Electronic Supplementary Information

A light-driven molecular machine based on stiff stilbene

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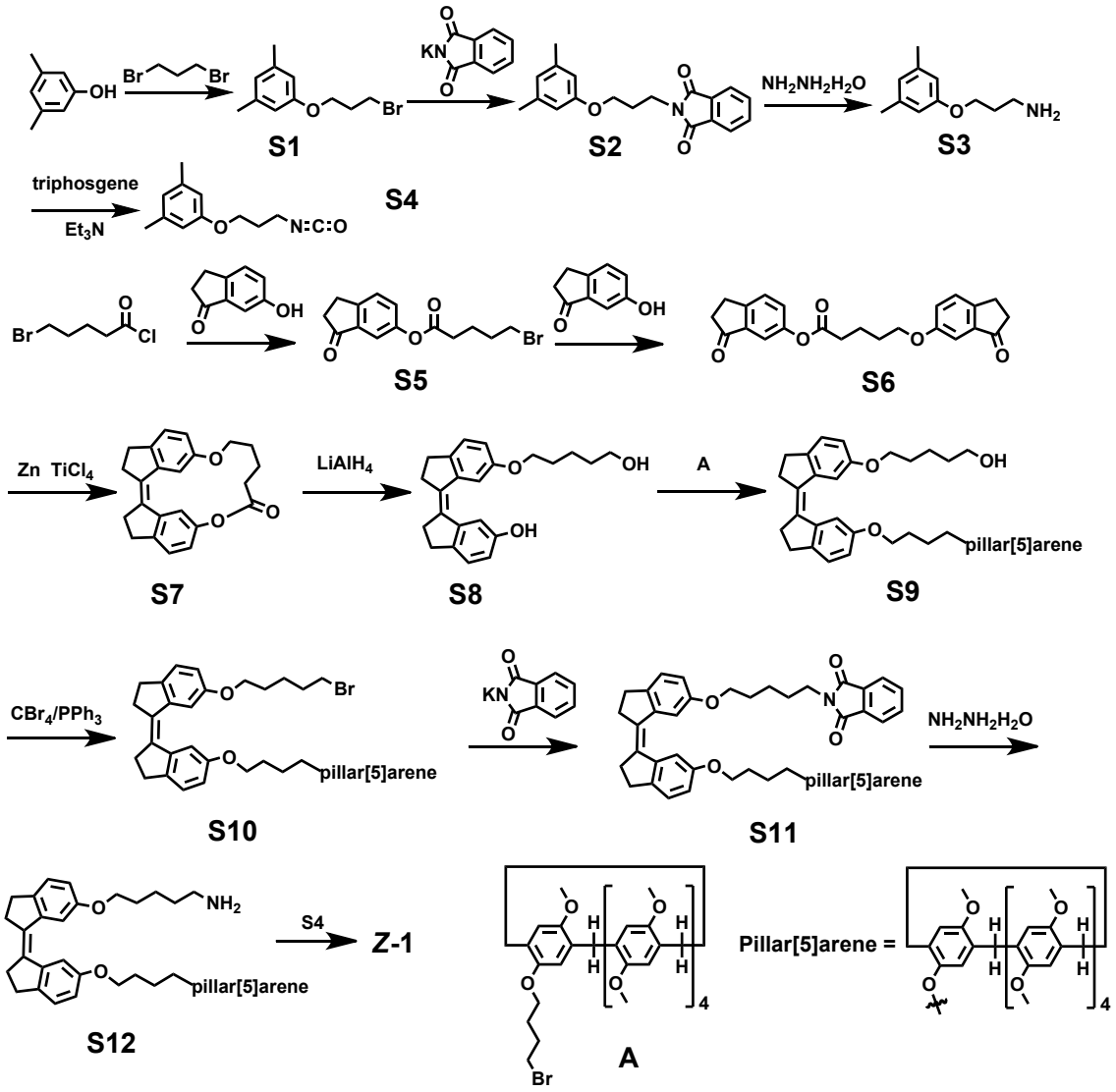
Contents

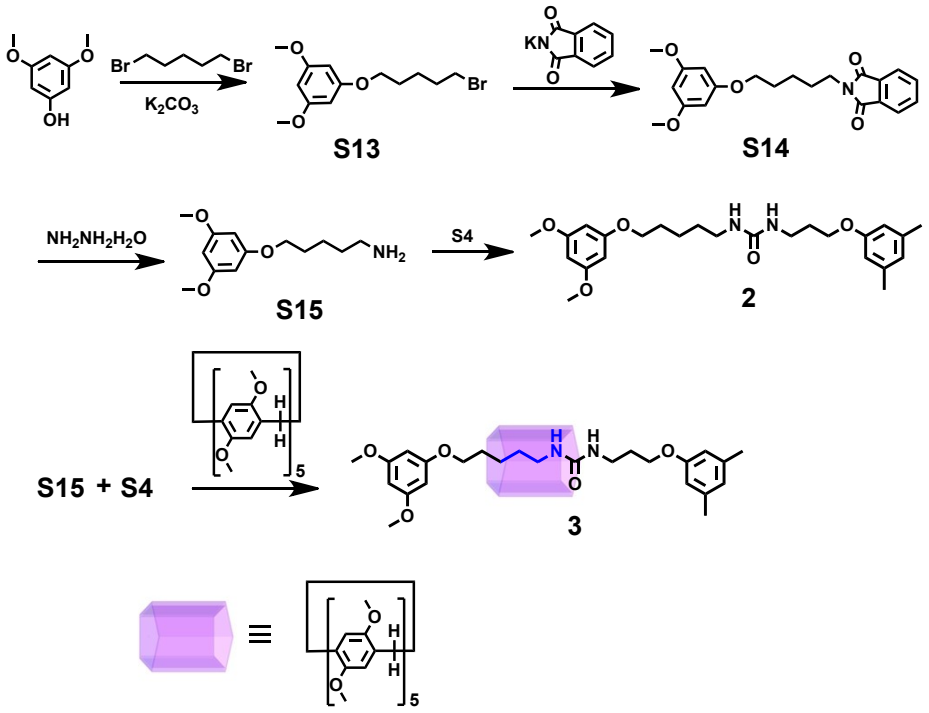
1. Materials and methods

Unless otherwise noted, chemicals and reagents 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 spectra were measured on a Bruker Daltonics Apex IV spectrometer. The photoisomerization reactions were carried out by using a xenon lamp (500 W) or a high-pressure Hg lamp (500 W) with a filter. Absorption spectra were recorded on a Hitachi U-3900 spectrophotometer. High performance liquid chromatography was performed on a Hitachi L-2000 with UV-vis detector L-2420, pump L-2130 and Rheodyne 7725i manual injector using YMC silica gel column (column: 25 cm by 4.6 mm (ID), stationary phase size: 5 μm diameter).

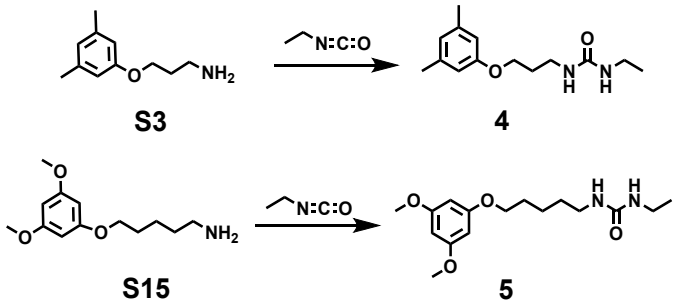
2. Synthesis of compound *Z*-1, *E*-1, 2, 3, 4, 5.



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



Scheme S2. Synthesis of compound **2**, **3**.



Scheme S3. Synthesis of compound **4**, **5.**

1-(3-bromopropoxy)-3,5-dimethylbenzene, S1. To a stirred solution of 1,3-dibromopropane (19.8 g, 98.1 mmol) in acetone (250 mL) was added K_2CO_3 (15.0 g, 108.0 mmol) and 3,5-dimethylphenol (2.0 g, 16.4 mmol) and the mixture was stirred at 70°C overnight. After the reaction was completed, the solid was removed by filtration and the solvent was removed under reduced pressure to afford 3.8 g of product. Yield: 94%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.66 (s, 1H), 6.59 (s, 2H), 4.11 (t, 2H, *J* = 5.6Hz), 3.64 (t, 2H, *J* = 6.2 Hz), 2.34 (m, 8H).

2-(3-(3,5-dimethylphenoxy)propyl)isoindoline-1,3-dione, S2. A solution of **S1** (3.1 g, 12.6 mmol) and potassium phthalimide (7.0 g, 37.8 mmol) in 30 mL DMF was heated at 40°C 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 (40/1, v/v) as eluent to afford 3.7 g of **S2**. Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (m, 2H), 7.73 (m, 2H), 6.56 (s, 1H), 6.42 (s, 2H), 4.00 (t, 2H, *J* = 6.0 Hz), 3.90 (t, 2H, *J* = 6.8 Hz), 2.24 (s, 6H), 2.16 (m, 2H).

3-(3,5-dimethylphenoxy)propan-1-amine, S3. To a solution of **S2** (1.0 g, 3.2 mmol) in CH_2Cl_2 (10 mL) and CH_3OH (10 mL) under N_2 atmosphere, hydrazine monohydrate (2.0 mL, 2.0 g, 40.0 mmol) was added and the mixture was heated at 50°C overnight. After evaporation, the mixture was dissolved in 100 mL 15% aqueous NaOH and then extracted with CH_2Cl_2 (50 mL, 3 times), the combined organic phase was washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford 0.4 g of product. Yield: 72%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.60 (s, 1H), 6.55 (s, 2H), 4.03 (t, 2H, *J* = 6.2 Hz), 2.91 (t, 2H, *J* = 6.8 Hz), 2.30 (s, 6H), 1.91 (m, 2H).

1-(3-isocyanatopropoxy)-3,5-dimethylbenzene, S4. To a solution of **S3** (0.1 g, 0.8 mmol) in dry CH_2Cl_2 (3 ml) was added triethylamine (0.5 ml, 0.3 g, 3.4 mmol) and triphosgene (0.08 g, 0.3 mmol), then the mixture was stirred at room temperature for 1 h and **S4** was obtained. We used **S4** for subsequent addition reactions without further purification.

3-oxo-2,3-dihydro-1H-inden-5-yl 5-bromopentanoate, S5. To a solution of 6-hydroxy-1-indanone (1.0 g, 6.8 mmol) in dry THF (200 mL) was added triethylamine (1.4 mL, 1.0 g, 10.2 mmol) and 5-bromovaleryl chloride (2.0 g, 10.0 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 1.9 g of product. Yield: 89%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, 1H, *J* = 8.0 Hz), 7.44 (d, 1H, *J* = 1.6 Hz), 7.31 (dd, 1H, *J* = 8.4 Hz, 2.4 Hz), 3.46 (t, 2H, *J* = 6.4 Hz), 3.14 (t, 2H, *J* = 5.6 Hz), 2.74 (t, 2H, *J* = 5.6 Hz), 2.62 (t, 2H, *J* = 6.4 Hz), 2.00 (m, 2H), 1.92 (m, 2H).

3-oxo-2,3-dihydro-1H-inden-5-yl 5-((3-oxo-2,3-dihydro-1H-inden-5-yl)oxy)pentanoate, S6. To a solution of **S5** (1.9 g, 6.0 mmol) of DMF (9 mL) was added 6-hydroxyindanone (1.0 g, 6.4 mmol) and K_2CO_3 (2.4 g, 17.3 mmol), then the mixture was stirred at 60°C 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 (20:1, v/v) as eluent to afford 0.8 g product. Yield: 37%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, 1H, *J* = 8.0 Hz), 7.42 (d, 1H, *J* = 1.6 Hz), 7.37 (d, 1H, *J* = 8.0 Hz), 7.31 (dd, 1H, *J* = 8.4 Hz, 2.4 Hz), 7.20 (d, 1H, *J* = 2Hz), 7.17 (dd, 1H, *J* = 8.4 Hz, 2.4 Hz), 4.05 (t, 2H, *J* = 5.6 Hz), 3.12 (t, 2H, *J* = 6.4 Hz), 3.05 (t, 2H, *J* = 5.6 Hz), 2.70 (t, 2H, *J* = 6.0 Hz), 1.94 (m, 4H).

S7. To a stirred suspension of zinc powder (5.3 g, 81.6 mmol) in 120 mL dry THF, $TiCl_4$ (2.5 mL, 5.2 g, 27.2 mmol) was added over 2 min at 0°C. The resulting slurry was heated at 80°C reflux for 3 h, then pyridine (1.1 mL, 1.1 g, 13.6 mmol) was added. A THF solution (50 mL) of **S6** (0.8 g, 2.2 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 0.7 g of product. Yield: 90%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, 1H, *J* = 2.0 Hz), 7.53 (d, 1H, *J* = 2.0 Hz), 7.26 (overlapped with $CDCl_3$, 1H), 7.15 (d, 1H, *J* = 8.0 Hz),

6.88 (dd, 1H, *J* = 8.0 Hz, 2.0 Hz), 6.76 (dd, 1H, *J* = 8.0 Hz, 2.0 Hz), 4.00 (t, 2H, *J* = 7.6 Hz), 3.00 (t, 2H, *J* = 6.0 Hz), 2.88 (m, 6H), 2.58 (t, 2H, *J* = 6.0 Hz), 1.92 (m, 4H).

(Z)-6'-((5-hydroxypentyl)oxy)-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6-ol, S8. To a stirred solution of **S7** (0.7 g, 2.0 mmol) in dry THF (100 mL) was added $LiAlH_4$ (0.3 g, 8.0 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 (20:1, v/v) as eluent to afford 0.6 g of product. Yield: 80%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, 1H, *J* = 2.0 Hz), 7.59 (d, 1H, *J* = 2.0 Hz), 7.17 (d, 1H, *J* = 8.4 Hz), 7.11 (d, 1H, *J* = 8.0 Hz), 6.72 (dd, 1H, *J* = 8.0 Hz, 2.0 Hz), 6.66 (dd, 1H, *J* = 8.0 Hz, 2.4 Hz), 3.97 (t, 2H, *J* = 6.6 Hz), 3.67 (t, 2H, *J* = 6.0 Hz), 2.89 (t, 4H, *J* = 6.4 Hz), 2.80 (t, 4H, *J* = 6.4 Hz), 1.79 (m, 2H), 1.63 (m, 2H), 1.54 (m, 2H).

Pseudorotaxane, S9. A solution of **S8** (0.4 g, 1.2 mmol), **A** (1.7 g, 2.0 mmol) and K_2CO_3 (0.6 g, 4.0 mmol) in 10 mL DMF was heated at 60°C 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 (10/1, v/v) as eluent to afford 1.1 g of product. Yield: 85%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, 1H, *J* = 3.2 Hz), 7.58 (d, 1H, *J* = 1.6 Hz), 7.31 (d, 1H, *J* = 8.0 Hz), 7.22 (d, 1H, *J* = 8.4 Hz), 6.96-6.81 (m, 12H), 4.07 (t, 2H, *J* = 6.0 Hz), 3.97 (t, 2H, *J* = 6.2 Hz), 3.82-3.61 (m, 37H), 2.98 (m, 6H), 2.86 (t, 4H, *J* = 6.2 Hz), 2.14 (m, 2H), 2.05 (m, 2H), 1.67 (m, 2H), 0.03 (m, 2H), -0.05 (t, 1H, *J* = 6.4 Hz), -1.97 (m, 2H), -2.18 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.12, 157.51, 150.99, 150.79, 150.70, 150.52, 150.48, 150.45, 150.12, 141.85, 141.67, 140.86, 140.21, 135.98, 135.22, 129.23, 129.09, 128.63, 128.59, 128.54, 128.45, 128.03, 125.95, 125.39, 117.09, 115.18, 114.83, 114.22, 113.74, 113.71, 113.50, 113.45, 113.22, 111.99, 111.78, 108.26, 68.82, 68.08, 67.31, 62.84, 56.91, 56.78, 55.79, 55.61, 55.53, 55.48, 55.41, 55.33, 53.48, 35.53, 35.41, 30.04, 29.60, 29.43, 26.20, 26.15, 26.61, 26.15, 18.15. HR-ESI-MS: m/z calcd for $[M+H]^+$ $C_{71}H_{81}O_{13}$: 1141.56717; found: 1141.56468, error: 2.2 ppm.

Pseudorotaxane, S10. To a stirred solution of **S9** (0.8 g, 0.7 mmol) in 5 mL dry CH_2Cl_2 containing 10 drops of acetone, CBr_4 (0.5 g, 1.4 mmol) and PPh_3 (0.4 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 0.7 g of product. Yield: 86%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, 1H, *J* = 1.6 Hz), 7.56 (d, 1H, *J* = 1.6 Hz), 7.27 (d, 1H, *J* = 8.4 Hz), 7.23 (d, 1H, *J* = 8.4 Hz), 7.01-6.75 (m, 12H), 4.05 (t, 2H, *J* = 6.0 Hz), 3.95 (t, 2H, *J* = 6.2 Hz), 3.85-3.59 (m, 37H), 3.26 (t, 2H, *J* = 7.6 Hz), 2.98 (t, 4H, *J* = 6.4 Hz), 2.87 (t, 4H, *J* = 6.4 Hz), 2.04 (m, 4H), 0.53 (t, 2H, *J* = 4.8 Hz), 0.24 (m, 2H), -1.37 (m, 2H), -1.62 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.10, 157.68, 150.70, 150.64, 150.56, 150.43, 150.36, 150.25, 149.72, 142.02, 141.74, 140.98, 140.53, 136.38, 135.95, 135.29, 128.76, 128.67, 128.60, 128.50, 128.46, 128.42, 128.35, 128.22, 128.15, 128.04, 127.09, 125.98, 125.59, 116.81, 114.51, 114.02, 113.95, 113.47, 113.37, 113.26, 113.13, 113.07, 110.10, 108.59, 69.32, 68.55, 67.56, 56.22, 55.96, 55.75, 55.48, 55.32, 35.60,

35.52, 32.88, 30.13, 30.06, 29.35, 29.24, 29.21, 26.94, 26.29, 23.67, 20.51, 19.16. HR-ESI-MS: m/z calcd for $[M+Na]^+$ $C_{71}H_{79}O_{12}Br$: 1225.46471; found: 1225.46331, error: 1.1 ppm.

S11. A solution of **S10** (0.7 g, 0.6 mmol) and potassium phthalimide (0.7 g, 3.8 mmol) in 30 mL DMF was heated at 40°C 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 (25/1, v/v) as eluent to afford 0.7 g of **S11**. Yield: 92%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (m, 2H), 7.79 (m, 2H), 7.64 (d, 1H, *J* = 2.0 Hz), 7.62 (d, 1H, *J* = 2.0 Hz), 7.27 (d, 1H, *J* = 8.4 Hz), 7.23 (d, 1H, *J* = 8.4 Hz), 6.78-6.72 (m, 12H), 4.00 (t, 2H, *J* = 6.0 Hz), 3.91 (t, 2H, *J* = 6.4 Hz), 3.86 (t, 2H, *J* = 6.4 Hz), 3.76-3.59 (m, 39H), 2.92 (t, 4H, *J* = 6.4 Hz), 2.81 (t, 4H, *J* = 6.4 Hz), 1.96 (m, 4H), 1.78 (m, 2H), 1.70 (m, 2H), 1.48 (m, 2H).

Pseudorotaxane, S12. To a solution of **S11** (0.7 g, 0.6 mmol) in CH_2Cl_2 (10 mL) and CH_3OH (10 mL) under N_2 atmosphere, hydrazine monohydrate (2.0 mL, 2.0 g, 40.0 mmol) was added and the mixture was heated at 50°C overnight. After evaporation, the mixture was dissolved in 100 mL 15% aqueous NaOH and then extracted with CH_2Cl_2 (50 mL, 3 times), the combined organic phase was washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford 0.6 g of product. Yield: 91%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, 1H, *J* = 3.2 Hz), 7.66 (d, 1H, *J* = 1.6 Hz), 7.34 (d, 1H, *J* = 8.0 Hz), 7.26 (overlapped with $CDCl_3$, 1H), 6.96-6.69 (m, 12H), 5.38 (t, 1H, *J* = 6.4 Hz) 5.16 (t, 1H, *J* = 6.4 Hz), 4.10 (t, 2H, *J* = 6.0 Hz), 4.01 (t, 2H, *J* = 6.0 Hz), 3.85-3.66 (m, 37H), 3.19 (t, 2H, *J* = 8.0 Hz,), 3.00 (t, 4H, *J* = 6.4 Hz), 2.89 (t, 4H, *J* = 6.4 Hz), 2.16 (m, 4H), 0.59 (t, 2H, *J* = 6.4 Hz), 0.30 (m, 2H), -1.90 (m, 2H), -2.11 (m, 2H).

Rotaxane, *Z*-1. To a solution of **S4** in CH_2Cl_2 (5 mL) was added **S12** (0.3g, 0.3 mmol) in the ice bath, Then the mixture was stirred for 10 h, after the reaction was completed, the resulting mixture was removed under reduced pressure and the further purification was carried out by column chromatography using CH_2Cl_2/Et_2O (50/1, v/v) as eluent to afford 250 mg *Z*-**1**. Yield: 70%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, 1H, *J* = 1.2 Hz), 7.59 (d, 1H, *J* = 1.2 Hz), 7.30 (d, 1H, *J* = 5.6 Hz), 7.21 (d, 1H, *J* = 5.6 Hz), 6.96-6.81 (m, 12H), 6.61 (m, 3H), 4.87 (br, 1H), 4.05-3.92 (m, 6H). 3.86-3.64 (m, 37H), 3,32 (m, 2H), 3.12 (s, 1H), 3.05 (s, 1H), 2.98 (t, 4H, *J* = 6.4 Hz), 2.86 (m, 5H), 2.31 (s, 6H), 2.05 (m, 4H), 1.94 (br, 2H), 0.90 (m, 2H), 0.15 (br, 2H), -2.03 (br, 2H), -2.16 (br, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.27, 158.08, 157.72, 157.51, 151.07, 150.94, 150.89, 150.62, 150.52, 150.47, 141.89, 141.67, 140.90, 140.30, 139.38, 136.01, 135.24, 129.30, 129.26, 129.20, 129.14, 129.01, 128.98, 128.78, 128.74, 128.37, 125.97, 125.43, 122.77, 117.03, 115.07, 114.82, 114.67, 114.58, 114.37, 114.31, 114.25, 113.69, 113.24, 112.49, 112.07, 111.71, 108.36, 68.77, 68.09, 67.55, 65.94, 56.90, 56.82, 56.69, 56.63, 56.59, 56.45, 56.41, 55.81, 55.38, 40.25, 37.65, 35.53, 35.41, 30.88, 30.05, 29.84, 29.53, 29.36, 29.30, 29.22, 26.66, 26.16, 26.07, 21.59, 19.88, 14.21. HR-ESI-MS: m/z calcd for $[M+H]^+$ $C_{83}H_{97}N_2O_{14}$: 1345.69343; found: 1345.69409, error: 0.5 ppm.

Rotaxane, *E*-1. We irradiate a solution of *Z*-**1** (30 mg) with a Xe lamp and a narrow band filter centered at 387 ± 5 nm for about 2-2.5 h and further purification was carried out by column

chromatography using CH_2Cl_2/Et_2O (50/1, v/v) as eluent to afford 27 mg *E*-**1**. Yield: 90%. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.22 (m, 4H), 6.94-6.62 (m, 12H), 6.52 (s, 1H), 6.24 (s, 2H), 4.29(m, 5H), 4.05 (t, 1H, *J* = 6.4 Hz), 3.81-3.34 (m, 37H), 3.20 (m, 5H), 3.06 (m, 5H), 2.84 (s, 1H), 2.37 (s, 6H), 2.02 (s, 1H), 1.82 (m, 6H), 1.52 (m, 4H), 1.19 (m, 2H), -0.01 (br, 2H), -1.65 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.54, 157.43, 157.33, 156.96, 152.73, 151.69, 151.63, 151.33, 151.19, 150.48, 150.33, 150.06, 149.97, 144.67, 144.47, 140.55, 140.04, 138.21, 135.64, 135.58, 130.73, 130.39, 130.09, 129.85, 128.95, 128.86, 128.81, 128.53, 128.48, 126.90, 125.63, 121.51, 118.57, 117.29, 116.96, 116.12, 115.94, 115.41, 114.42, 113.86, 113.06, 112.85, 112.31, 112.16, 111.19, 69.22, 68.69, 64.38, 59.29, 57.67, 57.32, 56.70, 56.06, 55.90, 55.85, 55.66, 55.01, 53.49, 40.67, 34.69, 34.05, 33.94, 31.04, 31.00, 30.94, 30.50, 30.31, 29.91, 29.83, 29.35, 29.10, 28.57, 26.06, 27.44, 26.85, 26.60, 24.27, 21.60. HR-ESI-MS: m/z calcd for $[M+H]^+$ $C_{83}H_{97}N_2O_{14}$: 1345.69343; found: 1345.89572, error: 1.7 ppm.

1-((5-bromopentyl)oxy)-3,5-dimethoxybenzene, S13. To a stirred solution of 1,5-dibromopentane (33.9 g, 147.4 mmol) in acetone (250 mL) was added K_2CO_3 (15.0 g, 108.0 mmol) and 3,5-dimethoxyphenol (3.0 g, 24.5 mmol) and the mixture was stirred at 70°C overnight. After the reaction was completed, the solid was removed by filtration and the solvent was removed under reduced pressure to afford 6.4 g of product. Yield: 95%. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.08 (s, 3H), 3.92 (t, 2H, *J* = 6.4 Hz), 3.76 (s, 6H), 3.43 (t, 2H, *J* = 6.8 Hz), 1.92 (m, 2H), 1.79 (m, 2H), 1.61 (m, 2H).

2-(5-(3,5-dimethoxyphenoxy)pentyl)isoindoline-1,3-dione, S14. A solution of **S13** (3.7 g, 13.8mmol) and potassium phthalimide (3.9 g, 21.0 mmol) in 30 mL DMF was heated at 40°C 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 (25/1, v/v) as eluent to afford 4.0 g of **S14**. Yield: 98%. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.84 (m, 2H), 7.71 (m, 2H), 6.06 (3, 3H), 3.91 (t, 2H, *J* = 5.6 Hz), 3.76 (s, 6H), 3.72 (t, 2H, *J* = 7.2 Hz), 1.78 (m, 4H), 1.52 (m, 2H).

5-(3,5-dimethoxyphenoxy)pentan-1-amine, S15. To a solution of **S14** (1.0 g, 3.4 mmol) in CH_2Cl_2 (10 mL) and CH_3OH (10 mL) under N_2 atmosphere, hydrazine monohydrate (2.0 mL, 2.0 g, 40.0 mmol) was added and the mixture was heated at 50°C overnight. After evaporation, the mixture was dissolved in 100 mL 15% aqueous NaOH and then extracted with CH_2Cl_2 (50 mL, 3 times), the combined organic phase was washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford 0.6 g of product. Yield: 91%. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.07 (s, 3H), 3.91 (t, 2H, *J* = 6.4 Hz), 3.76 (s, 6H), 2.71 (t, 2H, *J* = 6.4 Hz), 1.78 (t, 2H, *J* = 6.4 Hz), 1.49 (m, 4H).

1-(5-(3,5-dimethoxyphenoxy)pentyl)-3-(3-(3,5-dimethylphenoxy)propyl)urea, 2. To a solution of **S4** (0.1 g, 0.5 mmol) in CH_2Cl_2 (5 mL) was added **S15** (0.1 g, 0.4 mmol) in the ice bath and stirred at room temperature for 1 h. After the reaction was completed, the resulting mixture was removed under reduced pressure and the further purification was carried out by column chromatography using CH_2Cl_2/CH_3OH (40/1, v/v) as eluent to afford 30 mg **2**. Yield:

19%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.59 (s, 1H), 6.51 (s, 2H), 6.06 (s, 3H), 4.93 (t, 1H, *J* = 6.4 Hz), 4.73 (t, 1H, *J* = 6.4 Hz), 3.98 (t, 2H, *J* = 6.0 Hz), 3.88 (t, 2H, *J* = 6.4 Hz), 3.75 (s, 6H), 3.34 (t, 2H, *J* = 6.0 Hz), 3.14 (t, 2H, *J* = 6.0 Hz), 2.27 (s, 6H), 1.95 (m, 2H), 1.73 (m, 2H), 1.49 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.74, 161.15, 158.96, 158.63, 139.35, 122.86, 112.51, 93.77, 93.23, 67.94, 65.97, 55.41, 40.62, 38.19, 30.16, 30.03, 29.08, 23.61, 21.47. HR-ESI-MS: m/z calcd for $[M+H]^+$ $C_{25}H_{37}N_2O_5$: 445.26970 ; found: 445.27032 , error: 1.4 ppm.

Rotaxane, 3. To a solution of **S4** (0.1 g, 0.5 mmol) in CH_2Cl_2 (5 mL) was added **S15** (0.1 g, 0.4 mmol) and pillar[5]arene (0.5 g, 0.7 mmol). Then the mixture was stirred at ice bath for 1 h. After the reaction was completed, the resulting mixture was removed under reduced pressure and the further purification was carried out by column chromatography using CH_2Cl_2/Et_2O (50/1, v/v) as eluent to afford 54 mg **3**. Yield: 13%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.95 (d, 10H, *J* = 4.4 Hz), 6.63 (m, 3H), 6.11 (m, 3H), 4.94 (b, 1H), 4.02 -3.75 (m, 48H), 3.34 (b, 2H), 3.09 (b, 1H), 2.93 (b, 2H), 2.33 (s, 6H), 1.86 (m, 2H), 1.32 (m, 2H), -0.15 (br, 2H), -1.87 (br, 2H), -2.13 (br, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.80, 161.47, 159.24, 157.81, 150.97, 150.69, 139.33, 129.09, 128.82, 122.76, 114.58, 113.99, 112.50, 94.19, 91.59, 68.27, 65.90, 56.59, 55.94, 55.40, 40.18, 37.65, 30.66, 29.30, 28.97, 26.95, 21.56, 19.61. HR-ESI-MS: m/z calcd for $[M+H]^+$ $C_{70}H_{87}N_2O_{15}$: 1195.61010 ; found: 1195.61029 , error: 0.2 ppm.

1-(3-(3,5-dimethylphenoxy)propyl)-3-ethylurea, 4. To a solution of **S3** (0.4 g, 2.4 mmol) in dry CH_2Cl_2 (5 ml) was added ethyl isocyanate (0.2 g, 3.0 mmol), Then the mixture was stirred at room temperature for 10 h, After the reaction was completed, the resulting mixture was removed under reduced pressure and the further purification was carried out by column chromatography using CH_2Cl_2/CH_3OH (40/1, v/v) as eluent to afford 500 mg **4**. Yield: 85%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.60 (s, 1H), 6.51 (s, 2H), 4.88 (t, 1H, *J* = 6.4 Hz), 4.60 (t, 1H, *J* = 6.4 Hz), 3.99 (t, 2H, *J* = 6.0 Hz), 3.34 (m, 2H), 3.17 (m, 2H), 2.27 (s, 6H), 1.94 (m, 2H), 1.11 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.28, 158.90, 138.98, 122.46, 112.31, 65.46, 53.33, 37.34, 34.89, 30.08, 21.24, 15.43. HR-ESI-MS: m/z calcd for $[M+H]^+$ $C_{14}H_{23}N_2O_2$: 251.17540; found: 251.17546, error: 0.2 ppm.

1-(5-(3,5-dimethoxyphenoxy)pentyl)-3-ethylurea, 5. To a solution of **S15** (0.2 g, 0.7 mmol) in dry CH_2Cl_2 (5 ml) was added ethyl isocyanate (0.2 g, 3.0 mmol). Then the mixture was stirred at room temperature for 10 h, After the reaction was completed, the resulting mixture was removed under reduced pressure and the further purification was carried out by column chromatography using CH_2Cl_2/CH_3OH (40/1, v/v) as eluent to afford 135 mg **5**. Yield: 68%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.07 (s, 3H), 4.23 (m, 2H), 3.91 (t, 2H, *J* = 6.4 Hz), 3.76 (s, 6H), 3.19 (m, 4H), 1.78 (m, 2H), 1.55 (m, 4H), 1.13 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.63, 161.06, 159.01, 93.66, 93.09, 67.88, 55.31, 40.26, 35.10, 30.21, 29.04, 23.55, 15.56. HR-ESI-MS: m/z calcd for $[M+H]^+$ $C_{16}H_{27}N_2O_4$: 311.19653; found: 311.19666, error: 0.4 ppm.

3. Characterization of compound *Z*-1, *E*-1, 2, 3, 4, 5.

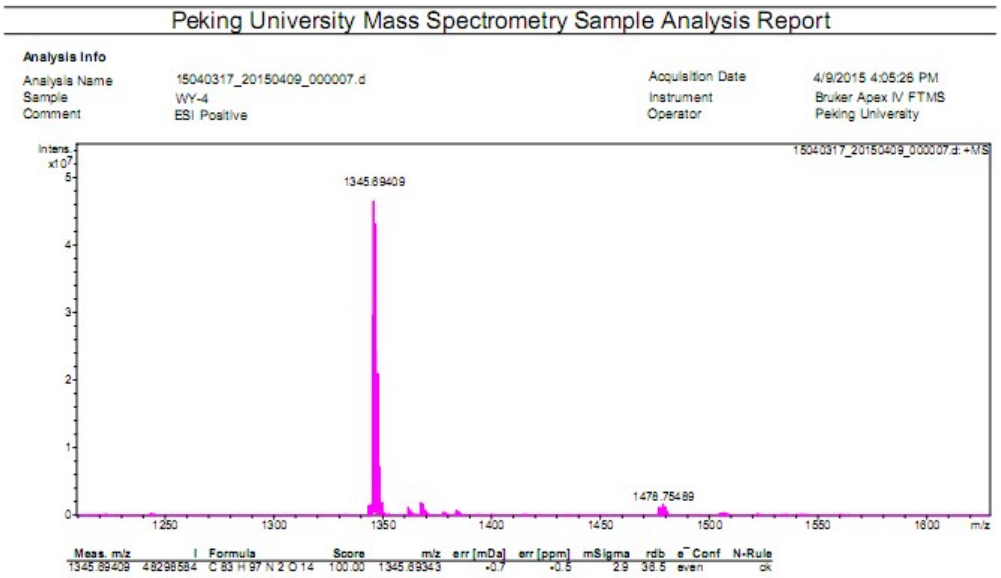


Fig. S1. HR-ESI-MS spectrum of *Z*-**1**.

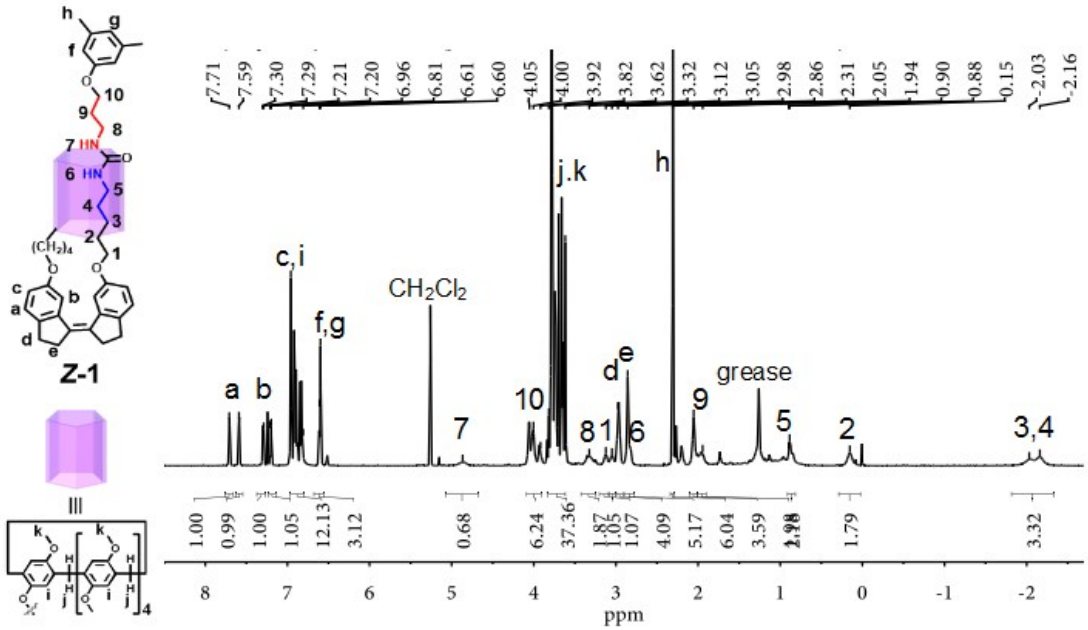


Fig. S2. ^{1}H NMR spectrum of *Z*-**1** ($CDCl_3$, 400 MHz, 298 K).

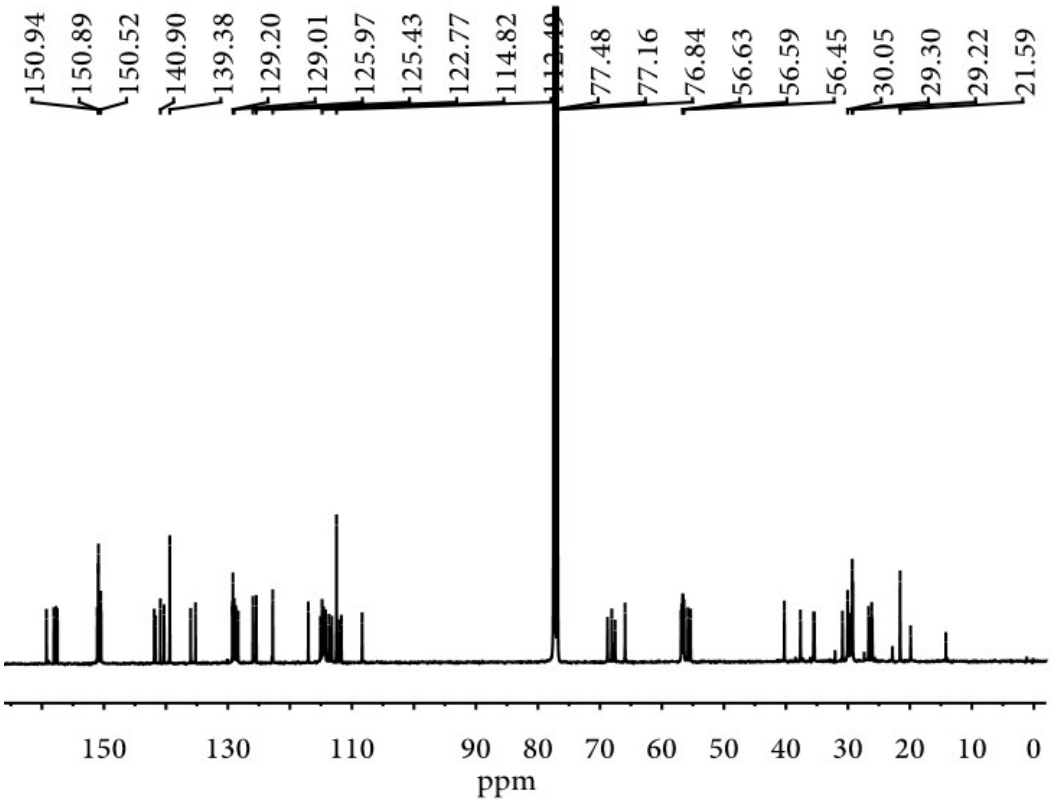


Fig. S3. ^{13}C NMR spectrum of *Z*-**1** ($CDCl_3$, 100 MHz, 298 K).

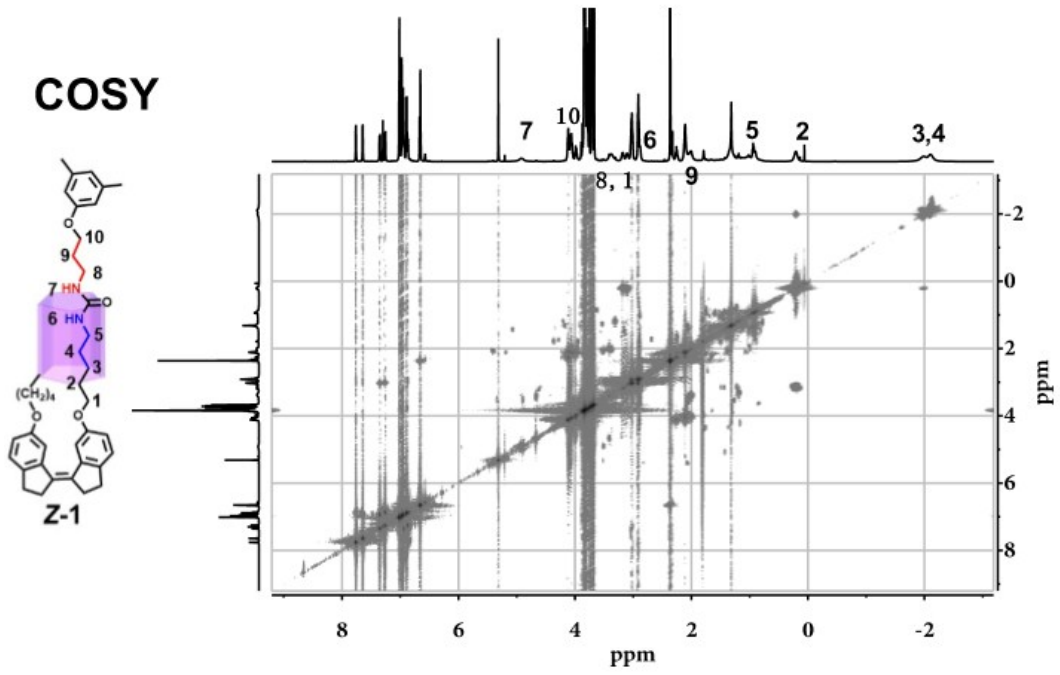


Fig. S4. COSY spectrum of *Z*-**1** ($CDCl_3$, 600 MHz, 298 K).

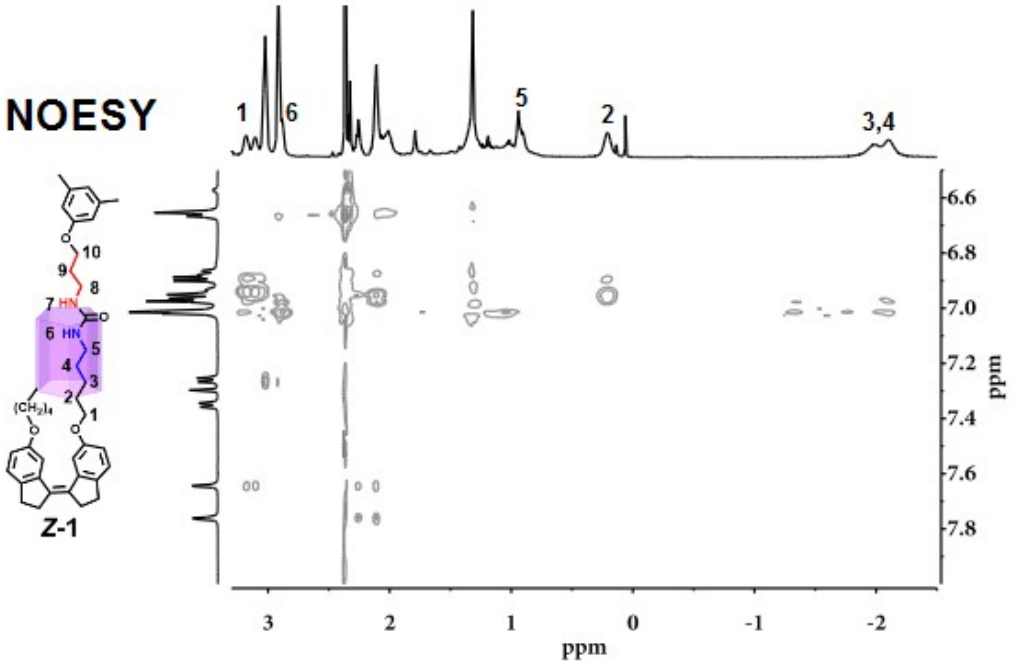


Fig. S5. NOESY spectrum of *Z*-**1** ($CDCl_3$, 600 MHz, 298 K).

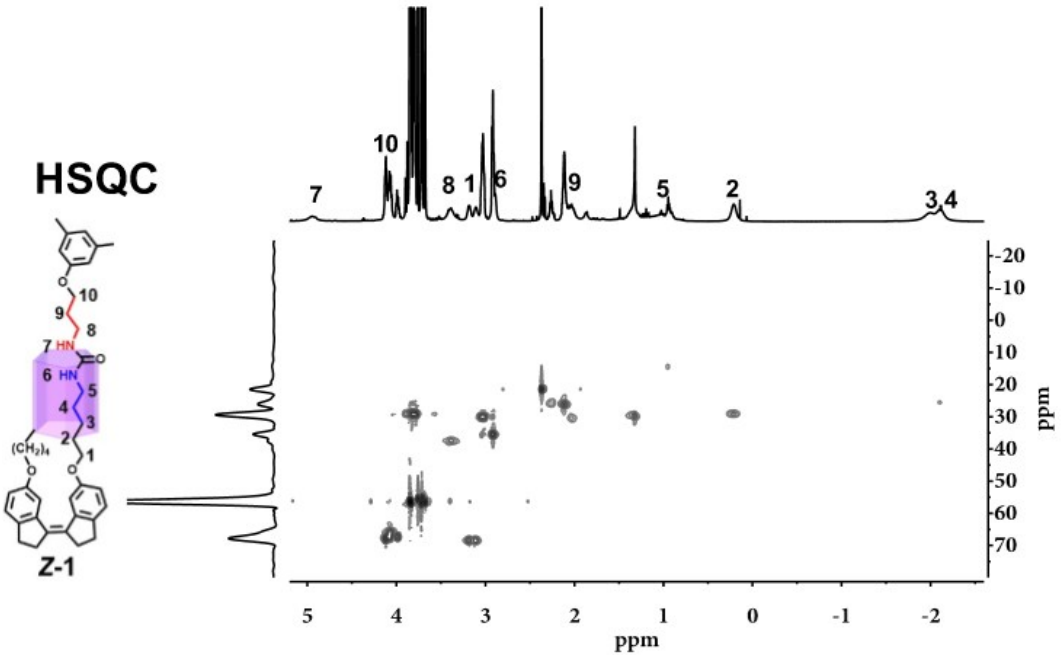


Fig. S6. HSQC spectrum of *Z*-**1** ($CDCl_3$, 600 MHz, 298 K).

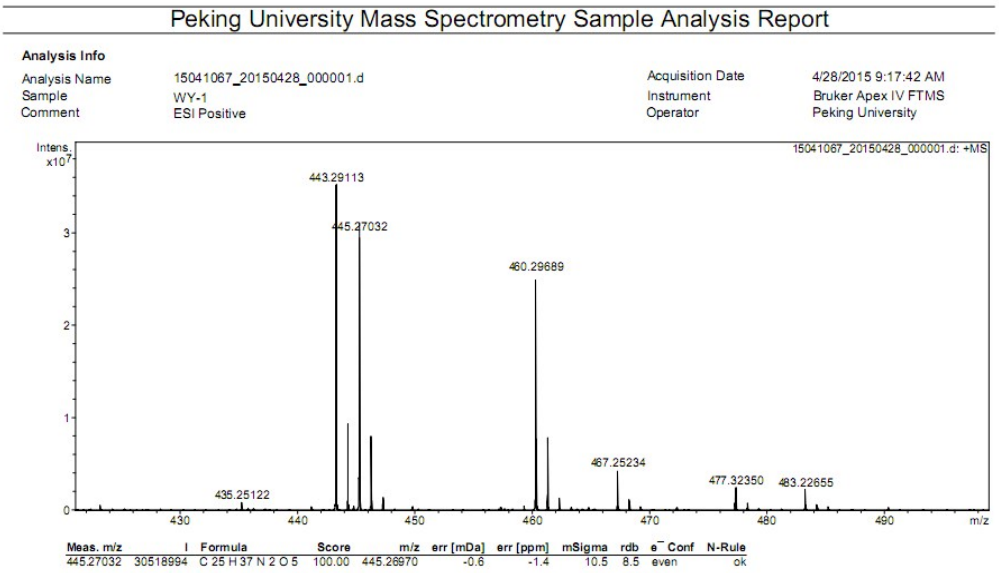


Fig. S7. HR-ESI-MS spectrum of **2**.

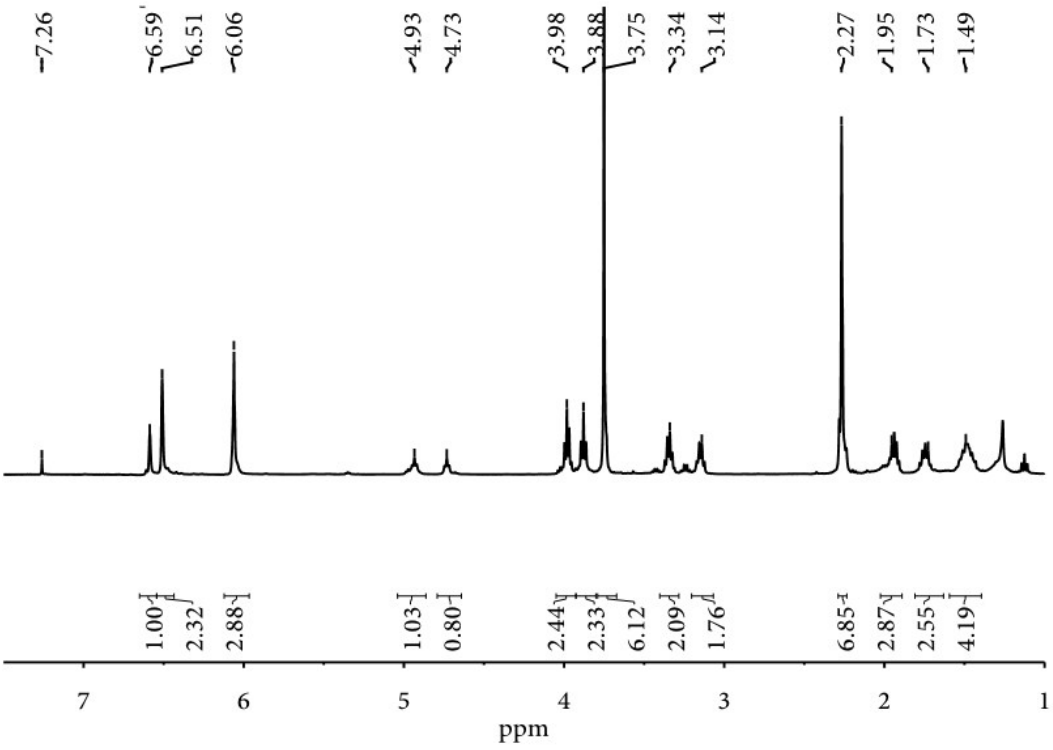


Fig. S8. ^{1}H NMR spectrum of **2** ($CDCl_3$, 400 MHz, 298 K).

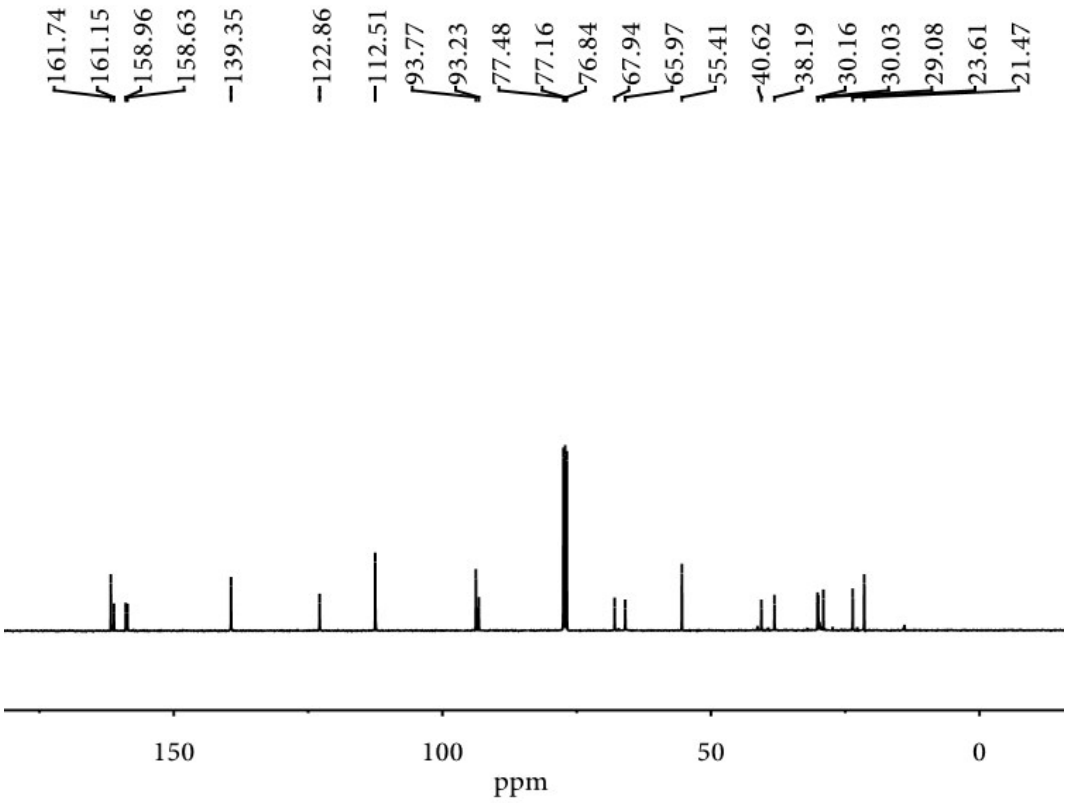


Fig. S9. ^{13}C NMR spectrum of **2** ($CDCl_3$, 100 MHz, 298 K).

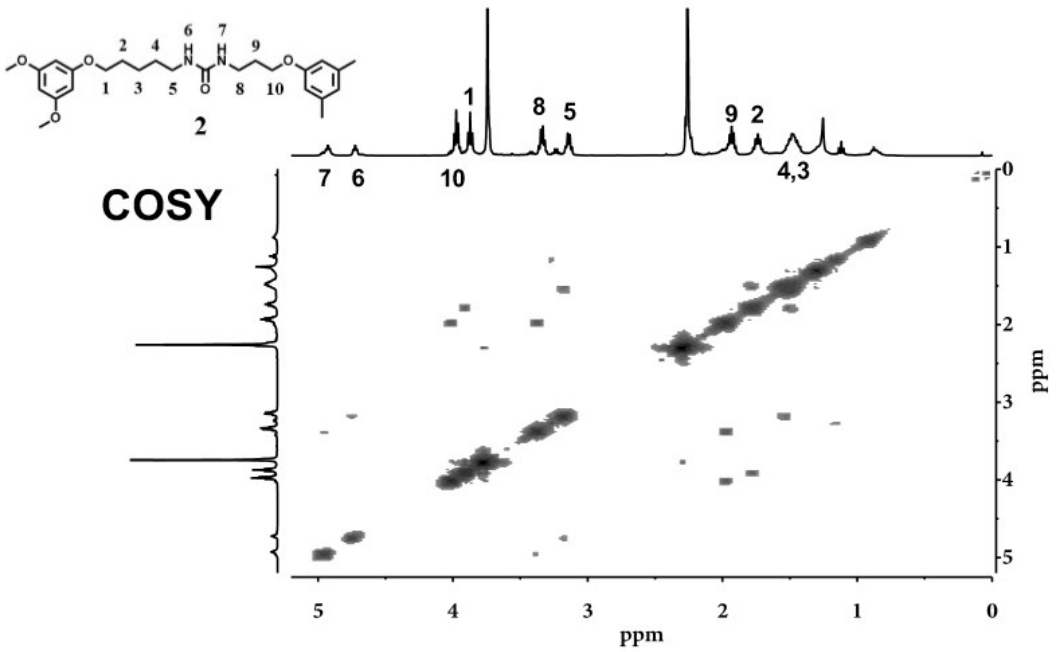


Fig. S10. COSY spectrum of **2** ($CDCl_3$, 600 MHz, 298 K).

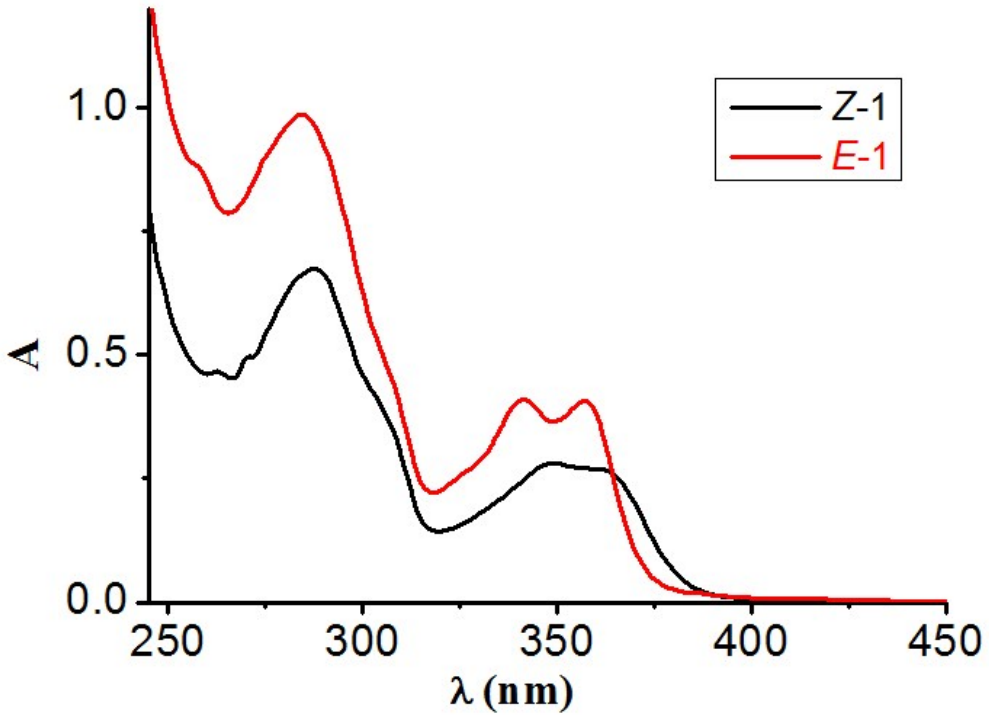


Fig. S11. UV-visible spectra of *Z*-**1** and *E*-**1** in CH_2Cl_2 (c = 20.0 μM).

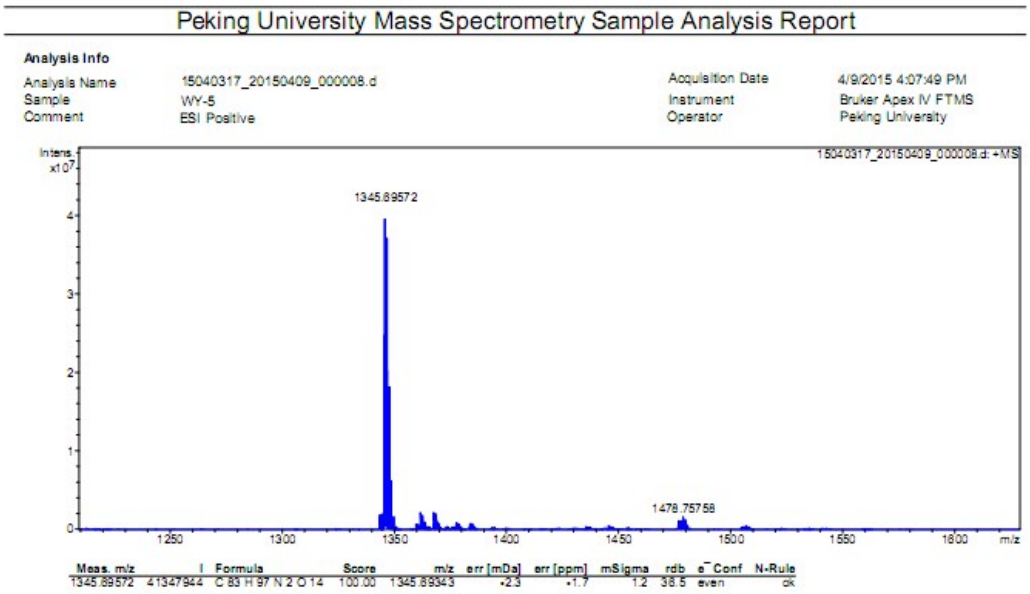


Fig. S12. HR-ESI-MS spectrum of *E*-**1**.

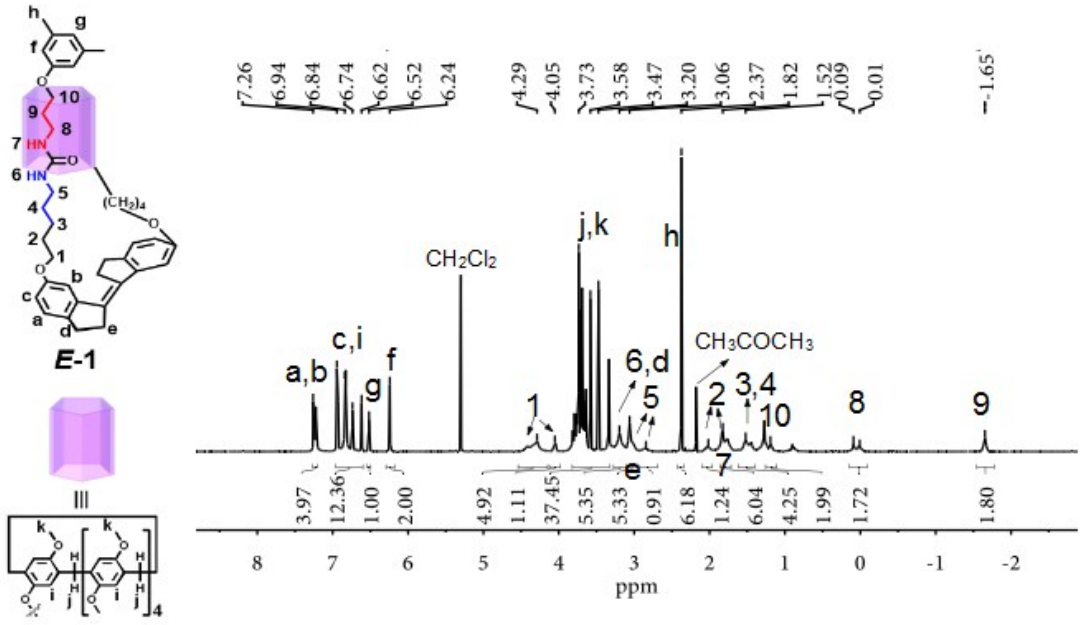


Fig. S13. ^{1}H NMR spectrum of *E*-**1** ($CDCl_3$, 400 MHz, 298 K).

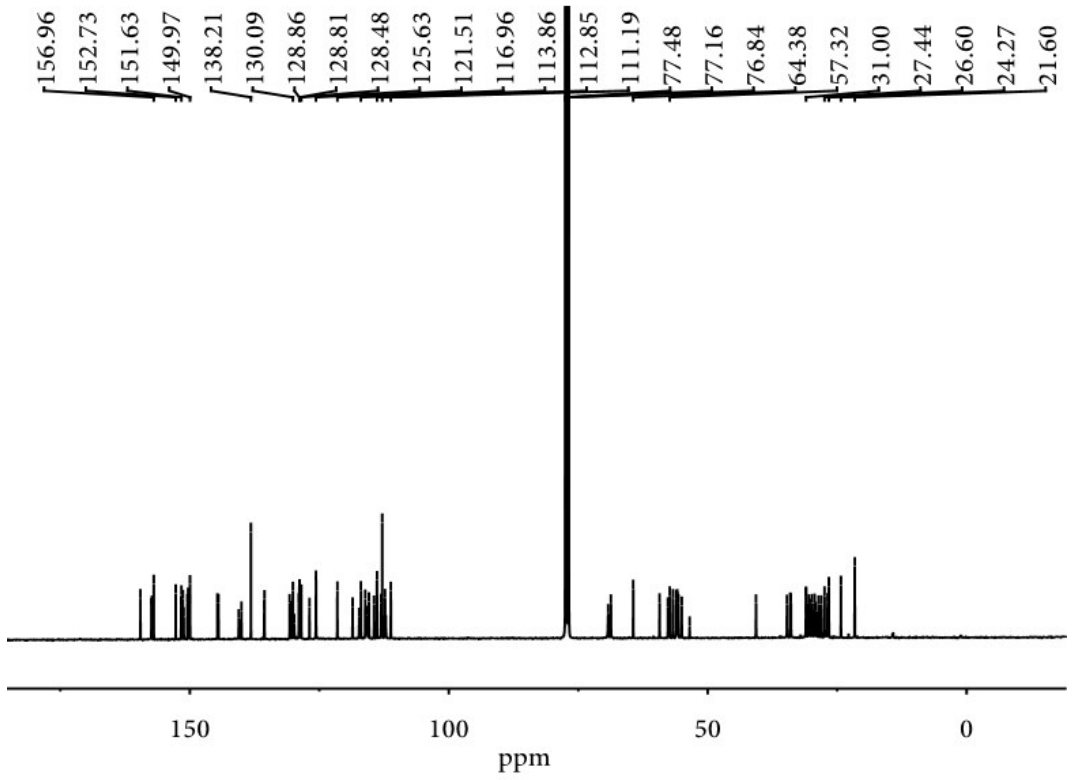


Fig. S14. ^{13}C NMR spectrum of *E*-**1** ($CDCl_3$, 100 MHz, 298 K).

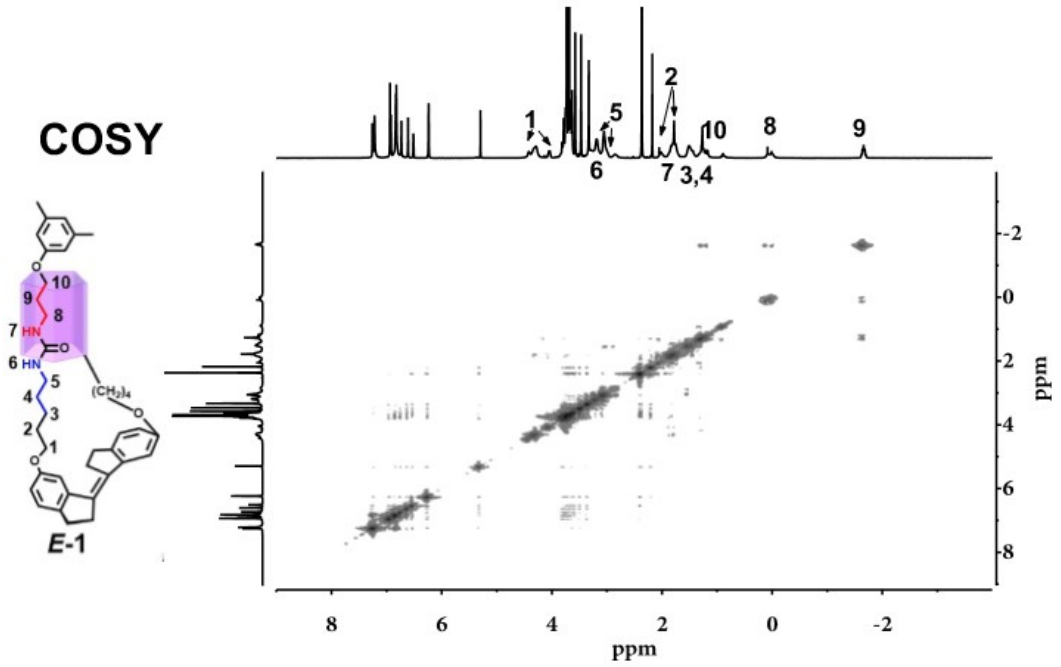


Fig. S15. COSY spectrum of *E*-**1** ($CDCl_3$, 600 MHz, 298 K).

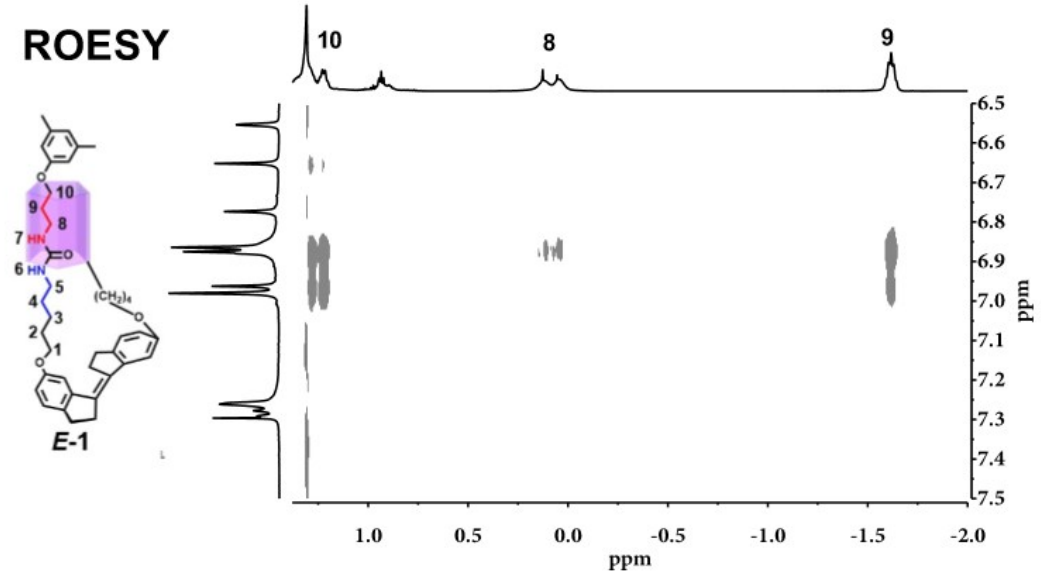


Fig. S16. ROESY spectrum of *E*-**1** ($CDCl_3$, 600 MHz, 298 K).

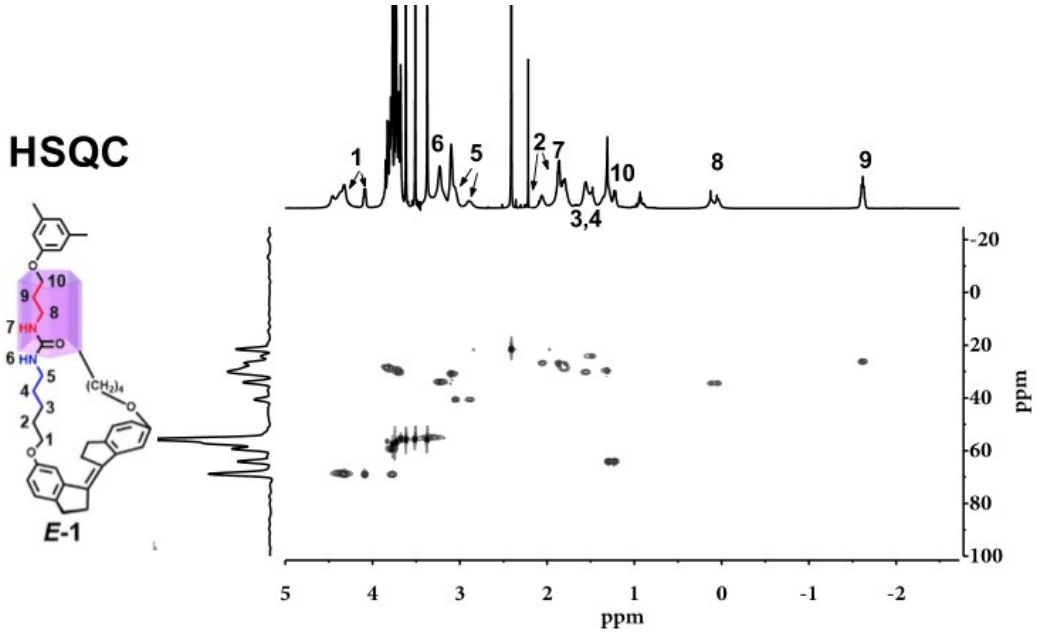


Fig. S17. HSQC spectrum of *E*-**1** ($CDCl_3$, 600 MHz, 298 K).

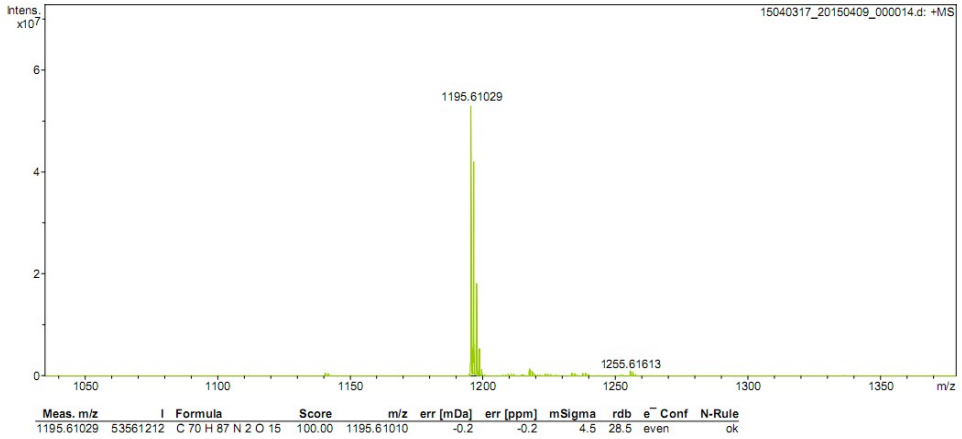


Fig. S18. HR-ESI-MS spectrum of **3.**

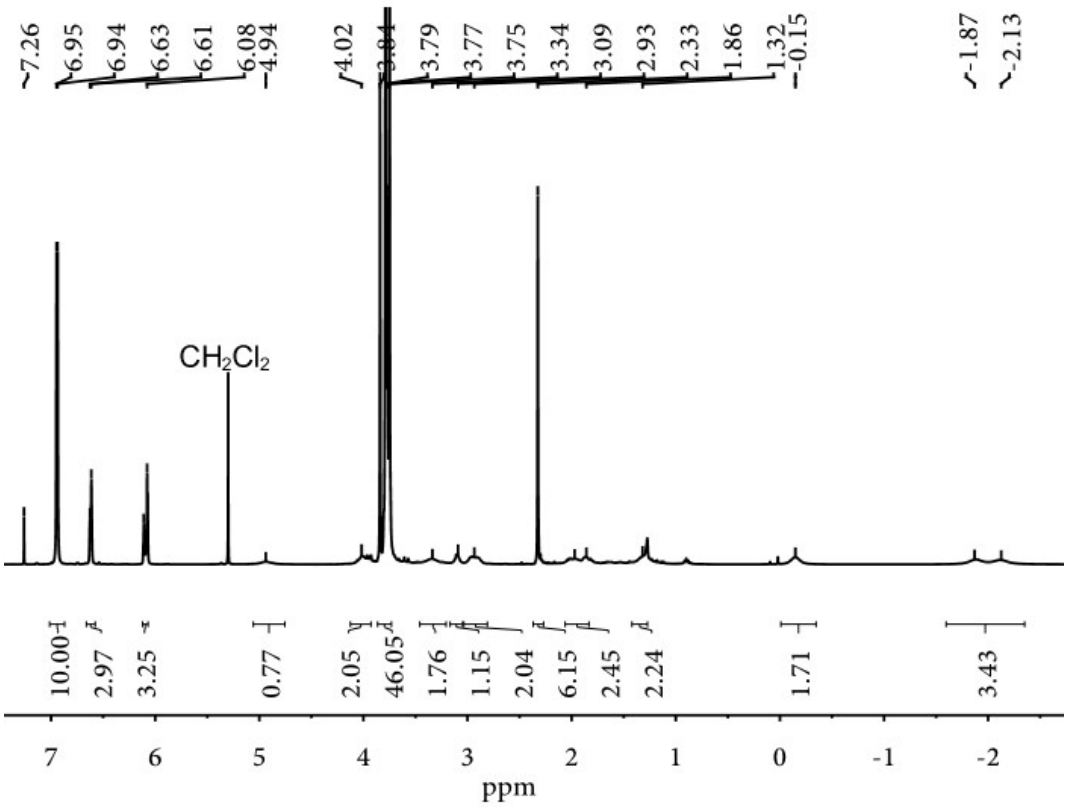


Fig. S19. ^{1}H NMR spectrum of **3** ($CDCl_3$, 400 MHz, 298 K).

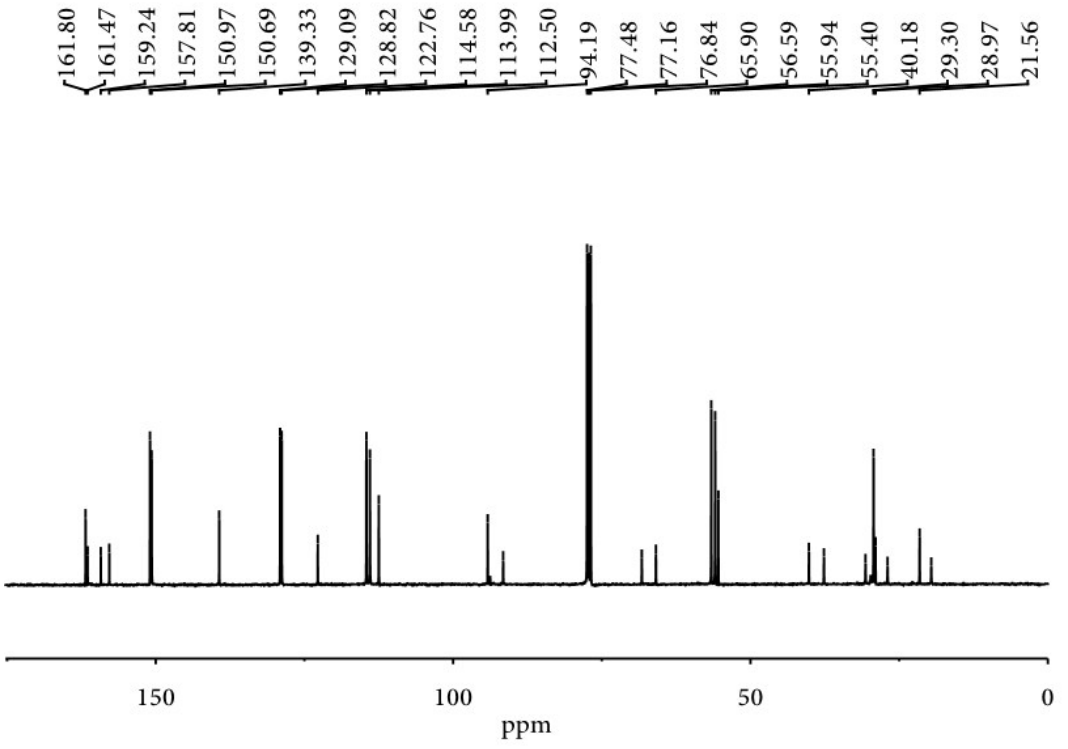


Fig. S20. ^{13}C NMR spectrum of **3** ($CDCl_3$, 100 MHz, 298 K).

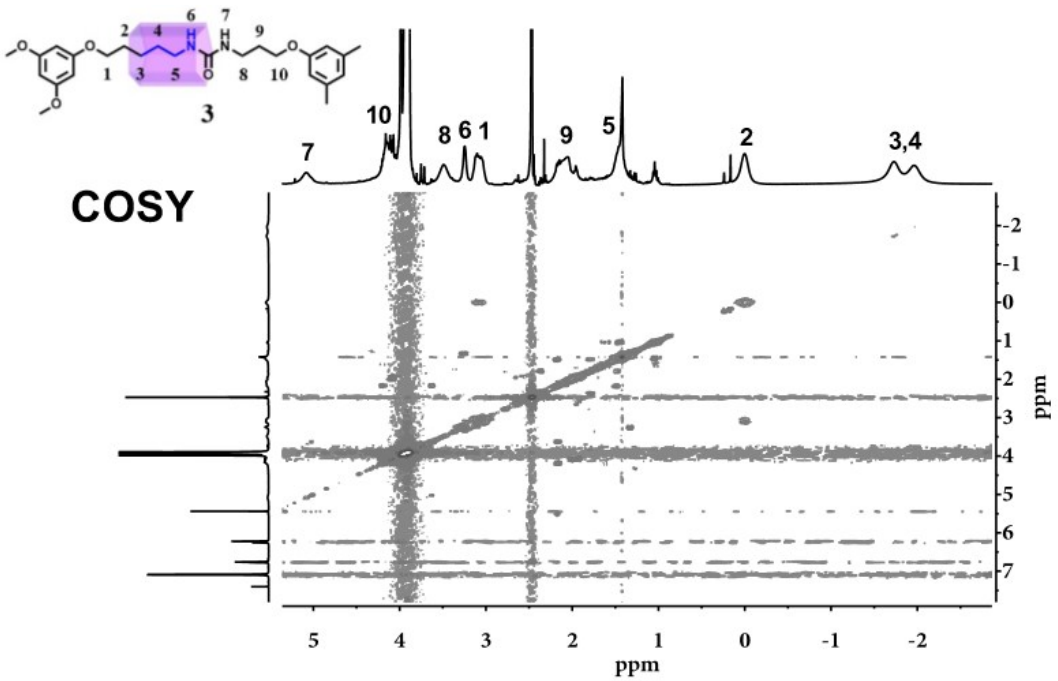


Fig. S21. COSY spectrum of **3** ($CDCl_3$, 600 MHz, 298 K).

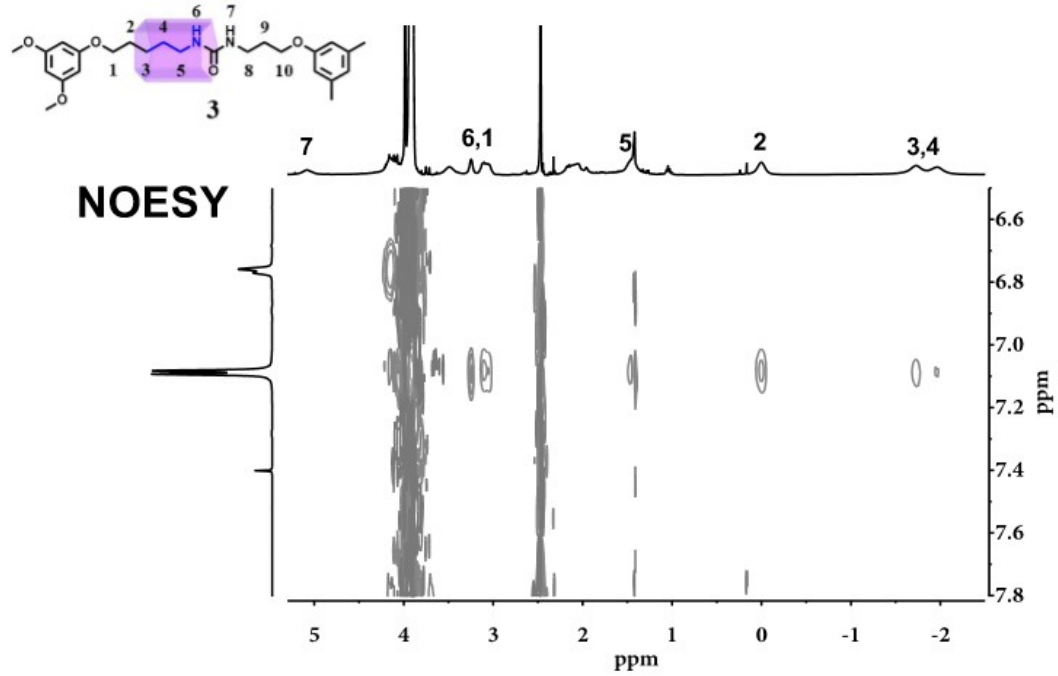


Fig. S22. NOESY spectrum of **3** ($CDCl_3$, 600 MHz, 298 K).

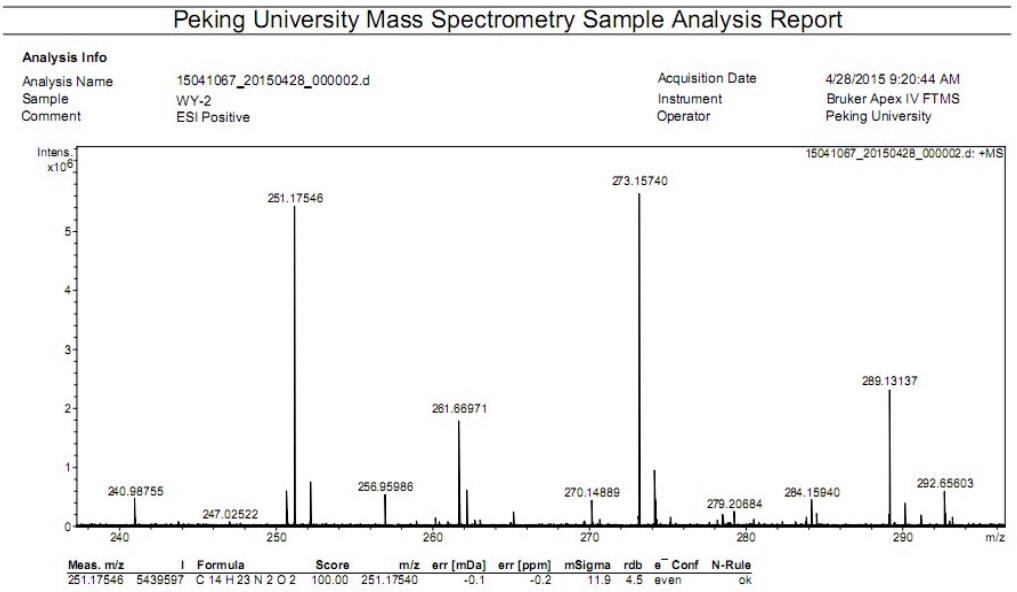


Fig. S23. HR-ESI-MS spectrum of **4**.

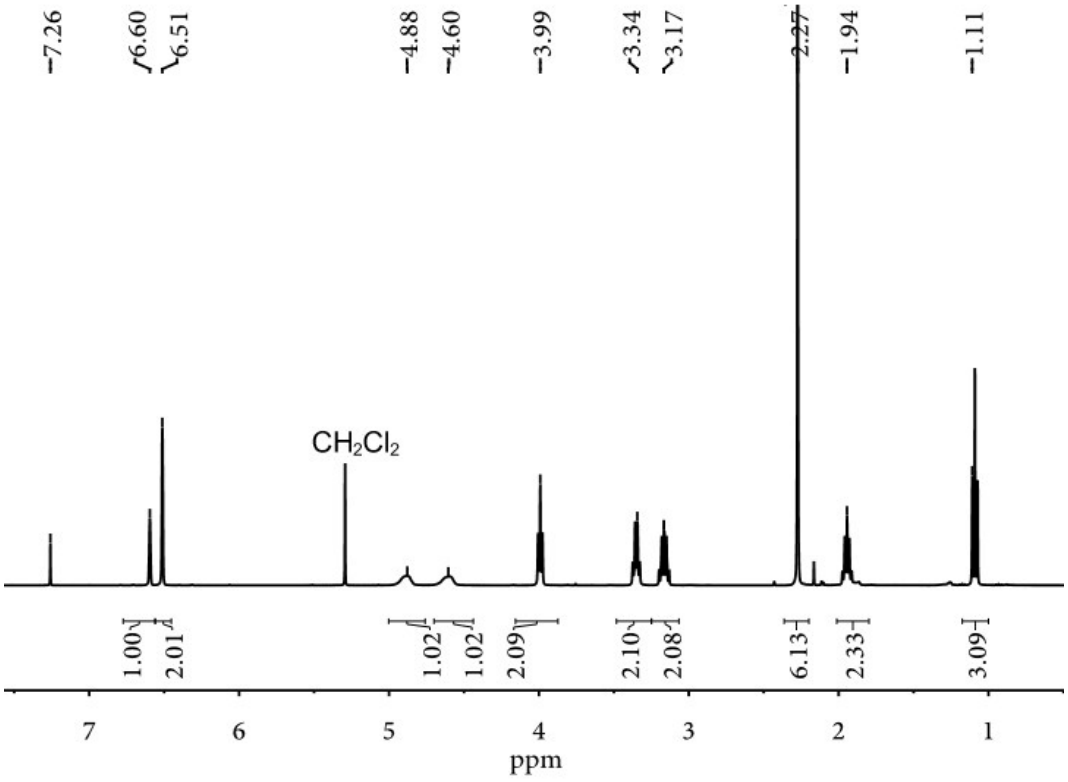


Fig. S24. ^{1}H NMR spectrum of **4** ($CDCl_3$, 400 MHz, 298 K).

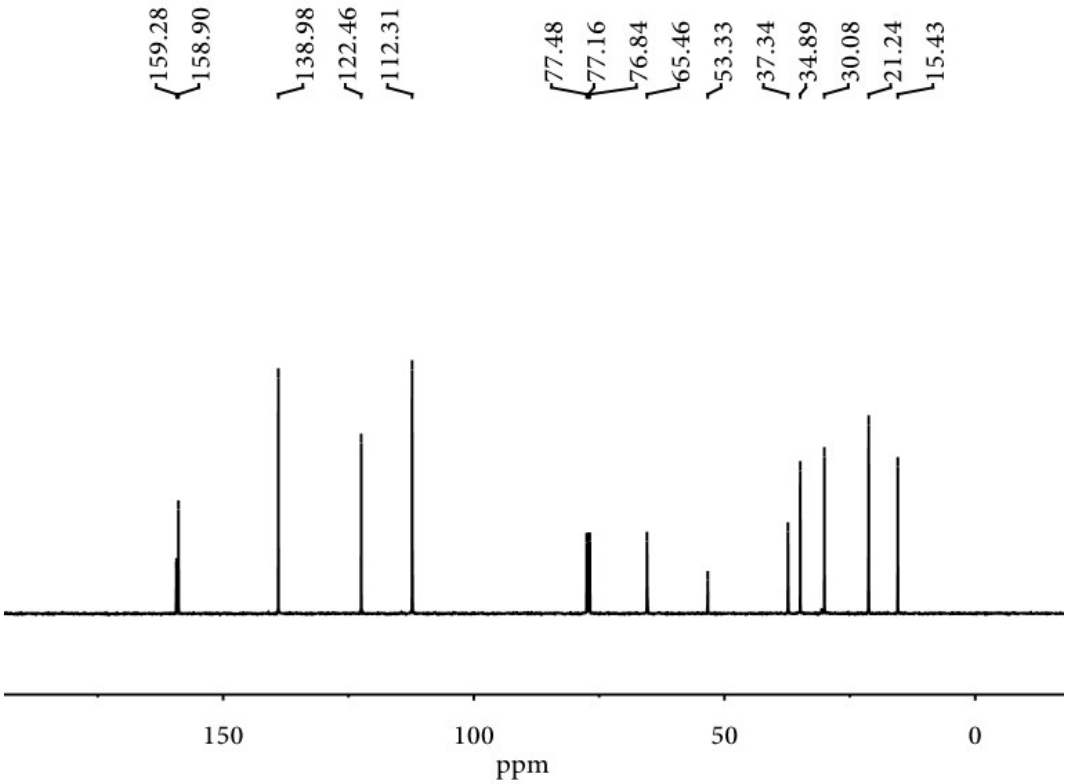


Fig. S25. ^{13}C NMR spectrum of **4** ($CDCl_3$, 100 MHz, 298 K).

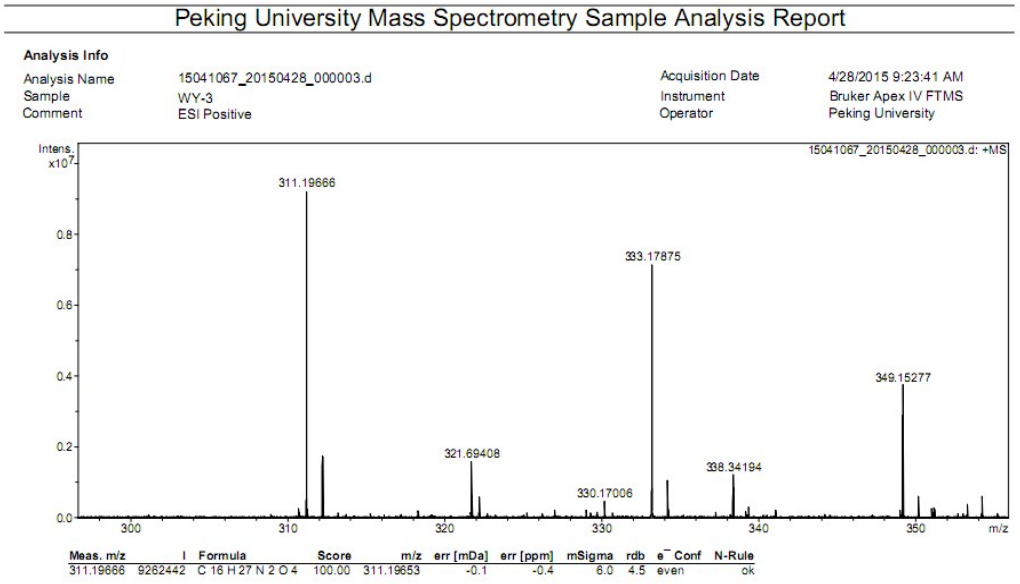


Fig. S26. HR-ESI-MS spectrum of **5**.

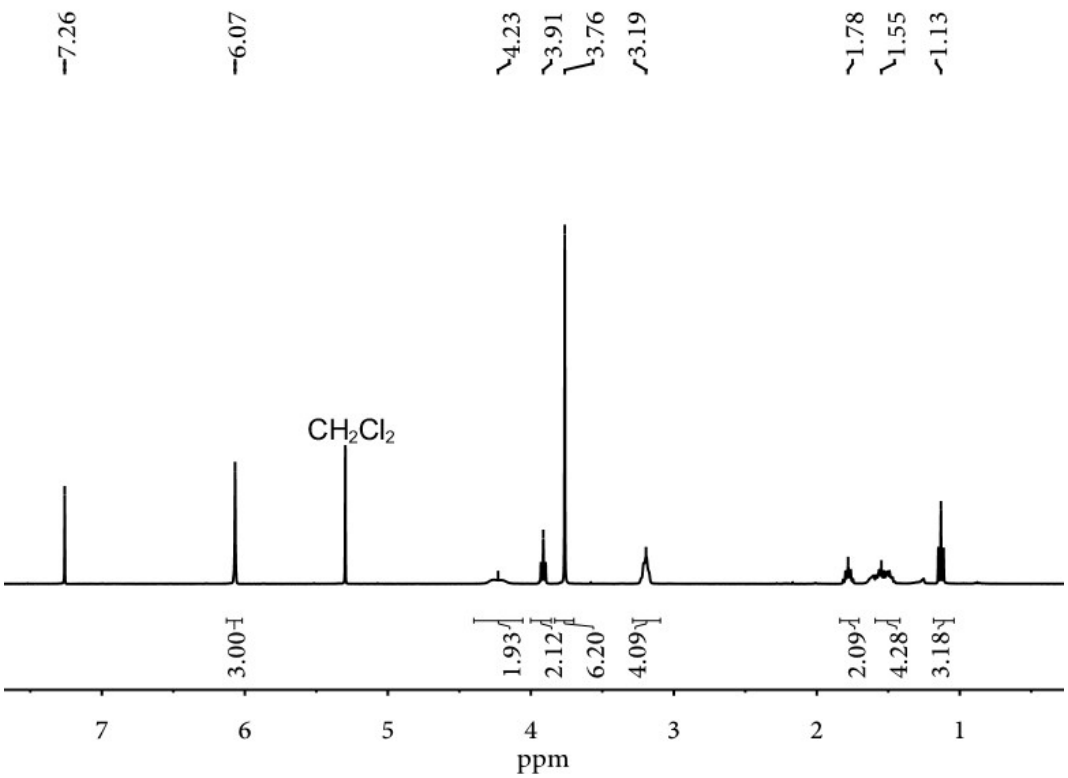


Fig. S27. ^{1}H NMR spectrum of **5** ($CDCl_3$, 400 MHz, 298 K).

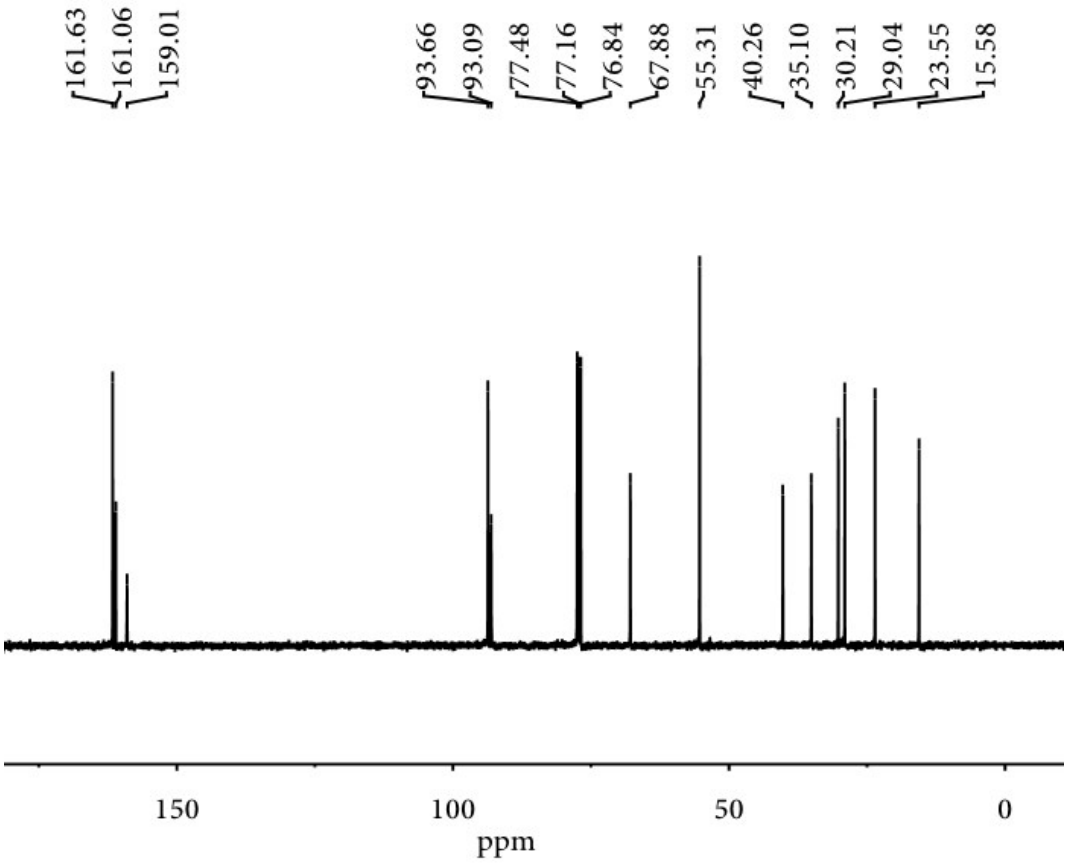
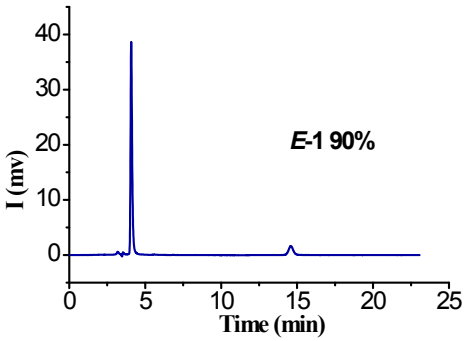
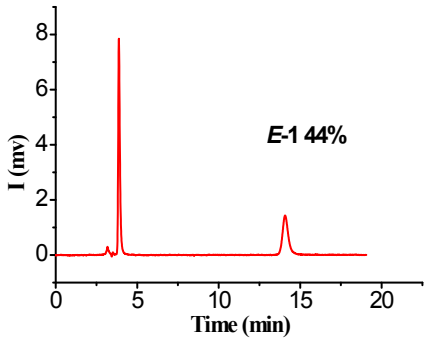
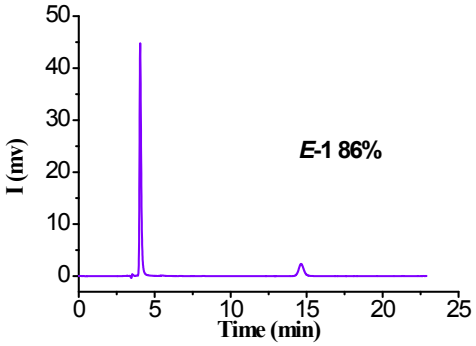


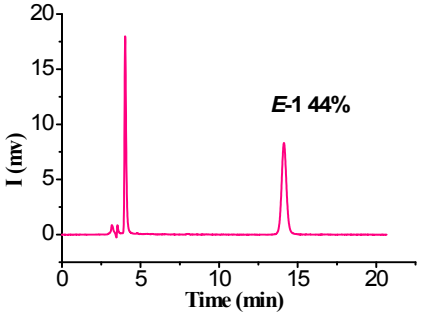
Fig. S28. ^{13}C NMR spectrum of **5** ($CDCl_3$, 100 MHz, 298 K).

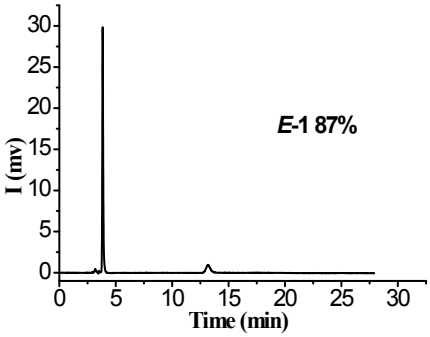
4. Cycling between Z-1 and E-1 upon irradiation.

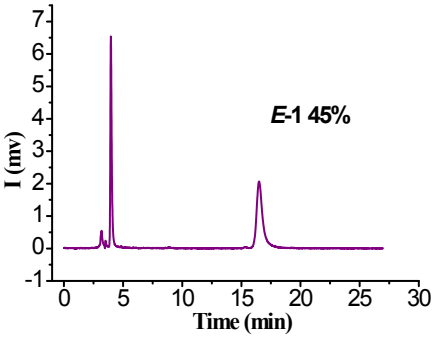


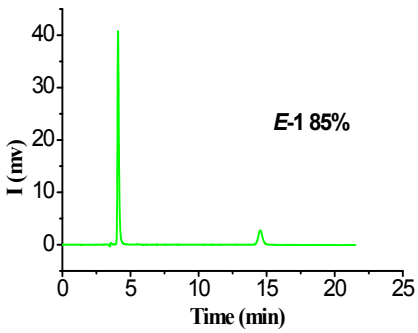


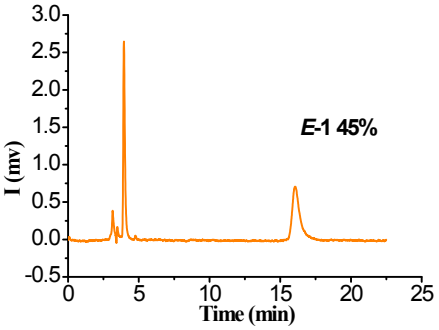












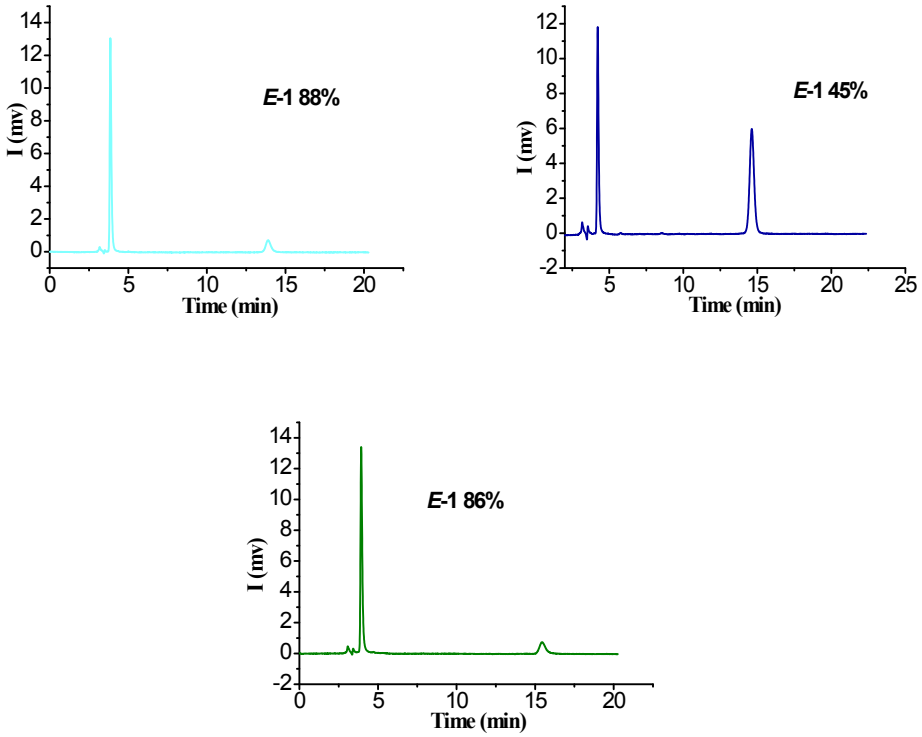


Fig. S29. HPLC of the photostationary mixtures obtained by repeated irradiation of *E*-**1** at 387 nm (left chromatograms) and 360 nm (right chromatograms) observed at 350 nm; eluent: 20% EtOAc + 80% CH_2Cl_2, flowrate 1ml/min, ambient temperature[1].

5. Changes in the chemical shifts of protons H1-H10 of *Z*-1, *E*-1 and 3 compared to 2 in $CDCl_3$.

Table S1. Chemical shift changes of protons H1-H10 on *Z*-**1** compared with **2** in chloroform-*d*.

Protons of **2**	1	2	3	4	5	6	7	8	9	10
δ	3.879	1.744	1.485	1.485	3.140	4.732	4.934	3.340	1.954	3.982
Protons of *Z*-**1**	1	2	3	4	5	6	7	8	9	10
δ	3.141	0.173	-2.012	-2.142	0.885	2.846	4.882	3.344	1.963	3.981
Δδ	0.738	1.571	3.497	3.627	2.255	1.886	0.052	-0.004	-0.009	0.001

Table S2. Chemical shift changes of protons H1-H10 on *E*-**1** compared with **2** in chloroform-*d*.

Protons of **2**	1	2	3	4	5	6	7	8	9	10
δ	3.879	1.744	1.485	1.485	3.140	4.732	4.934	3.340	1.954	3.982
Protons of *E*-**1**	1	2	3	4	5	6	7	8	9	10
δ	4.037	1.752	1.482	1.482	2.955	3.188	1.762	0.040	-1.656	1.192
Δδ	-0.158	-0.008	0.003	0.003	1.185	1.544	3.172	3.300	3.610	2.790

Table S3. Chemical shift changes of protons H1-H10 on **3** compared with **2** in chloroform-*d*.

Protons of **2**	1	2	3	4	5	6	7	8	9	10
δ	3.879	1.744	1.485	1.485	3.140	4.732	4.934	3.340	1.954	3.982
Protons of **3**	1	2	3	4	5	6	7	8	9	10
δ	2.935	0.149	-1.87	-2.125	1.859	1.319	4.938	3.337	1.971	4.071
Δδ	0.944	1.595	3.355	3.610	1.821	1.640	-0.004	0.003	0.017	-0.035

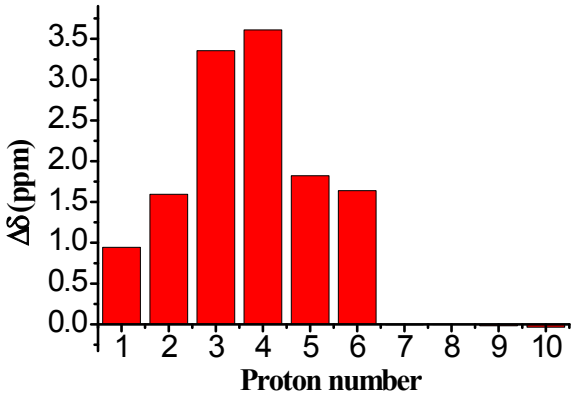


Fig. S30. Chemical shift changes of protons H1-H10 of **3** compared to **2** in chloroform-*d*.

6. Determination of the association constants.

To determine the association constant between pillar[5]arene (P5A) and **4** or **5** (guest), proton NMR titrations were done with solutions which had a constant concentration of P5A (1.6 mM) and varying concentrations of **4** (or **5**). The binding constants were obtained by non-linear least-squares fitting of the difference in the chemical shift proton H_c of P5A, $\Delta\delta$, in the absence of **4** or **5** and in its presence at concentration [G][2]:

$$\Delta\delta = (\Delta\delta_\infty /[P5A]_0)\ (0.5[G]+0.5([P5A]_0 + 1/K_a)-(0.5\ ([G]^2+(2[G](1/K_a-[P5A]_0)) + (1/K_a + [P5A]_0)^2)^{0.5}))$$

where $\Delta\delta_\infty$ is the chemical shift change of H_c when P5A host is completely complexed, $[P5A]_0$ is the fixed initial concentration of P5A.

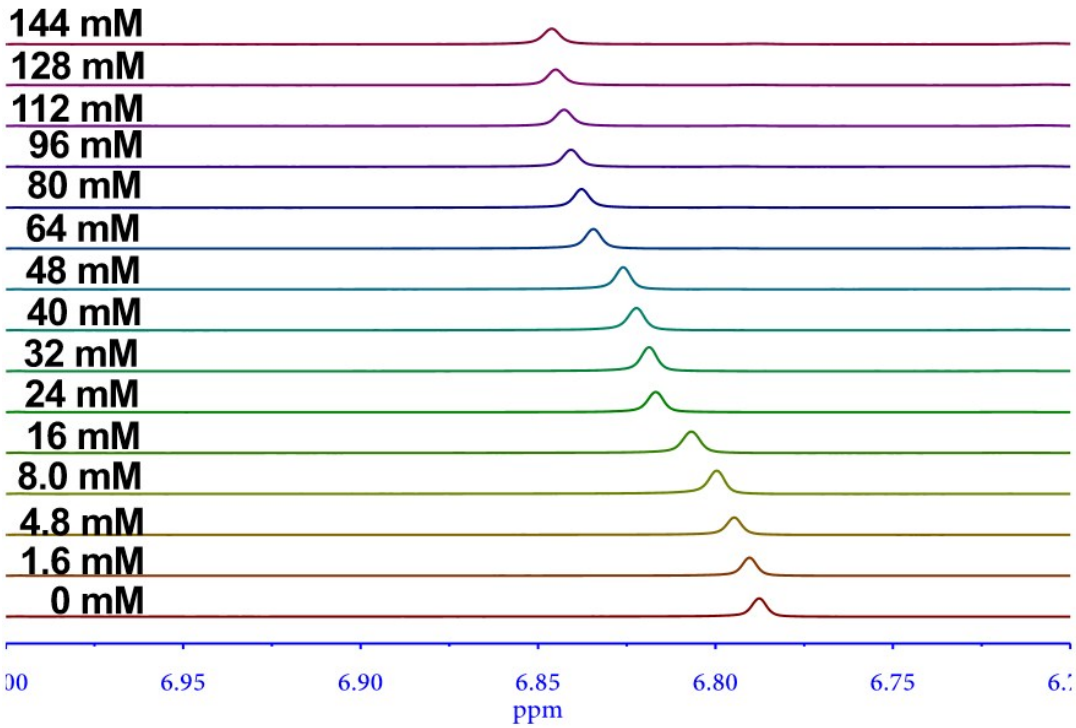


Fig. S31. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25°C) of Pillar[5]arene at a concentration of 1.6 mM upon addition of **4** : (1) 0 mM (2) 1.6 mM (3) 4.8 mM (4) 8 mM (5) 16 mM (6) 24 mM (7) 32 mM (8) 40 mM (9) 48 mM (10) 64 mM (11) 80 mM (12) 96 mM (13) 112 mM (14) 128 mM.

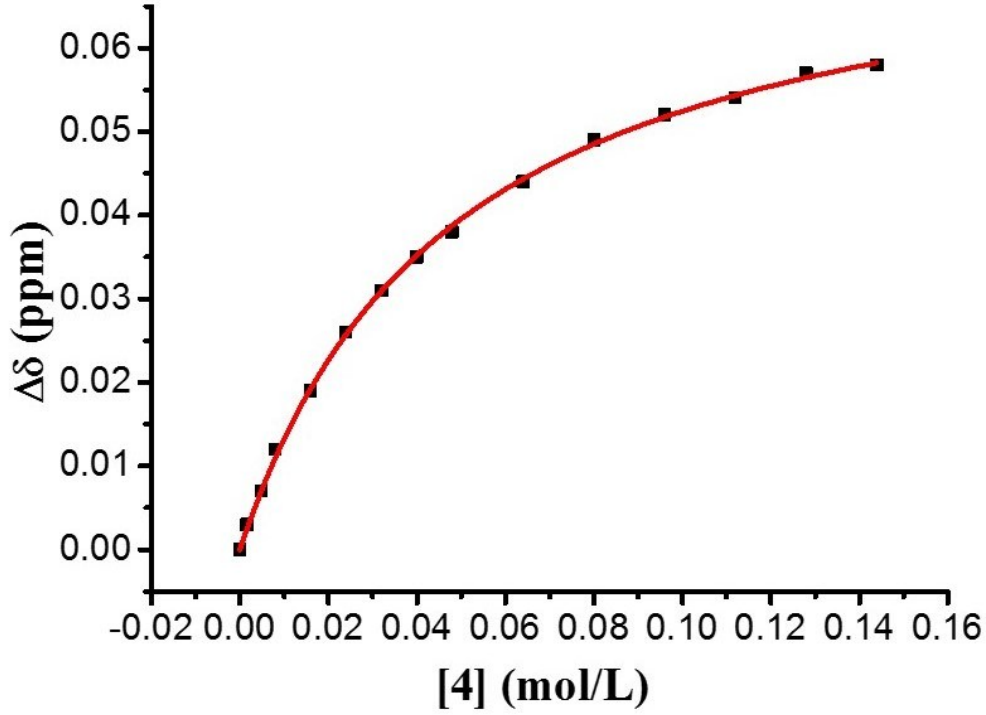


Fig. S32. The non-linear curve-fitting (NMR titrations) for the complexation of pillar[5]arene host (1.6 mM) with **4** in $CDCl_3$ at 298 K. The concentration of 4 was 0, 1.6, 4.8, 8, 16, 24, 32, 40, 48, 64, 80, 96, 112, 128 and 144 mM.

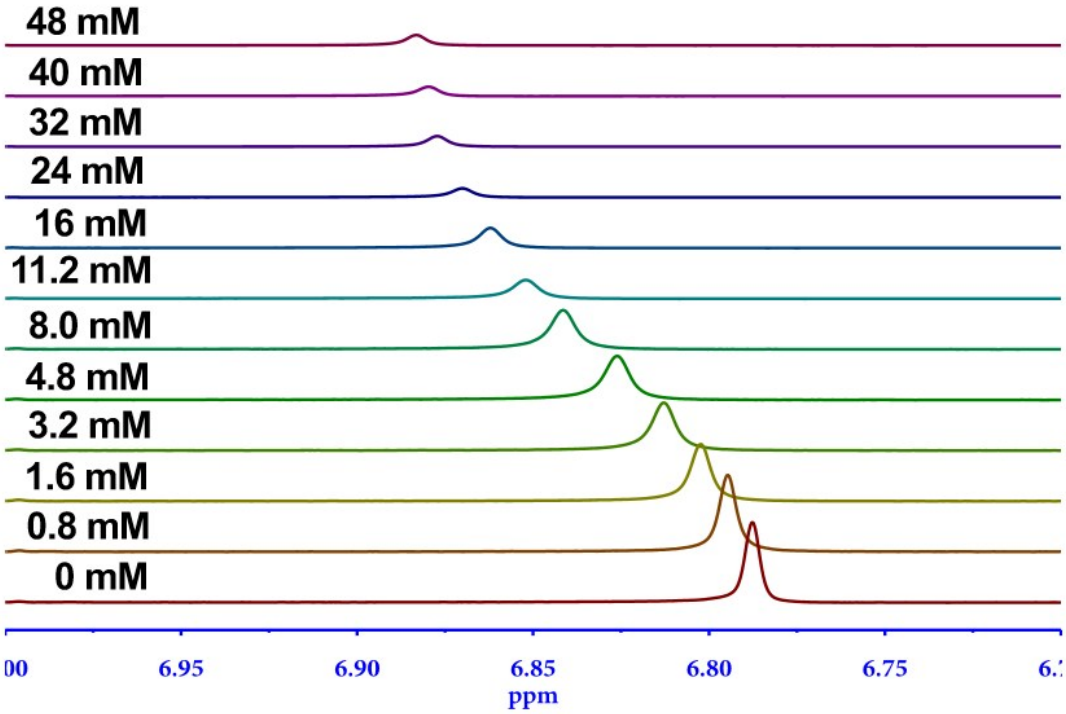


Fig. S33. Partial ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of pillar[5]arene at a concentration of 1.6 mM upon addition of **5** : (1) 0 mM (2) 0.8 mM (3) 1.6 mM (4) 3.2 mM (5) 4.8 mM (6) 8mM (7) 11.2 mM (8) 16 mM (9) 24 mM (10) 32 mM (11) 40 mM (12) 48 mM.

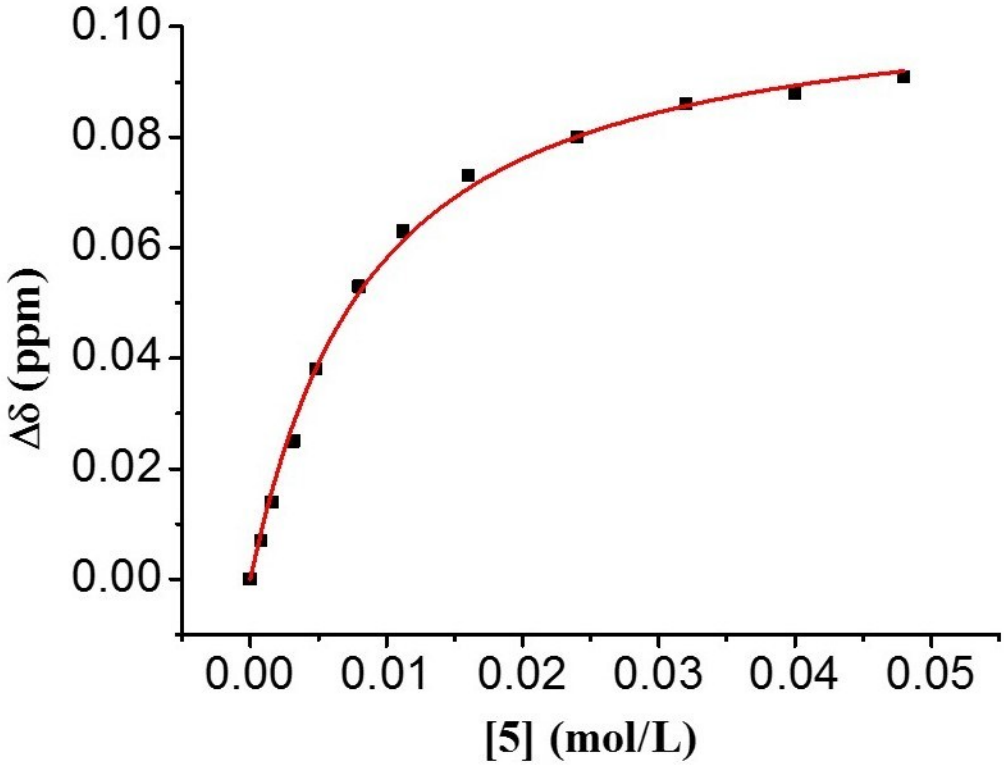
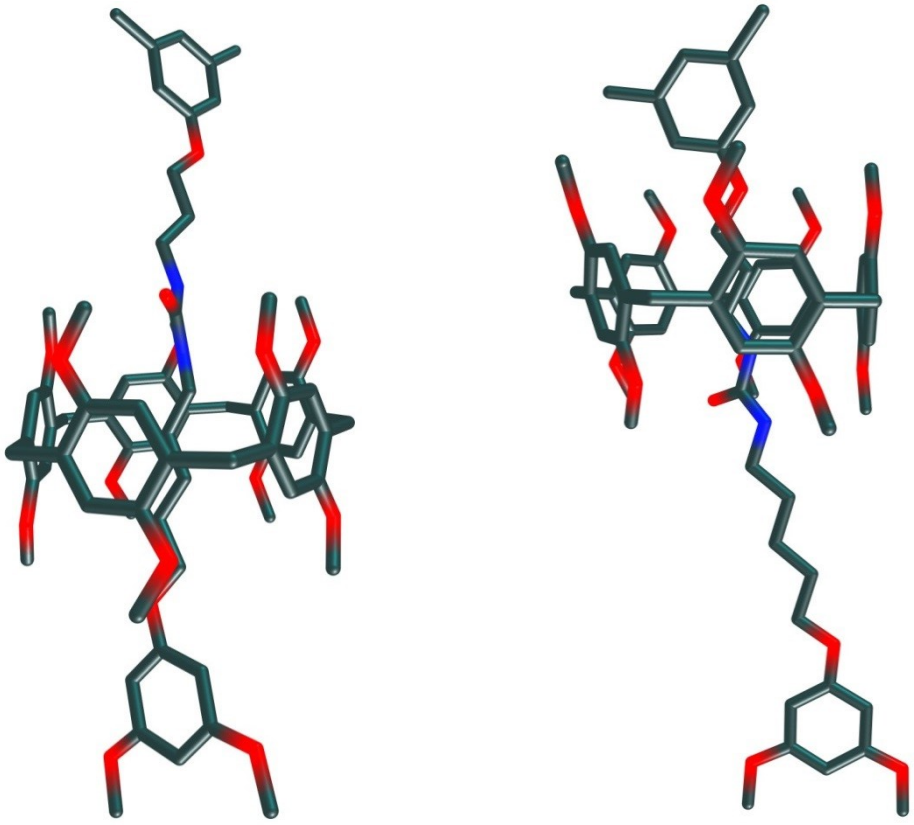


Fig. S34. The non-linear curve-fitting (NMR titrations) for the complexation of pillar[5]arene host (1.6 mM) with **5** in $CDCl_3$ at 298 K. The concentration of **5** was 0, 0.8, 1.6, 3.2, 4.8, 8, 11.2, 16, 24, 32, 40, 48 mM.

7. Quantum-chemical calculations

All optimizations were performed in Gaussian 09.E01 using the Berny algorithm. The conformational ensembles of **1** and **3** were built by systematically varying the torsions of all rotable bonds of the axle that were not encapsulated by pillar[5]arene (and of the strap connecting stiff stilbene with pillar[5]arene in **1**). The resulting guess structures were first optimized at the BLYP/6-31G(d) level in vacuum, followed by reoptimization of all unique conformers at the B3LYP/6-31G(d) level. Single-point energies of all conformers were calculated at the CAM-B3LYP/6-31+G(d) level. The molecules were too large to allow frequency calculations. Assuming that all conformers have the same thermodynamic corrections allowed us to calculate the relative electronic energies of conformational ensembles, $E_{\{\}}$, as $E_{\{\}} = -RT\ln\left(\sum_{i=1}^{n} e^{-(E_i - E_o)/RT}\right)$, where E_o is the electronic energy of the global conformational minimum of **1** or **3**, E_i is the i^{th} conformer of *Z*-**1**, *Z*-**1**', *E*-**1**, *E*-**1**' (Fig. 5, main text) or **3** or **3**' (Fig. S35)



3 **3'**

Fig. S35. Calculated minimum-energy molecular geometries of model rotaxane **3** with the "wheel" at the A (**3**) and B (**3')** stations, respectively.

8. References.

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