S2-1**<sup>[2]</sup> (3.3 g, 6.9 mmol) in dry DMF (10 mL) was added to a suspension of sodium hydride (1.6 g, 69 mmol) in dry DMF (20 mL) at 0 °C, and the mixture was stirred for 1 h. 4-Pentenyl 4-methylbenzenesulfonate (5.0 g, 21 mmol) in dry DMF (10 mL) was added dropwise to the solution and stirred at 0 °C for 12 h. After addition of methanol (excess amount) at 0 °C, the solvent was removed under reduced pressure. The residue was dissolved in EtOAc and washed successively with 3M HCl aq., satd. aq.  $\text{NaHCO}_3$ , water, and brine, then dried over  $\text{MgSO}_4$ , filtered, and concentrated. The crude product was purified by silica gel column

chromatography (eluent; EtOAc,  $R_f = 0.4$ ) to give a crown ether **2** (2.8 g, 5.1 mmol, 74%) as a white solid.

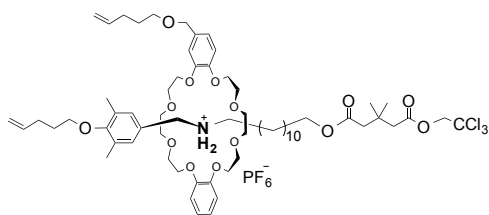
m.p. 56.2 – 58.0 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 298 K)  $\delta$  6.92 - 6.84 (br, 7H, Ar), 5.90 - 5.76 (m, 1H), 5.07 – 4.94 (m, 2H), 4.42 (s, 2H), 4.20 - 4.14 (m, 8H), 3.96 - 3.91 (m, 8H), 3.87 - 3.83 (br, 8H), 3.46 (t, 2H,  $J = 7$  Hz), 2.15 (q, 2H,  $J = 7$  Hz), 1.71 (quint., 2H,  $J = 7$  Hz) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 298 K)  $\delta$  149.3, 148.7, 138.7, 132.2, 121.8, 121.1, 115.1, 114.5, 114.1, 114.0, 73.1, 71.7, 70.3, 69.94, 69.87, 69.80, 30.8, 29.3 ppm; IR (NaCl)  $\nu$  3064, 2928, 2867, 2799, 1594, 1519, 1455, 1430, 1356, 1335, 1260, 1177, 1139, 1093, 1059, 964, 920, 849, 824, 808, 782, 735, 592  $\text{cm}^{-1}$ ; HR-MS FAB Calcd for  $\text{C}_{30}\text{H}_{42}\text{O}_9$   $[\text{M}+\text{H}]^+$ ,  $m/z = 546.2829$ ; Found,  $m/z = 546.2826$ .

### Synthesis of temporary stabilized [1]rotaxane end-cap agent



**Scheme S3.** Synthesis of temporary stabilized [1]rotaxane end-cap agent **5**.

### Synthesis of [2]rotaxane **3**

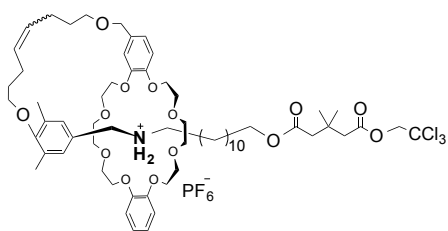


To a solution of *sec*-ammonium salt **1** (2.0 g, 3.6 mmol), crown ether **2** (2.6 g, 4.7 mmol), and 3,3-dimethylglutaric acid mono 2,2,2-trichloroethyl ester (4.2 g, 15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added PBU<sub>3</sub> (0.90 mL, 3.6 mmol) and *N,N'*-diisopropylcarbodiimide (2.8 mL, 18 mmol) at room temperature, and the solution was stirred for 12 h. The reaction mixture was then poured into *n*-hexane (500 mL), and the precipitates were collected by decantation and purified by SiO<sub>2</sub> column chromatography (CHCl<sub>3</sub> / EtOAc = 1 / 1) and recycling preparative GPC to give [2]rotaxane **3** (3.7 g, 2.7 mmol, 75%) as a yellow foam.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K) δ 7.10 (br, 2H), 7.00 (s, 2H), 6.97 - 6.80 (m, 7H), 5.96 - 5.76 (m, 2H), 5.14 - 4.95 (m, 4H), 4.75 (s, 2H), 4.50 - 4.45 (m, 2H), 4.43 (s, 2H), 4.30 - 4.04 (m, 10H), 3.96 - 3.75 (m, 8H), 3.73 - 3.41 (m, 12H), 3.10 (br, 2H), 2.63 (s, 2H), 2.47 (s, 2H), 2.30 (q, 2H, *J* = 6 Hz), 2.19 - 2.10 (m, 8H), 1.90 (quint., 2H, *J* = 6 Hz), 1.77 - 1.57 (m, 4H), 1.49 - 0.96 (m, 26H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) δ 172.2, 170.6, 156.9, 147.8, 147.3, 138.6, 138.4, 132.7, 131.7, 130.5, 127.9, 122.2, 121.3, 115.5, 115.1, 113.0, 112.8, 112.5, 95.3, 74.3, 72.8, 72.0, 71.1, 70.6, 70.1, 68.8, 68.6, 64.8, 52.3, 49.3, 45.5, 45.1, 33.1, 30.7, 30.6, 29.9,

29.85, 29.78, 29.65, 29.4, 29.3, 29.0, 28.1, 27.1, 26.9, 26.4, 16.7 ppm; IR (NaCl)  $\nu$  3645, 3163, 3074, 2928, 2855, 1750, 1729, 1640, 1594, 1506, 1453, 1254, 1221, 1125, 1108, 1058, 954, 842, 743, 557  $\text{cm}^{-1}$ ; HR-MS FAB Calcd for  $\text{C}_{65}\text{H}_{99}\text{NO}_{14}\text{Cl}_3$   $[\text{M}-\text{PF}_6]^+$ ,  $m/z = 1222.6131$ ;  
Found,  $m/z = 1222.6024$ .

### Synthesis of [1]rotaxane **4**

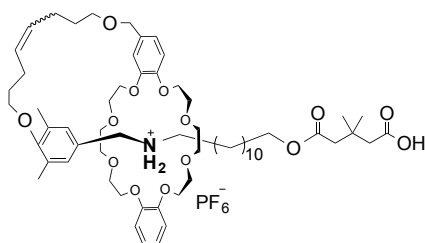


To a solution of **3** (1.5 g, 1.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (110 mL), Grubbs catalyst 2<sup>nd</sup> generation (9.3 mg, 0.11 mmol) was added, evacuated three times and filled with argon. The solution was heated to reflux and stirred for 24 h. The reaction mixture was cooled to room temperature and evaporated. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and poured into *n*-hexane (300 mL), and the precipitates were collected by decantation and purified by silica gel column chromatography ( $\text{CHCl}_3$  / EtOAc = 1 / 1) and preparative GPC to give rotaxane **4** (1.3 g, 1.0 mmol, 87%) as a brown foam.

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  172.1, 170.5, 156.6, 156.2, 148.0, 147.9, 147.8, 147.2, 146.5, 145.7, 132.7, 132.4, 131.3, 131.1, 130.7, 130.6, 130.02, 129.95, 129.8, 122.1, 121.7, 121.55,

121.50, 120.4, 119.7, 112.47, 112.40, 111.53, 111.47, 111.3, 110.4, 95.3, 74.2, 72.7, 72.1, 71.9, 71.7, 71.6, 71.1, 70.93, 70.86, 70.6, 69.8, 69.3, 68.6, 68.1, 67.9, 67.8, 67.6, 64.7, 52.2, 49.0, 45.5, 45.0, 33.0, 31.1, 29.9, 29.8, 29.6, 29.5, 29.0, 28.6, 28.0, 27.3, 27.1, 26.8, 26.3, 24.4, 23.8, 16.8, 16.3 ppm; IR (NaCl)  $\nu$  3161, 3072, 2927, 2856, 1749, 1730, 1594, 1506, 1454, 1354, 1254, 1221, 1107, 1058, 956, 843, 749, 557  $\text{cm}^{-1}$ ; MALDI-TOF-MS Calcd for  $\text{C}_{63}\text{H}_{95}\text{Cl}_3\text{NO}_{14} [\text{M}-\text{PF}_6]^+$ ,  $m/z = 1194.58$  ; Found:  $m/z = 1194.60$ .

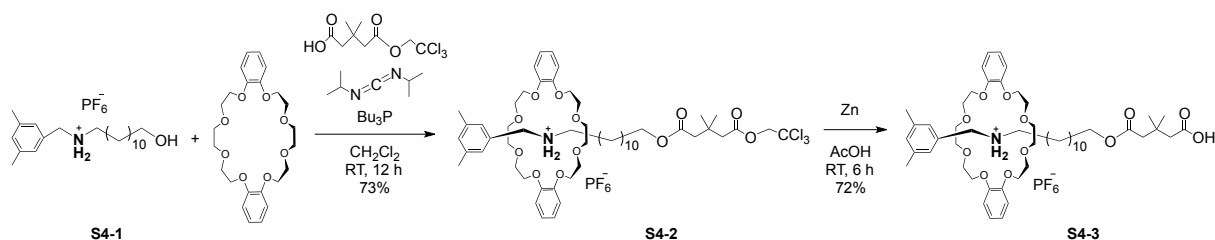
### Synthesis of temporary stabilized [1]rotaxane 5



To a solution of rotaxane 4 (1.2 g, 0.89 mmol) in AcOH (9.0 mL) was added activated Zn powder (0.58 g, 8.9 mmol) at room temperature, and the solution was stirred for 6 h. The reaction mixture was filtered, poured into  $\text{CH}_2\text{Cl}_2$ , and washed successively with water, satd. aq.  $\text{NaHCO}_3$ , and brine. The organic layer was dried over  $\text{MgSO}_4$ , filtered and concentrated. The crude product was purified by preparative GPC ( $\text{CHCl}_3$ ) to give [1]rotaxane 5 (0.98 g, 0.80 mmol, 90%) as a yellow foam.

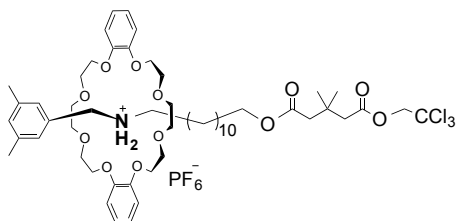
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  175.8, 173.1, 156.7, 156.2, 148.03, 147.96, 147.88, 147.3, 146.63, 146.60, 145.8, 132.7, 132.4, 131.3, 131.2, 130.7, 130.6, 130.5, 130.1, 130.0, 129.8, 127.3, 127.0, 121.8, 121.7, 121.6, 121.5, 120.5, 119.8, 112.5, 112.4, 111.55, 111.50, 111.4, 110.4, 72.7, 72.2, 72.0, 71.7, 71.6, 71.12, 71.09, 70.95, 70.89, 70.6, 69.8, 69.3, 68.1, 67.9, 67.8, 67.7, 67.6, 64.6, 52.3, 49.1, 47.1, 46.0, 33.0, 31.1, 29.8, 29.7, 29.5, 29.0, 28.6, 27.9, 27.3, 27.0, 26.3, 24.4, 23.9, 16.8, 16.3 ppm; IR (NaCl)  $\nu$  3161, 3068, 2926, 2856, 1727, 1591, 1506, 1454, 1254, 1221, 1124, 1106, 1059, 955, 842, 751, 557  $\text{cm}^{-1}$ ; MALDI-TOF-MS Calcd for  $\text{C}_{61}\text{H}_{94}\text{NO}_{14} [\text{M}-\text{PF}_6]^+$ ,  $m/z = 1064.67$  ; Found:  $m/z = 1064.61$ .

## 2.2 Synthesis of temporary stabilized [2]rotaxane end-cap agent S4-3



**Scheme S4.** Synthesis of temporary stabilized [2]rotaxane end cap agent S4-3.

## Synthesis of [2]rotaxane S4-2



To a solution of ammonium hexafluorophosphate **S4-1**<sup>[3]</sup> (1.0 g, 2.2 mmol), dibenzo-24-crown-8-ether (1.3 g, 2.8 mmol), and 3,3-dimethylglutaric acid mono 2,2,2-trichloroethyl ester (2.5 g, 8.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (9.0 mL) was added PBU<sub>3</sub> (0.53 mL, 2.2 mmol) and *N,N'*-diisopropylcarbodiimide (1.7 mL, 11 mmol) at room temperature, and the solution was stirred for 12 h. The reaction mixture was then poured into *n*-hexane (500 mL), and the precipitates were collected by decantation and purified by SiO<sub>2</sub> column chromatography (CHCl<sub>3</sub> / EtOAc = 1 / 1) and recycling preparative GPC to give rotaxane **S4-2** (1.9 g, 1.6 mmol, 73%) as a yellow foam.

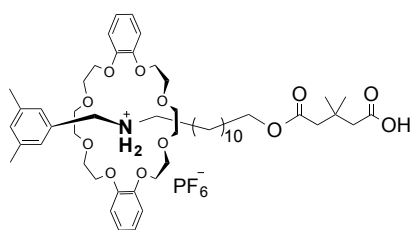
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K)  $\delta$  7.11 (br, 2H), 7.00 (s, 2H), 6.96 - 6.85 (m, 9H), 4.75 (s, 2H), 4.55 - 4.50 (m, 2H), 4.29 - 4.04 (m, 10H), 3.90 - 3.70 (m, 8H), 3.68 - 3.40 (m, 8H), 3.10 (br, 2H), 2.62 (s, 2H), 2.47 (s, 2H), 2.20 (m, 6H), 1.69 - 1.49 (m, 4H), 1.45 - 0.94 (m, 22H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K)  $\delta$  172.2, 170.6, 147.9, 138.7, 132.7, 131.0, 127.7, 122.2, 113.1, 95.3, 74.3, 71.1, 70.6, 68.7, 64.8, 52.6, 49.4, 45.6, 45.1, 33.1, 29.9, 29.8, 29.7, 29.6, 29.3, 29.0, 28.3, 28.1, 27.3, 27.0, 26.8, 26.4, 24.1, 23.9, 23.7, 23.6, 21.6, 13. ppm; IR (NaCl)  $\nu$  3631, 3168,



2929, 2859, 1750, 1727, 1594, 1505, 1453, 1253, 1212, 1123, 1108, 1057, 953, 841, 742, 557

$\text{cm}^{-1}$ ; HR-MS FAB Calcd for  $\text{C}_{54}\text{H}_{81}\text{NO}_{12}\text{Cl}_3$   $[\text{M}-\text{PF}_6]^+$ ,  $m/z = 1040.4819$ ; Found,  $m/z = 1040.4824$ .

### Synthesis of temporary stabilized [2]rotaxane end-cap agent S4-3



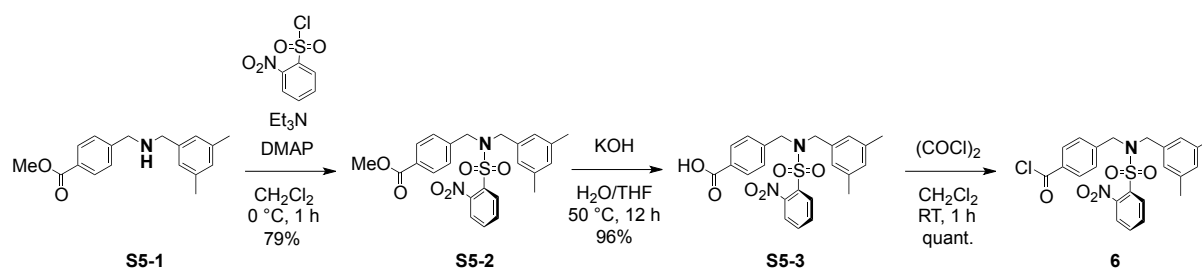
To a solution of [2]rotaxane **S4-2** (1.5 g, 1.3 mmol) in AcOH (13 mL) was added activated Zn powder (0.85 g, 13 mmol) at room temperature, and the solution was stirred for 6 h. The reaction mixture was filtered, poured into  $\text{CH}_2\text{Cl}_2$ , and washed successively with water, satd. aq.  $\text{NaHCO}_3$ , and brine. The organic layer was dried over  $\text{MgSO}_4$ , filtered, and concentrated. The crude product was purified by preparative GPC to give rotaxane **S4-3** (0.99 g, 0.93 mmol, 72%) as a yellow foam.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  7.13 (br, 2H), 6.99 (s, 2H), 6.96 - 6.87 (m, 9H), 4.56 - 4.50 (m, 2H), 4.29 - 4.03 (m, 10H), 3.88 - 3.82 (m, 8H), 3.69 - 3.40 (m, 8H), 3.09 (br, 2H), 2.46 (s, 2H), 2.41 (s, 2H), 2.21 (m, 6H) 1.70 - 0.94 (m, 26H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  177.6, 173.1, 147.9, 138.6, 132.7, 131.0, 127.7, 122.2, 113.1, 71.1, 70.6, 68.6, 64.6, 52.6, 49.4, 47.7,

46.2, 33.0, 29.8, 29.72, 29.65, 29.56, 29.3, 29.0, 28.18, 28.09, 27.9, 27.3, 27.0, 26.8, 26.3, 24.7, 24.5, 24.11, 24.06, 14.2, 14.0 ppm; IR (NaCl)  $\nu$  3631, 3168, 2929, 2859, 1750, 1727, 1594, 1505, 1453, 1253, 1212, 1123, 1108, 1057, 953, 841, 742, 557  $\text{cm}^{-1}$ ; HR-MS FAB Calcd for  $\text{C}_{52}\text{H}_{80}\text{NO}_{12}$   $[\text{M}-\text{PF}_6]^+$ ,  $m/z = 910.5675$ ; Found,  $m/z = 910.5683$ .

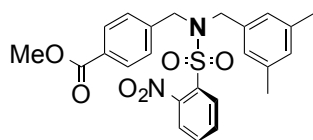
## 2.3 Synthesis of axle polymer

### Synthesis of benzoyl chloride 6



**Scheme S5.** Synthesis of benzoyl chloride derivative **6** for initiator of polymerization.

### Synthesis of methyl benzoate S5-2

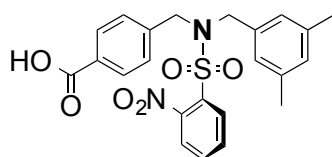


To a solution of amine **S5-1**<sup>[4]</sup> (13 g, 45 mmol), triethylamine (13 mL, 90 mmol) and *N,N*-dimethyl-4-aminopyridine (0.55 g, 4.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (230 mL), 2-nitrobenzenesulfonyl chloride (0.55 g, 4.5 mmol) were added at 0 °C and stirred for 1 h.

The reaction mixture was quenched by adding satd. aq. NaHCO<sub>3</sub> and washed successively with satd. aq. NaHCO<sub>3</sub>, water, and brine. The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude product was purified by silica gel column chromatography (*n*-hexane / EtOAc = 2 / 1, *R<sub>f</sub>* = 0.4) to give methyl benzoate **S5-2** (9.5 g, 44 mmol, 79%) as a white solid.

m.p. 125.8 – 126.5 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K) δ 7.98 (d, 1H, *J* = 8 Hz), 7.94 (d, 2H, *J* = 7 Hz), 7.75 – 7.68 (m, 2H), 7.64 – 7.56 (m, 1H), 7.22 (d, 2H, *J* = 7 Hz), 6.87 (s, 1H), 6.62 (s, 2H), 4.55 (s, 2H), 4.40 (s, 2H), 3.93 (s, 3H), 2.20 (s, 6H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) δ 167.1, 148.1, 141.2, 138.6, 134.8, 134.5, 134.0, 132.2, 131.4, 130.2, 130.0, 128.5, 126.5, 124.6, 52.6, 51.2, 50.9, 21.5 ppm; IR (NaCl) ν 3085, 3061, 3021, 2954, 2921, 1719, 1610, 1543, 1435, 1356, 1281, 1163, 1112, 1080, 1019, 919, 851, 776, 654, 581 cm<sup>-1</sup>; HR-MS FAB Calcd for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>, *m/z* = 469.1433; Found, *m/z* = 469.1434

### Synthesis of benzoic acid **S5-3**

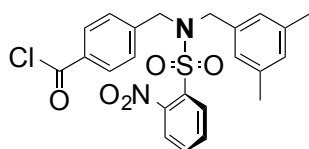


To a solution of **S5-2** (9.0 g, 41 mmol) in THF (80 mL), 1M KOH (40 mL) was added at room temperature. The reaction mixture was heated to 50 °C and stirred for 8 h. The

mixture was cooled to room temperature and added hydrochloric acid for making the solution acidic. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with 3M HCl and brine, then dried over MgSO<sub>4</sub>, filtrated, and concentrated. Benzoic acid **S5-3** (17 g, 40 mmol, 96%) was obtained as a white solid.

m.p. 195.2 – 196.5 °C; <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 298 K) δ 12.9 (br, 1H), 8.07 - 8.02 (m, 2H), 7.91 (dt, 1H, *J* = 1 Hz, 8 Hz), 7.82 (d, 2H, *J* = 8 Hz), 7.79 (dt, 1H, *J* = 1 Hz, 8 Hz), 7.24 (d, 2H, *J* = 8 Hz), 6.81 (s, 1H), 6.59 (s, 2H), 4.53 (s, 2H), 4.38 (s, 2H), 2.21 (s, 6H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) δ 167.9, 148.2, 141.8, 138.2, 135.6, 135.5, 133.3, 132.9, 130.9, 130.8, 130.2, 129.8, 128.8, 126.8, 125.1, 51.9, 51.6, 21.5 ppm; IR (NaCl) ν 3093, 3066, 2979, 2917, 2871, 1683, 1608, 1544, 1423, 1344, 1288, 1161, 1126, 1080, 911, 852, 780, 740, 654, 571 cm<sup>-1</sup>; HR-MS FAB Calcd for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>, *m/z* = 455.1277; Found, *m/z* = 455.1273.

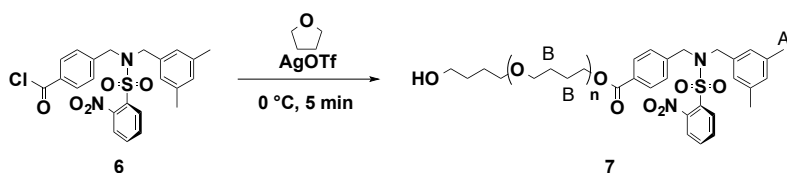
### Synthesis of benzoyl chloride **6**



To a solution of **S5-3** (1.0 g, 2.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), oxalyl chloride (0.57 mL, 6.6 mmol) was added dropwise at 0 °C. The mixture was stirred for 2 h at room temperature. The mixture was cooled to room temperature, and the solvent and excess oxalyl chloride were

distilled off under reduced pressure. The residue was dried *in vacuo* to give a benzoyl chloride **6** as a yellow oil quantitatively.

### Synthesis of axle polymer **7**



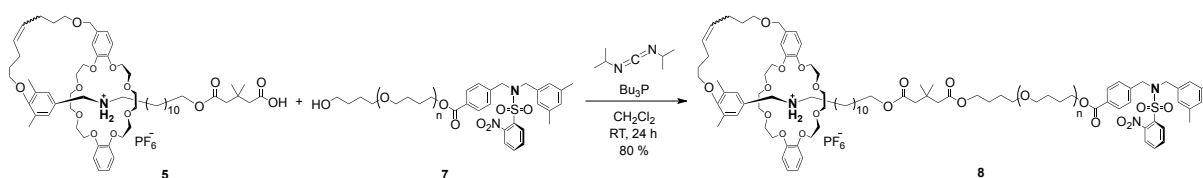
#### *Scheme S6. Synthesis of axle polymer **7**.*

To a solution of **6** (1.0 g, 2.2 mmol) in dry THF (100 mL), silver trifluoromethanesulfonate (5.7 g, 22 mmol) was added at 0 °C and stirred for 5 min. The reaction mixture was quenched by adding water and extracted with CHCl<sub>3</sub>. The combined organic layer was washed successively with water and brine, then dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude product was purified by preparative GPC to give axle polymer **7** as a yellow solid.

$M_{n,NMR}$  2.2 kDa (This value was calculated using the integrals of signal H<sub>A</sub> (2.21 ppm) and H<sub>B</sub> (1.70-1.58 ppm));  $M_{n,SEC}$  3.5 kDa,  $M_w/M_n = 1.13$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K)  $\delta$  7.98 (d, 1H,  $J = 9$  Hz), 7.94 (d, 2H,  $J = 8$  Hz), 7.74 – 7.70 (m, 2H), 7.63 – 7.57 (m, 1H), 7.21 (d, 2H,  $J = 8$  Hz), 6.87 (s, 1H), 6.63 (s, 2H), 4.54 (s, 2H), 4.40 (s, 2H), 4.35 (t, 2H,  $J = 6$  Hz), 3.66 (q, 2H,  $J$

= 6 Hz), 3.51 - 3.38 (m, 4H × n), 2.54 (br, 1H), 2.21 (s, 6H), 1.91 - 1.79 (m, 2H), 1.70 - 1.58 (m, 4H × n) ppm; IR (NaCl)  $\nu$  3457, 2941, 2862, 2800, 1718, 1545, 1454, 1367, 1276, 1111, 851, 778  $\text{cm}^{-1}$ .

## 2.4 Synthesis of macromolecular [1]rotaxane

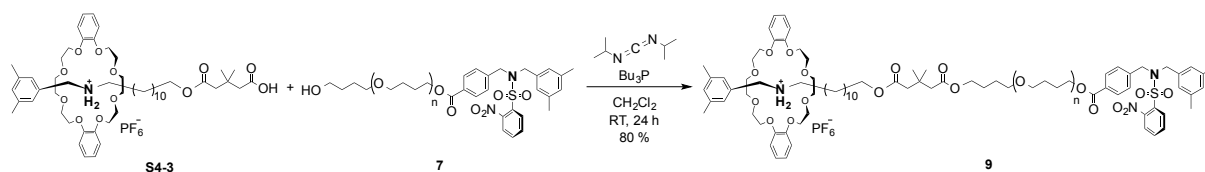


### *Scheme S7. Synthesis of macromolecular [1]rotaxane 8.*

To a solution of temporary stabilized [1]rotaxane end-cap agent **5** (1.57 g, 1.3 mmol) and axle polymer **7** (0.75 g, 0.35 mmol) in  $\text{CH}_2\text{Cl}_2$  (4.0 mL) was added  $\text{Bu}_3\text{P}$  (0.11 mL, 0.43 mmol) and *N,N'*-diisopropylcarbodiimide (0.44 mL, 2.81 mmol) at room temperature, and the solution was stirred for 24 h. The reaction mixture was then poured into *n*-hexane, and the precipitates were collected by decantation and purified by silica gel column chromatography (eluent ;  $\text{CHCl}_3$ ) and preparative GPC to give a macromolecular [1]rotaxane **8** (0.93 g, 0.28 mmol, 80%) as a yellow oil.

$M_{n,SEC}$  3.2 kDa,  $M_{p,SEC}$  3.5 kDa,  $M_w/M_n = 1.16$ ; IR (NaCl)  $\nu$  3161, 3074, 2936, 2856, 2796, 1723, 1594, 1544, 1507, 1448, 1367, 1252, 1221, 1111, 959, 843, 741, 557  $\text{cm}^{-1}$ .

## 2.5 Synthesis of macromolecular [2]rotaxane



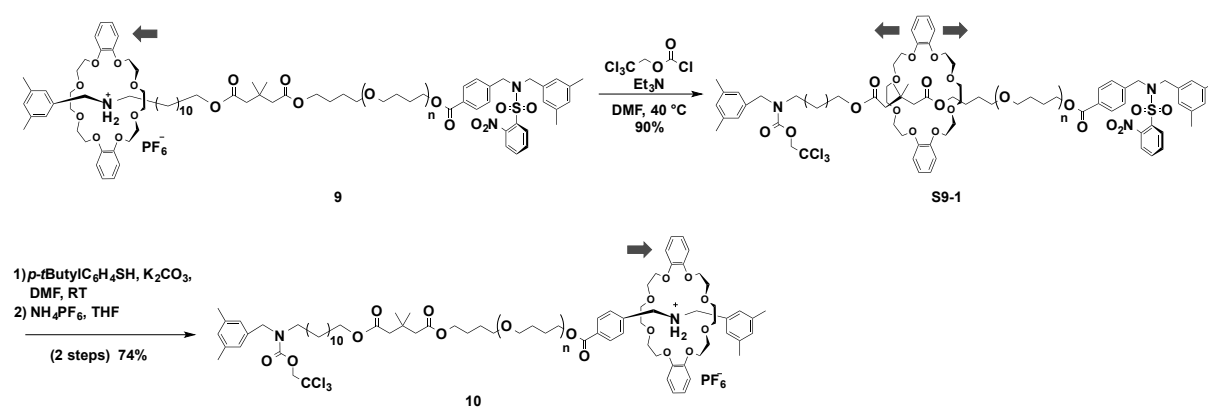
### *Scheme S8. Synthesis of macromolecular [2]rotaxane 9*

To a solution of temporary stabilized [2]rotaxane end-cap agent **S4-3** (1.0 g, 0.95 mmol) and axle polymer **7** (0.50 g, 0.23 mmol) in  $\text{CH}_2\text{Cl}_2$  (2.0 mL) was added  $\text{Bu}_3\text{P}$  (0.24 mL, 0.95 mmol) and  $N,N'$ -diisopropylcarbodiimide (0.18 mL, 1.2 mmol) at room temperature, and the solution was stirred for 24 h. The reaction mixture was poured into *n*-hexane, and the precipitates were collected by decantation and purified by silica gel column chromatography (eluent ;  $\text{CHCl}_3$ ) and preparative GPC to give a macromolecular [2]rotaxane **9** (0.59 g, 0.18 mmol, 80%) as a yellow oil.

$M_{n,SEC}$  3.2 kDa,  $M_w/M_n = 1.12$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 298 K)  $\delta$  7.98 (d, 1H,  $J = 9$  Hz), 7.94 (d, 2H,  $J = 8$  Hz), 7.74 – 7.70 (m, 2H), 7.63 – 7.57 (m, 1H), 7.21 (d, 2H,  $J = 8$  Hz), 6.99 (s, 2H), 6.87 (s, 1H), 6.96 - 6.75 (m, 9H), 6.63 (s, 2H), 4.54 (s, 2H), 4.56 - 4.50 (m, 2H), 4.40 (s, 2H), 4.35 (t, 2H,  $J = 7$  Hz), 4.29 - 4.03 (m, 10H), 3.88 - 3.82 (m, 8H), 3.69 - 3.40 (m, 8H), 3.51 - 3.38 (m, 2H  $\times$  n), 3.09 (br, 2H), 2.41 (s, 4H), 2.21 (s, 12H), 1.91 - 1.79 (m, 2H), 1.70 - 1.58

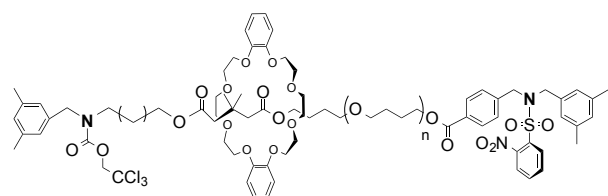
(m, 2H × n), 1.70 - 0.94 (m, 26H) ppm; IR (NaCl)  $\nu$  3164, 3064, 2941, 2856, 2795, 2740, 2075, 1942, 1723, 1611, 1546, 1505, 1455, 1369, 1252, 1207, 1112, 957, 844, 754, 707, 654, 557  $\text{cm}^{-1}$ .

## 2.6 Transposition of wheel component in model macromolecular [2]rotaxane



**Scheme S9.** Transposition of wheel component in model macromolecular [2]rotaxane

## Synthesis of macromolecular [2]rotaxane S9-1



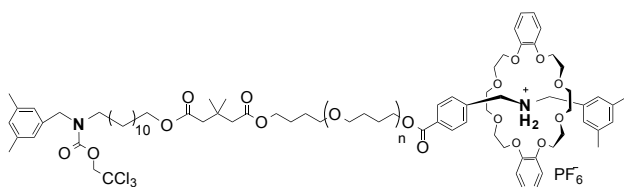
To a solution of macromolecular [2]rotaxane **9** (75 mg, 0.028 mmol) in DMF (1.5 mL) was added triethylamine (0.39 mL, 2.8 mmol) and 2,2,2-trichloroethyl chloroformate (0.19 mL, 1.4 mmol) at room temperature. The mixture was heated to 40 °C and stirred for 12 h. The reaction mixture was then poured into water, and the precipitates were collected by



decantation and purified by preparative GPC to give a macromolecular [2]rotaxane **S9-1** (69 mg, 0.025 mmol, 90%) as a brown oil.

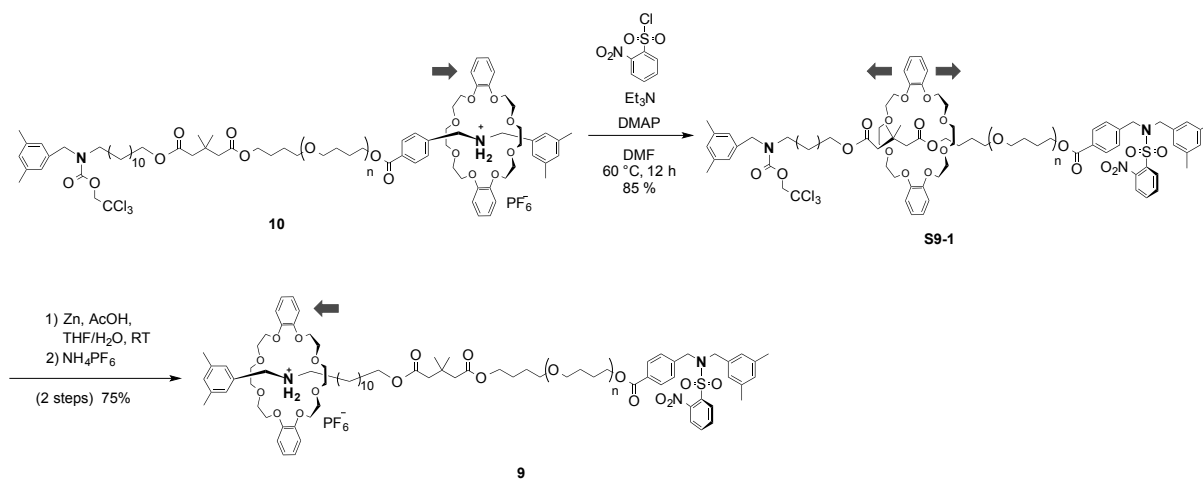
$M_{n,SEC}$  3.7 kDa,  $M_w/M_n = 1.13$ ; IR (NaCl)  $\nu$  3472, 3157, 3066, 2930, 2856, 2794, 2739, 1723, 1611, 1546, 1505, 1455, 1369, 1275, 1252, 1212, 1111, 957, 844, 754, 557  $\text{cm}^{-1}$ .

### Synthesis of macromolecular [2]rotaxane **10**



To a solution of macromolecular [2]rotaxane **S9-1** (50 mg, 0.016 mmol) in DMF (1.0 mL) was added  $\text{K}_2\text{CO}_3$  (0.22 g, 1.6 mmol) and 4-*tert*-butylbenzenethiol (0.14 mL, 0.79 mmol) and stirred for 24 h at room temperature. The reaction mixture was poured into water, and the precipitates were collected by decantation. The collected precipitates were dissolved in satd.  $\text{NH}_4\text{PF}_6/\text{THF}$  solution and stirred for 12 h at room temperature. The solution was concentrated under the reduced pressure. The residue was dissolved in  $\text{CHCl}_3$  and washed with water, then dried over  $\text{MgSO}_4$ , filtered, and concentrated. The product was purified by preparative GPC to give a macromolecular [2]rotaxane **10** (36 mg, 0.012 mmol, 74%) as a yellow oil.

$M_{n,SEC}$  3.3 kDa,  $M_w/M_n = 1.12$ ; IR (NaCl)  $\nu$  2938, 2855, 2795, 1718, 1504, 1449, 1366, 1273, 1249, 1212, 1112, 957, 843, 555  $\text{cm}^{-1}$ .



**Scheme S10.** Reverse transposition of wheel component in model macromolecular [2]rotaxane

### Synthesis of macromolecular [2]rotaxane **S9-1** from **10**

To a solution of macromolecular [2]rotaxane **10** (25 mg, 0.0083 mmol) in DMF (0.7 mL) was added triethylamine (0.12 mL, 0.83 mmol), *N,N*-dimethyl-4-aminopyridine (10 mg, 0.083 mmol), and 2-nitrobenzenesulfonyl chloride (38 mg, 0.12 mmol) at room temperature. The mixture was heated to 60 °C and stirred for 12 h. The reaction mixture was poured into *n*-hexane, and the precipitates were collected by decantation and purified by preparative GPC to give a macromolecular [2]rotaxane **S9-1** (22 mg, 0.0071 mmol, 85%) as a yellow foam.

IR (NaCl)  $\nu$  3472, 3157, 3066, 2930, 2856, 2794, 2739, 1723, 1611, 1546, 1505, 1455, 1369, 1275, 1252, 1212, 1111, 957, 844, 754, 557  $\text{cm}^{-1}$ .

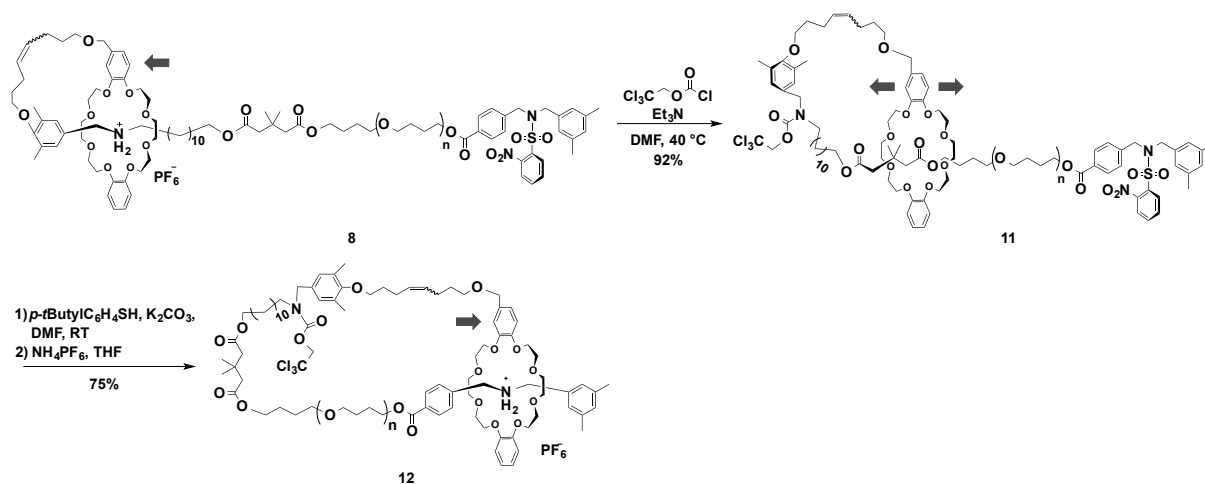
### **Synthesis of macromolecular [2]rotaxane **9** from **S9-1****

To a solution of macromolecular [2]rotaxane **S9-1** (15 mg, 0.0048 mmol) in THF (0.5 mL) and water (0.3 mL) was added AcOH (0.2 mL) and activated Zn powder (31 mg, 0.48 mmol) at room temperature, and the mixture was stirred for 24 h. The solvent was removed under reduced pressure, and the residue was resolved in  $\text{CHCl}_3$ . and the solution was washed with satd. aq.  $\text{NH}_4\text{PF}_6$  and water. The organic layer was dried over  $\text{MgSO}_4$ , filtered and concentrated. The precipitates were purified by preparative GPC to give a macromolecular [2]rotaxane **9** (9.6 mg, 0.0036 mmol, 75%) as a yellow foam.

IR (NaCl)  $\nu$  3164, 3064, 2941, 2856, 2795, 2740, 2075, 1942, 1723, 1611, 1546, 1505, 1455, 1369, 1252, 1207, 1112, 957, 844, 754, 707, 654, 557  $\text{cm}^{-1}$ .

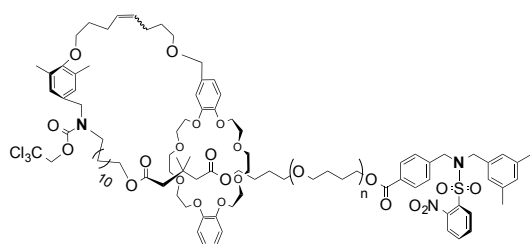
## 2.7 Reversible polymer structural transformation

### 2.7.1 Polymer structural transformation from linear polymer to cyclic polymer



**Scheme S11.** Polymer structural transformation from linear polymer to cyclic polymer

### Synthesis of macromolecular [1]rotaxane **11**

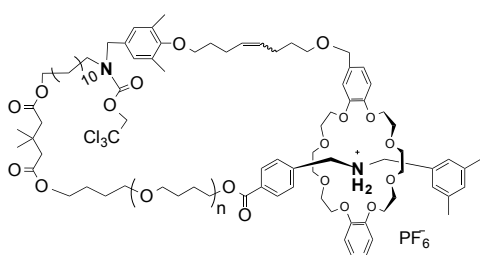


To a solution of macromolecular [1]rotaxane **8** (64 mg, 0.019 mmol) in DMF (0.5 mL) was added triethylamine (0.027 mL, 0.19 mmol) and 2,2,2-trichloroethyl chloroformate (0.013 mL, 0.097 mmol) at room temperature. The mixture was heated to  $40^\circ\text{C}$  and stirred for 12 h. The reaction mixture was poured into water, and the precipitates were collected by

decantation and purified by preparative GPC to give macromolecular [1]rotaxane **11** (59 mg, 0.018 mmol, 92%) as a brown oil.

$M_{n,SEC}$  3.1 kDa,  $M_{p,SEC}$  3.2 kDa,  $M_w/M_n = 1.20$ ; IR (NaCl)  $\nu$  2937, 2856, 2795, 1719, 1544, 1506, 1448, 1367, 1252, 1217, 1112, 961, 851  $\text{cm}^{-1}$ .

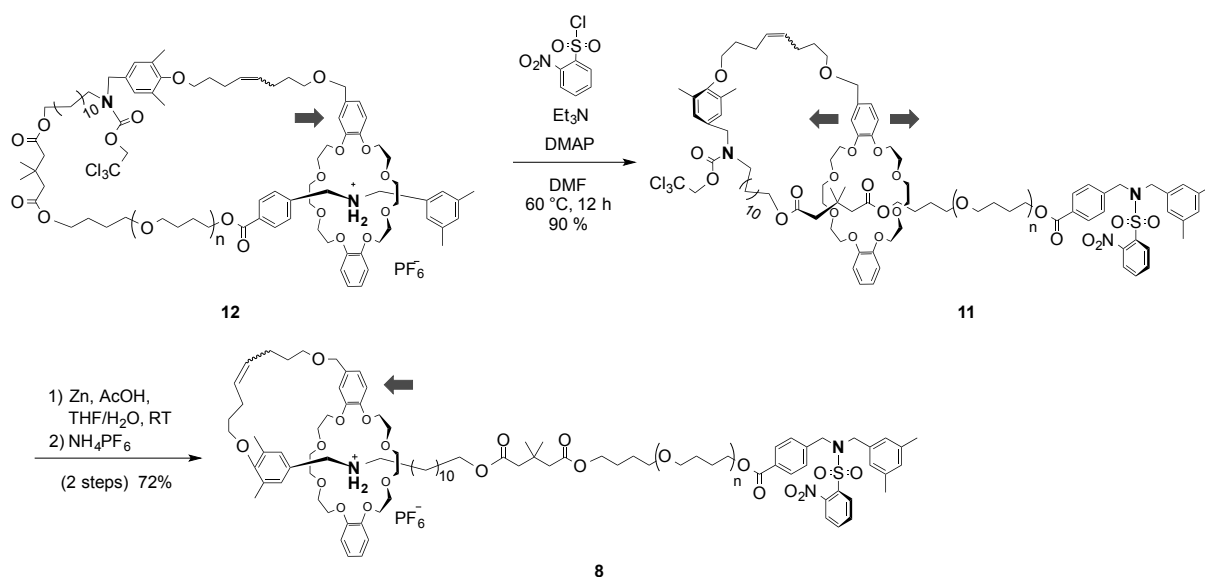
### Synthesis of macromolecular [1]rotaxane **12**



To a solution of macromolecular [1]rotaxane **11** (35 mg, 0.011 mmol) in DMF (1.0 mL) was added  $\text{K}_2\text{CO}_3$  (0.15 g, 1.1 mmol) and 4-*tert*-butylbenzenethiol (0.088 g, 0.53 mmol), and the mixture was stirred for 24 h at room temperature. The reaction mixture was poured into water, and the precipitates were collected by decantation. The collected precipitates were dissolved in satd.  $\text{NH}_4\text{PF}_6/\text{THF}$  solution and stirred for 12 h at room temperature. The solution was concentrated under the reduce pressure. The residue was dissolved in  $\text{CHCl}_3$ , and washed with water, then dried over  $\text{MgSO}_4$ , filtered, and concentrated. The product was purified by preparative GPC to give a macromolecular [1]rotaxane **12** (27 mg, 0.0083 mmol, 75%) as a yellow oil.

$M_{n,SEC}$  2.7 kDa,  $M_{p,SEC}$  2.8 kDa,  $M_w/M_n = 1.19$ ; IR (NaCl)  $\nu$  2938, 2855, 2795, 1718, 1504, 1449, 1366, 1273, 1249, 1212, 1112, 957, 843, 555  $\text{cm}^{-1}$ .

## 2.7.2 Polymer structural transformation from cyclic polymer to linear polymer



**Scheme S12.** Polymer structural transformation from cyclic polymer to linear polymer

### Synthesis of macromolecular [1]rotaxane 11 from 12

To a solution of macromolecular [1]rotaxane **12** (20 mg, 0.0061 mmol) in DMF (0.5 mL) was added triethylamine (0.085 mL, 0.61 mmol), *N,N*-dimethyl-4-aminopyridine (7.5 mg, 0.061 mmol), and 2-nitrobenzenesulfonyl chloride (27 mg, 0.12 mmol) at room temperature. The mixture was heated to 60 °C and stirred for 12 h. The reaction mixture was poured into

*n*-hexane, and the precipitates were collected by decantation and purified by preparative GPC to give a macromolecular [1]rotaxane **11** (18 mg, 0.0055 mmol, 90%) as a yellow foam.

IR (NaCl)  $\nu$  2937, 2856, 2795, 1719, 1544, 1506, 1448, 1367, 1252, 1217, 1112, 961, 851  $\text{cm}^{-1}$ .

### **Synthesis of macromolecular[1]rotaxane **8** from **11****

To a solution of macromolecular [1]rotaxane **11** (10 mg, 0.0054 mmol) in THF (0.5 mL) and water (0.3 mL) was added AcOH (0.2 mL) and activated Zn powder (35 mg, 0.54 mmol) at room temperature, and the mixture was stirred for 24 h. The solvent was removed under reduced pressure, and the residue was resolved in  $\text{CHCl}_3$ , and the solution was washed with satd. aq.  $\text{NH}_4\text{PF}_6$  and water. The organic layer was dried over  $\text{MgSO}_4$ , filtered and concentrated. The precipitates were purified by preparative GPC to give a macromolecular [1]rotaxane **8** (13 mg, 0.0039 mmol, 72%) as a yellow foam.

IR (NaCl)  $\nu$  3161, 3074, 2936, 2856, 2796, 1723, 1594, 1544, 1507, 1448, 1367, 1252, 1221, 1111, 959, 843, 741, 557  $\text{cm}^{-1}$ .

### 3. References

- [1] Purification of Laboratory Chemicals, 5th ed. (Eds.: W. L. F. Armarego, C. L. L. Chai),  
ELSEVIER: Oxford, **2003**.
- [2] S. J. Loeb, D. A. Tramontozzi, *Org. Biomol. Chem.* **2005**, *3*, 1393-1401.
- [3] D. Aoki, S. Uchida, K. Nakazono, Y. Koyama, T. Takata, *ACS Macro Lett.* **2013**, *2*,  
461-465.
- [4] H. Kawasaki, N. Kihara, T. Takata, *Chem. Lett.* **1999**, *28*, 1015–1016.



## 4. Spectra of Synthesized Compounds

### 4.1 $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

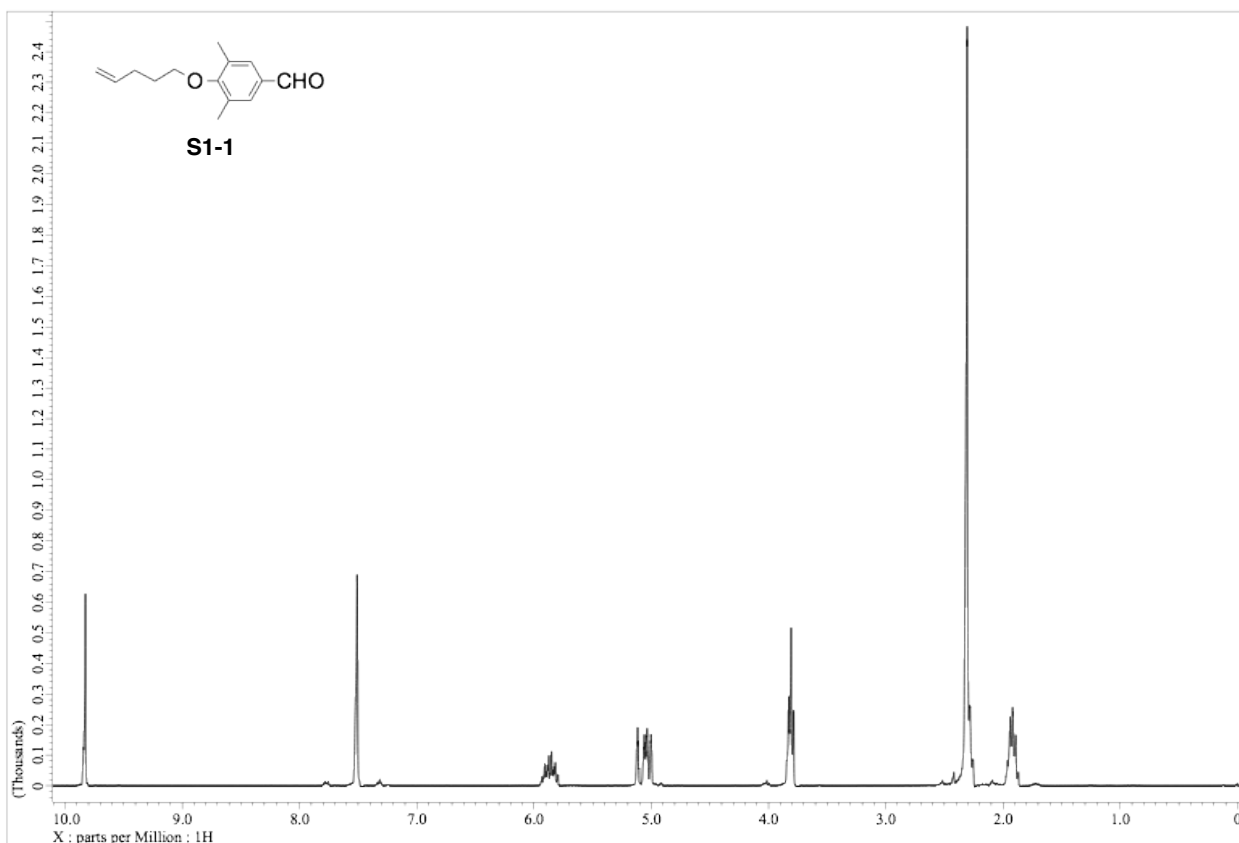


Figure S1.  $^1\text{H}$  NMR spectrum of S1-1 (300 MHz,  $\text{CDCl}_3$ , 298 K).

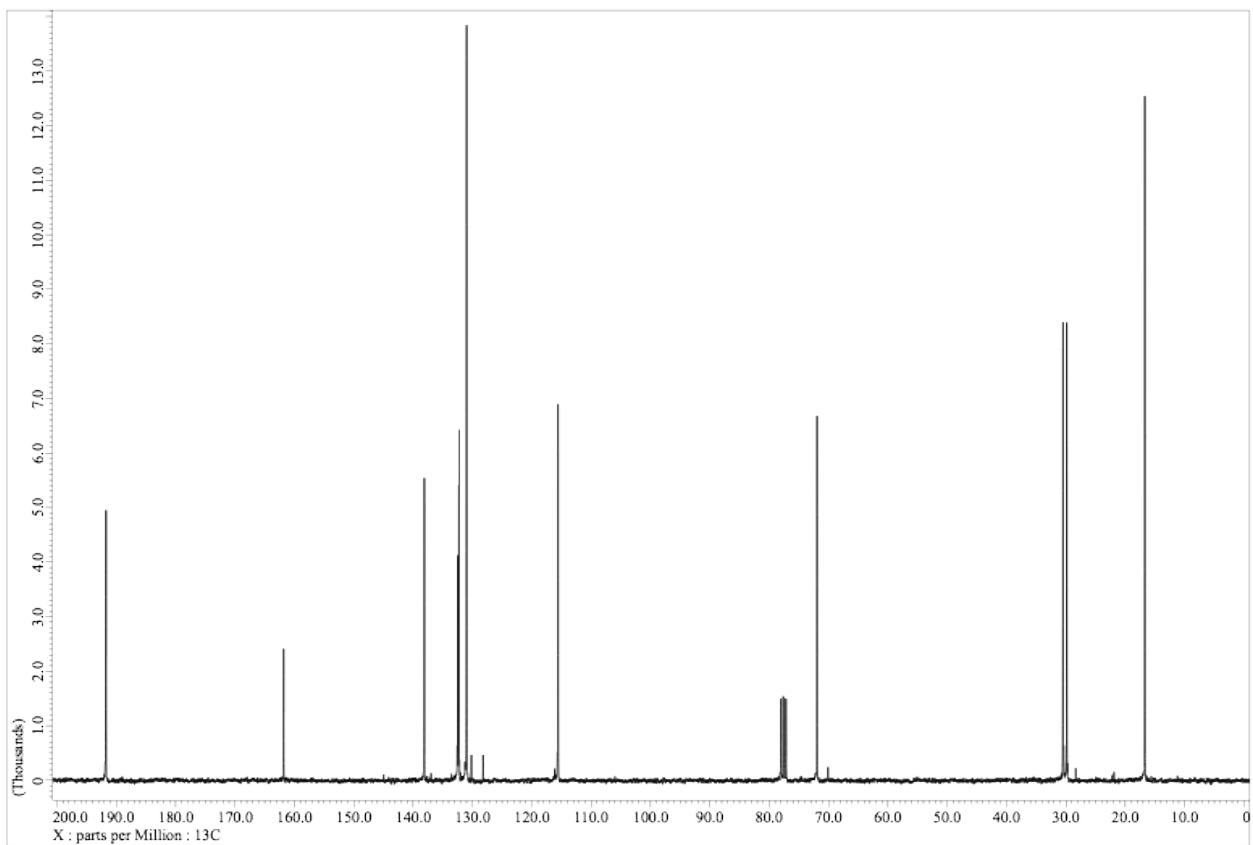


Figure S2.  $^{13}\text{C}$  NMR spectrum of S1-1 (75 MHz,  $\text{CDCl}_3$ , 298 K).

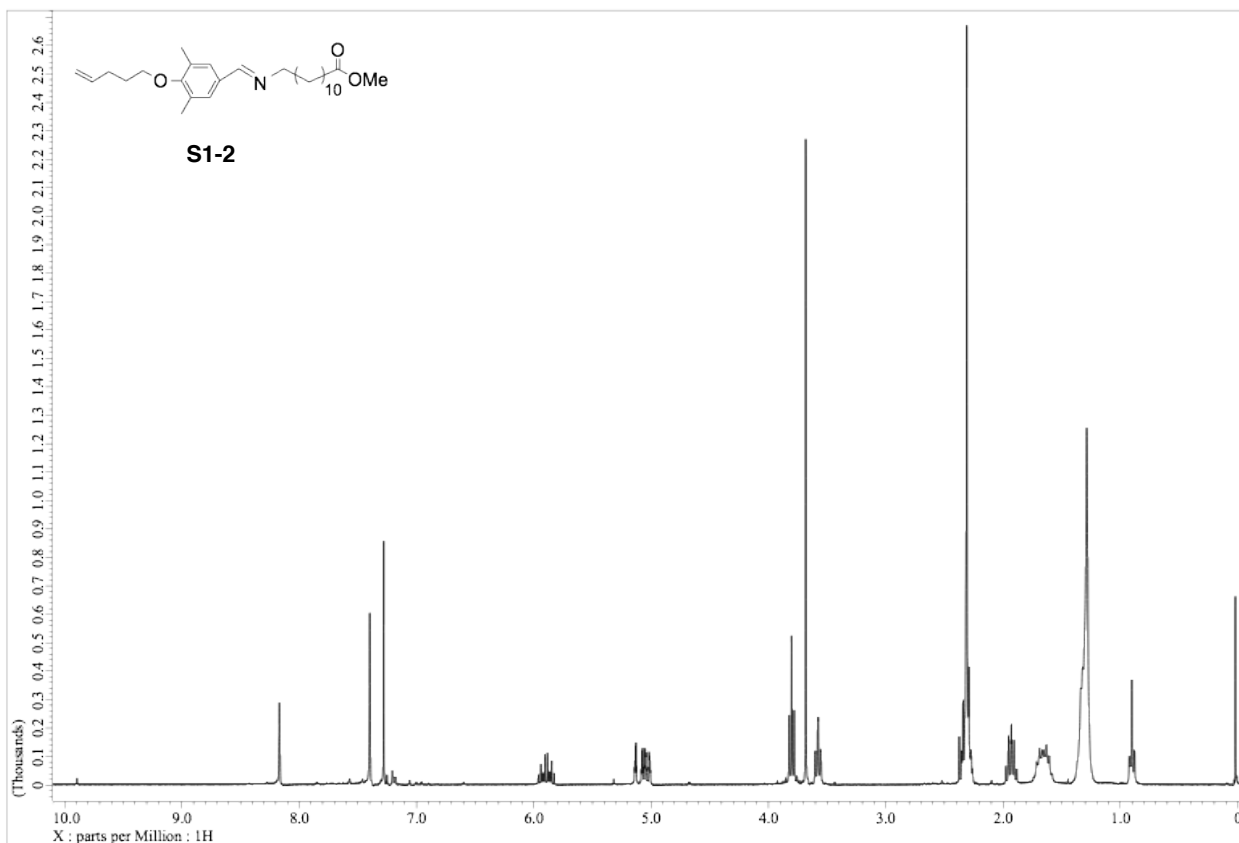


Figure S3. <sup>1</sup>H NMR spectrum of S1-2 (300 MHz, CDCl<sub>3</sub>, 298 K).

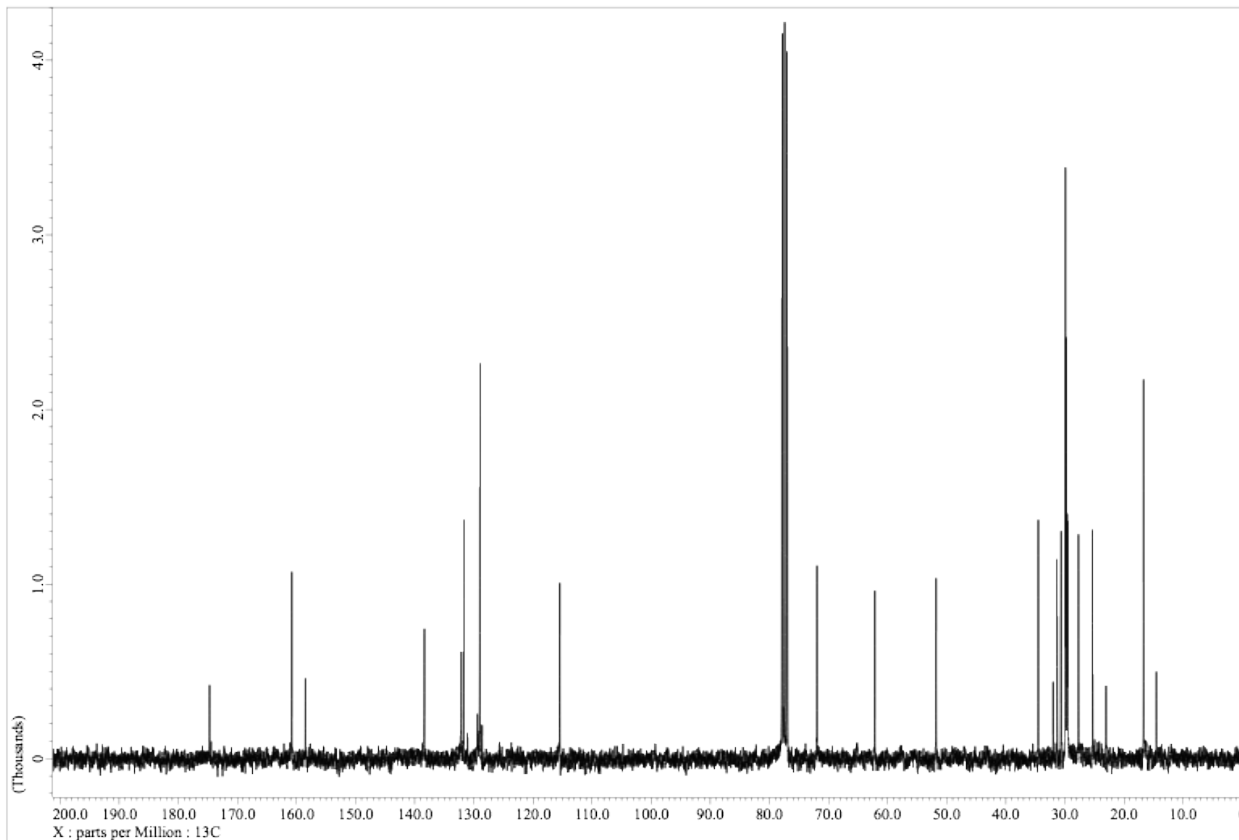


Figure S4. <sup>13</sup>C NMR spectrum of S1-2 (75 MHz, CDCl<sub>3</sub>, 298 K).

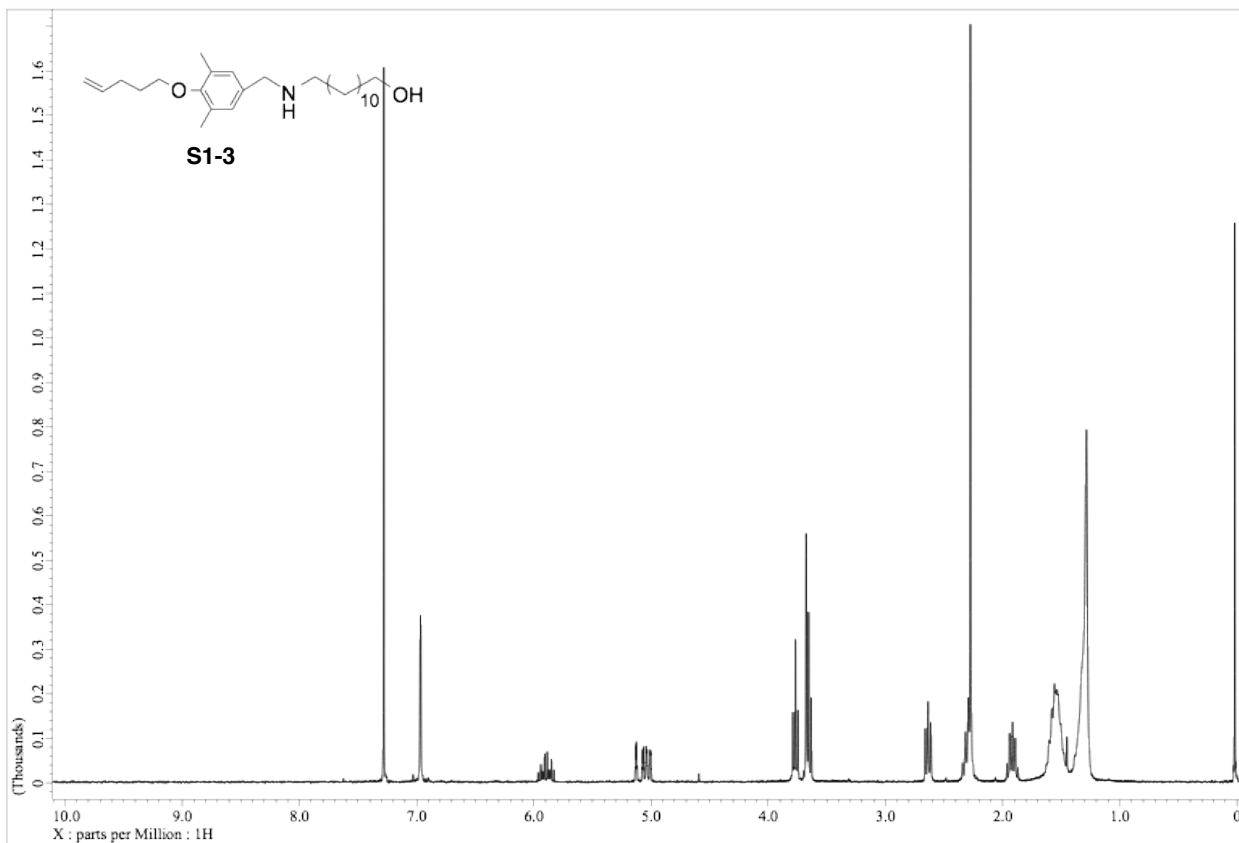


Figure S5. <sup>1</sup>H NMR spectrum of S1-3 (300 MHz, CDCl<sub>3</sub>, 298 K).

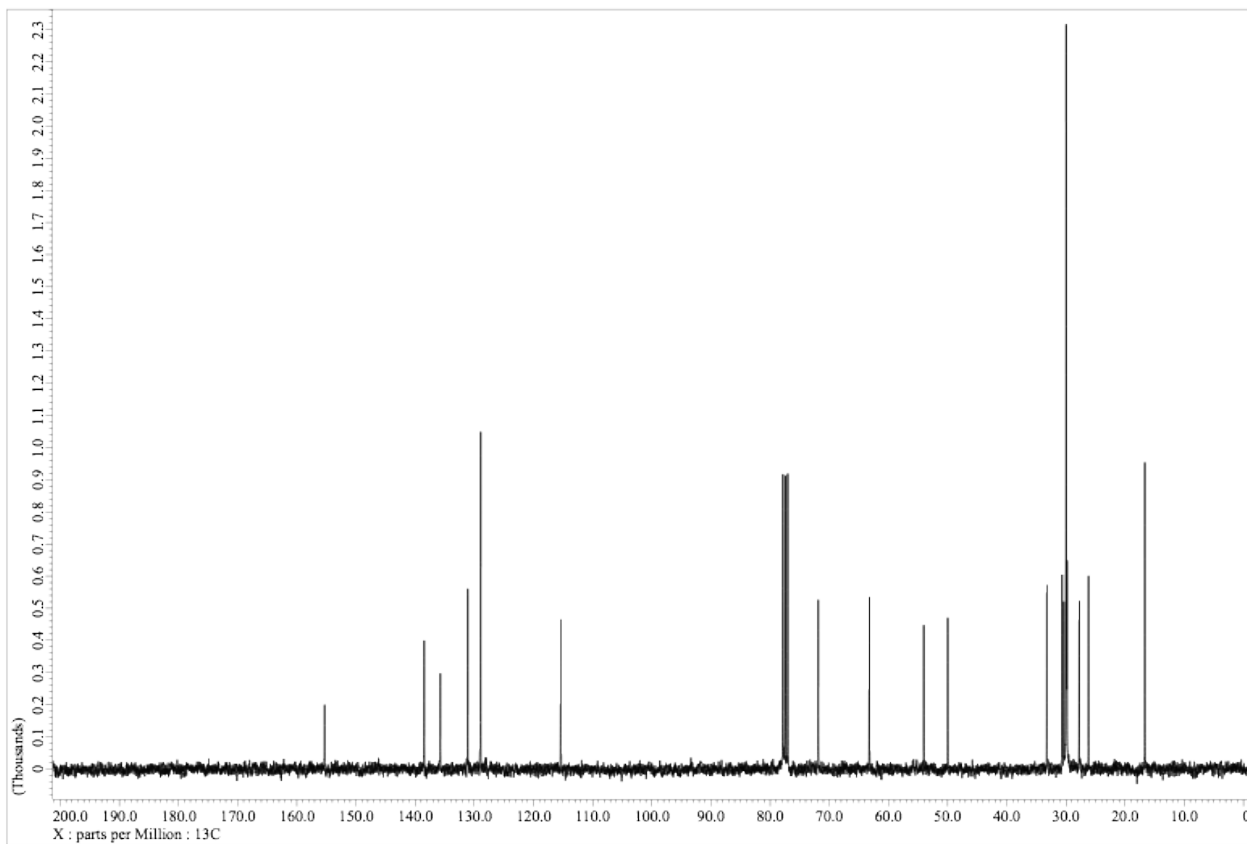


Figure S6. <sup>13</sup>C NMR spectrum of S1-3 (75 MHz, CDCl<sub>3</sub>, 298 K).

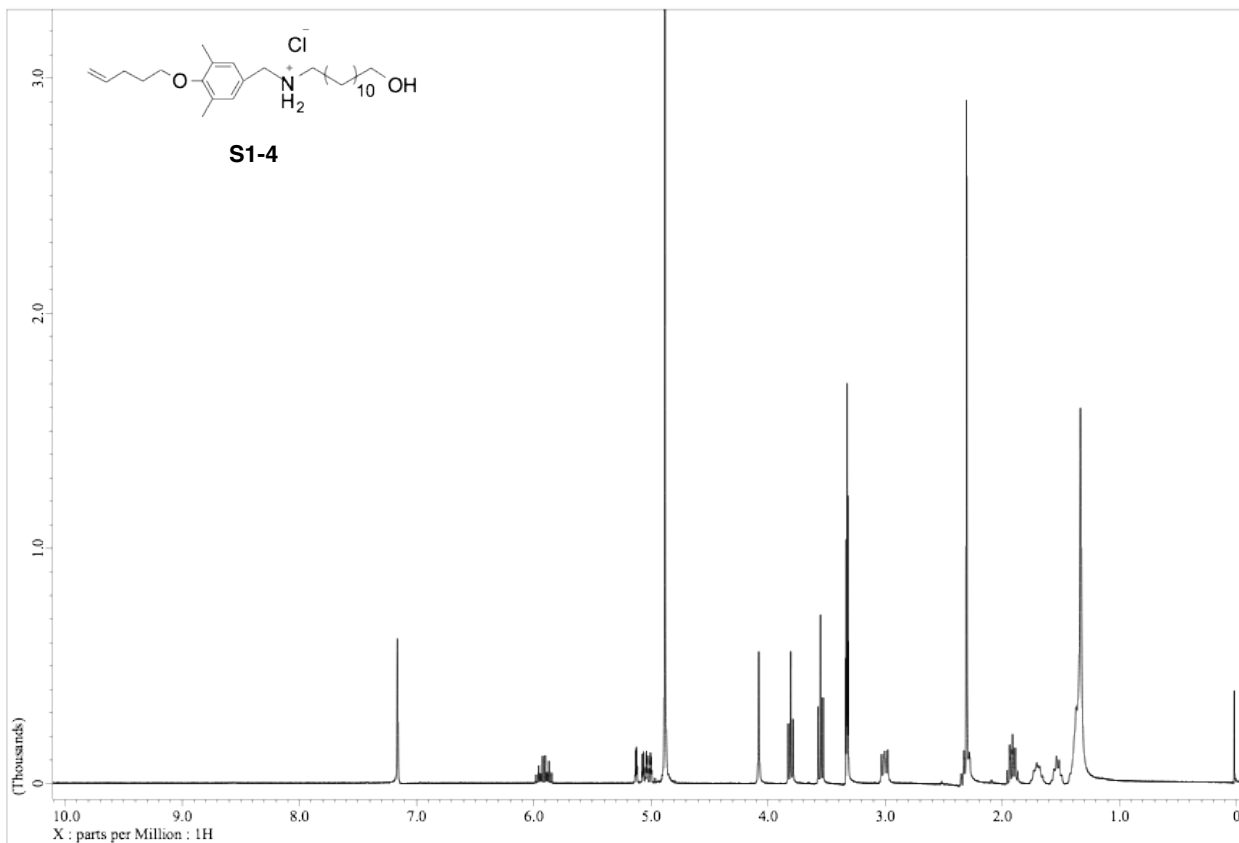


Figure S7.  $^1\text{H}$  NMR spectrum of S1-4 (300 MHz,  $\text{CD}_3\text{OD}$ , 298 K).

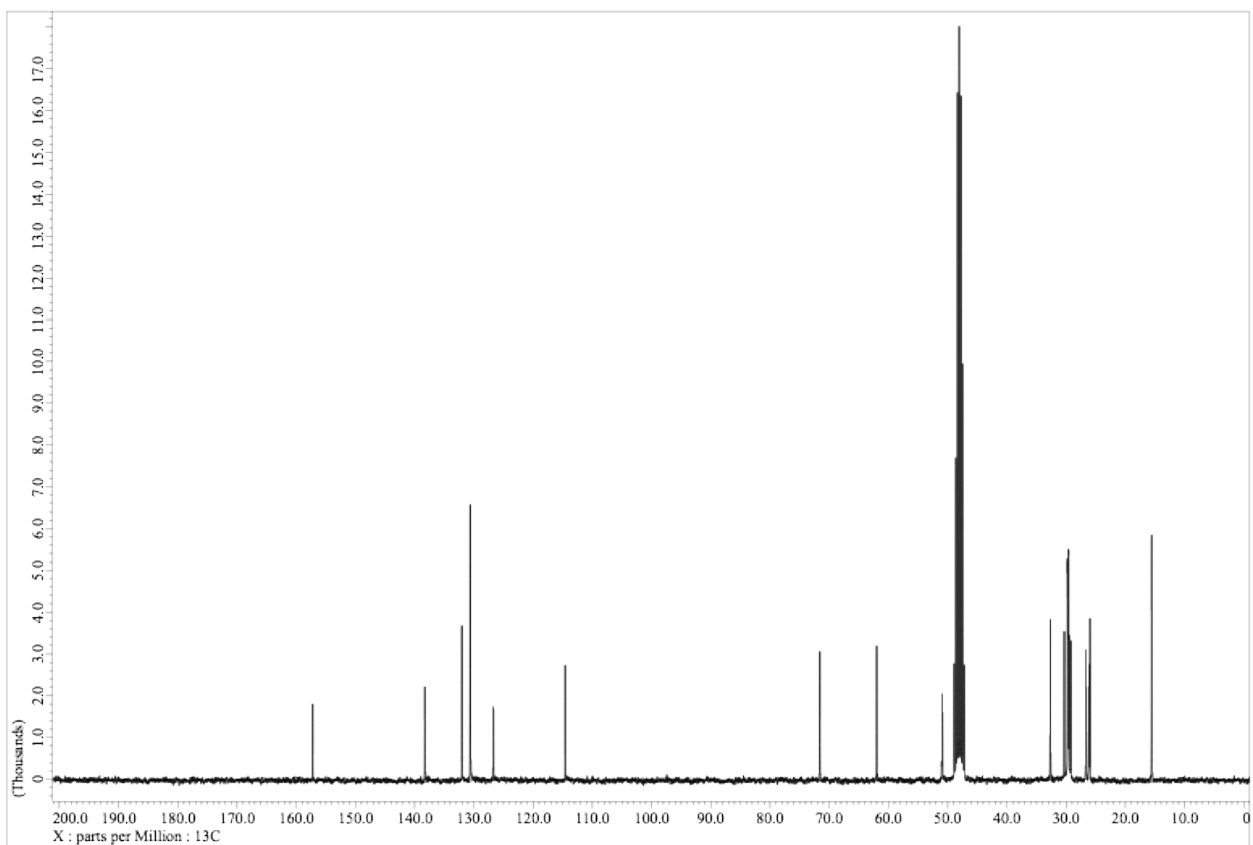


Figure S8.  $^{13}\text{C}$  NMR spectrum of S1-4 (75 MHz,  $\text{CD}_3\text{OD}$ , 298 K).

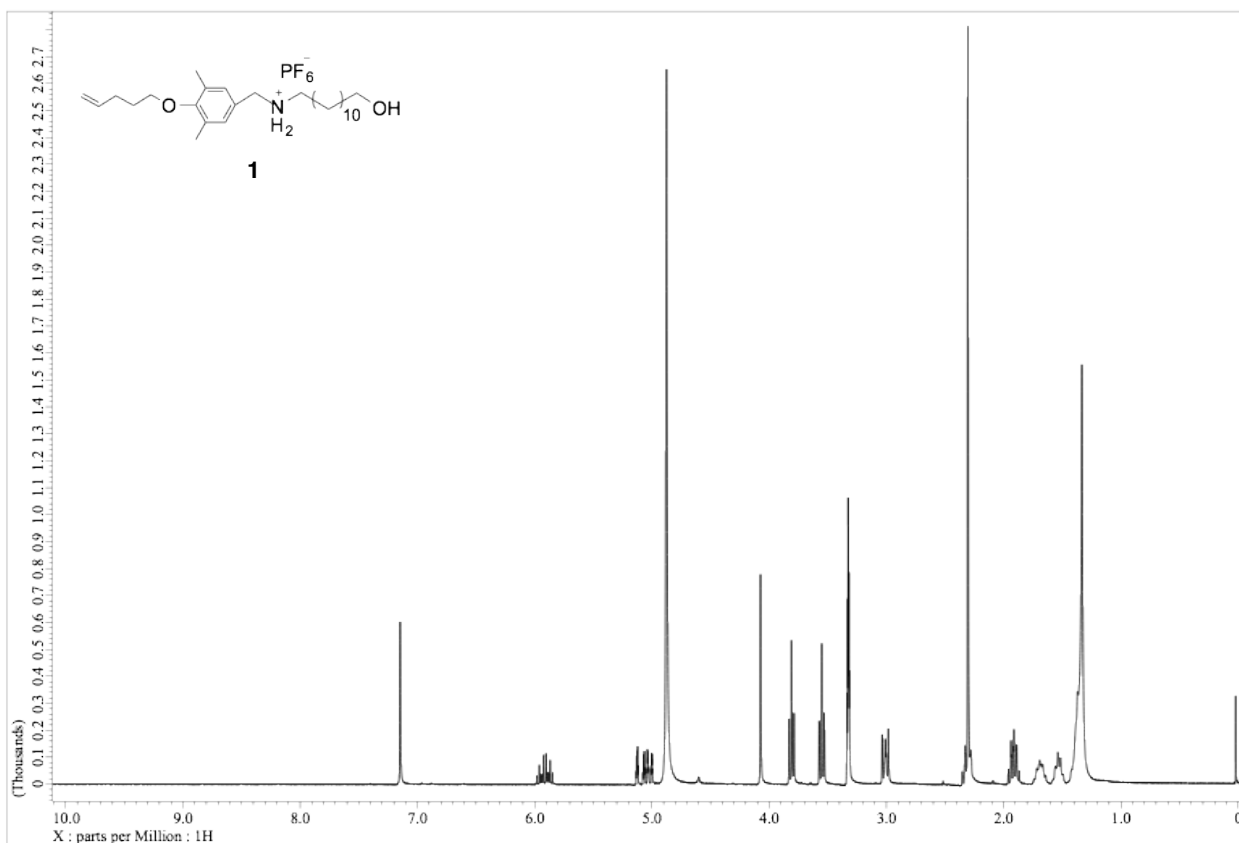


Figure S9. <sup>1</sup>H NMR spectrum of 1 (300 MHz, CD<sub>3</sub>OD, 298 K).

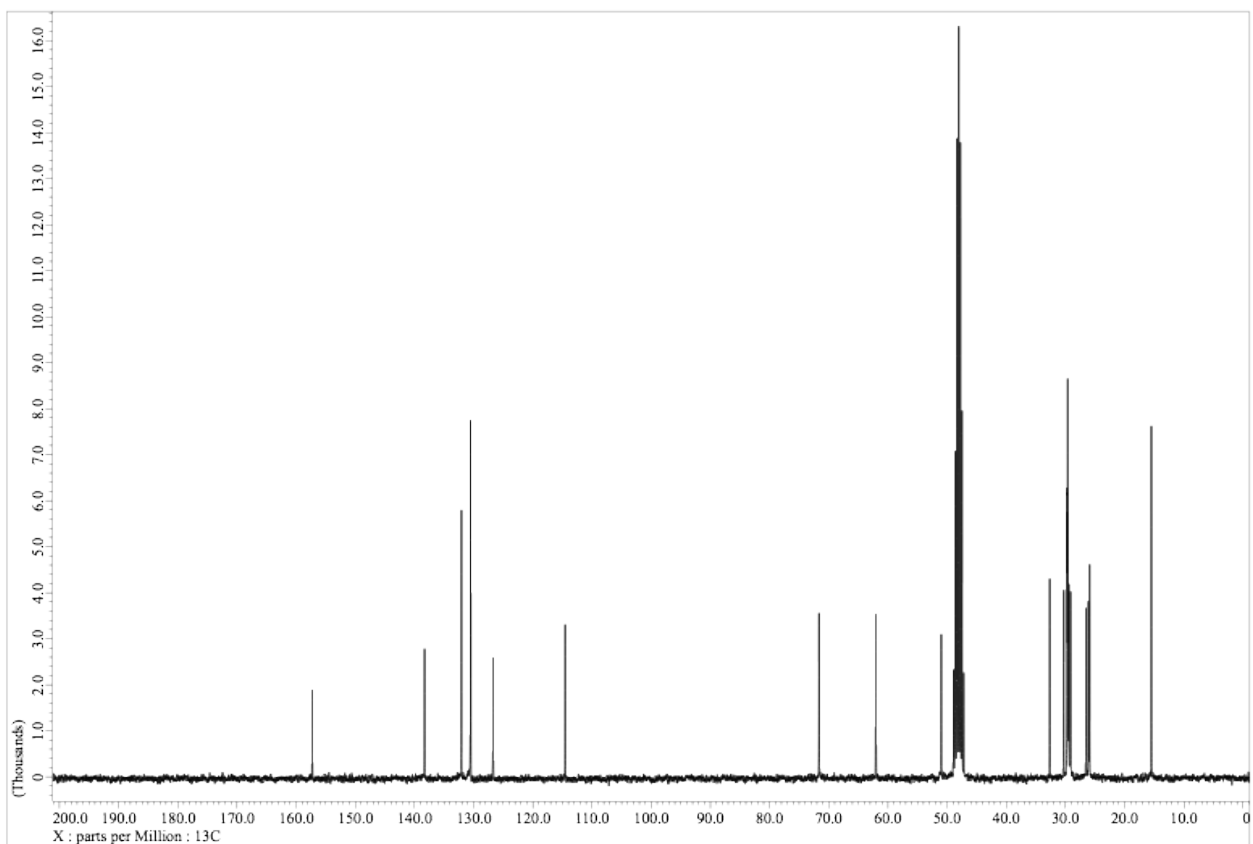


Figure S10. <sup>13</sup>C NMR spectrum of 1 (75 MHz, CD<sub>3</sub>OD, 298 K).

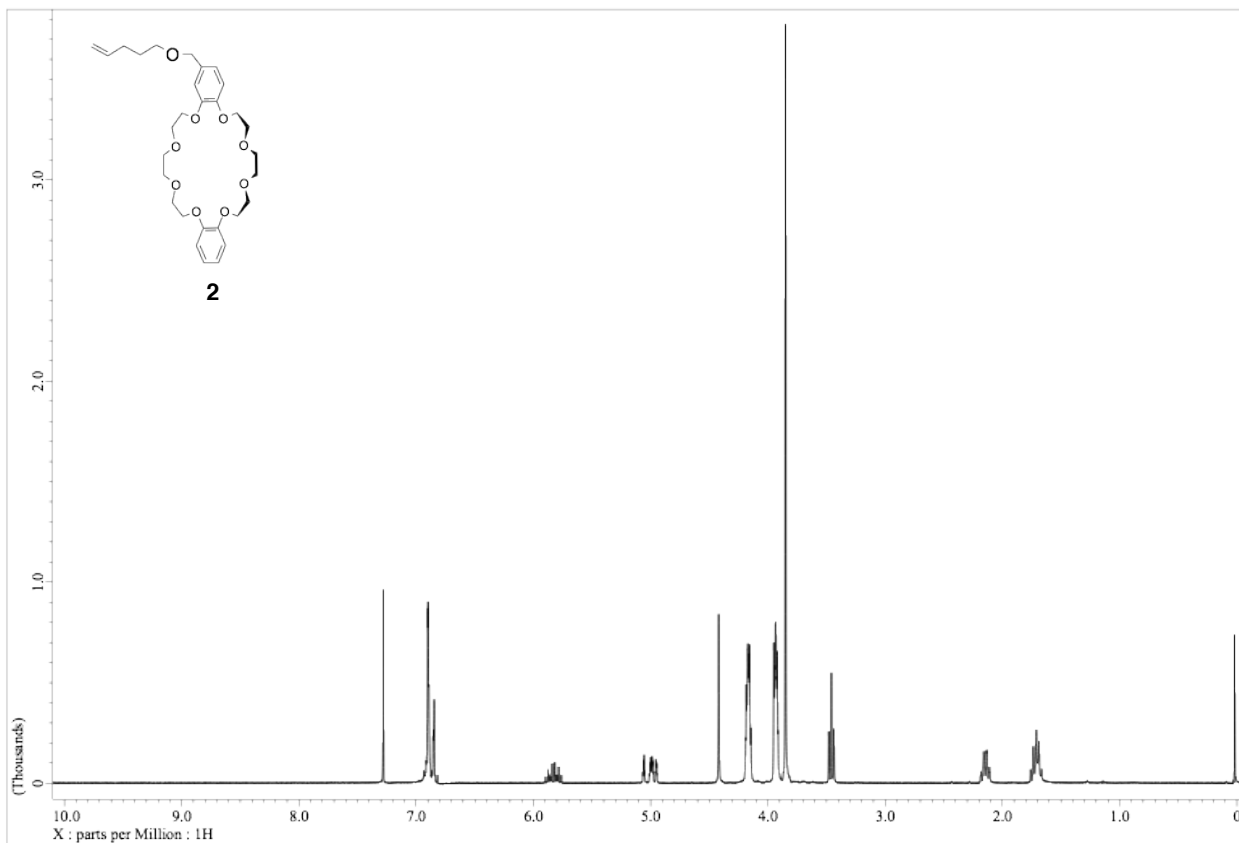


Figure S11.  $^1\text{H}$  NMR spectrum of **2** (300 MHz,  $\text{CDCl}_3$ , 298 K).

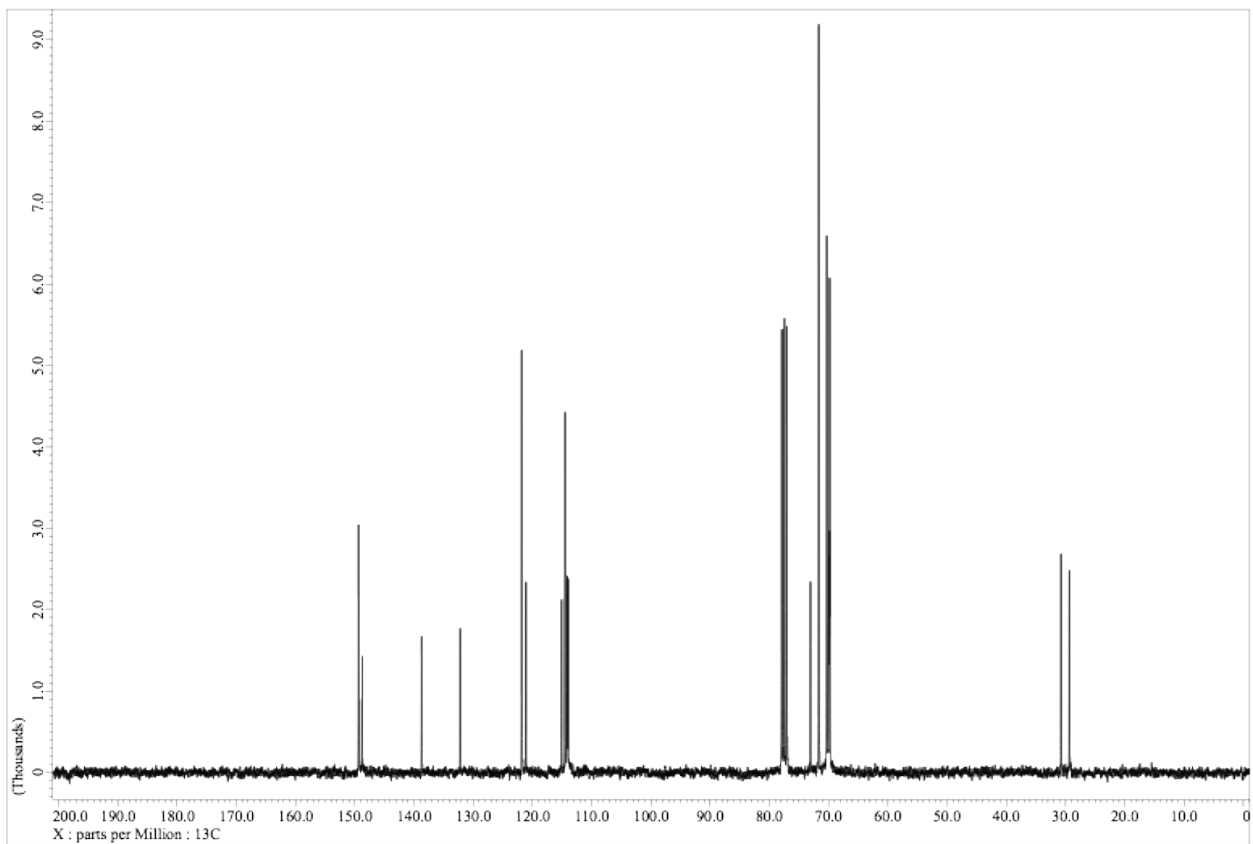
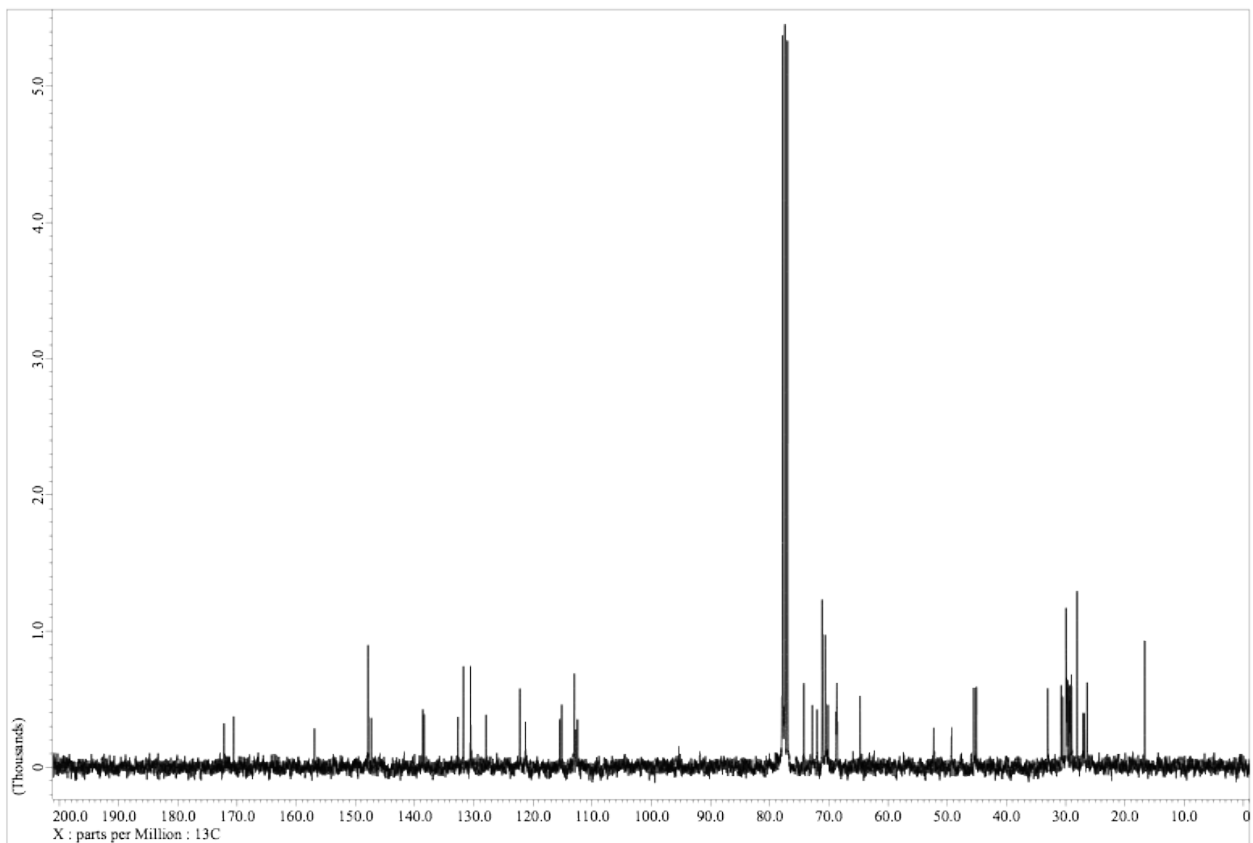
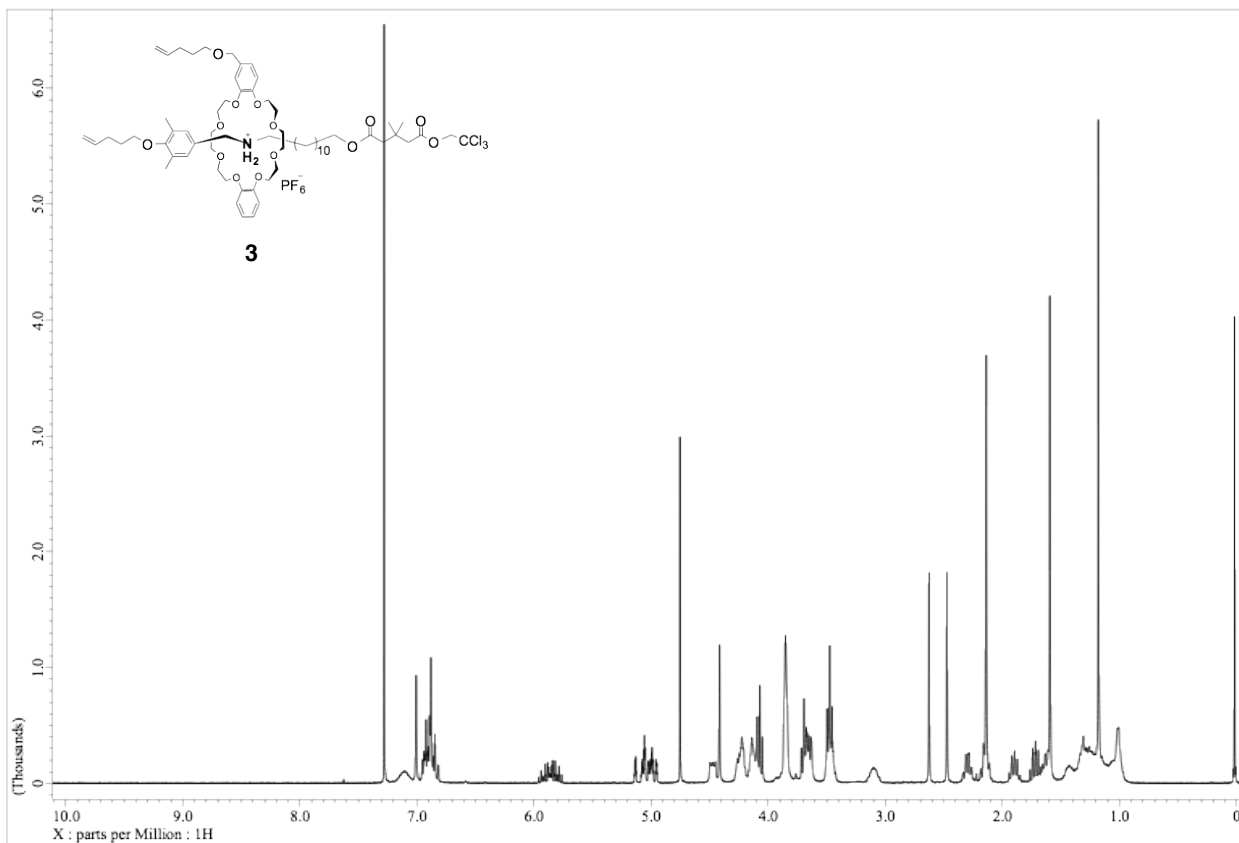


Figure S12.  $^{13}\text{C}$  NMR spectrum of **2** (75 MHz,  $\text{CDCl}_3$ , 298 K).



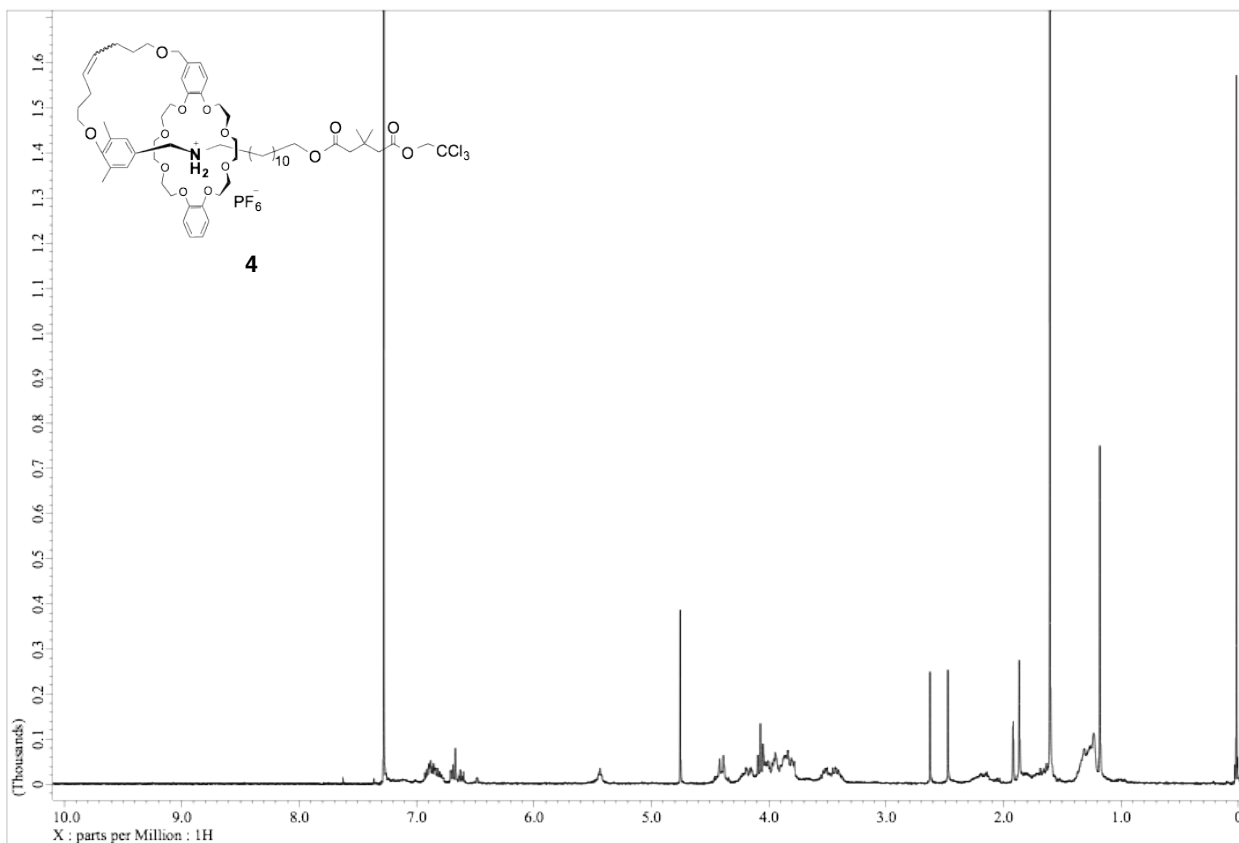


Figure S15.  $^1\text{H}$  NMR spectrum of **4** (300 MHz,  $\text{CDCl}_3$ , 298 K).

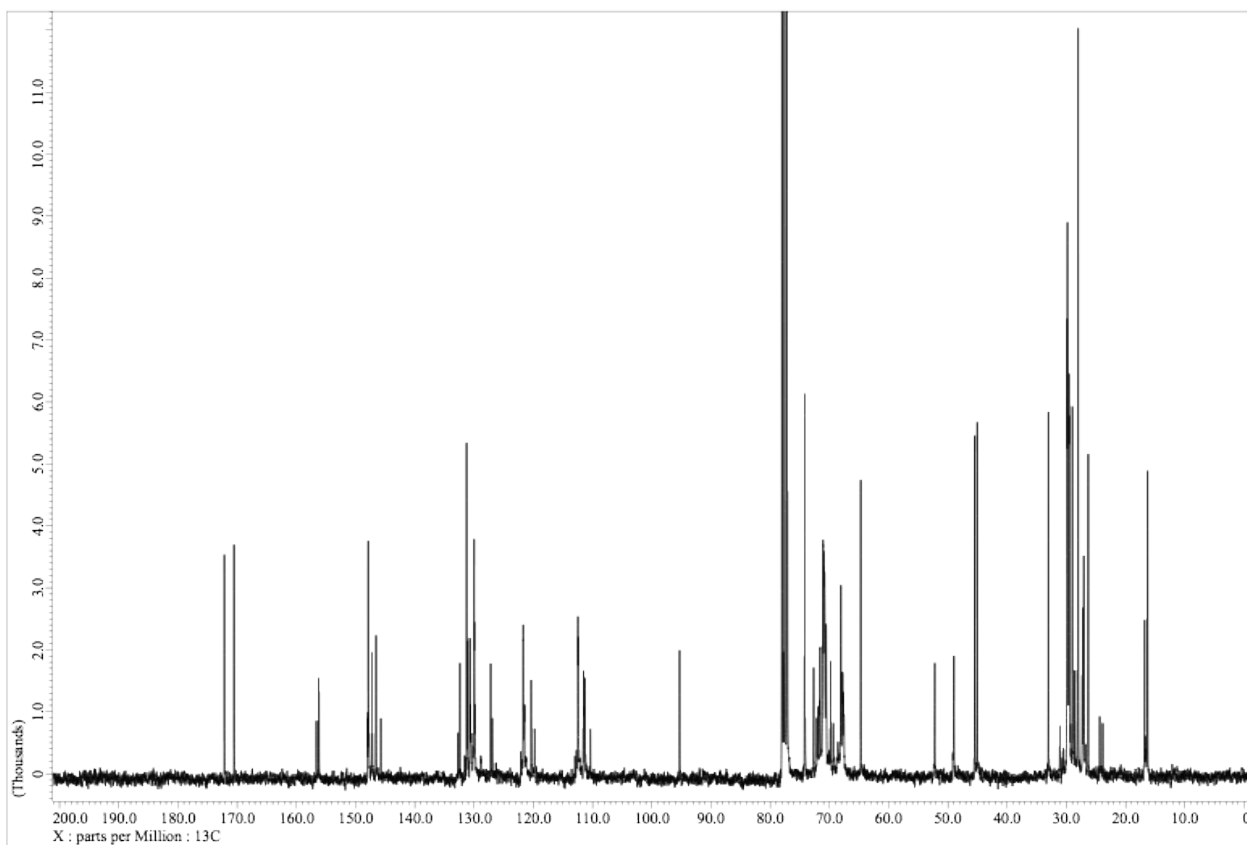


Figure S16.  $^{13}\text{C}$  NMR spectrum of **4** (75 MHz,  $\text{CDCl}_3$ , 298 K).



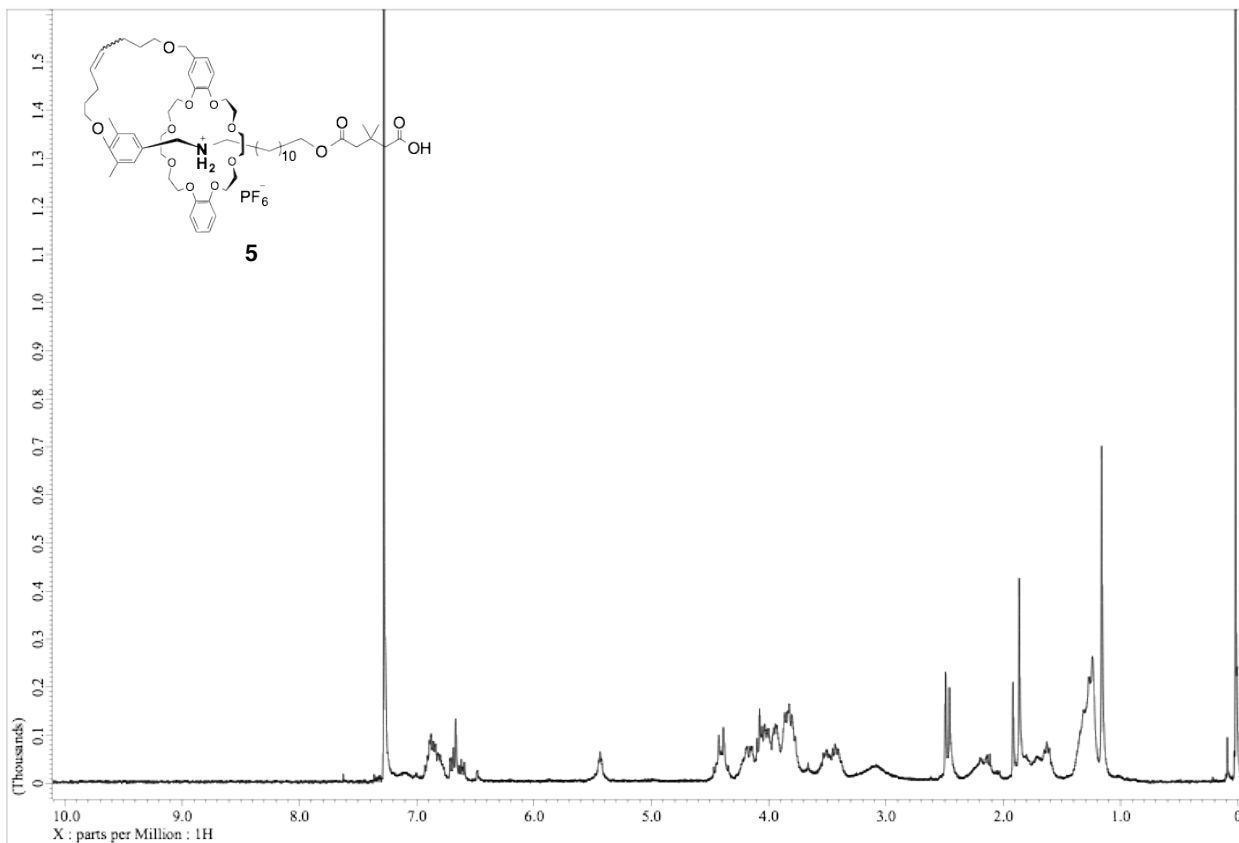


Figure S17.  $^1\text{H}$  NMR spectrum of **5** (300 MHz,  $\text{CDCl}_3$ , 298 K).

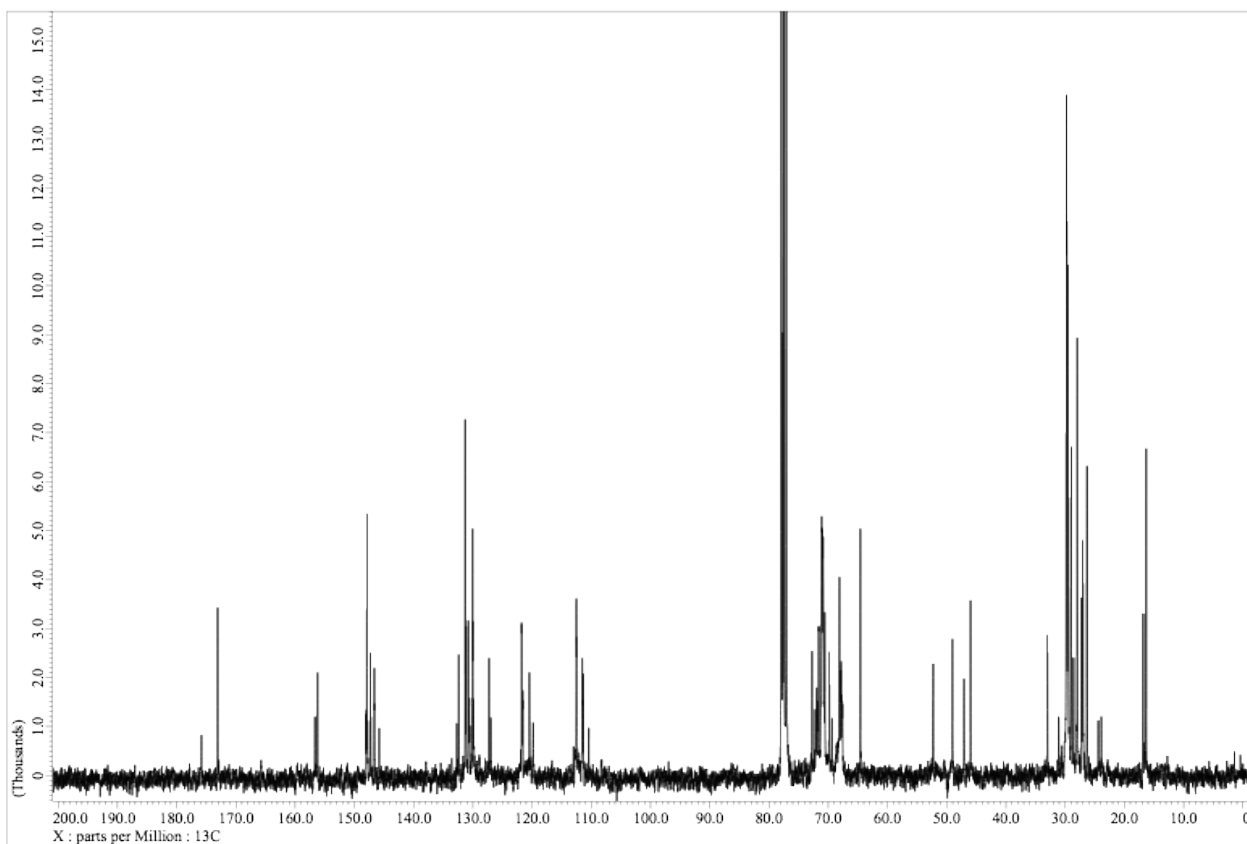


Figure S18.  $^{13}\text{C}$  NMR spectrum of **5** (75 MHz,  $\text{CDCl}_3$ , 298 K).

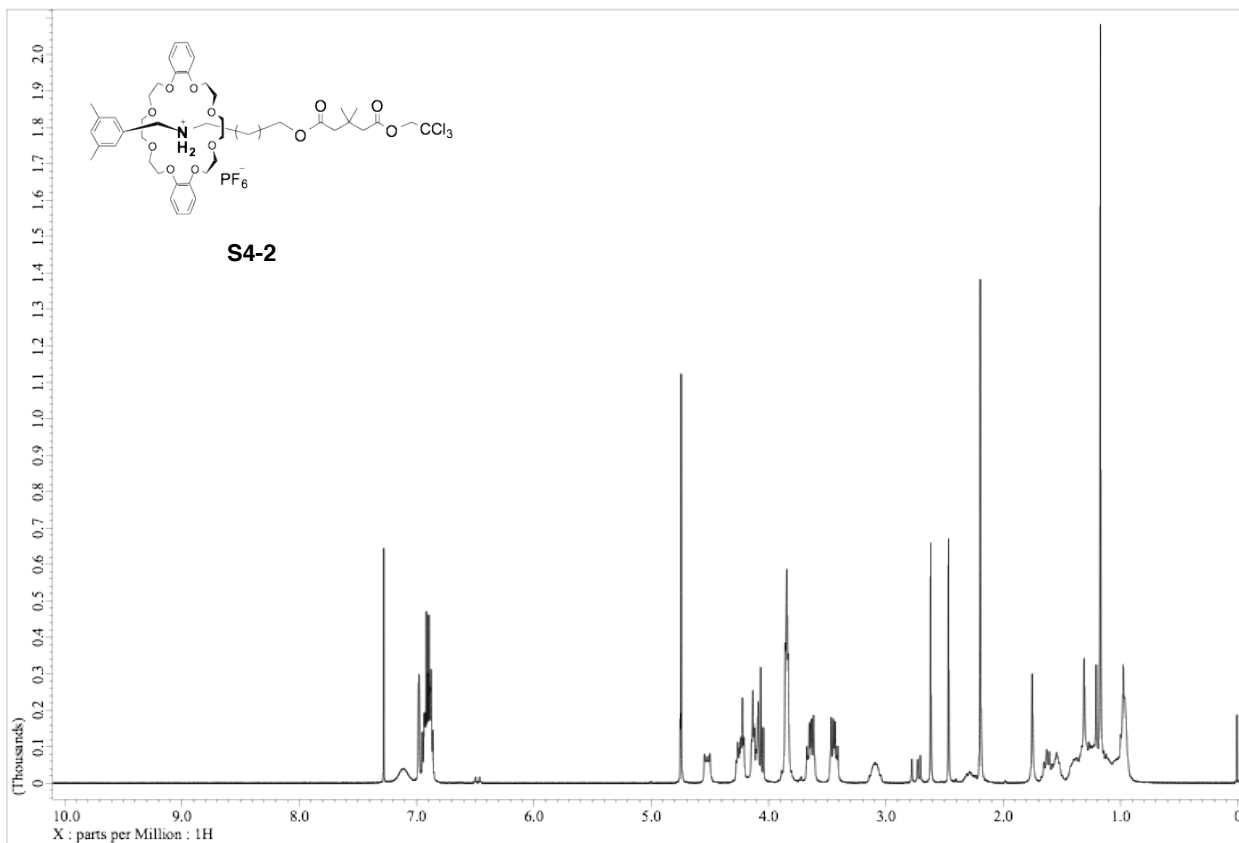


Figure S19.  $^1\text{H}$  NMR spectrum of S4-2 (300 MHz,  $\text{CDCl}_3$ , 298 K).

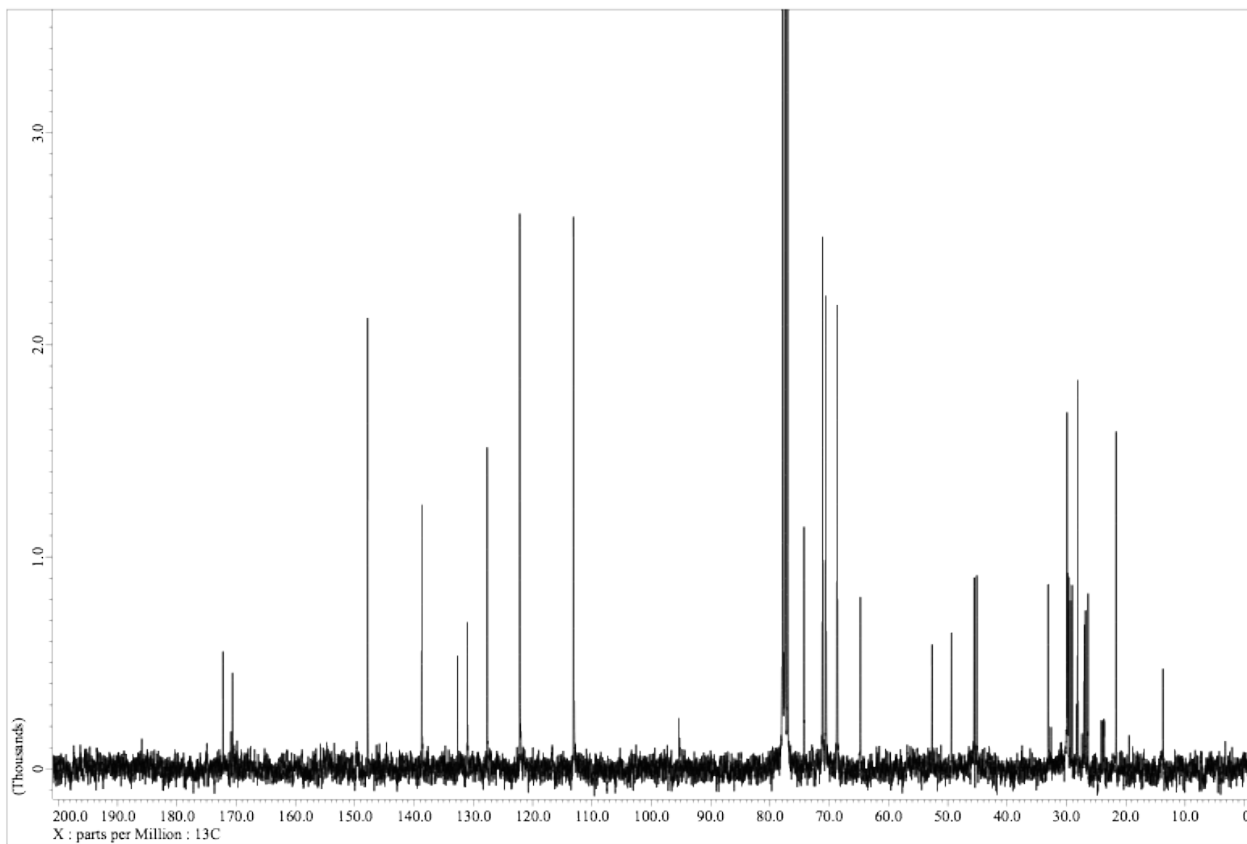


Figure S20.  $^{13}\text{C}$  NMR spectrum of S4-2 (75 MHz,  $\text{CDCl}_3$ , 298 K).

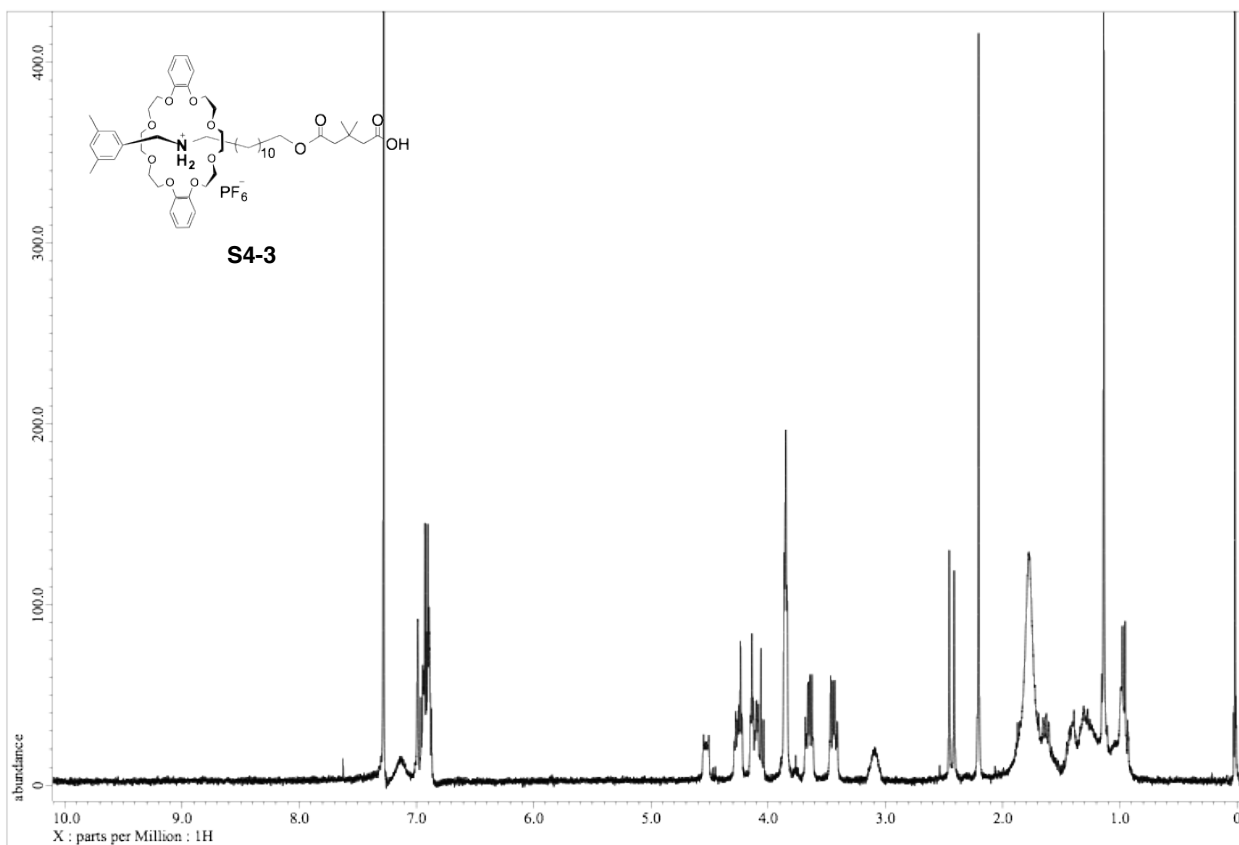


Figure S21. <sup>1</sup>H NMR spectrum of S4-3 (300 MHz, CDCl<sub>3</sub>, 298 K).

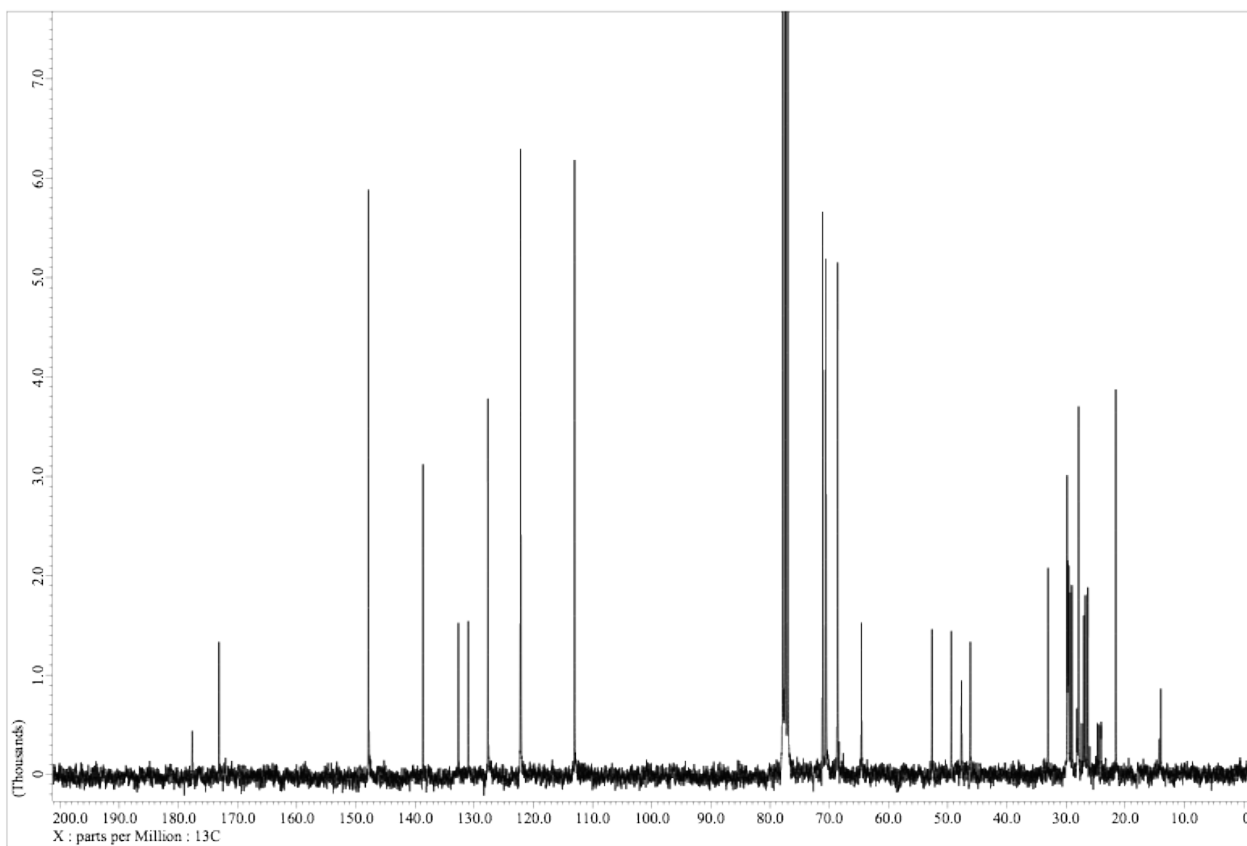
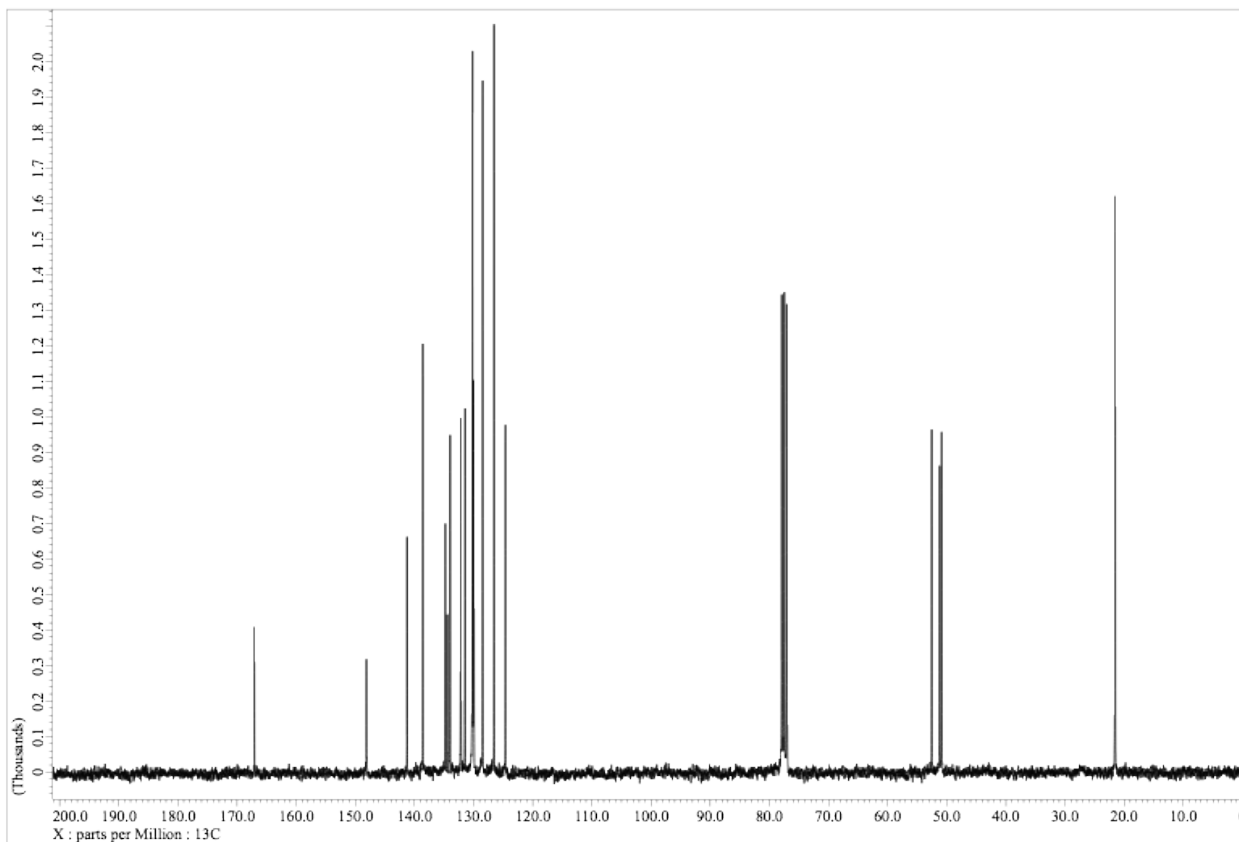
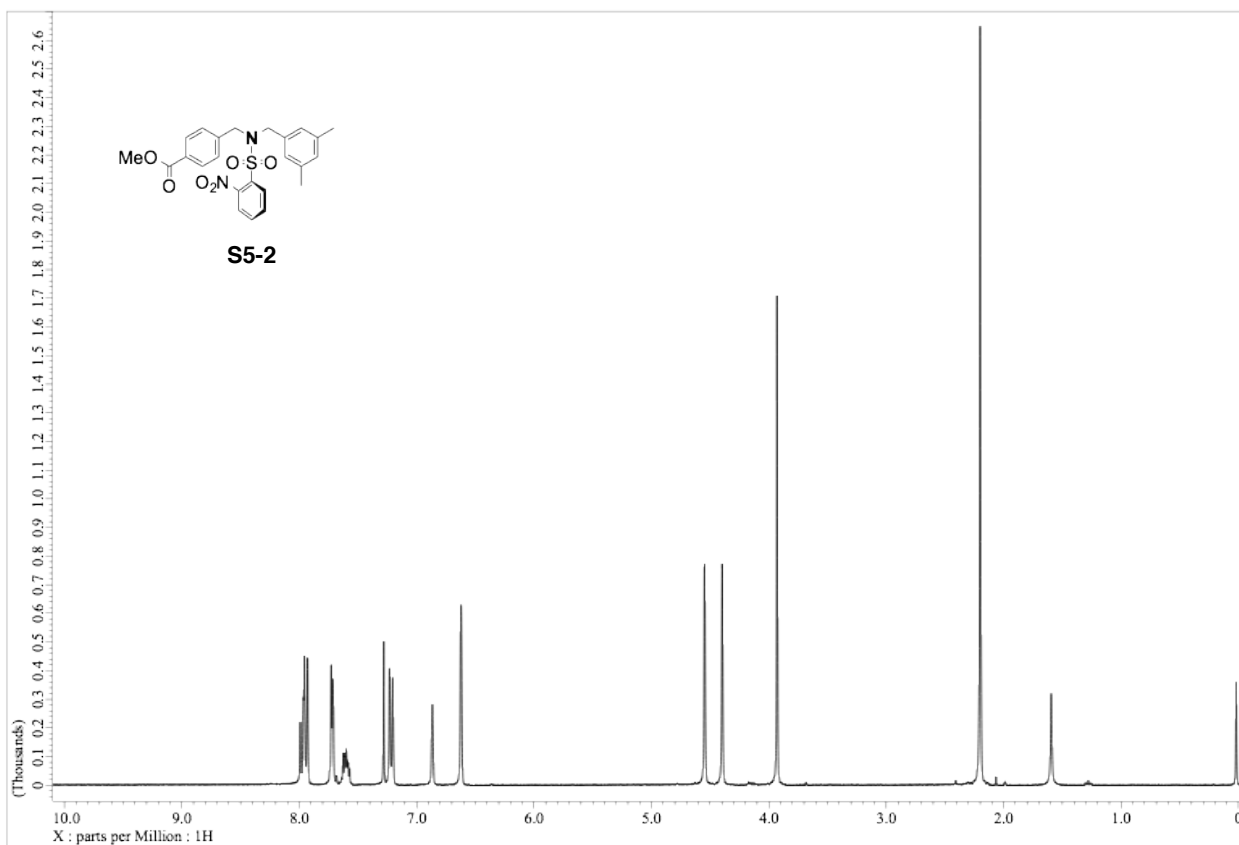


Figure S22. <sup>13</sup>C NMR spectrum of S4-3 (75 MHz, CDCl<sub>3</sub>, 298 K).



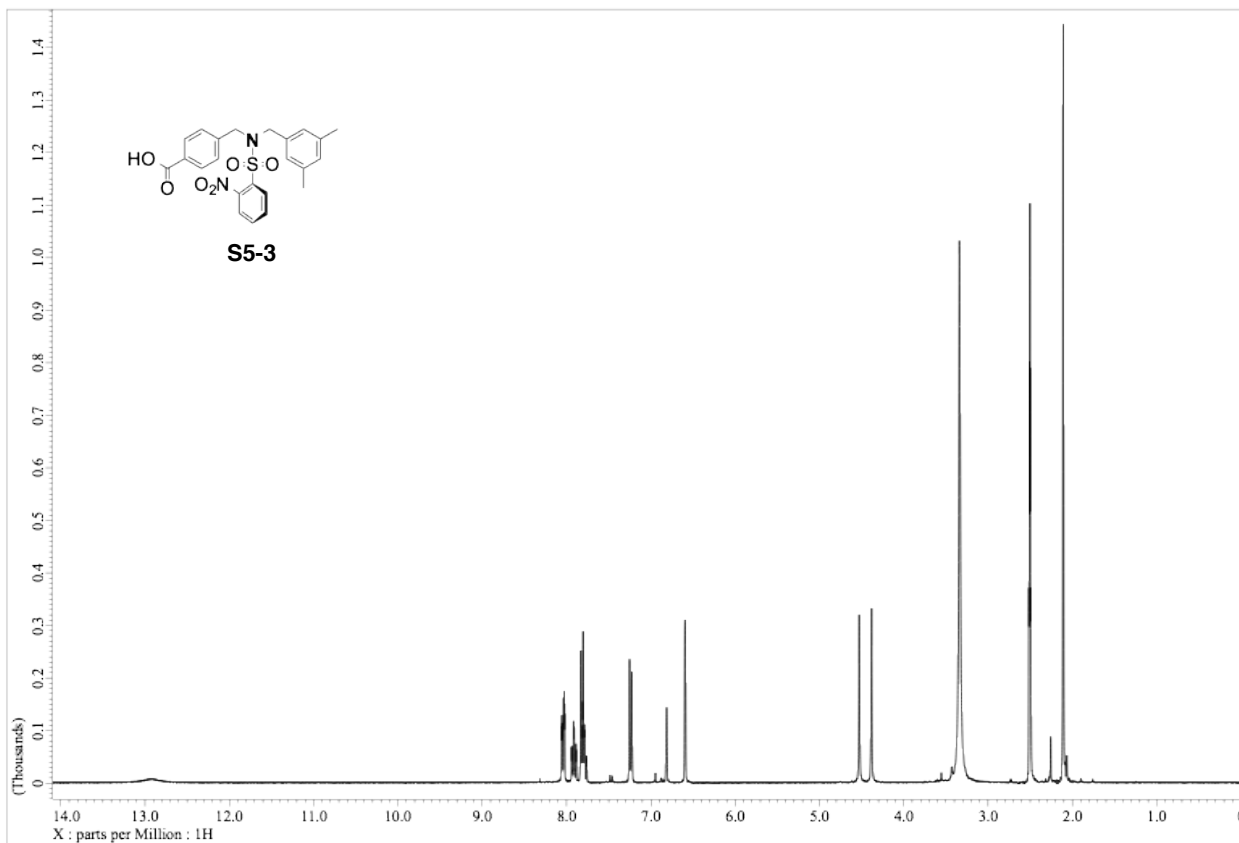


Figure S25. <sup>1</sup>H NMR spectrum of S5-3 (300 MHz, CD<sub>3</sub>OD, 298 K).

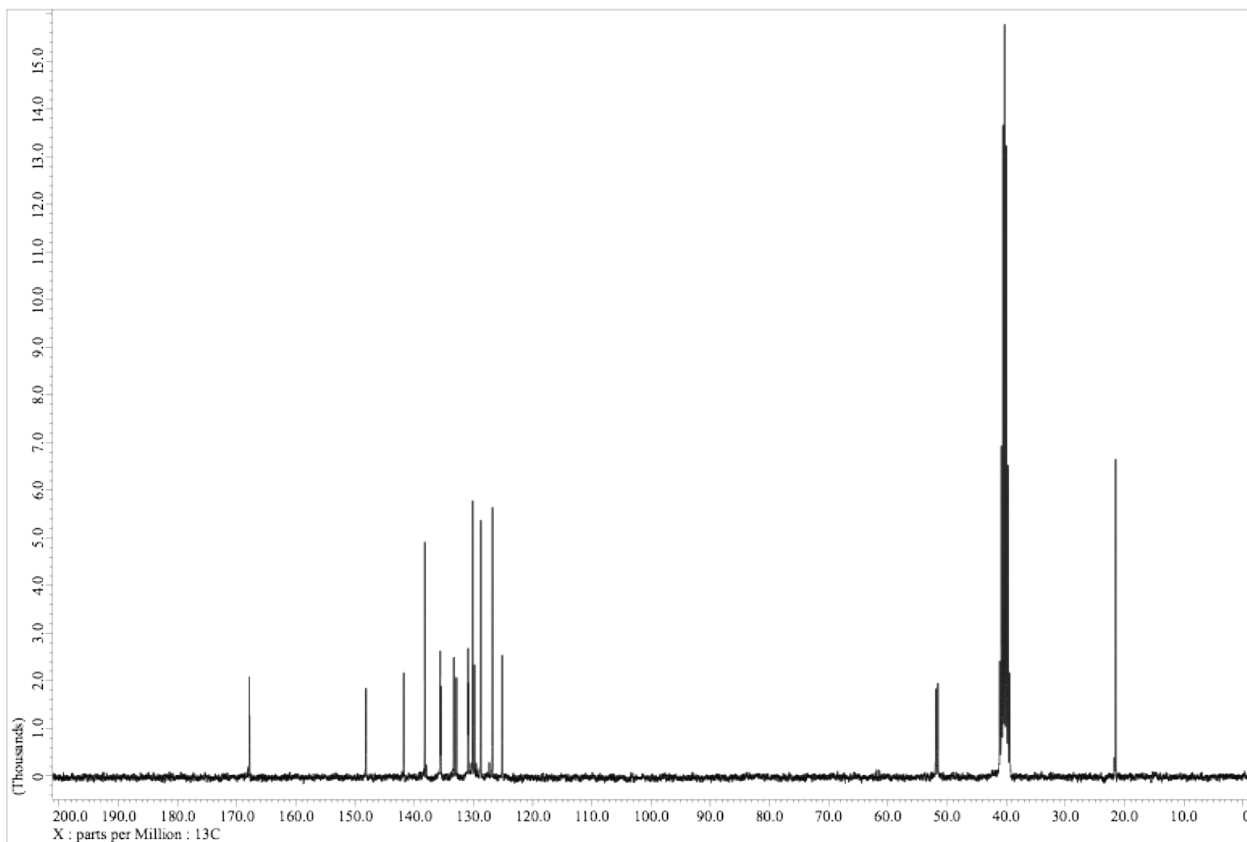


Figure S26. <sup>13</sup>C NMR spectrum of S5-3 (75 MHz, CD<sub>3</sub>OD, 298 K).

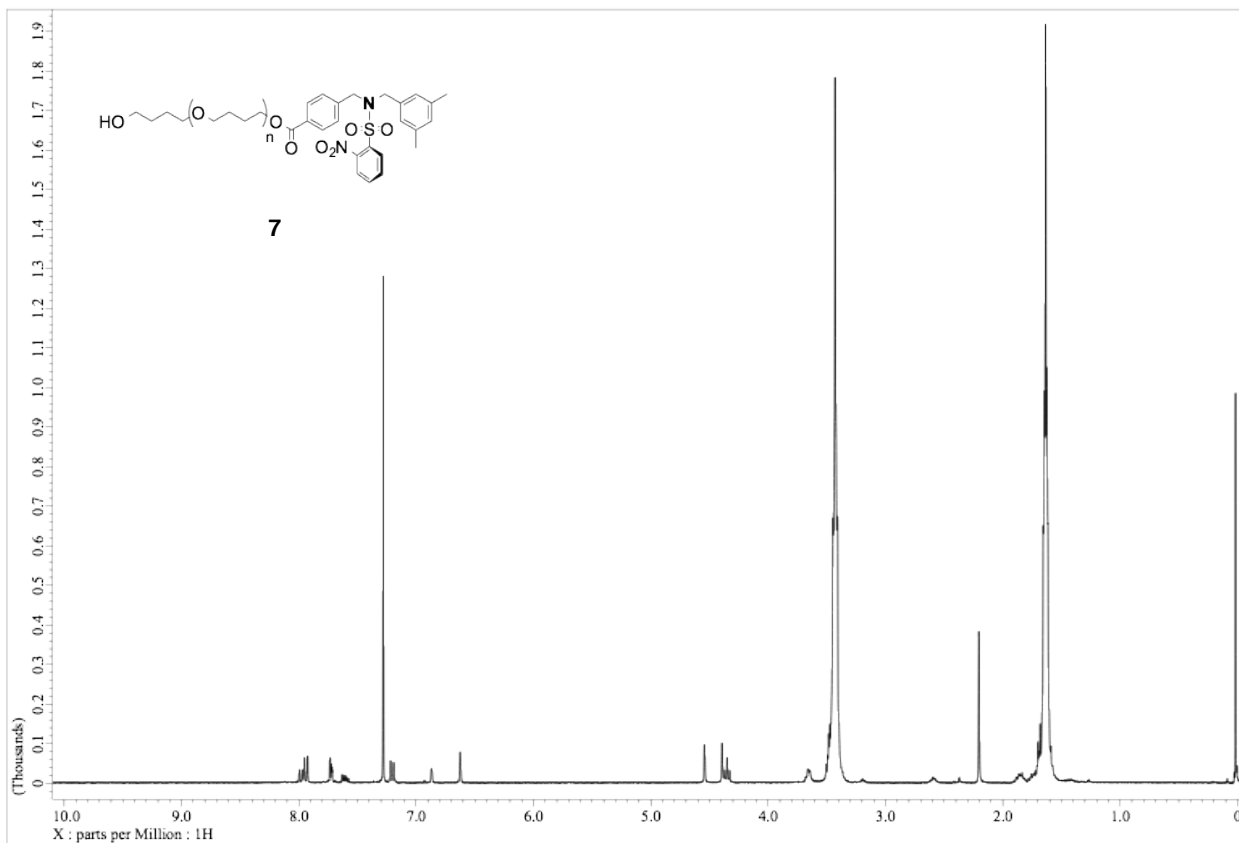


Figure S27. <sup>1</sup>H NMR spectrum of 7 (300 MHz, CDCl<sub>3</sub>, 298 K).

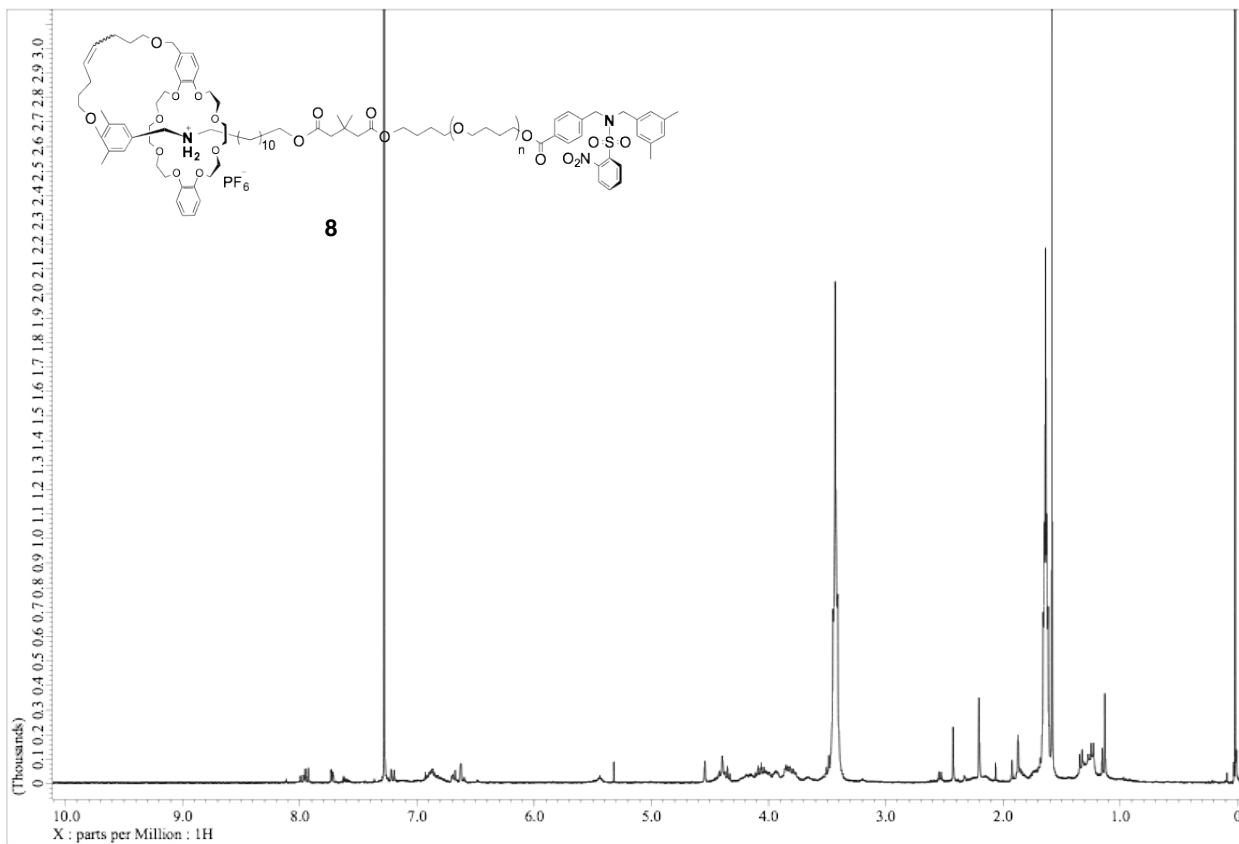
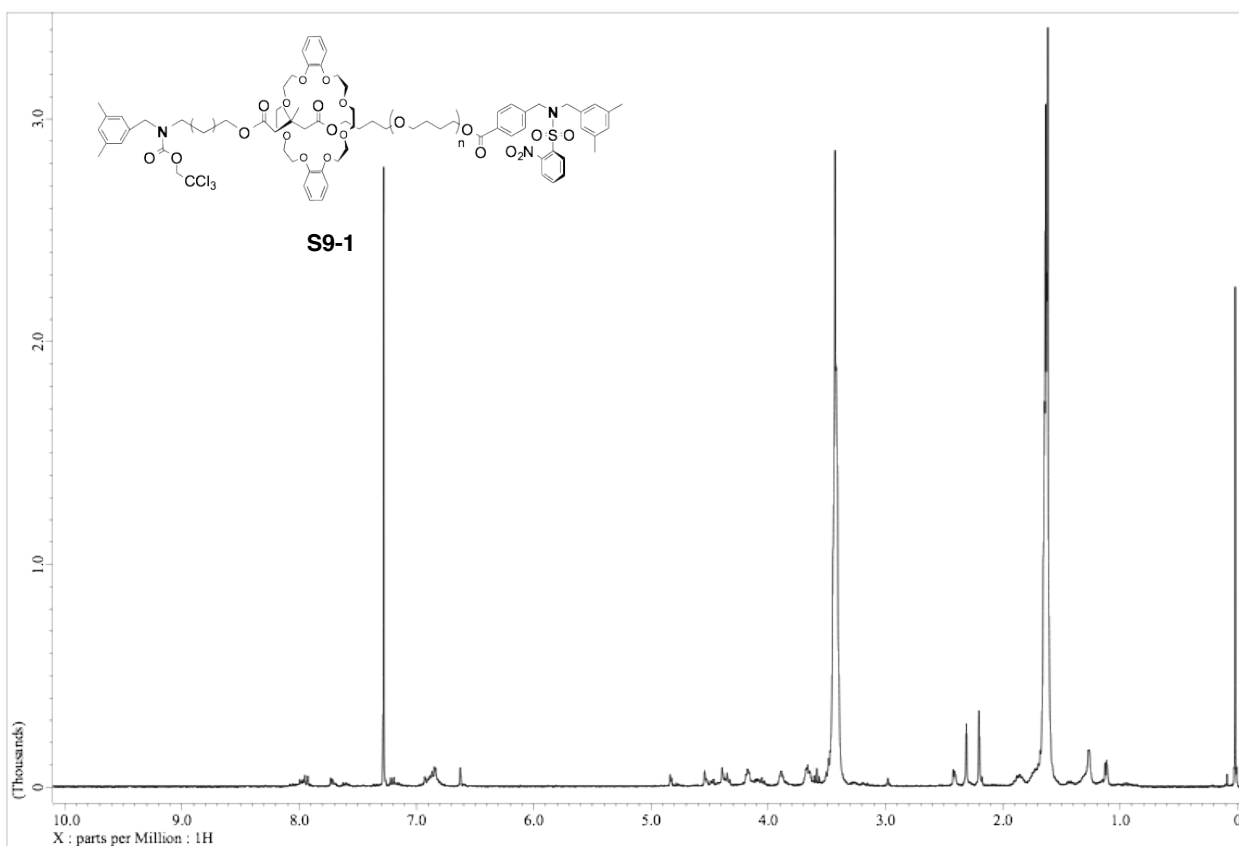
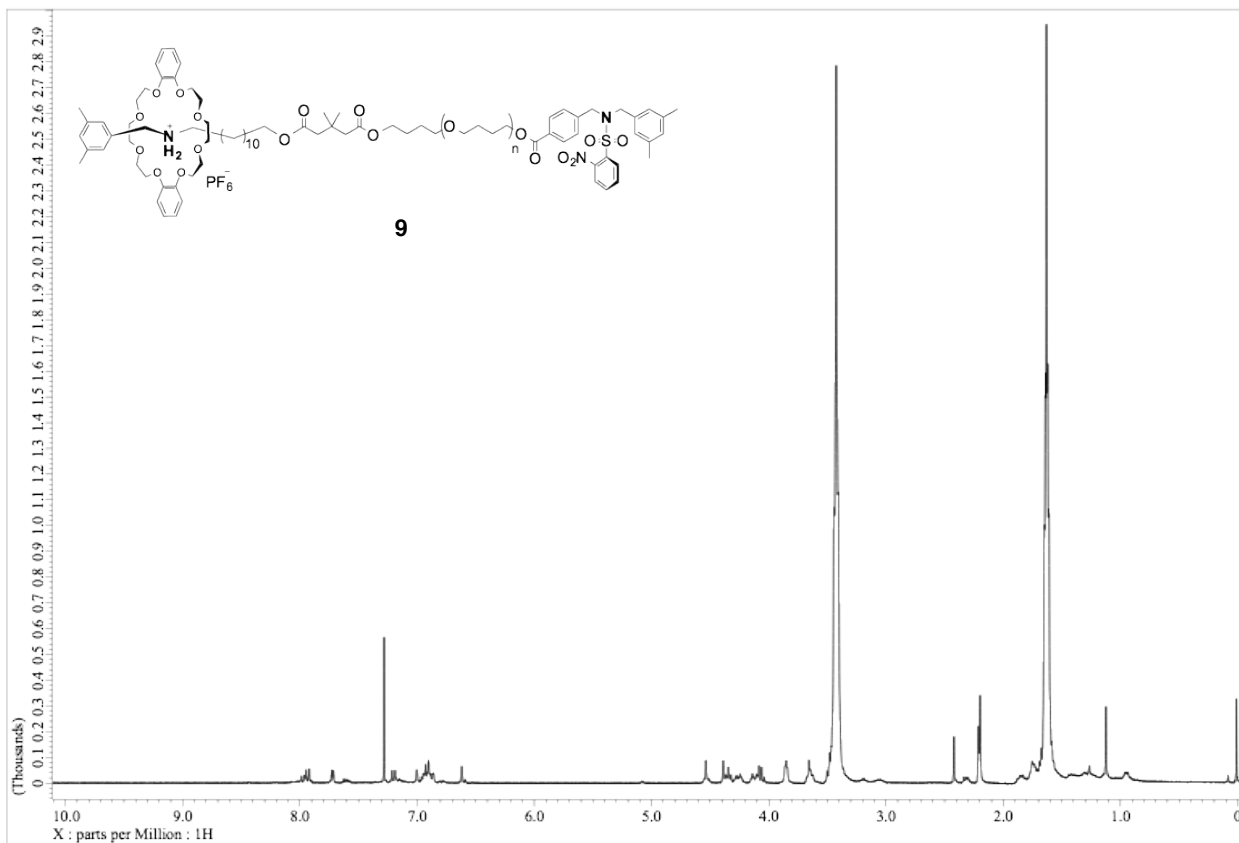


Figure S28. <sup>1</sup>H NMR spectrum of 8 (300 MHz, CDCl<sub>3</sub>, 298 K).



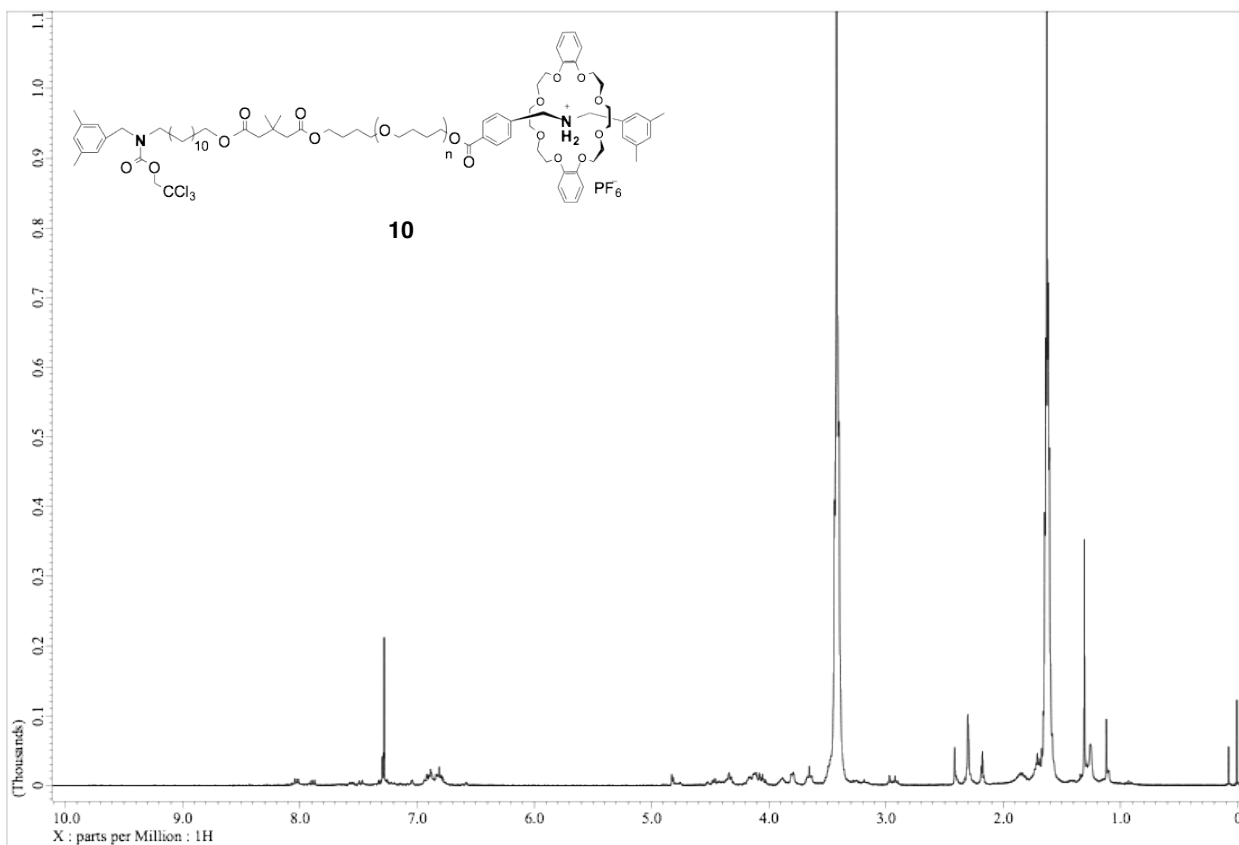


Figure S31. <sup>1</sup>H NMR spectrum of 10 (300 MHz, CDCl<sub>3</sub>, 298 K).

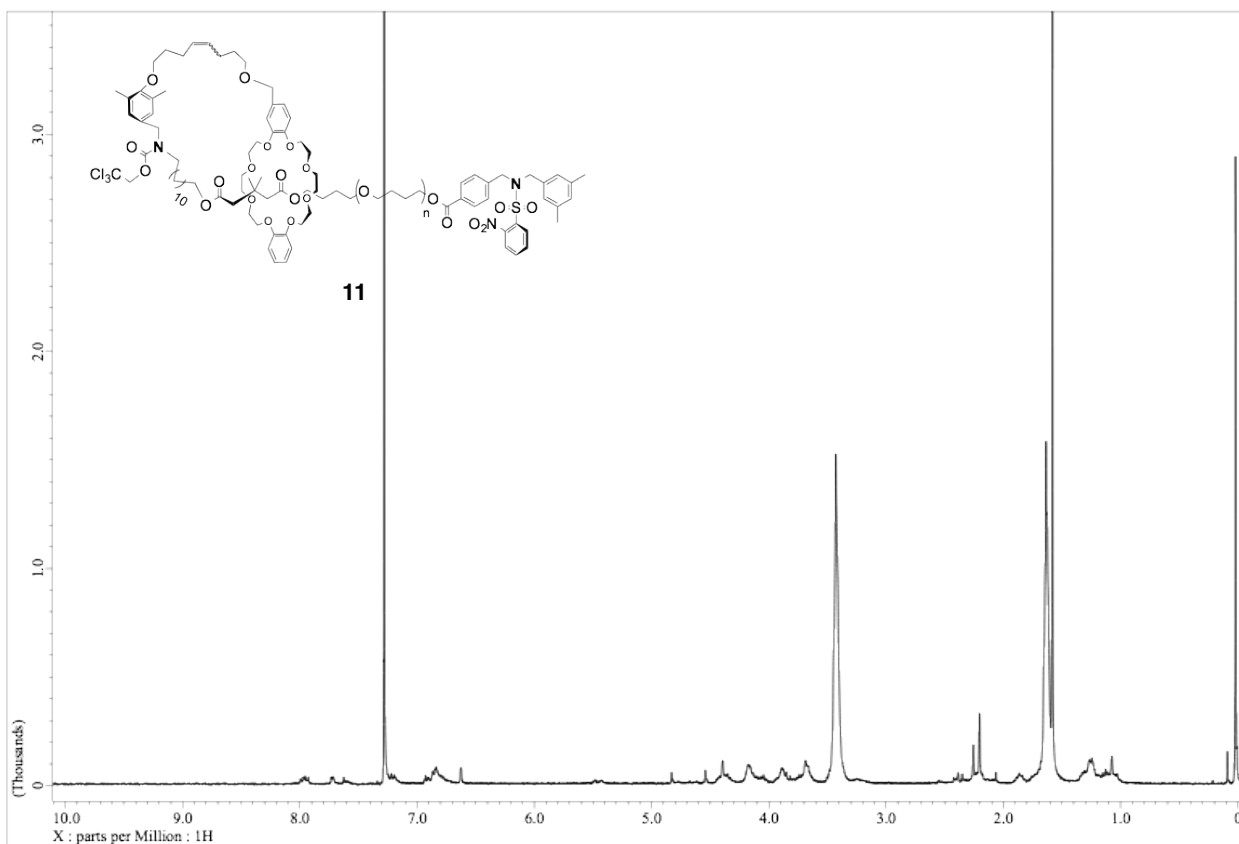


Figure S32. <sup>1</sup>H NMR spectrum of 11 (300 MHz, CDCl<sub>3</sub>, 298 K).



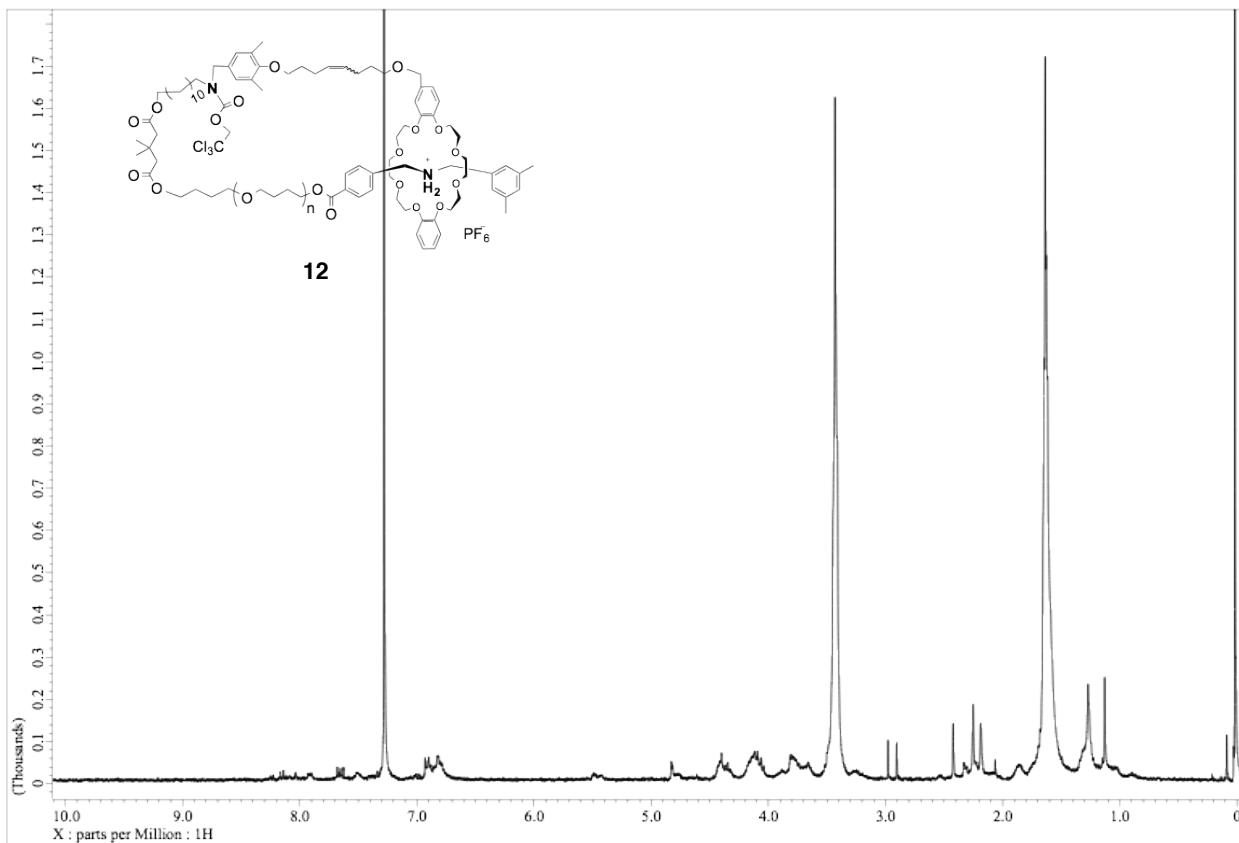
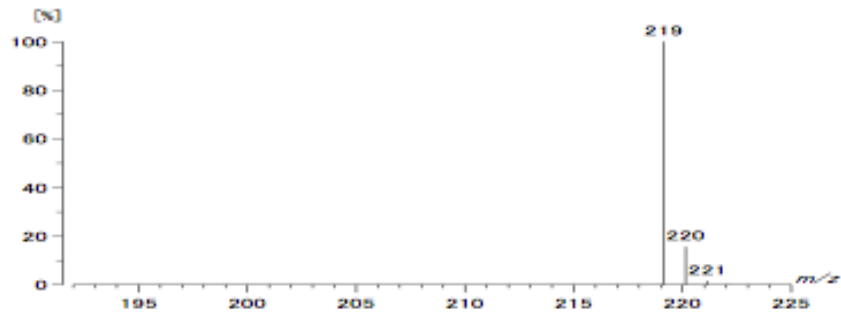


Figure S33.  $^1\text{H}$  NMR spectrum of **12** (300 MHz,  $\text{CDCl}_3$ , 298 K).

## 4.2 Mass spectra

[ Molecular Formula ]  
Data : ogawa2013-001-218-HR Date : 26-Aug-2013 10:19  
Molecular Formula : C14 H19 O2  
Elements : C 100.0, H 100.0, N 5.0, O 20.0  
Mass Tolerance : 2mmu  
Unsaturation (U.S.) : -0.5 - 40.0



[ Mass Spectrum ]  
Data : ogawa2013-001-218-HR Date : 26-Aug-2013 10:19  
Inlet : Direct Ion Mode : FAB+  
Scan# : 13

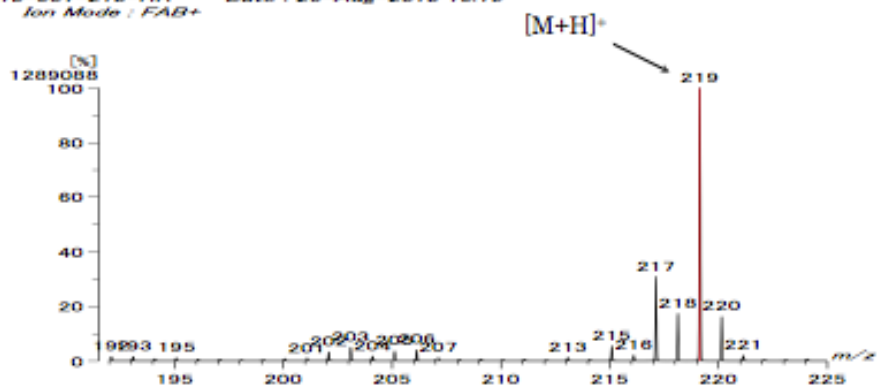
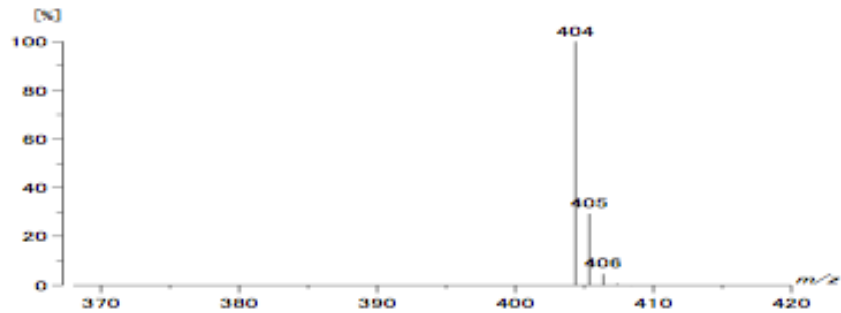


Figure S34. FAB HR-MS spectrum of S1-1.

[ Molecular Formula ]  
Data : ogawa2013-003-403-HR Date : 26-Aug-2013 10:45  
Molecular Formula : C26 H46 N O2  
Elements : C 100.0, H 100.0, N 5.0, O 20.0  
Mass Tolerance : 2mmu  
Unsaturation (U.S.) : -0.5 - 40.0



[ Mass Spectrum ]  
Data : ogawa2013-003-403-HR Date : 26-Aug-2013 10:45  
Inlet : Direct Ion Mode : FAB+  
Scan# : 11

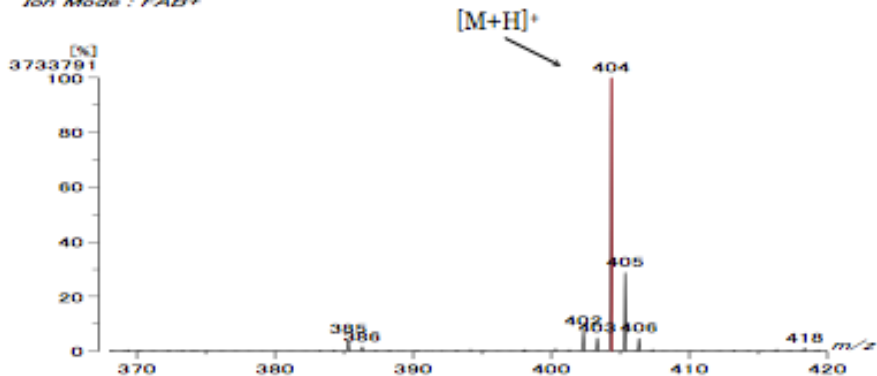


Figure S35. FAB HR-MS spectrum of S1-3.

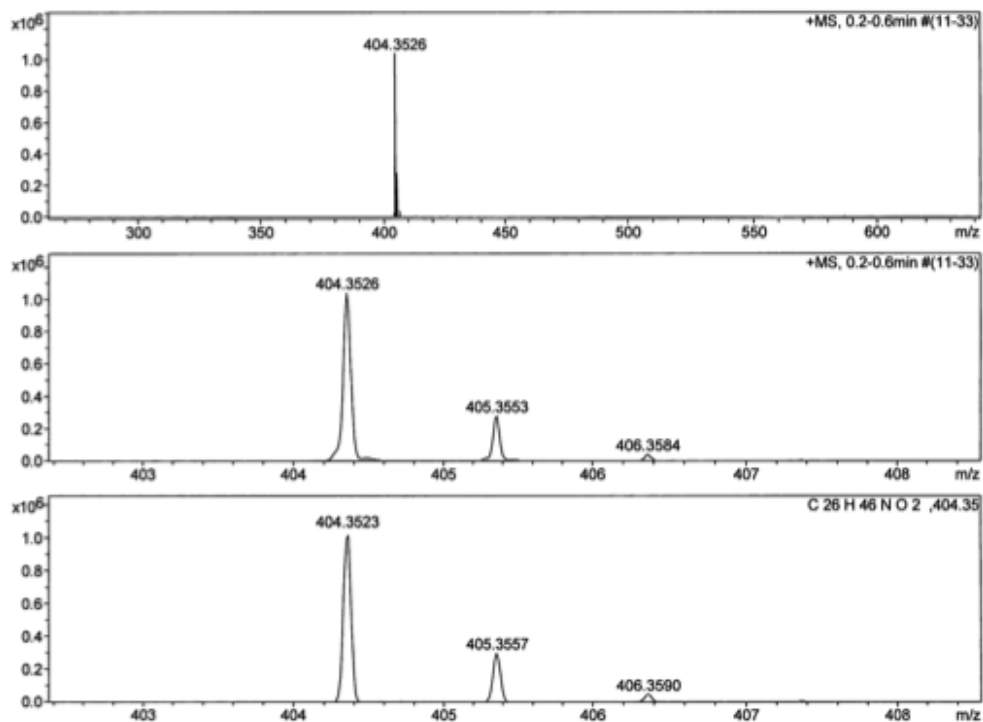


Figure S36. ESI-TOF-MS spectrum of S1-3.

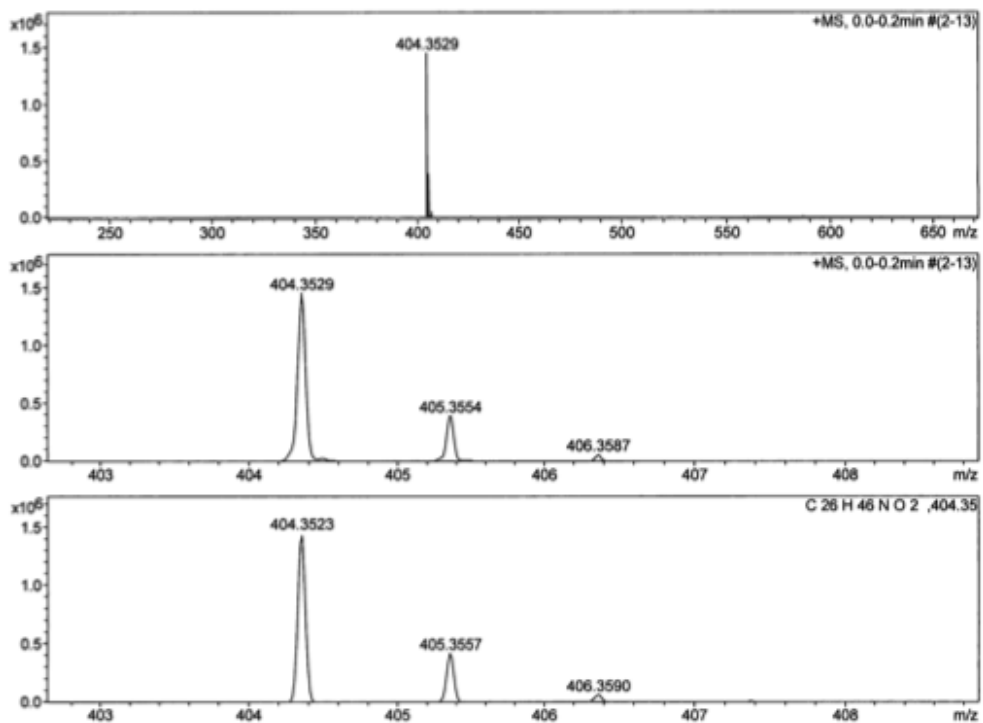
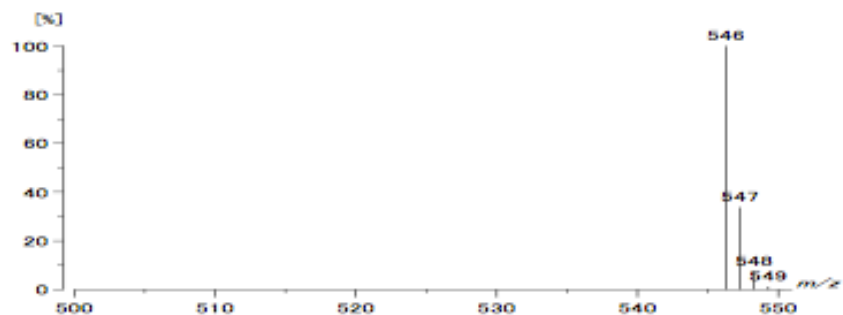


Figure S37. ESI-TOF-MS spectrum of 1.

[ Molecular Formula ]  
 Data : ogawa2013-002-546-HR Date : 26-Aug-2013 11:53  
 Molecular Formula : C<sub>30</sub>H<sub>42</sub>O<sub>9</sub>  
 Elements : C 100/0, H 100/0, N 5/0, O 20/0  
 Mass Tolerance : 2mmu  
 Unsaturation (U.S.) : -0.5 - 40.0



[ Mass Spectrum ]  
 Data : ogawa2013-002-546-HR Date : 26-Aug-2013 11:53  
 Inlet : Direct Ion Mode : FAB+  
 Scan# : 24

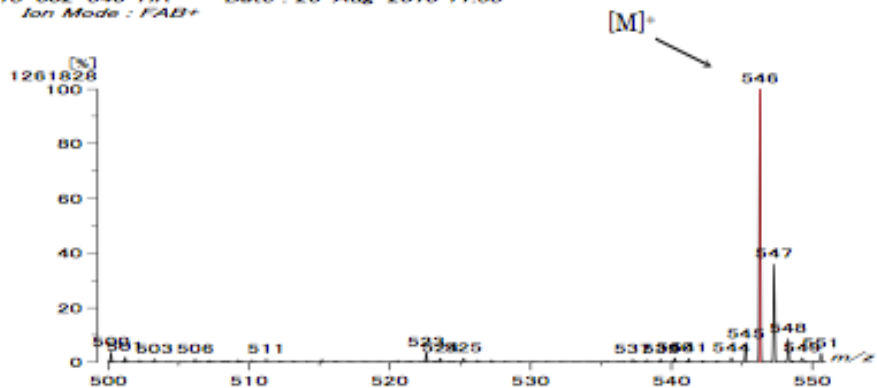
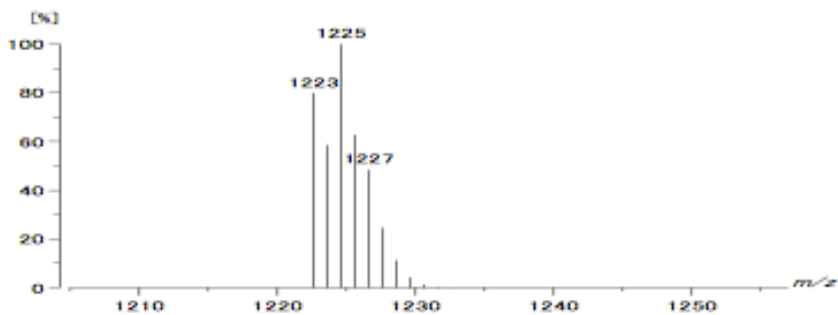


Figure S38. FAB HR-MS spectrum of 2.

[ Molecular Formula ]  
 Data : ogawa2013-008-1367-HR Date : 26-Aug-2013 12:37  
 Molecular Formula : C<sub>65</sub>H<sub>99</sub>N<sub>3</sub>O<sub>14</sub>Cl<sub>3</sub>  
 Elements : C 100/1, H 100/1, 35Cl 3/0, 37Cl 3/0, N 1/0, O 20/0  
 Mass Tolerance : 1.1mmu  
 Unsaturation (U.S.) : -0.5 - 16.0



[ Mass Spectrum ]  
 Data : ogawa2013-008-1367-HR Date : 26-Aug-2013 12:37  
 Inlet : Direct Ion Mode : FAB+  
 Scan# : 22

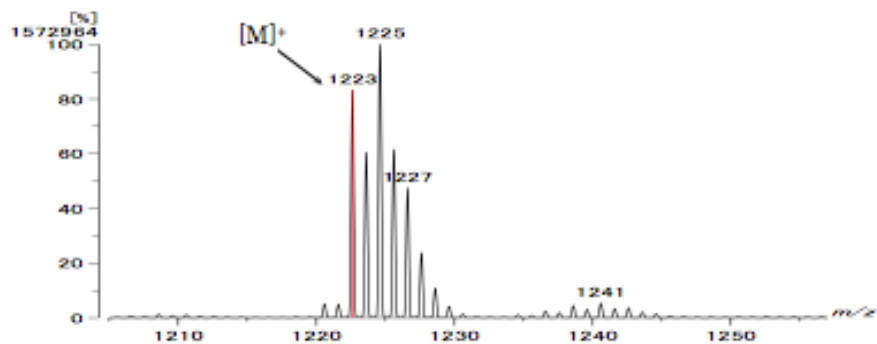


Figure S39. FAB HR-MS spectrum of 3.

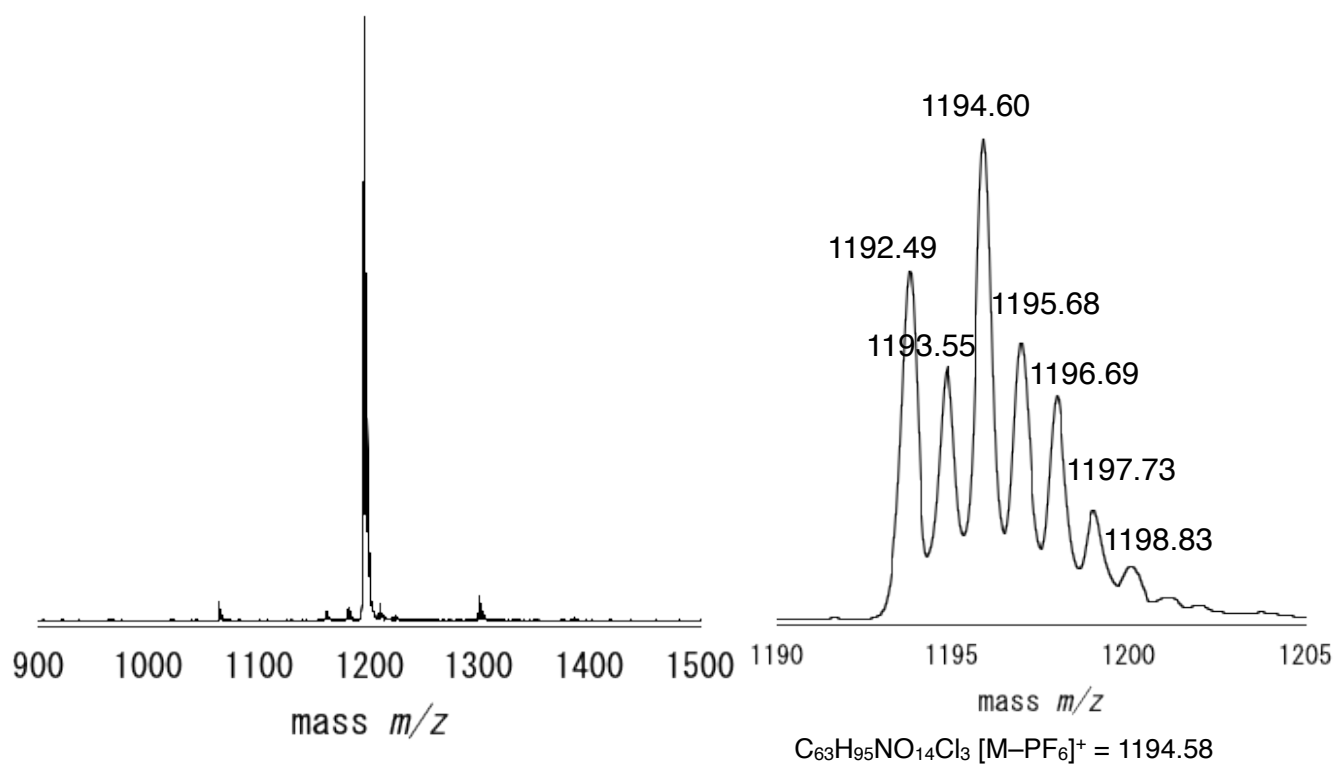


Figure S40. MALDI-TOF-MS spectrum of 4.

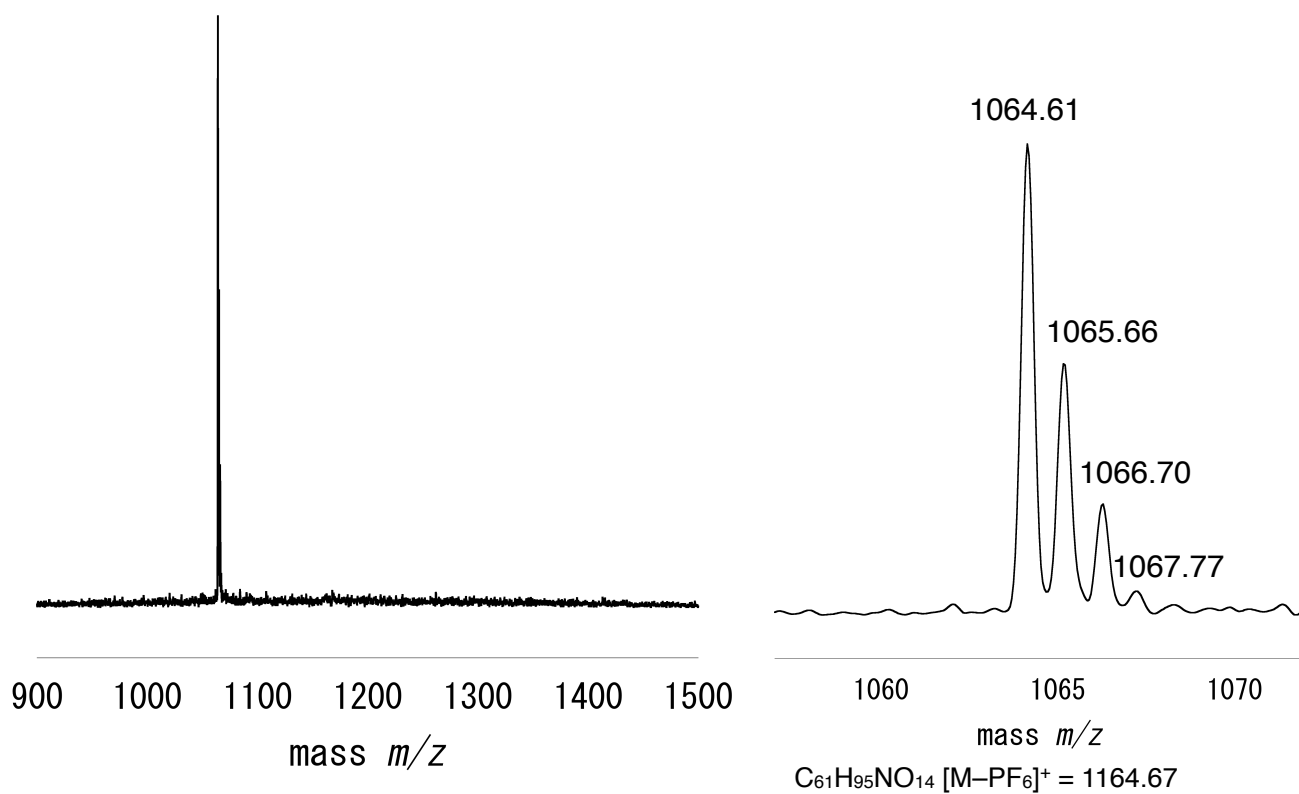
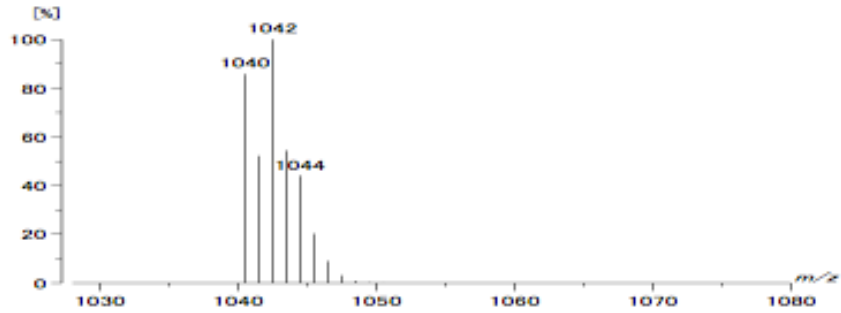


Figure S41. MALDI-TOF-MS spectrum of 5.

[ Molecular Formula ]  
 Data : ogawa2013-006-1185-HR Date : 26-Aug-2013 12:27  
 Molecular Formula : C<sub>54</sub> H<sub>81</sub> Cl<sub>3</sub> N O<sub>12</sub>  
 Elements : C 100/0, H 100/0, 35Cl 3/0, 37Cl 3/0, N 5/0, O 20/0  
 Mass Tolerance : 1mmu  
 Unsaturation (U.S.) : -0.5 - 15.0



[ Mass Spectrum ]  
 Data : ogawa2013-006-1185-HR Date : 26-Aug-2013 12:27  
 Inlet : Direct Ion Mode : FAB+  
 Scan# : 15

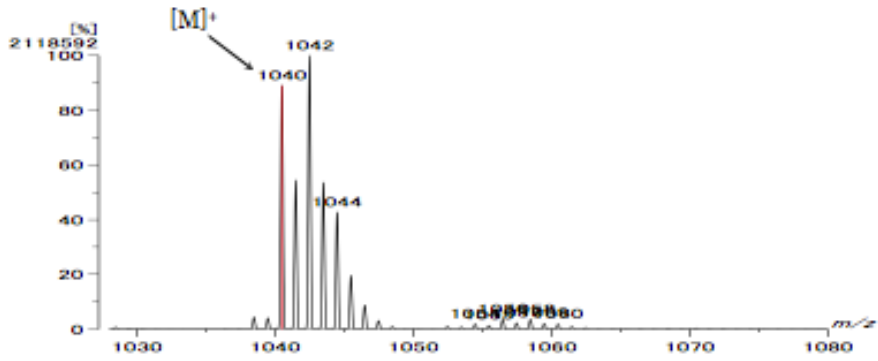
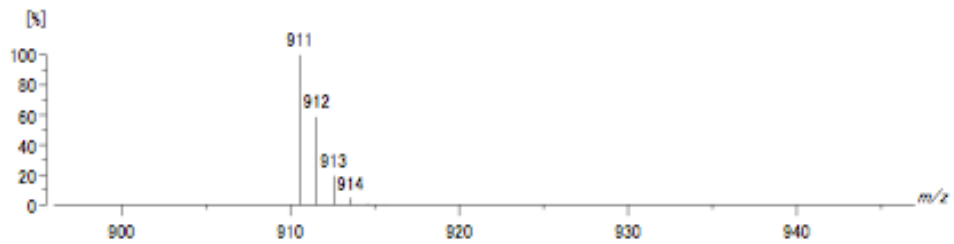


Figure S42. FAB HR-MS spectrum of S4-2.

[ Molecular Formula ]  
 Data : ogawa2013-007-1055-HR Date : 26-Aug-2013 12:17  
 Molecular Formula : C<sub>52</sub> H<sub>80</sub> N O<sub>12</sub>  
 Elements : C 100/0, H 100/0, N 5/0, O 20/0  
 Mass Tolerance : 2mmu  
 Unsaturation (U.S.) : -0.5 - 40.0



[ Mass Spectrum ]  
 Data : ogawa2013-007-1055-HR Date : 26-Aug-2013 12:17  
 Inlet : Direct Ion Mode : FAB+  
 Scan# : 14

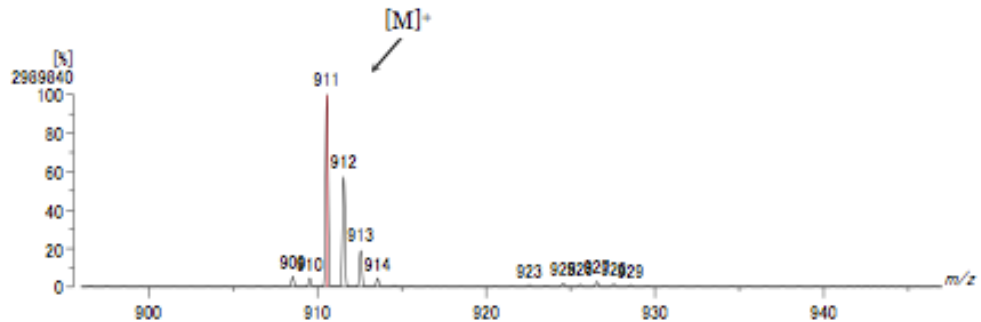
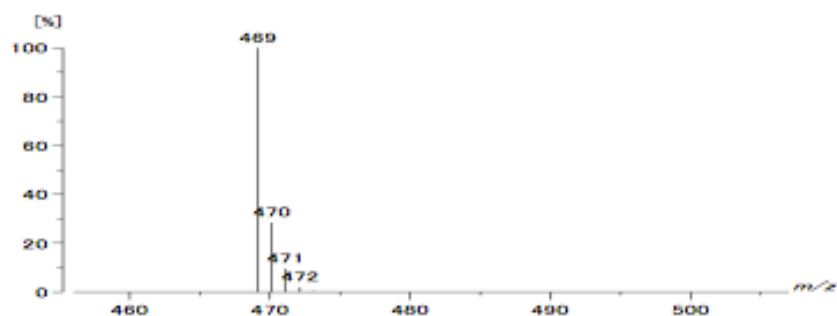


Figure S43. FAB HR-MS spectrum of S4-3.

[ Molecular Formula ]  
 Data : ogawa2013-004-468-HR Date : 26-Aug-2013 11:37  
 Molecular Formula : C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O<sub>6</sub>S  
 Elements : C 100.0, H 100.0, N 5.0, O 20.0, S 1.0, Na 1.0  
 Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 2mmu if m/z > 2  
 Unsaturation (U.S.) : -0.5 - 15.0



[ Mass Spectrum ]  
 Data : ogawa2013-004-468-HR Date : 26-Aug-2013 11:37  
 Inlet : Direct Ion Mode : FAB+  
 Scan# : 13

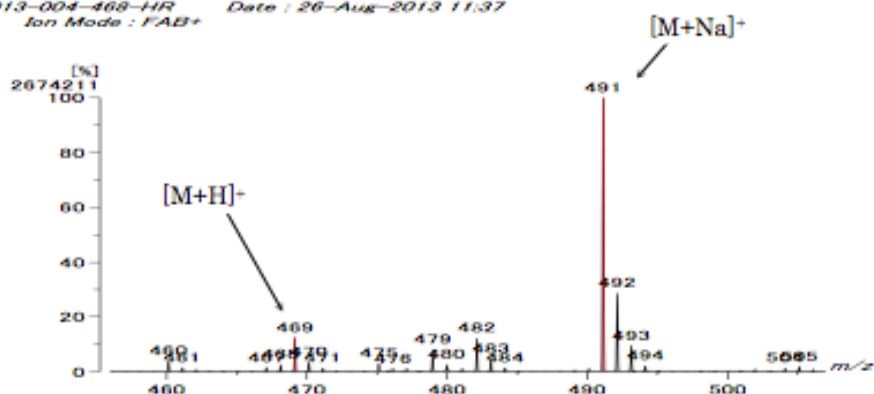
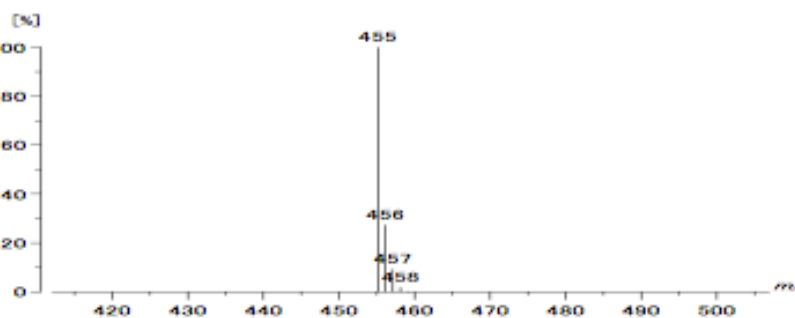


Figure S44. FAB HR-MS spectrum of S5-2.

[ Molecular Formula ]  
 Data : ogawa2013-005-454-HR Date : 26-Aug-2013 11:10  
 Molecular Formula : C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub>S  
 Elements : C 100.0, H 100.0, N 5.0, O 20.0, S 1.0, Na 1.0  
 Mass Tolerance : 1mmu  
 Unsaturation (U.S.) : -0.5 - 15.0



[ Mass Spectrum ]  
 Data : ogawa2013-005-454-HR Date : 26-Aug-2013 11:10  
 Inlet : Direct Ion Mode : FAB+  
 Scan# : 12

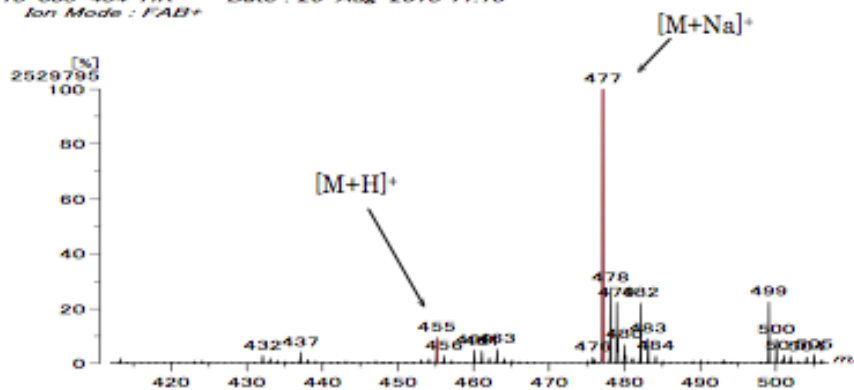


Figure S45. FAB HR-MS spectrum of S5-3.

### 4.3 FT-IR spectra

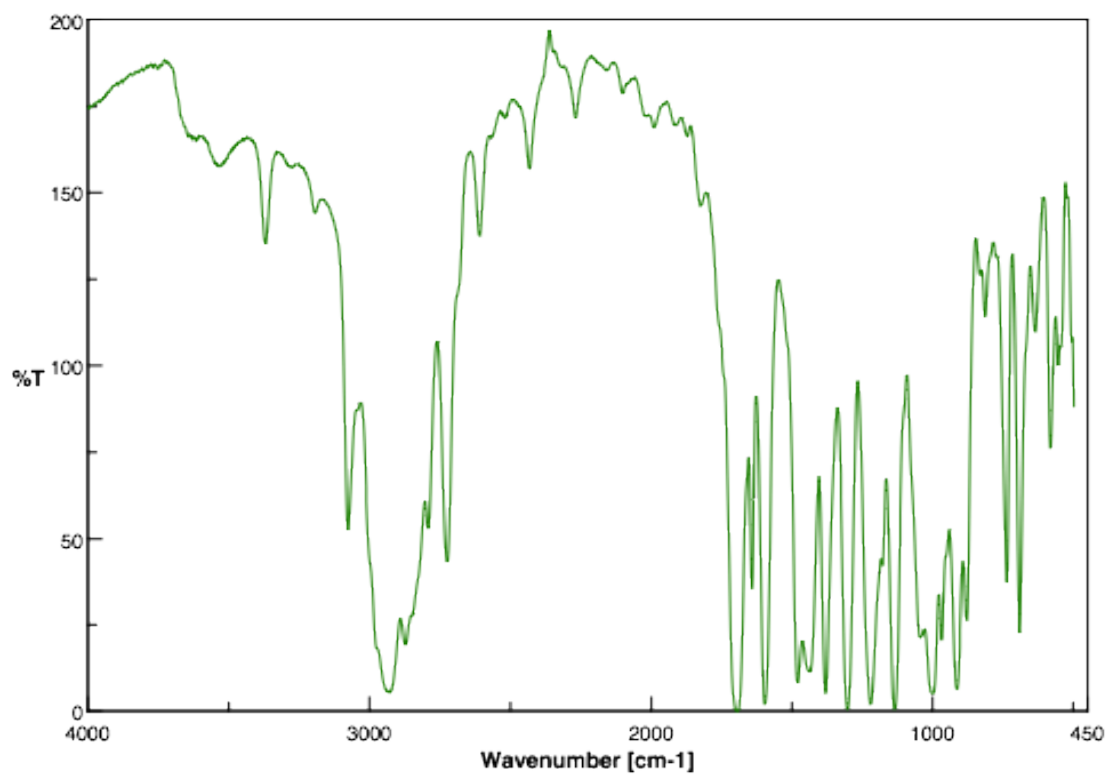


Figure S46. FT-IR spectrum of S1-1 (NaCl).

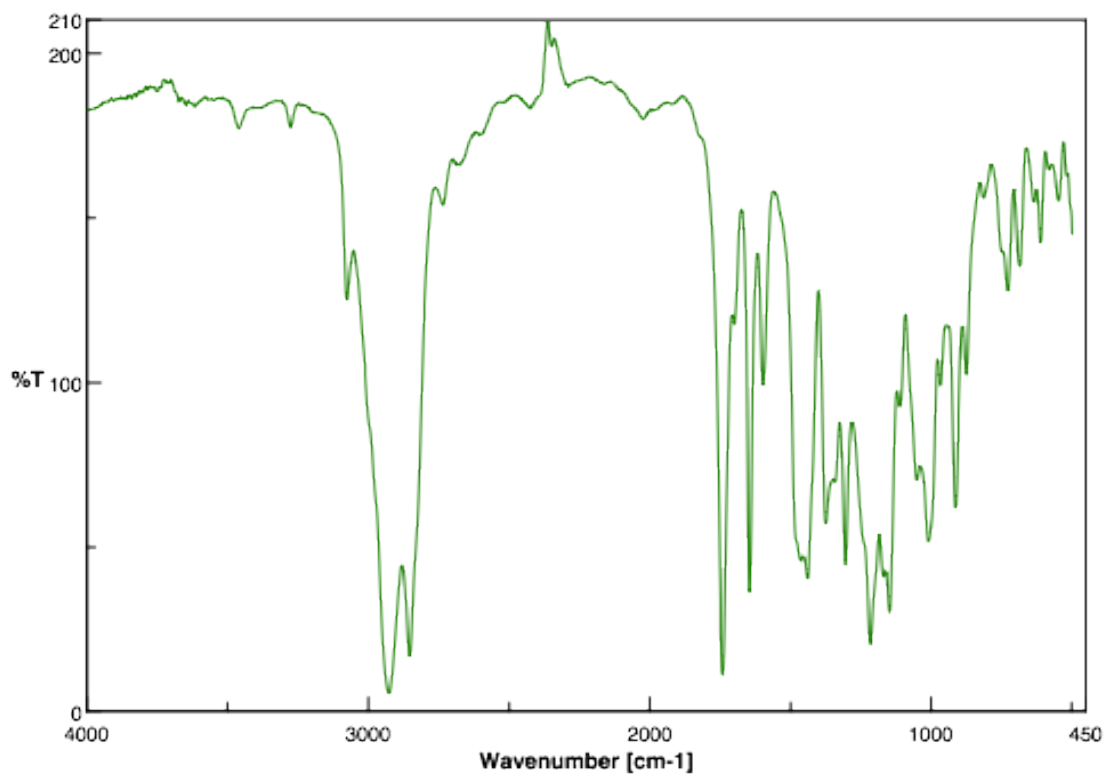


Figure S47. FT-IR spectrum of S1-2 (NaCl).



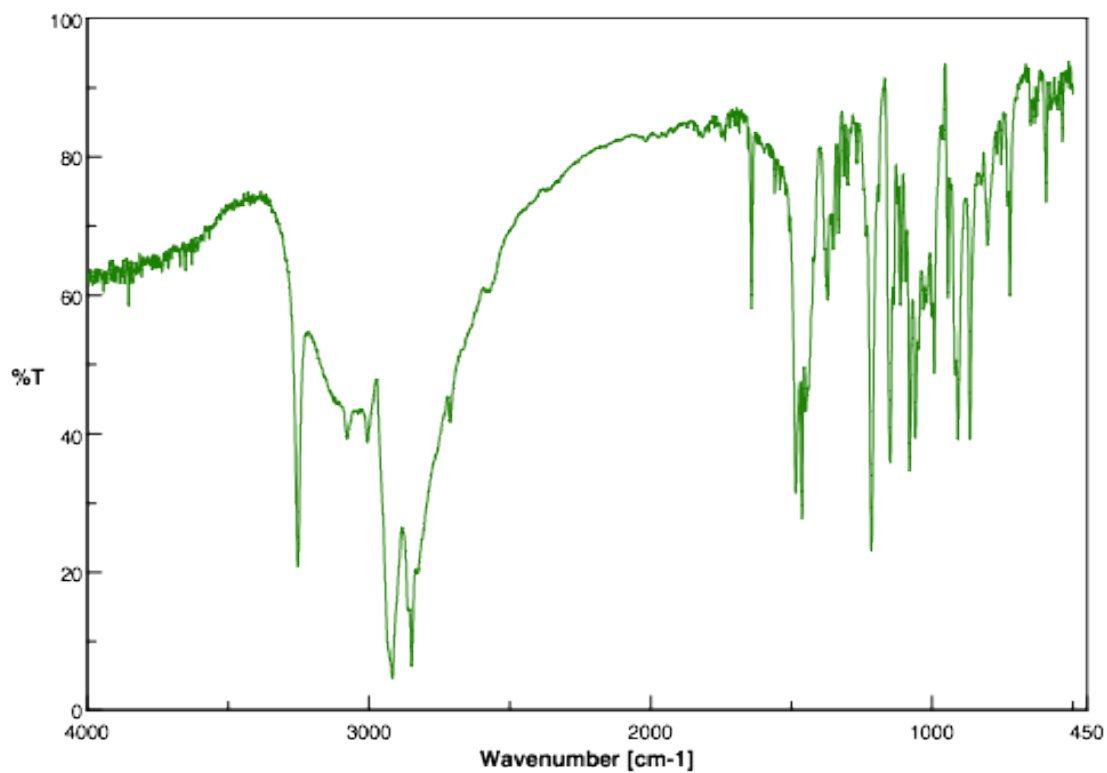


Figure S48. FT-IR spectrum of S1-3 (NaCl).

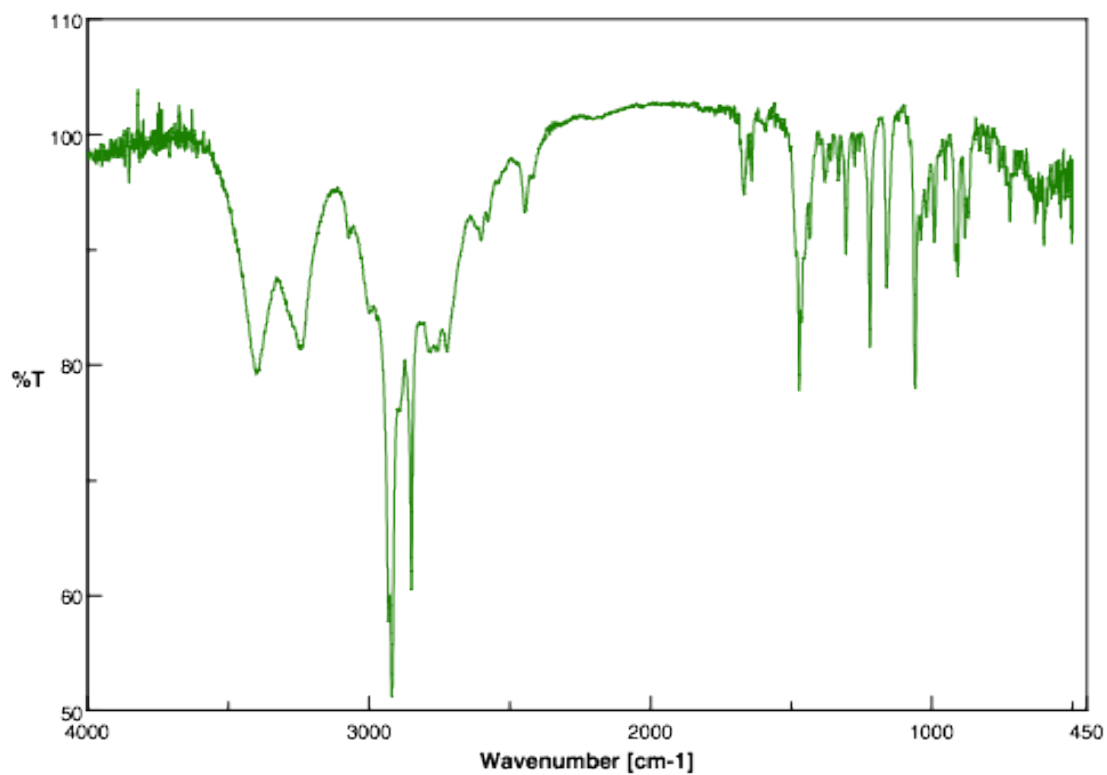


Figure S49. FT-IR spectrum of S1-4 (NaCl).

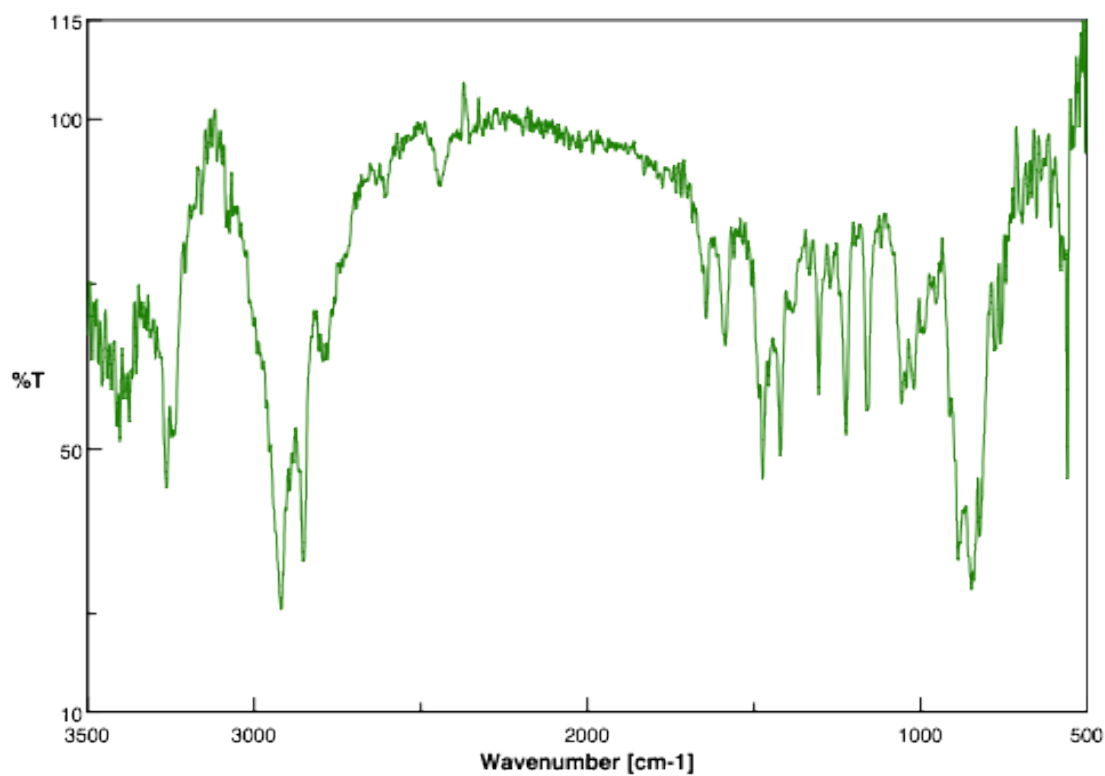


Figure S50. FT-IR spectrum of 1 (NaCl).

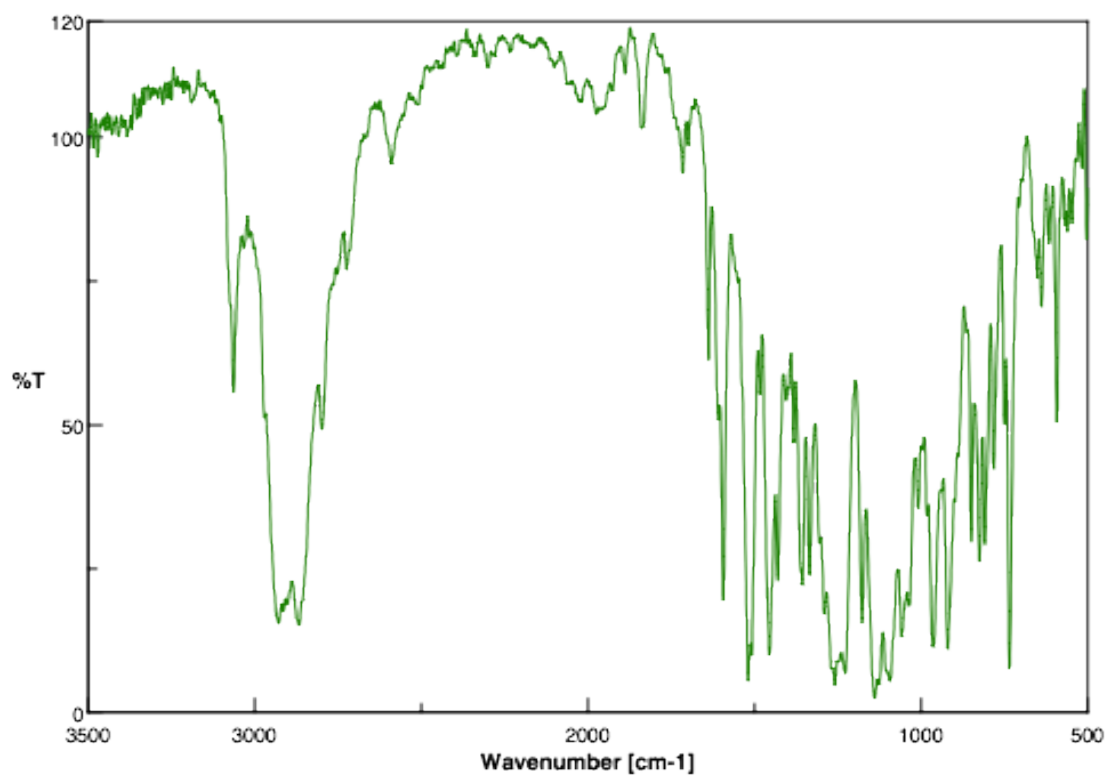


Figure S51. FT-IR spectrum of 2 (NaCl).

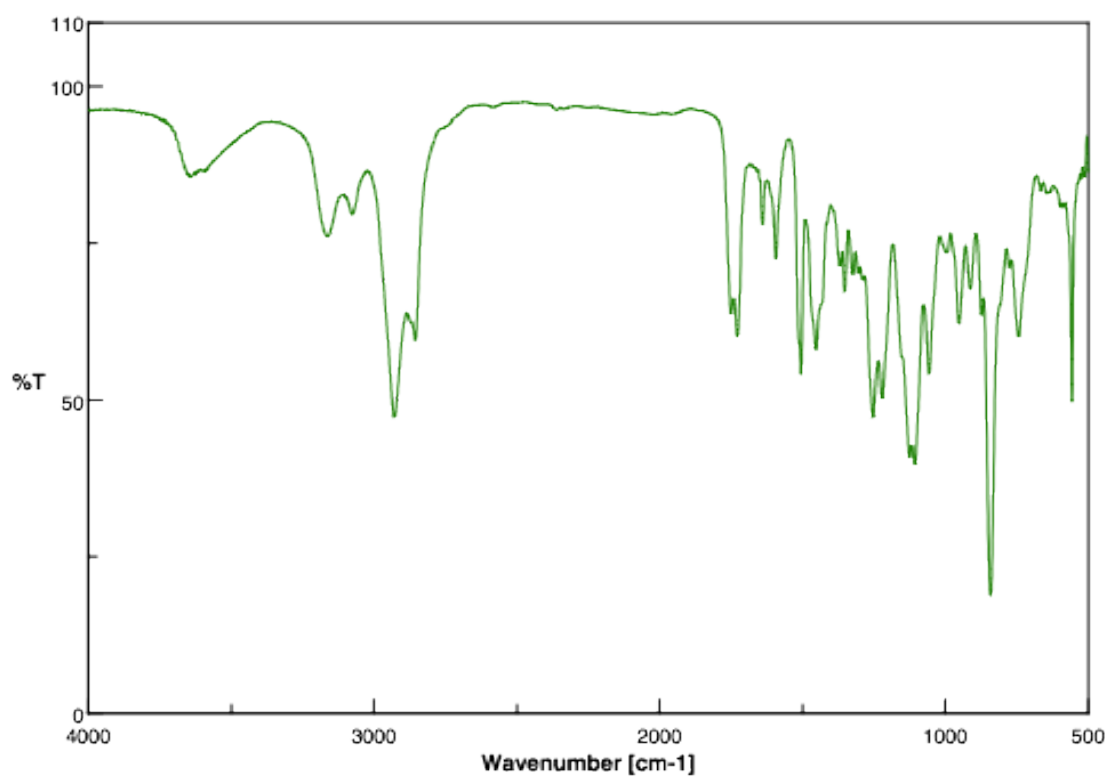


Figure S52. FT-IR spectrum of 3 (NaCl).

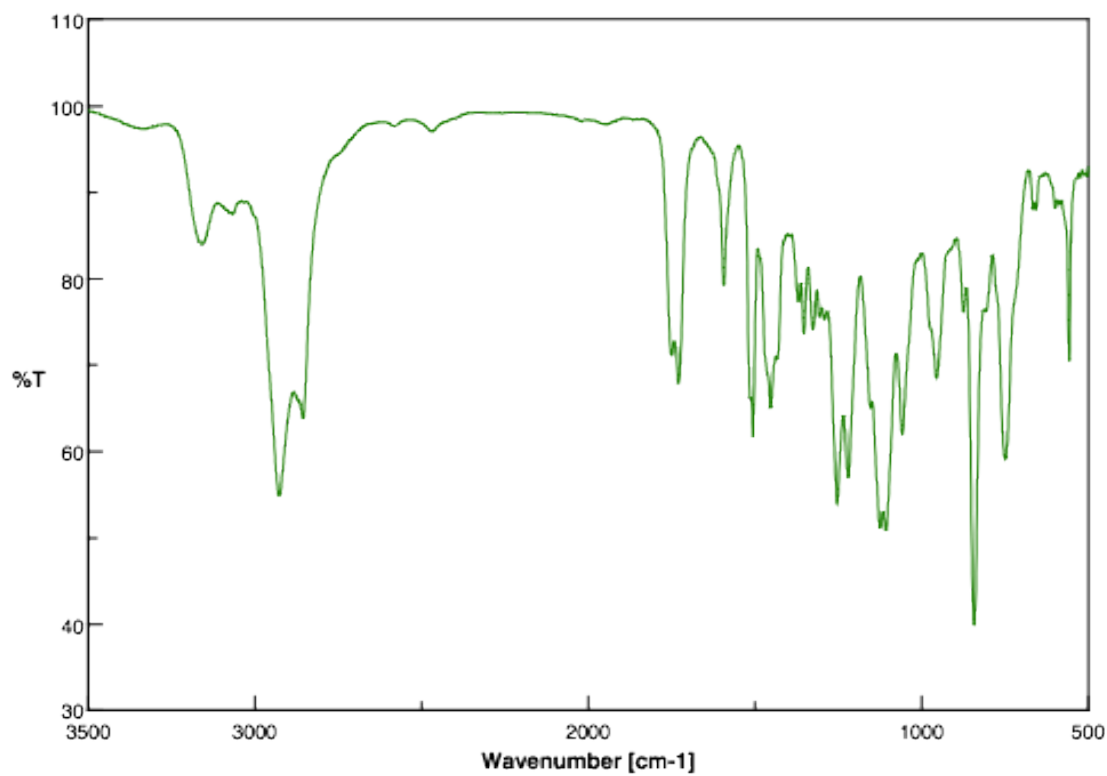


Figure S53. FT-IR spectrum of 4 (NaCl).

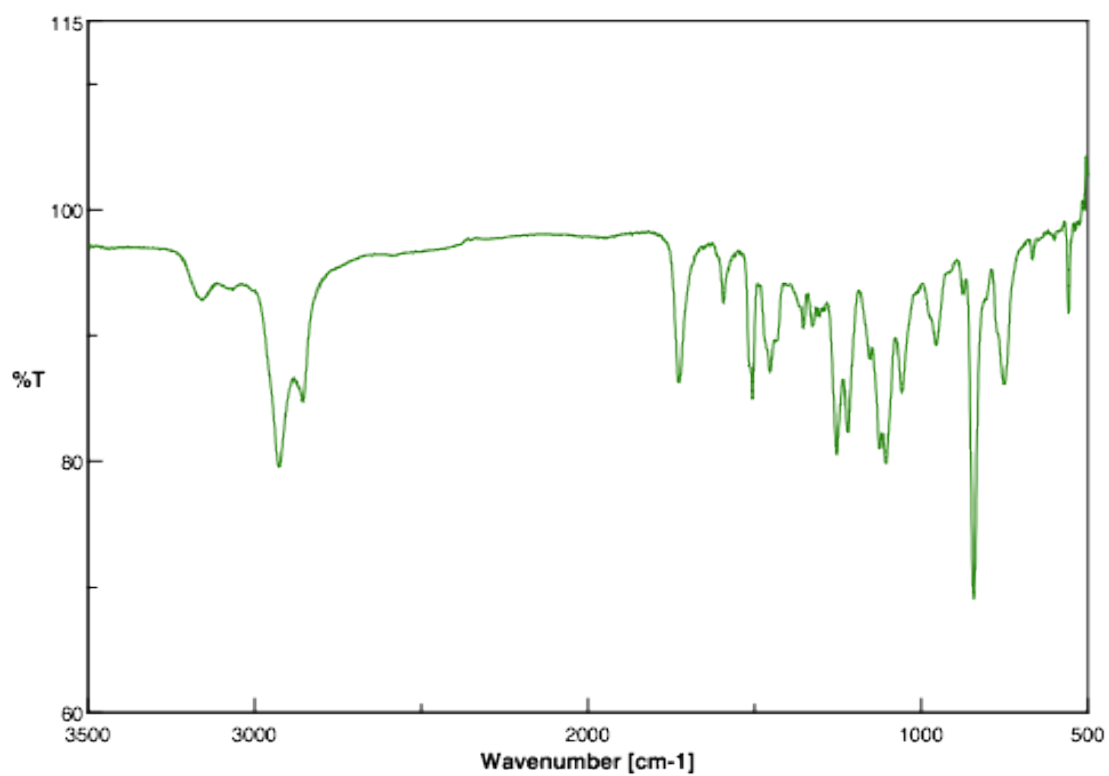


Figure S54. FT-IR spectrum of 5 (NaCl).

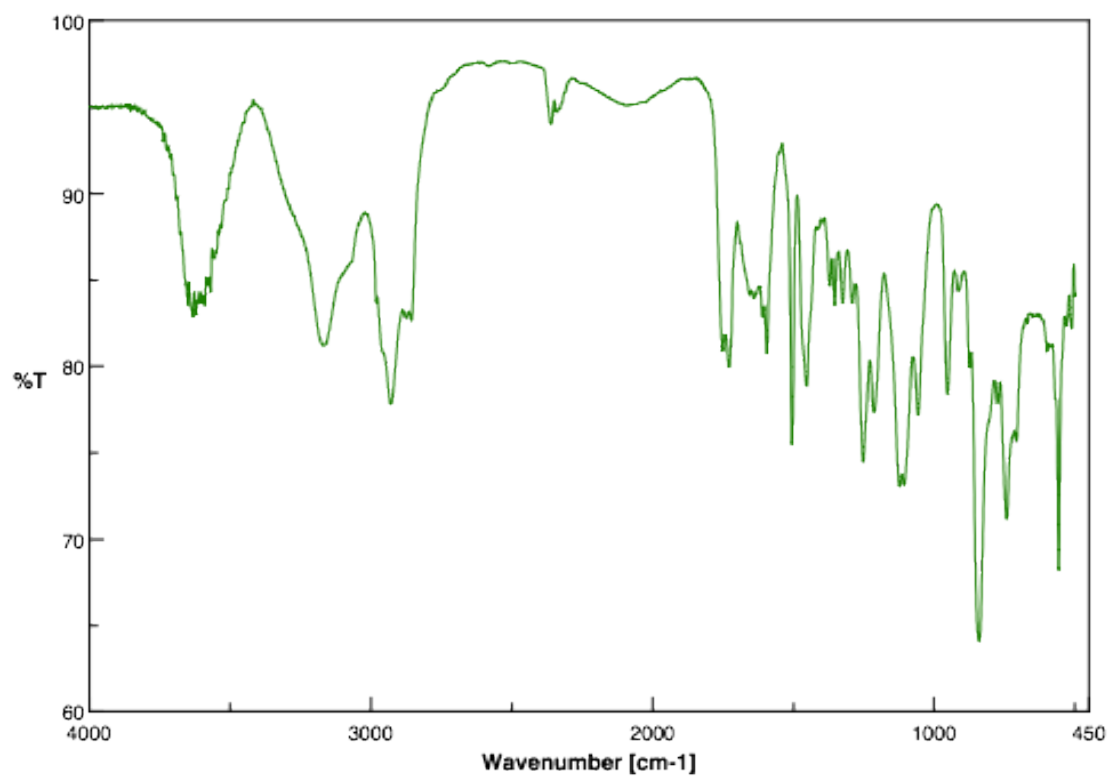


Figure S55. FT-IR spectrum of S4-2 (NaCl).

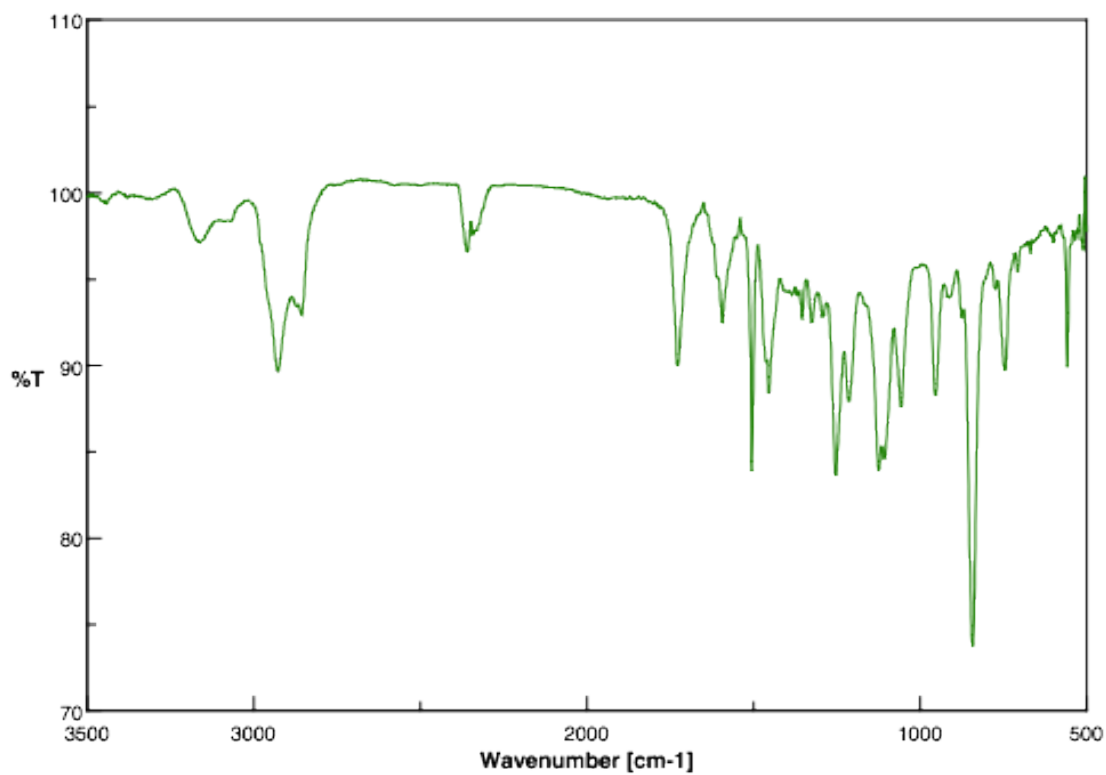


Figure S56. FT-IR spectrum of S4-3 (NaCl).

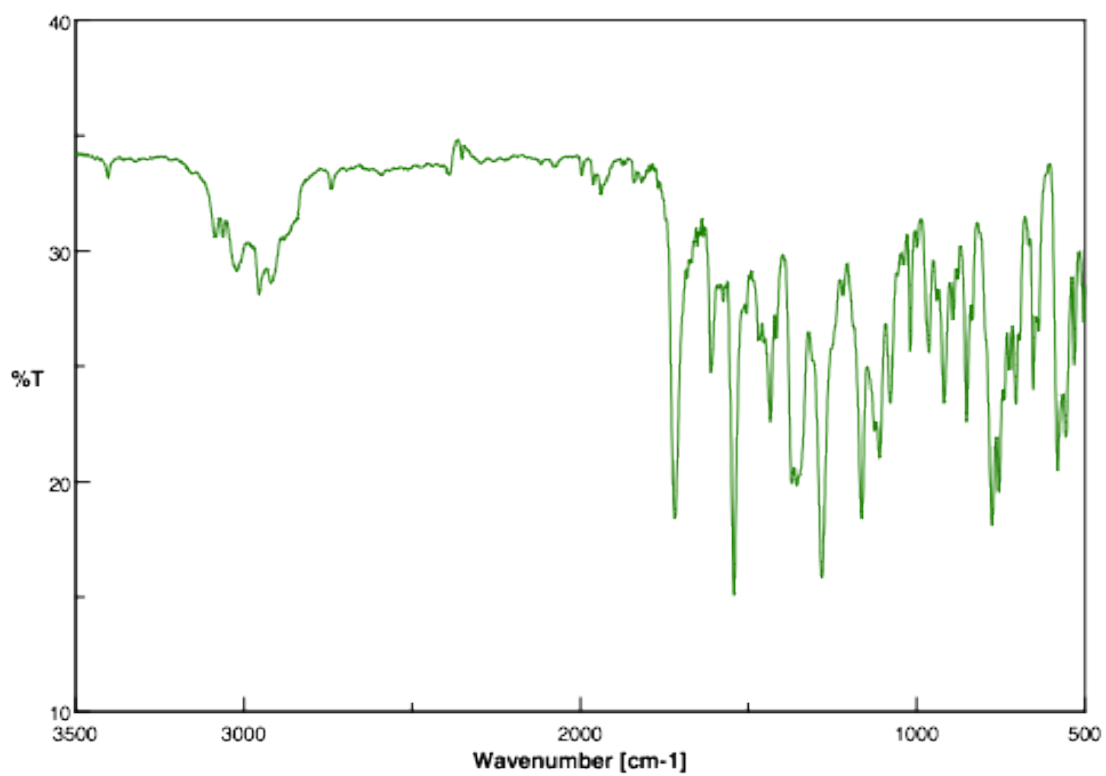


Figure S57. FT-IR spectrum of S5-2 (NaCl).

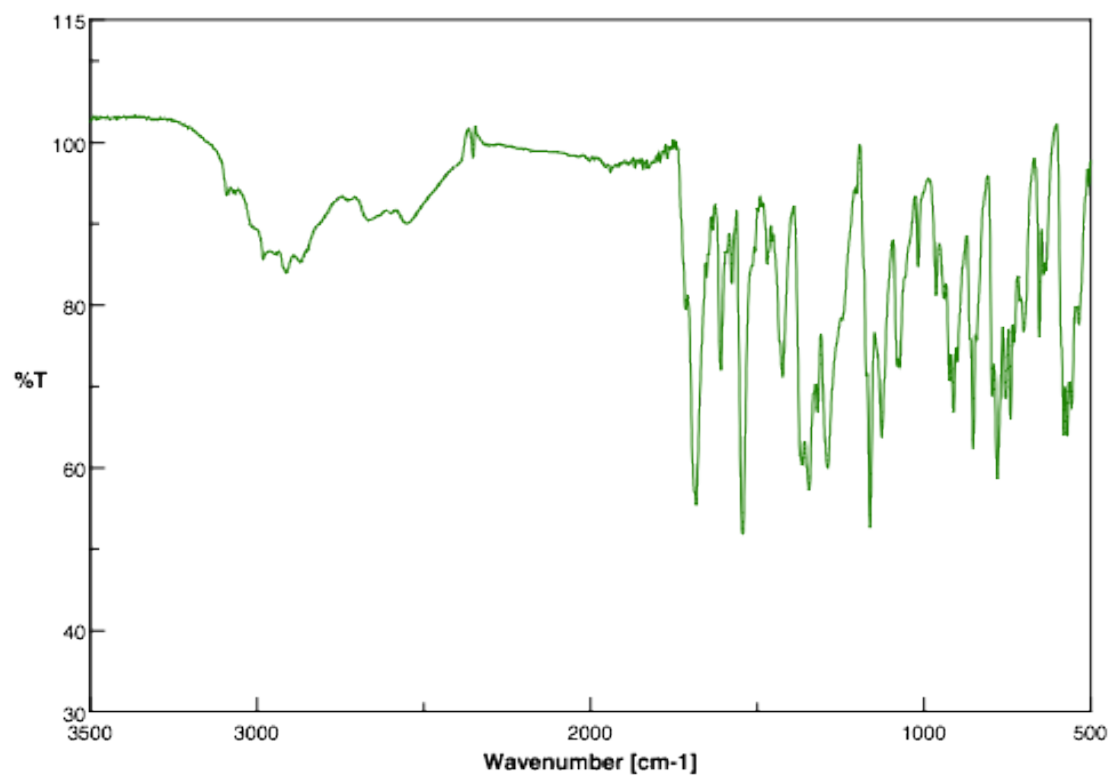


Figure S58. FT-IR spectrum of S5-3 (NaCl).

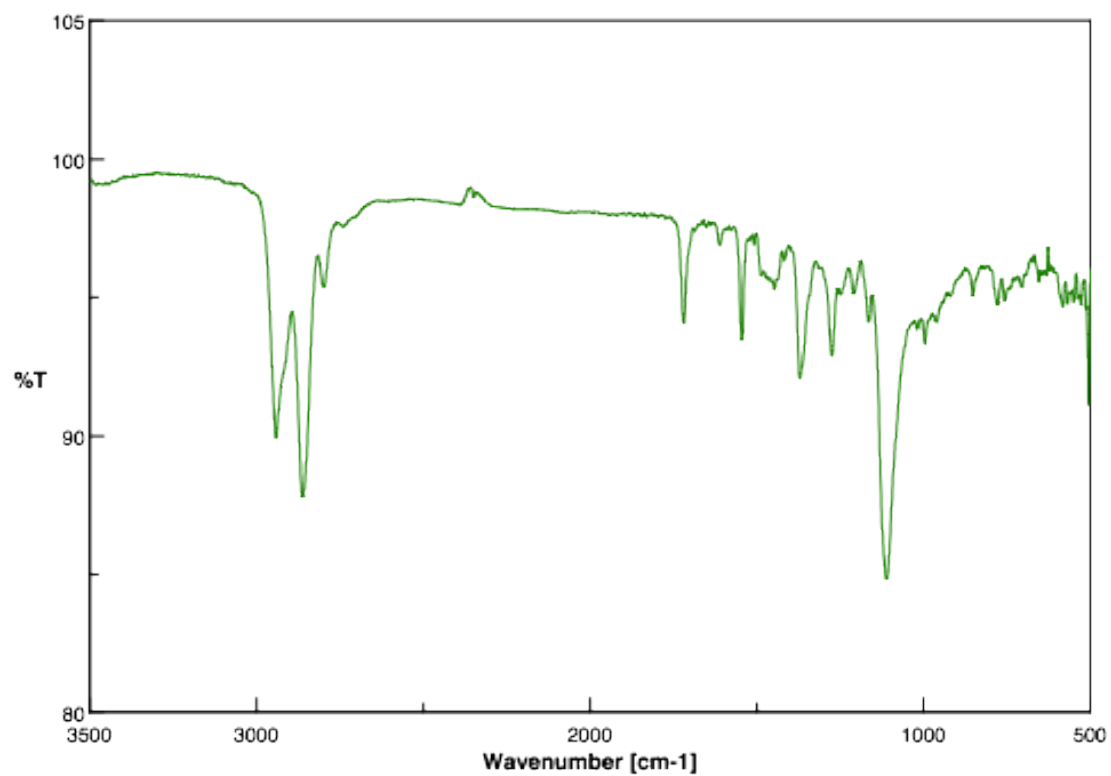


Figure S59. FT-IR spectrum of 7 (NaCl).

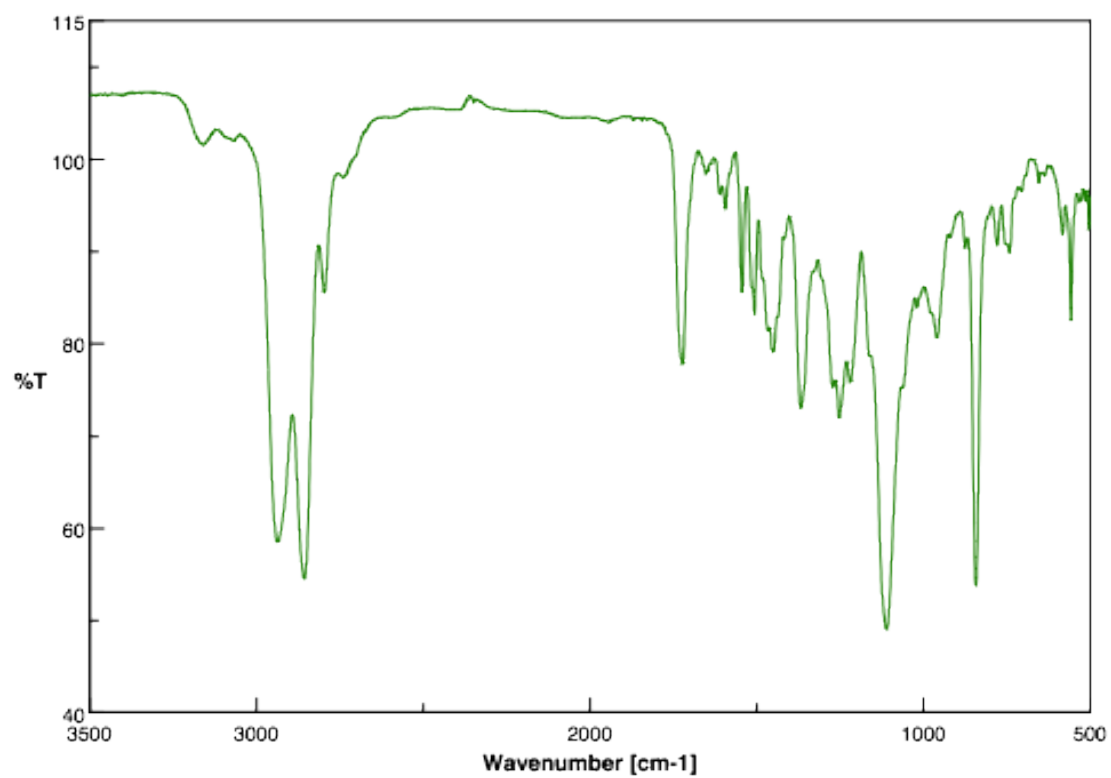


Figure S60. FT-IR spectrum of 8 (NaCl).

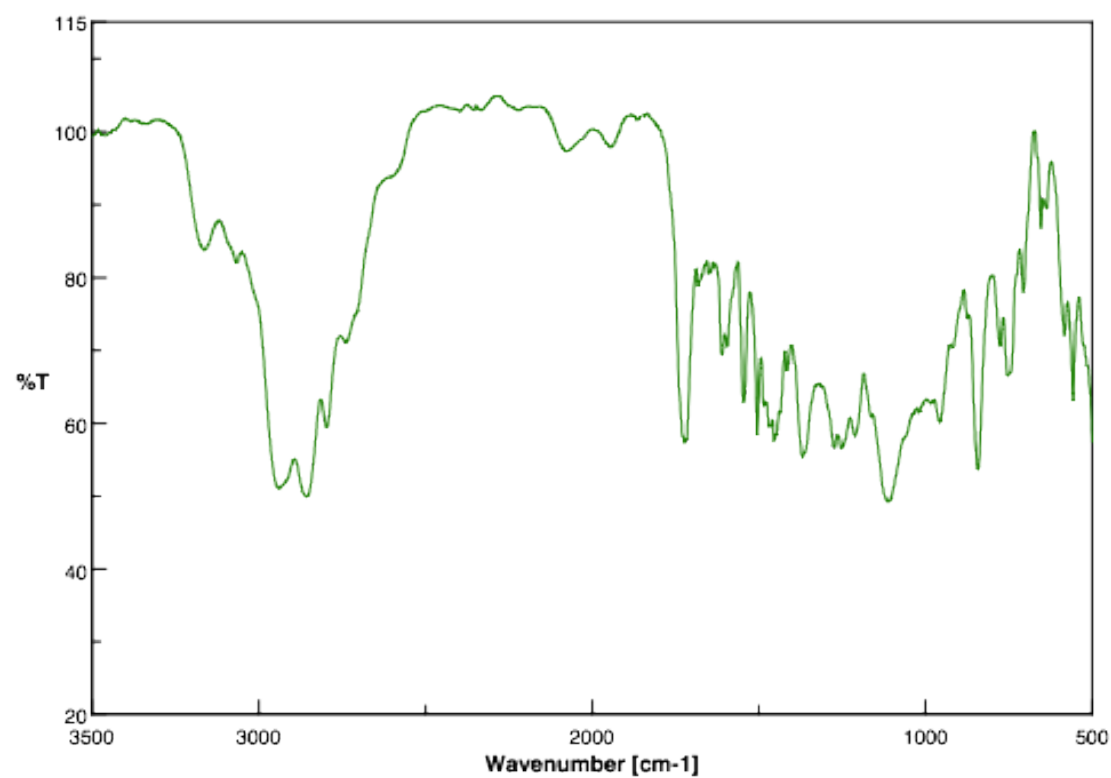


Figure S61. FT-IR spectrum of 9 (NaCl).

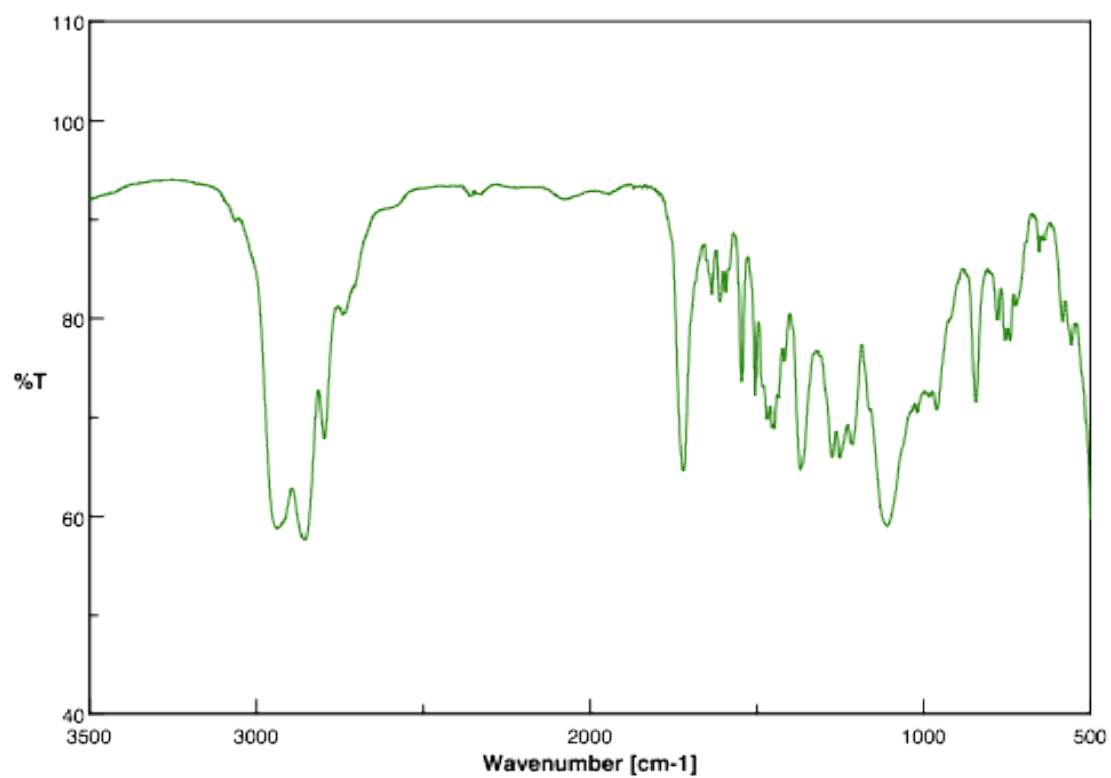


Figure S62. FT-IR spectrum of S9-1 (NaCl).

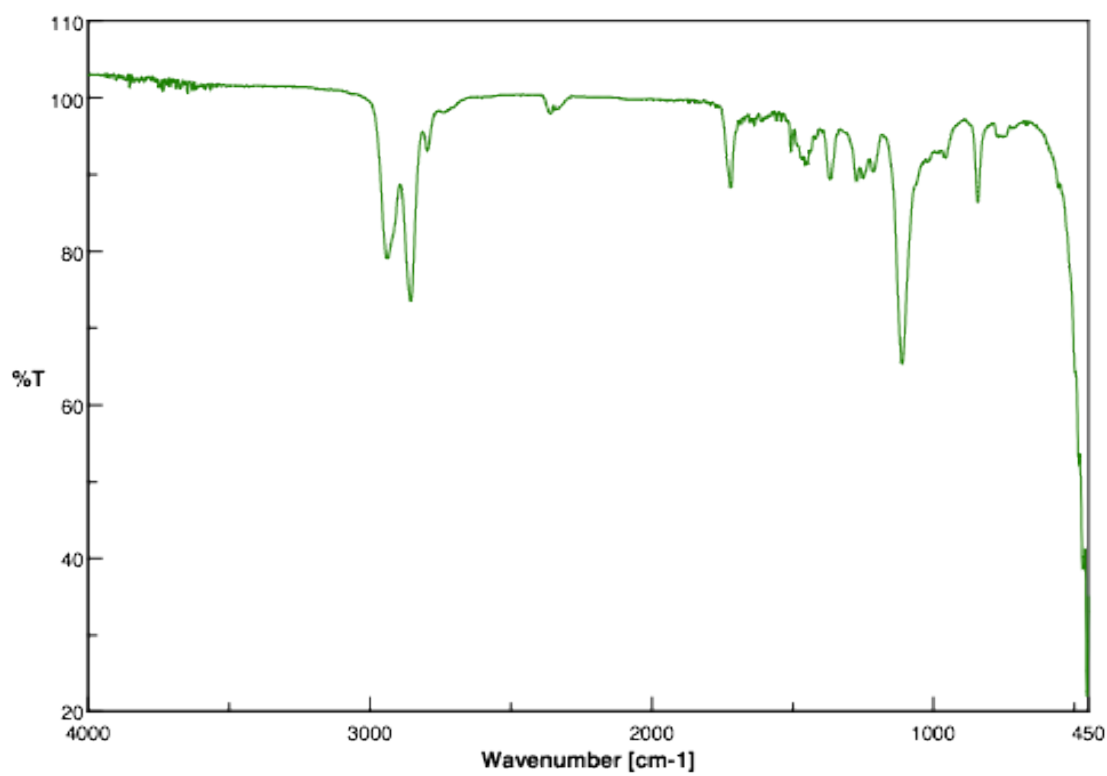


Figure S63. FT-IR spectrum of 10 (NaCl).



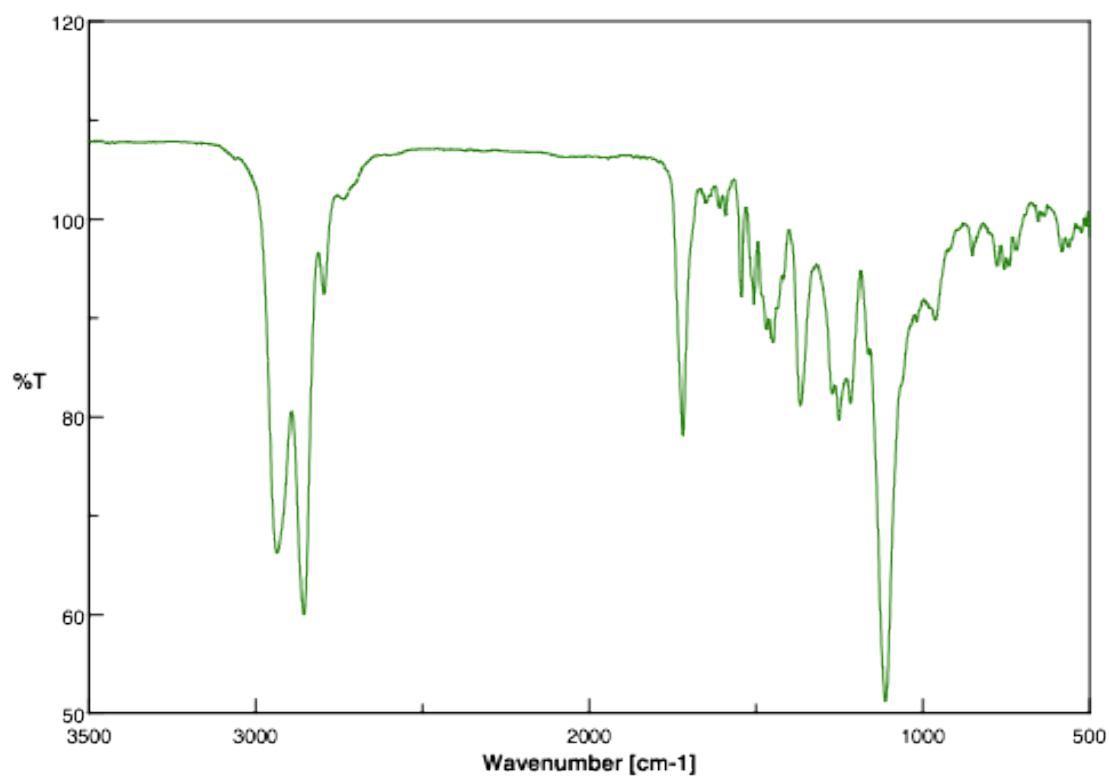


Figure S64. FT-IR spectrum of 11 (NaCl).

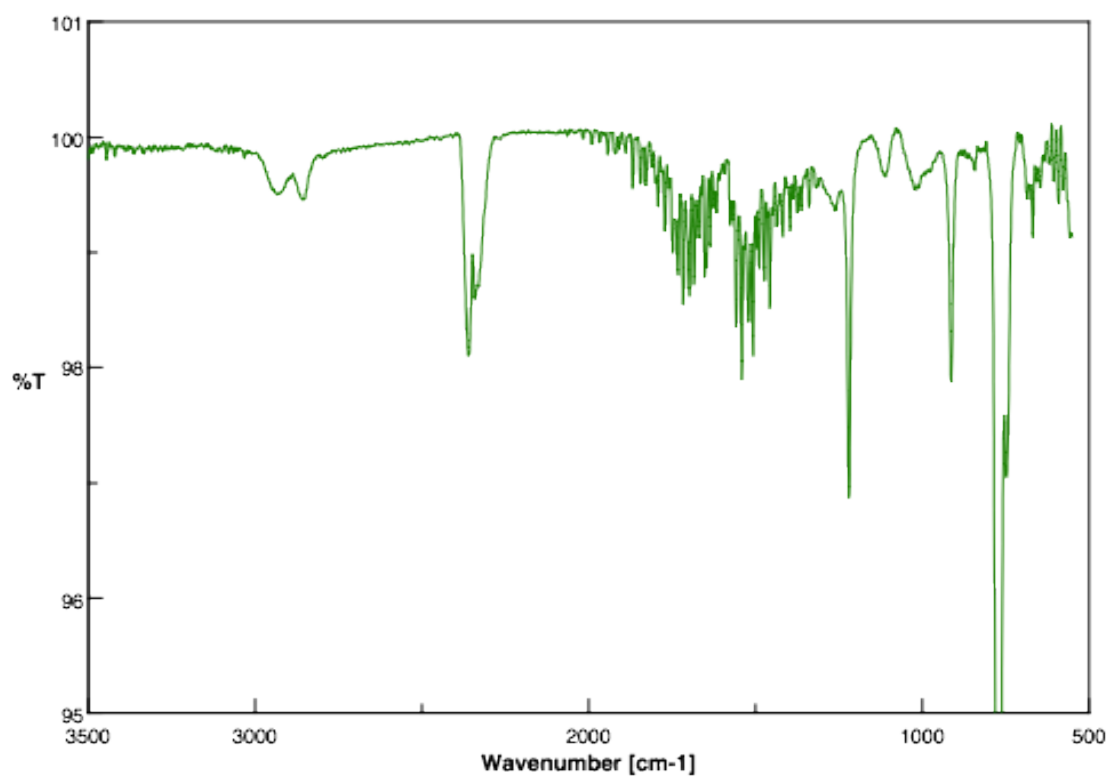


Figure S65. FT-IR spectrum of 12 (NaCl).

#### 4.4 MALDI-TOF-MS spectra

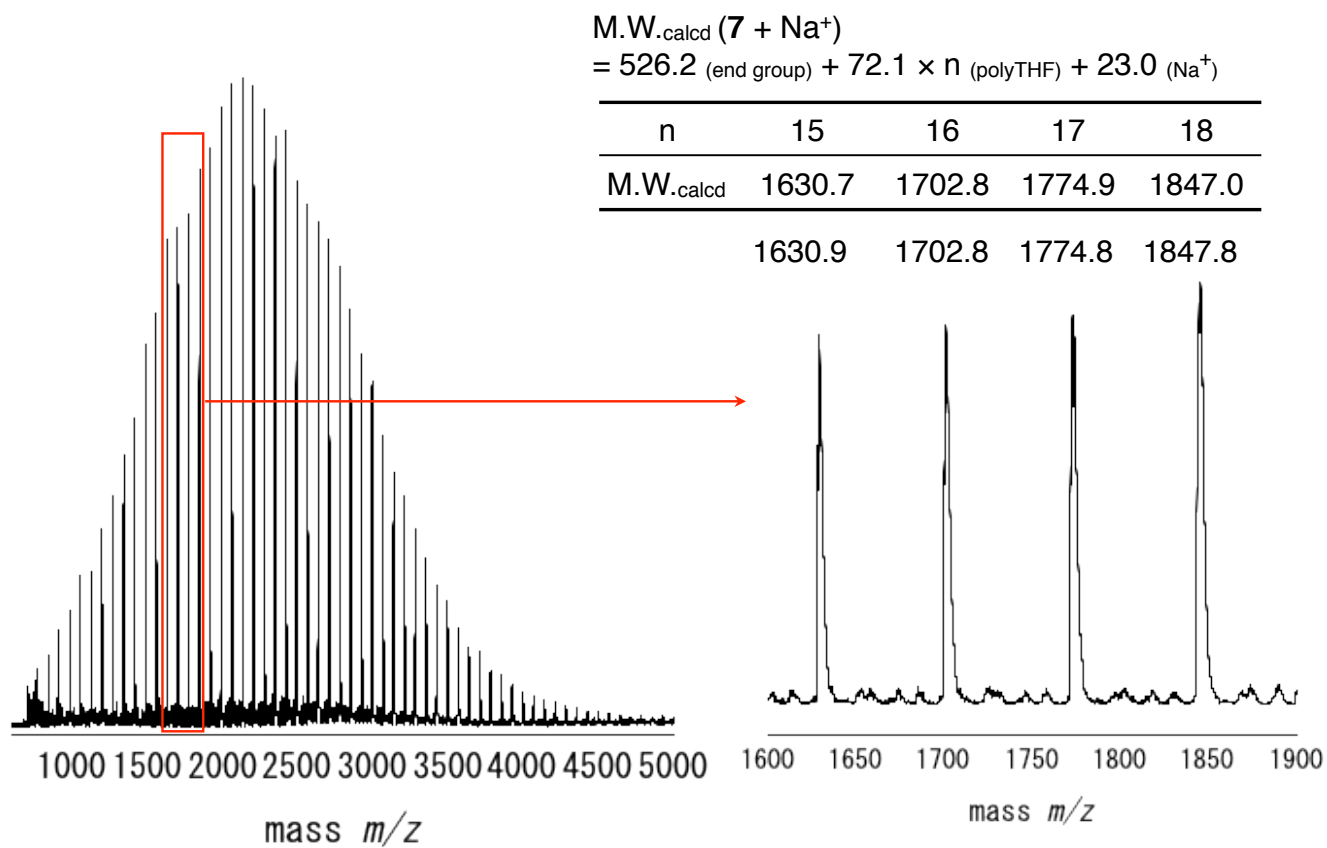


Figure S66. MALDI-TOF-MS spectrum of **7**.

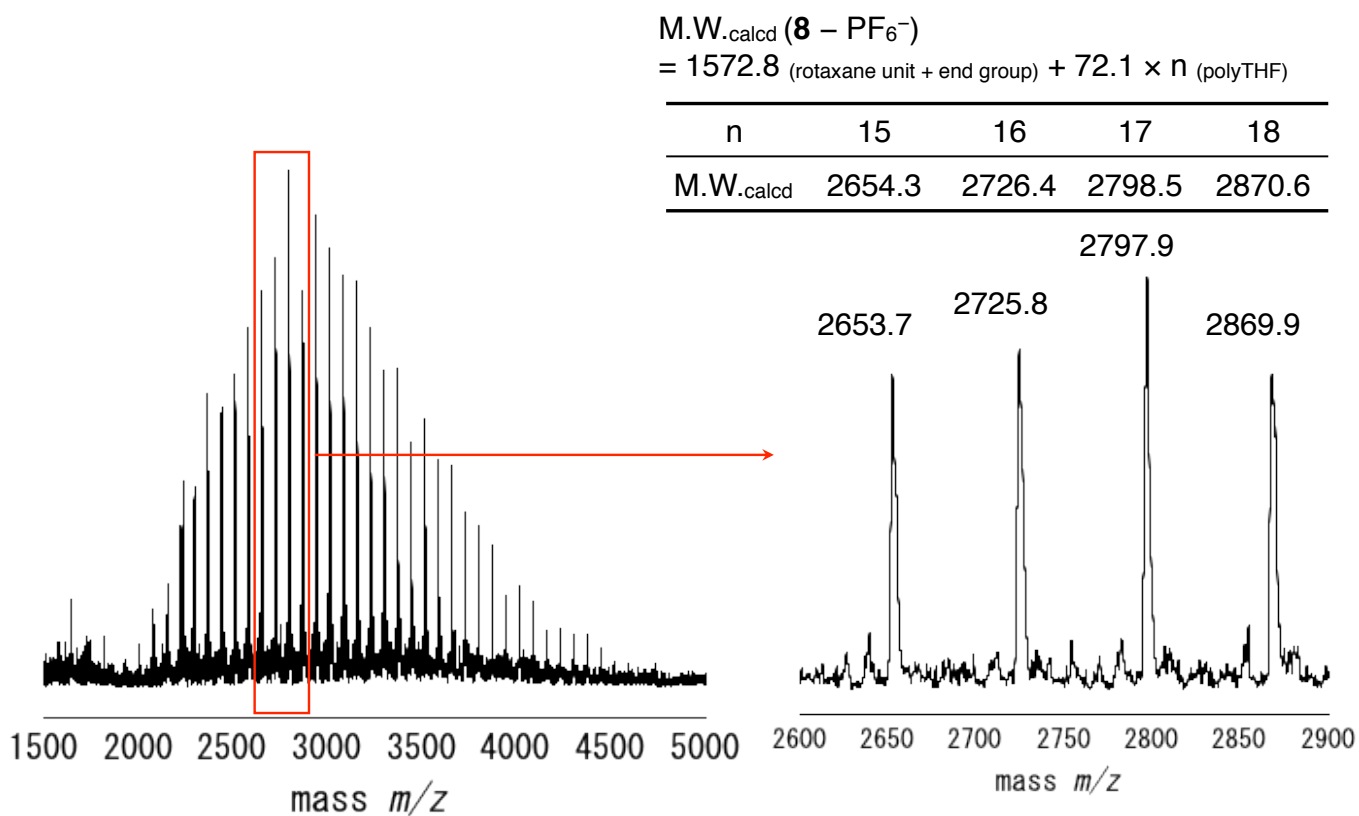


Figure S67. MALDI-TOF-MS spectrum of **8**.

$$\begin{aligned} & \text{M.W.}_{\text{calcd}} (\mathbf{9} - \text{PF}_6^-) \\ & = 1418.7 (\text{rotaxane unit} + \text{end group}) + 72.1 \times n (\text{polyTHF}) \end{aligned}$$

n	15	16	17	18
M.W. <sub>calcd</sub>	2500.2	2572.3	2644.4	2716.5

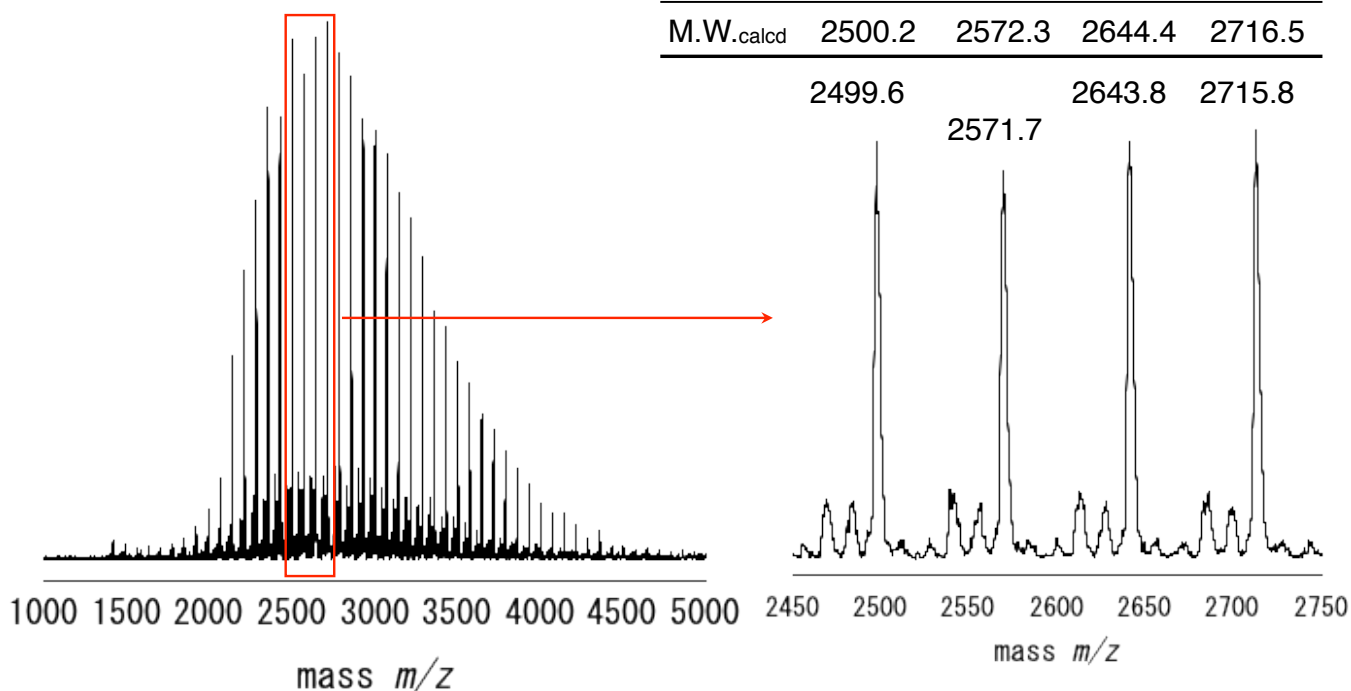


Figure S68. MALDI-TOF-MS spectrum of **9**.

$$\begin{aligned} & \text{M.W.}_{\text{calcd}} (\mathbf{S9-1} + \text{Na}^+) \\ & = 1591.6 (\text{rotaxane unit} + \text{end group}) + 72.1 \times n (\text{polyTHF}) + 23.0 (\text{Na}^+) \end{aligned}$$

n	15	16	17	18
M.W. <sub>calcd</sub>	2696.1	2768.2	2840.3	2912.4

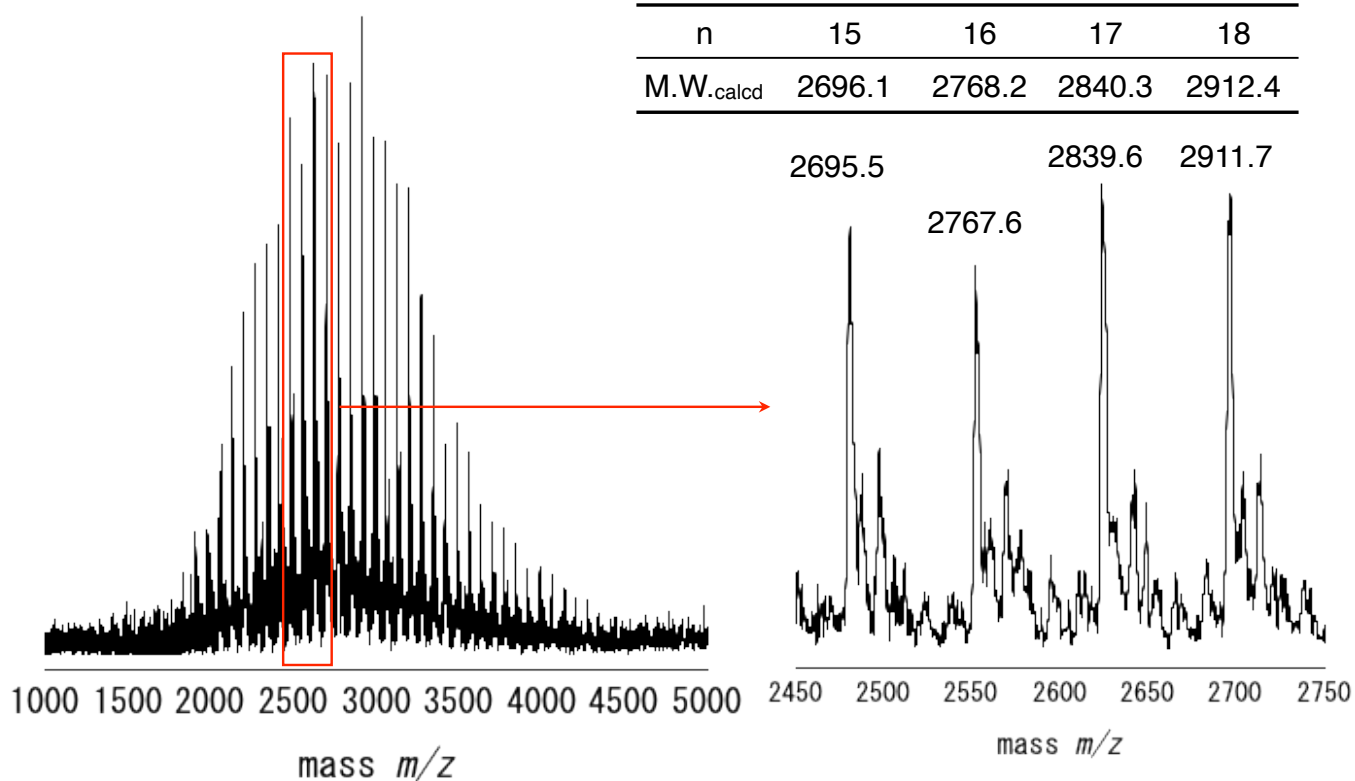


Figure S69. MALDI-TOF-MS spectrum of **S9-1**.

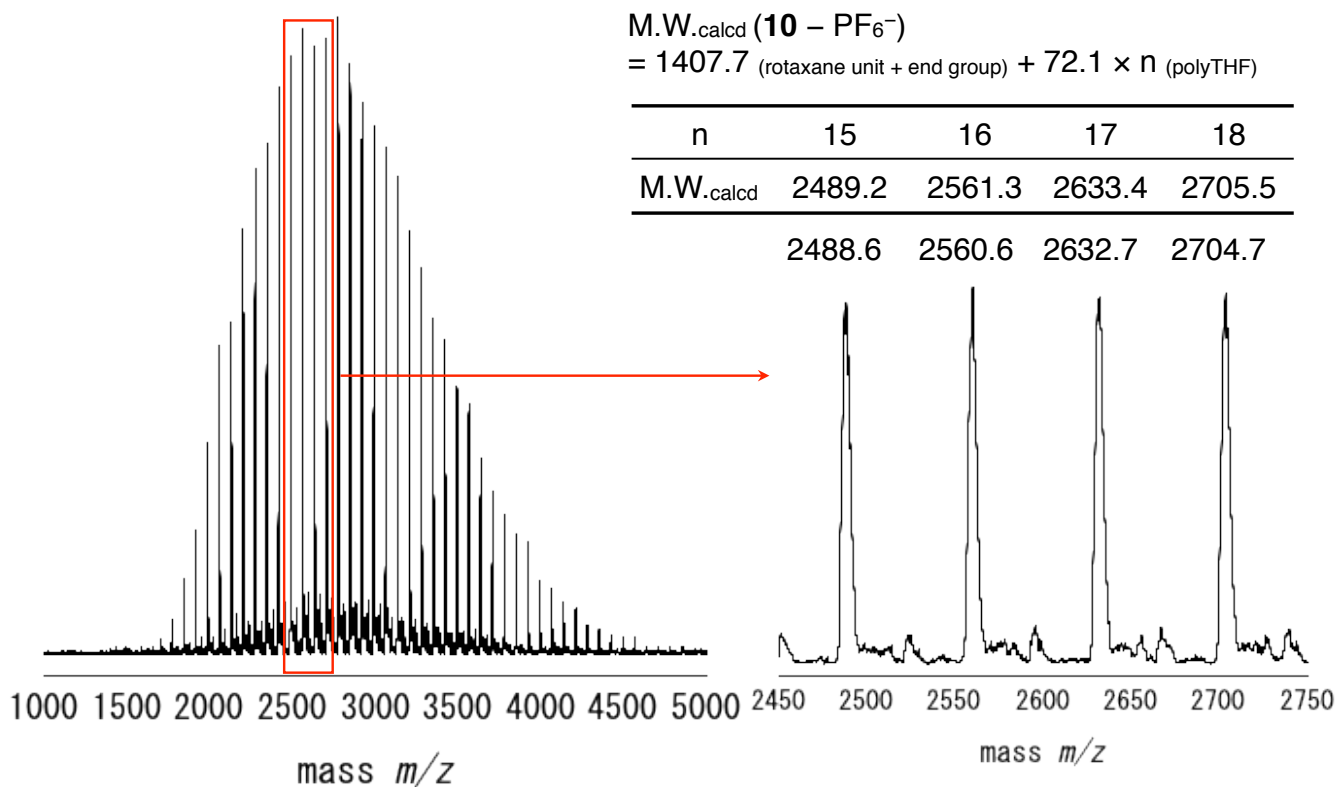


Figure S70. MALDI-TOF-MS spectrum of **10**.

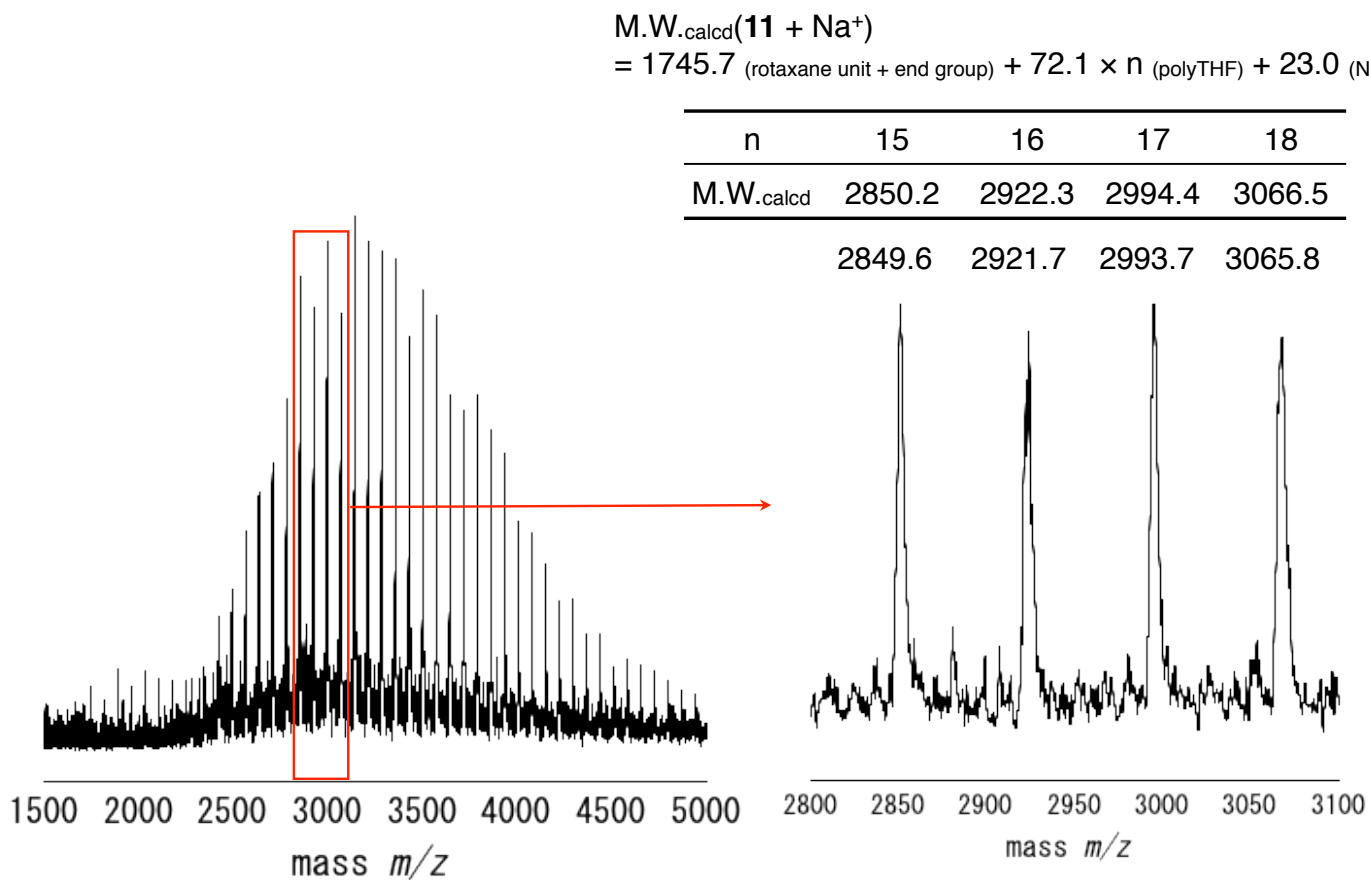


Figure S71. MALDI-TOF-MS spectrum of **11** from **8**.

$$\begin{aligned} \text{M.W.}_{\text{calcd}} (\mathbf{12} - \text{PF}_6^-) \\ = 1561.8 (\text{rotaxane unit} + \text{end group}) + 72.1 \times n (\text{polyTHF}) \end{aligned}$$

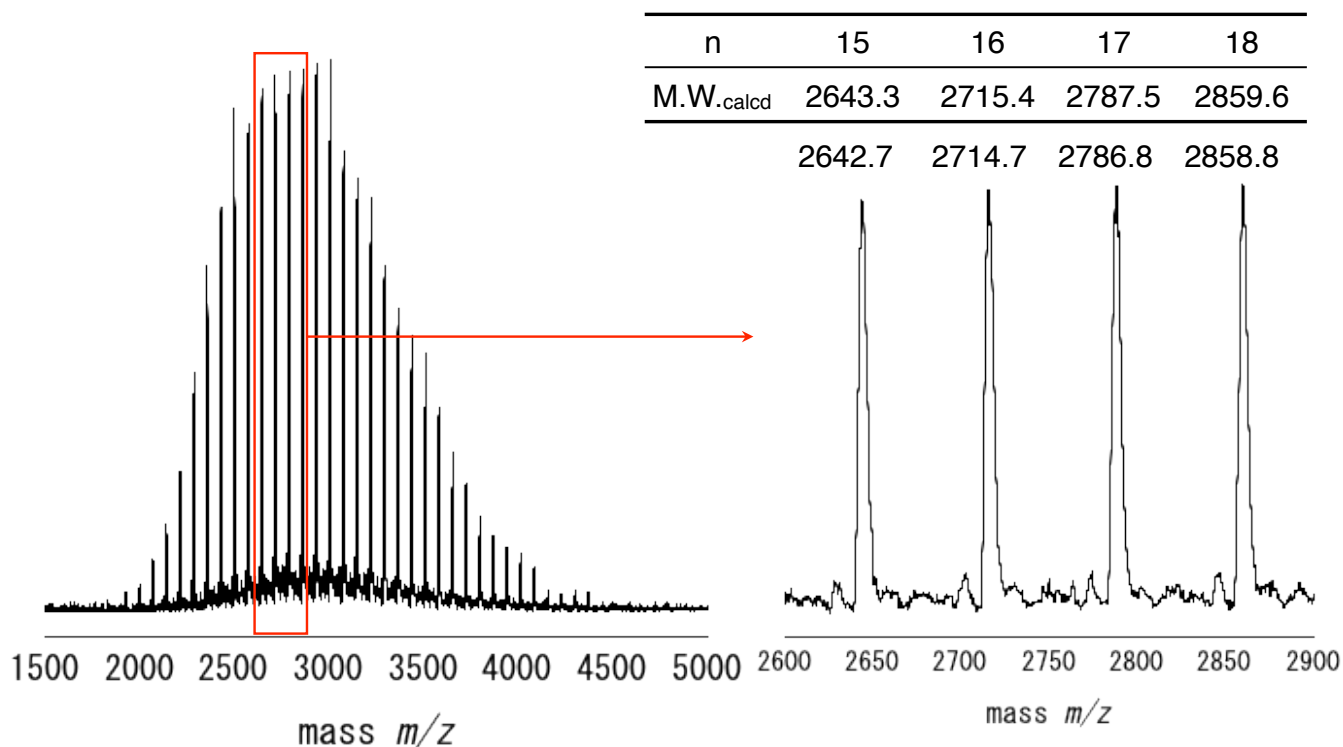


Figure S72. MALDI-TOF-MS spectrum of **12** from **11**.

$$\begin{aligned} \text{M.W.}_{\text{calcd}} (\mathbf{11} + \text{Na}^+) \\ = 1745.7 (\text{rotaxane unit} + \text{end group}) + 72.1 \times n (\text{polyTHF}) + 23.0 (\text{Na}^+) \end{aligned}$$

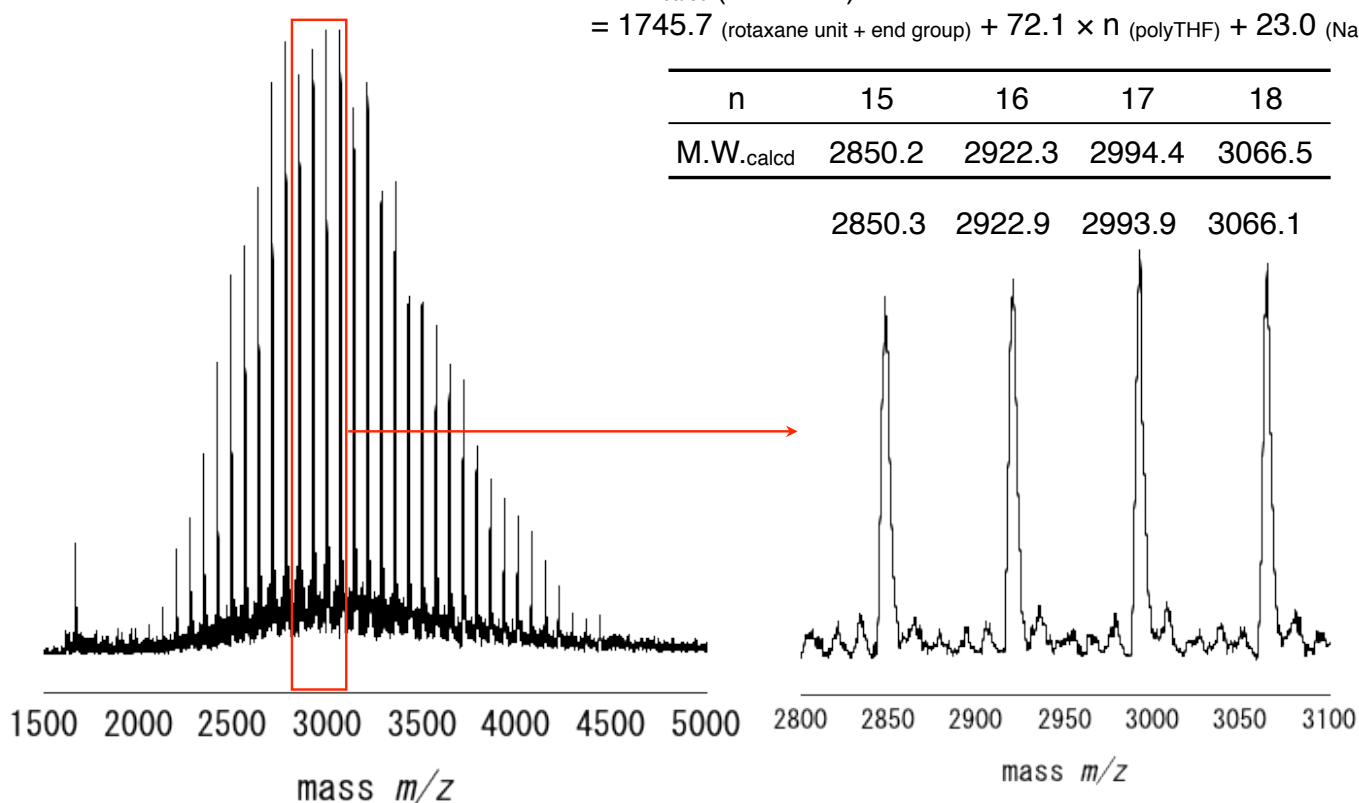


Figure S73. MALDI-TOF-MS spectrum of **11** from **12**.

$$\text{M.W.}_{\text{calcd}} (\mathbf{8} - \text{PF}_6^-) = 1572.8 \text{ (rotaxane unit + end group)} + 72.1 \times n \text{ (polyTHF)}$$

n	15	16	17	18
M.W. <sub>calcd</sub>	2654.3	2726.4	2798.5	2870.6

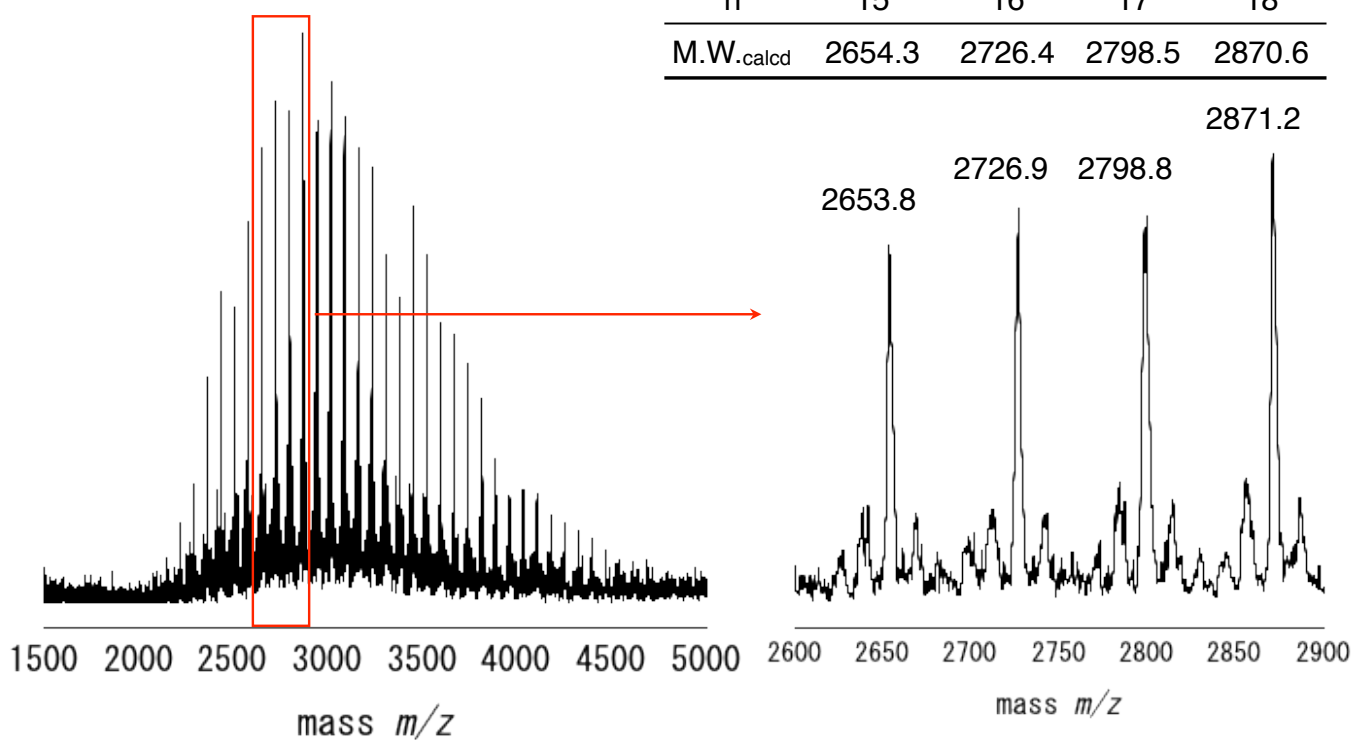


Figure S74. MALDI-TOF-MS spectrum of **8** from **11**.

## 5. SEC profiles

### 5.1 SEC profile of 7

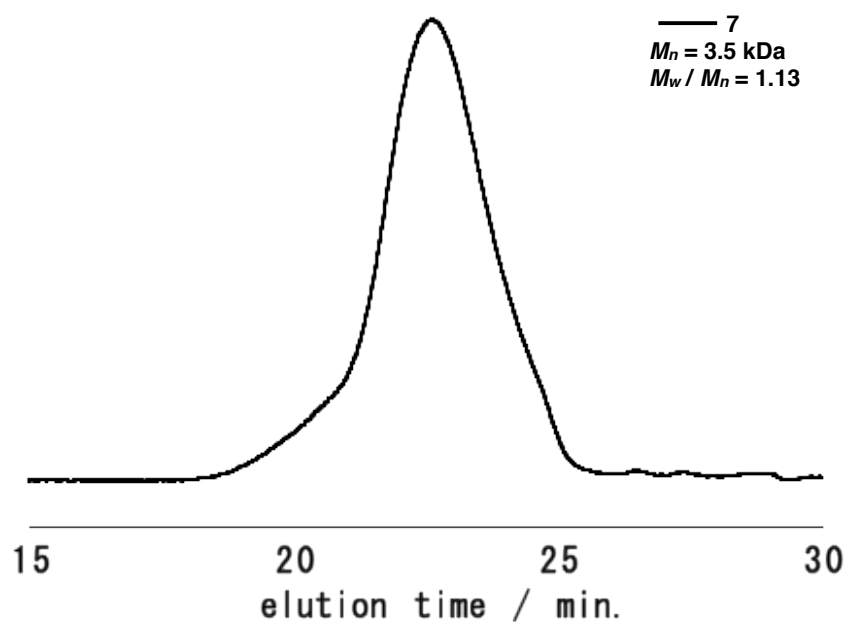


Figure S75. SEC profile of the axle polymer 7

### 5.2 SEC profiles of model macromolecular [2]rotaxanes 9, S9-1, and 10

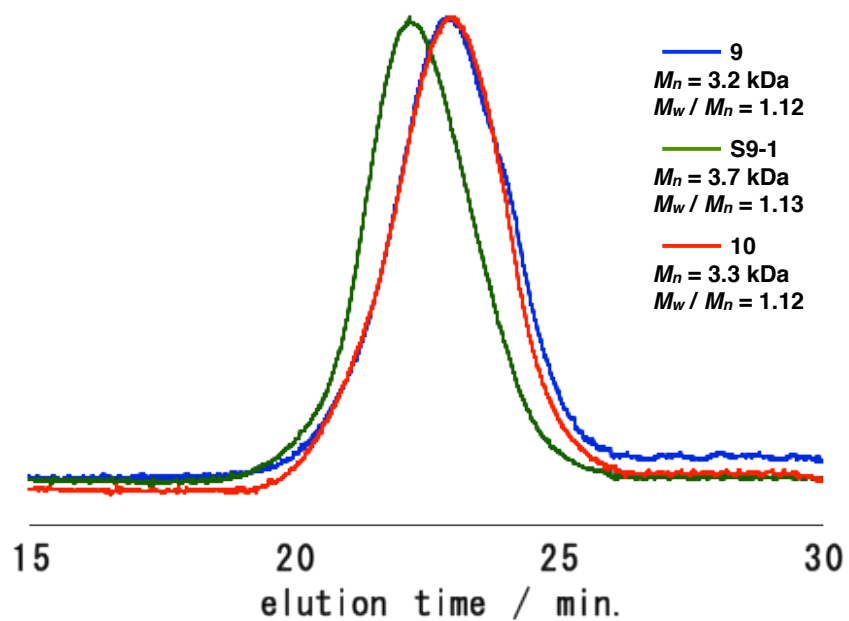


Figure S76. SEC profiles of the macromolecular [2]rotaxanes 9, S9-1, and 10

### 5.3 SEC profiles of macromolecular [1]rotaxanes 8, 11, and 12

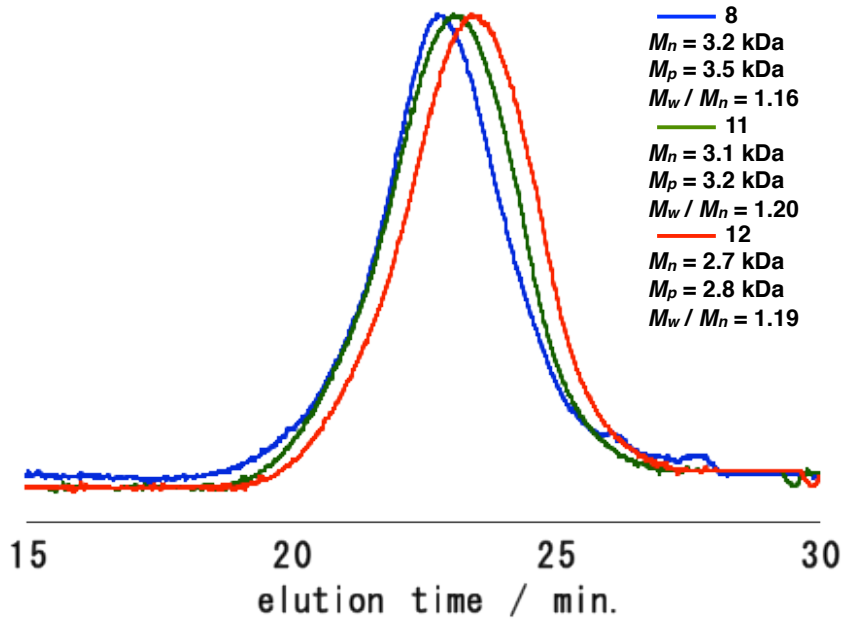


Figure S77. SEC profiles of the macromolecular [1]rotaxanes 8, 11, and 12

### 5.4 Calculation of the intrinsic viscosity ratio $\eta_{12} / \eta_8$

According to theories of SEC universal calibration, the polymers of different families with the same retention time possess the same hydrodynamic volume, indicating

$$\eta_{PS} \cdot M_{PS} = \eta_{PTHF} \cdot M_{PTHF} \cdot \dots \cdot (1)$$

where  $\eta_{PS}$  and  $\eta_{PTHF}$  are the intrinsic viscosity of the hypothetical monodisperse sample. For polystyrene(PS) in DMF at 35 °C, can be calculated using

$$\eta_{PS} = K \cdot M_{PS}^a = 31.8 \times 10^{-3} \times M_{PS}^{0.603} \cdot \dots \cdot (2)$$

With assigning the  $M_p$  value based on the PS standards ( $M_{p8} = 3500$  and  $M_{p12} = 2800$ ) obtained by SEC analysis to the  $M_{PS}$  in eq.2, and the combination of eq.1 and eq.2 lead to the following equation.

$$\eta_{PTHF} = \eta_{PS} \cdot M_{PS} / M_{PTHF}$$

$$\eta_8 = \eta_{PS} \cdot M_p(8) / M_{PTHF}(8) = 31.8 \times 10^{-3} \times 35^{0.603} \times 35 / M_{PTHF}(8)$$

$$\eta_{12} = \eta_{PS} \cdot M_p(12) / M_{PTHF}(12) = 31.8 \times 10^{-3} \times 28^{0.603} \times 28 / M_{PTHF}(12)$$

$$M_{PTHF}(8) \approx M_{PTHF}(12)$$

The ratio of intrinsic viscosity  $\eta_{12} / \eta_8$  is

$$\begin{aligned} \eta_{12} / \eta_8 &= \eta_{PS} \cdot M_p(12) / \eta_{PS} \cdot M_p(8) \\ &= 31.8 \times 10^{-3} \times 28^{0.603} \times 28 / 31.8 \times 10^{-3} \times 35^{0.603} \times 35 \\ &= \underline{0.70} \end{aligned}$$



## 6. DOSY spectra and diffusion coefficients $D$

### 6.1 DOSY spectra and diffusion coefficient of macromolecular [1]rotaxane 8

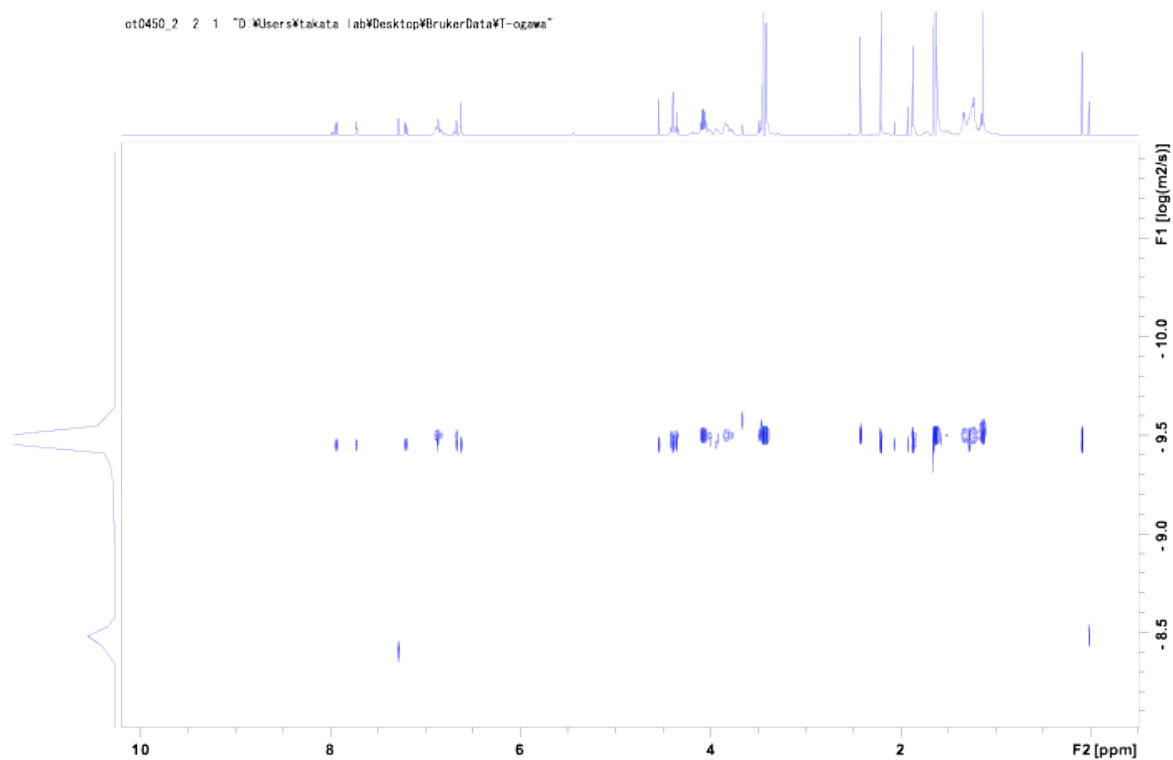


Figure S78. 2D DOSY spectrum of 8 (500 MHz, CDCl<sub>3</sub>, 298 K).

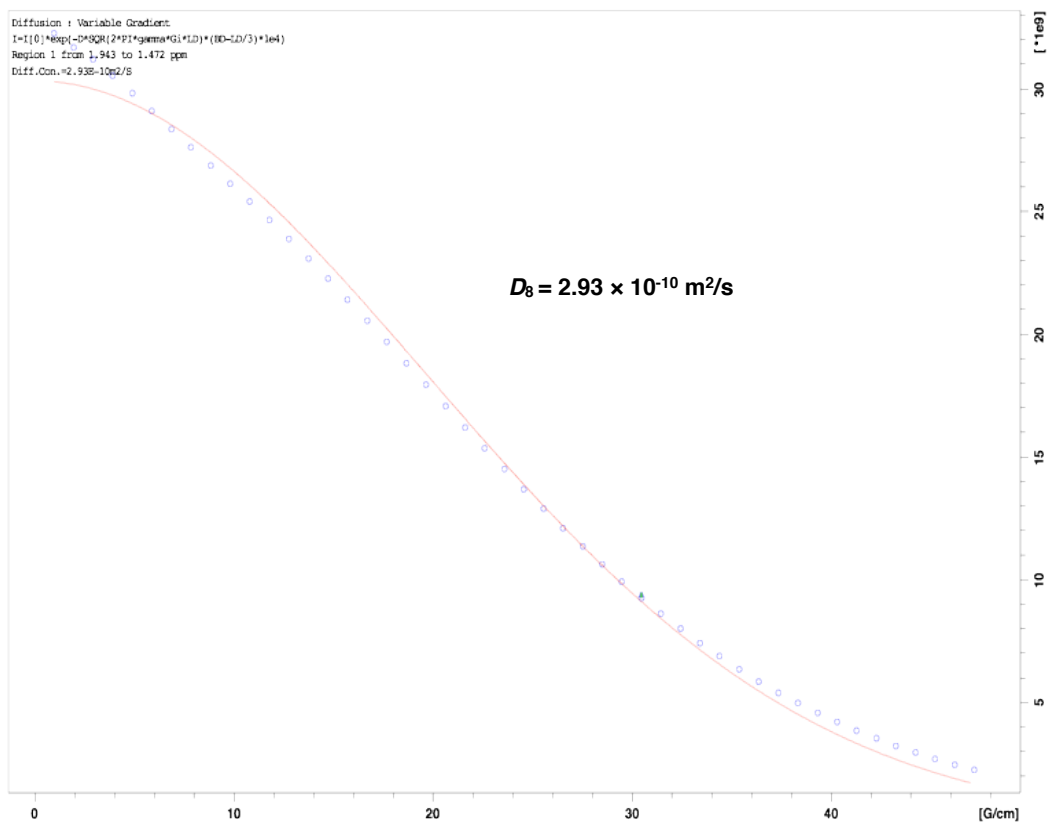


Figure S79. Diffusion coefficient  $D$  of 8

## 6.2 DOSY spectra and diffusion coefficient of macromolecular [1]rotaxane 12

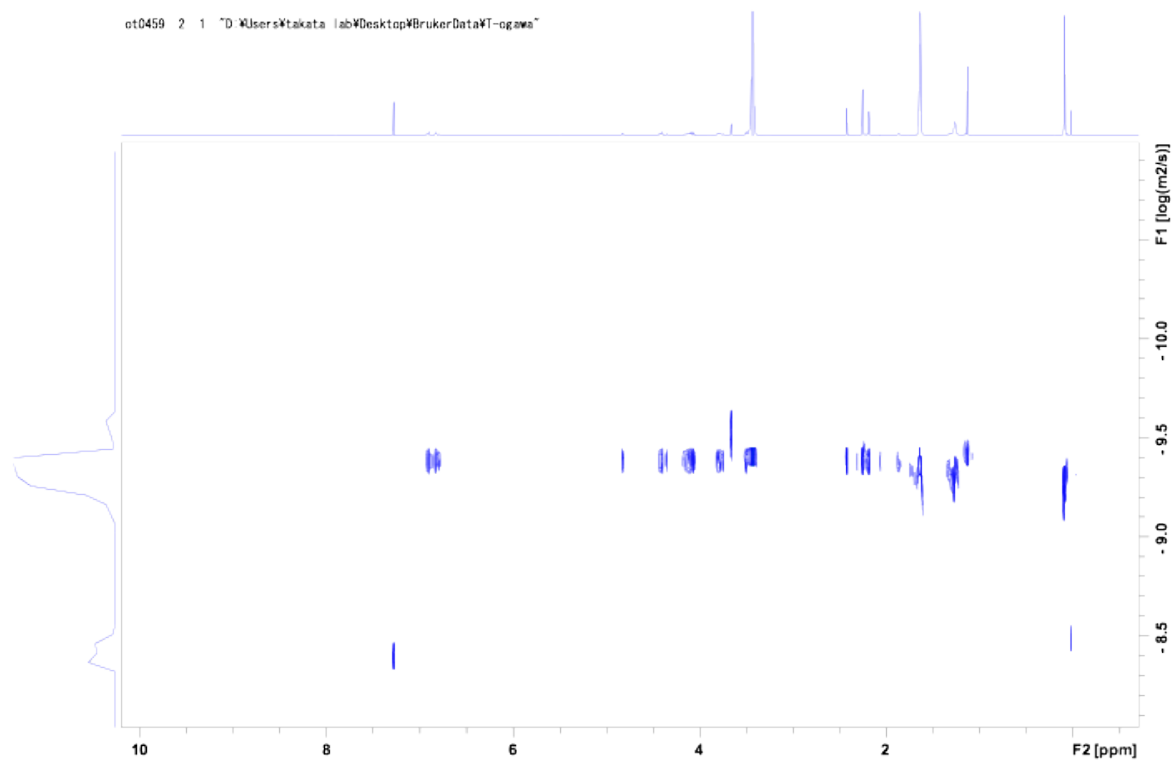


Figure S80. 2D DOSY spectrum of 12 (500 MHz, CDCl<sub>3</sub>, 298 K).

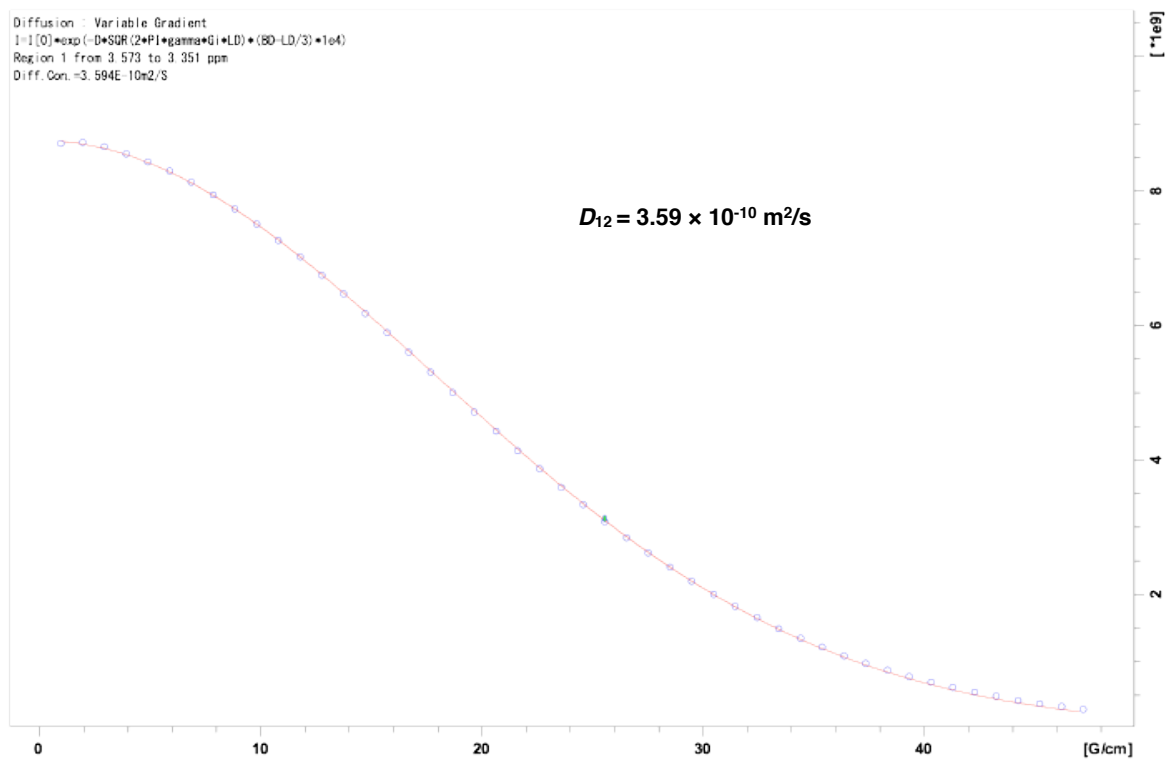


Figure S81. Diffusion coefficient  $D$  of 12