Electronic Supplementary Information

Photoresponsive supramolecular self-assembly of monofunctionalized pillar[5]arene based on stiff stilbene

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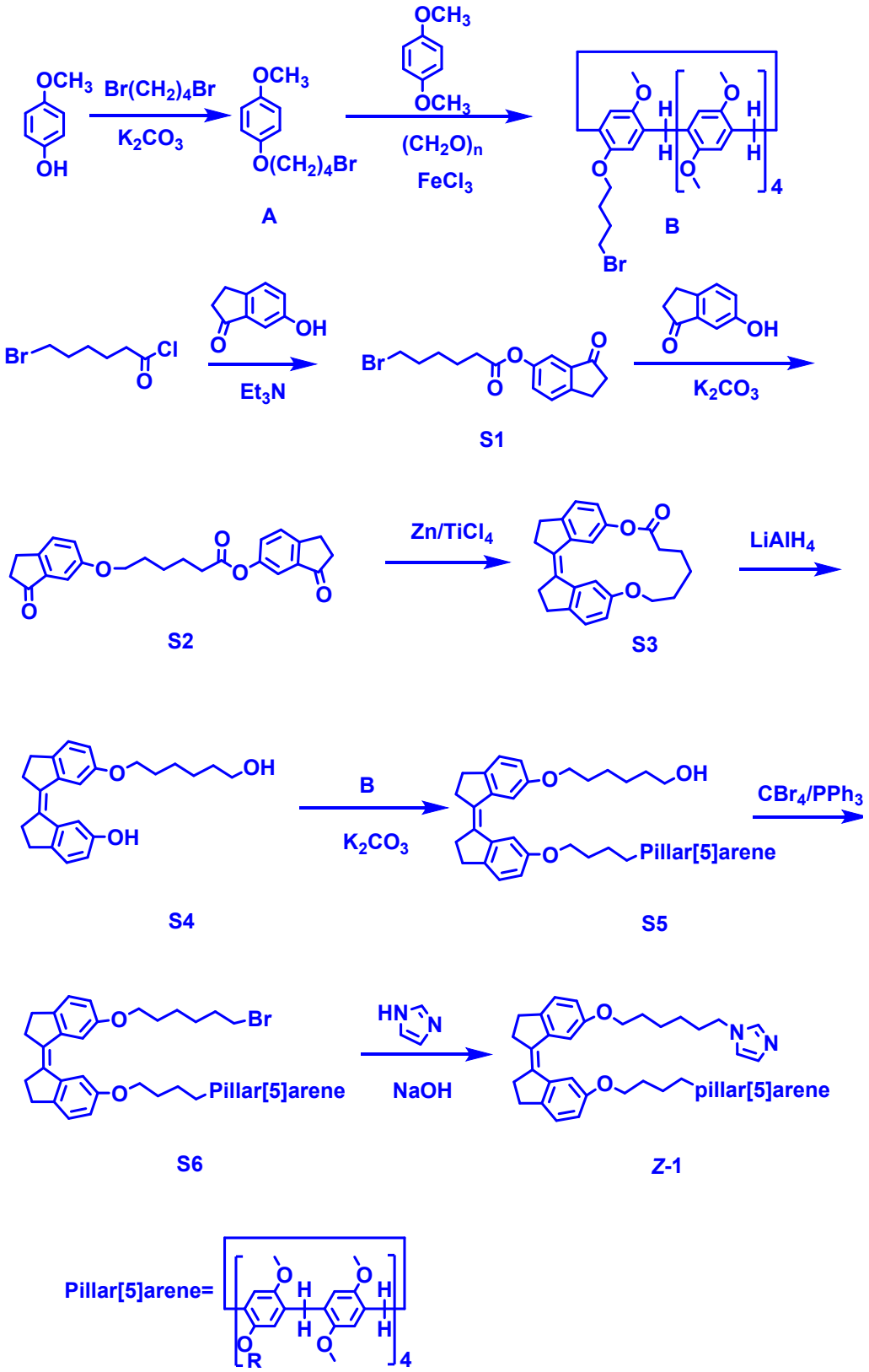
Contents

1. Materials and methods.

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. NMR spectra were recorded with a Bruker Avance 400 spectrometer or a Bruker Avance 600 spectrometer. High-resolution mass spectrometey experiments were performed with a Bruker Daltonics Apex IV spectrometer. The photoisomerization reactions were carried out by using a xenon lamp (500 W) with filter. Viscosity measurements were carried out with a micro-Ubbelohde dilution viscometer at 18℃ in chloroform.

2. Synthesis of compound *Z*-1 and *E*-1.



Scheme S1. Synthesis of compound *Z*-**1**

Preparation of compound A.

To a stirred solution of 1,4-dibromobutane (6.47 g, 30 mmol) in acetone (150 mL) was added K_2CO_3 (4.14 g, 30 mmol) and 4-methylbenzophenone (0.62 g, 5 mmol) and the mixture was stirred at 70 ℃ overnight. After the reaction was completed, the solid was removed by filtration and the solvent was removed under reduced pressure to afford 1.2 g of product. Yield: 92%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.83 (s, 4H), 3.95 (t, 2H, J = 6 Hz), 3.77 (s, 3H), 3.49 (t, 2H, J = 6.8 Hz), 2.07 (m, 2H), 1.92 (m, 2H).

Preparation of compound B.

To a solution of **A** (0.26 g, 1 mmol), 1,4-dimethoxybenzene (2.21 g, 16 mmol) and paraformaldehyde (1.5 g, 50 mmol) in dry CH_2Cl_2 (500 mL) under N_2 atmosphere for 0.5 h, then anhydrous $FeCl_3$ (0.41 g, 2.5 mmol) was added. The mixture was stirred at room temperature under N_2 atmosphere for 5 h. After the reaction was completed, the resulting mixture was washed with water, brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure and further purification was carried out by column chromatography using CH_2Cl_2 as eluent to afford 0.42 g of product as a white solid. Yield: 48%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.83-6.72 (m, 10H), 3.77-3.63 (m, 39H), 3.08 (br, 2H), 1.69 (br, 2H), 1.25 (br, 2H).

Preparation of compound S1.

To a solution of 6-hydroxy-1-indanone (1.0 g, 6.76 mmol) in dry THF (200 mL) was added triethylamine (1.4 mL, 1.02 g, 10.2 mmol) and 6-bromohexanoyl chloride(1.73 g, 8.1 mmol), then the mixture was stirred at room temperature for 3 h. After the reaction was completed, the resulting mixture was washed with aqueous K_2CO_3 and dried over Na_2SO_4. The solution was removed under reduced pressure to afford 1.87 g of product. Yield: 90%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, 1H, J = 8.4 Hz), 7.44 (d, 1H, J = 2 Hz), 7.31 (dd, 1H, J = 8.4 Hz, 2 Hz), 3.44 (t,

2H, *J* = 6.8 Hz), 3.13 (t, 2H, *J* = 5.6 Hz), 2.73 (t, 2H, *J* = 5.6 Hz), 2.60 (t, 2H, *J* = 7.2 Hz), 1.93 (m, 2H), 1.79 (m, 2H), 1.56 (m, 2H).

Preparation of compound S2.

To a solution of **S1** (1.87 g, 5.8 mmol) of DMF (9 mL) was added 6-hydroxyindanone (0.85 g, 5.8 mmol) and K_2CO_3 (2.38 g, 17.3 mmol), then the mixture was stirred at 60 ℃ overnight. After the reaction was completed, ethyl acetate (200 mL) was added and the organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the further purification was carried out by column chromatography using CH_2Cl_2/Et_2O (100:1, v/v) as eluent to afford 0.97 g product. Yield: 40%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, 1H, *J* = 8.4 Hz), 7.44 (d, 1H, *J* = 2.0 Hz), 7.37 (d, 1H, *J* = 8.4 Hz), 7.30 (dd, 1H, *J* = 8.4 Hz, 2.0 Hz), 7.19 (d, 1H, *J* = 2Hz), 7.17 (dd, 1H, *J* = 8.4 Hz, 2 Hz), 4.02 (t, 2H, *J* = 6.4 Hz), 3.13 (t, 2H, *J* = 6.0 Hz), 3.06 (t, 2H, *J* = 5.6 Hz), 2.72 (m, 4H), 2.62 (t, 2H, *J* = 7.2 Hz), 1.85 (m, 4H), 1.61 (m, 2H).

Preparation of compound S3.

To a stirred suspension of zinc powder (4.6 g, 70 mmol) in 120 mL dry THF, $TiCl_4$ (2.6 mL, 4.5 g, 23.5 mmol) was added over 2 min at 0 ℃. The resulting slurry was heated at reflux for 3 h, and pyridine (1 mL, 0.95 g, 12 mmol) was added. A THF solution (50 mL) of **S2** (0.92 g, 2.35 mmol) was added over a 5 h period by syringe pump to the refluxing reaction mixture. The reflux was continued for 0.5 h after the addition was completed. Upon cooling to room temperature, the reaction mixture was poured into saturated aqueous K_2CO_3 (100 mL) and stirred until the organic phase was separated. The combined organic phase was evaporated under reduced pressure, CH_2Cl_2 (100 mL) was added and washed with water. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford 0.62 g of product. Yield: 73%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, 1H, *J* = 2.0 Hz), 7.58 (d, 1H, *J* = 2 Hz), 7.24 (d, 1H, *J* = 8 Hz), 7.17 (d, 1H, *J* = 8Hz), 6.91

(dd, 1H, *J* = 8 Hz, 2 Hz), 6.80 (dd, 1H, *J* = 8 Hz, 2 Hz), 4.09 (t, 2H, *J* = 5.6 Hz), 2.97 (t, 2H, *J* = 6.8 Hz), 2.89 (t, 2H, *J* = 6.8 Hz), 2.80 (m, 4H), 2.54 (t, 2H, *J* = 6.0 Hz), 1.83 (m, 2H), 1.69 (m, 4H).

Preparation of compound S4.

To a stirred solution of **S3** (0.59 g, 1.63 mmol) in dry THF (100 mL) was added $LiAlH_4$ (0.34 g, 8 mmol) cautiously and the resulting mixture was stirred overnight. The reaction was quenched with methanol and the solid was removed by filtration. The filtrate was concentrated to a small volume, CH_2Cl_2 (100 mL) was added and under reduced pressure and further purification was carried out by column chromatography using CH_2Cl_2/CH_3OH (100:1, v/v) as eluent to afford 0.45 g of product. Yield: 80%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, 1H, *J* = 2.0 Hz), 7.57 (d, 1H, *J* = 2 Hz), 7.17 (d, 1H, *J* = 8.4 Hz), 7.14 (d, 1H, *J* = 8.0 Hz), 6.75 (dd, 1H, *J* = 8.0 Hz, 2.0 Hz), 6.76 (dd, 1H, *J* = 8.0 Hz, 2.4 Hz), 6.44(s, 1H), 3.97 (t, 2H, *J* = 6.6 Hz), 3.72 (m, 2H), 2.89 (m, 4H), 2.81 (m, 4H), 1.82 (m, 2H), 1.60 (m, 2H), 1.51 (m, 4H).

Preparation of compound S5.

A solution of **S4** (0.45 g, 1.23 mmol), **B** (1.74 g, 2 mmol), and potassium phthalimide (0.55 g, 4 mmol) in 10 mL DMF was heated at 60 ℃ overnight. After the reaction was completed, 120 mL of brine was added and then extracted with EtOAc (50 mL, 3 times), the combined organic phase was washed with brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure and the further purification was carried out by column chromatography using CH_2Cl_2/Et_2O (100/1, v/v) as eluent to afford 0.9 g of product. Yield: 64%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, 1H, *J* = 3.2 Hz), 7.60 (d, 1H, *J* = 1.6 Hz), 7.24 (d, 1H, *J* = 8 Hz), 7.21 (d, 1H, *J* = 8.4 Hz), 6.95-6.75 (m, 12H), 4.05 (t, 2H, *J* = 6 Hz), 3.95 (t, 2H, *J* = 6.2 Hz), 3.79-3.64 (m, 37H), 3.48 (t, 2H, *J* = 6.6 Hz), 2.97 (t, 4H, *J* = 6.4 Hz), 2.85 (t, 4H, *J* = 6.2 Hz), 2.08 (m, 4H), 1.85 (m, 2H), 0.66 (m, 2H), 0.18 (t, 1H, *J* = 6.4 Hz), -0.74 (m, 2H), -1.68 (m, 2H), -2.15 (m, 2H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 157.98, 157.53, 150.54,

150.48, 150.45, 150.38, 150.02, 141.89, 141.71, 140.96, 140.50, 135.78, 135.43, 128.68, 128.48, 128.45, 128.40, 128.36, 128.34, 128.32, 128.24, 125.93, 125.69, 116.22, 114.95, 114.01, 113.84, 113.63, 113.45, 113.40, 113.38, 113.33, 113.24, 109.37, 108.83, 69.36, 68.26, 67.82, 62.99, 55.86, 55.80, 55.55, 55.52, 55.50, 55.48, 55.43, 35.55, 35.49, 30.42, 30.05, 29.30, 29.27, 29.24, 29.17, 26.89, 26.17, 25.13, 22.51. HR-ESI-MS: m/z calcd for $[M+H]^+$ $C_{72}H_{83}O_{13}$: 1155.58282; found: 1155.58386, error: -0.9 ppm.

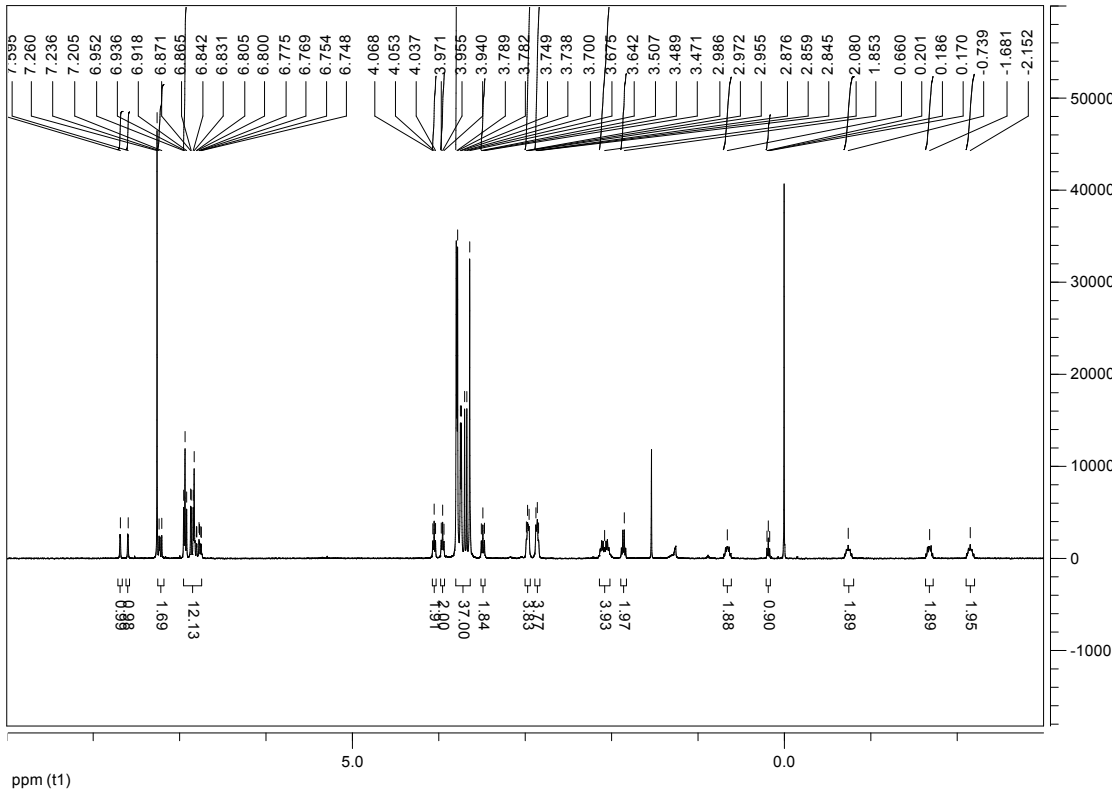


Figure S2(a). ^{1}H NMR spectra of **S5** ($CDCl_3$, 400 MHz).

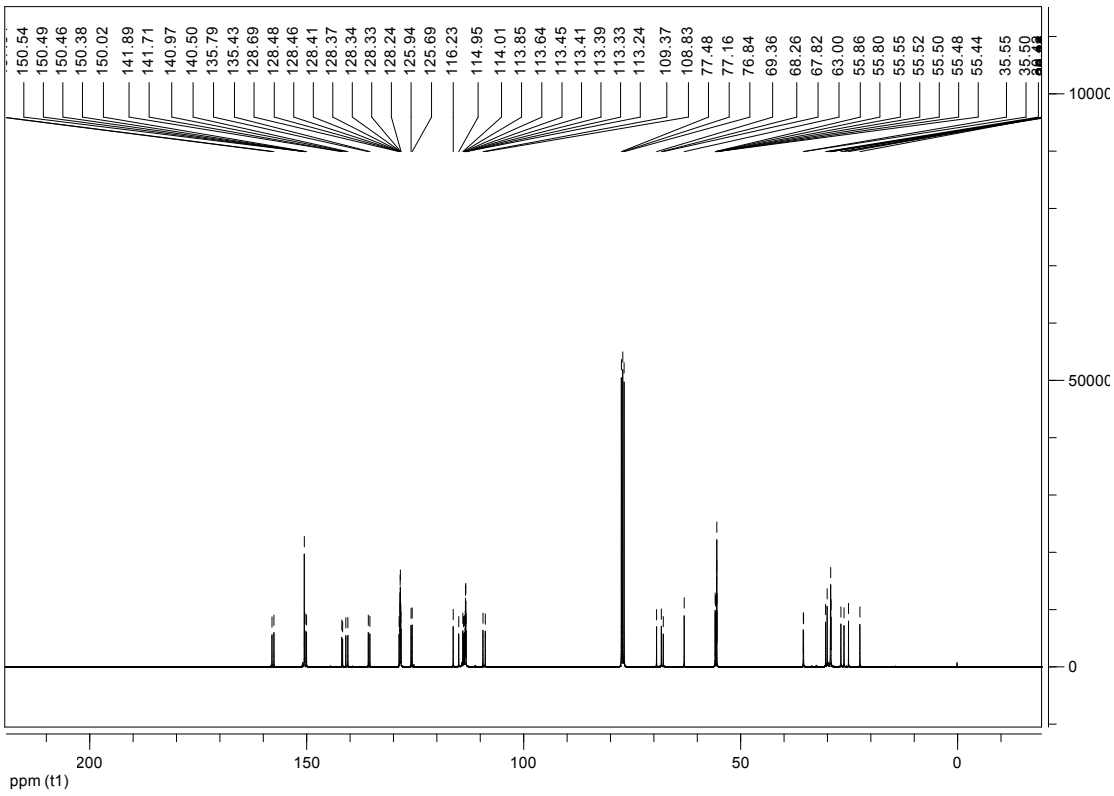


Figure S2(b). ^{13}C NMR spectra of **S5** ($CDCl_3$, 100 MHz).

Preparation of compound S6.

To a stirred solution of **S5** (0.8 g, 0.7 mmol) in 5 mL dry CH_2Cl_2 containing 10 drops of acetone, CBr_4 (0.46 g, 1.4 mmol) and PPh_3 (0.37 g, 1.4 mmol) was added in sequence. The resulting mixture was stirred for 10 min and then purified immediately with column chromatography eluting with petroleum ether/CH_2Cl_2/Et_2O (10:10:1, v/v/v) to afford 0.72 g of product. Yield: 85%. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, 1H, J = 1.6 Hz), 7.64 (d, 1H, J = 1.6 Hz), 7.28 (d, 1H, J = 8.4 Hz), 7.22 (d, 1H, J = 8.4 Hz), 6.96-6.75 (m, 12H), 4.08 (t, 2H, J = 6 Hz), 3.95 (t, 2H, J = 6.2 Hz), 3.84-3.63 (m, 37H), 3.41 (t, 2H, J = 7.6 Hz), 2.96 (t, 4H, J = 6.4 Hz), 2.86 (t, 4H, J = 6.4 Hz), 2.07 (m, 4H), 1.38 (m, 2H), 0.63 (m, 2H), -0.91 (m, 2H), -1.13 (m, 2H), -1.92 (m, 2H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 157.91, 157.43, 150.71, 150.57, 150.40, 150.35, 150.31, 149.92, 141.83, 141.65, 140.92, 140.42, 135.85, 135.37, 128.83, 128.66, 128.44, 128.35, 128.30, 128.24, 128.19, 128.18, 128.15, 128.03, 125.92, 125.56, 116.18, 114.64, 114.57, 113.93, 113.46, 113.33, 113.09, 112.97, 112.92, 112.89, 112.87, 110.66, 108.87, 68.71, 68.12, 67.89, 56.56, 56.15, 55.59, 55.45, 55.39, 55.37, 35.49, 35.42, 33.45, 31.93, 30.00, 29.92, 29.41, 29.26,

29.21, 29.16, 29.11, 26.86, 26.76, 26.20, 23.21. HR-ESI-MS: m/z calcd for M^+ $C_{72}H_{81}BrO_{12}$: 1216.49059; found: 1216.49303, error: -2.0 ppm.

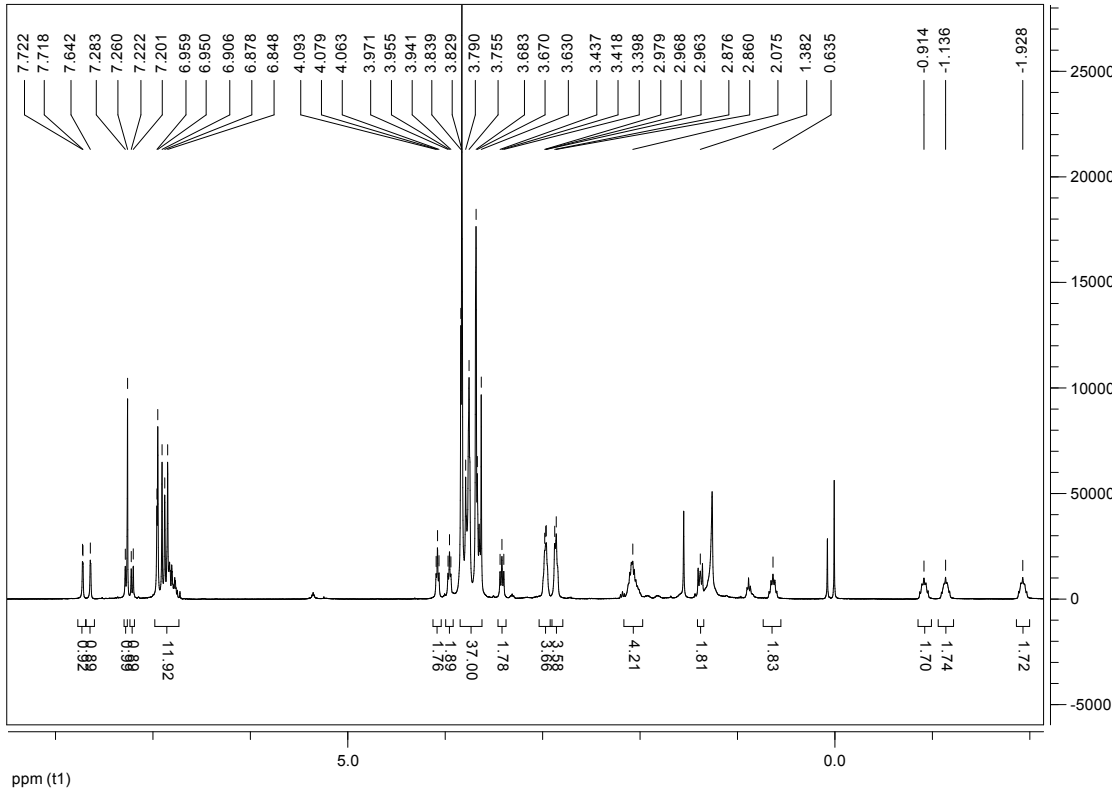


Figure S3(a). ^{1}H NMR spectra of **S6** ($CDCl_3$, 400 MHz).

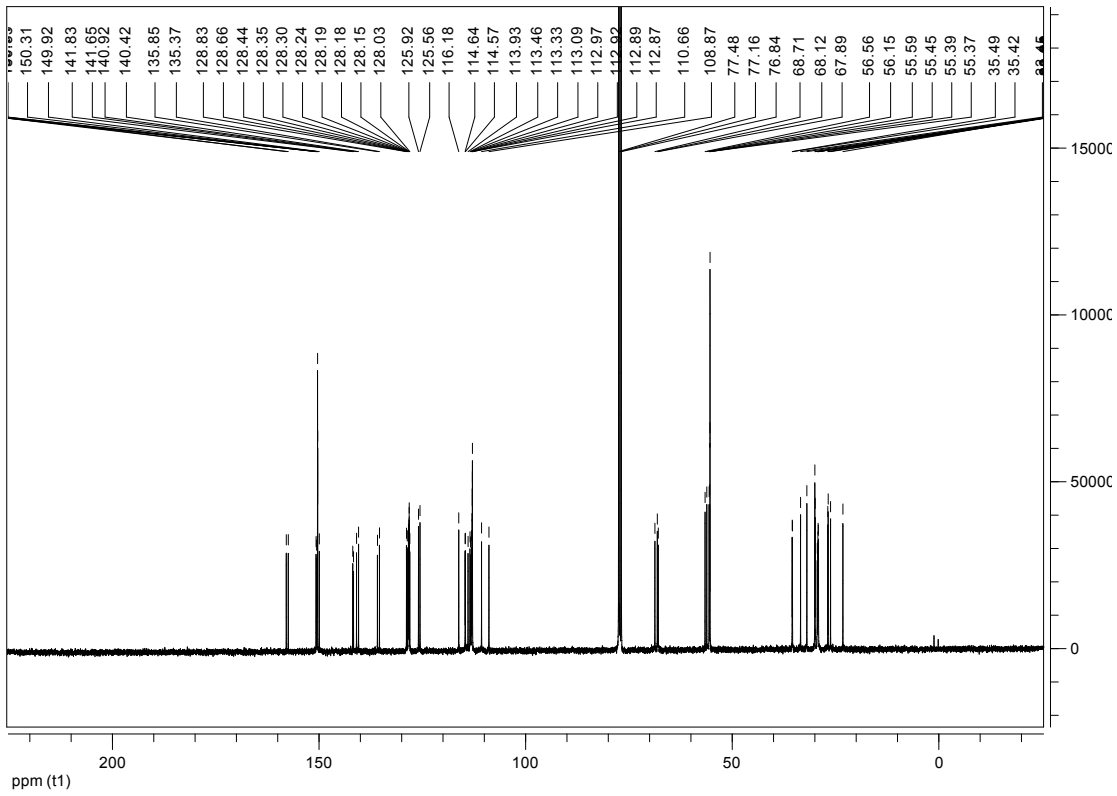


Figure S3(b). ^{13}C NMR spectra of **S6** ($CDCl_3$, 100 MHz).

Preparation of compound *Z*-1.

A mixture of imidazole (0.37 g, 5.4 mmol) and NaOH (86.4 mg, 2.16 mmol) in DMF (7 mL) was heated at 60 ℃ for 2 h, and then **S5** (656.4 mg, 0.54 mmol) was added. The mixture was maintained at 60 ℃ for 40 min. Upon cooling to room temperature, 120 mL brine was added and then extracted with EtOAc (50 mL, 3 times), the combined organic phase was washed with brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure and the further purification was carried out by column chromatography using CH_2Cl_2/CH_3OH (50:1) as eluent to afford 631.8 mg of ***Z*-1**. Yield: 97%. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, 1H, *J* = 2 Hz), 7.69 (d, 1H, *J* = 2 Hz), 7.26 (d, 1H, *J* =8.4 Hz), 7.22 (d, 1H, *J* = 8.4 Hz), 6.98-6.69 (m, 14H), 6.09 (s, 1H), 4.10 (m, 3H), 3.08 (m, 1H), 3.76-3.54 (m, 39H), 2.95 (t, 4H, *J* = 5.8 Hz), 2.85 (t, 4H, *J* = 6 Hz), 2.09 (m, 4H), 1.16 (br, 2H), 0.84 (br, 2H), -0.13 (br, 2H), -1.13(br, 2H), -1.5 (br, 2H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 157.79, 157.49, 150.63, 150.57, 150.50, 150.48, 150.45, 150.42, 150.22, 141.85,

141.67, 141.00, 140.71, 136.56, 135.75, 135.54, 128.86, 128.79, 128.73, 128.61, 128.56, 128.55, 128.42, 128.21, 127.19, 125.87, 125.73, 118.93, 115.38, 115.25, 114.55, 114.01, 113.95, 113.83, 113.78, 113.64, 113.49, 113.45, 113.43, 109.71, 109.62, 68.72, 68.54, 68.27, 56.33, 55.81, 55.77, 55.71, 55.63, 55.60, 55.58, 45.23, 35.48, 35.45, 30.90, 29.98, 29.69, 29.36, 29.06, 28.97, 27.14, 27.09, 26.37, 24.29. HR-ESI-MS: m/z calcd for $[M+H]^+$ $C_{75}H_{85}N_2O_{12}$: 1205.60970; found: 1205.61012, error: -0.3 ppm.

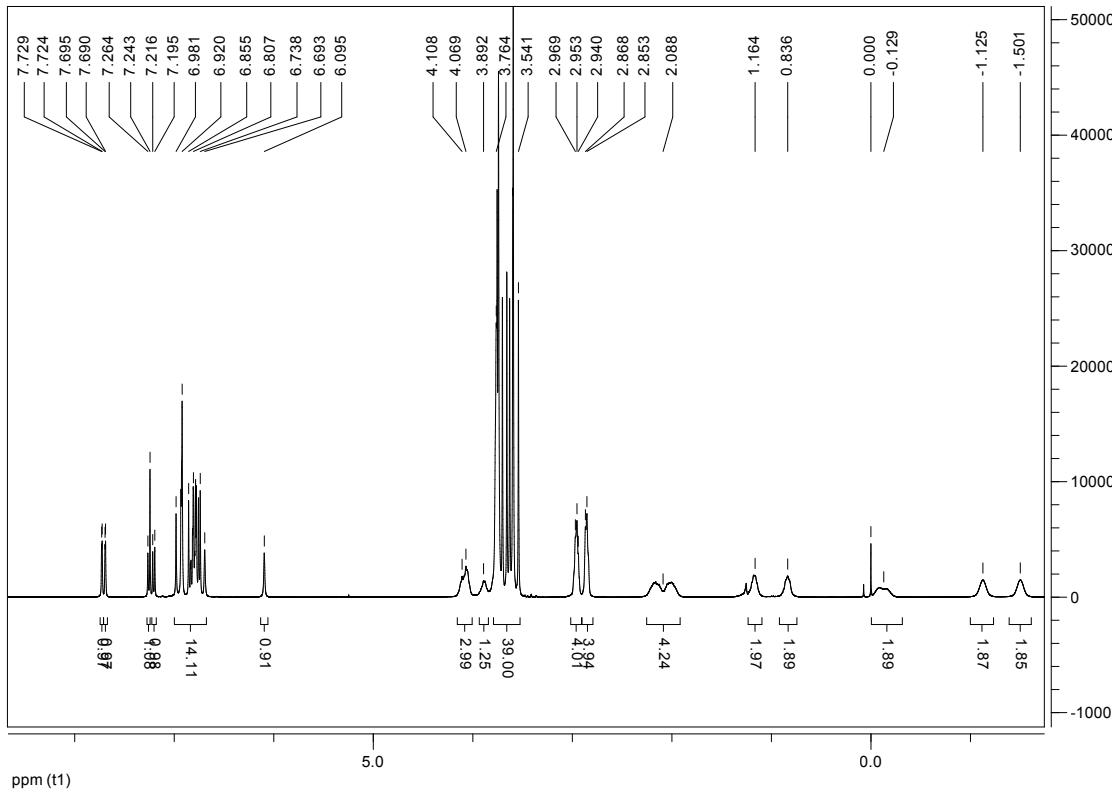


Figure S4(a). ^{1}H NMR spectra of *Z*-**1** ($CDCl_3$, 400 MHz).

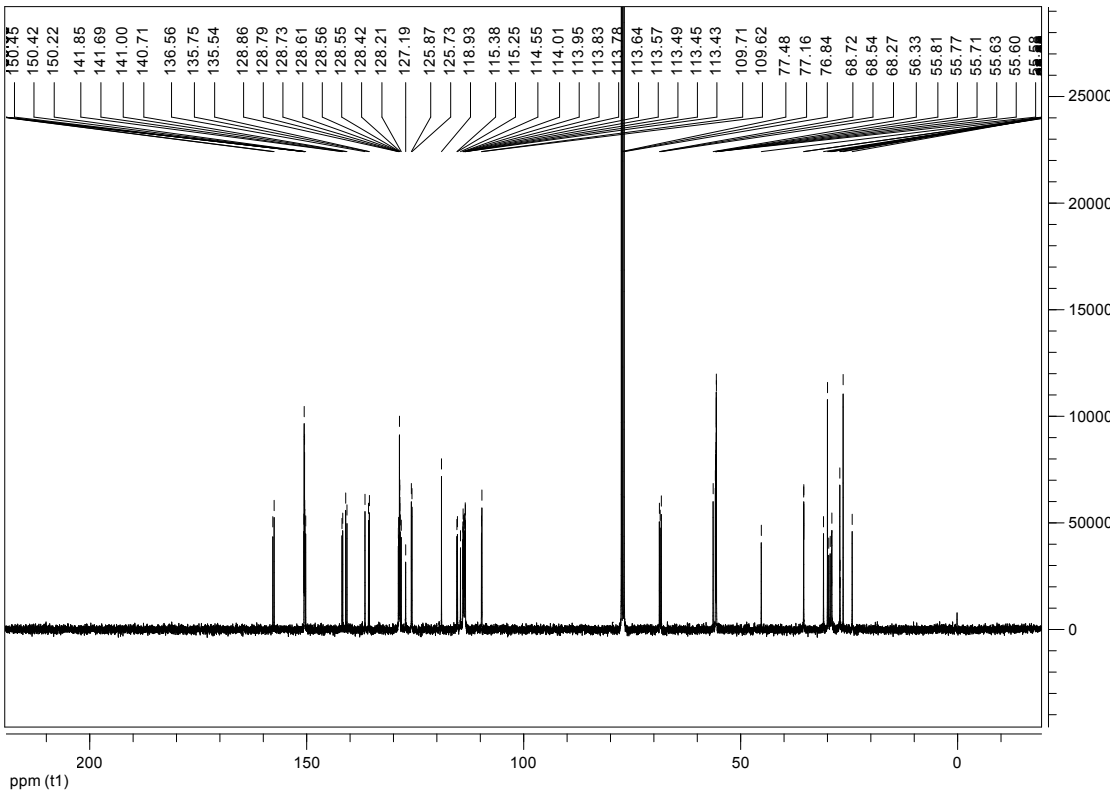


Figure S4(b). ^{13}C NMR spectra of *Z*-**1** ($CDCl_3$, 100 MHz).

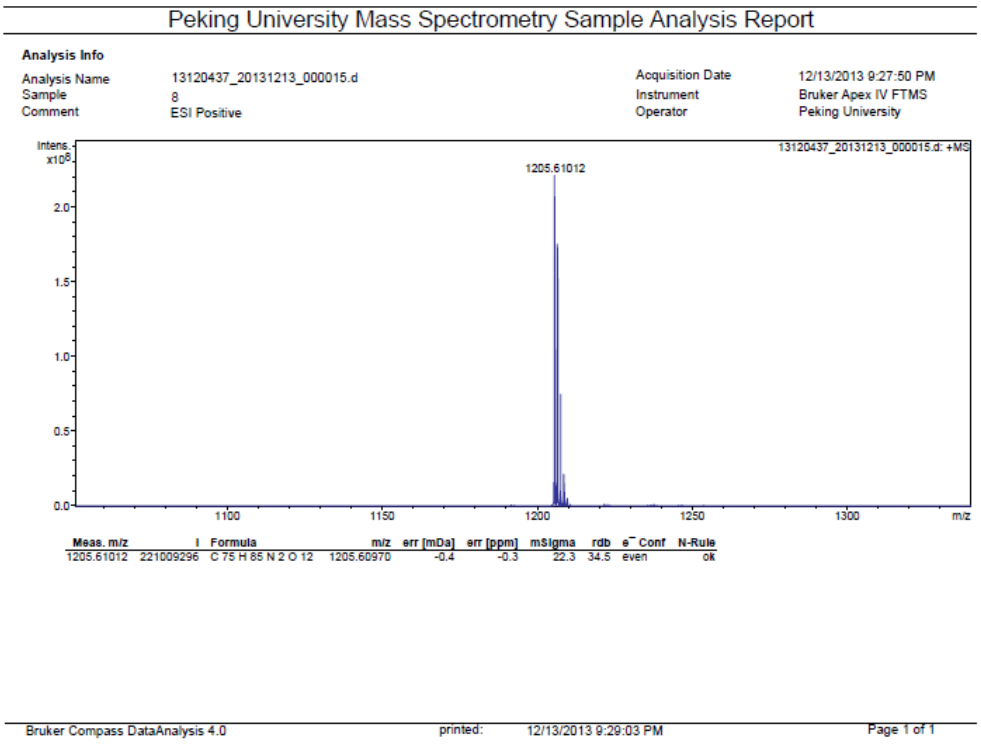


Figure S4(c). HR-ESI-MS spectra of *Z*-**1** .

Preparation of compound *E*-1.

E-**1** was produced by irradiating a solution of *Z*-**1** with a Xe lamp and a narrow band filter centered at 387 ± 5 nm for about 2-2.5 h. The integral area of the proton signal (7.7 ppm) of *Z*-**1** in ^{1}H NMR spectra is only about 3% of the integral area of *E*-**1** proton signal, which revealed the almost completely conversion.

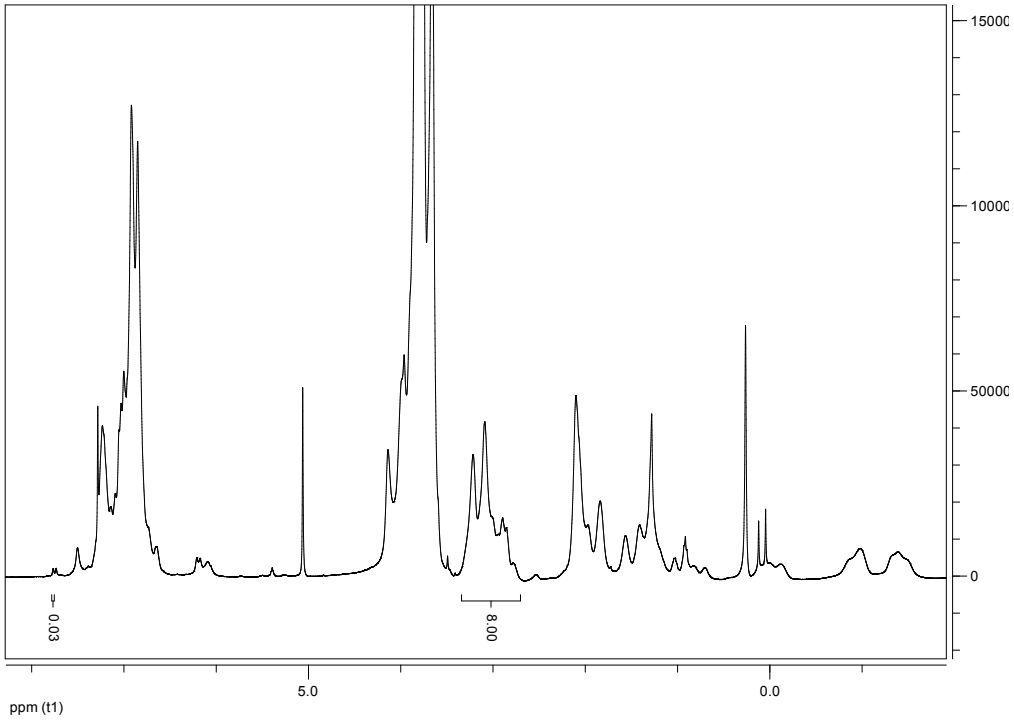


Figure S5. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of *E*-**1.**

3. ^{1}H NMR spectra of *E*-2.

E-**2** was produced by irradiating a solution of protonated *Z*-**1** with a Xe lamp and a narrow band filter centered at 387 ± 5 nm for about 2-2.5 h. The proton signal (7.7 ppm) of protonated *Z*-**1** in ^{1}H NMR spectra is almost disappeared, which revealed the almost completely conversion.

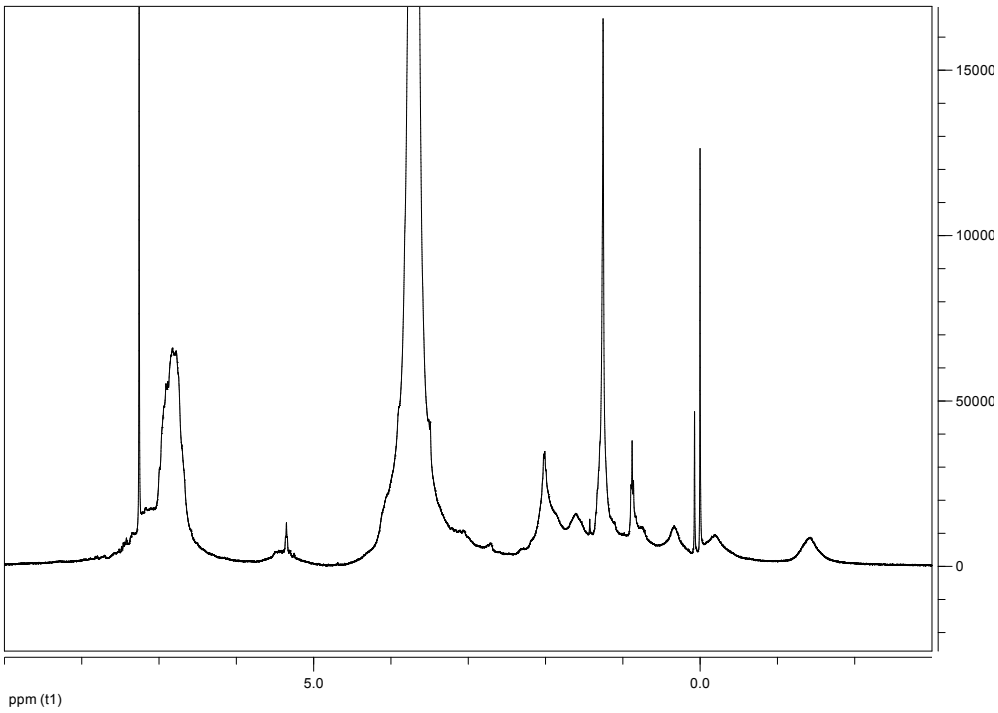


Figure S6. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of *E*-**2.**

4. ^{1}H NMR spectra of *Z*-1 at 5 mM.

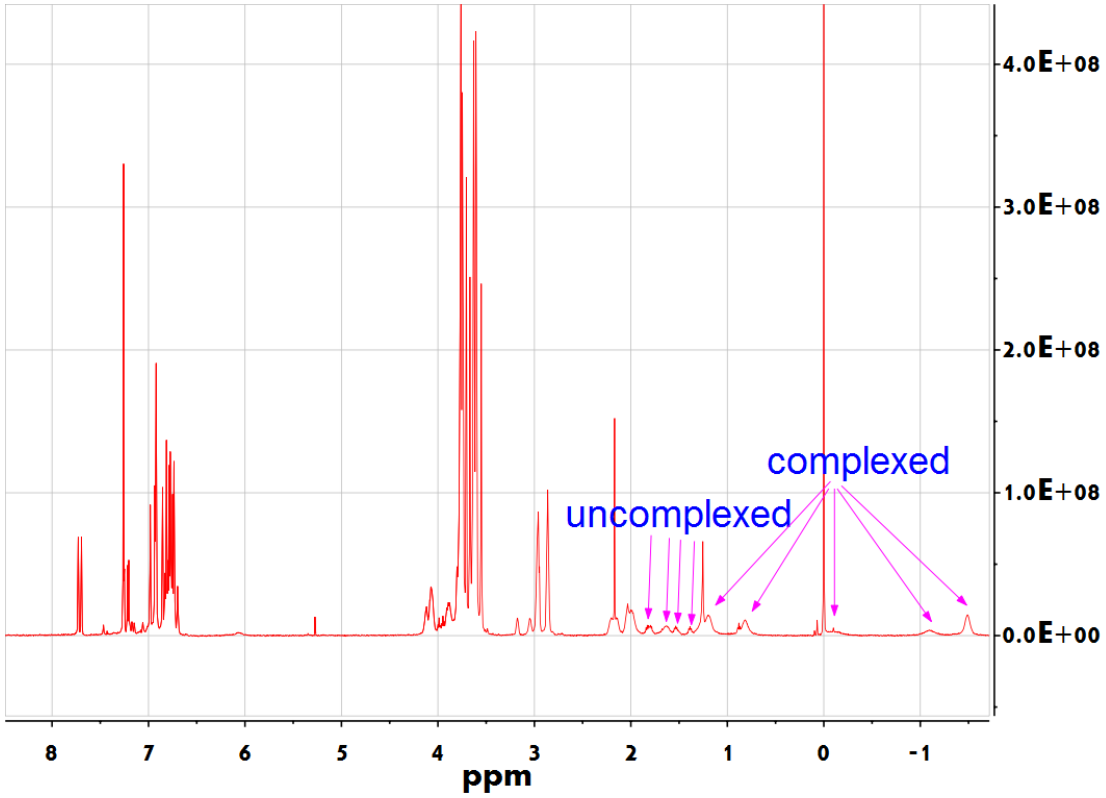


Figure S7. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of *Z*-**1** at 5 mM.

The ^{1}H NMR spectra of *Z*-**1** at 5 mM showed large upfield shifts even below 0 ppm for the alkyl protons H2-H6, indicating the alkyl part entered into the cavity of pillar[5]arene. The uncomplexed signals of the alkyl protons at 2.0-1.5ppm suggested the complexation was a slow-exchanging system.

5. 2-D COSY spectra of *Z*-1 at 150 mM.

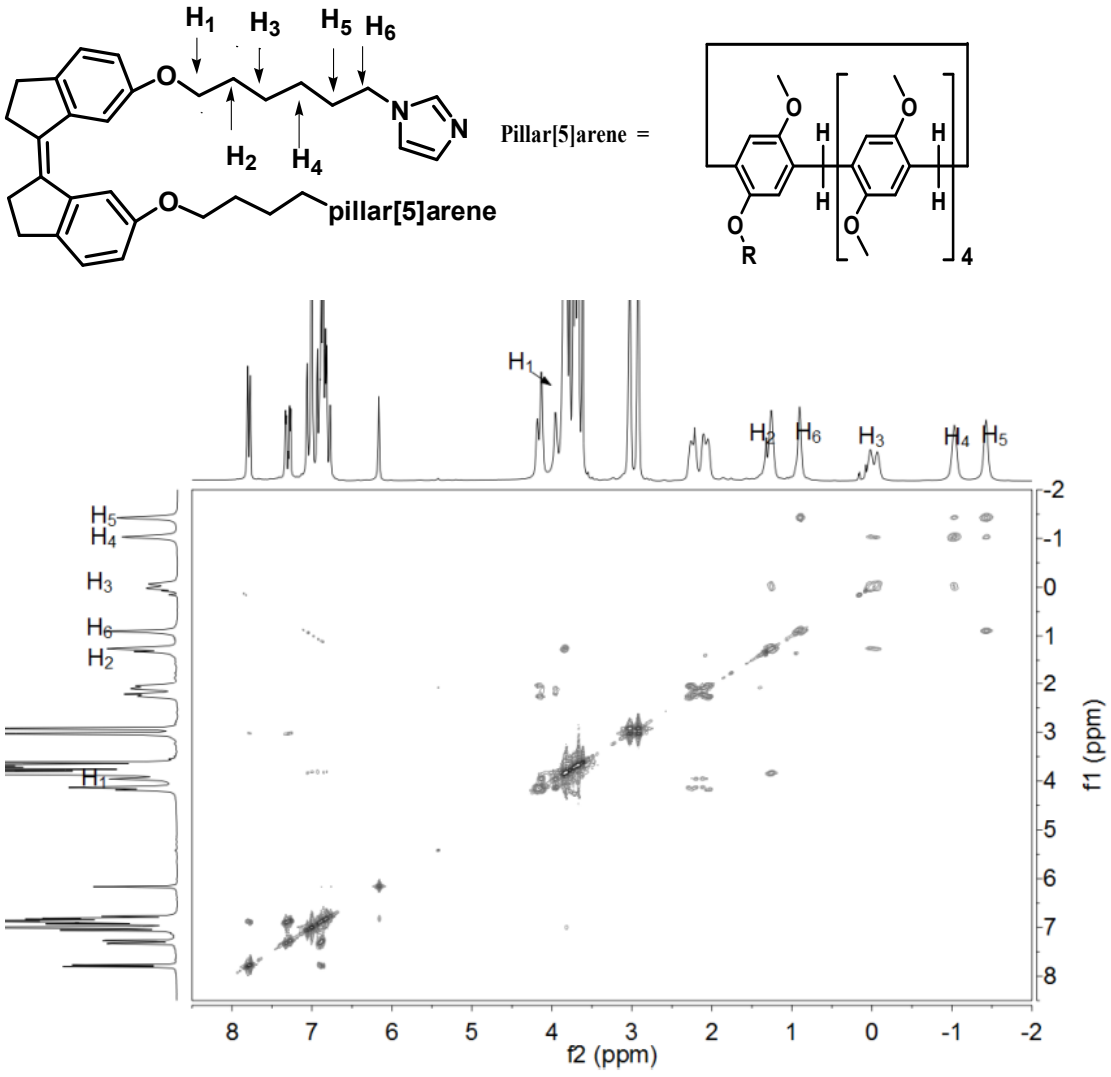
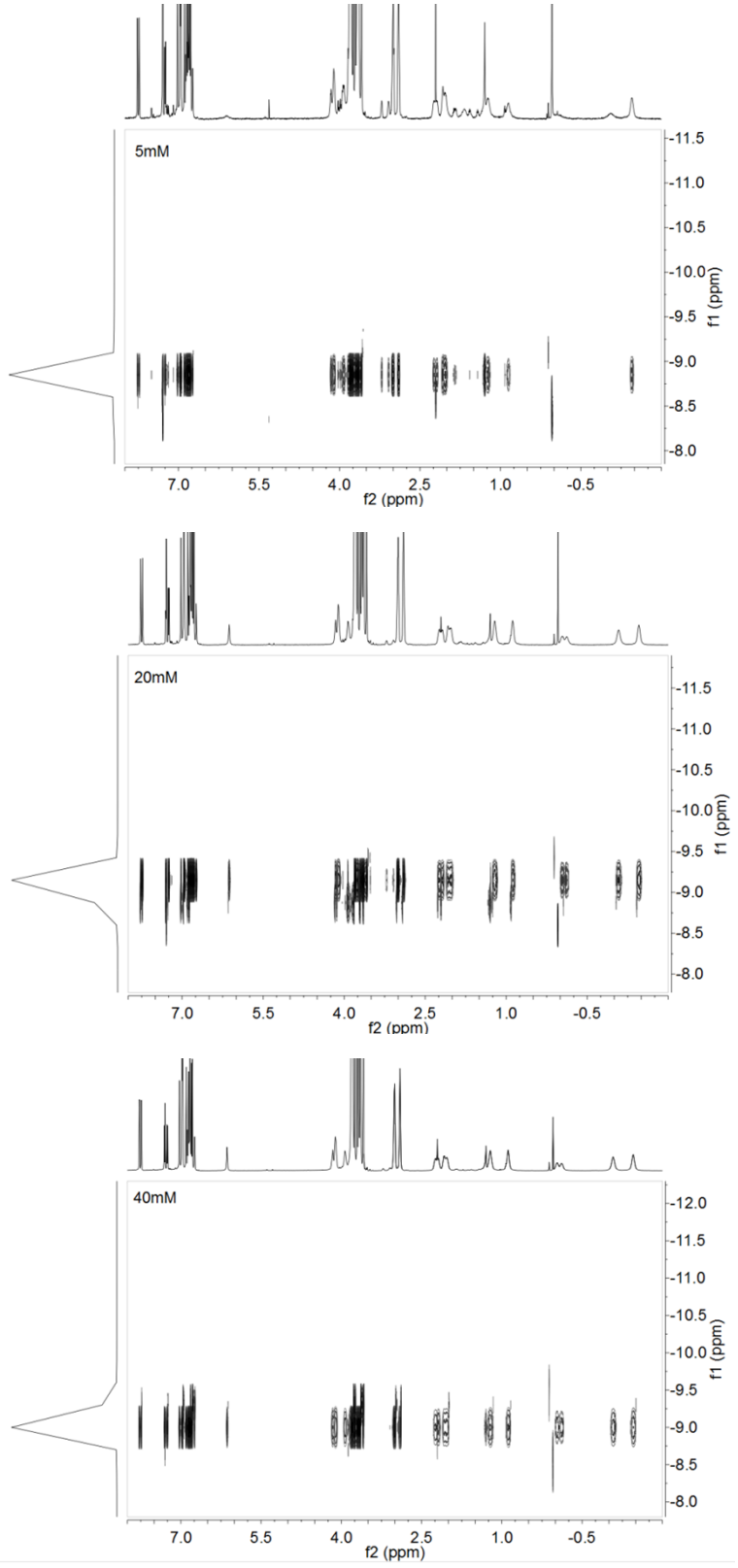


Figure S8. COSY spectrum of a chloroform-d solution of 150 mM *Z*-**1**.

6. DOSY spectra of Z-1 at 5-150 mM.



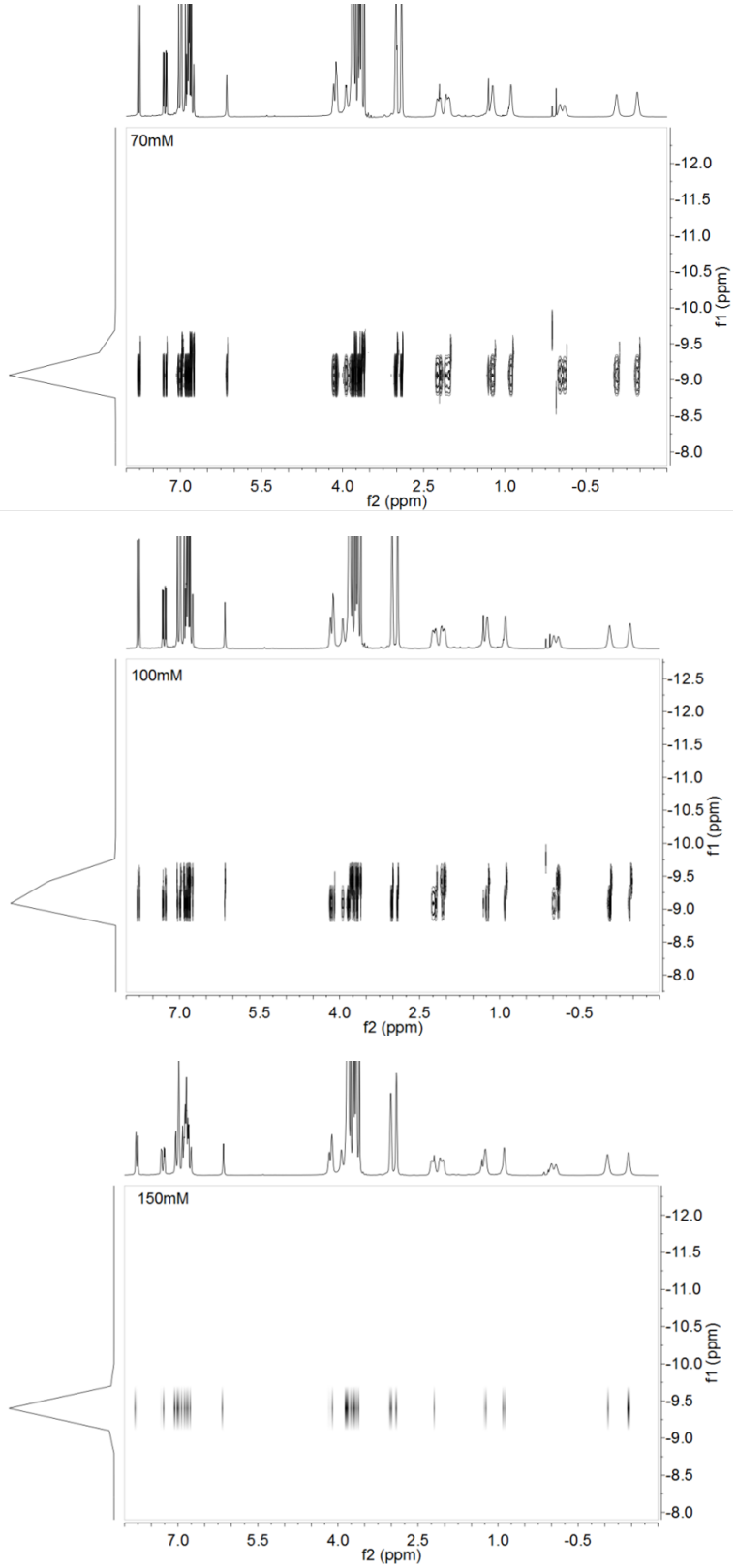
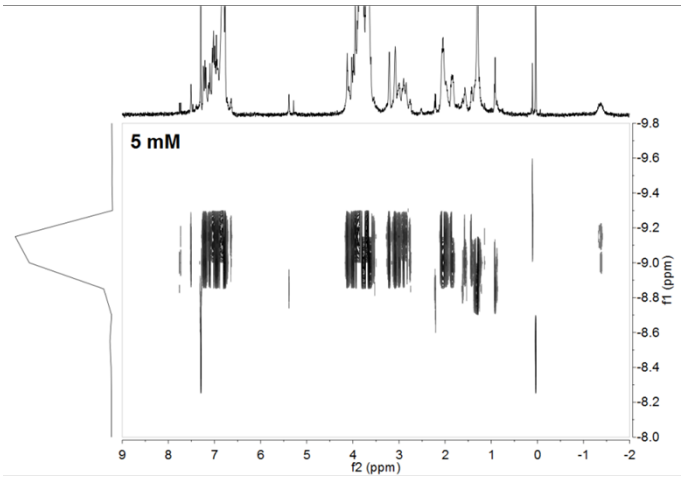
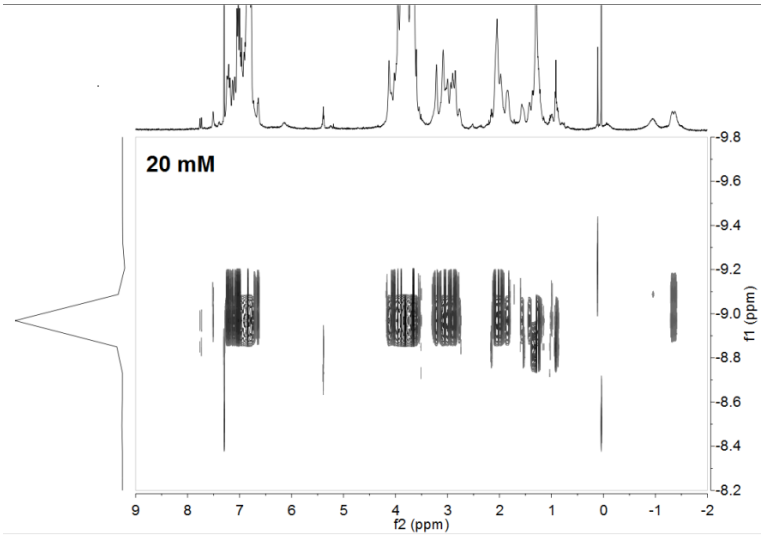
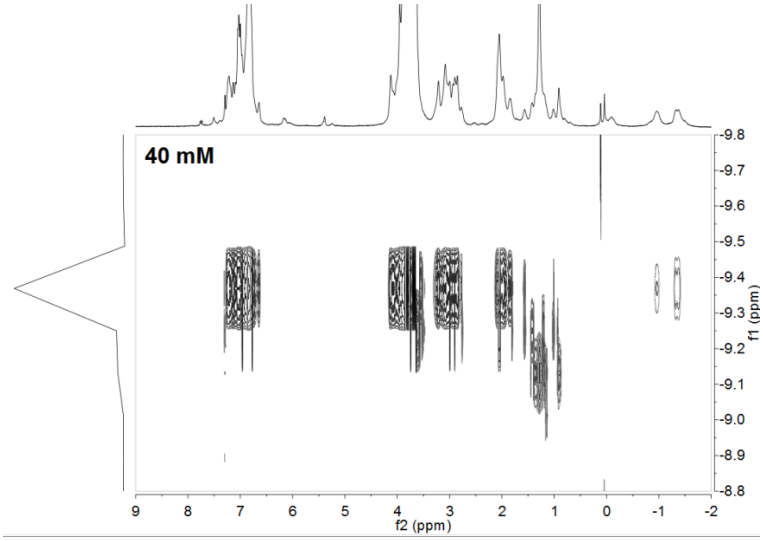


Figure S9. DOSY spectra of *Z*-**1** at 5, 20, 40, 70, 100, 150 mM in $CDCl_3$.

7. DOSY spectra of *E*-1 at 5-150 mM.







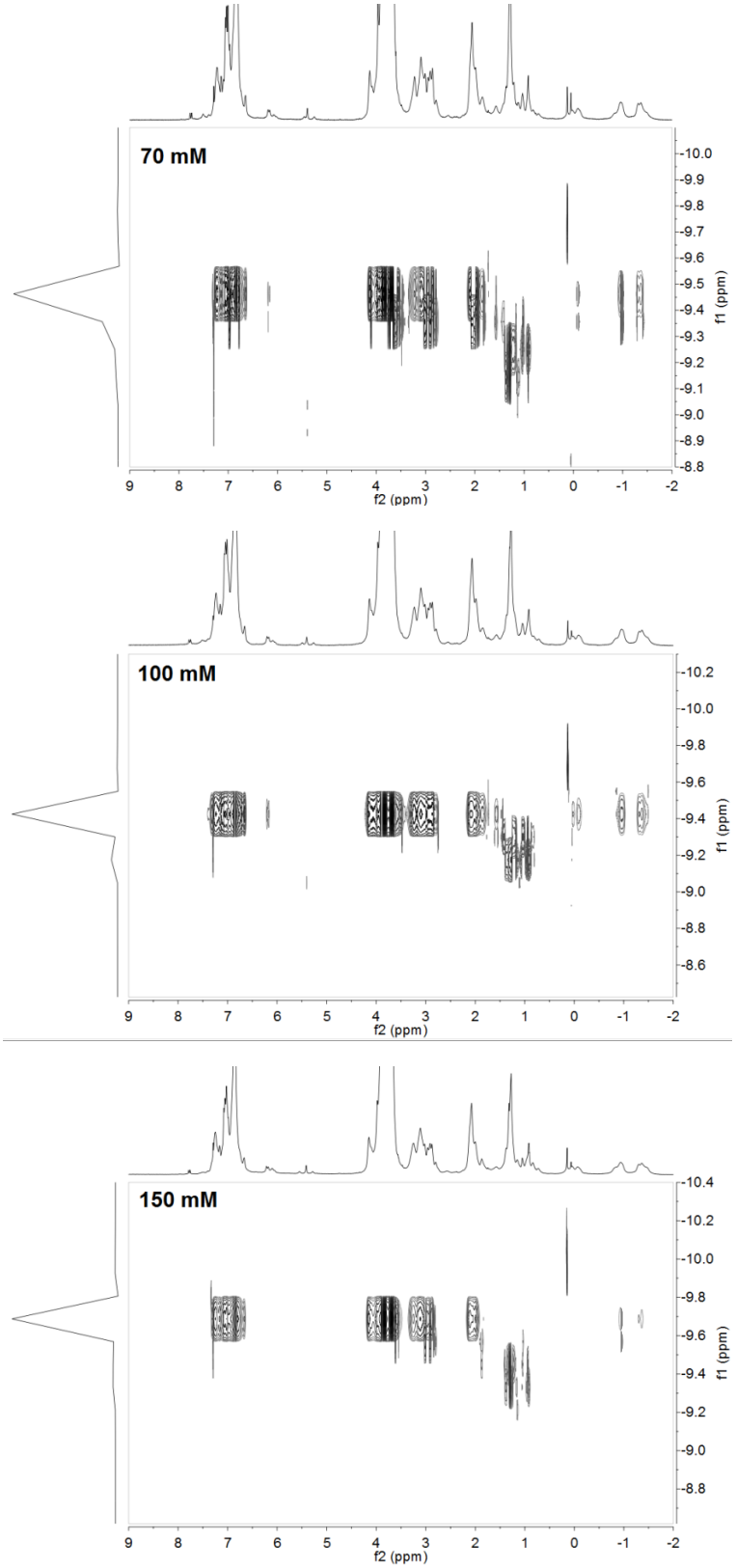
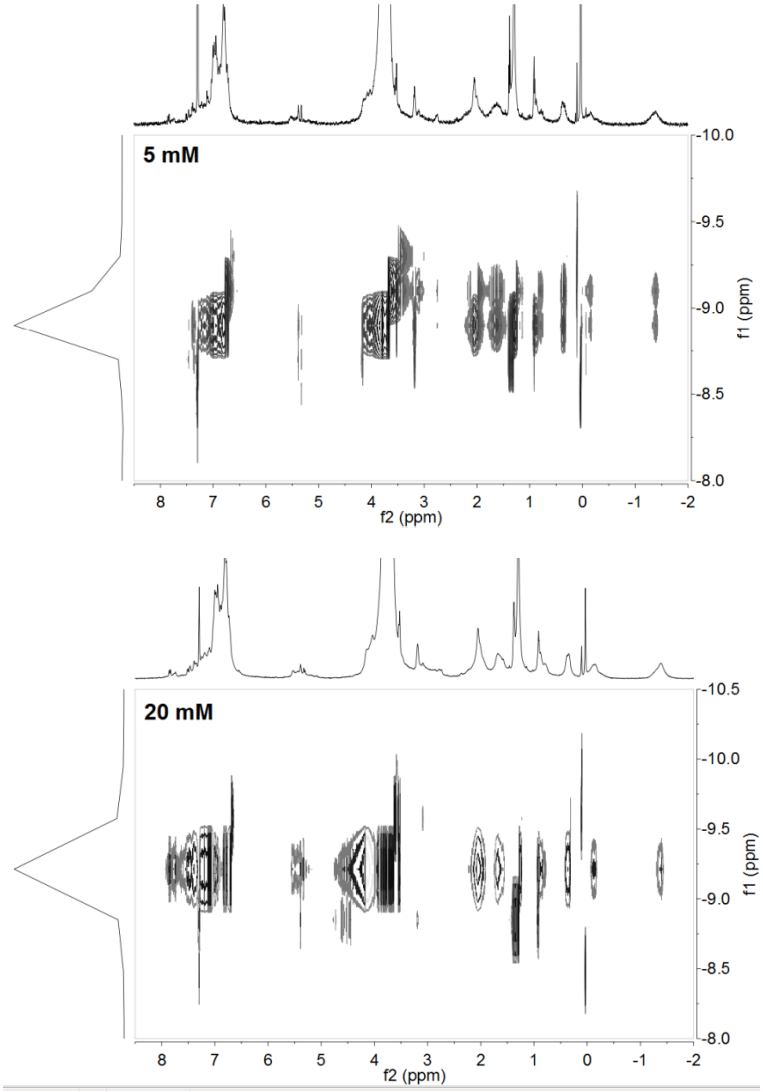


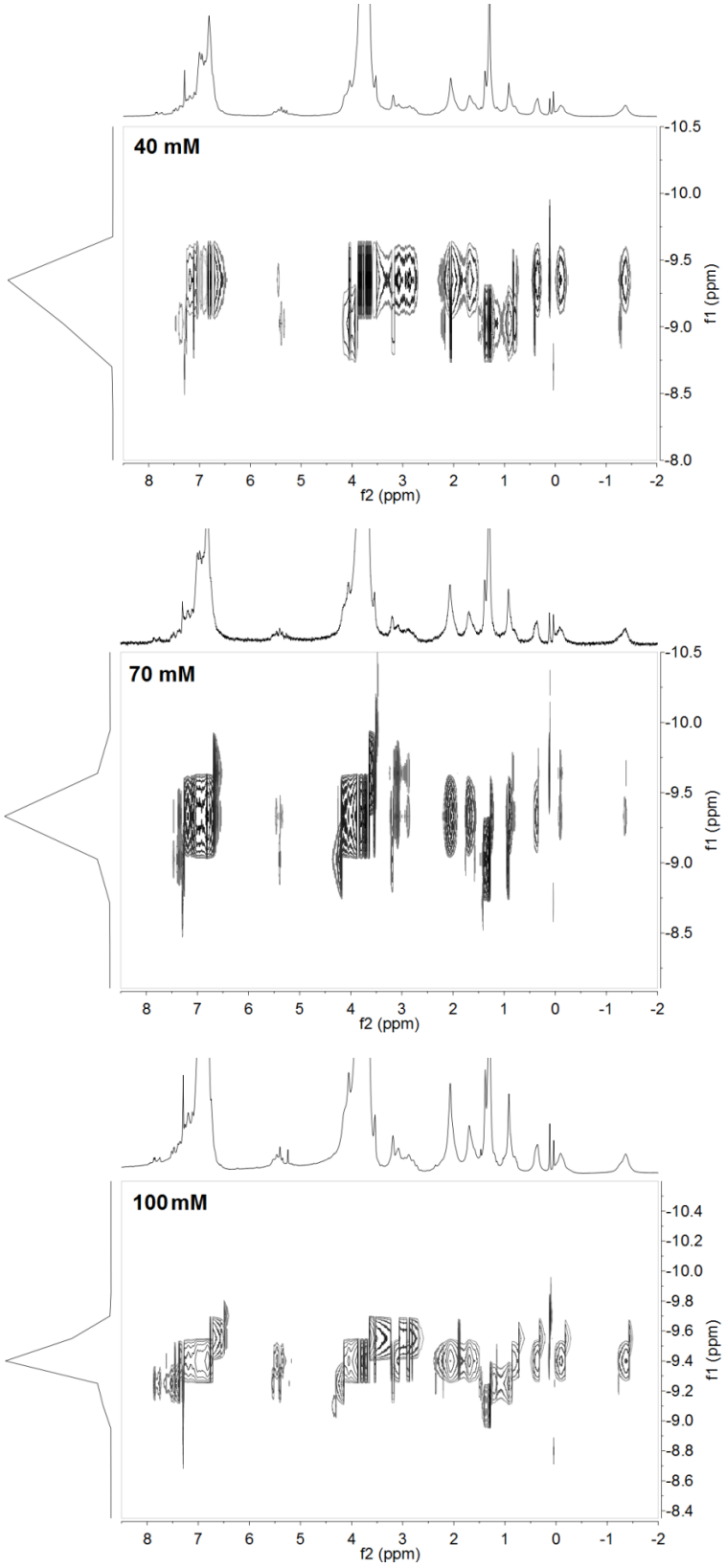
Figure S10. DOSY spectra of *E*-**1** at 5, 20, 40, 70, 100, 150 mM in $CDCl_3$.

The 2-D DOSY spectra of *E*-**1** at 40-150 mM revealed several sets of signals with different diffusion coefficients, which indicated the

existence of several sizes of different aggregates. The observation of a sharp decrease in the diffusion coefficient upon concentration of *E*-**1** increasing suggested the formation of linear polymers.[1]

8. DOSY spectra of *E*-2 at 5-150 mM.




40 mM
70 mM
100 mM
f1 (ppm)
f2 (ppm)

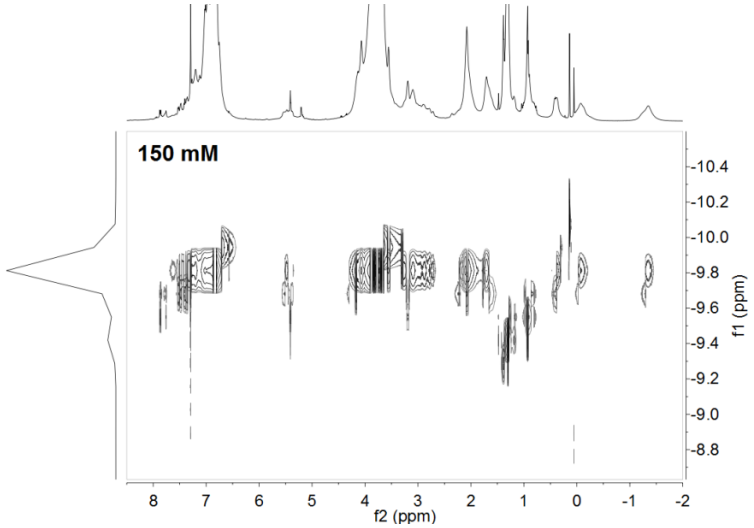


Figure S11. DOSY spectra of *E*-**2** at 5, 20, 40, 70, 100, 150 mM in $CDCl_3$.

The 2-D DOSY spectra of *E*-**2** at 40-150 mM showed several sets of signals with different diffusion coefficients, demonstrating that there were several sizes of different aggregates in *E*-**2** system. When the concentration of *E*-**2** increases, the diffusion coefficient decreases significantly. The decrease is bigger than that of *E*-**1**, suggesting protonation of *E*-**1** increases its degree of polymerization.

9. Reference.

1. F. Wang, J. Q. Zhang, X. Ding, S. Y. Dong, M. Liu, B. Zheng, S. J. Li, L. Wu, Y. H. Yu, H. W. Gibson, F. H. Huang, *Angew. Chem., Int. Ed*., 2010, **122**, 1108-1112.