Supramolecular crowns: a new class of cyclic hydrogen-bonded cavitands

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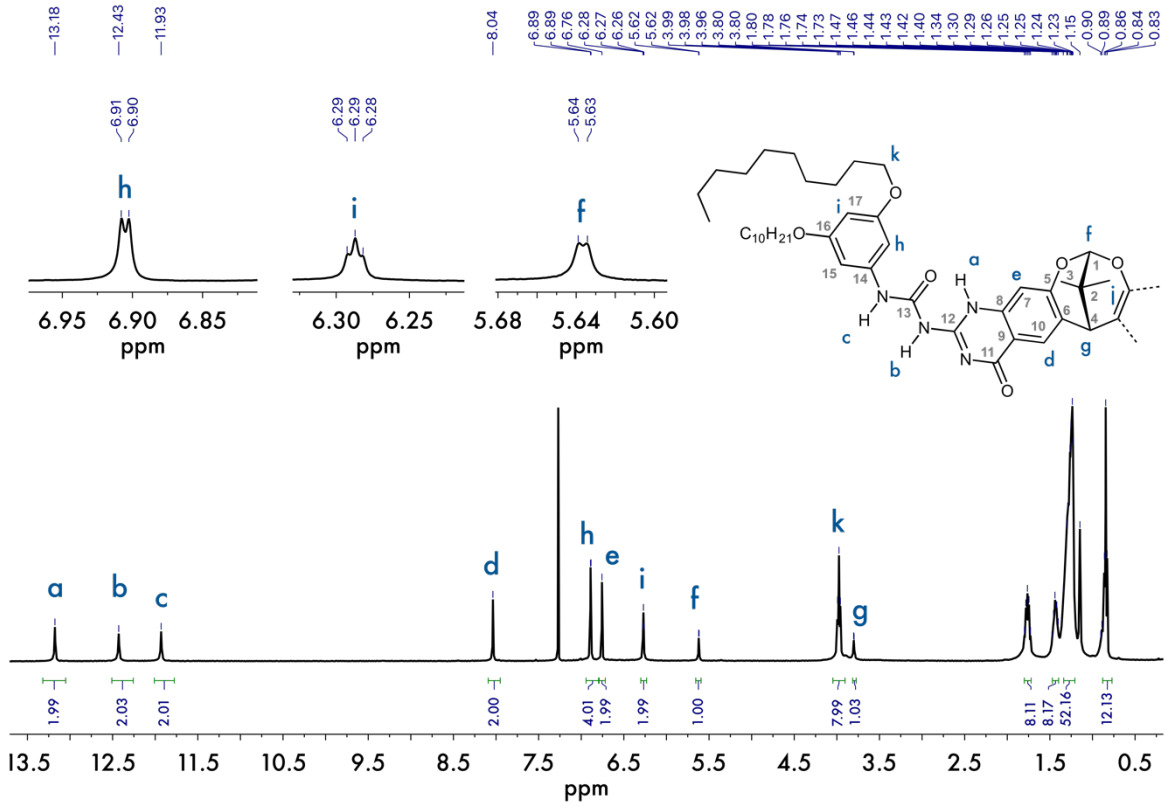

Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

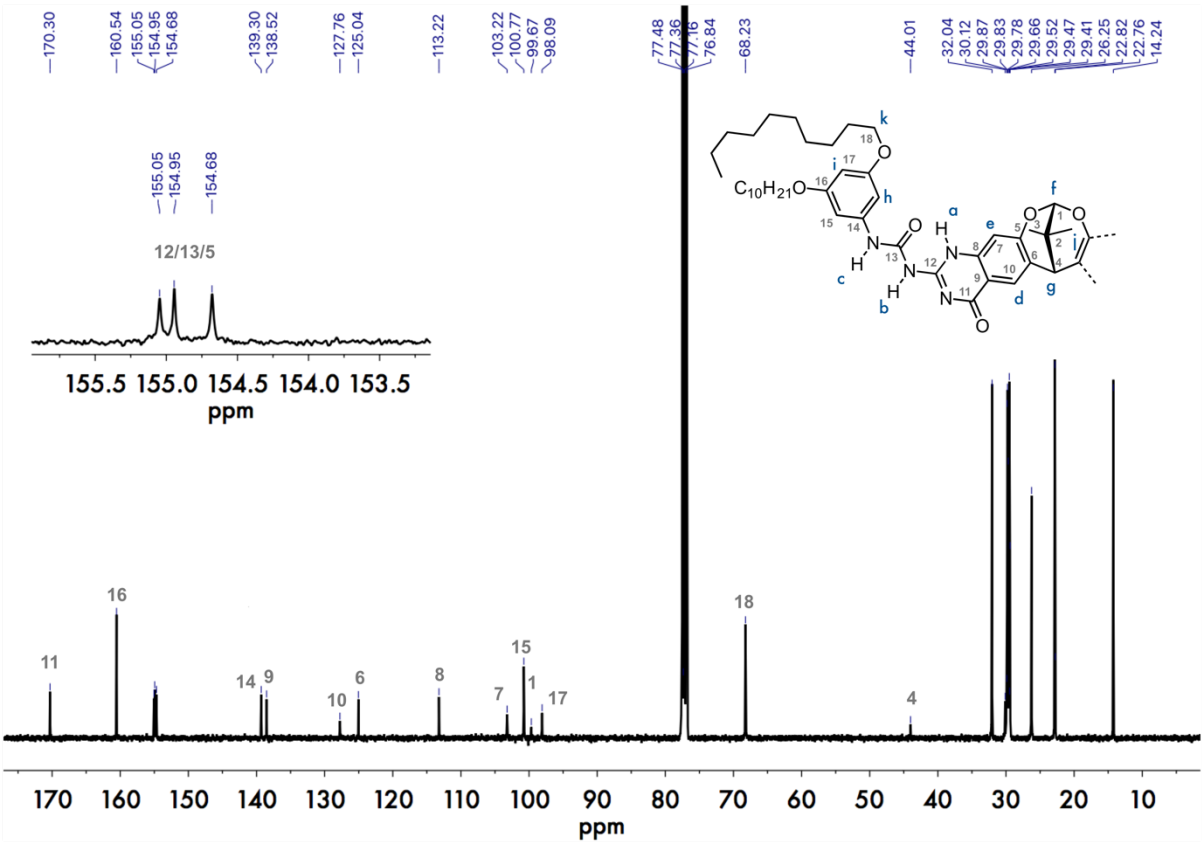

Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

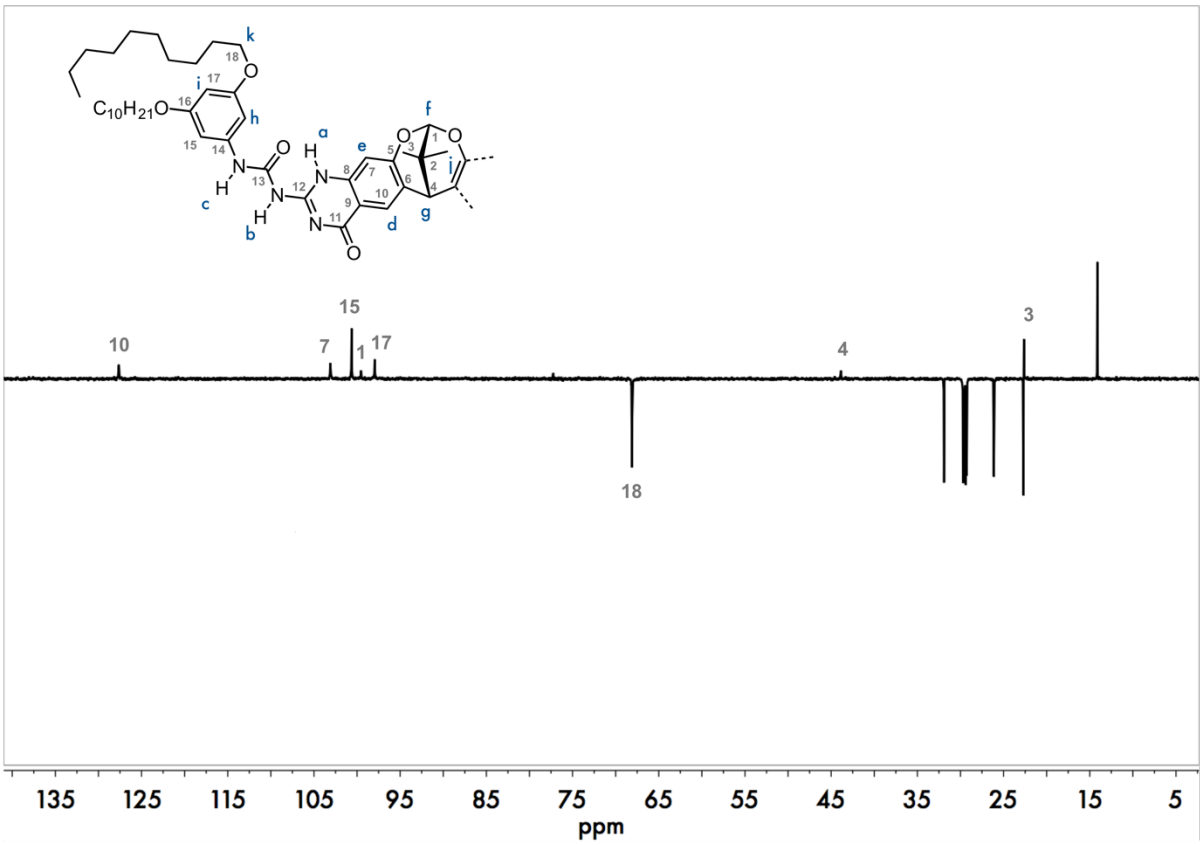

Figure S3. DEPT-135 spectrum of **1** in $CDCl_3$.

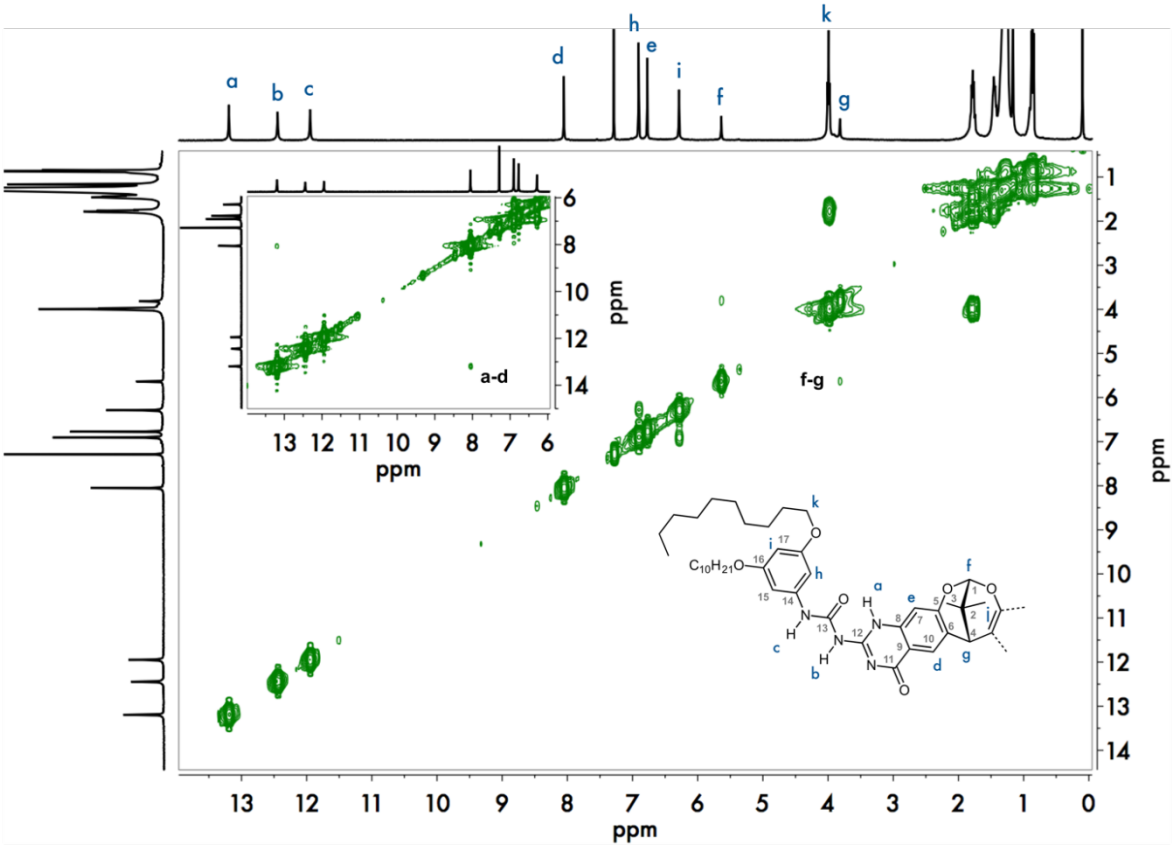

Figure S4. COSY spectrum of **1** in $CDCl_3$.

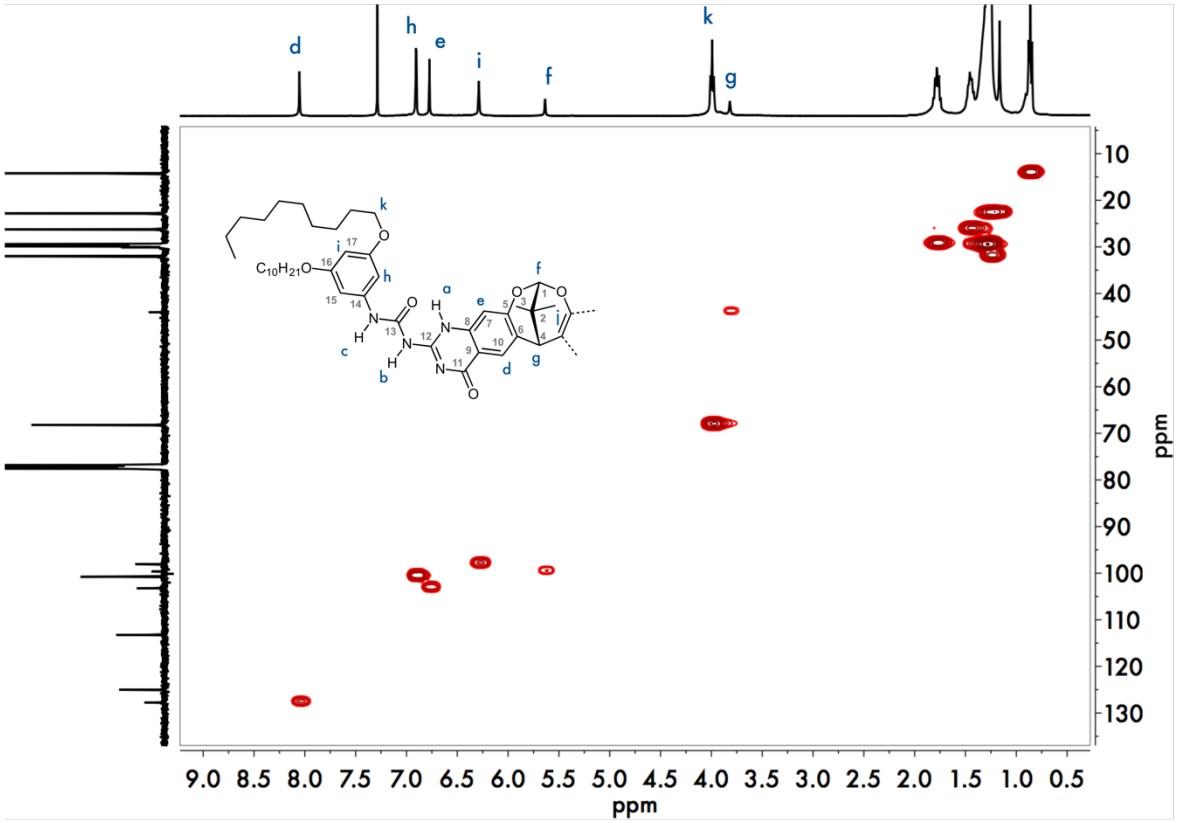

Figure S5. HSQC spectrum of **1** in $CDCl_3$.

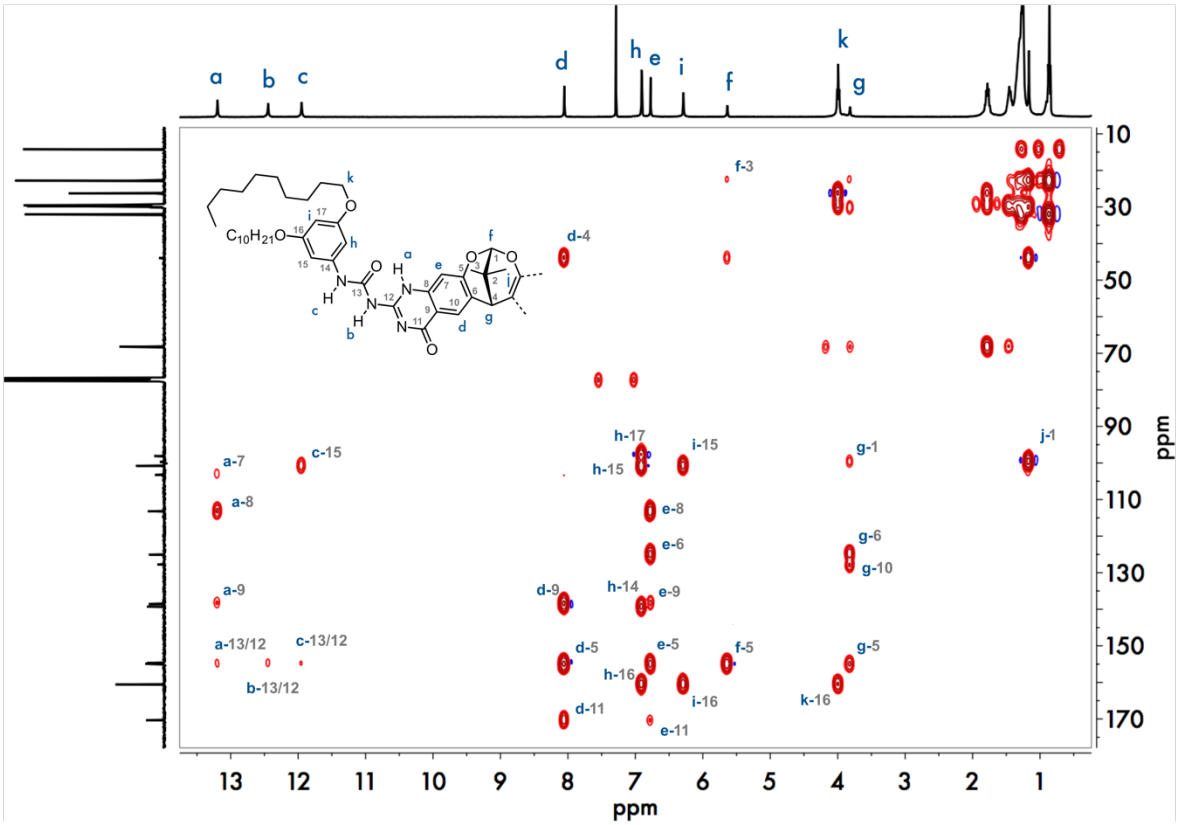

Figure S6. HMBC spectrum of **1** in $CDCl_3$.

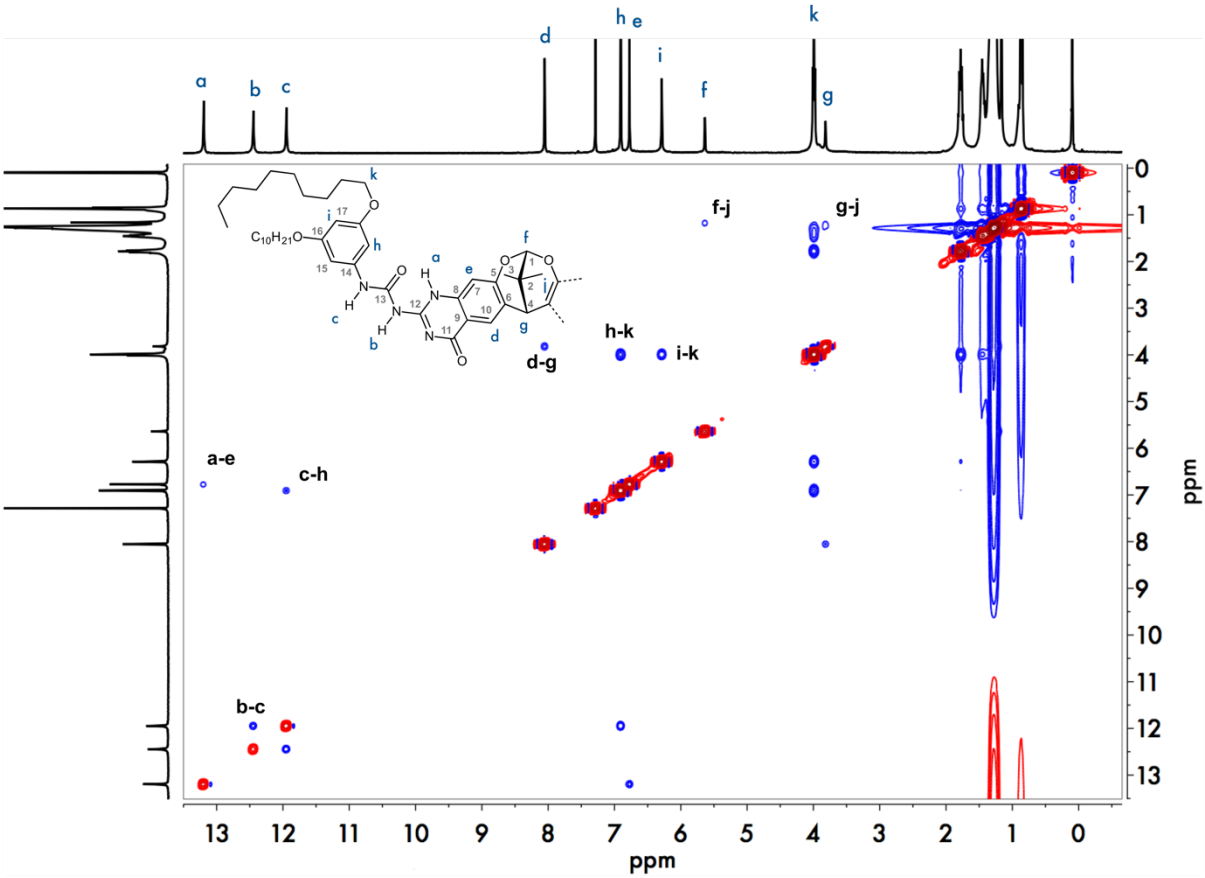

Figure S7. ROESY spectrum of **1** in $CDCl_3$.

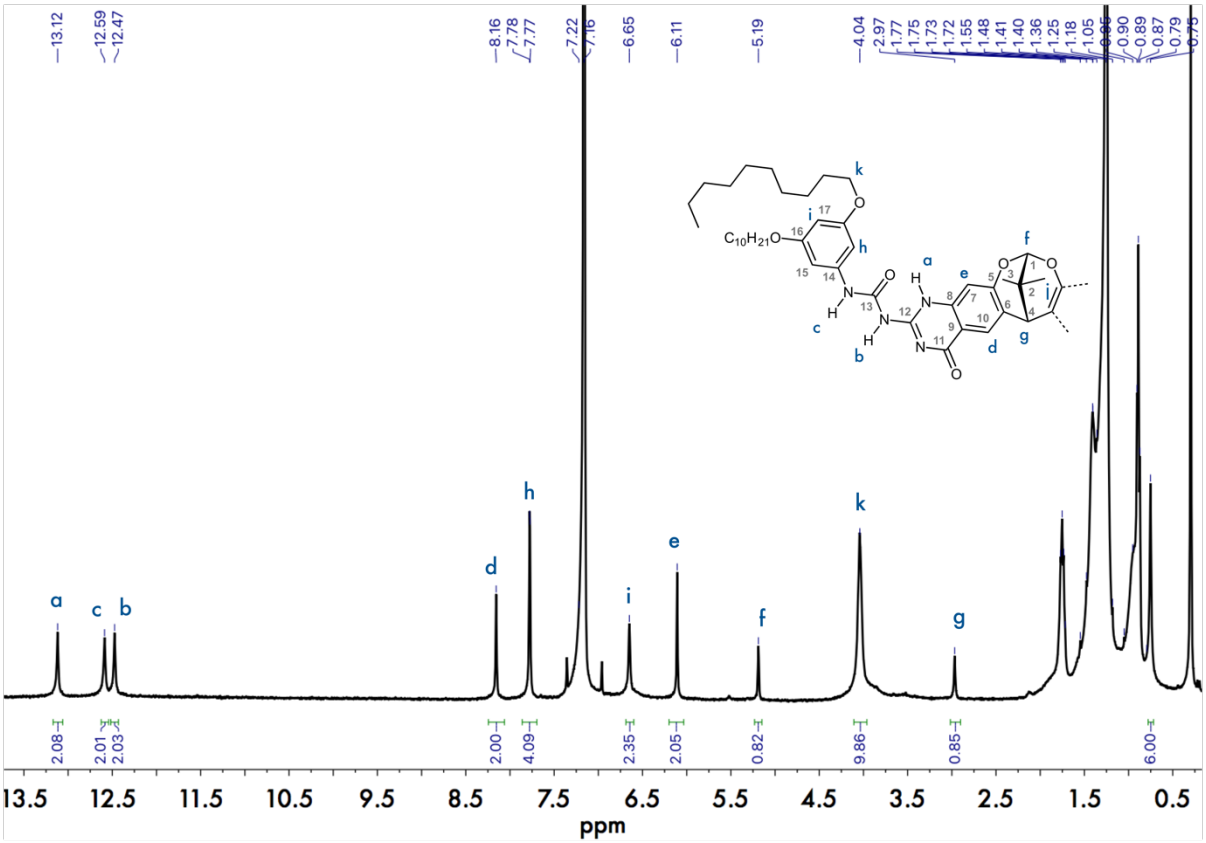

Figure S8. ^1H NMR spectrum of **1** in benzene-d_6.

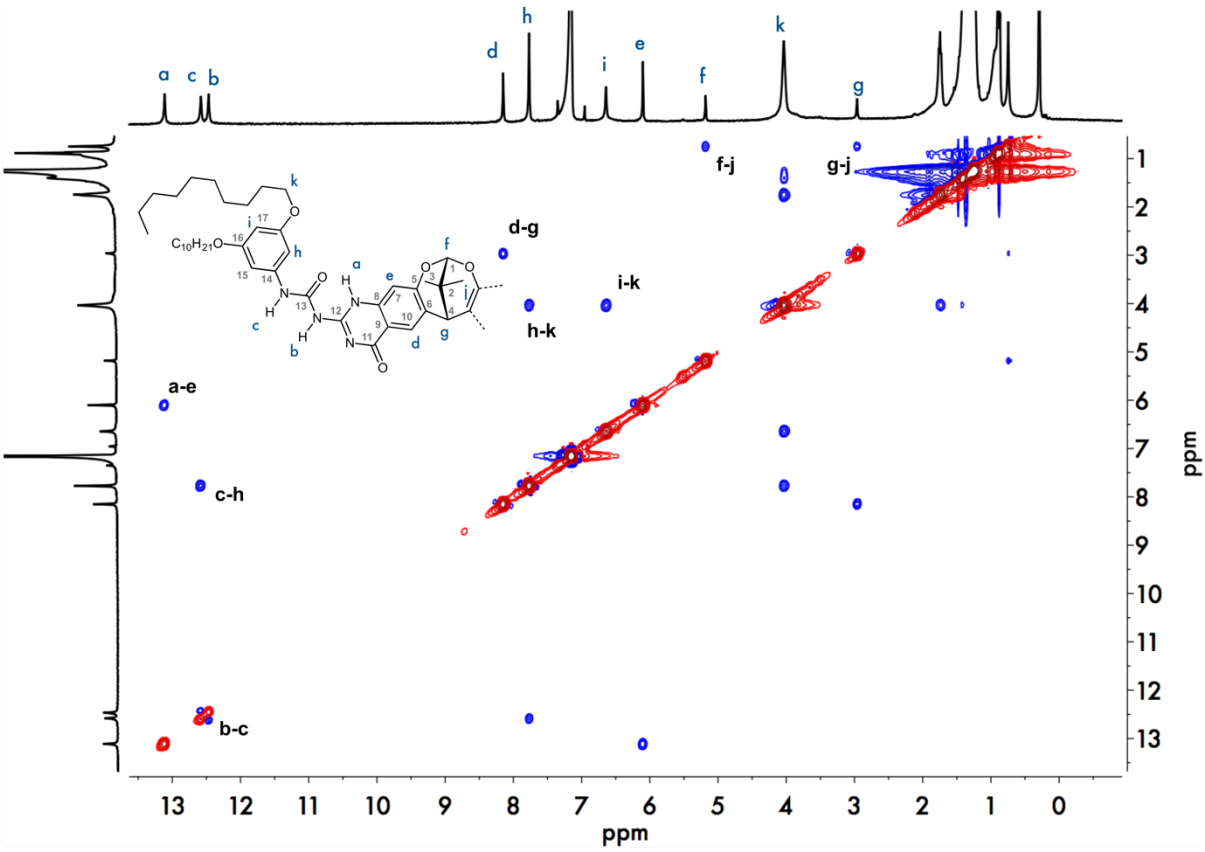

Figure S9. ROESY spectrum of **1** in benzene-d_6.

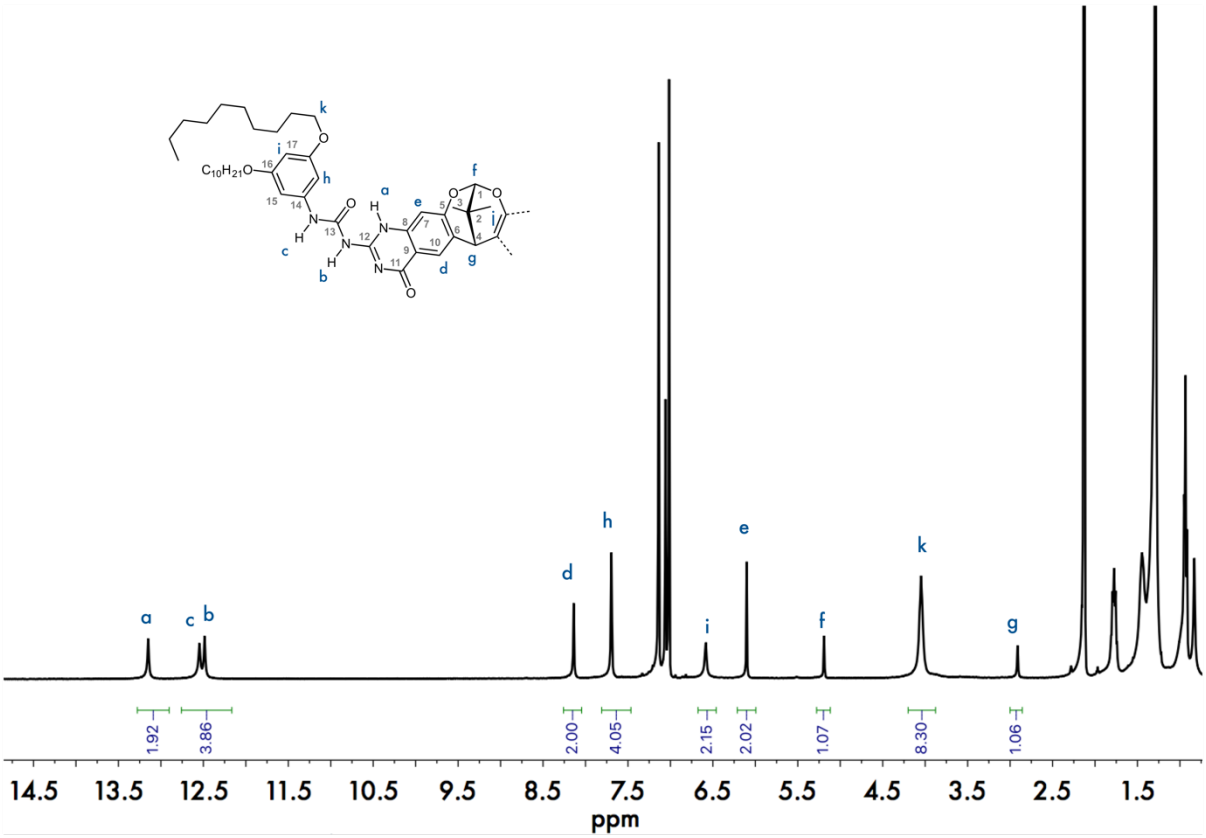

Figure S10. ^{1}H NMR spectrum of **1** in toluene-d_8.

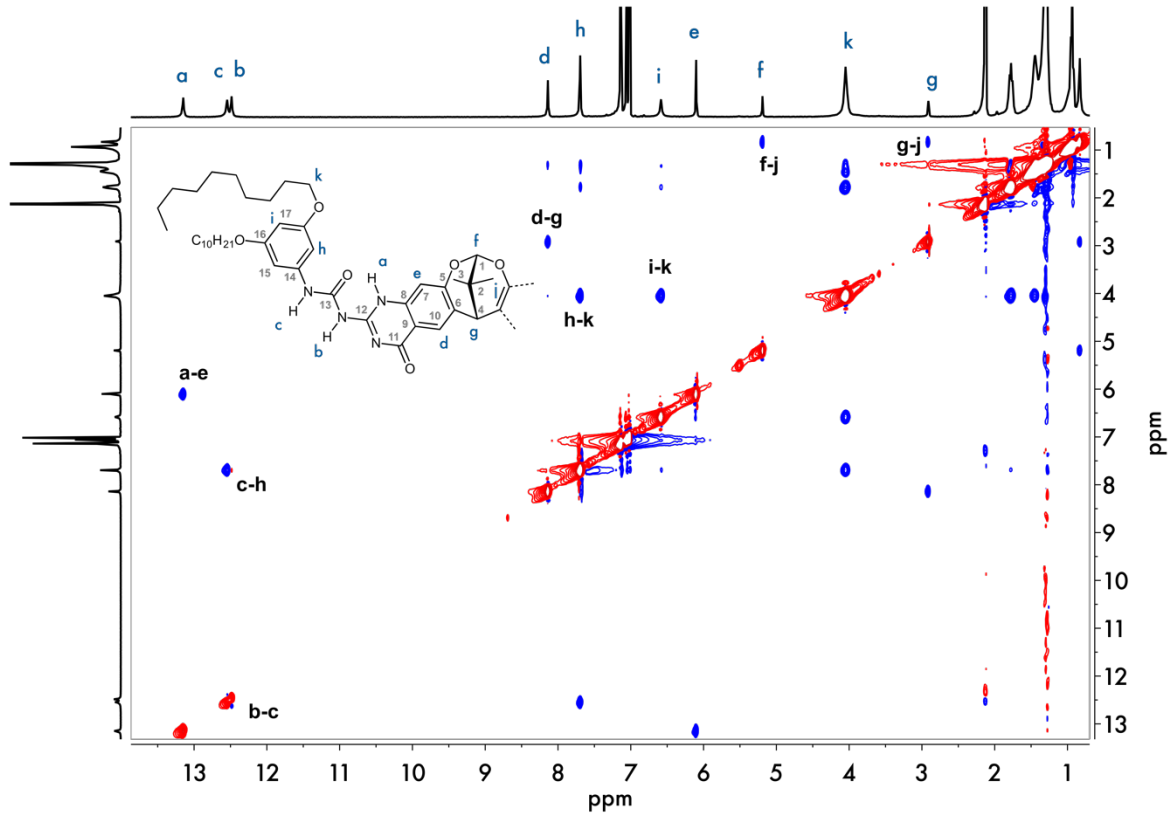

Figure S11. ROESY spectrum of **1** in toluene-d_8.

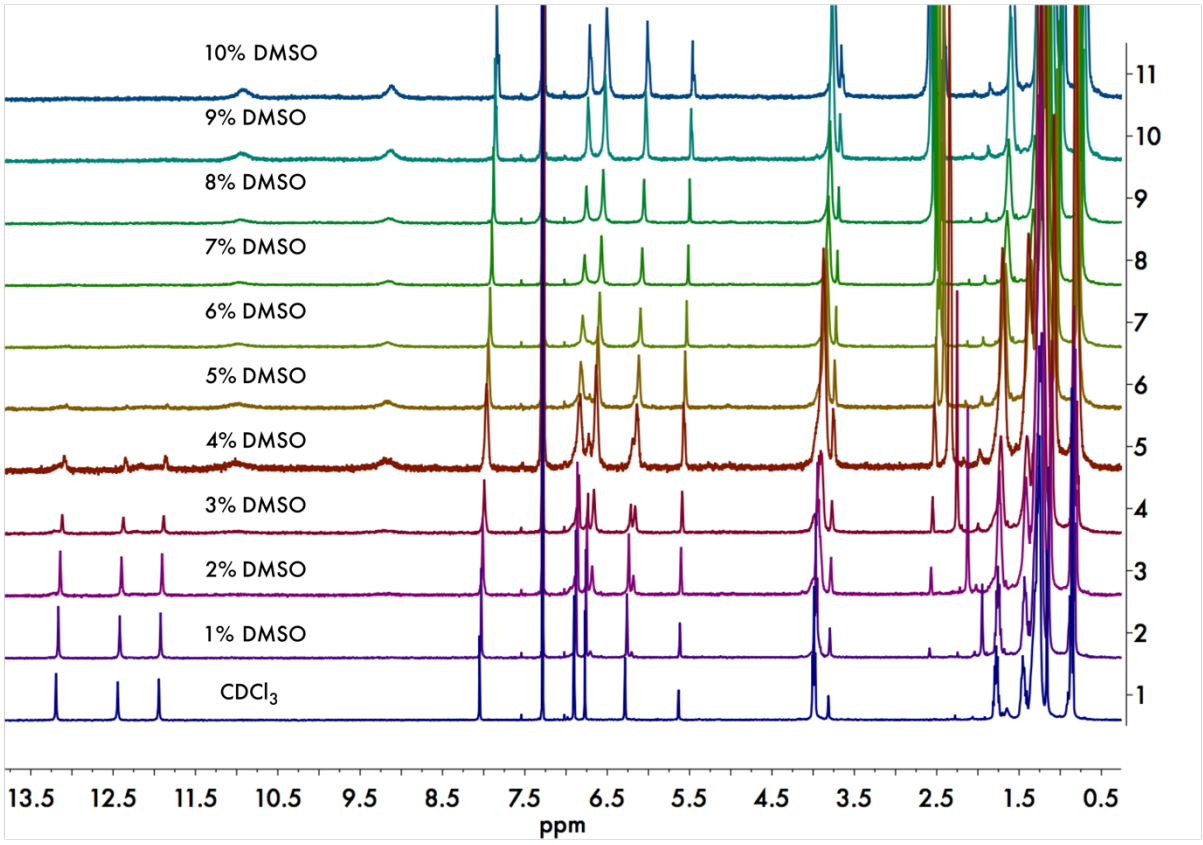

Figure S12. Titration NMR of **1** in $CDCl_3$ with DMSO-d_6.

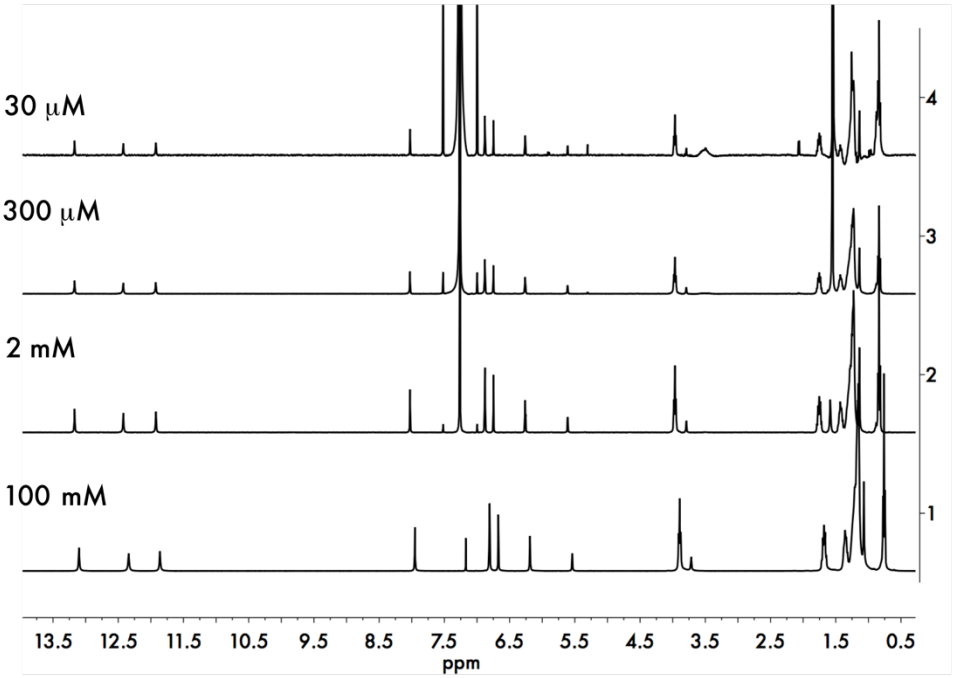

Figure S13. Dillution NMR of **1** in $CDCl_3$.

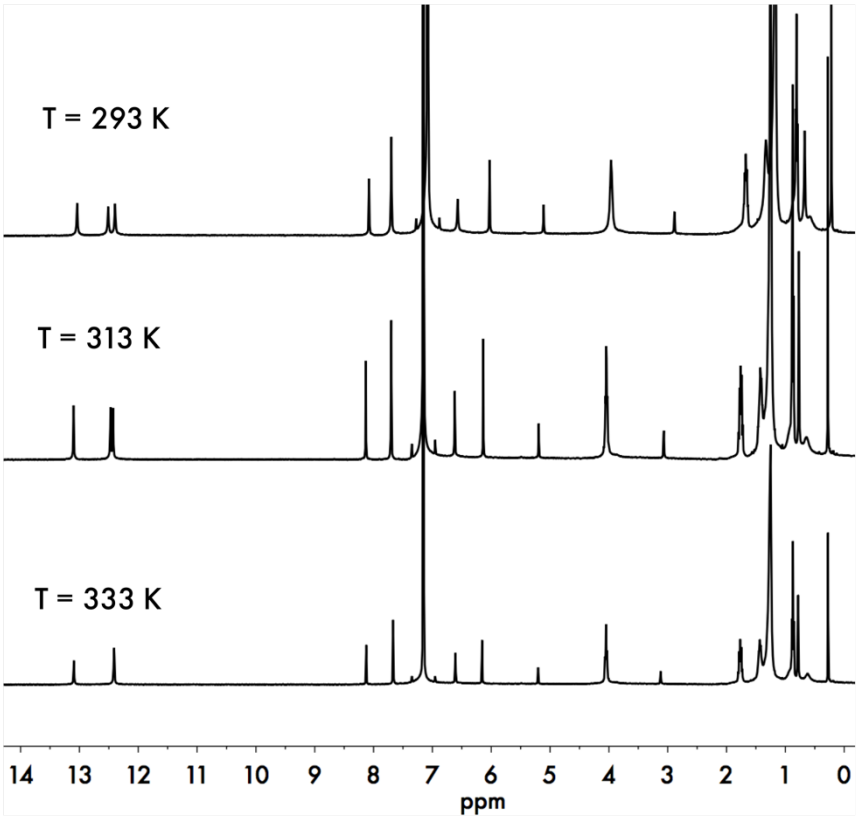

Figure S14. Variable temperature NMR of **1** (5.3 mM) in benzene-d_6.

Diffusion ordered NMR spectroscopy (DOSY)

DOSY experiments were performed on a 400 MHz Bruker Avance NMR spectrometer equipped with an Accustar z-axis gradient amplifier and an ATMA BBO probe with a z-axis gradient coil. All experiments were run using insert tubes and without spinning to avoid convection. All calculations were performed using standard applications in Bruker Topspin and MestReNova software. Diffusion was measured at 22 °C using standard Bruker pulse sequence, stegp1s, employing a stimulated echo sequence and 1 spoil gradient with a diffusion gradient, δ, set to 2 ms and the diffusion time, Δ, to 120 ms. The rectangular gradient pulses applied ranged from 2%-98% of the maximum gradient output of 48.15 Gauss/cm. The number of gradient steps was set to be 128. Individual rows of the quasi-2-D diffusion databases were phased, baseline corrected and aligned. At least three peaks were analyzed for each compound. Compound **5** was used as an internal non-aggregating reference.

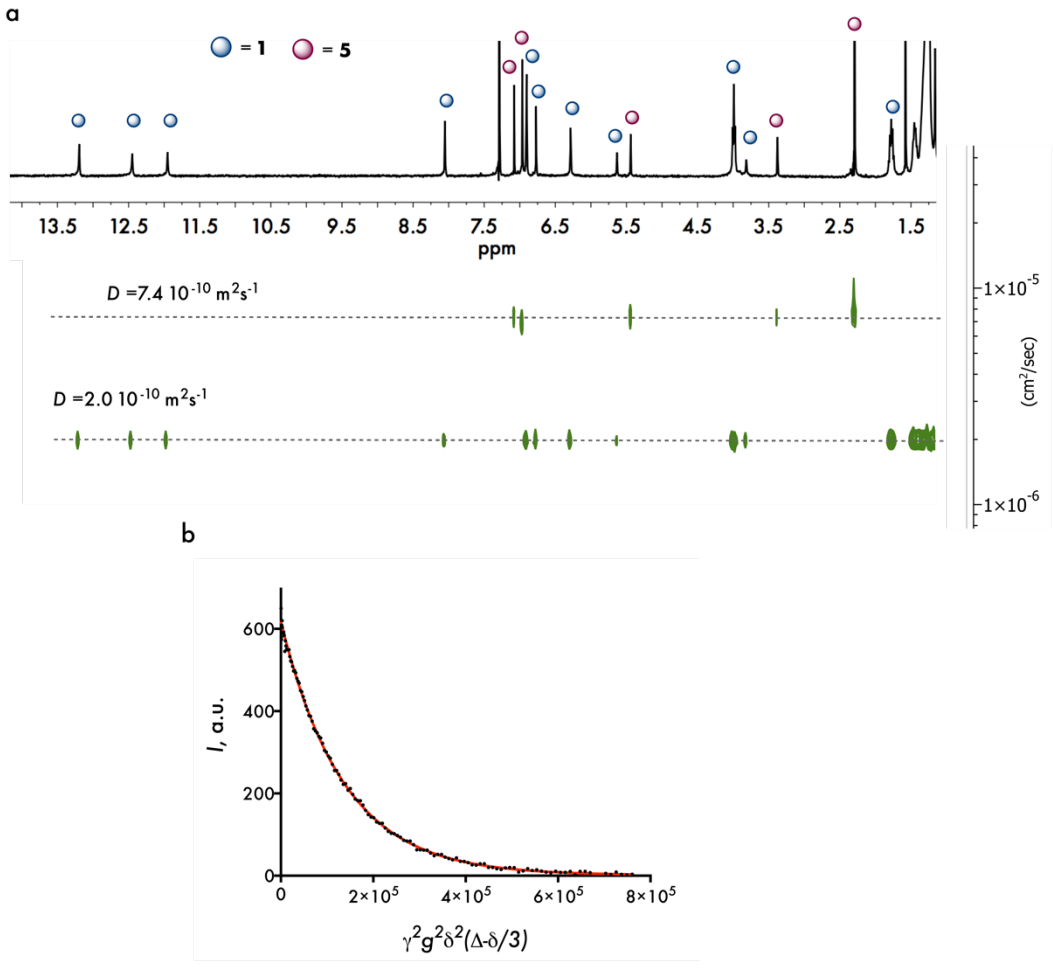

Figure S15. a) DOSY spectrum of a mixture of **1** and **5** in $CDCl_3$ with diffusion coefficients indicated; b) An example of fitting of peak intensity at 5.47 ppm to mono-exponential decay model.

Determination of stability constant *K*

The stock solution of **1** ($c_T(1)$ = 100 mM) was prepared in mixed solvent system ($CDCl_3$/3% (v/v)DMSO-d_6). The experiment was performed by diluting stock solution and recording ^{1}H NMR spectra. Integration of NH resonance (δ = 13.18 ppm) and proton **d** (combined resonance for free monomer and aggregate) resonance provided the relative quantities of aggregate and aggregate + monomer, respectively. For instance, the spectrum in Fig. S16 gives integral value of 1.0 for the aggregate and 1.38 for the sum of aggregate and monomer, corresponding to 0.38 integral value for monomer. Correcting these values by the number of protons in monomer and aggregate, respectively, the concentrations of monomer c_M and aggregate c_{agg} were calculated based on c_T(n), where n = number of experiment. The plot was constructed using c_{agg} and c_M^4 and fitted to tetramer-monomer equilibrium model. The slope of the fitted line corresponds to 1/*K*, where $K = c_{agg}/c_M^4$ (Fig. S17). Although some resonances of individual monomeric species in 6.0-7.0 ppm range were appearing, their integration required spectrum deconvolution, compromising the precision. Dilution experiments were done in 100 mM – 13 mM range.

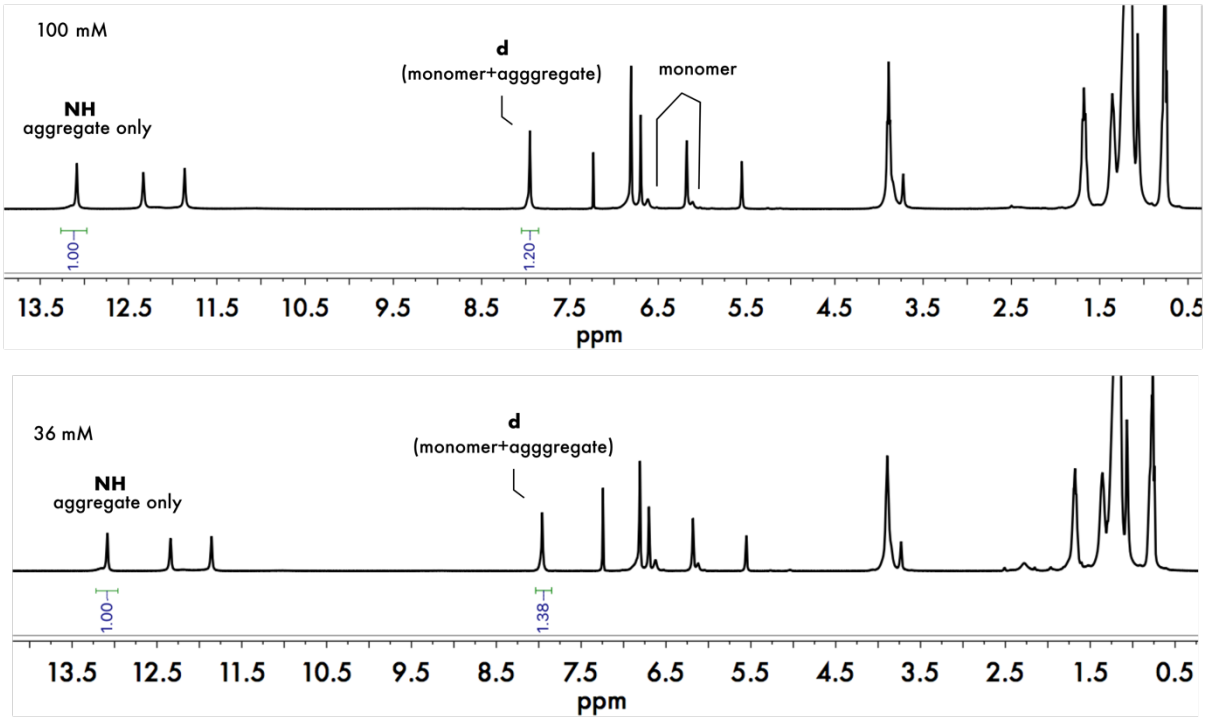

Figure S16. Selected examples of NMR dilution experiments in $CDCl_3$/3% (v/v)DMSO-d_6 mixture.

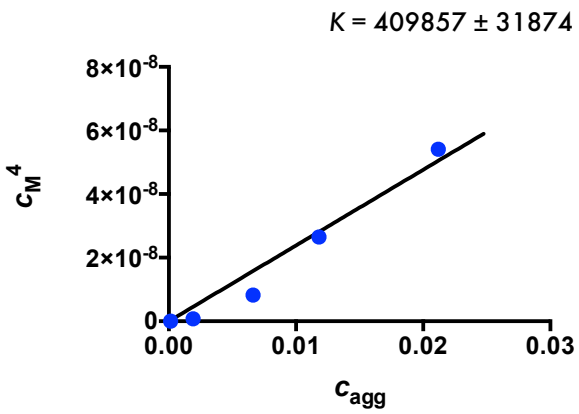

Figure S17. Fitting of experimentally determined concentrations of monomer (c_M) and tetramer (c_{agg}) to monomer-tetramer equilibrium model.

Gel permeation chromatography (GPC).

GPC analysis was performed on Agilent 1260 Infinity GPC/SEC system. (Column: PLGel 10 µm; Mobile phase: toluene; Column temperature: 25°C; Flow rate: 1 mL/min; Injection volume: 20 µL; Sample concentration: 1-3 mg/mL).

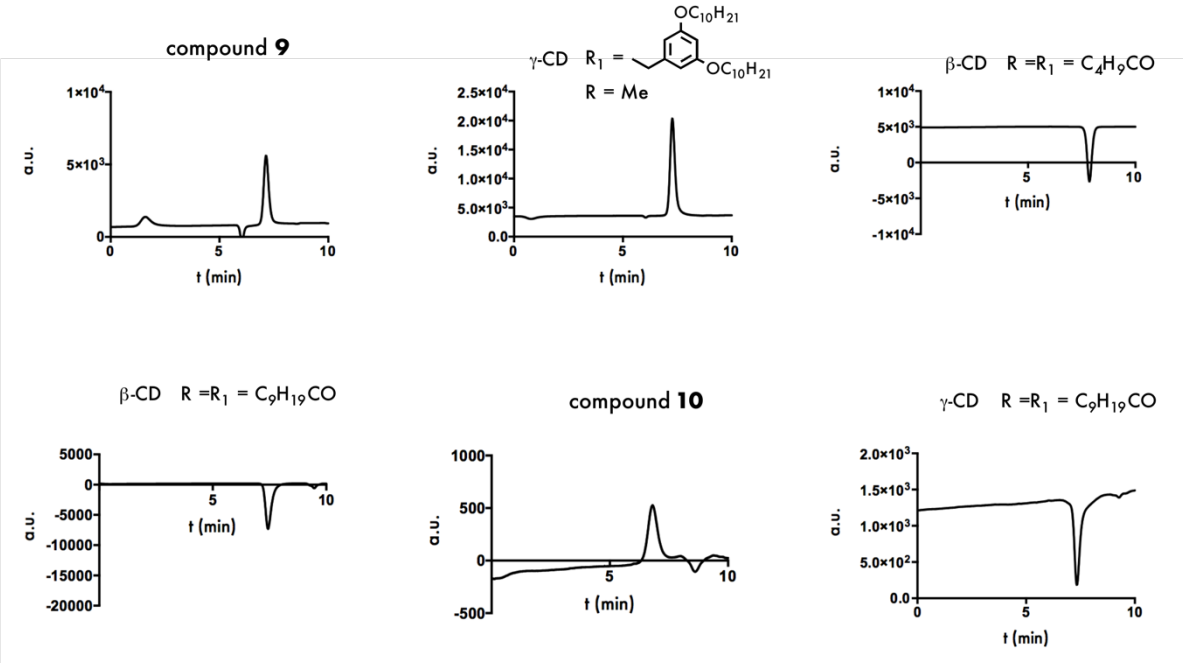

Figure S18. GPC traces of standards used to construct calibration curve.

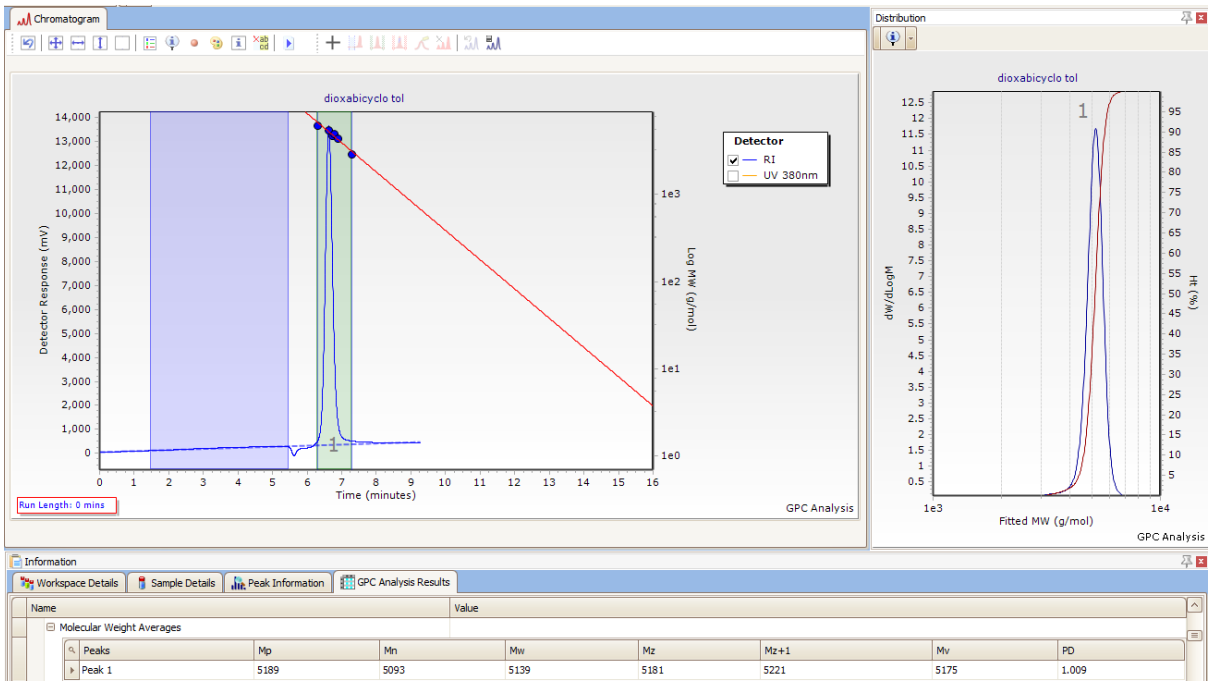

Figure S19. Screenshot of GPC trace analysis of compound **1** (Agilent GPC/SEC software).