

# **CHEMISTRY**

---

## **A EUROPEAN JOURNAL**

### Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2009

**Sequence Specific Self-Sorting of the Binding Sites of a Ditopic Guest by  
Cucurbituril Homologues and Subsequent Formation of a  
*Hetero*[4]pseudorotaxane**

Gizem Celtek,<sup>[a]</sup> Müge Artar,<sup>[a]</sup> Oren A. Scherman,<sup>[b]</sup> and Dönüs Tuncel\*<sup>[a]</sup>

*[a] Chemistry Department and Institute of Materials Science and Nanotechnology*

*Bilkent University*

*06800 Ankara, Turkey*

*Fax: (+90) 3122664068*

*E-mail: [dtuncel@fen.bilkent.edu.tr](mailto:dtuncel@fen.bilkent.edu.tr)*

*[b] Dr. O.A. Scherman*

*Melville Laboratory for Polymer Synthesis, Chemistry Department*

*University of Cambridge*

*Cambridge, CB2 1EW, United Kingdom*

## SUPPORTING INFORMATION

### CONTENTS

EXPERIMENTAL SECTION	S3
MALDI-TOF-MS AND NMR DATA	S4
<b>FIGURE S1:</b> $^1\text{H}$ NMR (400 MHz, $\text{D}_2\text{O}$ , 25 °C) spectra of <b>Axle A</b> ; the addition of (a) 0 equiv of CB6 (b) 0.5 equiv of CB6, (c) 1 equiv of CB6, (d) 2.2 equiv of CB6.	S4
<b>FIGURE S2:</b> Proposed structure of CB7-Axle A and $^1\text{H}$ NMR (400 MHz, $\text{D}_2\text{O}$ , 25 °C) spectra of Axle A; the addition of (a) 0 equiv of CB7 (b) 0.4 equiv of CB7, (c) 0.9 equiv of CB7, (c) 1.3 equiv of CB7.	S4
<b>FIGURE S3:</b> Structure of CB8-Axle A and $^1\text{H}$ NMR (400 MHz, $\text{D}_2\text{O}$ , 25 °C) spectra of Axle A; the addition of (a) 0 equiv of CB8 (b) 0.5 equiv of CB8, (c) 1.2 equiv of CB8.	S5
<b>FIGURE S4:</b> COSY-NMR spectrum Axle A.	S6
<b>FIGURE S5:</b> COSY-NMR spectrum of [3]pseudorotaxane of CB8 with Axle A.	S7
<b>FIGURE S6:</b> NOESY-NMR spectrum of [3]pseudorotaxane of CB8 with Axle A.	S8
<b>FIGURE S7:</b> HMQC-NMR spectrum of [3]pseudorotaxane of CB8 with Axle A.	S9
<b>FIGURE S8:</b> MALDI-mass spectrum of CB8-Axle A.	S10
<b>FIGURE S9:</b> MALDI-mass spectrum of CB7-Axle A.	S11
<b>FIGURE S10:</b> MALDI-mass spectrum of Axle A+1CB8+2CB6.	S11
<b>Figure S11:</b> The COSY-NMR spectra (400 MHz, 25 °C, $\text{D}_2\text{O}$ ) of 96 h later after addition of 2 equiv CB6 to <b>Axle A</b> +CB8.	S12

## Experimental Section

CB6, CB7, CB8, *N,N'*-Bis-(2-azido-ethyl)-dodecane-1,12-diamine.2HCl, were prepared according to literature.<sup>[5b, 6d, 7]</sup> All other reagents and solvents were of the commercial reagent grade and used without further purification except where noted. Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance DPX-400 MHz spectrometer. In all cases, samples were dissolved in D<sub>2</sub>O with DSS (3-(trimethylsilyl)-1-propanesulfonic acid sodium salt) as an external standard. Mass spectra were taken on Applied Biosystems MALDI-TOF MS mass spectrometer equipped with a YAG-Laser ( $\lambda = 335$  nm) at 10<sup>-7</sup> Torr and delayed extraction mode (delay 300 ns) by changing the laser intensity, if necessary. All spectra were acquired in reflector mode using 20 kV acceleration potential and they were the average of 60 laser shots. Then, data were transferred to a personal computer for further processing. 2,4,6-Trihydroxyacetophenone (THAP) was chosen as the MALDI matrix.

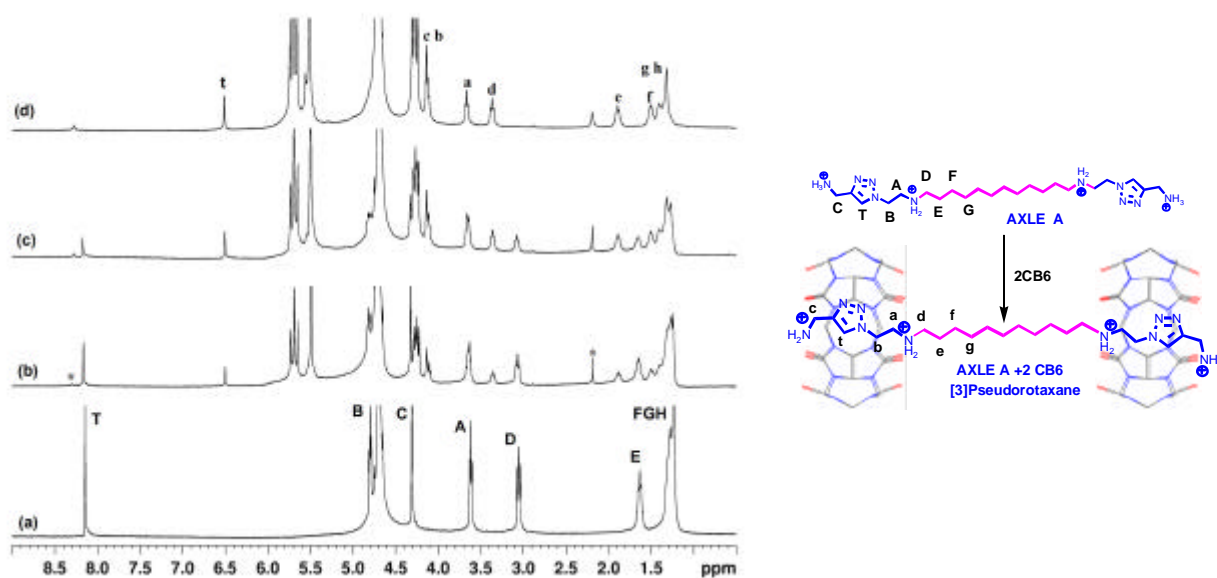
**Synthesis of *N,N'*-Bis-[1-(2-amino-ethyl)-1H-[1,2,3]triazol-4-ylmethyl]-dodecane-1,12-diamine:** *N,N'*-Bis-(2-azido-ethyl)-dodecane-1,12-diamine.2HCl (150 mg, 0.36 mmol), propargylamine.HCl (83 mg, 0.91 mmol) were dissolved in an ethanol-water mixture (5 ml, 2:3, v/v). Subsequently CuSO<sub>4</sub>.5H<sub>2</sub>O (4.5 mg, 0.015 mmol) and sodium ascorbate (7.5 mg, 0.036 mmol) were added. After stirring at rt overnight, the mixture was poured into water (5 ml) and 1M NaOH solution (2 ml) was added. It was stirred for 30 min and extracted with chloroform. Organic phase was collected and the solvent was removed under reduced pressure. The remaining solid residue was suspended in water and stirred further 30 min. White precipitates were collected by filtration and dried under high vacuum 3h. (170 mg, 92%). M.p. 122-123 °C; Elemental Analysis calcd (%) for C<sub>22</sub>H<sub>44</sub>N<sub>10</sub> C, 58,90; H, 9,89; N, 31,22; found: C, 58,63; H, 10,01; N, 31,07

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): d 1.18 (m, 8H, **F,G,H**), 1.38 (m, 2H, **E**), 1.51 (m, 6H, -NH), 2.54 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, **D**), 3.03 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, **A**), 3.92 (s, 2H, **C**), 4.37 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, **B**), 7.47 (s, 1H, **T**); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O, 25 °C): d 27.4, 29.6, 29.7, 30.2, 37.7, 49.6, 49.7, 50.4, 122.8 (triazole, = CH), 148.8 (triazole, = CR).

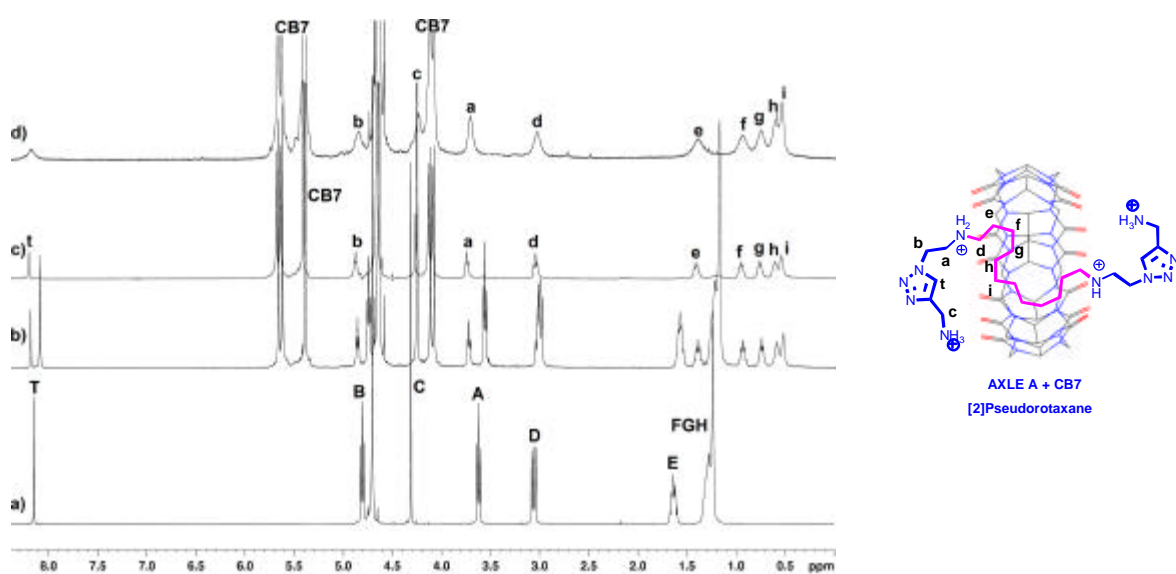
Hydrochloride salt of the ditriazole **Axle A** compound was prepared by dissolving it in diluted HCl solution. After stirring overnight at rt, the solvent was removed under reduced pressure and the solid residue was washed with THF. It was dried under high vacuum 5h. (180 mg, 95%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): d 1.30 (m, 8H, **F,G,H**), 1.65 (m, 2H, **E**), 3.05 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, **D**), 3.56 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, **A**), 4.35 (s, 2H, **C**), 4.85 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, **B**), 8.12 (s, 1H, **T**);

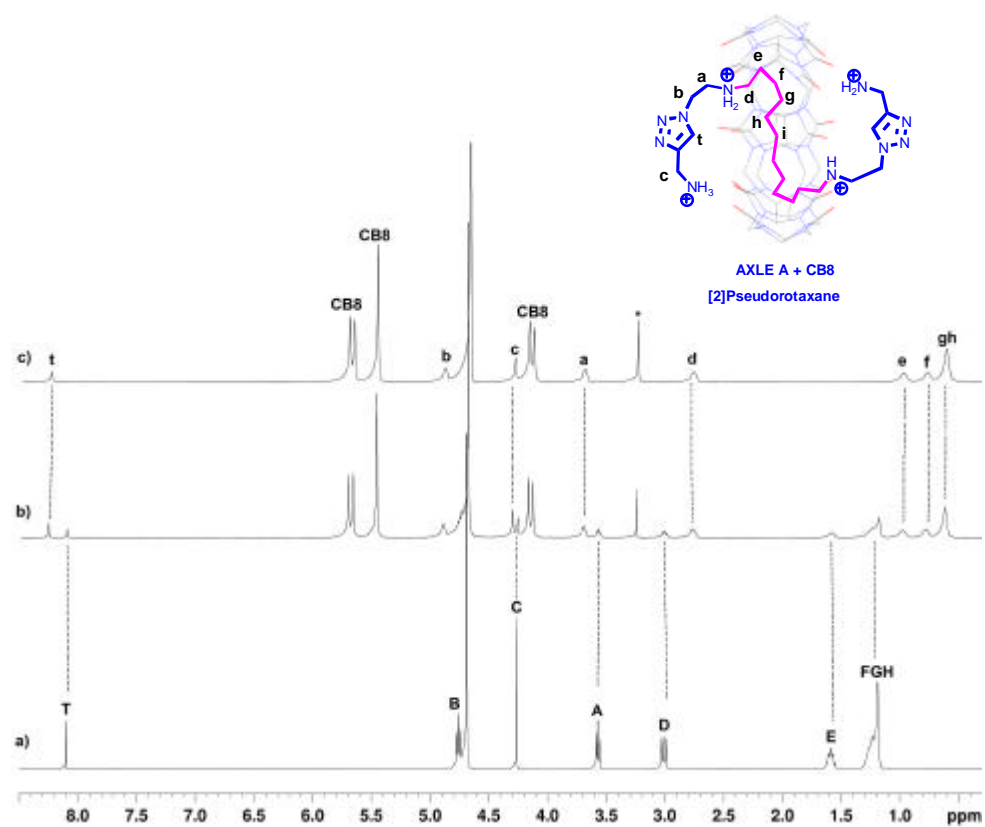
## NMR and MALDI-MS Spectra



**Figure S1.**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ , 25  $^\circ\text{C}$ ) spectra of Axle A; the addition of (a) 0 equiv of CB6 (b) 0.5 equiv of CB6, (c) 1 equiv of CB6, (d) 2.2 equiv of CB6 (\* denotes impurities).



**Figure S2:** Proposed structure of CB7-Axle A and  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ , 25  $^\circ\text{C}$ ) spectra of Axle A; the addition of (a) 0 equiv of CB7 (b) 0.4 equiv of CB7, (c) 0.9 equiv of CB7, (c) 1.3 equiv of CB7.



**Figure S3:** Structure of CB8-Axle A and  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ , 25  $^\circ\text{C}$ ) spectra of Axle A; the addition of (a) 0 equiv of CB8 (b) 0.5 equiv of CB8, (c) 1.2 equiv of CB8.

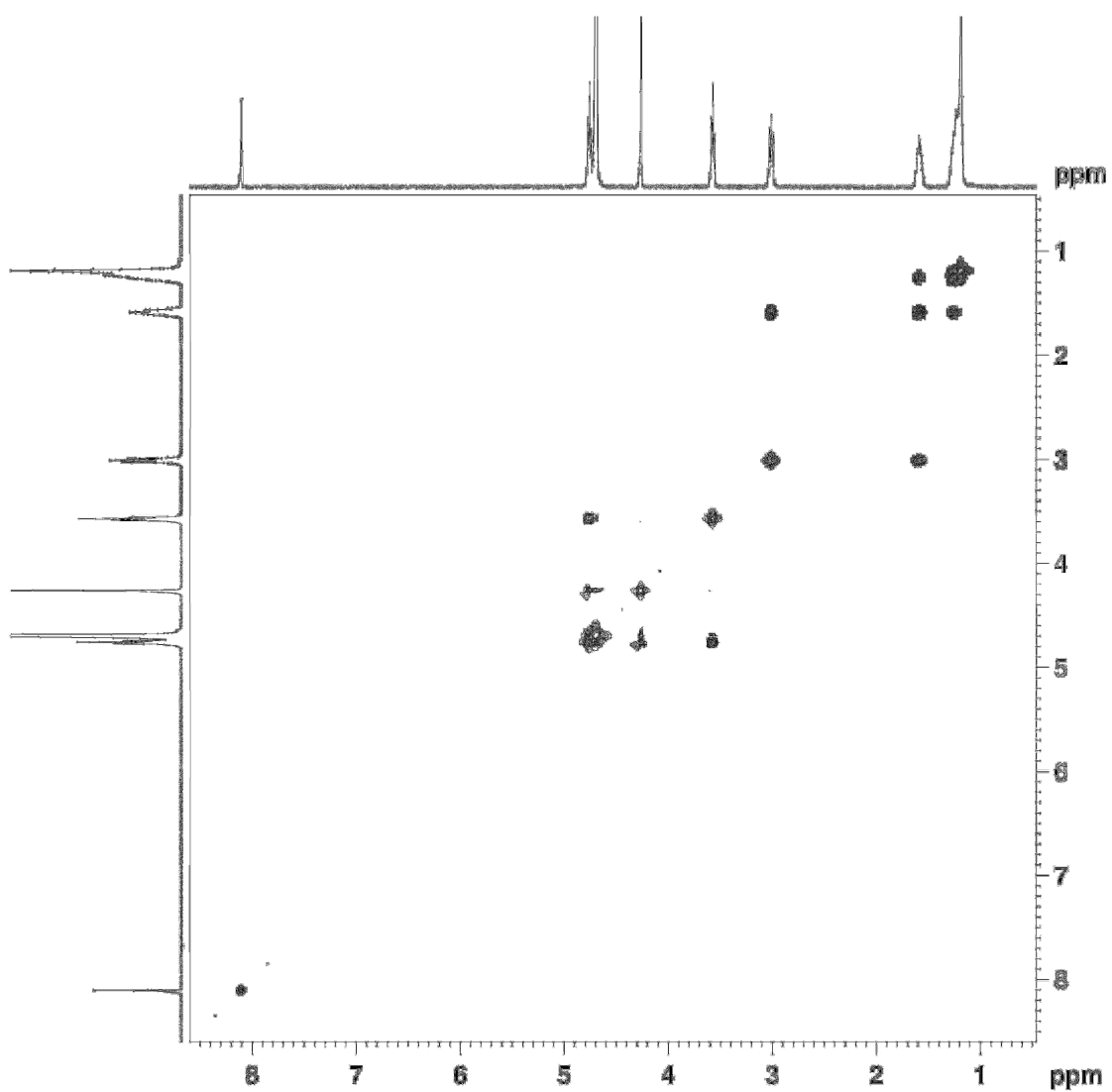


Figure S4: COSY-NMR spectrum Axle A.

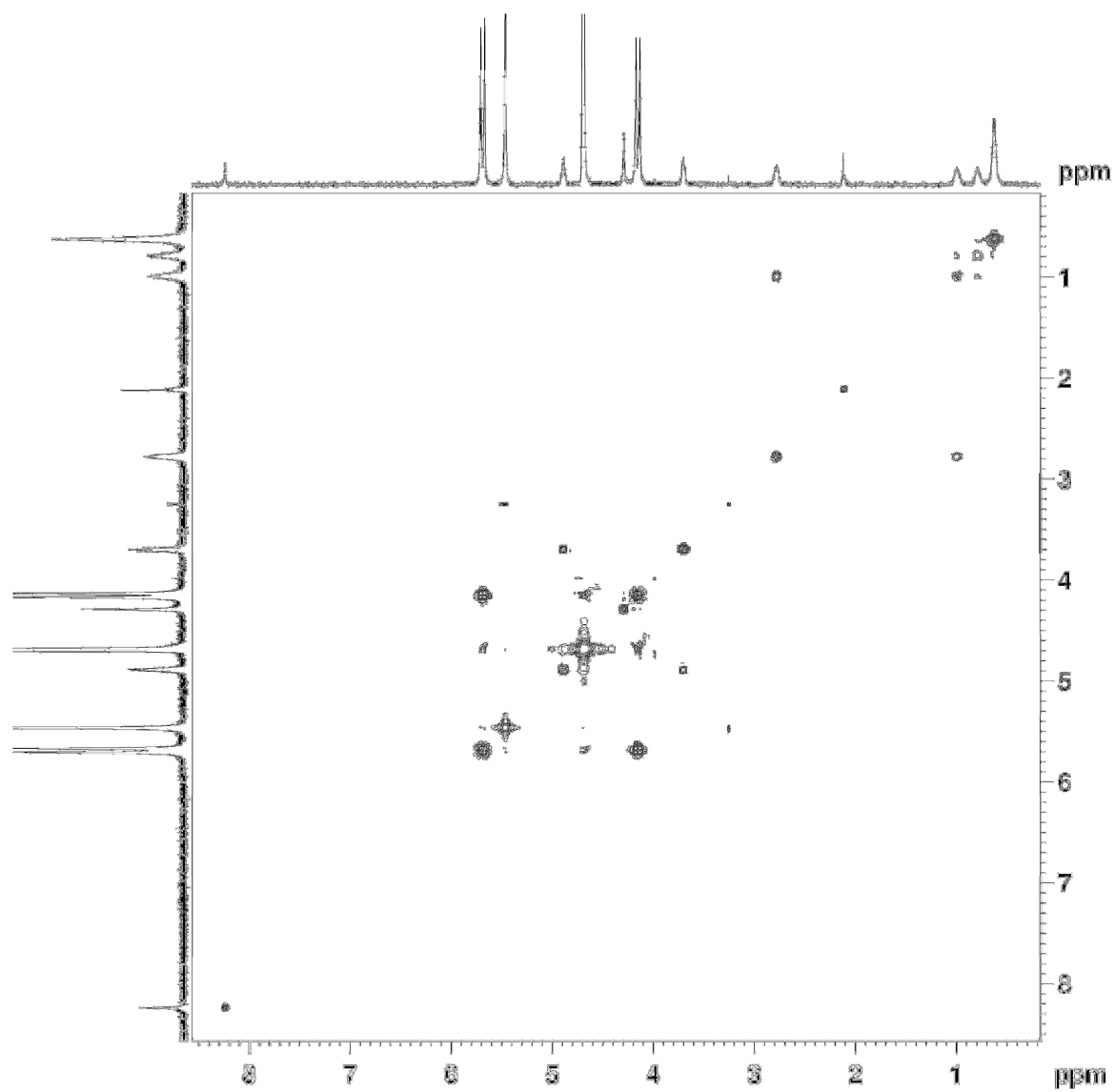


Figure S5: COSY-NMR spectrum of [3]pseudorotaxane of CB8 with Axle A.



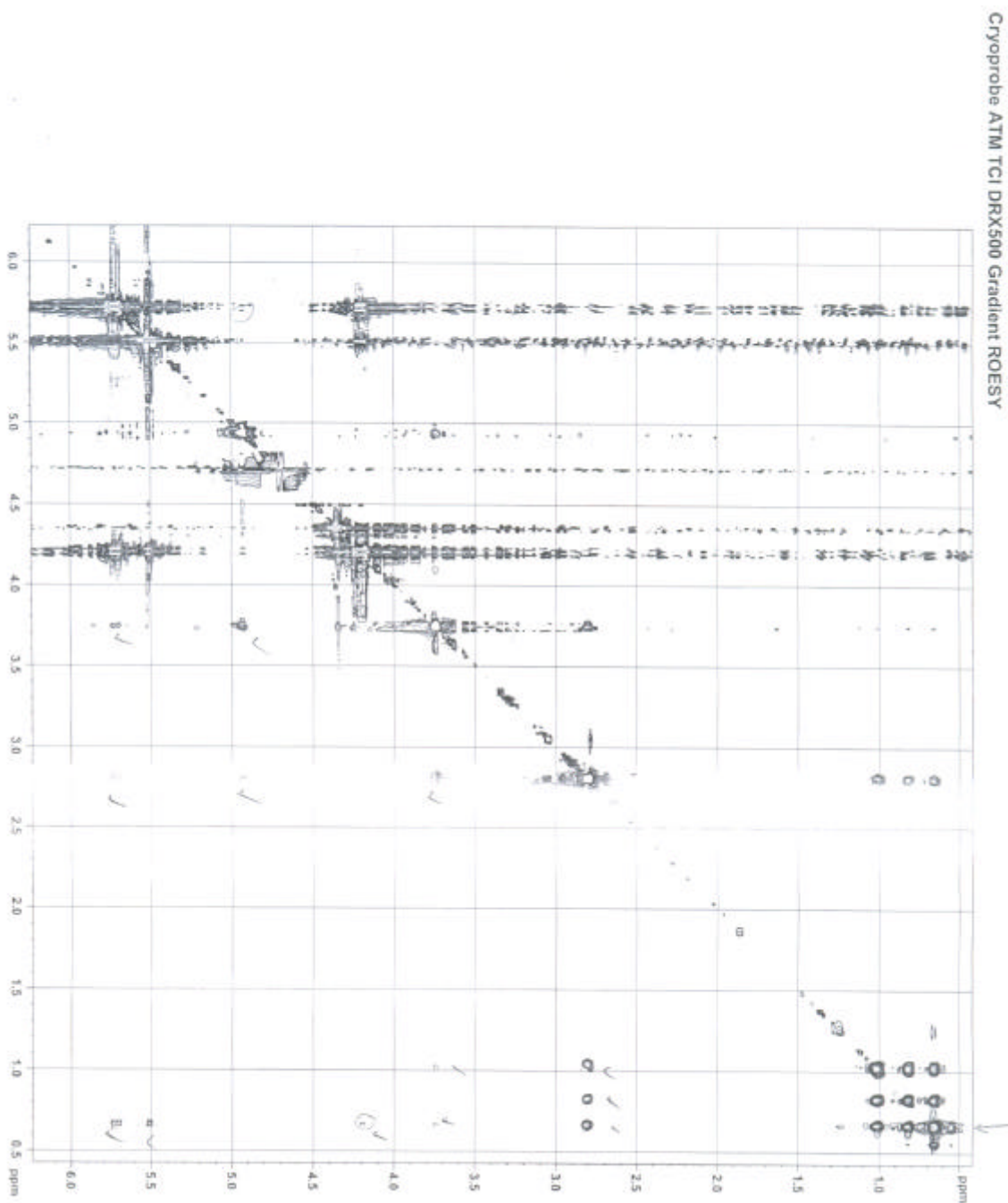


Figure S6: NOESY-NMR spectrum of [3]pseudorotaxane of CB8 with Axle A.

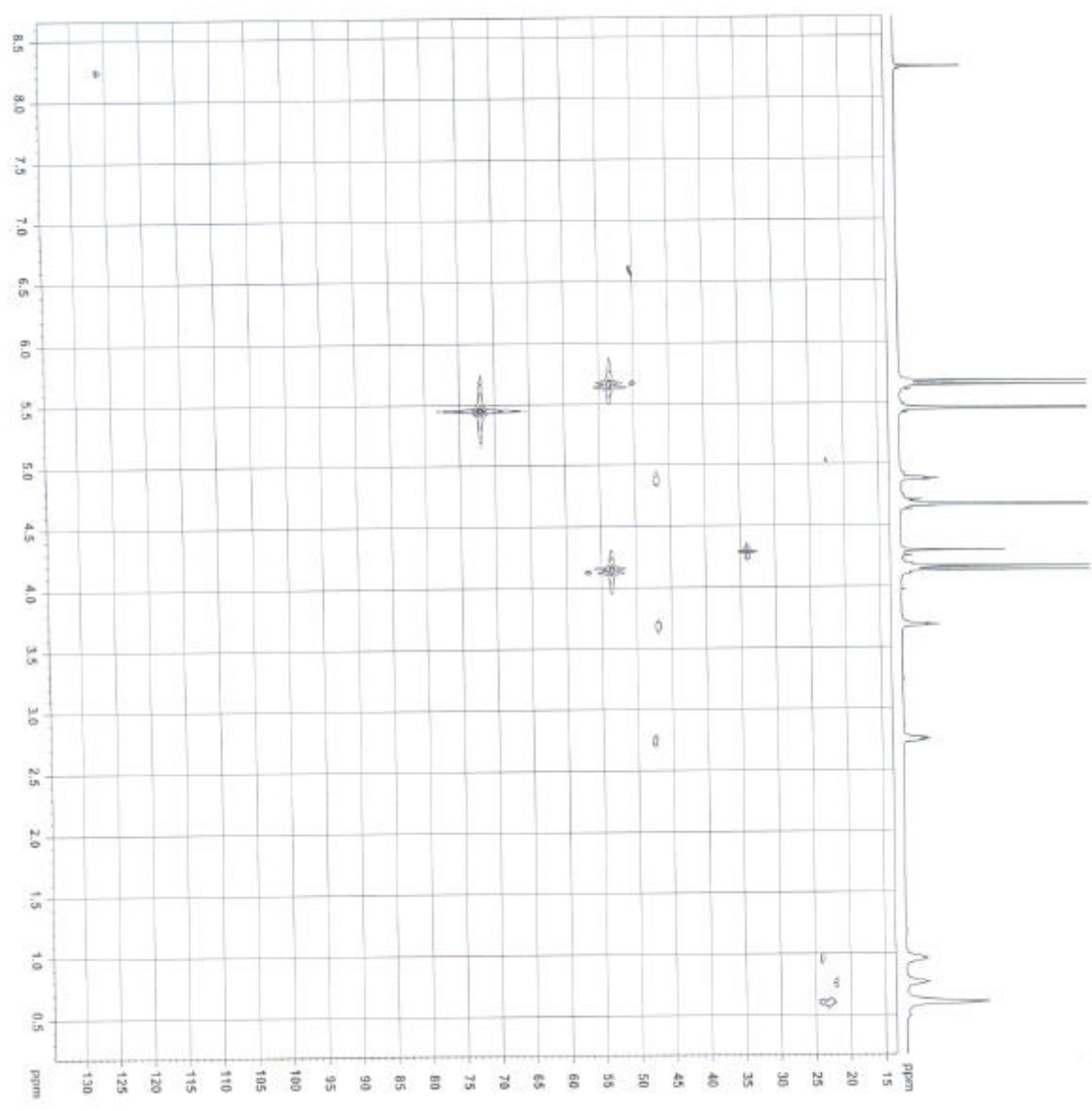


Figure S7: HMQC-NMR spectrum of [3]pseudorotaxane of CB8 with Axle A.

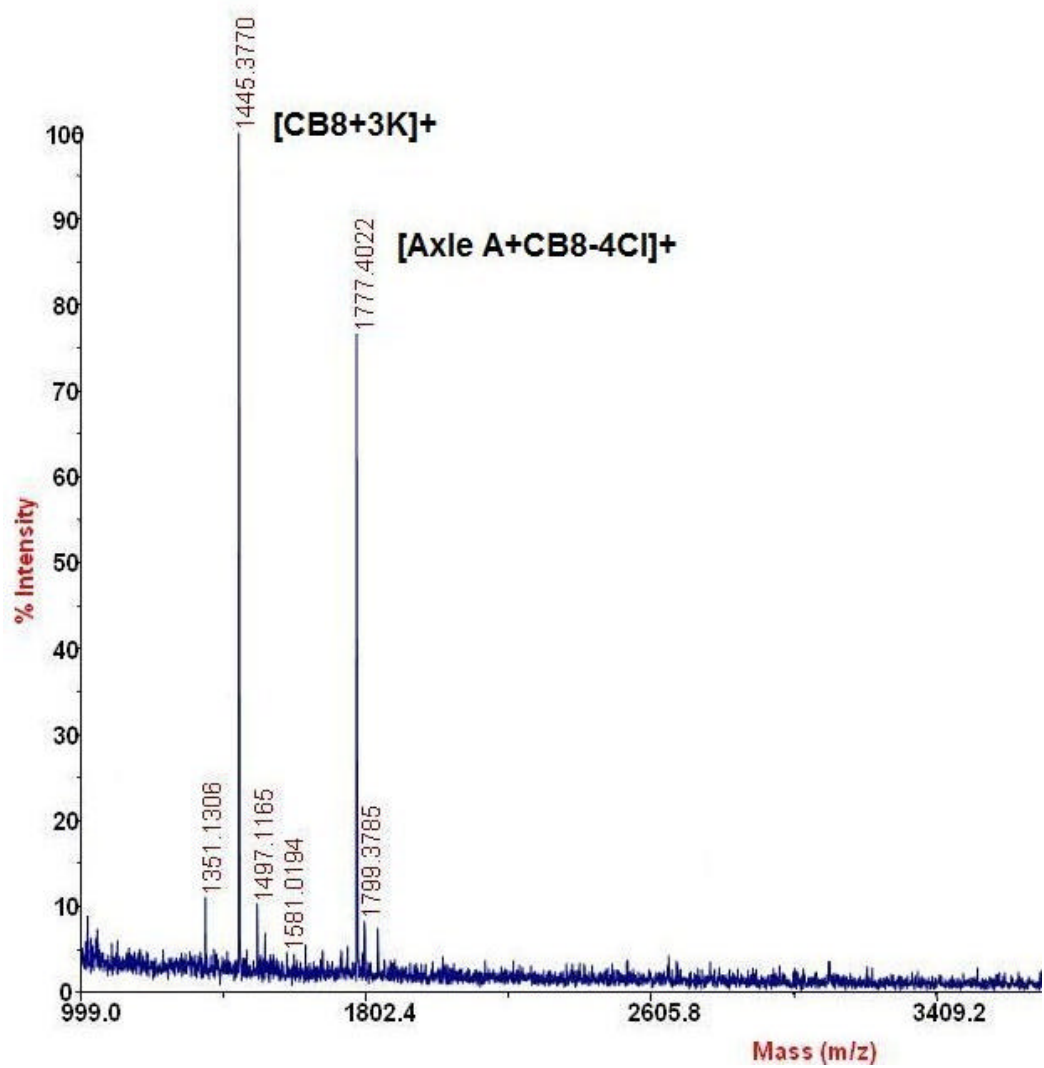


Figure S8: MALDI-mass spectrum of CB8-Axle A.

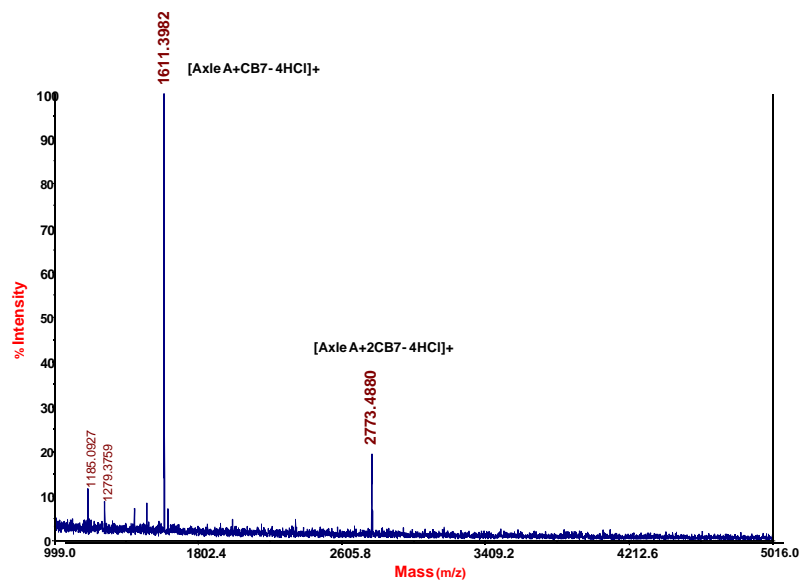


Figure S9: MALDI-mass spectrum of CB7-Axle A.

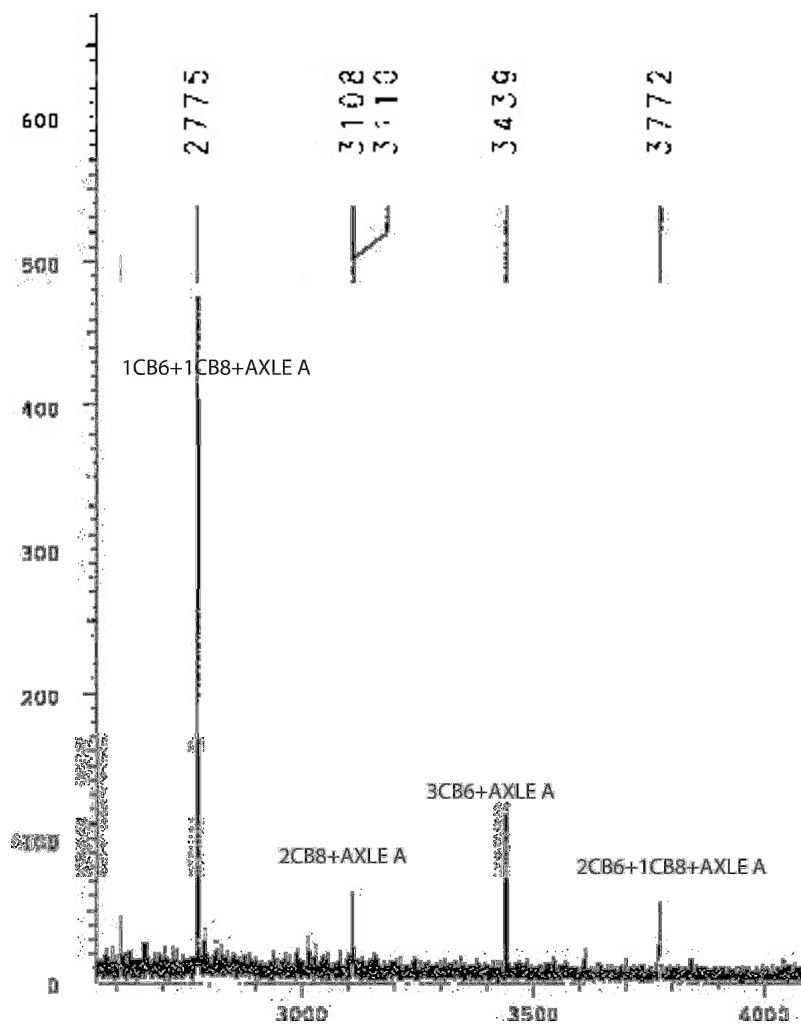
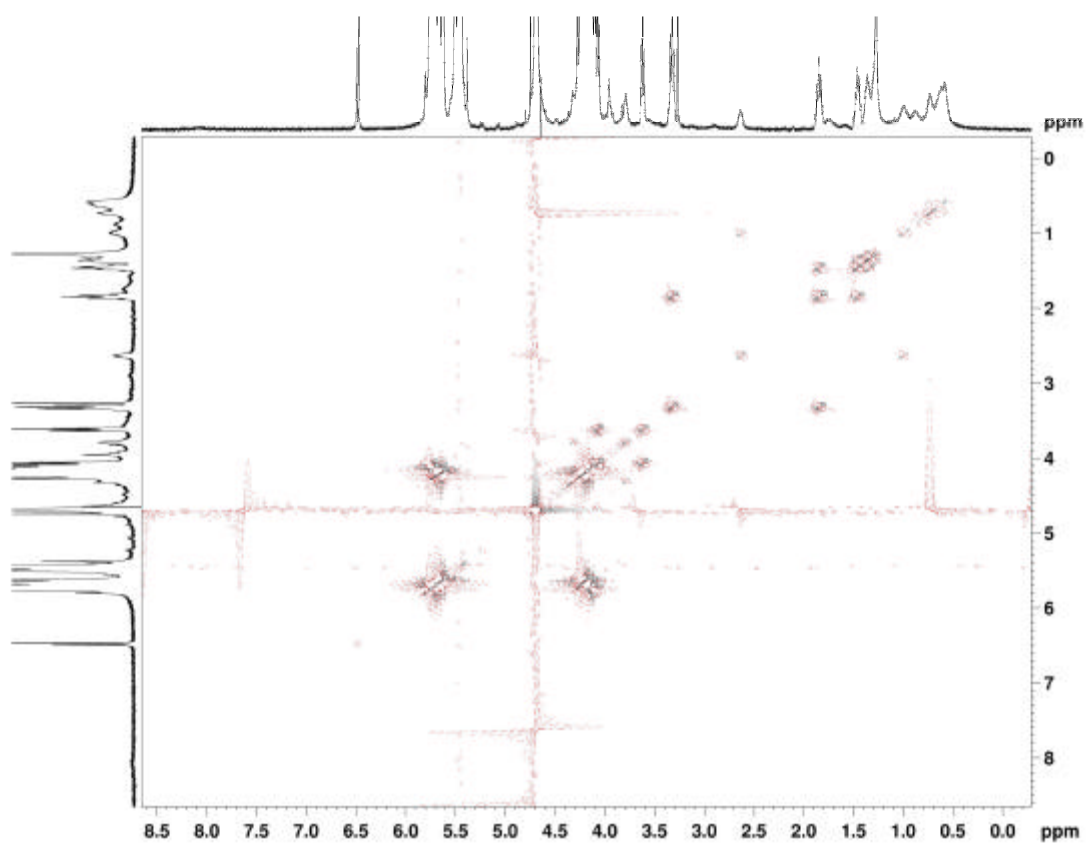


Figure S10: MALDI-mass spectrum of Axle A+1CB8+2CB6.



**Figure S11:** The COSY-NMR spectra (400 MHz, 25 °C, D<sub>2</sub>O) of 96 h later after addition of 2 equiv CB6 to Axle A+CB8.