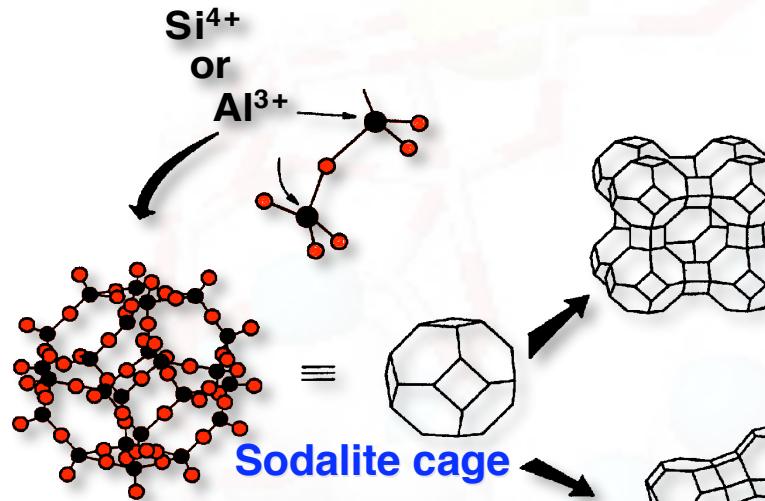
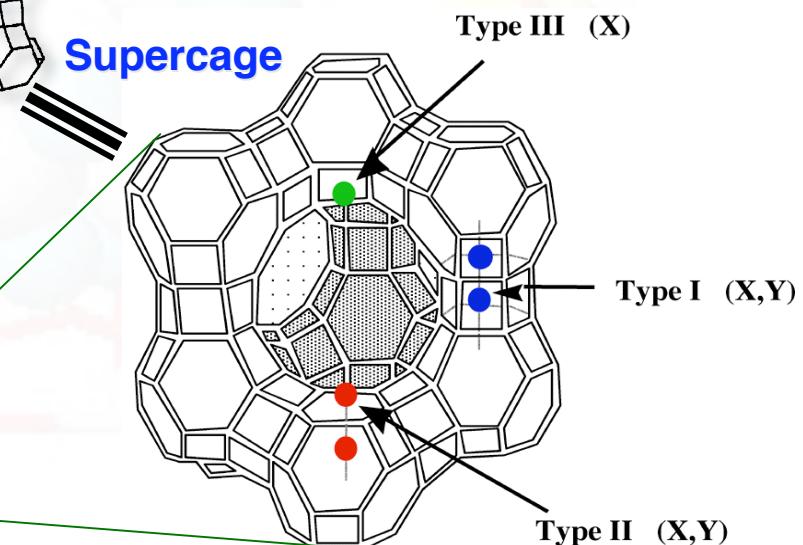
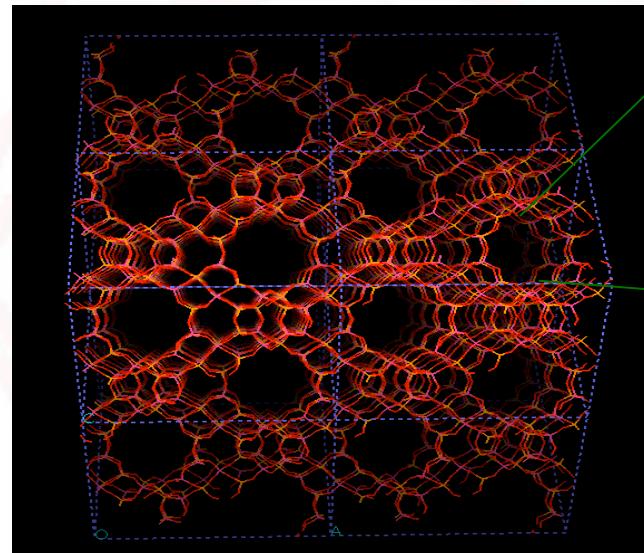


# Characteristics of Zeolite



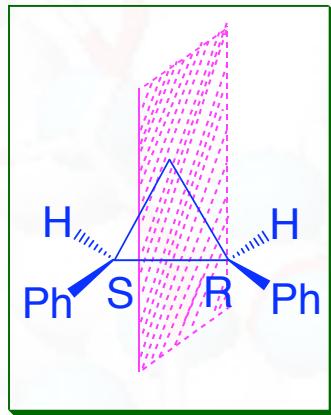
- Crystalline white powder
- Microporous solid
- Large surface area
- Well defined large pores
- Channels and cages

## Faujasite Y

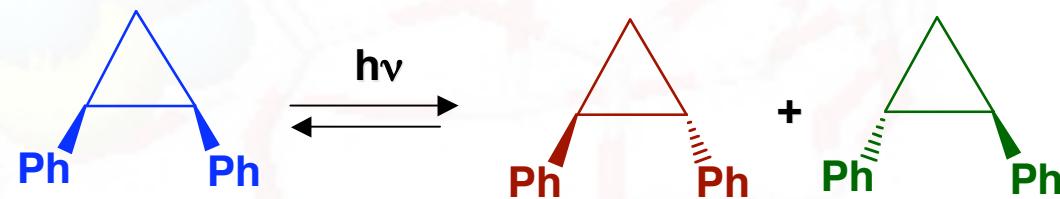


# Asymmetric Induction

## Chirality in Diphenylcyclopropane Systems.....

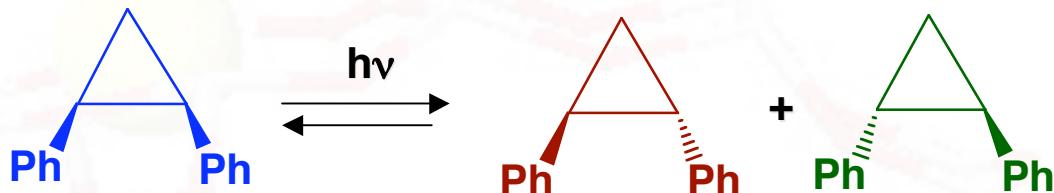


*Cis - Meso - Optically inactive*

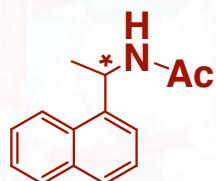


*Optically active*

*Singlet State or Triplet State*



Hammond, G. S. and Cole, R. S.  
*J. Am. Chem. Soc.* **1965**, p-3256



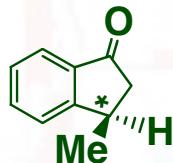
**ee = 6.7%**

Horner, L. and Klaus, J.  
*Liebigs Ann. Chem.*, **1979**, p-1232



**ee = 4.0 %**

Ouannes, C. Beugelmans, R. and Roussi, G.  
*J. Am. Chem. Soc.*, **1973**, p-8472



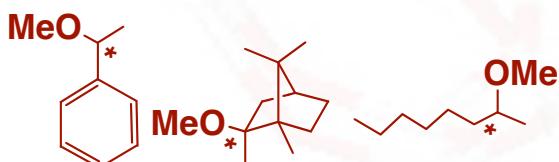
**ee = 3.0%**

Vondenhof, M. and Mattay, J.  
*Chem. Ber.*, **1990**, p-2457



**ee = 3.5%**

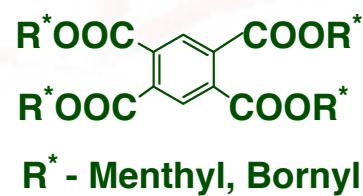
Faljoni, A. Zinner, K. and Weiss, R. G.  
*Tetrahedron lett.*, **1974**, p-1127



As chiral solvents

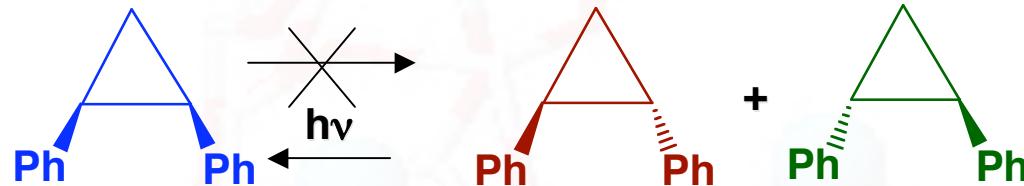
**ee = 2.3%**

Inoue, Y. Shimoyama, H. Yamasaki, N. and Tai, A.  
*Chem. lett.*, **1991**, p-593

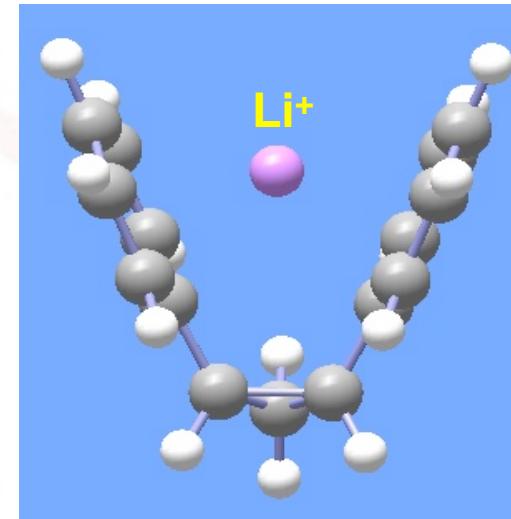


**ee = 10.4 %**

# ZEOLITES



V. Ramamurthy, et.al. JACS, 2000, (122), 4815–4816.

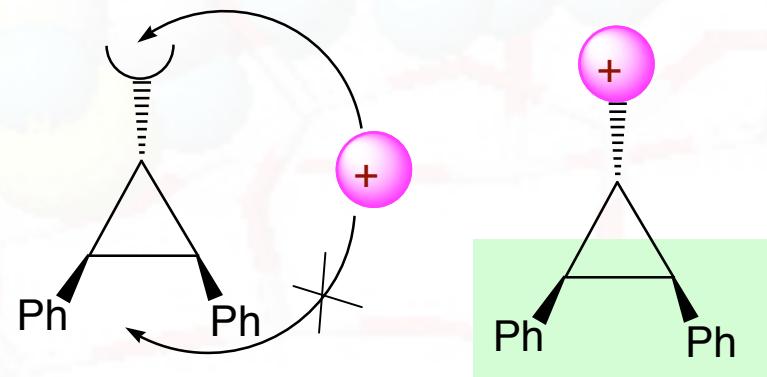


$\text{BA} = 66.83 \text{ kcal/mol}$

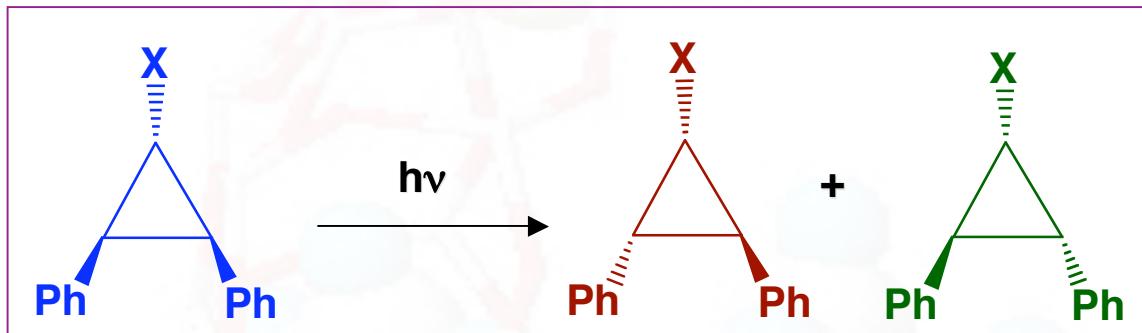
B3LYP / 6-31G\*

Steering the photoisomerization towards the trans-isomer...

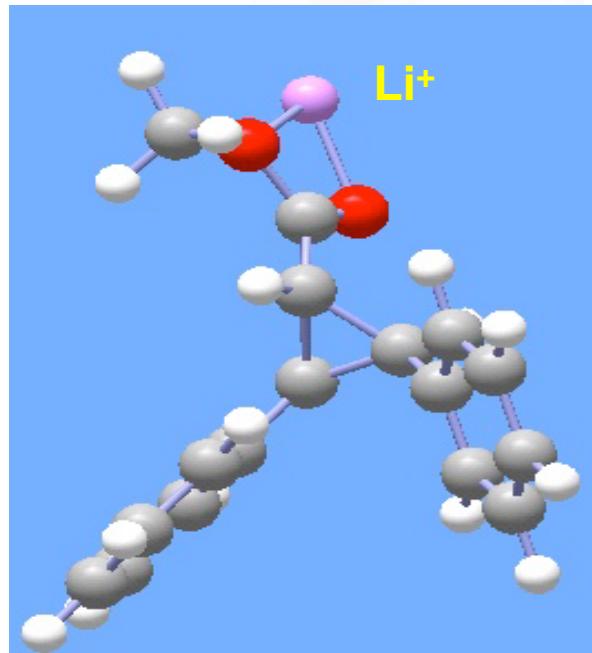
Two sites available for  
the cation to bind



# Need for substitution at the 1-position....

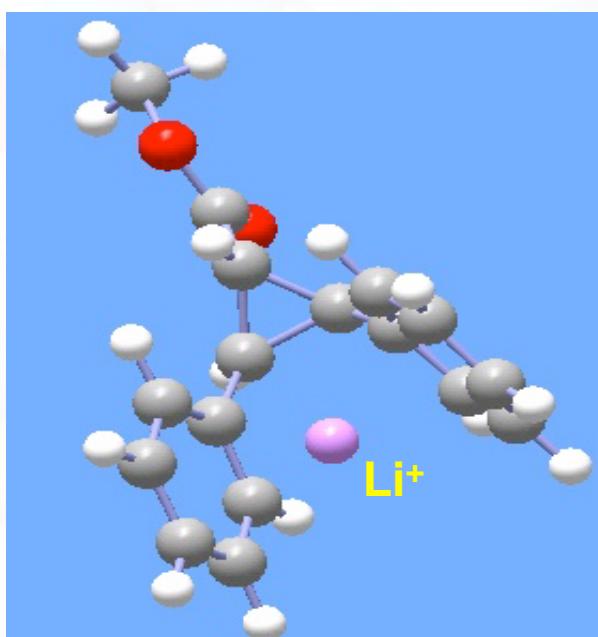


X = -COOR = Ester  
X = -CONHR = Amide  
X = COAr = Ketones



BA = 65.70 kcal/mol

B3LYP / 6-31G\*

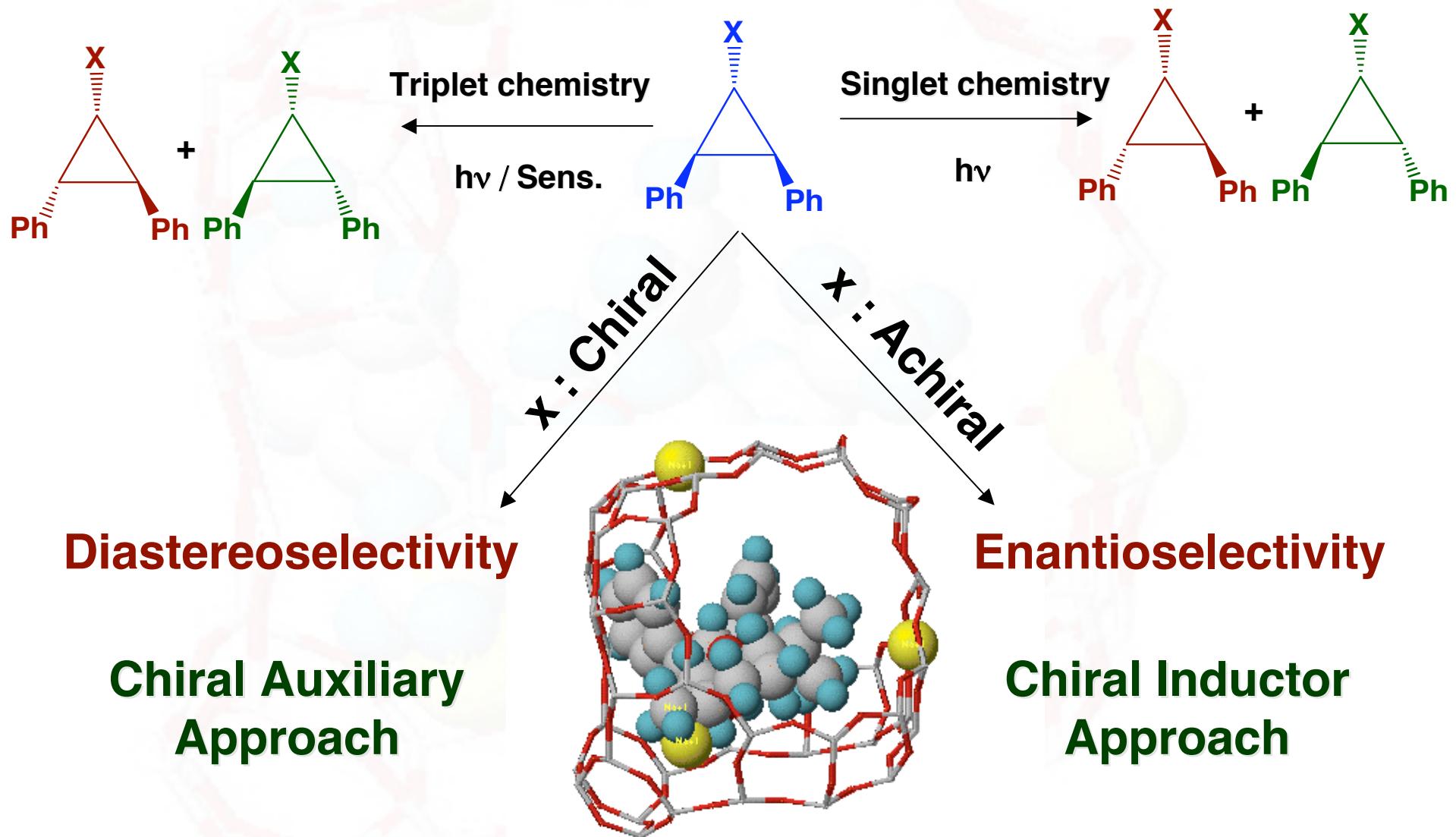


BA = 64.69 kcal/mol

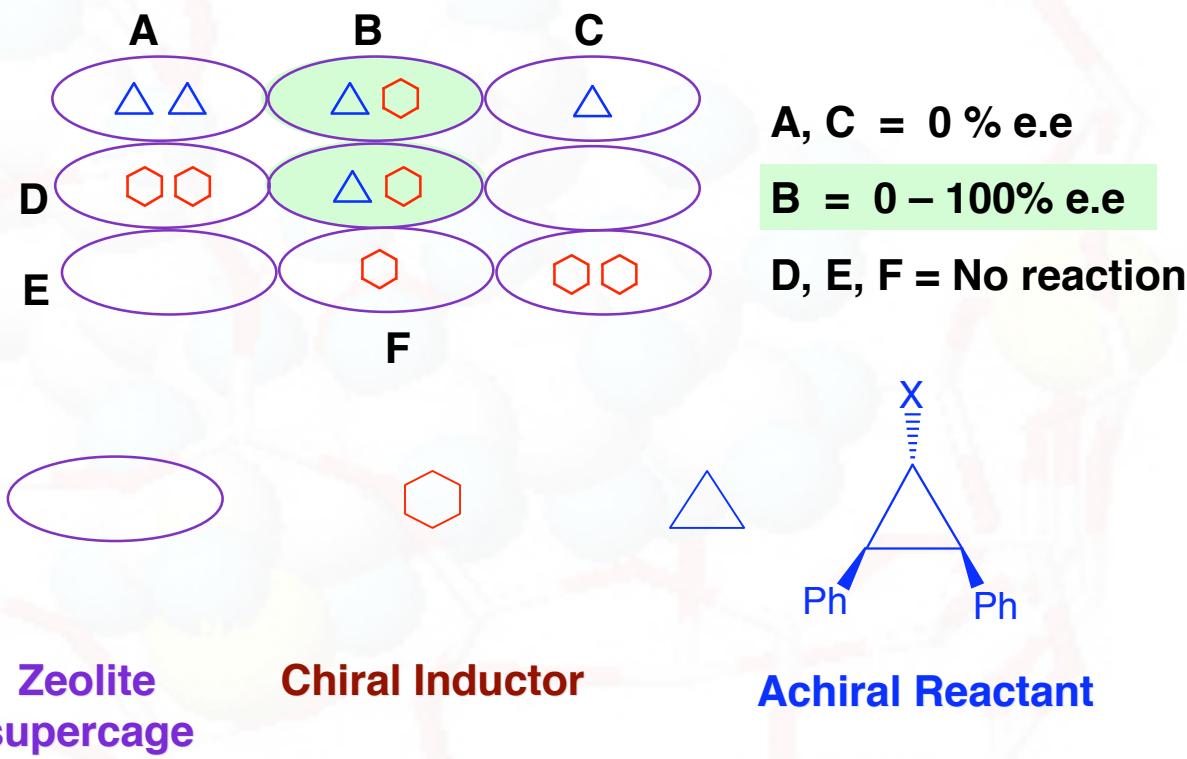
X=COOMe	Zeolite	Cis : Trans
	LiY	45 : 55
	NaY	39 : 61
	KY	40 : 60
	RbY	39 : 61
	CsY	37 : 63

4'-methoxyacetophenone  
as sensitizer

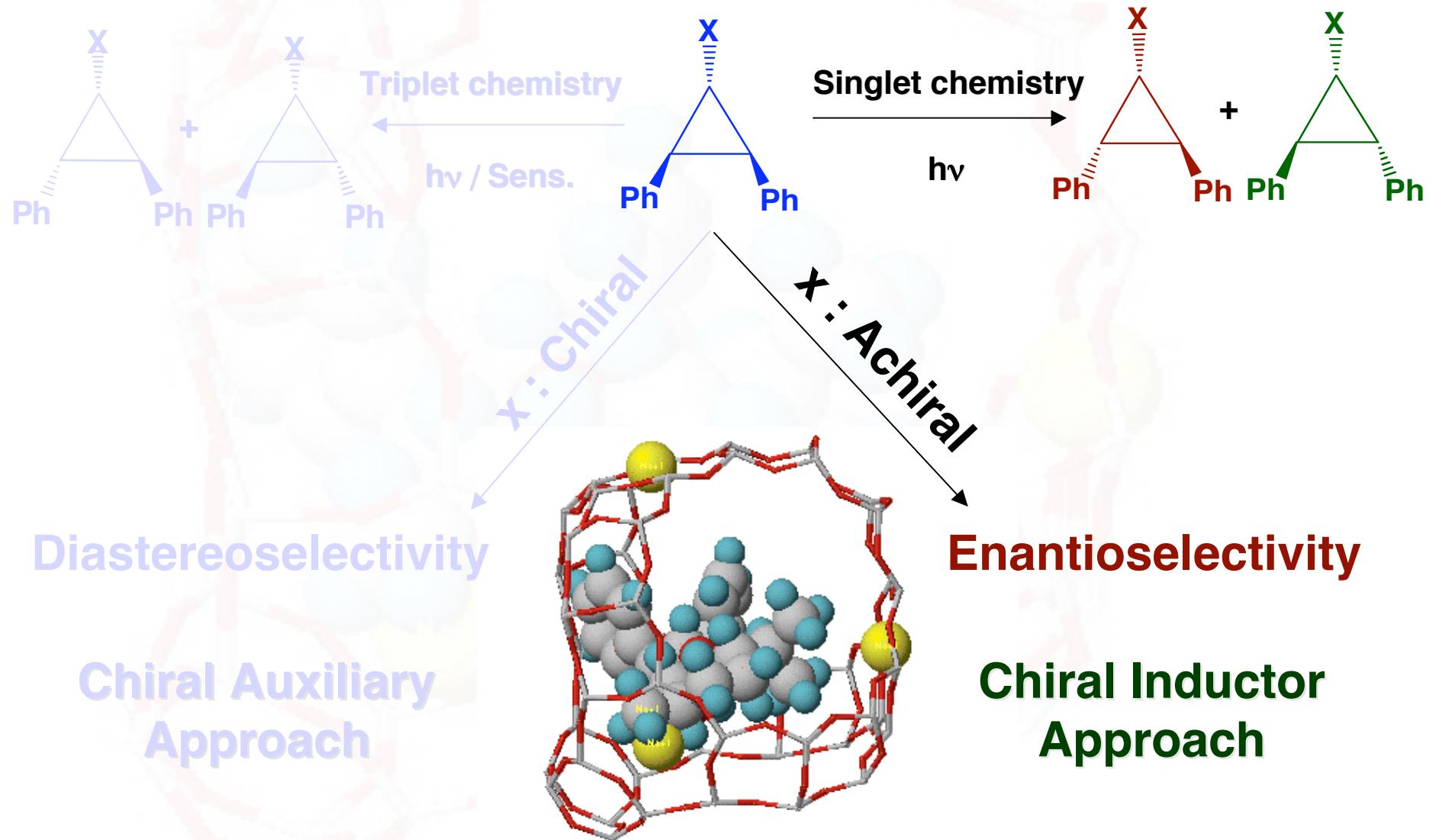
# Asymmetric Induction within Zeolites



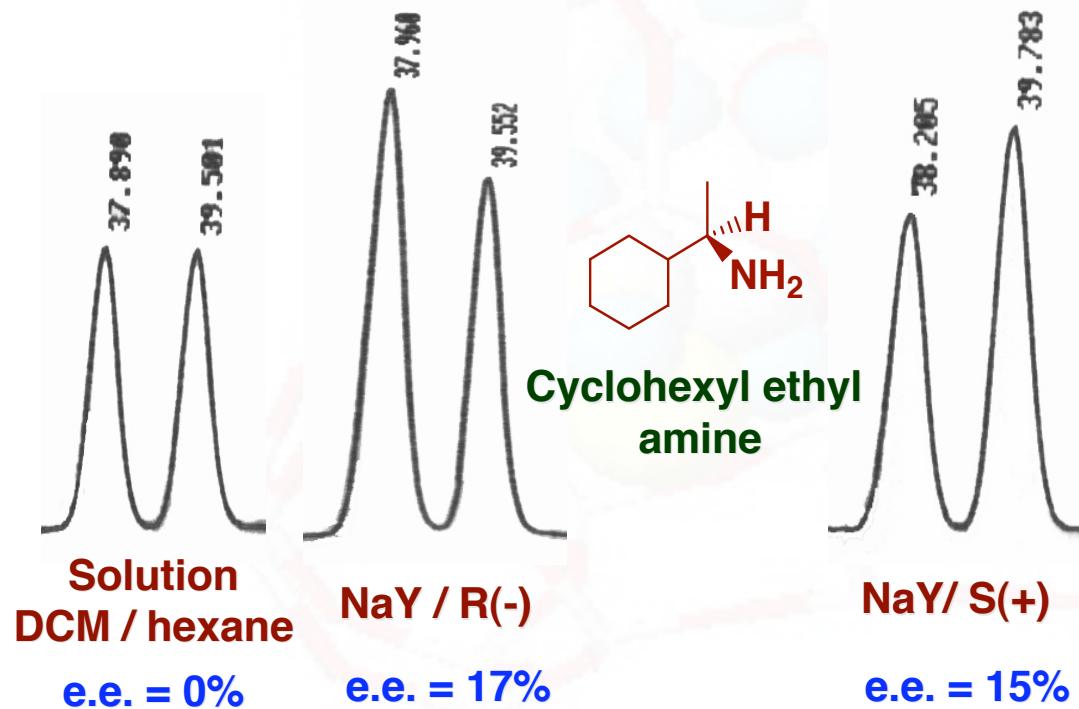
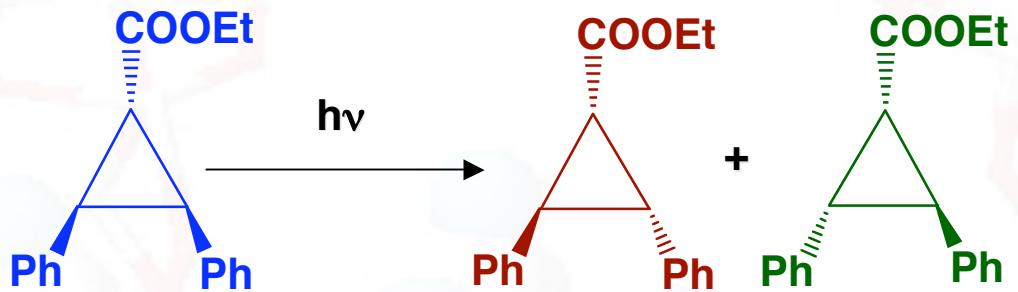
# Chiral Inductor Approach



# Asymmetric Induction within Zeolites

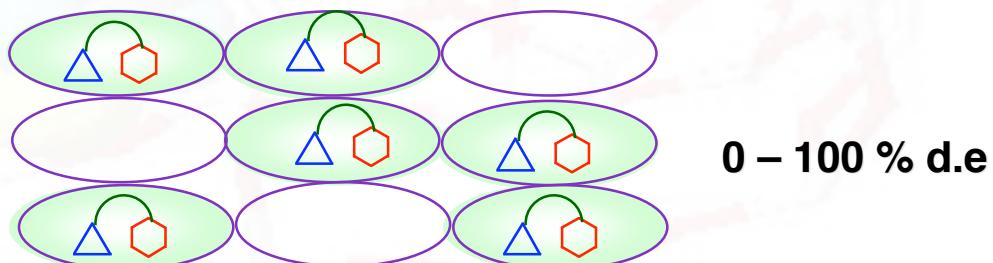
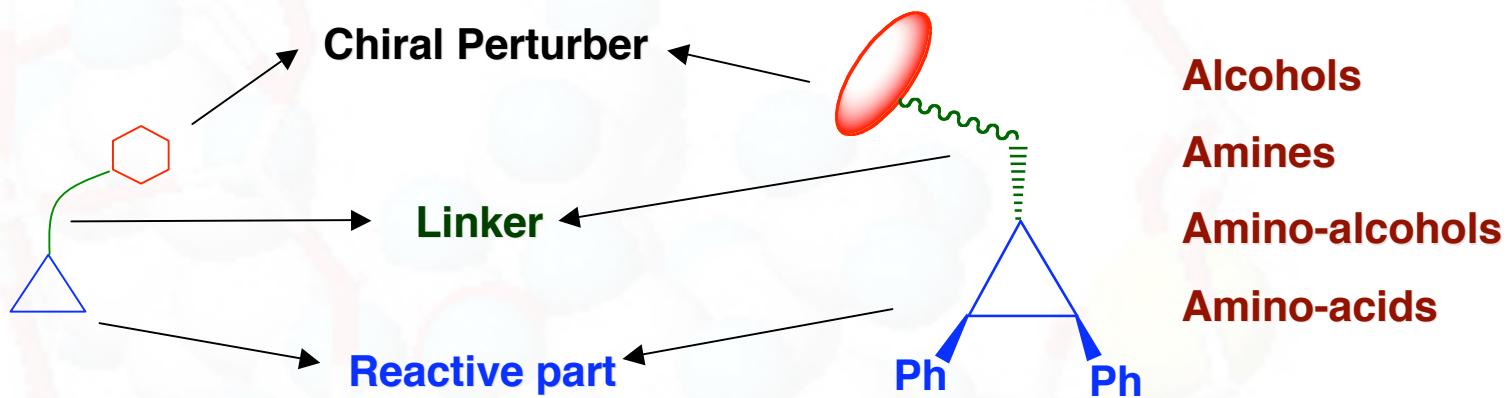


# Enantioselectivity – Chiral Inductor Approach

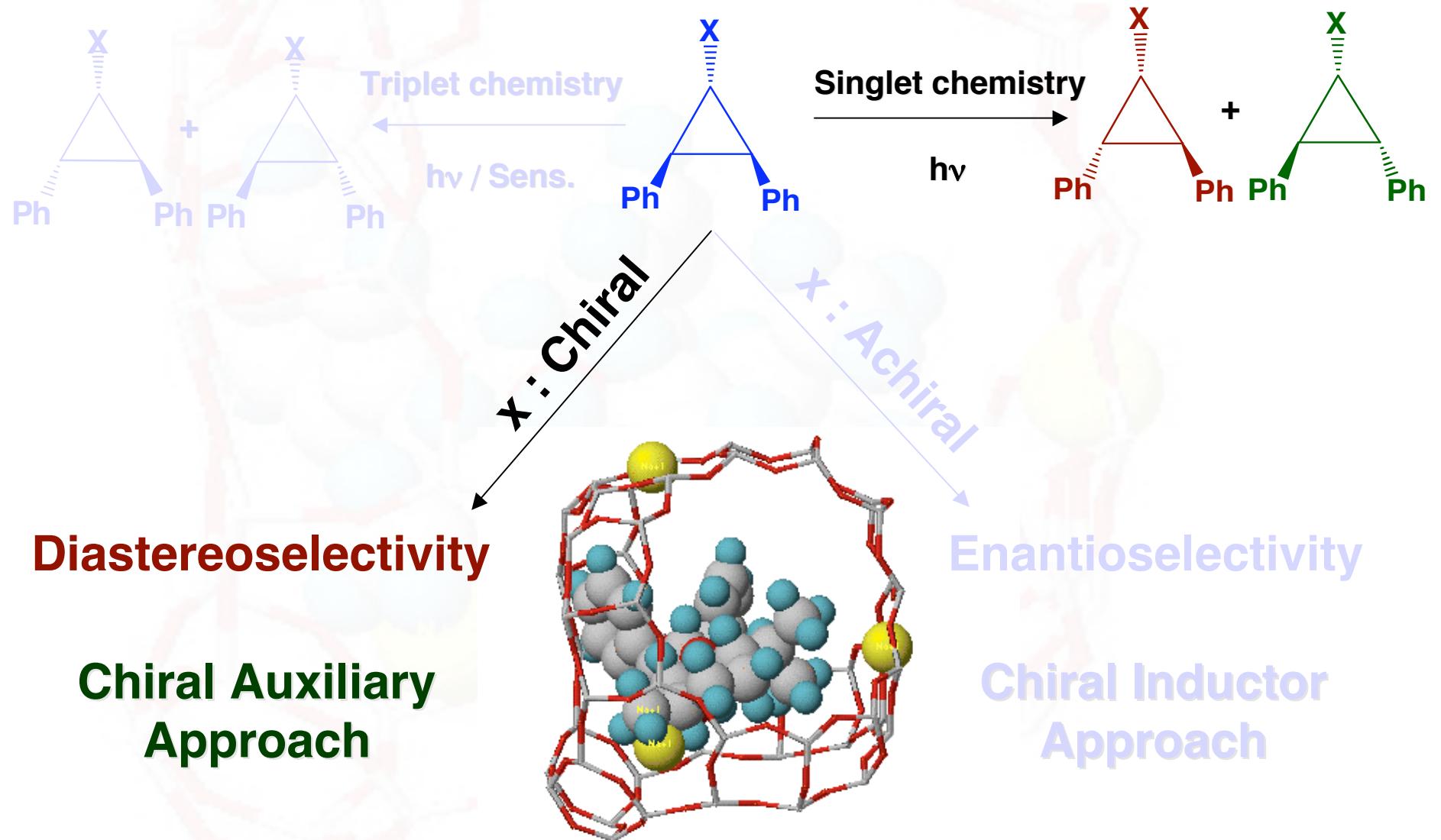


	D(+)-Norephedrine 5% (B)
	(+)-Pseudoephedrin 5% (B)
	(-)-Menthol 0%
	S(-)-Phenylethyl amine 0%

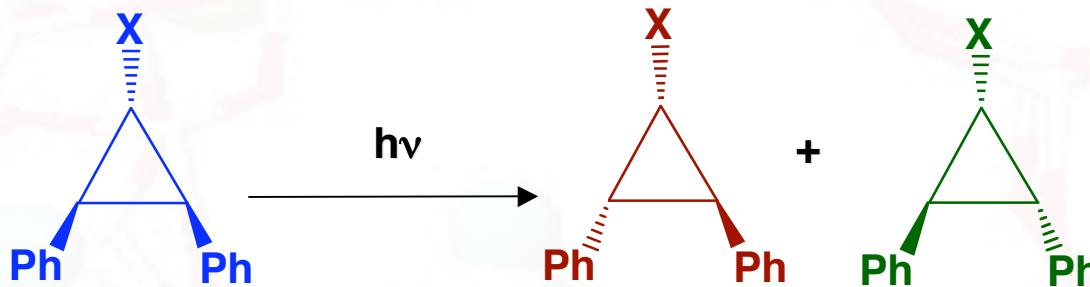
# Chiral Auxiliary Approach



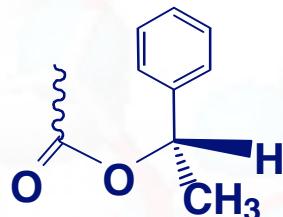
# Asymmetric Induction within Zeolites



# Selected Examples



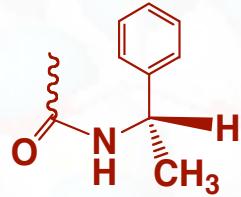
## Esters



1-Phenylethyl

LiY : 78%

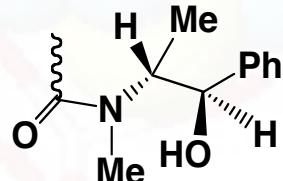
## Amides



1-Phenylethyl

LiY : 80%

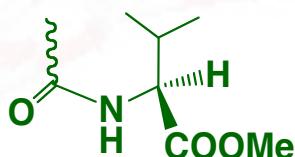
## Amino Alcohols



(-) -Pseudoephedrine

NaY : 89%

## Amino Acids



L-Valine methyl ester

LiY : 83%

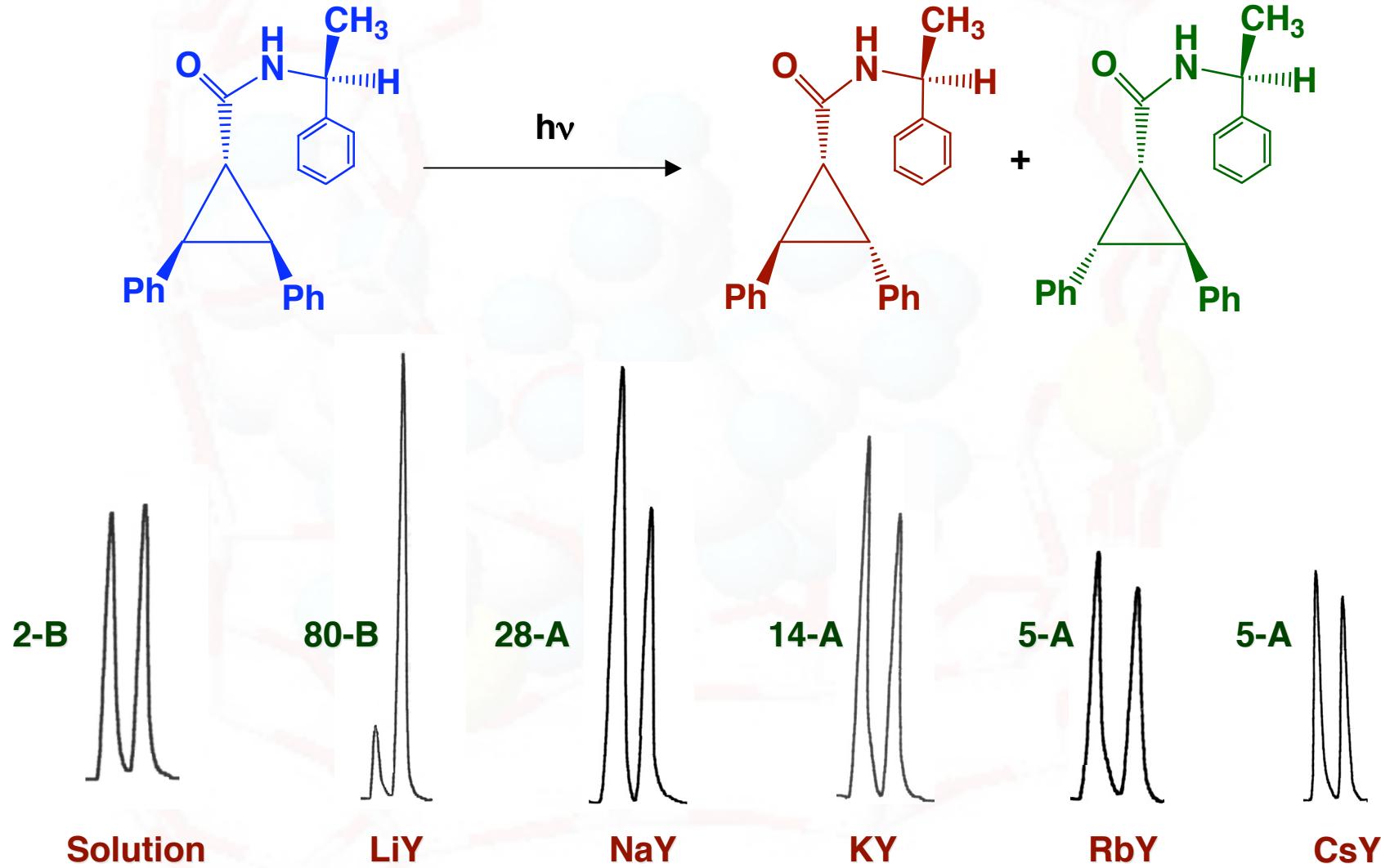
# **Asymmetric Photoreactions Within Zeolites**

**Modest to Good Chiral Induction**

**Factors that Control Asymmetric Induction**

**Generalization**

# Chiral Induction Depends on the Alkali Metal Ion



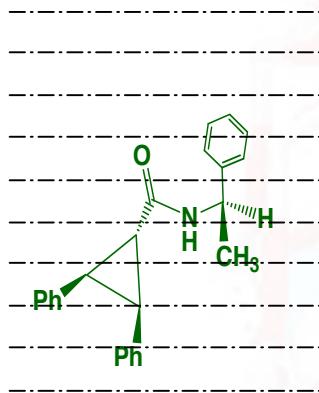
# Asymmetric Photoreactions Within Zeolites

Modest to Good Chiral Induction

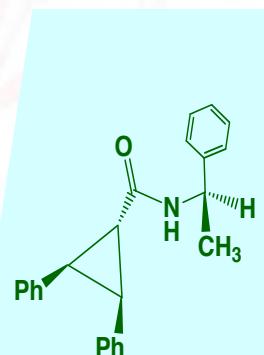
Chiral Induction Depends on

- Type of cations in the zeolite

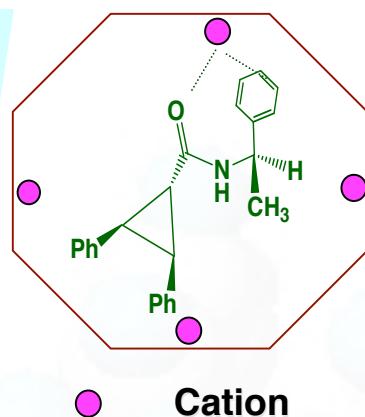
## Solution (Isotropic media)



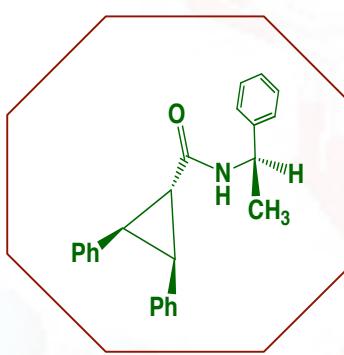
## Silica



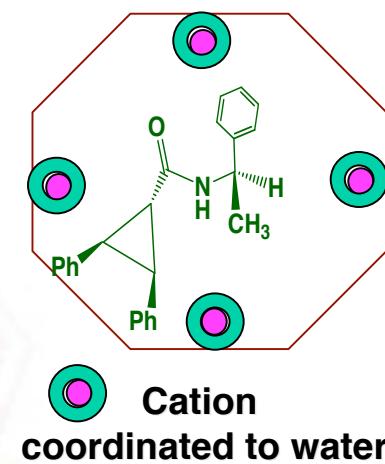
## Zeolite-Y moisture free



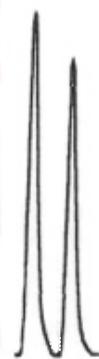
## Zeolite-Y with less # of cations



## Zeolite -Y wet



2-B



8-A



80-B



10-A



8-A

LiY (DRY)

Si/ Al = 2.4

Cations/unitcell: 64

LiY

Si/ Al = 40

Cations/unitcell: 5

LiY (WET)

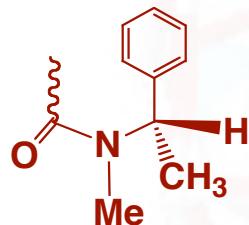
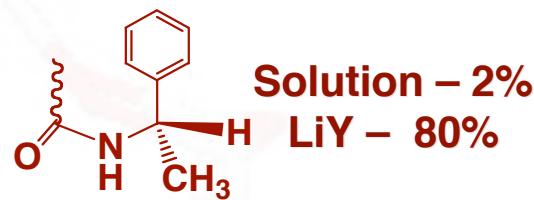
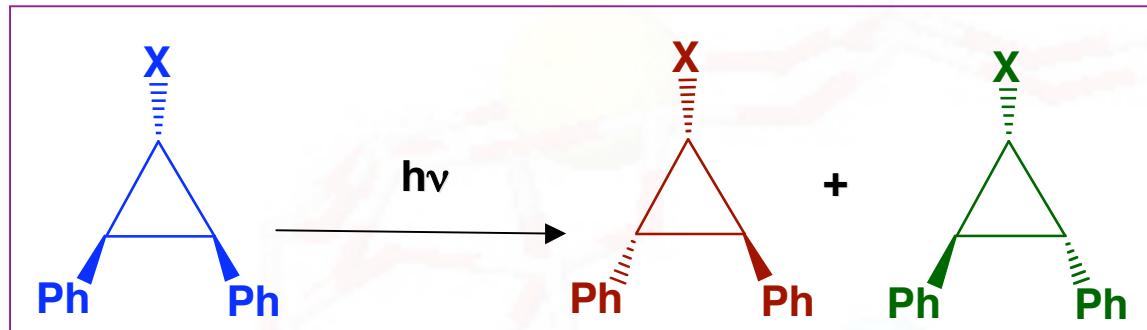
Si/ Al = 2.4

# Asymmetric Photoreactions Within Zeolites

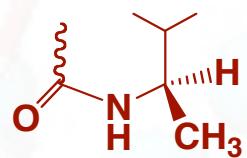
## Modest to Good Chiral Induction

### Chiral Induction Depends on

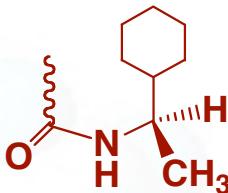
- Type of cations in the zeolite
- Water Content
- Number of Cations (Si/Al ratio)



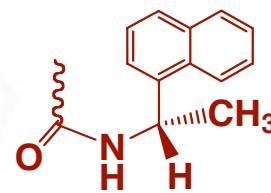
Solution – 5%  
NaY – 15%



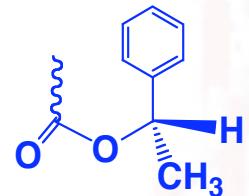
Solution – 2%  
CsY – 23%



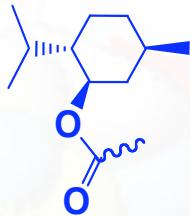
Solution – 2%  
CsY – 37%



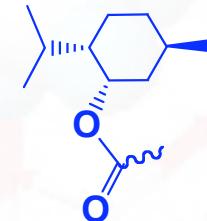
Solution – 0%  
LiY – 70%



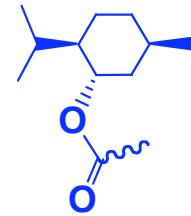
Solution – 4 %  
NaY – 78%



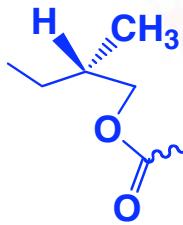
Solution – 4%  
NaY – 55%



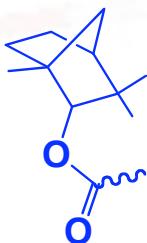
Solution – 5%  
NaY – 32%



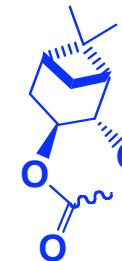
Solution – 3%  
NaY – 40%



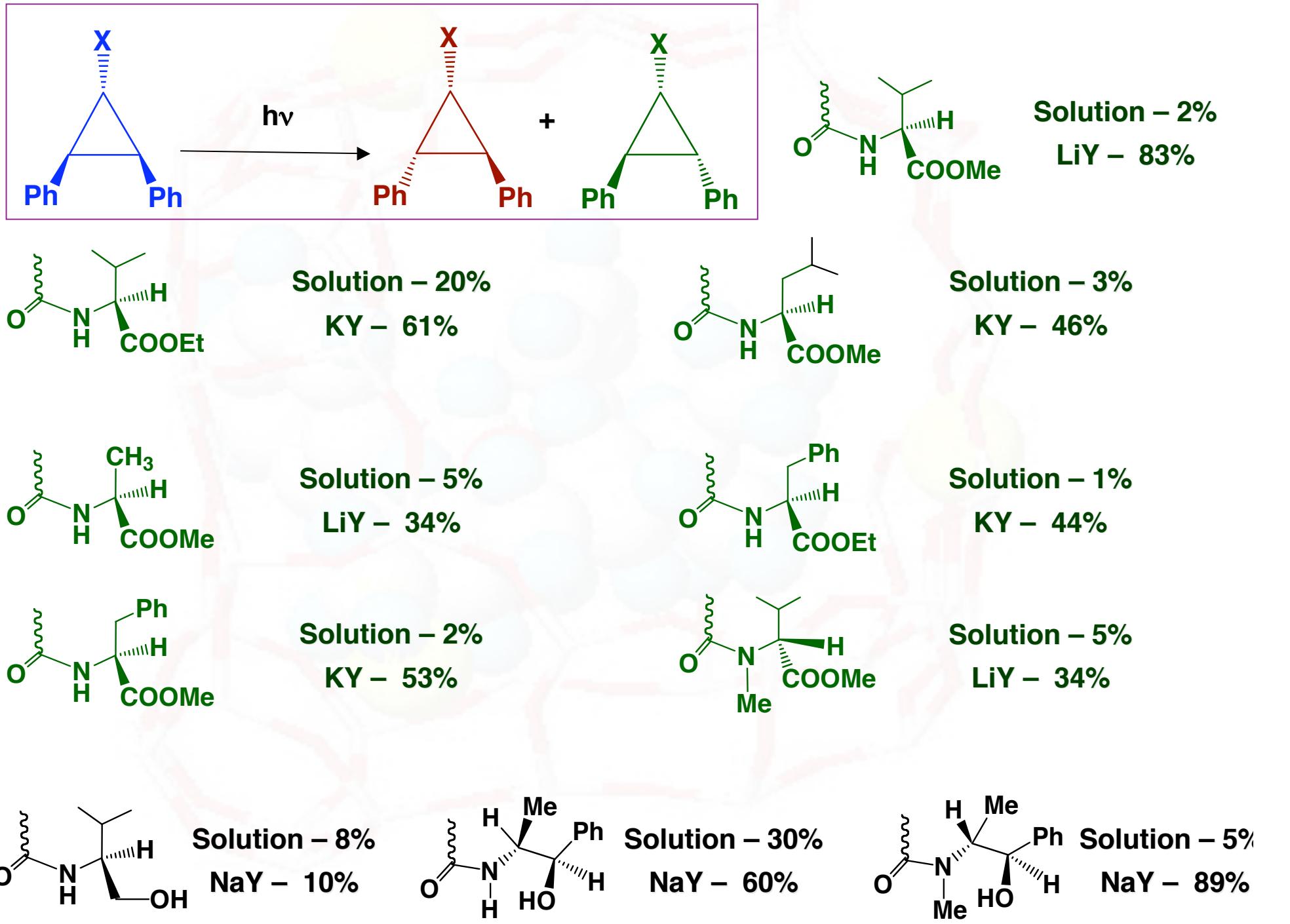
Solution – 0%  
NaY – 19%



Solution – 4%  
NaY - 16%

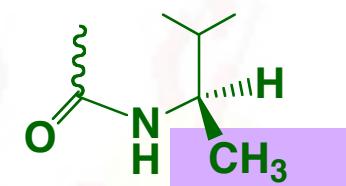
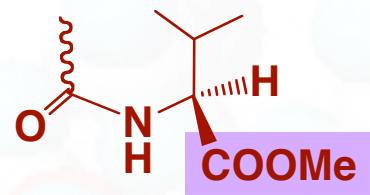
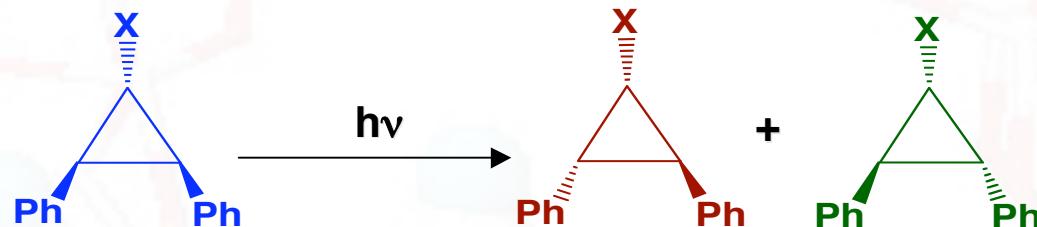


Solution – 5%  
CsY – 13%



# Role of Cation-Carbonyl Dipolar Interaction

## Carboalkoxy vs Alkyl



Zeolite

% d.e.

% d.e.

LiY

83-B

7-A

NaY

28-A

7-A

KY

80-A

7-B

RbY

47-A

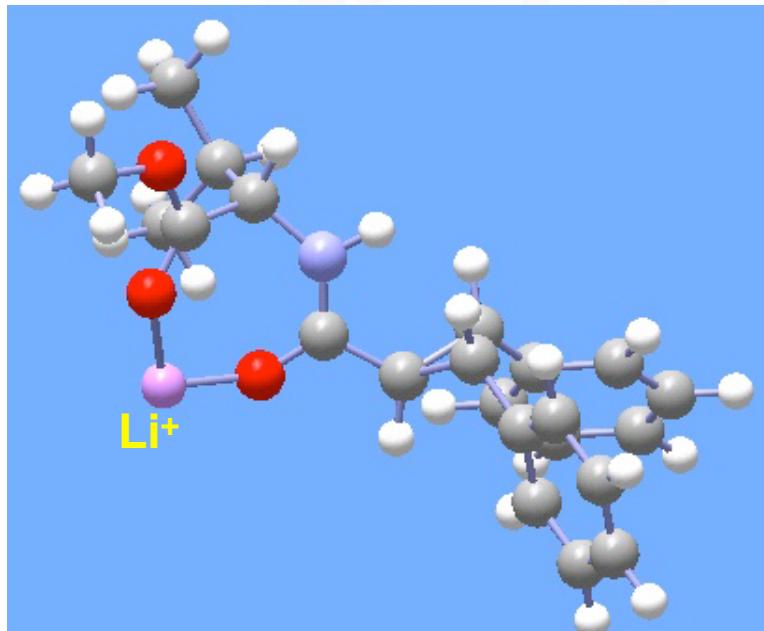
12-B

Solution

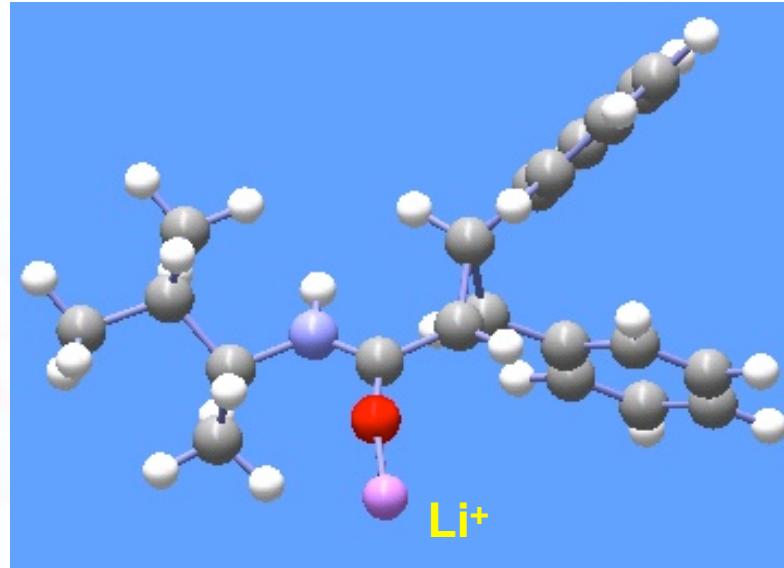
2-B

2-B

# Role of Cation-Carbonyl Dipolar Interaction

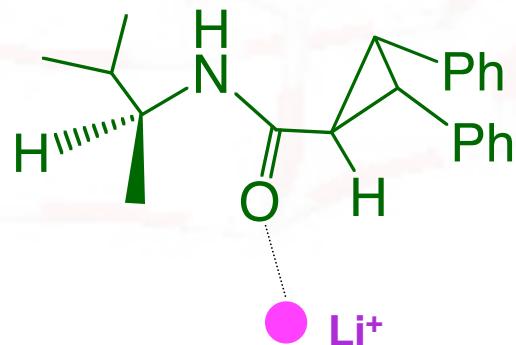
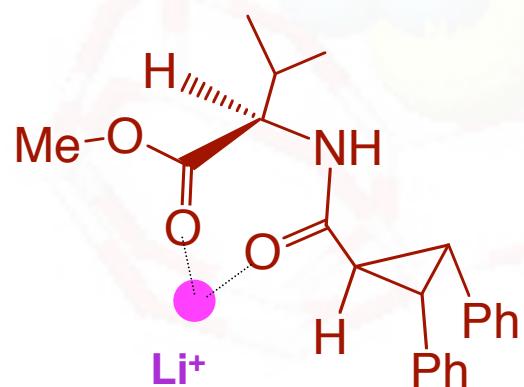


**BA = 104.10 kcal/mol**



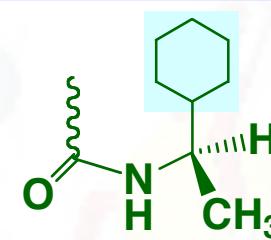
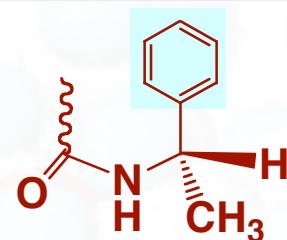
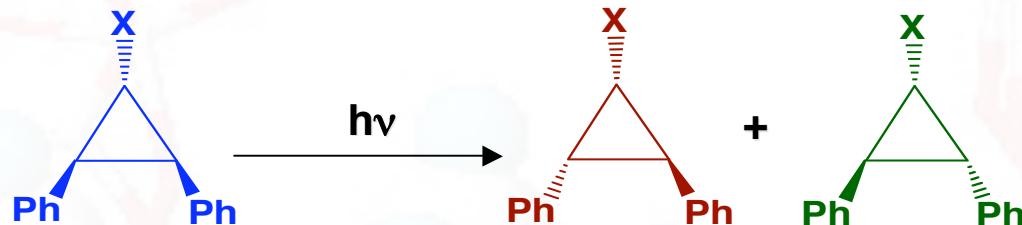
**HF / 3–21G**

**BA = 79.63 kcal/mol**



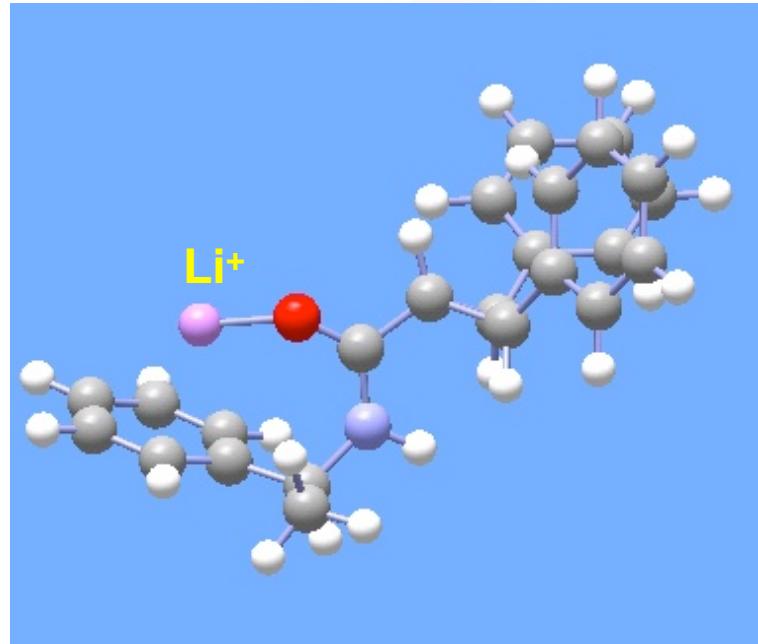
# Role of Cation- $\pi$ Quadrupolar Interaction

## Phenyl vs Cyclohexyl

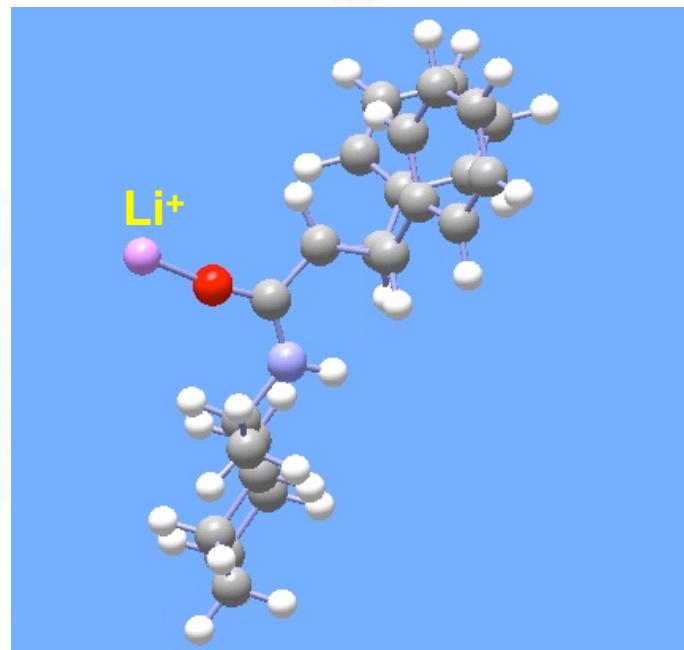


Zeolite	% d.e.	% d.e.
LiY	80-B	29-B
NaY	28-A	24-A
KY	14-A	26-A
RbY	5-A	29-A
CsY	5-A	37-A
Solution	2-B	2-B

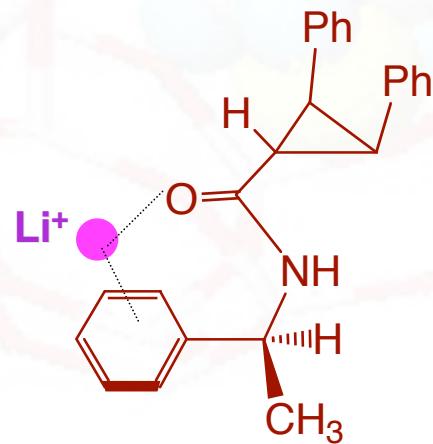
# Role of Cation- $\pi$ Quadrupolar Interaction



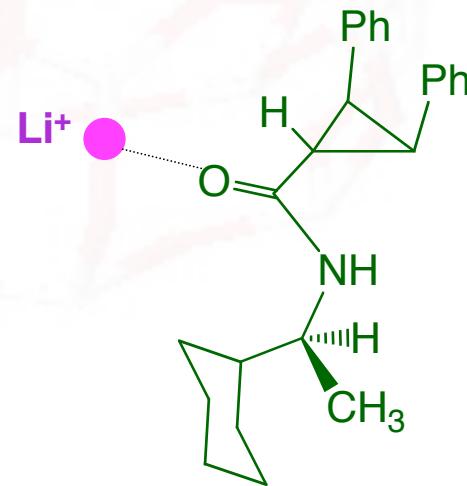
**BA = 91.3 kcal/mol**



**HF / 3-21G**



**BA = 80.26 kcal/mol**



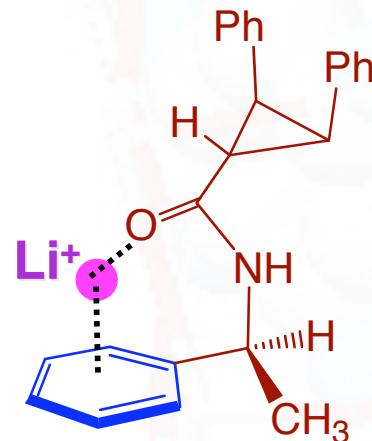
# Asymmetric Photoreactions Within Zeolites

## Modest to Good Chiral Induction

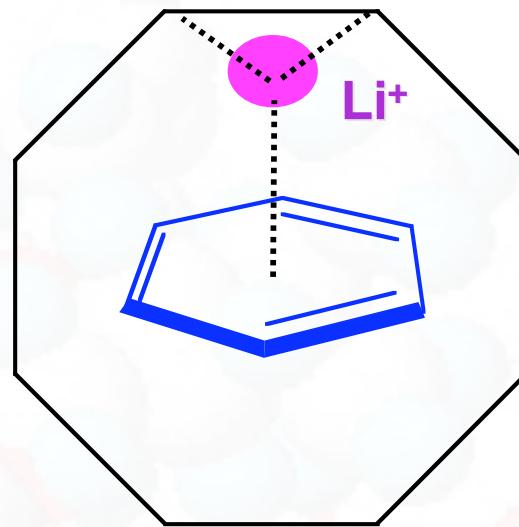
### Chiral Induction Depends on

- Type of cations in the zeolite
- Water Content
- Number of Cations (Si/Al ratio)
- Chiral Perturber
  - Anchoring of chiral perturber  
Cation-aromatic or cation-carbonyl interactions

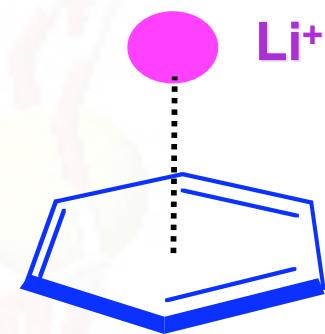
# Gas Phase Based Computational Studies Could be a Good Starting Point



Gas phase



Inside zeolite

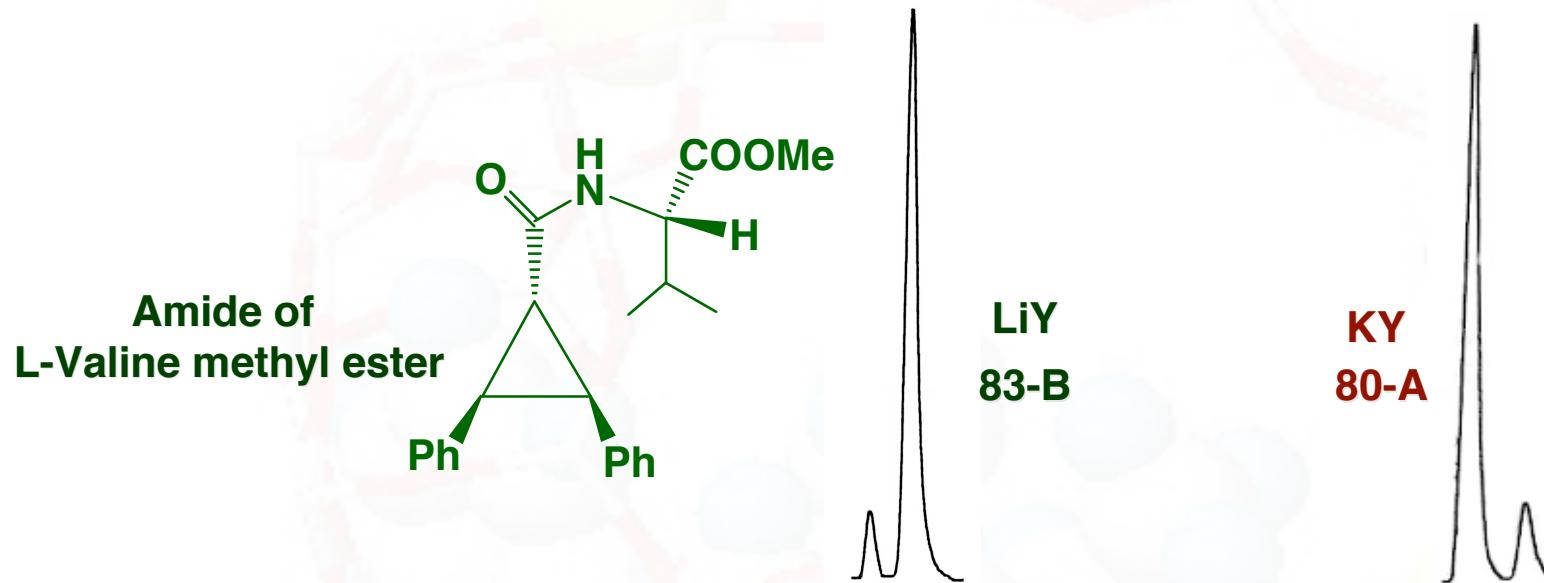


Gas phase

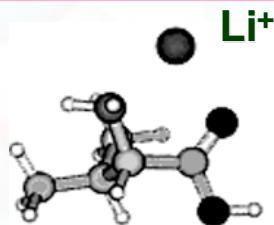
**Smaller binding energy compared to  
gas phase**

**Trend likely to remain the same**

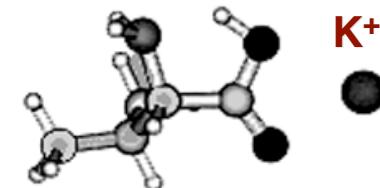
# Cation Dependent Diastereomer Switch



Williams, E. A. et. al.,  
JACS, 123, 12255–12265, (2001)

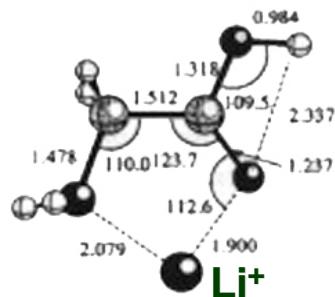


Valine

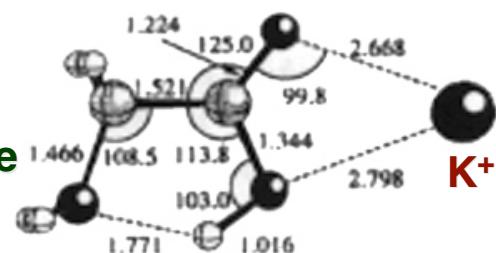


Bowers, M. T. et. al.,  
JACS, 2001, 122, 3458–3464, (2000)

NO – Co-ordination

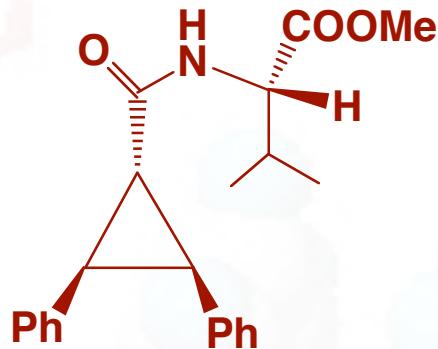


Glycine



OO – Co-ordination

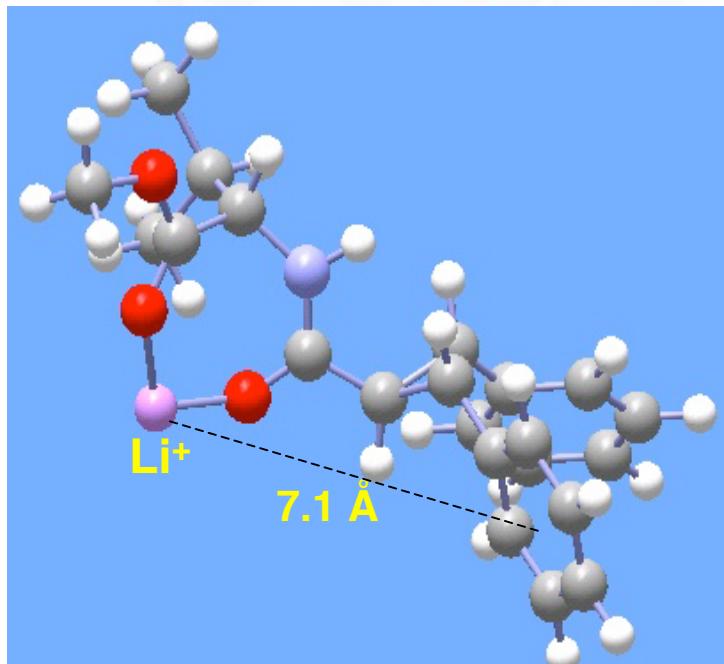
# $\text{Li}^+$ (vs) $\text{K}^+$ – Cation Dependent Diastereomer Switch



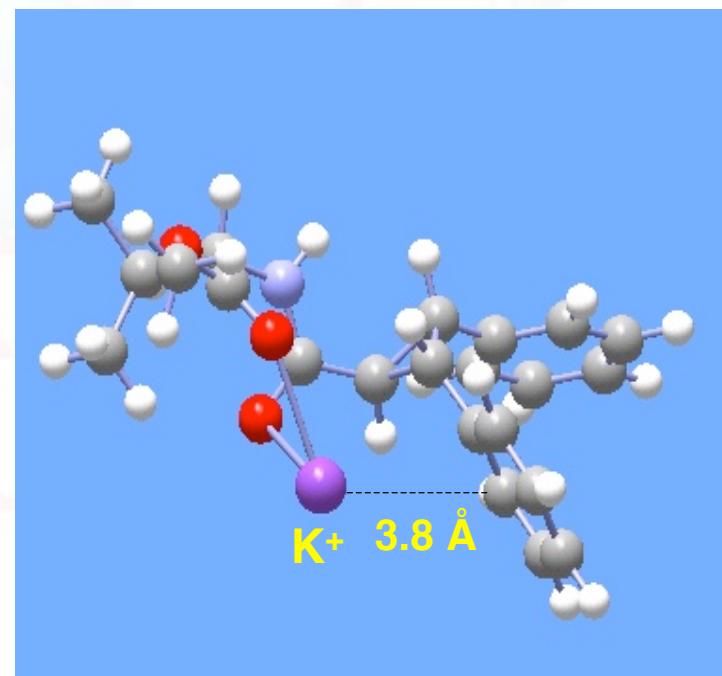
HF / 3–21G

Amide of L-valine methyl ester

BA = 104.10 kcal/mol

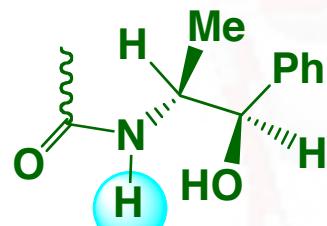
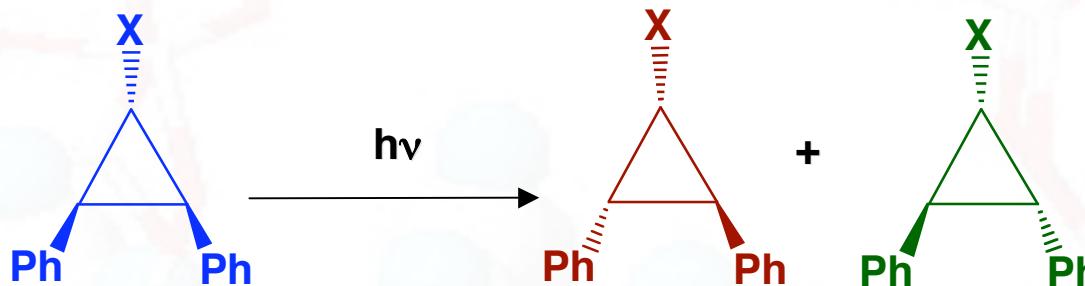


BA = 53.33 kcal/mol



# Comparison of Norephedrine and Pseudoephedrine

## Effect of 'N-Methyl' Group



**Amide of  
Norephedrine**

% d.e.

**25-B**

**60-A**

**13-A**

**2-A**

**0**

**30-A**  
**Solution  
(DCM/hexane)**

Medium

**LiY**

**NaY**

**KY**

**RbY**

**CsY**

**Solution  
(DCM/hexane)**

**Amide of  
Pseudoephedrine**

% d.e.

**59-A**

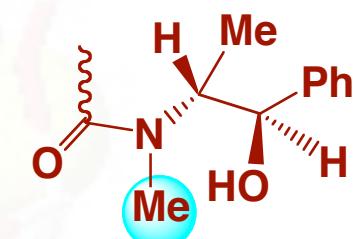
**89-A**

**15-A**

**9-A**

**8-A**

**21-A**

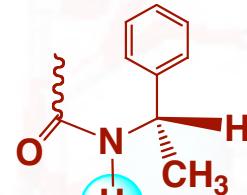


**Switching**

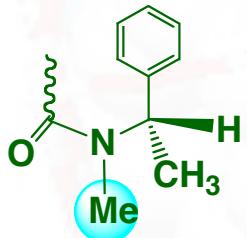
**No Switching**

# Effect of N-Methyl Substitution on Diastereomer Switch

## NH (vs) N-Methyl S(-)-1-phenylethyl amide

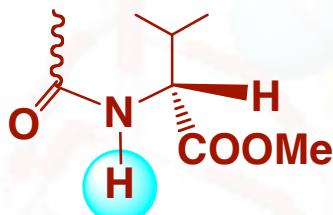


Solution	Li	Na	K	Rb	Cs
2-B	80-B	28-A	14-A	5-A	5-A

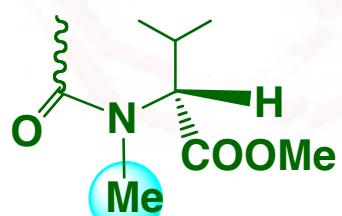


3-A	17-A	30-A	20-A	5-A	6-A
-----	------	------	------	-----	-----

## NH (vs) N-Methyl L-Valine Methyl ester

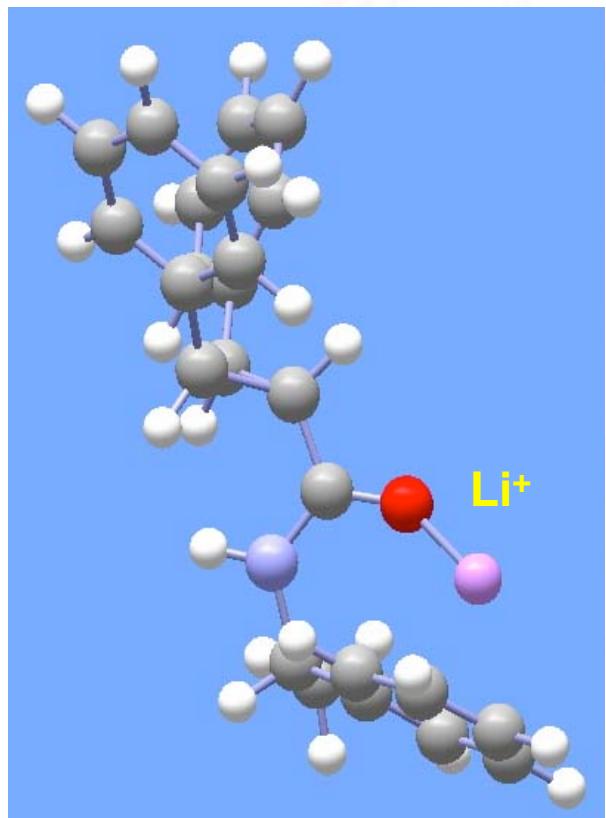


Solution	Li	Na	K	Rb	Cs
----------	----	----	---	----	----



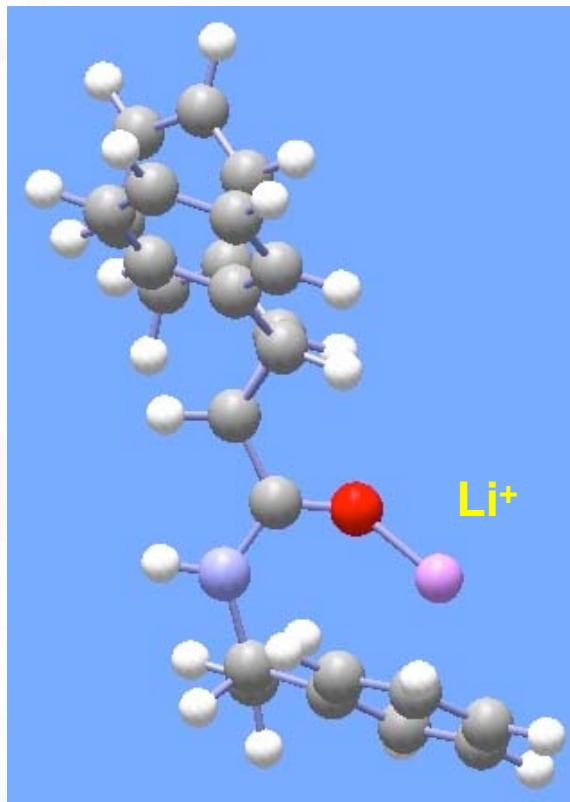
2-B	83-B	28-A	80-A	47-A	5-A
-----	------	------	------	------	-----

## (N-Me and NH) 1-phenylethyl amide – Conformations



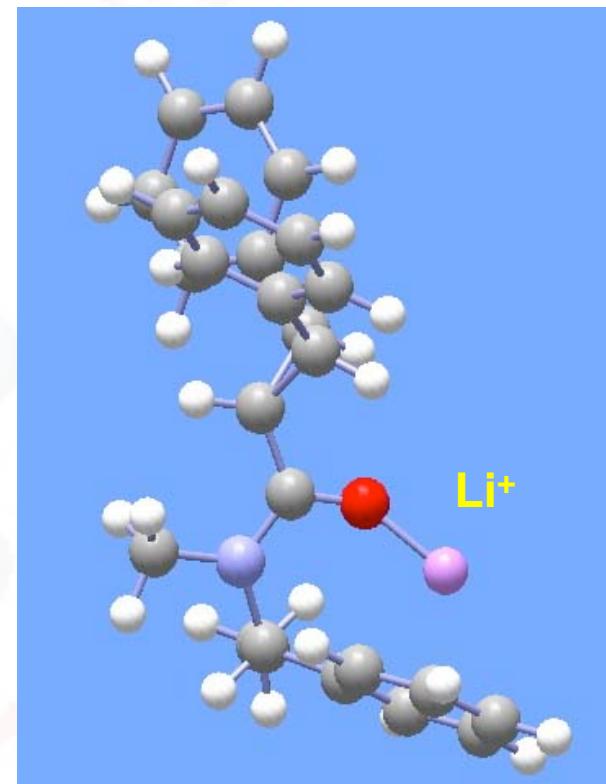
NH-*cis-trans*

BA = 91.30 kcal/mol



NH-*trans-trans*

BA = 89.79 kcal/mol



N-methyl-*trans-trans*

BA = 90.67 kcal/mol

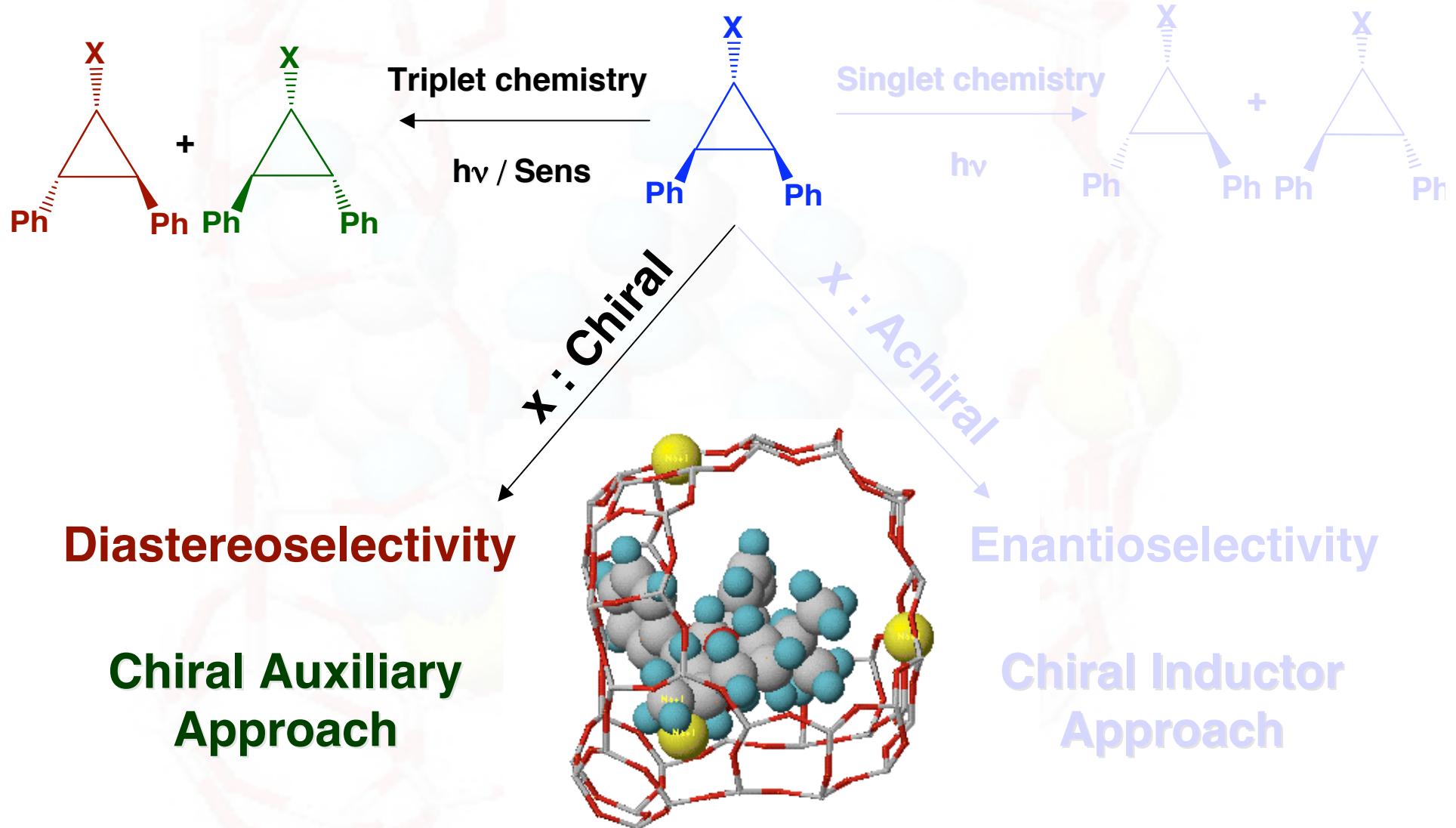
# Asymmetric Photoreactions Within Zeolites

## Modest to Good Chiral Induction

### Chiral Induction Depends on

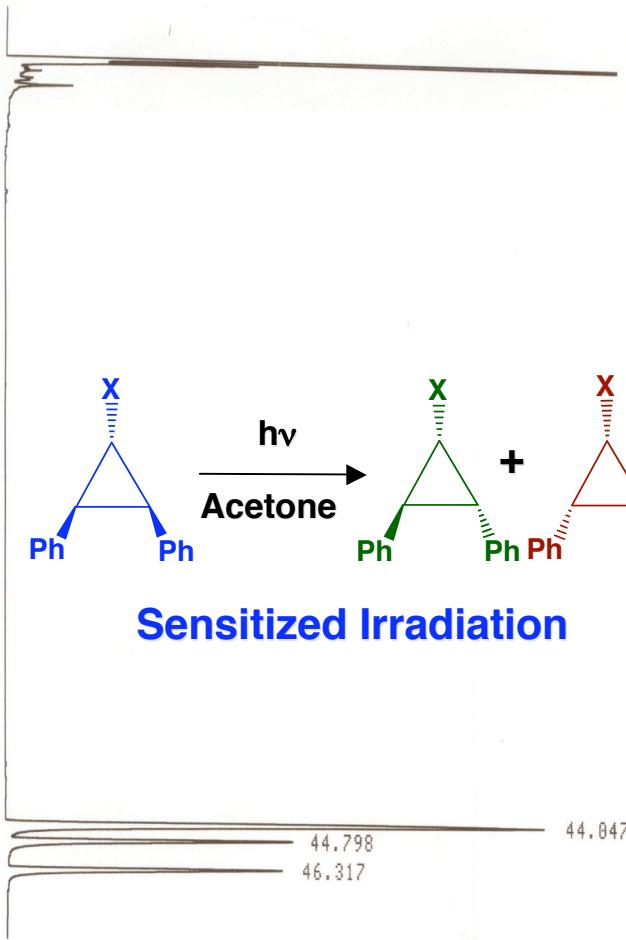
- Type of cations in the zeolite
- Water Content
- Number of Cations (Si/Al ratio)
- Chiral Perturber
  - Anchoring of chiral perturber  
Cation-aromatic or cation-carbonyl interactions
- Cation binding - Diastereomer switch
  - Controlling diastereomer switch by N-methylation

# Asymmetric Induction within Zeolites

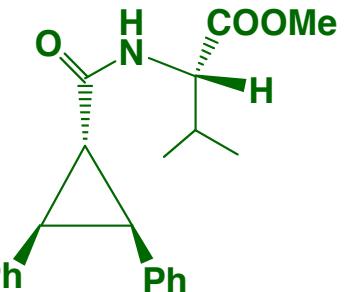
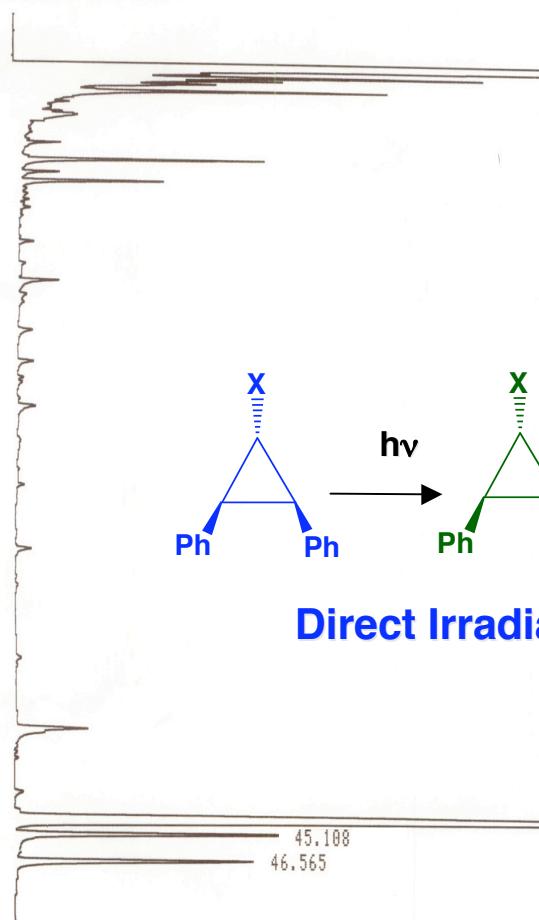


# Triplet vs Singlet Photochemistry

DPCP-LVME / ACETONE



SOL / QUARTZ / DPCP-LVME /



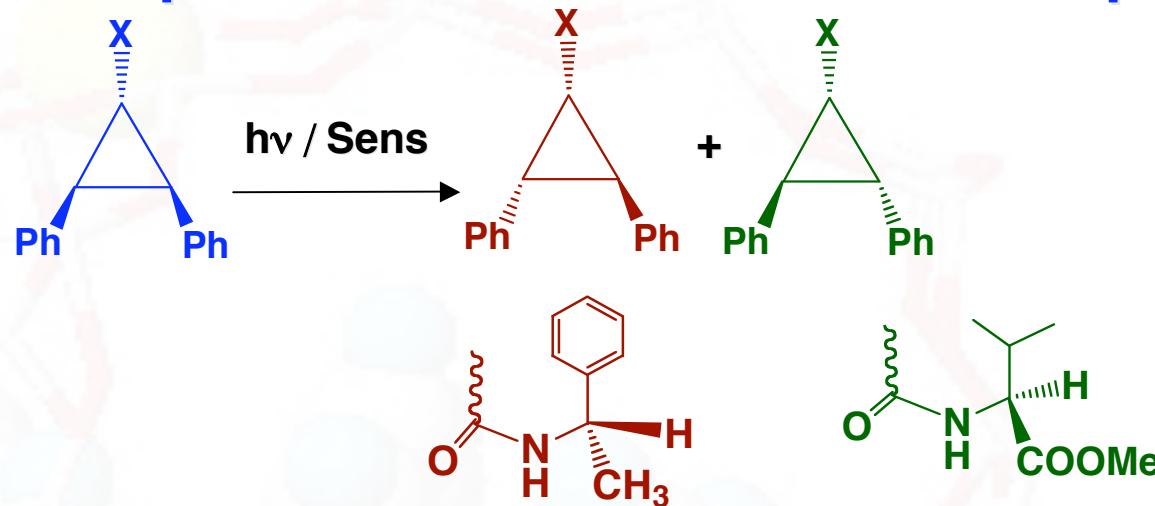
CR501 CHROMATOPAC  
CHANNEL NO 1  
SAMPLE NO 0  
REPORT NO 21

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	44.047	54376			54.9137	
2	44.798	22375			22.5957	
3	46.317	22270			22.4906	
TOTAL		99021			100	

CR501 CHROMATOPAC  
CHANNEL NO 1  
SAMPLE NO 0  
REPORT NO 18

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	44.504	137658			76.9736	
2	45.108	20774			11.6161	
3	46.565	20406			11.4104	
TOTAL		178839			100	

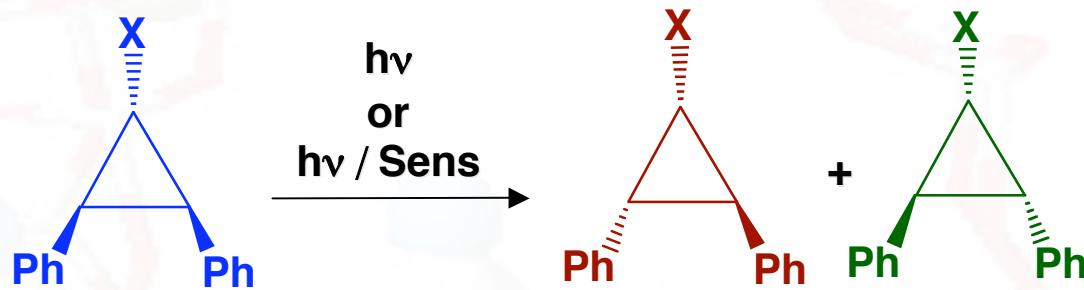
# Diastereoselective photoisomerization from the triplet state



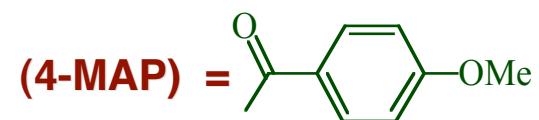
Sensitizer	% de (KY)	% de (KY)
Acetophenone	75-A	85-A
4'-Methoxyacetophenone	61-A	81-A
4'-Cyanoacetophenone	57-A	43-A
4'-Methylacetophenone	50-A	78-A
4'-Fluoroacetophenone	45-A	36-A
4'-Chloroacetophenone	40-A	71-A
Xanthone	30-A	40-A

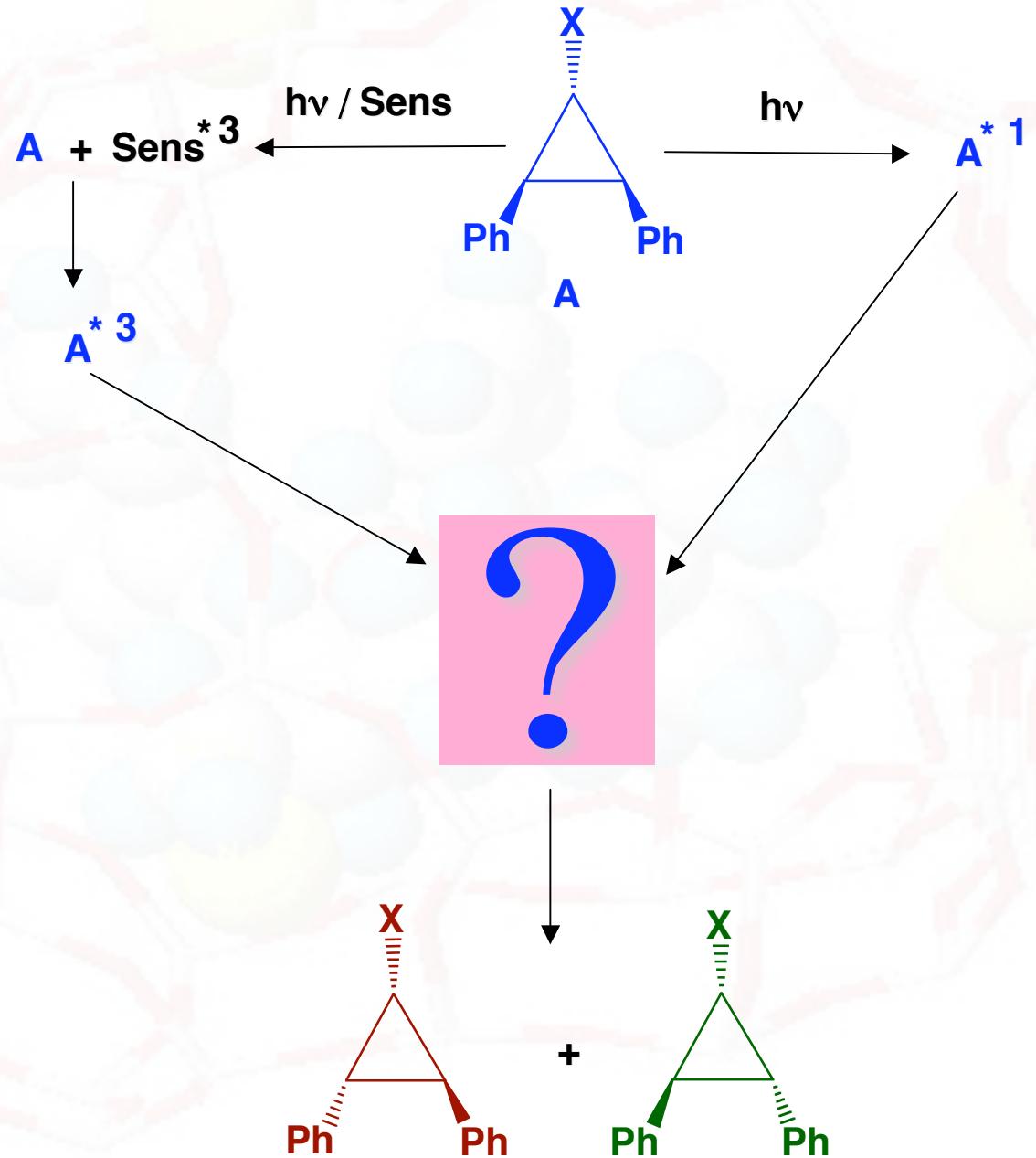
Efforts to sensitize the reaction with fluorenone ( $E_T = 50.4$  kcal/mol) and Acetonaphthone ( $E_T = 59.7$  kcal/mol) were unsuccessful.

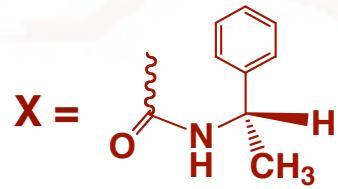
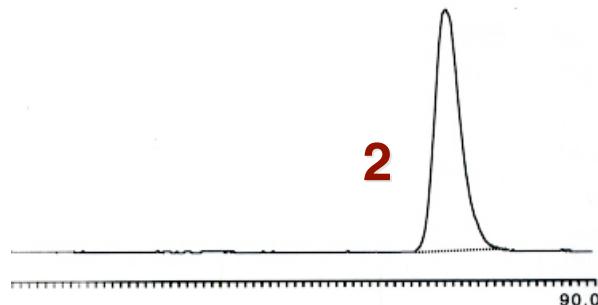
# Diastereoselectivity - Dependence on Reactive State



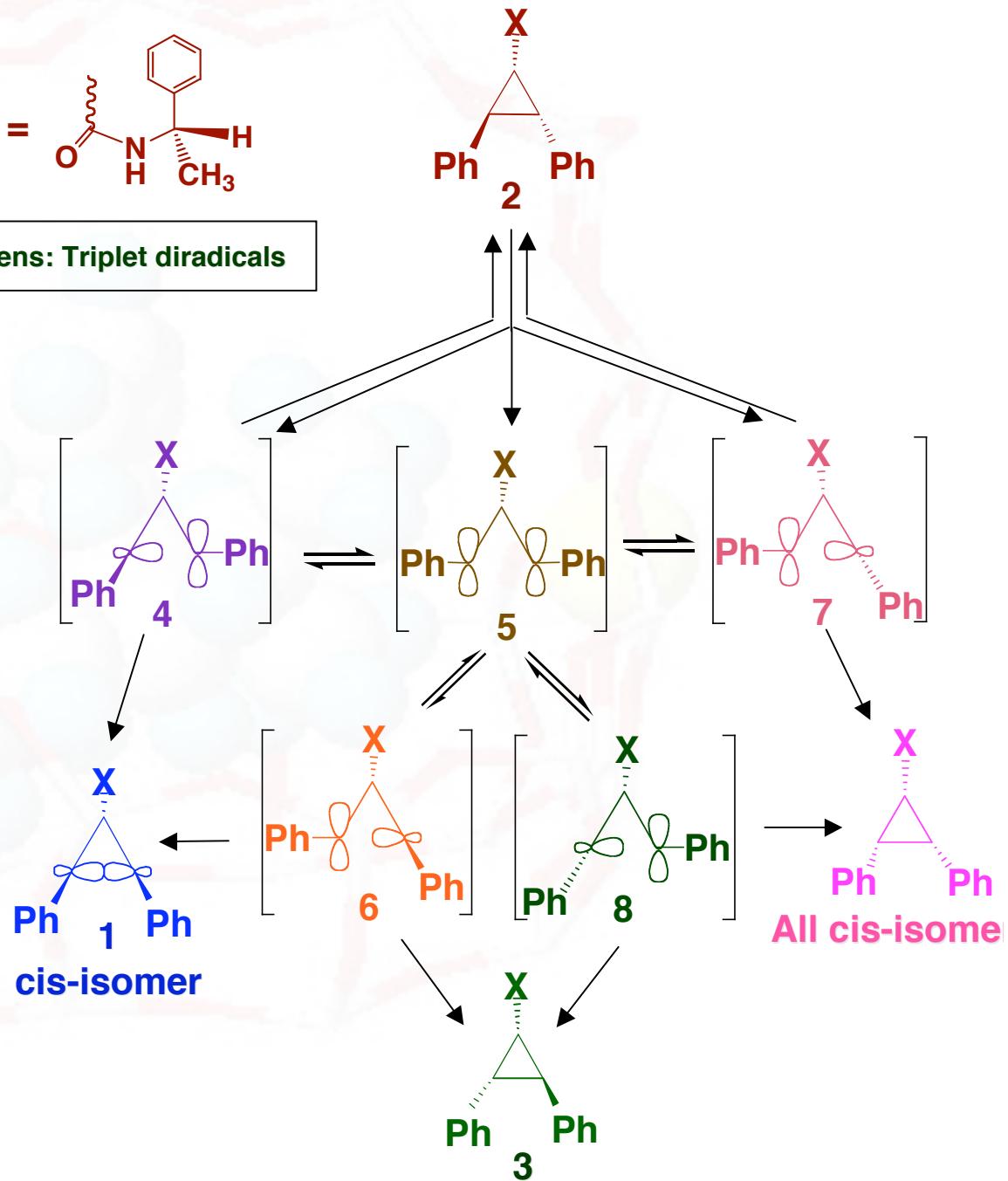
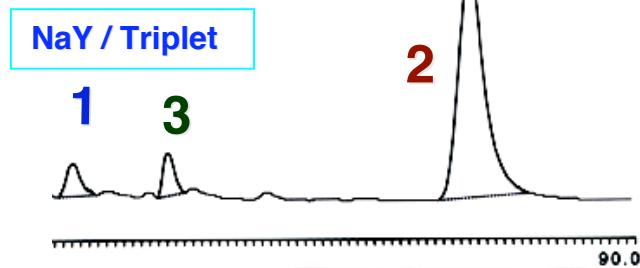
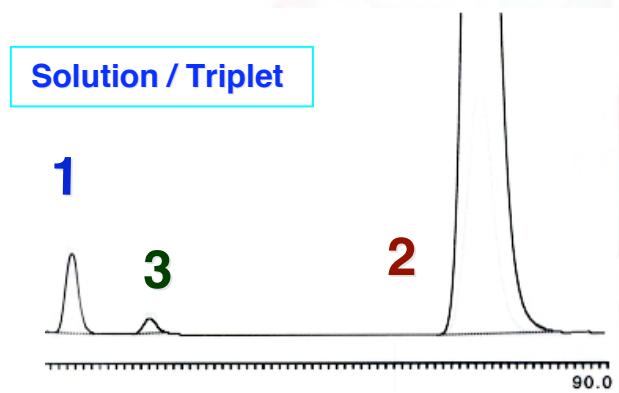
<b>Method</b>	KY	NaY	KY	KY	NaY	NaY	NaY
<b>Direct</b>	14-A	30-A	80-A	14-B	60-A	19-A	
<b>Sens<sup>3</sup> (4-MAP)</b>	61-A	51-A	81-A	17-B	59-B	44-B	

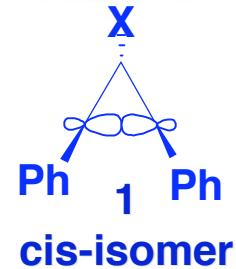
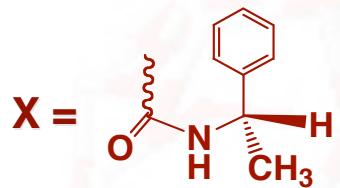




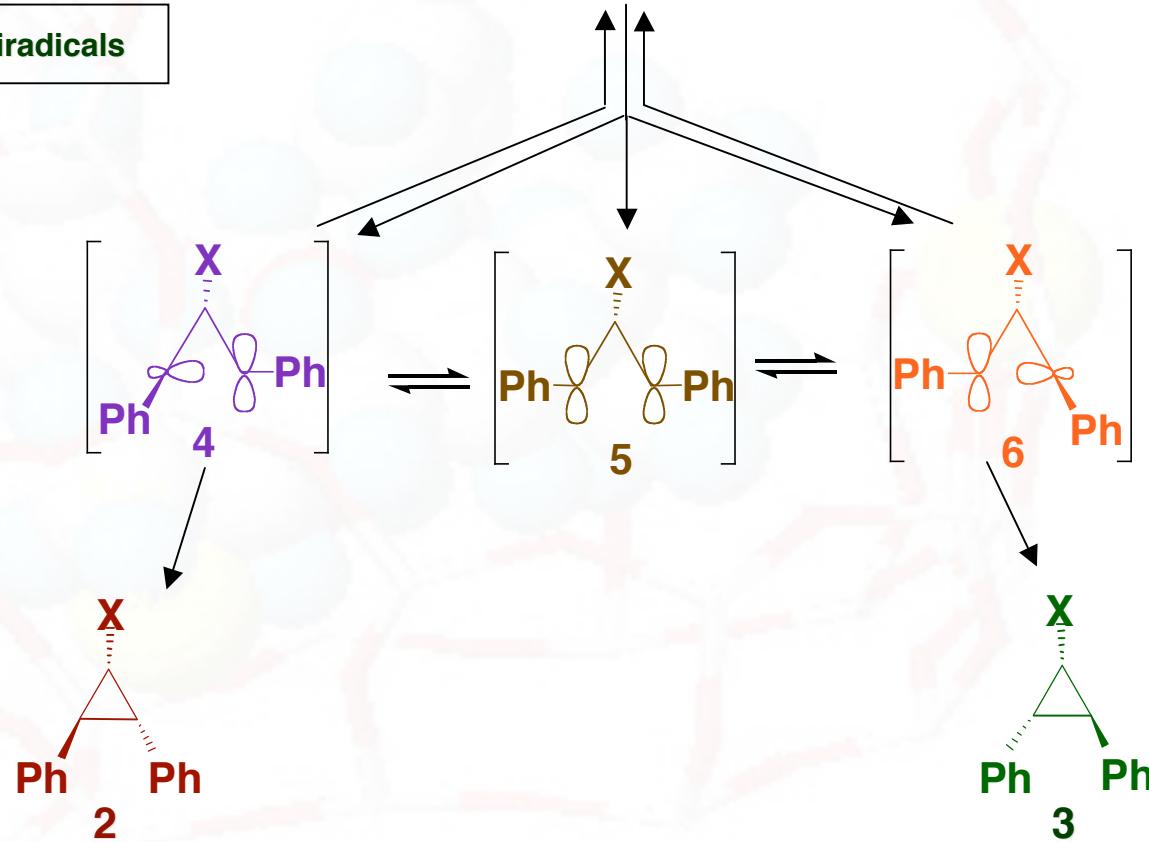


$h\nu / \text{Sens: Triplet diradicals}$

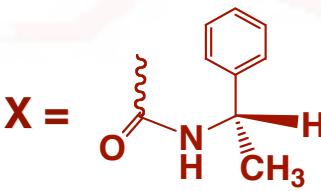
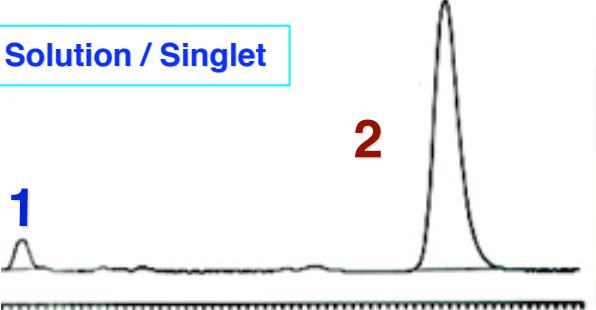
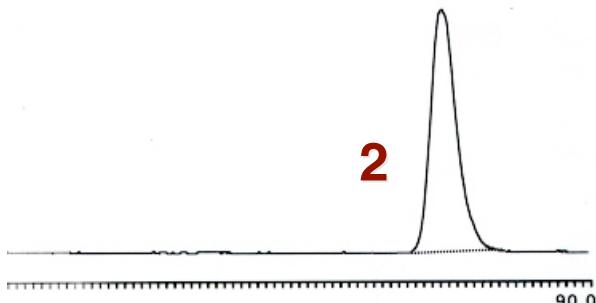




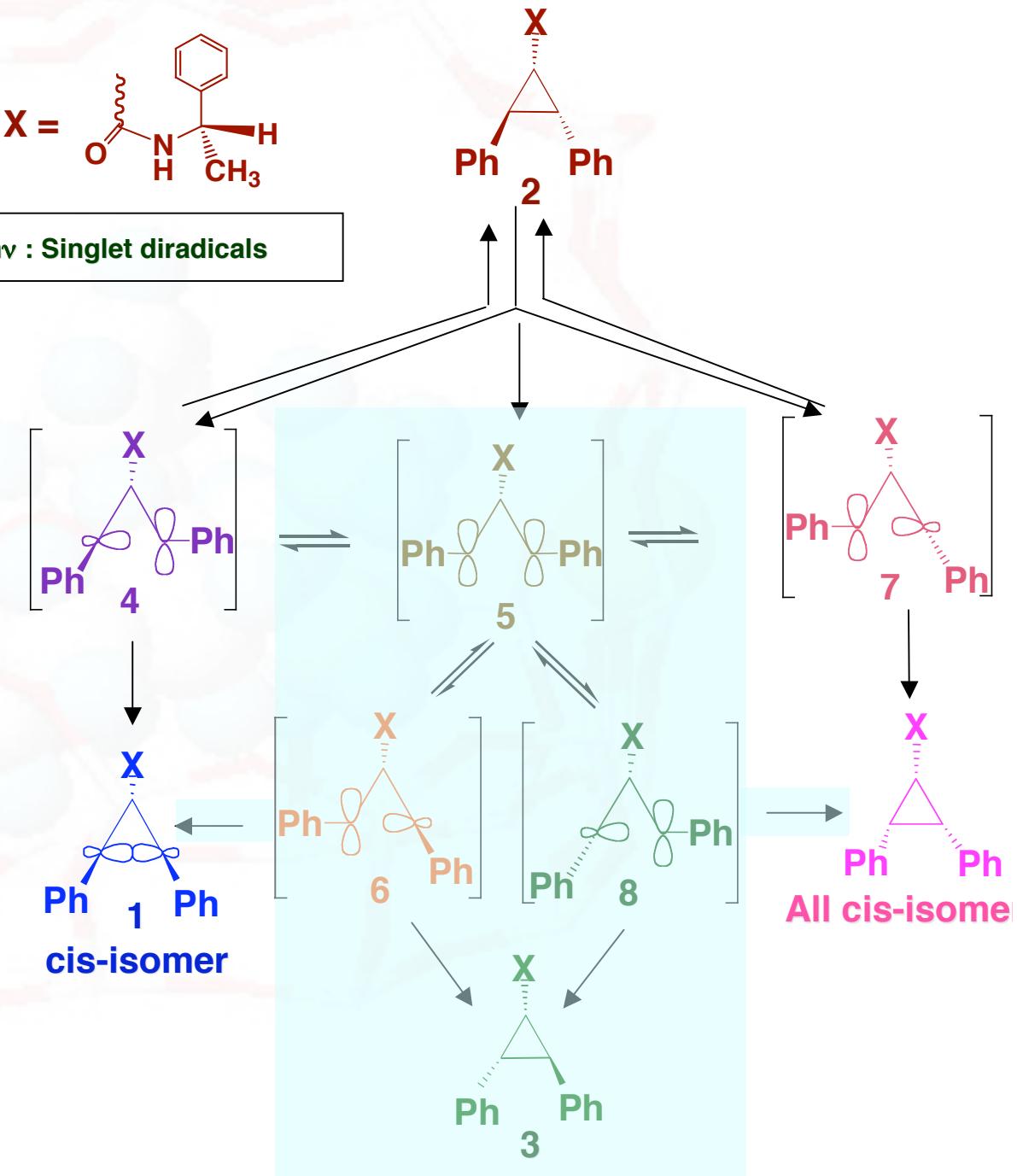
$h\nu / \text{Sens: Triplet diradicals}$



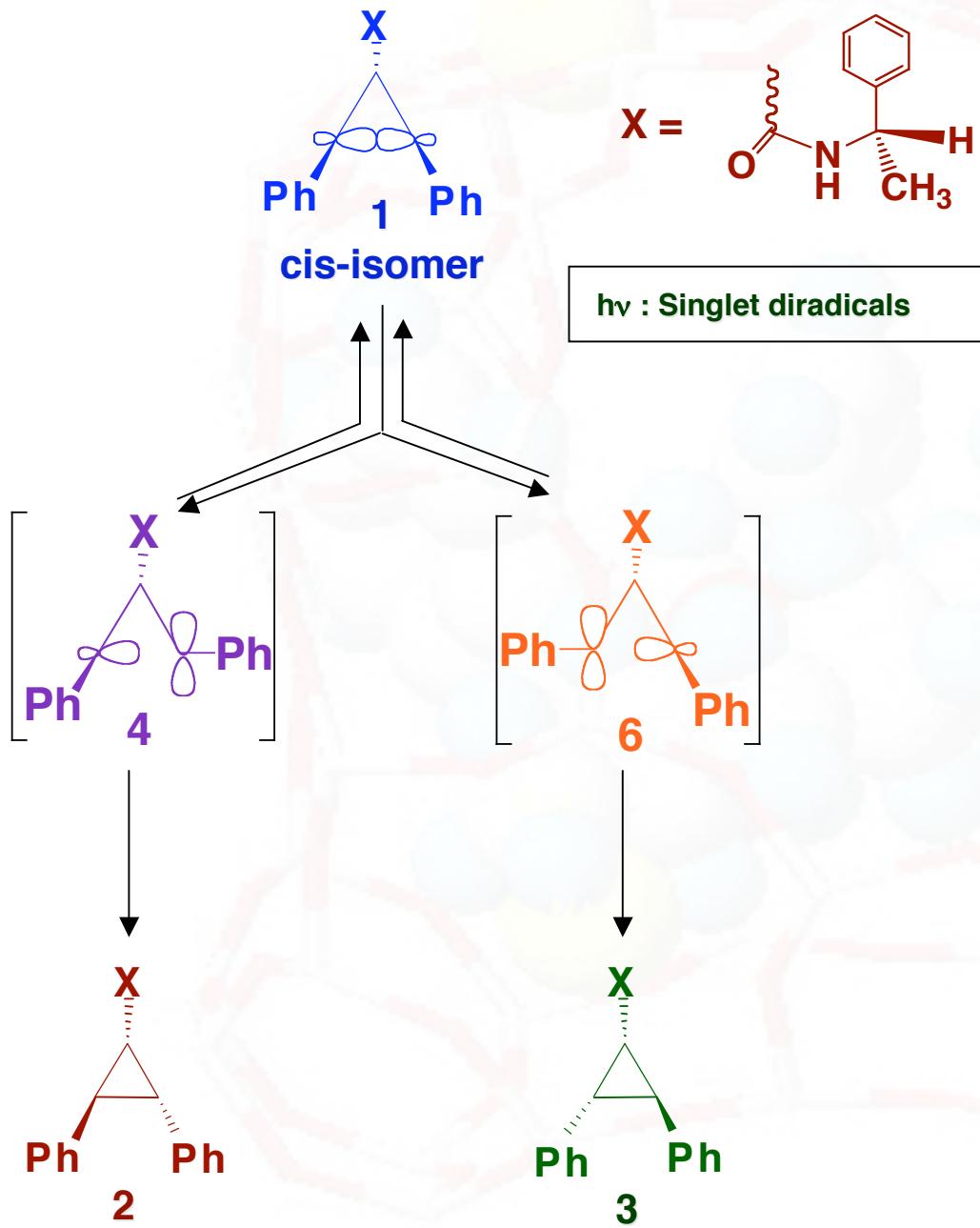
**Relative reactivity of diradicals determines the diastereoselectivity**



$h\nu$  : Singlet diradicals

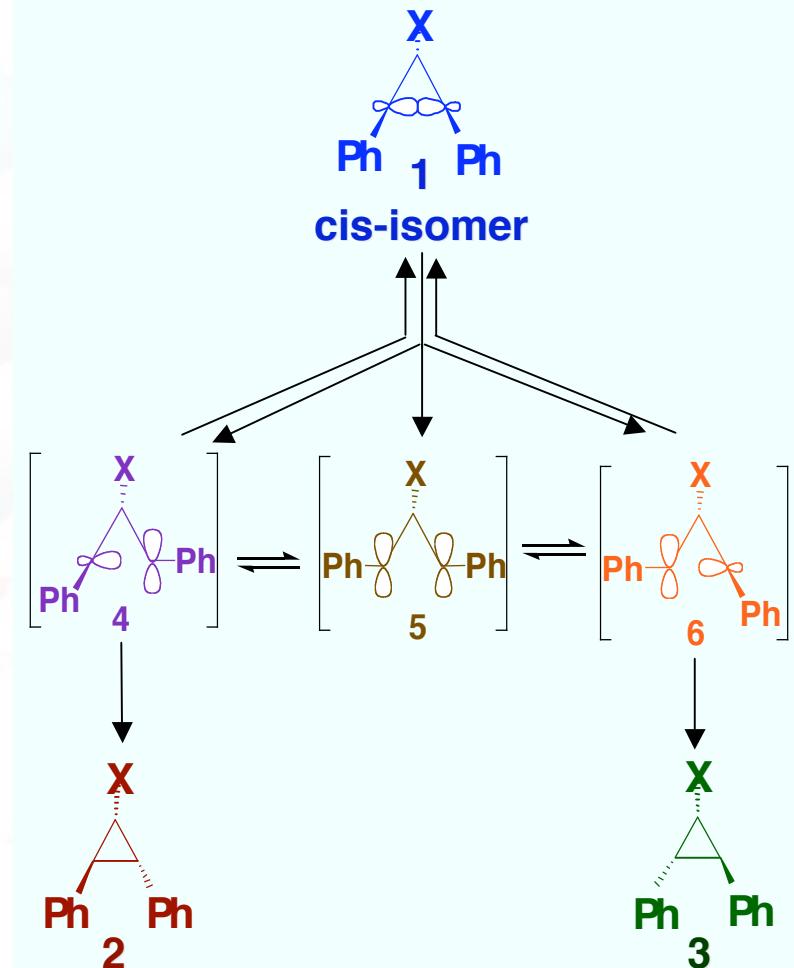


## Singlet chemistry

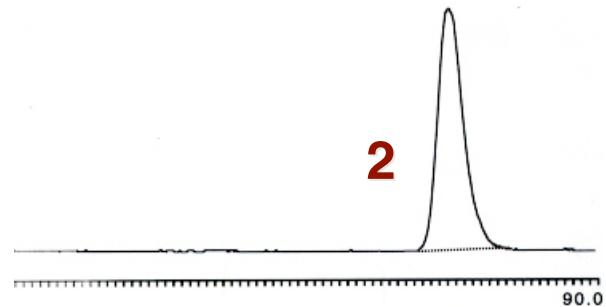


## Solution chemistry

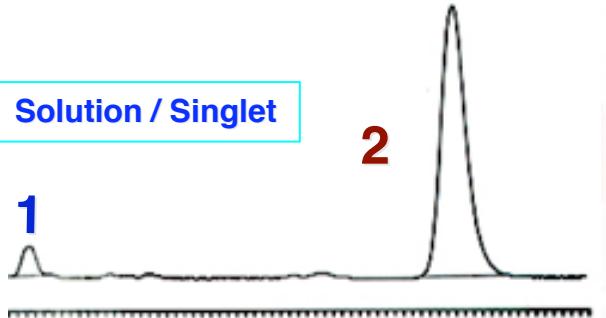
### Triplet Chemistry



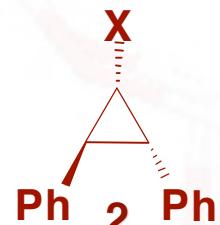
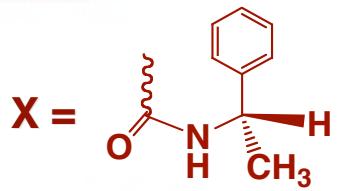
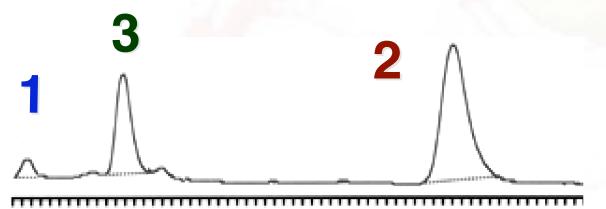
**There is no equilibrium between the diradicals**



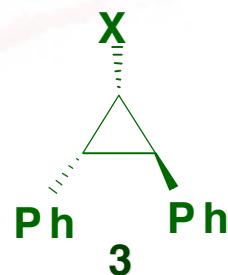
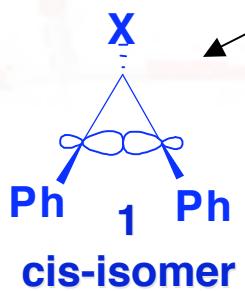
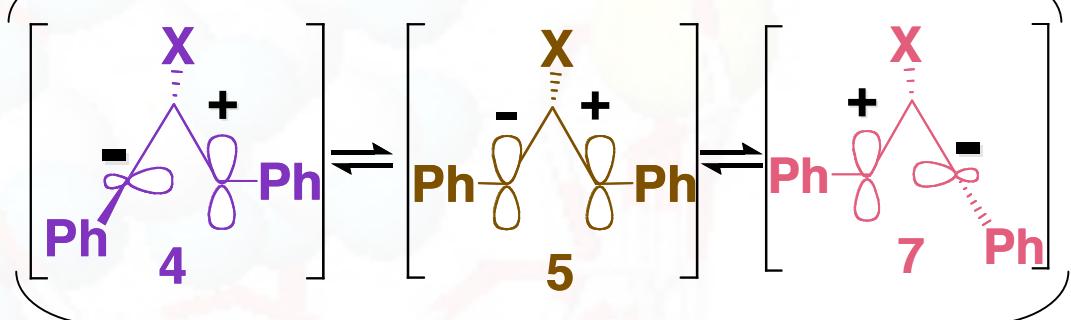
Solution / Singlet



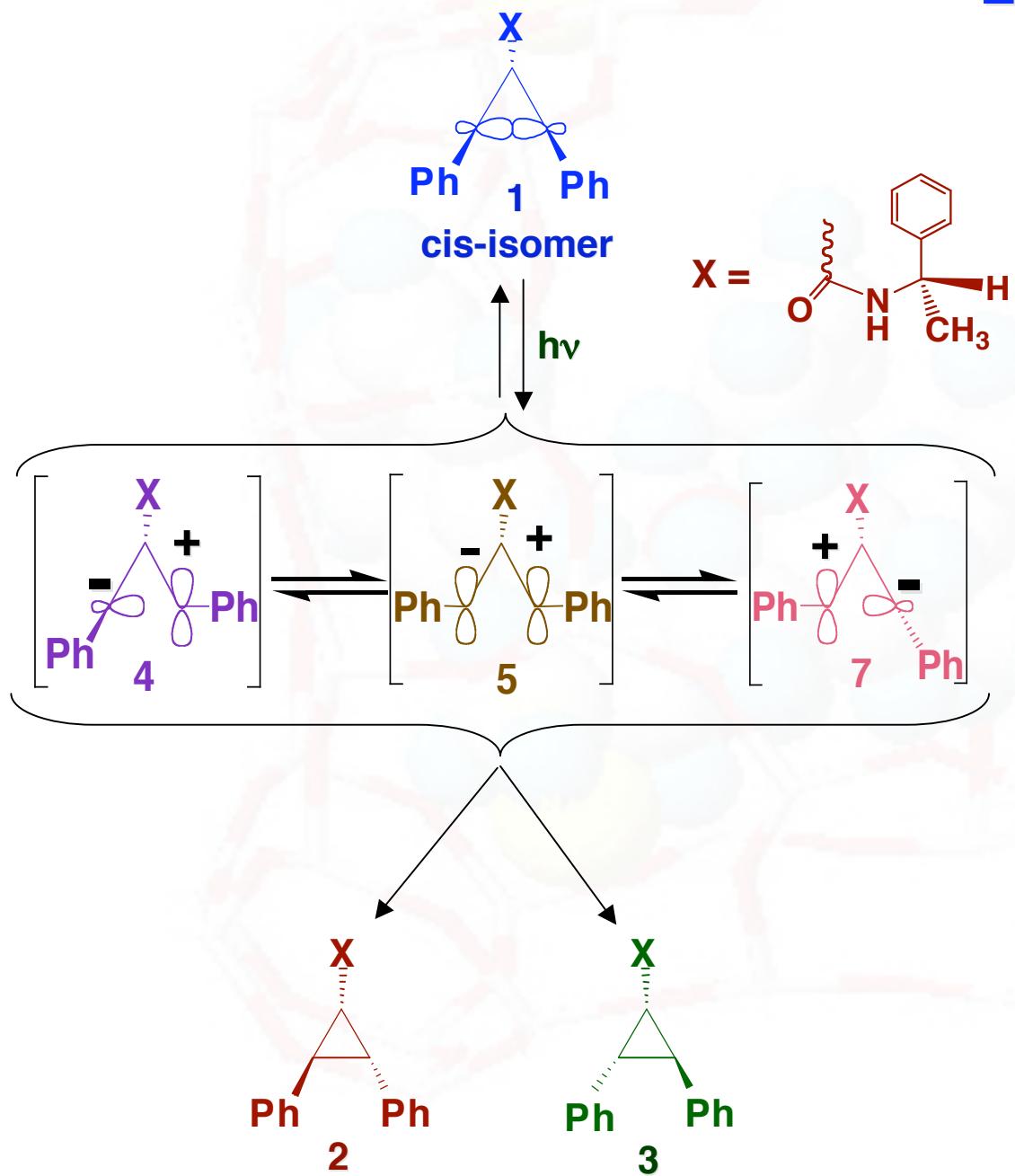
NaY / Singlet



$h\nu$

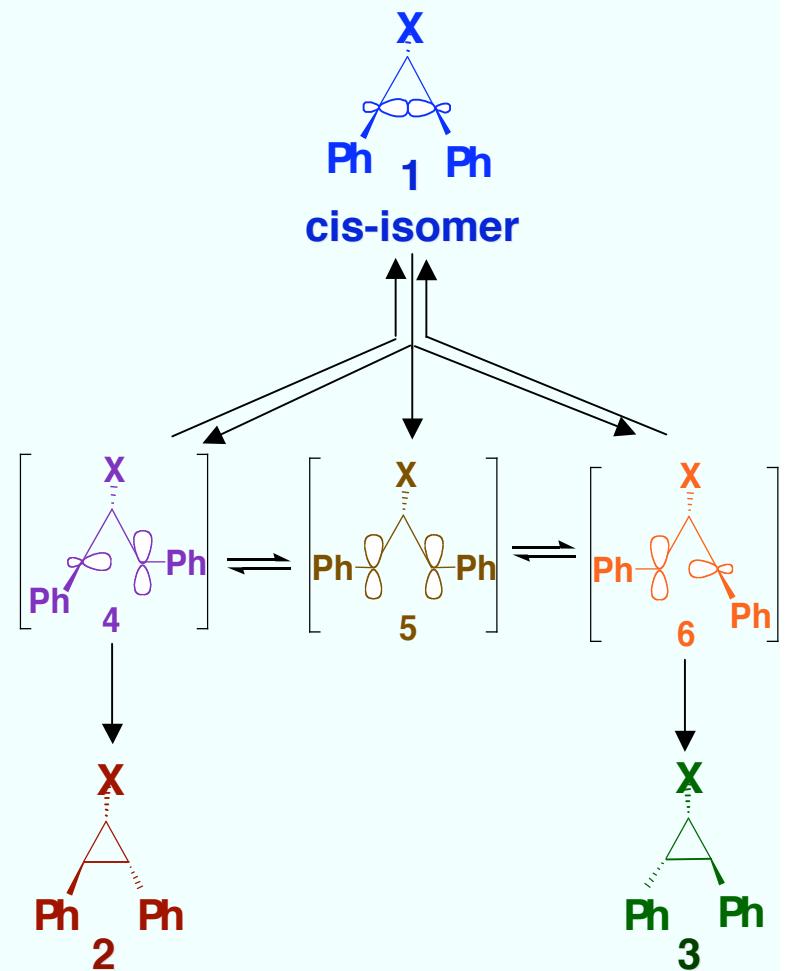


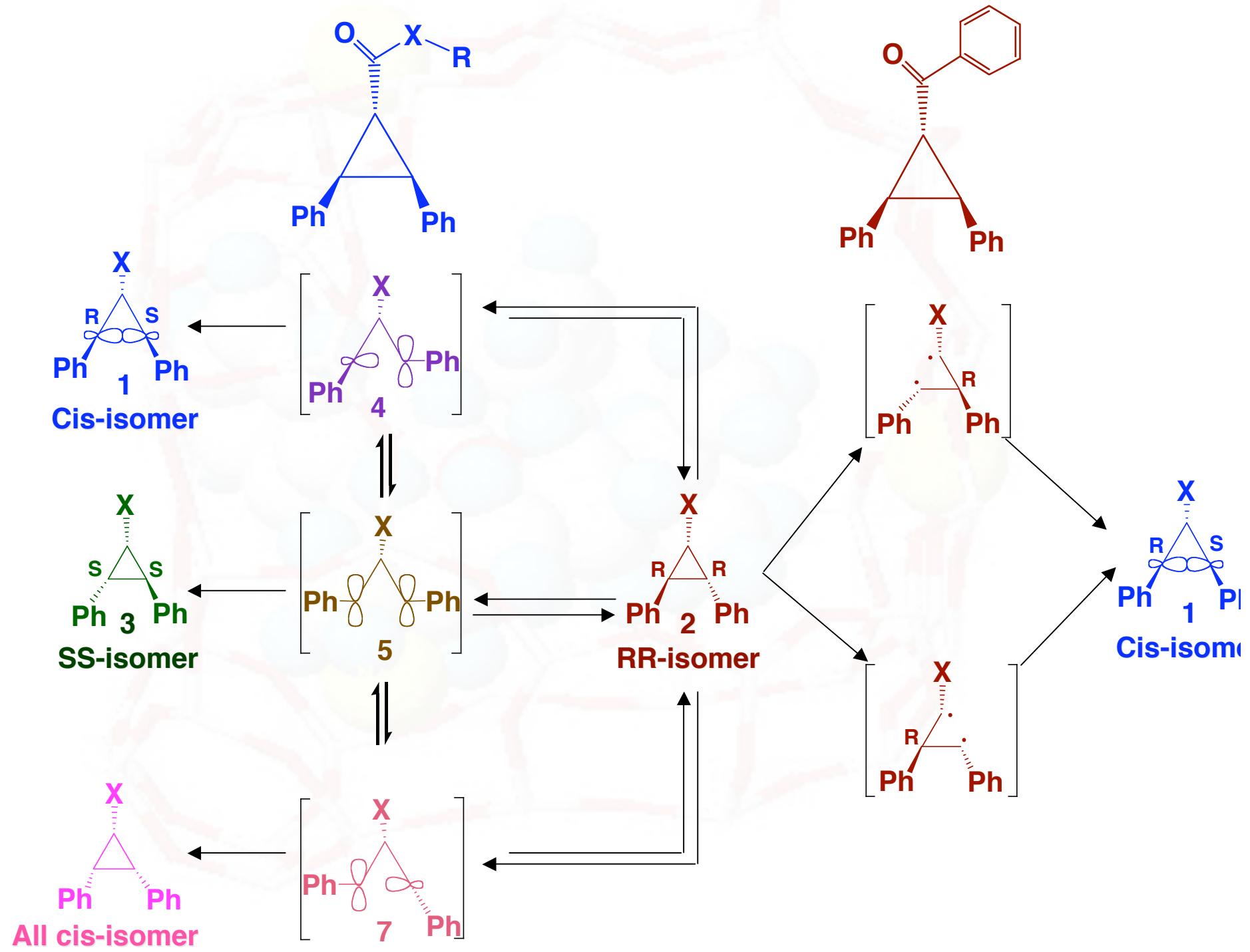
## Singlet chemistry

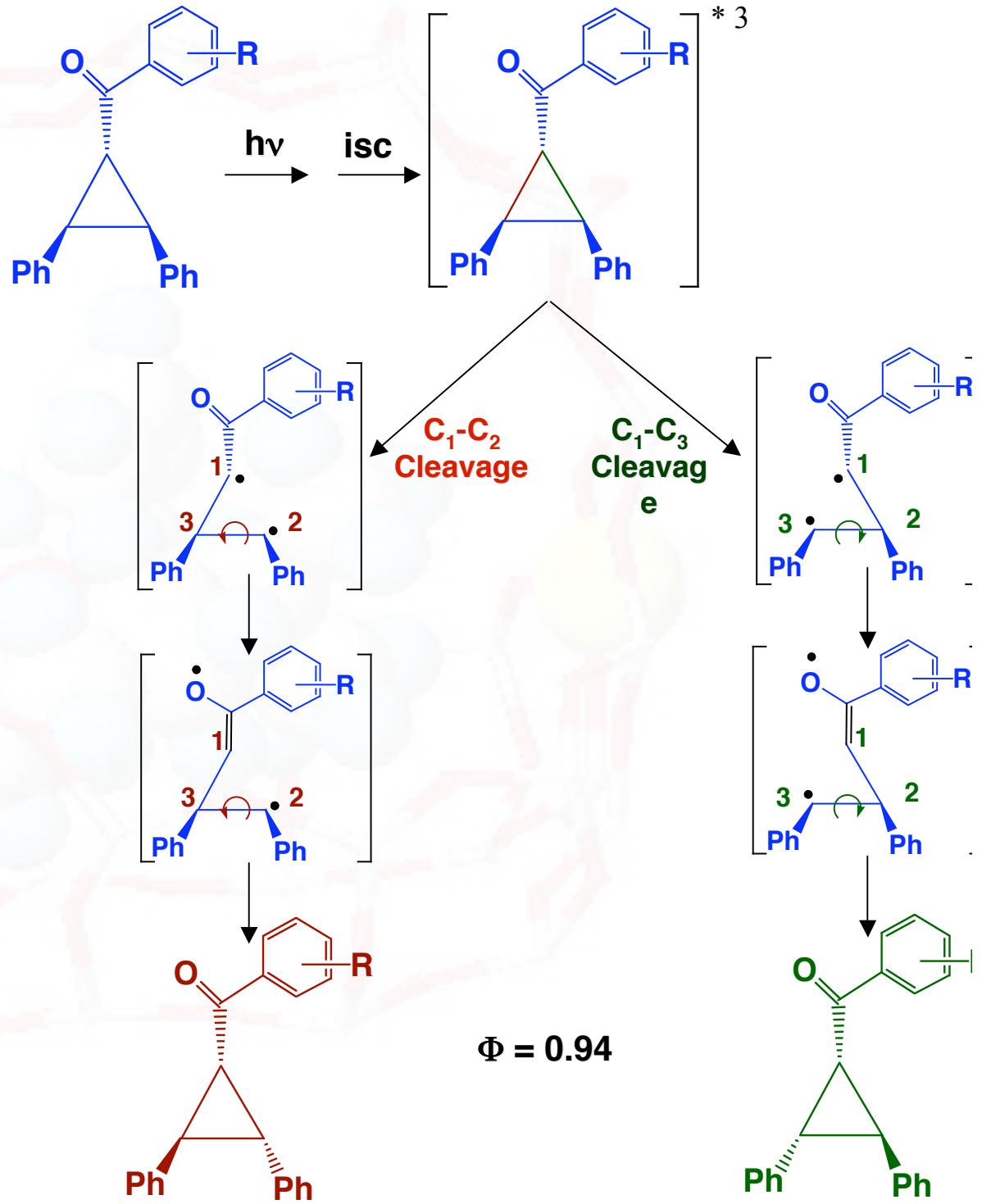
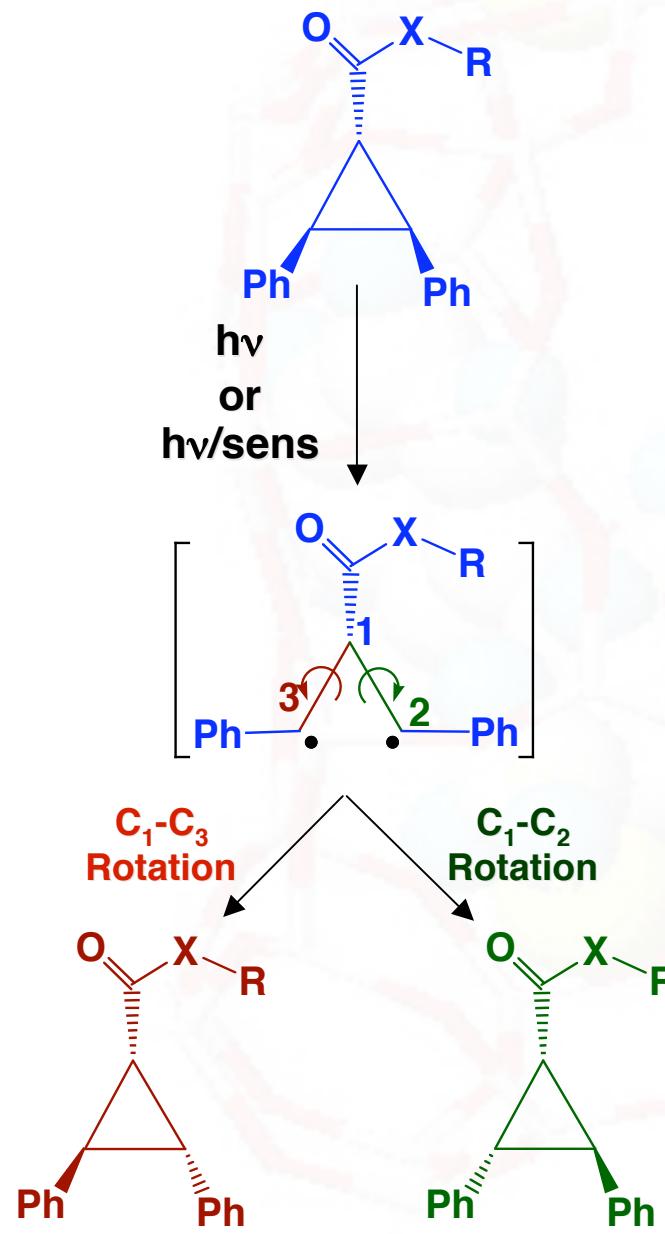


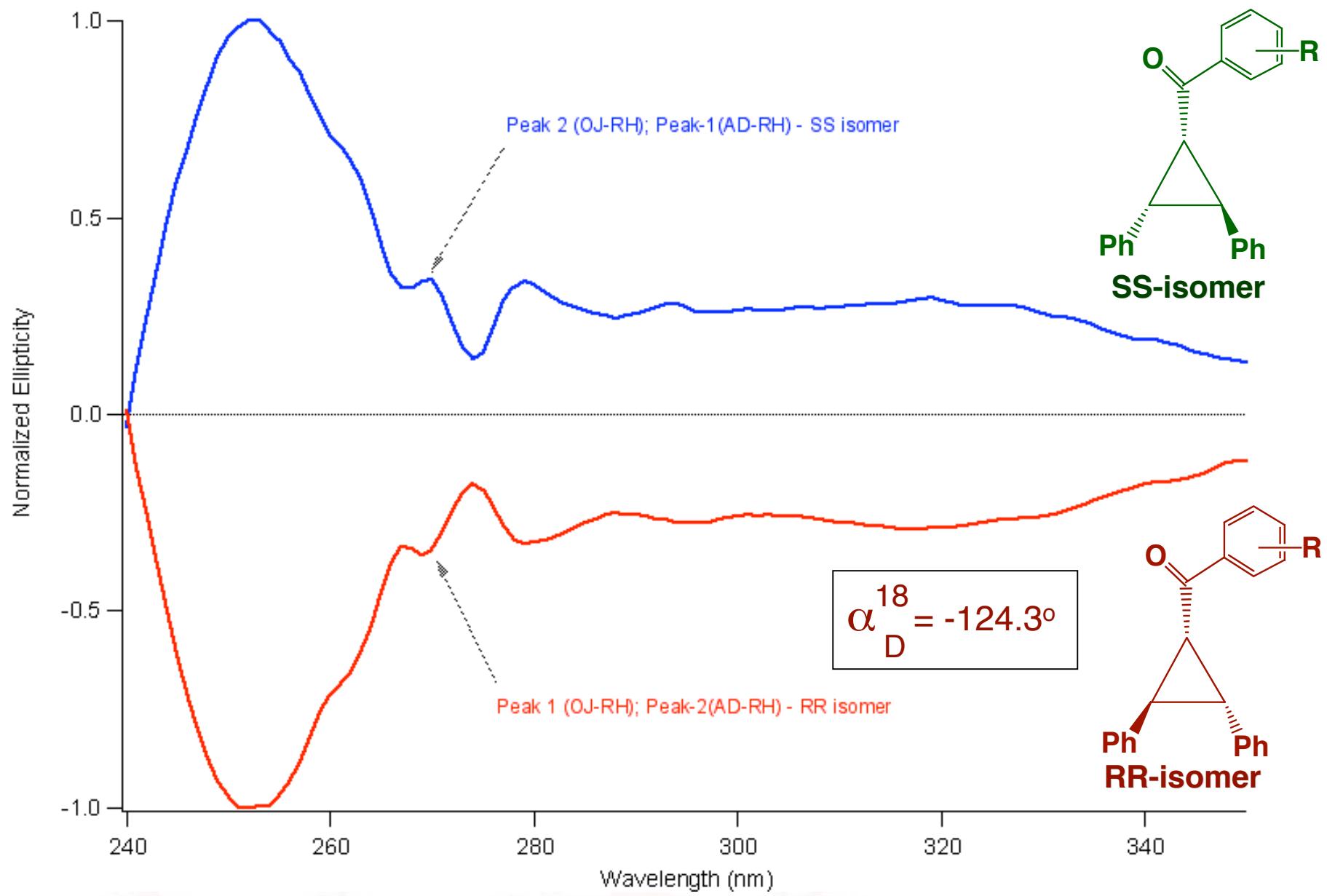
## Zeolite chemistry

### Triplet chemistry



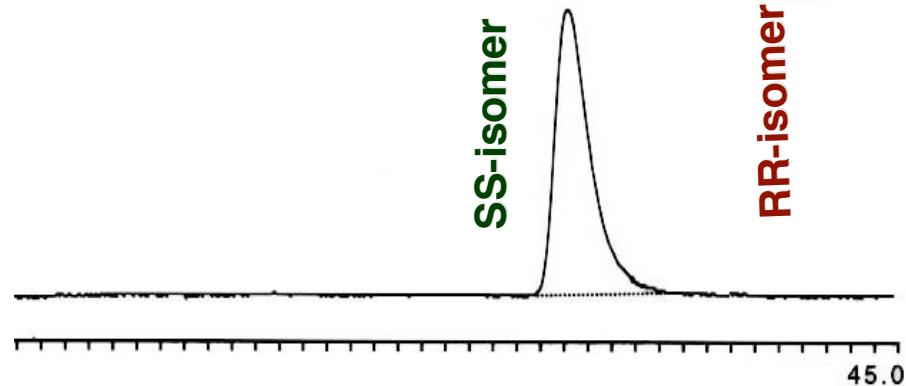




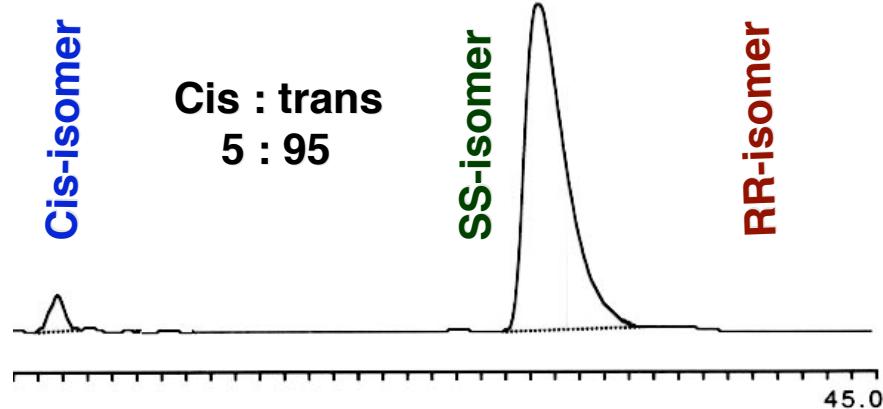


$$\alpha_D^{25} = -136^\circ$$

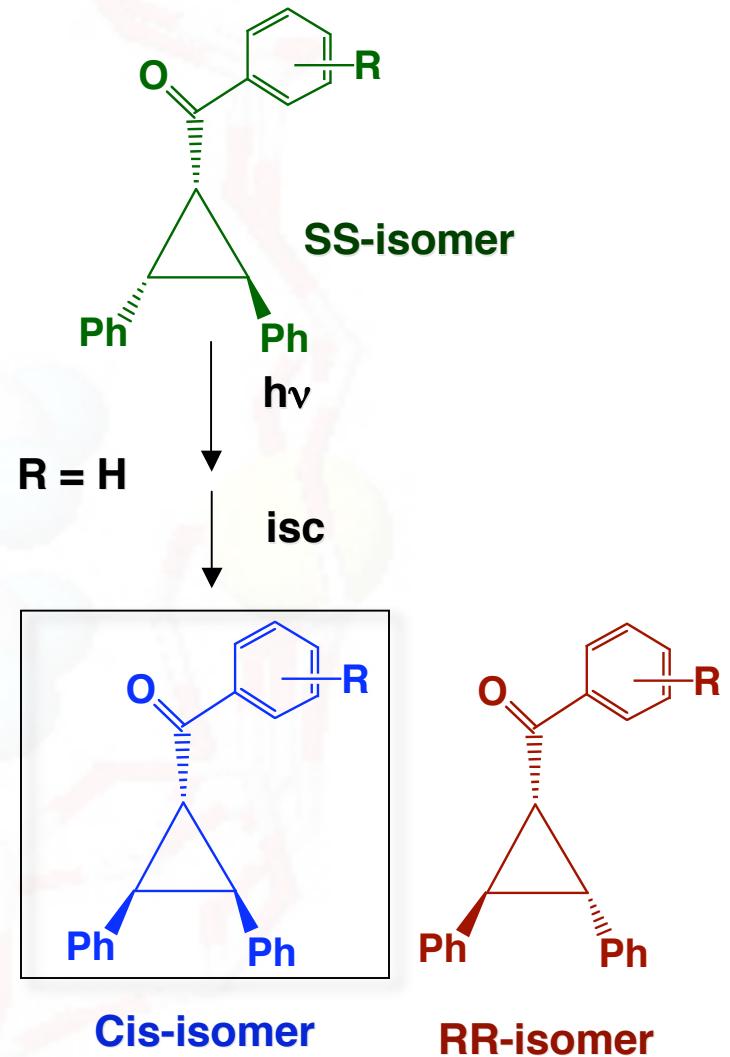
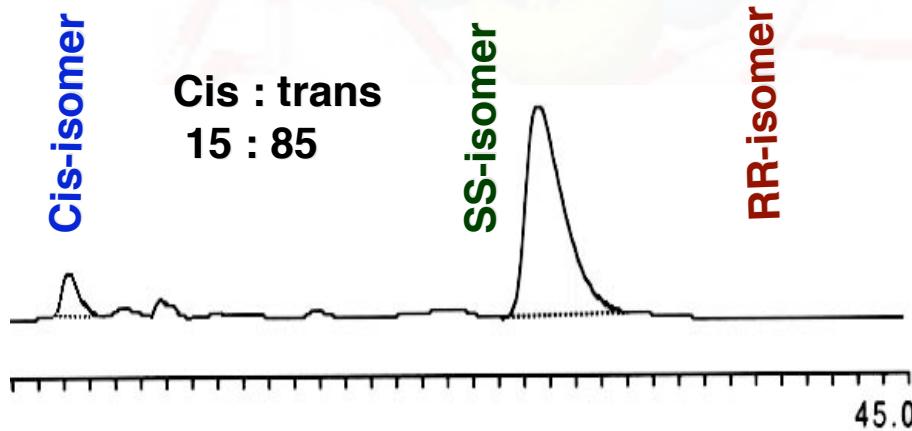
**RR-isomer**  
J. Chem. Soc., Perkin Trans, 1, 2000, (19), 3267–3276.

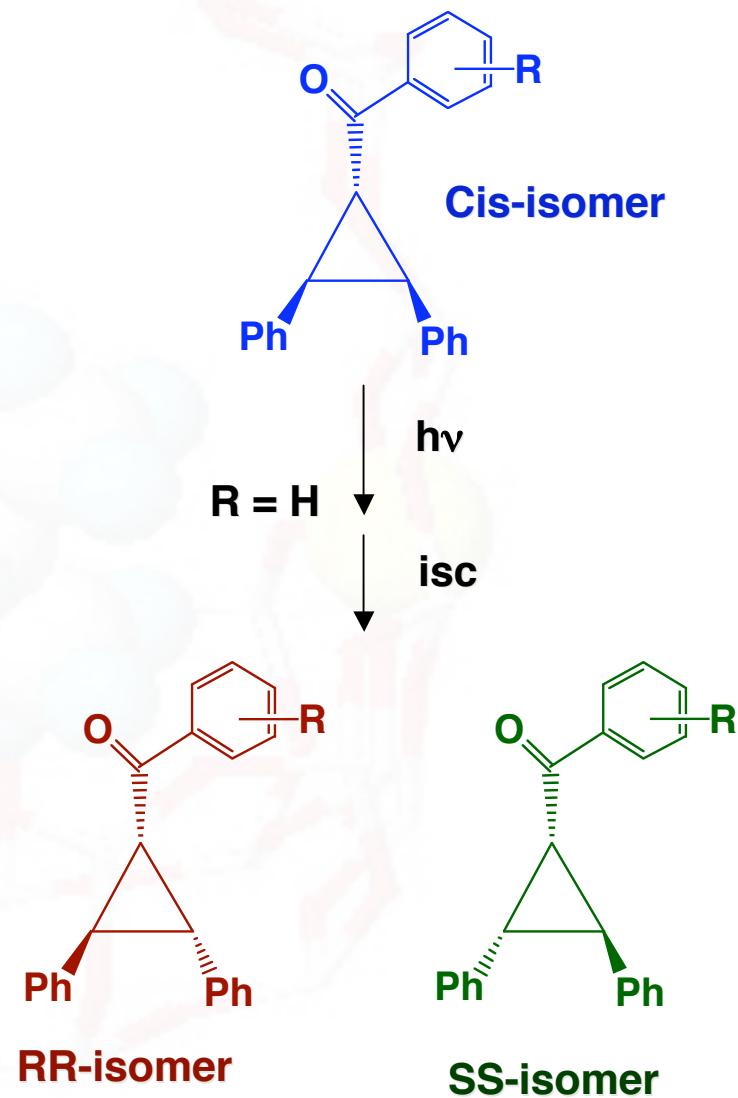
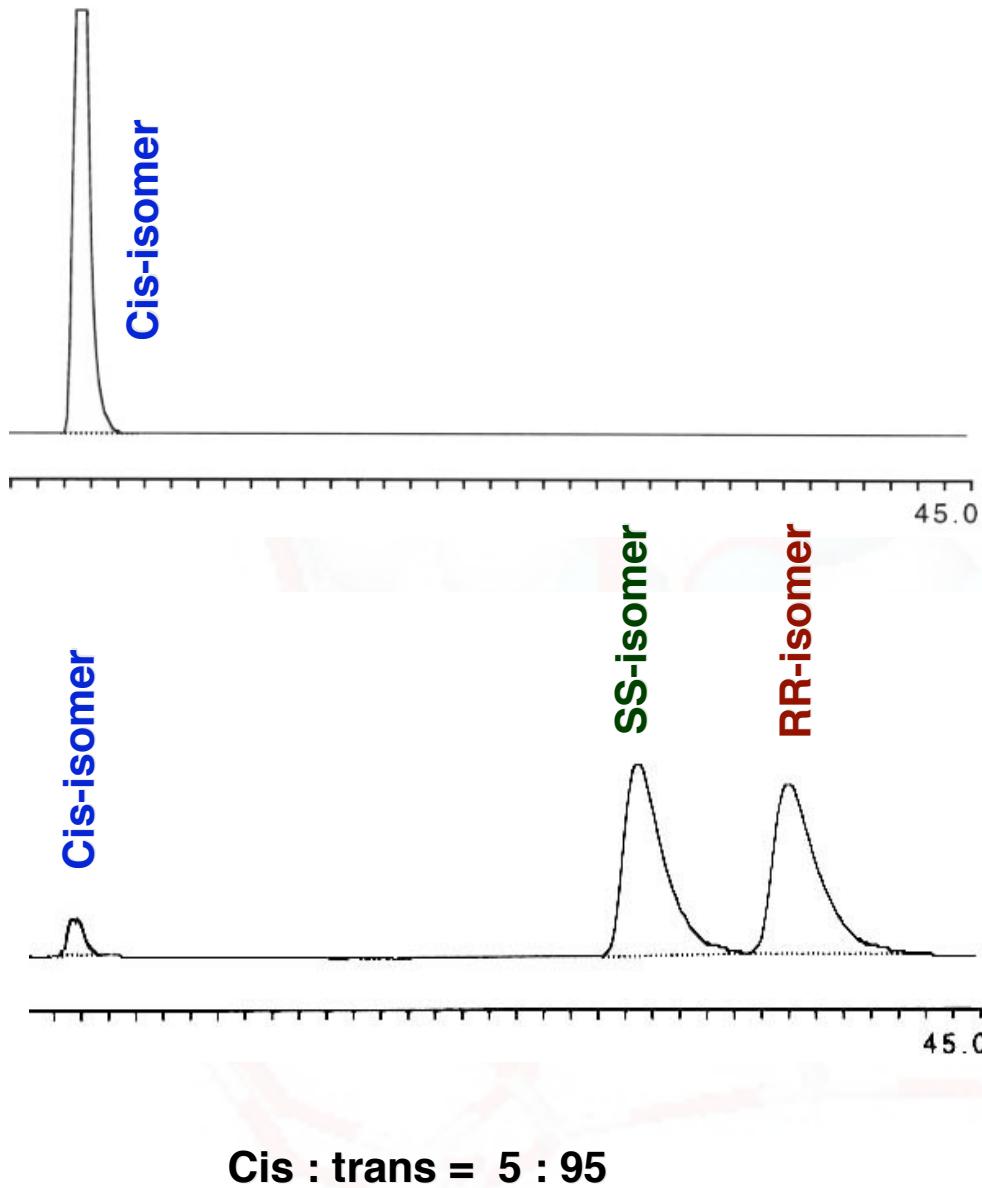


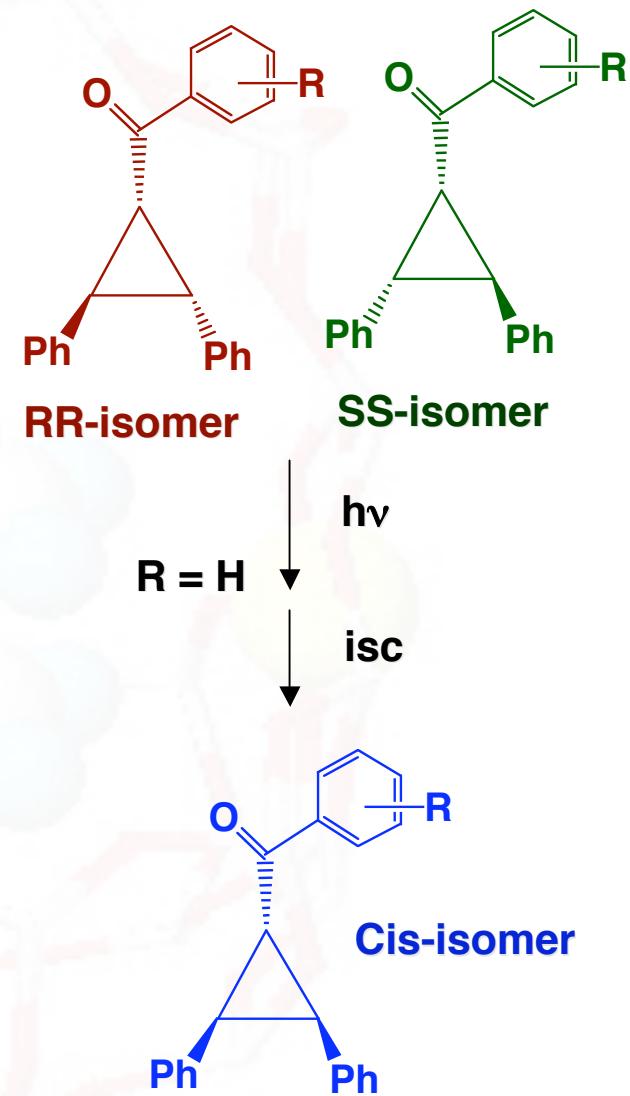
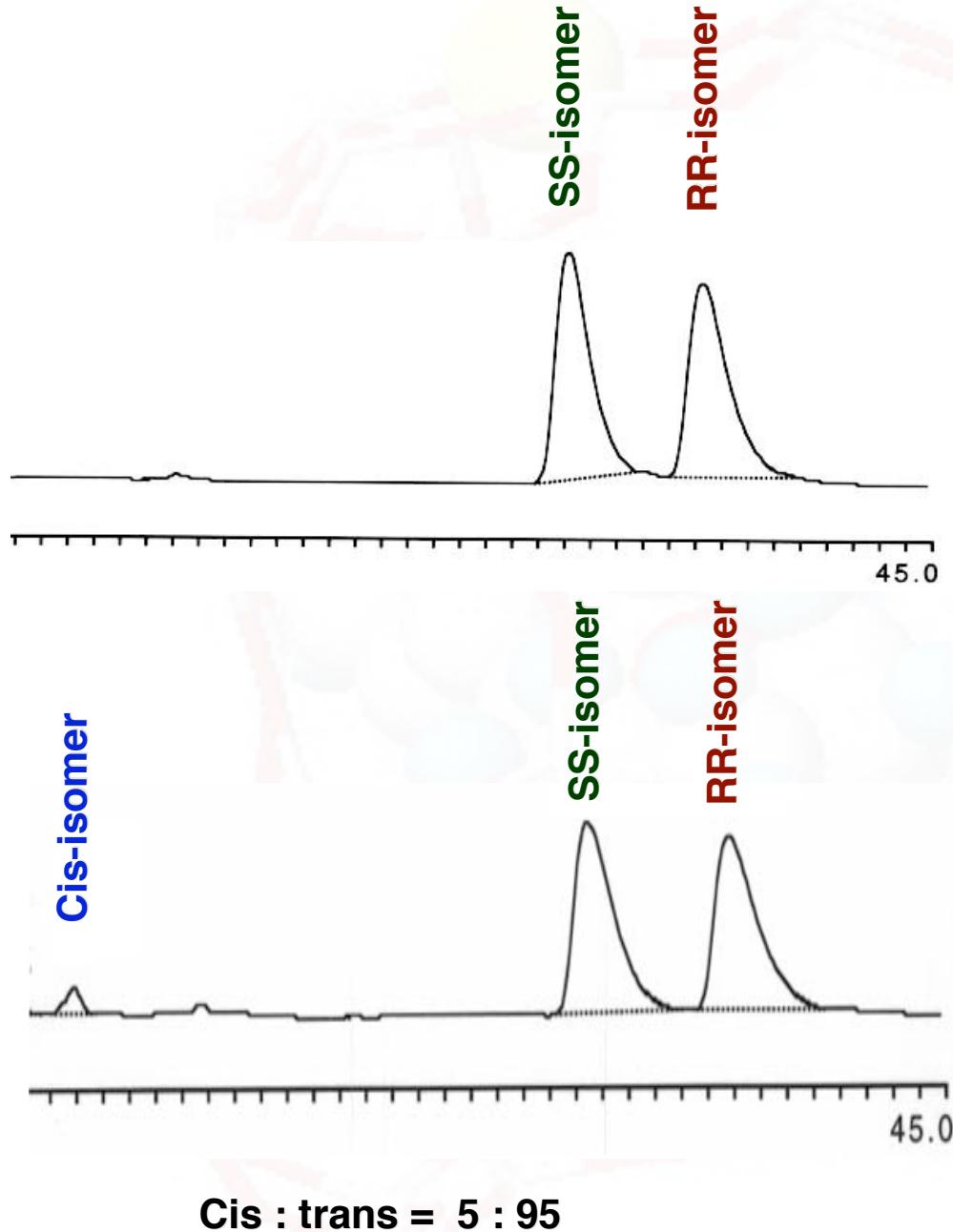
## SOLUTION

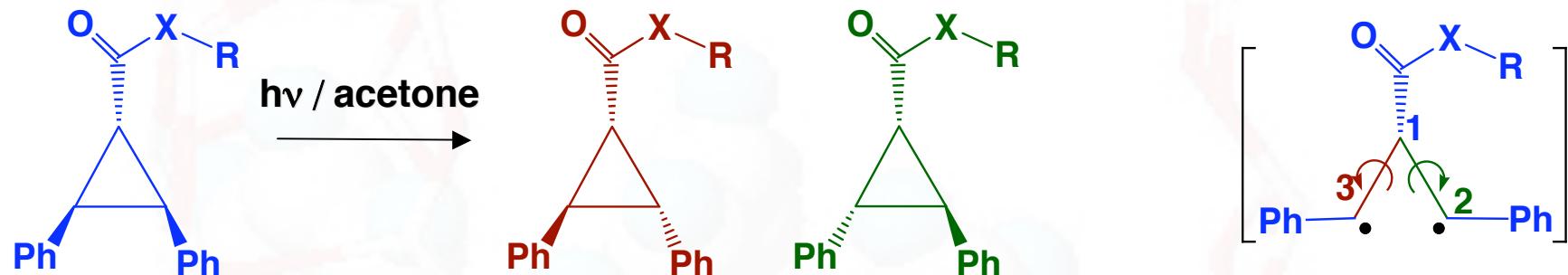


## ZEOLITE

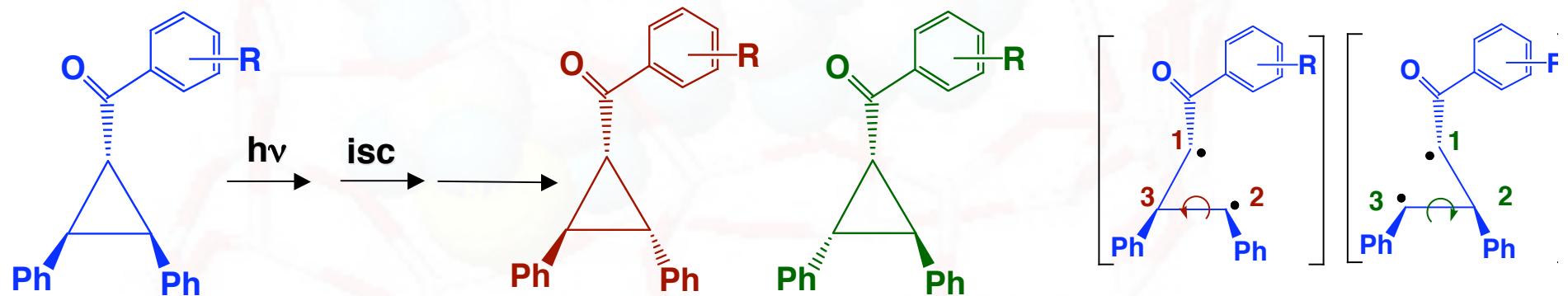




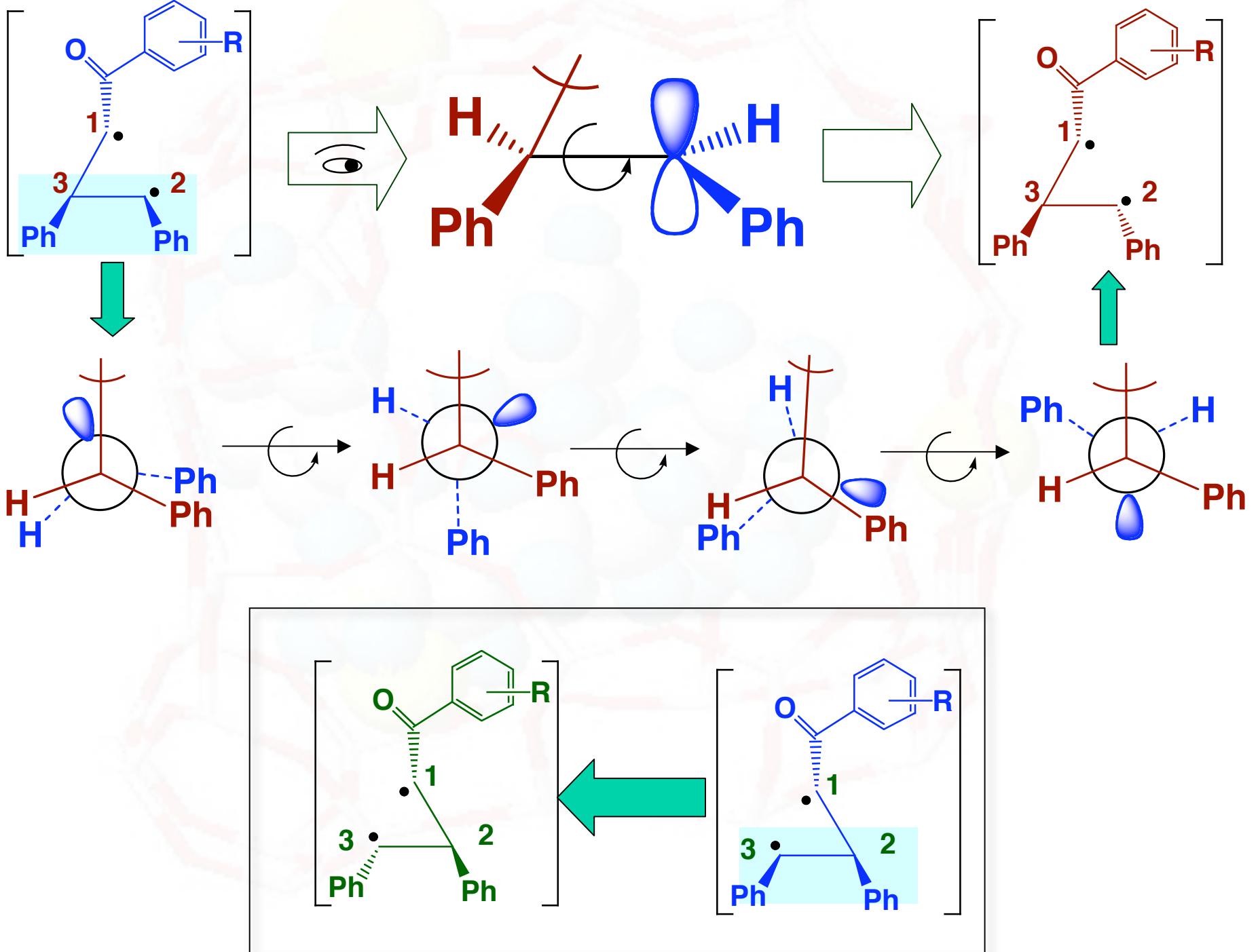


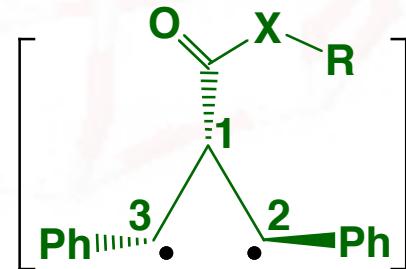
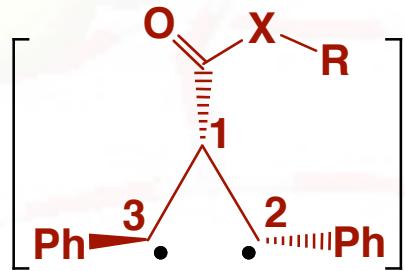
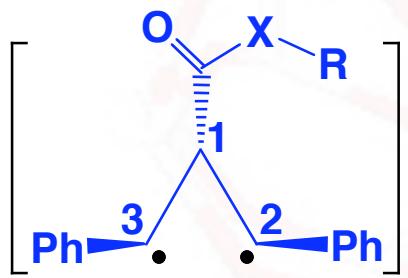
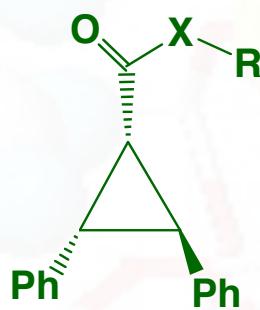
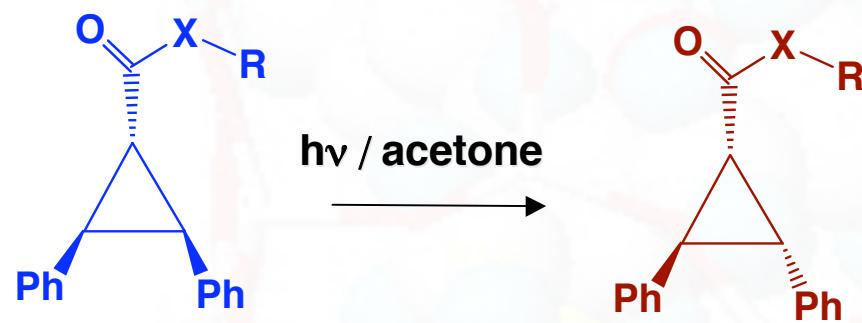
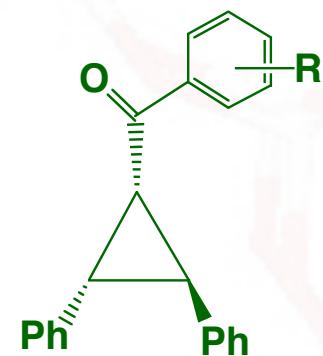
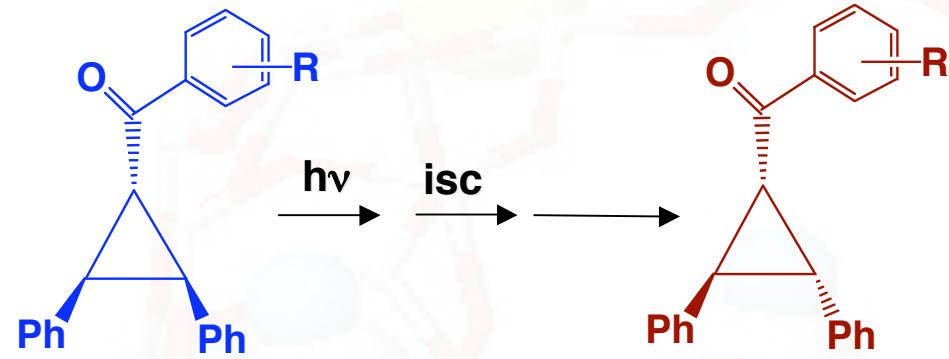


**Cis : trans = 45 : 55**



**Cis : trans = 5 : 95**



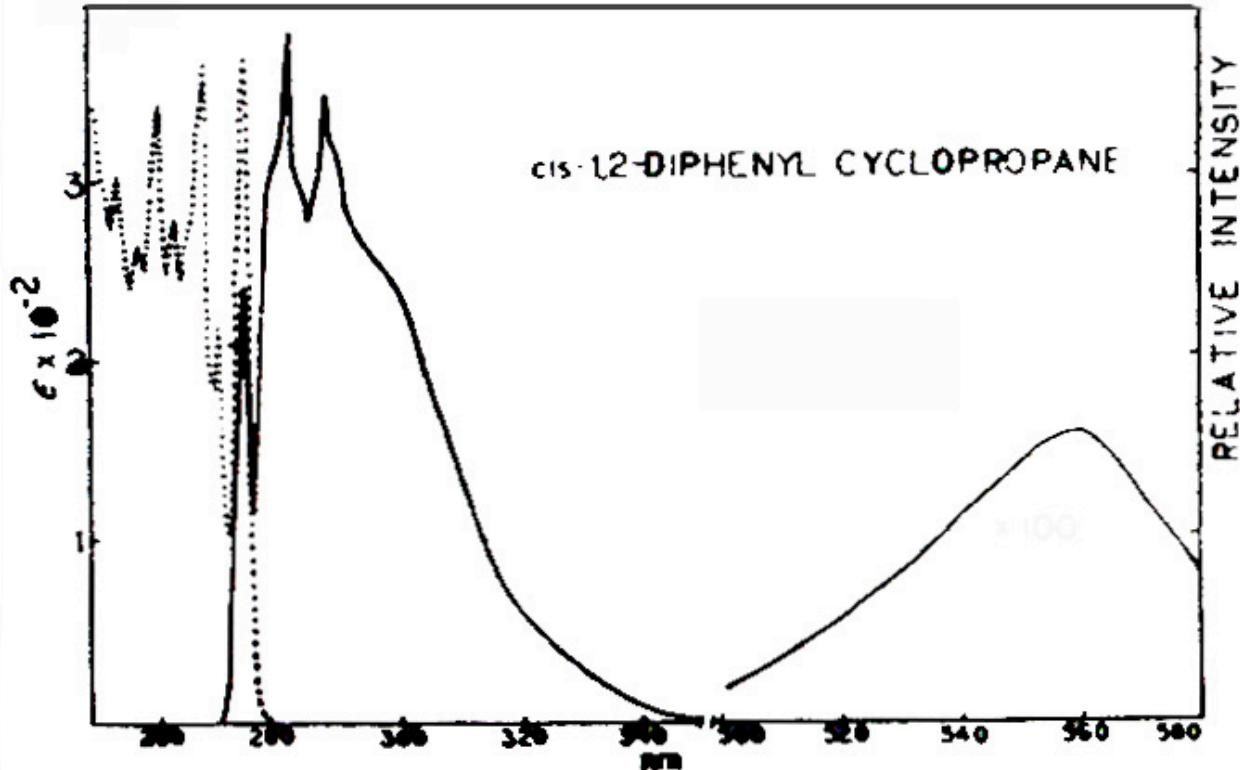
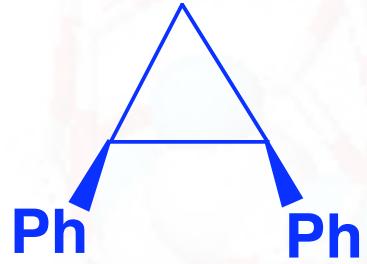


# Asymmetric Photoreactions Within Zeolites

## Modest to Good Chiral Induction

### Chiral Induction Depends on

- Type of cations in the zeolite
- Water Content
- Number of Cations (Si/Al ratio)
- Chiral Perturber
  - Anchoring of chiral perturber  
Cation- $\pi$  or cation-carbonyl interactions
- Cation binding - Diastereomer switch
  - Controlling diastereomer switch by N-methylation
- Reactive State ( $S_1$  vs  $T_1$ )
- Mechanism of the Reaction



Becker, R. S.; Edwards, L.; Bost, R.; Elam, M.; Griffin, G.; JACS, 94, 6584-6591, (1972).

**Singlet energy  $\sim 102$  kcal/mole**

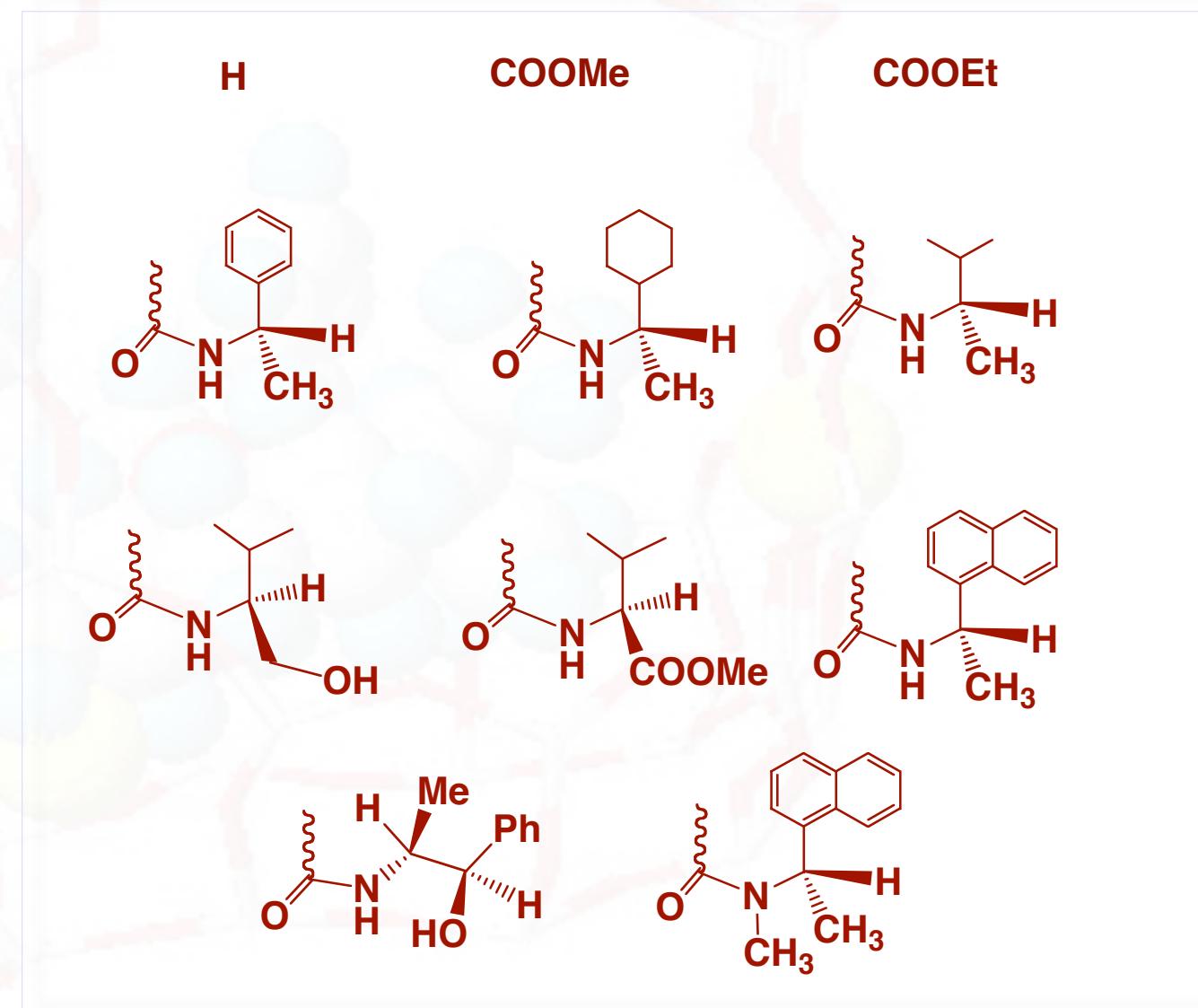
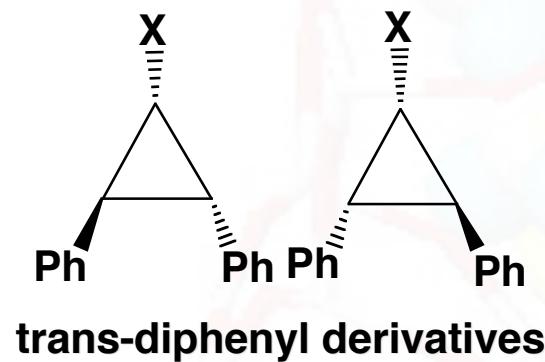
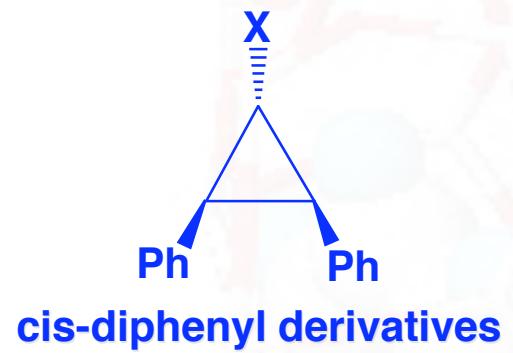
**Triplet energy  $\sim 53$  kcal/mole**

**Phosphorescence ( $\tau_p$ ) = 8 msec**

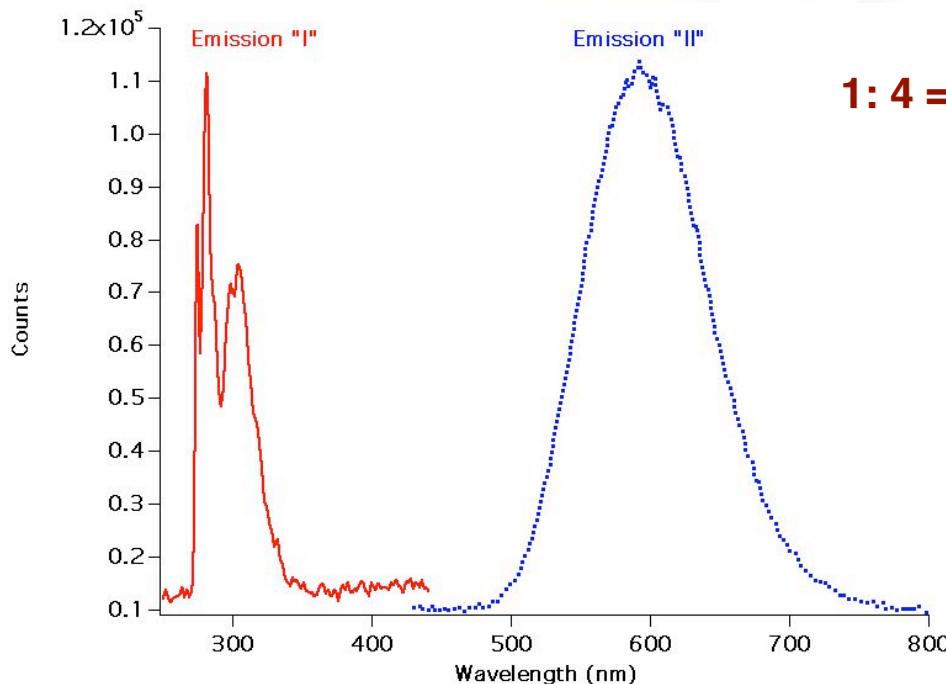
**Medium = 3-Methylpentane glass**

**Temperature = 77K**

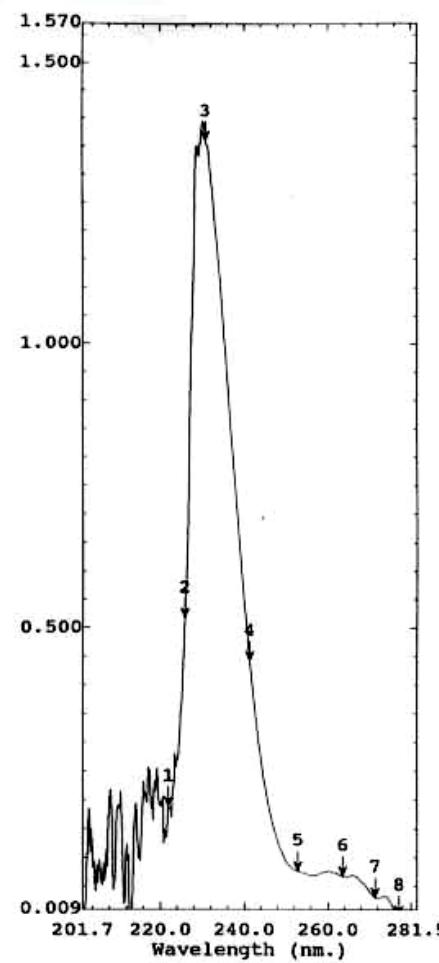
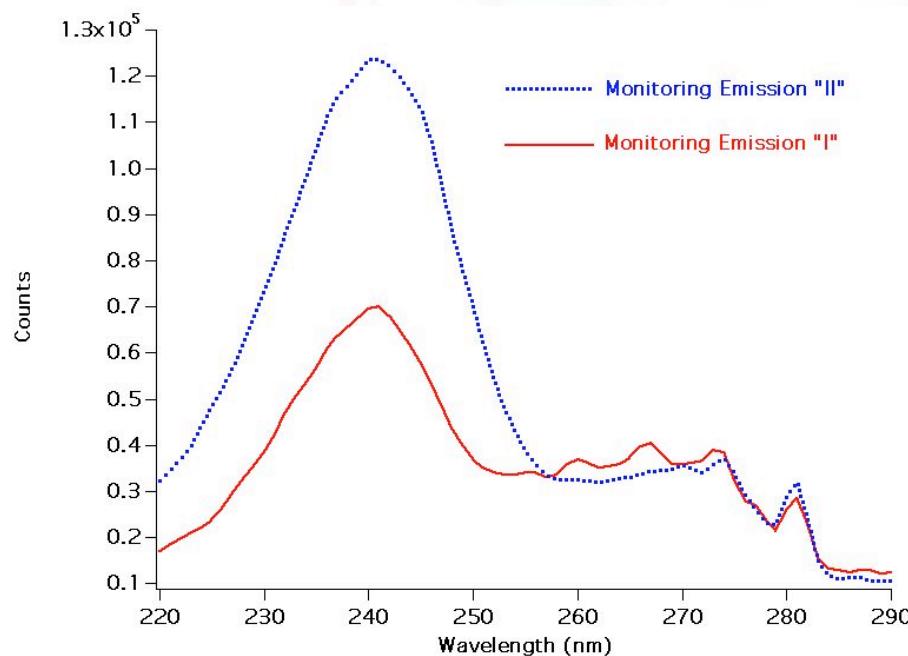
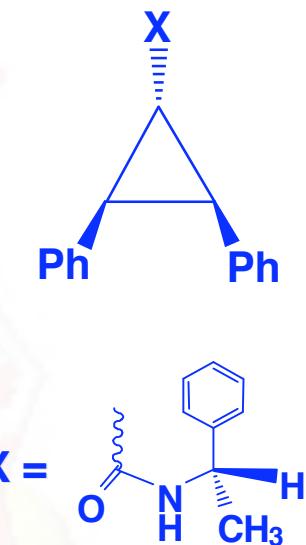
**Efforts to sensitize the reaction with fluorenone ( $E_T = 50.4$  kcal/mol) and acetonaphthone ( $E_T = 59.7$  kcal/mol) were unsuccessful.**



# Emission from *cis*-diphenylcyclopropane derivatives

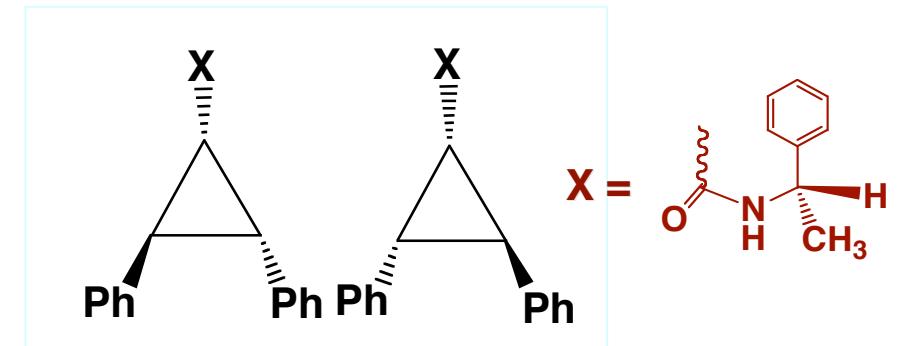
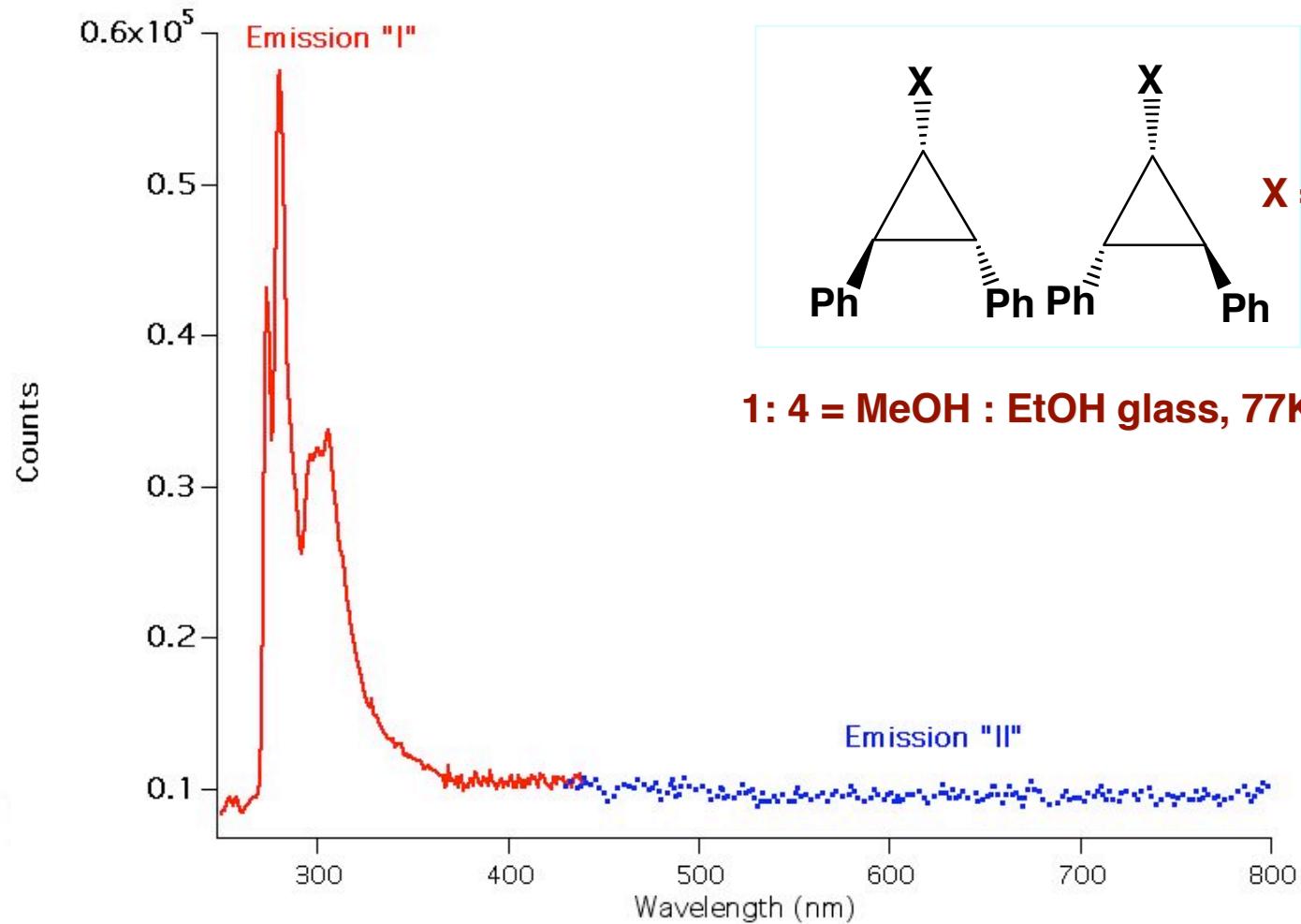


1: 4 = MeOH : EtOH glass, 77K



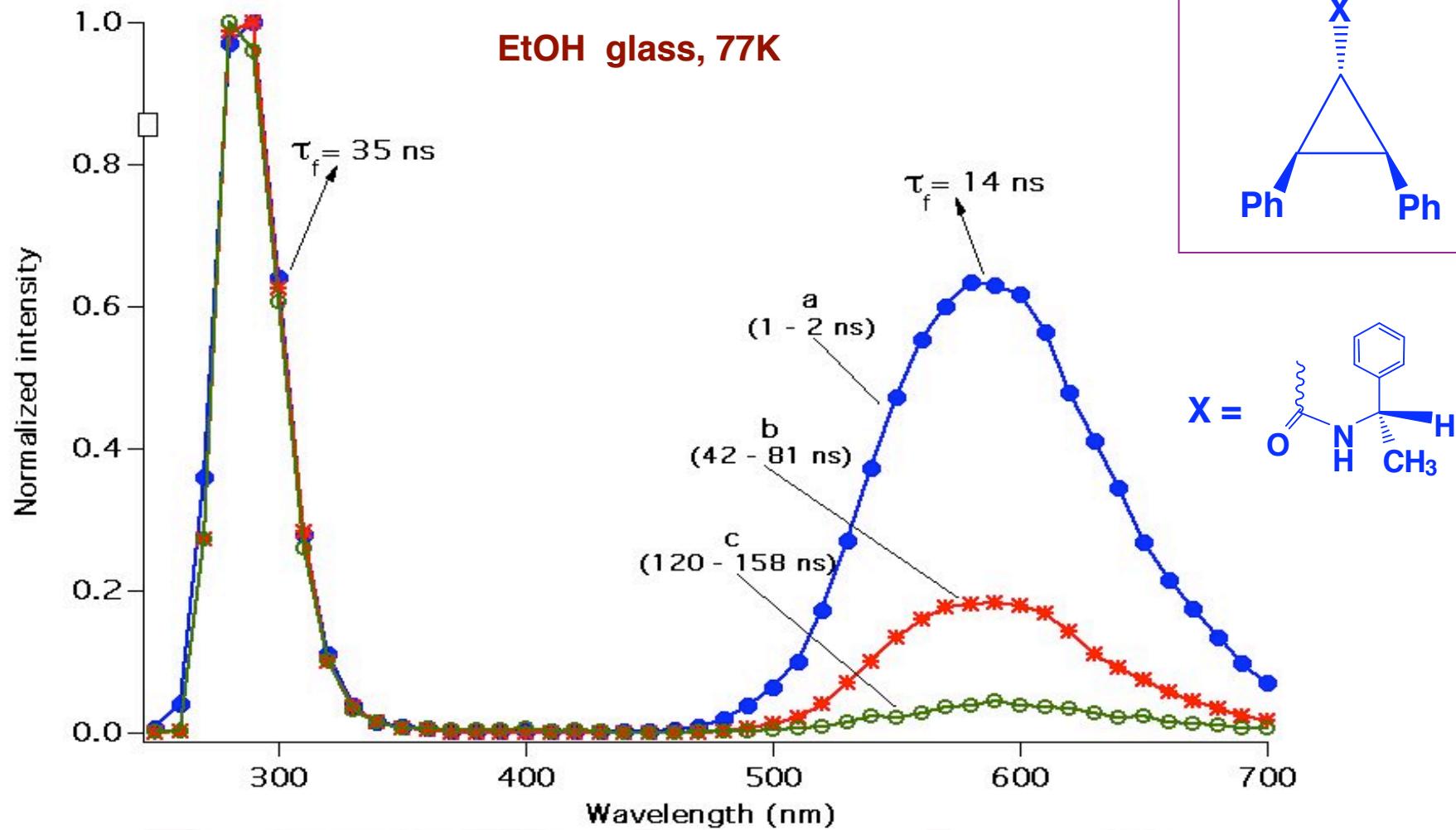
No.	Wavelength (nm.)	Ab
1	221.80	0.1
2	225.80	0.5
3	230.80	1.3
4	241.20	0.4
5	252.80	0.0
6	263.60	0.0
7	271.40	0.0
8	277.20	-0.0

# Emission from *trans*-diphenylcyclopropane derivatives



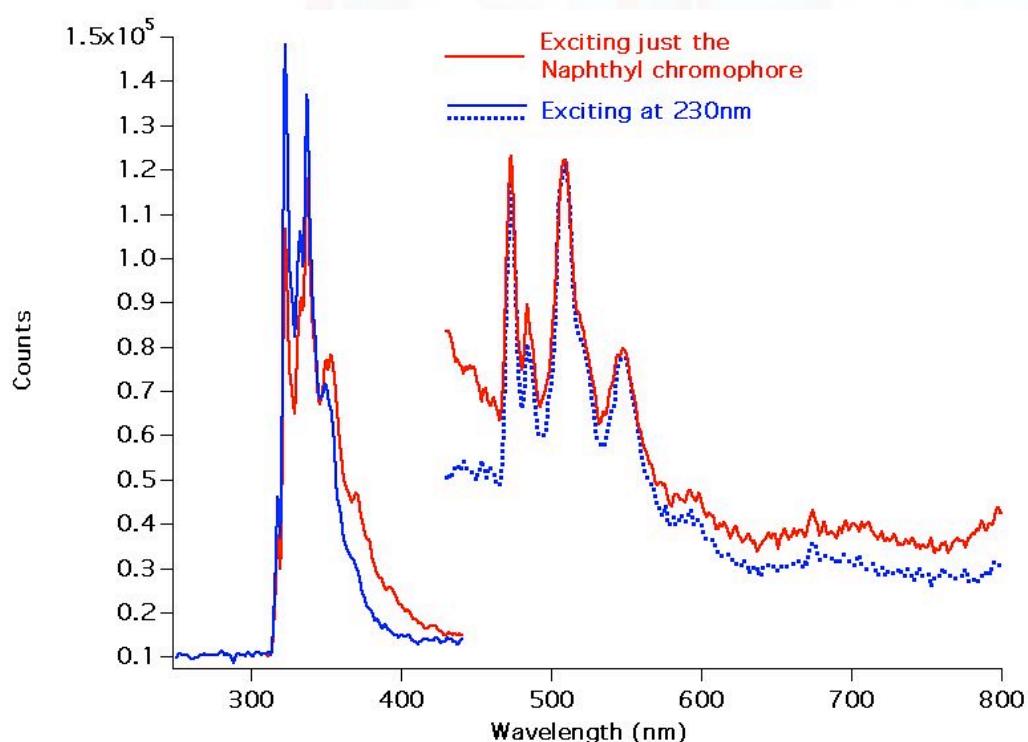
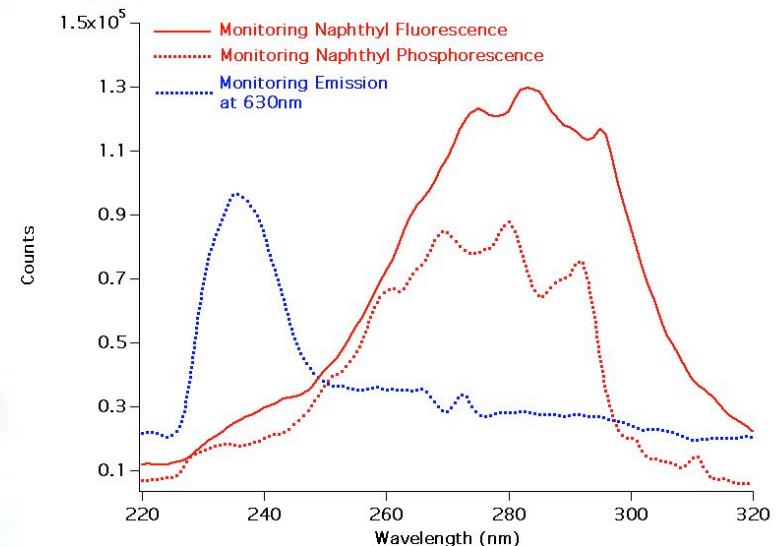
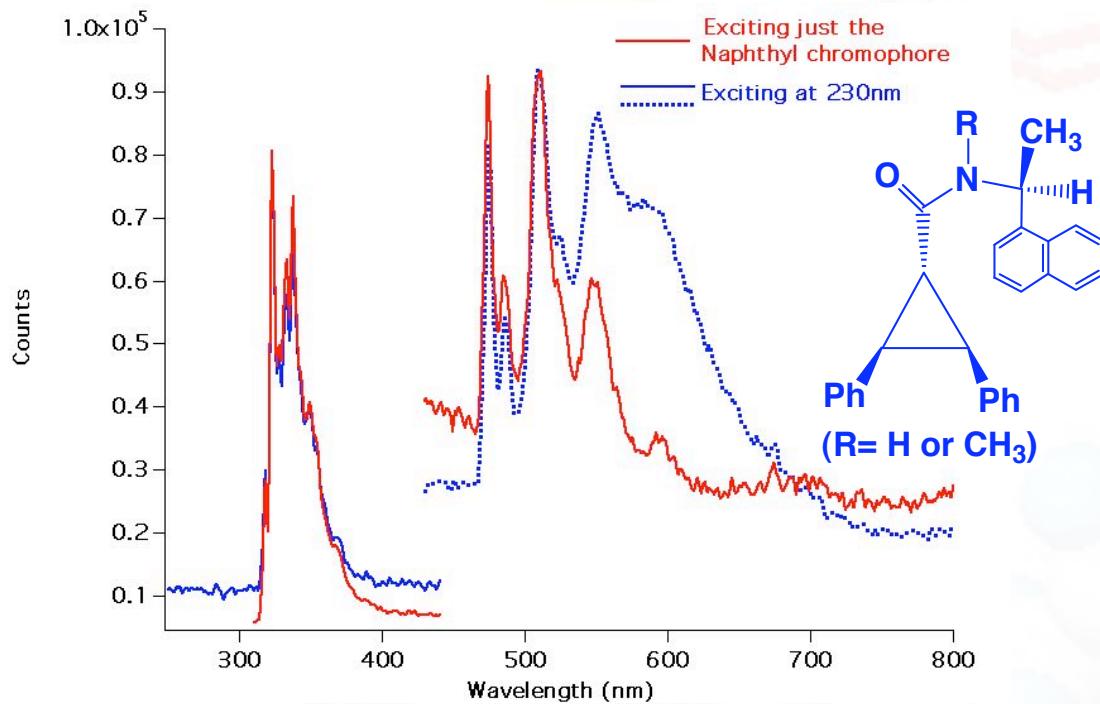
1: 4 = MeOH : EtOH glass, 77K

## Time resolved Emission

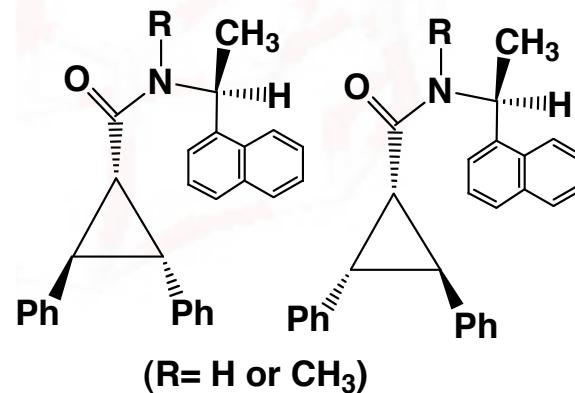


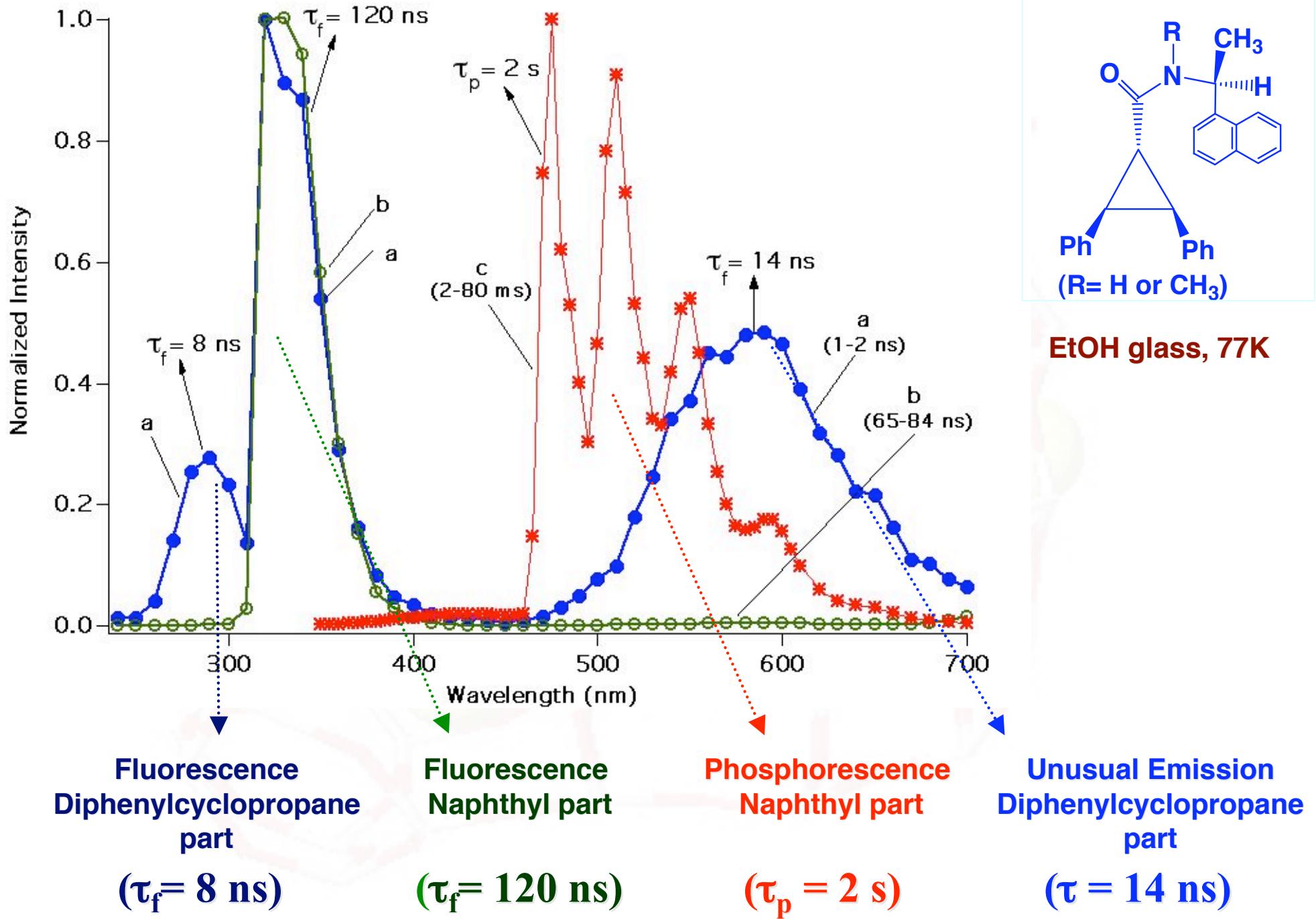
$(\tau = 14 \text{ ns})$

$(\tau_p) = 8 \text{ msec}$  JACS, 94, 6584-6591, (1972).



**1: 4 = MeOH : EtOH glass, 77K**



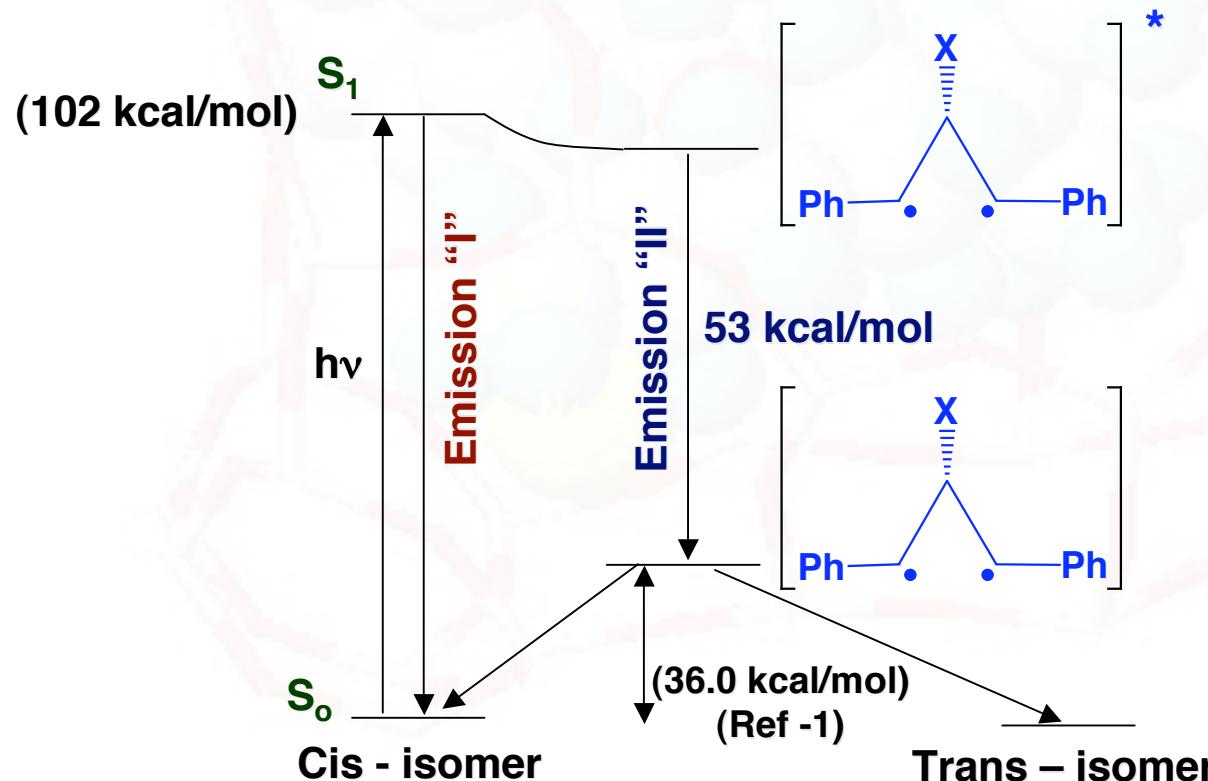


# Structureless emission ?

Lifetime is too short to be phosphorescence.

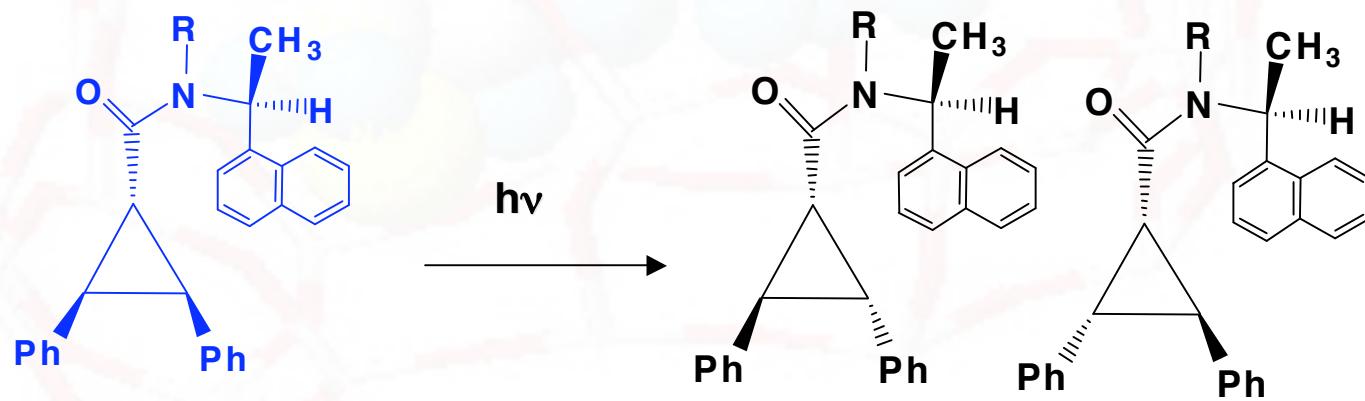
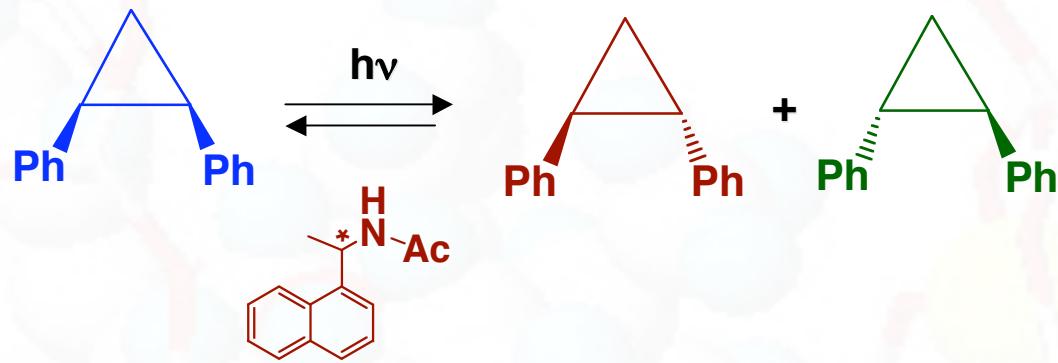
Based on triplet sensitization results the emission is at a lower energy to be phosphorescence.

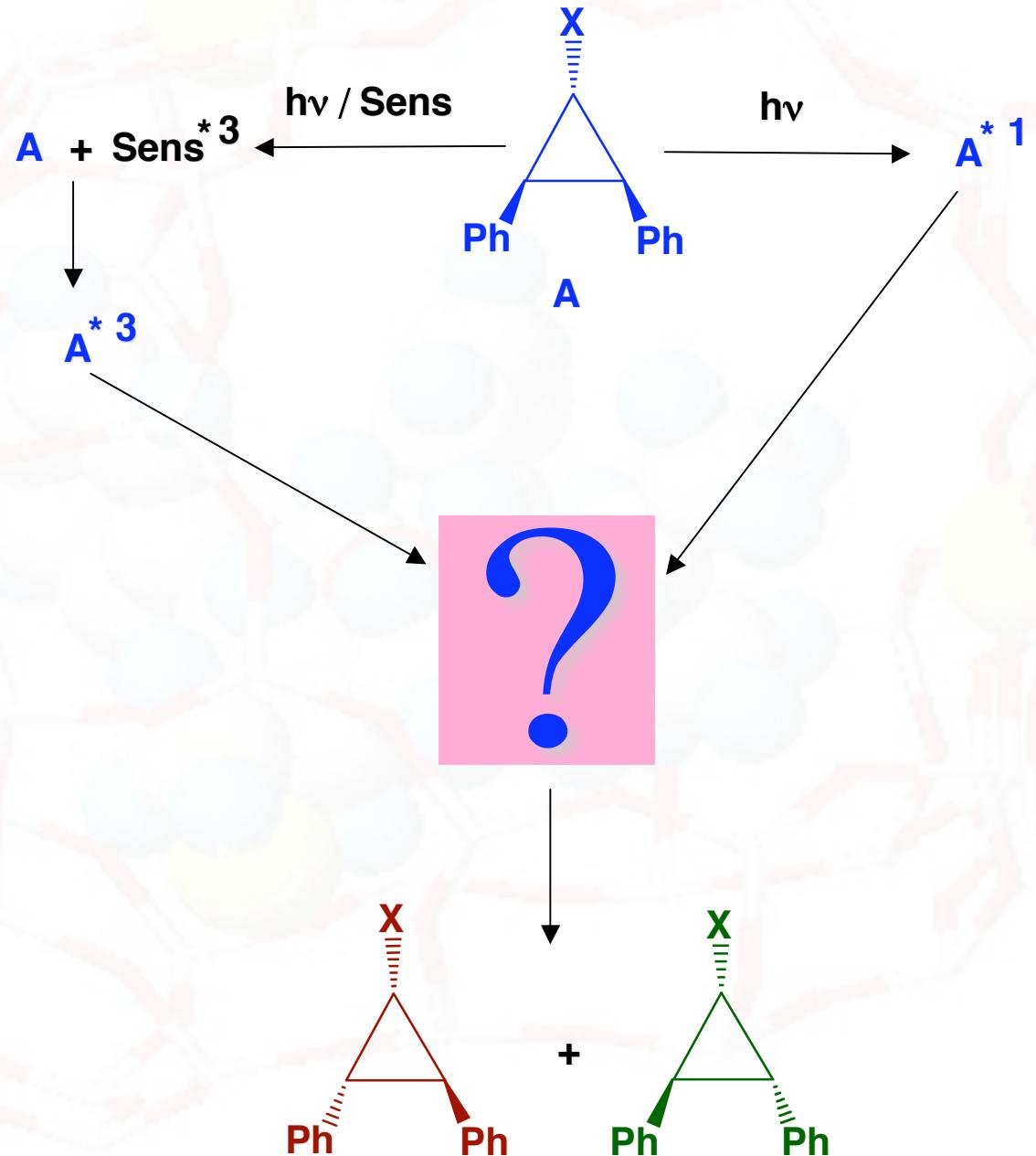
Resembles the emission from benzyl radicals (510 – 700 nm).

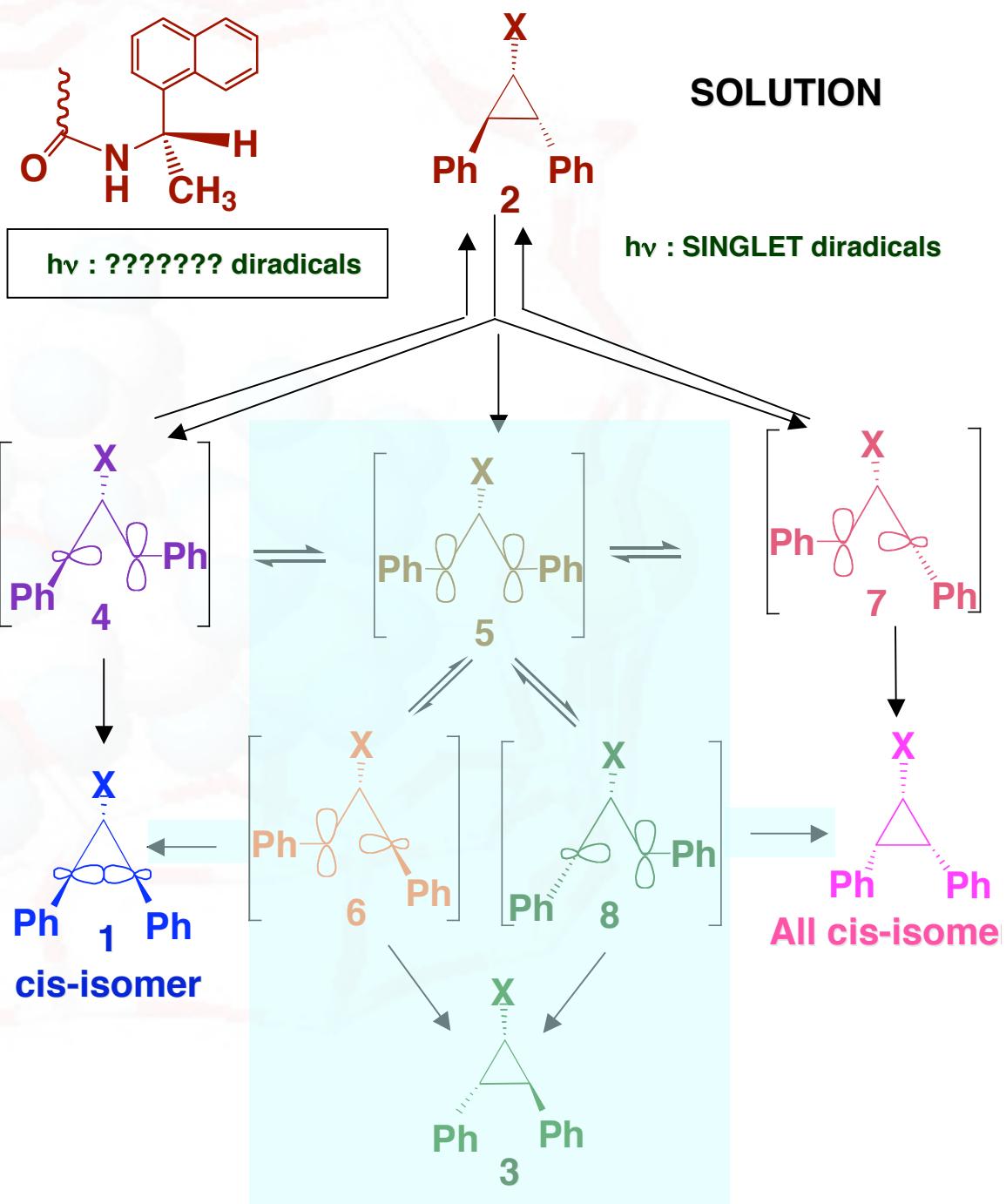
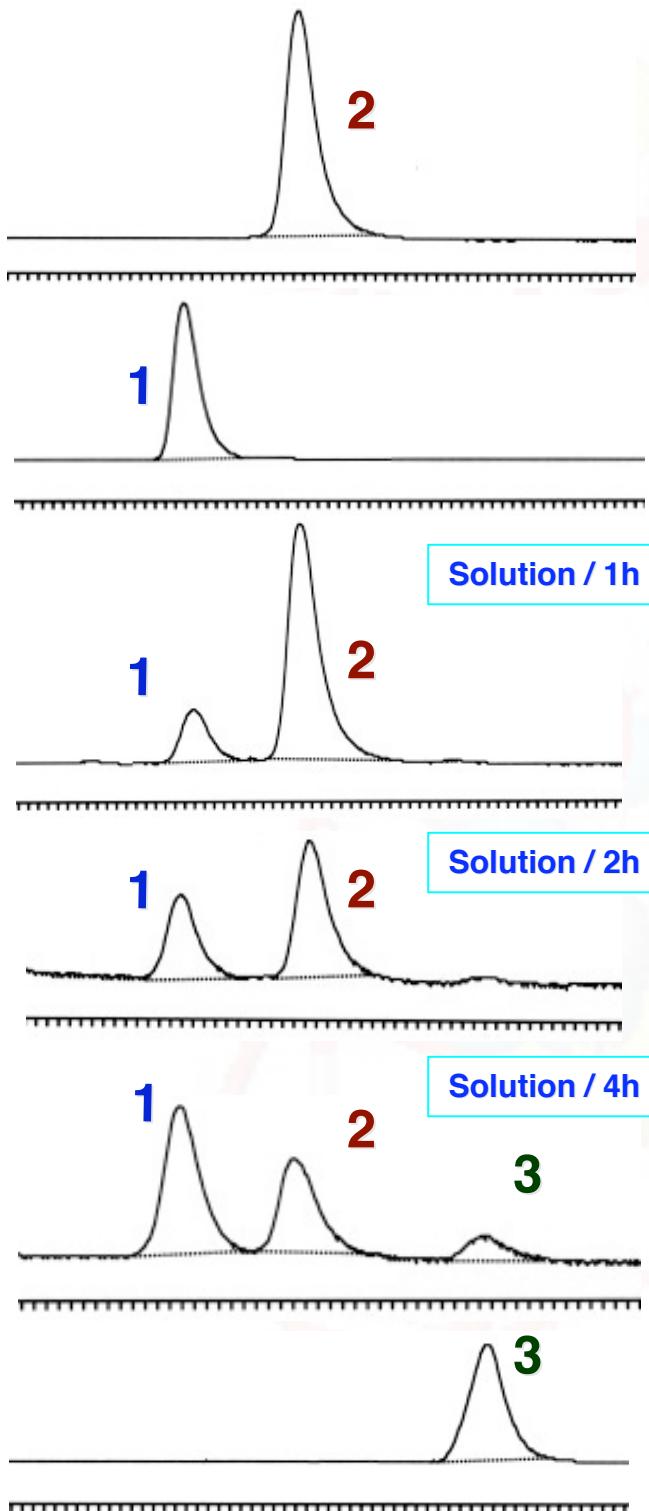


Ref-1 :  
Tetrahedron Lett., 2951–2953, (196)

# Role of Naphthalene in photoisomerization of Diphenylcyclopropane

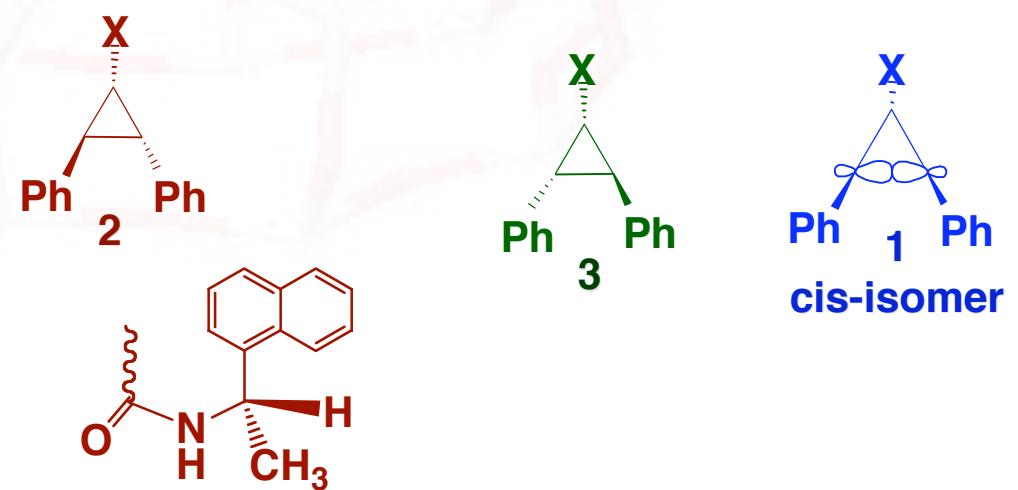
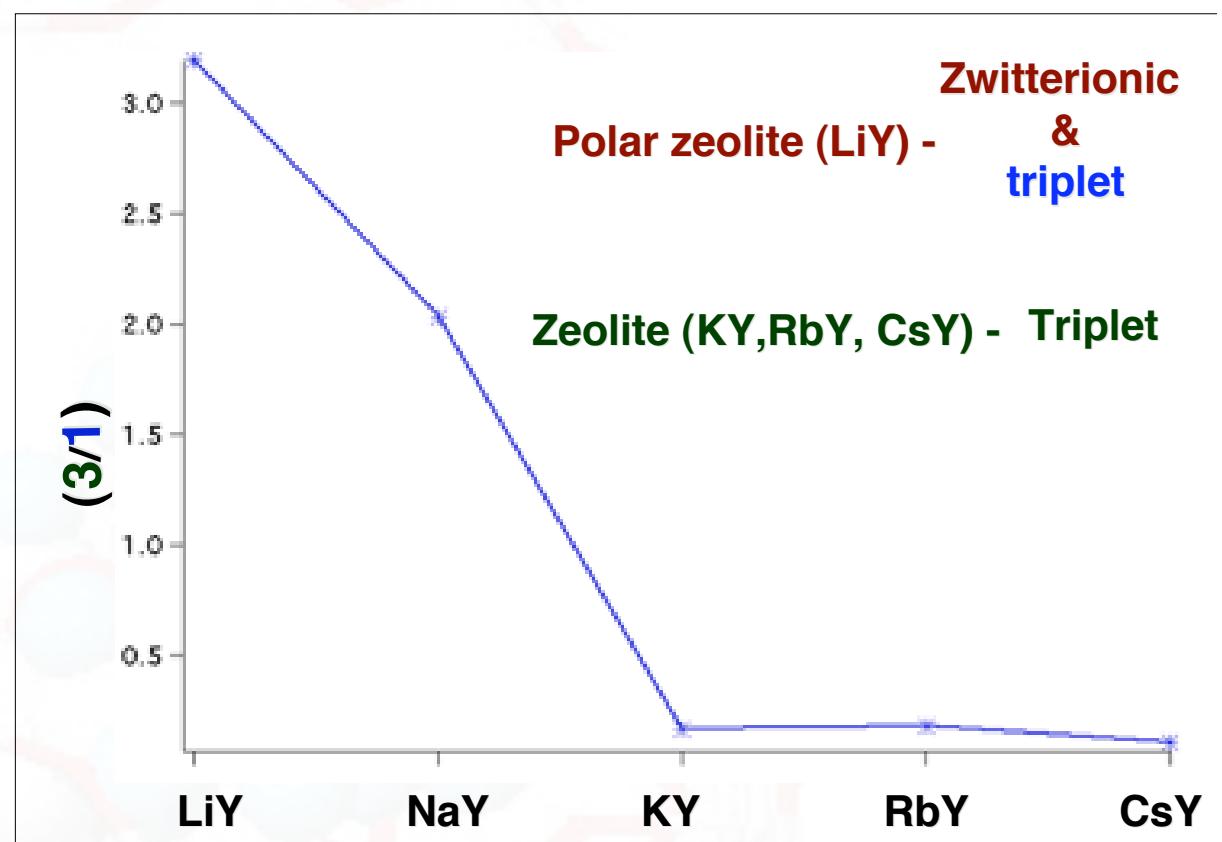
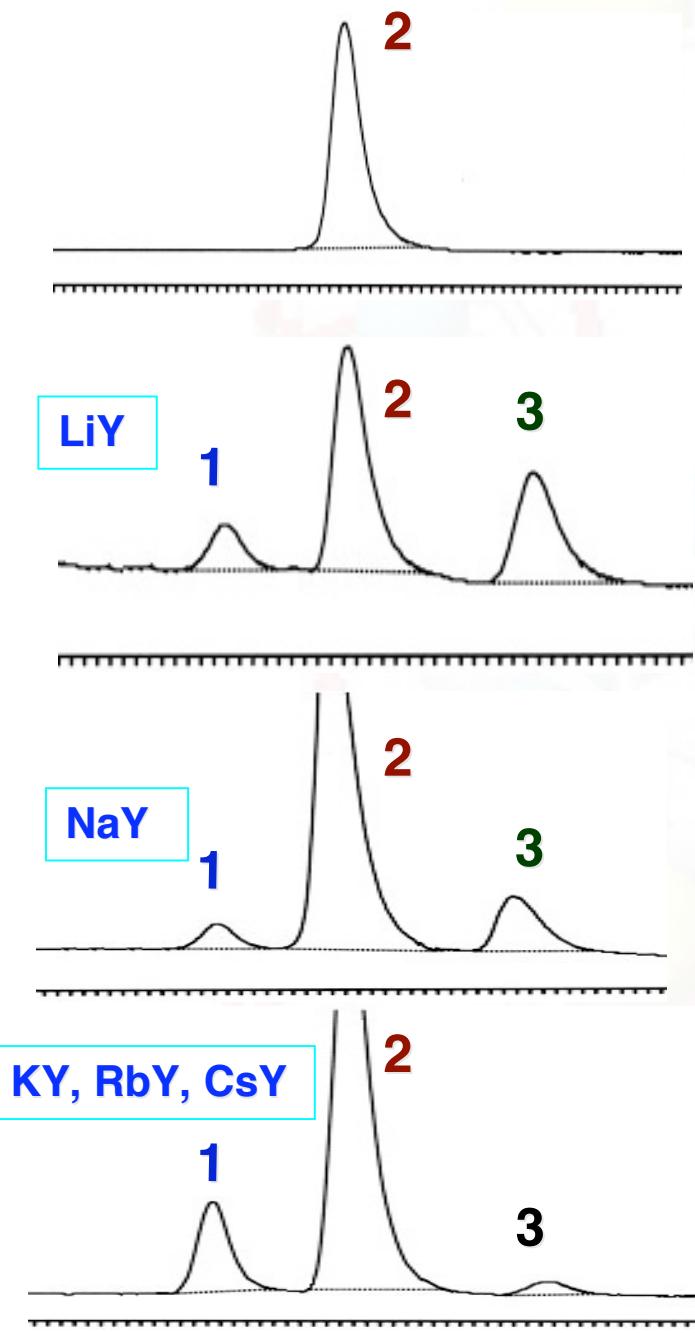






## ZEOLITE

$h\nu$  : ??????? diradicals



# Conclusions

➤ Influence of the Chiral Perturber – Increased Within Zeolite

- Stereoselectivity                  Reactive spin state

➤ Photo-isomerization within Zeolites

- Direct excitation                  Proceeds possibly via 1,3-zwitterionic intermediates
- Triplet sensitization              Proceeds via equilibrated 1,3-diradicals

➤ Photo-isomerization in Solution

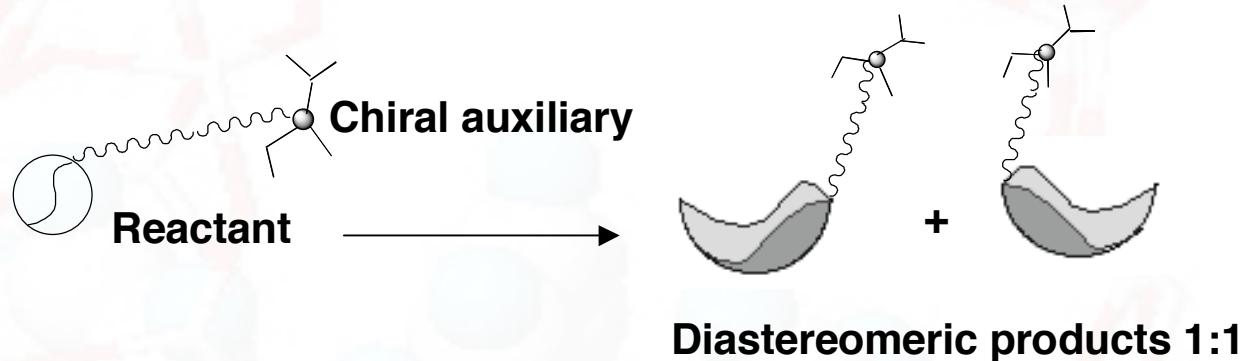
- Direct excitation                  Adiabatic processes may be involved, especially at 77K
- Proceeds via non-equilibrated 1,3-diradicals
- Triplet state not involved
- Triplet sensitization              Triplet energy of DPCP derivatives above 69 kcal/mol
- Proceeds via equilibrated 1,3-diradicals

➤ Role of Naphthyl chromophore in Photo-isomerization of diphenylcyclorpropane

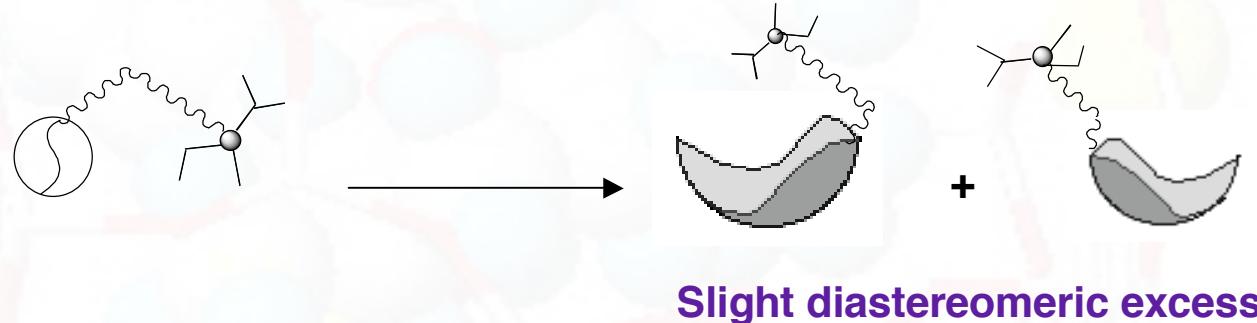
- Direct excitation                  Proceeds possibly via  
1,3—singlet diradical (solution)  
zwitterionic / 1,3-Triplet diradical (Nature of zeolite)

# A Model

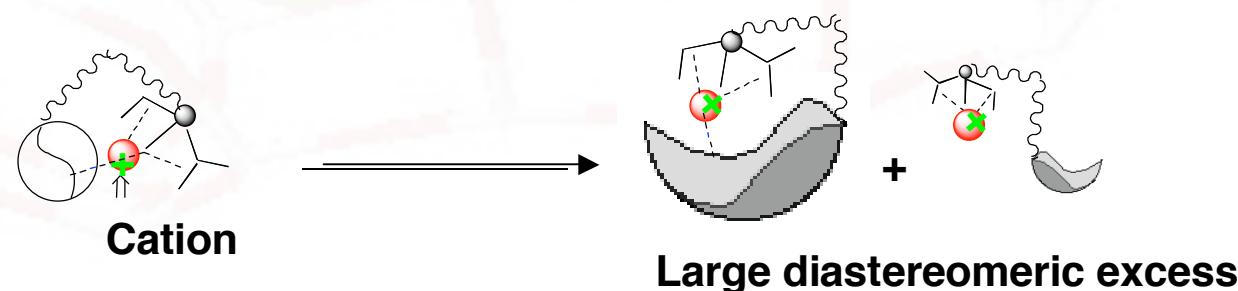
## Isotropic media



## Confined space (Role of confinement)



## Inside zeolites (Role of cations and confinement)



# Conclusions

## ➤ Influence of the Chiral Perturber – Increased Within Zeolite

- Stereoselectivity                                  Cations
- Water content
- Nature of the chiral perturber
- Reactive spin state

## ➤ Photo-isomerization within Zeolites

- Direct excitation                                    Proceeds possibly via 1,3-zwitterionic intermediate
- Triplet sensitization                                Proceeds via equilibrated 1,3-diradicals

## ➤ Photo-isomerization in Solution

- Direct excitation                                    Adiabatic processes may be involved, especially at 77K
- Proceeds via non-equilibrated 1,3-diradicals
- Triplet state not involved
- Triplet sensitization                                Triplet energy of DPCP derivatives above 69 kcal/mol
- Proceeds via equilibrated 1,3-diradicals

## **Acknowledgement**

**Prof. V. Ramamurthy**

**Ramamurthy group members**

**Prof. Nicholas. J. Turro and Dr. Steffan Jockusch**

**Prof. John. R. Scheffer and Kenneth. C. W. Chong**

**Prof. J. Chandrasekhar and Dr. R. B. Sunoj**

**NSF**