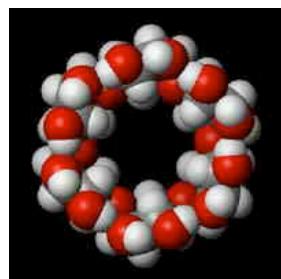
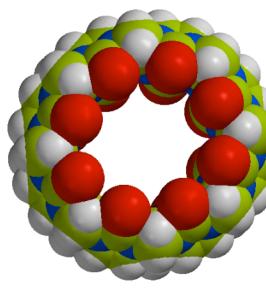


Supramolecular Photochemistry

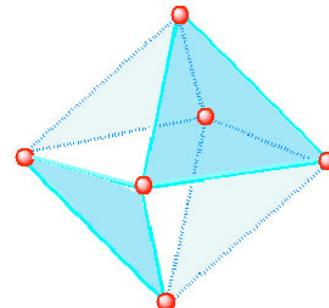
- Objective:** To conduct product selective photoreactions in water or in solid state
To alter the photophysical properties of molecules
- Problem:** Organic compounds generally are either poorly soluble or insoluble in water and not all molecules are crystalline.
- Solution:** Use water soluble hosts to solubilize organic molecules
Use confining hosts to achieve product selectivity
Use weak interactions to manipulate molecules



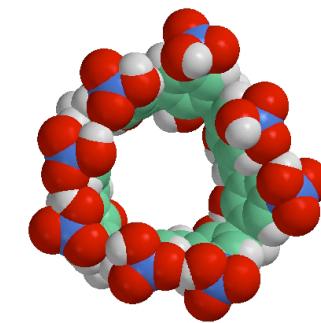
Cyclodextrins



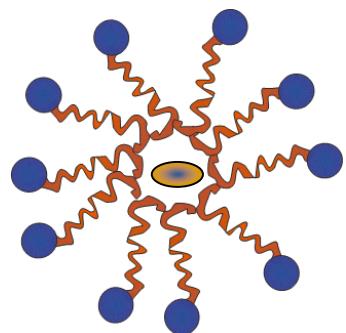
Cucurbiturils



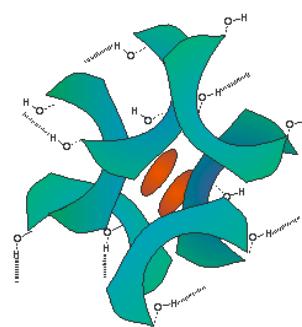
Pd Nano Cage



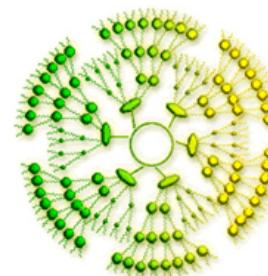
Calixarenes



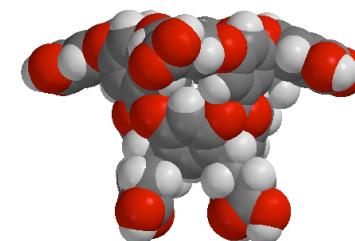
SDS / CTAC



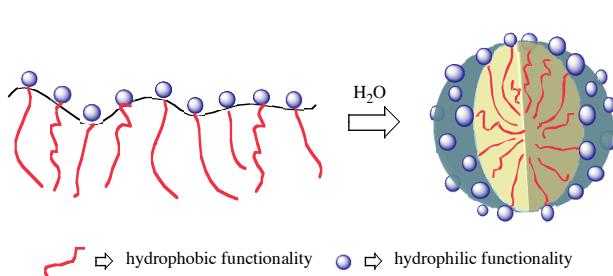
NaCh / NaDCh



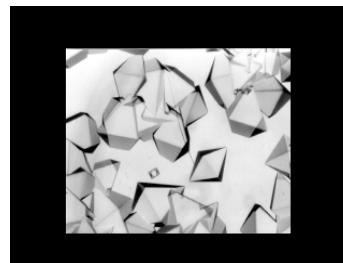
Dendrimers



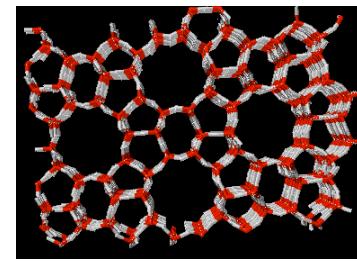
Octa acid



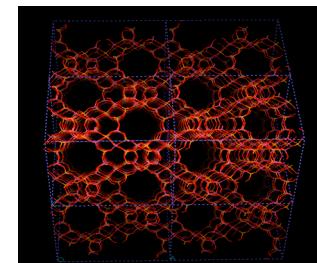
Water soluble polymer



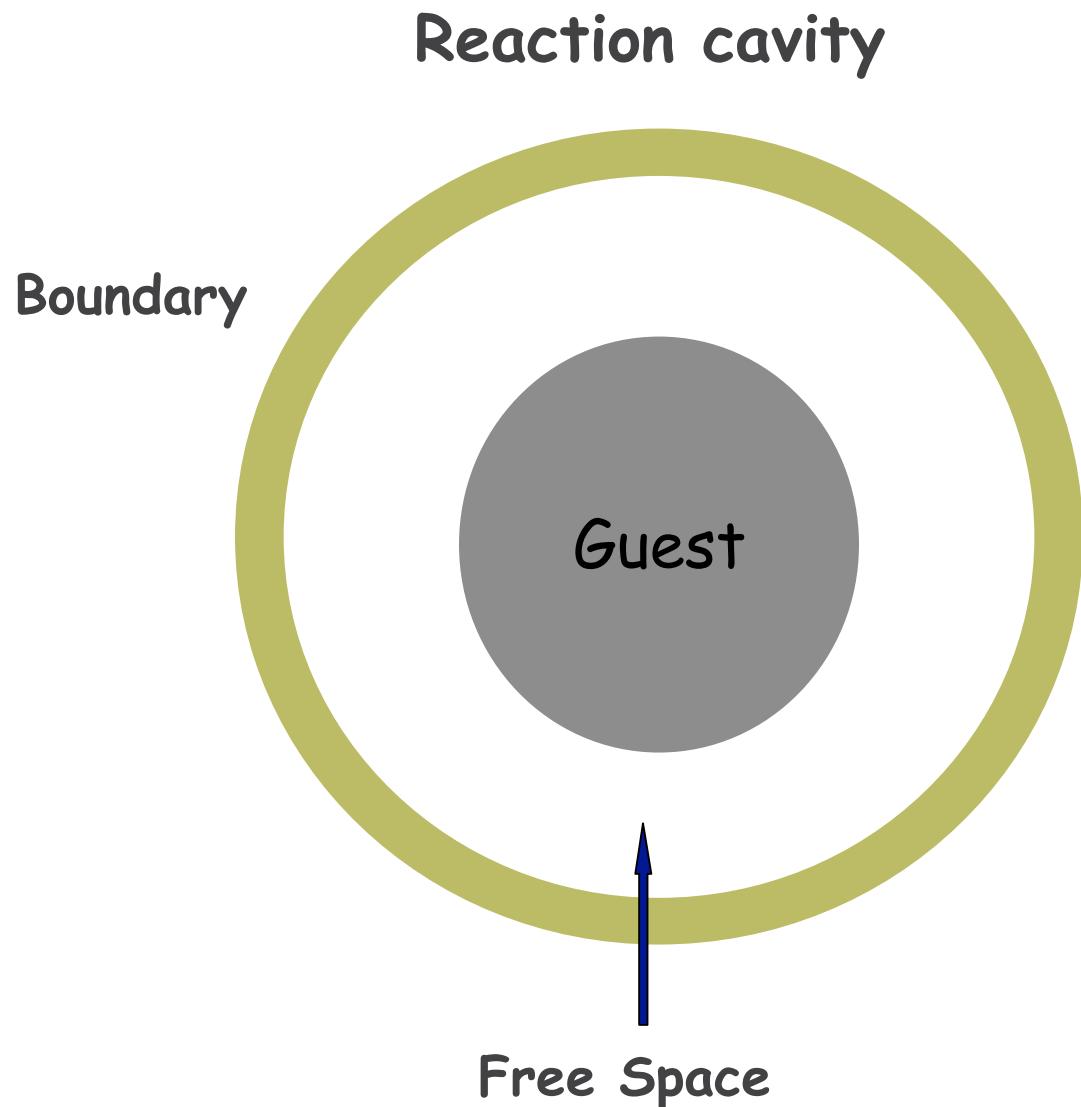
Crystals



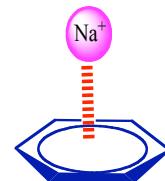
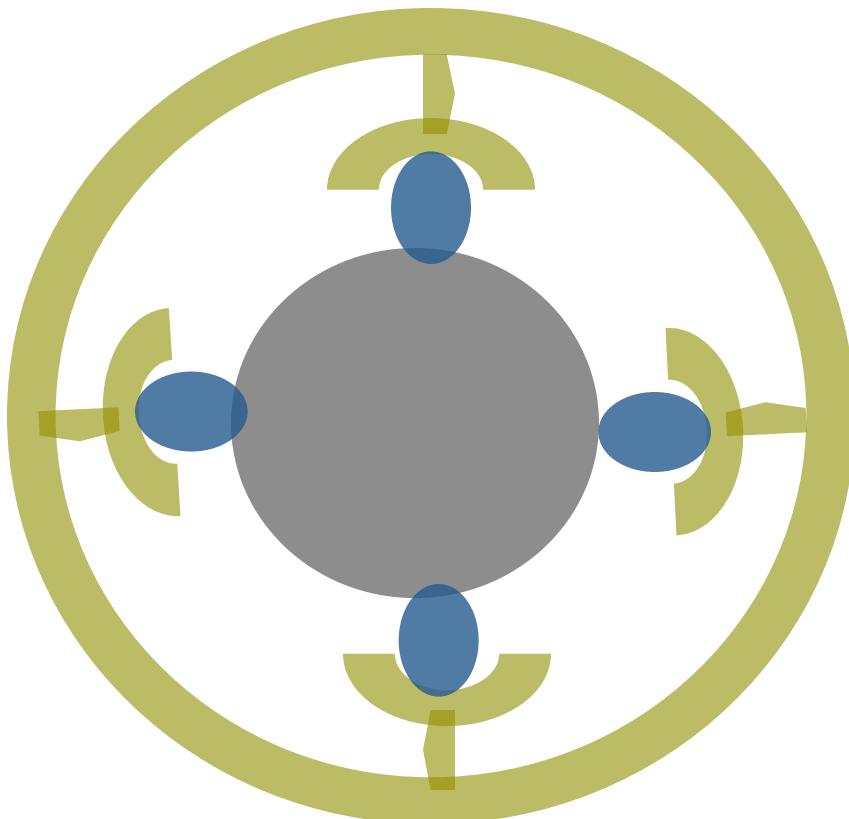
Zeolites



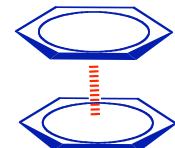
Supramolecular Containers



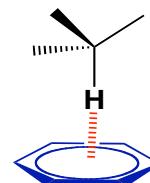
Role of Weak Interactions



Cation--- π



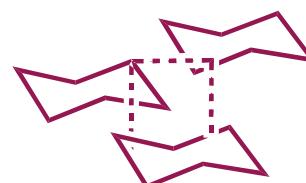
π --- π



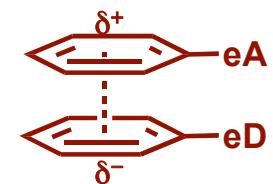
C-H--- π



Hydrogen bond



van der Waals

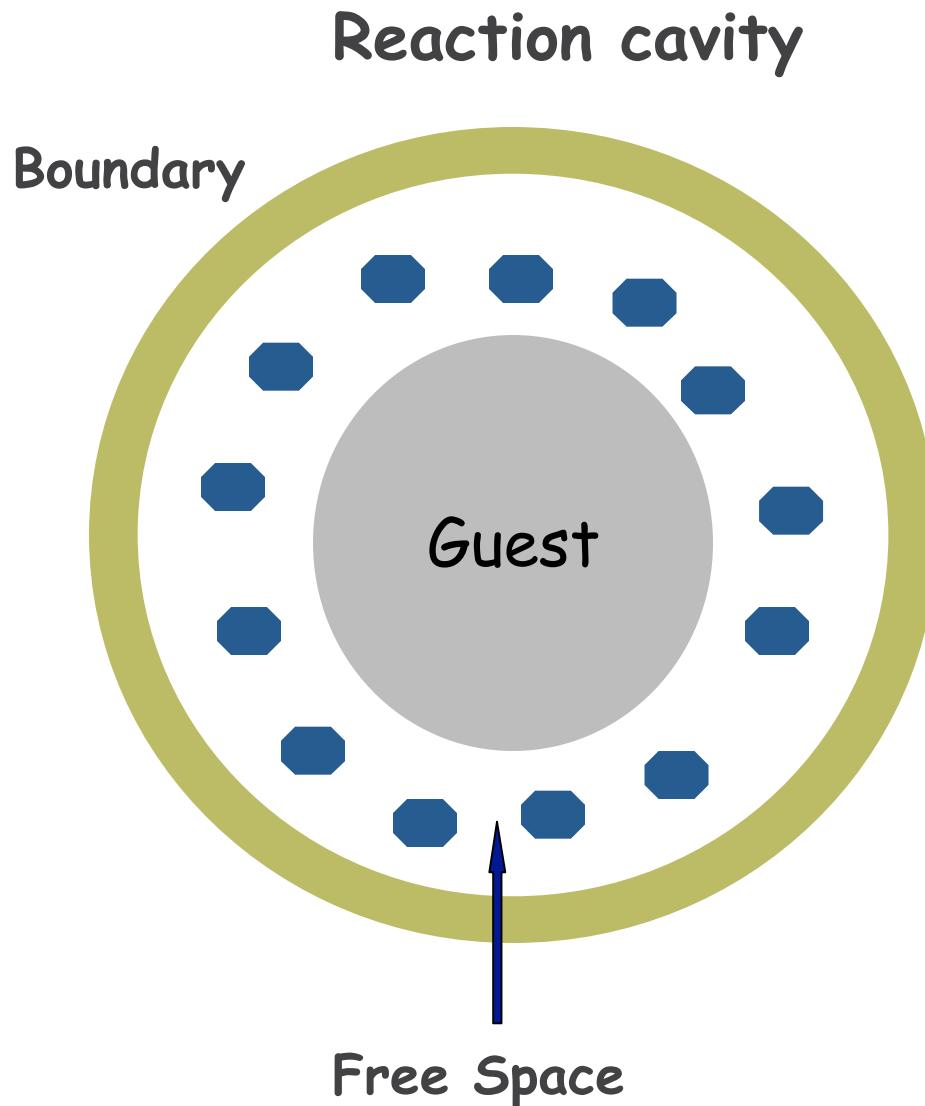


Charge transfer

Supramolecular Container Store



Supramolecular Containers

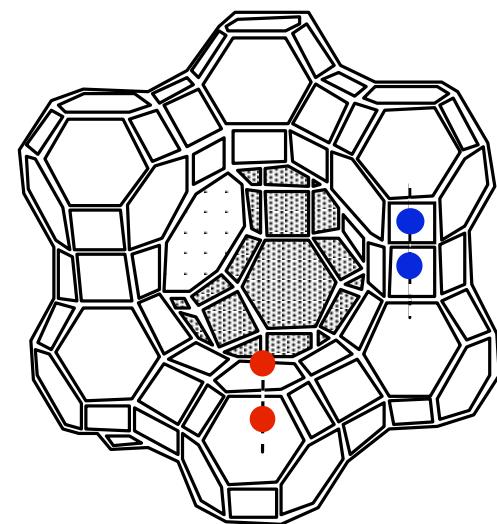
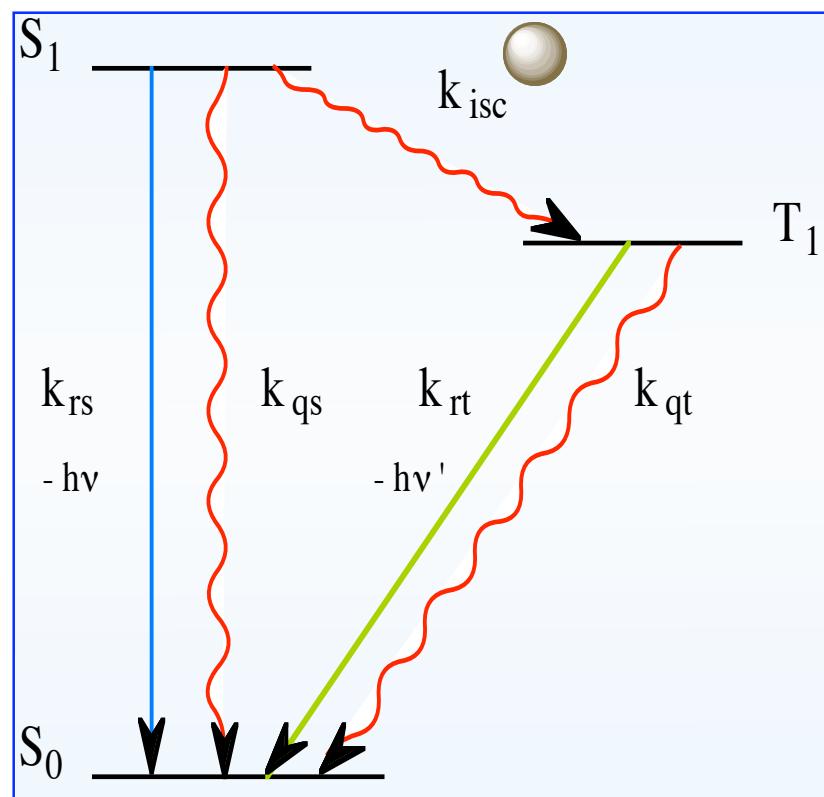


The Crow and the Pitcher



Controlling the free space

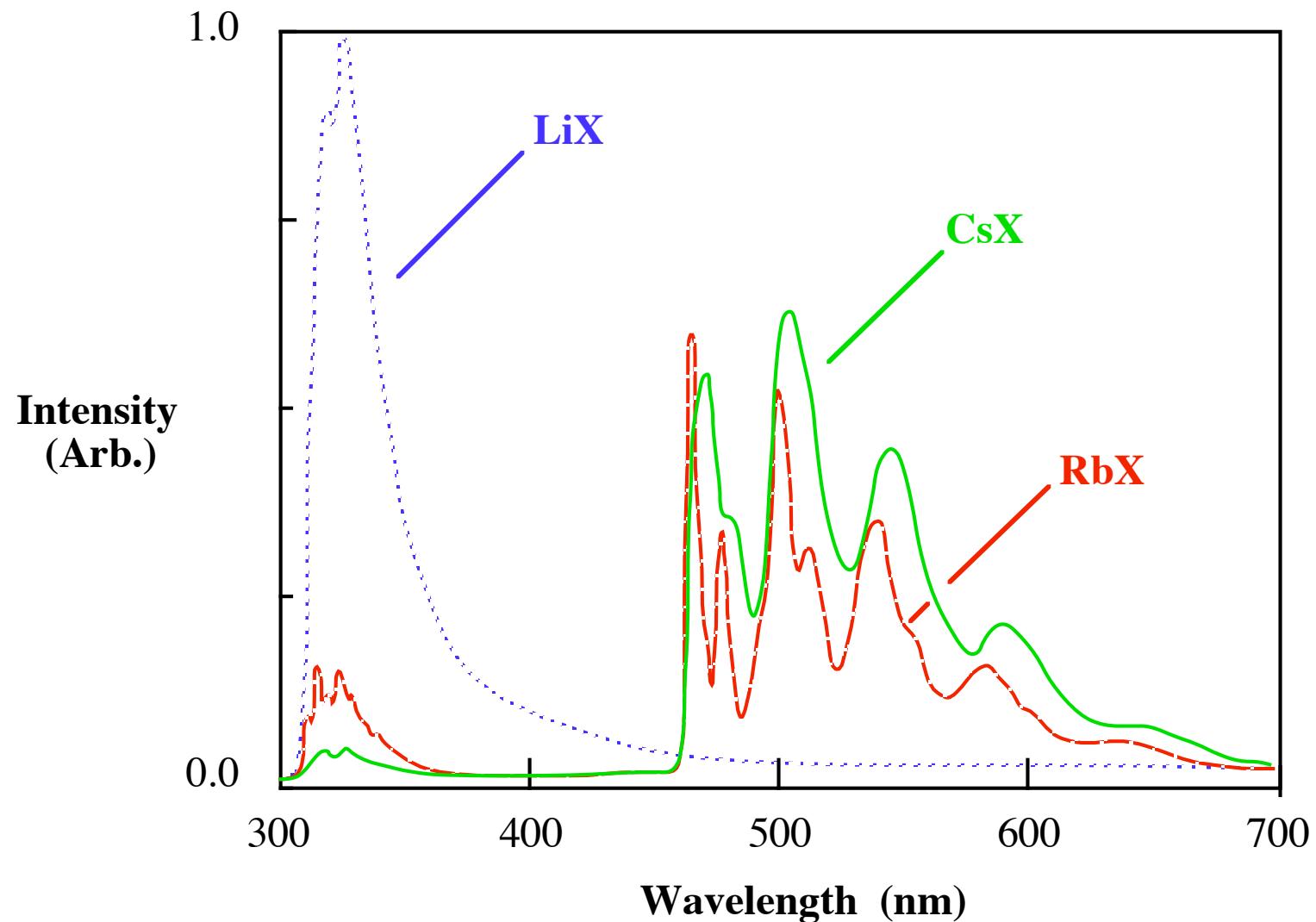
Heavy Cations Enhance S_1 to T_1 Crossing



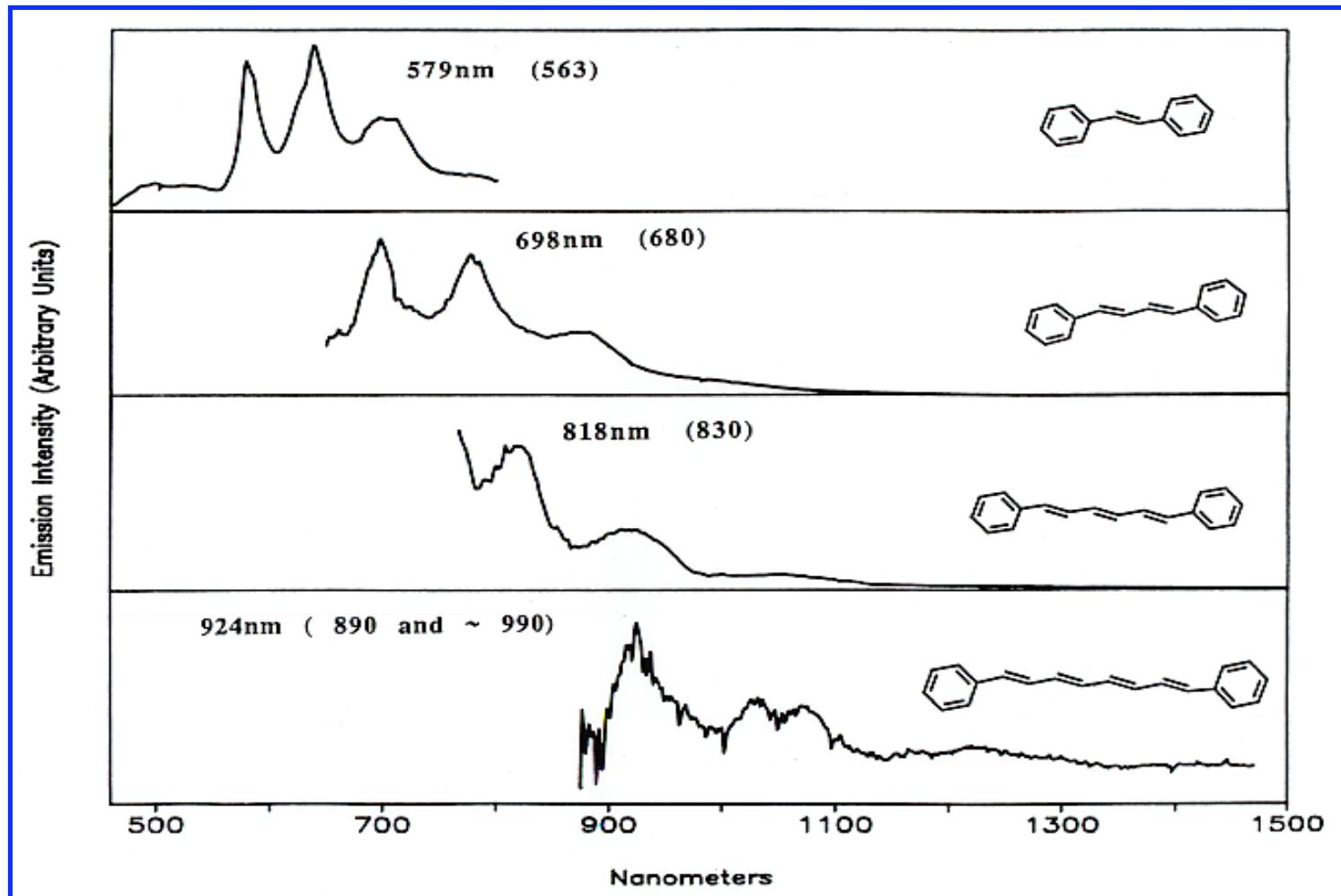
Induced Intersystem Crossing Depends on the SOC of the Alkali Ion

Atom	Ionic Radius of the Cation (Å)	Spin-Orbit Coupling ζ cm ⁻¹
Li	0.86 (+)	0.23
Na	1.12	11.5
K	1.44	38
Rb	1.58	160
Cs	1.84	370
Tl	1.40	3410
Pb	1.33 (2+)	5089

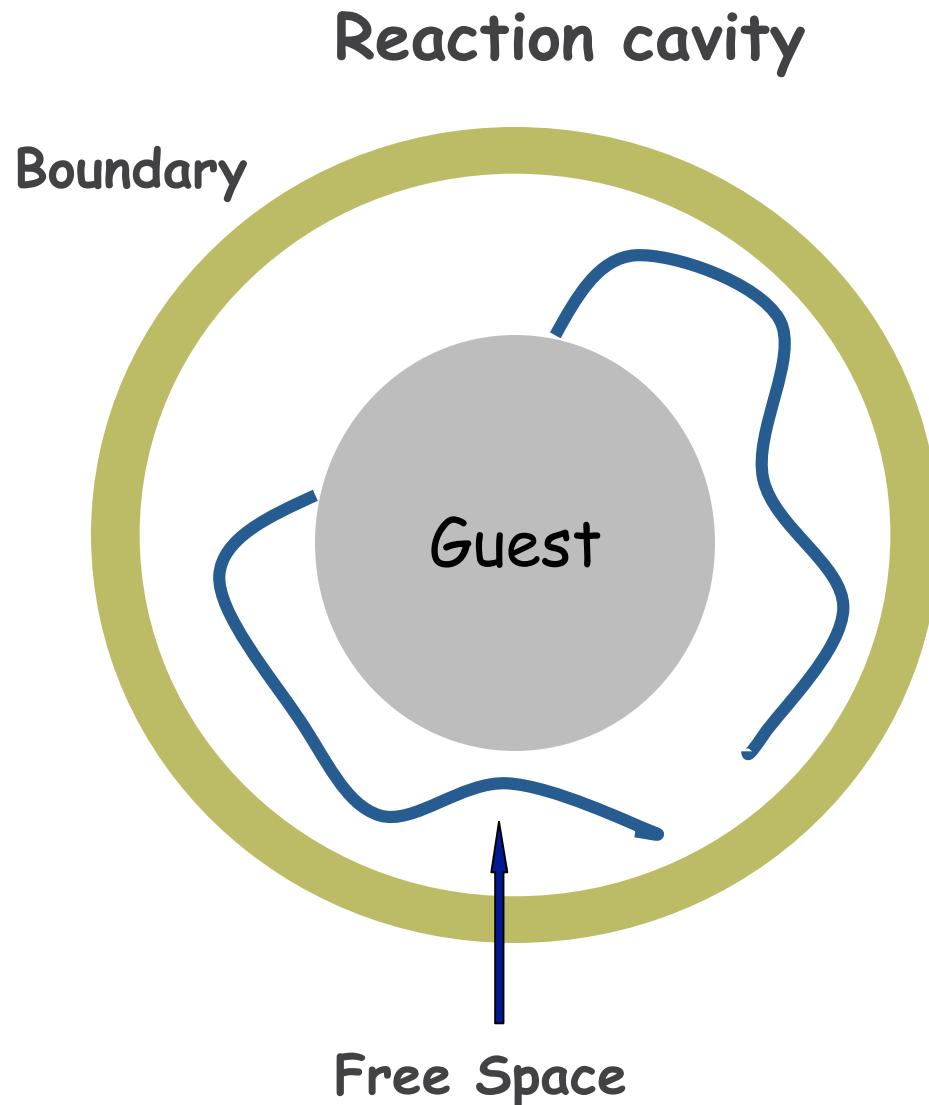
Emission Spectra of Naphthalene Included in MY Zeolites



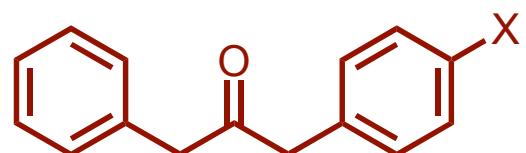
Phosphorescence from Diphenyl Polyenes



Supramolecular Containers



Controlling the free space

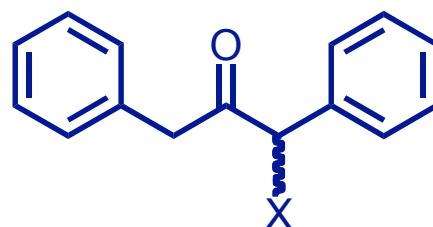


$X = \text{CH}_2\text{CH}_3$

$X = (\text{CH}_2)_2\text{CH}_3$

$X = (\text{CH}_2)_3\text{CH}_3$

$X = (\text{CH}_2)_4\text{CH}_3$



$X = \text{CH}_3$

$X = \text{CH}_2\text{CH}_3$

$X = (\text{CH}_2)_2\text{CH}_3$

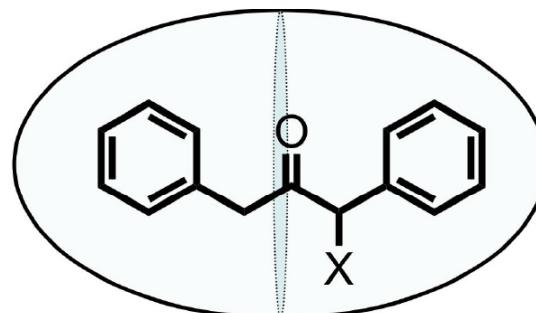
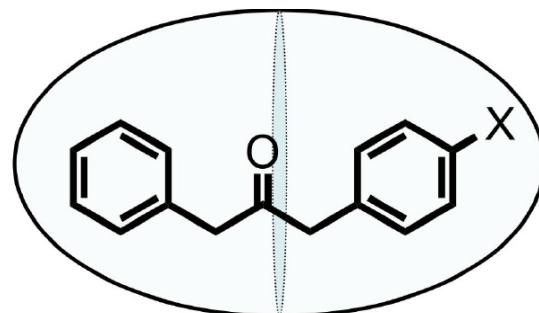
$X = (\text{CH}_2)_3\text{CH}_3$

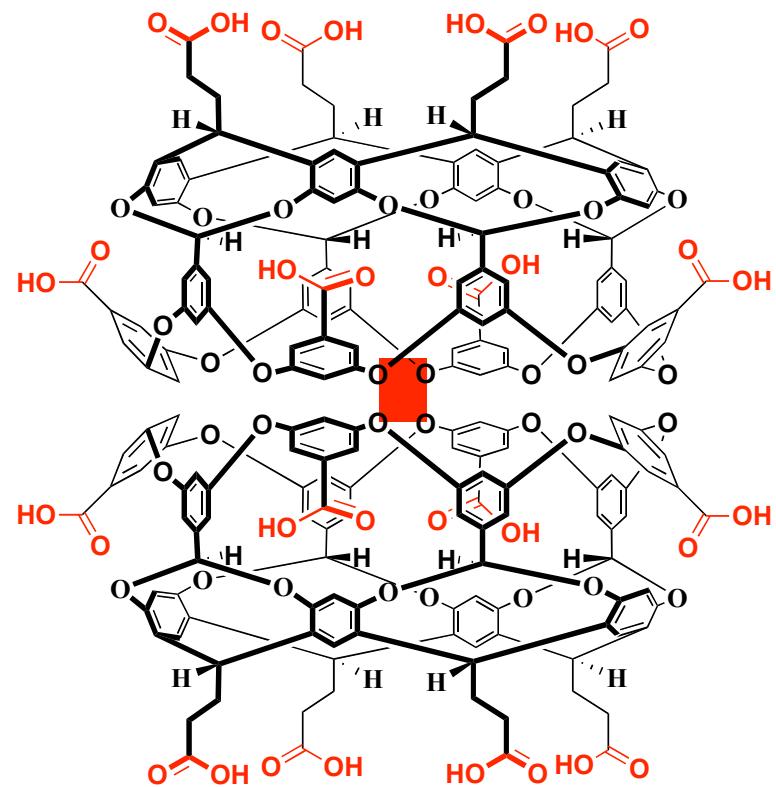
$X = (\text{CH}_2)_4\text{CH}_3$

$X = (\text{CH}_2)_5\text{CH}_3$

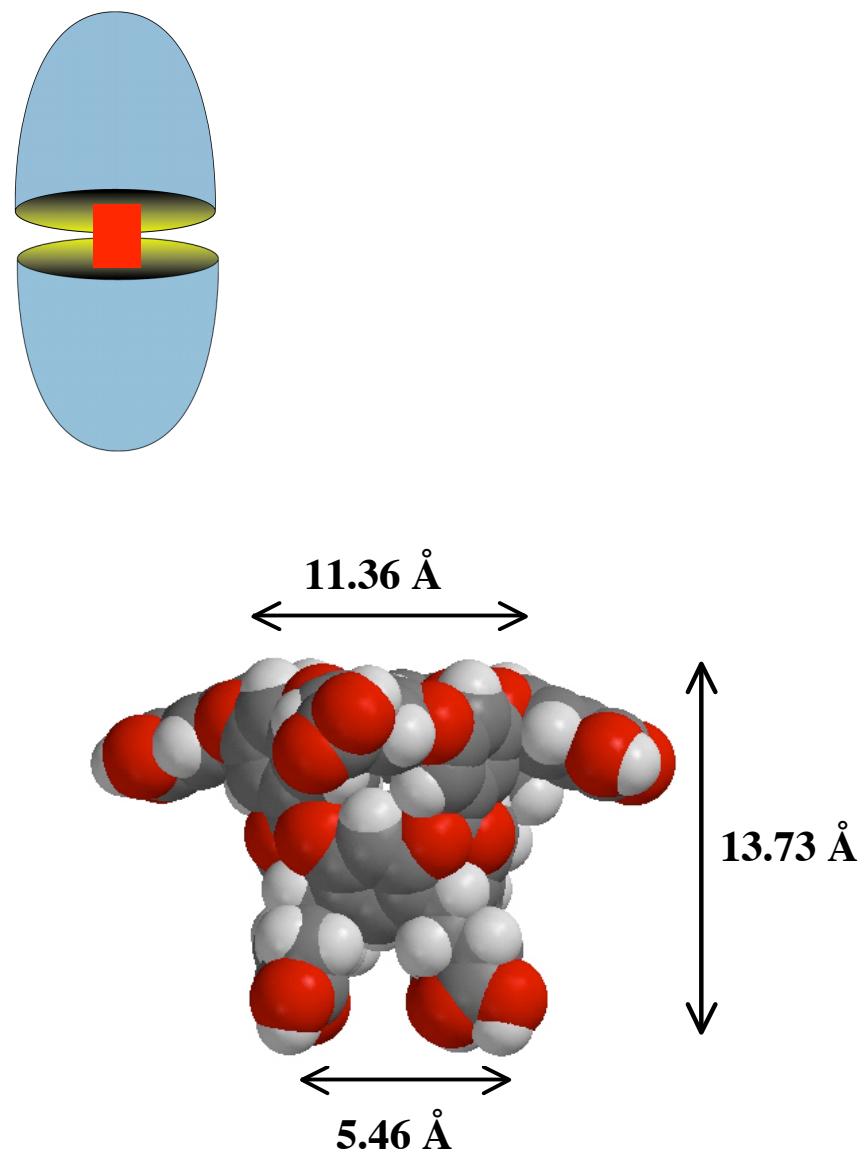
$X = (\text{CH}_2)_6\text{CH}_3$

$X = (\text{CH}_2)_7\text{CH}_3$

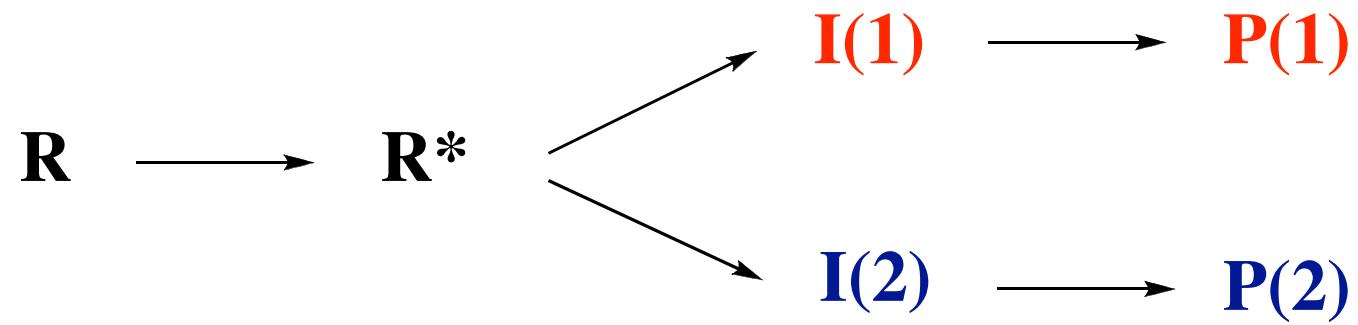
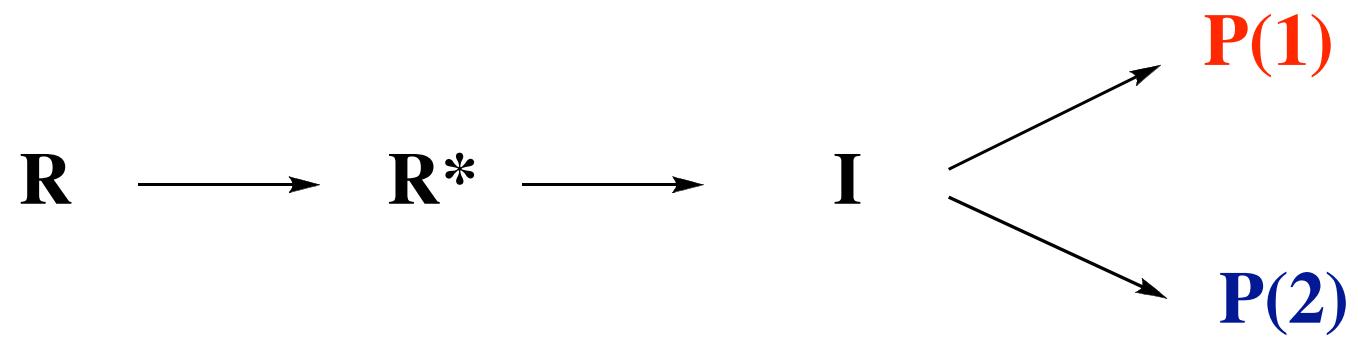




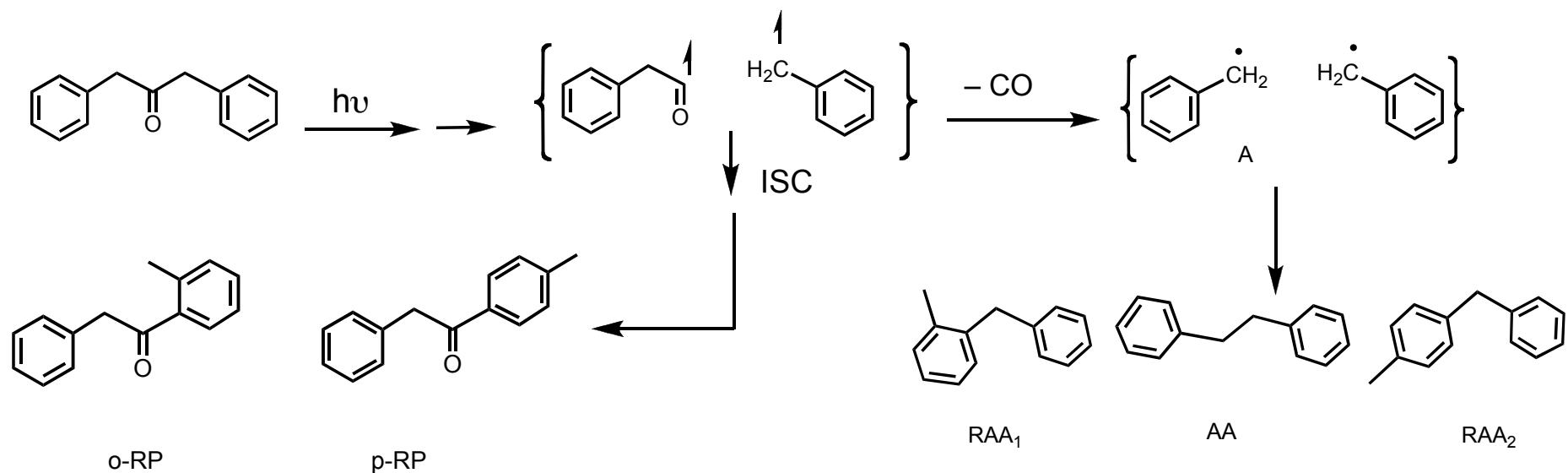
Octa acid (OA)
Water soluble at pH 9



C. L. D. Gibb, and B. C. Gibb, *J. Am. Chem. Soc.*, 2004, 126, 11408-11409.

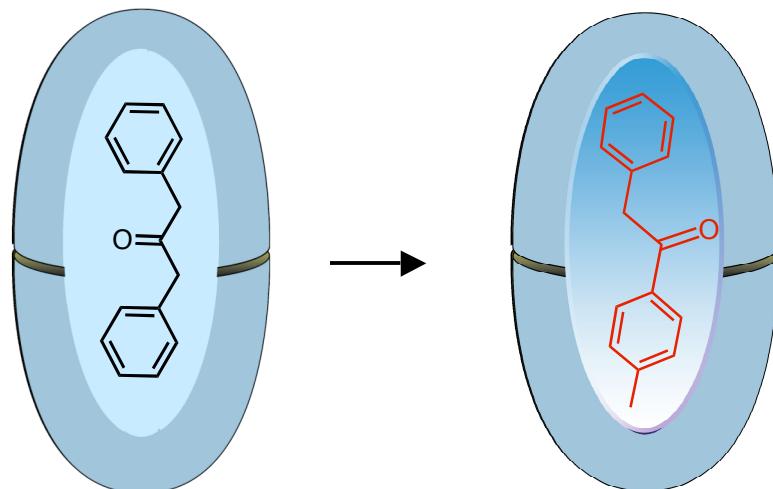


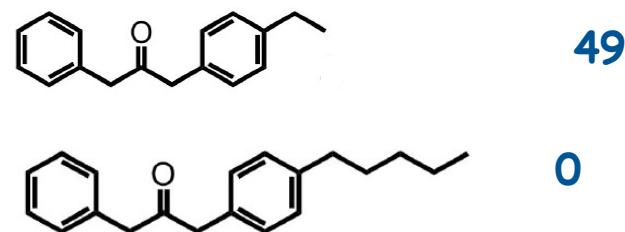
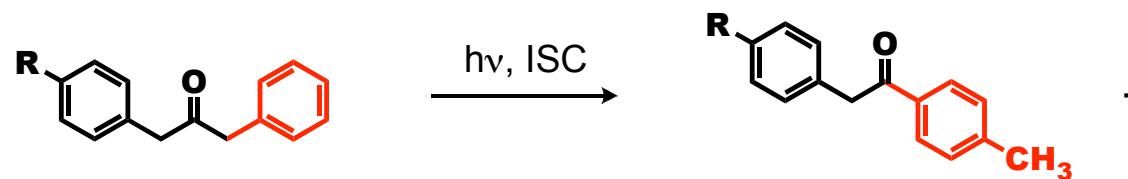
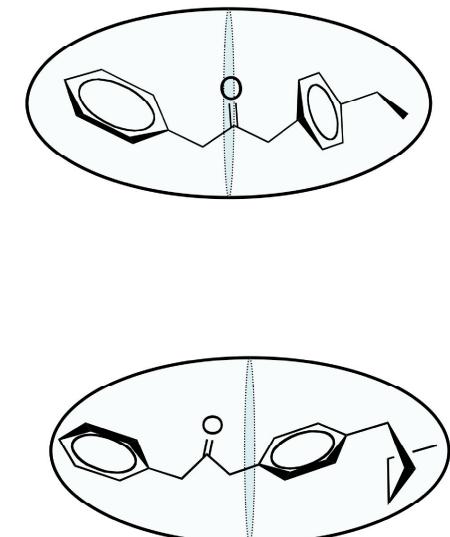
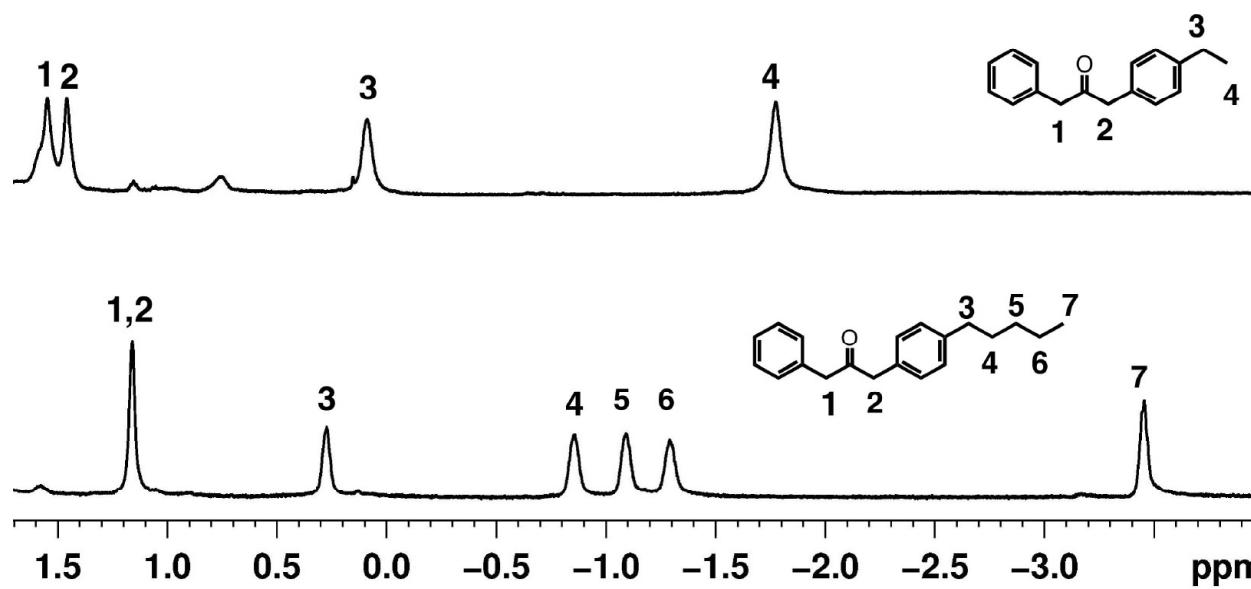
The primary radical pair prefers to rotate than decarbonylate

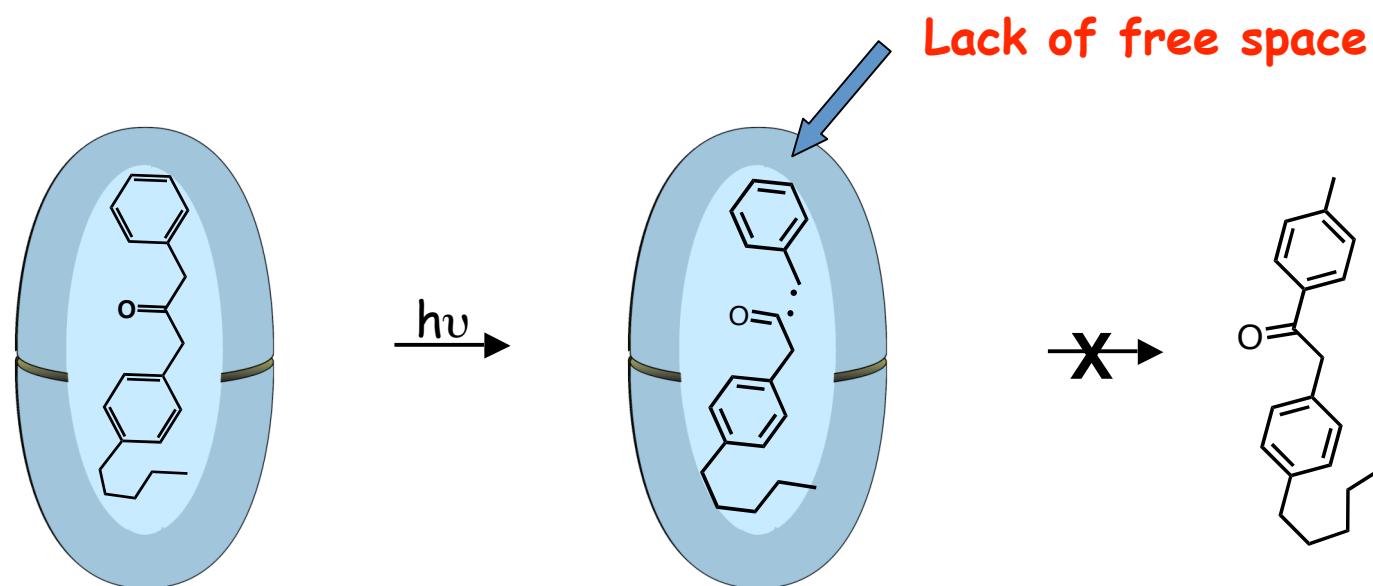
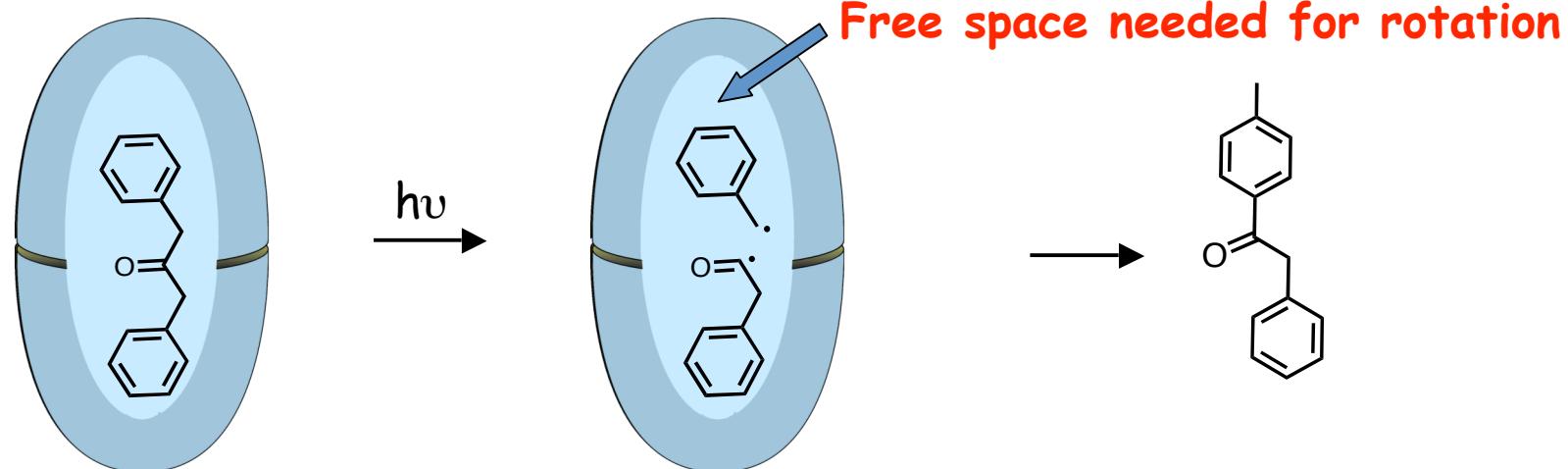
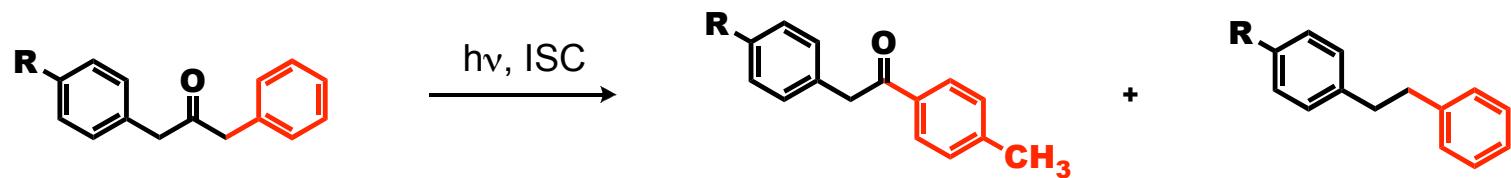


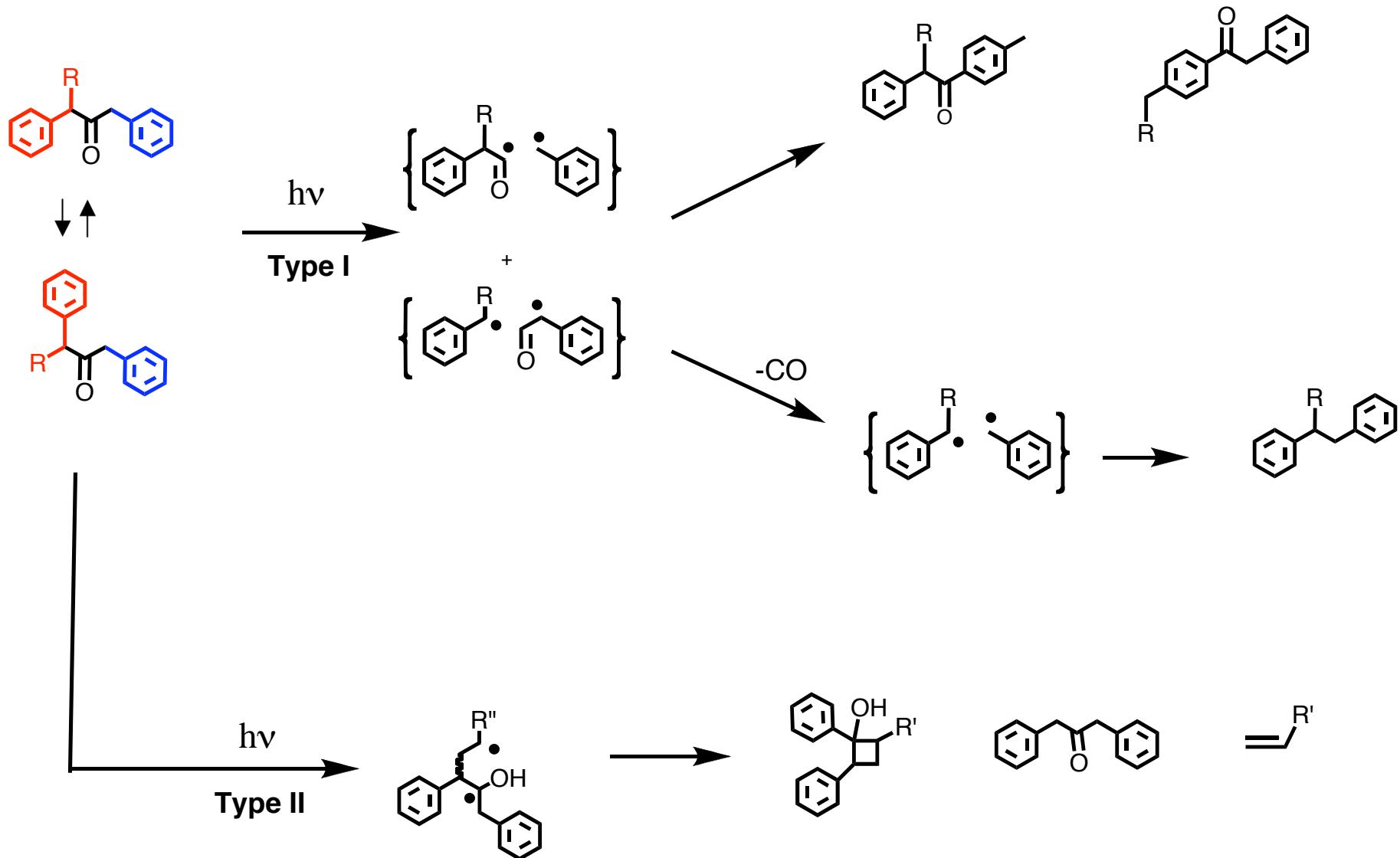
Relative product distribution (%)

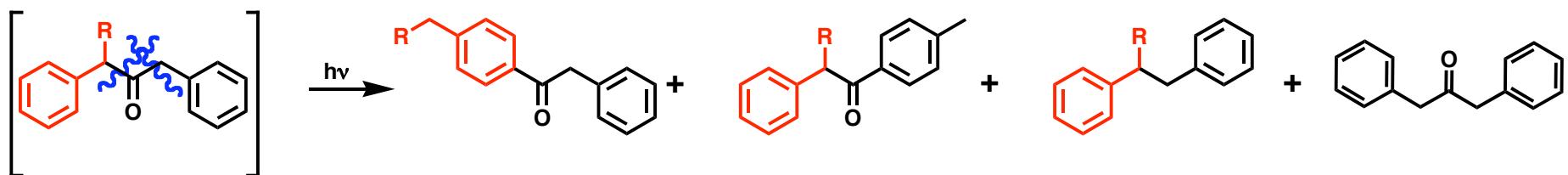
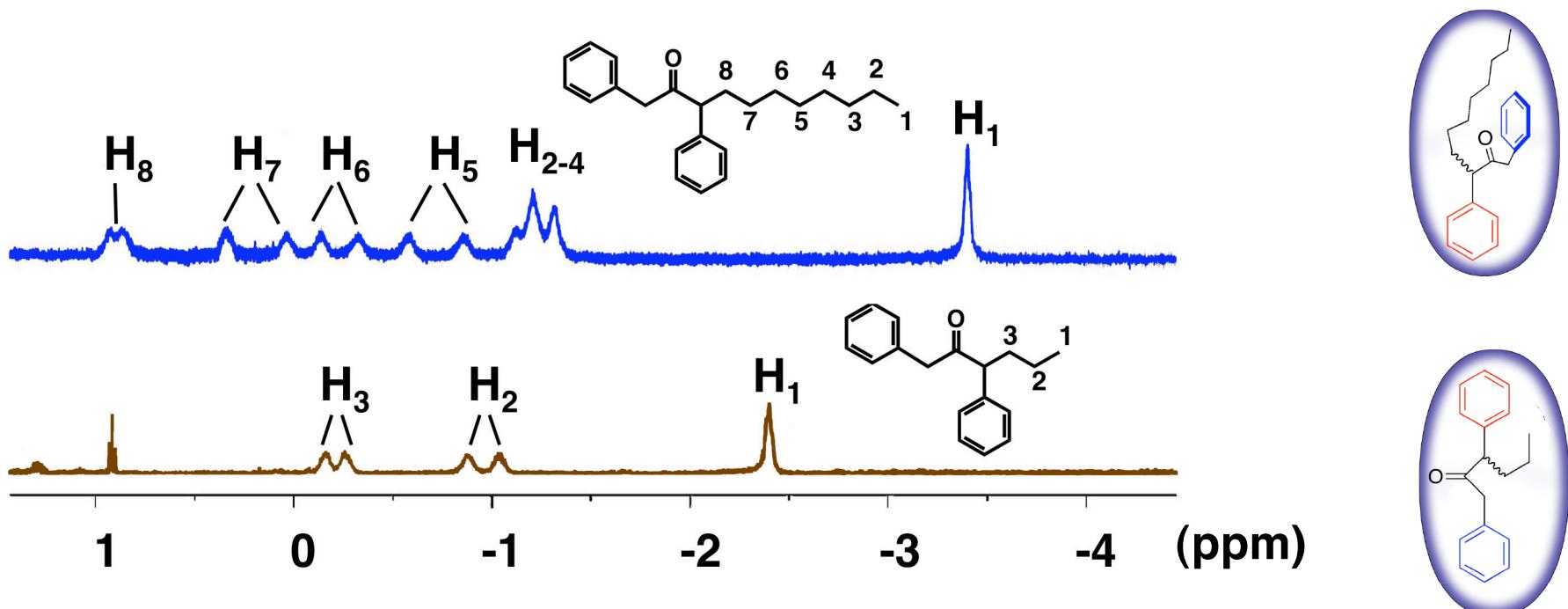
Medium	RAA ₁ +RAA ₂	AA	p-RP
Hexane	--	>99	--
Octa acid	10	34	56





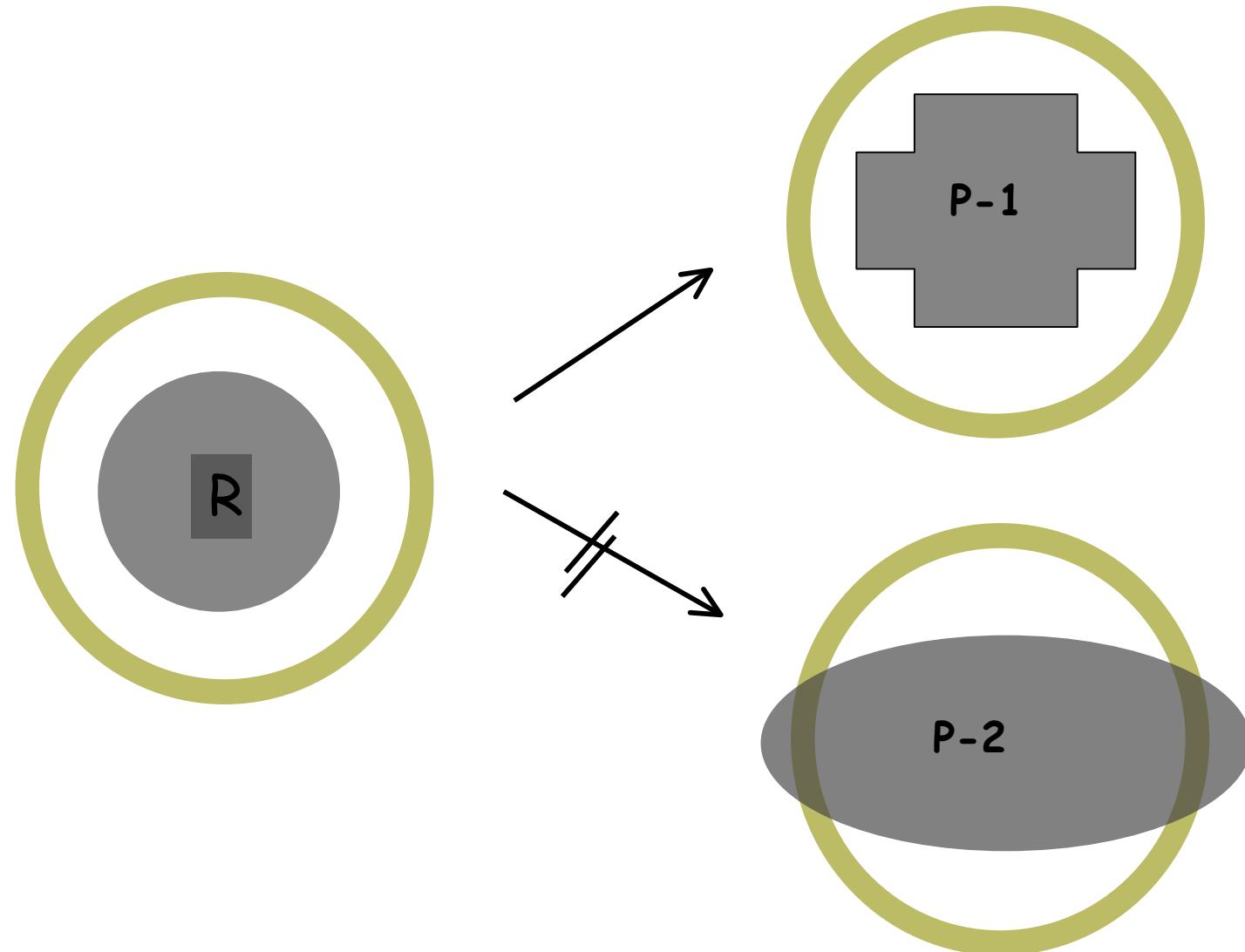




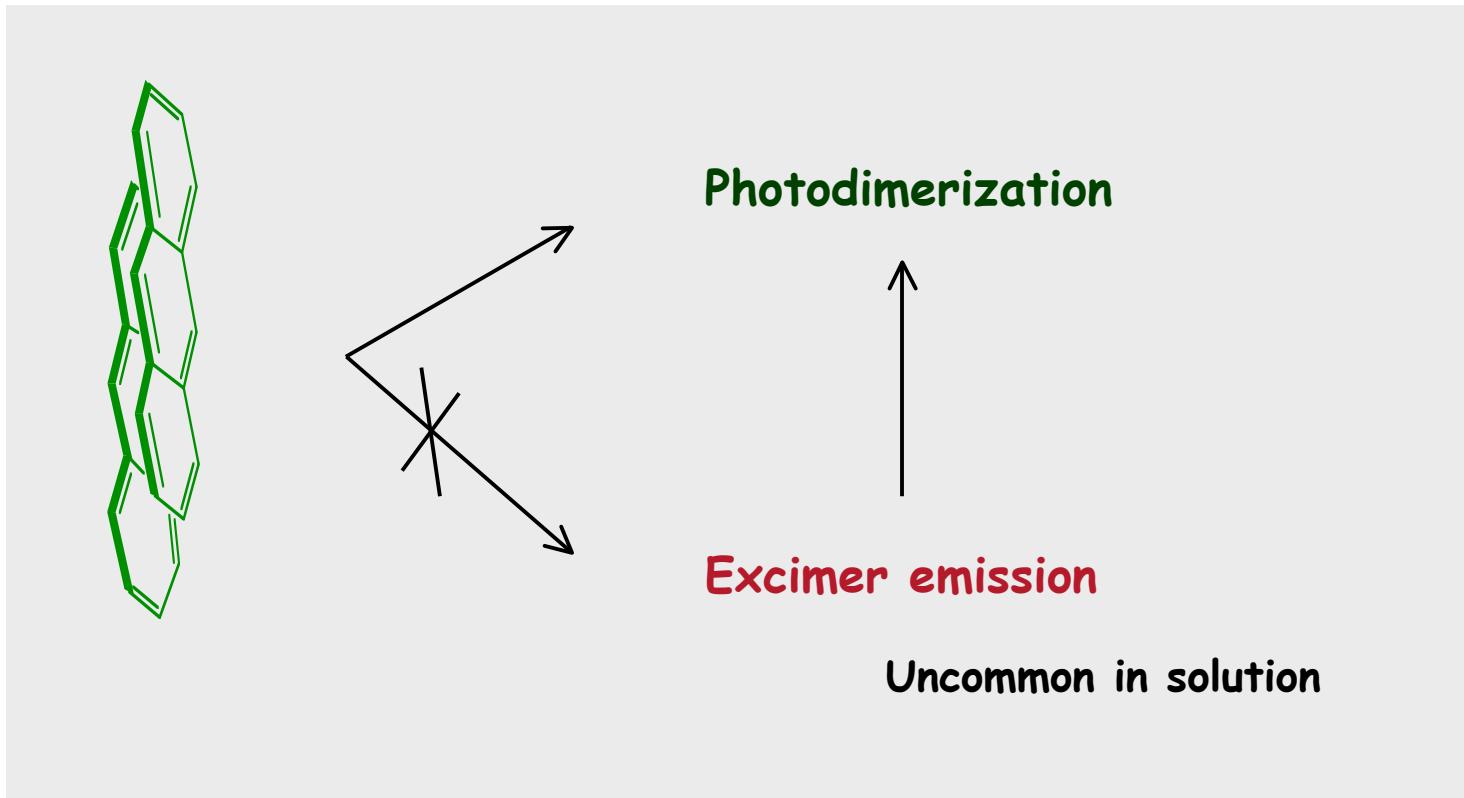


$-\text{C}_3\text{H}_7$	35	4	50	11
$-\text{C}_8\text{H}_{17}$	-	-	10	90

Role of Free Space: Product Must Fit the Reaction Cavity

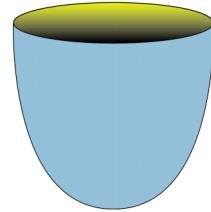


Photochemistry and Photophysics of Anthracene



OA-anthracene complex

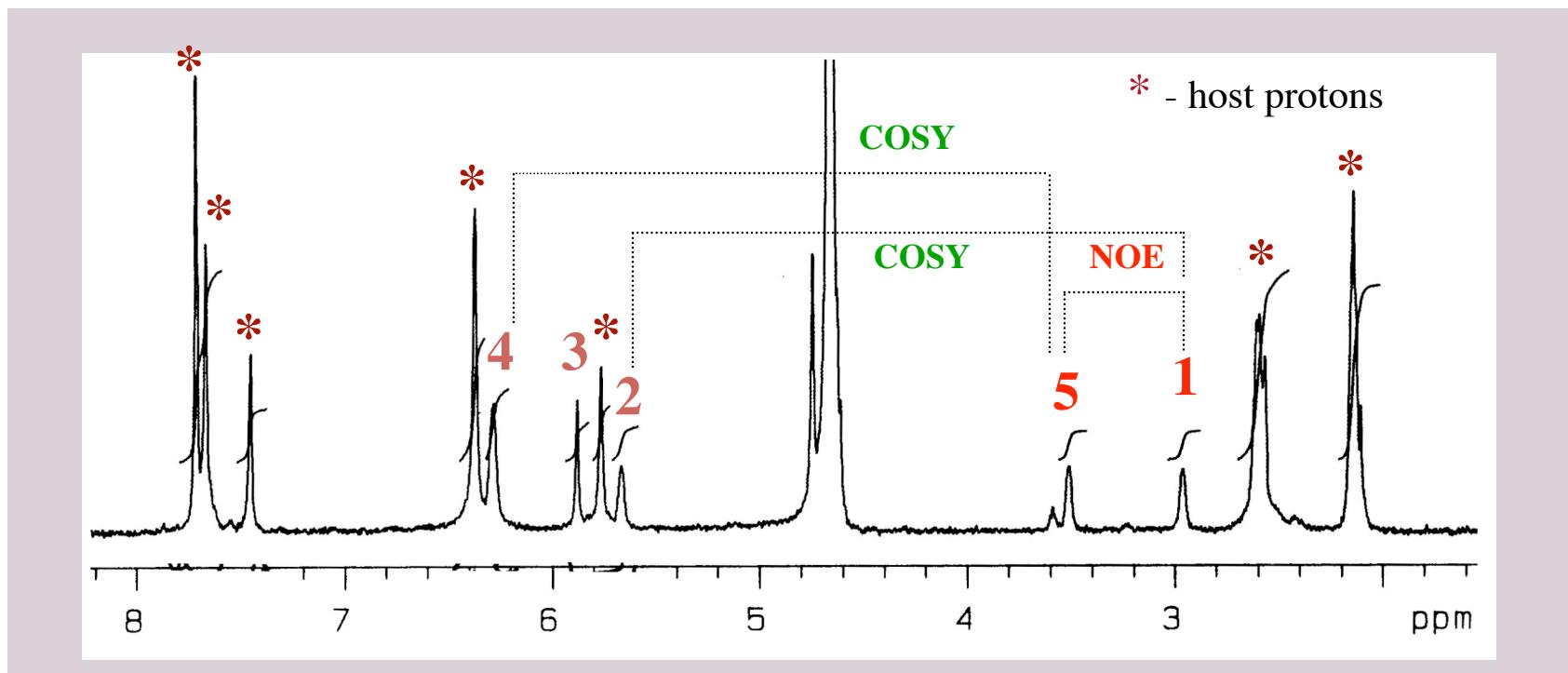
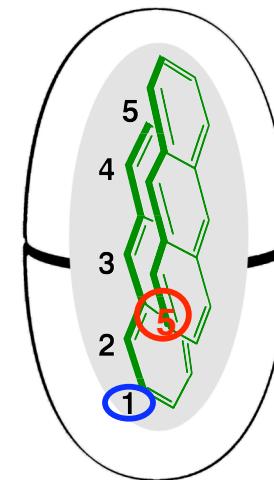
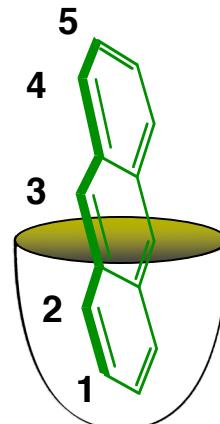
Octa Acid



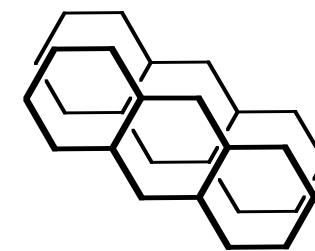
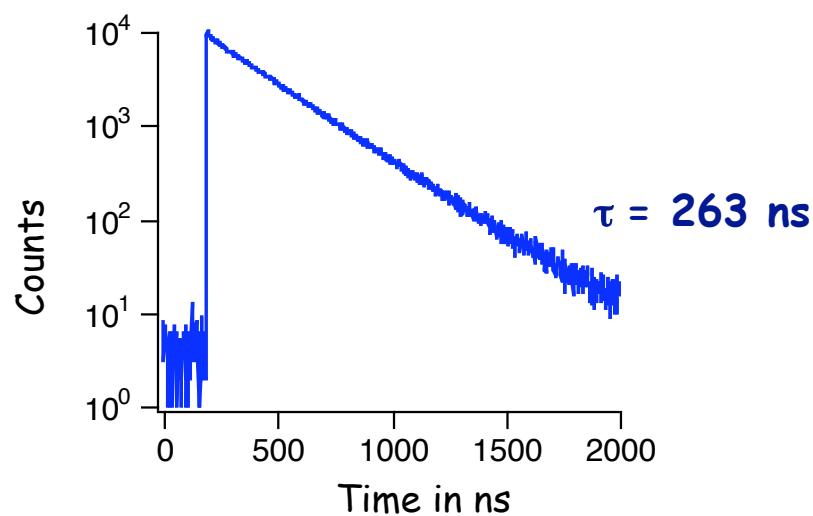
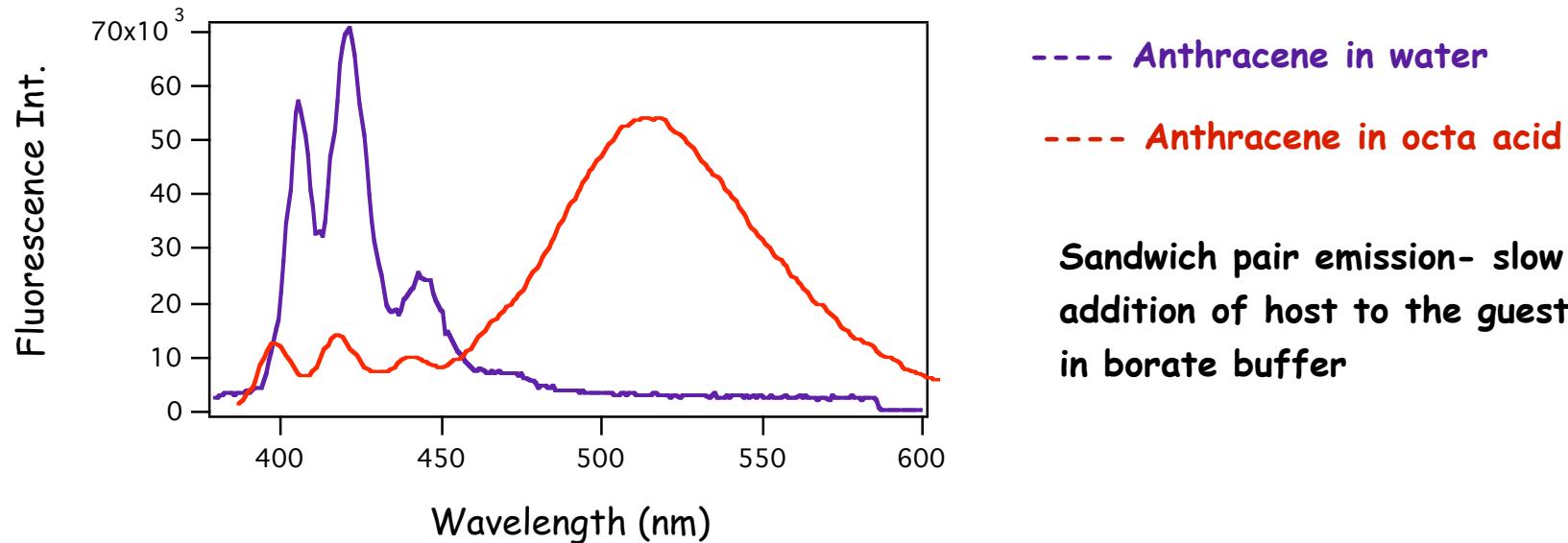
Anthracene



Five Signals

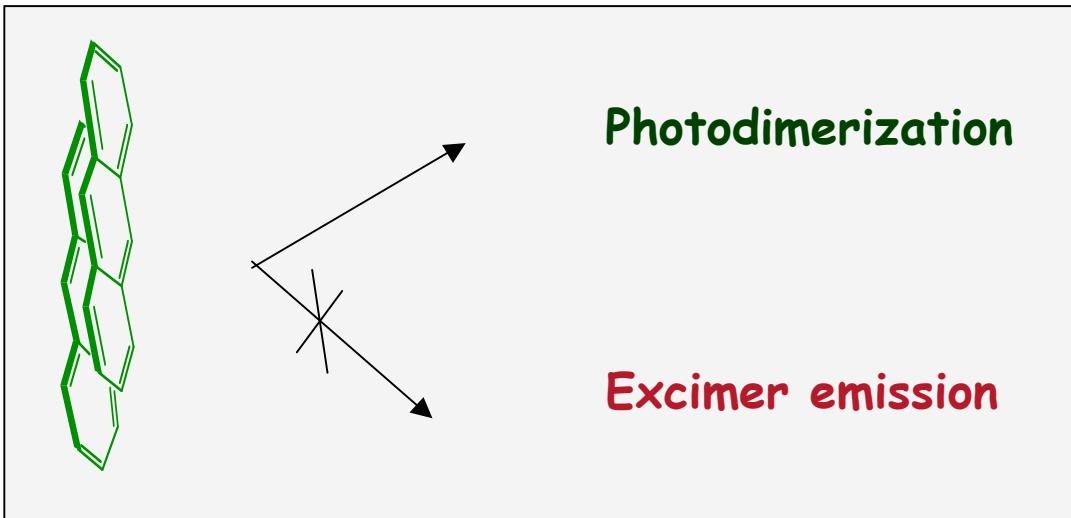


Photophysics of OA-anthracene complex

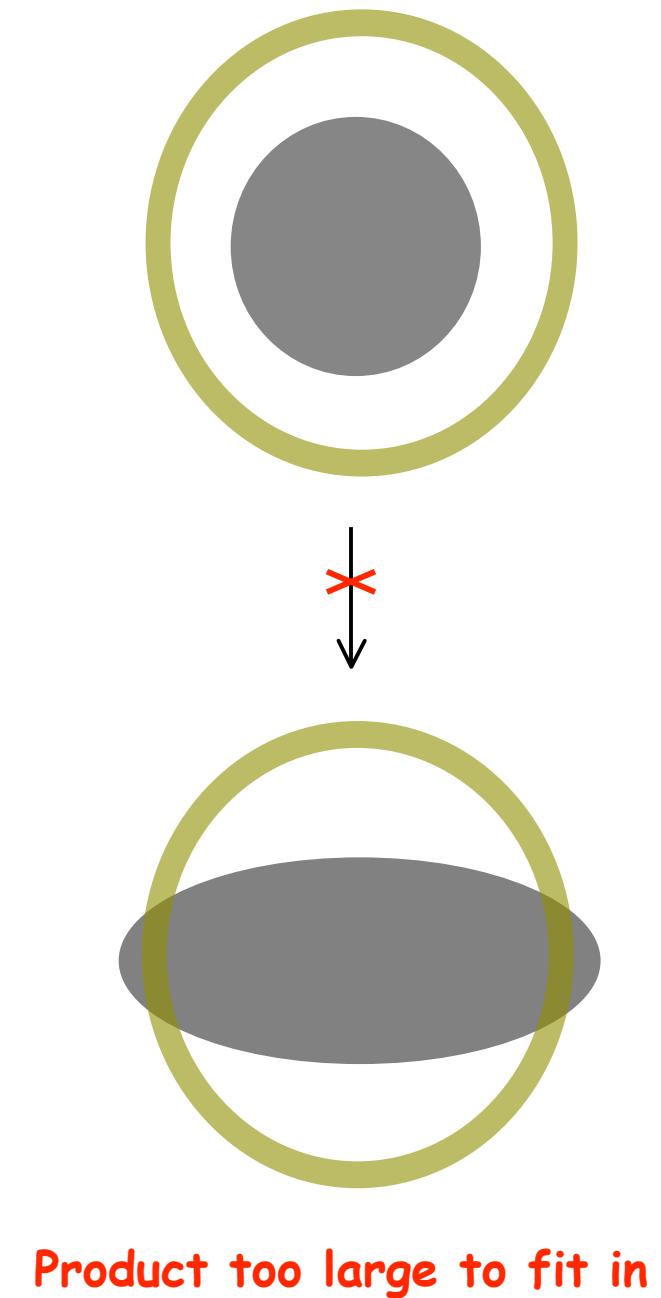
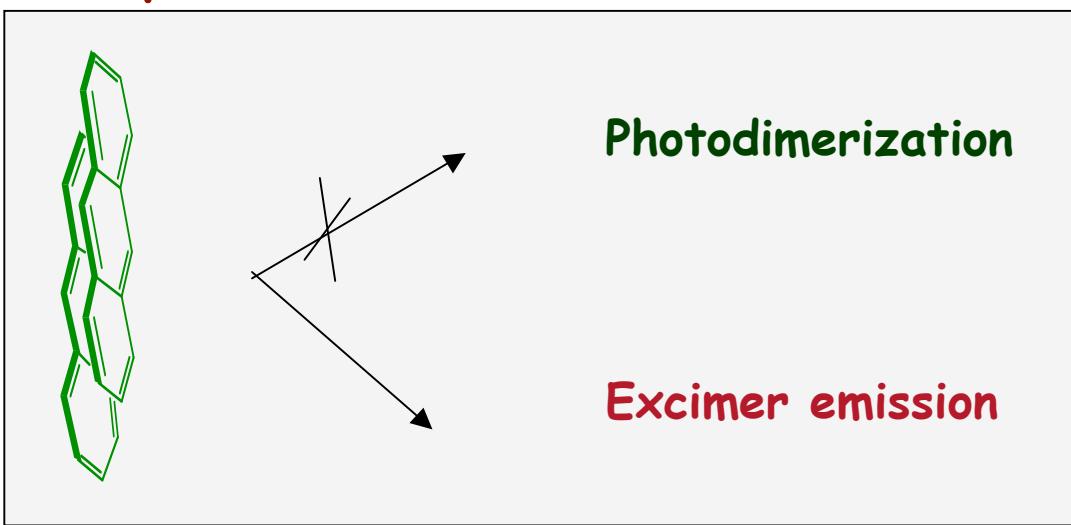


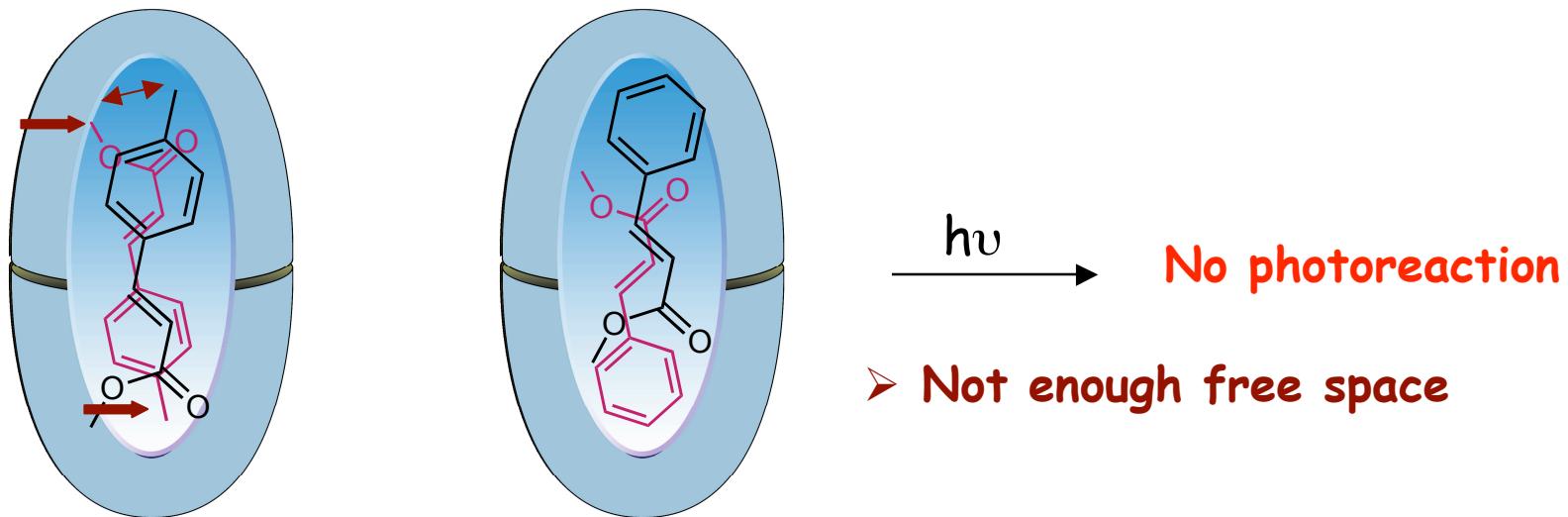
Sandwich excimer - τ 210 - 225 ns

Isotropic solution

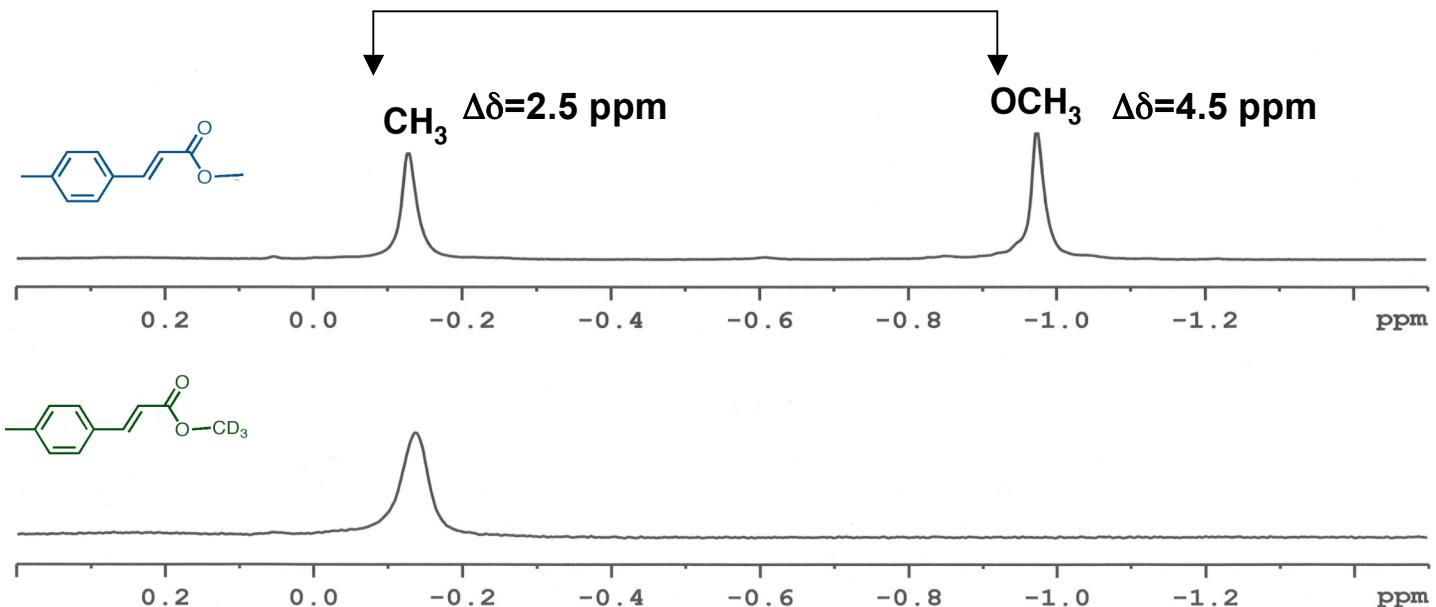


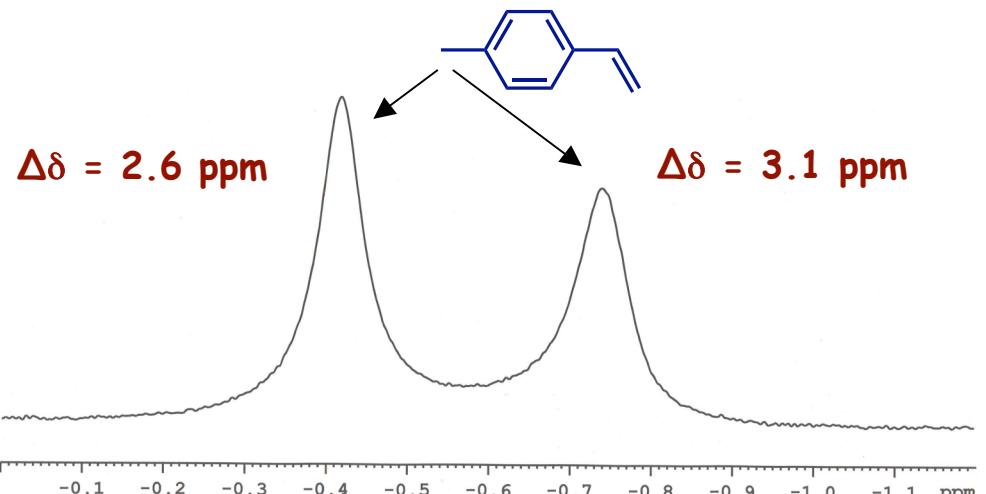
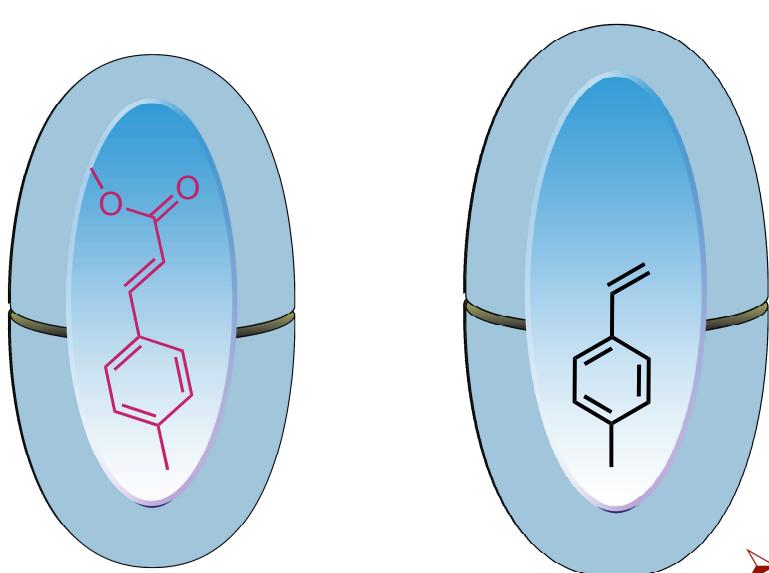
OA complex



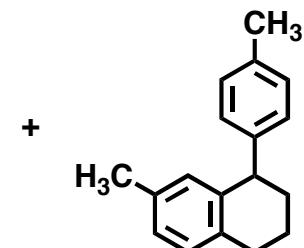
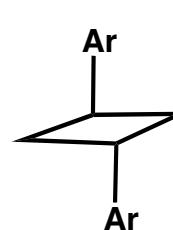
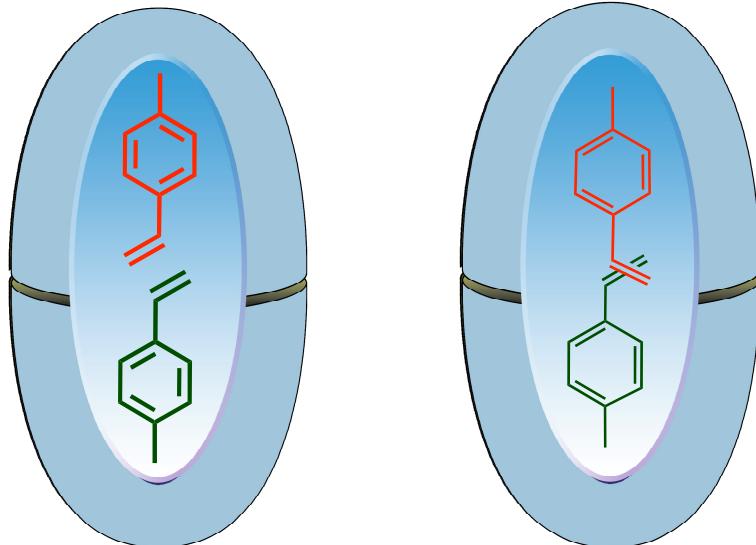


NOE

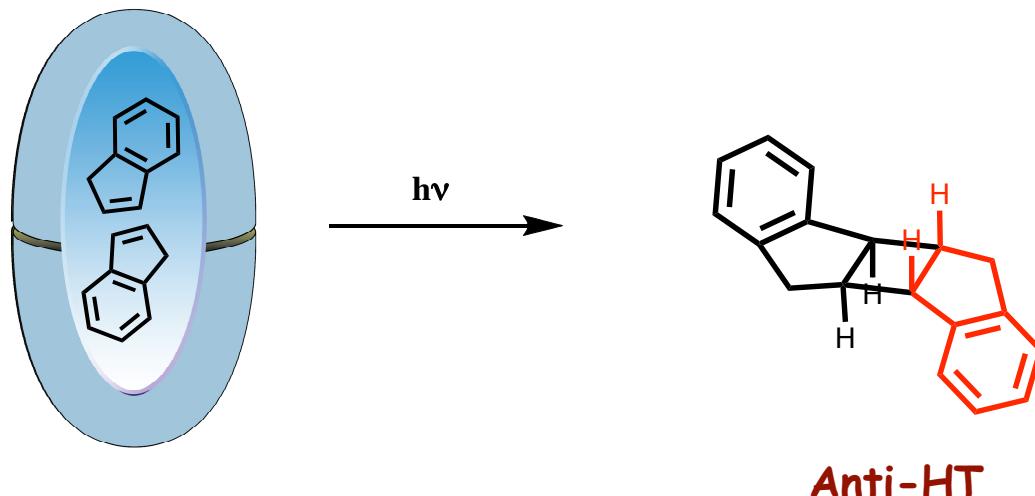
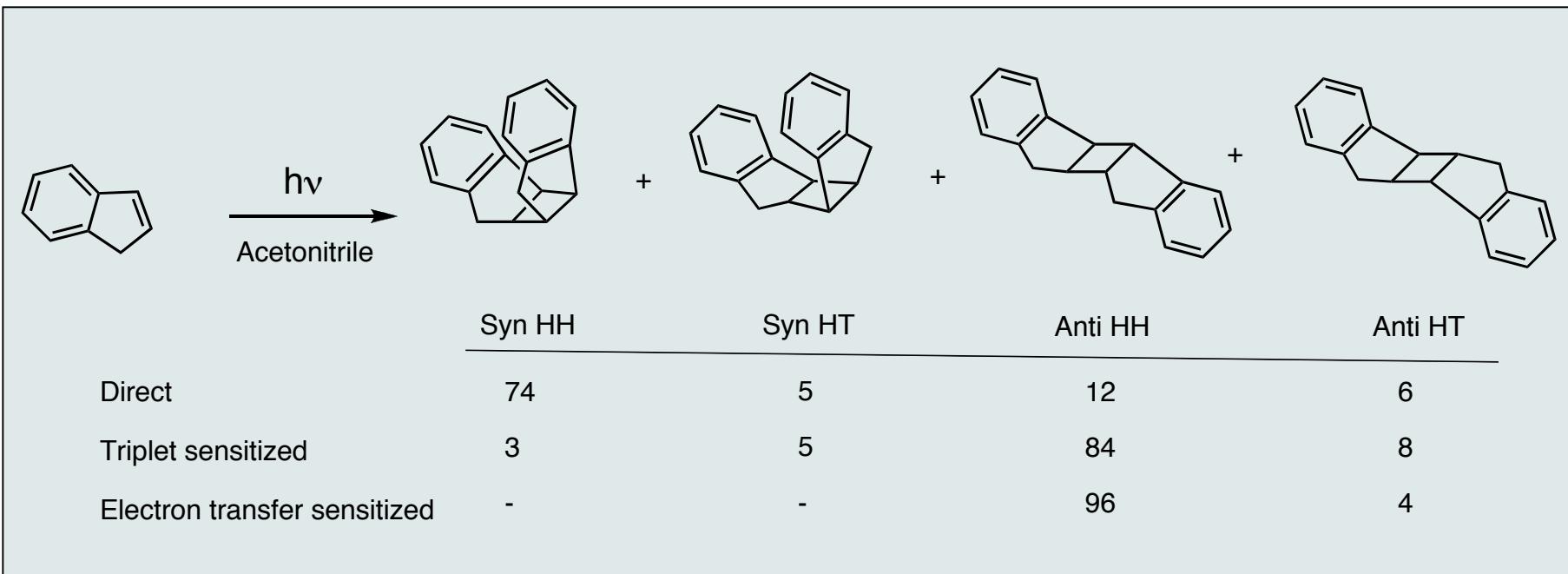




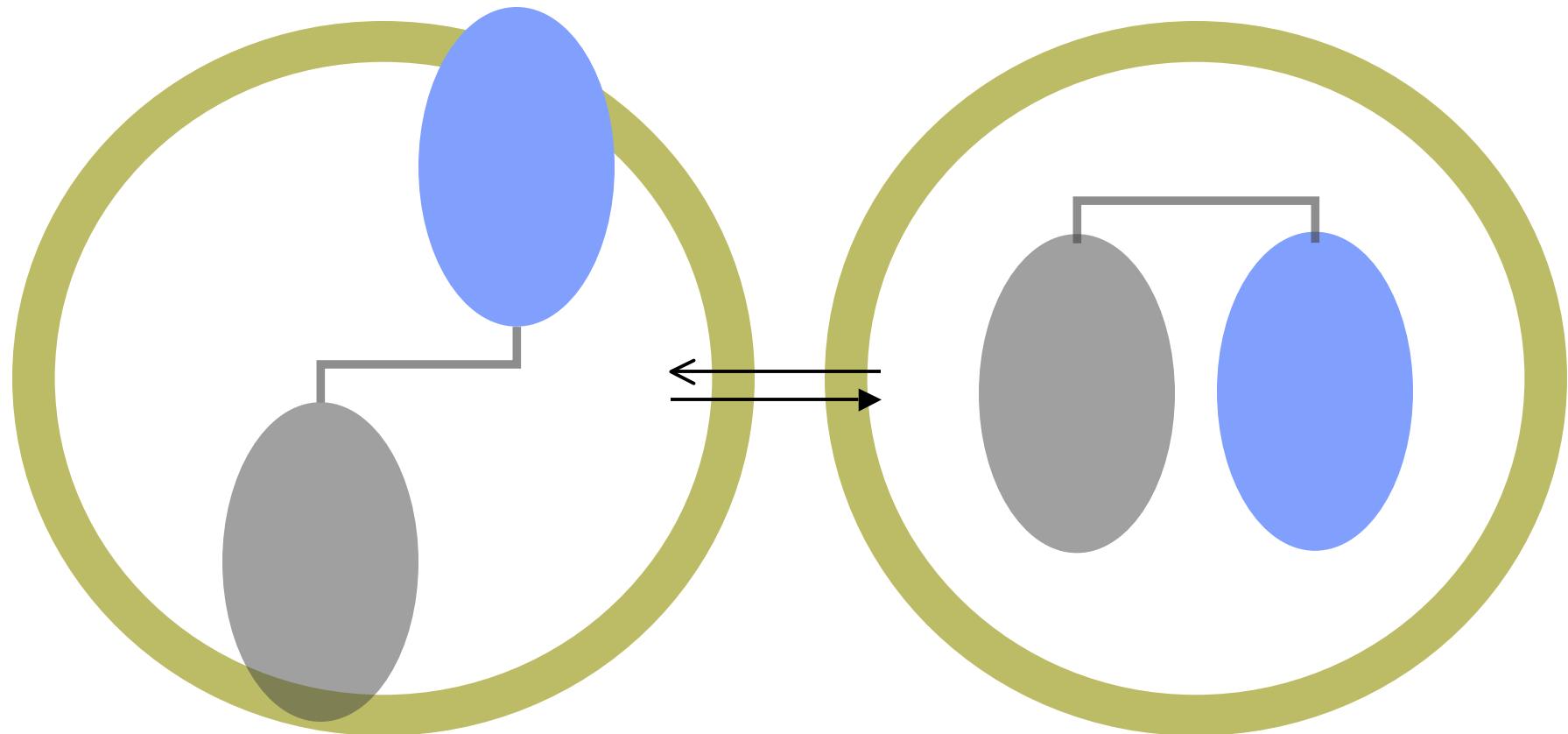
- Pre-organized for dimerization
- Enough free space to accommodate the dimers



Dimer ratio: 55:45
NMR integration ratio: 53:47

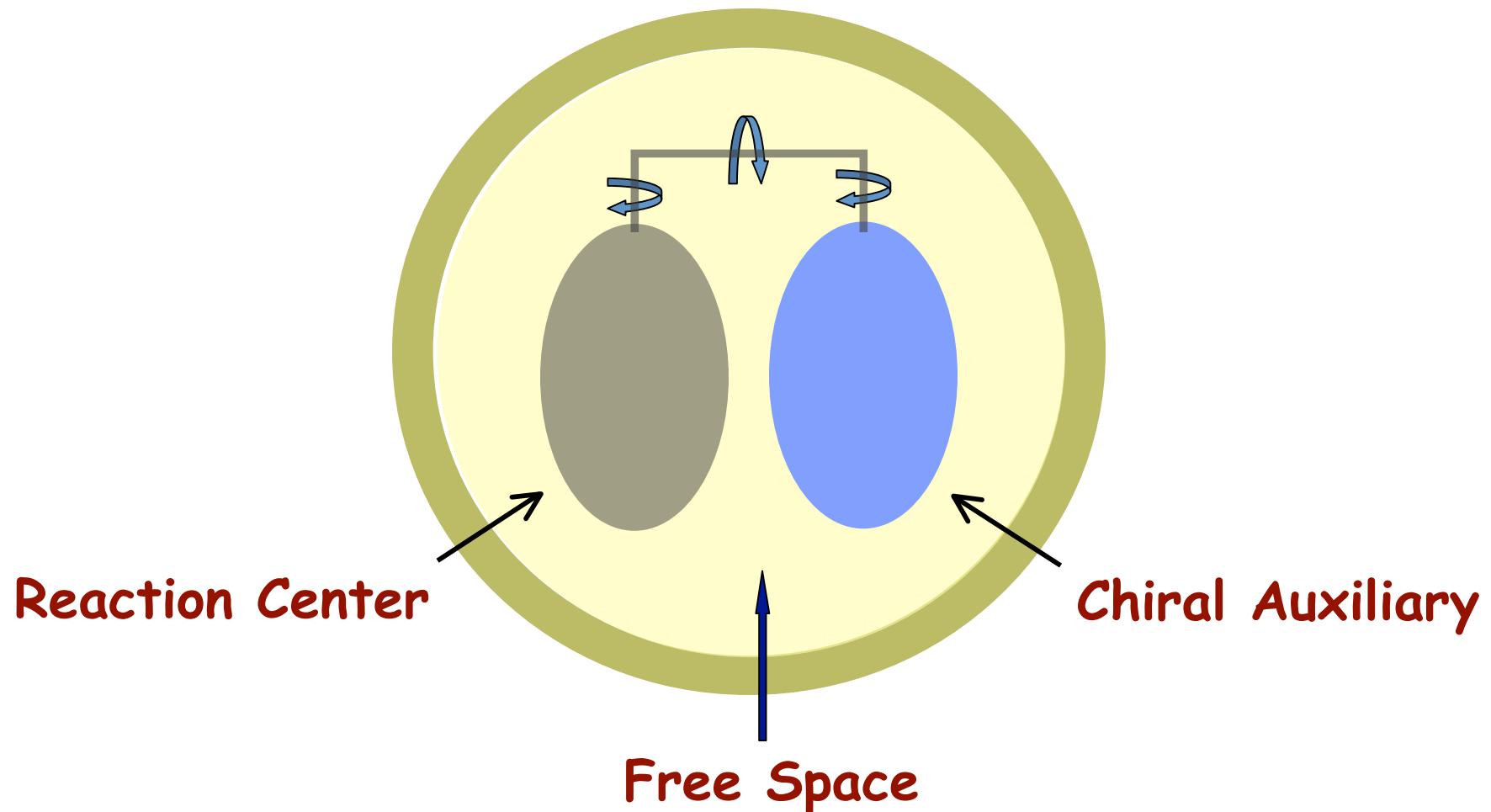


Conformational Control and Rotational Restriction

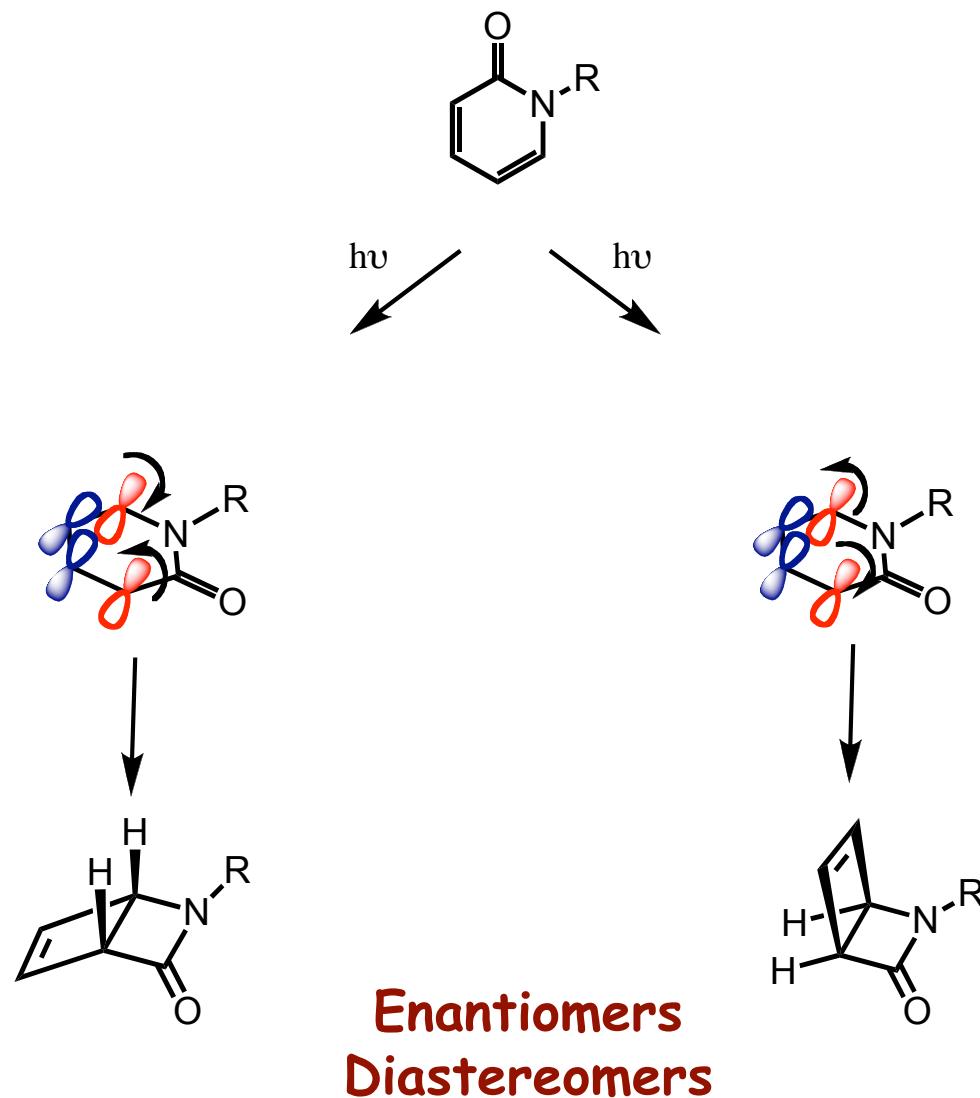


Role of Free Space

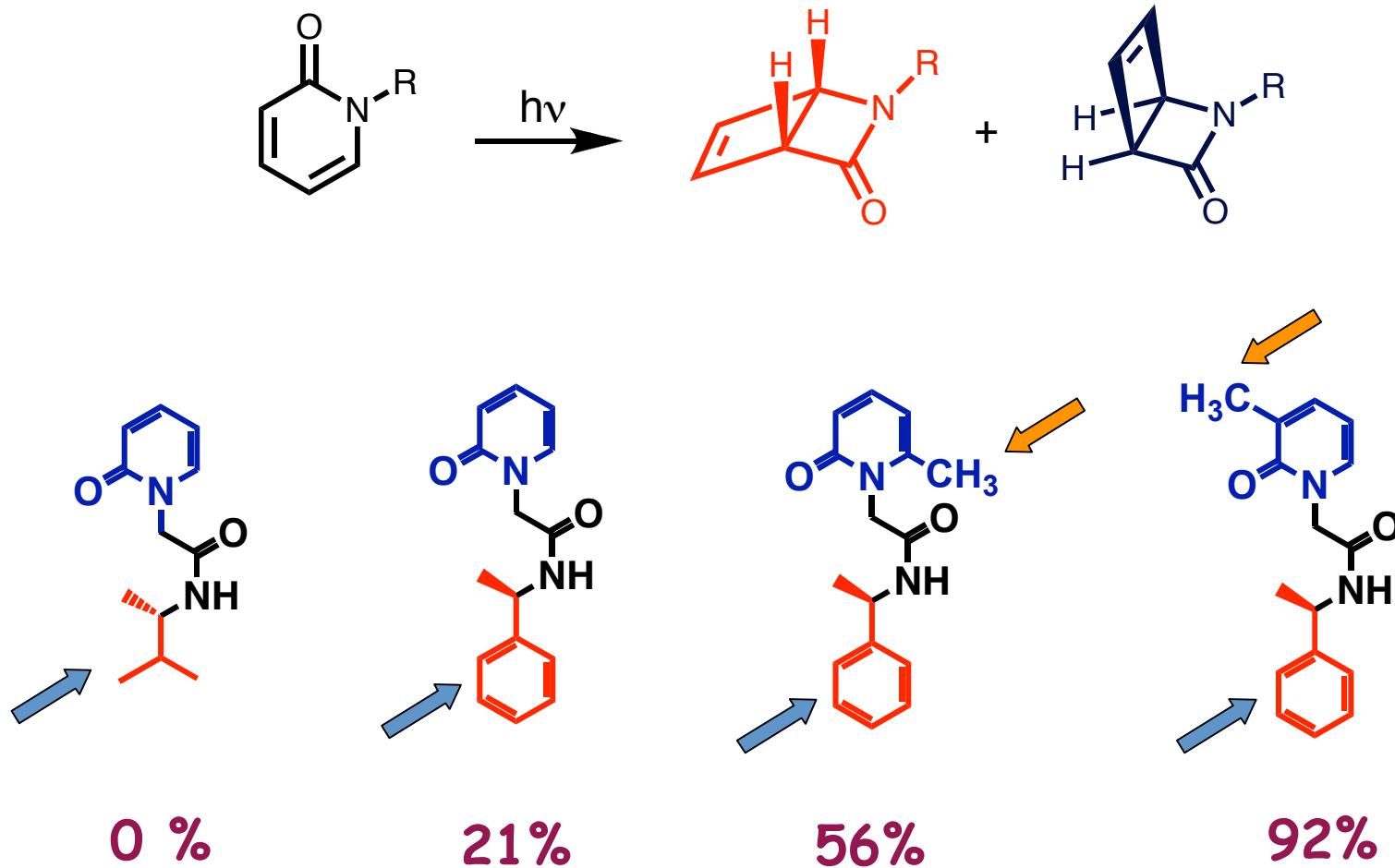
Conformational Control and Rotational Restriction

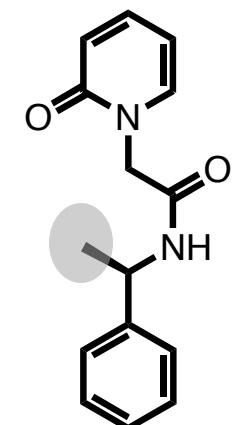
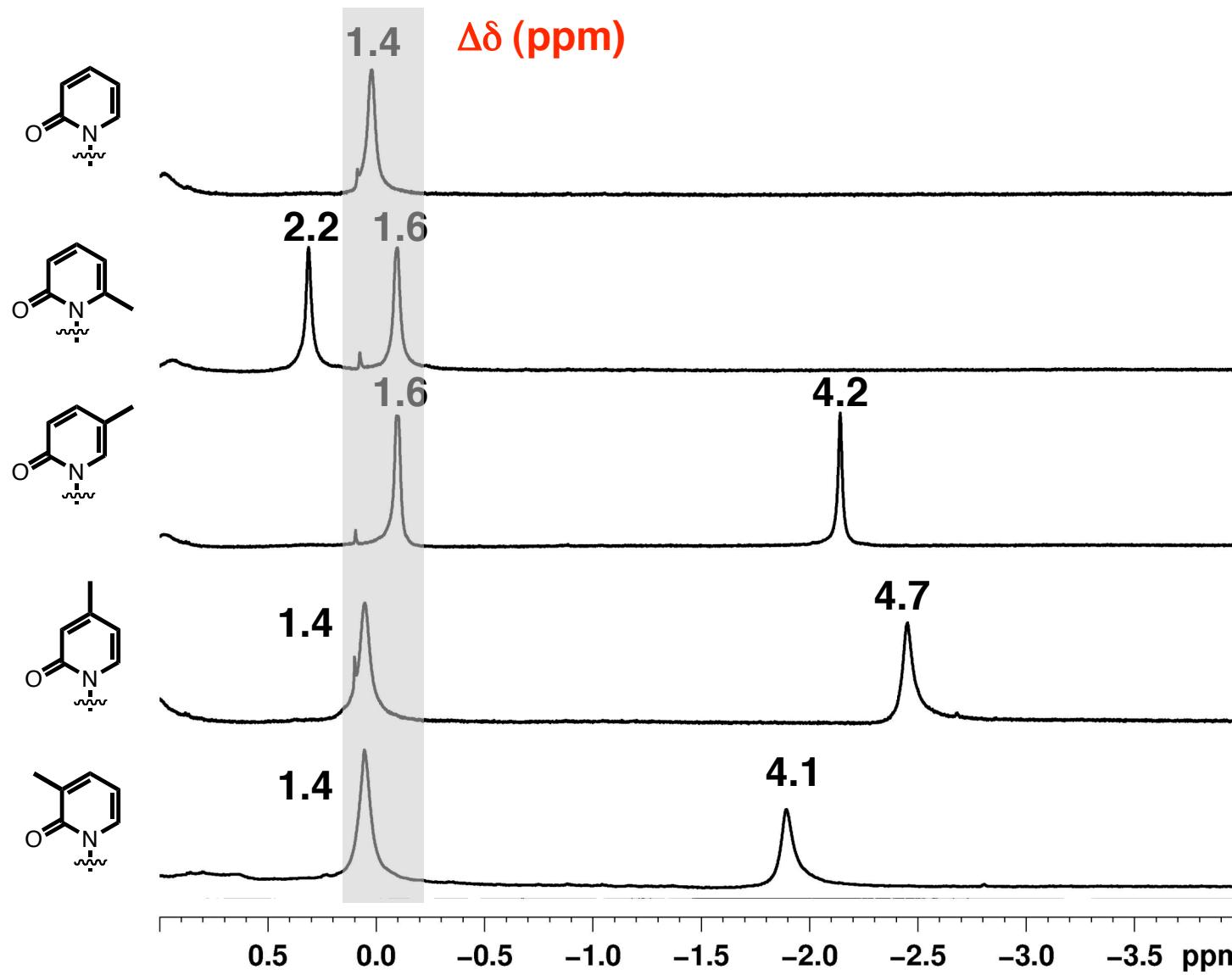


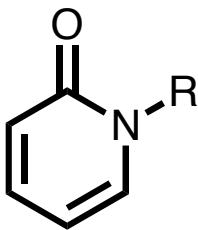
Amplified Chiral Induction in a Supramolecular Assembly



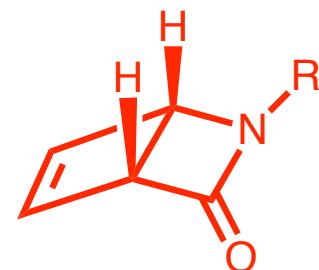
Importance of phenyl group and methyl substitution



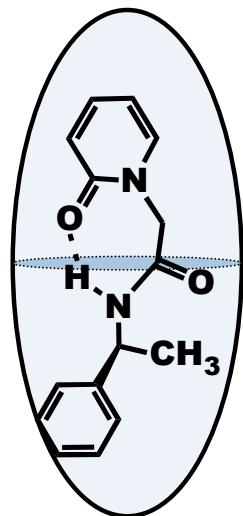
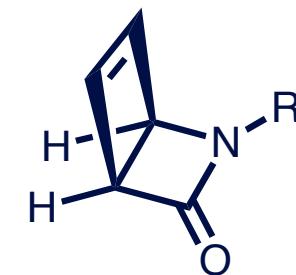




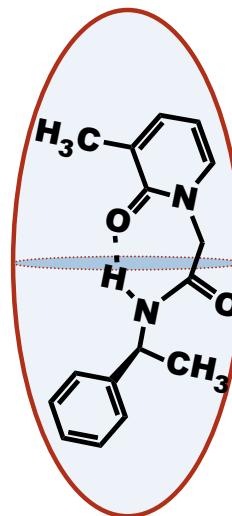
$\text{h}\nu$



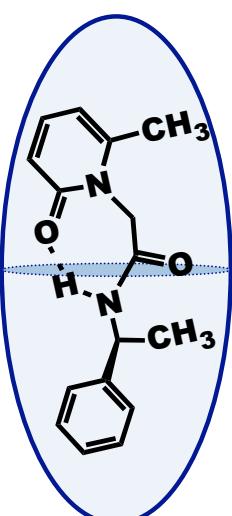
+



21%

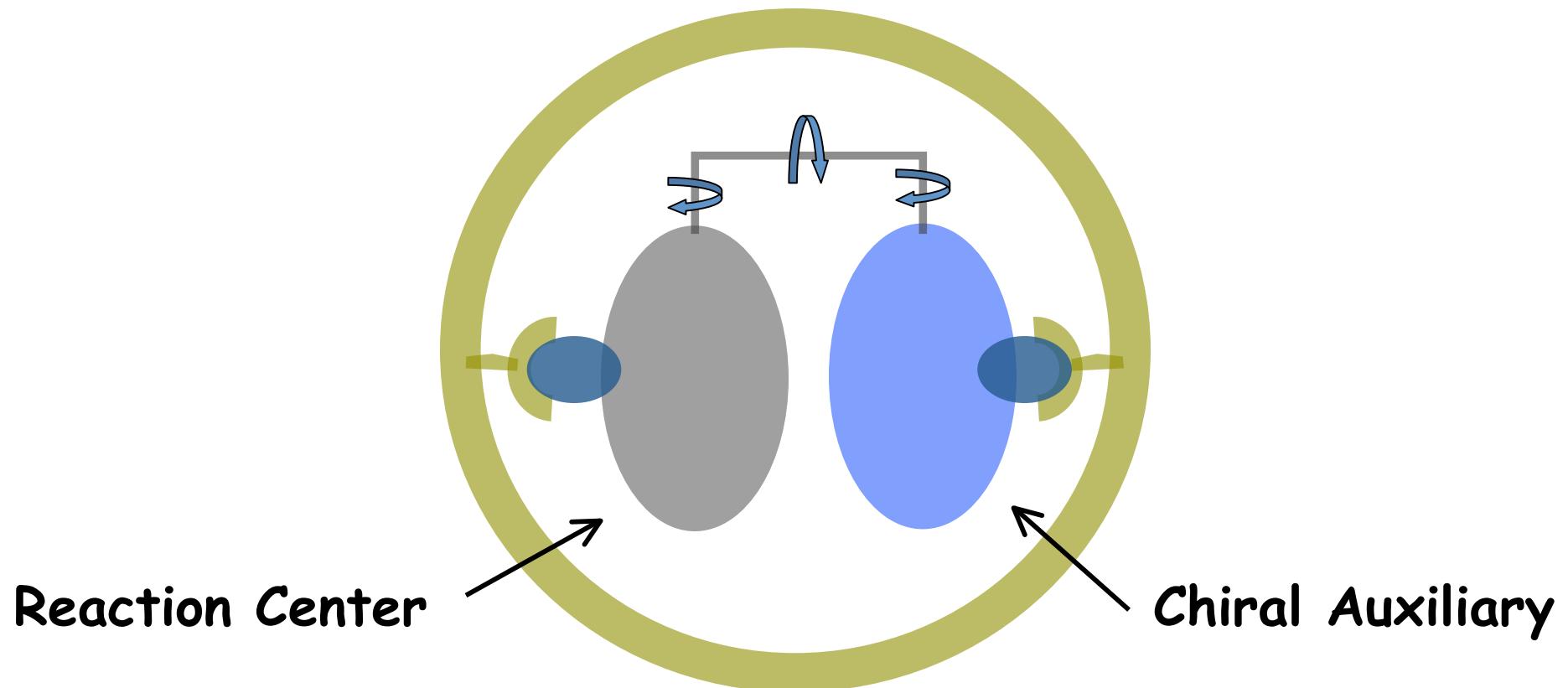


92%

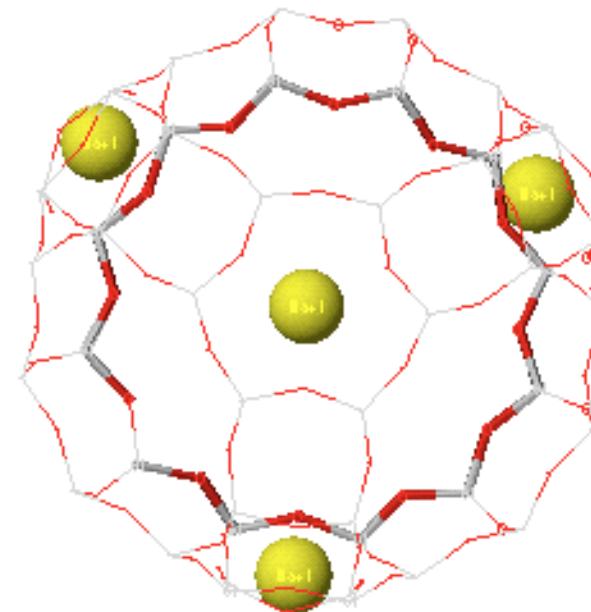
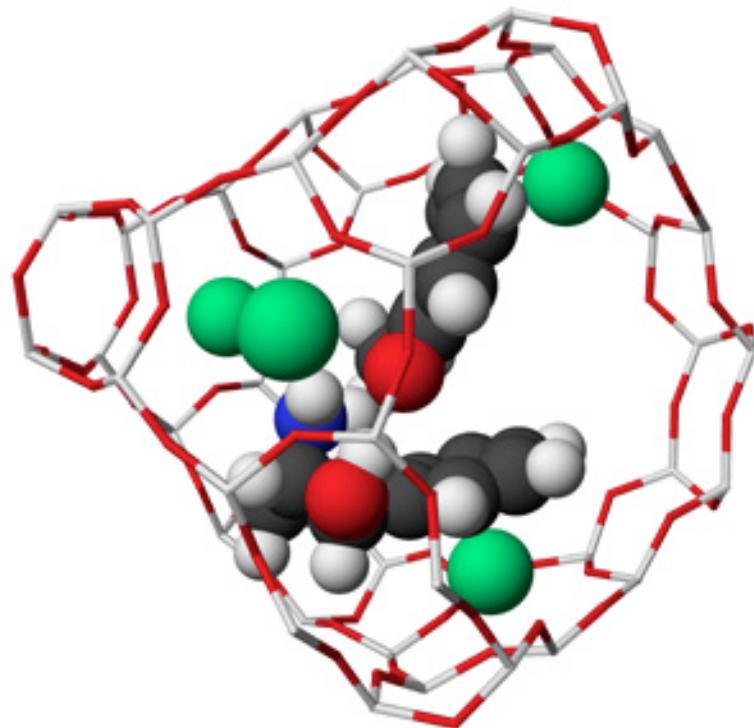


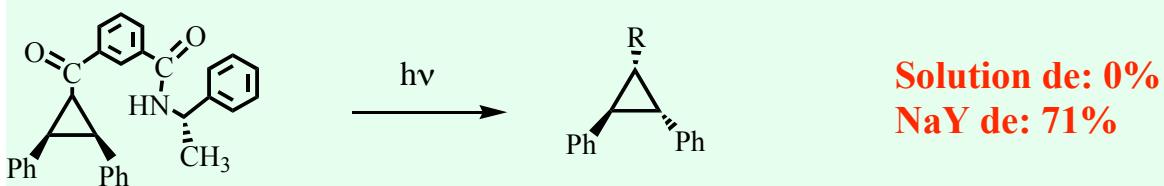
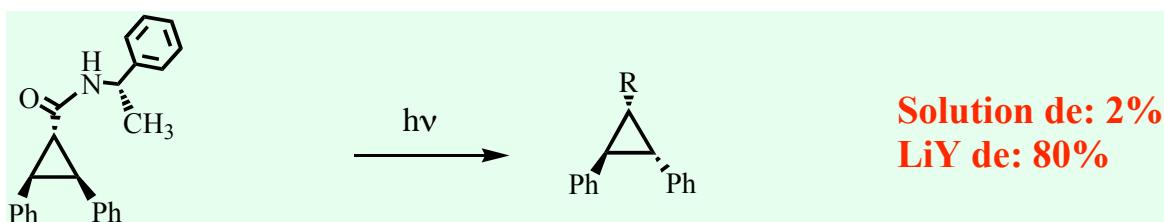
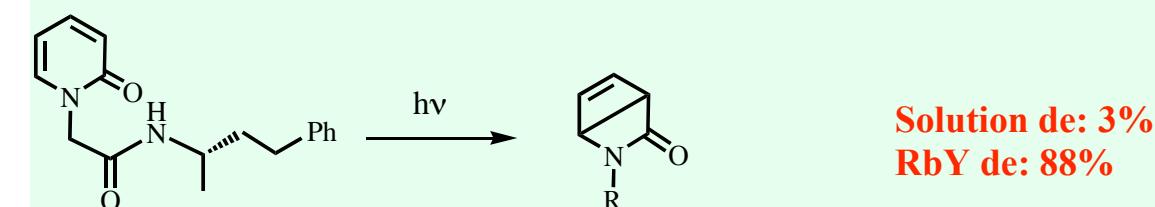
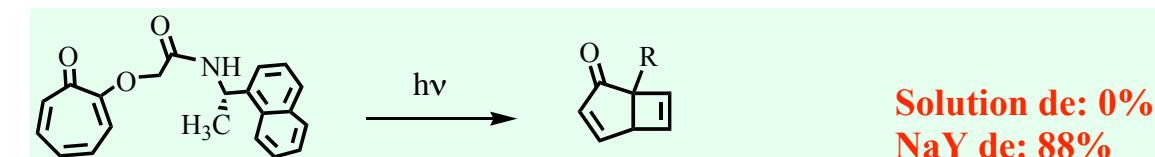
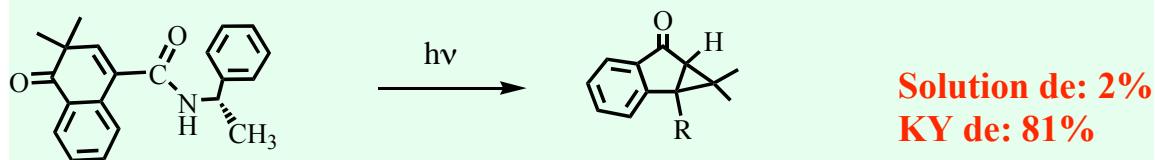
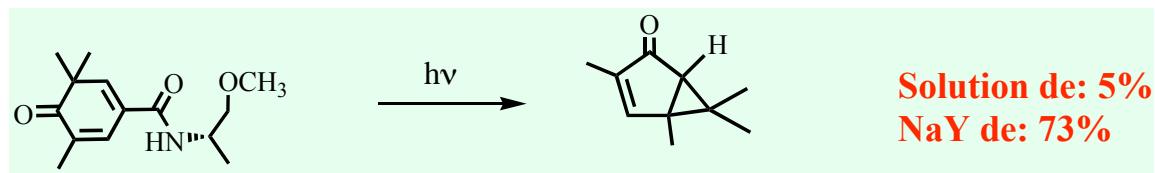
56%

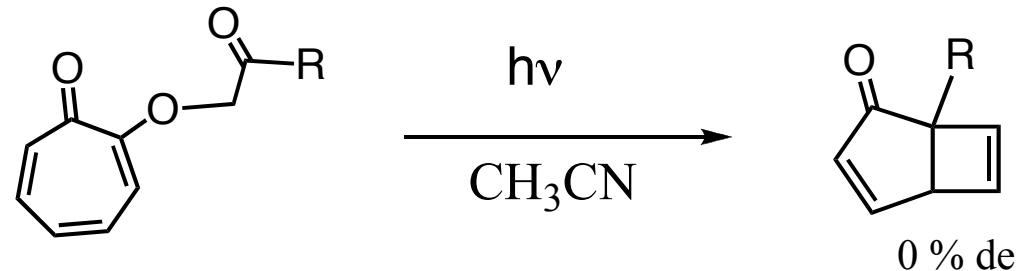
Conformational Control and Rotational Restriction



Asymmetric Photoreactions Within Zeolites







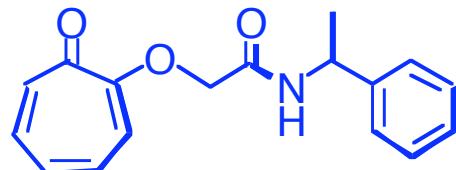
85 % de (NaY)



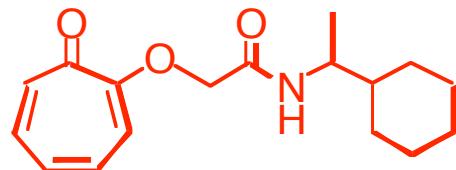
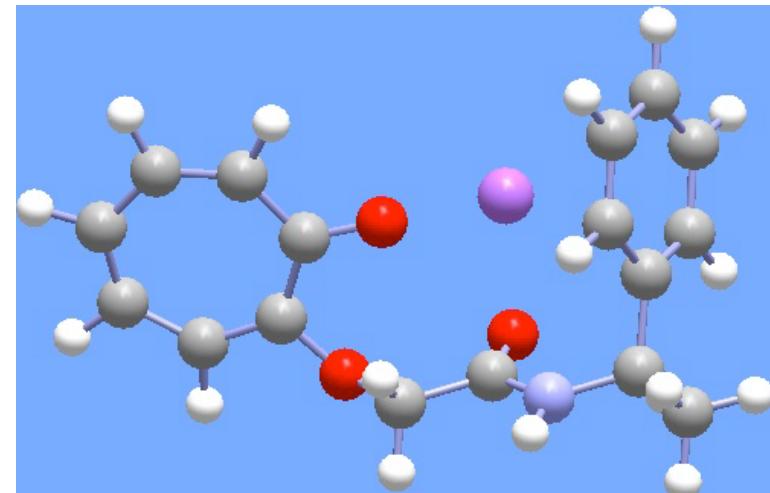
45 % de (NaY)

Importance of Cation-Chiral Auxiliary Binding: Phenyl vs Cyclohexyl

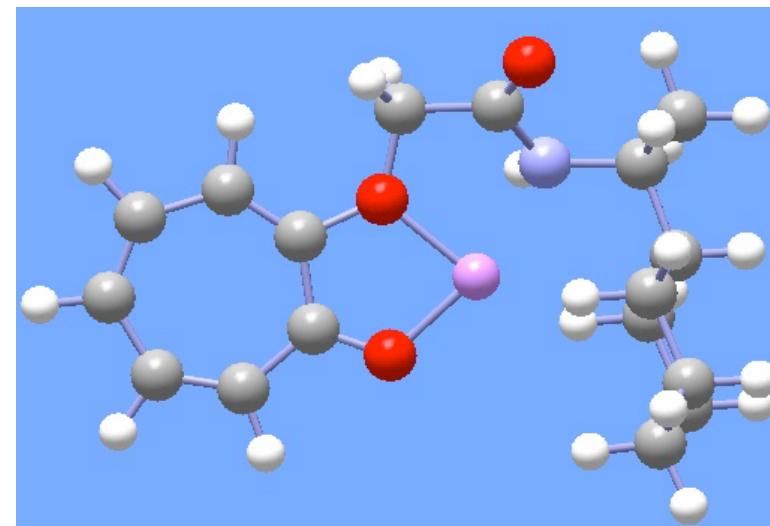
Gaussian 98 HF/ 3-21G *



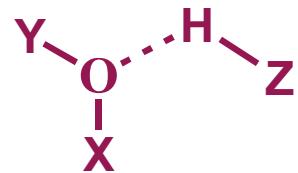
B.E (Na⁺ complex) = -96.89 kcal/mol



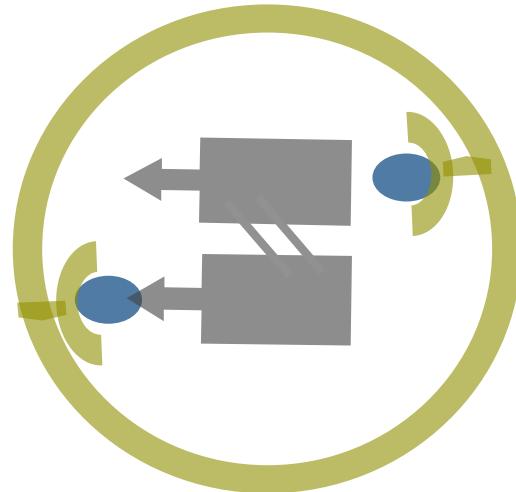
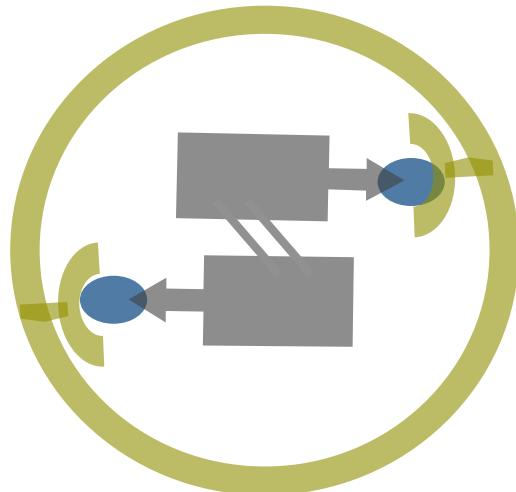
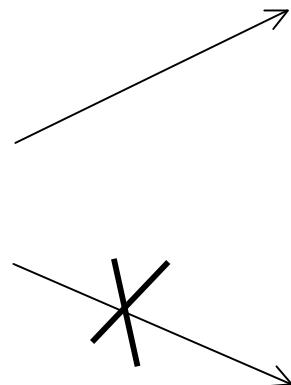
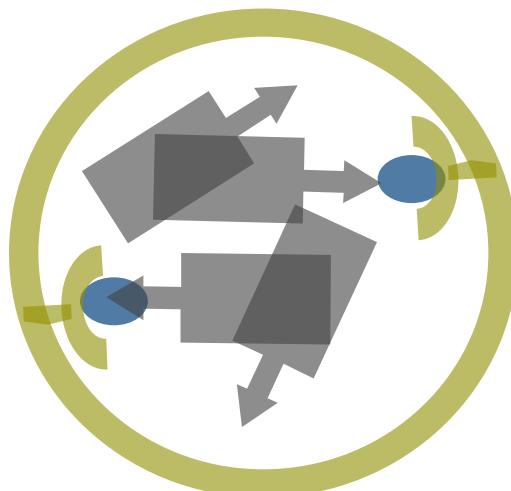
B.E (Na⁺ complex) = -75.49 kcal/mol



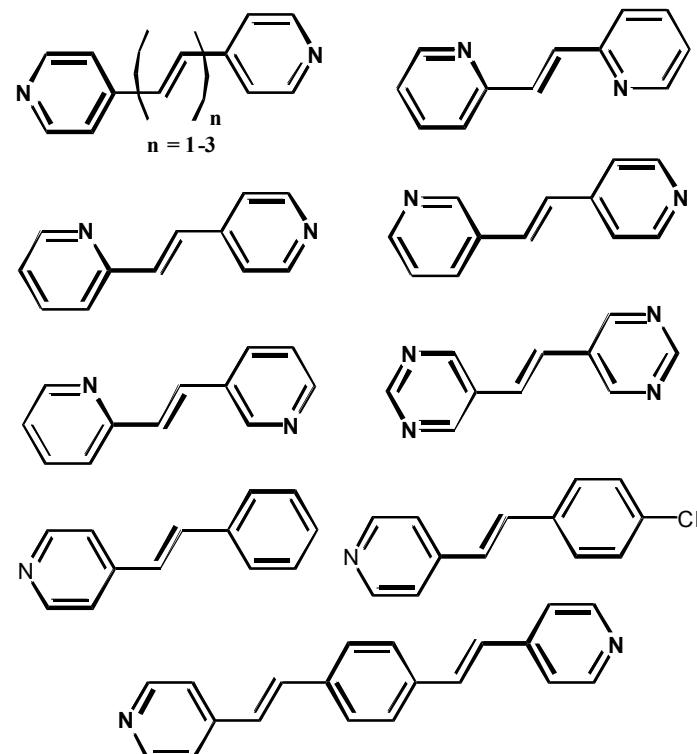
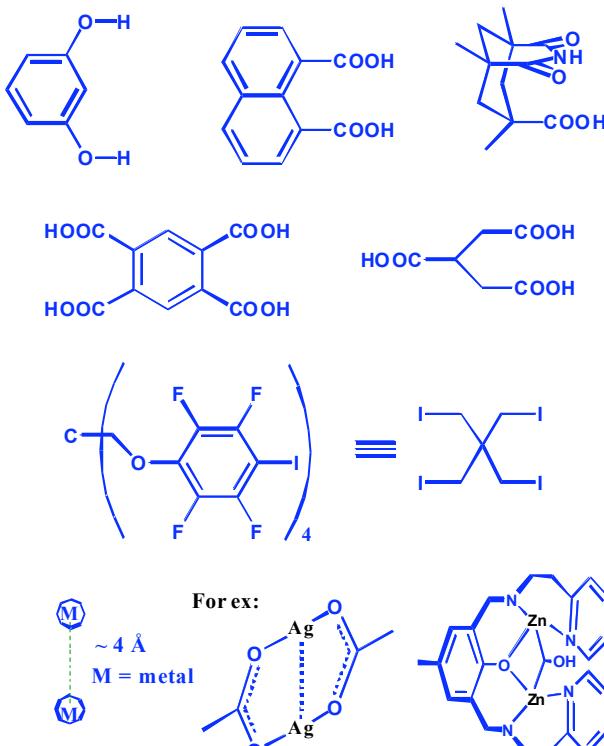
Pre-organization Through Weak Interactions



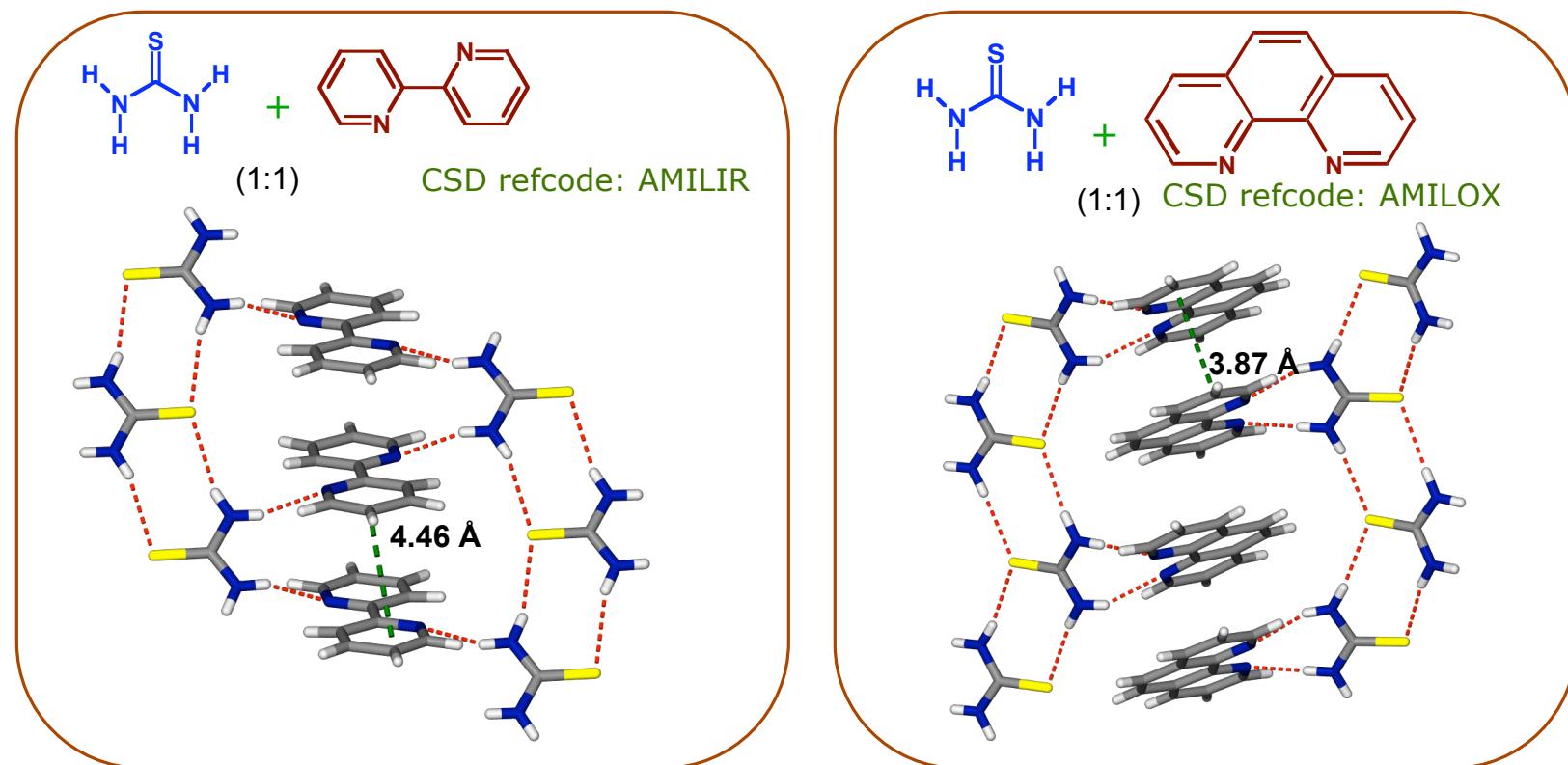
Hydrogen bond



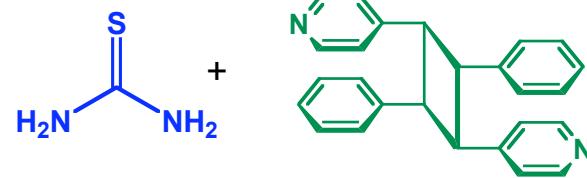
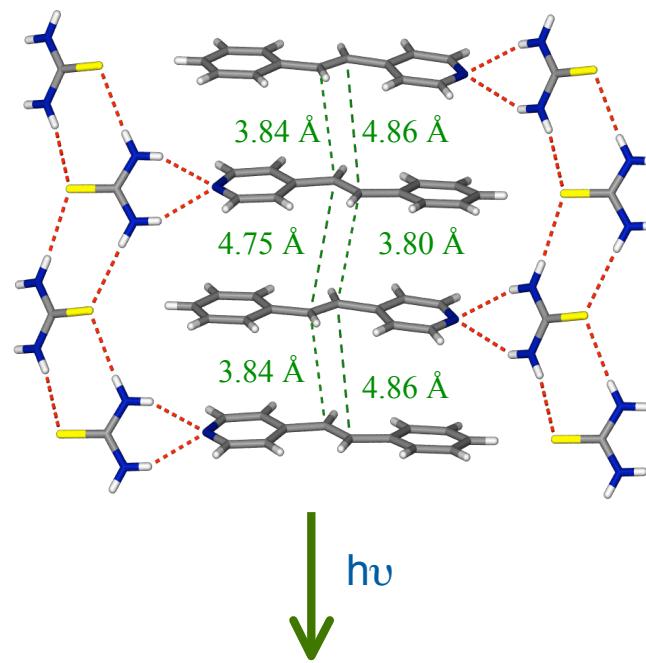
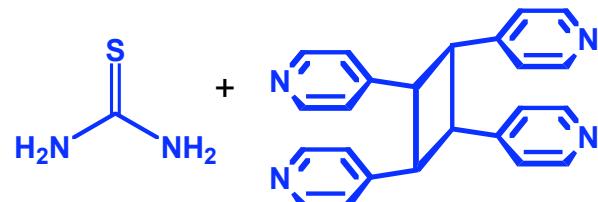
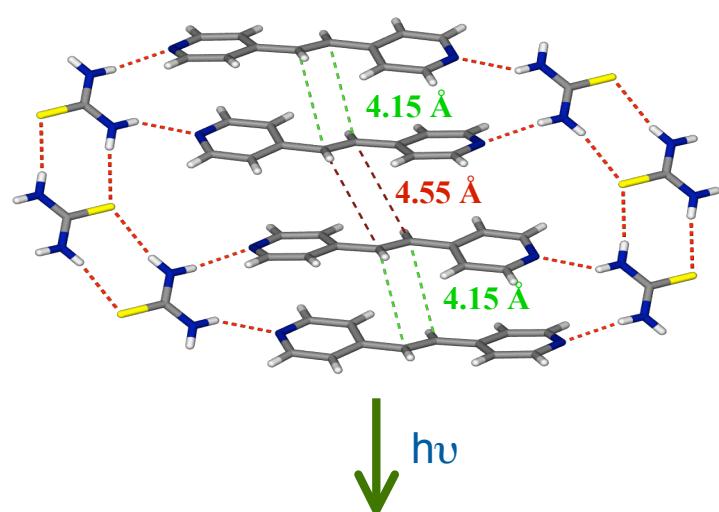
Overview of templated dimerization of olefins in solid-state



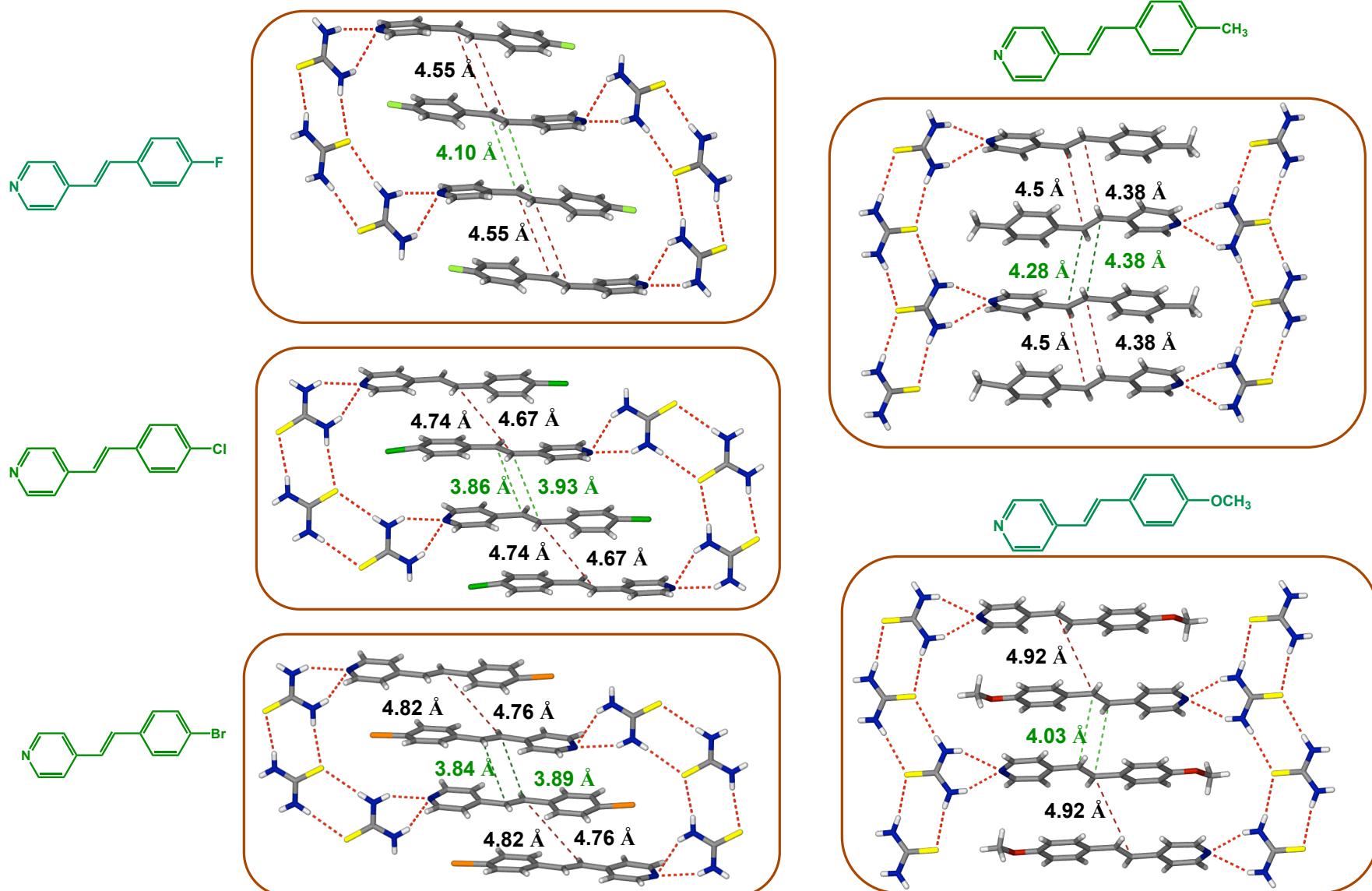
Thiourea as a possible template (Cambridge Structural Database)



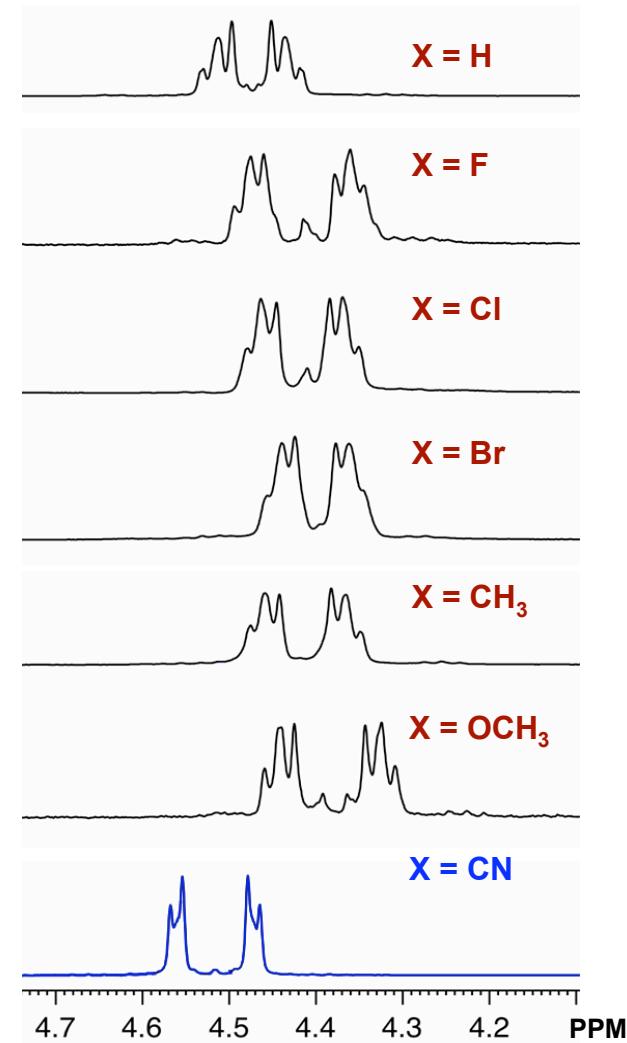
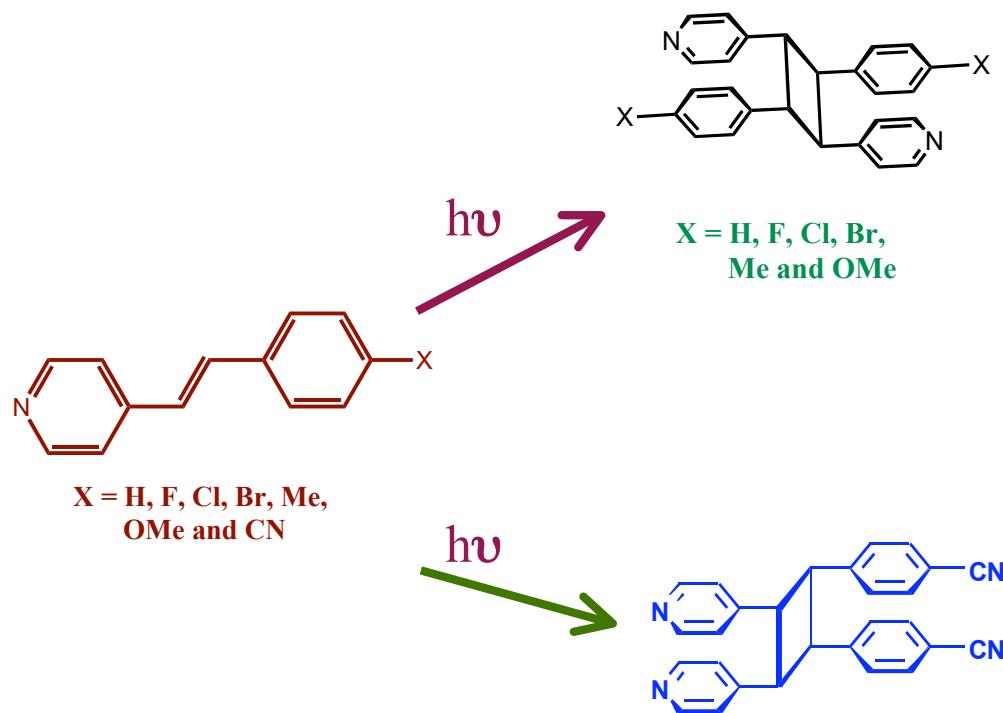
Photodimerization of 4,4'-bispyridyl ethylene and 4-stilbazole templated by thiourea



Thiourea templated photodimerization of stilbazoles – A general trend

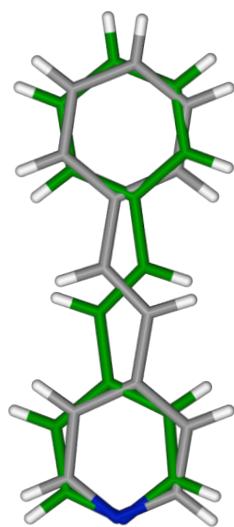
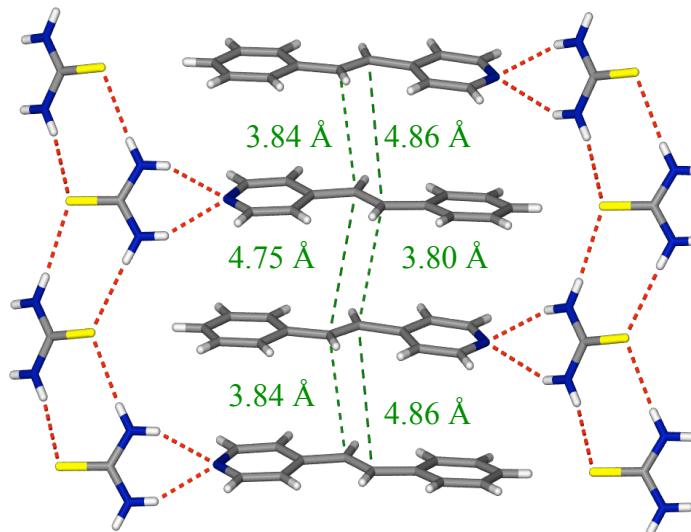
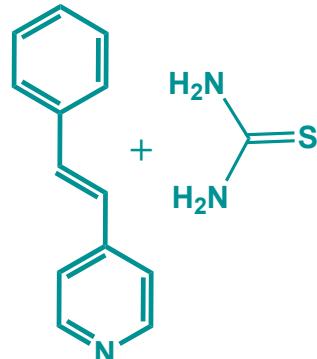
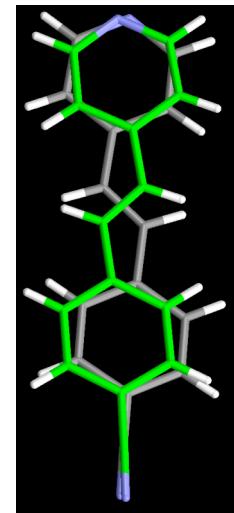
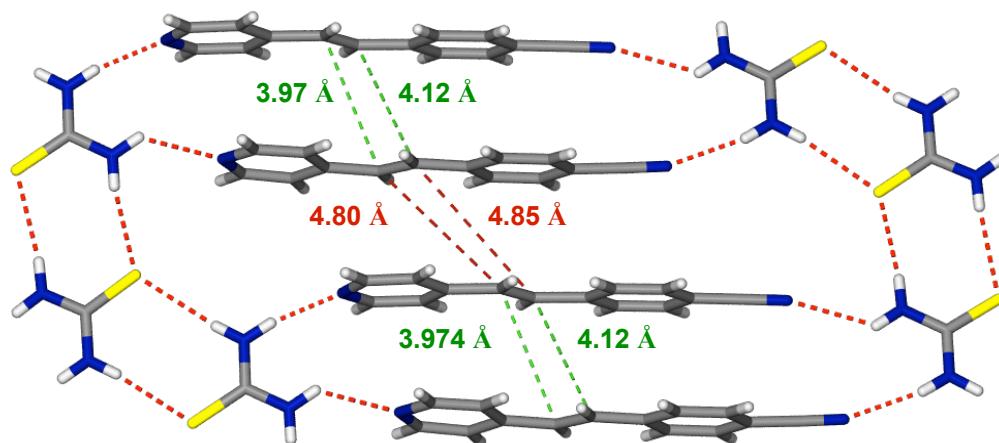
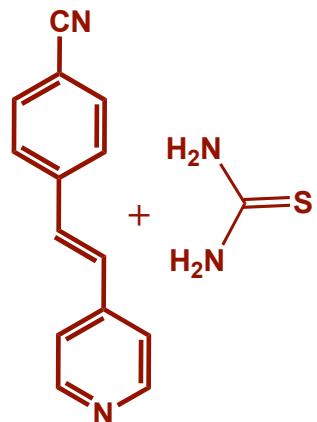


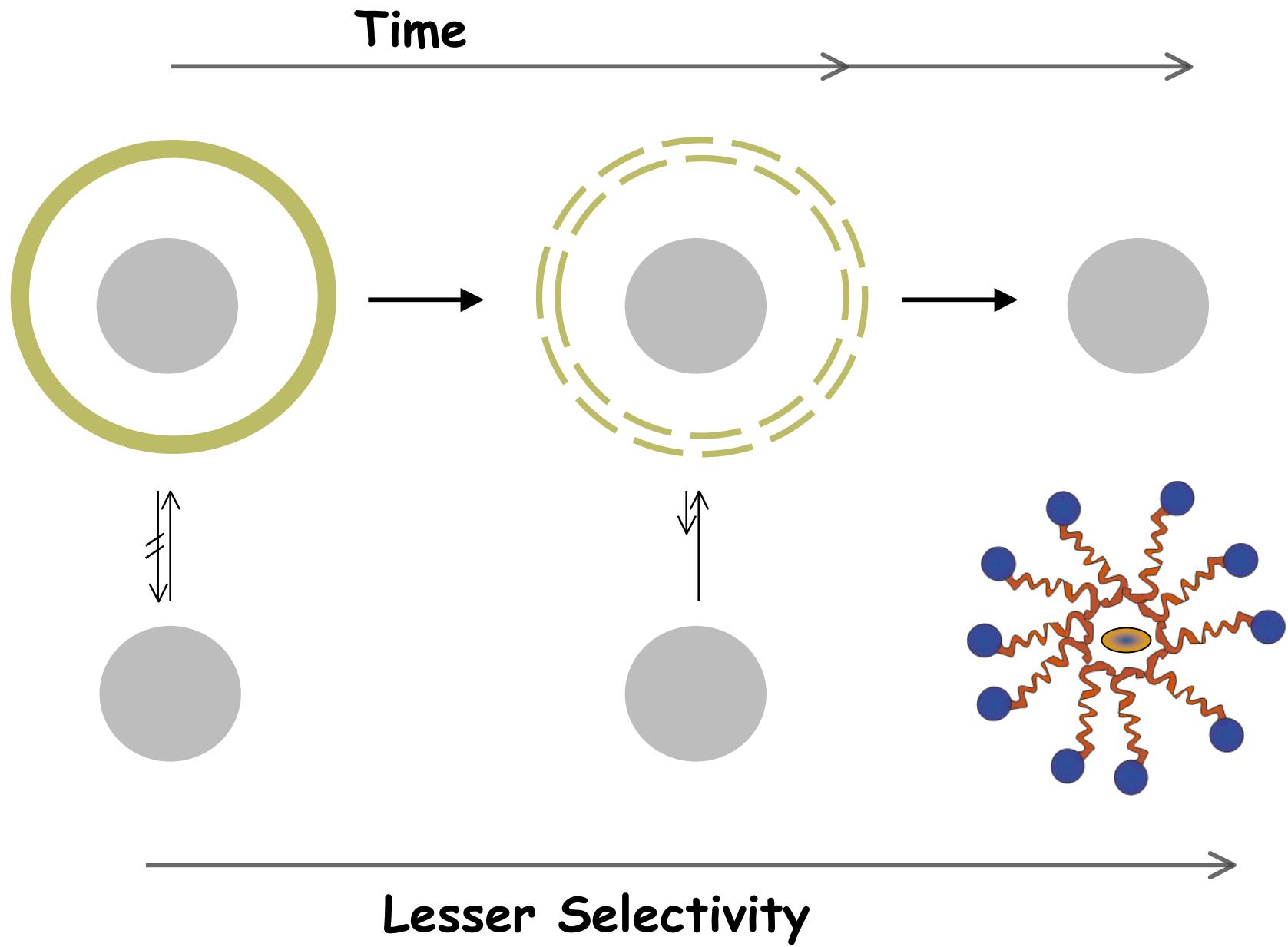
An overview of photochemistry of stilbazoles in thiourea co-crystals



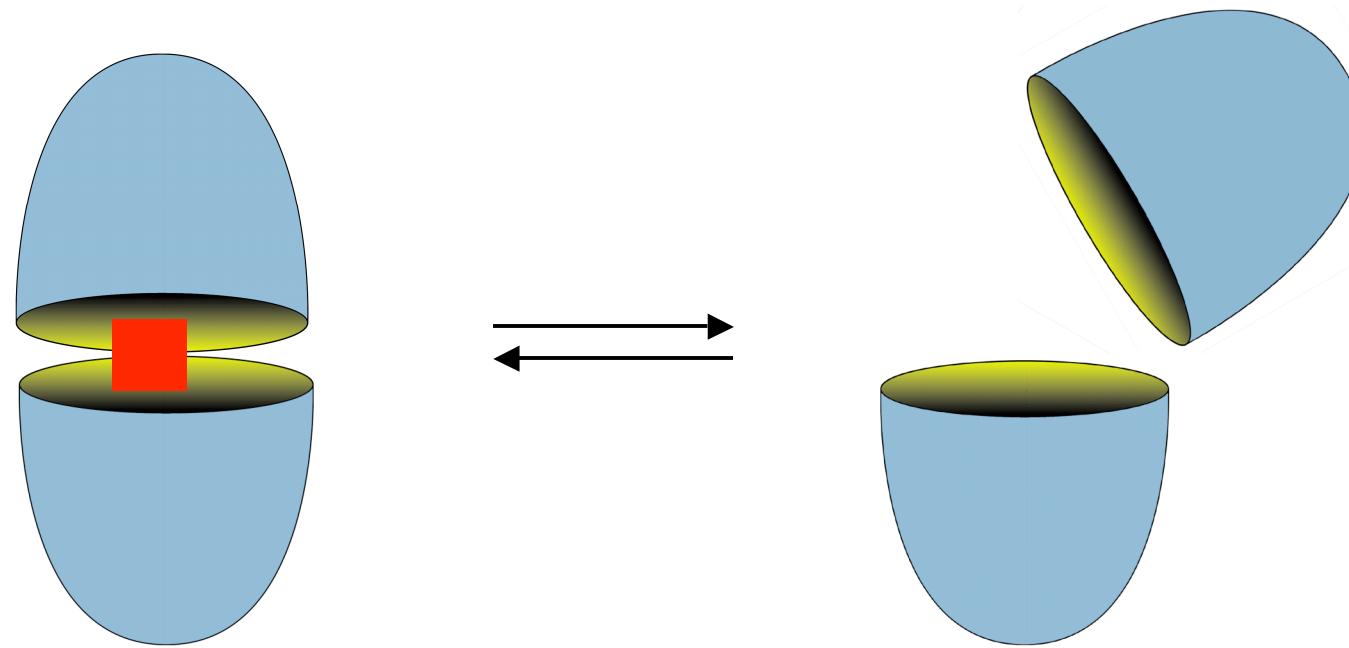
^1H NMR (CDCl_3) of cyclobutane protons in dimer products

Anomalous orientation of 4-cyanostilbazole in thiourea co-crystals



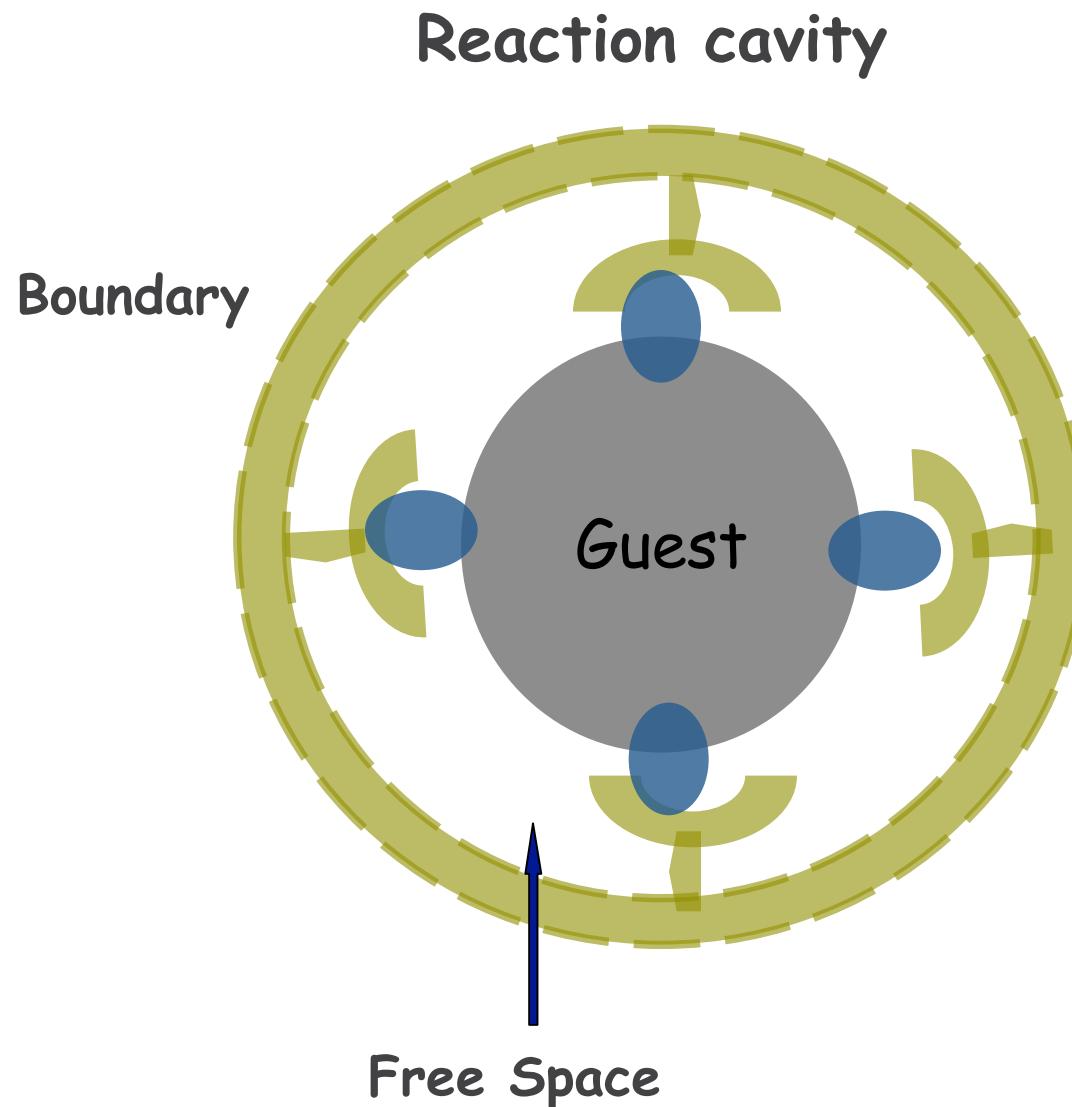


Dynamic Capsule

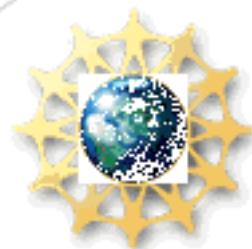


The opening-closing time may vary with the guest.

Controlling Reactions with Supramolecular Containers



Thanks for financial support



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