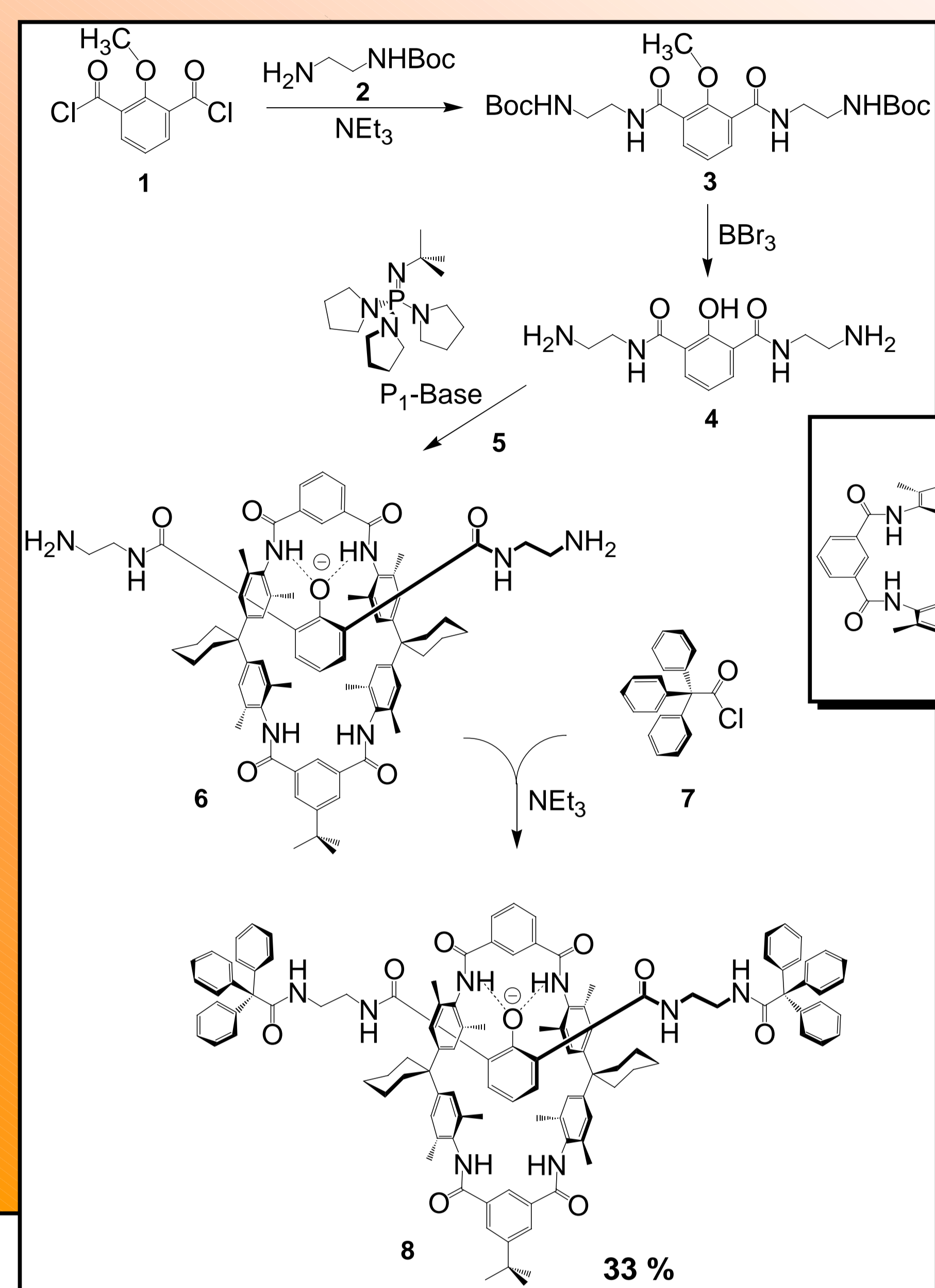


# Novel Template Effect for the Preparation of [2]Rotaxanes with Functionalized Center Pieces

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## I. Synthesis

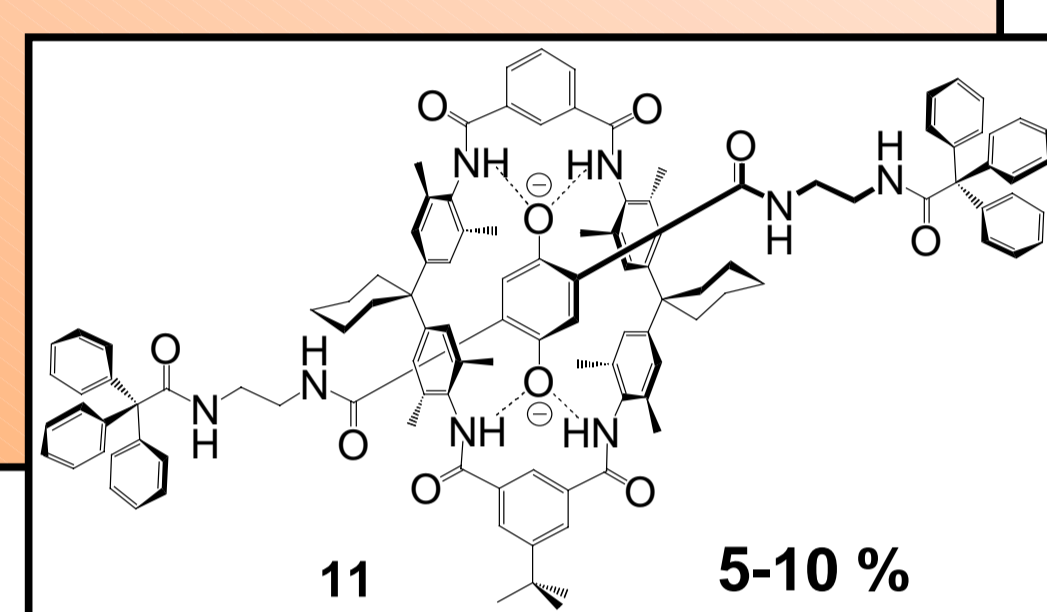
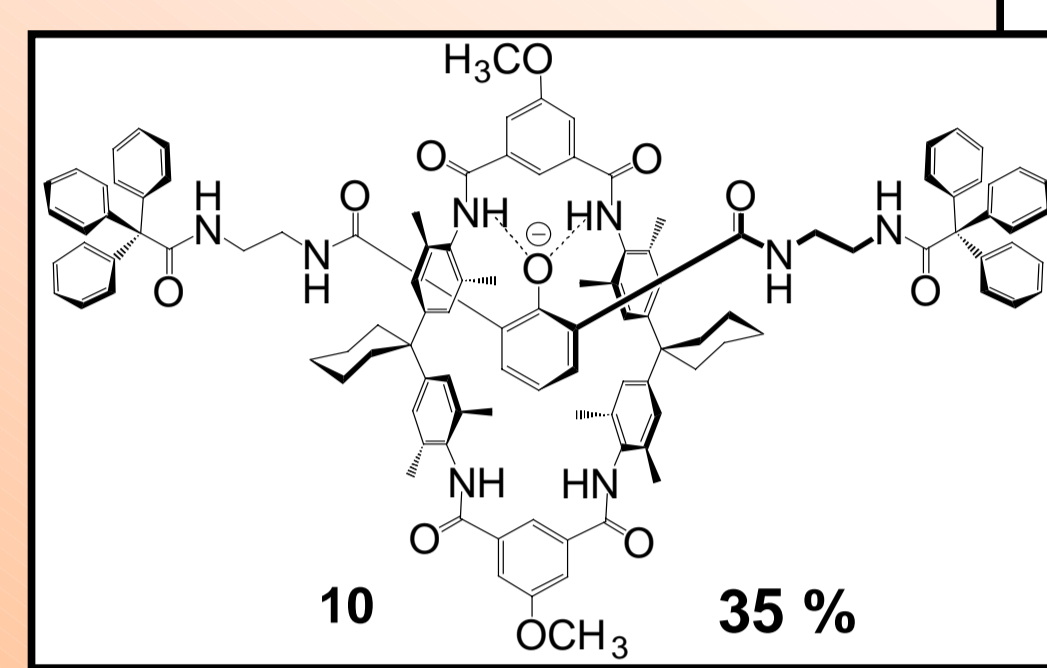
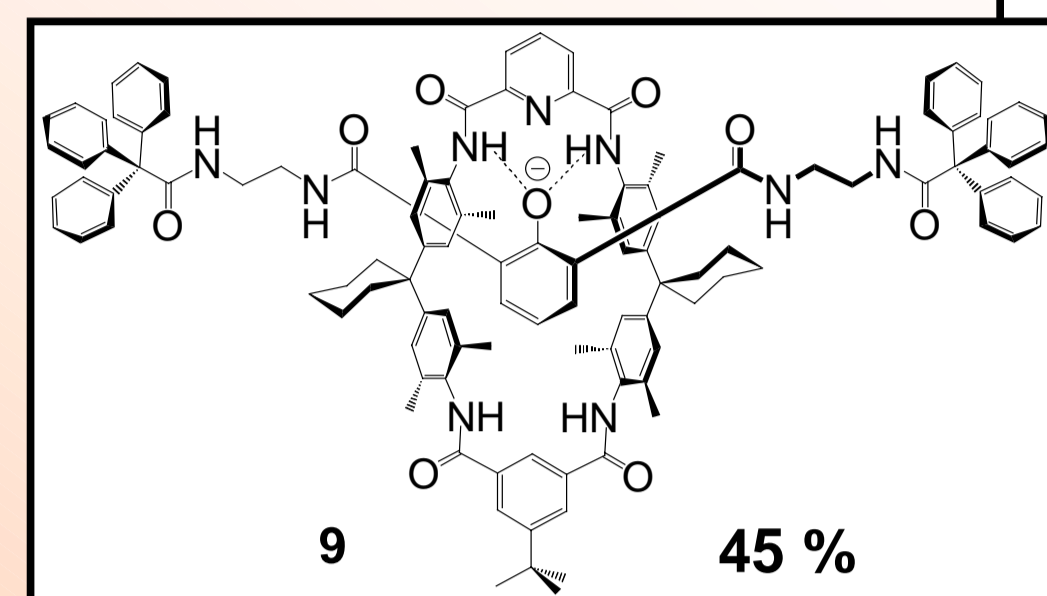


[2]Rotaxanes can be synthesized by using a novel anion template effect, in which a phenolate anion can be threaded through a tetralactam macrocycle by hydrogen bonding

This anion template effect is not limited to phenol derivatives as center pieces. It can also be used with hydroquinone center pieces, however with somewhat lower yields

Methylation of phenolate center piece with MeI did not occur

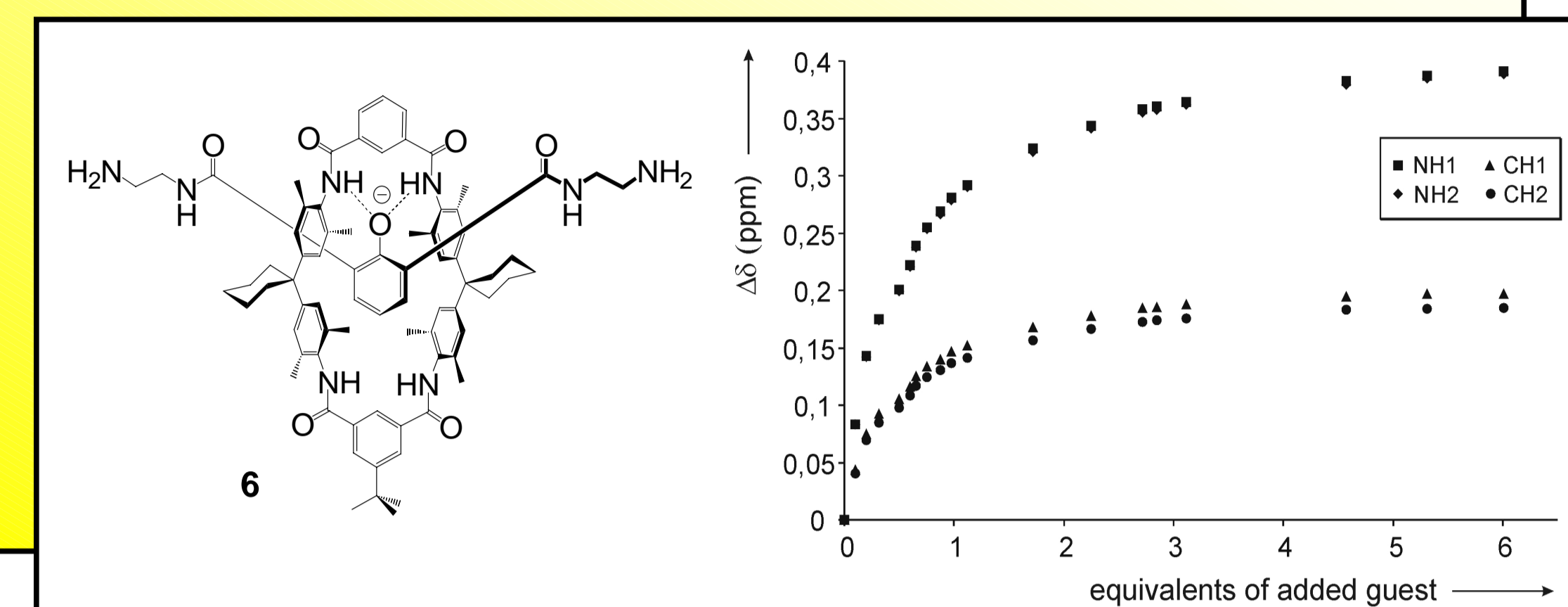
Wheel serves as a non-covalent protecting group and thus confirms rotaxane structure



## II. Anion Binding to Macrocycle 5

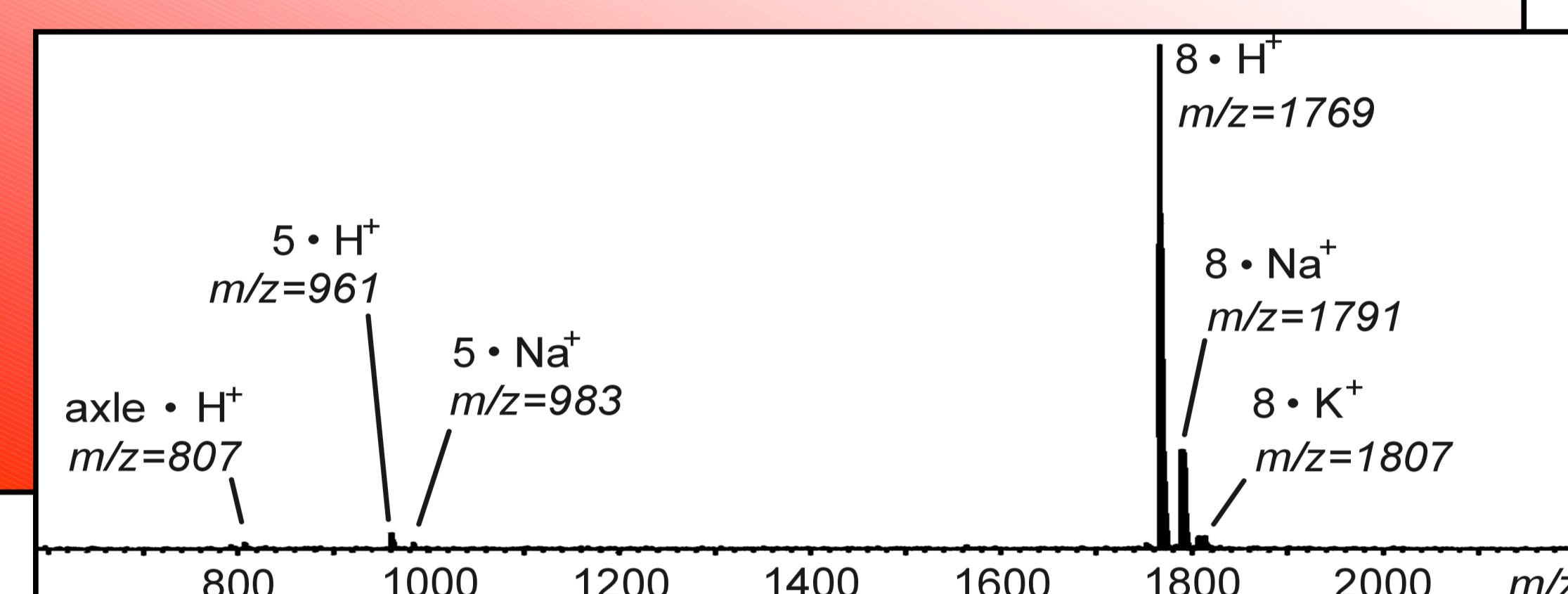
Strong bonding of center piece 4 to macrocycle 5 is confirmed by determination of a binding constant in a NMR titration

Even in a competitive solvent mixture such as DMSO:CH<sub>2</sub>Cl<sub>2</sub> = 1:1, a high binding constant of  $K = 2.200 \pm 700 \text{ M}^{-1}$  is found

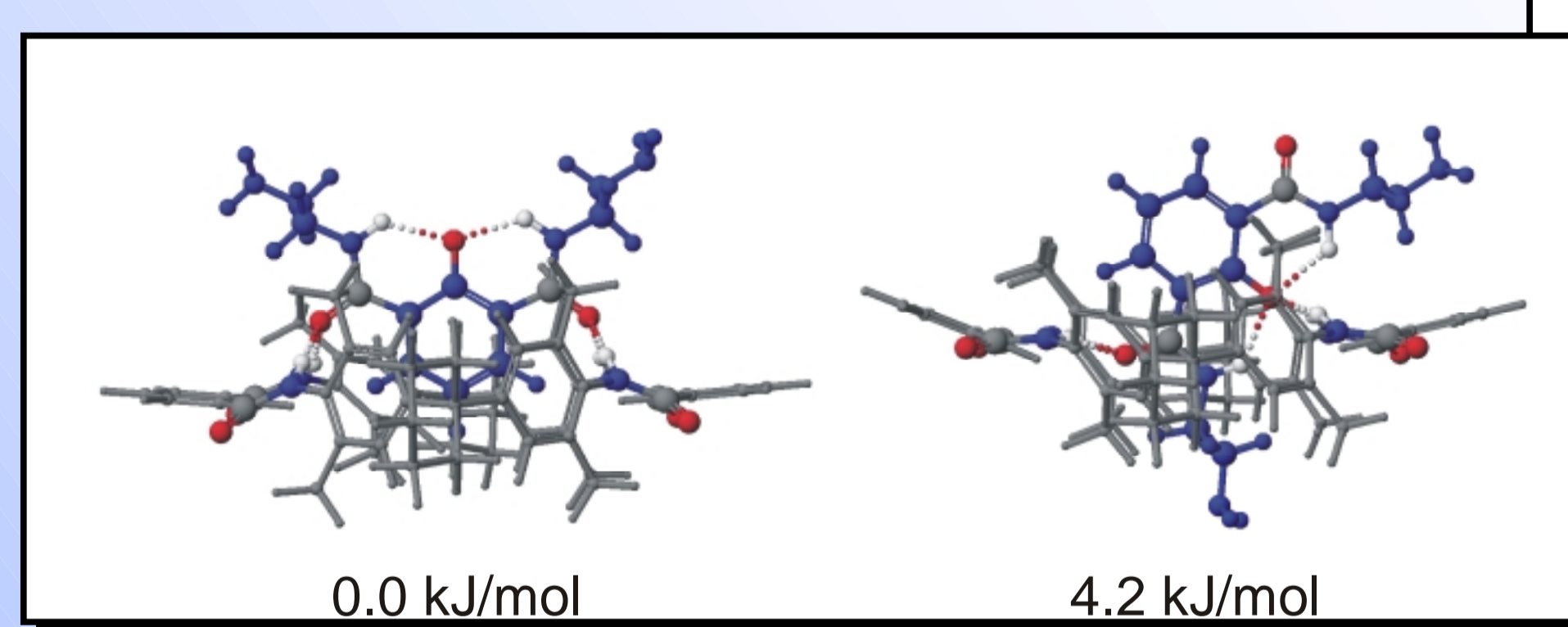
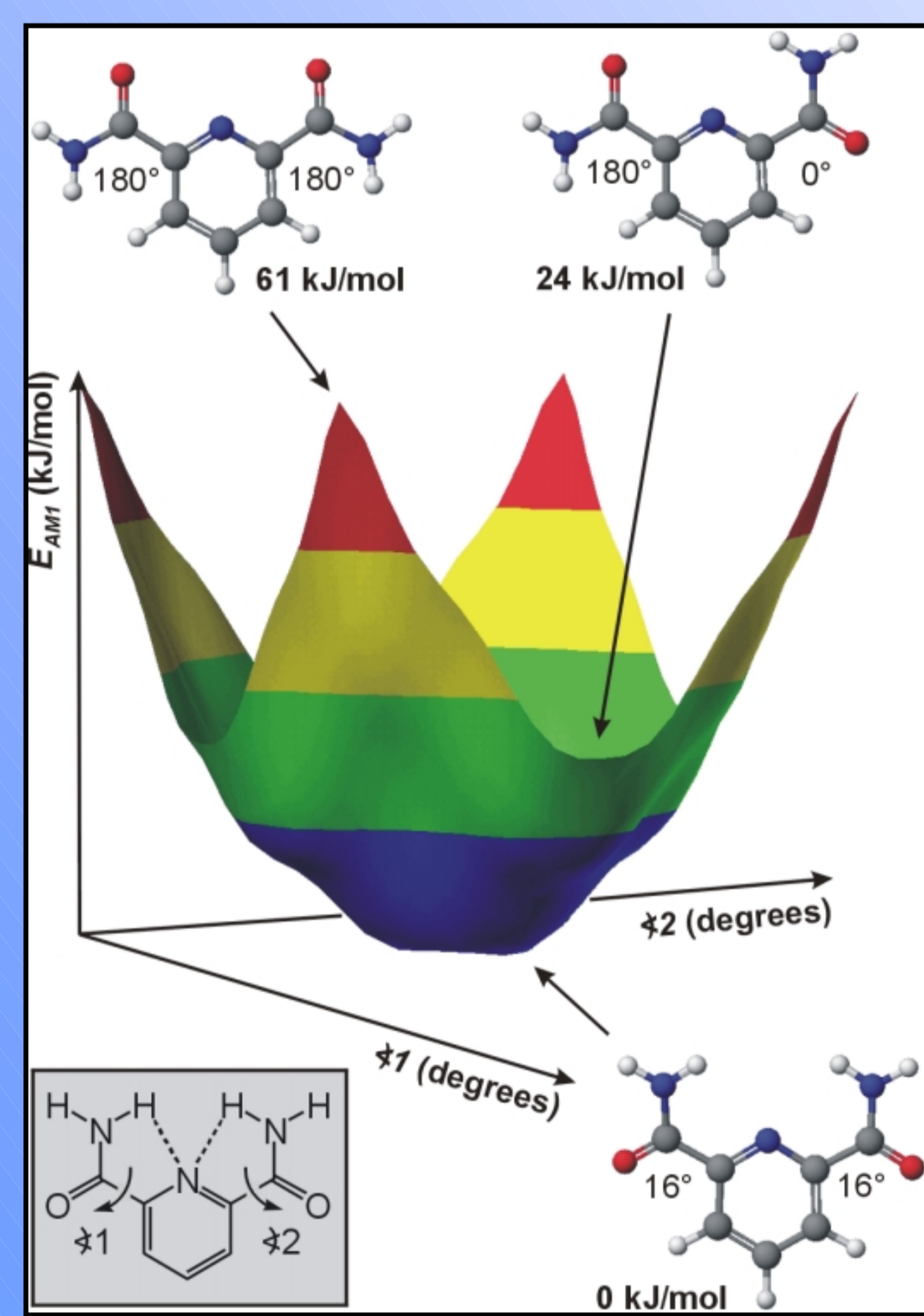
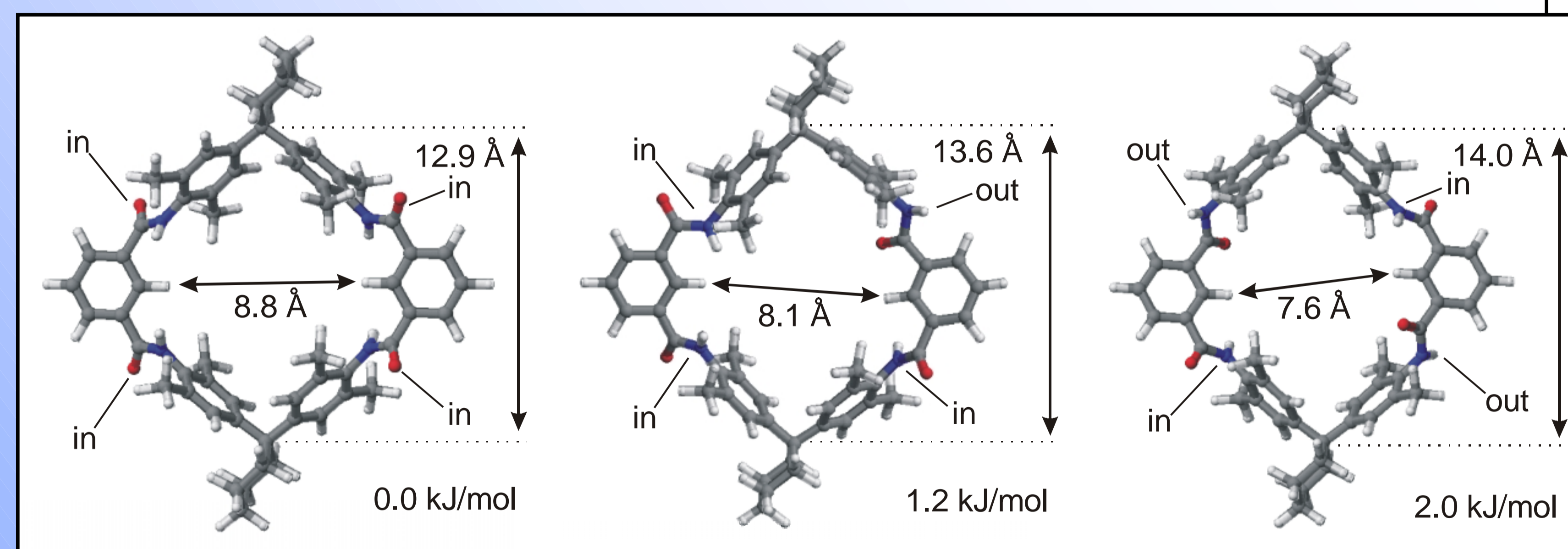


## III. MALDI-MS

The MALDI mass spectrum is almost fragment free and thus indicates that molecule 8 indeed possesses a rotaxane structure



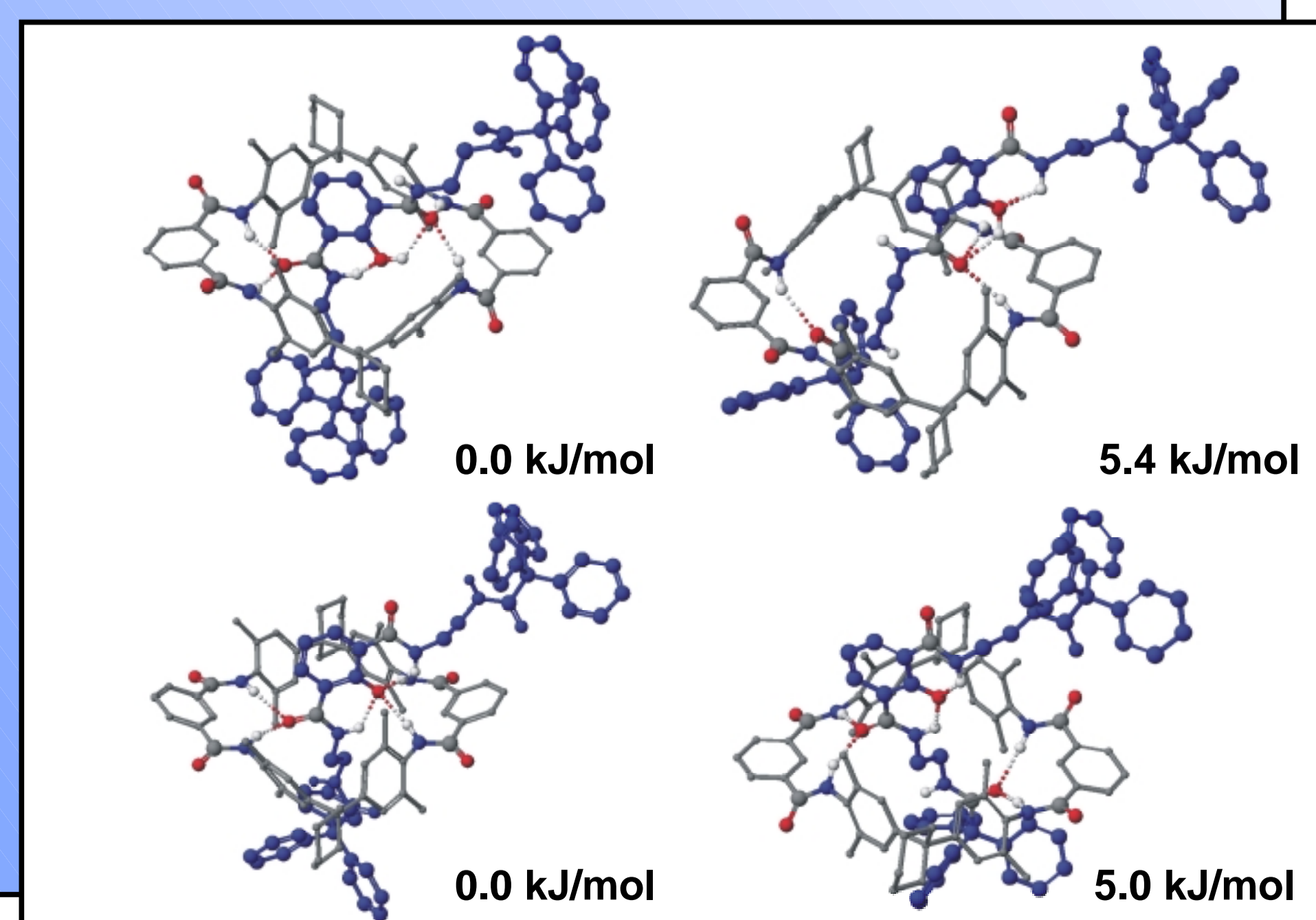
## IV. Molecular Modeling



The tetralactam macrocycle is flexible with respect to the *in* and *out* conformations of the amide groups

Instead, the only stable conformation (*in/in*) of the pyridine unit in the pyridine macrocycle is shown in the Ramachandran plot of the potential energy surface for rotation about angles 1 and 2

A non-threaded center piece/wheel complex likely competes with the threaded complex in the synthesis; rotaxane yields therefore are lower than expected from a high binding constant (33 – 45%)



Different positions of the wheel on the neutral or anionic axle cause different energies of axle/wheel complex

For both, the protonated and deprotonated rotaxanes, two types of conformations are found with comparable energies:

Type I: Wheel located around axle center piece  
Type II: Wheel positioned on one of the spacers between stopper and center piece

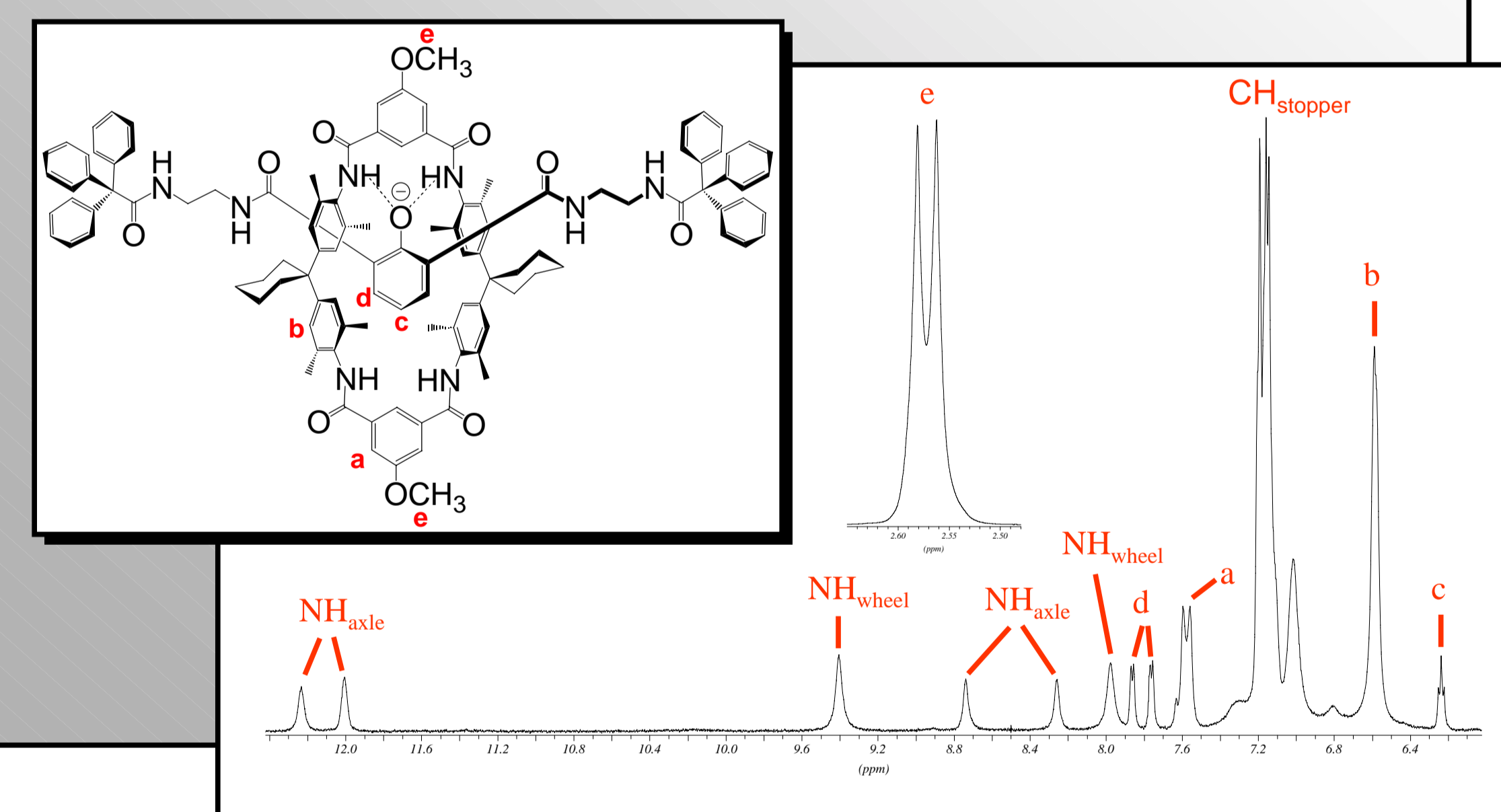
## V. Molecular Shuttles?

Proton signals in the <sup>1</sup>H-NMR spectrum of the deprotonated rotaxane 8 in CH<sub>2</sub>Cl<sub>2</sub> at 248 K indicate slow shuttling and rotational motion of the wheel

Two sets of signals for the wheel are observed in line with the conclusion that rotation around the axle is slow

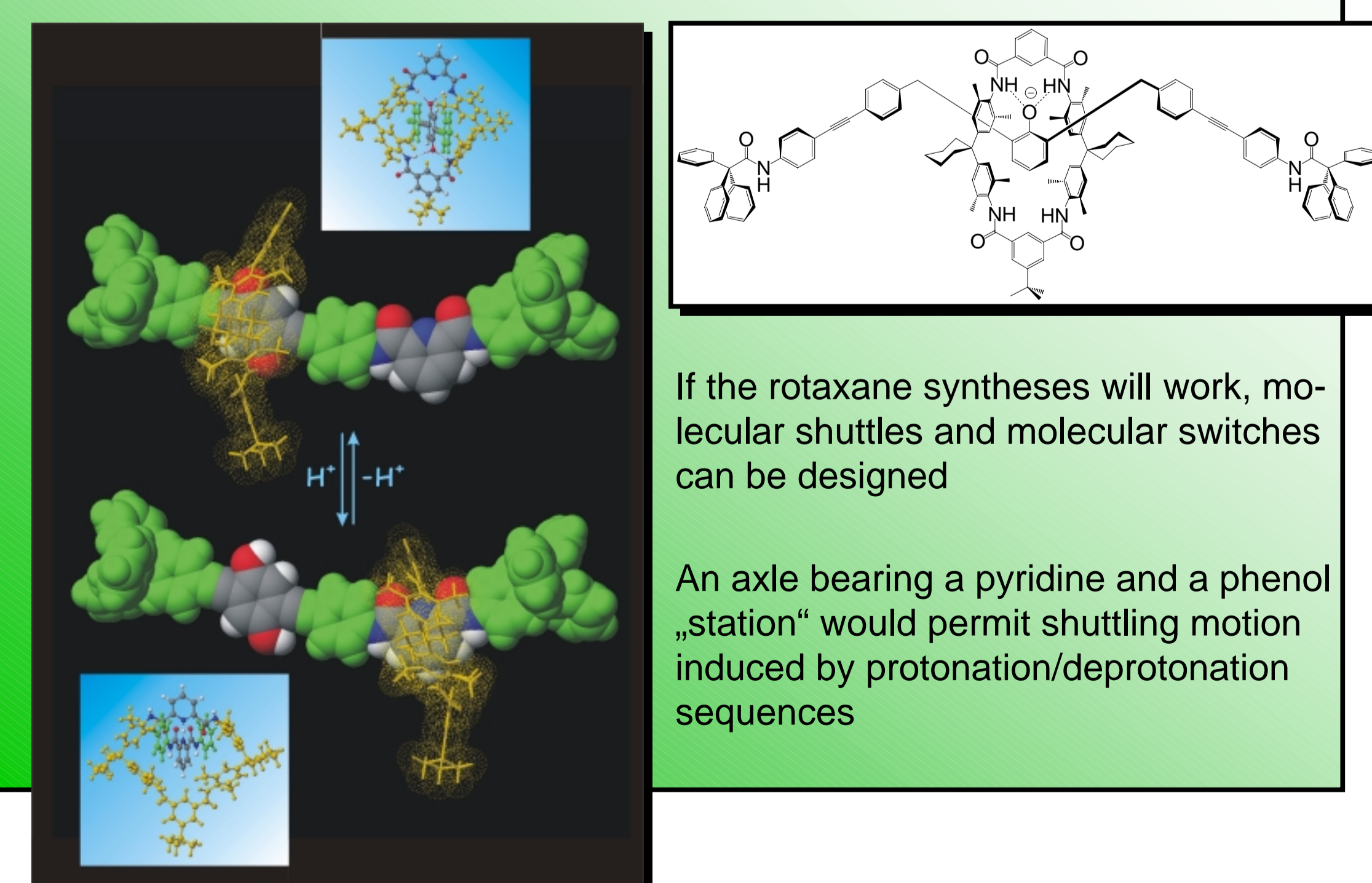
The axle protons also appear twice indicating a slow shuttling of the wheel along the axle

Further studies with the protonated rotaxanes are needed for comparison



## VI. Outlook

This new anion template effect will now be combined with organometallic rotaxane syntheses, in which catalytic cross coupling reactions are used



If the rotaxane syntheses will work, molecular shuttles and molecular switches can be designed

An axle bearing a pyridine and a phenol „station“ would permit shuttling motion induced by protonation/deprotonation sequences

## Acknowledgement

We are grateful to Prof. Dr. Fritz Vögtle for revealing his knowledge in rotaxane chemistry. P. Ghosh thanks the Alexander-von-Humboldt foundation for a postdoctoral fellowship. C. A. Schalley acknowledges a Liebig fellowship from the Fonds der Chemischen Industrie and financial support from the Deutsche Forschungsgemeinschaft.