

Electronic Supplementary Information

Guest Differentiation and Fingerprinting Based on the Conformational Diversity of a Dynamic Corannulene-based Cage

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1. General Procedures and Materials

Throughout the Supporting Information a large number of chemical structures or chemical equilibriums have been used to schematically illustrate the labelling of the protons and the interconversions between different stereoisomers. Notably, despite that only two conformers of the cage are shown for clarity in some cases, there are in fact two pair of enantiomers presented in the systems in all the cases.

Cage **1** was prepared according to the procedure we reported recently.¹ The detailed definition of the cage conformers can be found in Part 1 of the Supporting Information of the paper.^{S1} Per-deuterated solvents for NMR spectroscopy like chloroform-*d* (CDCl₃), acetonitrile-*d*₃ (CD₃CN), dichloromethane-*d*₂ (CD₂Cl₂), methanol-*d*₄ (CD₃OD), acetone-*d*₆ and dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) were obtained from commercial sources. Other commercially available chemicals were obtained from either Alfa Aesar, Aldrich or Acros and used without further purification.

Analytical TLC was carried out using tapered silica plates with a preadsorbent zone. Column chromatography was carried out on flash grade silica gel, using 0 – 20 psig pressure, or a Chromatotron centrifugal thin-layer chromatograph (Model 7924T, T-Squared Technology, Inc.), performed at ambient pressure.

NMR spectra were obtained with a Bruker spectrometer (¹H, 400, 500, and 600 MHz) or a JEOL Delta spectrometer (¹H, 400 and 600 MHz). The probe temperatures for the measurements were calibrated with neat ethylene glycol (for temperature in range of 313–393 K) and neat methanol (for temperature in range of 203–313 K) according to the literature^{S2}, by observation of the chemical-shift separation between the OH resonances and CH₂ (or CH₃) resonances in ethylene glycol or methanol. The chemical shifts of the deuterated reagents reference were as follows: chloroform-*d* (¹H: 7.26 ppm;

^{13}C : 77.2 ppm); acetonitrile- d_3 (^1H : 2.05 ppm; ^{13}C : 118.26 ppm)); dichloromethane- d_2 (^1H : 5.31 ppm; ^{13}C : 53.84 ppm); methanol- d_4 (^1H : 3.31 ppm; ^{13}C : 49.00 ppm); acetone- d_6 (^1H : 2.05 ppm; ^{13}C : 29.84 ppm) ; dimethyl sulfoxide- d_6 (^1H : 2.50 ppm; ^{13}C : 39.52 ppm). In the cases of the deuterium solvent mixtures, tetramethylsilane (TMS, ^1H : 0.00 ppm) was used as the reference. Typical 1D FID was subjected to exponential multiplication with a line broadening exponent (LB) of 0.3 Hz (for ^1H) and 1.0 Hz (for ^{13}C). 2D NOESY was recorded with the mixing time of 300 ms.

Exact mass spectra (ESI) were acquired on GCT spectrometer.

2. Relationships among Equilibrium Constants in the Studied System

When a supramolecular host with multiple conformers coexisting in dynamical equilibrium binds a specific guest, multiple, different complexes corresponding to those conformers will form resultantly. The simplest example is that the host exists as a mixture of two conformers (denoted H_1 and H_2) in equilibrium. In such the case, the hosts and the complexes are related by the following equilibria, as we have illustrated in the main text,



where G is the guest; H_1G and H_2G are the host-guest complexes; K_H , K_{a1} , K_{a2} and K_{HG} are the corresponding equilibrium constants (in which K_{a1} and K_{a2} can also be called complexation/binding constants).

The basic equations for K_{a1} and K_{a2} are the following,

$$K_{a1} = \frac{[H_1G]}{[H_1] \cdot [G]} \quad (S5)$$

$$K_{a2} = \frac{[H_2G]}{[H_2] \cdot [G]} \quad (S6)$$

$$[H]_0 = [H_1] + [H_2] + [H_1G] + [H_2G] \quad (S7)$$

$$[G]_0 = [G] + [H_1G] + [H_2G] \quad (S8)$$

where $[H]_0$ is the initial (total) concentration of host molecules, $[G]_0$ is the initial (total) concentration of guest molecules, $[H_1]$, $[H_2]$, $[G]$, $[H_1G]$ and $[H_2G]$ are equilibrium concentrations of the corresponding species (the free host, free guest and complexes) in the system, respectively.

Equations (S5) and (S6) can be written in other forms,

$$[H_1G] = K_{a1} \cdot [H_1] \cdot [G] \quad (S9)$$

$$[H_2G] = K_{a2} \cdot [H_2] \cdot [G] \quad (S10)$$

Define the coefficient of conformational distribution (CCD) of the host upon complexing the guest as,

$$CCD_{\frac{H_1G}{H_2G}} = \frac{[H_1G]}{[H_2G]} \quad (S11)$$

Combining the Equations (S1), (S4), (S9) and (S10) gives,

$$CCD_{\frac{H_1G}{H_2G}} = \frac{1}{K_{HG}} = \frac{K_{a1} \cdot [H_1] \cdot [G]}{K_{a2} \cdot [H_2] \cdot [G]} = \frac{K_{a1}}{K_{a2}} \cdot \frac{1}{K_H} \quad (S12)$$

As mentioned in the main text, considering K_H is constant for a given host at a given condition, Equation (S12) indicates that CCD is essentially a kind of comprehensive equilibrium constant, being just a reflection of the difference between H_1 and H_2 in association affinity for a specific guest. Notably, for determination of CCD, i.e., $1/K_{HG}$, there is no need to determine the analytical concentrations of the free hosts, the free guests and the specific concentrations of each product species (in Equations (S7) and (S8)) in the mixture.

3. Encapsulation of Adamantane in Cage 1

3.a Summary of Studies on Encapsulation of Adamantane.

Adamantane (**2**) was first used as the guest to explore the complexation properties of **1**. The purposes of the studies are to verify the encapsulation of the guests in the cage, the changes in conformational distribution of the cage induced by the encapsulation, and the "CCD–microscopic equilibrium constants" relationship described in Equation 1 (in the main text).

¹H NMR Titration Experiments. ¹H NMR titration experiments were carried out according to the procedure as follows. To a solution of cage **1** (1 mM, 0.5 mL) in 7:93 (v/v) CD₃CN/CDCl₃, a solution of adamantane (**2**) (100 mM) in the same solvent was gradually added. In this process, a series of ¹H NMR spectra of the sample was recorded by a Bruker Avance 600 MHz (¹H) spectrometer at 298 K. Totally 14 points were recorded in these processes. To estimate the standard deviations of the determined equilibrium constants and CCD (*vide infra*), the investigation was repeated for totally three times. An example of the obtained spectra is shown in Figure S1.

The assignments of the ¹H NMR spectra of the complexes were performed based on the corresponding ¹H–¹H NOESY, ¹H–¹H COSY, ¹H–¹³C HSQC, and ¹H–¹³C HMBC experiments (see Figures S7–S10, Part 3.d in this Supporting Information).

In other two runs, the spectra were recorded at 273 K and 253 K by a 400 MHz (¹H) spectrometer (Figures S2–S3). These two sets of spectra clearly showed how signals of the complexes aggregated in the case of 298 K. Of particular interest is the spectral changes at 253 K, which showed still the appearance of two new set of signals of **2**⊂**1**, though only one set of signals corresponding to *P,M,P/M,P,M* species can be observed in the absence of guests at such temperature (Figure S3). This qualitatively manifested that the energy gap between **2**⊂[(*P,M,P*)/(*M,P,M*)-**1**] and **2**⊂[(*P,P,P*)/(*M,M,M*)-**1**] is much lower than that between (*P,M,P*)/(*M,P,M*)-**1** and (*P,P,P*)/(*M,M,M*)-**1**.

Equilibrium Constants. Determination of K_a for the complexations of **2** with $(P,M,P)/(M,P,M)$ -**1** or $(P,P,P)/(M,M,M)$ -**1** at 298 K were based on Equations (S5)–(S8). To make the elaborations more readable, we designated $(P,M,P)/(M,P,M)$ -**1** and $(P,P,P)/(M,M,M)$ -**1** as the host **H1** and **H2**, respectively; and guest **2** was designated as **G**. For the determinations on K_{a1} and K_{a2} , the relative amounts of free hosts and the complexes, i.e., **H1**, **H2**, **H1G** and **H2G**, can be obtained by integrations of the H_d and H_d' signals of the corresponding species in the NMR spectra. The absolute analytical concentrations of these species and the free guest were obtained by taking the initial concentrations of the cages and the guest ($[H]_0$ and $[G]_0$ in Equations (S7) and (S8)) into considerations.

To reduce the error arising from the NMR integrations, only part of spectra was used for the calculations. $CCD_{H1G/H2G}$, K_H , K_{a1} , K_{a2} and $K_{a1}/(K_{a2} \cdot K_H)$ were first determined independently based on each of the spectra investigable; and the final values were reported as the mean of the data obtained from those runs. Summary of the calculations are shown in Table S1.

VT 1H NMR measurements. The measurements were carried out on a 600 MHz (1H) NMR spectroscopy, with 93:7 (v/v) $CDCl_3/CD_3CN$ as the solvent. The range of temperature investigated were chosen based on the physical properties of the solvents (Chloroform-*d*: M.p., -63.5 °C; B.p. 61 – 62 °C. Acetonitrile-*d*₃: M.p., -48 °C; B.p. 81 – 82 °C). In the measurements, a series of 1H NMR spectra of the sample at various temperature were recorded; each 1H NMR spectrum was recorded after the sample was maintained at the stated temperature for 10 minutes. The obtained spectra are shown in Figure S4.

Thermodynamic parameters for $2 \subset [(P,M,P)/(M,P,M)$ -1**] $\rightleftharpoons 2 \subset [(P,P,P)/(M,M,M)$ -**1**]**
conversion. The parameters were obtained through the same way as that we previously reported^{S1}: Relative amounts of the complex species were derived from the VT 1H NMR spectra (Figure S4); the

obtained equilibrium constants (K_{HG} in Equation (S4)) were then used to calculate standard reaction Gibbs energy using Gibbs free energy isotherm equation:

$$\Delta G = -RT \ln K \quad (S13)$$

The enthalpic (ΔH) and entropic (ΔS) contributions to the interconversion were calculated from Van't Hoff plot (Equation (S14)):

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (S14)$$

The obtained Van't Hoff plot is shown in Figure S5. Summary and plots of sectioned numerical fits to Van't Hoff equation is shown in Table S2 and Figure S6.

Table S1. Summary of the ^1H NMR titration studies on the complexation of (*P,M,P*)/(*M,P,M*)-**1** (**H1**) and (*P,P,P*)/(*M,M,M*)-**1** (**H2**) with **2** (**G**) in 93:7 (v/v) $\text{CDCl}_3/\text{CD}_3\text{CN}$ at 298 K: relative amounts (Rel. amt., a.u.) and equilibrium concentrations (mM) of the species in the systems, equilibrium constants (K_{a1} and K_{a2} , M^{-1}), and $\text{CCD}_{\text{H1G/H2G}}$ of the cage.^a

G (equiv)	Run	Rel. amt. H1	Rel. amt. H2	Rel. amt. H1G	Rel. amt. H2G	[H1]	[H2]	[G]	[H1G]	[H2G]	K_H	K_{a1}^b ($\times 10^3$)	K_{a2}^c ($\times 10^4$)	$\text{CCD}_{\text{H1G/H2G}}$	$K_{a1}/(K_{a2} \times K_H)$	General Results
1.0	1	1.00	0.23	2.55	1.26	0.20	0.05	0.24	0.51	0.25	0.23	10.45	2.23	2.02	2.02	$K_H = 0.22 \pm 0.03$ $K_{a1}^d = (6.26 \pm 1.80) \times 10^3 \text{ M}^{-1}$; $K_{a2}^d = (1.37 \pm 0.44) \times 10^4 \text{ M}^{-1}$ $\frac{K_{a1}}{K_{a2}} \cdot \frac{1}{K_H} = 2.08 \pm 0.05$ $\text{CCD}_{\text{H1G/H2G}}^e = 2.08 \pm 0.05$
	2	1.00	0.20	2.04	1.01	0.24	0.05	0.28	0.48	0.24	0.20	7.18	1.75	2.01	2.01	
	3	1.00	0.20	2.15	1.04	0.23	0.05	0.27	0.49	0.24	0.27	7.84	1.87	2.07	2.07	
1.2	1	1.00	0.20	3.05	1.47	0.17	0.04	0.41	0.53	0.26	0.30	7.46	1.79	2.07	2.07	
	2	1.00	0.20	2.48	1.20	0.20	0.04	0.45	0.51	0.25	0.20	5.57	1.34	2.08	2.08	
	3	1.00	0.20	2.61	1.23	0.20	0.04	0.44	0.52	0.24	0.20	5.96	1.42	2.12	2.12	
1.6	1	1.00	0.27	4.26	2.09	0.13	0.04	0.77	0.56	0.27	0.24	5.56	1.02	2.04	2.04	
	2	1.00	0.24	3.82	1.89	0.14	0.03	0.78	0.55	0.27	0.21	4.91	1.02	2.03	2.03	
	3	1.00	0.22	3.80	1.75	0.15	0.03	0.78	0.56	0.26	0.20	4.88	1.01	2.17	2.17	
2.0	1	1.00	0.30	7.51	3.64	0.08	0.02	1.10	0.60	0.29	0.20	6.80	1.09	2.06	2.06	
	2	1.00	0.21	4.70	2.19	0.12	0.03	1.15	0.58	0.27	0.22	4.09	0.92	2.15	2.15	
	3	1.00	0.22	5.04	2.38	0.12	0.03	1.14	0.58	0.28	0.22	4.42	0.97	2.12	2.12	

^a Relative amount of the cage and complex species were derived from the ^1H NMR signals at ca. 8.81 ppm (H_d of **H1**), 8.75 ppm (H_d of **H1G**), 8.45 ppm (H_d of **H2**) and 8.50 ppm (H_d of **H2G**) shown in Figure S1. ^b The association constant of **H1** and **G**. ^c The association constant of **H2** and **G**. ^d The mean and the standard deviation of the association constant. ^e The mean and the standard deviation of the coefficient of conformational distribution.

3.b Selected ^1H NMR Spectra Obtained from Adamantane Titrations

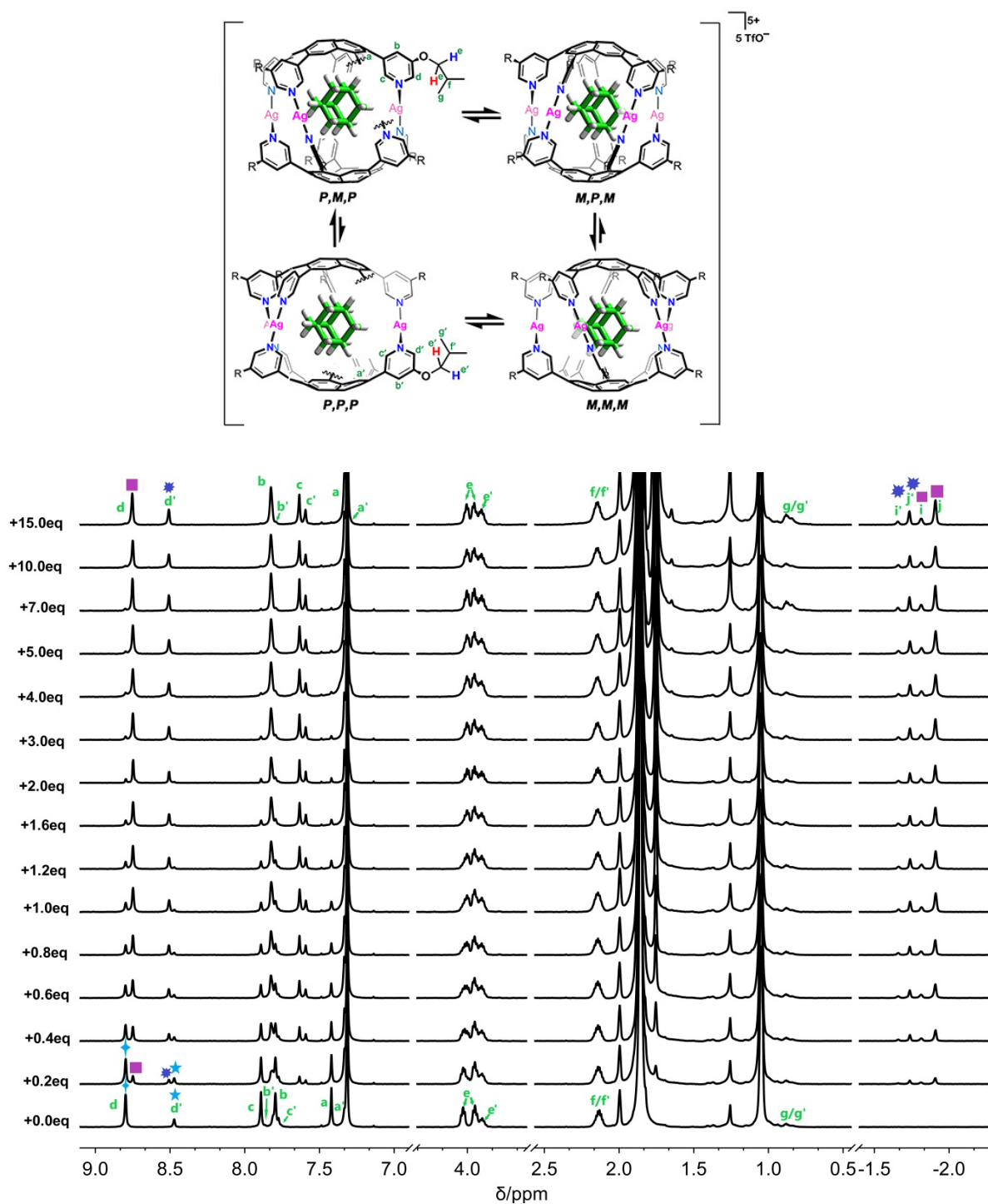


Figure S1. Example of changes of ^1H NMR spectra (600 MHz, **298 K**, 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (1 mM) upon the addition of adamantane (**2**). ✧ = $(P,M,P)/(M,P,M)$ -**1**, ★ = $(P,P,P)/(M,M,M)$ -**1**, ■ = **2** $\subset$ $(P,M,P)/(M,P,M)$ -**1**, ⬠ = **2** $\subset$ $(P,P,P)/(M,M,M)$ -**1**.

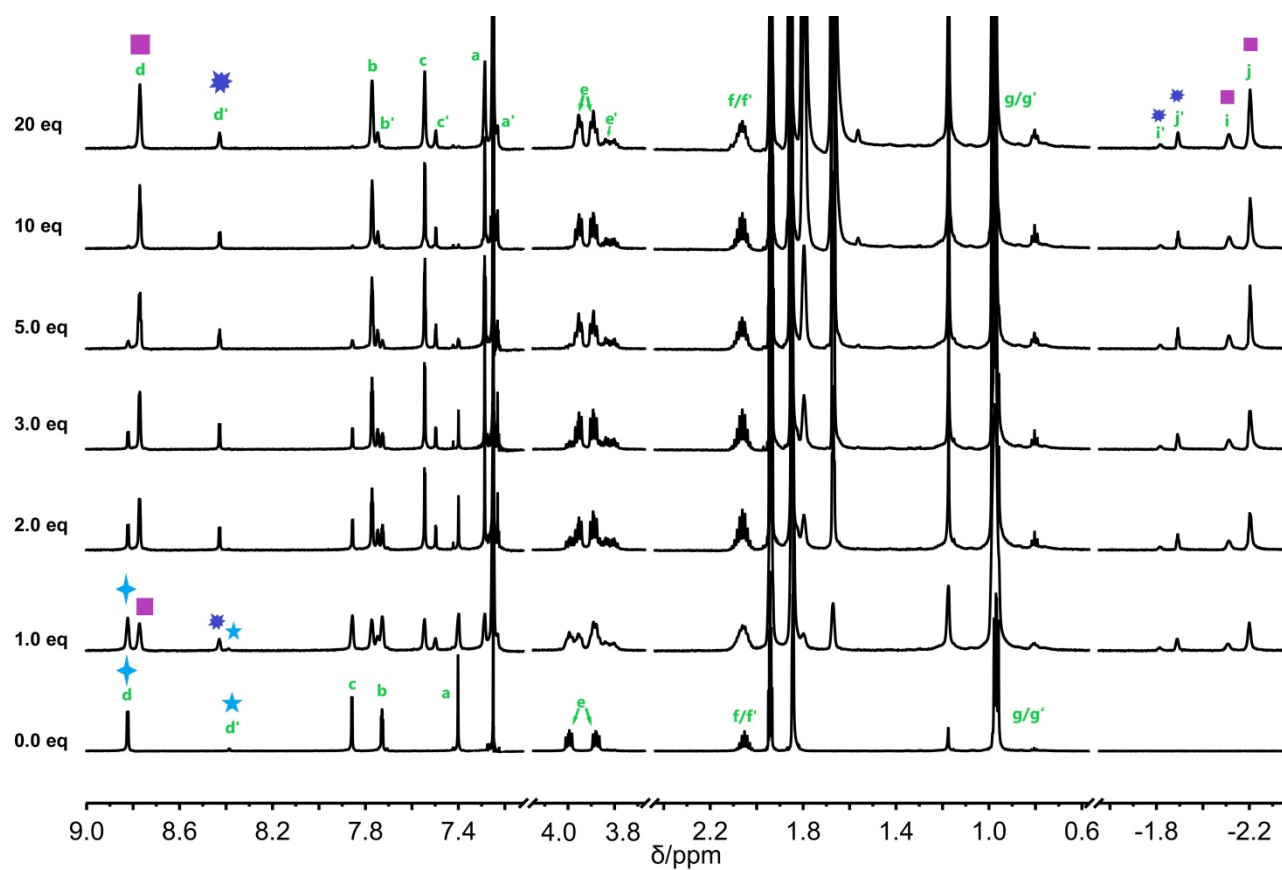


Figure S2. Changes of ^1H NMR spectra (400 MHz, 273 K, 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (1 mM) upon the addition of adamantane (**2**). ★ = $(P,M,P)/(M,P,M)$ -**1**, ★ = $(P,P,P)/(M,M,M)$ -**1**, ■ = $\mathbf{2} \subset (P,M,P)/(M,P,M)$ -**1**, ★ = $\mathbf{2} \subset (P,P,P)/(M,M,M)$ -**1**.

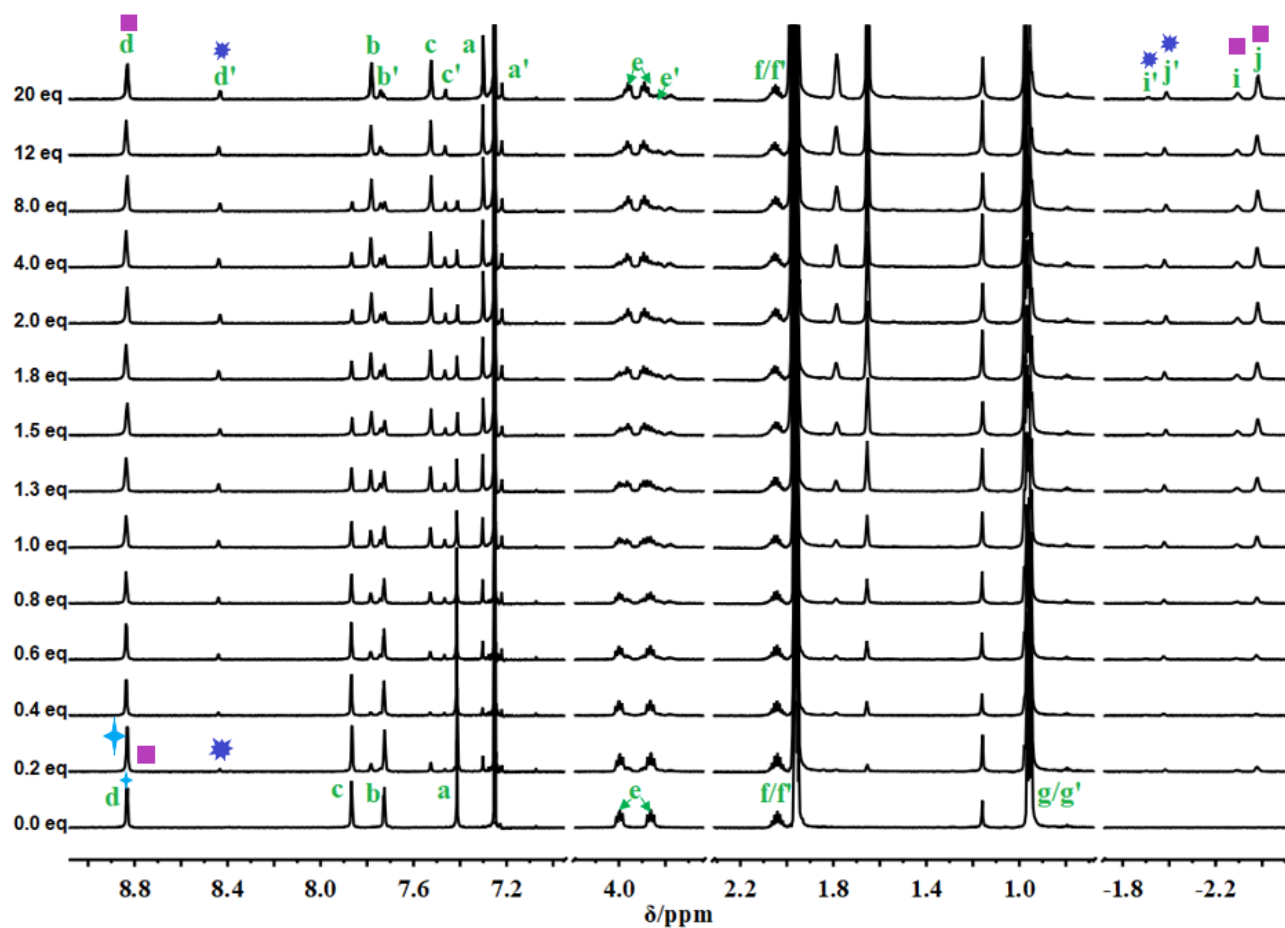


Figure S3. Changes of ^1H NMR spectra (400 MHz, **253 K**, 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (1 mM) upon the addition of adamantane (**2**). $\star = (P,M,P)/(M,P,M)$ -**1**, $\star = (P,P,P)/(M,M,M)$ -**1**, $\blacksquare = 2 \subset (P,M,P)/(M,P,M)$ -**1**, $\star = 2 \subset (P,P,P)/(M,M,M)$ -**1**.

3.c VT ^1H NMR Spectra of **2** $\subset$ **1**

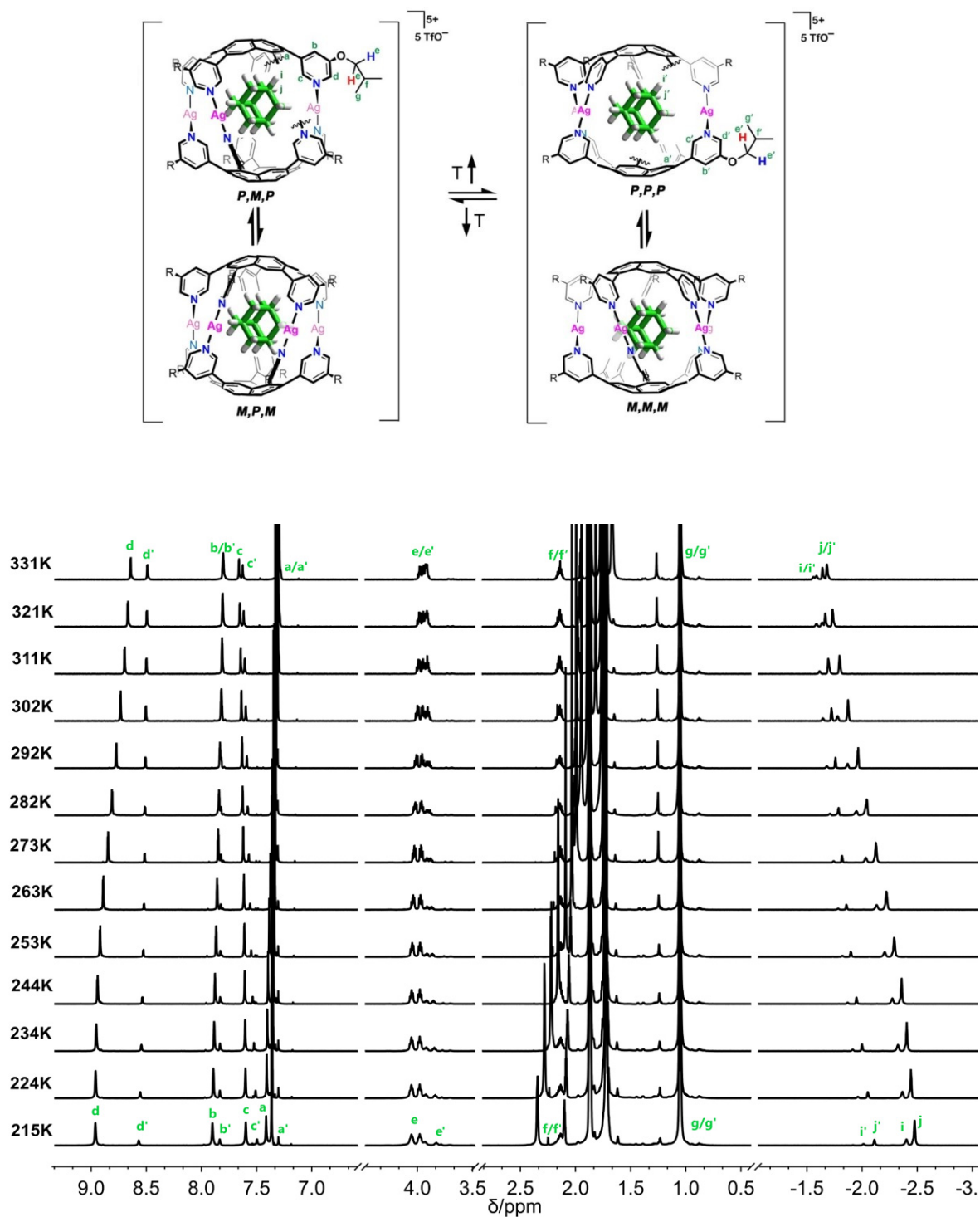


Figure S4. VT ^1H NMR spectra (600 MHz, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$, 1 mM) of **2** $\subset$ **1** (prepared by mixing **1** with 20 equivalents of **2**).

Table S2. Summary of sectioned numerical fits to Van't Hoff equation for the equilibrium of **2** $\subset$ $(P,M,P)/(M,P,M)$ -**1** $\rightleftharpoons$ **2** $\subset$ $(P,P,P)/(M,M,M)$ -**1** in 93:7 (v/v) $\text{CDCl}_3/\text{CD}_3\text{CN}$.

$\Delta G = -RT\ln K; \quad \ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} = -0.50322\frac{\Delta H}{T} + 0.50322\Delta S; \quad R = 1.9872$					
T (K)	$n_{P,M,P/M,P,M}/n_{P,P,P/M,M,M}^a$	K	ΔG (kcal·mol ⁻¹)	ΔH (kcal·mol ⁻¹)	ΔS (cal·mol ⁻¹ ·K ⁻¹)
330.54	1.39	1.39	-0.22	$\Delta H = 1.93$ $\Delta S = -5.22$	
320.88	1.47	1.47	-0.25		
311.21	1.67	1.67	-0.32		
301.55	1.92	1.92	-0.39	$\Delta H = -4.61$ $\Delta S = -14.01$	
291.88	2.44	2.44	-0.52		
282.22	3.23	3.23	-0.66		
272.55	4.35	4.35	-0.80		
262.89	5.26	5.26	-0.87	$\Delta H = 0.66$ $\Delta S = 5.80$	
253.22	5.00	5.00	-0.81		
243.56	4.76	4.76	-0.76		
233.89	4.76	4.76	-0.73		
224.23	4.76	4.76	-0.70		
214.56	4.76	4.76	-0.67		

^a Molar ratio of **2** $\subset$ $(P,M,P)/(M,P,M)$ -**1** to **2** $\subset$ $(P,P,P)/(M,M,M)$ -**1**, derived from the integration of H_d and H_d' in the ¹H NMR spectra.

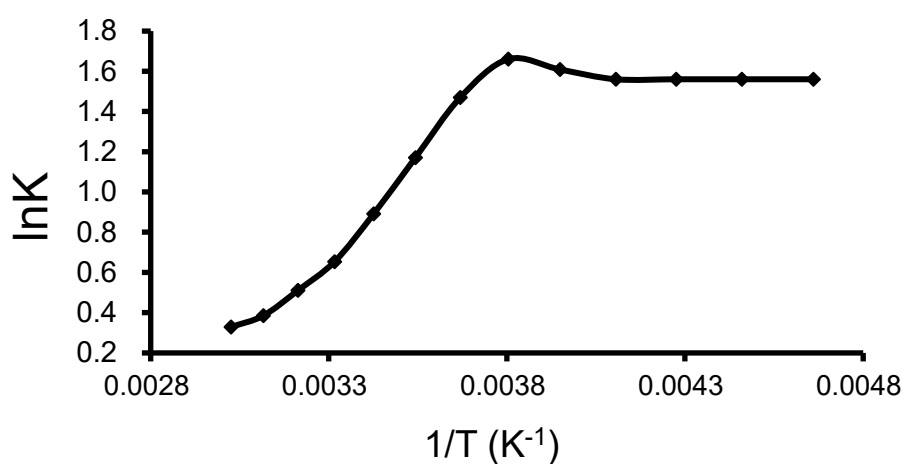


Figure S5. Van't Hoff Plot of the interconversion between the $P,P,P/M,M,M$ and the $P,M,P/M,P,M$ conformers of **1** with **2** included.

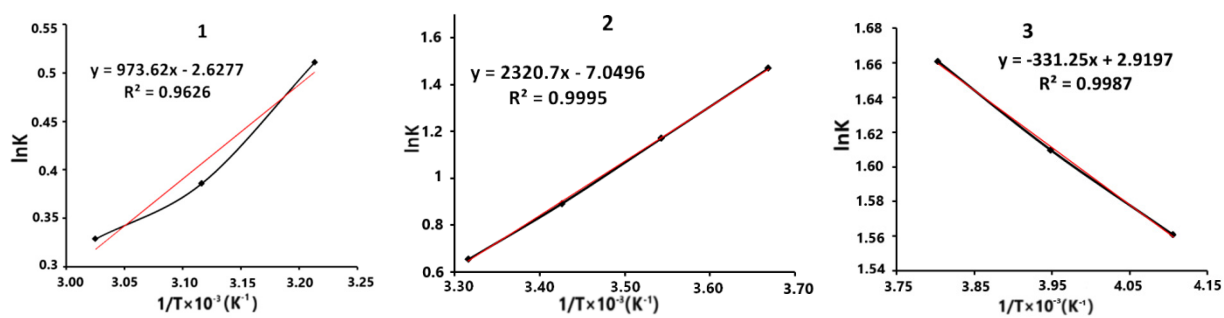
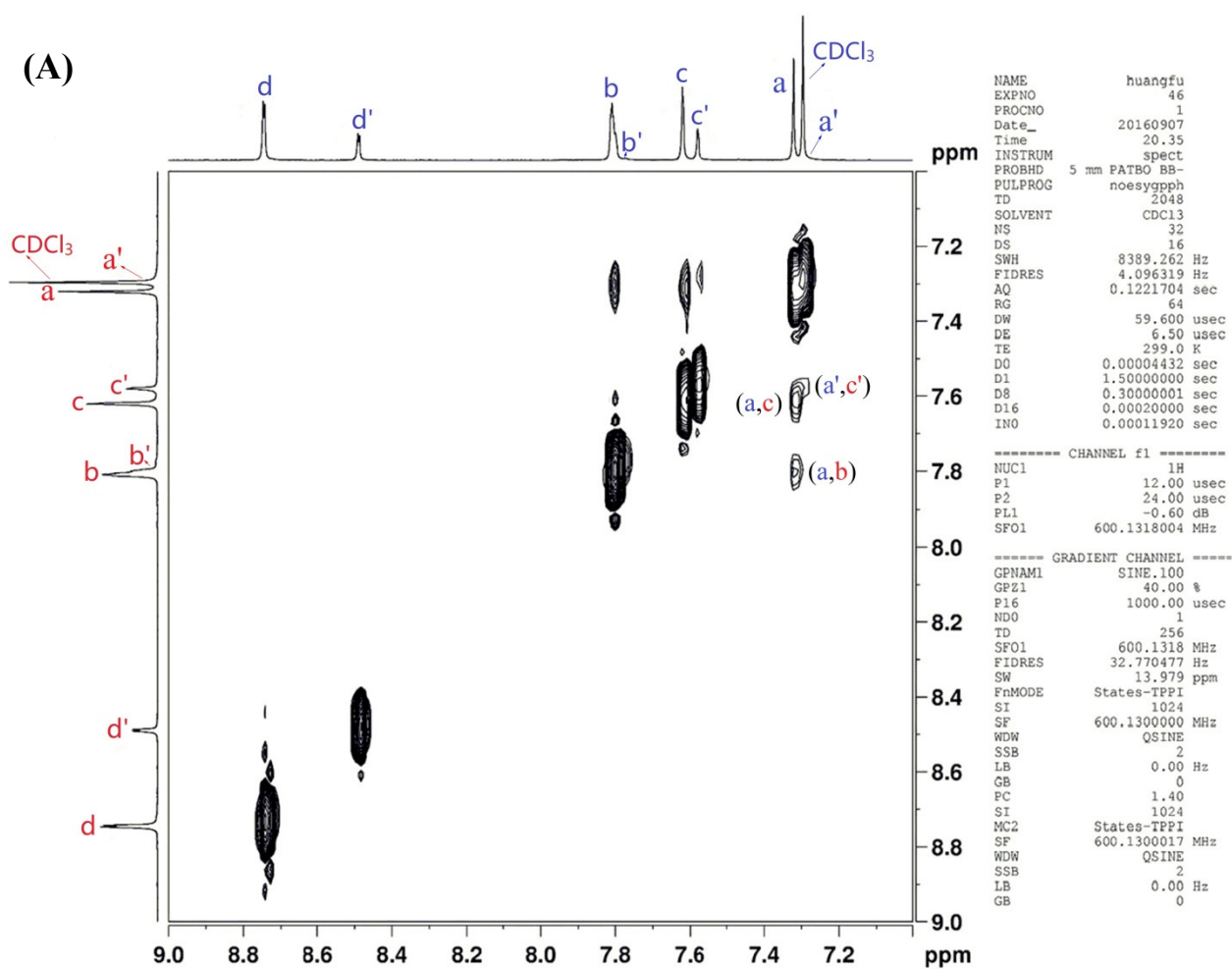
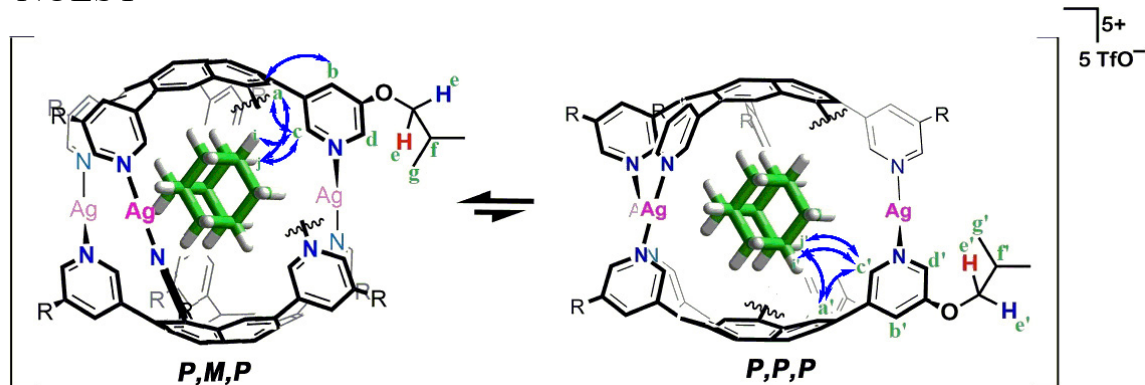


Figure S6. The sectioned Van't Hoff Plot of the interconversion between the $P,P,P/M,M,M$ and the $P,M,P/M,P,M$ conformers for **1** with **2** included.

3.d 2D NMR Spectra for 2c1

NOESY



(B)

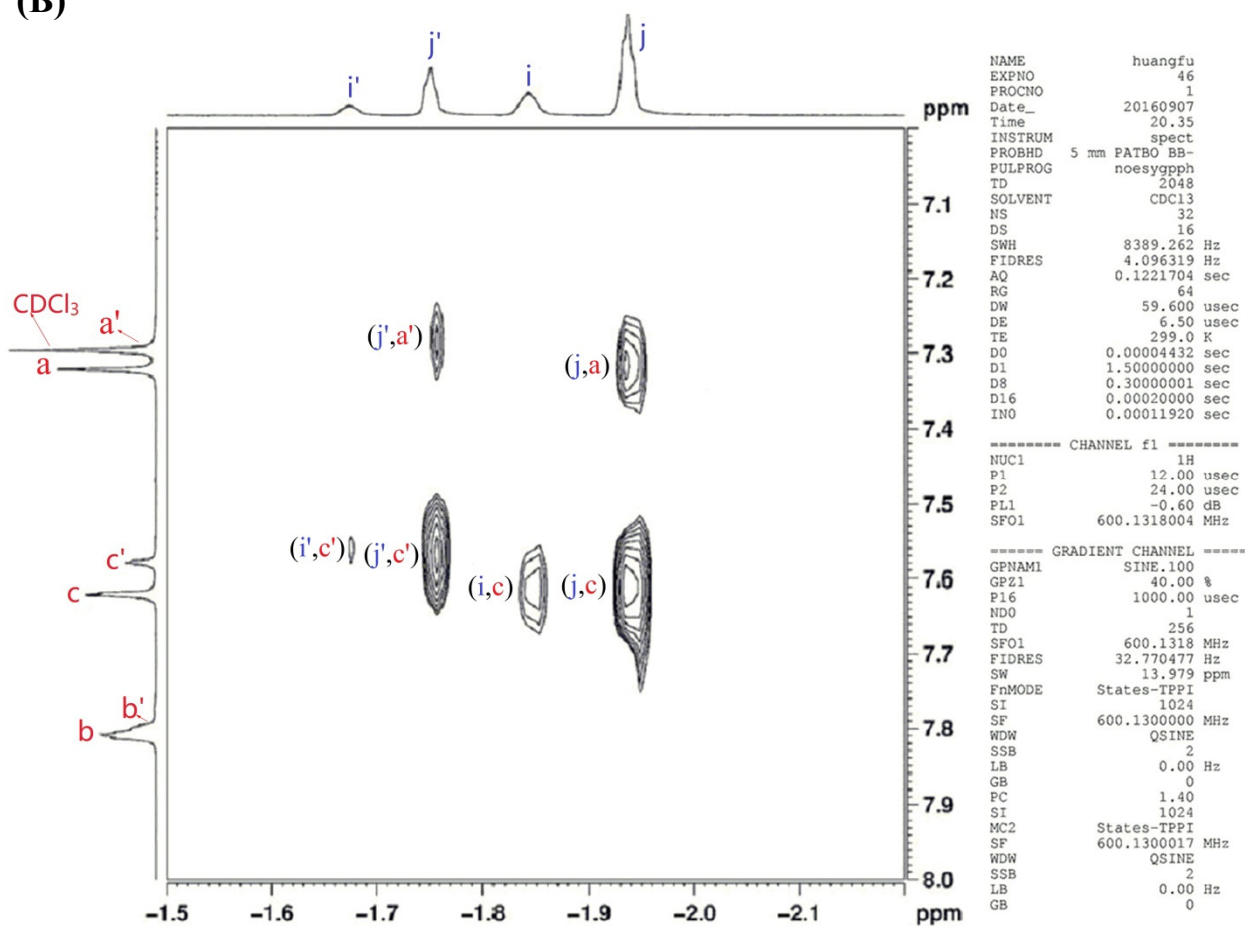
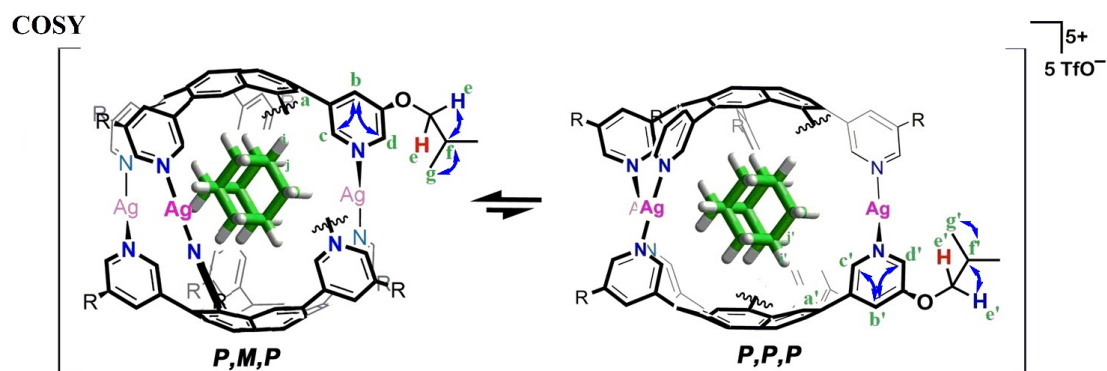
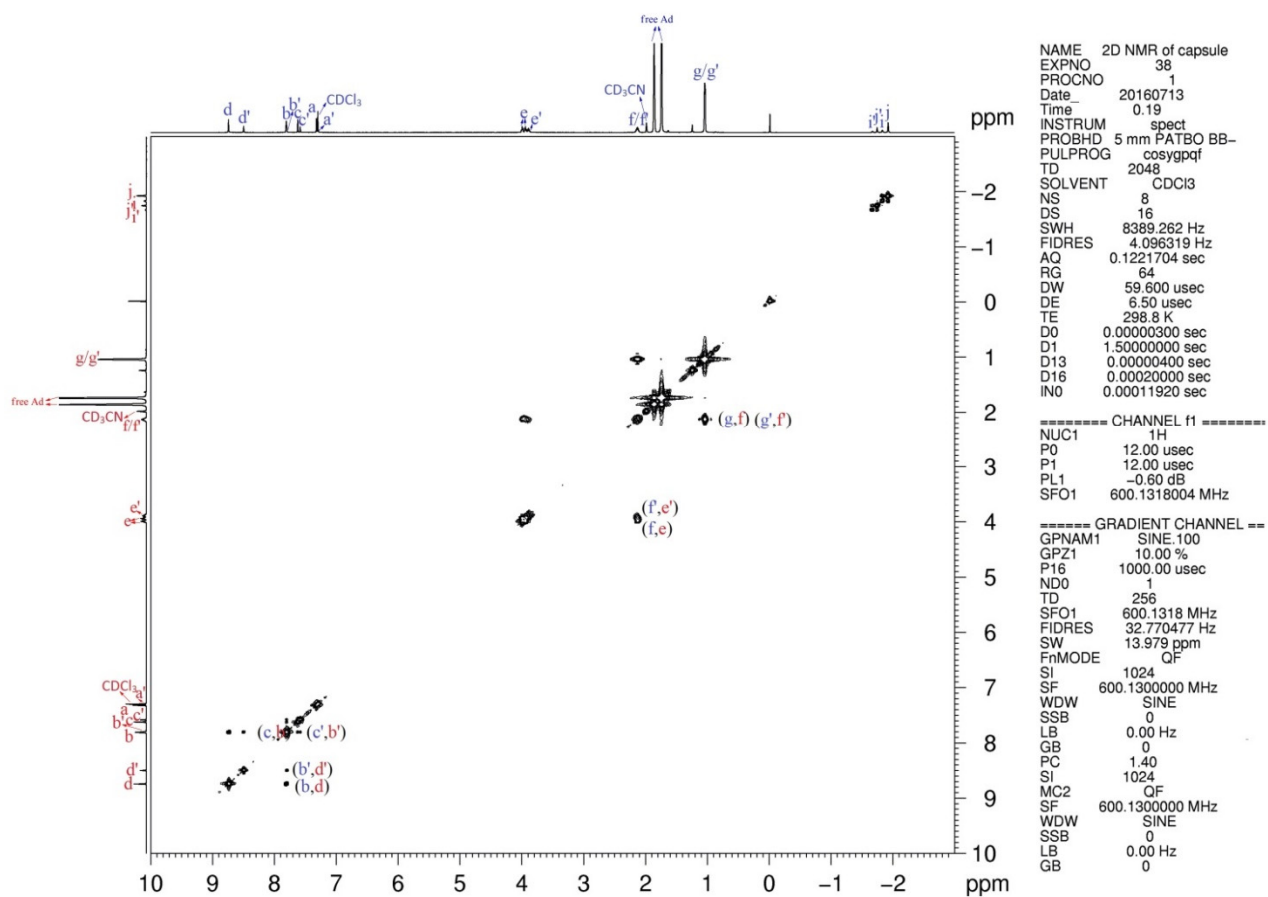


Figure S7. (A) Partial ^1H - ^1H NOESY spectrum (600 MHz, 298 K, 93:7 (v/v) $\text{CDCl}_3/\text{CD}_3\text{CN}$, 4 mM) of **2****c****1** complex (prepared by mixing **1** with 20 equiv. of **2**). (B) Zoom of the spectrum A.



(A)



(to be continued)

(B)

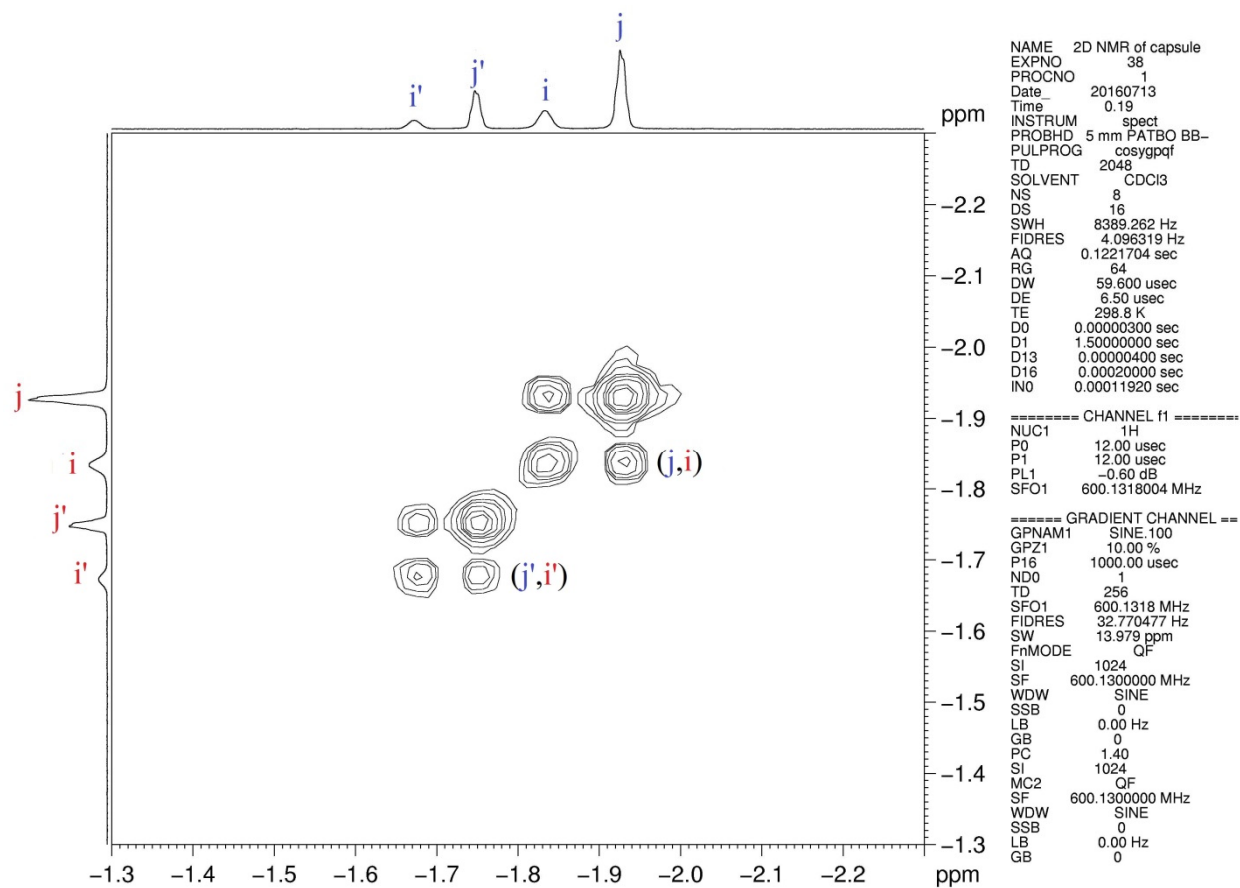
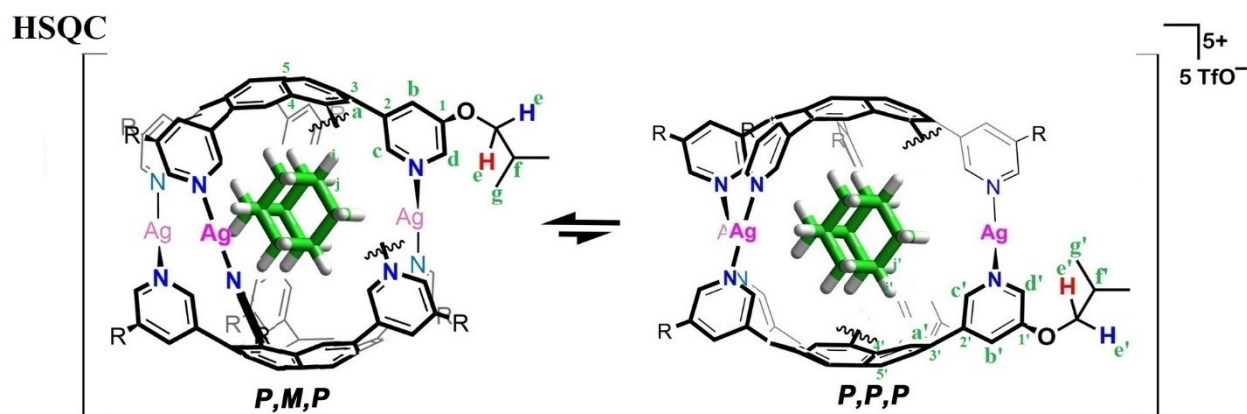
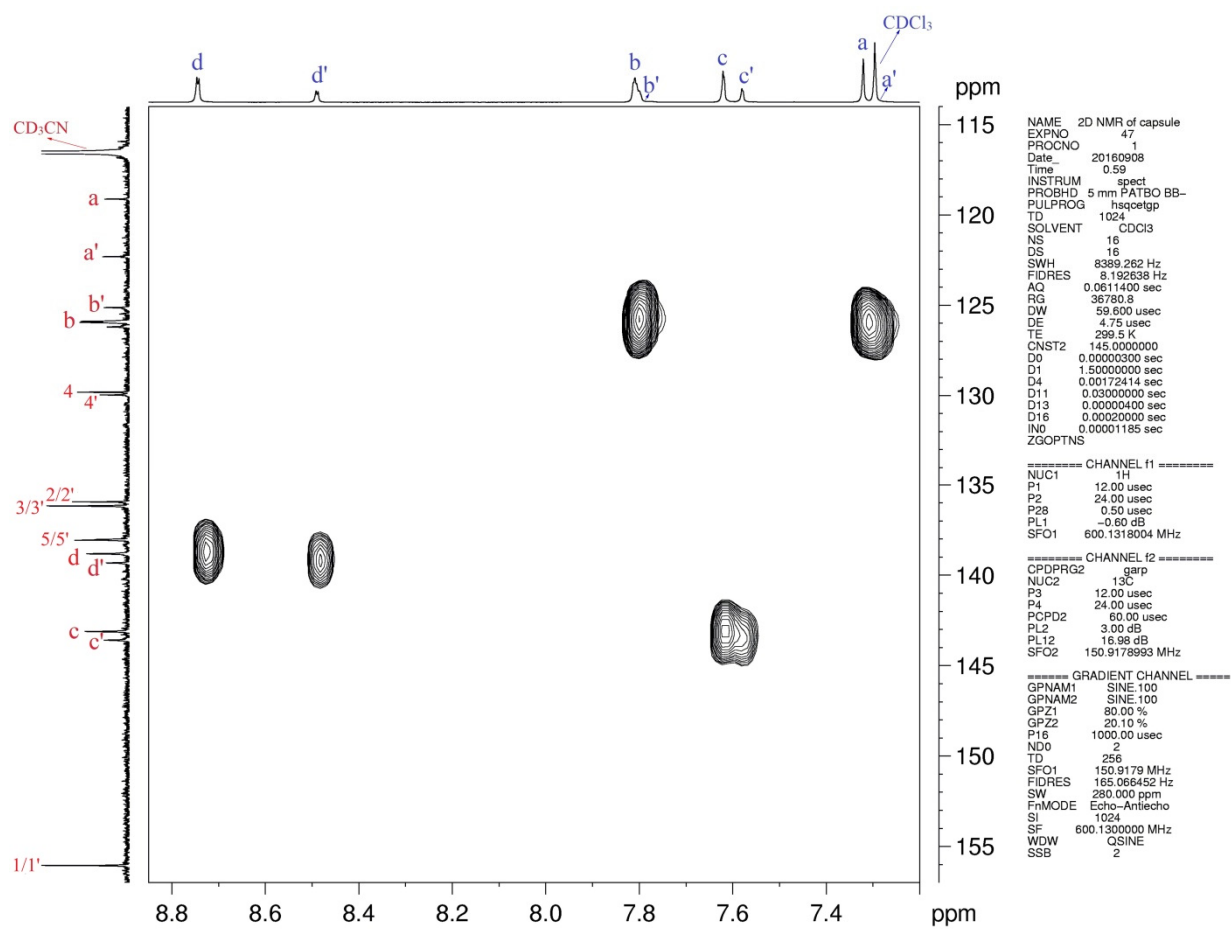


Figure S8. (A) Partial ^1H - ^1H COSY spectrum (600 MHz, 298 K, 93:7 (v/v) $\text{CDCl}_3/\text{CD}_3\text{CN}$, 4 mM) of **2**·**1** (prepared by mixing **1** with 20 equiv. of **2**). (B) Zoom of the spectrum A.



(A)



(to be continued)

(B)

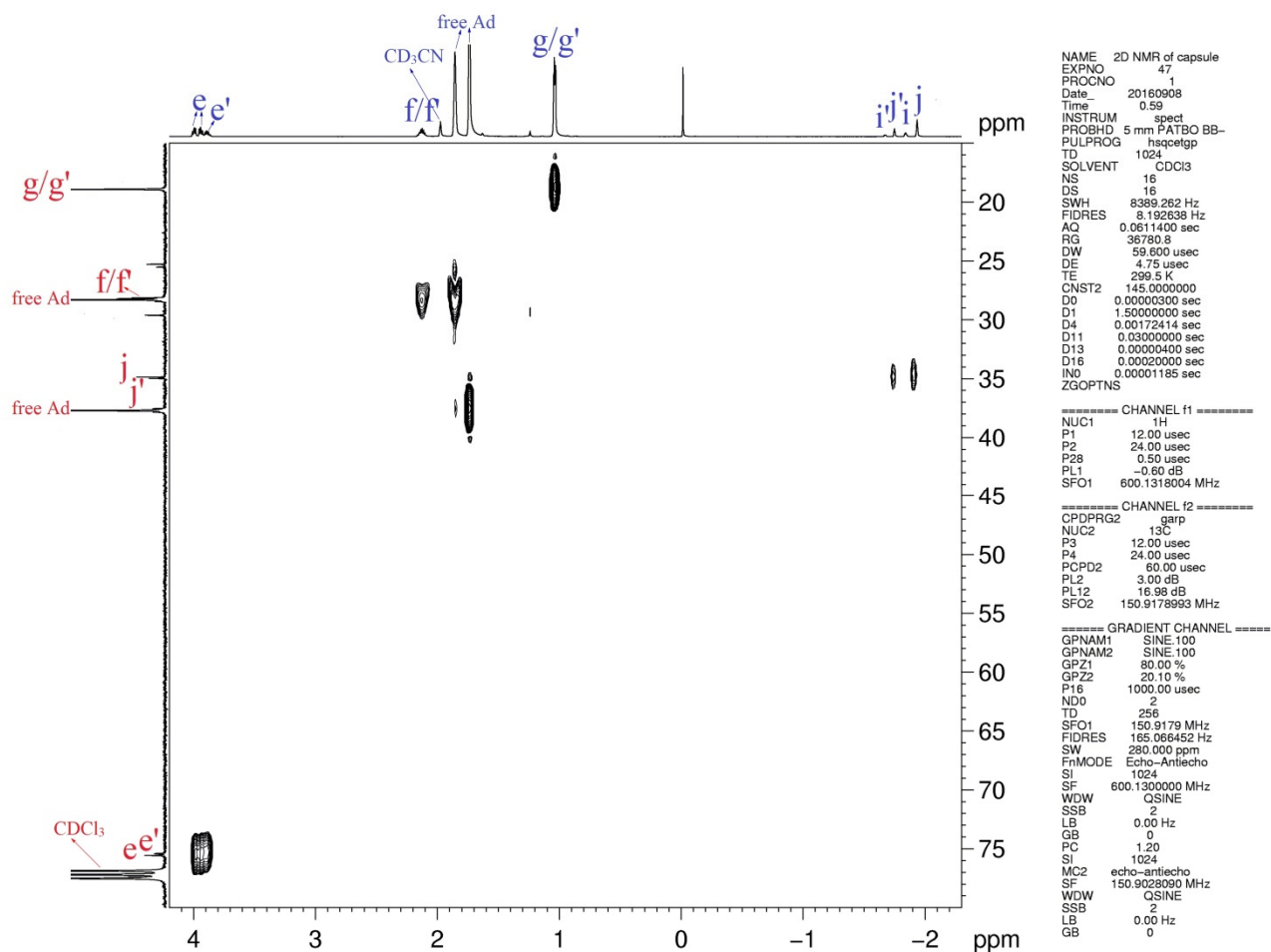
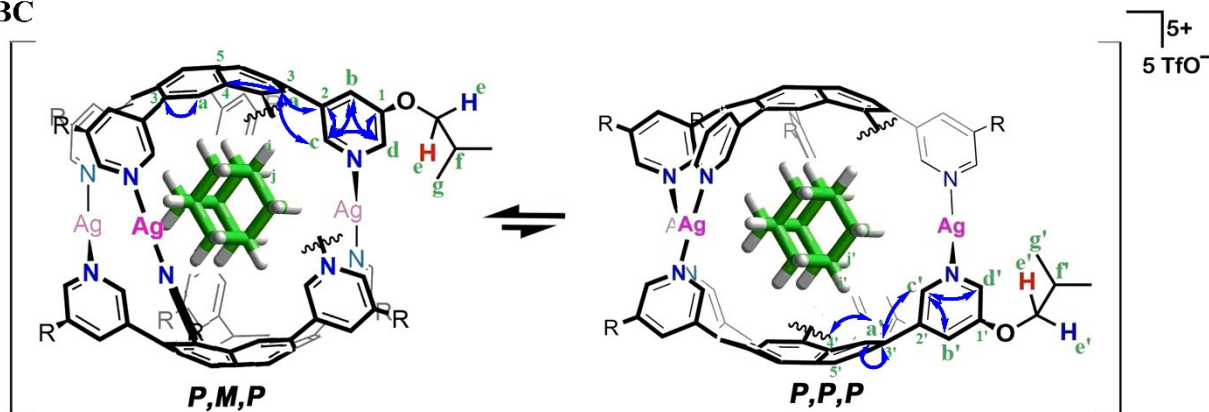
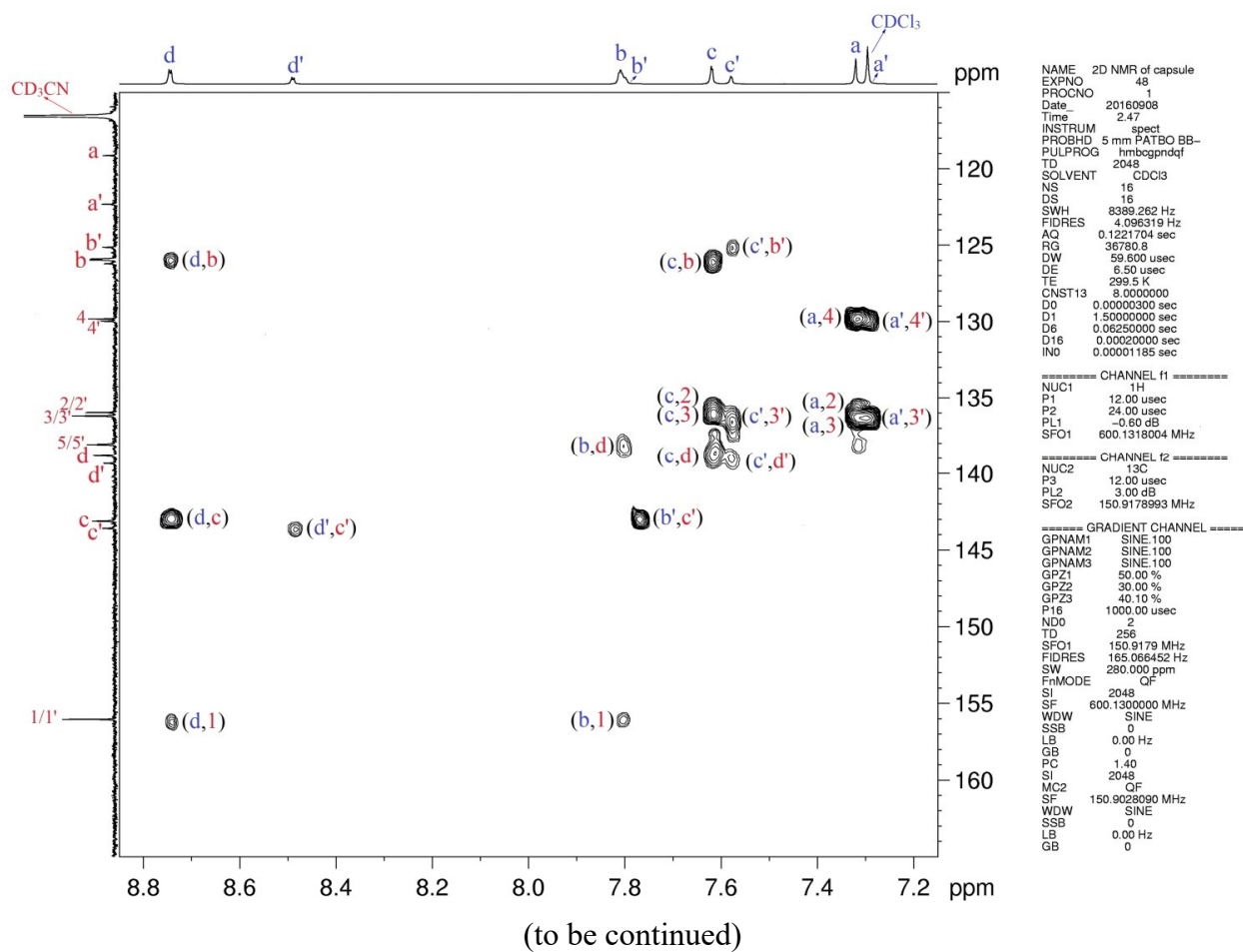


Figure S9. (A) Partial ^1H - ^{13}C HSQC spectrum (600 MHz, 298 K, 93:7 (v/v) $\text{CDCl}_3/\text{CD}_3\text{CN}$, 4 mM) of **2**·**1** (prepared by mixing **1** with 20 equiv. of **2**). (B) Zoom of the spectrum A.

HMBC



(A)



(B)

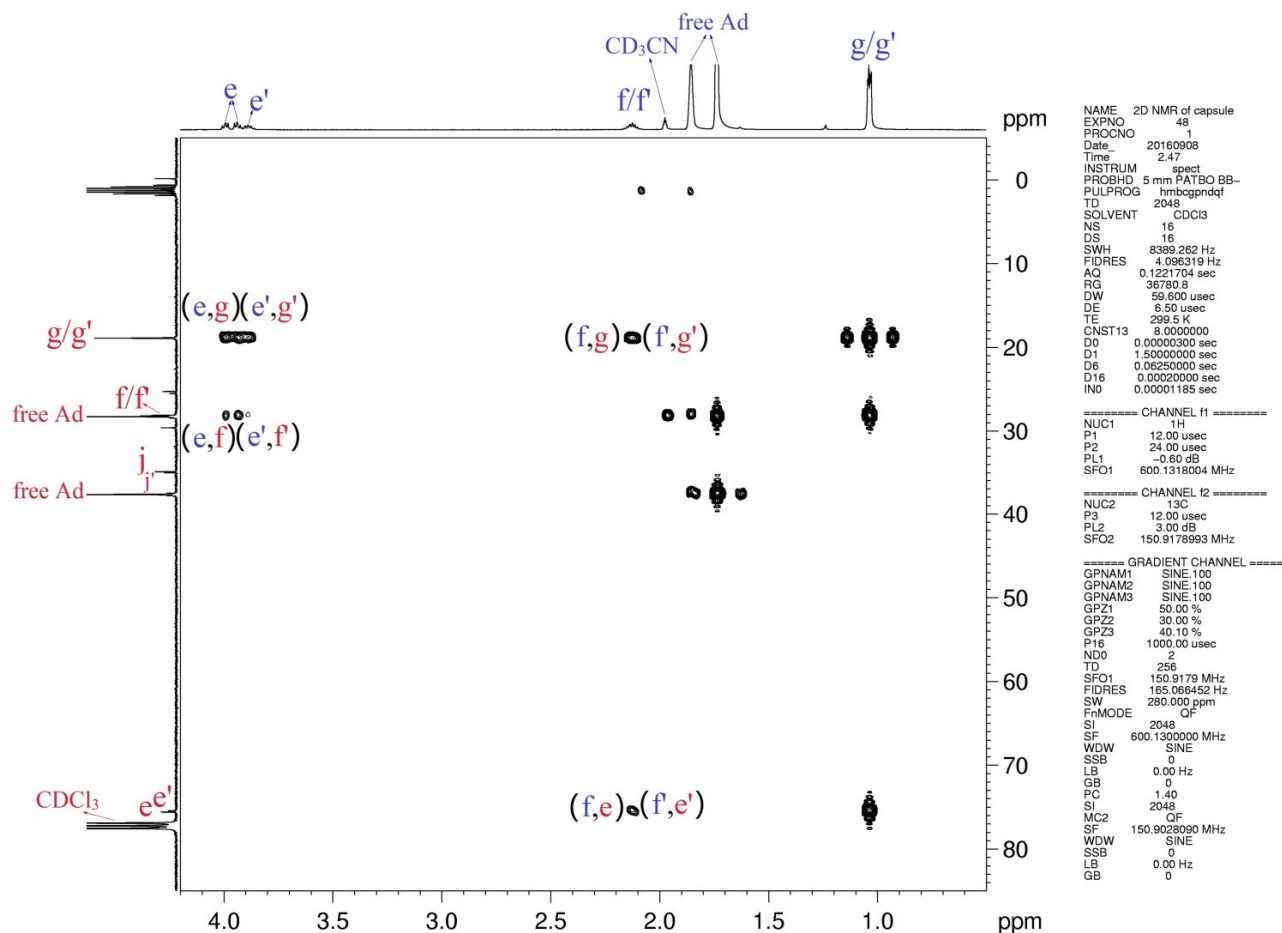


Figure S10. (A) Partial ^1H - ^{13}C HMBC spectrum (600 MHz, 298 K, 93:7 (v/v) $\text{CDCl}_3/\text{CD}_3\text{CN}$, 4 mM) of **2**·**1** (prepared by mixing **1** with 20 equiv. of **2**). (B) Zoom of the spectrum A.

3.e DOSY NMR Spectra of 2 $\subset$ 1

Sample of complex was prepared by mixing cage **1** with 20 equivalents of adamantane, using 93:7 (v/v) CDCl₃/CD₃CN as the solvent. Diffusion NMR experiments were carried out on a Bruker Advance III (¹H, 600 MHz) instrument at 298 K using triple resonance broad-band probe with ATM (5 mm PATBO BB-1H/19F/D Z-GRD) and a Diff30 pulsed field gradient amplifier. The obtained data were processed using the T1/T2 relaxation procedure implemented in Topspin 2.1 software package, where each 2D column was nonlinear-fitted separately. Due to the aggregation of some signals, attenuations of only two aromatic protons signals for each pair of complexes, including H_a and H_c of **2** $\subset$ (P,M,P)/(M,P,M)-**1** and H_a, H_c of **2** $\subset$ (P,P,P)/(M,M,M)-**1**, were employed for the fitting. Diffusion constants were reported as mean of the values obtained from these two runs.

The obtained diffusion coefficients (**D**) are summarized in Table S3. Examples for simulated diffusion decay curves are shown in Figures S12–S13.

Table S3. Summary of diffusion coefficients (*D*, m²·s⁻¹) of **2** $\subset$ (P,M,P)/(M,P,M)-**1** and **2** $\subset$ (P,P,P)/(M,M,M)-**1** in 93:7 (v/v) CDCl₃/CD₃CN at 298 K.^a

Species	Data Sets and <i>D</i>	Run 1	Run 2	Mean (<i>D</i>)	δ^b (Mean(<i>D</i>))
2 $\subset$ (P,M,P)/(M,P,M)- 1	Peak	H _a , 8.74	H _c , 7.62	/	/
	<i>D</i> (×10 ⁻¹⁰)	2.601	2.629	2.615	0.020
2 $\subset$ (P,P,P)/(M,M,M)- 1	Peak	H _a , 8.50	H _c , 7.58	/	/
	<i>D</i> (×10 ⁻¹⁰)	2.624	2.489	2.557	0.095

^a The diffusion coefficients were derived from the DOSY experiments by using the T1/T2 Relaxation procedure implemented in Topspin 2.1 software package. The data sets employed for the fitting were denoted by the labels of the protons (the labels of the atoms are shown in Figure S11) or the chemical shift of the peaks. Throughout the table, the unit of diffusion coefficients, including *D* and the mean *D*, is m²·s⁻¹. The unit of chemical shift is ppm. ^b Standard derivation of the mean *D*.

DOSY

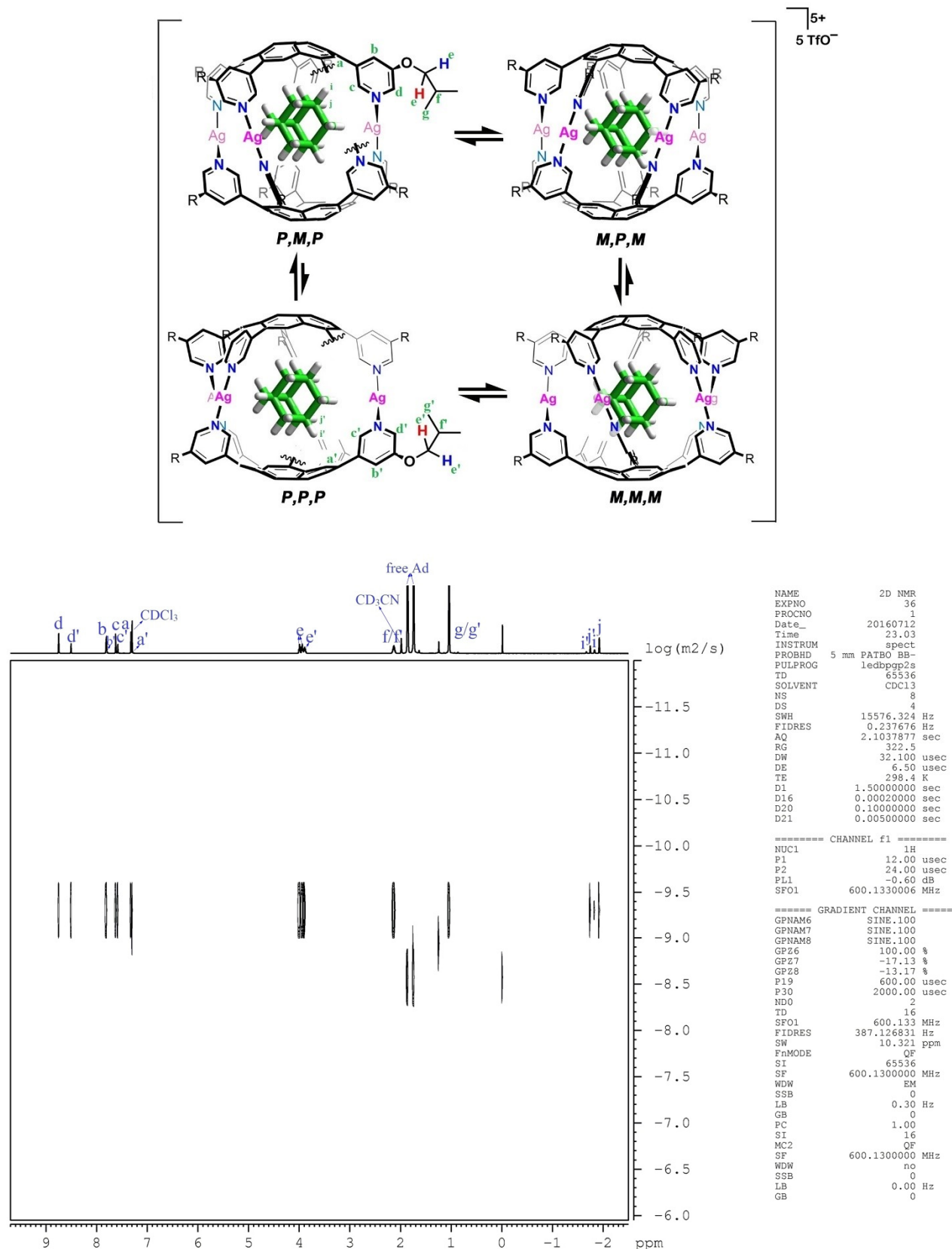


Figure S11. Part of the DOSY spectrum (600 MHz, 298 K, 4 mM) of **2** ⊂ **1** in 93:7 (v/v) CDCl₃/CD₃CN.

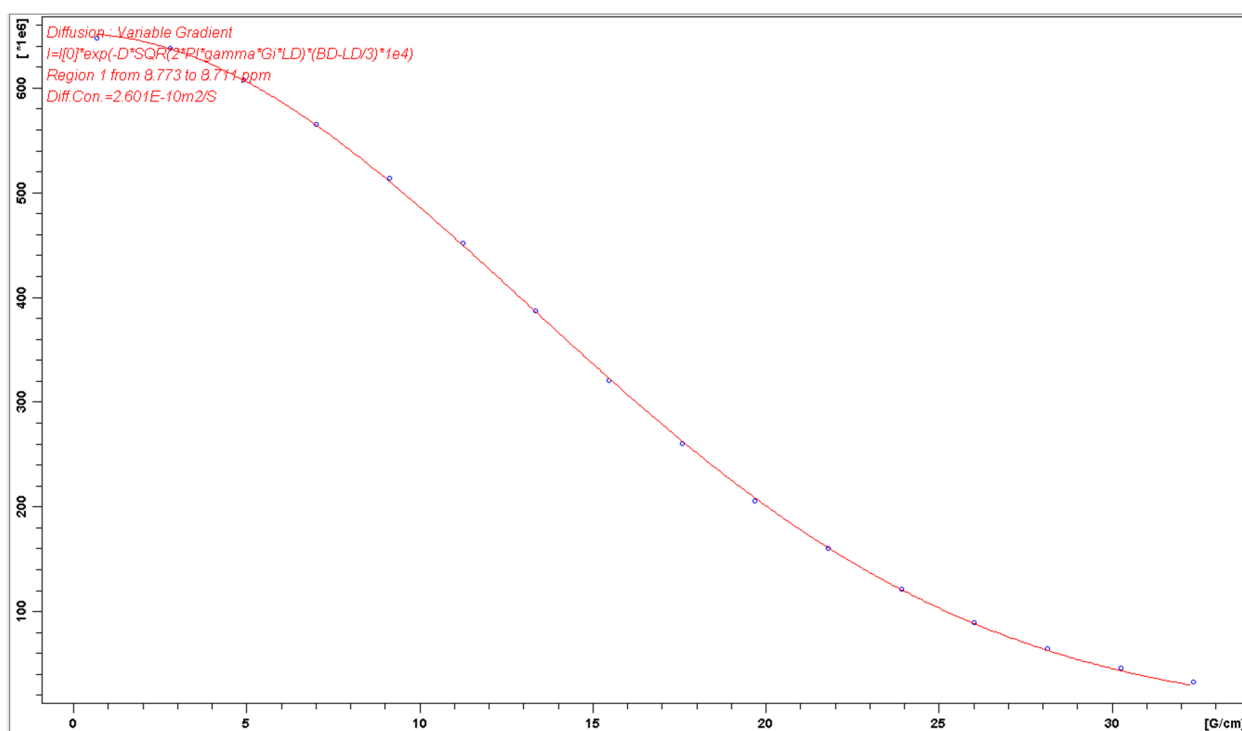


Figure S12. Simulated diffusion decay curve for the signal of H_a (peak at 8.74 ppm) of 2 ⊂ (P,M,P)/(M,P,M)-1.

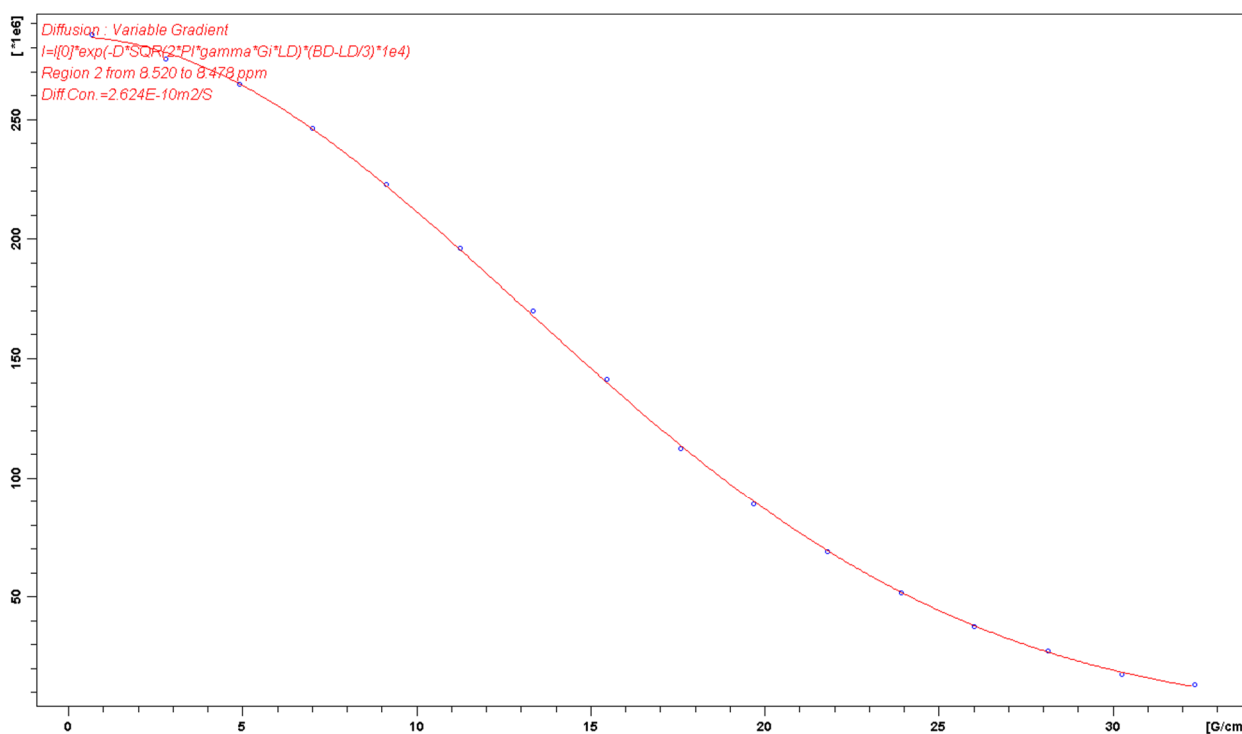


Figure S13. Simulated diffusion decay curve for the signal of H_d (peak at 8.50 ppm) of 2 ⊂ (P,P,P)/(M,M,M)-1.

3.f HRMS-ESI Spectrum of 2⊂1

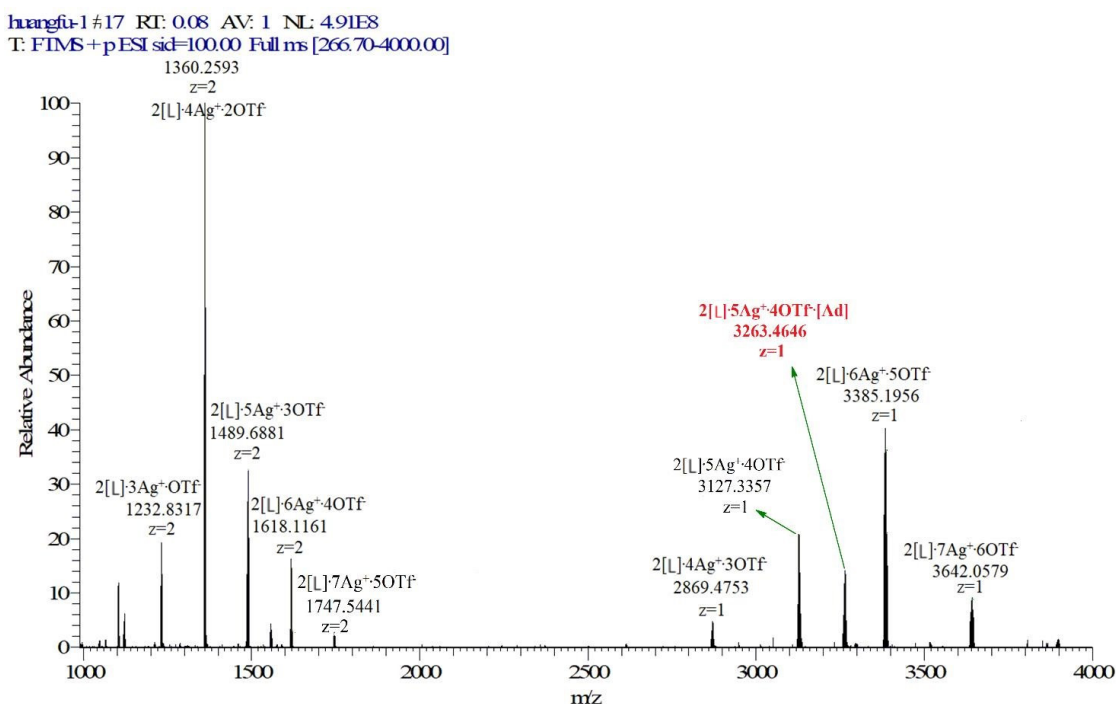


Figure S14. HRMS-ESI spectrum of 2⊂1, which was obtained in the positive ion mode using 7% CH₃CN within CHCl₃ as the mobile flow phase, in which the ligand for 1 are labeled "L". Despite that most of 2 got released from the complexes during the analysis, signals of 2⊂1 was still observable. Table S4 shows the summary of data corresponding to the experimental and the simulated expanded isotopic cluster of the complexes.

Table S4. Summary of the HRMS-ESI data of the expanded isotopic cluster for the cage complex.

Species	Charge	Spectrum patterns	Chemical Formula	Data
2[1]·5Ag ⁺ ·4OTf·[2]	+1		C ₁₄₄ H ₁₄₆ N ₁₀ O ₂₂ F ₁₂ S ₄ Ag ₅ at M ⁺	Found: 3263.4749 (100.0%, 5.0 ppm), 3264.4514 (96.4%, -2.5 ppm), 3265.4659 (77.7%, 1.9 ppm), 3262.4626 (76.0%, 1.1 ppm), 3266.4836 (58.1%, 7.2 ppm), 3261.4452 (54.4%, -3.8 ppm), 3267.4594 (48.5%, -0.4 ppm), 3260.4739 (30.7%, 4.7 ppm), 3268.4753 (29.3%, 4.3 ppm).

4. Differentiation of Adamantane and Its Derivatives

As the first group of differentiation objects in our proof-of-concept studies, three kinds of adamantane-based guest molecules, including adamantane (**2**), 1-fluoroadamantane (**2b**) and 1-chloroadamantane (**2c**), were investigated at 298 K. The associated ^1H NMR titration experiments on **2b** and **2c** were carried out through the same procedure as that for **2** described above (Section 3.a in this Supporting Information), in which a solution of **2b** or **2c** (100 mM) in 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$ was gradually added into the solution of **1** (1 mM, 0.5 mL) in the same solvent mixture. As same as that in the case of **2**, the investigations on **2b** and **2c** were repeated for totally three times.

Examples of the ^1H NMR titration spectra regarding to **2**, **2b** and **2c** are shown in Figure S1 and Figures S15–S16.

CCD Determinations. Relative amounts of $P,M,P/M,P,M$ and $P,P,P/M,M,M$ conformers used for CCD determinations were derived from the integrations of H_d and $\text{H}_\text{d'}$ of the complex species in the ^1H NMR spectra. Notably, different from that in the cases of association constant determinations (Table S1) in which only part of ^1H NMR spectra are useful for the calculations, most of spectra obtained from the ^1H NMR titration experiments can be utilized for the CCD determination.

Obtained data are summarized in Table S5.

Table S5. Summary of CCDs of cage **1** upon encapsulation of adamantane (**2**), 1-fluoroadamantane (**2b**) and 1-chloroadamantane (**2c**) in 7:93 (v/v) CD₃CN/CDCl₃ at 298 K.^a

2					2b					2c				
Equiv	Run1	Run2	Run 3	Mean ^b	Equiv	Run1	Run2	Run 3	Mean ^b	Equiv	Run1	Run2	Run 3	Mean ^b
0.2	1.82	1.92	1.92	1.89	1	1.25	1.06	1.06	1.13	1	0.78	0.78	0.74	0.77
0.4	2.13	2.08	2.04	2.08	2	1.41	1.28	1.28	1.32	2	0.85	0.87	0.83	0.85
0.6	2.08	1.96	2.00	2.01	3	1.43	1.37	1.37	1.39	3	0.86	0.90	0.82	0.86
0.8	2.04	2.08	2.13	2.08	4	1.45	1.39	1.37	1.40	4	0.87	0.88	0.86	0.87
1	2.04	2.00	2.08	2.04	5	1.43	1.41	1.41	1.42	5	0.91	0.88	0.86	0.89
1.2	2.08	2.08	2.13	2.10	6	1.45	1.43	1.43	1.44	6	0.89	0.92	0.85	0.89
1.6	2.04	2.04	2.17	2.09	8	1.47	1.41	1.43	1.44	8	0.92	0.93	0.88	0.91
2	2.04	2.13	2.13	2.10	10	1.52	1.43	1.43	1.46	10	0.93	0.92	0.88	0.91
3	2.08	2.13	2.22	2.14	15	1.47	1.45	1.45	1.46	15	0.95	0.93	0.92	0.93
4	2.08	2.17	2.22	2.16	20	1.49	1.45	1.45	1.46	20	0.93	0.93	0.89	0.92
5	2.17	2.22	2.27	2.22	25	1.43	1.49	1.45	1.46	25	0.94	0.93	0.93	0.94
7	2.33	2.33	2.17	2.28	Mean(CCD) ^c				1.40	Mean(CCD) ^c				0.88
10	2.13	2.13	2.13	2.13	σ(Mean CCD) ^d				0.10	σ(Mean CCD) ^d				0.05
15	2.17	2.13	2.04	2.11										
Mean(CCD) ^c				2.10										
σ(Mean CCD) ^d				0.09										

^a Data were derived the ¹H NMR integrations of signals of H_d and H_{d'}. ^b the mean CCD value of the three sets of data. ^c the overall mean CCD of all sets of data. ^d Standard deviation of the overall mean value.

Example of ^1H NMR Titration Spectra

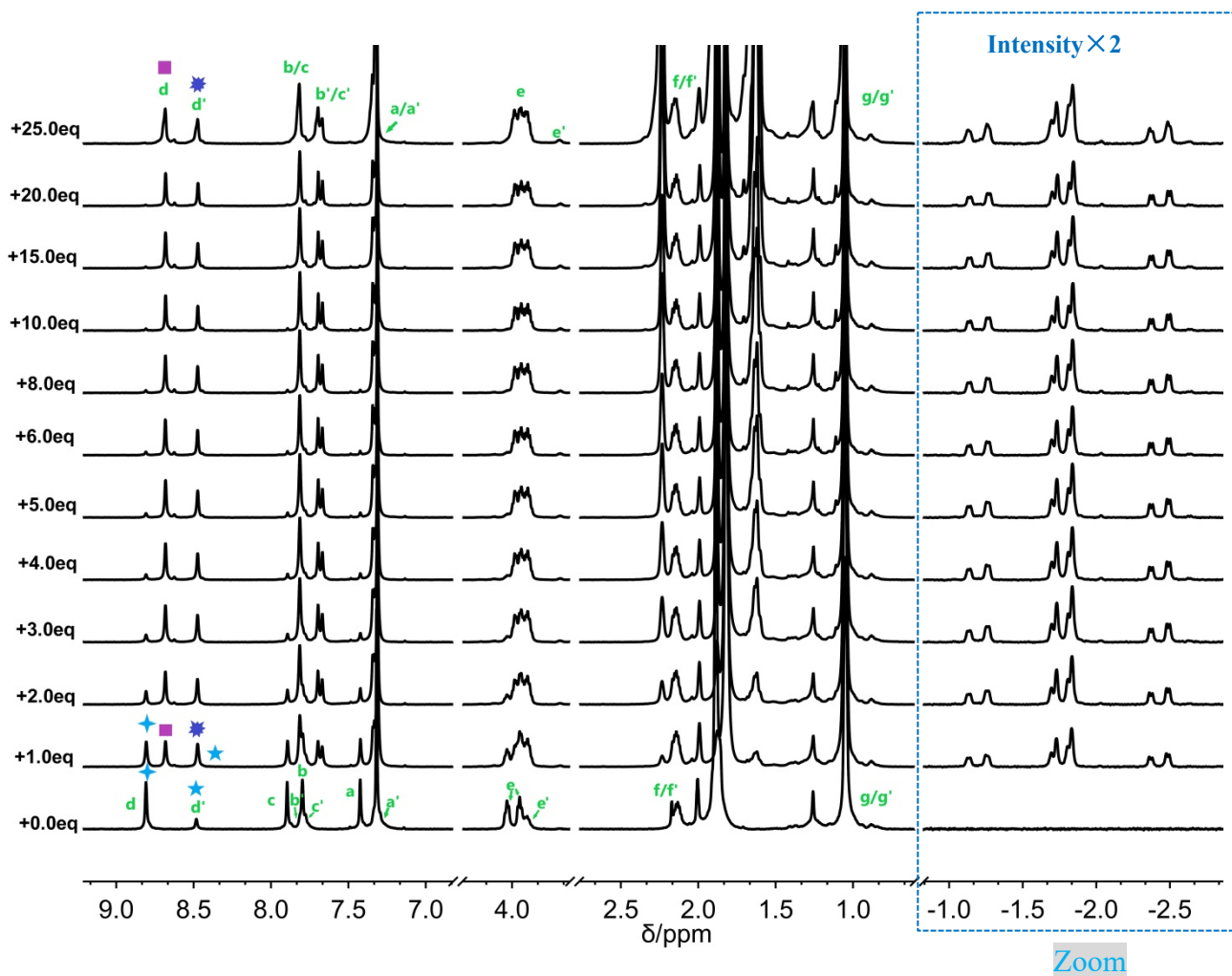


Figure S15. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (1 mM) upon the addition of 1-fluoroadamantane (**2b**) (100 mM). $\star = (P,M,P)/(M,P,M)\text{-1}$, $\star = (P,P,P)/(M,M,M)\text{-1}$, $\blacksquare = 2b \subset (P,M,P)/(M,P,M)\text{-1}$, $\star = 2b \subset (P,P,P)/(M,M,M)\text{-1}$.

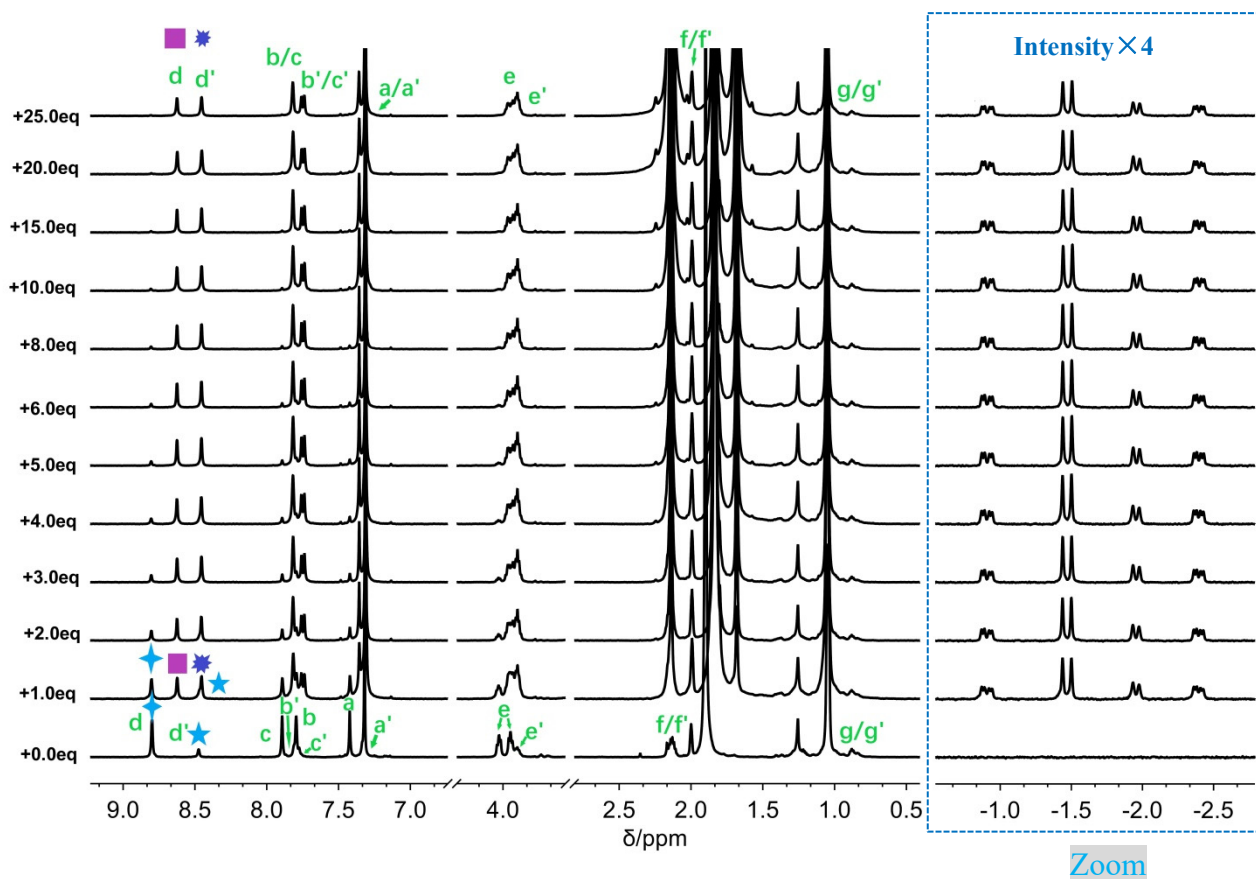


Figure S16. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (1 mM) upon the addition of 1-chloroadamantane (**2c**) (100 mM). $\blacklozenge = (P,M,P)/(M,P,M)$ -**1**, $\star = (P,P,P)/(M,M,M)$ -**1**, $\blacksquare = 2\text{c} \subset (P,M,P)/(M,P,M)$ -**1**, $\blacklozenge = 2\text{c} \subset (P,P,P)/(M,M,M)$ -**1**.

5. Differentiation of Three Bridged Bicyclic Compounds

In this proof-of-concept study, three kinds of bridged bicyclic compounds, including (*1S*)-(-)-camphanic acid (**3a**), (*S*)-(+)-ketopininc acid (**3b**), and bicyclo[2.2.2]octane-1,4-dicarboxylic acid (**3c**), were investigated. Due to the poor solubility of **3c** in most of the common solvents, the mother solutions of **3a–c** were prepared uniformly in DMSO-*d*₆. In the ¹H NMR titration experiments, to a solution of molecular cage **1** (1 mM, 0.5 mL) in 7:93 (v/v) CD₃CN/CDCl₃, a solution of **3a** (150 mM) or **3c** (150 mM) or **3b** (500 mM) in DMSO-*d*₆ was gradually added. A series of ¹H NMR spectra of the samples were recorded at 298 K. The investigation on each guest was repeated for 3 times. Examples of the obtained ¹H NMR spectra are shown in Figures S17–S19. Relative amounts of *P,M,P/M,P,M* and *P,P,P/M,M,M* conformers were derived from the integrations of H_d and H_{d'} of the complex species in the NMR spectra. The obtained CCDs are summarized in Table S6.

Table S6. Summary of CCDs of cage **1** upon encapsulation of (*1S*)-(-)-camphanic acid (**3a**), (*S*)-(+)-ketopininc acid (**3b**) and bicyclo[2.2.2]octane-1,4-dicarboxylic acid (**3c**) in 7:93 (v/v) CD₃CN/CDCl₃ with the presence of different amount of DMSO-*d*₆ at 298 K. ^a

V _{DMSO} /V _{Total} (%)	3a							3b							3c						
	Equiv	Run1	Run2	Run3	Mean ^b	σ ^c		Equiv	Run1	Run2	Run3	Mean ^b	σ ^c		Equiv	Run1	Run2	Run3	Mean ^b	σ ^c	
0.79	1.2	1.27	1.33	1.37	1.32	0.05		4	0.93	0.93	0.92	0.93	0.01		1.2	1.56	1.61	1.61	1.60	0.03	
1.19	1.8	1.39	1.41	1.43	1.41	0.02		6	0.98	1.00	1.00	0.99	0.01		1.8	1.82	1.85	1.89	1.85	0.03	
1.57	2.4	1.43	1.49	1.47	1.46	0.03		8	1.05	1.05	1.03	1.05	0.01		2.4	1.92	1.96	2.00	1.96	0.04	
1.96	3.0	1.54	1.56	1.52	1.54	0.02		10	1.12	1.10	1.10	1.11	0.01		3.0	2.13	2.22	2.17	2.17	0.05	
2.34	3.6	1.64	1.59	1.64	1.62	0.03		12	1.16	1.18	1.12	1.15	0.03		3.6	2.22	2.27	2.33	2.27	0.05	
2.72	4.2	1.69	1.64	1.79	1.71	0.07		14	1.22	1.19	1.18	1.20	0.02		4.2	2.38	2.44	2.44	2.42	0.03	
3.10	4.8	1.79	1.72	1.75	1.75	0.03		16	1.30	1.27	1.23	1.27	0.03		4.8	2.56	2.50	2.56	2.54	0.04	
3.47	5.4	1.79	1.79	1.75	1.78	0.02		18	1.39	1.32	1.28	1.33	0.05		5.4	2.63	2.63	2.70	2.66	0.04	
3.85	6.0	1.89	1.79	1.82	1.83	0.05		20	1.45	1.37	1.32	1.38	0.07		6.0	2.78	2.78	2.78	2.78	0.00	
4.21	6.6	1.92	1.89	1.89	1.90	0.02		22	1.56	1.49	1.41	1.49	0.08		6.6	2.78	2.86	2.86	2.83	0.05	
4.58	7.2	2.08	1.92	2.00	2.00	0.08		24	1.64	1.56	1.43	1.54	0.11		7.2	3.13	3.03	2.94	3.03	0.09	

^a Data were derived the ¹H NMR integrations of signals of H_d and H_{d'}. ^b the mean CCD value of the three sets of data. ^c Standard deviation of the mean CCD value.

Example of ^1H NMR Titration Spectra

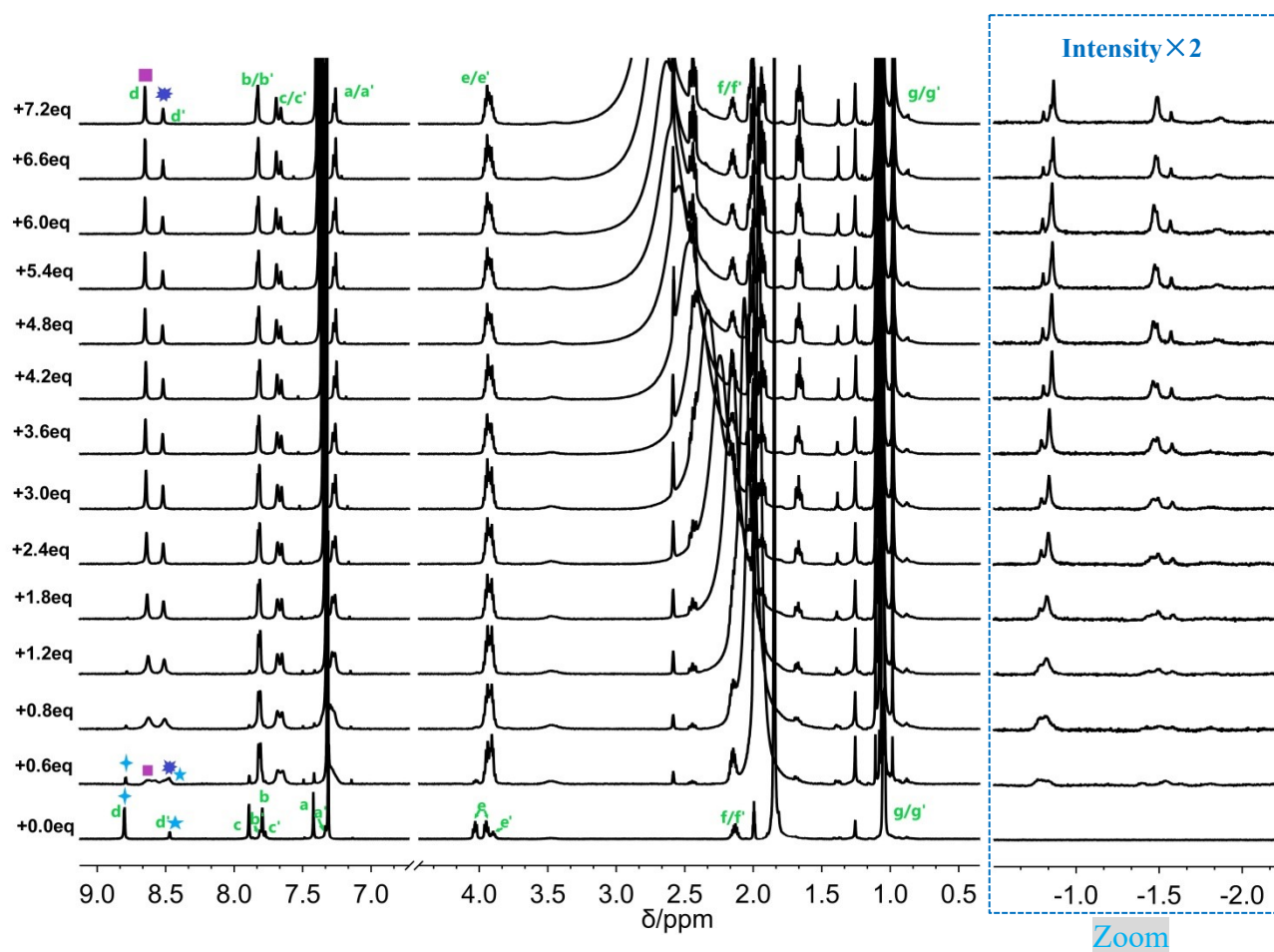


Figure S17. Changes of ^1H NMR spectra (600 MHz, 298 K) of molecular cage **1** (1 mM, 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) upon the addition of *(1S)*-(-)-camphanic acid (**3a**) (150 mM in $\text{DMSO}-d_6$). $\star$ = *(P,M,P)/(M,P,M)*-**1**, $\star$ = *(P,P,P)/(M,M,M)*-**1**, $\blacksquare$ = **3a** $\subset$ *(P,M,P)/(M,P,M)*-**1**, $\star$ = **3a** $\subset$ *(P,P,P)/(M,M,M)*-**1**.

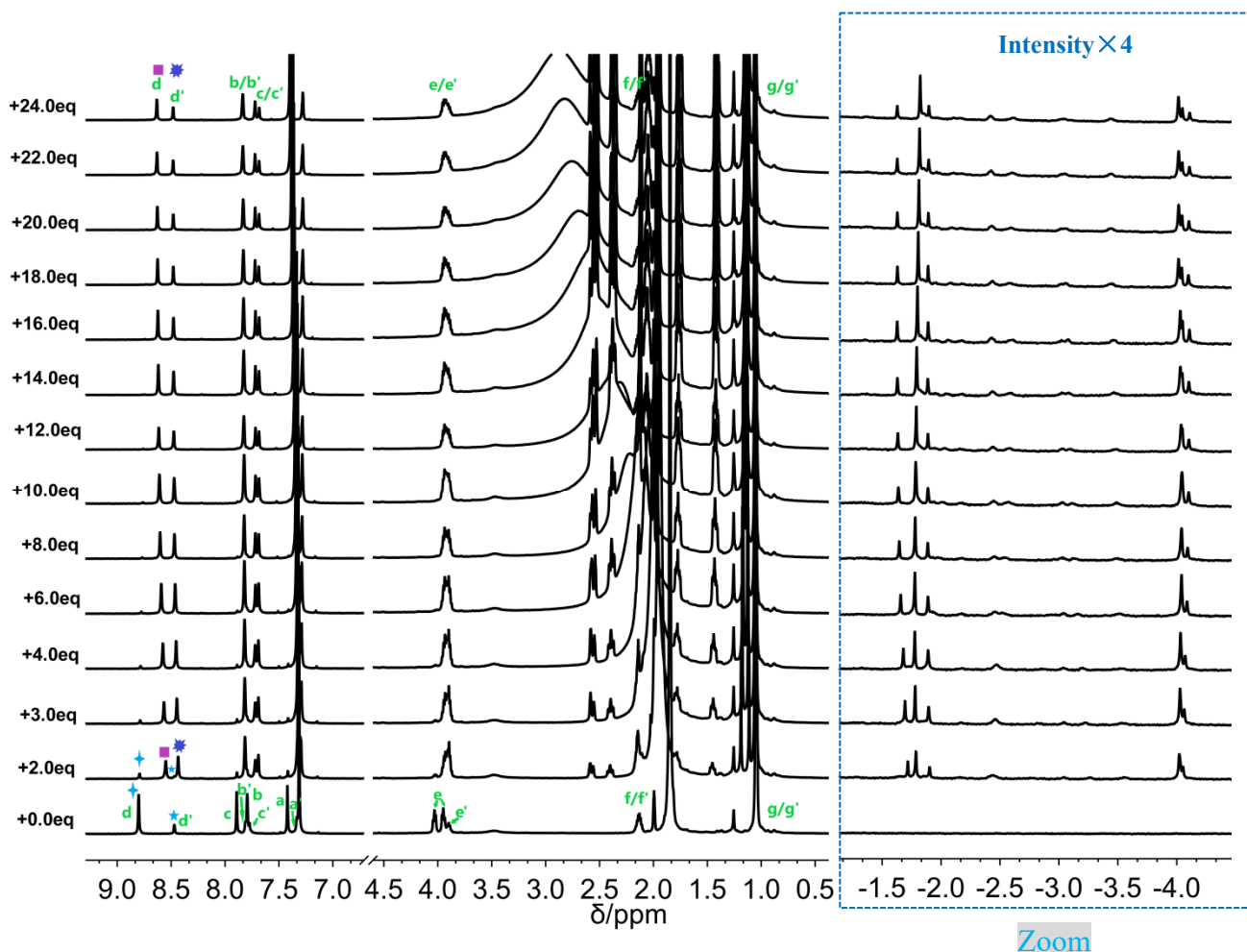


Figure S18. Changes of ^1H NMR spectra (600 MHz, 298 K) of molecular cage **1** (1 mM, 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) upon the addition of *(S)*-(+)-ketopinic acid (**3b**) (500 mM in $\text{DMSO}-d_6$). $\star = (P,M,P)/(M,P,M)$ -**1**, $\star = (P,P,P)/(M,M,M)$ -**1**, $\blacksquare = \mathbf{3a} \subset (P,M,P)/(M,P,M)$ -**1**, $\star = \mathbf{3a} \subset (P,P,P)/(M,M,M)$ -**1**.

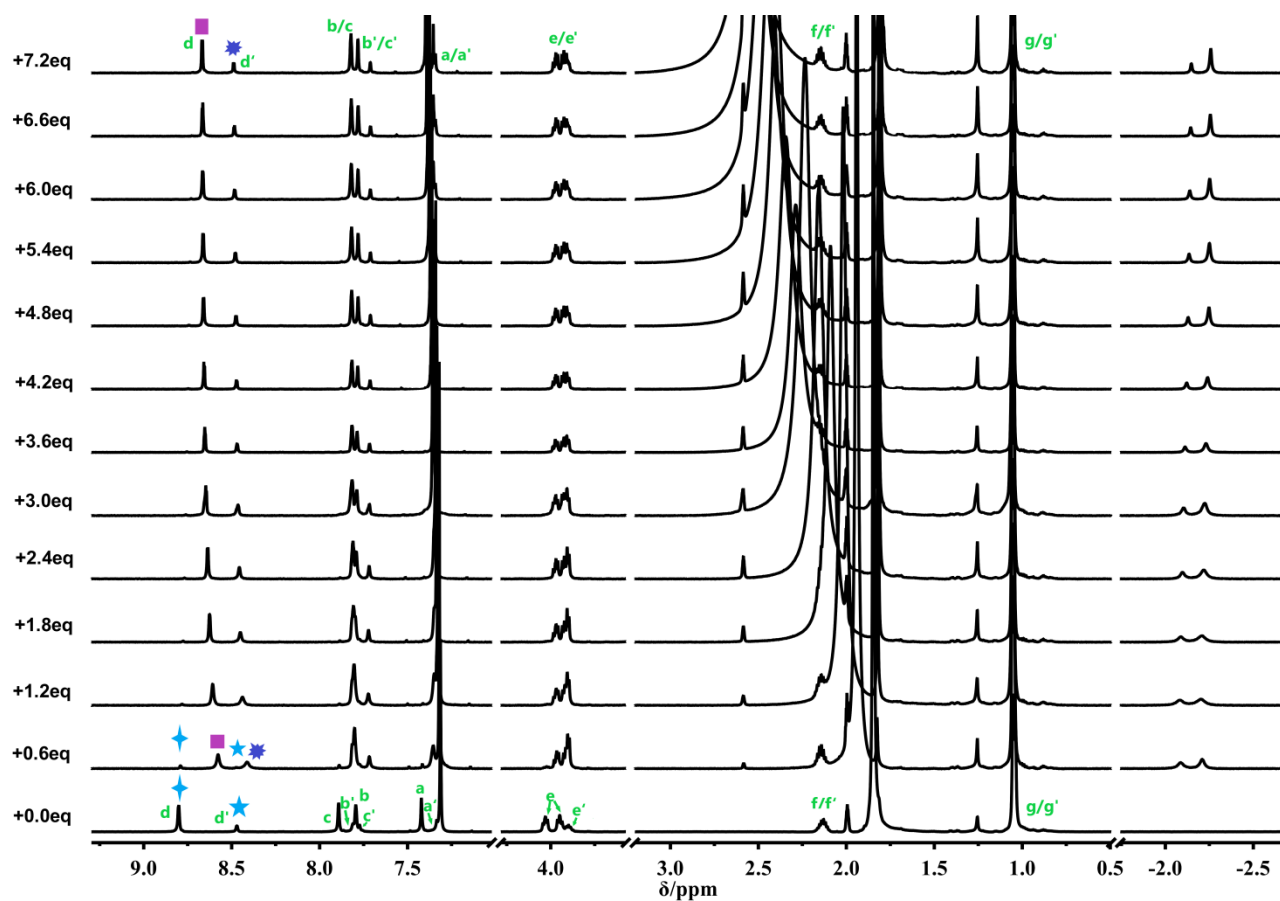


Figure S19. Changes of ^1H NMR spectra (600 MHz, 298 K) of molecular cage **1** (1 mM, 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) upon the addition of bicyclo[2.2.2]octane-1,4-dicarboxylic acid (**3c**) (150 mM in $\text{DMSO}-d_6$). $\star = (P,M,P)/(M,P,M)$ -**1**, $\star = (P,P,P)/(M,M,M)$ -**1**, $\blacksquare = 3c \subset (P,M,P)/(M,P,M)$ -**1**, $\star = 3c \subset (P,P,P)/(M,M,M)$ -**1**.

6. Differentiation of Three Adamantanediols Isomers

Three kinds of adamantanediols, including *trans*-1,4-adamantanediol (**4a**), *cis*-1,4-adamantanediol (**4b**), and *rac*-1,2-adamantanediol (**4c**), were investigated in the study. The preparations of **4a–c** are described in Section 10 in this Supporting Information.

¹H NMR Titration Experiments. Since the compounds of **4a–c** (in particular **4a–b**) are hardly or just slightly soluble in many common solvents but have a very good solubility in DMSO-*d*₆, the mother solutions of **4a–c** were thus prepared using DMSO-*d*₆ as the solvent. To a solution of molecular cage **1** (1 mM, 0.5 mL) in 7:93 (v/v) CD₃CN/CDCl₃, a solution of **4a** or **4b** or **4c** (100 mM) in DMSO-*d*₆ was gradually added. In this process, a series of ¹H NMR spectra of the sample was recorded at 298 K. To estimate the standard deviation, the investigation on each guest molecule was repeated for totally three times. Examples of the obtained ¹H NMR spectra are shown in Figures S20–S22. Relative amounts of guest⊂[(*P,P,P*)/(*M,M,M*)-**1**] and guest⊂[(*P,M,P*)/(*M,P,M*)-**1**] were derived from the integrations of H_d and H_{d'} of the complex species in the NMR spectra. The CCDs derived from the ¹H NMR spectra are summarized in Table S7.

Table S7. Summary of CCDs of cage **1** upon encapsulation of *trans*-1,4-adamantanediol (**4a**), *cis*-1,4-adamantanediol (**4b**) and *rac*-1,2-adamantanediol (**4c**) in 7:93 (v/v) CD₃CN/CDCl₃ with the presence of different amount of DMSO-*d*₆ at 298 K. ^a

		4a					4b					4c				
V _{DMSO} /V _{Total} (%)	Equiv	Run1	Run2	Run3	Mean ^b	σ ^c	Run1	Run2	Run3	Mean ^b	σ ^c	Run1	Run2	Run3	Mean ^b	σ ^c
0.79	0.8	1.96	1.89	1.89	1.91	0.04	1.64	1.69	1.69	1.68	0.03	1.56	1.61	1.56	1.58	0.03
0.99	1.0	1.96	1.92	1.89	1.92	0.04	1.69	1.69	1.79	1.73	0.05	1.56	1.64	1.61	1.60	0.04
1.19	1.2	1.96	2.00	2.00	1.99	0.02	1.75	1.69	1.79	1.75	0.05	1.61	1.67	1.61	1.63	0.03
1.38	1.4	2.13	1.96	2.00	2.03	0.09	1.72	1.72	1.85	1.77	0.07	1.61	1.67	1.61	1.63	0.03
1.57	1.6	2.04	2.00	2.04	2.03	0.02	1.79	1.75	1.89	1.81	0.07	1.64	1.69	1.67	1.67	0.03
1.77	1.8	2.08	2.08	2.08	2.08	0.00	1.82	1.82	1.92	1.85	0.06	1.69	1.72	1.69	1.70	0.02
1.96	2.0	2.17	2.13	2.17	2.16	0.03	1.96	1.82	1.96	1.91	0.08	1.69	1.72	1.69	1.70	0.02

^a Data were derived the ¹H NMR integrations of signals of H_d and H_{d'}. ^b the mean CCD value of the three sets of data. ^c Standard deviation of the mean CCD value.

Example of ^1H NMR Titration Spectra

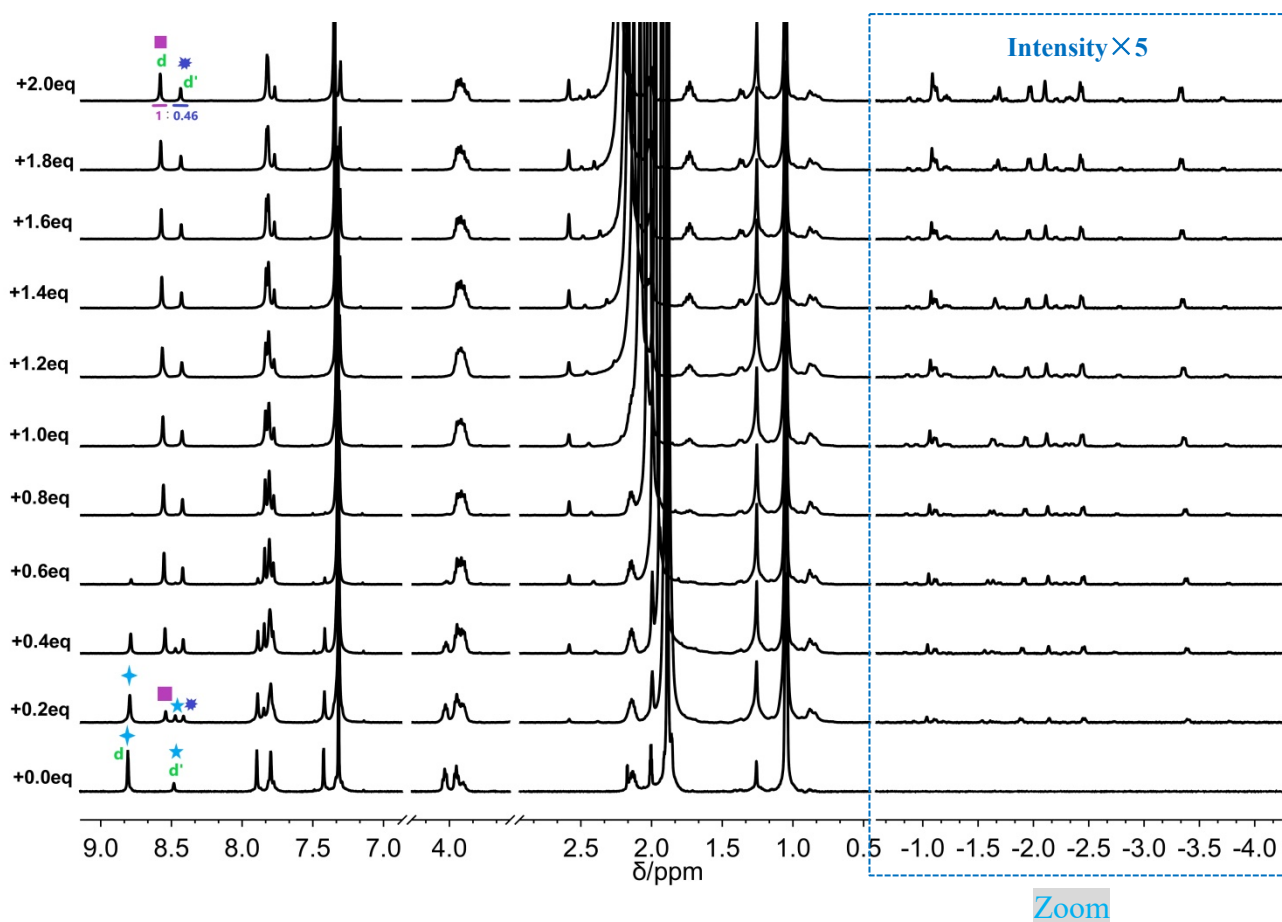


Figure S20. Changes of ^1H NMR spectra (600 MHz, 298 K) of molecular cage **1** (1 mM, 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) upon the addition of *trans*-1,4-adamantanediol (**4a**) (100 mM in $\text{DMSO}-d_6$). $\star = (P,M,P)/(M,P,M)$ -**1**, $\star = (P,P,P)/(M,M,M)$ -**1**, $\blacksquare = 4a \subset (P,M,P)/(M,P,M)$ -**1**, $\star = 4a \subset (P,P,P)/(M,M,M)$ -**1**.

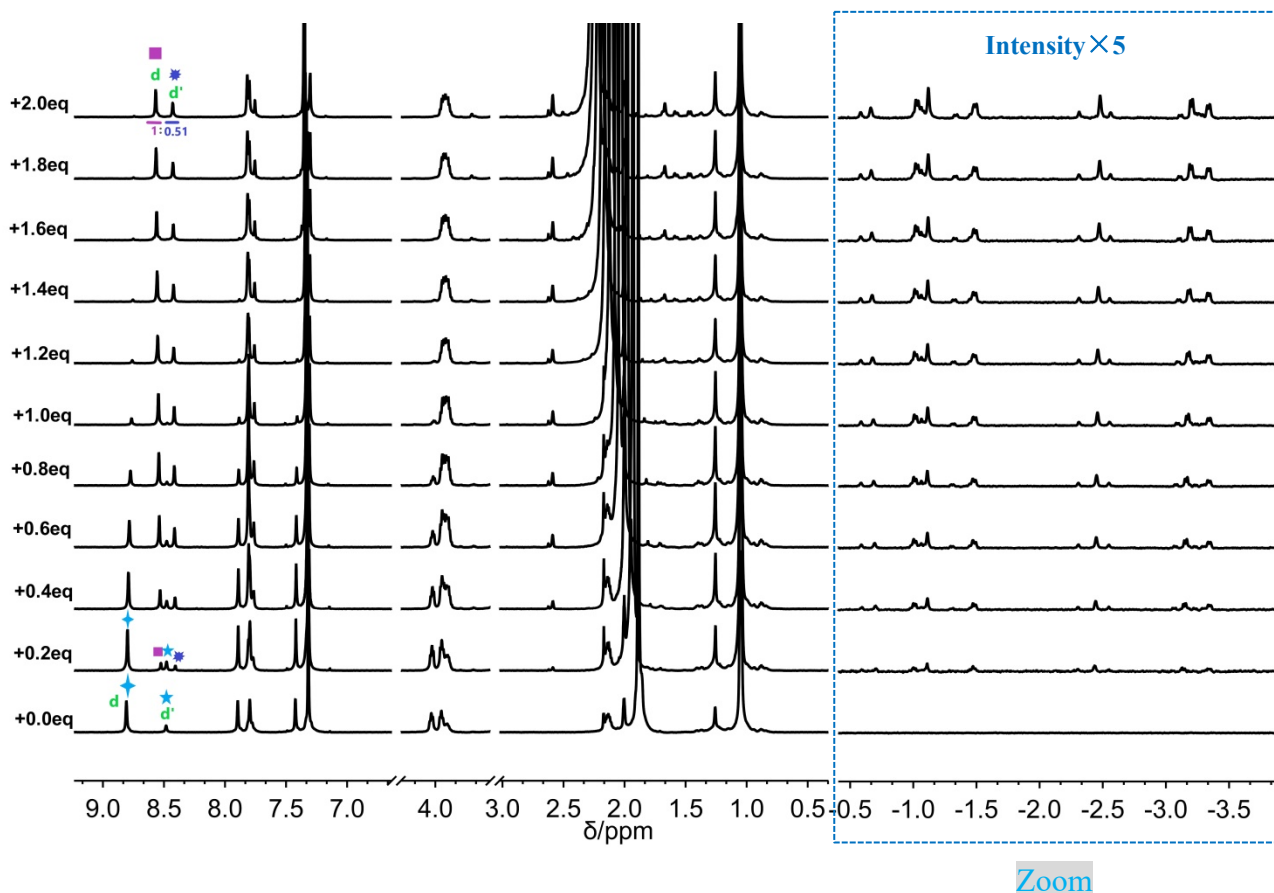


Figure S21. Changes of ^1H NMR spectra (600 MHz, 298 K) of molecular cage **1** (1 mM, 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) upon the addition of *cis*-1,4-adamantanediol (**4b**) (100 mM in $\text{DMSO}-d_6$). $\blacklozenge = (P,M,P)/(M,P,M)\text{-1}$, $\blackstar = (P,P,P)/(M,M,M)\text{-1}$, $\blacksquare = 4b \subset (P,M,P)/(M,P,M)\text{-1}$, $\blacklozenge = 4b \subset (P,P,P)/(M,M,M)\text{-1}$.

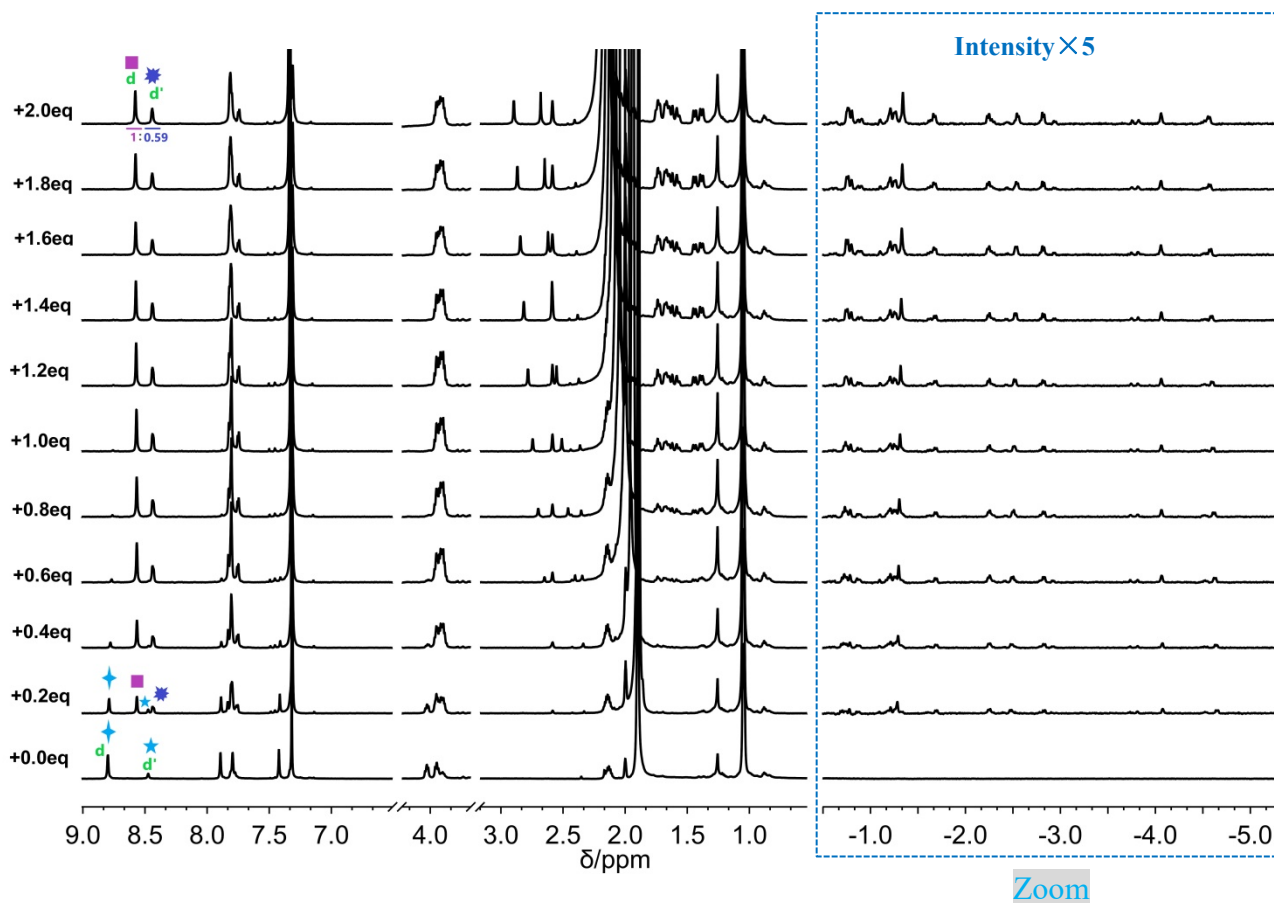


Figure S22. Changes of ^1H NMR spectra (600 MHz, 298 K) of molecular cage **1** (1 mM, 7:93 (v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) upon the addition of *rac*-1,2-adamantanediol (**4c**) (100 mM in $\text{DMSO}-d_6$). $\blacklozenge = (P,M,P)/(M,P,M)\text{-1}$, $\star = (P,P,P)/(M,M,M)\text{-1}$, $\blacksquare = 4\text{c} \subset (P,M,P)/(M,P,M)\text{-1}$, $\star = 4\text{c} \subset (P,P,P)/(M,M,M)\text{-1}$.

7. Solvent Effect on CCD

In this study, conformational distributions of cage **1** in different solvents were studied. Three different solvent mixture systems, including (i) CD₃CN/CDCl₃, (ii) CD₂Cl₂/CDCl₃ with the presence of constant 7% (v/v_{total}) CD₃CN, and (iii) CD₃OD/CDCl₃ were investigated.

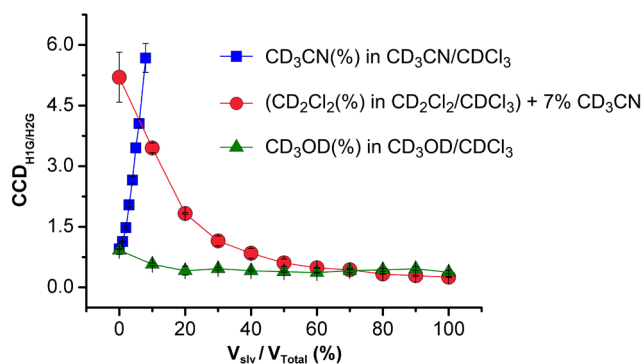
In the case of CD₃CN/CDCl₃, to cage **1** in CDCl₃, CD₃CN was gradually added and the ¹H NMR spectra were recorded at 298 K accordingly. In the other cases, cage **1** was independently dissolved into different solvent mixtures and its ¹H NMR spectrum was recorded at 298 K. The investigations on each solvent mixture system were repeated for three times. Examples of the obtained ¹H NMR spectra are shown in Figures S24–S26. Relative amounts of *P,M,P/M,P,M* and *P,P,P/M,M,M* conformers were derived from the integration of H_d and H_{d'} of the complexes in the spectra. The obtained CCDs are summarized in Table S8.

As shown in Figure 23, at 298 K, increasing the fraction of CD₃CN in the mixture of CD₃CN/CDCl₃ resulted in obvious increase of CCD_{H1G/H2G} (Figure S24). Though the cage started to collapse in the presence of 10% or more CD₃CN, at least when the amount of CD₃CN was varied from 0% to 8%, CCD_{H1G/H2G} substantially changed from 0.95 to 5.68 (Figure S23). Significant changes with different trend were also observed when changing the ratio of CD₂Cl₂ to CDCl₃ in the mixture of CD₂Cl₂/CDCl₃/7% (v/v_{total}) CD₃CN (Figure S23). Obviously, solvent has a strong influence on CCD. Furthermore, the solvent systems can thus even be distinguished, and the standard curves for determining the solvents fractions in the corresponding systems are able to be constructed. In the case of CD₃OD/CDCl₃, CCD_{H1G/H2G} kept almost constant thus hardly giving a standard curve for solvent fraction determination (Figure S23); nevertheless, characteristic curve like this is still helpful for qualitatively distinguishing CD₃OD/CDCl₃ from the other two systems.

Table S8. Summary of CCDs of **1** in different solvent mixture at 298 K. ^a

CD ₃ CN/CDCl ₃						CD ₂ Cl ₂ /CDCl ₃ /7% (v/v _{total}) CD ₃ CN						CD ₃ OD/CDCl ₃					
CD ₃ CN(%)	Run1	Run2	Run3	Mean ^b	σ ^c	CD ₂ Cl ₂ (%)	Run1	Run 2	Run 3	Mean ^b	σ ^c	CD ₃ OD(%)	Run1	Run2	Run3	Mean ^b	σ ^c
0	0.95	0.93	0.96	0.95	0.01	0	5.56	7.14	5.56	6.08	0.92	0	0.80	0.97	0.98	0.92	0.10
1	1.12	1.15	1.12	1.13	0.01	10	3.45	3.57	3.33	3.45	0.12	10	0.58	0.54	0.59	0.57	0.03
2	1.47	1.45	1.52	1.48	0.03	20	1.85	1.82	1.82	1.83	0.02	20	0.49	0.47	0.29	0.41	0.11
3	2.00	2.04	2.08	2.04	0.04	30	1.22	1.01	1.22	1.15	0.12	30	0.49	0.45	0.44	0.46	0.03
4	2.70	2.70	2.56	2.66	0.08	40	0.92	0.70	0.91	0.84	0.12	40	0.41	0.43	0.39	0.41	0.02
5	3.45	3.45	3.45	3.45	0.00	50	0.67	0.50	0.65	0.61	0.09	50	0.39	0.37	0.40	0.39	0.02
6	4.00	4.00	4.17	4.06	0.10	60	0.48	0.48	0.49	0.48	0.01	60	0.36	0.37	0.37	0.37	0.01
8	5.88	5.88	5.26	5.68	0.36	70	0.44	0.43	0.43	0.44	0.00	70	0.38	0.38	0.48	0.42	0.06
9	5.88	5.88	5.26	5.68	0.36	80	0.34	0.33	0.33	0.33	0.01	80	0.45	0.39	0.46	0.44	0.04
10	5.26	5.88	5.56	5.57	0.31	90	0.30	0.28	0.29	0.29	0.01	90	0.48	0.41	0.49	0.46	0.04
						100	0.25	0.26	0.24	0.25	0.01	100	0.35	0.36	0.42	0.38	0.04

^a Data were derived the ¹H NMR integrations of signals of H_d and H_{d'}. ^b the mean CCD value of the three sets of data. ^c Standard deviation of the mean CCD value.

**Figure S23.** Plots of CCD of **1** vs. volumetric fraction of a particular solvent in the solvent mixture ($V_{\text{slv}}/V_{\text{Total}}$). Solvent molecules function as the guests in such cases.

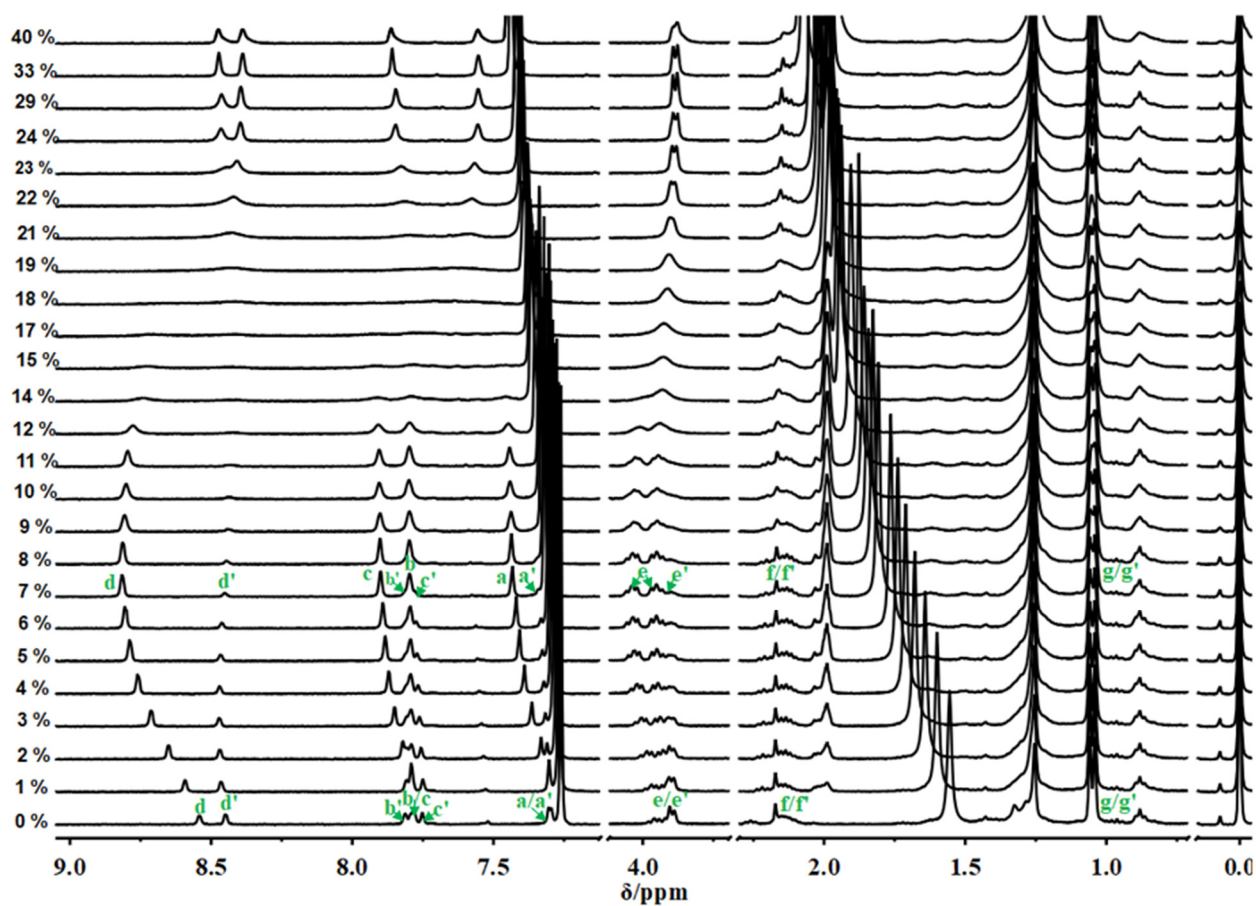


Figure S24. Changes of ^1H NMR spectra (400 MHz, 298 K, CDCl_3) of molecular cage **1** (initial conc. = 1 mM) upon addition of CD_3CN .

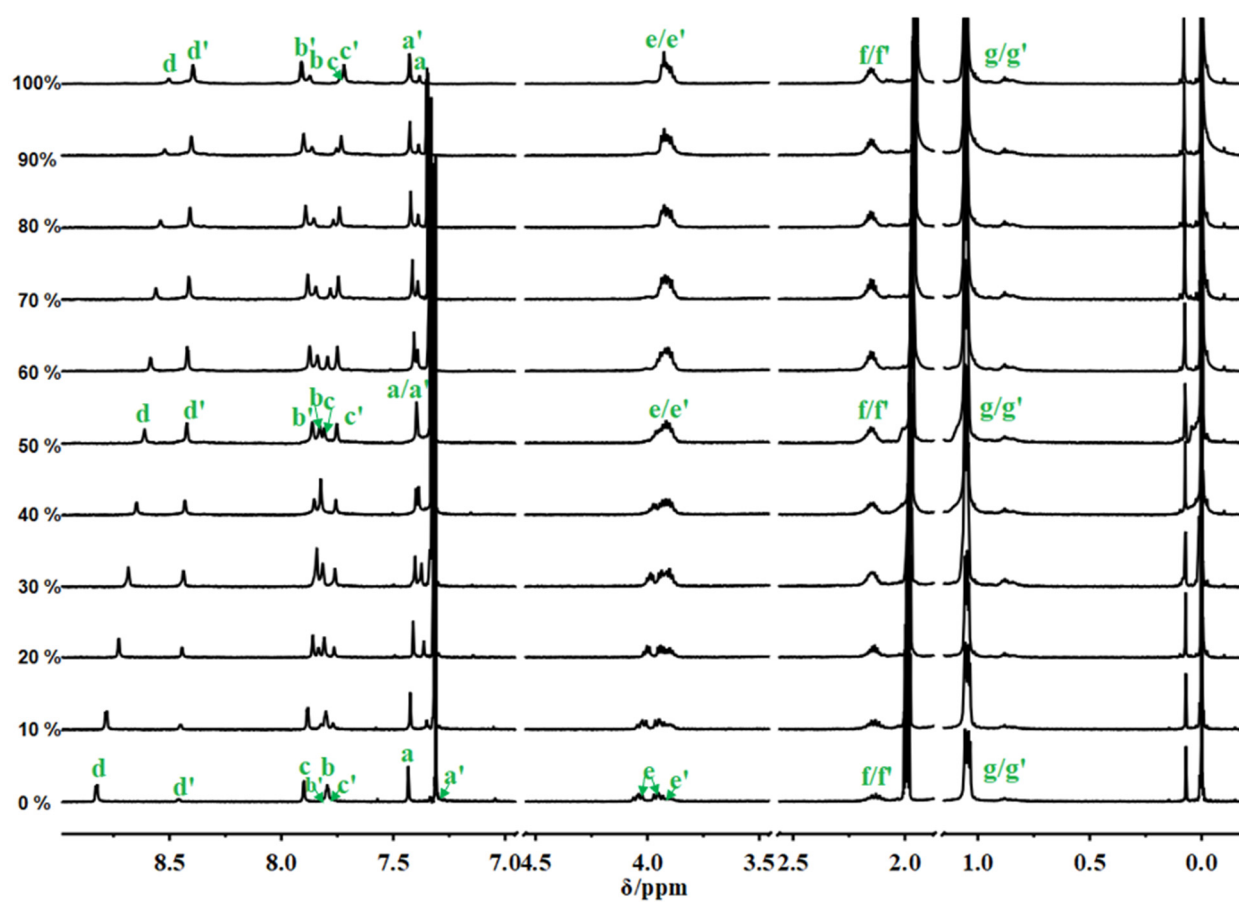


Figure S25. Changes of ^1H NMR spectra (400 MHz, 298 K, 1 mM) of **1** upon changing the ratio of CD_2Cl_2 to CDCl_3 in solvent system of $\text{CD}_2\text{Cl}_2/\text{CDCl}_3/7\%$ ($\text{v}/\text{v}_{\text{total}}$) CD_3CN .

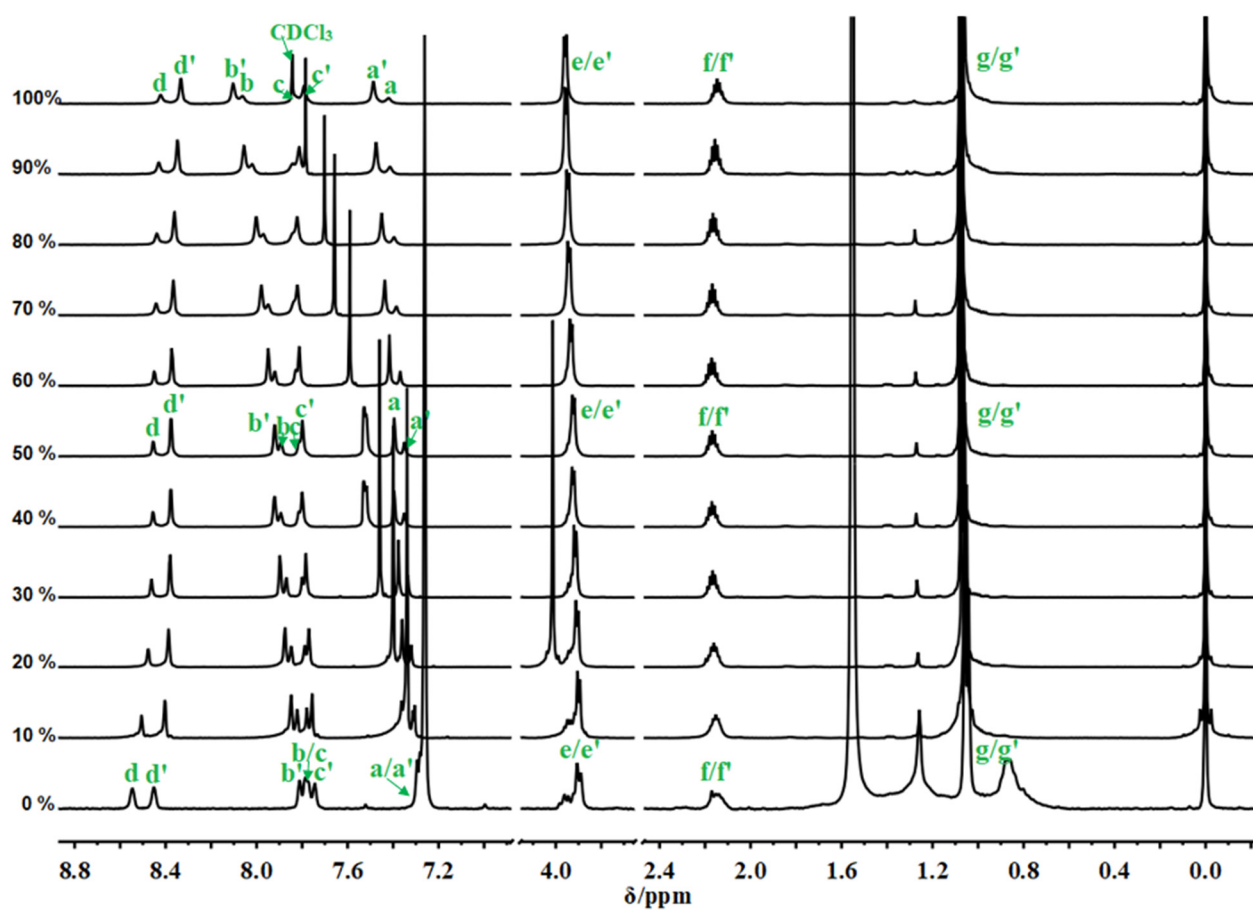


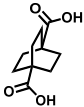
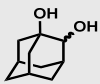
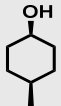
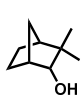
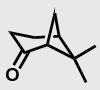
Figure S26. Changes of ^1H NMR spectra (400 MHz, 298 K, 1 mM) of **1** upon increasing the fraction of CD_3OD in the solvent mixture of $\text{CD}_3\text{OD}/\text{CDCl}_3$.

8. Fingerprinting and Identification of Analytes

In this study, screening of possible guests was first carried out using ^1H NMR titrations. Two different solvent mixture systems, including (i) 2:7:91 (v/v/v) DMSO- d_6 /CD $_3$ CN/CDCl $_3$ and (ii) 7:93 (v/v) CD $_3$ CN/CDCl $_3$, were investigated successively. Parameters (CCD, proton H $_a$ resonance shift) for each guest were derived from the obtained spectra. These parameters, which are regarded as the "fingerprints" of the guests in our study and summarized in Tables S9–S10, were used to plot the scatterplots shown in Figure 4 and Figure 5 in the main text. Next, to verify where these fingerprints can really be utilized for analyte identifications, we examined some guest species in a crude sample and a sample of mixture, and the obtained parameters of guest species in these samples were compared with those of the pure compounds to verify whether the species can be identified in such cases.

Table S9. Summary of CCDs (CCD-1)^a and chemical shifts (CS-1)^b of cage **1** upon encapsulation of guests (**2–10**) in 2:7:91 (v/v/v) DMSO- d_6 /CD $_3$ CN/CDCl $_3$ at 298 K.

Label	Structure	CCD-1						CS-1/ppm				
		Equiv.	Run1	Run2	Run3	Mean ^c	σ^d	Run1	Run2	Run3	Mean ^e	σ^f
2		15	3.030	2.899	3.040			8.761	8.761	8.765		
		20	3.030	2.976	3.125	3.035	0.093	8.761	8.761	8.760	8.761	0.002
		25	3.067	2.941	3.205			8.761	8.761	8.759		
2b		40	2.381	2.381	2.381			8.705	8.705	8.705		
		60	2.381	2.381	2.381	2.394	0.026	8.706	8.706	8.705	8.705	0.001
		80	2.440	2.440	2.381			8.705	8.704	8.704		
2c		60	1.351	1.351	1.370			8.653	8.653	8.653		
		100	1.370	1.370	1.351	1.370	0.016	8.654	8.654	8.653	8.654	0.001
		150	1.389	1.389	1.389			8.654	8.654	8.654		
3a		3	1.544	1.559	1.519	1.541 ^g	0.020 ^g	8.644	8.643	8.642	8.643	0.001
3b		10	1.123	1.103	1.102	1.109 ^g	0.012 ^g	8.608	8.608	8.606	8.607	0.001

3c		3	2.128	2.224	2.171	2.174 ^g	0.048 ^g	8.640	8.647	8.647	8.645	0.004
4a		2	2.174	2.125	2.174	2.158 ^g	0.028 ^g	8.597	8.580	8.582	8.586	0.009
4b		2	1.962	1.820	1.961	1.914 ^g	0.082 ^g	8.569	8.563	8.570	8.567	0.004
4c		2	1.693	1.724	1.694	1.704 ^g	0.018 ^g	8.578	8.579	8.576	8.578	0.002
5		10	2.500	2.440	2.500			8.668	8.676	8.667		
		20	2.564	2.500	2.500	2.522	0.056	8.668	8.675	8.670	8.671	0.004
		30	2.564	2.500	2.632			8.670	8.676	8.667		
6		200	3.350	3.251	3.330			8.730	8.728	8.729		
		300	3.394	3.387	3.344	3.334	0.097	8.726	8.725	8.725	8.724	0.005
		500	3.467	3.362	3.125			8.717	8.721	8.718		
<i>(S)</i> -7		320	1.613	1.587	1.587			8.637	8.637	8.639		
		400	1.587	1.613	1.587	1.601	0.014	8.638	8.638	8.638	8.638	0.001
		500	1.613	1.613	1.613			8.639	8.639	8.639		
<i>(R)</i> -7		320	1.563	1.587	1.613			8.638	8.638	8.637		
		400	1.613	1.640	1.587	1.602	0.023	8.639	8.638	8.637	8.638	0.001
		500	1.587	1.613	1.613			8.638	8.639	8.639		
8		640	1.592	1.580	1.472			8.641	8.642	8.639		
		800	1.580	1.615	1.473	1.552	0.076	8.641	8.641	8.639	8.641	0.001
		1000	1.607	1.632	1.421			8.641	8.642	8.639		
9		640	1.909	1.808	1.900			8.658	8.656	8.657		
		800	1.868	1.826	1.886	1.894	0.058	8.660	8.657	8.658	8.658	0.001
		1000	2.004	1.934	1.909			8.660	8.658	8.659		
10		640	2.257	2.275	2.313			8.705	8.706	8.705		
		800	2.317	2.241	2.361	2.321	0.054	8.707	8.707	8.709	8.708	0.002
		1000	2.381	2.378	2.370			8.709	8.710	8.710		

^a Data were derived from the ¹H NMR integrations of signals of H_d and H_d. ^b The ¹H NMR chemical shifts of proton H_d. ^c The overall mean CCD of all sets of data. ^d Standard deviation of the overall CCDs. ^e The overall mean chemical shift of all sets of data. ^f Standard deviation of the overall CS-1s. ^g Data were quoted from Tables S6–S7.

Table S10. Summary of CCDs (CCD-2)^a and chemical shifts (CS-2)^b of cage **1** upon encapsulation of guests (**2–10**) in 7:93 (v/v) CD₃CN/CDCl₃ at 298 K.

Label	Structure	CCD-2						CS-2/ppm				
		Equiv.	Run1	Run2	Run3	Mean ^c	σ ^d	Run1	Run2	Run3	Mean ^e	σ ^f
2		7						8.753	8.753	8.750		
		10				2.103 ^g	0.091 ^g	8.751	8.749	8.749	8.751	0.003
		15						8.754	8.754	8.745		
2b		15						8.675	8.683	8.683		
		20				1.397 ^g	0.099 ^g	8.677	8.683	8.683	8.681	0.004
		25						8.676	8.683	8.684		
2c		15						8.626	8.620	8.627		
		20				0.884 ^g	0.048 ^g	8.622	8.620	8.625	8.624	0.004
		25						8.626	8.618	8.628		
3a		7	0.629	0.637	0.637			8.549	8.549	8.553		
		10	0.637	0.633	0.625	0.631	0.007	8.552	8.549	8.551	8.550	0.002
		20	0.617	0.637	0.625			8.549	8.551	8.548		
3b		10	0.662	0.662	0.671			8.508	8.506	8.507		
		15	0.699	0.662	0.685	0.678	0.015	8.506	8.506	8.506	8.506	0.001
		20	0.690	0.680	0.694			8.505	8.506	8.505		
5		10	1.613	1.613	1.639			8.631	8.631	8.631		
		15	1.695	1.640	1.639	1.626	0.014	8.631	8.631	8.631	8.631	0.001
		20	1.667	1.613	1.613			8.633	8.632	8.630		
6		320	1.450	1.485	1.450			8.694	8.694	8.691		
		400	1.515	1.442	1.478	1.483	0.030	8.693	8.691	8.692	8.692	0.002
		500	1.515	1.515	1.493			8.687	8.691	8.691		
(S)- 7		320	0.971	0.990	0.952			8.602	8.598	8.598		
		400	0.970	0.952	0.952	0.964	0.013	8.602	8.598	8.599	8.600	0.002
		500	0.962	0.971	0.952			8.602	8.599	8.598		
(R)- 7		320	0.971	0.962	0.952			8.599	8.598	8.598		
		400	0.962	0.962	0.943	0.965	0.012	8.598	8.599	8.599	8.598	0.001
		500	0.980	0.971	0.980			8.599	8.597	8.598		
8		640	0.964	0.947	0.934			8.595	8.594	8.593		
		800	1.006	1.020	0.964	0.989	0.039	8.592	8.593	8.595	8.594	0.001
		1000	1.031	1.047	0.990			8.592	8.596	8.595		
9		640	1.236	1.262	1.310			8.632	8.633	8.632		
		800	1.269	1.223	1.261	1.285	0.045	8.633	8.632	8.631	8.632	0.001
		1000	1.351	1.333	1.320			8.632	8.632	8.632		
10		640	1.455	1.432	1.502			8.681	8.682	8.683		
		800	1.434	1.520	1.444	1.469	0.037	8.684	8.685	8.682	8.683	0.001
		1000	1.522	1.477	1.439			8.684	8.683	8.685		

^a Data were derived from the ¹H NMR integrations of signals of H_d and H_{d'}. ^b The chemical shifts of the H_d resonance. ^c the overall mean CCD of all sets of data. ^d Standard deviation of the overall CCDs. ^e The overall mean chemical shift of all sets of data. ^f Standard deviation of the overall CS-2s. ^g Data were quoted from Table S5.

8.a Molecular Fingerprinting in 2:7:91 (v/v/v) DMSO-*d*₆/CD₃CN/CDCl₃

To a 10 mL volumetric flask, 700 μ L CD₃CN and 200 μ L DMSO-*d*₆ was added by microsyringe, followed by the addition of CDCl₃ to the level of the etched line to give a solvent mixture of 2:7:91 (v/v/v) DMSO-*d*₆/CD₃CN/CDCl₃. Cage **1** and the potential guest compounds was independently dissolved into the solvent mixture, giving rise to solutions of the cage and the potential guests in 2:7:91 (v/v/v) DMSO-*d*₆/CD₃CN/CDCl₃.

To a solution of **1** (0.5 mL), different guest solutions was gradually added respectively, and a series of ¹H NMR spectra were recorded at 298 K. The investigation on each guest was repeated for 3 times. Seven new guest species, including 1-adamantanol (**5**), *cis*-4-methylcyclohexanol (**6**), (1*R*)-(+)-camphor ((*R*)-**7**), (1*S*)-(–)-camphor ((*S*)-**7**), (1*R*)-endo-(+)-fenchyl alcohol (**8**), (1*R*)-(+)-nopinone (**9**) and (1*S*)-(β)-pinene (**10**), were screened out. Complexations of **1** with **2**, **2b** and **2c** were also explored in such a solvent condition. Examples of the obtained ¹H NMR spectra are shown in Figures S27–S36.

Parameters (CCD, proton H_a resonance shift) were derived from the obtained ¹H NMR spectra.

All the data are summarized in Table S9.

Example of ^1H NMR Titration Spectra

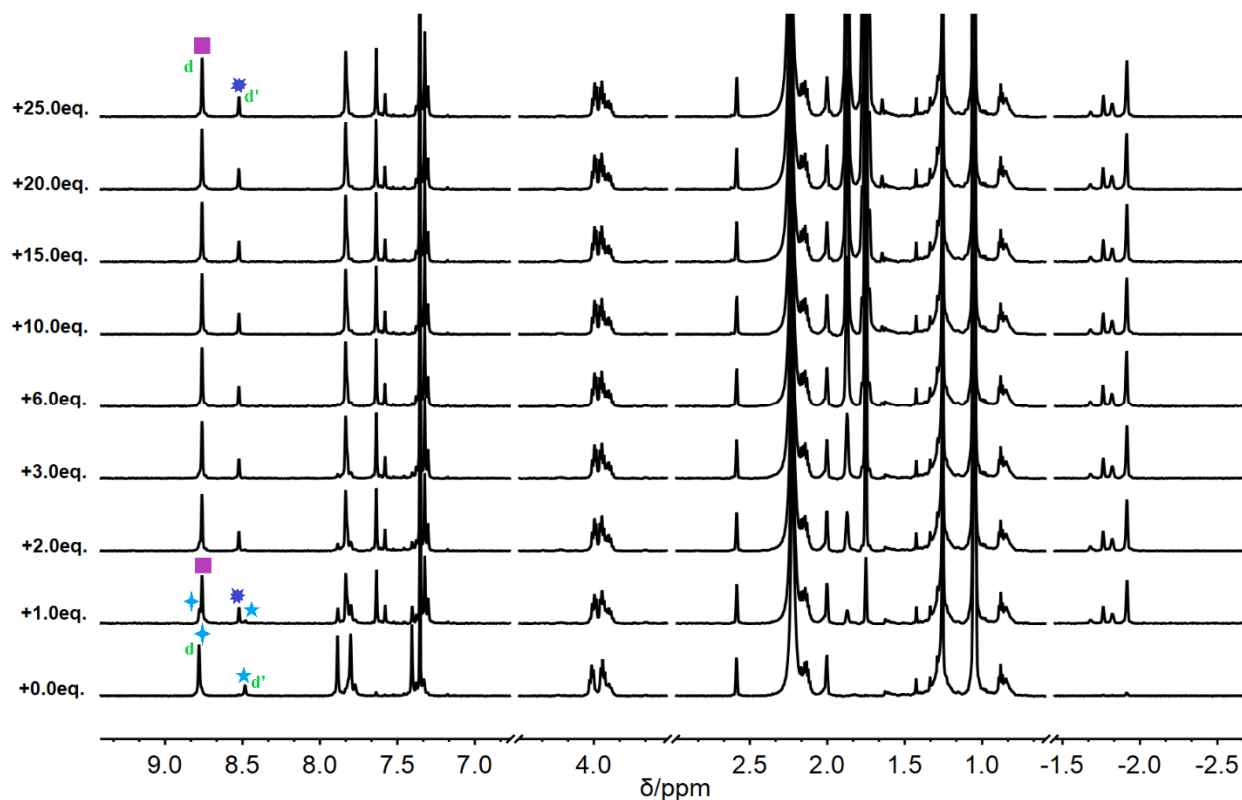


Figure S27. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) $\text{DMSO}-d_6/\text{CD}_3\text{CN}/\text{CDCl}_3$) of cage **1** (1 mM) upon the addition of adamantane (**2**) (500 mM).

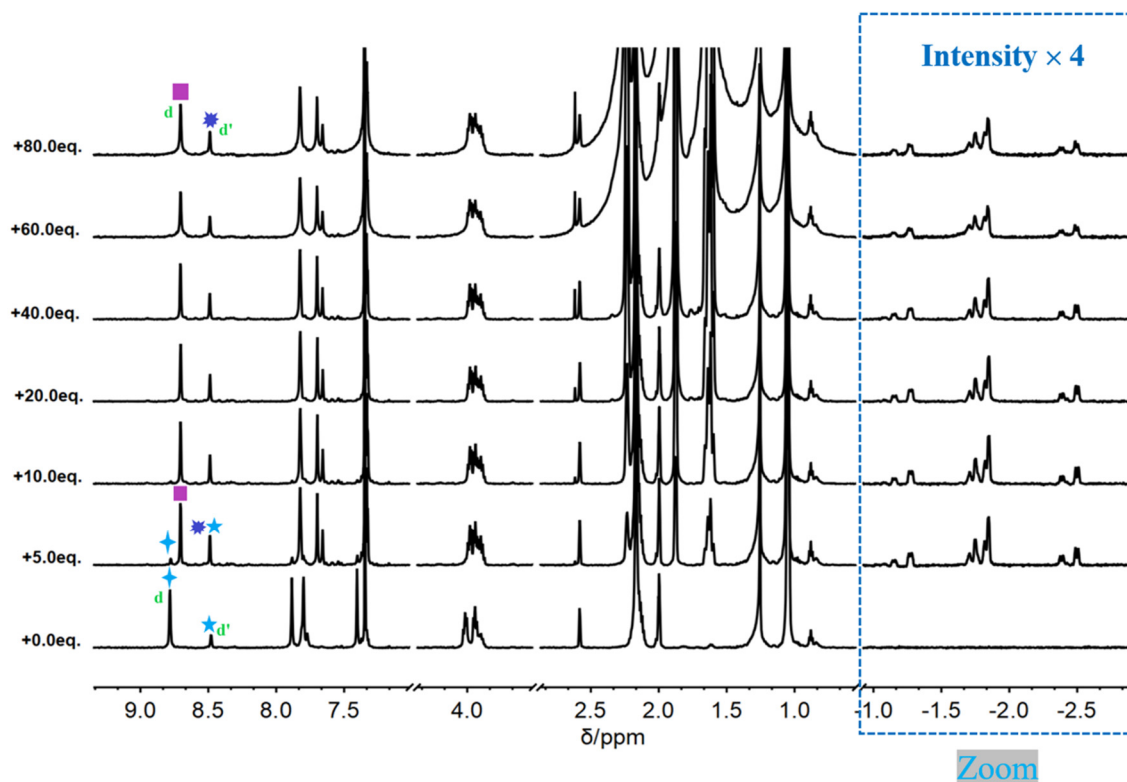


Figure S28. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) $\text{DMSO}-d_6/\text{CD}_3\text{CN}/\text{CDCl}_3$) of cage **1** (1 mM) upon the addition of 1-fluoroadamantane (**2b**) (2.5 M).

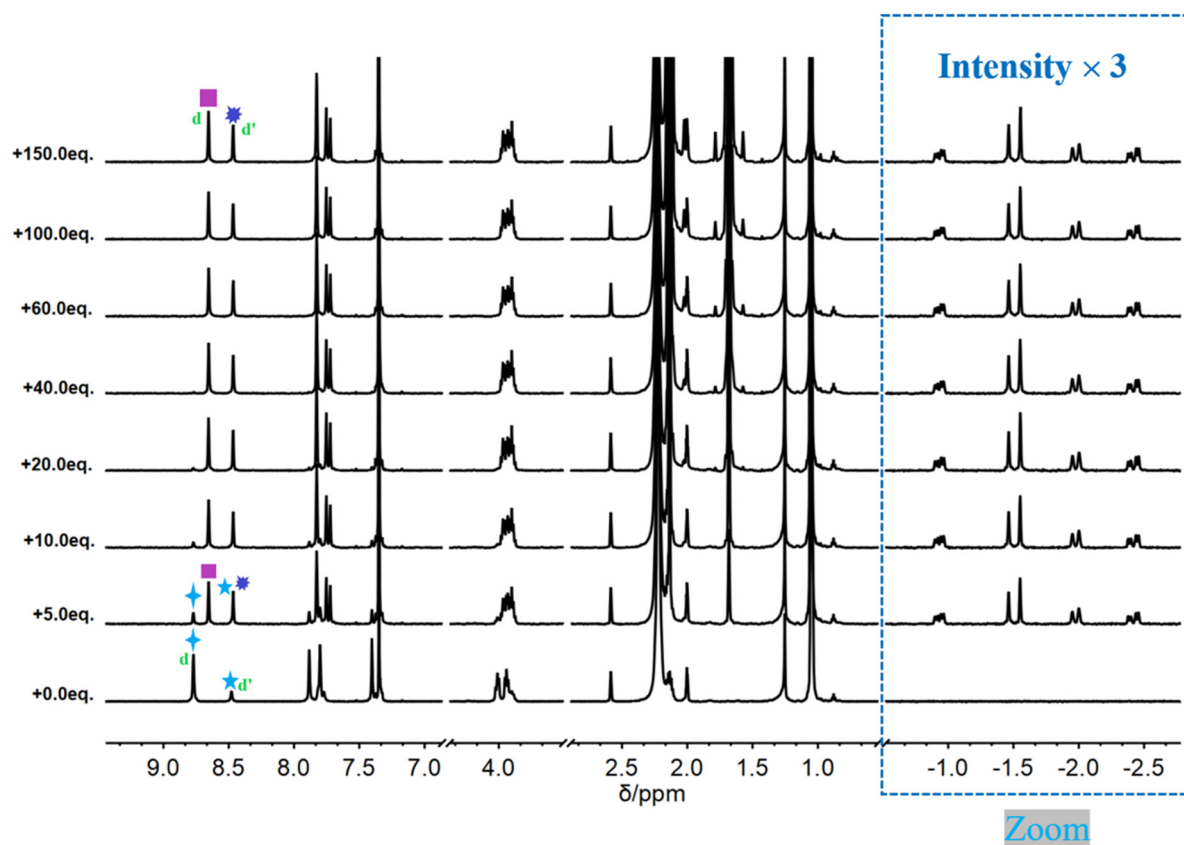


Figure S29. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) DMSO- d_6 /CD $_3$ CN/CDCl $_3$) of cage **1** (1 mM) upon the addition of 1-chloroadamantane (**2c**) (5 M).

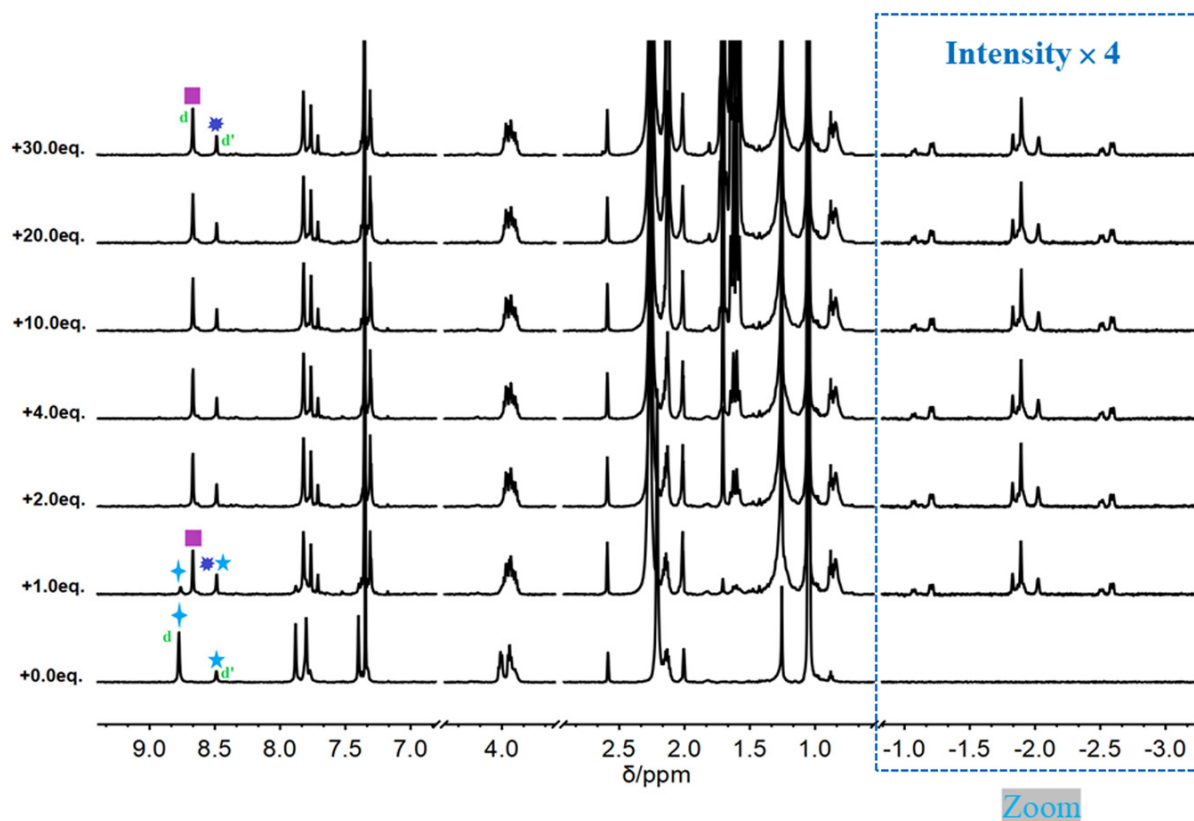


Figure S30. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) DMSO- d_6 /CD $_3$ CN/CDCl $_3$) of cage **1** (1 mM) upon the addition of 1-adamantanol (**5**) (1 M).

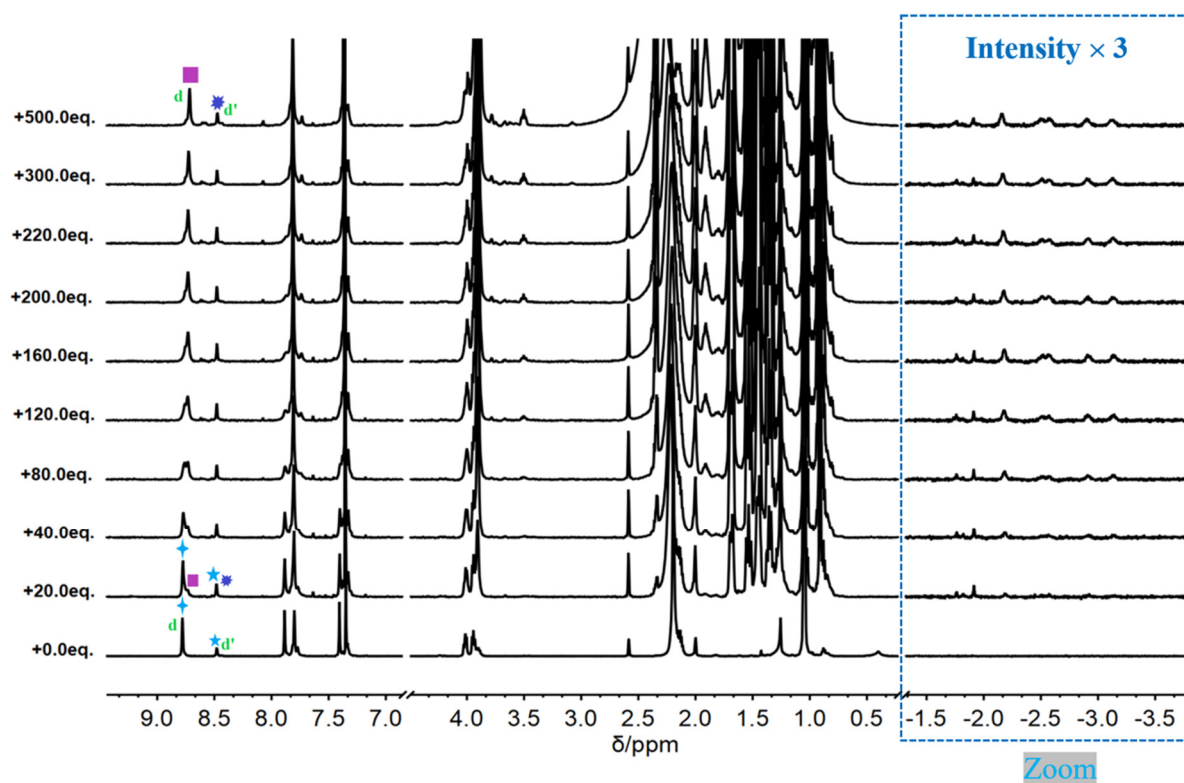


Figure S31. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) $\text{DMSO-}d_6/\text{CD}_3\text{CN}/\text{CDCl}_3$) of cage **1** (1 mM) upon the addition of *cis*-4-methylcyclohexanol (**6**) (10 M).

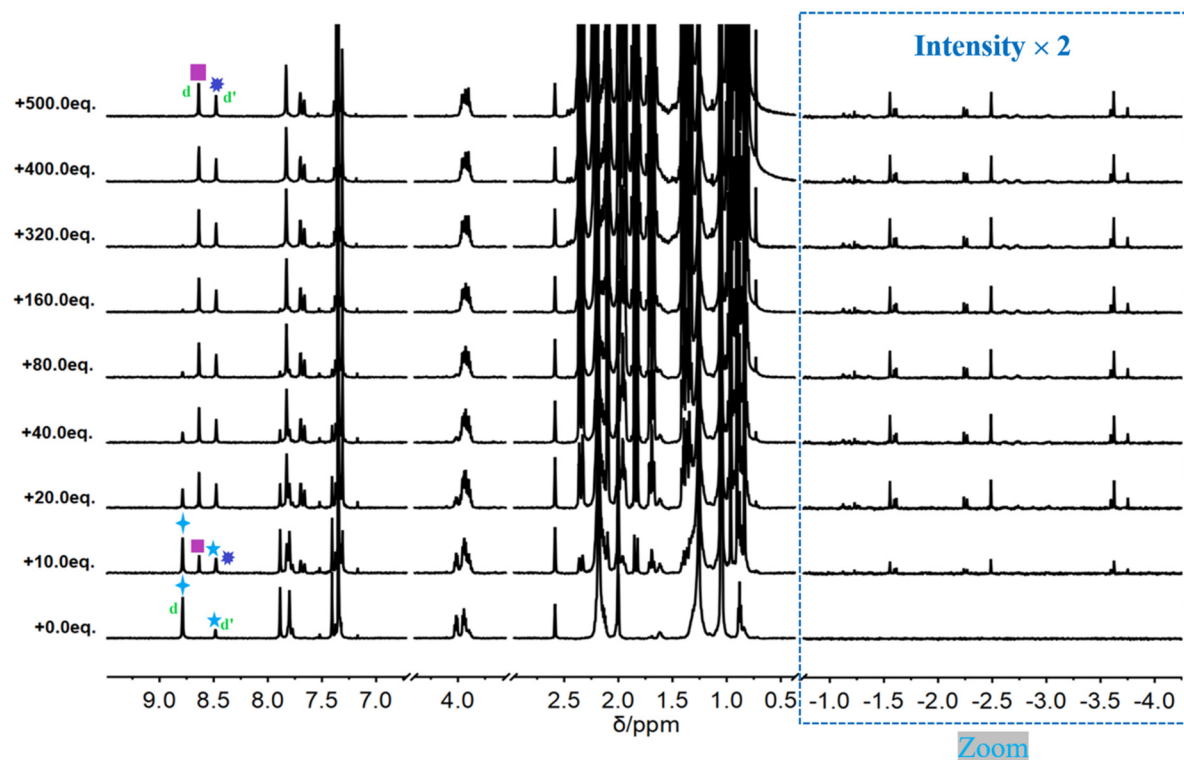


Figure S32. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) $\text{DMSO-}d_6/\text{CD}_3\text{CN}/\text{CDCl}_3$) of cage **1** (1 mM) upon the addition of (1*S*)-(-)-camphor ((*S*)-**7**) (10 M).

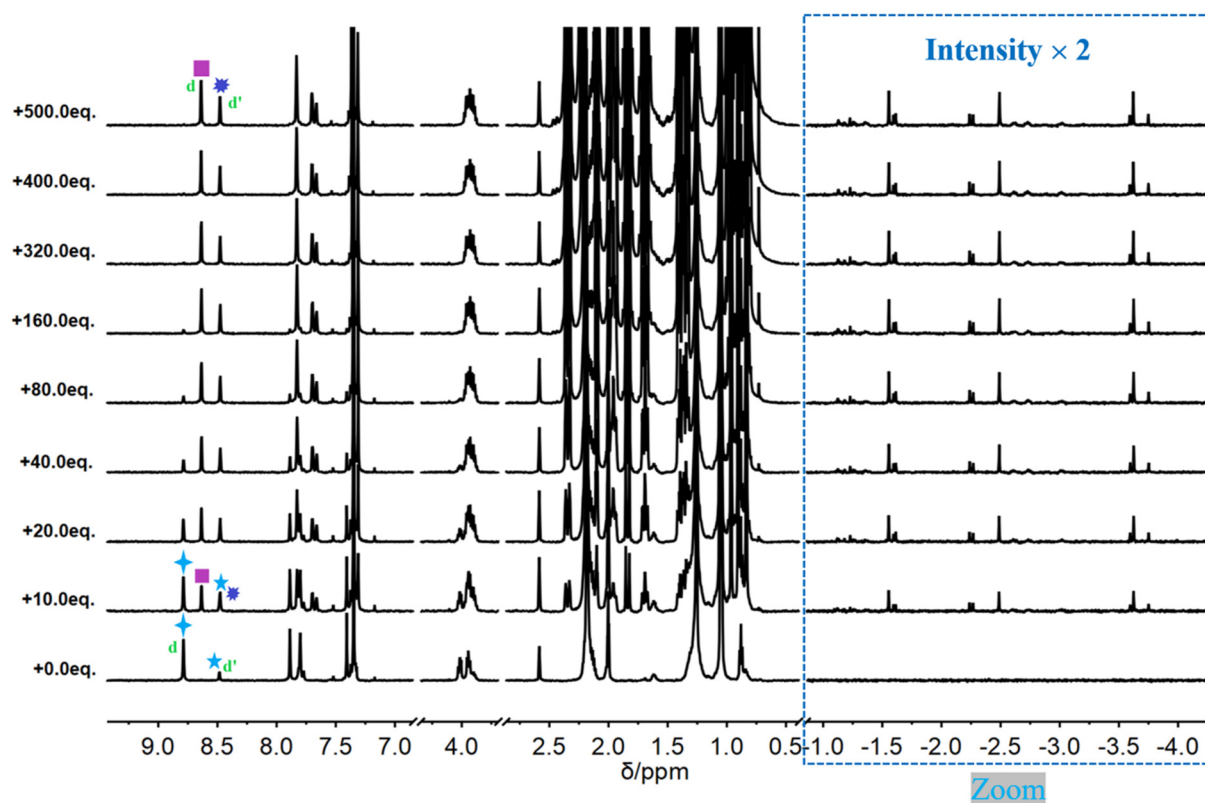


Figure S33. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) $\text{DMSO}-d_6/\text{CD}_3\text{CN}/\text{CDCl}_3$) of cage **1** (1 mM) upon the addition of (1*R*)-(+)-camphor ((*R*)-**7**) (10 M).

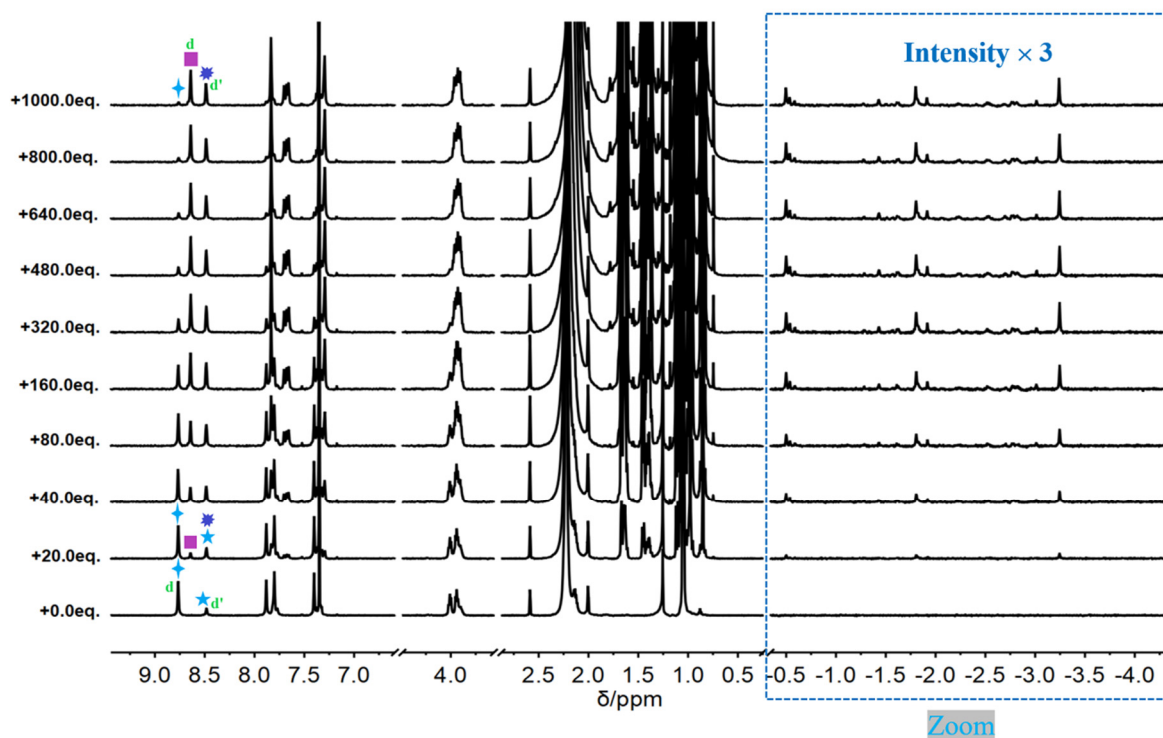


Figure S34. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) $\text{DMSO}-d_6/\text{CD}_3\text{CN}/\text{CDCl}_3$) of cage **1** (1 mM) upon the addition of (1*R*)-endo-(+)-fenchyl alcohol (**8**) (20 M).

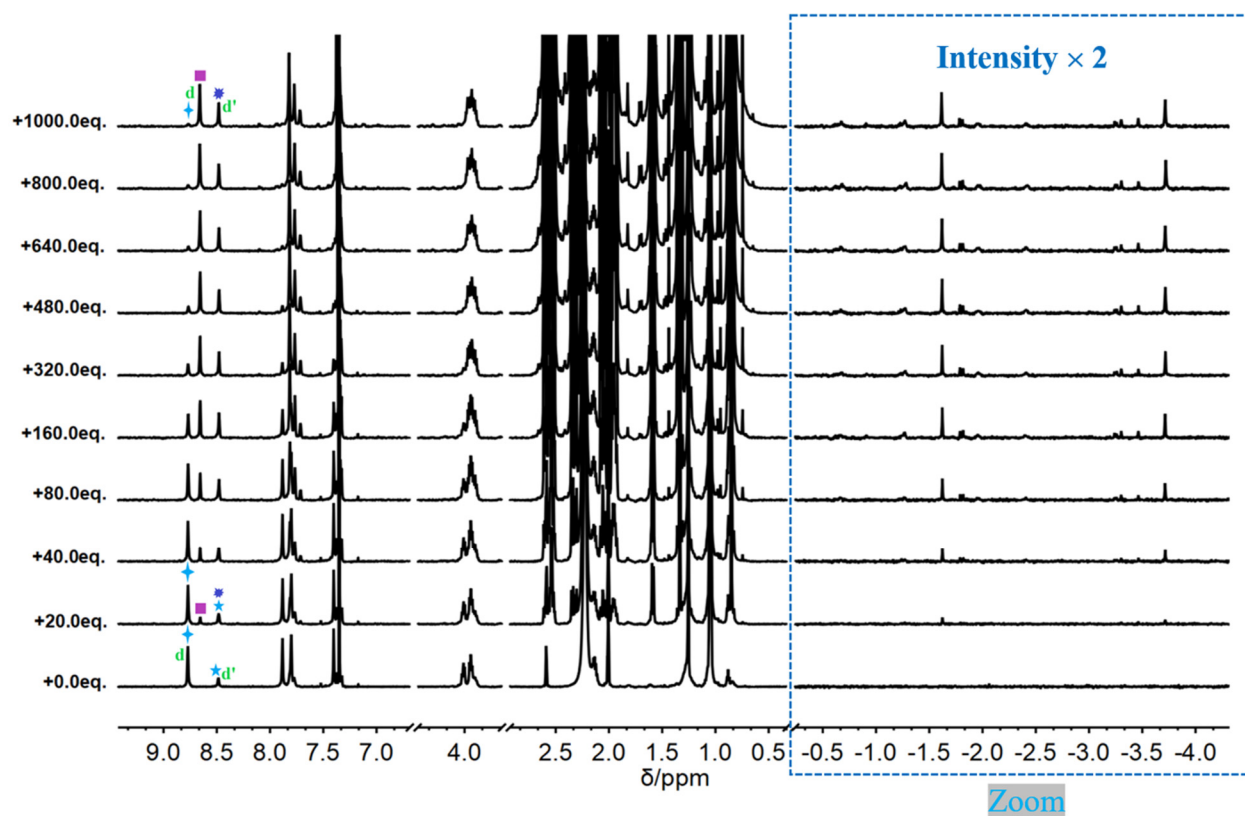


Figure S35. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) $\text{DMSO-}d_6/\text{CD}_3\text{CN}/\text{CDCl}_3$) of cage **1** (1 mM) upon the addition of (1*R*)-(+)-nopinone (**9**) (20 M).

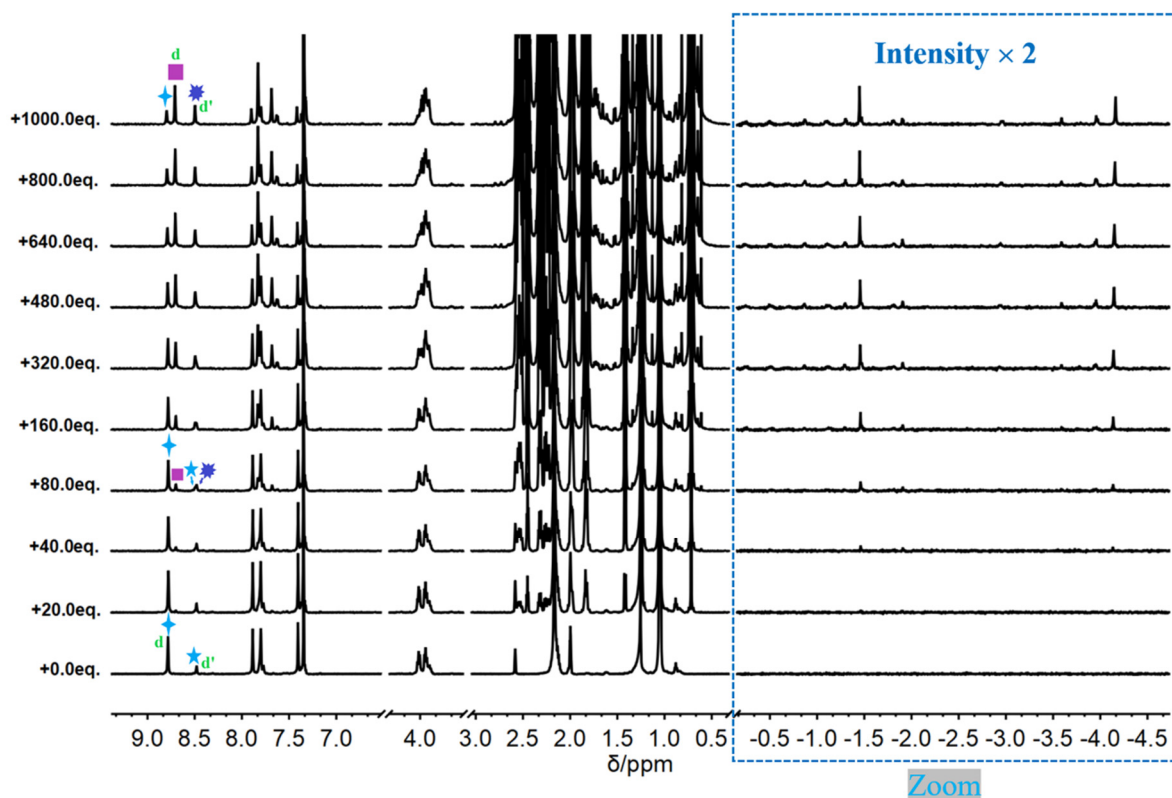


Figure S36. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) $\text{DMSO-}d_6/\text{CD}_3\text{CN}/\text{CDCl}_3$) of cage **1** (1 mM) upon the addition of (1*S*)- β -pinene (**10**) (20 M).

8.b Molecular Fingerprinting in 7:93 (v/v) CD₃CN/CDCl₃

To a 10 mL volumetric flask, 700 μ L CD₃CN was added by microsyringe, followed by the addition of CDCl₃ to give a mixture of 7:93 (v/v) CD₃CN/CDCl₃. Cage **1** and the guest compounds was independently dissolved into above solvent mixture. Next, to a solution of **1** (0.5 mL) in 7:93 (v/v) CD₃CN/CDCl₃, a guest solution was gradually added, and a series of ¹H NMR spectra were recorded at 298 K. The investigation on each guest was repeated for 3 times. **3c**, **4a**, **4b** and **4c** have not been investigated in this part of study due to their poor solubility in 7:93 (v/v) CD₃CN/CDCl₃. All the obtained parameters are summarized in Table S10. Examples of the obtained ¹H NMR spectra relating to solvent of 7:93 (v/v) CD₃CN/CDCl₃ are shown in Figures S37–S45, Figure S1, and Figures S15–S16.

Example of ¹H NMR Titration Spectra

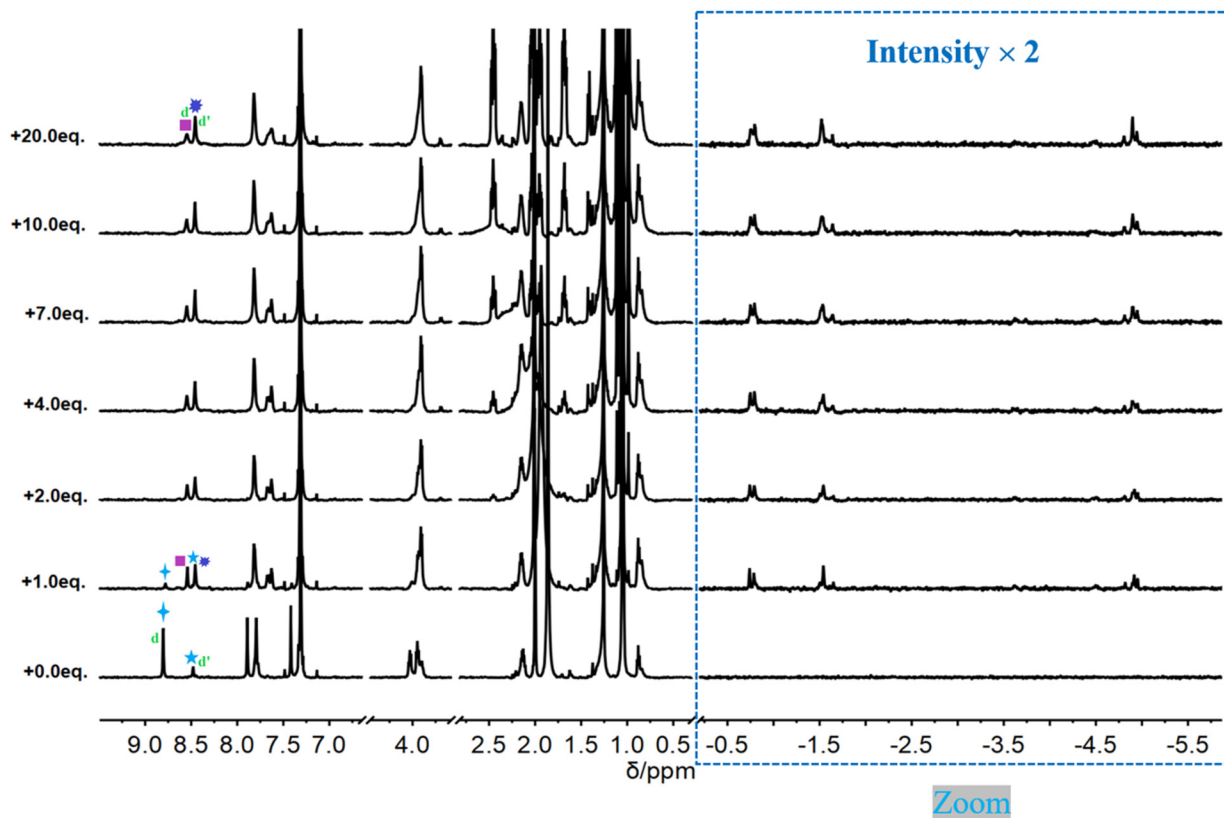


Figure S37. Changes of ¹H NMR spectra (600 MHz, 298 K, 7:93(v/v) CD₃CN/CDCl₃) of cage **1** (0.5 mM) upon the addition of (1*S*)-(-)-camphoric acid (**3a**) (500 mM).

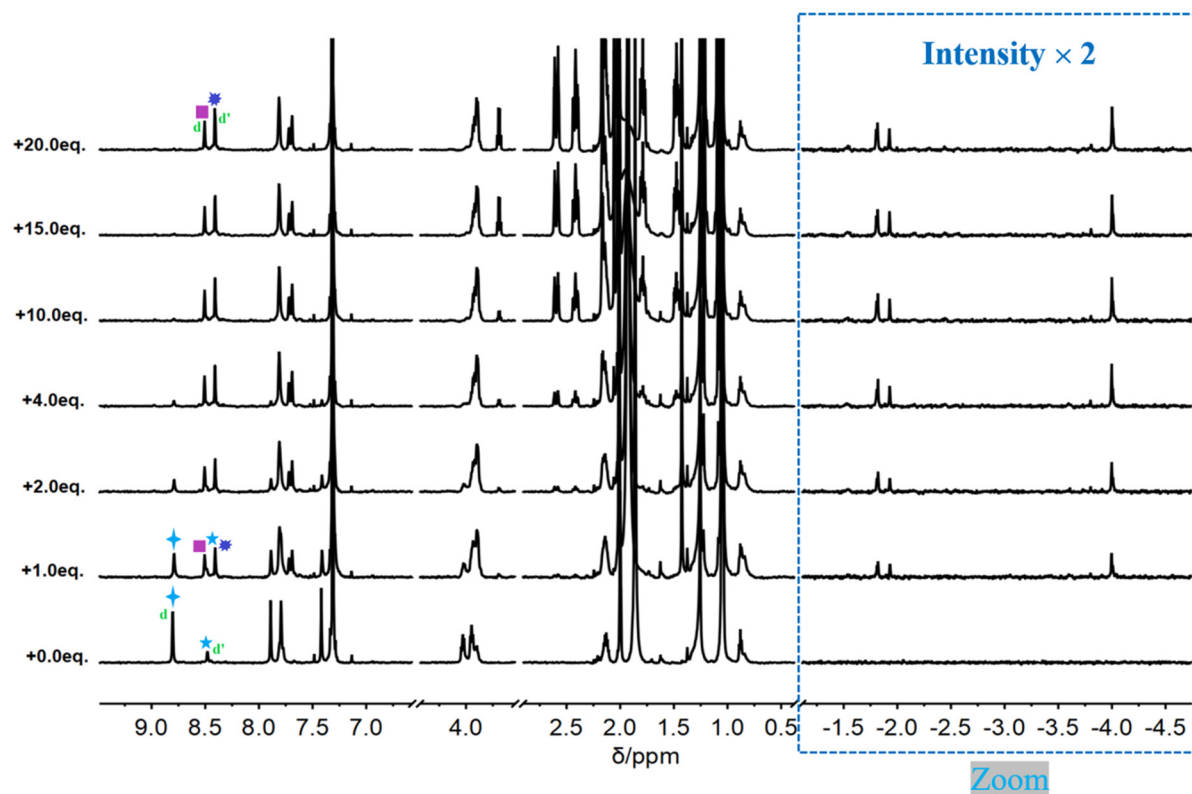


Figure S38. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (0.5 mM) upon the addition of (*S*)-(+)-ketopinic acid (**3b**) (500 mM).

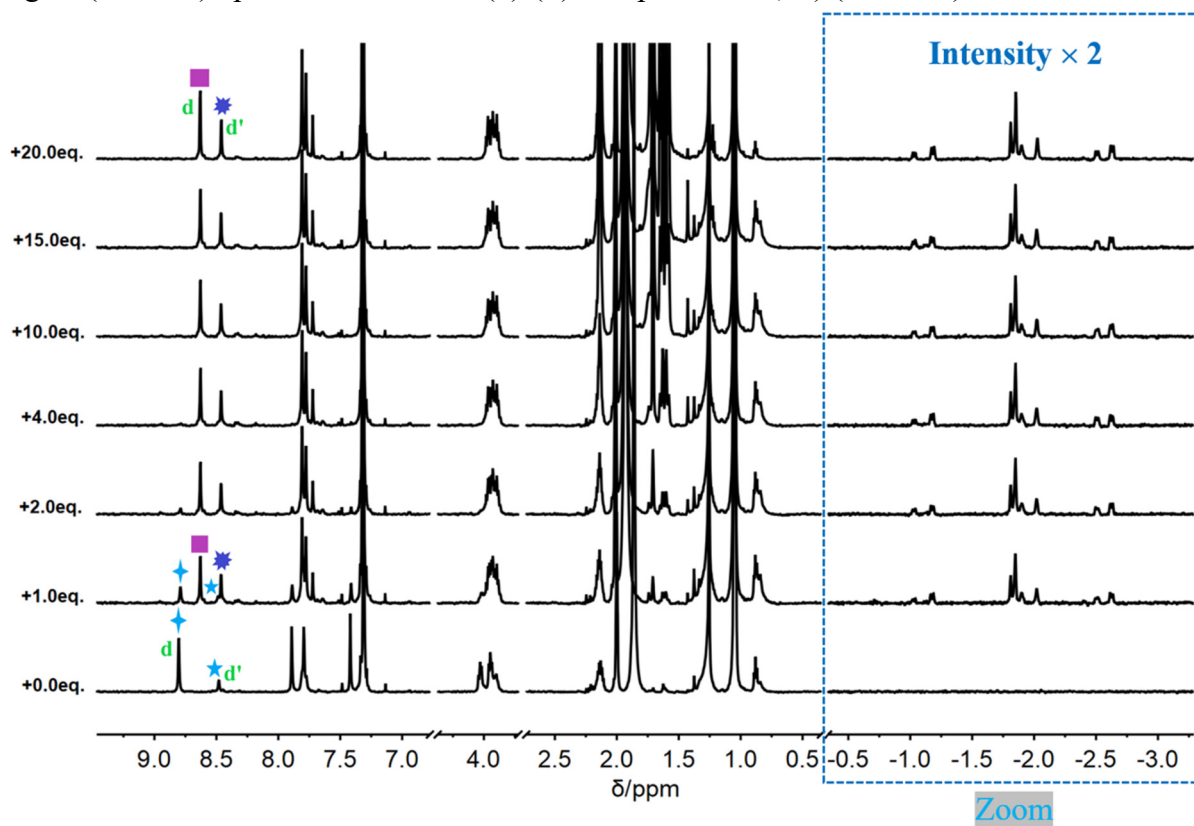


Figure S39. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (0.5 mM) upon the addition of 1-adamantanol (**5**) (500 mM).

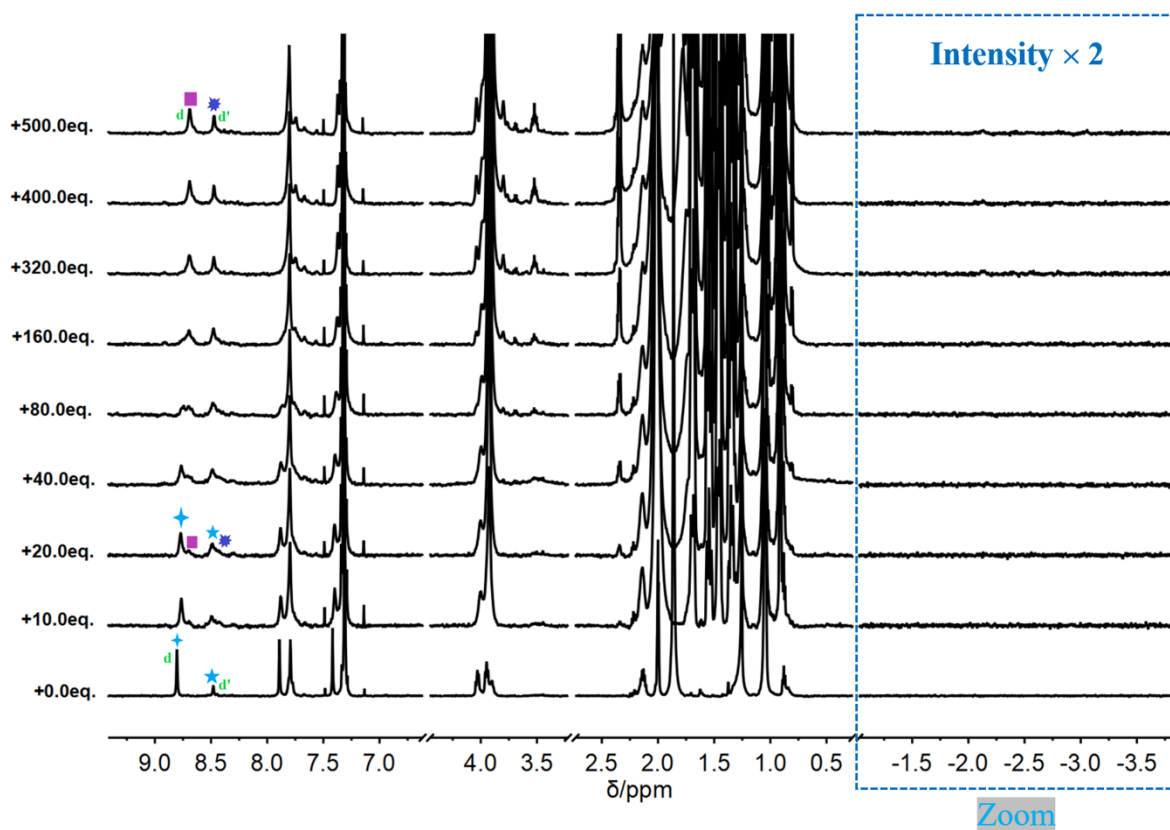


Figure S40. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (0.5 mM) upon the addition of *cis*-4-methylcyclohexanol (**6**) (5 M).

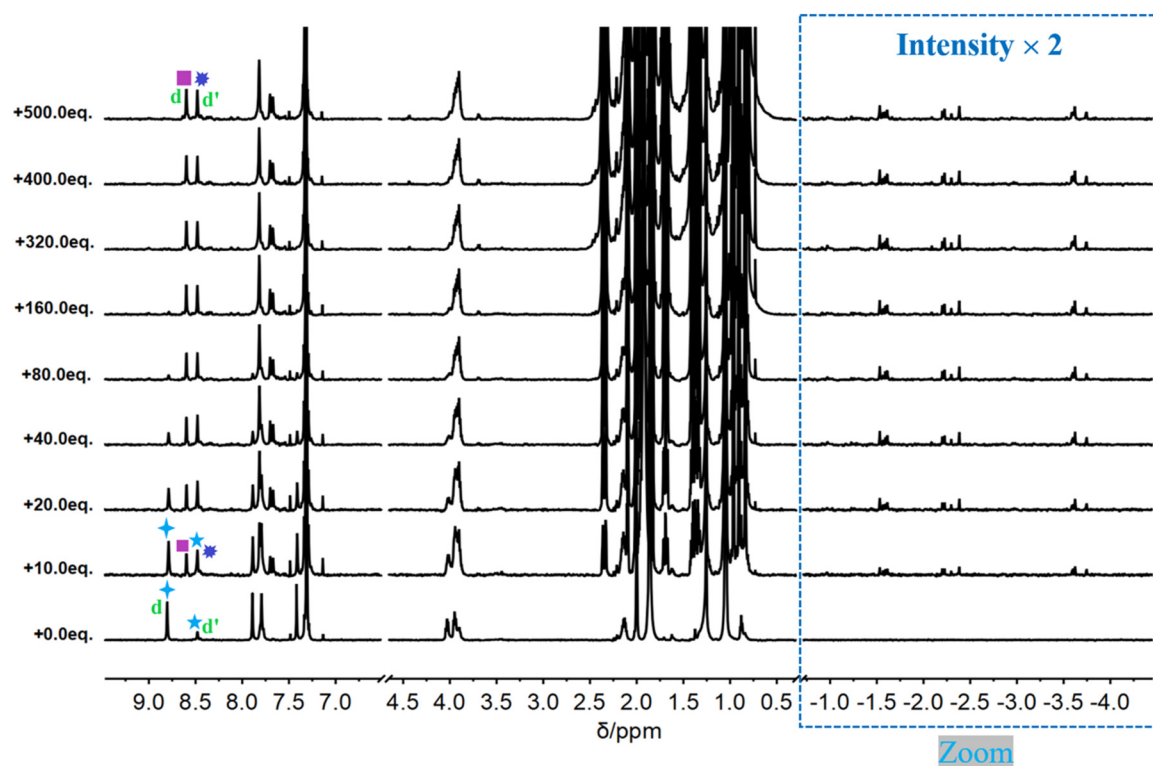


Figure S41. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (0.5 mM) upon the addition of (1*S*)-(-)-camphor ((*S*)-**7**) (5 M).

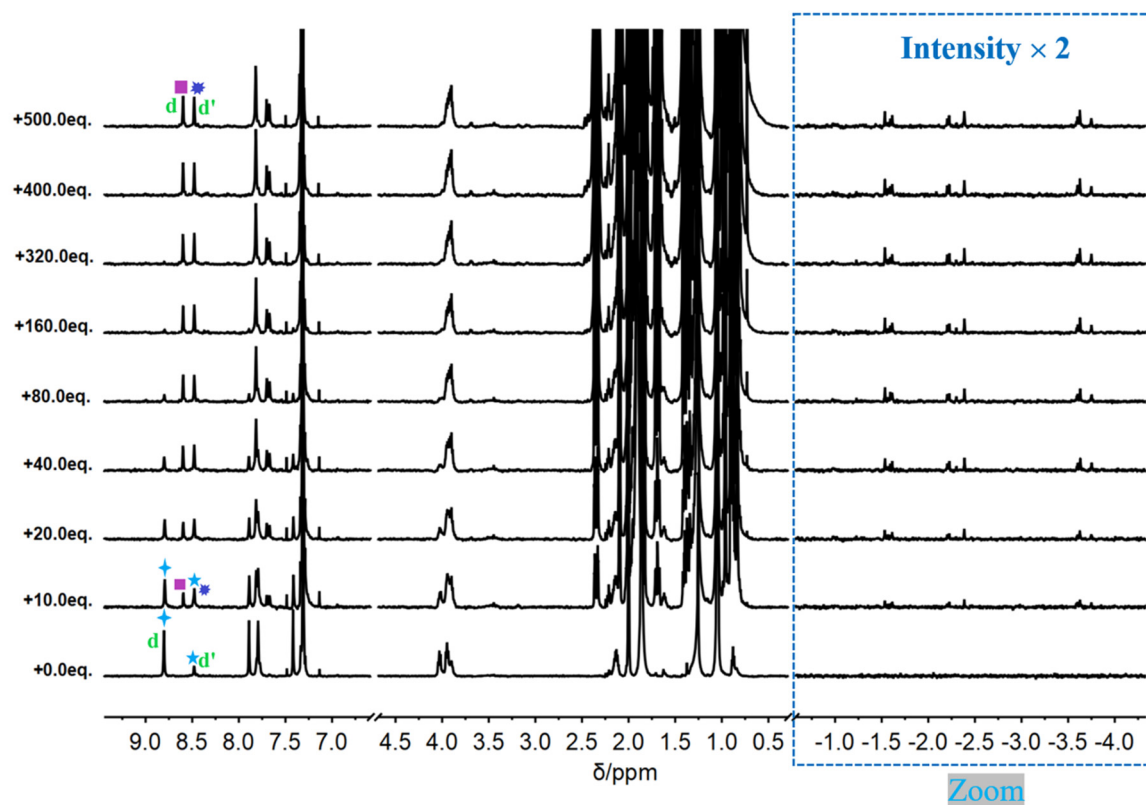


Figure S42. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (0.5 mM) upon the addition of (1*R*)-(+)-camphor ((*R*)-**7**) (5 M).

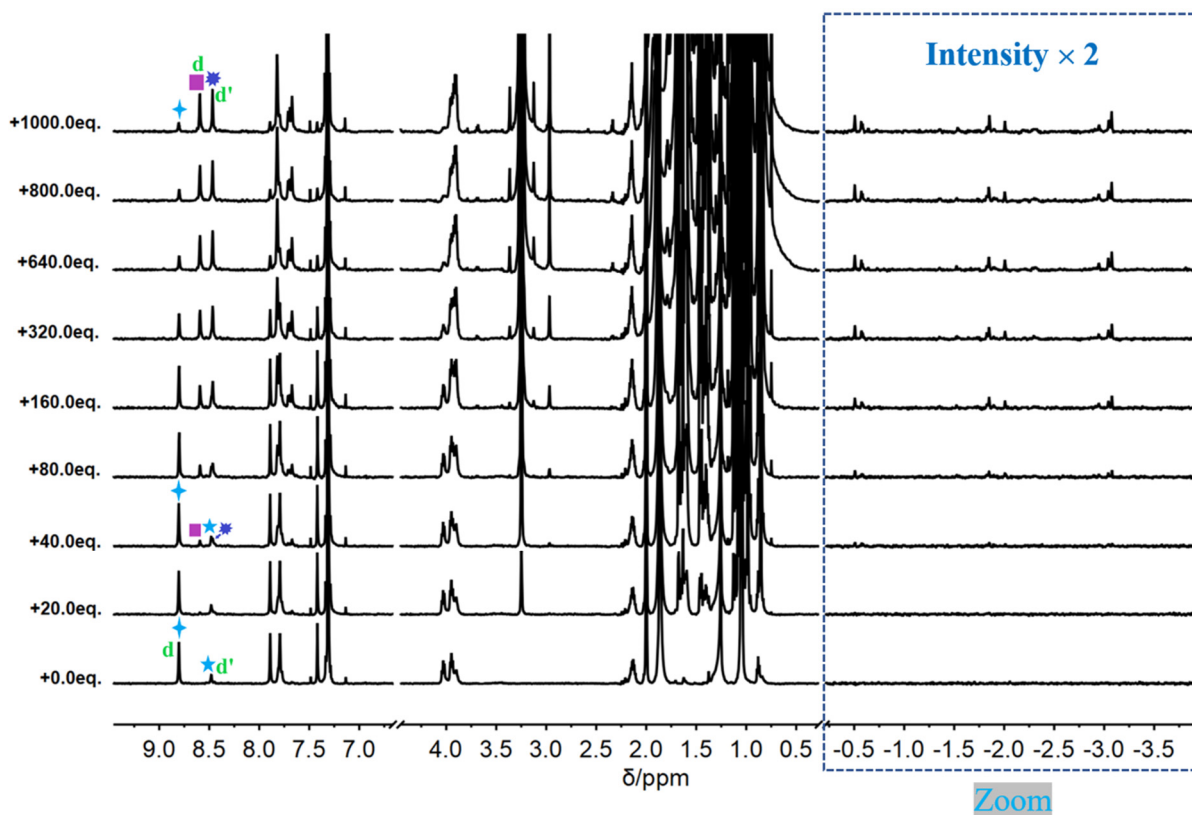


Figure S43. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (0.5 mM) upon the addition of (1*R*)-endo-(+)-fenchyl alcohol (**8**) (10 M).

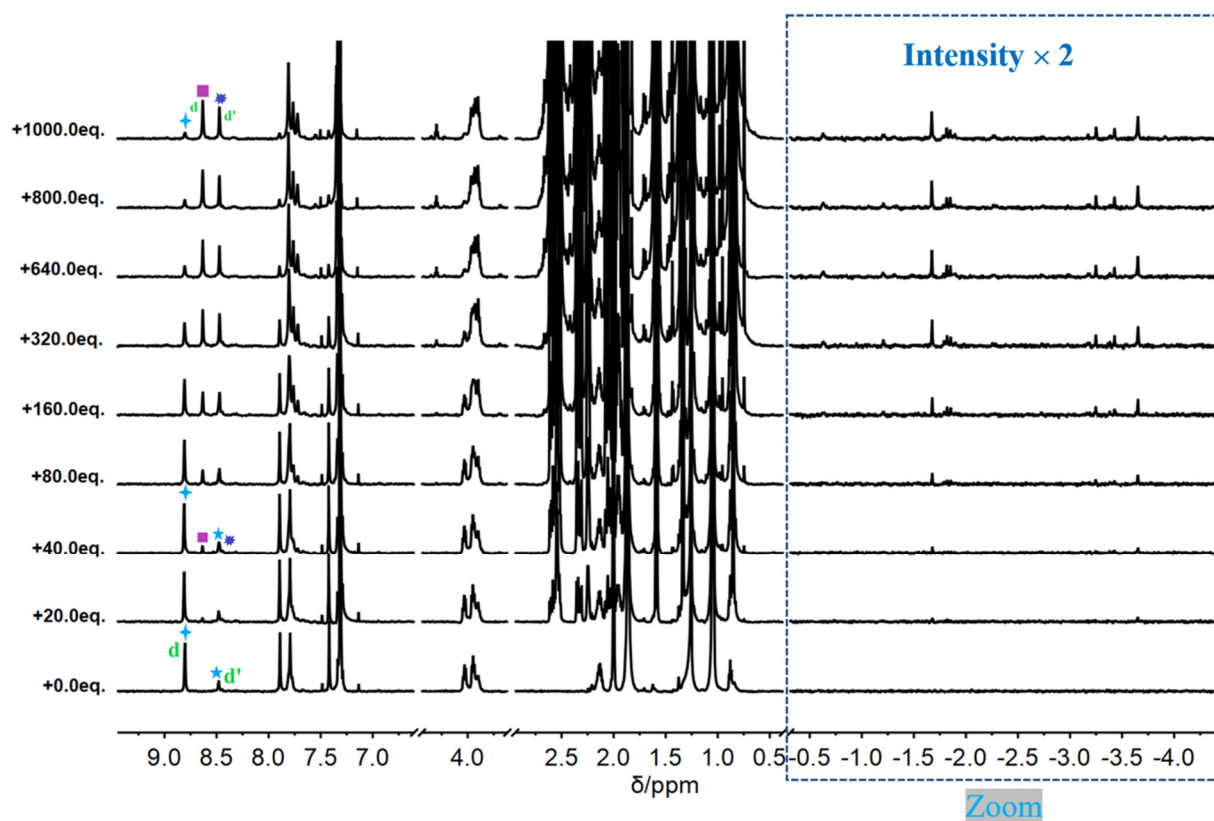


Figure S44. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (0.5 mM) upon the addition of (1*R*)-(+)-nopinone (**9**) (10 M).

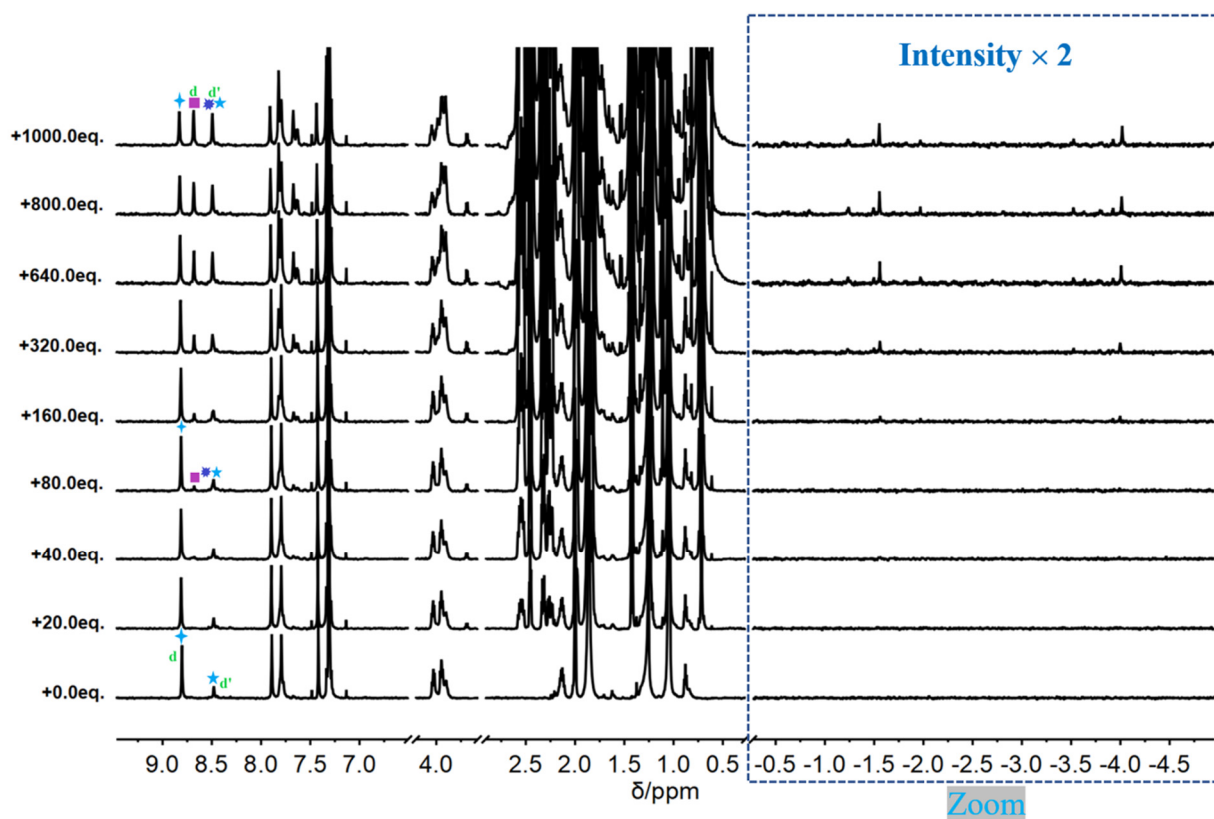


Figure S45. Changes of ^1H NMR spectra (600 MHz, 298 K, 7:93(v/v) $\text{CD}_3\text{CN}/\text{CDCl}_3$) of molecular cage **1** (0.5 mM) upon the addition of (1*S*)-(β)-pinene (**10**) (10 M).

8.c Identification of Analytes in Samples of Mixture

Identification of 2 in the mixture of 2 and tricyclo[5.2.1.0(2,6)]decan-8-one. A series of stock solutions of a mixture of adamantane (**2**) and *tricyclo[5.2.1.0(2,6)]decan-8-one*, with different molar ratio but a constant total concentration of 600 mM, in 2:7:91 (v/v/v) DMSO-*d*₆/CD₃CN/CDCl₃ were prepared in advance. Then, to a solution of **1** (1 mM, 0.5 mL) in 2:7:91 (v/v/v) DMSO-*d*₆/CD₃CN/CDCl₃, a solution of above guest mixtures was gradually added. ¹H NMR spectra of this series of samples were recorded at 298 K. The obtained ¹H NMR spectra are shown in Figure S47, and the derived data are summarized in Table S11.

Identification of analytes in a mixture of 2, 2b and 2c. A 1:1:1 (molar ratio) mixture of **2**, **2b** and **2c** was first dissolved into 2:7:91 (v/v/v) DMSO-*d*₆/CD₃CN/CDCl₃ to give a stock solution of the target mixture (500 mM: 500 mM: 500 mM). The solution (10 μL) was then added into cage **1** (1 mM, 0.5 mL) in 2:7:91 (v/v/v) DMSO-*d*₆/CD₃CN/CDCl₃, and a ¹H NMR spectrum of the resultant sample was recorded at 298 K. The obtained spectrum is shown in Figure 4a(e) (in the main text) and Figure S46. The derived data are shown in Table S11.

Table S11. Summary of CCDs^a and H_d chemical shifts (CS)^b of cage **1** in the presence of analyte mixtures in 2:7:91 (v/v/v) DMSO-*d*₆/CD₃CN/CDCl₃ at 298 K.

Sample	Content	Equiv.	CCD	CS (ppm)
mixture : 2+2b+2c	 +	10	2.941	8.759
	 +	10	2.380	8.704
		10	1.370	8.654
2+impurity		2/10	3.030	8.760
	 + 	6/6	2.941	8.757
		10/2	3.030	8.758

^a Data were derived from the ¹H NMR integrations of signals of H_d and H_e. ^b Chemical shifts of the proton H_d.

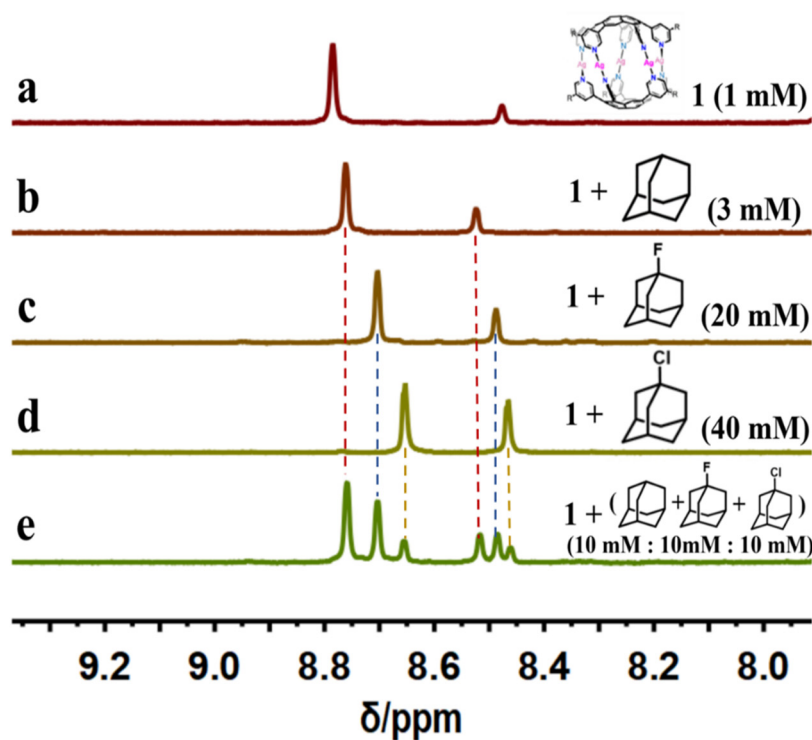


Figure S46. ¹H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) DMSO-*d*₆/CD₃CN/CDCl₃) of **1** (1 mM) in the absence and the presence of pure compounds or a compounds mixture. (a) ¹H NMR spectra of cage **1**. (b-d) ¹H NMR spectras of **1** upon the addition of (b) adamantane (**2**) (3 mM), (c) 1-fluoroadamantane (**2b**) (20 mM), and (d) 1-chloroadamantane (**2c**) (40 mM). (e) ¹H NMR spectra of molecular cage **1** upon the addition of the mixture of adamantane (**2**) (10 mM), 1-fluoroadamantane (**2b**) (10 mM) and 1-chloroadamantane (**2c**) (10 mM).

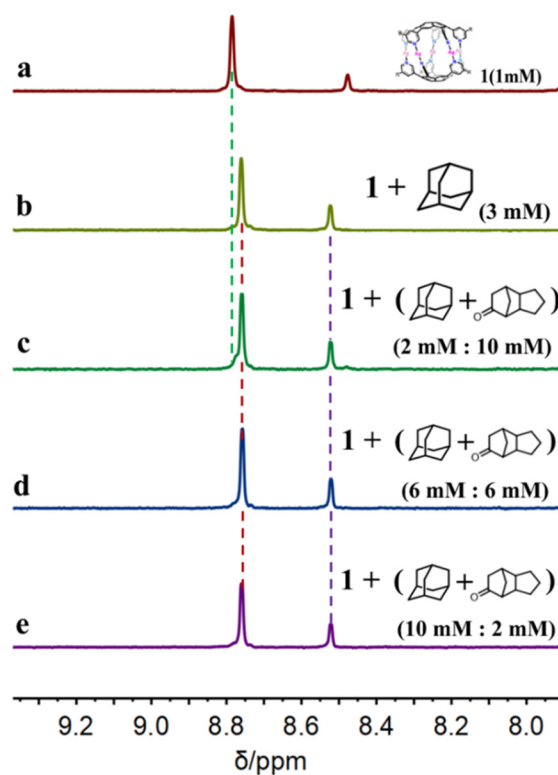


Figure S47. Changes of ^1H NMR spectra (600 MHz, 298 K, 2:7:91 (v/v/v) $\text{DMSO-}d_6/\text{CD}_3\text{CN}/\text{CDCl}_3$) of cage **1** (1 mM) upon the addition of mixtures of compounds: (a) Cage **1**. (b) Cage **1** in the presence of adamantane (**2**) (3 mM). (c-e) Cage **1** in the presence of the mixtures of adamantane (**2**) and *tricyclo[5.2.1.0(2,6)]decan-8-one* in different proportions.

9. Computational Details

DFT calculations, performed by the Gaussian 09 program package^{S3} under Linux operating system, were applied to determine the stationary structures of **2**⊂**1** as well as the investigated guest molecules, including **2**, 1-fluoroadamantane (**2b**) and 1-chloroadamantane (**2c**), (*1S*)-(–)-camphanic acid (**3a**), (*S*)-(+)-ketopininc acid (**3b**), and bicyclo[2.2.2]octane-1,4-dicarboxylic acid (**3c**), *trans*-1,4-adamantanediol (**4a**), *cis*-1,4-adamantanediol (**4b**), and *rac*-1,2-adamantanediol (**4c**). For the cage-guest complexes, the calculations were carried out using 30 processing cores with 100 GB physical memory (National Supercomputing Center–Shenzhen, China), whereas for the guests, 12 processing cores and 8 GB physical memory were used (Supercomputing Center, Beijing Normal University).

2⊂**1** Complexes. As the same as that in the case of **1**,^{S1} the minima of the cage/guest complexes were obtained by full system optimization at the B3LYP//LANL2DZ/ 6-31G(d)//CPCM-UAHF levels of theory, using LANL2DZ pseudopotential for Ag and 6-31G(d) basis set for the rest atoms. Dispersion was taken into account using Grimme's empirical dispersion correction (D3 version)^{S4} with Becke–Johnson damping function^{S5} (empiricaldispersion=gd3bj). The conductor-like polarizable continuum calculation model (CPCM) for chloroform solvent was used for the computation^{S6–7}, in which the default static dielectric constant value of chloroform was replaced with the average of the ones of chloroform and acetonitrile, weighted by the 93:7 (chloroform/acetonitrile) fraction ratio of these two solvents. Notably, as we stated in our previous paper,^{S1} most solvent models, including the one used in our computational calculations, are not based on explicit solvent molecules that can interact with solute molecules but instead model the solvent as a polarizable continuum. The energies are reported with the lowest electronic energies of the corresponding complexes; vibrational frequencies were not computed due to the huge calculative workload (181

atoms, 546 degrees of freedom in the 1st order CPHF) on the condition of our limited computation resources.

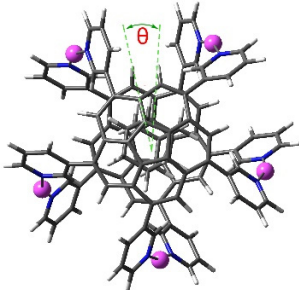
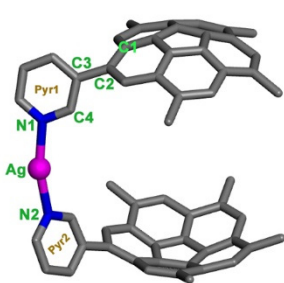
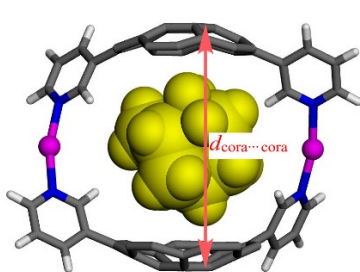
1:1 Complexes of **2** with $[\text{Ag}_5\text{L}_2]^{5+}$ (**2** $\subset$ $[\text{Ag}_5\text{L}_2]^{5+}$), the isolated states which could be regarded as the cases when the complexes are highly solvated, were optimized. The optimizations were carried out on the four stereoisomers of the complexes, including **2** $\subset$ $[(P,M,P)\text{-Ag}_5\text{L}_2]^{5+}$, **2** $\subset$ $[(M,P,M)\text{-Ag}_5\text{L}_2]^{5+}$, **2** $\subset$ $[(P,P,P)\text{-Ag}_5\text{L}_2]^{5+}$ and **2** $\subset$ $[(M,M,M)\text{-Ag}_5\text{L}_2]^{5+}$. To reduce the computational cost, we just calculated a simplified structure of **1**, in which all the *iso*-butoxy side chains were replaced with hydrogen atoms.

The obtained geometries and the corresponding energies as well as the structural parameters are summarized in Tables S12–S13. The sizes of the complexes are especially shown in Figure S49, in which the diameters reported are derived from the average distances between two hydrogen atoms being directed *exo* in two spatially adjacent pyridyl groups, respectively (Figure S48), utilizing the general geometric calculation formulas. For comparison, the geometries of $(P,M,P)\text{-Ag}_5\text{L}_2]^{5+}$, $[(M,P,M)\text{-Ag}_5\text{L}_2]^{5+}$, $[(P,P,P)\text{-Ag}_5\text{L}_2]^{5+}$ and $[(M,M,M)\text{-Ag}_5\text{L}_2]^{5+}$ which optimized at the same level of theory and method² were also illustrated in Figure S49.

Guest Molecules. Guests **2** – **4c** were investigated in our computations. Considering that all these molecules are pretty rigid such that their geometries are hardly affected by the solvent circumstances, their unconstrained geometries were optimized in the gas phase at B3LYP//6-31+G(d,p) levels of theory. The shape and size of the molecules are represented as a product of three longest atom-atom distances along one of three roughly perpendicular coordinates; volumes of the molecules are reported based on the CPK mode.

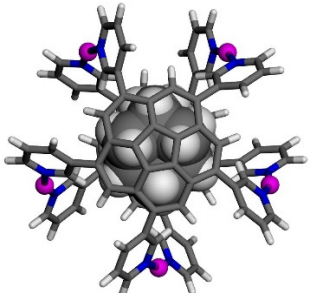
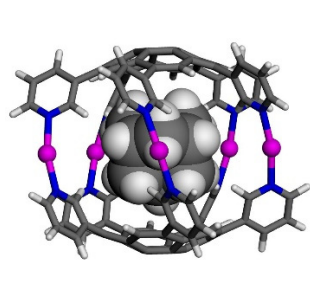
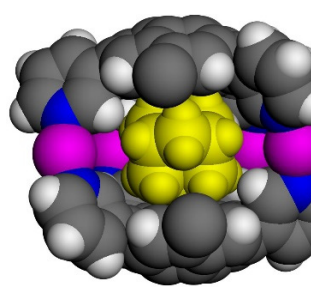
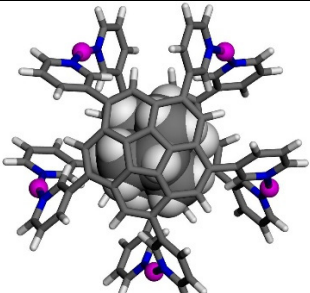
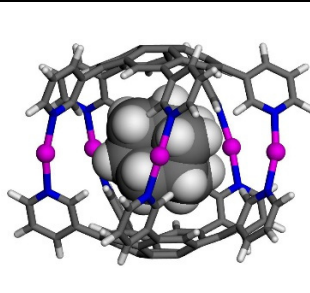
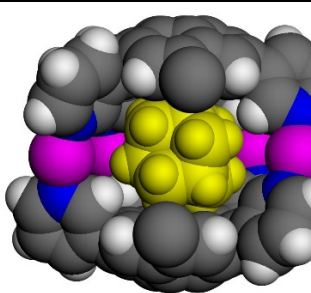
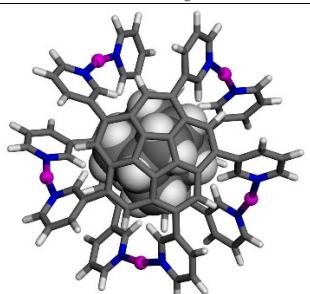
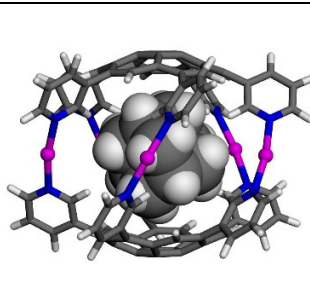
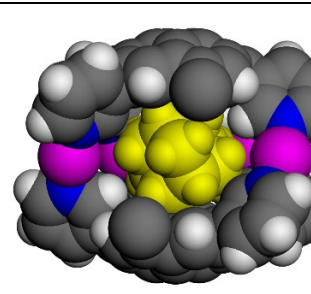
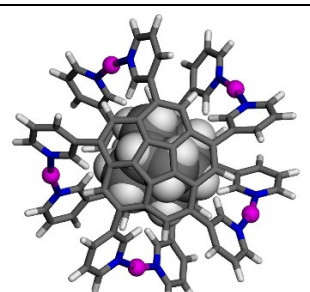
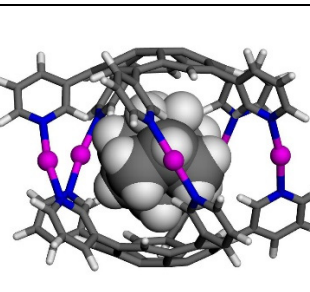
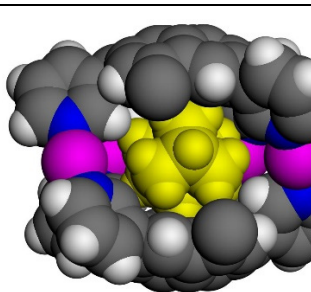
All the obtained geometries and the corresponding structural parameters are summarized in Table S14.

Table S12. The DFT//B3LYP//LANL2DZ/6-31G(d) calculations with Grimme's dispersion correction for the minima of 1:1 complexes of adamantane (**2**) and isolated $[\text{Ag}_5\text{L}_2]^{5+}$ in different conformers ($2\subset[(\text{conformation})\text{-Ag}_5\text{L}_2]^{5+}$) in a solvent model: energies (E° , hartree), relative energies (kcal mol⁻¹) and the important parameters for the geometries.^{a,b}

									
Geometry	E°	Rel. energies ^c	θ^d ($^\circ$)	Dihedral Angel (Pyr1/Pyr2) ^e ($^\circ$)	Dihedral Angel (C1-C2-C3-C4) ($^\circ$)	Dihedral Angel (C3-C4-N1-Ag) ($^\circ$)	$\varphi_{\text{N1}\cdots\text{Ag}\cdots\text{N2}}^f$ ($^\circ$)	$d_{\text{N1}\cdots\text{Ag}}^g$ (Å)	$d_{\text{cora}\cdots\text{cora}}^h$ (Å)
$2\subset[(P,M,P)\text{-Ag}_5\text{L}_2]^{5+}$	-5126.8763009	0.00	19.48	60.54~61.90	124.26~126.38	169.46~171.29	164.17~ 165.82	2.1692~ 2.1743 2.1707~ 2.1726	10.83
					124.51~125.71	170.05~170.91			
$2\subset[(M,P,M)\text{-Ag}_5\text{L}_2]^{5+}$	-5126.8761630	0.09	19.00	60.90~61.84	46.96~48.16	-172.02~-169.30	165.15~ 165.50	2.1693~ 2.1726 2.1704~ 2.1716	10.87
					47.44~48.04	-170.85~-170.07			
$2\subset[(P,P,P)\text{-Ag}_5\text{L}_2]^{5+}$	-5126.8693606	4.36	7.54	46.00~47.39	54.61~58.69	-177.37~-174.46	167.89~ 168.54	2.1716~ 2.1742 2.1701~ 2.1759	10.37
					54.10~57.24	-177.65~-172.42			
$2\subset[(M,M,M)\text{-Ag}_5\text{L}_2]^{5+}$	-5126.8693065	4.39	6.16	45.46~46.78	113.42~116.99	174.18~177.44	167.94~ 168.62	2.1706~ 2.1740 2.1704~ 2.1750	10.37
					114.40~118.07	172.40~177.81			

^a In a chloroform solvent-model, in which the default static dielectric constant value were replaced with the average of the ones of chloroform and acetonitrile, weighted by the 93:7 (chloroform/acetonitrile) fraction ration of these two solvents. ^b Model for elaboration the structural parameters is shown at the top of the table. The two pyridyl rings that coordinates with the same silver cation denotes "pyr1" and "pyr2", respectively. For clarity, some of the atoms were deleted. Notably, some parameters are different between the two layers, which are thus dividedly given and separated by dotted lines. ^c Relative energy with relative to that of the most stable conformer. 1 Hartree = 627.5095 kcal mol⁻¹. ^d Torsion angle between the two corannulene units. ^e The dihedral angle between the planes of two pyridyl rings that coordinates with the same silver cation. ^f The bond angles of the N1⋯Ag⋯N2 coordination bond. ^g The N1⋯Ag distance. ^h The length of the cage when the guest is included.

Table S13. Summary of the illustration of the DFT optimized structures of $2 \subset [(P,P,P)\text{-Ag}_5\text{L}_2]^{5+}$: top and side view, side view with partial groups omitted for clarity.

$2 \subset [(P,M,P)\text{-Ag}_5\text{L}_2]^{5+}$			
$2 \subset [(M,P,M)\text{-Ag}_5\text{L}_2]^{5+}$			
$2 \subset [(P,P,P)\text{-Ag}_5\text{L}_2]^{5+}$			
$2 \subset [(M,M,M)\text{-Ag}_5\text{L}_2]^{5+}$			

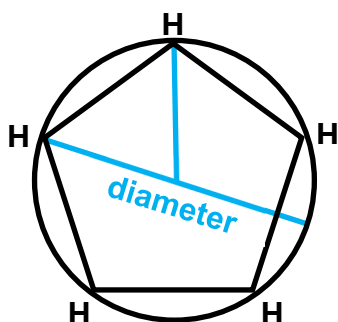


Figure S48. The diameters of the cage-guest complexes reported are derived from the average distances between two hydrogen atoms being directed *exo* in two spatially adjacent pyridyl groups (denoted **H**), respectively, utilizing the general geometric calculation formulas.

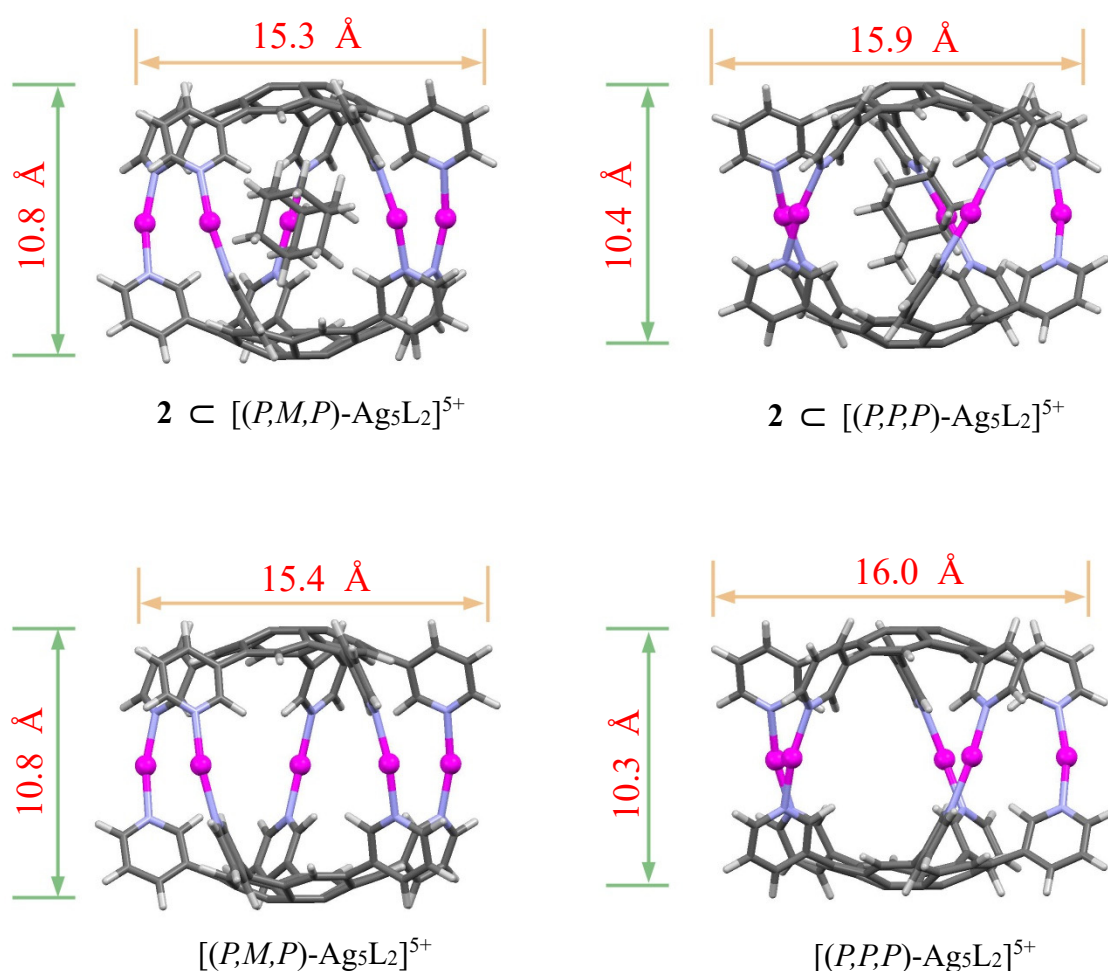
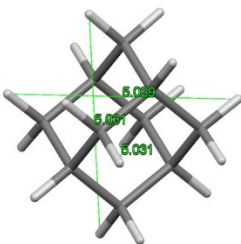
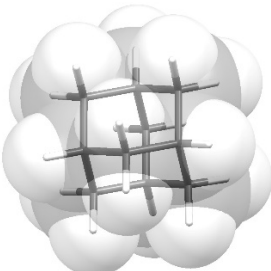
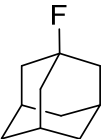
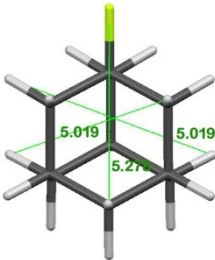
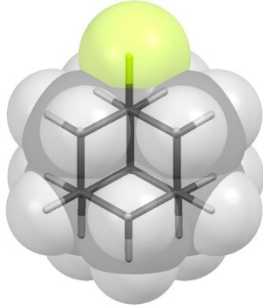
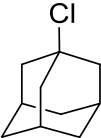
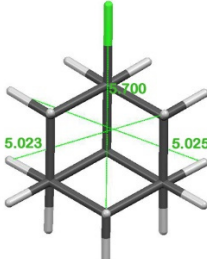
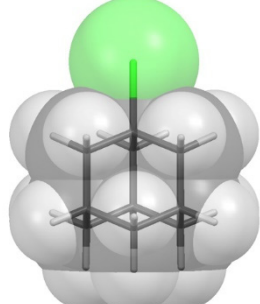
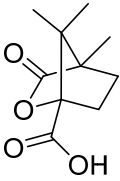
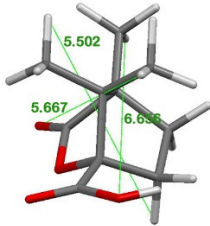
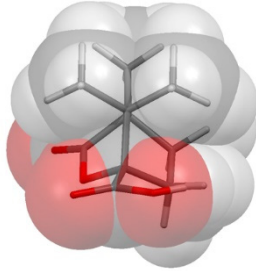
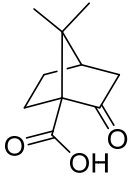
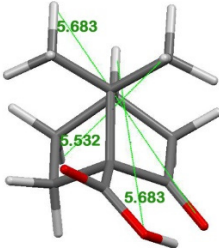
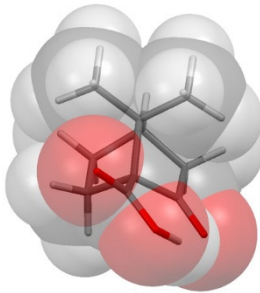
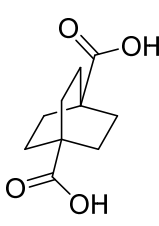
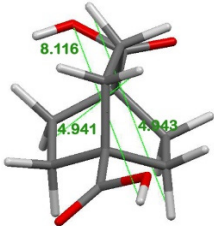
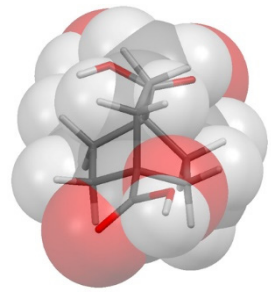
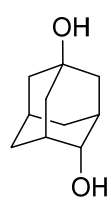
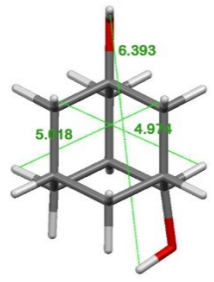
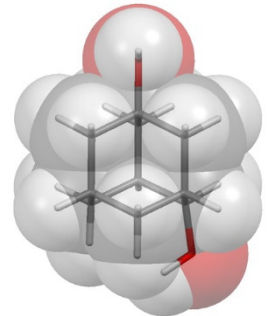
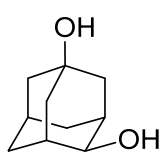
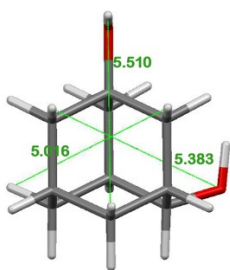
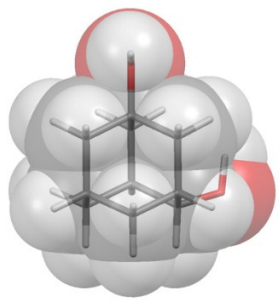
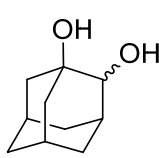
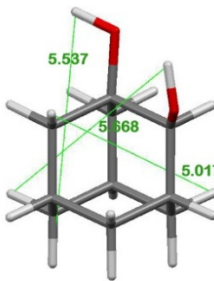
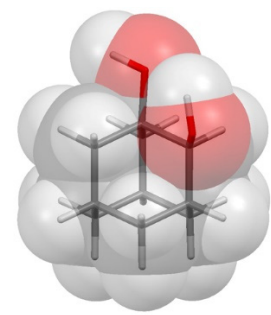
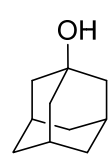
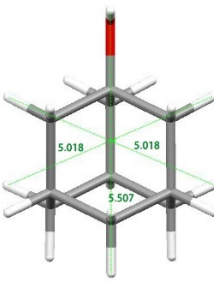
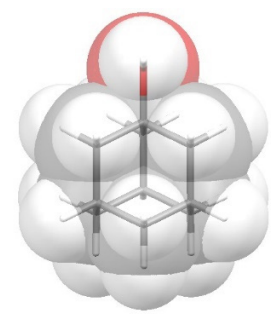


Figure S49. The sizes of $2 \subset 1$ cage complexes as well as the isolated cages. As examples, the species in *P,M,P* and *P,P,P* conformations are shown.

Table S14. Size, Corey–Pauling–Koltun (CPK) volume and illustration of the DFT optimized structures of guests **2**, **2b–c**, **3a–c** and **5–10**.

Guest	Chemical Structure	Shape and Size (Å × Å × Å)	CPK Volume (Å ³)	Molecular Structure
2		 5.03 × 5.03 × 5.03	159.85	
2b		 5.28 × 5.02 × 5.02	164.67	
2c		 5.70 × 5.02 × 5.03	173.85	
3a		 6.66 × 5.50 × 5.67	195.19	
3b		 5.68 × 5.68 × 5.53	184.97	

3c		 $8.12 \times 4.94 \times 4.94$	191.35	
4a		 $6.39 \times 5.02 \times 4.97$	174.54	
4b		 $5.51 \times 5.02 \times 5.38$	174.54	
4c		 $5.54 \times 5.67 \times 5.02$	174.50	
5		 $5.51 \times 5.02 \times 5.02$	167.22	

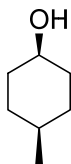
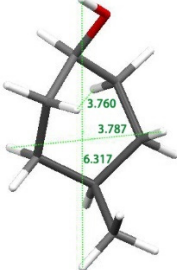
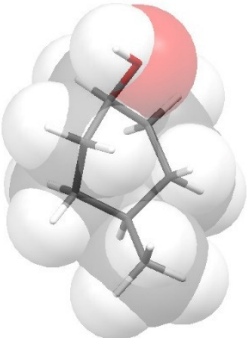
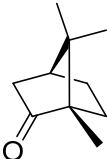
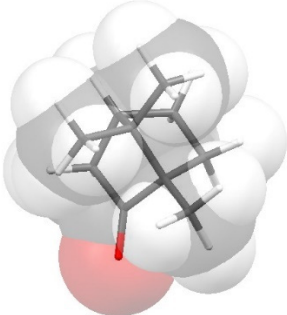
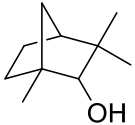
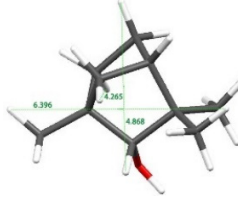
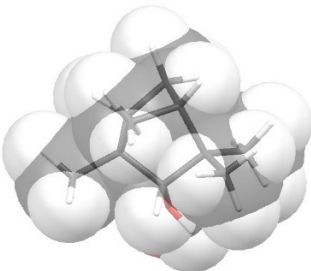
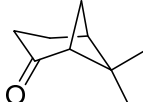
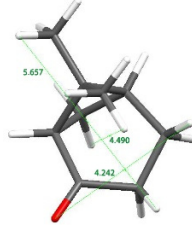
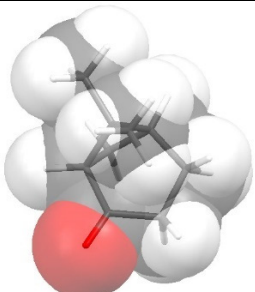
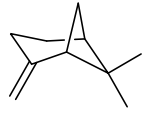
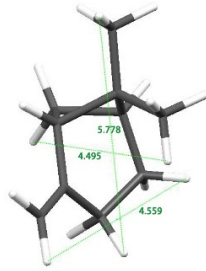
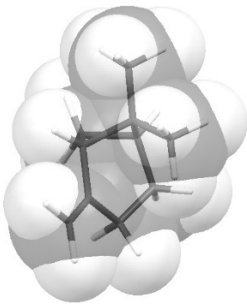
6		 $6.32 \times 3.79 \times 3.76$	138.01	
(S)-7		 $5.24 \times 5.10 \times 4.61$	176.46	
8		 $6.40 \times 4.87 \times 4.27$	181.88	
9		 $5.66 \times 4.49 \times 4.24$	159.58	
10		 $5.78 \times 4.56 \times 4.60$	171.26	

Table S15. The DFT B3LYP//6-31+G(d,p) calculations for guests **2**, **2b–c**, **3a–c** and **4a–c**: energies (E° , hartree), zero point vibrational energies (ZPVE, hartree), lowest vibrational frequencies (cm^{-1}), and dipole moments (μ , D).

geometry	Medium	E°	ZPVE	$E^\circ + \text{ZPVE}$	RMS gradient ($\times 10^{-6}$) ^a	Lowest vibrational frequencies	μ
2	gas	−390.75425258	0.242814	−390.511439	31	310.6, 314.7	0.00
2b	gas	−490.00545455	0.234671	−489.770784	49	263.9, 264.7	2.53
2c	gas	−850.35754901	0.233433	−850.124116	45	209.8, 209.9	2.56
3a	gas	−690.44820884	0.231241	−690.216968	3	31.0, 131.4	7.09
3b	gas	−615.22157496	0.22832	−614.993255	9	52.6, 113.0	7.42
3c	gas	−690.46912476	0.235419	−690.233706	2	18.5, 34.0	3.71
4a	gas	−541.20013683	0.250679	−540.949458	3	168.3, 193.1	2.56
4b	gas	−541.20085601	0.250889	−540.949967	6	163.5, 229.4	2.58
4c	gas	−541.20506108	0.251189	−540.953872	6	173.5, 246.0	2.30

^a In Cartesian coordinates.

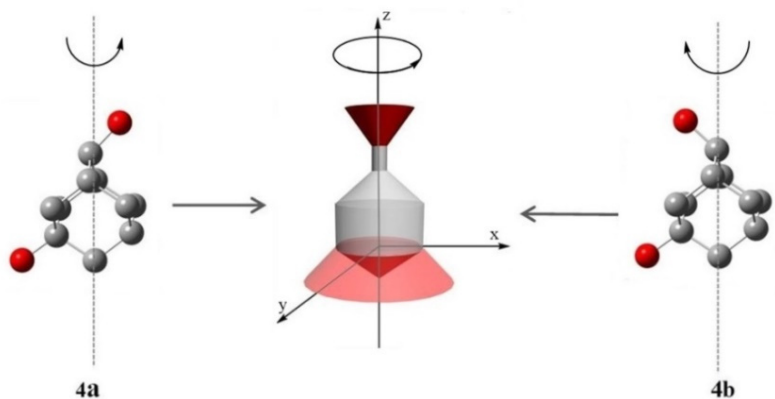


Figure S50. Cartoon illustration: rotation of two molecules along certain axes would give the same or very closed size and shape in terms of their solid of revolution.

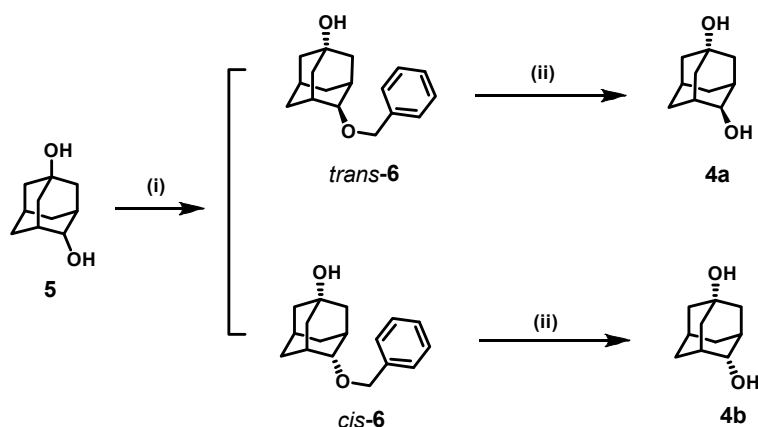
10. Synthesis and Characterization of Adamantanediols 4a–c

10.a Synthesis of Adamantanediols 4a–c

Commercial 1,4-adamantanediol (**5**) is a mixture of a pair of geometric isomers; and we used a chemical method to resolve them (Figure S51). Initially, mono-*O*-benzylation of the commercial **5** by benzyl chloride to give a mixture of diastereomers of *trans*-**6** and *cis*-**6**,^{S8} which were carefully isolated by regular silica gel column chromatography. Further reductive debenzylation^{S9} of *trans*-**6** and *cis*-**6** gave rise to the resolved target compounds of *trans*-1,4-adamantanediol (**4a**) and *cis*-1,4-adamantanediol (**4b**), respectively. The successful resolution was verified by the corresponding ¹H NMR spectra of the compounds (Figure S54).

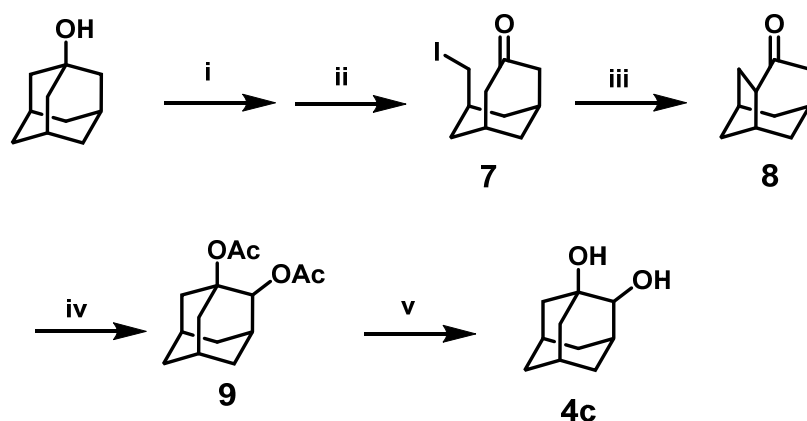
Rac-1,2-adamantanediol (**4c**) was prepared according to a known procedure (Figure S52).^{S10–14}

Figure S51. Resolution of isomeric 1,4-adamantanediol ^a

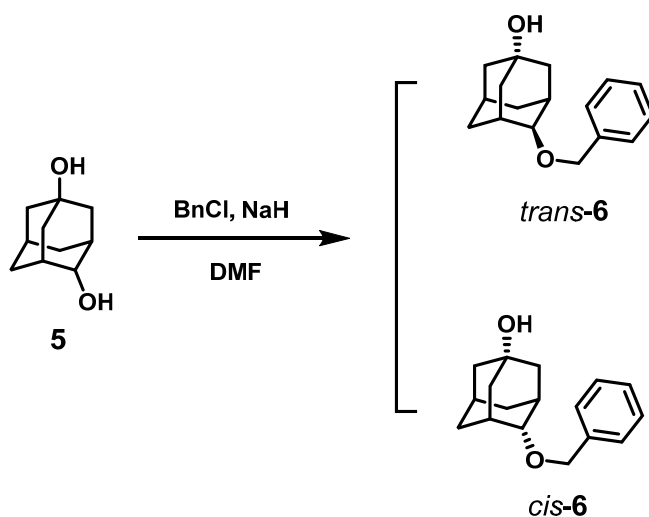


^a Reagents and conditions: (i) benzyl chloride, NaH, DMF, room temperature, 15 h; (ii) H₂, Pd/C, EtOH, 5 M HCl, 18 bar, 60 °C, 2 days.

Figure S52. Synthesis of *rac*-1,2-adamantanediol ^a, S10–14



^a Reagents and conditions: (i) Pb(OAc)₄, I₂, anhydrous benzene, 70–75 °C, 2 h; (ii) room temperature, 1 h; (iii) KOH, anhydrous MeOH, reflux, 3 h; (iv) Ac₂O, BF₃, room temperature, 6 h, 60 °C, 1 h; (v) K₂CO₃, anhydrous MeOH, reflux, 0.5 h.

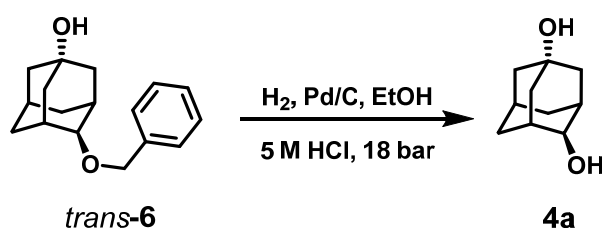


***trans/cis*-4-(Benzyloxy)adamantane-1-ol (*trans*-6 and *cis*-6)^{S8}:** To a solution of racemic 1,4-adamantanediol (400 mg, 2.36 mmol) and NaH (114.12 mg, 4.76 mmol) in dry DMF (20 mL) was added benzyl chloride (328.36 μ L, 2.86 mmol). The obtained solution was stirred for 15 hours at room temperature. The resulting solution was extracted with ethyl acetate and the combined organic layers were washed with brine for at least 3 times, dried over anhydrous Na₂SO₄ and evaporated in vacuo. The residue was purified on silica gel column chromatography (dichloromethane/EtOAc, 20/1) to afford *trans*-6 (182 mg, white amorphous solid, yield: 59%) and *cis*-6 (163 mg, white amorphous

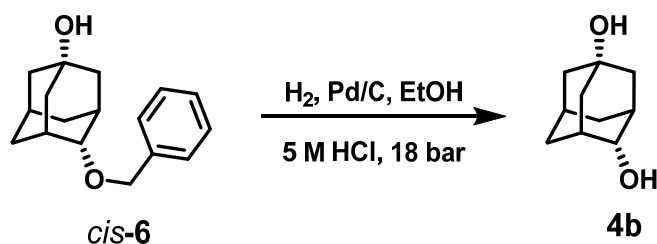
solid, yield: 53%) .

trans-**6**: ^1H NMR (400 MHz, CDCl_3) δ = 7.32 (ddd, J = 29.2, 18.6, 7.8 Hz, 5H), 4.53 (s, 2H), 3.55 (s, 1H), 2.24 (s, 2H), 2.11 – 2.06 (m, 3H), 1.74 (d, J = 9.2 Hz, 6H), 1.37 (d, J = 12.2 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ = 139.7, 128.8, 127.8, 80.5, 77.7, 77.5, 77.3, 70.2, 68.5, 45.9, 44.0, 34.0, 30.7, 30.4.

cis-**6**: ^1H NMR (400 MHz, CDCl_3) δ = 7.35 (m, 5H), 4.53 (s, 2H), 3.40 (s, 1H), 2.34 (s, 2H), 2.12 – 2.05 (m, 3H), 1.69 (s, 4H), 1.50-1.47 (d, J = 11.6 Hz, 3H), 1.32 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ = 139.7, 128.8, 127.8 (s), 79.7, 77.7, 77.5, 77.3, 69.8, 68.2, 45.5, 40.1, 35.4, 34.9, 30.3.



trans-1,4-adamantanediol (**4a**)^{S9}: Pd/C (10 mg, 10%) and 3 drops of 5 M HCl in EtOH were added to a solution of *trans*-**6** (100 mg, 0.39 mmol) in EtOH (9.0 mL). The mixture was stirred under H_2 (18 bar) at 60 °C by an oil bath for 2 days. After the reaction was completed, the mixture was filtered and the solvent was removed under reduced pressure. The compound **4a** was recrystallized from ethyl acetate. (26.83 mg; white amorphous solid, yield: 41%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 4.50 (s, 1H), 4.27 (s, 1H), 3.59 (s, 1H), 1.90 (d, J = 11.5 Hz, 3H), 1.77 (s, 2H), 1.51 (q, J = 12.0, 10.9 Hz, 6H), 1.15 (d, J = 11.1 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO}-d_6$) δ = 72.2, 66.2, 46.1, 44.1, 36.4, 30.2, 30.0.



***cis*-1,4-adamantane-1,4-diol (4b)**^{S9}: Pd/C (10 mg, 10%) and one drop of 5 M HCl in EtOH were added to a solution of *cis*-6 (100 mg, 0.39 mmol) in EtOH (9.0 mL). The mixture was stirred under H₂ (18 bar) at 60 °C by an oil bath for 2 days. After the reaction was completed, the mixture was filtered and the solvent was removed under reduced pressure. The compound **4b** was recrystallized from ethyl acetate. (22.10 mg, white amorphous solid, yield: 34%). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 4.49 (s, 1H), 4.19 (s, 1H), 3.53 – 3.40 (m, 1H), 1.88 (d, *J* = 12.8 Hz, 5H), 1.47 (q, *J* = 16.9, 14.5 Hz, 6H), 1.20 (d, *J* = 10.2 Hz, 2H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ = 71.5, 66.3, 45.9, 37.2, 35.3, 29.5.

***rac*-1,2-adamantane-1,2-diol (4c)**: The compound was synthesized according to the procedure reported in the literatures.^{S10–14} ¹H NMR (400 MHz, CDCl₃) δ = 3.65 (s, 1H), 2.17 (d, *J* = 2.2 Hz, 1H), 2.09 (d, *J* = 12.1 Hz, 4H), 1.92 (d, *J* = 12.7 Hz, 1H), 1.81 (s, 1H), 1.79 – 1.71 (m, 2H), 1.71 – 1.61 (m, 3H), 1.49 – 1.36 (m, 2H), 1.25 (s, 1H) (*lit.*: ¹H NMR (400 MHz, CDCl₃)^{S10–14} δ = 3.67 (dd, *J* = 9.0 Hz, 4.0 Hz, 1H), 3.1 (br, 2H), 1.2–2.4 (br, 15H)). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ = 76.4, 75.9, 75.6, 75.3, 69.0, 42.1, 37.2, 34.7, 34.3, 29.0, 28.4, 28.1.

10.b ^1H NMR Spectra of 4a, 4b and the Commercial Mixture

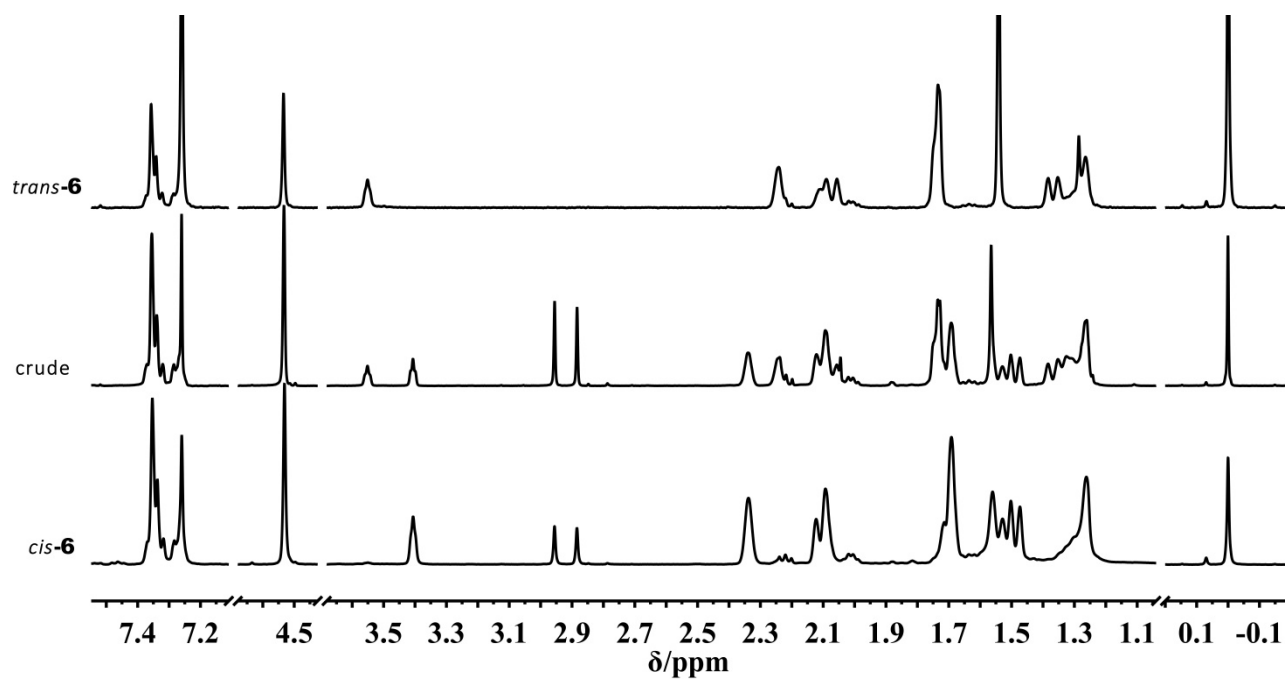


Figure S53. ^1H NMR contract spectra (400 MHz, CDCl_3 , 298 K) of compound *trans*-6, *cis*-6 and the crude before isolation.

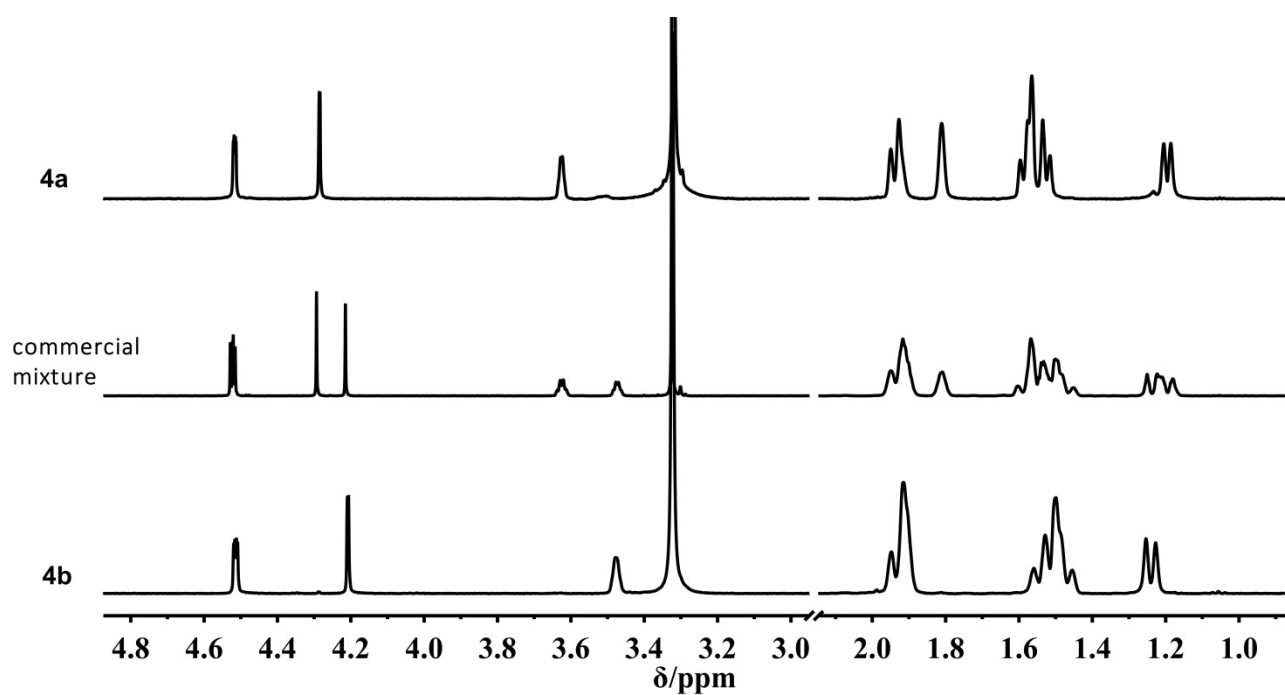


Figure S54. ^1H NMR contract spectra (400 MHz, $\text{DMSO}-d_6$, 298 K) of compound 4a, 4b and commercial mixture.

11. Optimized Geometries/Coordinate Outputs of DFT Calculations

2c [(P,M,P)-Ag ₅ L ₂] ⁵⁺ (in 7:93 (v/v) CD ₃ CN/CDCl ₃):							2c [(M,P,M)-Ag ₅ L ₂] ⁵⁺ (in 7:93 (v/v) CD ₃ CN/CDCl ₃):						
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)				Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)			
			X	Y	Z					X	Y	Z	
1	6	0	4.275874	-3.488629	4.550135		1	6	0	-4.961127	-2.423708	-4.566955	
2	6	0	5.220724	-4.319750	3.952739		2	6	0	-6.108859	-2.928832	-3.960261	
3	6	0	5.765501	-3.955367	2.724492		3	6	0	-6.000770	-3.563961	-2.726061	
4	7	0	5.401718	-2.820706	2.095092		4	7	0	-4.815700	-3.702182	-2.099712	
5	6	0	3.903872	-2.296652	3.911095		5	6	0	-3.720832	-2.579895	-3.931398	
6	6	0	4.496136	-2.013637	2.677718		6	6	0	-3.705999	-3.223817	-2.691551	
7	1	0	3.834199	-3.751857	5.510384		7	1	0	-5.018362	-1.922387	-5.532226	
8	1	0	5.537023	-5.244538	4.430243		8	1	0	-7.082940	-2.834939	-4.435240	
9	1	0	4.212791	-1.119921	2.126034		9	1	0	-2.773132	-3.337454	-2.144076	
10	6	0	-1.531870	5.316244	4.519632		10	6	0	5.480856	-0.852765	-4.544652	
11	6	0	-1.945470	4.136521	3.884521		11	6	0	4.577361	0.004648	-3.900278	
12	6	0	-2.586894	4.258497	2.649676		12	6	0	4.950876	0.520113	-2.656744	
13	7	0	-2.823749	5.443482	2.058829		13	7	0	6.124577	0.232718	-2.065293	
14	6	0	-1.788885	6.544820	3.915101		14	6	0	6.703077	-1.138354	-3.940220	
15	6	0	-2.436094	6.573446	2.682780		15	6	0	6.993166	-0.580118	-2.698342	
16	1	0	-1.024690	5.266905	5.482304		16	1	0	5.228753	-1.279204	-5.514668	
17	6	0	-5.637777	0.189424	4.462829		17	6	0	2.559284	5.006054	-4.470097	
18	6	0	-6.873589	0.307177	3.829716		18	6	0	3.191986	6.073857	-3.837520	
19	6	0	-7.056433	-0.282009	2.581359		19	6	0	2.735241	6.491402	-2.590459	
20	7	0	-6.069682	-0.963849	1.967652		20	7	0	1.697134	5.890290	-1.976666	
21	6	0	-4.611304	-0.534198	3.838765		21	6	0	1.466306	4.386914	-3.847061	
22	6	0	-4.881676	-1.088823	2.585838		22	6	0	1.078461	4.867314	-2.593795	
23	1	0	-5.468937	0.642182	5.438997		23	1	0	2.898088	4.659009	-5.445362	
24	1	0	-7.693244	0.850492	4.294727		24	1	0	4.033513	6.583067	-4.302058	
25	1	0	-4.107985	-1.633184	2.049609		25	1	0	0.257392	4.398152	-2.056934	
26	6	0	-2.020490	-5.233590	4.469086		26	6	0	-3.893946	4.024617	-4.484442	
27	6	0	-2.517136	-6.375502	3.845024		27	6	0	-4.718504	4.953689	-3.853738	
28	6	0	-1.999587	-6.752800	2.609157		28	6	0	-5.271602	4.640216	-2.615207	
29	7	0	-1.030910	-6.042984	1.997762		29	7	0	-5.030040	3.461947	-2.007515	
30	6	0	-0.999555	-4.499244	3.849114		30	6	0	-3.652305	2.788684	-3.867773	
31	6	0	-0.543146	-4.946992	2.606869		31	6	0	-4.242764	2.560817	-2.622312	
32	1	0	-2.408730	-4.916727	5.436172		32	1	0	-3.448563	4.245468	-5.453571	
33	1	0	-3.299649	-6.973075	4.307485		33	1	0	-4.935164	5.915482	-4.313386	
34	1	0	0.222650	-4.390610	2.071295		34	1	0	-4.056311	1.631180	-2.089627	
35	6	0	-3.263881	-0.700073	4.429192		35	6	0	0.747037	3.238414	-4.442195	
36	6	0	-2.679461	-1.965034	4.437619		36	6	0	-0.646036	3.243737	-4.454530	
37	6	0	-1.311348	-2.185268	4.836484		37	6	0	-1.422052	2.097272	-4.857094	
38	6	0	-0.680117	-1.088697	5.401482		38	6	0	-0.693105	1.063443	-5.423570	
39	6	0	-2.503305	0.472878	4.830477		39	6	0	1.490595	2.055075	-4.844914	
40	6	0	-1.267186	0.206771	5.398528		40	6	0	0.729323	1.048334	-5.418073	
41	6	0	-0.216305	1.164827	5.409086		41	6	0	1.154527	-0.308887	-5.430426	
42	6	0	-2.714899	1.845934	4.443365		42	6	0	2.824222	1.667939	-4.456575	
43	6	0	-1.692047	2.792288	4.448998		43	6	0	3.251688	0.341753	-4.465539	
44	6	0	-0.342959	2.426994	4.851233		44	6	0	2.351568	-0.727331	-4.870425	
45	6	0	1.020209	0.462252	5.419952		45	6	0	-0.004719	-1.132788	-5.444864	
46	6	0	2.185262	0.979981	4.876686		46	6	0	-0.028444	-2.407906	-4.902409	
47	6	0	2.115202	2.379888	4.487309		47	6	0	1.267714	-2.934745	-4.506140	
48	6	0	0.897945	3.057742	4.477003		48	6	0	2.396682	-2.118236	-4.493208	
49	6	0	0.733354	-0.930488	5.411472		49	6	0	-1.146470	-0.284750	-5.437379	
50	6	0	1.586021	-1.869758	4.853472		50	6	0	-2.358840	-0.661852	-4.881293	
51	6	0	2.898346	-1.367714	4.474624		51	6	0	-2.457007	-2.063173	-4.503019	
52	6	0	3.169370	-0.001072	4.491142		52	6	0	-1.333368	-2.886299	-4.519766	
53	6	0	-0.427081	-3.268805	4.437812		53	6	0	-2.778352	1.752485	-4.461390	
54	6	0	0.956688	-3.102829	4.451932		54	6	0	-3.211511	0.428287	-4.477539	
55	1	0	-3.261345	-2.794447	4.041272		55	1	0	-1.153341	4.120303	-4.056994	
56	1	0	0.886342	4.075935	4.093090		56	1	0	3.321422	-2.537870	-4.102657	
57	1	0	4.135337	0.329782	4.115377		57	1	0	-1.440875	-3.901465	-4.143093	
58	1	0	1.569946	-3.912602	4.061969		58	1	0	-4.204167	0.214241	-4.086825	
59	6	0	4.549442	3.054506	4.610142		59	6	0	0.854365	-5.429337	-4.612850	
60	6	0	3.316380	3.048475	3.941839		60	6	0	1.361591	-4.302900	-3.949367	
61	6	0	3.250667	3.682994	2.699732		61	6	0	1.948359	-4.499178	-2.697059	
62	7	0	4.303601	4.300549	2.135406		62	7	0	2.056377	-5.709394	-2.119262	
63	6	0	5.637525	3.704057	4.031604		63	6	0	0.975029	-6.683966	-4.019712	
64	6	0	5.479999	4.319080	2.792369		64	6	0	1.583378	-6.789225	-2.771853	
65	1	0	4.645027	2.567697	5.579825		65	1	0	0.383087	-5.319493	-5.588685	
66	1	0	-2.901723	3.372345	2.104394		66	1	0	4.273146	1.166302	-2.104574	
67	1	0	-1.492376	7.477189	4.390529		67	1	0	7.429471	-1.788852	-4.422343	
68	1	0	-3.683622	2.148126	4.050755		68	1	0	3.505770	2.418373	-4.061239	
69	1	0	2.325021	3.675732	2.128282		69	1	0	2.323399	-3.651060	-2.128644	
70	1	0	6.602563	3.738051	4.532400		70	1	0	0.603778	-7.577905	-4.515993	
71	1	0	6.500762	-4.578072	2.220125		71	1	0	-6.871715	-3.967647	-2.214982	
72	1	0	6.303707	4.833036	2.302424		72	1	0	1.693727	-7.748212	-2.271016	
73	1	0	-2.650685	7.510067	2.173407		73	1	0	7.931152	-0.783525	-2.186981	
74	1	0	-8.001595	-0.207498	2.048606		74	1	0	3.204127	7.316088	-2.058757	
75	1	0	-2.362404	-7.633759	2.084761		75	1	0	-5.915618	5.338367	-2.085565	
76	47	0	-0.372361	-6.352655	-0.047127		76	47	0	-5.582765	2.991430	0.038478	
77	6	0	2.159473	5.188853	-4.472340		77	6	0	3.790727	-4.147411	4.494757	
78	6	0	2.564157	6.372788	-3.860270		78	6	0	4.692968	-5.005592	3.870095	
79	6	0	3.183544	6.315416	-2.615025		79	6	0	4.376162	-5.531999	2.620730	
80	7	0	3.401254	5.145475	-1.983512		80	7	0	3.218994	-5.234314	1.997946	
81	6	0	2.399985	3.964893	-3.831047		81	6	0	2.576243	-3.846426	3.861625	
82	6	0	3.021964	4.001036	-2.580930		82	6	0	2.342501	-4.415758	2.607765	
83	1	0	1.673406	5.206151	-5.446921		83	1	0	4.015451	-3.721488	5.471718	
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85	1	0	3.198523	3.080017	-2.030209		85	1	0	1.429629	-4.185616	2.064031	
86	6	0	1.412005	-5.351394	-4.539944		86	6	0	-5.442171	1.002450	4.553654	
87	6	0	0.475863	-4.517161	-3.911925		87	6	0	-4.287343	1.485838	3.921739	
88	6	0	-0.037786	-4.934329	-2.681847		88	6	0	-4.443262	2.114301	2.683806	
89	7	0	0.316977	-6.088688	-2.090369		89	7	0	-5.638542	2.277855	2.088616	
90	6	0	1.771871	-6.553348	-3.934047		90	6	0	-6.681806	1.183088	3.944286	
91	6	0	1.205130	-6.892381	-2.708103		91	6	0	-6.744995	1.825301	2.710664	

92	1	0	1.841689	-5.062860	-5.498304	92	1	0	-5.365828	0.502445	5.518280
93	6	0	-4.649766	-2.905271	-4.625405	93	6	0	-0.656611	5.443665	4.617720
94	6	0	-5.681573	-3.631213	-4.033779	94	6	0	-0.877437	6.685043	4.025401
95	6	0	-6.176119	-3.224585	-2.797245	95	6	0	-0.300953	6.959001	2.788114
96	7	0	-5.683708	-2.145891	-2.156784	96	7	0	0.465356	6.055359	2.146242
97	6	0	-4.144631	-1.770695	-3.974211	97	6	0	0.155478	4.504502	3.965907
98	6	0	-4.698061	-1.437503	-2.735994	98	6	0	0.689067	4.861610	2.725105
99	1	0	-4.243580	-3.204480	-5.590800	99	1	0	-1.098101	5.203453	5.584034
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101	1	0	-4.317299	-0.586793	-2.176067	101	1	0	1.297316	4.155090	2.165569
102	6	0	-4.176966	3.627194	-4.582683	102	6	0	5.056292	2.255792	4.572028
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107	6	0	-2.834409	4.064598	-2.649081	107	6	0	4.880121	0.827110	2.659009
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111	6	0	-3.038947	-0.954309	-4.522217	111	6	0	0.427691	3.159589	4.520168
112	6	0	-3.153581	0.434288	-4.518959	112	6	0	1.733847	2.675119	4.518455
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114	6	0	-0.956613	0.665589	-5.420908	114	6	0	1.012072	0.594123	5.437609
115	6	0	-1.787060	-1.595424	-4.892812	115	6	0	-0.683527	2.301679	4.900069
116	6	0	-0.828741	-0.750902	-5.430210	116	6	0	-0.324888	1.078919	5.444893
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118	6	0	-1.303726	-2.895319	-4.500101	118	6	0	-2.066641	2.414815	4.509879
119	6	0	0.052765	-3.216033	-4.475108	119	6	0	-2.932237	1.322964	4.493603
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121	6	0	1.286705	0.154446	-5.389539	121	6	0	-0.402705	-1.220846	5.418400
122	6	0	2.540930	0.273575	-4.811744	122	6	0	-0.827049	-2.409681	4.845687
123	6	0	3.162130	-0.981541	-4.419546	123	6	0	-2.226701	-2.439899	4.451003
124	6	0	2.437830	-2.171865	-4.441243	124	6	0	-2.997736	-1.279403	4.468703
125	6	0	0.350526	1.224734	-5.393263	125	6	0	0.964040	-0.827011	5.421036
126	6	0	0.614989	2.457736	-4.819041	126	6	0	1.968880	-1.593114	4.851708
127	6	0	1.995157	2.664848	-4.409371	127	6	0	1.570241	-2.931629	4.445743
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131	1	0	-4.079896	0.866263	-4.146049	131	1	0	2.517908	3.328173	4.140467
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133	1	0	3.899576	1.796294	-4.010864	133	1	0	-0.024400	-4.287391	4.047768
134	1	0	-0.425733	4.220879	-4.035873	134	1	0	4.008227	-1.402618	4.069084
135	6	0	5.612711	-0.345458	-4.456902	135	6	0	-2.707008	-4.926611	4.484007
136	6	0	4.523129	-0.975633	-3.838159	136	6	0	-2.795833	-3.672959	3.862166
137	6	0	4.749280	-1.587403	-2.602901	137	6	0	-3.424317	-3.613106	2.616149
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139	6	0	6.861716	-0.376349	-3.839713	139	6	0	-3.259162	-6.041257	3.856421
140	6	0	6.996980	-1.016448	-2.610730	140	6	0	-3.871724	-5.888817	2.615417
141	1	0	5.481319	0.149656	-5.418133	141	1	0	-2.221334	-5.019909	5.454460
142	1	0	-0.738318	-4.304051	-2.139053	142	1	0	-3.573983	2.475930	2.139533
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144	1	0	-2.008139	-3.638211	-4.131600	144	1	0	-2.439963	3.364887	4.133044
145	1	0	3.930052	-2.051897	-2.059695	145	1	0	-3.485466	-2.669727	2.079109
146	1	0	7.728203	0.090713	-4.302677	146	1	0	-3.218348	-7.024316	4.320302
147	1	0	3.509445	7.215194	-2.098396	147	1	0	5.054712	-6.199397	2.094595
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152	47	0	5.946291	-2.325322	0.049200	152	47	0	-4.585033	-4.382221	-0.049242
153	47	0	4.039200	4.956300	0.082714	153	47	0	2.759010	-5.723319	-0.065964
154	47	0	-3.507222	5.344254	-0.001696	154	47	0	6.311248	0.861368	0.005268
155	47	0	-6.135322	-1.624589	-0.097405	155	47	0	1.121324	6.243752	0.084668
156	6	0	-1.473067	-0.109820	0.322581	156	6	0	0.491339	1.441178	-0.277334
157	6	0	-1.203544	-0.448001	-1.157919	157	6	0	0.085402	1.298947	1.203639
158	6	0	-0.971709	1.318076	0.622001	158	6	0	1.558878	0.380906	-0.617612
159	6	0	0.542637	1.407117	0.340704	159	6	0	0.986914	-1.030780	-0.371708
160	6	0	0.808374	1.063566	-1.140278	160	6	0	0.574075	-1.167185	1.108542
161	6	0	0.309282	-0.363878	-1.443383	161	6	0	-0.492969	-0.108618	1.452643
162	6	0	-0.723218	-1.108857	1.227631	162	6	0	-0.742561	1.223398	-1.176930
163	6	0	1.053233	-1.365248	-0.536998	163	6	0	-1.726456	-0.319134	0.550736
164	6	0	1.284194	0.401741	1.245606	164	6	0	-0.248181	-1.237413	-1.271533
165	6	0	0.790811	-1.028697	0.946562	165	6	0	-1.321921	-0.184305	-0.931833
166	1	0	1.323510	-1.741205	1.592438	166	1	0	-2.200047	-0.338084	-1.574645
167	1	0	-2.552389	-0.169493	0.524700	167	1	0	0.902308	2.445917	-0.454683
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169	1	0	-1.573203	-1.456598	-1.391167	169	1	0	-0.659488	2.062724	1.468812
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171	1	0	-1.514240	2.045482	-0.000665	171	1	0	2.455243	0.538245	0.000940
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173	1	0	0.301116	1.784536	-1.796588	173	1	0	1.448963	-1.043575	1.761895
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6	6	0	4.252098	1.934022	-2.581146	6	6	0	-4.193443	2.059788	-2.587120
7	1	0	5.721905	0.362090	-5.196909	7	1	0	-5.706331	0.531276	-5.203951
8	1	0	7.726184	1.363187	-4.061048	8	1	0	-7.681682	1.589278	-4.068872
9	1	0	3.292208	2.109108	-2.104568	9	1	0	-3.229374	2.207903	-2.110190
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22	6	0	-4.650676	1.071264	-2.391260	22	6	0	4.681765	0.944680	-2.385422
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24	1	0	-7.279005	3.481034	-3.758789	24	1	0	7.388084	3.259740	-3.764568
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27	6	0	0.541566	6.993956	-3.486942	27	6	0	-0.329295	7.011952	-3.485613
28	6	0	-0.185616	6.994910	-2.300389	28	6	0	0.395585	6.990992	-2.297895
29	7	0	-0.700871	5.862239	-1.782181	29	7	0	0.873498	5.842961	-1.777585
30	6	0	0.193465	4.612101	-3.639571	30	6	0	-0.056019	4.620199	-3.635897
31	6	0	-0.513747	4.702174	-2.437360	31	6	0	0.651349	4.688816	-2.432286
32	1	0	1.300205	5.761764	-5.095923	32	1	0	-1.123152	5.802999	-5.095238
33	1	0	0.945706	7.927470	-3.872426	33	1	0	-0.702912	7.957484	-3.872593
34	1	0	-0.925837	3.810441	-1.971686	34	1	0	1.035166	3.785025	-1.965562
35	6	0	-3.024785	1.541683	-4.212617	35	6	0	3.071962	1.459269	-4.208783
36	6	0	-2.138873	2.616603	-4.258849	36	6	0	2.217639	2.559374	-4.255742
37	6	0	-0.753255	2.460576	-4.630521	37	6	0	0.828062	2.443226	-4.627799
38	6	0	-0.434221	1.231745	-5.185773	38	6	0	0.474125	1.224341	-5.183674
39	6	0	-2.600709	0.204207	-4.600194	39	6	0	2.609353	0.134641	-4.596167
40	6	0	-1.339666	0.136581	-5.170165	40	6	0	1.347533	0.103527	-5.167558
41	6	0	-0.578753	-1.063330	-5.180242	41	6	0	0.552343	-1.073844	-5.178810
42	6	0	-3.172888	-1.071627	-4.245428	42	6	0	3.143683	-1.157303	-4.240440
43	6	0	-2.427457	-2.250030	-4.230531	43	6	0	2.364960	-2.313920	-4.227951
44	6	0	-1.027277	-2.253533	-4.630039	44	6	0	0.965719	-2.276953	-4.629116
45	6	0	0.797277	-0.709924	-5.200979	45	6	0	-0.812806	-0.681011	-5.201563
46	6	0	1.794646	-1.513845	-4.672553	46	6	0	-1.834088	-1.456421	-4.676308
47	6	0	1.364301	-2.852554	-4.297740	47	6	0	-1.442843	-2.807233	-4.301617
48	6	0	0.014319	-3.200199	-4.310615	48	6	0	-0.103217	-3.193200	-4.311545
49	6	0	0.886940	0.708183	-5.203254	49	6	0	-0.861484	0.739059	-5.202702
50	6	0	1.965077	1.398806	-4.672578	50	6	0	-1.920208	1.460332	-4.673879
51	6	0	3.107255	0.568183	-4.319537	51	6	0	-3.086948	0.662627	-4.324841
52	6	0	3.018376	-0.822644	-4.348685	52	6	0	-3.038347	-0.730330	-4.355375
53	6	0	0.392061	3.279589	-4.263684	53	6	0	-0.293500	3.294387	-4.260884
54	6	0	1.687717	2.768716	-4.315976	54	6	0	-1.603522	2.821306	-4.314967
55	1	0	-2.489537	3.574035	-3.879087	55	1	0	2.595518	3.506621	-3.876448
56	1	0	-0.249648	-4.192586	-3.951971	56	1	0	0.131476	-4.192574	-3.951883
57	1	0	3.880716	-1.387350	-4.001005	57	1	0	-3.917358	-1.270246	-4.010078
58	1	0	2.492501	3.406151	-3.956332	58	1	0	-2.389972	3.481179	-3.955212
59	6	0	2.530181	-5.103646	-4.254186	59	6	0	-2.668000	-5.026222	-4.258956
60	6	0	2.331494	-3.822212	-3.724424	60	6	0	-2.437516	-3.749669	-3.730044
61	6	0	3.042092	-3.482558	-2.569393	61	6	0	-3.142118	-3.390346	-2.577281
62	7	0	3.904849	-4.319056	-1.964908	62	7	0	-4.027632	-4.203882	-1.974239
63	6	0	3.425926	-5.970477	-3.629923	63	6	0	-3.587891	-5.868658	-3.636583
64	6	0	4.100210	-5.545323	-2.488945	64	6	0	-4.253774	-5.424947	-2.497856
65	1	0	1.992234	-5.409871	-5.150279	65	1	0	-2.135708	-5.347274	-5.153227
66	1	0	-1.544384	-3.618065	-2.072213	66	1	0	1.446786	-3.659698	-2.069452
67	1	0	-5.702952	-5.581247	-3.765532	67	1	0	5.539337	-5.743889	-3.778211
68	1	0	-4.188551	-1.116332	-3.858285	68	1	0	4.157215	-1.231314	-3.851999
69	1	0	2.898444	-2.513998	-2.098002	69	1	0	-2.975724	-2.424856	-2.106931
70	1	0	3.606509	-6.968848	-4.022380	70	1	0	-3.793714	-6.862249	-4.028755
71	1	0	7.389063	2.705225	-1.976969	71	1	0	-7.307485	2.919823	-1.983756
72	1	0	4.808438	-6.188784	-1.972236	72	1	0	-4.980218	-6.049047	-1.982663
73	1	0	-4.510962	-6.488541	-1.761900	73	1	0	4.325625	-6.619251	-1.773632
74	1	0	-7.662890	2.167099	-1.666354	74	1	0	7.730482	1.940315	-1.668481
75	1	0	-0.362953	7.910836	-1.741580	75	1	0	0.600921	7.901411	-1.739662
76	47	0	-1.745053	5.749741	0.118458	76	47	0	1.910758	5.698957	0.123685
77	6	0	5.802084	-1.178565	4.079187	77	6	0	-5.834758	-1.026691	4.076998
78	6	0	6.857161	-1.775895	3.390339	78	6	0	-6.904919	-1.595101	3.387070
79	6	0	6.590197	-2.507475	2.236451	79	6	0	-6.656854	-2.330615	2.231589
80	7	0	5.336502	-2.653189	1.763448	80	7	0	-5.407379	-2.507336	1.758032
81	6	0	4.495033	-1.335813	3.601238	81	6	0	-4.532267	-1.216466	3.598544
82	6	0	4.319837	-2.083268	2.434135	82	6	0	-4.376078	-1.965478	2.429496
83	1	0	5.984341	-0.599280	4.983242	83	1	0	-6.001960	-0.445032	4.982440
84	1	0	7.882276	-1.678260	3.741009	84	1	0	-7.927181	-1.471836	3.738014
85	1	0	3.330168	-2.210957	2.005917	85	1	0	-3.390286	-2.117590	2.000875
86	6	0	-3.845182	4.215908	4.329116	86	6	0	3.953278	4.106647	4.338741
87	6	0	-2.715546	3.589488	3.787656	87	6	0	2.809079	3.511363	3.792697
88	6	0	-2.173806	4.132063	2.619609	88	6	0	2.284981	4.070738	2.624478
89	7	0	-2.679422	5.217761	2.007763	89	7	0	2.821257	5.143631	2.016454
90	6	0	-4.366533	5.345966	3.700483	90	6	0	4.506071	5.223943	3.714147
91	6	0	-3.758765	5.822650	2.542463	91	6	0	3.914662	5.718753	2.555303
92	1	0	-4.302469	3.822836	5.236051	92	1	0	4.397611	3.699688	5.245988
93	6	0	-5.139039	-2.533879	4.207769	93	6	0	5.063340	-2.679120	4.208708
94	6	0	-6.373313	-2.674651	3.575261	94	6	0	6.293941	-2.853212	3.577385
95	6	0	-6.665565	-1.881623	2.469276	95	6	0	6.609668	-2.066681	2.473233
96	7	0	-5.786133	-0.978351	1.992673	96	7	0	5.756398	-1.138240	1.997242
97	6	0	-4.222965	-1.589132	3.726484	97	6	0	4.174601	-1.708323	3.727893
98	6	0	-4.600685	-0.835143	2.611692	98	6	0	4.574602	-0.963376	2.615078
99	1	0	-4.884939	-3.144290	5.073190	99	1	0	4.791144	-3.283671	5.072734
100	1	0	-7.107691	-3.393345	3.932409	100	1	0	7.007400	-3.592923	3.930424
101	1	0	-3.921210	-0.107116	2.181323	101	1	0	3.915937	-0.217019	2.183991
102	6	0	0.746922	-5.817664	4.119337	102	6	0	-0.905771	-5.800544	4.118844
103	6	0	0.472716	-7.013408	3.456940	103	6	0	-0.661243	-7.003140	3.457181
104	6	0	-0.313292	-6.989736	2.308664	104	6	0	0.124818	-6.999645	2.308631
105	7	0	-0.809034	-5.839134	1.811324	105	7	0	0.647756	-5.861913	1.809806
106	6	0	0.222899	-4.619682	3.617743	106	6	0	-0.353084	-4.616143	3.615734
107</											

108	1	0	1.355331	-5.808170	5.022585	108	1	0	-1.512641	-5.775529	5.022831
109	1	0	0.859691	-7.960820	3.825773	109	1	0	-1.070801	-7.940572	3.827141
110	1	0	-0.942532	-3.780227	2.000917	110	1	0	0.829220	-3.806369	1.996182
111	6	0	-2.863613	-1.419831	4.297319	111	6	0	2.819861	-1.502206	4.297253
112	6	0	-2.013104	-2.526050	4.295674	112	6	0	1.939395	-2.584645	4.294208
113	6	0	-0.610750	-2.430224	4.622881	113	6	0	0.539928	-2.450525	4.620714
114	6	0	-0.227036	-1.217738	5.170736	114	6	0	0.189855	-1.228329	5.169528
115	6	0	-2.376348	-0.102102	4.682469	115	6	0	2.368645	-0.171631	4.682001
116	6	0	-1.089496	-0.089799	5.194263	116	6	0	1.082826	-0.124462	5.194284
117	6	0	-0.282657	1.078899	5.193827	117	6	0	0.308274	1.065938	5.194923
118	6	0	-2.914337	1.203565	4.382706	118	6	0	2.942072	1.118960	4.382052
119	6	0	-2.122511	2.350980	4.350222	119	6	0	2.182055	2.287750	4.351282
120	6	0	-0.705229	2.293645	4.680430	120	6	0	0.763817	2.268943	4.682111
121	6	0	1.077805	0.672407	5.168422	121	6	0	-1.062794	0.696782	5.169482
122	6	0	2.089470	1.442065	4.618941	122	6	0	-2.053396	1.494574	4.621555
123	6	0	1.695422	2.797613	4.262038	123	6	0	-1.622259	2.839305	4.266048
124	6	0	0.361141	3.198480	4.323153	124	6	0	-0.277370	3.203235	4.326243
125	6	0	1.113186	-0.747385	5.159186	125	6	0	-1.136944	-0.721412	5.158509
126	6	0	2.151173	-1.478299	4.605476	126	6	0	-2.194760	-1.423345	4.605096
127	6	0	3.313965	-0.688147	4.224935	127	6	0	-3.335138	-0.601287	4.224692
128	6	0	3.277389	0.705795	4.258994	128	6	0	-3.260824	0.791166	4.260415
129	6	0	0.493303	-3.295129	4.230742	129	6	0	-0.587716	-3.284841	4.228819
130	6	0	1.809702	-2.836597	4.255146	130	6	0	-1.891087	-2.790554	4.254509
131	1	0	-2.415192	-3.465970	3.923499	131	1	0	2.315954	-3.534951	3.921935
132	1	0	0.124275	4.201867	3.976214	132	1	0	-0.012953	4.199772	3.979393
133	1	0	4.149125	1.239150	3.885753	133	1	0	-4.117303	1.348347	3.886614
134	1	0	2.579864	-3.506864	3.879435	134	1	0	-2.679800	-3.439388	3.879722
135	6	0	2.948498	5.001297	4.178711	135	6	0	-2.815570	5.076048	4.184392
136	6	0	2.677712	3.730627	3.655134	136	6	0	-2.578437	3.799273	3.659451
137	6	0	3.325635	3.366591	2.471472	137	6	0	-3.234382	3.454153	2.474507
138	7	0	4.191775	4.172423	1.830983	138	7	0	-4.077613	4.283648	1.833652
139	6	0	3.850263	5.834738	3.518651	139	6	0	-3.693846	5.934078	3.524198
140	6	0	4.456900	5.388340	2.348282	140	6	0	-4.310434	5.505625	2.352314
141	1	0	2.460676	5.325239	5.096971	141	1	0	-2.320362	5.385636	5.103641
142	1	0	-1.316384	3.667580	2.143379	142	1	0	1.416652	3.630350	2.144968
143	1	0	-5.237945	5.858828	4.101732	143	1	0	5.389551	5.712714	4.119073
144	1	0	-3.946869	1.300213	4.054757	144	1	0	3.976984	1.187446	4.054571
145	1	0	3.124260	2.404912	2.006061	145	1	0	-3.058573	2.487702	2.008600
146	1	0	4.086514	6.823837	3.904981	146	1	0	-3.904049	6.928707	3.911378
147	1	0	7.384300	-2.985980	1.668039	147	1	0	-7.463045	-2.787112	1.662085
148	1	0	5.165622	6.006261	1.801890	148	1	0	-5.001312	6.143323	1.805777
149	1	0	-4.134614	6.699543	2.020500	149	1	0	4.315136	6.586293	2.036069
150	1	0	-7.613619	-1.963751	1.942854	150	1	0	7.555692	-2.174371	1.947783
151	1	0	-0.554154	-7.899668	1.764008	151	1	0	0.344152	-7.915808	1.765324
152	47	0	4.948110	3.446917	-0.069261	152	47	0	-4.850866	3.583318	-0.069525
153	47	0	4.797909	-3.614541	-0.112898	153	47	0	-4.897046	-3.479455	-0.119243
154	47	0	-1.957712	-5.677656	-0.023188	154	47	0	1.801642	-5.732744	-0.025043
155	47	0	-6.018133	0.131753	0.136325	155	47	0	6.020010	-0.032138	0.143121
156	6	0	-1.049548	-0.703217	-0.925927	156	6	0	1.034542	-0.738162	-0.901981
157	6	0	-1.657634	-0.177852	0.388064	157	6	0	1.627319	-0.238571	0.429177
158	6	0	0.047281	-1.734073	-0.598876	158	6	0	-0.107591	-1.729067	-0.607599
159	6	0	1.148742	-1.066983	0.248578	159	6	0	-1.205286	-1.025023	0.214657
160	6	0	0.537303	-0.530897	1.557605	160	6	0	-0.608071	-0.516404	1.540972
161	6	0	-0.562984	0.498554	1.236460	161	6	0	0.536136	0.473917	1.252051
162	6	0	-0.424526	0.464774	-1.711125	162	6	0	0.472709	0.454241	-1.698211
163	6	0	0.050380	1.668493	0.442251	163	6	0	-0.014668	1.667350	0.447077
164	6	0	1.765820	0.106827	-0.537632	164	6	0	-1.758962	0.172321	-0.582910
165	6	0	0.670669	1.140960	-0.865851	165	6	0	-0.619123	1.166996	-0.878862
166	1	0	1.105539	1.975046	-1.433701	166	1	0	-1.009052	2.017685	-1.454476
167	1	0	-1.832456	-1.173083	-1.535156	167	1	0	1.815335	-1.233961	-1.493488
168	1	0	-2.104018	-1.009124	0.951807	168	1	0	2.030290	-1.085972	1.001629
169	1	0	-2.465474	0.537358	0.170738	169	1	0	2.464647	0.448702	0.234401
170	1	0	0.473845	-2.131875	-1.529276	170	1	0	-0.525436	-2.106256	-1.550419
171	1	0	-0.382964	-2.584628	-0.048667	171	1	0	0.276533	-2.597506	-0.051196
172	1	0	1.928856	-1.807846	0.477344	172	1	0	-2.017859	-1.737569	0.419370
173	1	0	0.116957	-1.355787	2.144845	173	1	0	-0.232543	-1.358006	2.135003
174	1	0	1.316440	-0.065260	2.173365	174	1	0	-1.385069	-0.024846	2.138745
175	1	0	-0.995732	0.872399	2.171601	175	1	0	0.958066	0.828972	2.199421
176	1	0	0.005044	0.094746	-2.648017	176	1	0	0.055149	0.102951	-2.647708
177	1	0	-1.198568	1.194034	-1.979227	177	1	0	1.279324	1.156214	-1.942937
178	1	0	-0.724356	2.415612	0.210828	178	1	0	0.792082	2.386851	0.239443
179	1	0	0.813639	2.173988	1.050544	179	1	0	-0.774707	2.197672	1.037948
180	1	0	2.223962	-0.258569	-1.466894	180	1	0	-2.205478	-0.174230	-1.524725
181	1	0	2.565225	0.575229	0.056028	181	1	0	-2.556177	0.667960	-0.008819

2 (in Gas Phase):						2b (in Gas Phase):					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)			Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z				X	Y	Z
1	6	0	-1.016153	-0.705266	0.928815	1	6	0	1.233870	-0.000293	-0.000213
2	6	0	-1.733300	0.397871	0.120147	2	6	0	0.748463	1.277485	-0.688926
3	6	0	0.107398	-0.069646	1.776972	3	6	0	0.747140	-1.235768	-0.761847
4	6	0	1.123694	0.635240	0.852136	4	6	0	-0.800067	-1.240462	-0.764723
5	6	0	-0.720982	1.104076	-0.808094	5	6	0	-0.798749	1.282867	-0.691681
6	6	0	0.401773	1.735590	0.044018	6	6	0	-1.312666	0.042479	-1.454783
7	6	0	-0.107340	0.069994	-1.777047	7	6	0	-1.311993	1.239339	0.763986
8	6	0	0.613364	-1.034237	-0.972897	8	6	0	-0.798671	-0.041982	1.456623
9	6	0	1.733135	-0.398058	-0.120339	9	6	0	-1.312374	-1.281160	0.691441
10	1	0	-2.192079	1.127174	0.801816	10	1	0	1.140583	1.312339	-1.712539
11	1	0	-2.547277	-0.039745	-0.473968	11	1	0	1.140547	2.151654	-0.155022
12	1	0	0.612860	-0.842617	2.372021	12	1	0	1.139557	-2.139622	-0.280216
13	1	0	-0.319102	0.651953	2.487187	13	1	0	1.139279	-1.211234	-1.785859
14	1	0	1.921017	1.086328	1.457482	14	1	0	-1.157591	-2.123077	-1.309277
15	1	0	-1.232509	1.887972	-1.382087	15	1	0	-1.156164	2.195665	-1.183984
16	1	0	-0.019921	2.487738	0.724872	16	1	0	-0.971209	0.072747	-2.497931
17	1	0	1.118309	2.258145	-0.604520	17	1	0	-2.410321	0.043661	-1.477426
18	1	0	0.600718	0.564196	-2.456377	18	1	0	-2.409666	1.258812	0.775886
19	1	0	-0.894265	-0.372743	-2.402991	19	1	0	-0.970353	2.127489	1.311835
20	1	0	1.048590	-1.768373	-1.663747	20	1	0	-1.156026	-0.071864	2.493328

21	1	0	2.472836	0.087856	-0.771294	21	1	0	-2.410015	-1.301574	0.702924
22	1	0	2.265823	-1.176407	0.443010	22	1	0	-0.970145	-2.199479	1.186651
23	1	0	-1.737113	-1.206036	1.588437	23	9	0	2.656550	-0.000595	-0.000601
24	6	0	-0.401648	-1.735498	-0.043770	24	6	0	0.748572	-0.041918	1.450717
25	1	0	0.095585	-2.536168	0.520760	25	1	0	1.140757	-0.941091	1.941125
26	1	0	-1.193122	-2.209675	-0.640242	26	1	0	1.140655	0.827409	1.992361
2c (in Gas Phase):						3a (in Gas Phase):					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)			Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z				X	Y	Z
1	6	0	0.929498	0.000053	-0.000039	1	6	0	1.454227	0.311890	0.118331
2	6	0	0.436259	0.721989	1.262231	2	6	0	1.317165	-1.208408	0.044230
3	6	0	0.437371	0.732037	-1.256471	3	6	0	1.150474	0.612949	1.624549
4	6	0	-1.111040	0.732699	-1.257441	4	6	0	-0.710742	-0.231344	0.347736
5	6	0	-1.112059	0.722639	1.262869	5	8	0	-0.017374	-1.496723	0.195229
6	6	0	-1.624604	1.456122	0.005466	6	6	0	-0.355153	0.247949	1.778759
7	6	0	-1.625585	-0.732930	1.257374	7	6	0	0.114822	0.722338	-0.592408
8	6	0	-1.111373	-1.455152	-0.005660	8	8	0	2.159019	-2.060805	-0.073808
9	6	0	-1.624987	-0.722928	-1.263196	9	6	0	2.773729	0.851530	-0.401691
10	1	0	0.821427	1.748002	1.276530	10	6	0	-2.174549	-0.441402	-0.028415
11	1	0	0.821750	0.214378	2.153938	11	6	0	-0.243508	2.211489	-0.482169
12	1	0	0.823088	0.231819	-2.152173	12	6	0	0.048196	0.308825	-2.072820
13	1	0	0.822810	1.758089	-1.262101	13	8	0	-2.566281	-1.318683	-0.750773
14	1	0	-1.463677	1.255824	-2.155168	14	8	0	-3.042585	0.492559	0.452077
15	1	0	-1.464837	1.238380	2.164765	15	1	0	1.340214	1.668457	1.839137
16	1	0	-1.281020	2.498966	0.010404	16	1	0	1.794828	0.025675	2.284317
17	1	0	-2.722176	1.480342	0.005323	17	1	0	-0.533318	-0.559897	2.492265
18	1	0	-2.723260	-0.744680	1.276466	18	1	0	-0.939717	1.114438	2.107015
19	1	0	-1.284247	-1.258484	2.159041	19	1	0	2.924988	0.594960	-1.453977
20	1	0	-1.464436	-2.493972	-0.010218	20	1	0	3.606518	0.419611	0.161192
21	1	0	-2.722613	-0.734082	-1.282947	21	1	0	2.818153	1.940744	-0.298263
22	1	0	-1.282994	-1.241097	-2.168833	22	1	0	0.463544	2.803302	-1.072354
23	17	0	2.782002	-0.000081	0.000518	23	1	0	-0.221401	2.601662	0.538096
24	6	0	0.436904	-1.454374	-0.006150	24	1	0	-1.239902	2.398337	-0.897176
25	1	0	0.821387	-1.972363	-0.892295	25	1	0	0.776798	0.884229	-2.652795
26	1	0	0.822471	-1.980671	0.874562	26	1	0	-0.943369	0.518200	-2.485667
3b (in Gas Phase):						3c (in Gas Phase):					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)			Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z				X	Y	Z
1	6	0	-1.915008	-0.236842	-0.050497	1	6	0	1.306369	0.057688	0.018900
2	6	0	-1.379514	-1.635161	-0.427322	2	6	0	0.754233	-0.185706	-1.412283
3	6	0	-1.799921	-0.120267	1.488630	3	6	0	0.803997	-1.097548	0.927851
4	6	0	0.338332	-0.022704	0.262187	4	6	0	-1.322503	-0.017221	0.051616
5	6	0	0.116809	-1.463230	-0.201503	5	6	0	-0.779344	-0.430656	-1.347106
6	6	0	-0.260149	-0.013731	1.718308	6	6	0	-0.733335	-0.983504	1.105213
7	6	0	-0.785237	0.724592	-0.559340	7	6	0	2.824718	0.103483	0.007977
8	6	0	1.762260	0.526671	0.205726	8	6	0	-2.851454	-0.136269	0.033136
9	6	0	-1.013780	2.194713	-0.172727	9	8	0	-3.453286	-1.140413	0.332242
10	6	0	-0.541626	0.678558	-2.080598	10	8	0	-3.551465	0.950039	-0.399515
11	8	0	1.999480	1.703218	0.378699	11	1	0	1.304850	-1.052994	1.901231
12	8	0	2.746655	-0.358290	-0.016665	12	1	0	1.077880	-2.055158	0.474896
13	1	0	-2.319525	0.762907	1.868019	13	1	0	-1.213992	-1.959214	1.009299
14	1	0	-2.233831	-0.990079	1.991336	14	1	0	-0.981296	-0.610518	2.105644
15	1	0	0.142909	-0.832429	2.321911	15	8	0	3.375151	-1.060082	-0.430014
16	1	0	0.026939	0.921517	2.203603	16	8	0	3.512136	1.044839	0.348029
17	1	0	-1.913726	2.561185	-0.681207	17	1	0	-2.958350	1.693909	-0.579284
18	1	0	-1.148215	2.354193	0.898097	18	6	0	0.734942	1.387760	0.552428
19	1	0	-0.165544	2.807370	-0.484500	19	6	0	-0.807344	1.411830	0.361028
20	1	0	-1.424902	1.046443	-2.614458	20	1	0	4.340225	-0.946628	-0.397534
21	1	0	0.297412	1.329970	-2.345626	21	1	0	1.205050	2.230391	0.038758
22	1	0	-0.313138	-0.318438	-2.468551	22	1	0	0.994063	1.491547	1.610922
23	1	0	2.366587	-1.260632	-0.145981	23	1	0	-1.051370	2.093151	-0.467550
24	1	0	-2.909527	-0.018216	-0.448727	24	1	0	-1.294843	1.808942	1.258463
25	8	0	0.977739	-2.319782	-0.350727	25	1	0	1.257808	-1.043173	-1.866025
26	1	0	-1.771283	-2.450524	0.190326	26	1	0	0.979950	0.687415	-2.035865
27	1	0	-1.558138	-1.910032	-1.471881	27	1	0	-1.287252	0.134768	-2.136744
4a (in Gas Phase):						4b (in Gas Phase):					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)			Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z				X	Y	Z
1	6	0	-1.478379	-0.277627	0.005831	1	6	0	1.242443	-0.568195	-0.009748
2	6	0	-1.379712	1.260317	0.030295	2	6	0	1.654302	0.917372	-0.015541
3	6	0	-0.775143	-0.851534	1.245740	3	6	0	0.393654	-0.863790	-1.256102
4	6	0	0.710180	-0.429853	1.249550	4	6	0	-0.871854	0.020806	-1.253765
5	6	0	0.102990	1.694481	0.027443	5	6	0	0.395722	1.812484	-0.006596
6	6	0	0.803276	1.111760	1.273973	6	6	0	-0.452888	1.507966	-1.259323
7	6	0	0.793192	1.154426	-1.243568	7	6	0	-0.438371	1.515030	1.257431
8	6	0	0.702817	-0.386868	-1.269733	8	6	0	-0.860070	0.028841	1.264482
9	6	0	1.387948	-0.989985	-0.021626	9	6	0	-1.718927	-0.249827	0.009912
10	1	0	-1.895485	1.638498	0.921575	10	1	0	2.268208	1.116021	-0.902662
11	1	0	-1.897509	1.677009	-0.846285	11	1	0	2.276473	1.130486	0.866201
12	1	0	-0.871980	-1.944038	1.238855	12	1	0	0.144018	-1.932779	-1.277586
13	1	0	-1.282092	-0.488627	2.147839	13	1	0	0.991310	-0.672684	-2.155263
14	1	0	1.214011	-0.851368	2.127337	14	1	0	-1.481371	-0.204038	-2.137003

15	1	0	0.163250	2.789969	0.045929	15	1	0	0.696919	2.867549	-0.011533
16	1	0	0.334356	1.494980	2.189124	16	1	0	0.119821	1.729900	-2.169078
17	1	0	1.851248	1.440961	1.310233	17	1	0	-1.342323	2.151286	-1.278019
18	1	0	1.840828	1.483705	-1.277803	18	1	0	-1.326605	2.159724	1.283784
19	1	0	0.316659	1.567827	-2.141955	19	1	0	0.144827	1.741457	2.159847
20	1	0	1.201072	-0.779178	-2.164185	20	1	0	-1.461082	-0.192054	2.154559
21	8	0	2.807612	-0.815389	-0.024528	21	1	0	-2.580666	0.427806	0.012883
22	1	0	1.261984	-2.078779	-0.040317	22	8	0	-2.314042	-1.550307	0.018602
23	8	0	-2.841777	-0.713388	0.074172	23	8	0	2.385797	-1.428719	-0.083474
24	6	0	-0.782727	-0.811290	-1.262705	24	6	0	0.404267	-0.858189	1.251801
25	1	0	-0.878155	-1.903734	-1.291213	25	1	0	0.149868	-1.925593	1.280063
26	1	0	-1.289293	-0.418866	-2.156399	26	1	0	1.004639	-0.660612	2.151409
27	1	0	-3.318086	-0.367516	-0.693471	27	1	0	2.954124	-1.257204	0.680450
28	1	0	3.015853	0.126409	0.022390	28	1	0	-1.621859	-2.222037	-0.034391

4c (in Gas Phase):

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.912321	-0.699489	-0.012027
2	6	0	0.088800	-1.539794	-0.825483
3	6	0	-1.029683	0.693962	-0.664859
4	6	0	0.340226	1.393033	-0.626410
5	6	0	1.473780	-0.854337	-0.811820
6	6	0	1.346125	0.550646	-1.440184
7	6	0	1.966867	-0.724098	0.645097
8	6	0	0.963136	0.119439	1.459208
9	6	0	0.829233	1.523080	0.831482
10	1	0	-0.282725	-1.652781	-1.851430
11	1	0	0.154484	-2.547959	-0.392321
12	8	0	-1.991179	1.509704	-0.001245
13	1	0	-1.338369	0.549333	-1.712682
14	1	0	0.228237	2.387716	-1.074129
15	1	0	2.183850	-1.456880	-1.392310
16	1	0	1.018272	0.468592	-2.484939
17	1	0	2.323610	1.049520	-1.450614
18	1	0	2.957830	-0.251716	0.664556
19	1	0	2.078191	-1.719824	1.095646
20	1	0	1.308536	0.208412	2.496894
21	1	0	1.798788	2.037908	0.849479
22	1	0	0.124905	2.131701	1.408026
23	8	0	-2.239179	-1.254124	-0.072250
24	6	0	-0.421694	-0.566745	1.440466
25	1	0	-1.147050	0.016011	2.017938
26	1	0	-0.358637	-1.567284	1.894137
27	1	0	-2.274239	-2.053556	0.470107
28	1	0	-2.799632	0.981978	0.076780

12. Routine ^1H NMR and ^{13}C NMR Spectra of Compounds

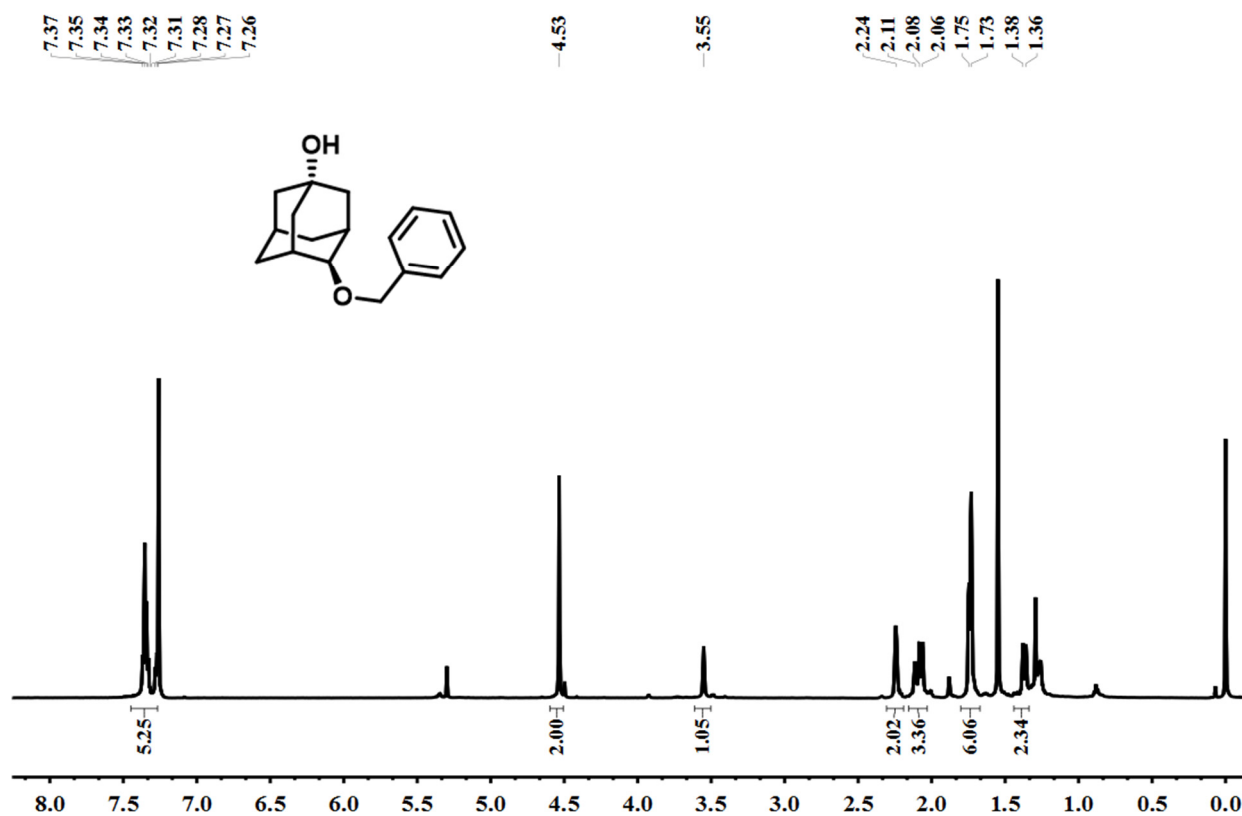


Figure S56. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of compound *trans*-6.

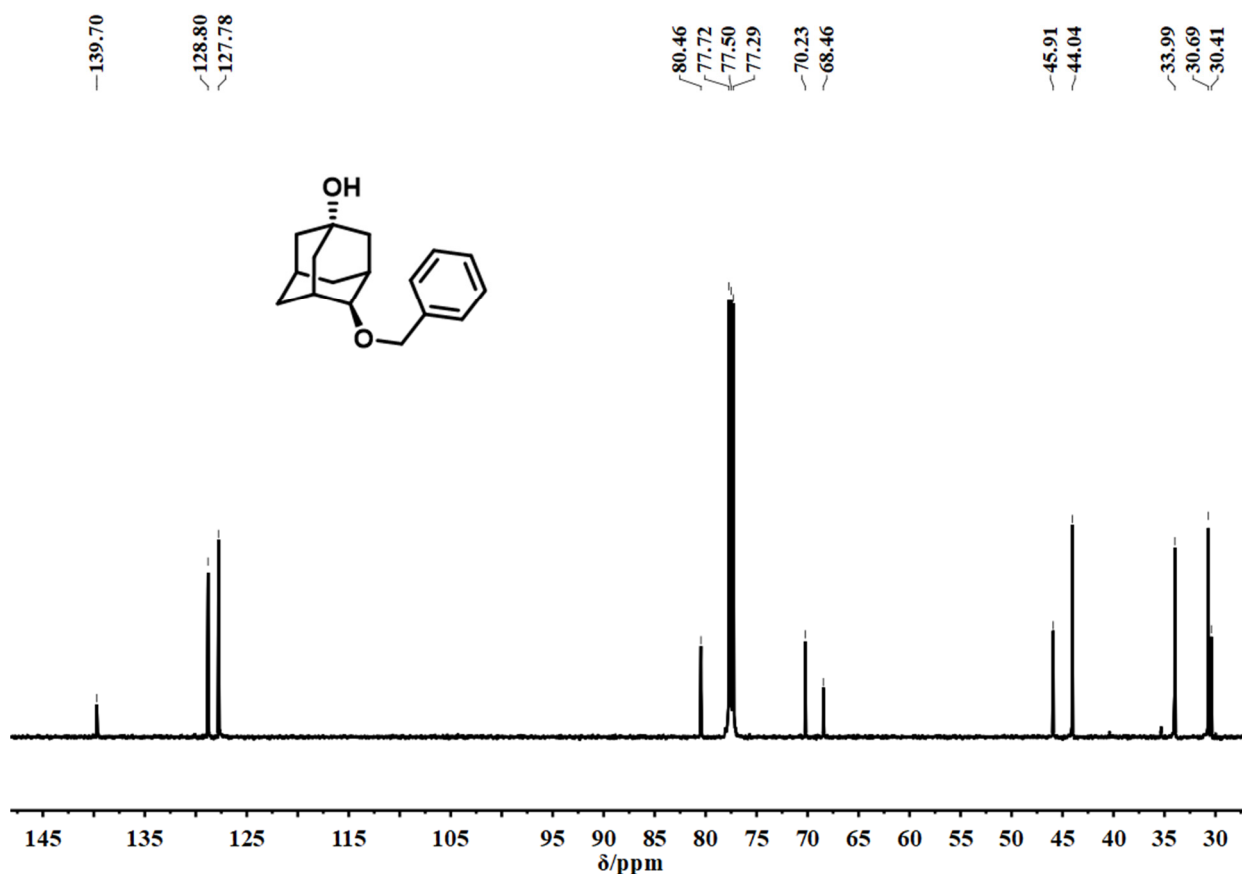


Figure S57. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (150 MHz, CDCl_3 , 298 K) of compound *trans*-6.

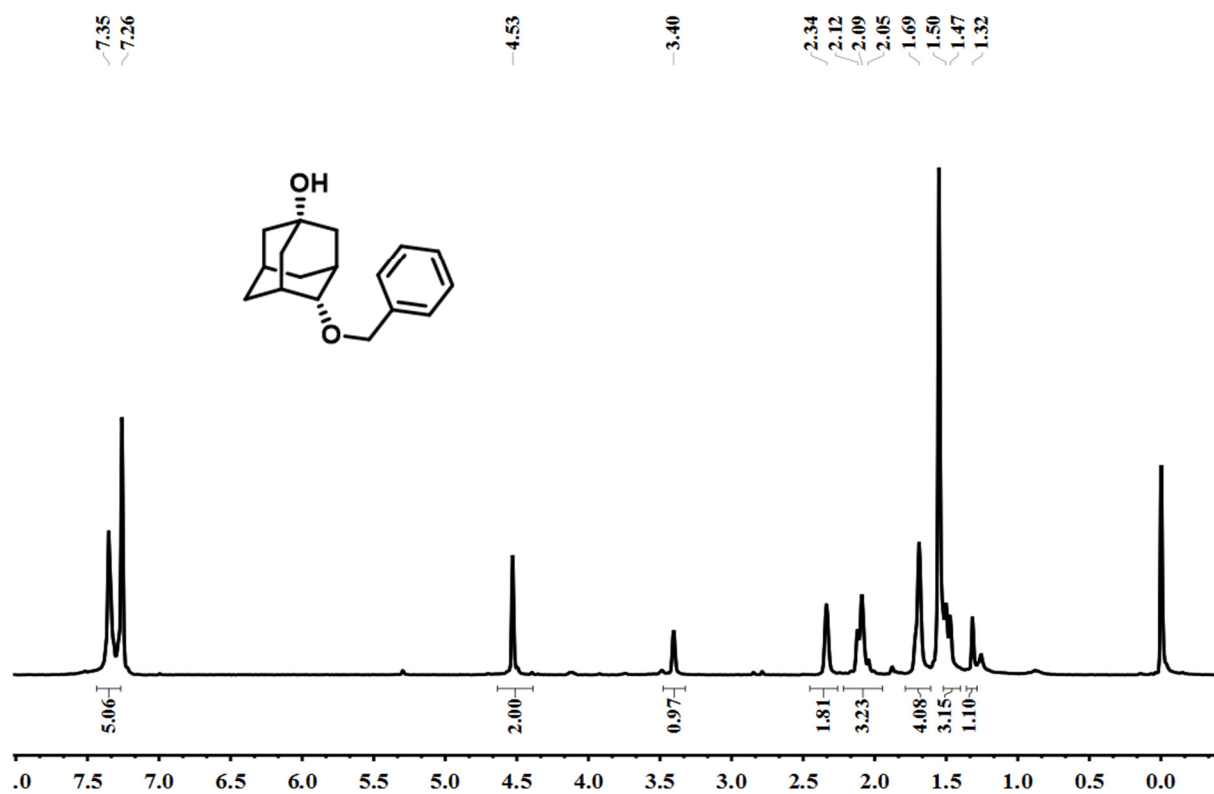


Figure S58. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of compound *cis*-6.

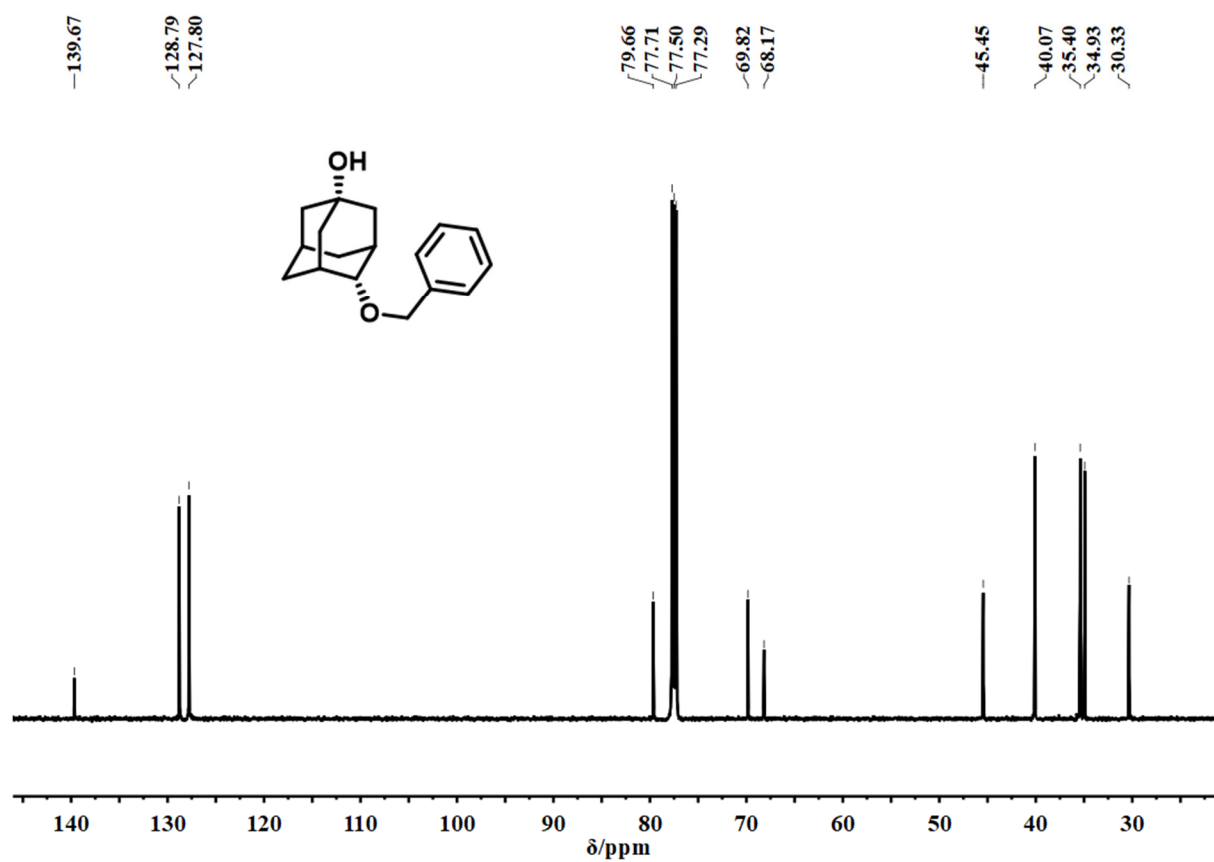


Figure S59. ¹³C{¹H} NMR spectrum (150 MHz, CDCl₃, 298 K) of compound *cis*-6.

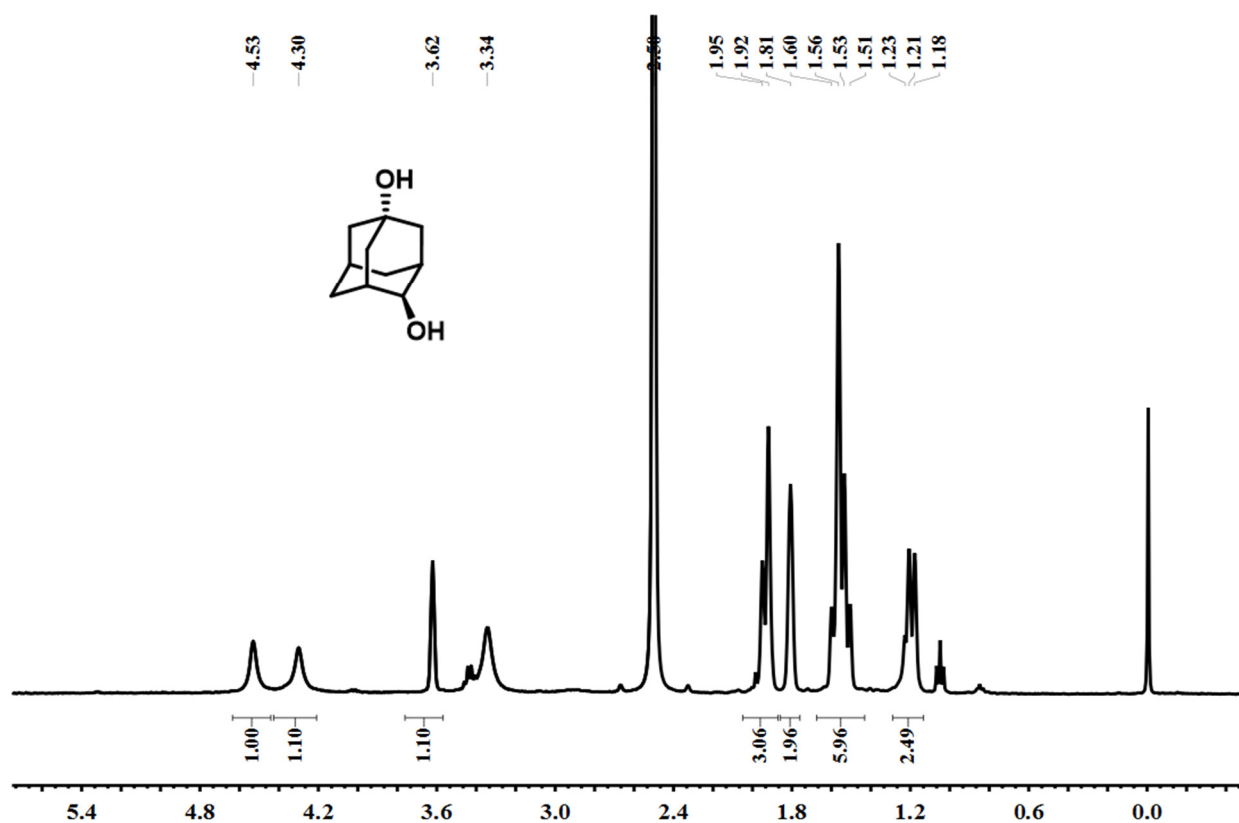


Figure S60. ^1H NMR spectrum (400 MHz, $\text{DMSO}-d_6$, 298 K) of compound 4a.

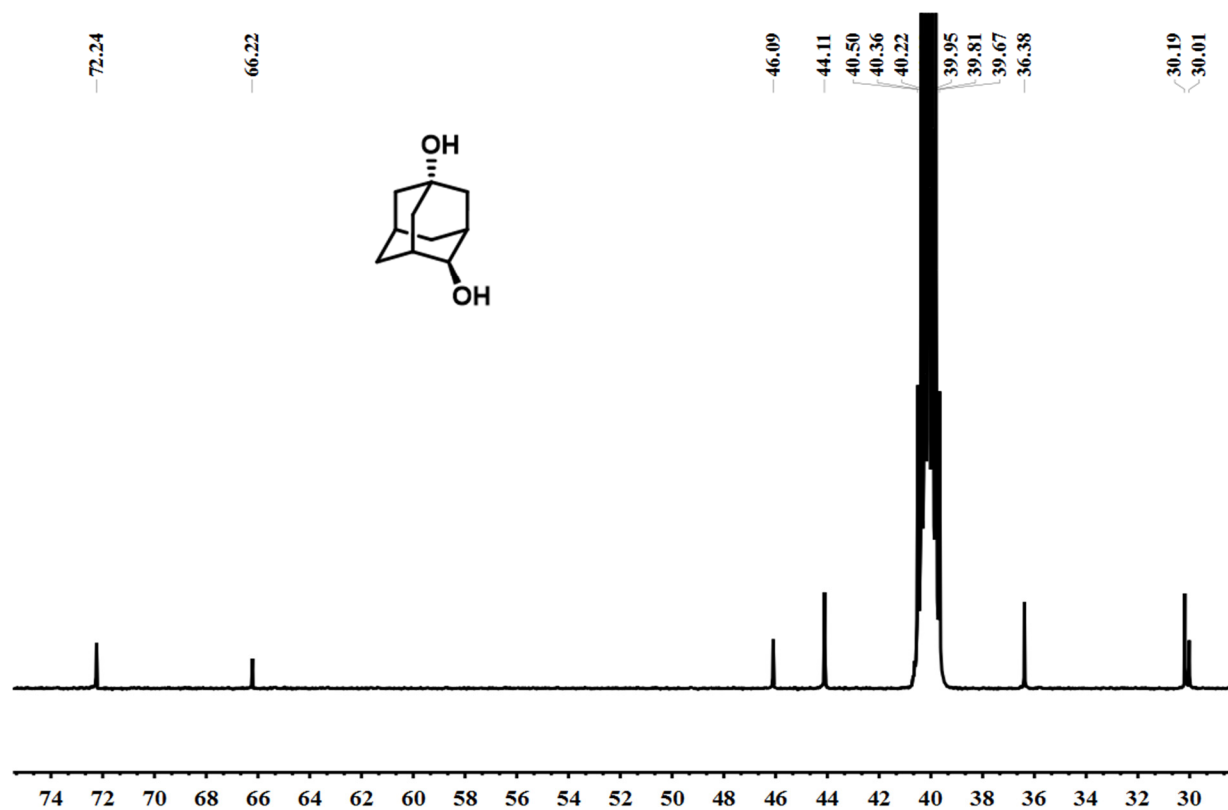


Figure S61. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, $\text{DMSO}-d_6$, 298 K) of compound 4a.

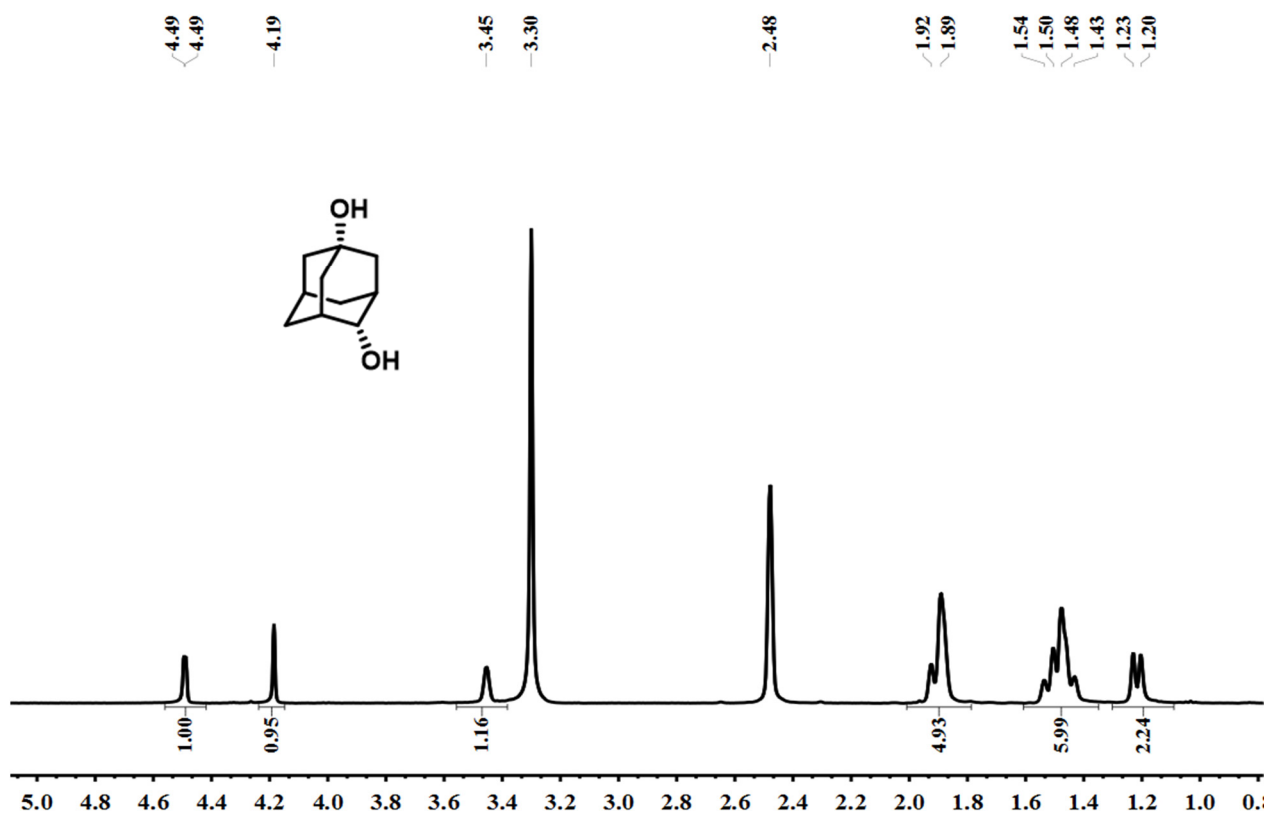


Figure S62. ¹H NMR spectrum (400 MHz, DMSO-*d*₆, 298 K) of compound **4b**.

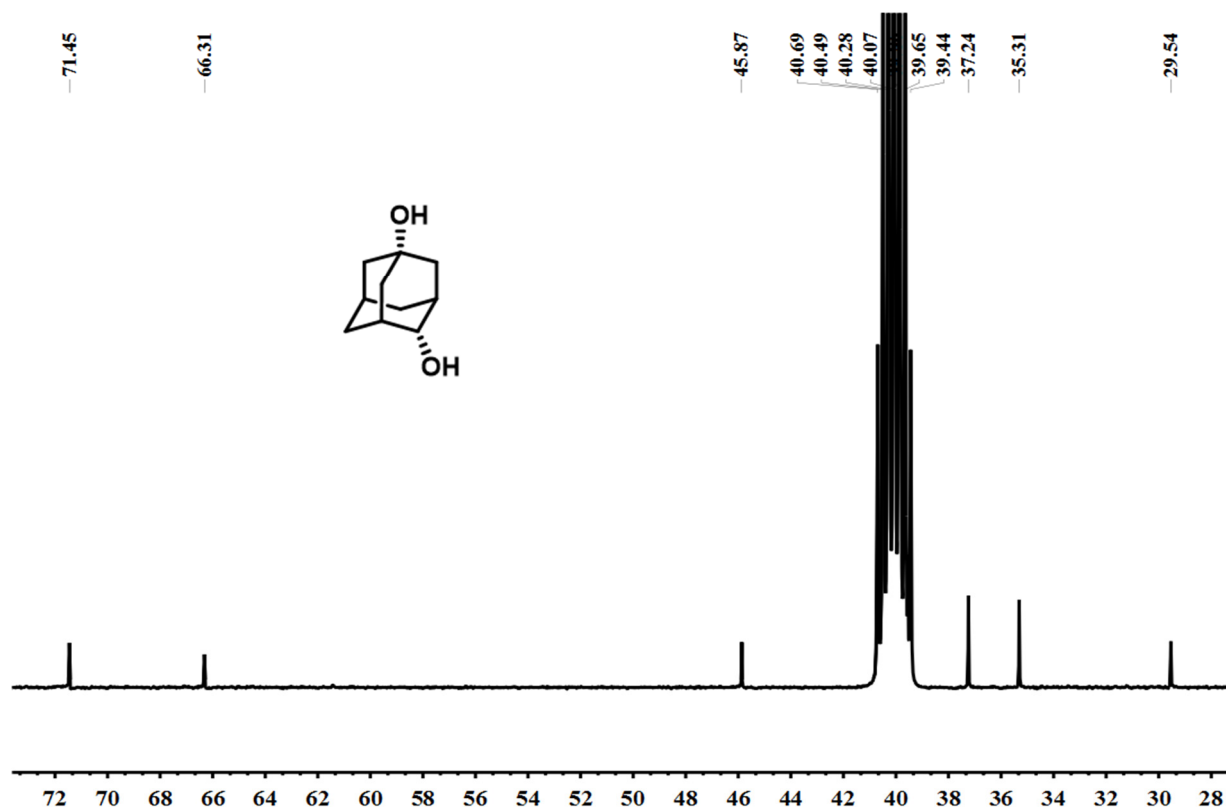


Figure S63. ¹³C{¹H} NMR spectrum (100 MHz, DMSO-*d*₆, 298 K) of compound **4b**.

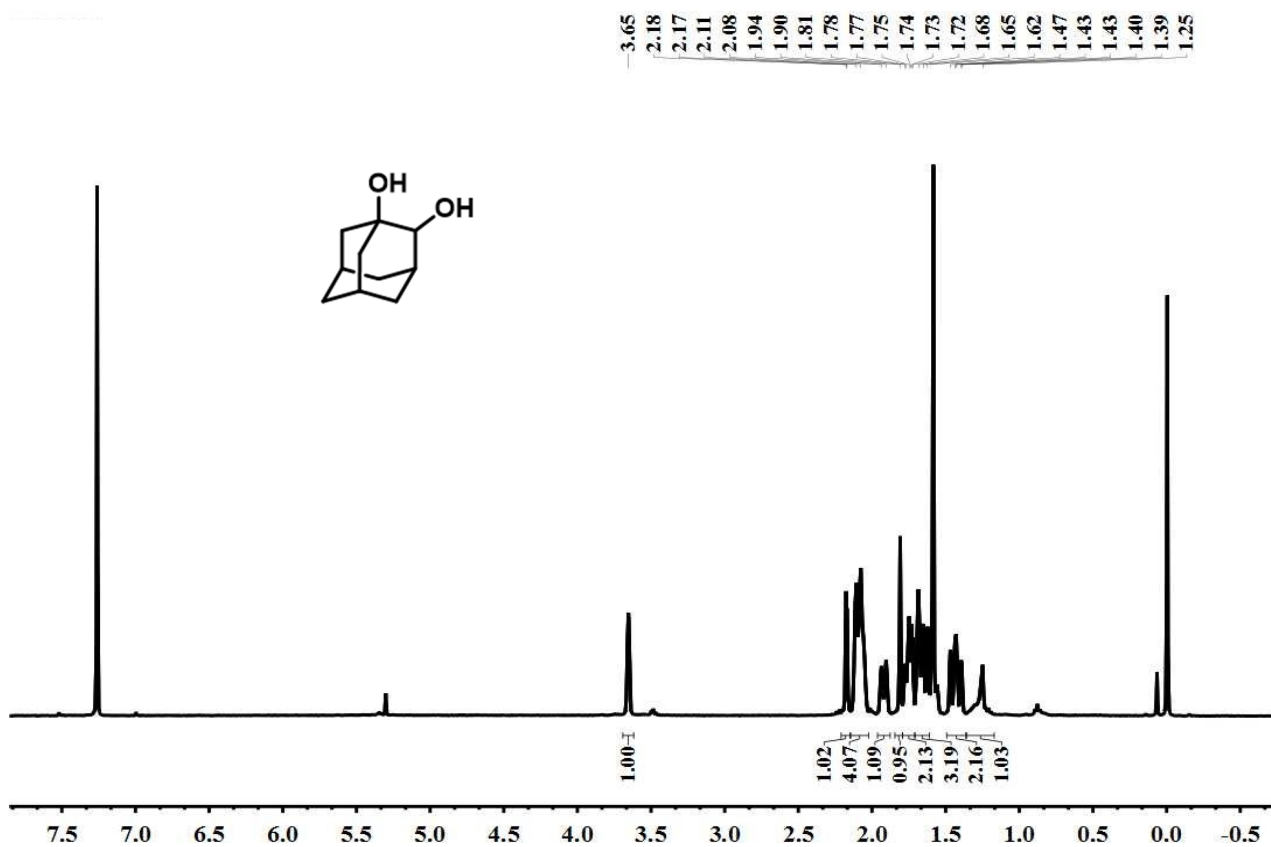


Figure S64. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of compound 4c.

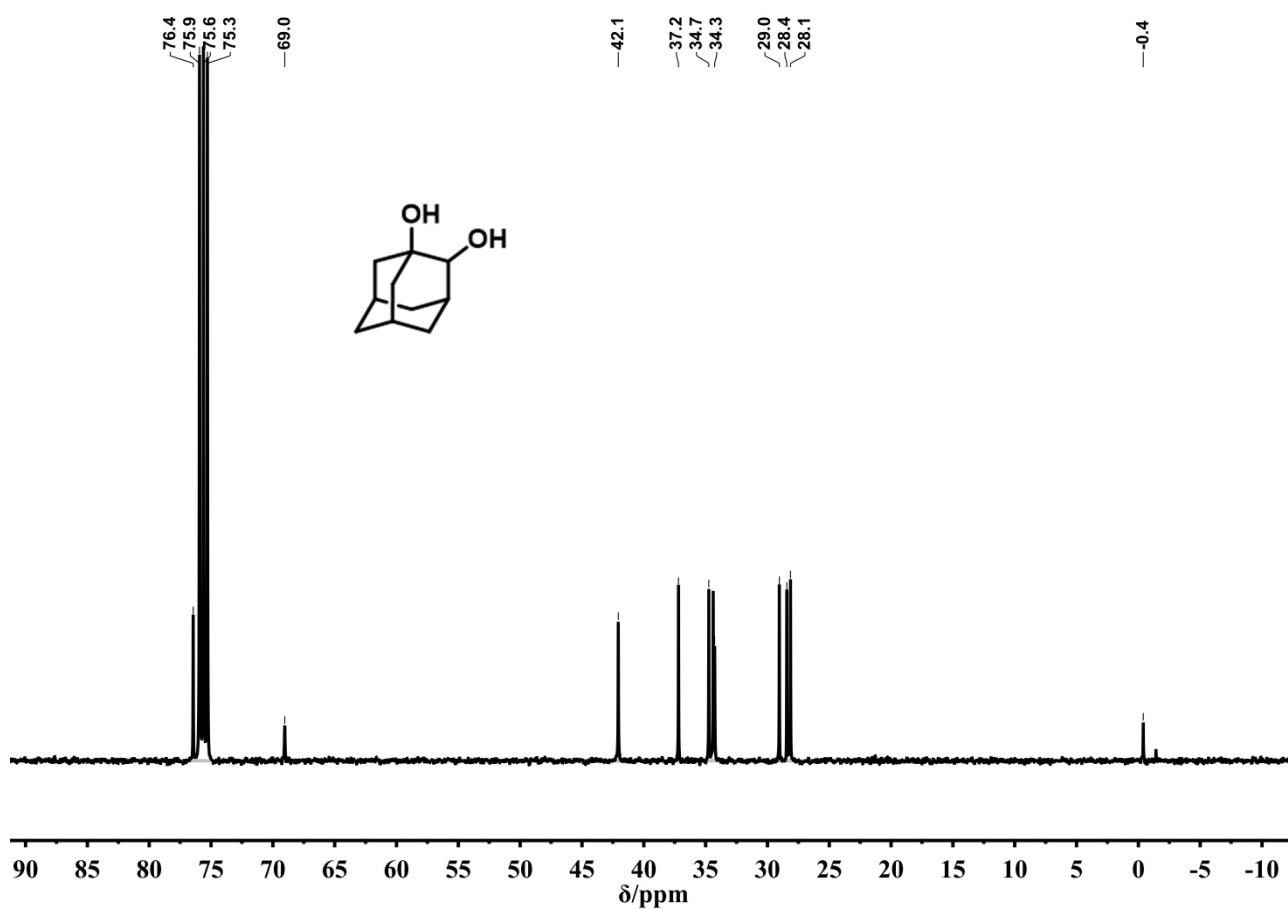


Figure S65. ¹³C{¹H} NMR spectrum (100 MHz, CDCl₃, 298 K) of compound 4c.

13. Supporting References

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