Stereochemistry of Molecules in Crystals (part 1, 2)

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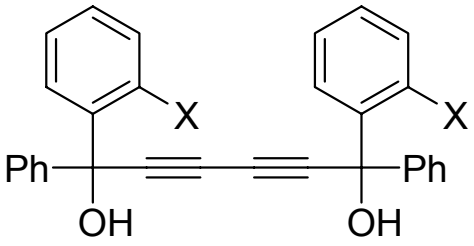
key word: solid state, host-guest complex

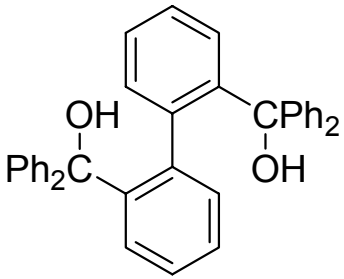
part 1: statistic aspect

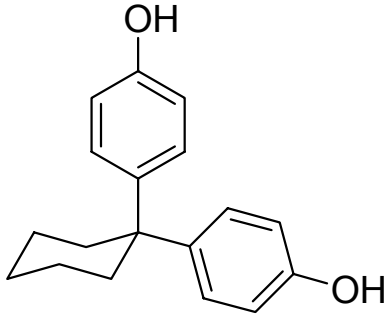
part 2: dynamic aspect

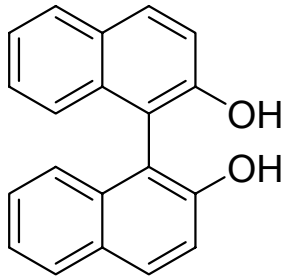
host:



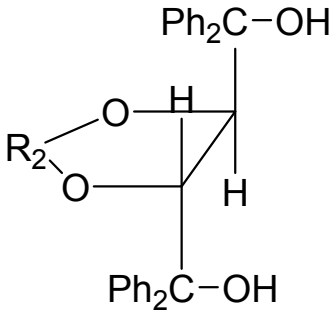
a: X = H
b: X = Cl (chiral)



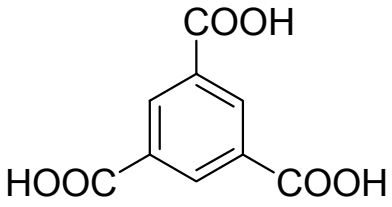


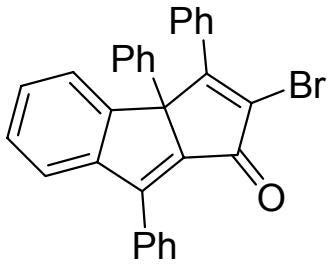


rac, chiral

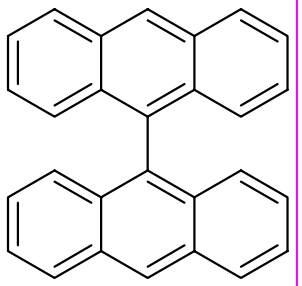


rac, chiral





rac, chiral



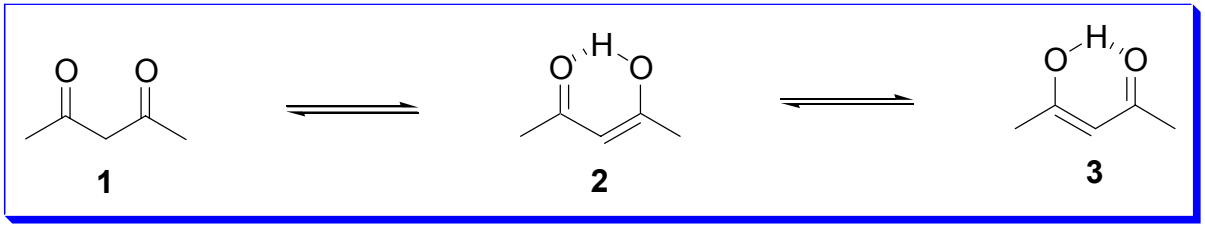
H-G complexation:

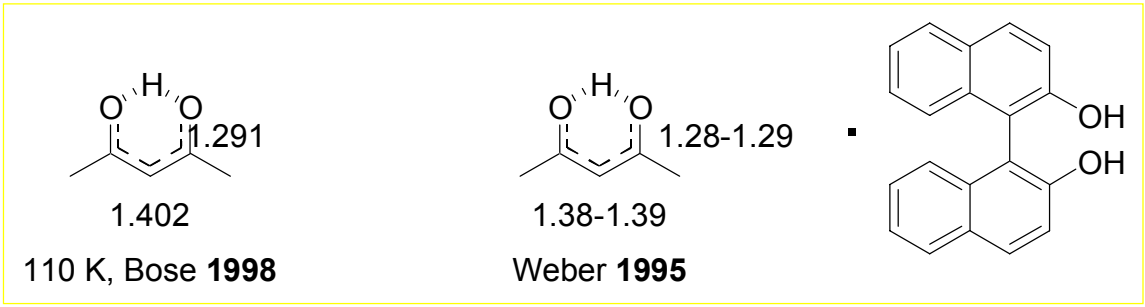
H/liq. G, H/gas G, H+G/solvent, H+G grinding

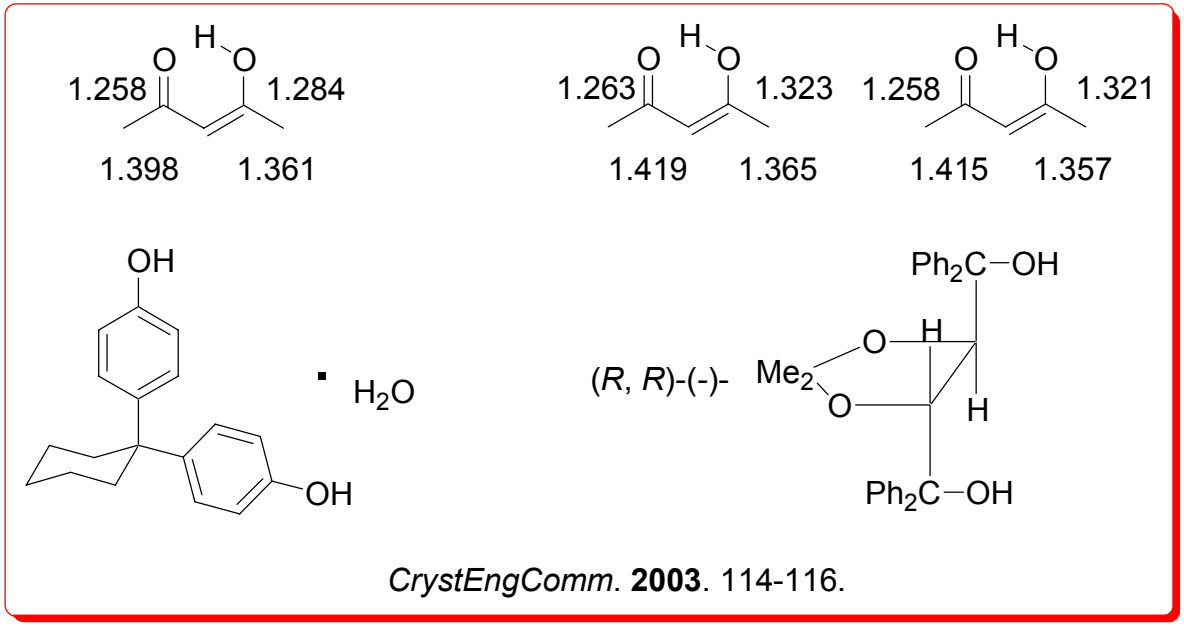
part 1: statistic aspect

(I) stereoisomers in inclusion crystals

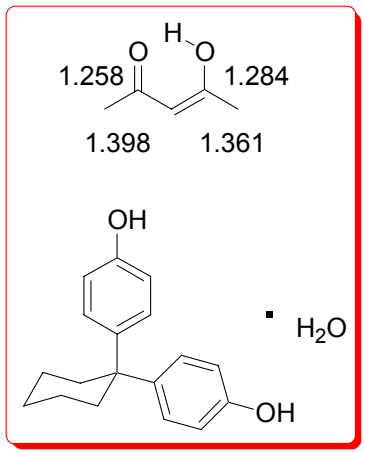
1) acetylacetone-enol form

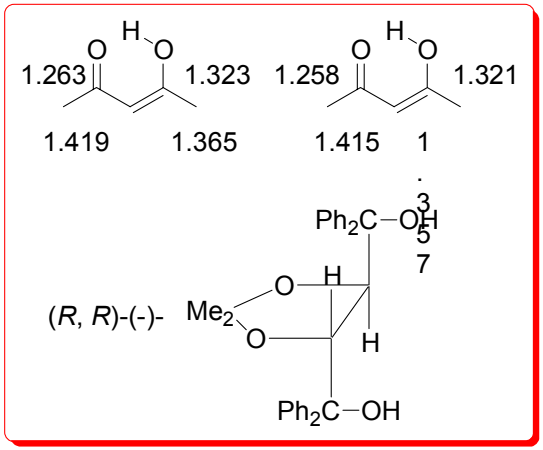


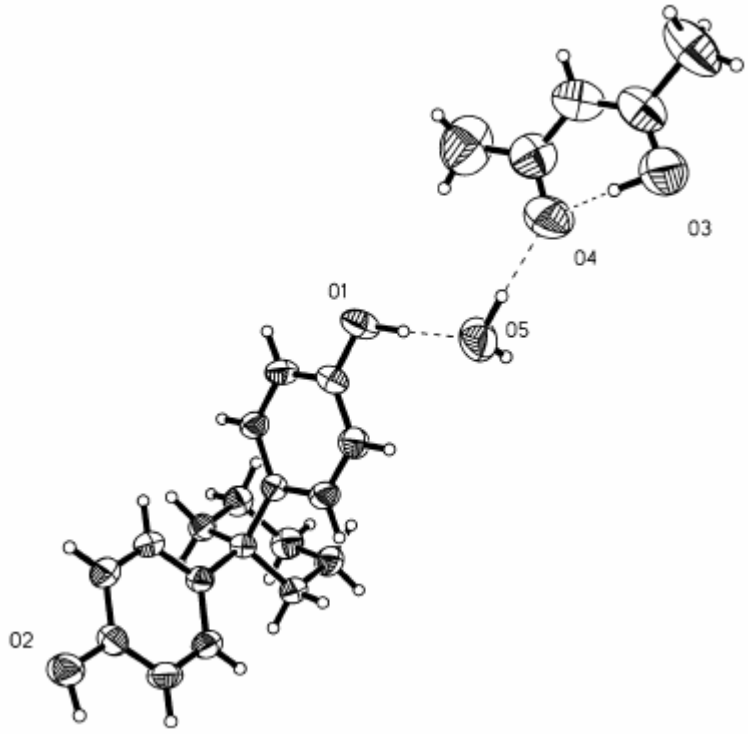




CrystEngComm. **2003**. 114-116.







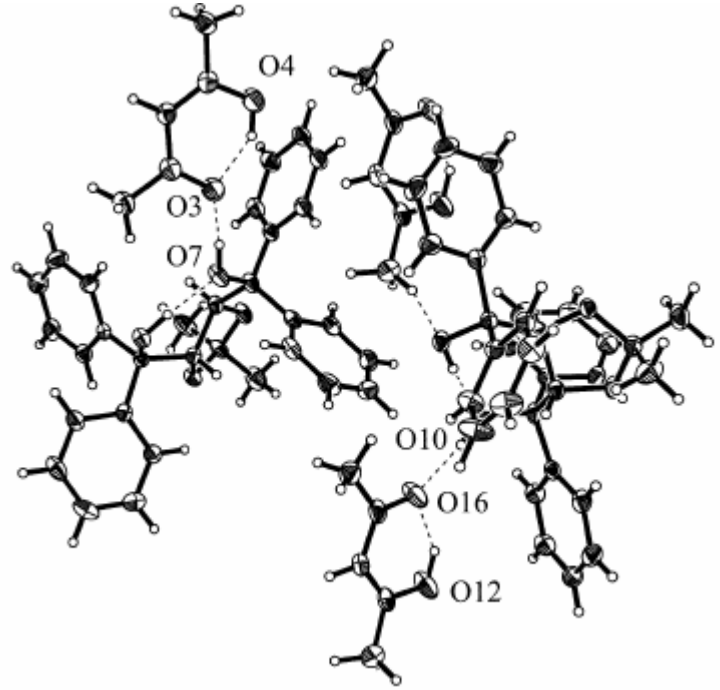
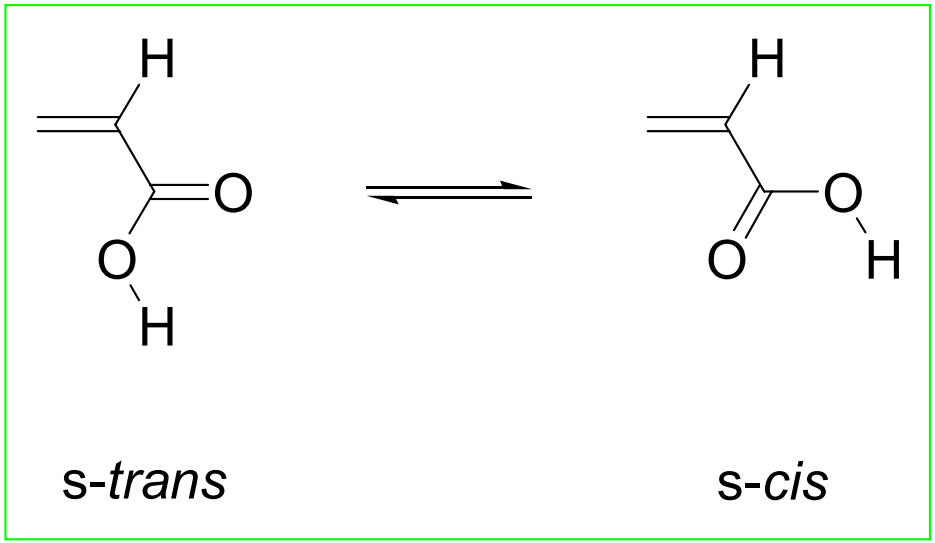
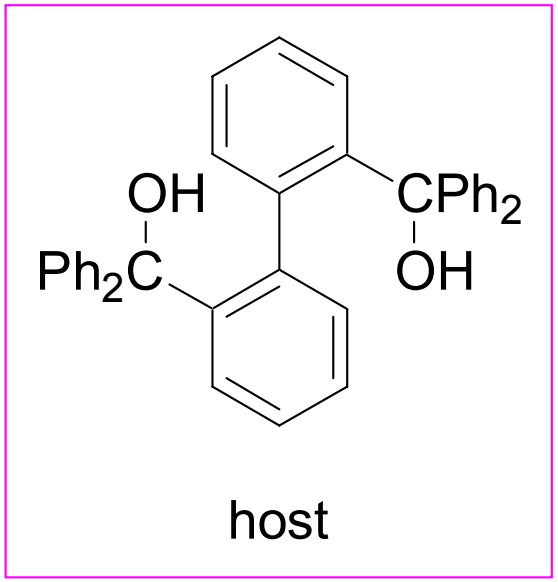


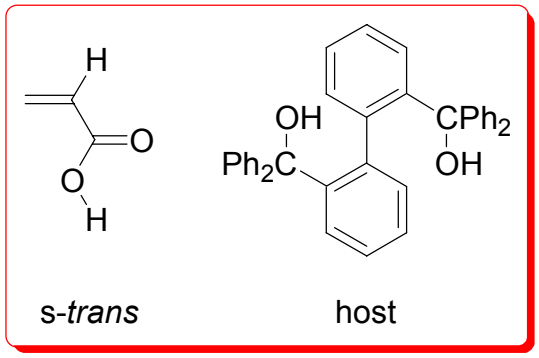
Fig. X-ray structures of inclusion complexes of acetylacetone.

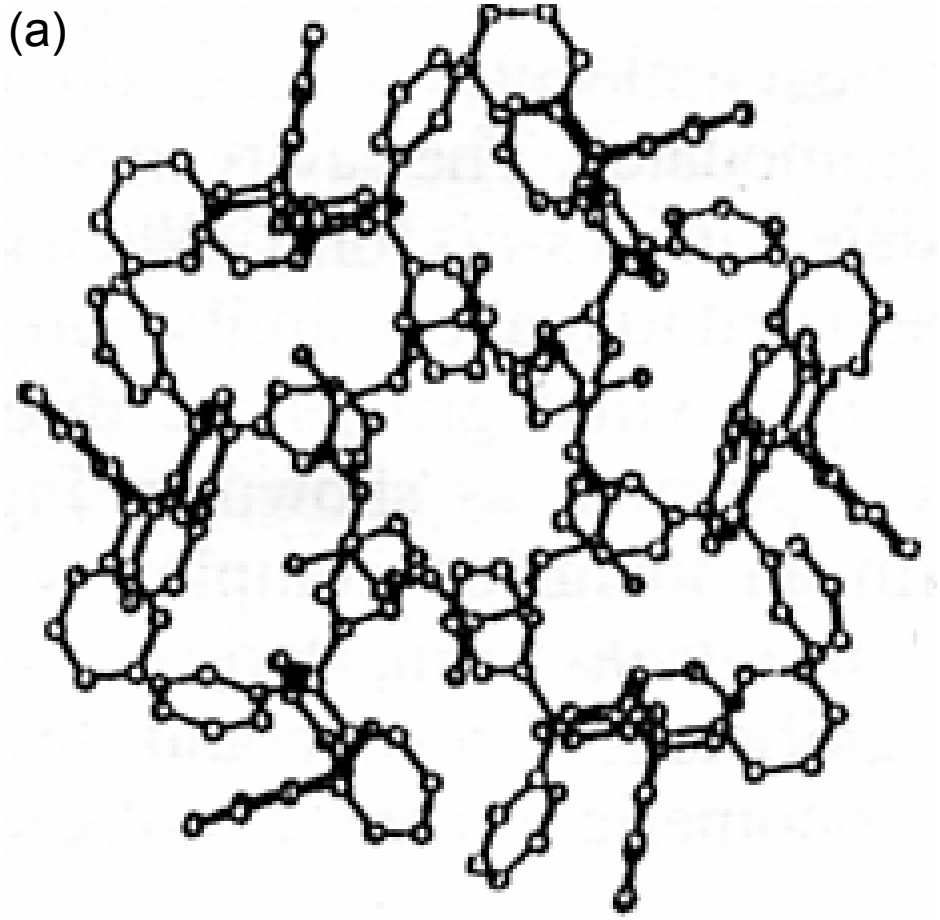
2) acylic acid-monomeric *s-trans* form





Chem. Comm. **1998**, 2502.





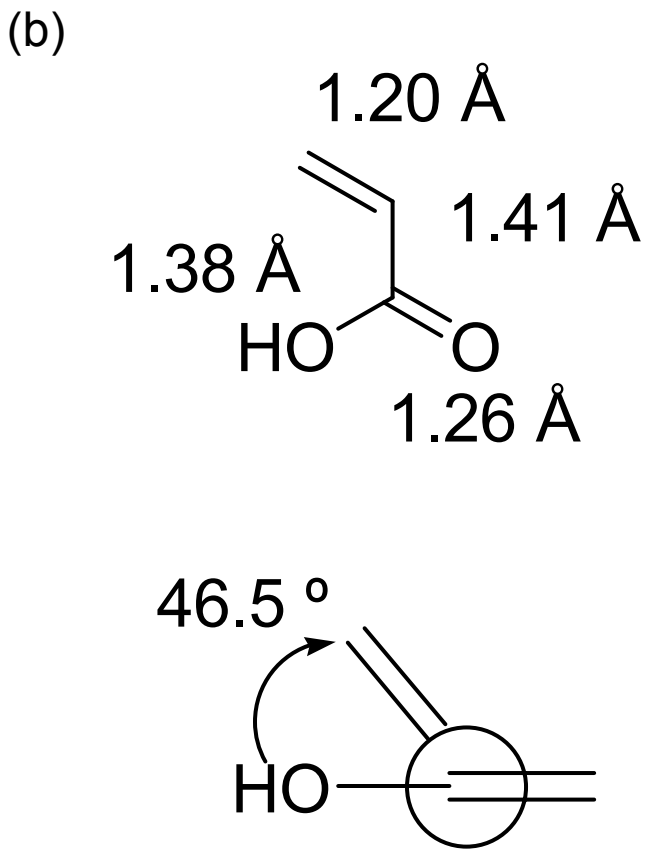
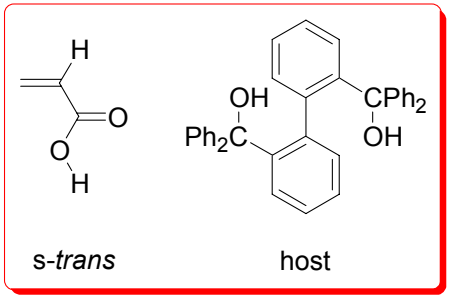
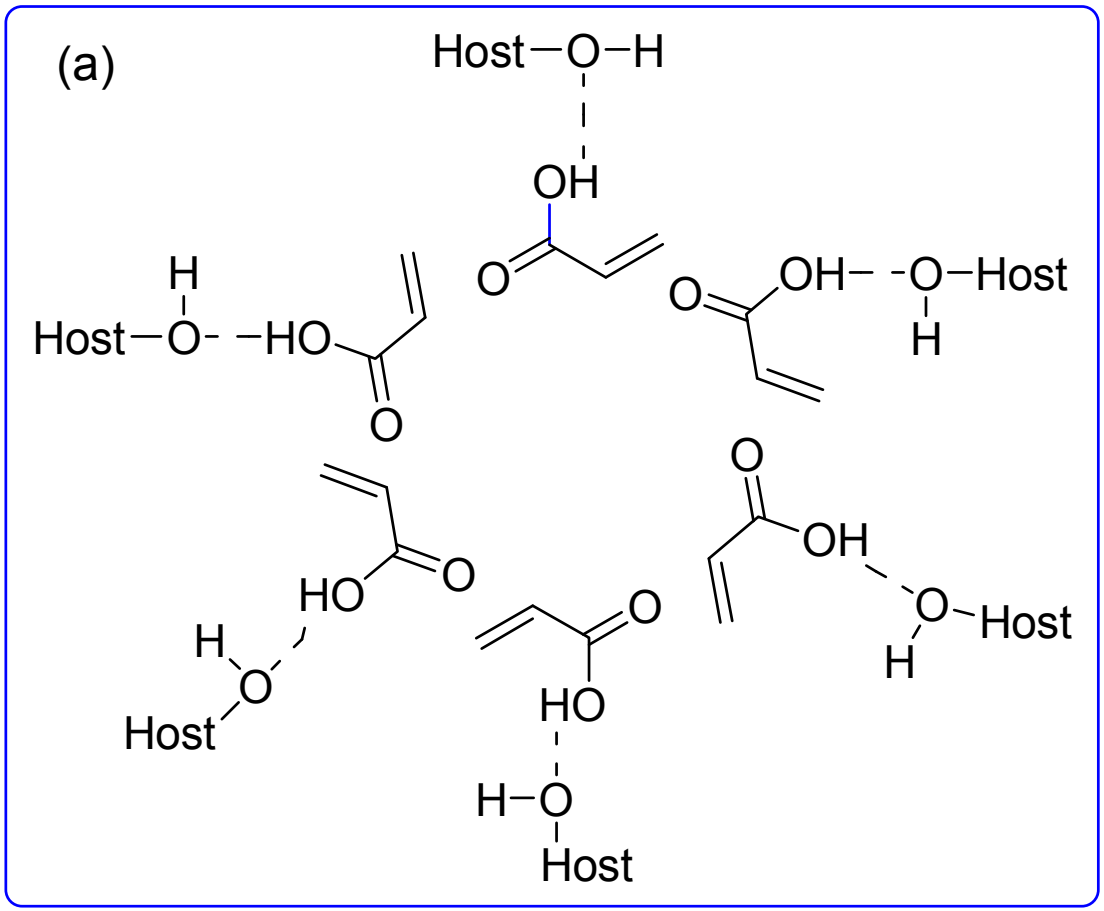


Fig. 3 X-Ray analytical data: (a) stereoview of the complex and (b) bond lengths and dihedral angle for *s*-trans-acrylic acid in the complex.





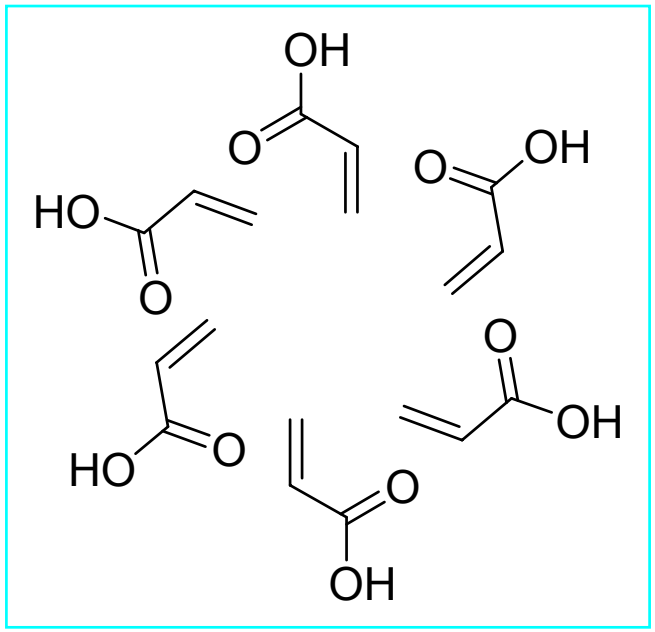
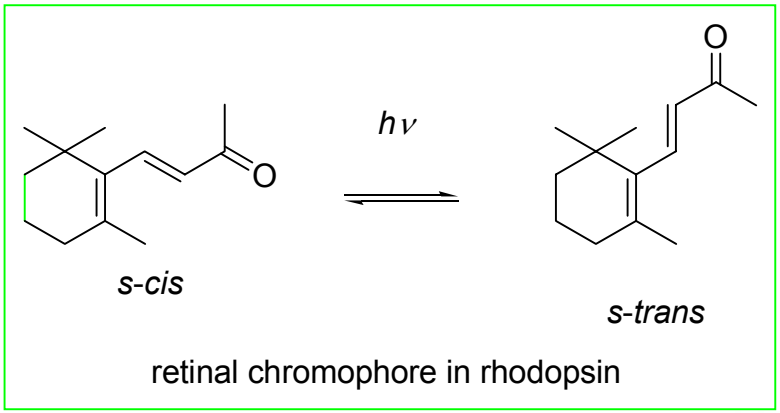
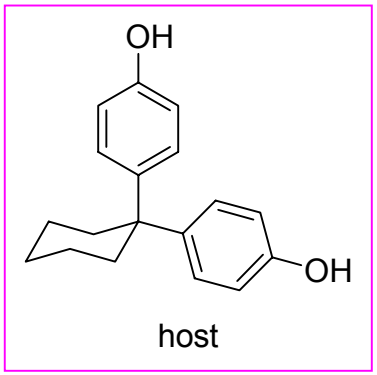
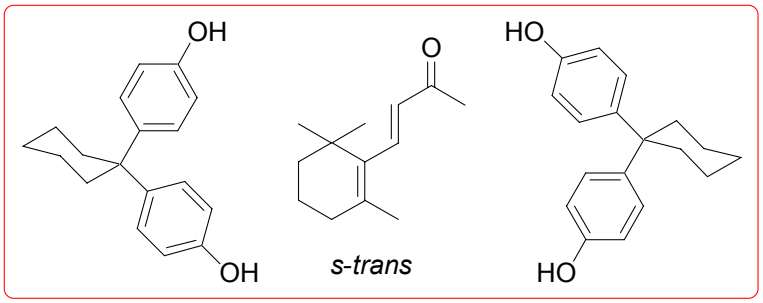


Fig. 4 Schematic drawing: (a) a circle of three *s*-trans-acrylic acid molecules in the complex and (b) a circle of three *s*-cis-acrylic acid molecules, both involving disorder.

3) β-ionone







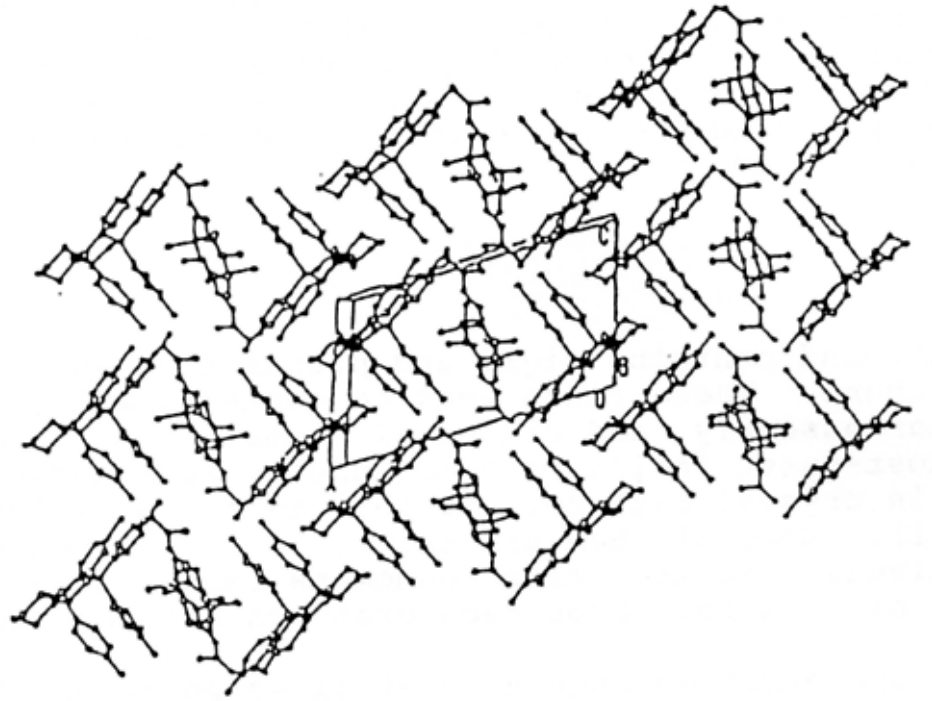
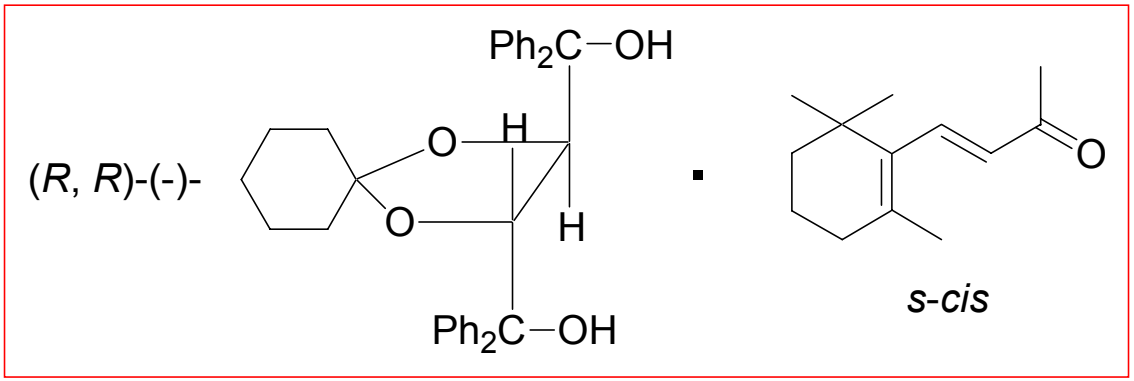
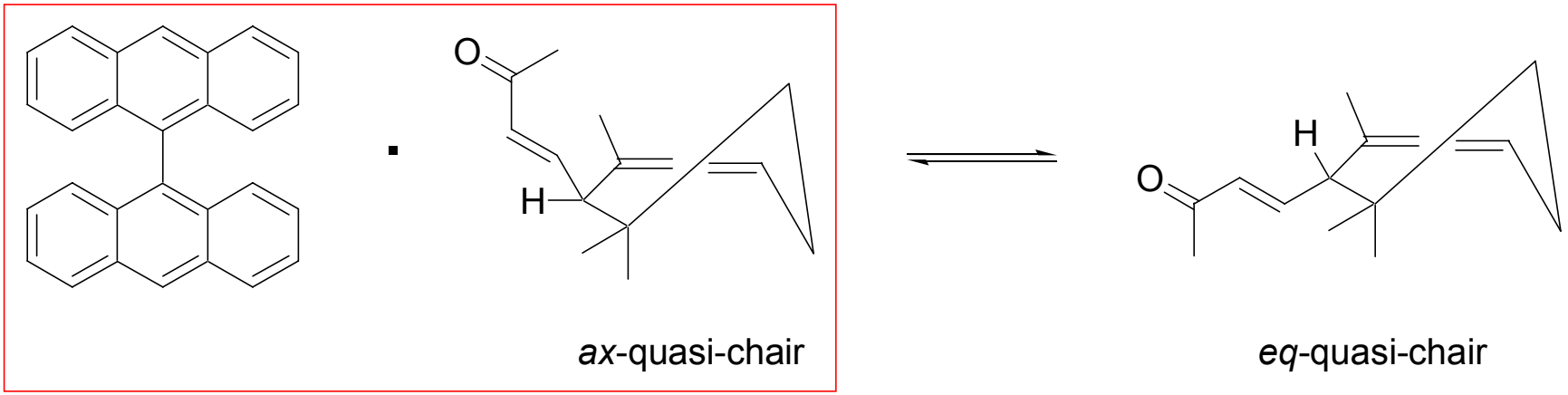


Fig. X-ray structure of the 2:1 complex.

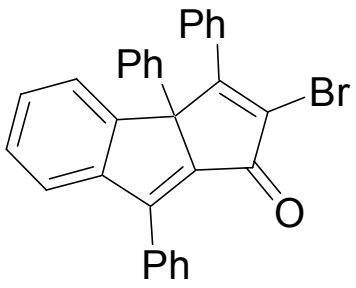


α-ionone

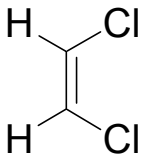


Angew. Chem. Int. Ed. Engl. **1990**, 662.
Pure Appl. Chem. **1990**, 417.
Bio. Org. Chem. **1991**, 157.

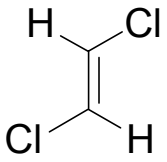
4) 1,2-dichloroethane



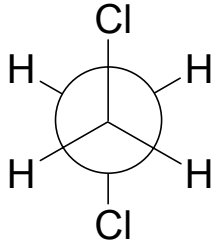
(*S*)-(-)-2



yes



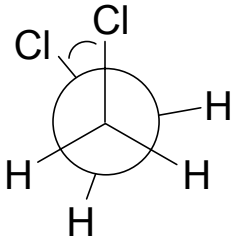
no



1a

trans

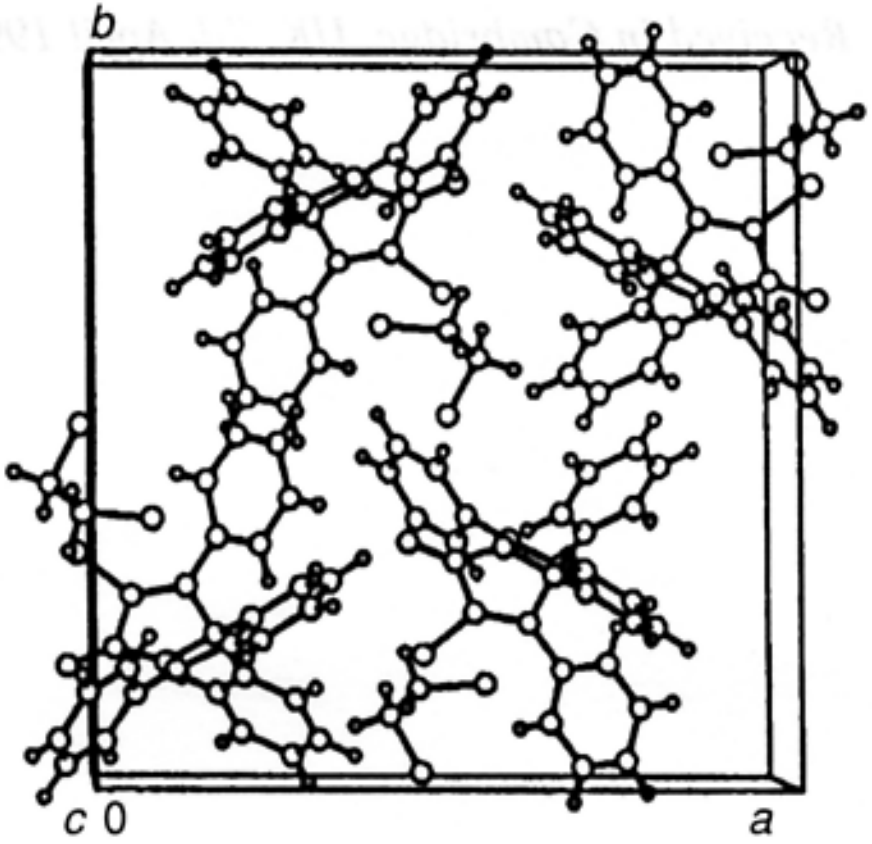
θ = 36 °



(*M*)-**1b**

eclipsed

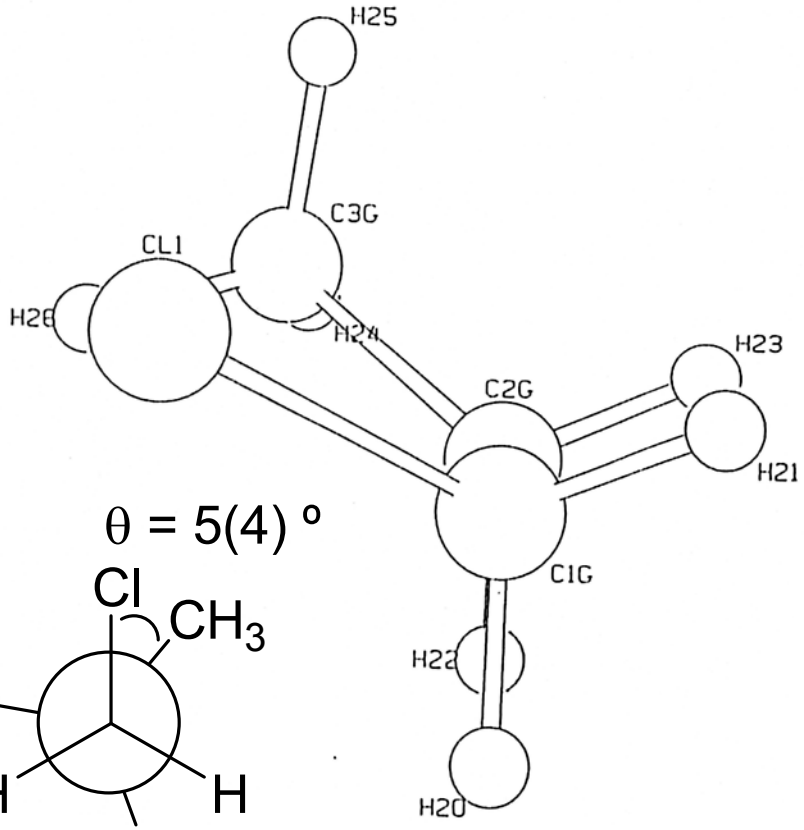
Cl···Cl
3.205 Å
(3.50 Å)



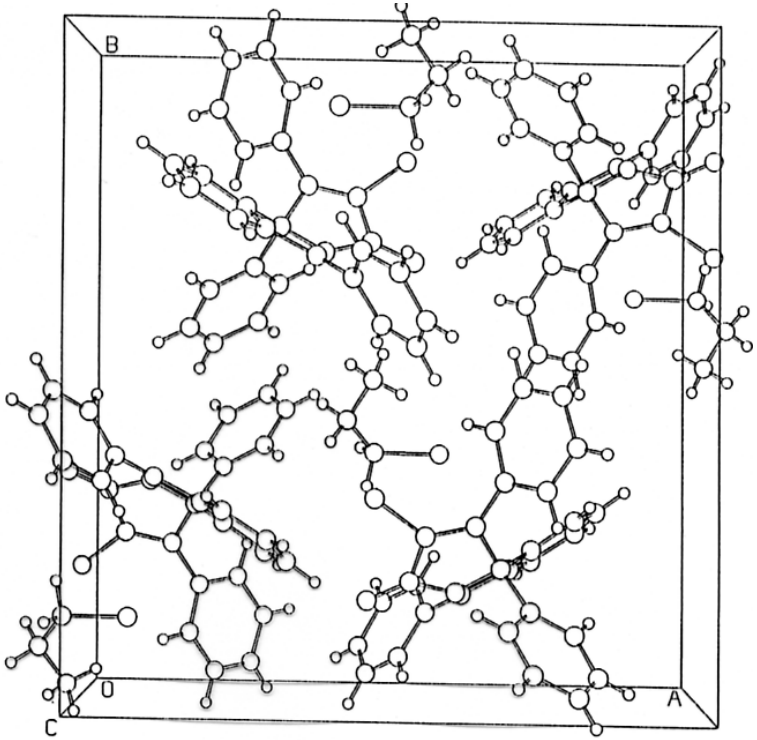
C=O ··· Cl

Fig. X-ray of a complex of *(M)*-**1b**.

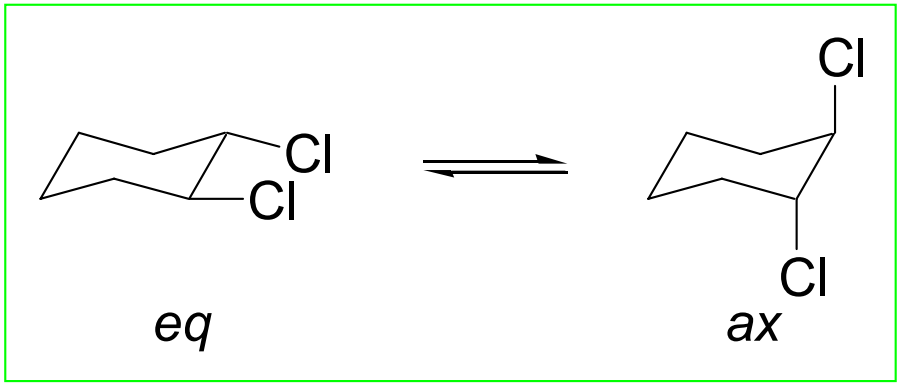
Chem. Comm. **1997**, 1227.

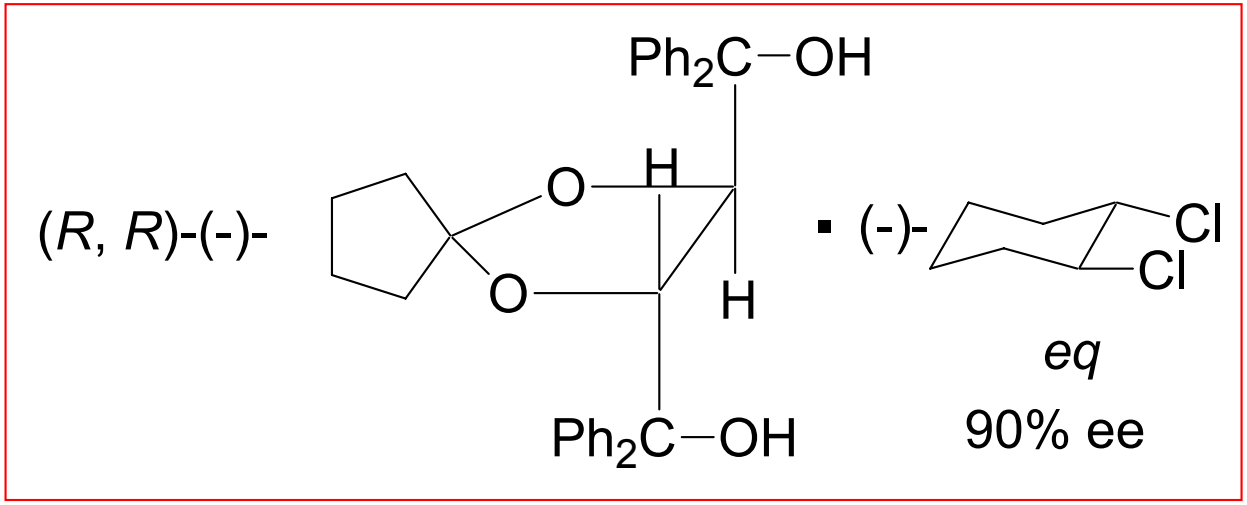


$\theta = 5(4)^{\circ}$



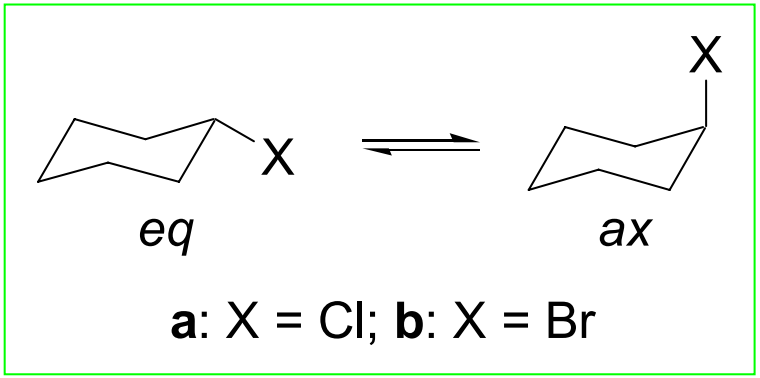
5) halocyclohexane –- di-*eq*

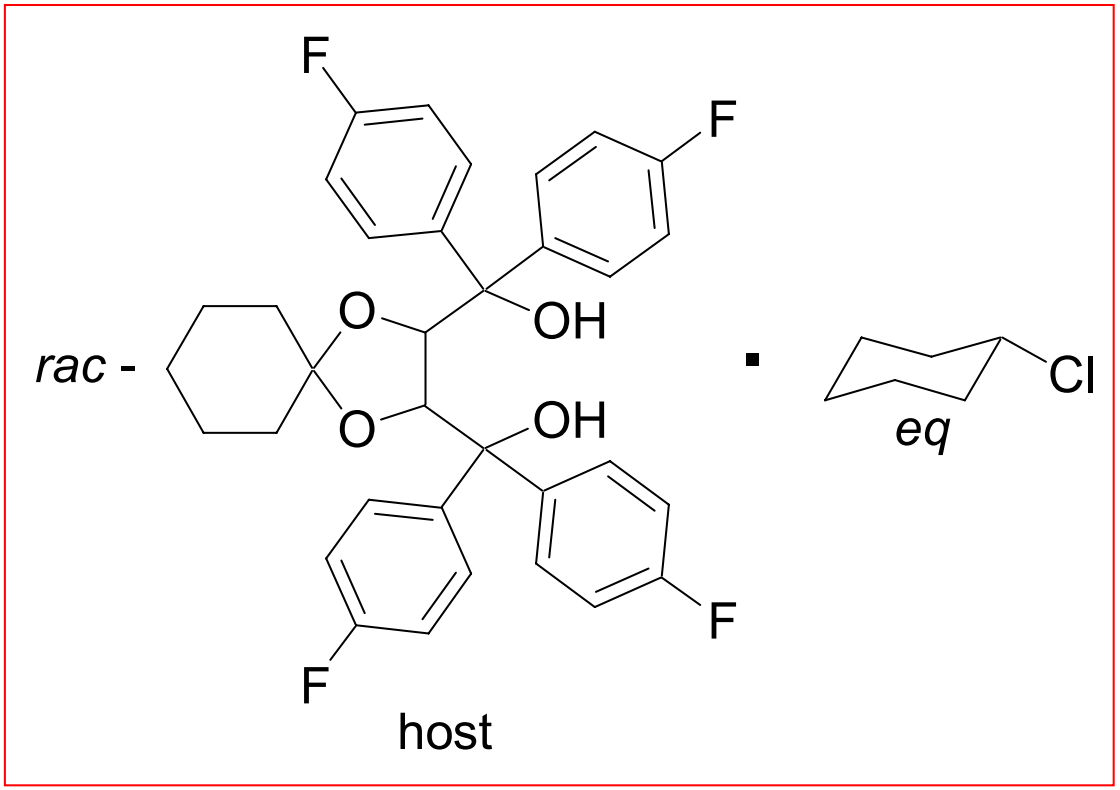




Supramol. Chem. **2001**, 175.

5) halocyclohexane – *eq*





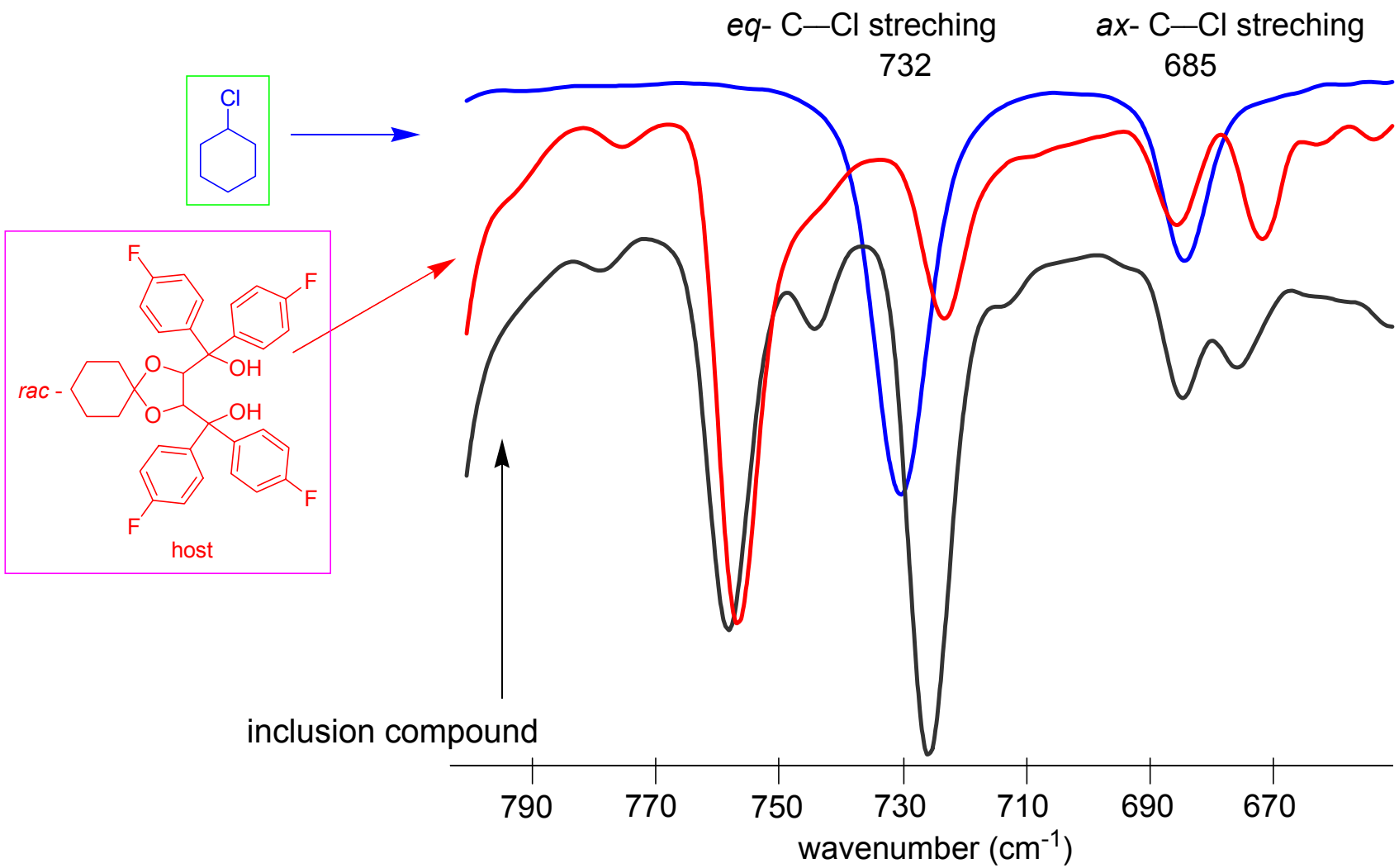


Fig. IR spectra with using ATR (attenuated total reflection).

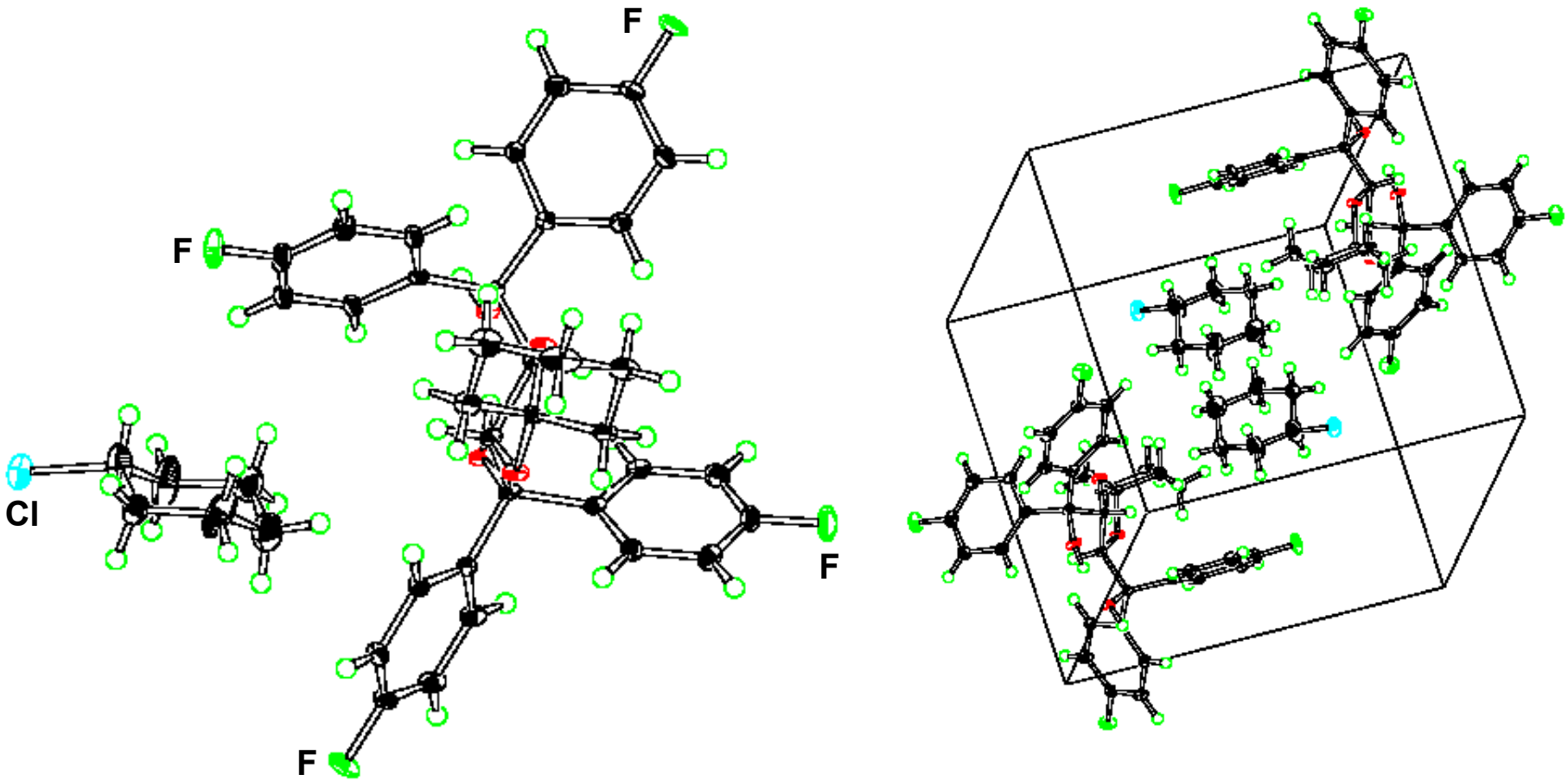
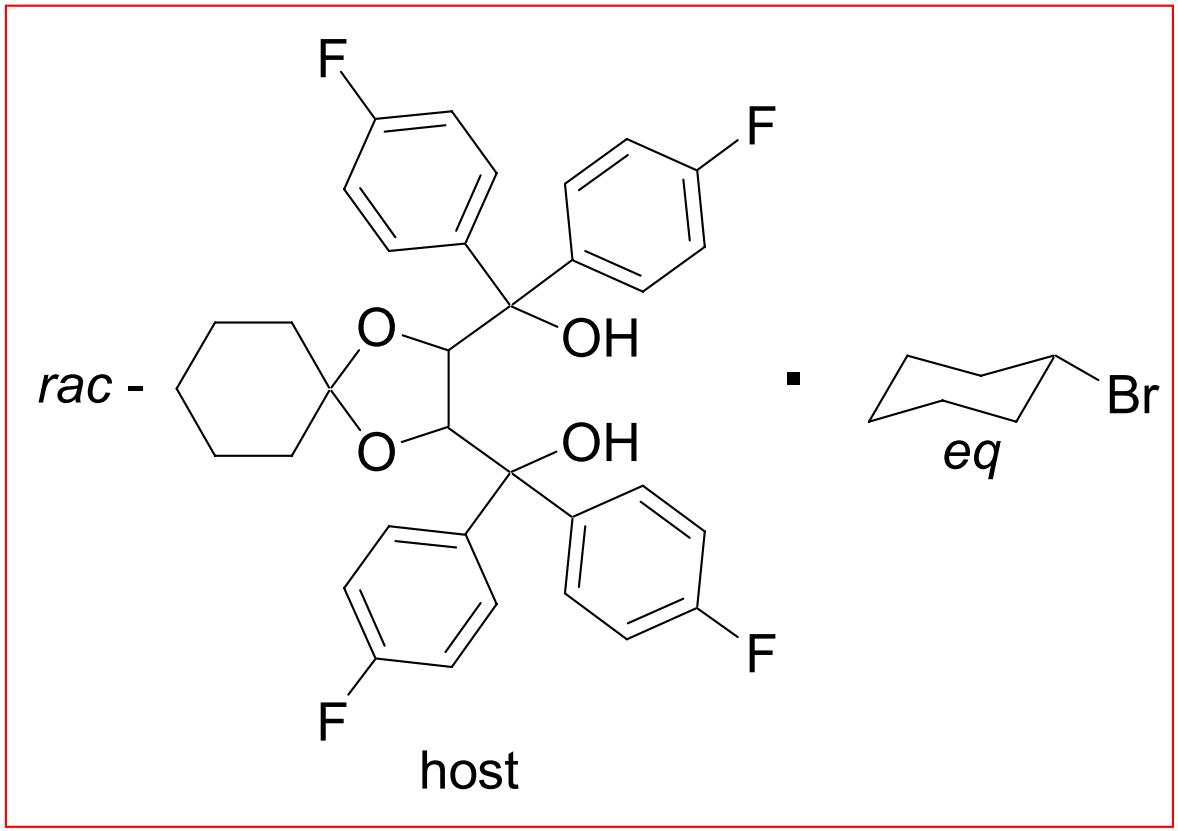
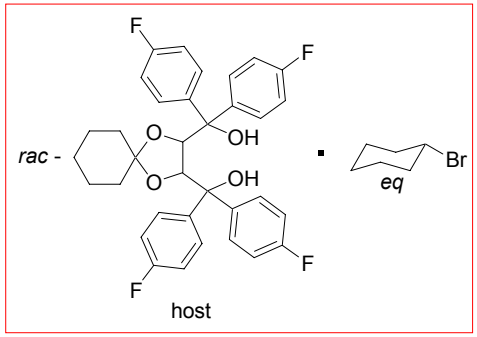


Fig. X-ray structure of the inclusion complex of *eq*-chlorocyclohexane.


F
F
O
OH
rac -
O
OH
F
F
host
·
Br
eq



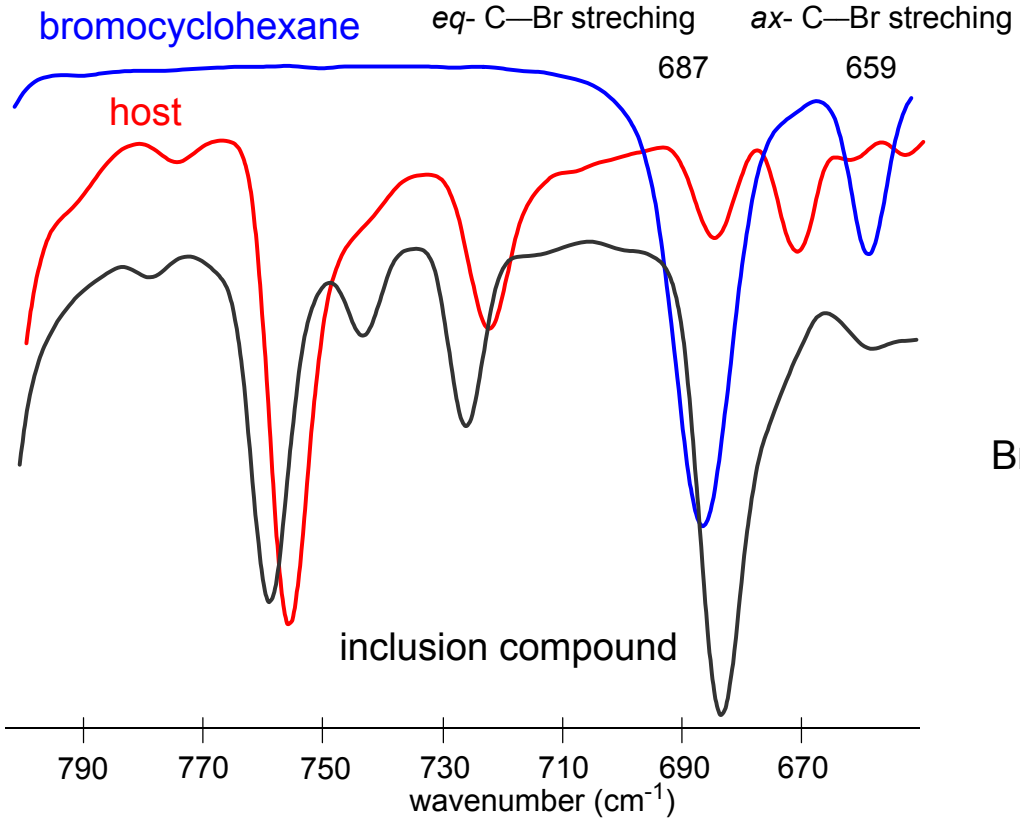


Fig. IR spectra with using ATR (attenuated total reflection).

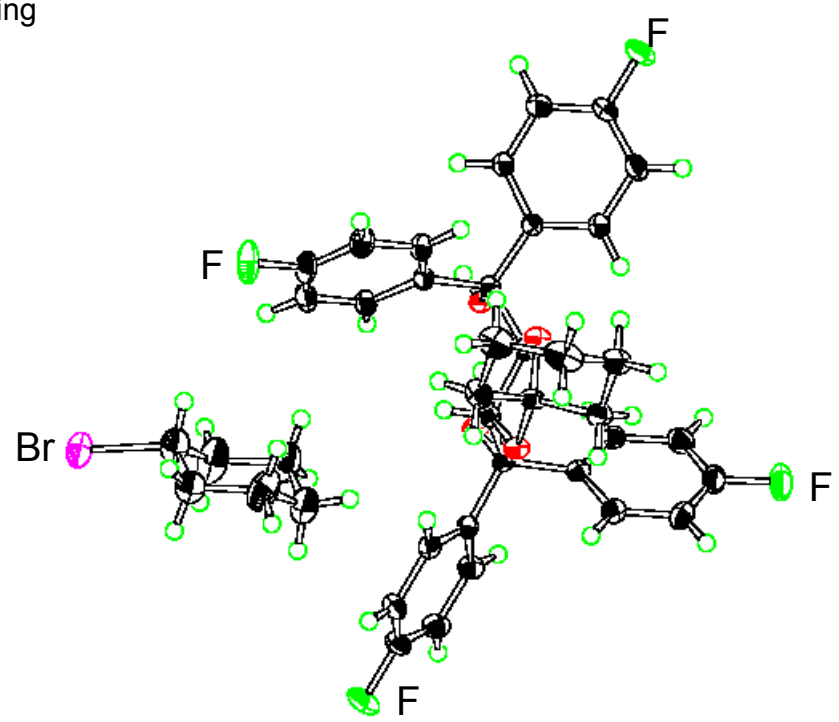
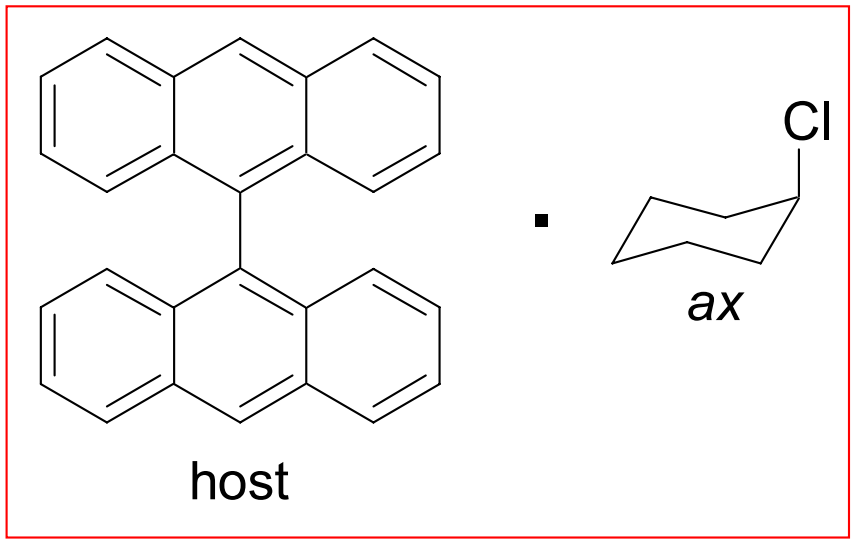


Fig. X-ray structure.

Chem. Comm. **2004**, 2354.

5) halocyclohexane – *ax*



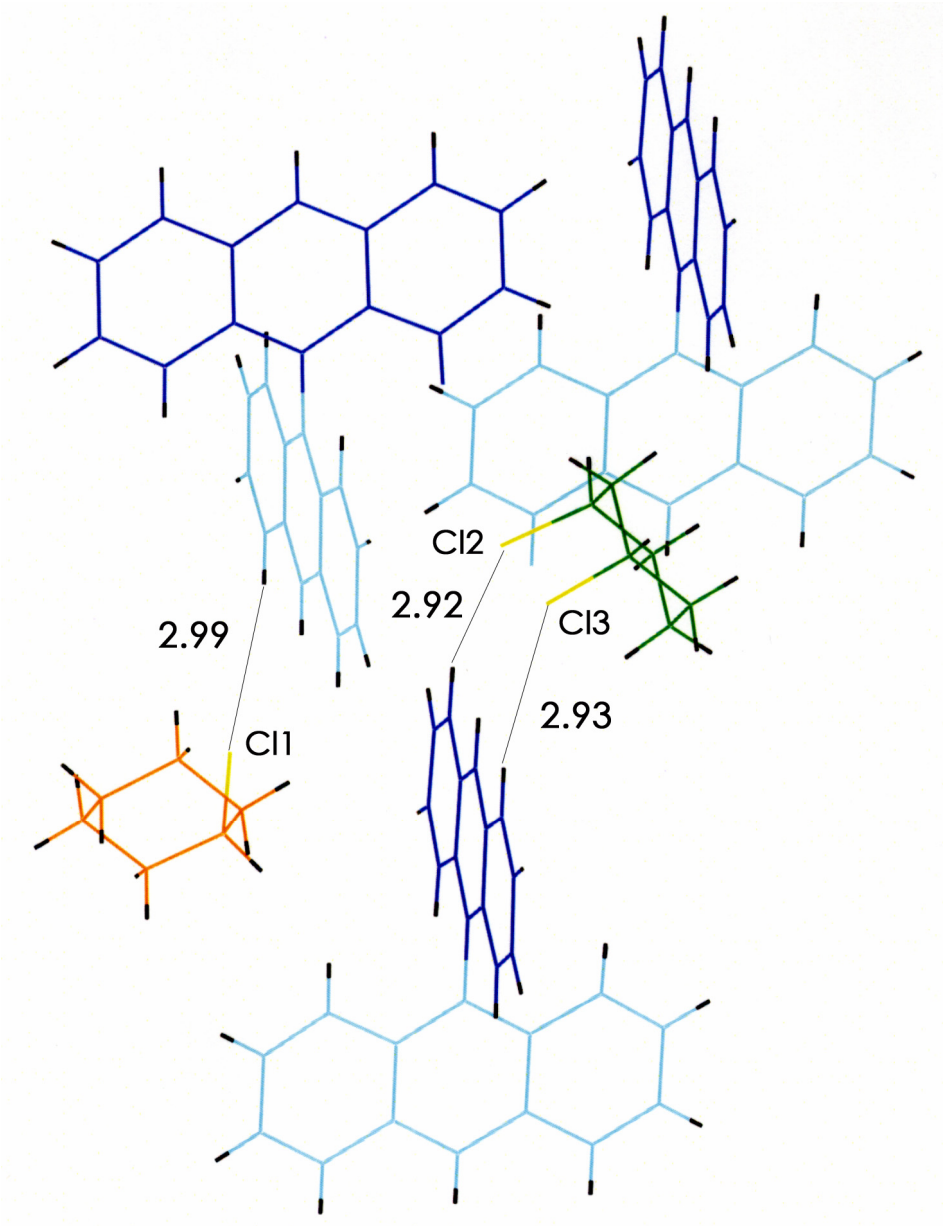


Fig. X-ray structure of the complex.

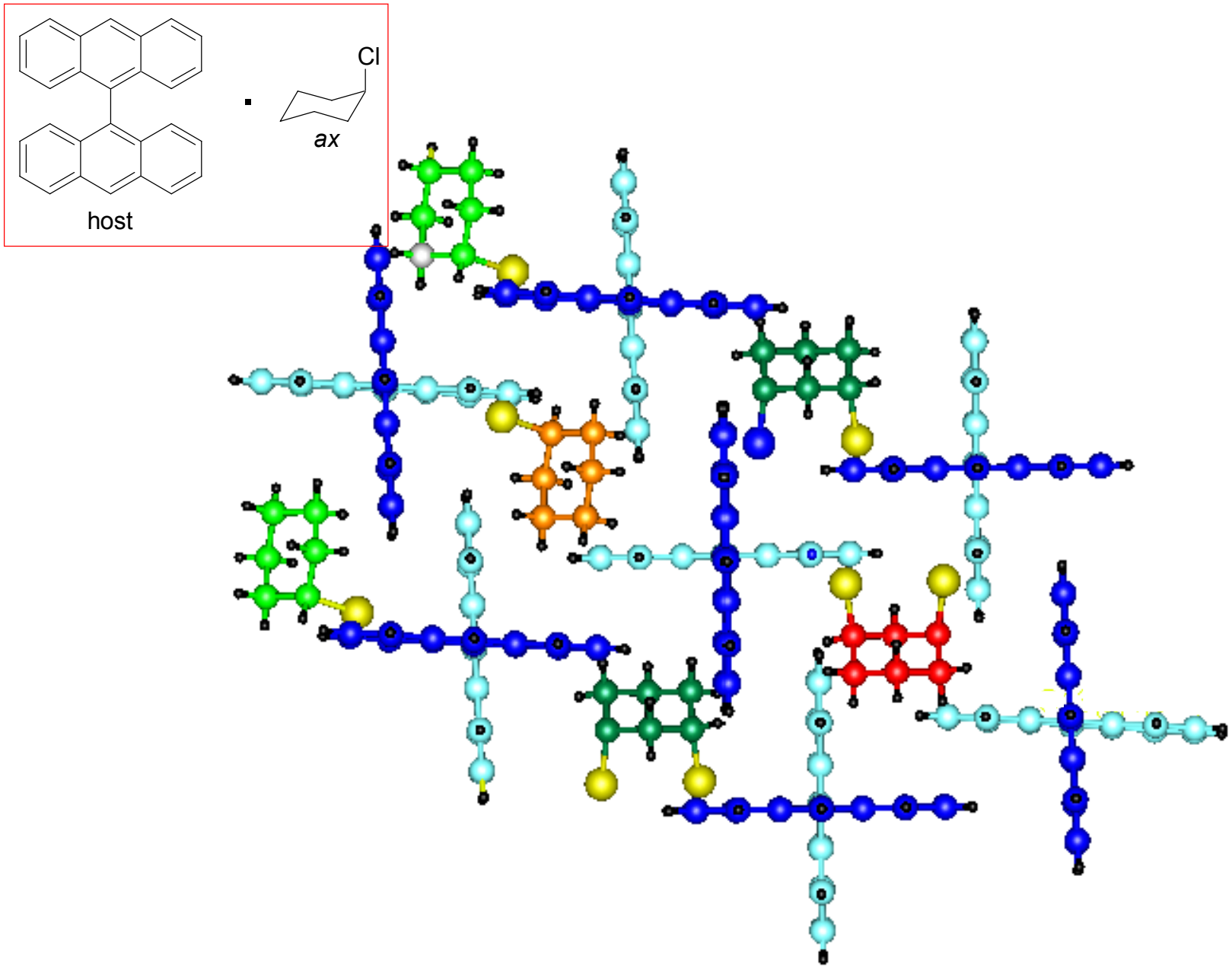
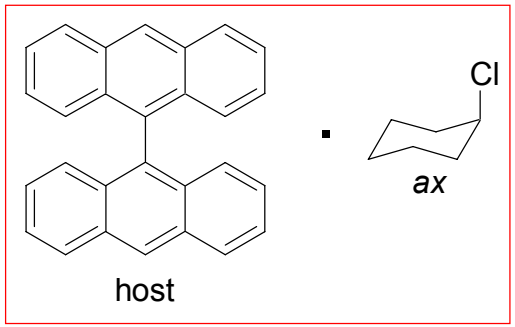


Fig. Packing diagram of *ax*-chlorocyclohexane complex which indicates the closest contacts.



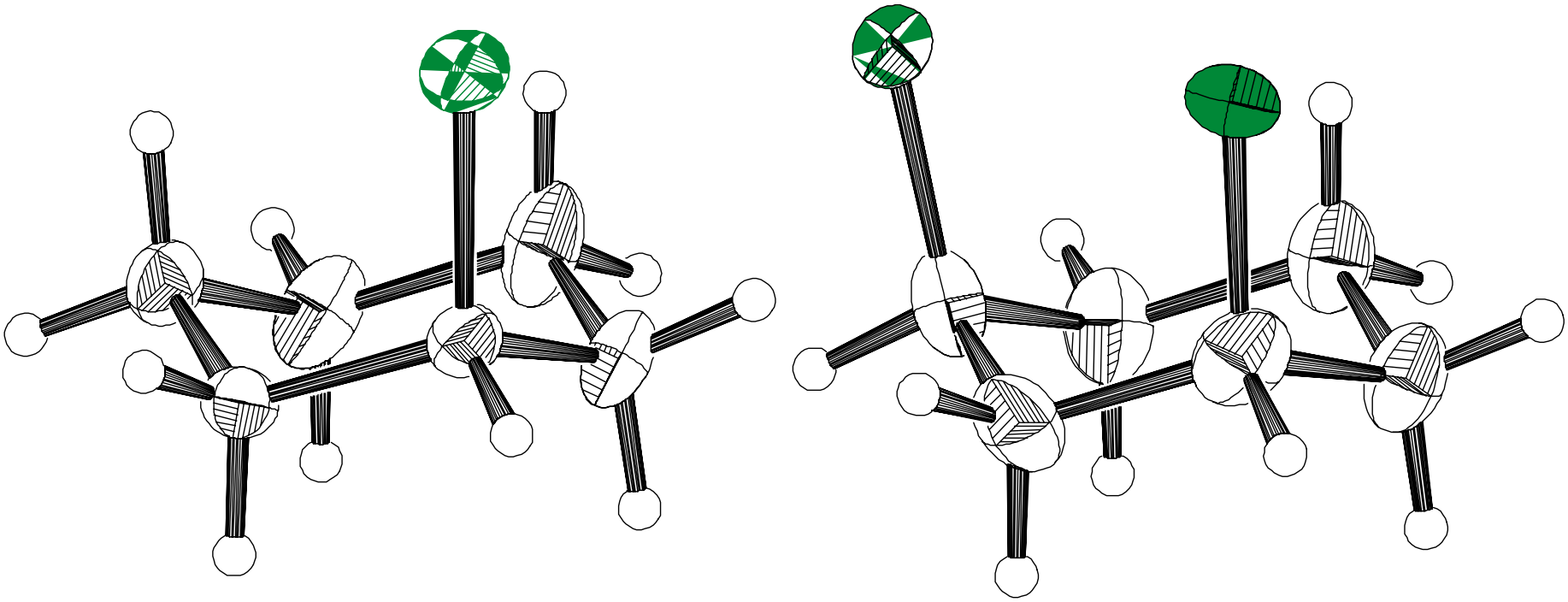
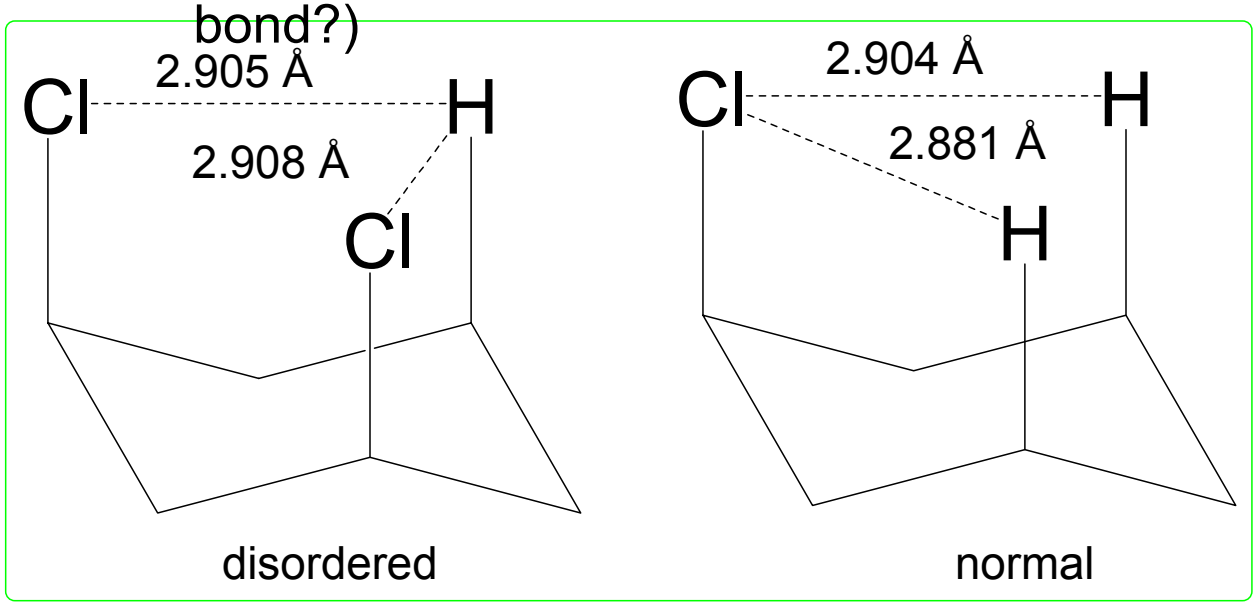
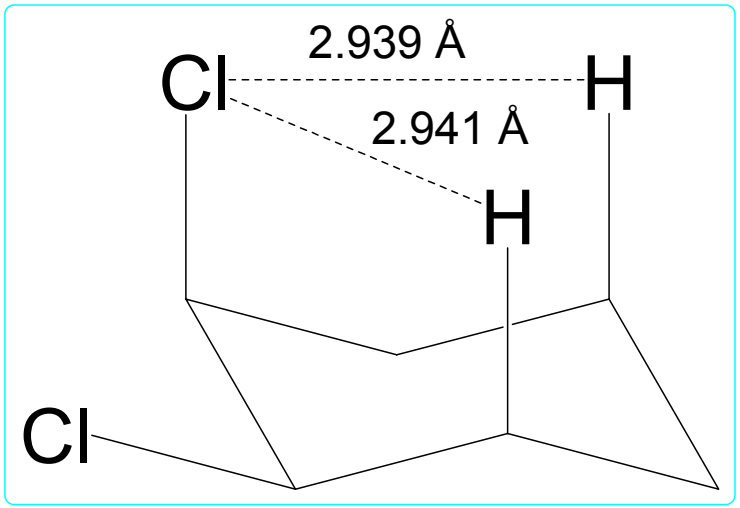


Fig. X-ray structure of normal and disordered *ax*-bromocyclohexane in the complex.

1,3-diaxial interaction (hydrogen bond?)





van der Walls radius; H, 1.20 Å, Cl , 1.75 Å

A schematic structure of *ax*-chlorocyclohexane

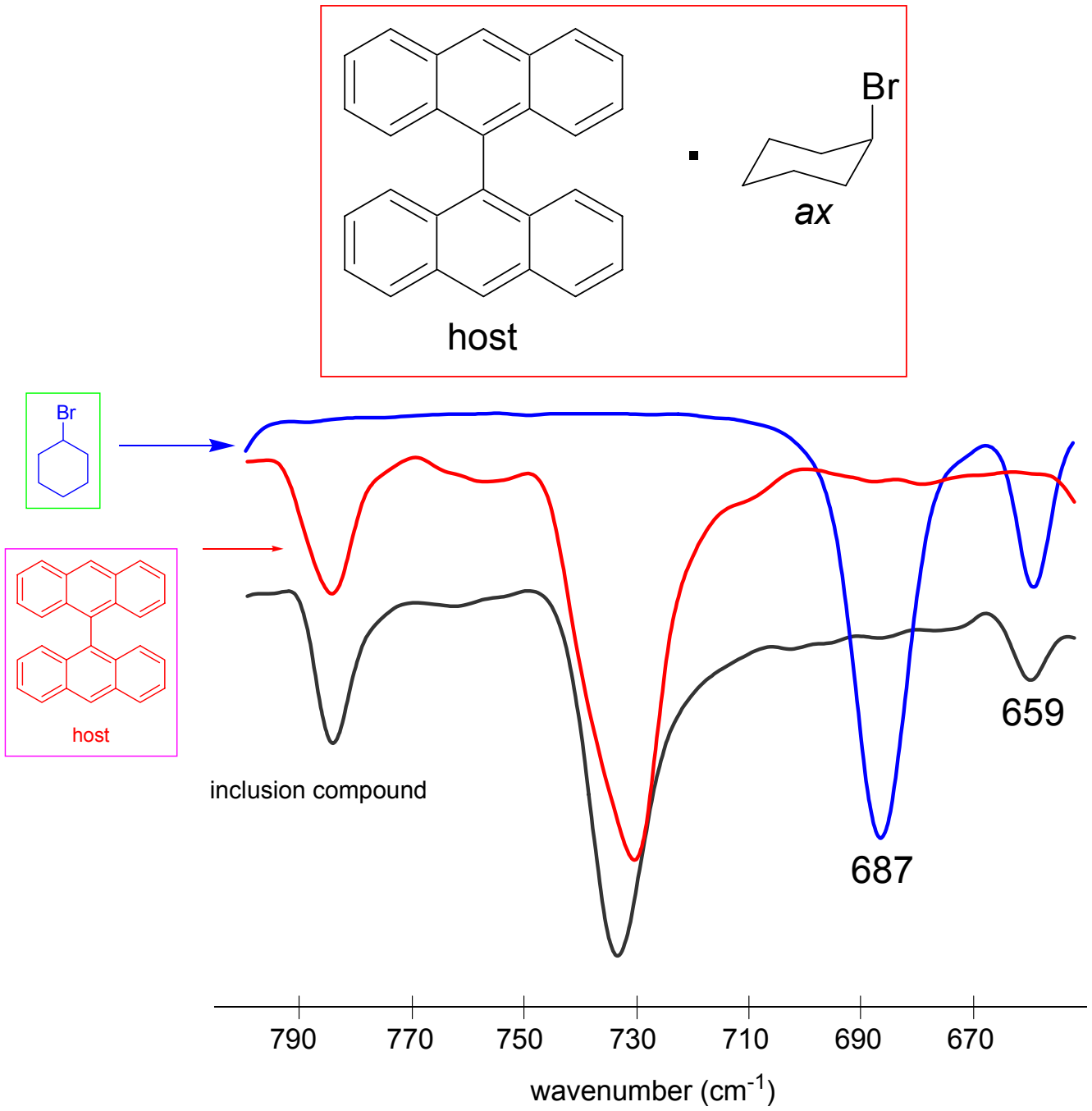


Fig. IR spectra with using the ATR.

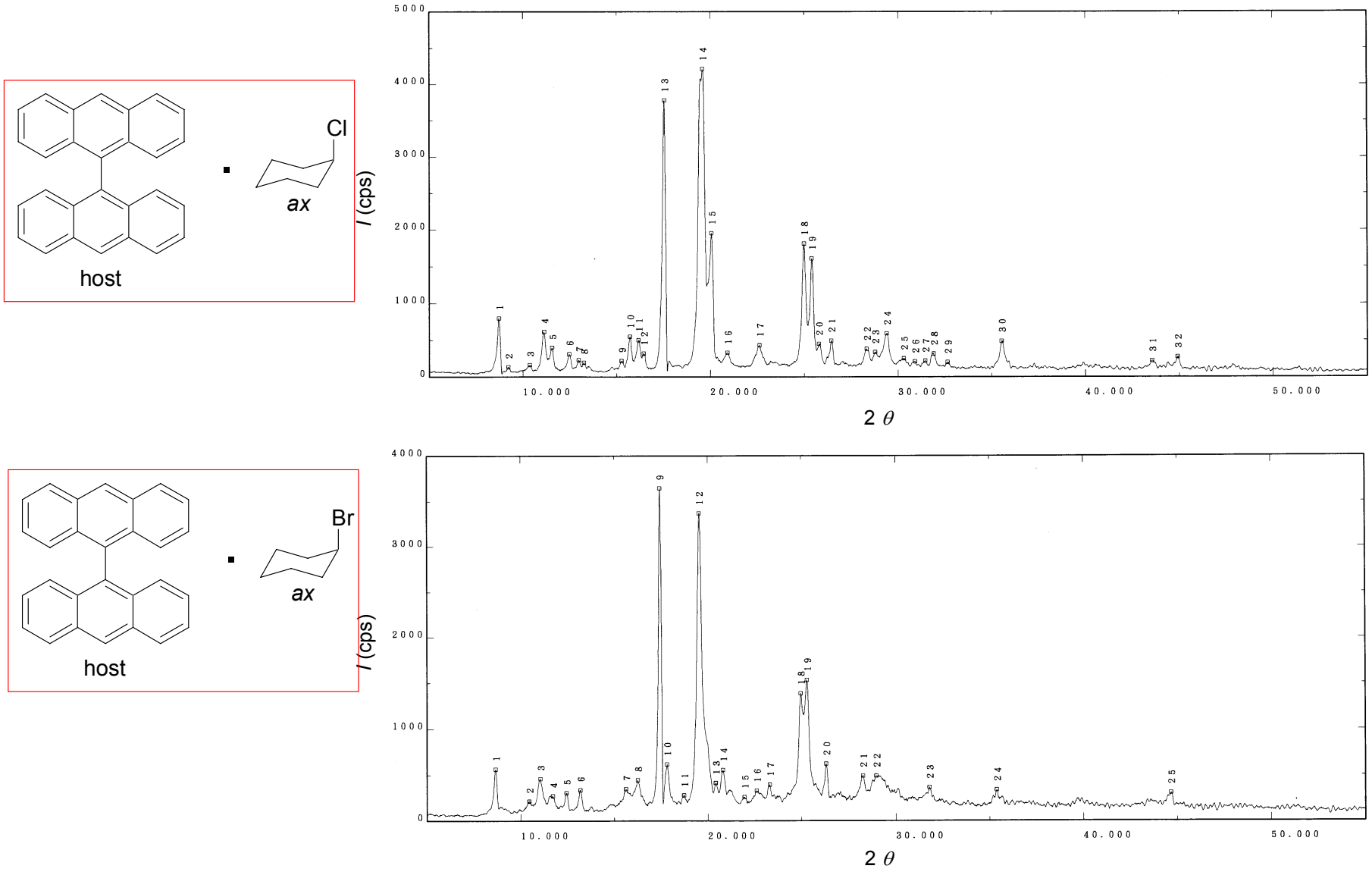
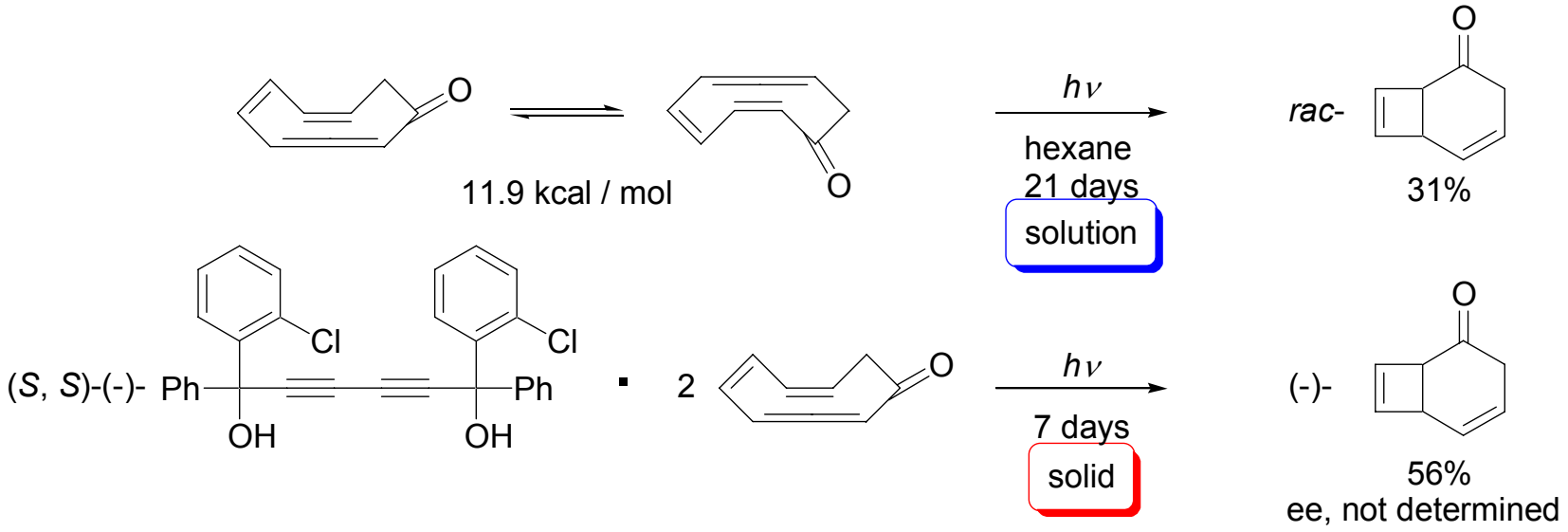


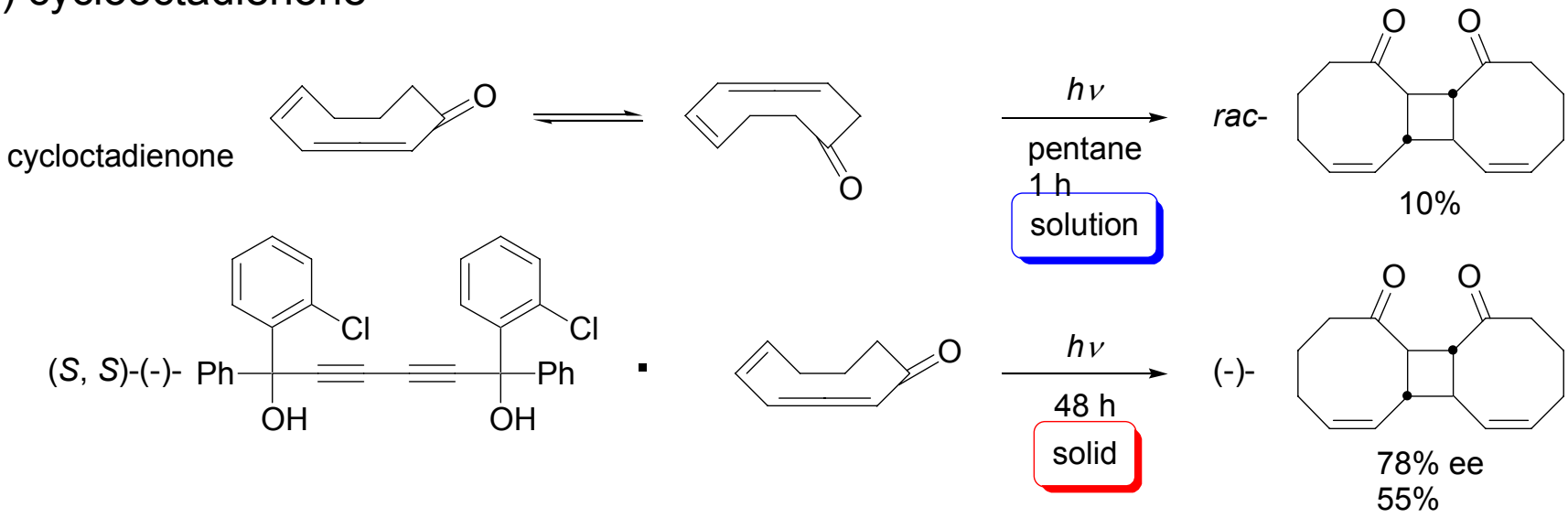
Fig . X-ray powder diffraction pattern

Chem. Comm. **2005**, 3646.

6) cyclooctatrienone

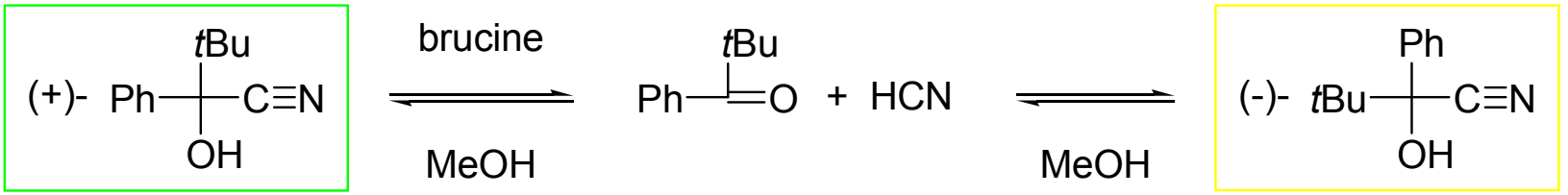


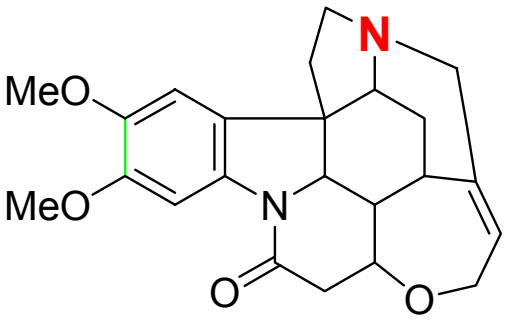
7) cyclooctadienone



Tetrahedron Lett. **1988**, 653, *J. Org. Chem*. **1990**, 4532.

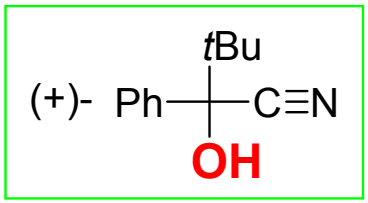
8) enantiomerization

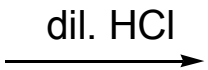


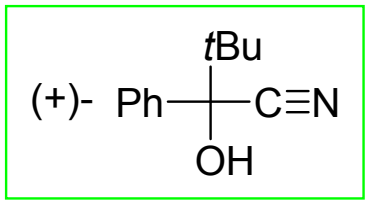


brucine

▪





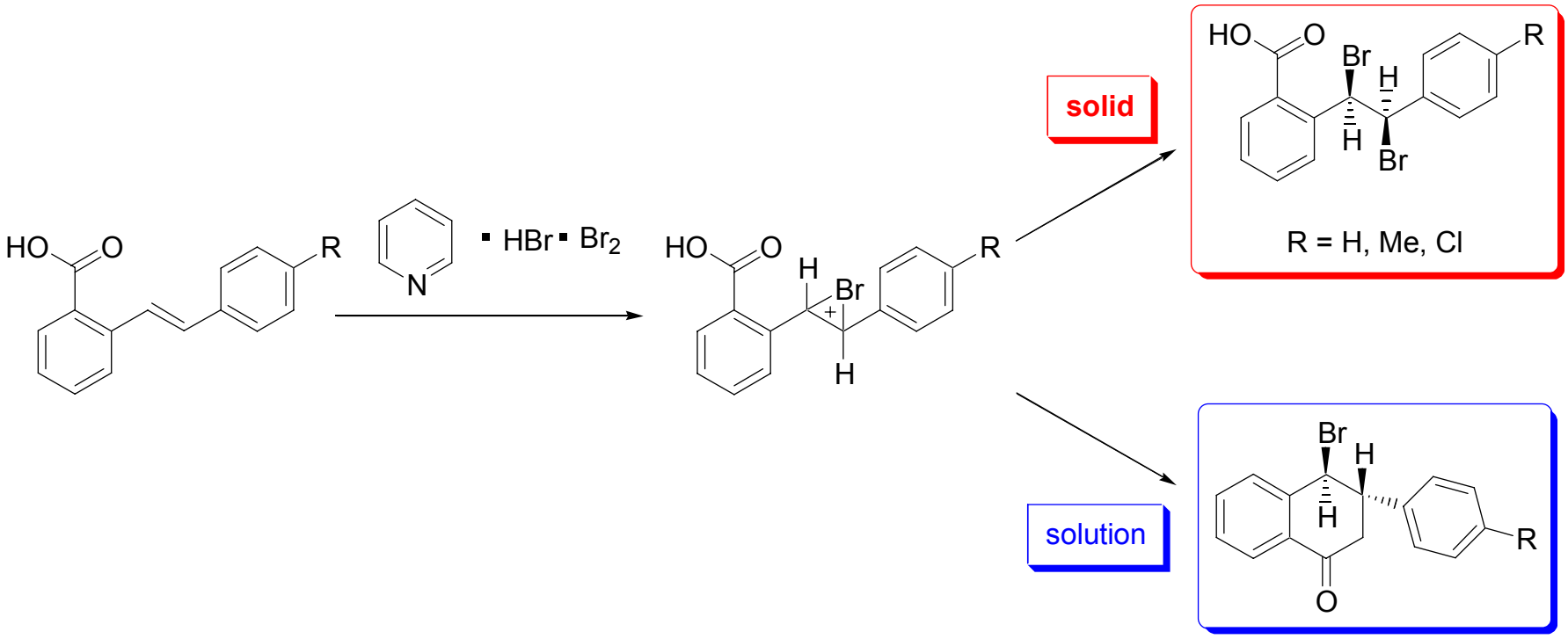


100% ee
100% yield

Chem. Lett. **1983**, 661.

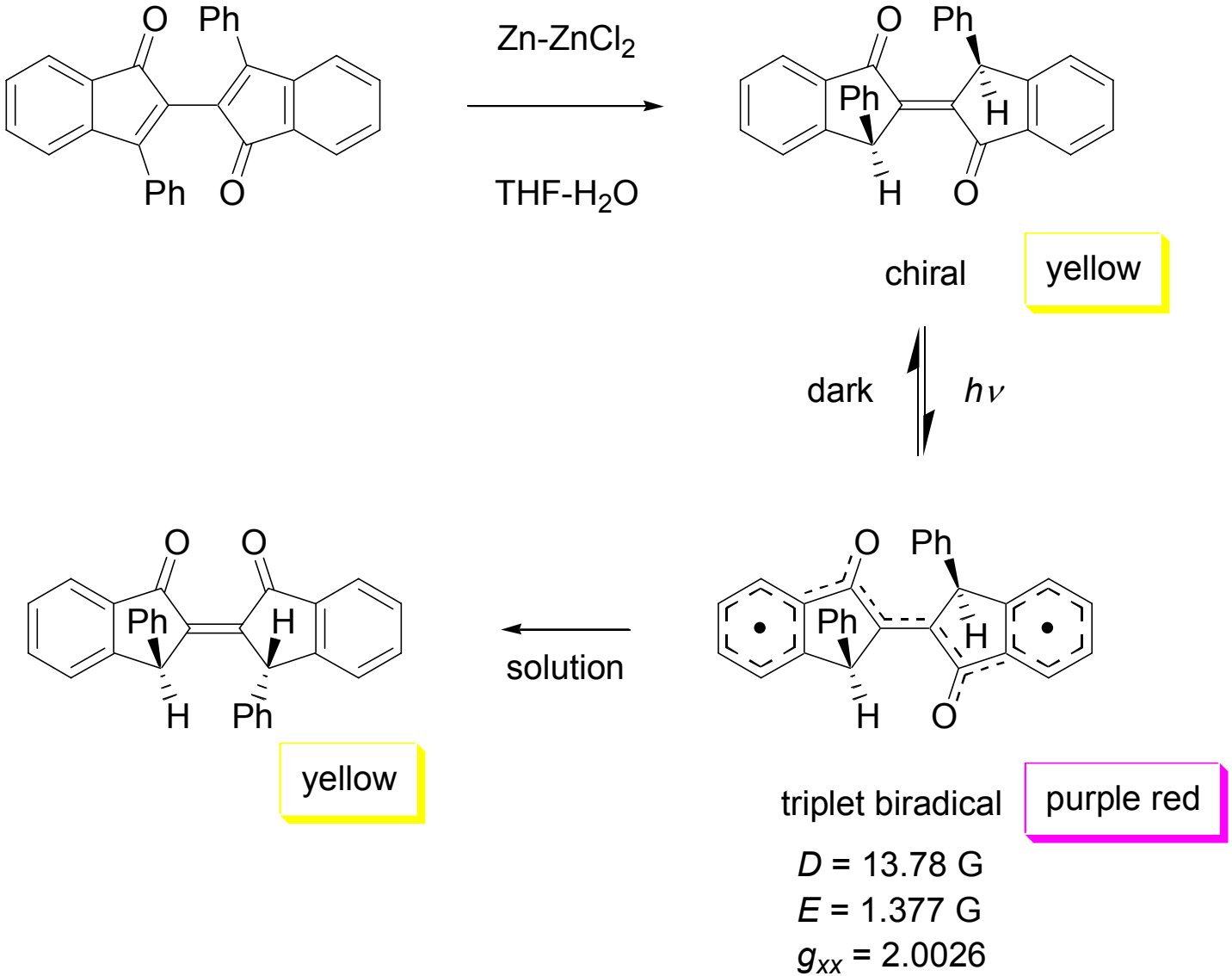
(II) stereoisomers in own crystals

1) neighboring group effect



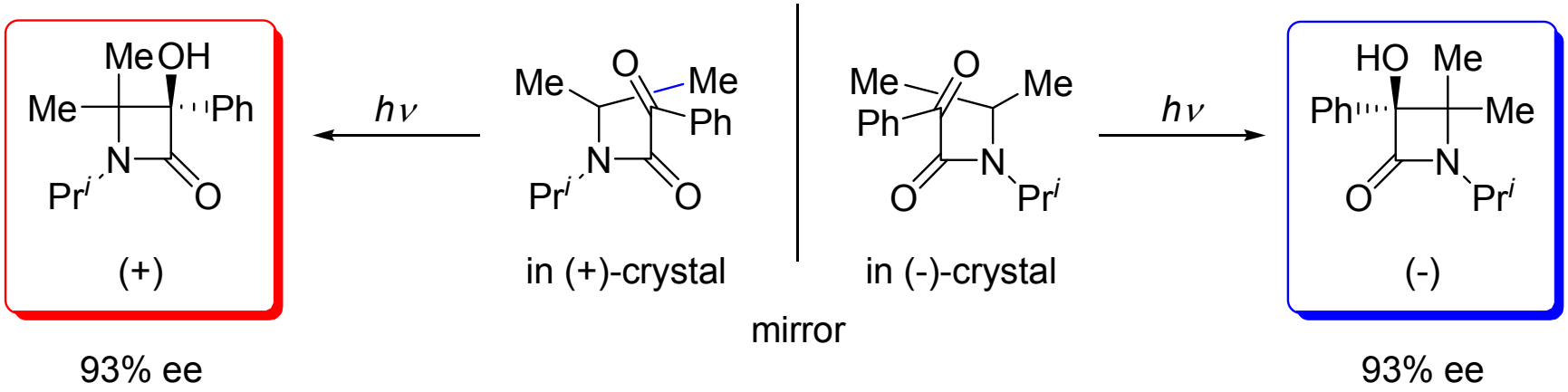
Acta Cryst. C53 **1997**, 620.

2) photochromism



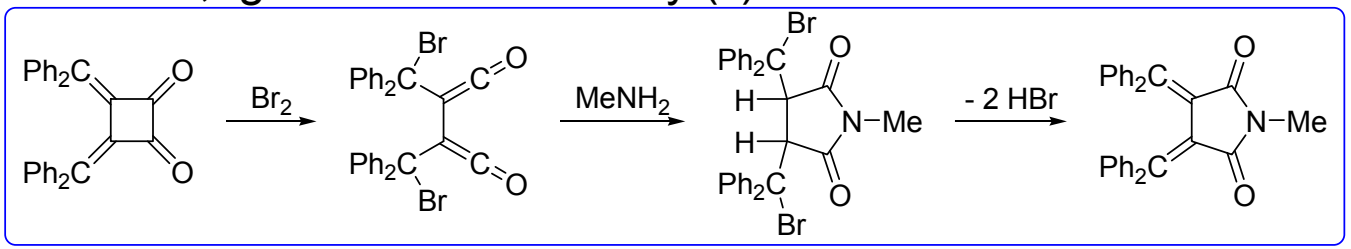
Chem. Comm. **2000**, 873.

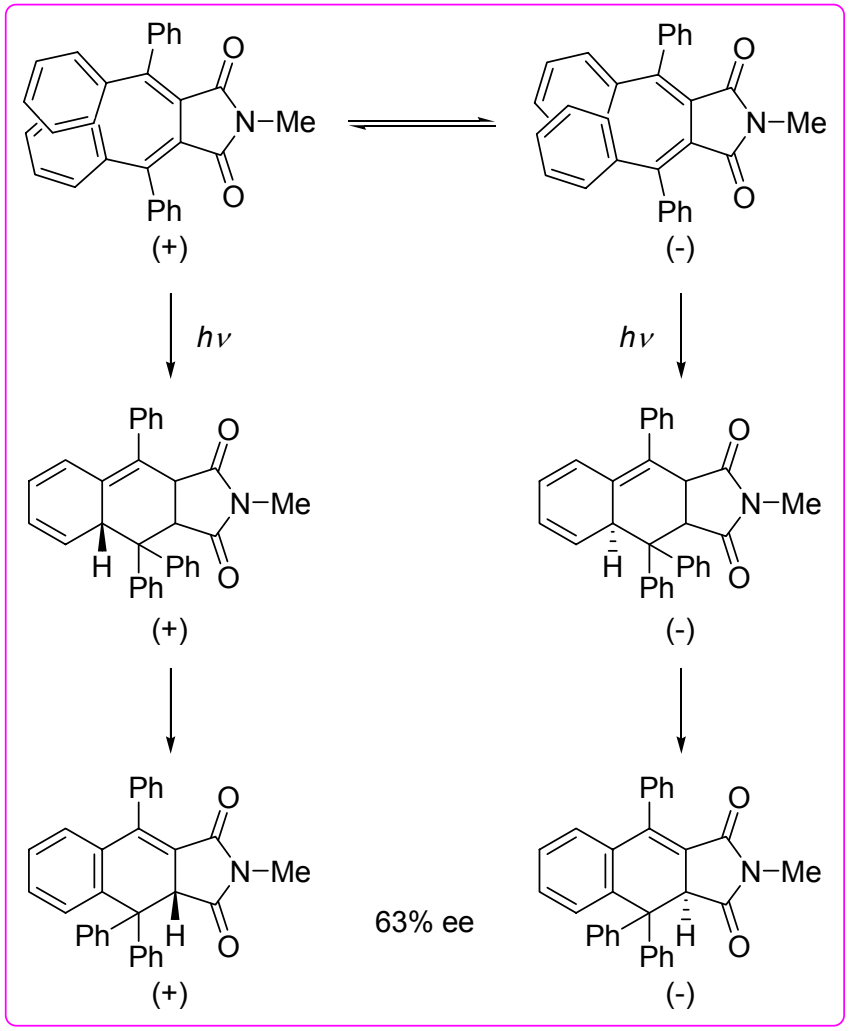
3) oxoamide, generation of chirality (i)



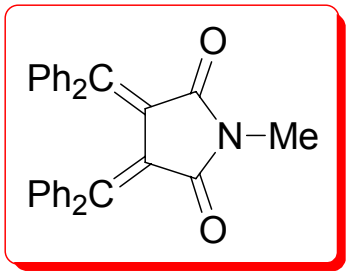
Chem. Comm. **1987**, 1413
J. Am. Chem. Soc. **1989**, 697.

4) succinamide, generation of chilality (ii)



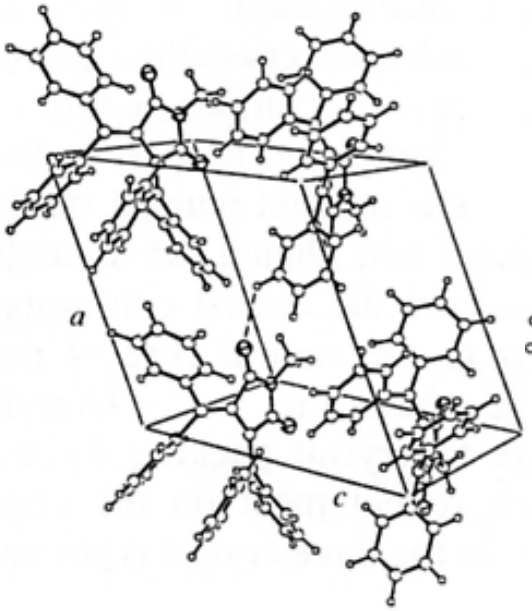


Supramol. Chem. **1994**, 87.
Acta Cryst. B51 **1995**, 856.



A
chiral

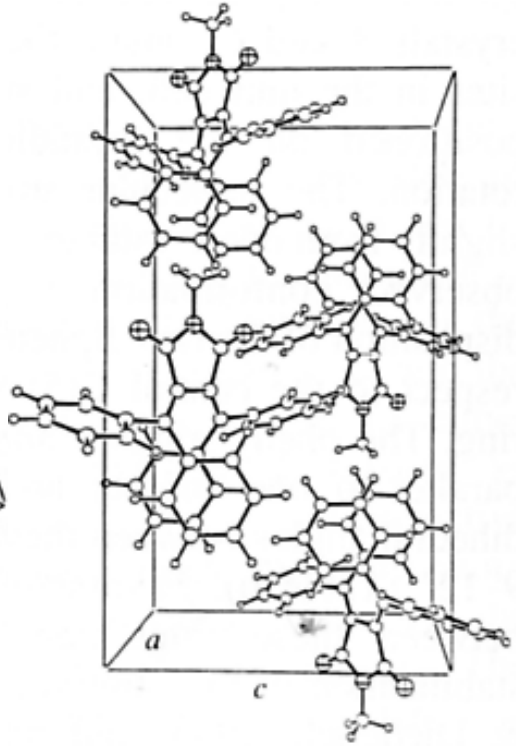
orange hexagonals
mp 260 ºC



P2₁

B
rac

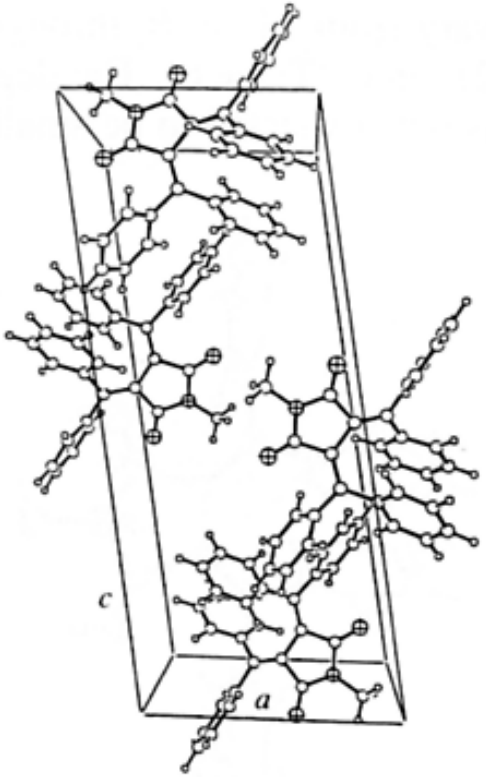
orange plates
302 ºC



Pbcn

C
rac

yellow plates
297 ºC



P2₁/n