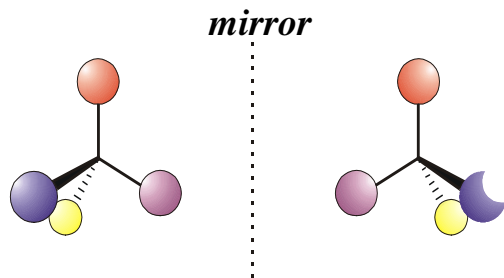




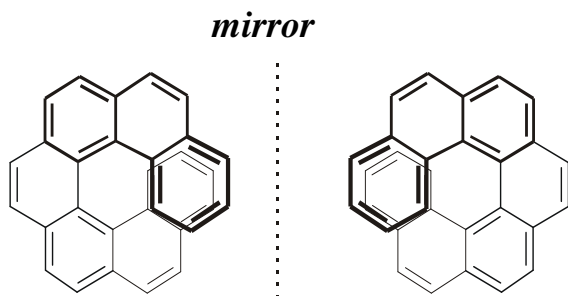
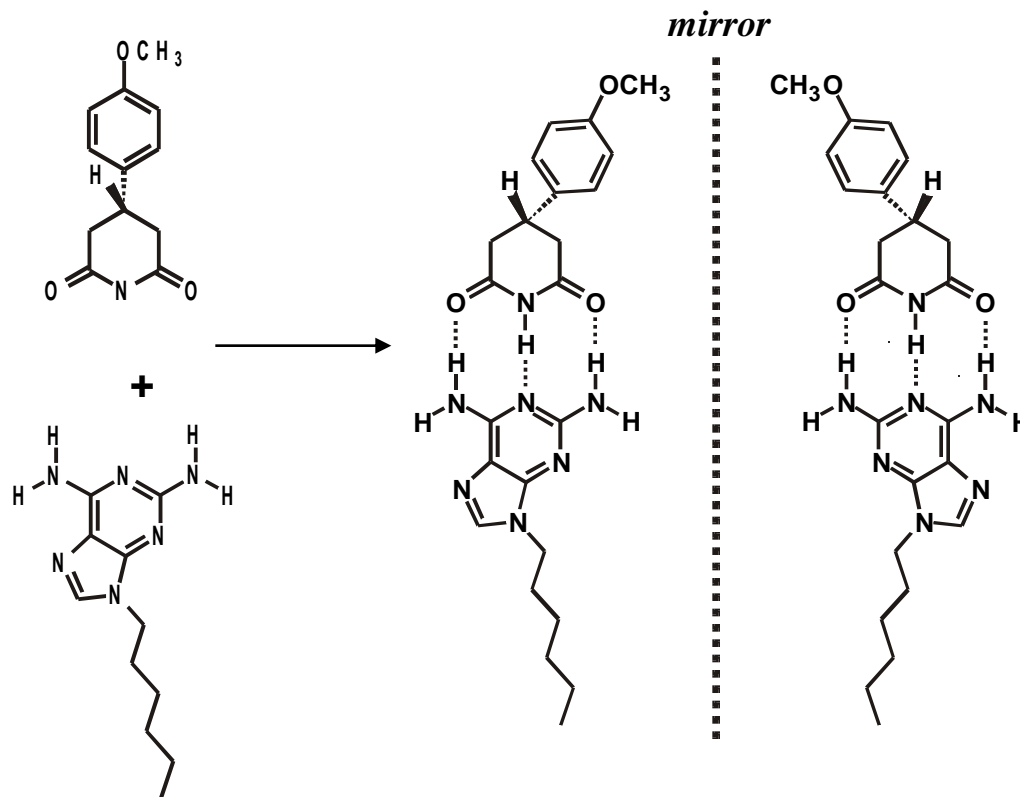
# Molecular and supramolecular chirality

## Molecular chirality



Van 't Hoff, Le Bell, 1874

## Supramolecular chirality

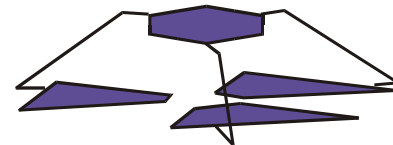
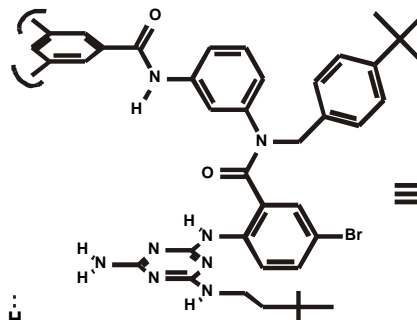
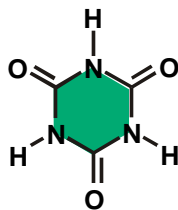
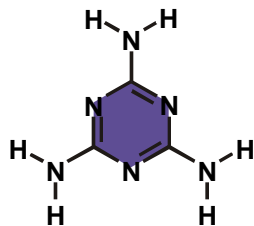


Newman, Lednicer  
*J. Am. Chem. Soc.*, 1956, 78, 4765

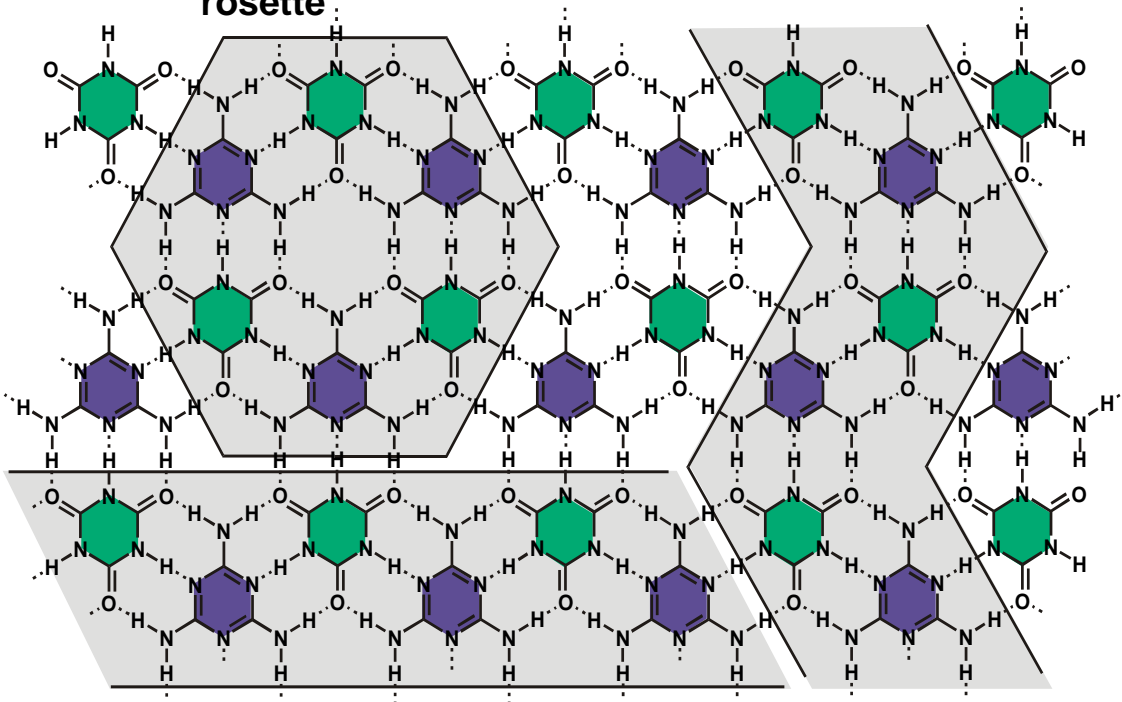
Lehn *et al.*  
*Helv. Chim. Act.*, 1998, 81, 1



# The Melamine-Cyanuric Acid lattice

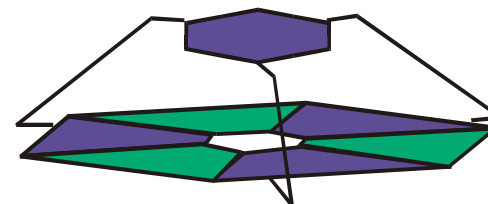
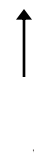


rosette



linear tape

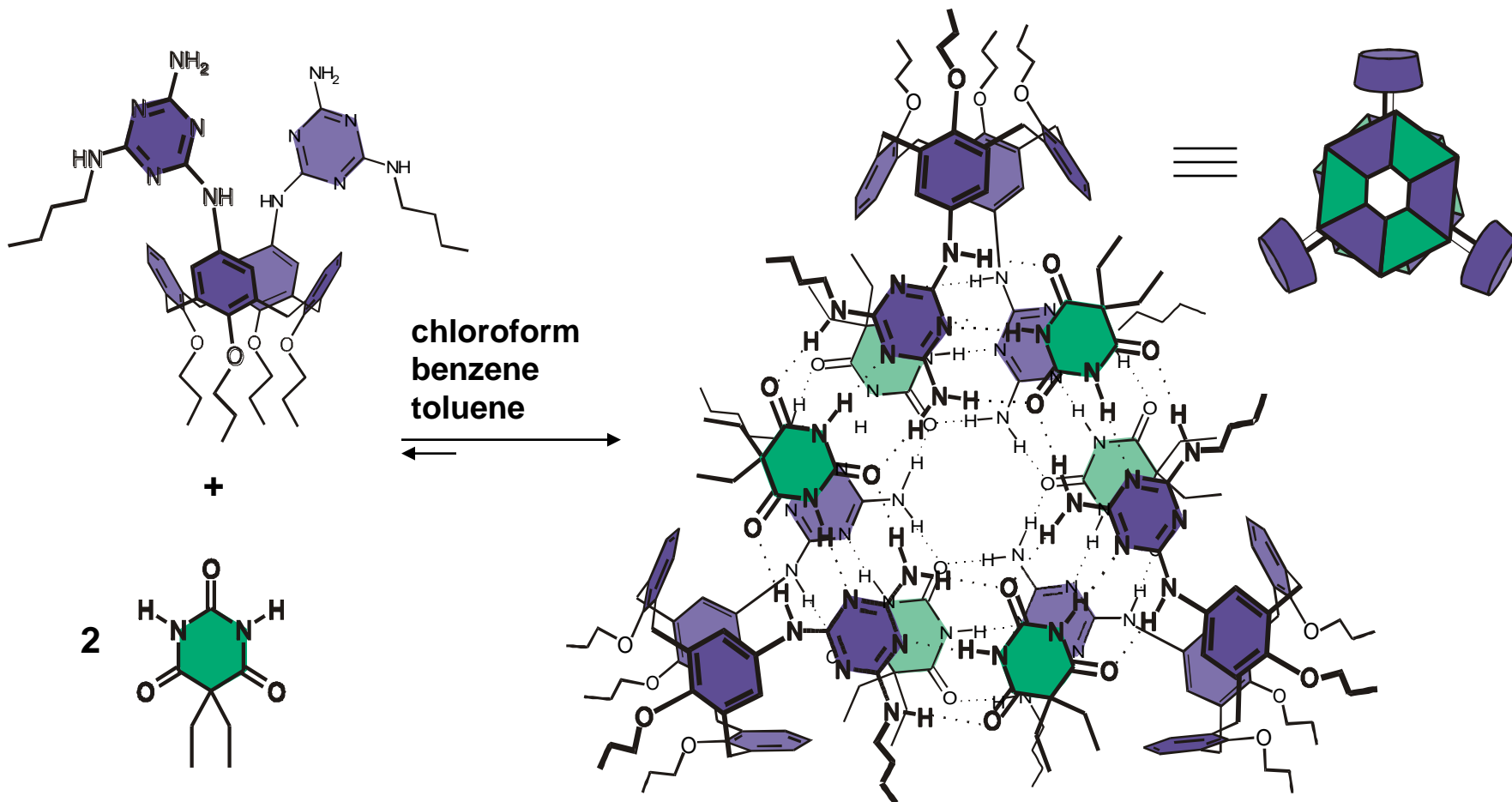
crinkled tape



Whitesides *et al.*  
*Acc. Chem. Res.* **1995**, *28*, 37-44



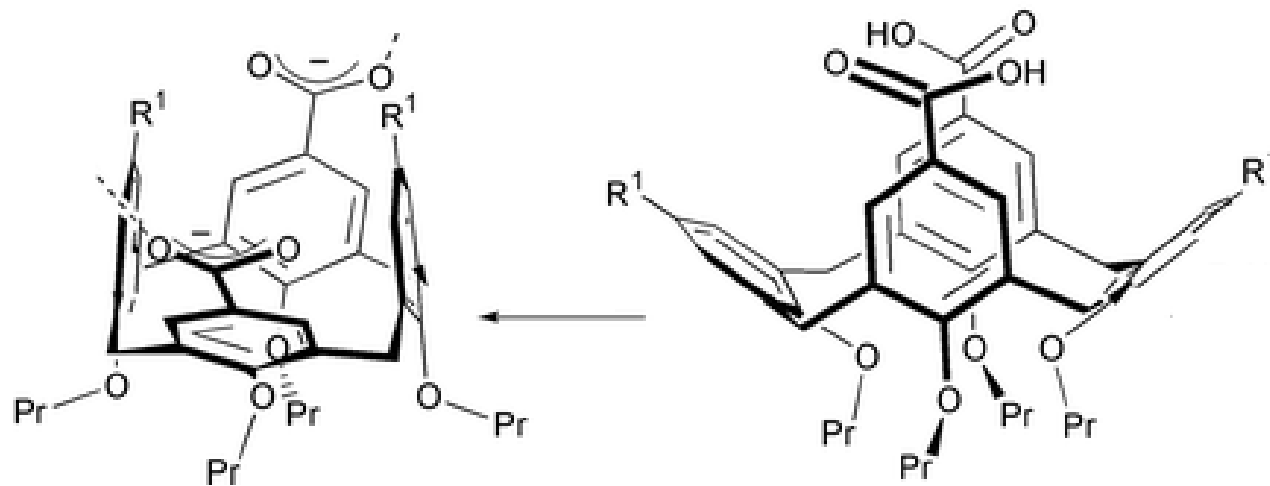
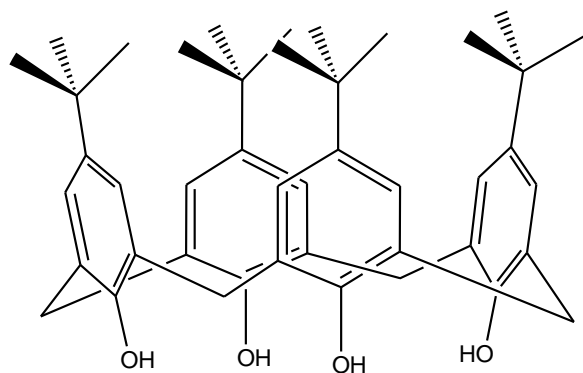
# Self-assembly of a calix[4]arene double rosette



Vreekamp *et al.*  
*Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1215

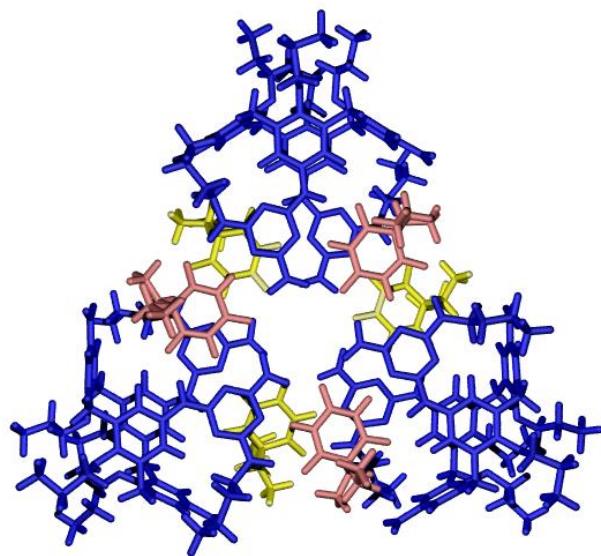


# Calix[4]arene cone and pinched cone conformations

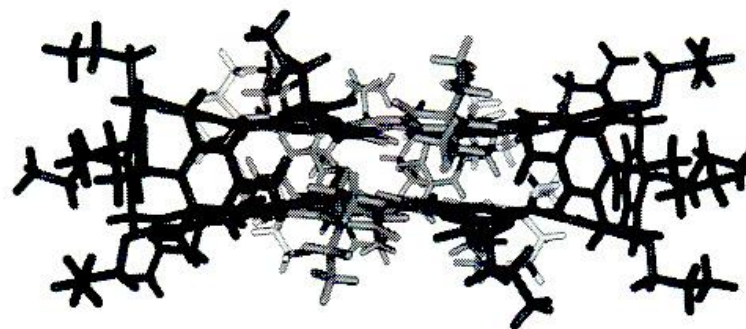




## X-Ray structure



*top view*



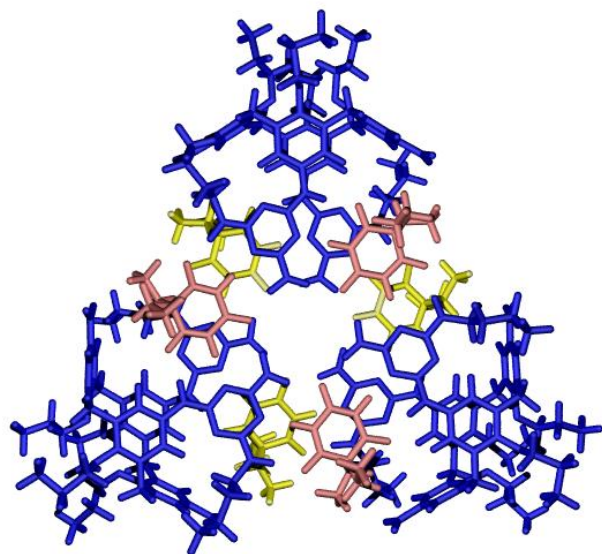
*side view*

Figure 3.4 X-Ray crystal structure of assembly  $Ib_3 \cdot (DEB)_6$ .<sup>[14]</sup>

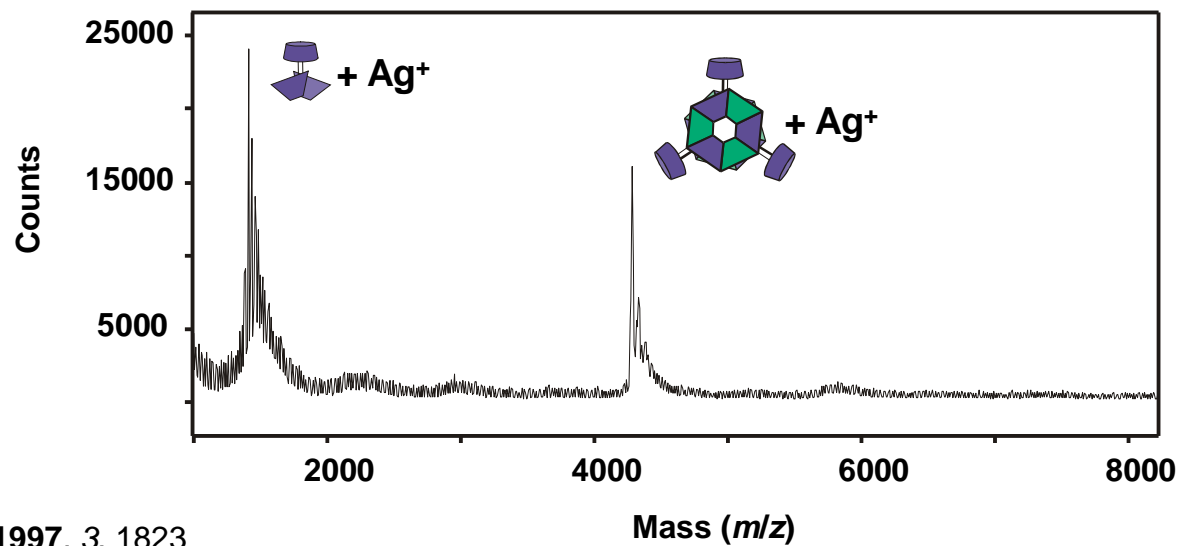
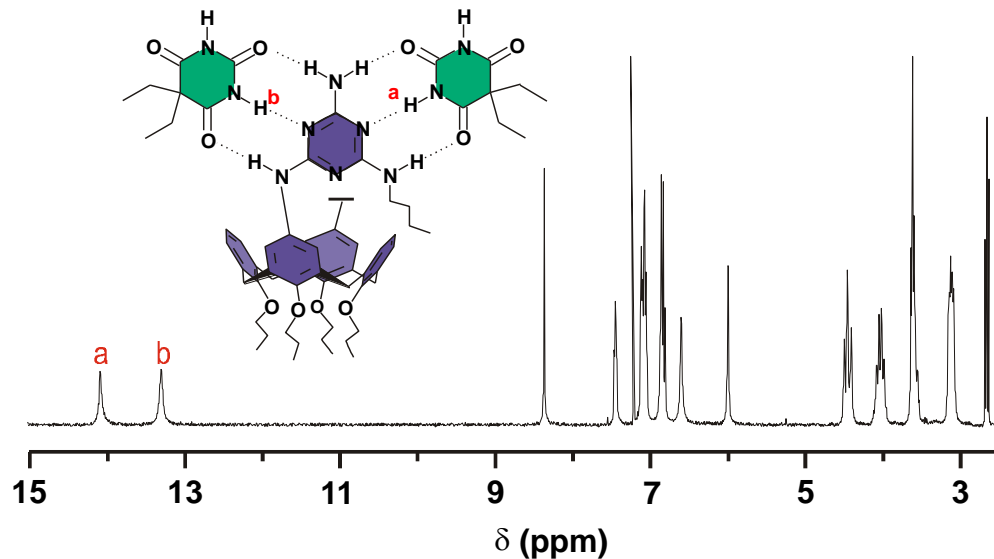


# Characterization

- $^1\text{H}$  NMR spectroscopy
- MALDI-TOF MS
- X-ray crystallography



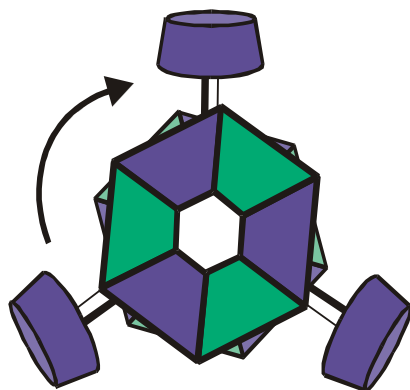
X-ray crystal structure



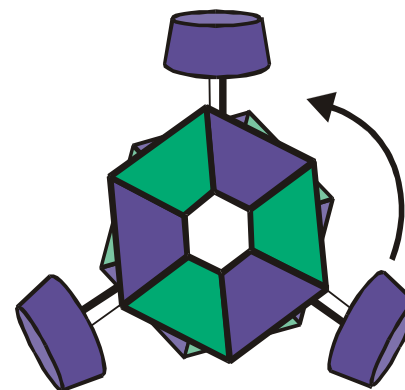




# Supramolecular chirality of the assembly

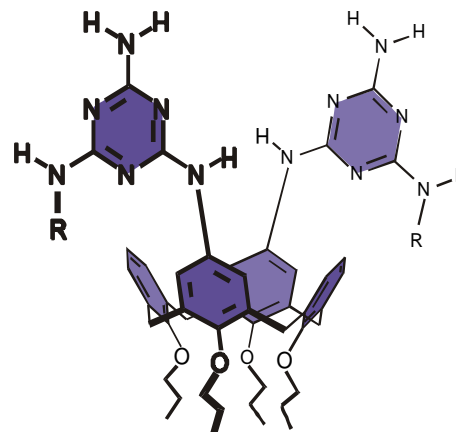
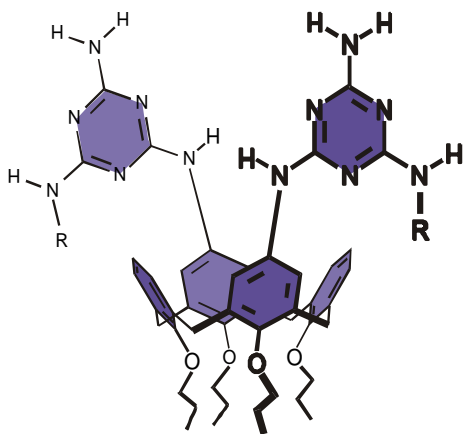


*mirror*



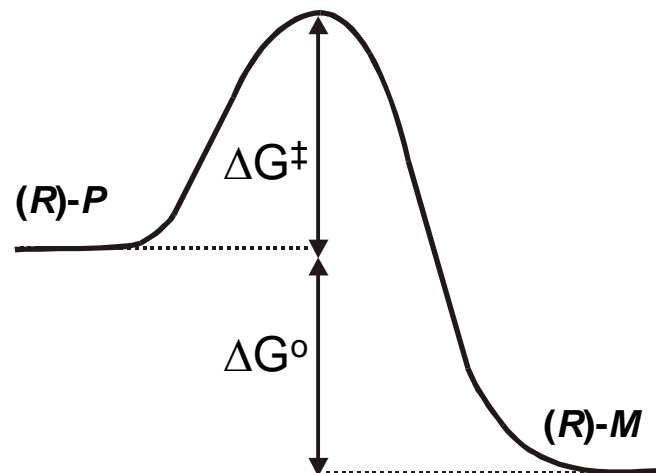
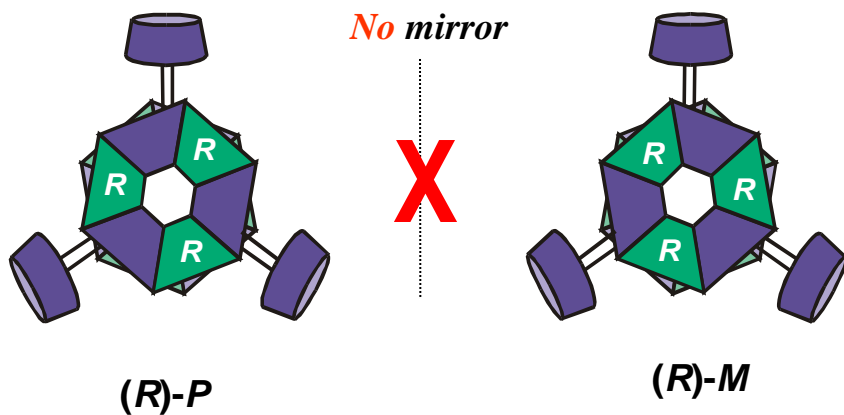
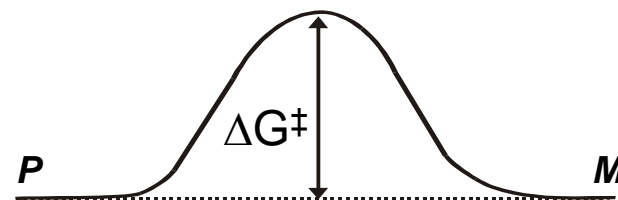
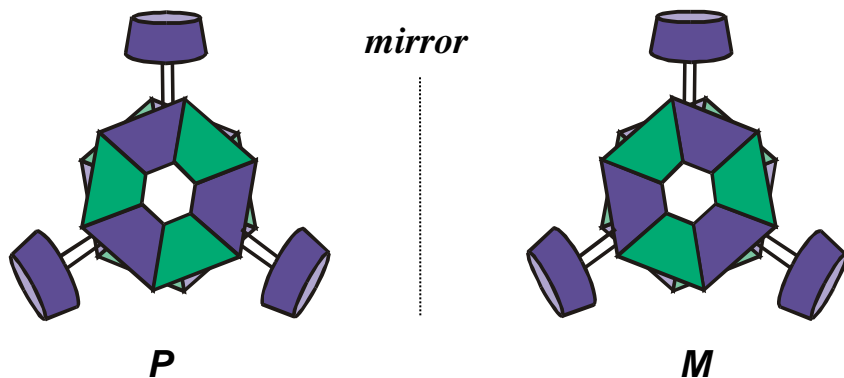
**(P)-D<sub>3</sub>**

**(M)-D<sub>3</sub>**



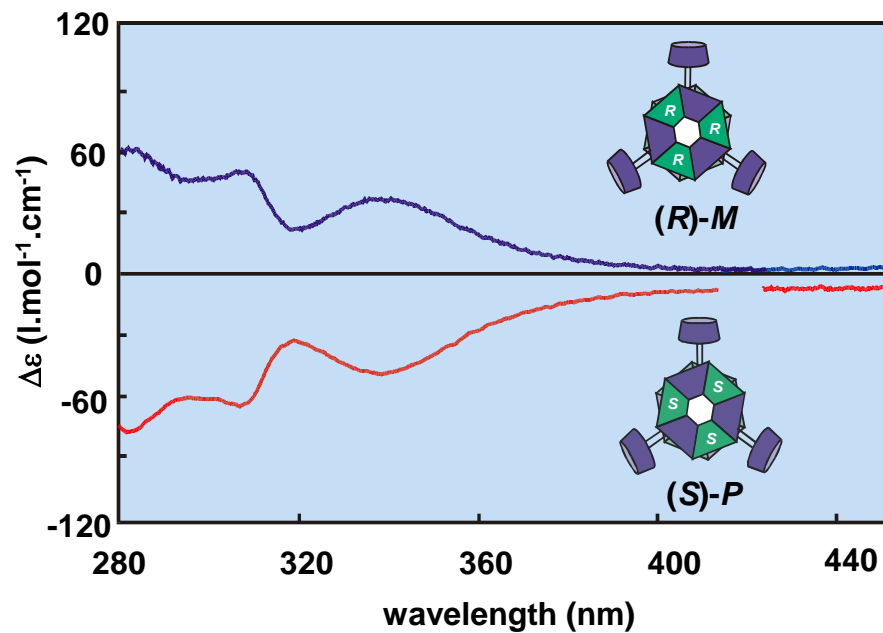
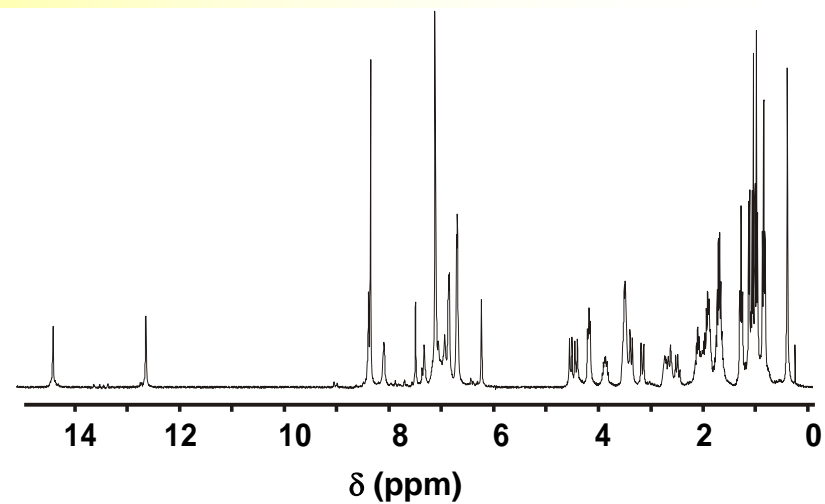
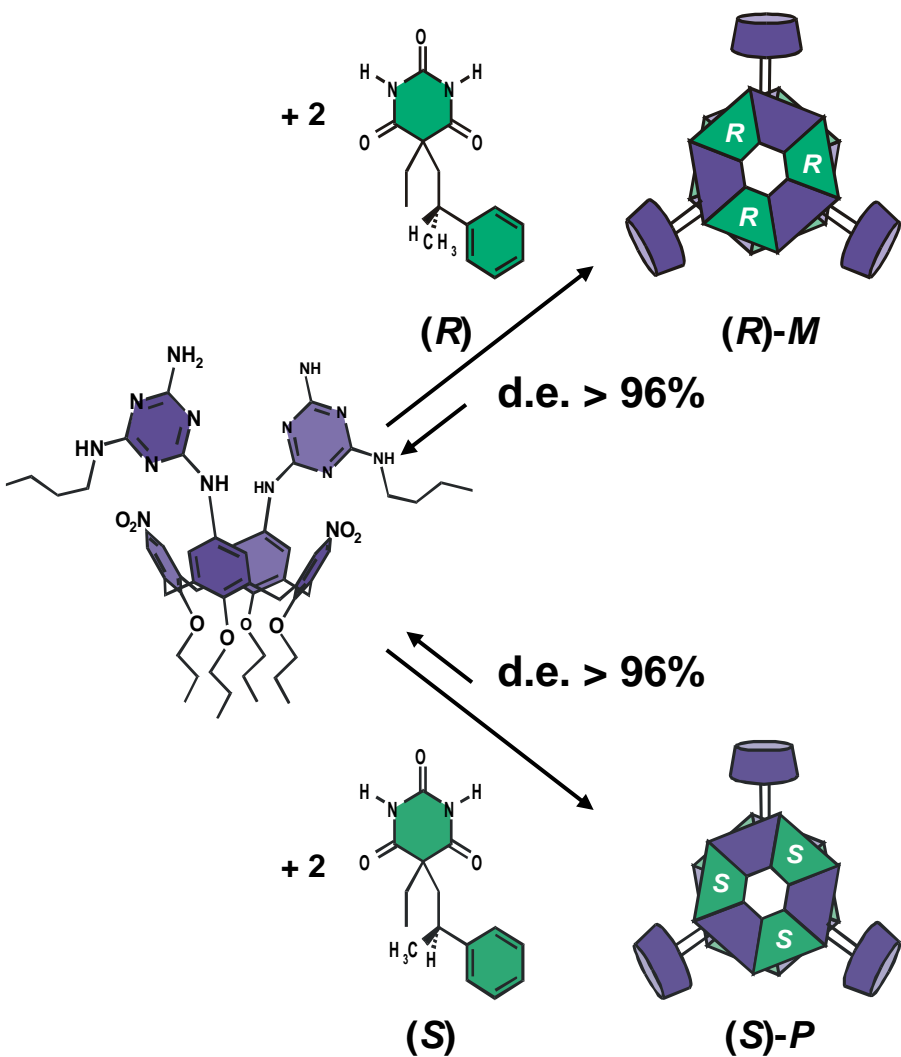


# Enantiomers vs diastereomers



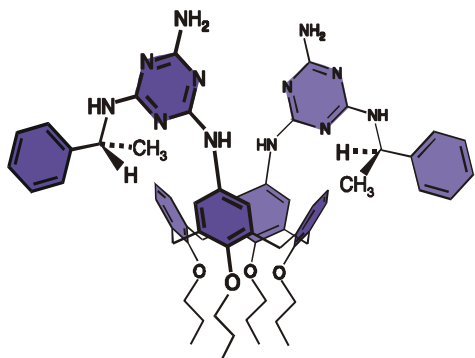


# Diastereoselective synthesis

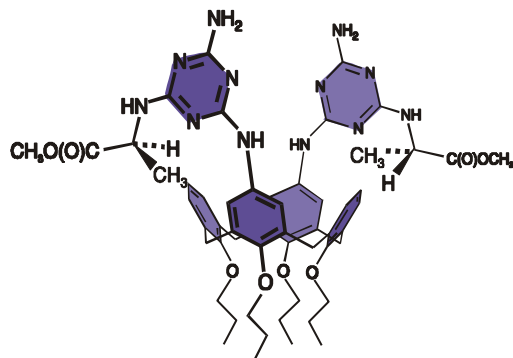




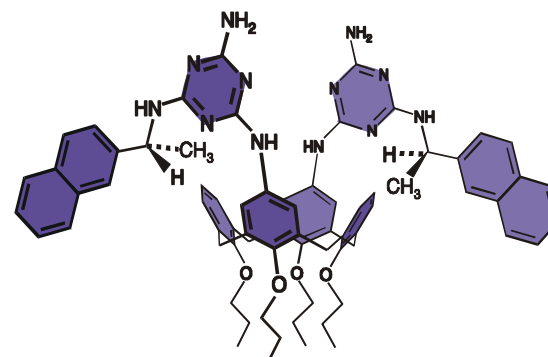
# Quantitative induction is a general phenomenon



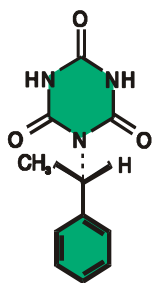
**(S,S)-(MePh)<sub>2</sub>**



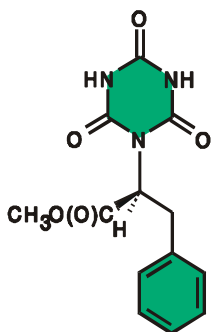
**(S,S)-(Ala)<sub>2</sub>**



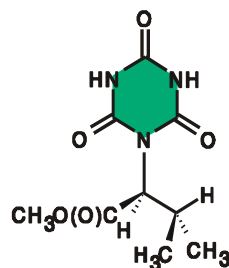
**(S,S)-(MeNap)<sub>2</sub>**



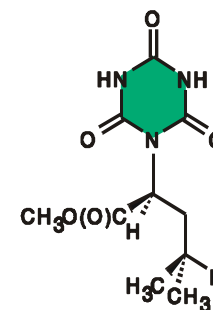
**(S)-MePhCYA**



**(S)-PheCYA**



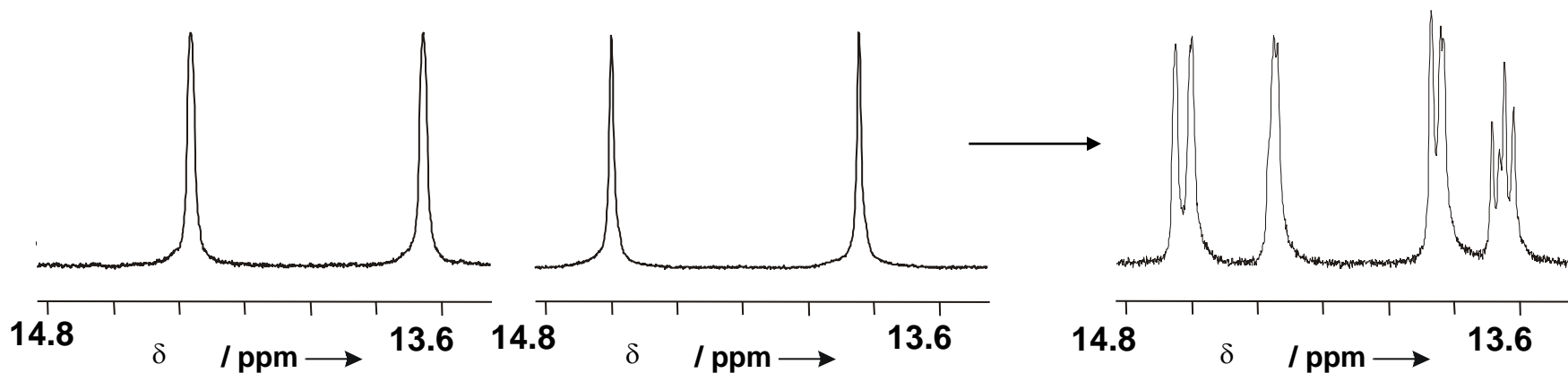
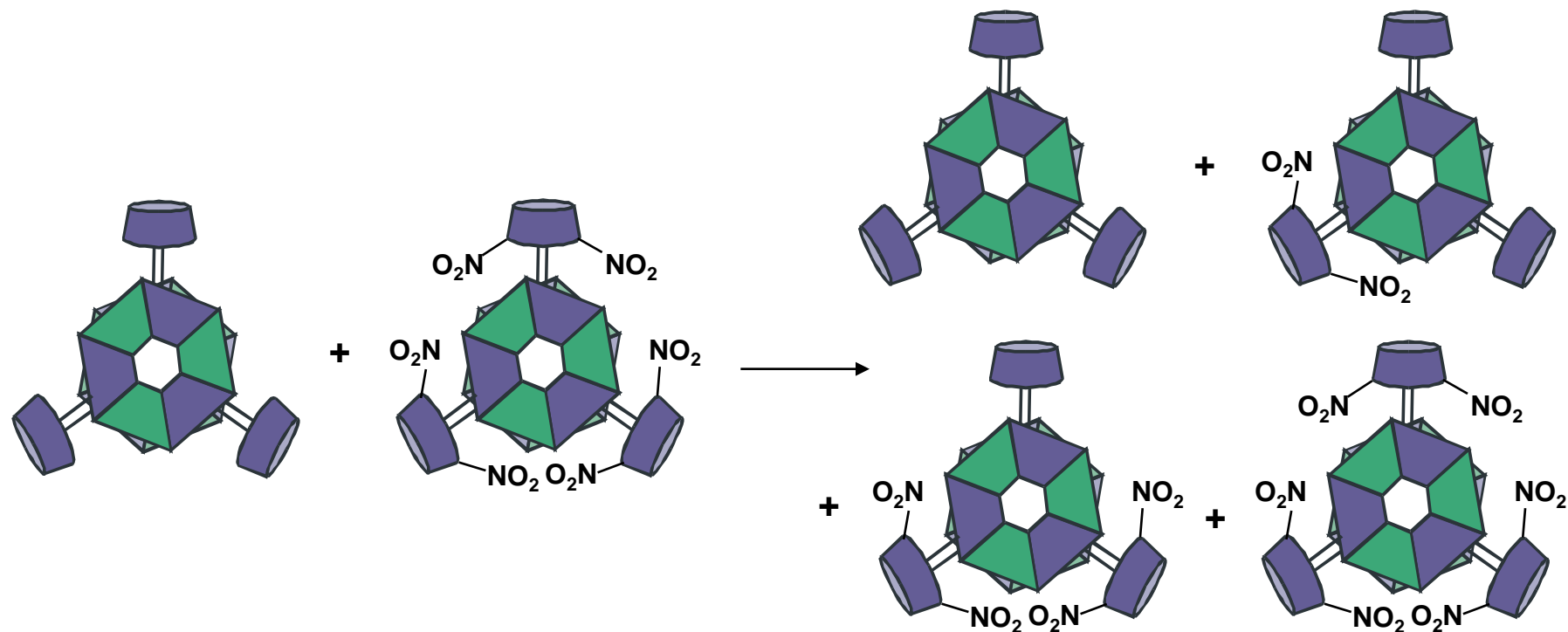
**(S)-ValCYA**



**(S)-LeuCYA**

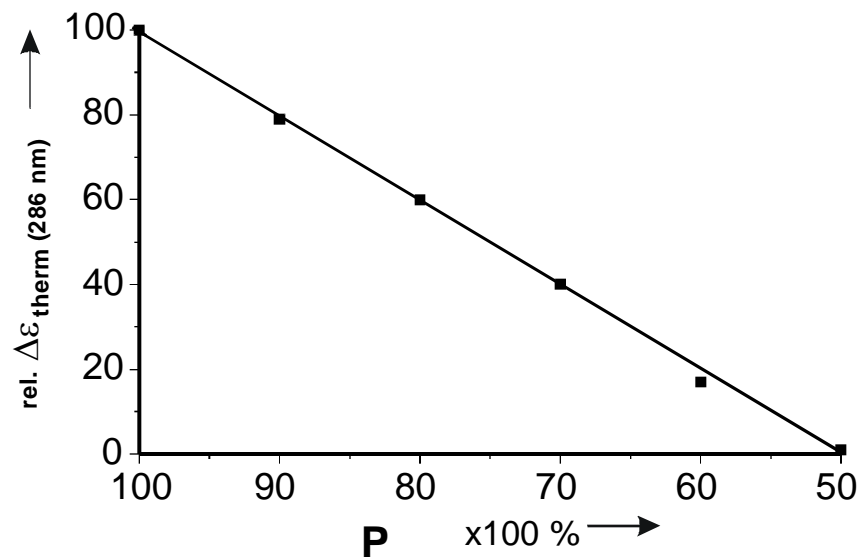
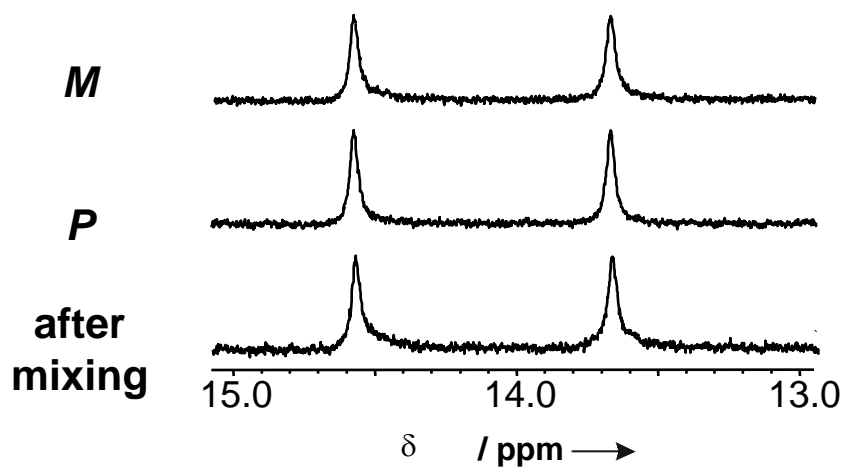
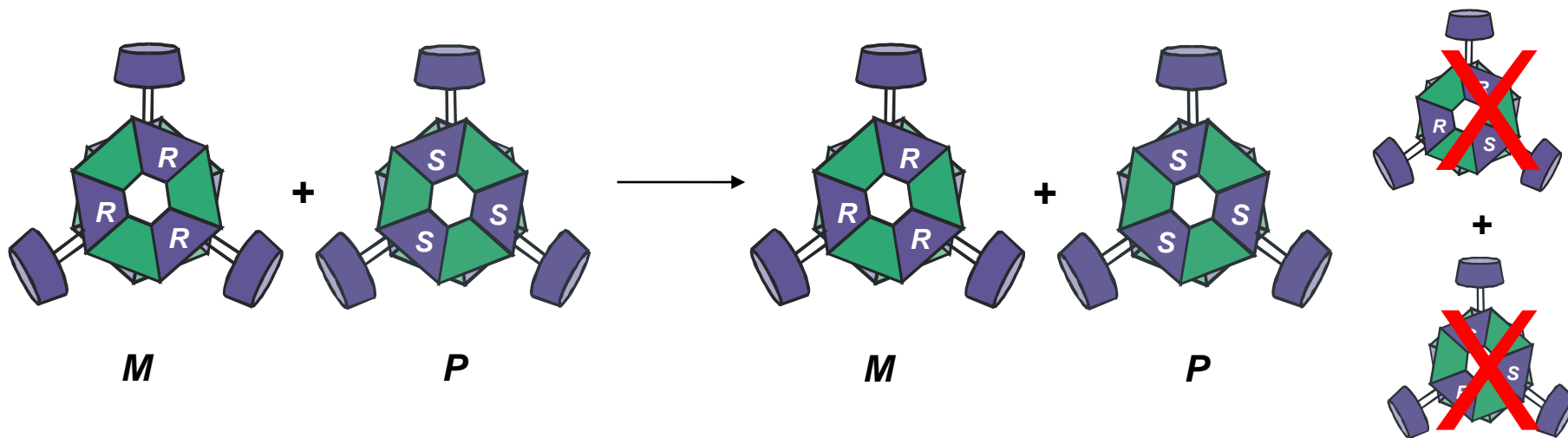


# Dynamic assemblies



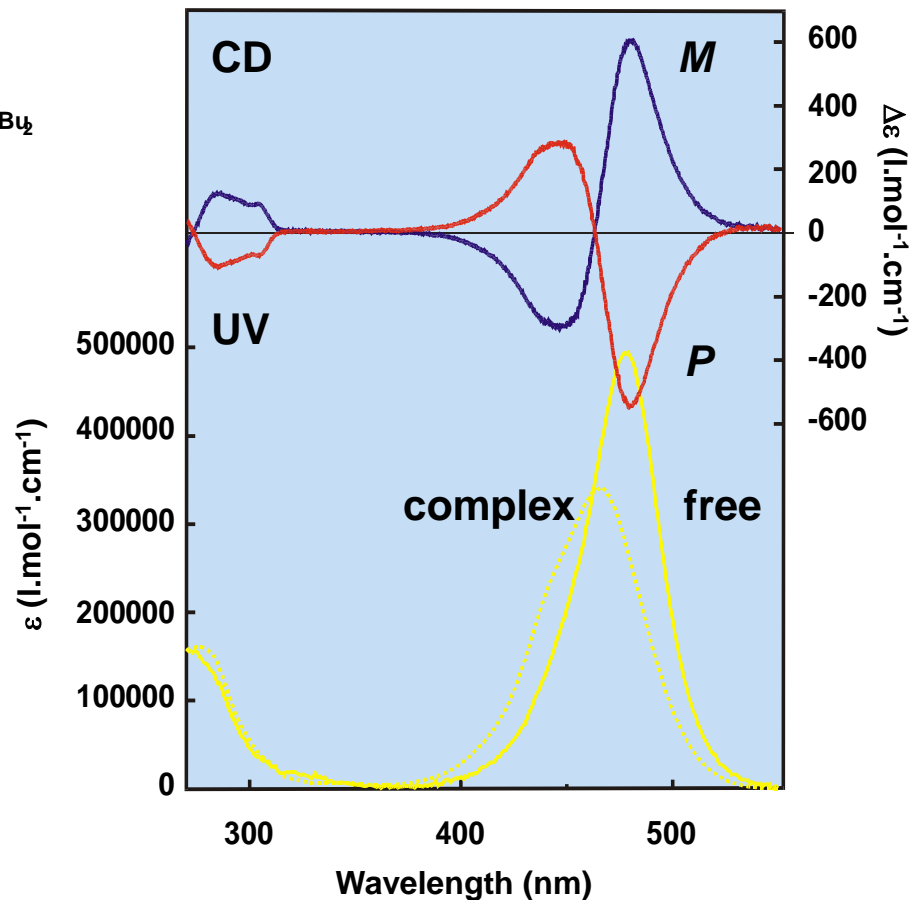
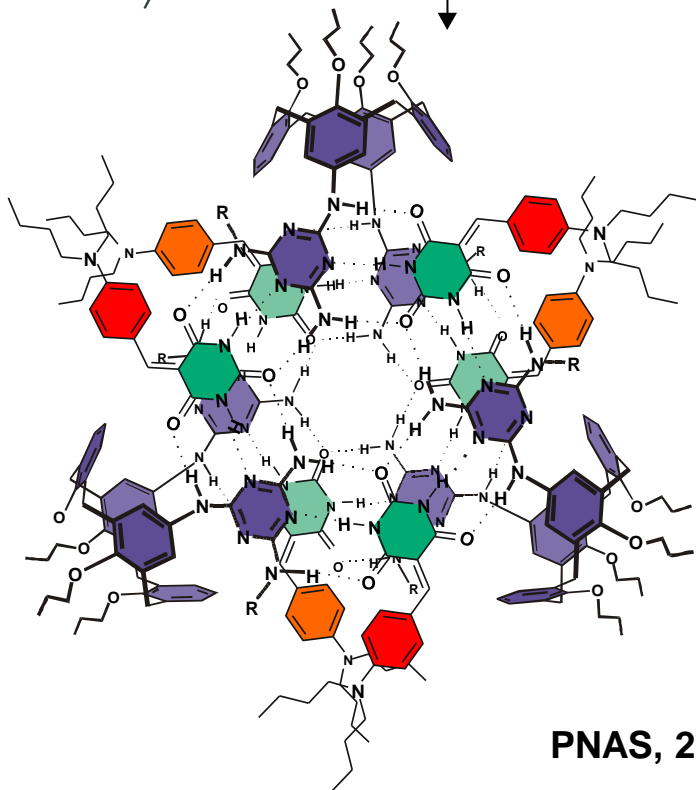
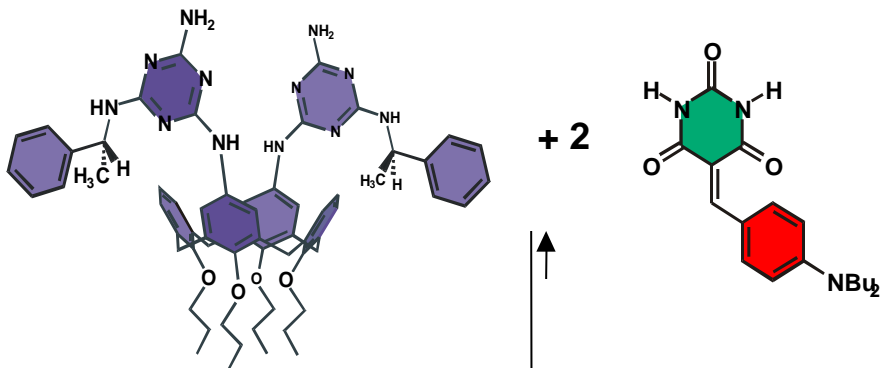


# Enantioselective self-resolution



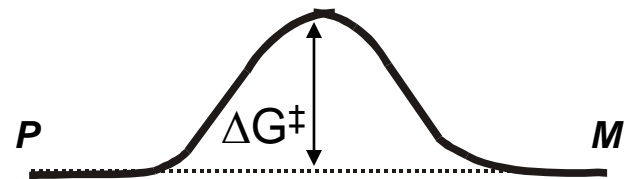
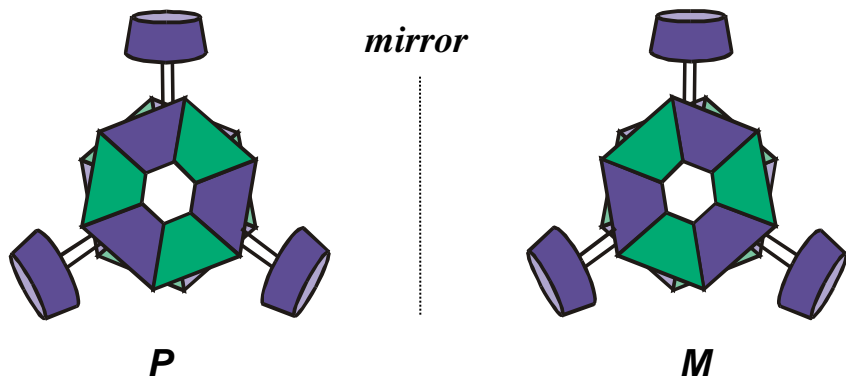
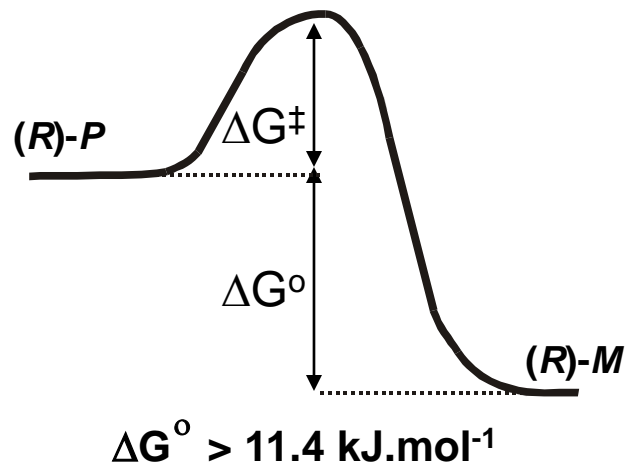
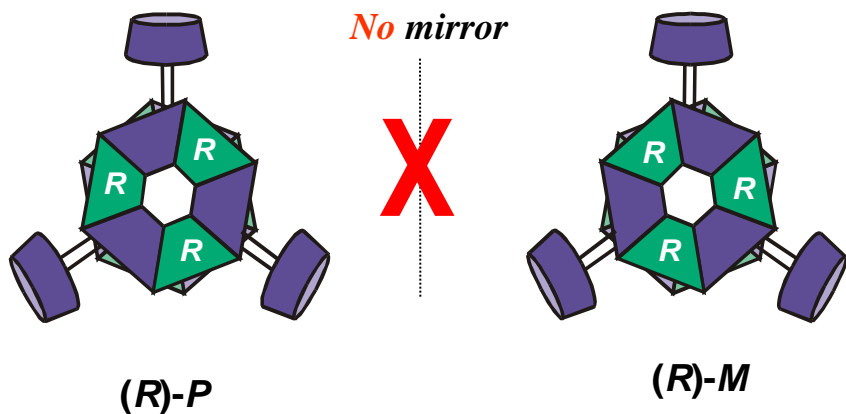


# Functions in a chiral environment



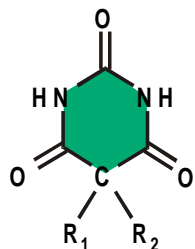


# Diastereomers vs enantiomers

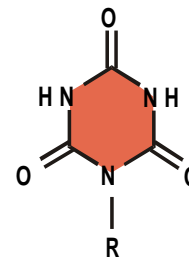




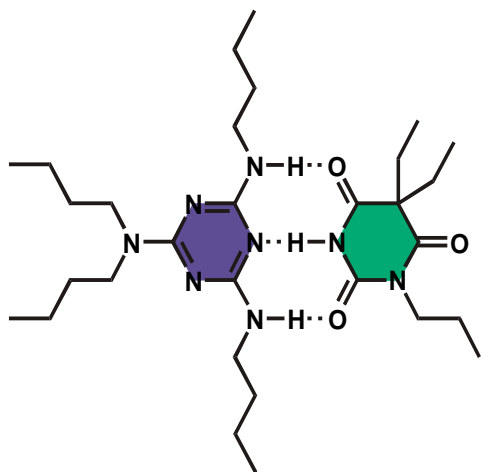
# Binding strength of barbiturates and cyanurates



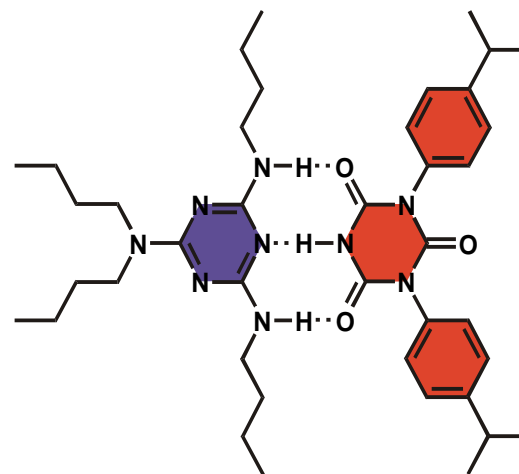
Barbiturates



Cyanurates



$$K_{\text{ass}} = 100 \pm 10 \text{ M}^{-1}$$

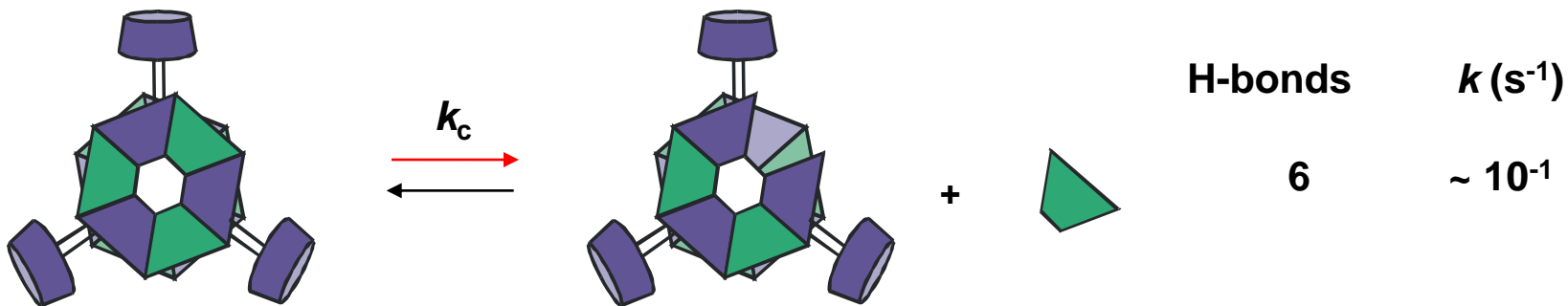


$$K_{\text{ass}} = 2200 \pm 800 \text{ M}^{-1}$$

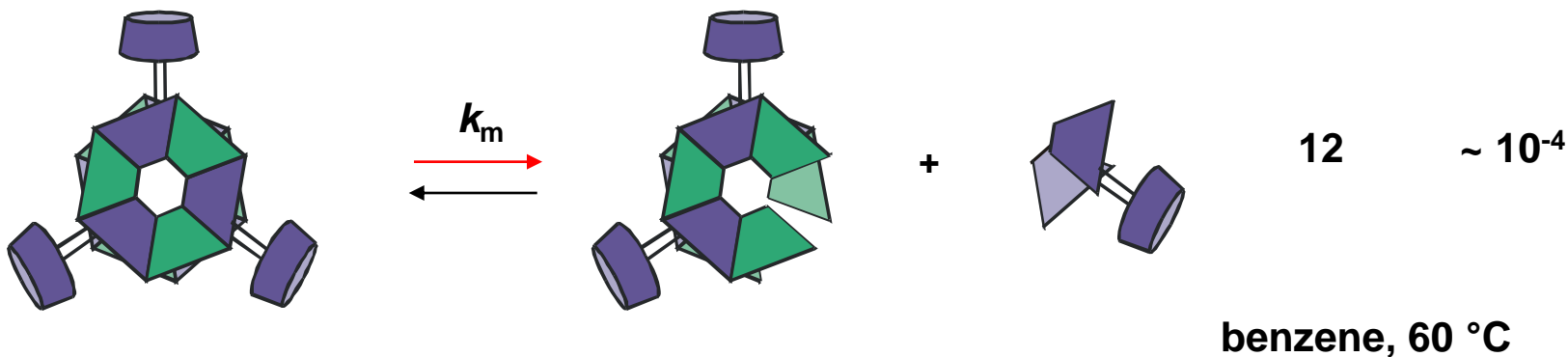


# Exchange rates in double rosette assemblies

## dissociation barbiturates/cyanurates:

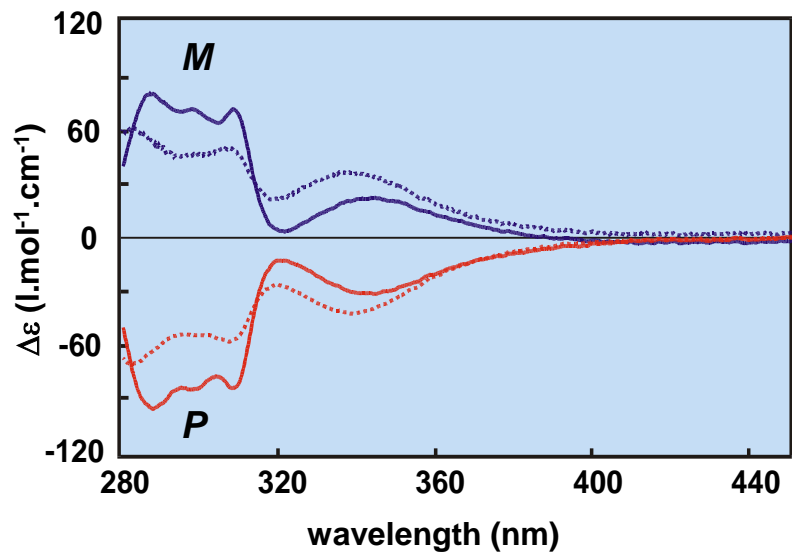
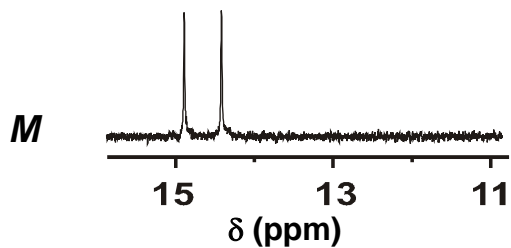
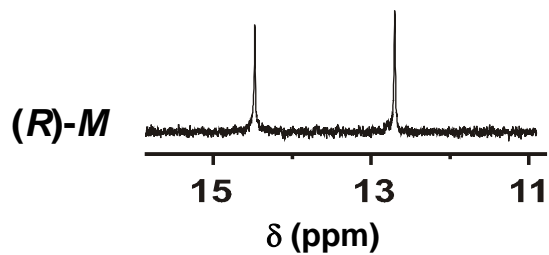
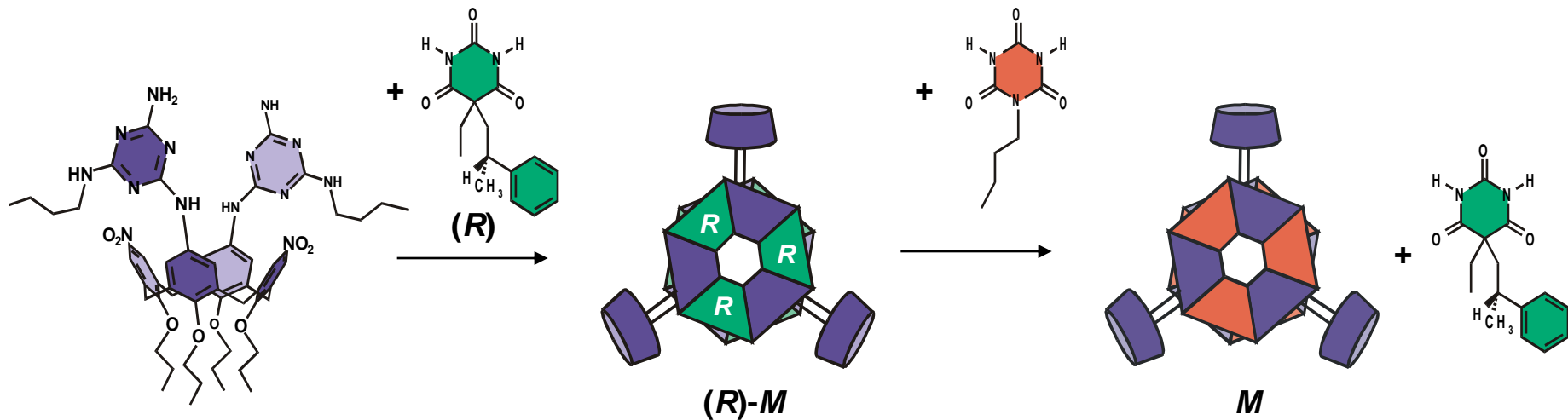


## dissociation dimelamines:



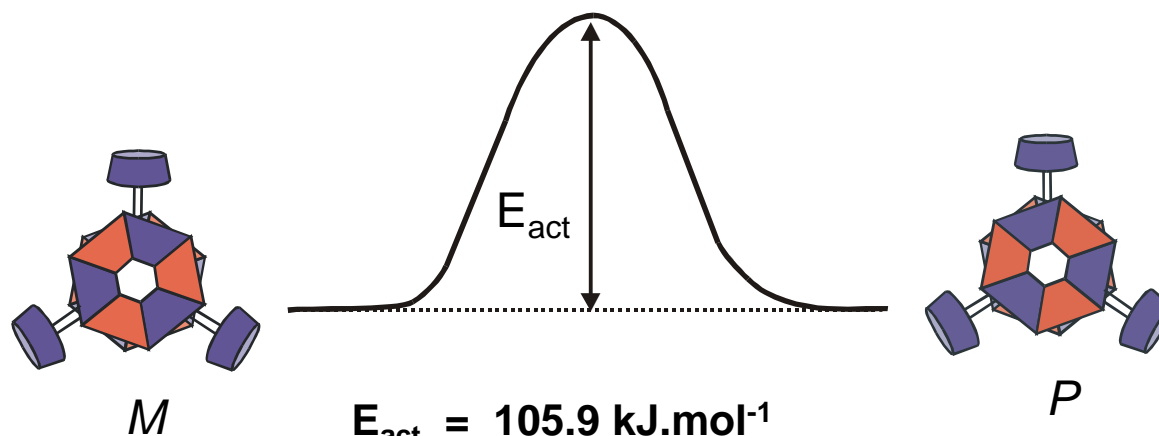
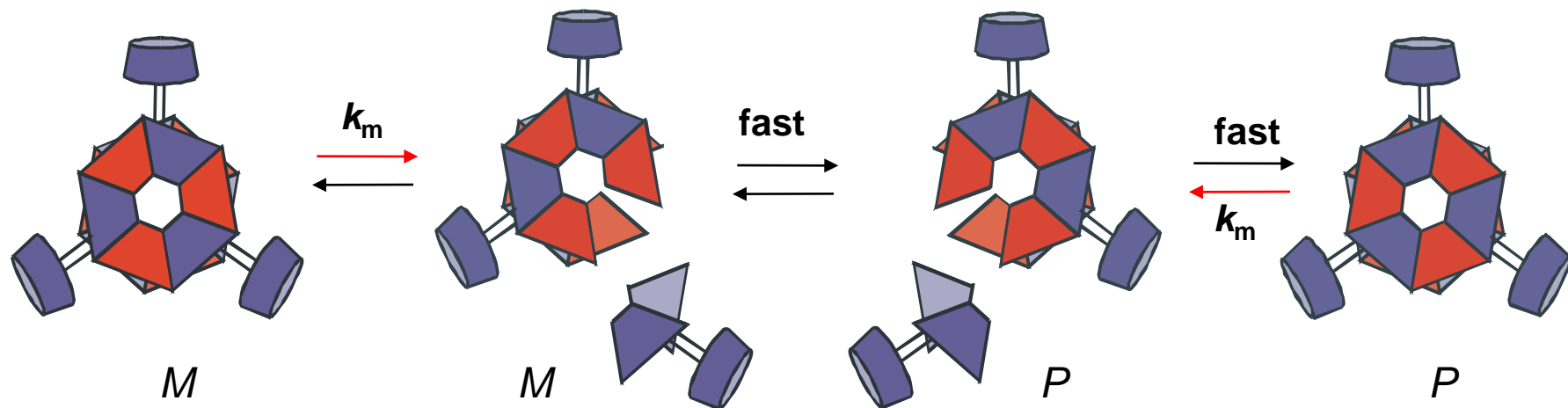


# Enantioselective synthesis





# Racemisation mechanism

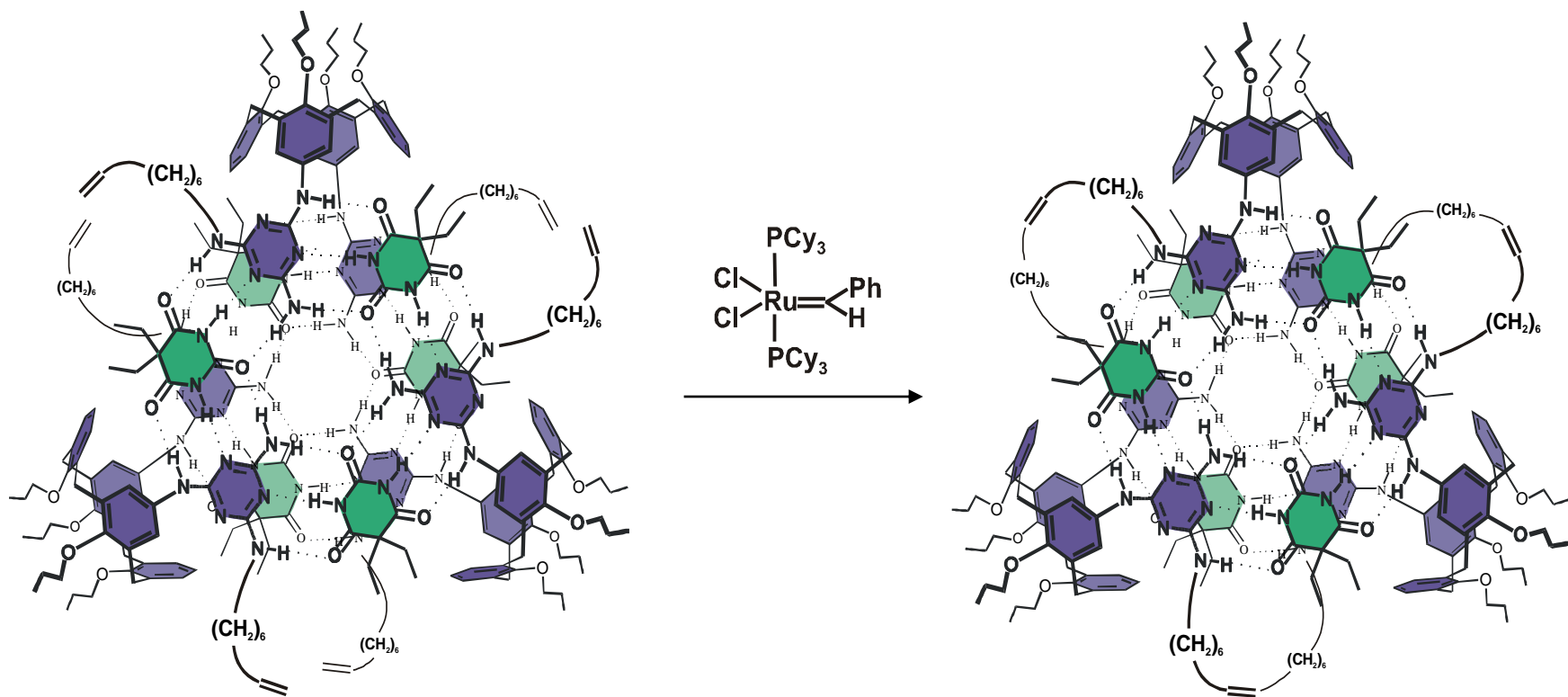


$$E_{act} = 105.9 \text{ kJ.mol}^{-1}$$

$$t_{1/2} \sim 4.5 \text{ days (18 } ^\circ\text{C, benzene)}$$

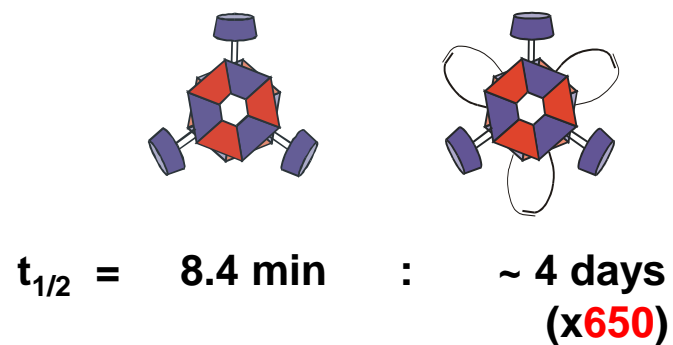
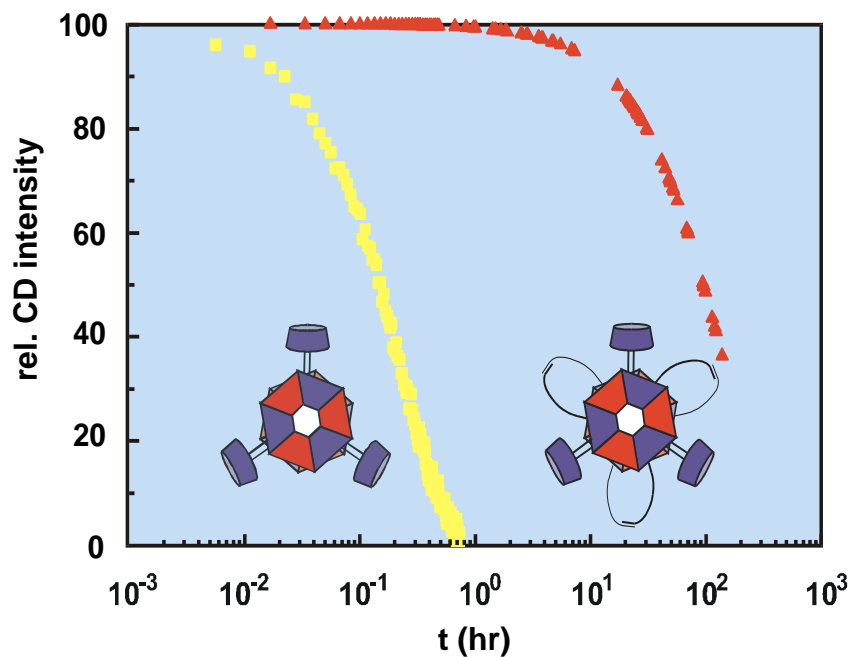
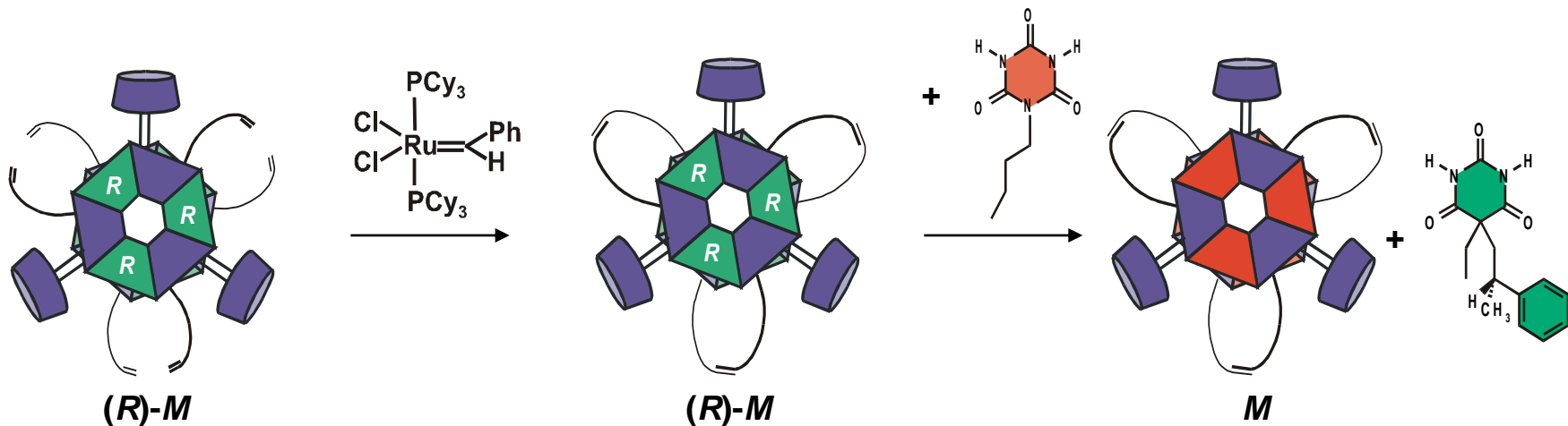


# Covalent postmodification





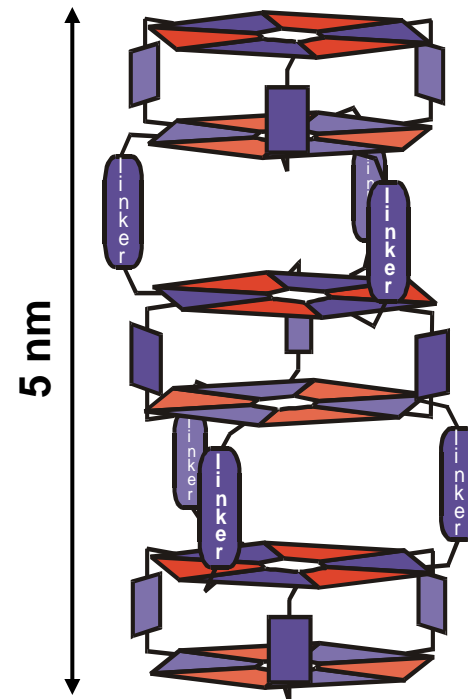
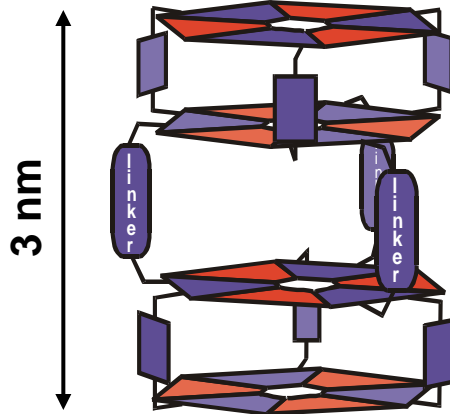
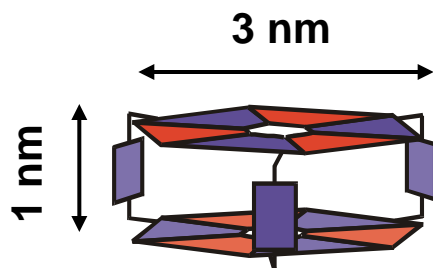
# Influence on the racemisation rate



chloroform, 50 °C



# Tetra- and hexarosette assemblies



*components*

9

15

21

*H-bonds*

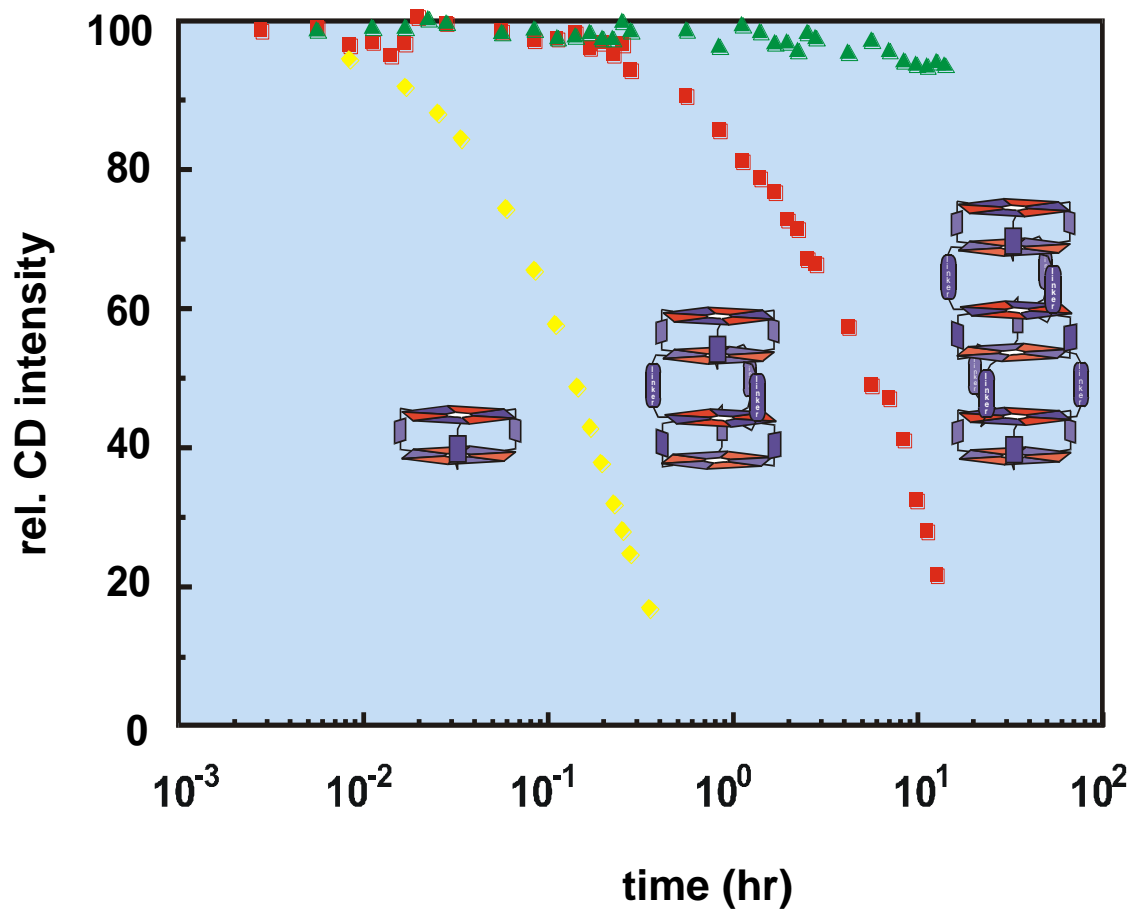
36

72

108



# Racemisation rates



$t_{1/2} = 8.4 \text{ min} : 5.5 \text{ hr} : > 6 \text{ days}$   
(x40) **x1100**

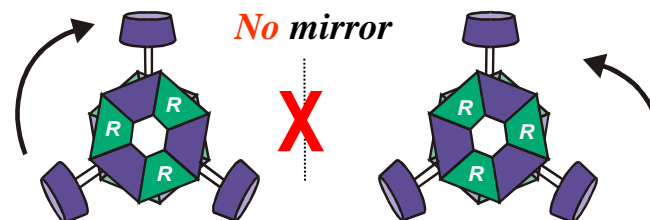
chloroform, 50 °C



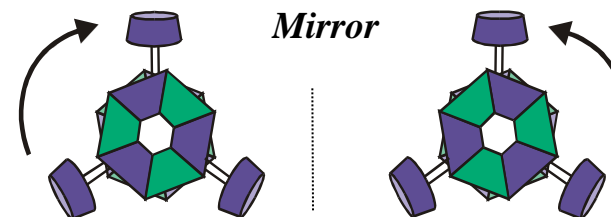
# Outline

Introduction of noncovalent synthesis

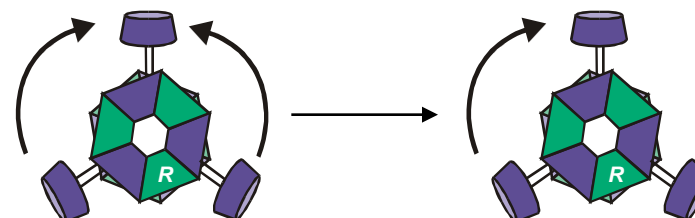
Diastereoselective synthesis



Enantioselective synthesis



**Amplification of chirality**

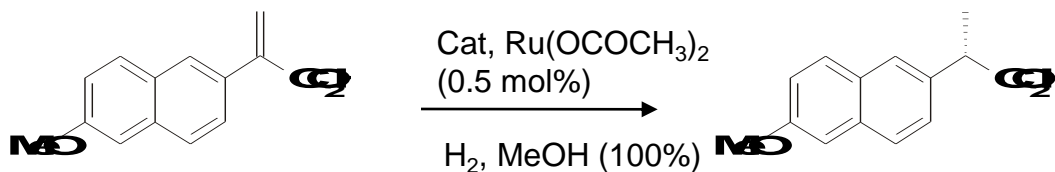




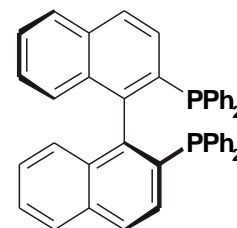
# Amplification of chirality

- Asymmetric catalysis

## Noyori asymmetric hydrogenation



Catalyst

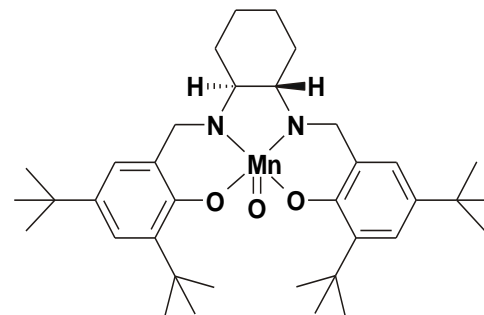
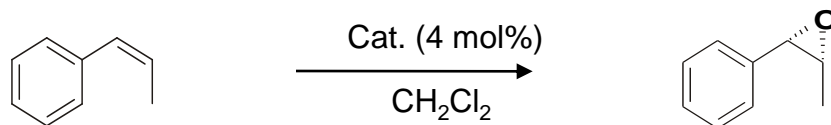


yield (%) e.e.(%)

92

97

## Jacobsen asymmetric epoxidation



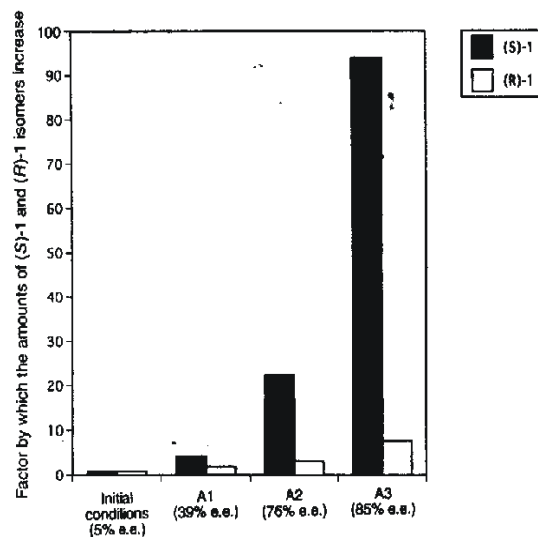
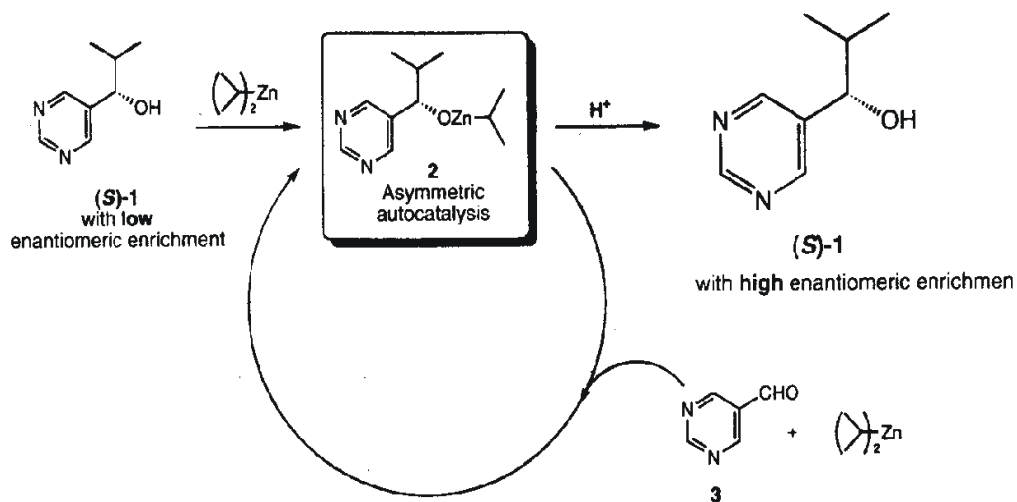
84

92



# Amplification of chirality

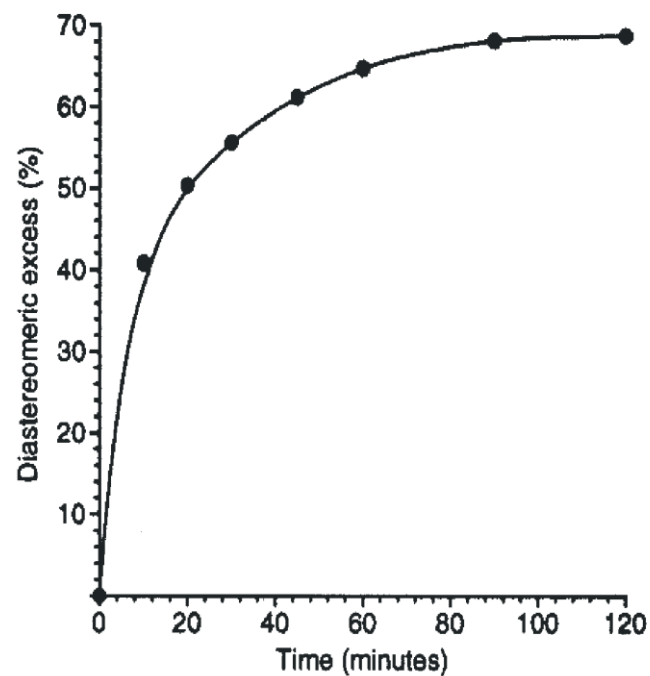
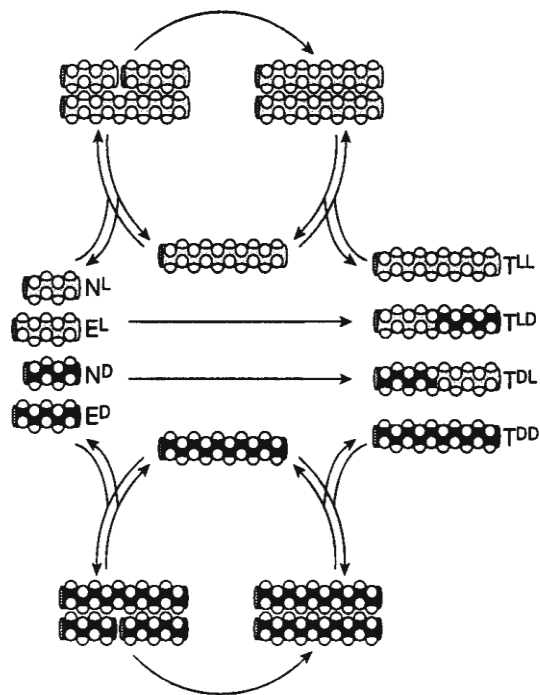
- Origin of homochirality



Soai *et al.* *Nature* 1995, 378, 767-768



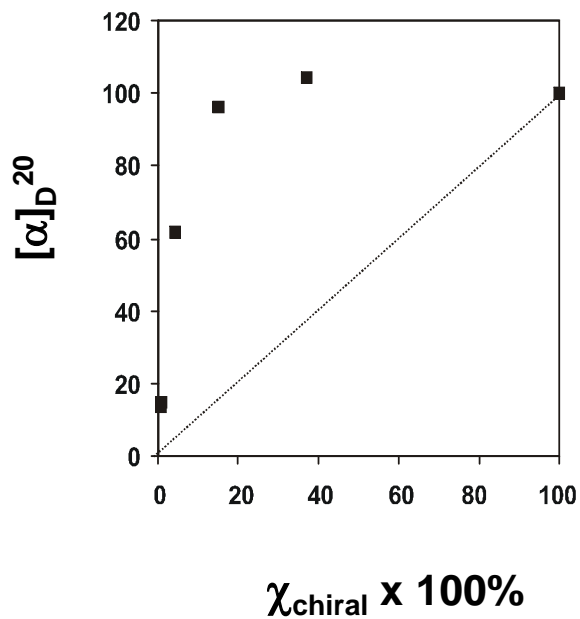
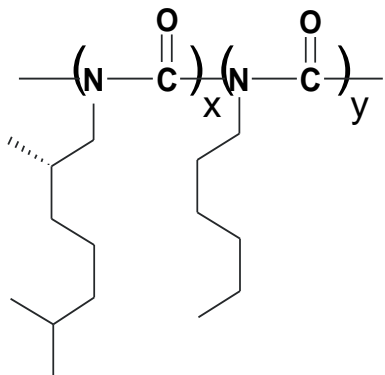
# A chiroselective peptide replicator



Ghadiri *et al.* *Nature* 2001, 398, 797-801



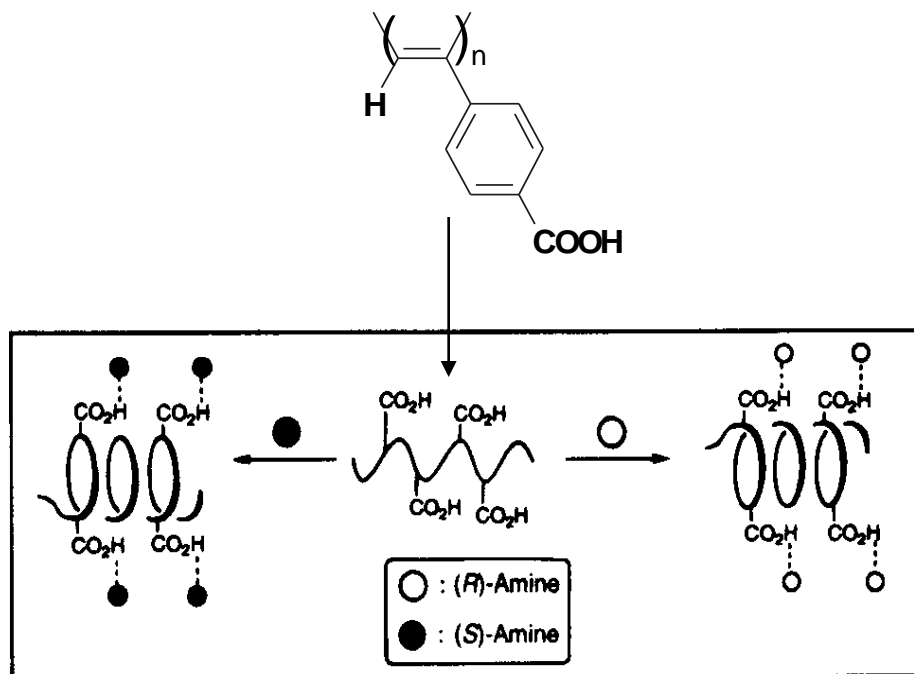
# Sergeants and Soldiers in polymers



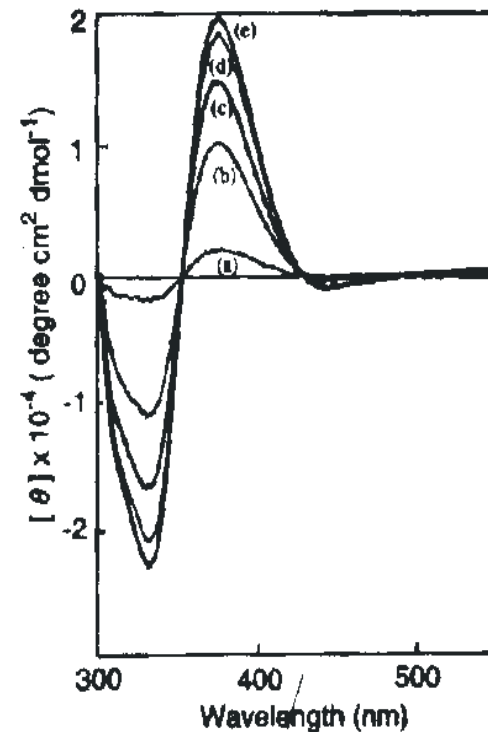
Green *et al.* *J.Am.Chem.Soc.* **1989**, 111, 6452-6453



# Application in non-covalent structures



Yashima *et al.* *J.Am.Chem.Soc.* **1997**, *119*, 6345-6359



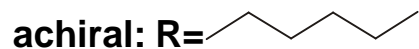
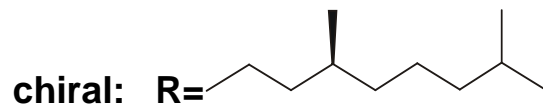
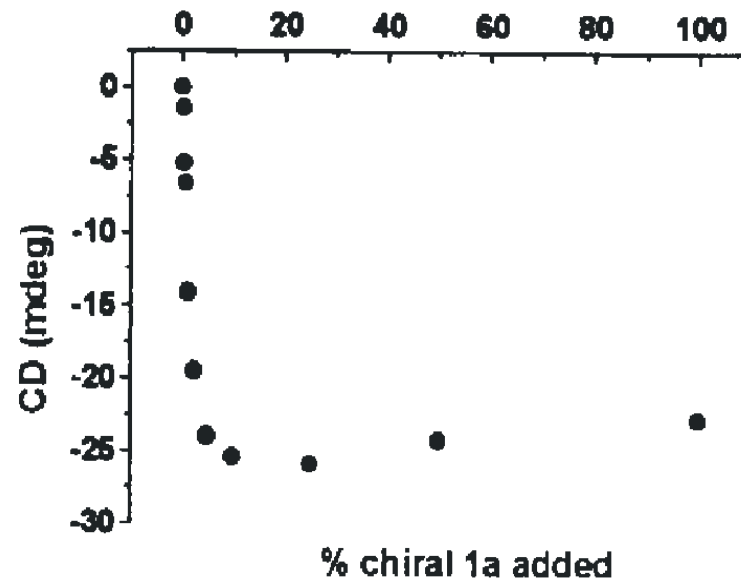
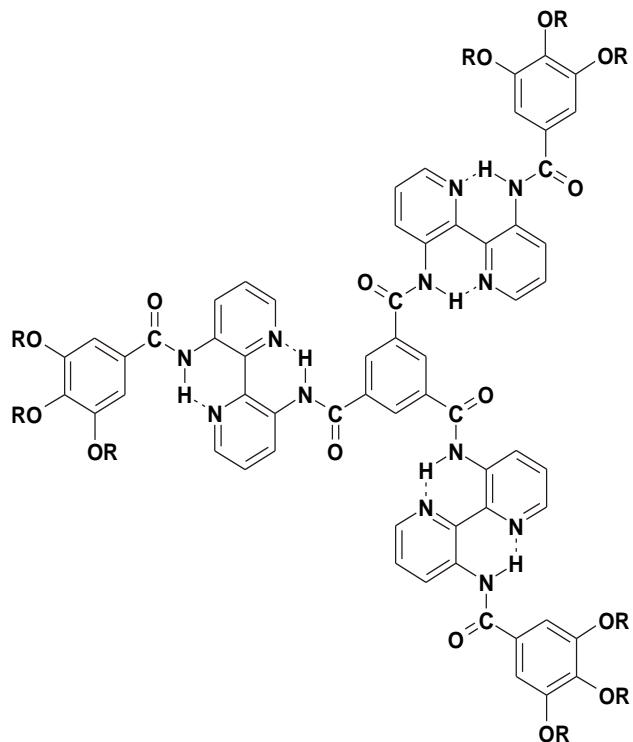
ratio polymer:chiral:achiral

a) 1 : 0.3 : 0

e) 1 : 0.3 : 5



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Meijer *et al.* *Angew.Chem.Int.Ed.Engl.* **1997**, *36*, 2648-2651



# Sergeants and Soldiers in rosette assemblies

