Stereochemistry of Molecules in Crystals (part 1, 2)

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key word: solid state, host-guest complex

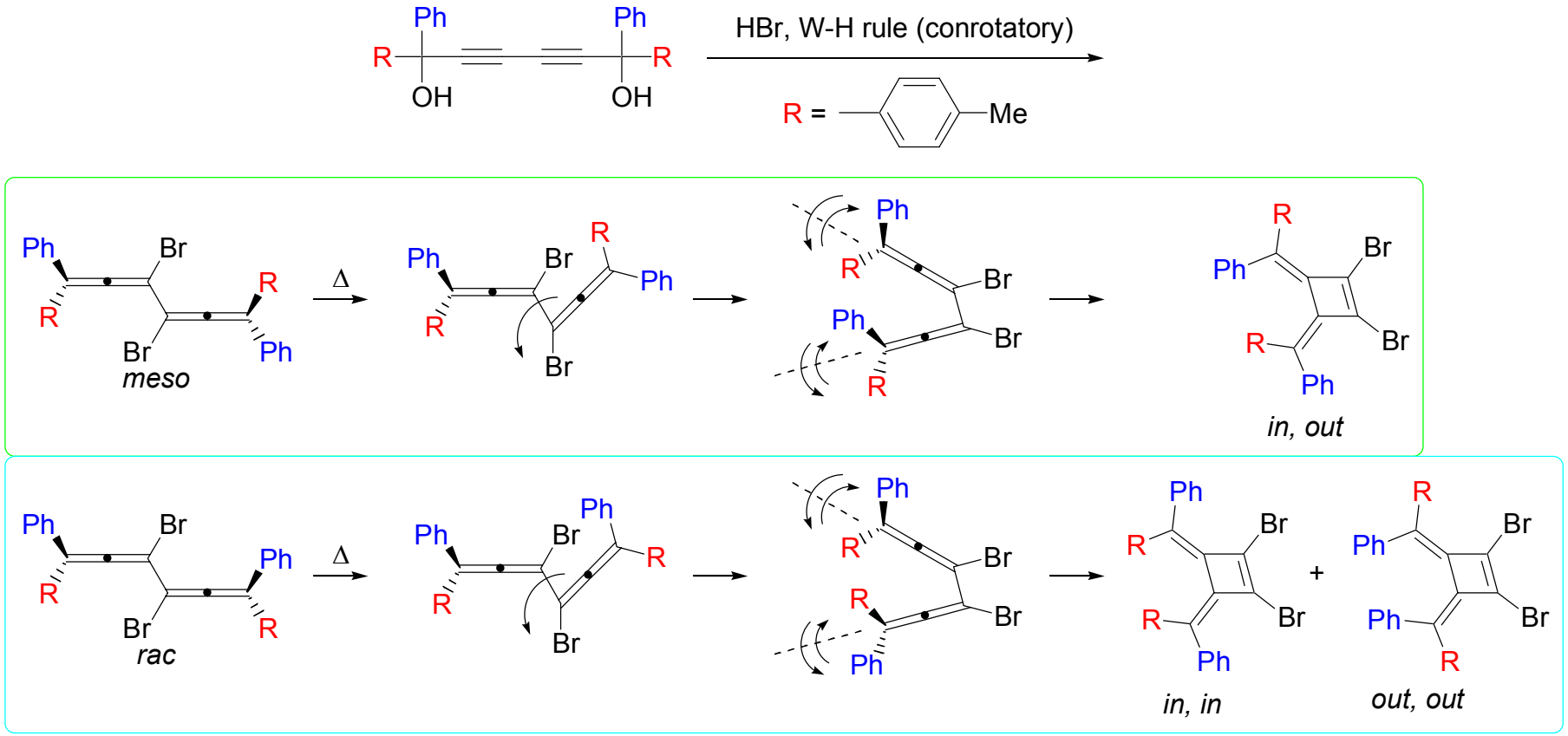
part 1: statistic aspect

part 2: dynamic aspect

part 2: dynamic aspect

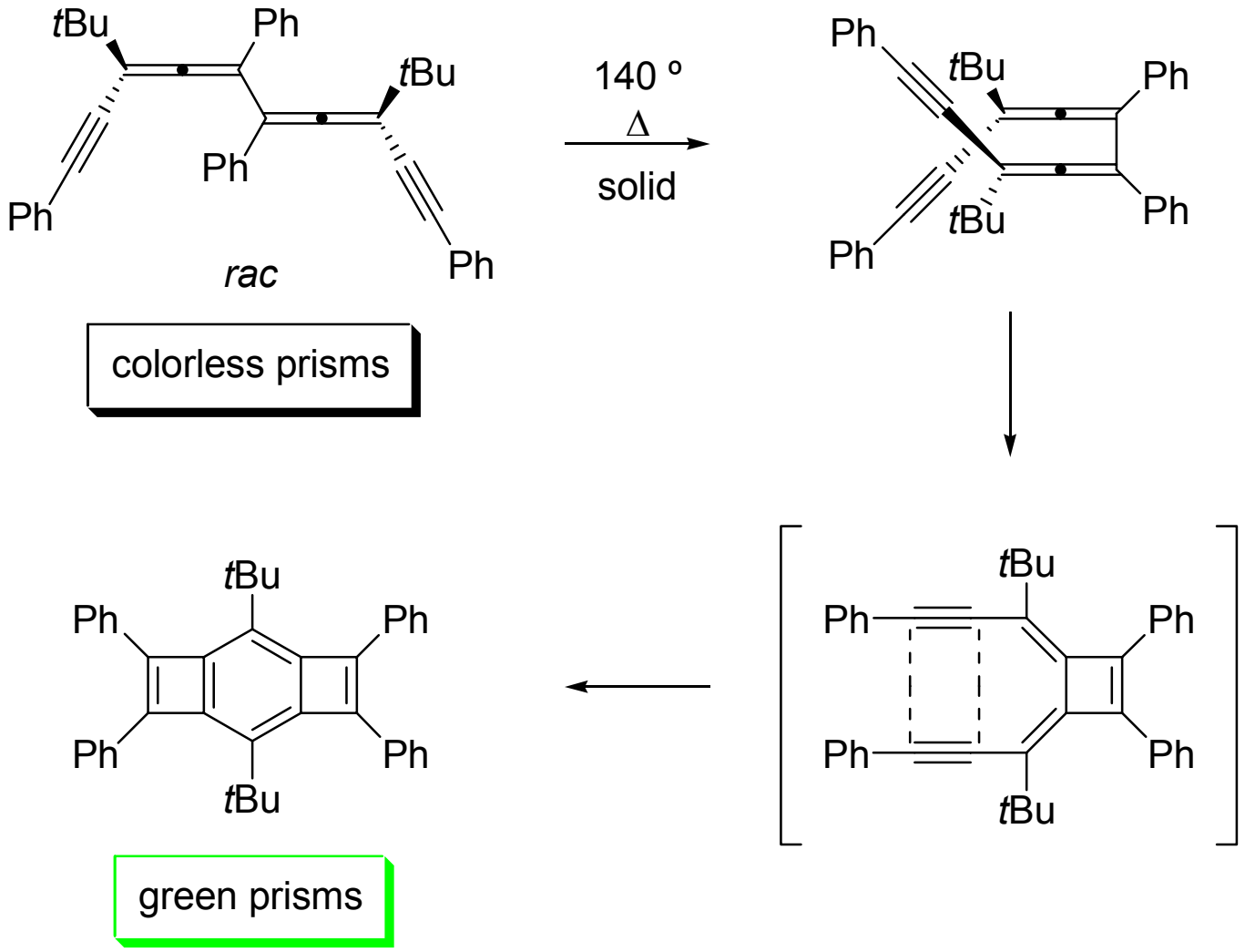
(I) Thermal cyclization of diallenes in own crystals

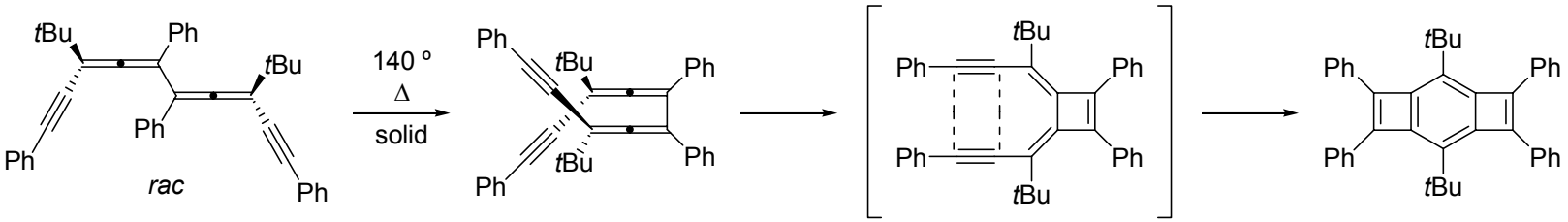
1) dimethylenecyclobutene



Angew. Chem. Int. Ed. **1988**, 2724.

2) benzodicyclobutadiene




tBu
Ph
tBu
Ph
Ph
rac
Ph
140 °
Δ
solid
Ph
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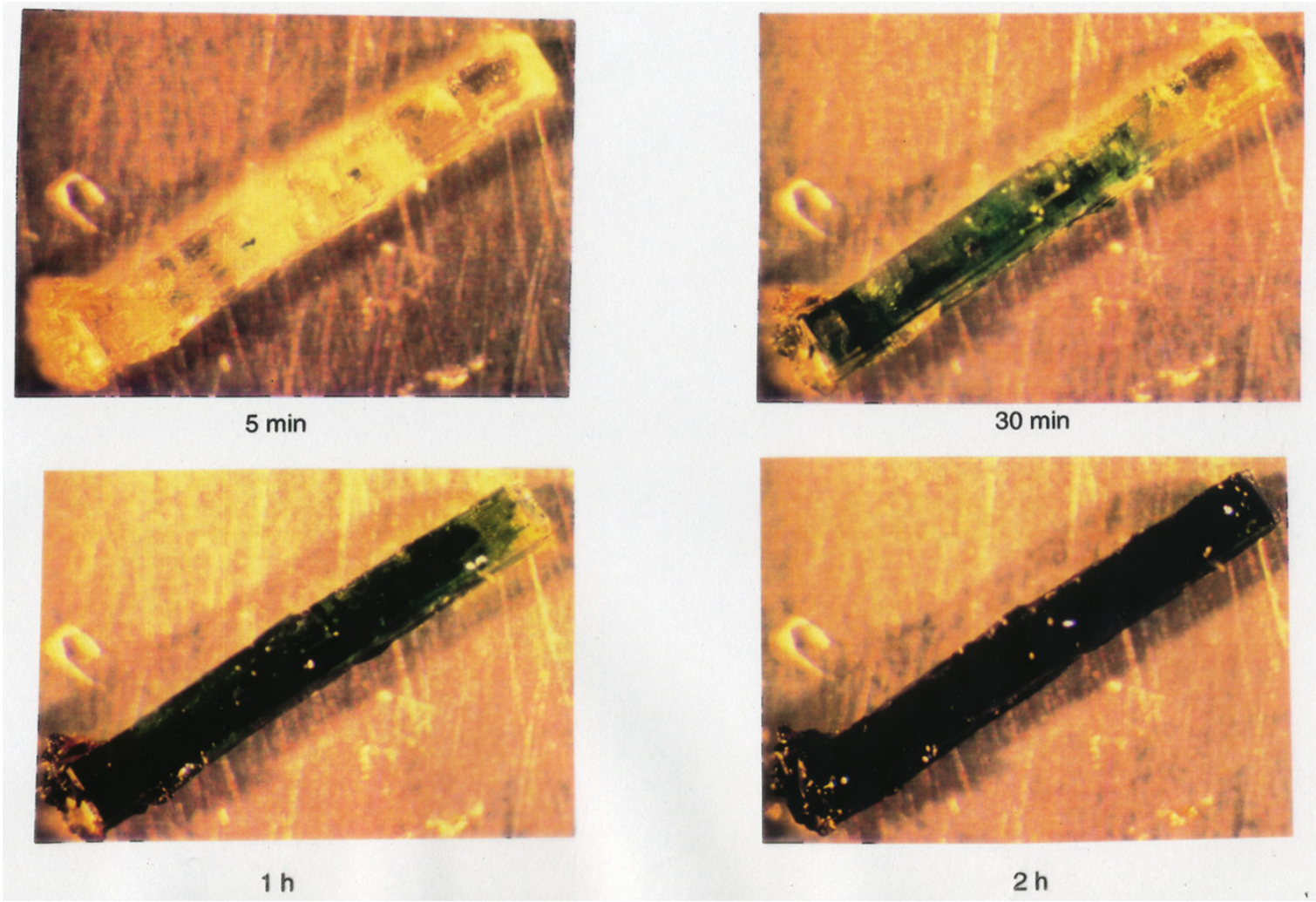
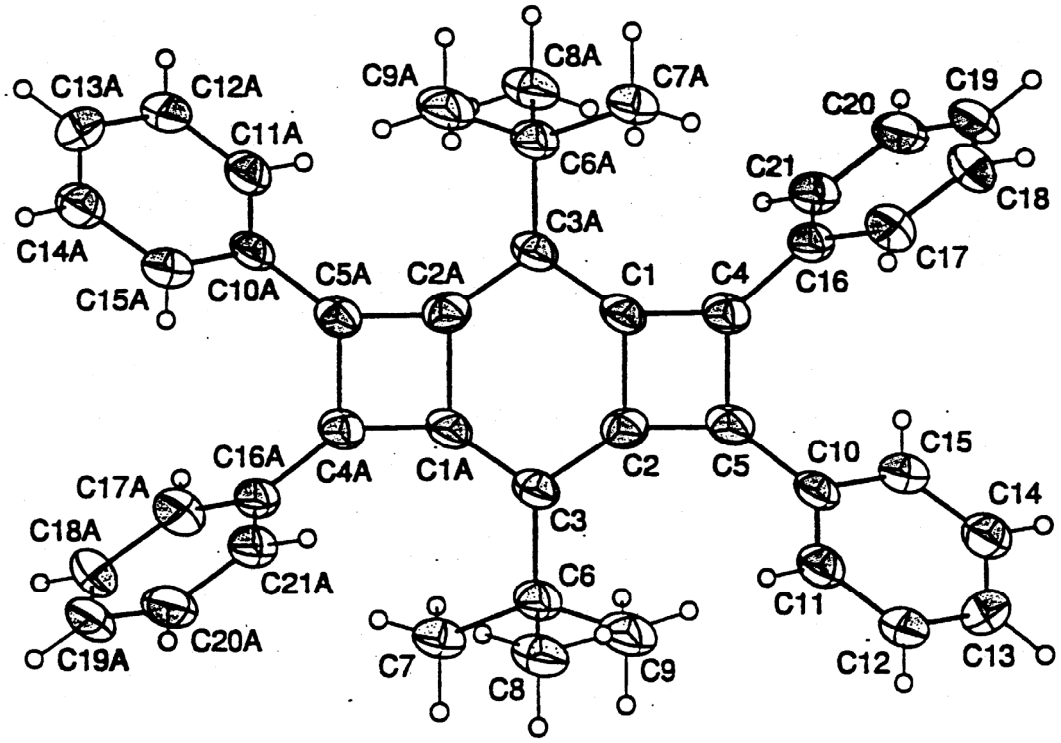
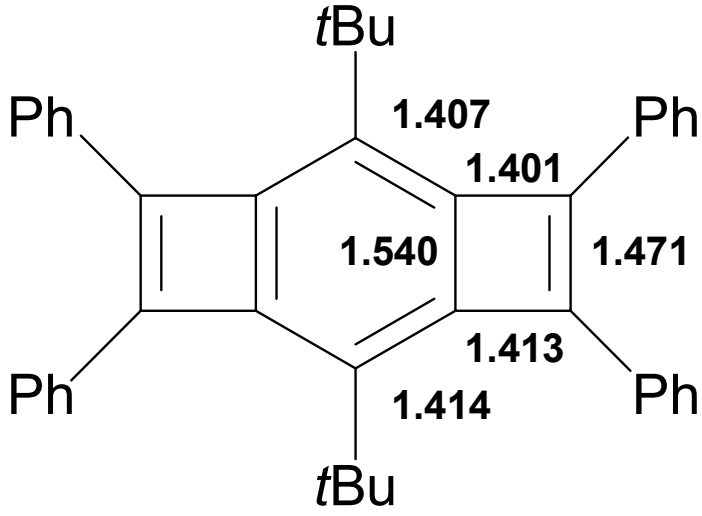
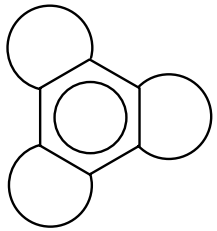

5 min
30 min
1 h
2 h

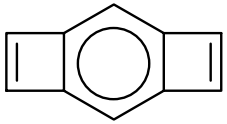




Chem. Commun. **1999**, 319.
Eur. J. Org. Chem. **2000**, 1377.



1



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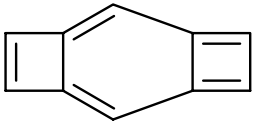
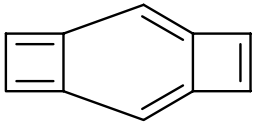
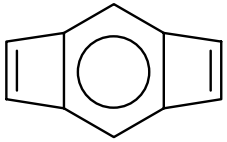


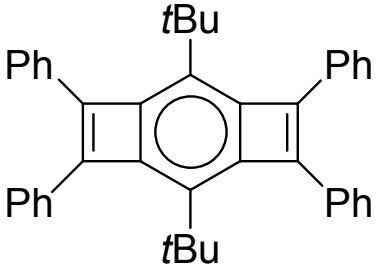
2b



2c

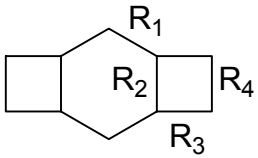


2d



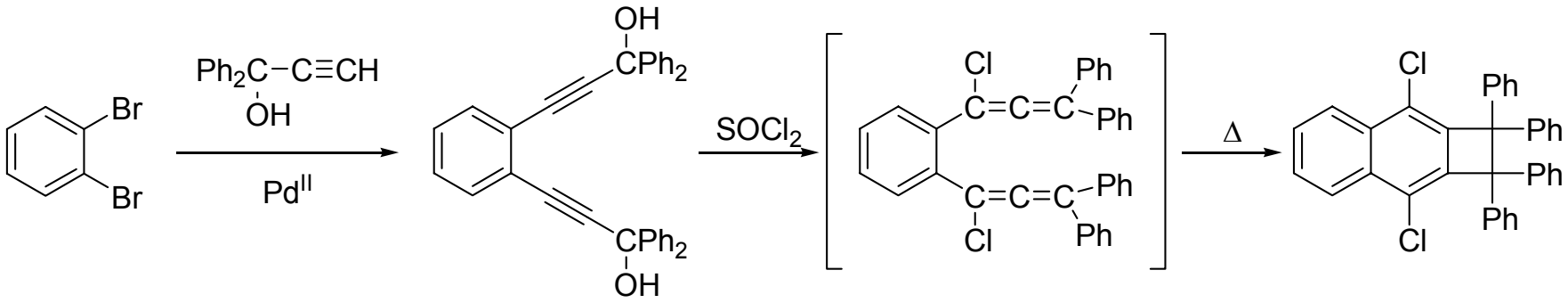
3

Table 1. Calculated (B3LYP/6-31G* and MP2/6-31G*) geometries and relative energies of the isomeres of **2.**

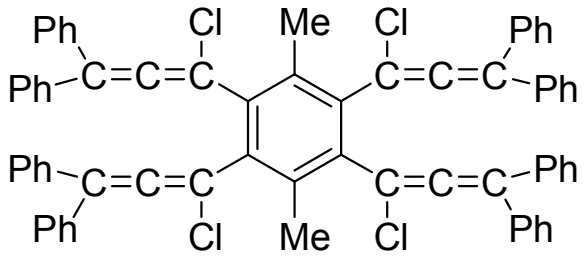


Isomer	Level	R_1	R_2	R_3	R_4	ΔE/kcal mol^{-1}
2a	MP2/6-31G*	1.3943	1.4082	1.5361	1.3456	00
2b	MP2/6-31G*	1.3898	1.5545	1.3921	1.4587	-3.7
2c	B3LYP/6-31G*	1.3944	1.4026	1.5430	1.3456	0
2d	B3LYP/6-31G*	1.3888	1.5461	1.3916	1.4583	-2.4

3) naphthocyclobutenes

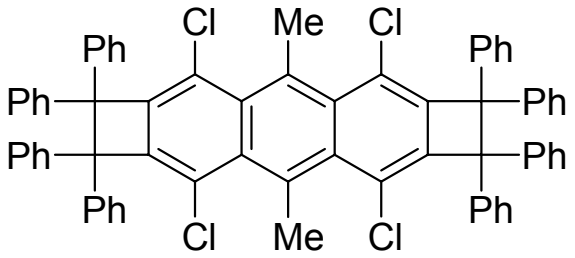


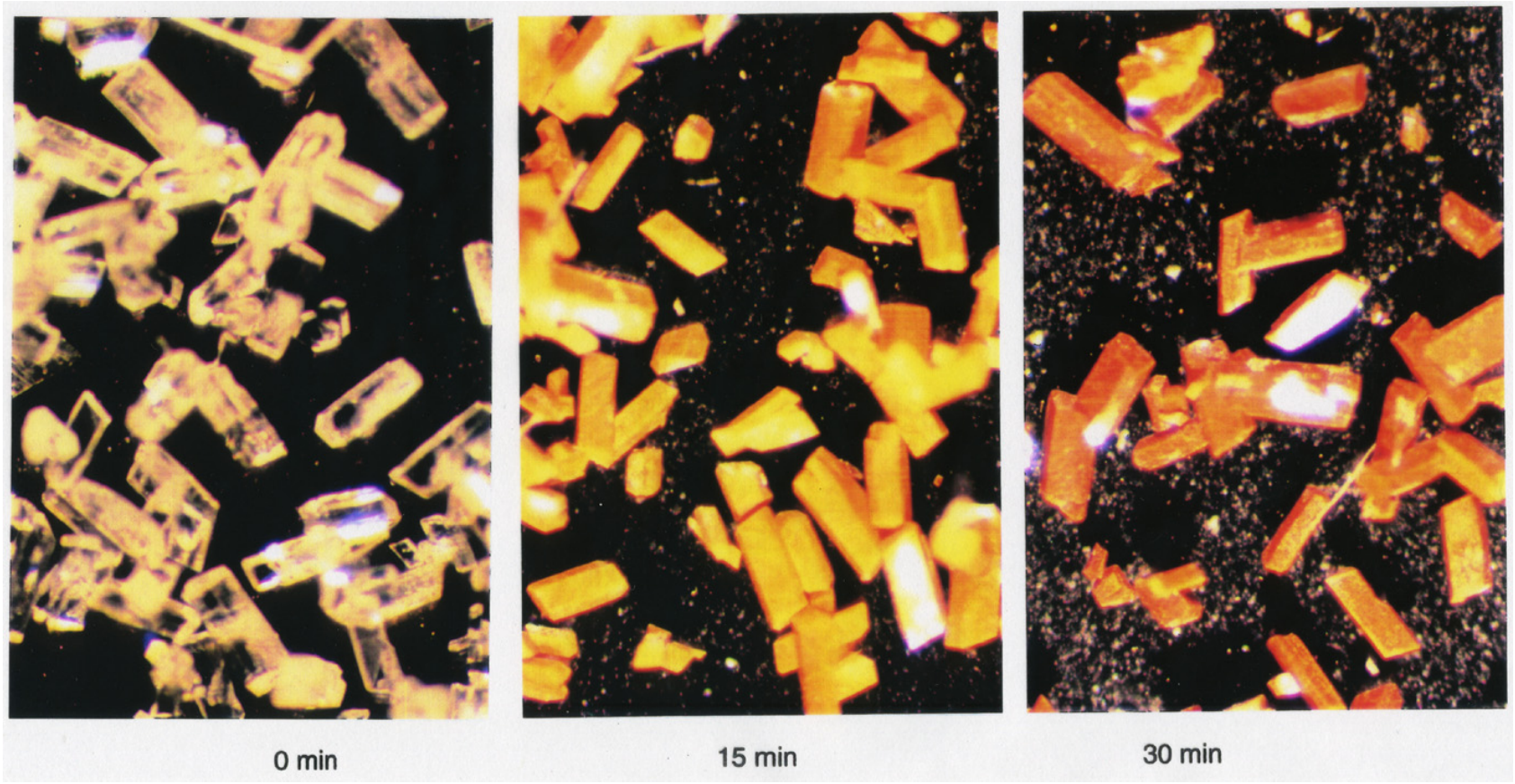
Angew. Chem. Int. Ed. **1994**, 1757.

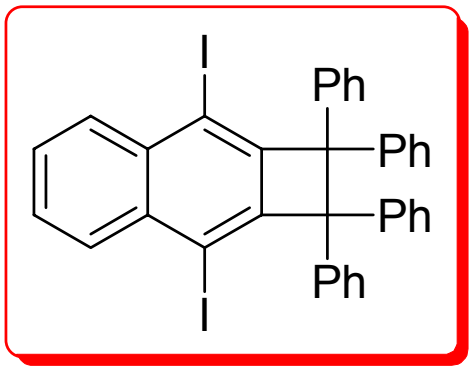


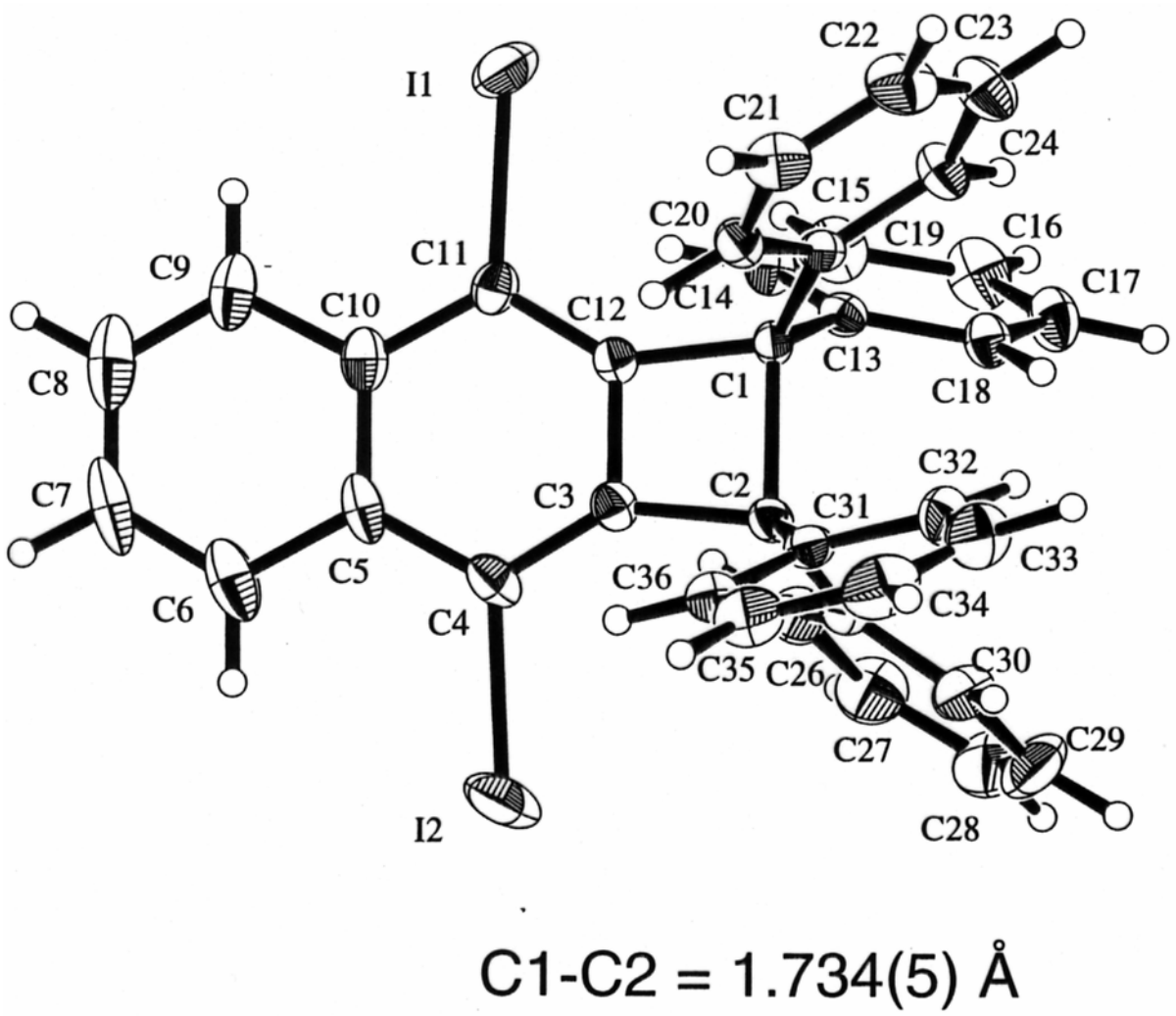
Δ

180 °C, 30 min
solid

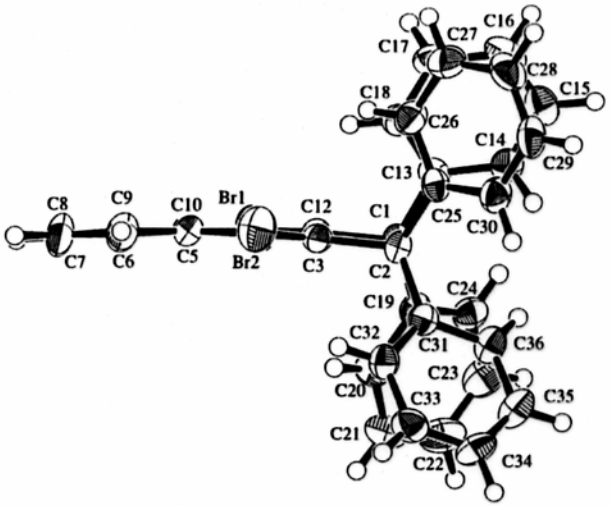




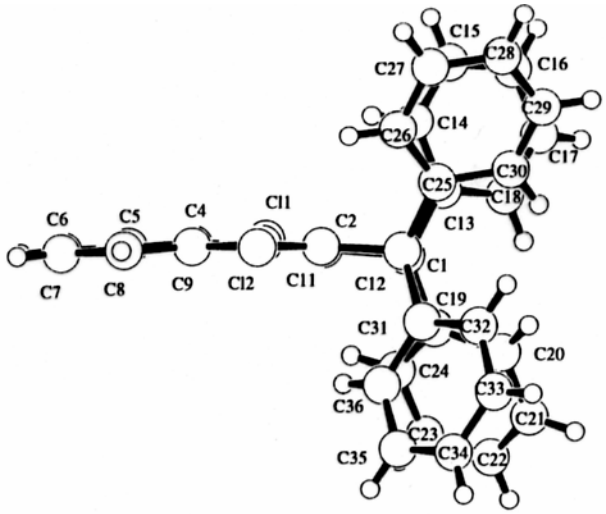

I
Ph
Ph
Ph
I


I1
C22
C23
C21
C24
C15
C20
C19
C16
C9
C11
C17
C10
C12
C14
C13
C8
C1
C18
C32
C7
C3
C2
C31
C33
C36
C5
C34
C6
C4
C35
C26
C30
C27
C29
I2
C28

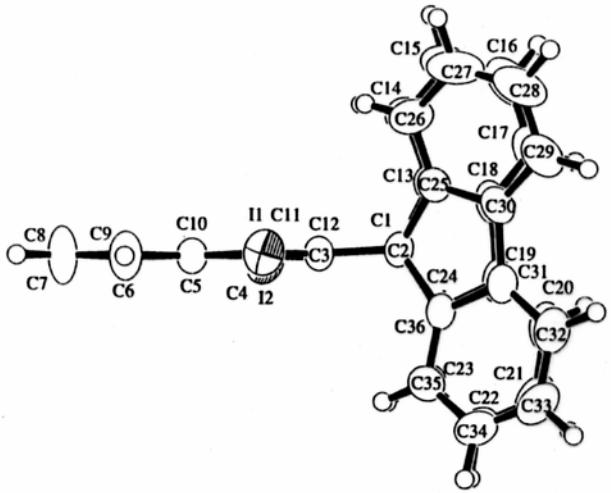
C1-C2 = 1.734(5) Å



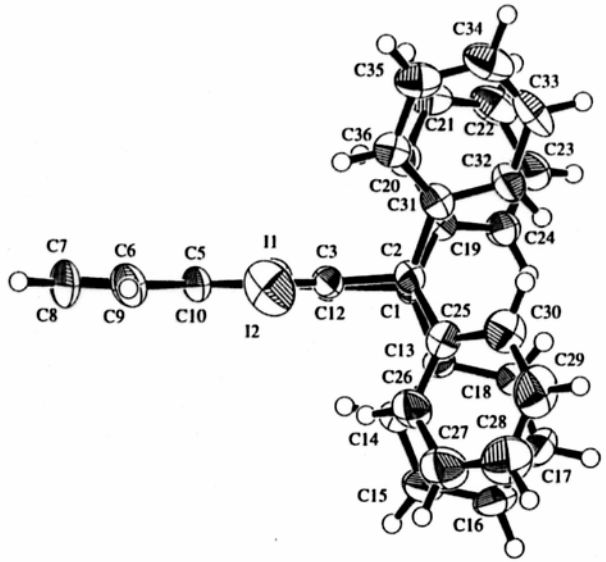
X = Br: bowed, eclipsed
C1-C2 = 1.712(5) Å



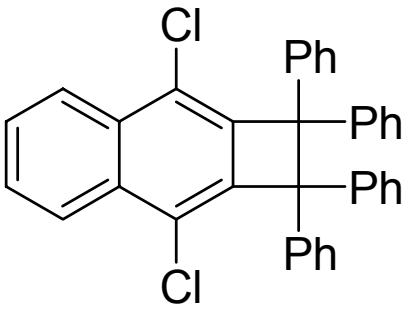
X = Cl: bowed, eclipsed
C1-C2 = 1.720(4) Å



X = I with fluorenyl: planar
C1-C2 = 1.724(5) Å



X = I: planar, guche
C1-C2 = 1.734(5) Å



Exptl. **1.720** Å

1.710 Å at 90 K

B3YLP/613G* **1.732** Å

M. Kertesz 1997

B3YLP/613G* **1.731** Å

P. v. R. Schleyer 1998

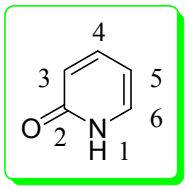
through bond interaction

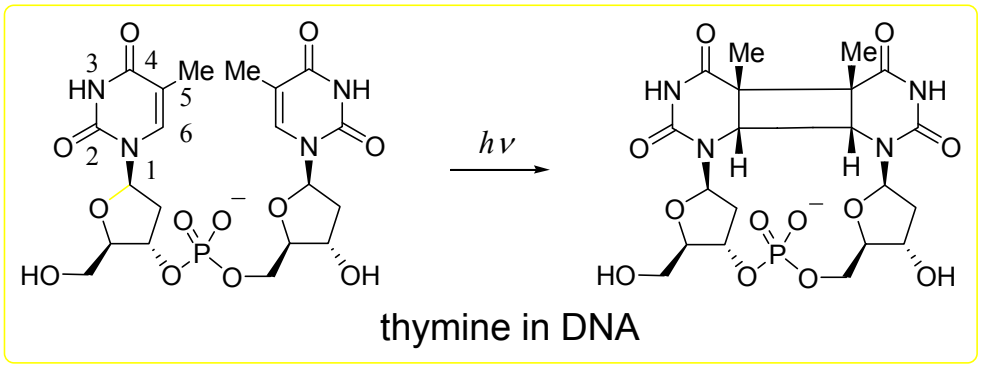
B3YLP/dz(2d, p) **1.708** Å

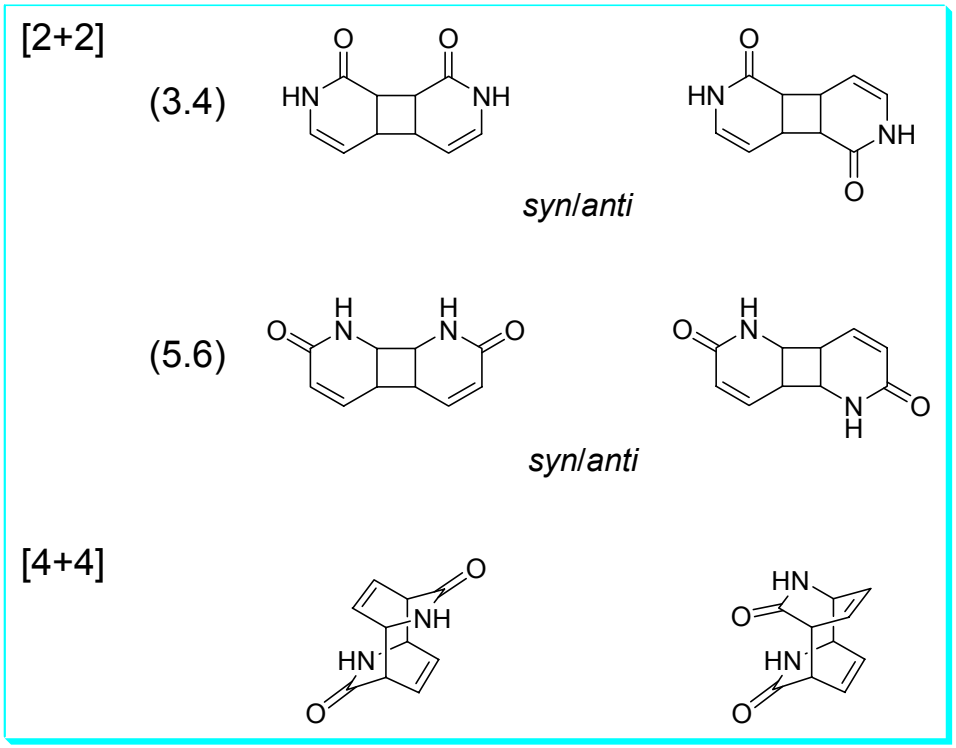
J. S. Siegel 1998

(II) Phase transitions in crystals

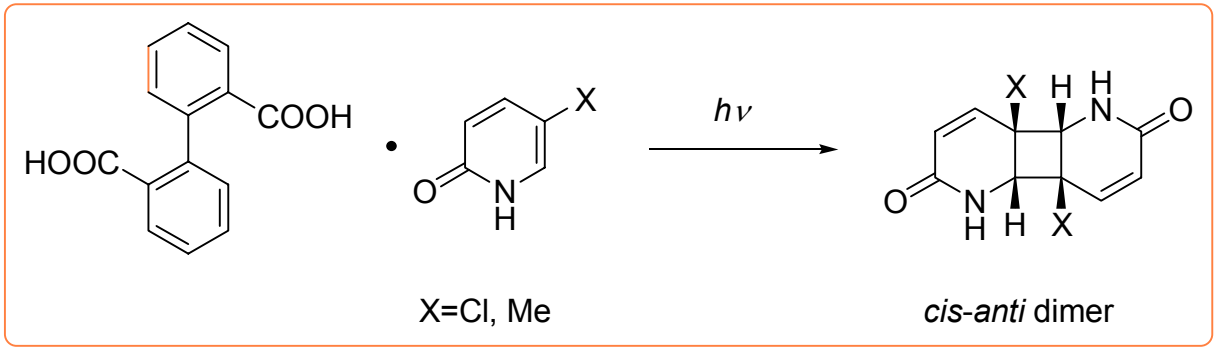
1) photodimerizatin of 2-pyridones





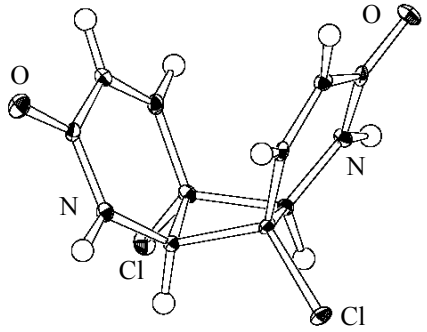


[2+2]

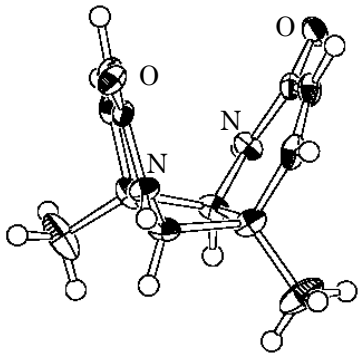


X=Cl, Me

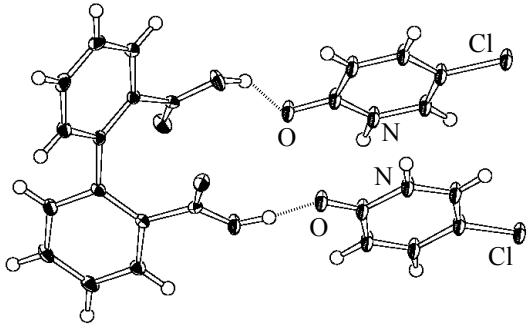
cis-anti dimer



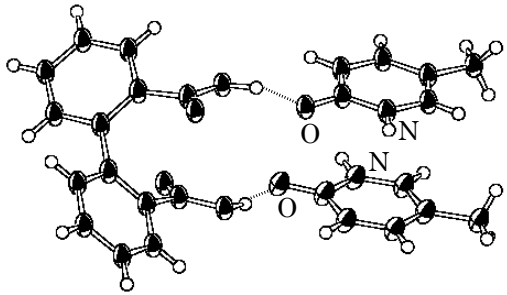
cis-anti dimer



cis-anti dimer

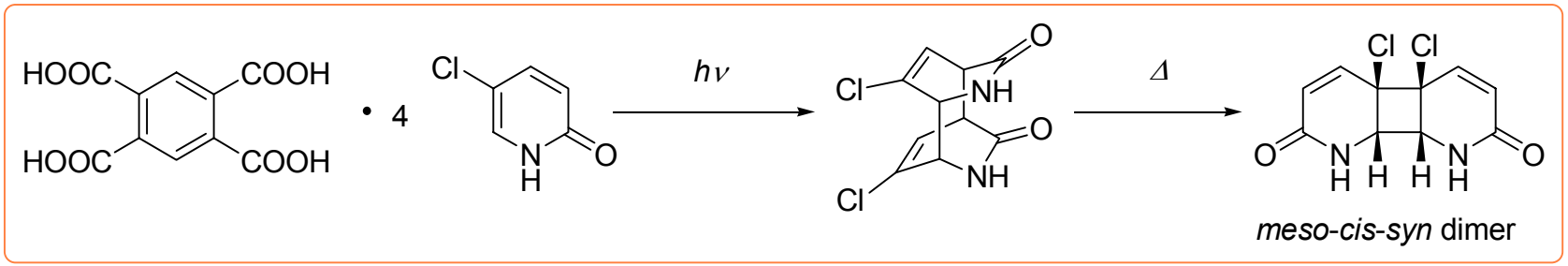


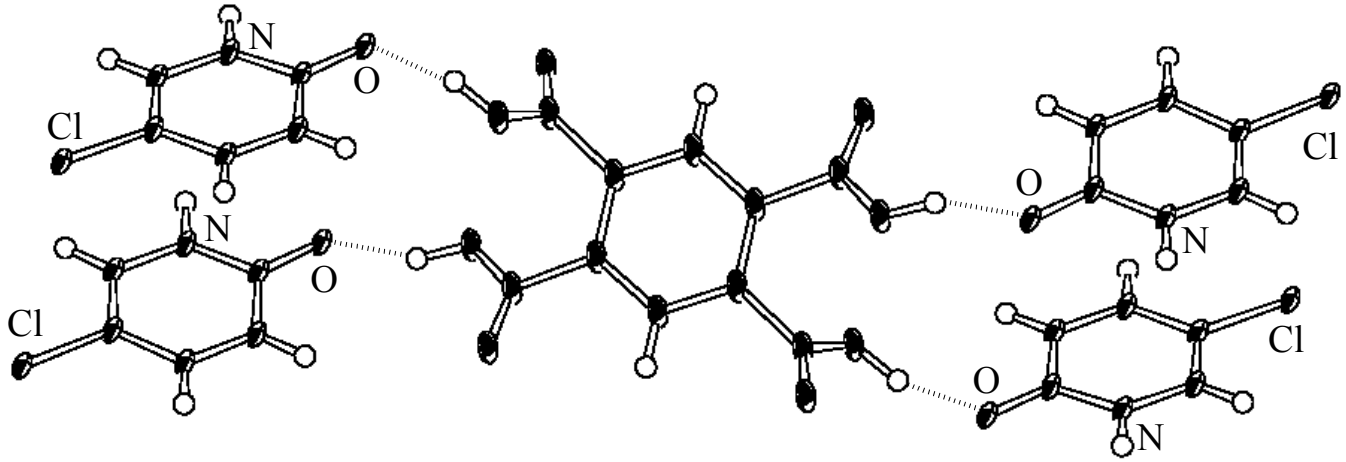
complex



complex

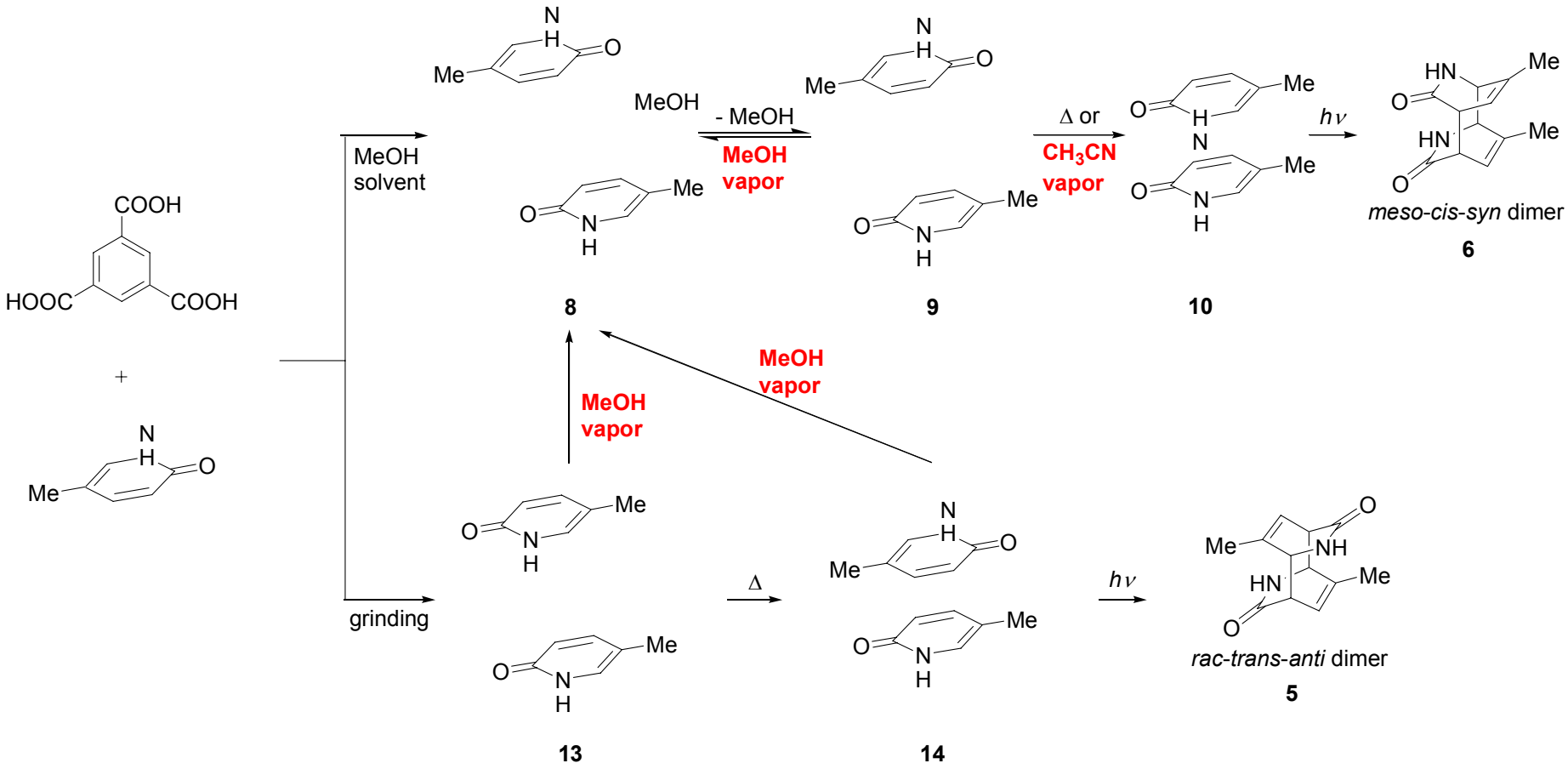
[4+4]





Chem. Commun., **2005**, 643; *Mendeleev Commun*., **2004**, 247; *Heterocycles*, **2004**, 383.

A reversible phase transition between photochemically nonreactive and reactive complexes



Scheme 1. Reversible phase transition between photochemically nonreactive and reactive complexes. For clarity host is omitted

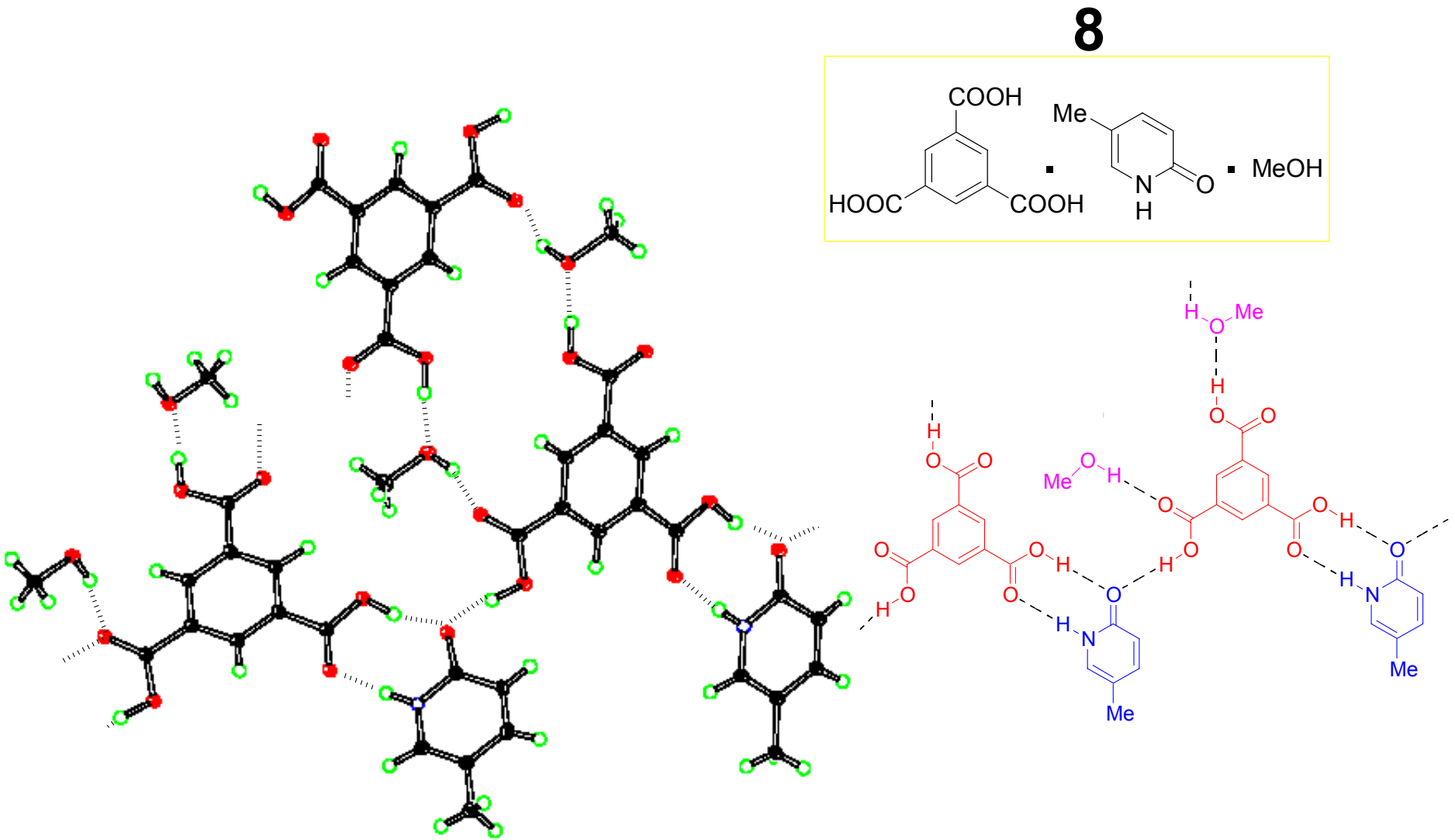
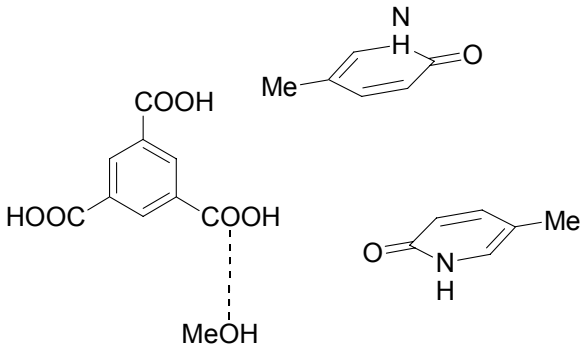


Fig. X-ray structure of **8** (top view)



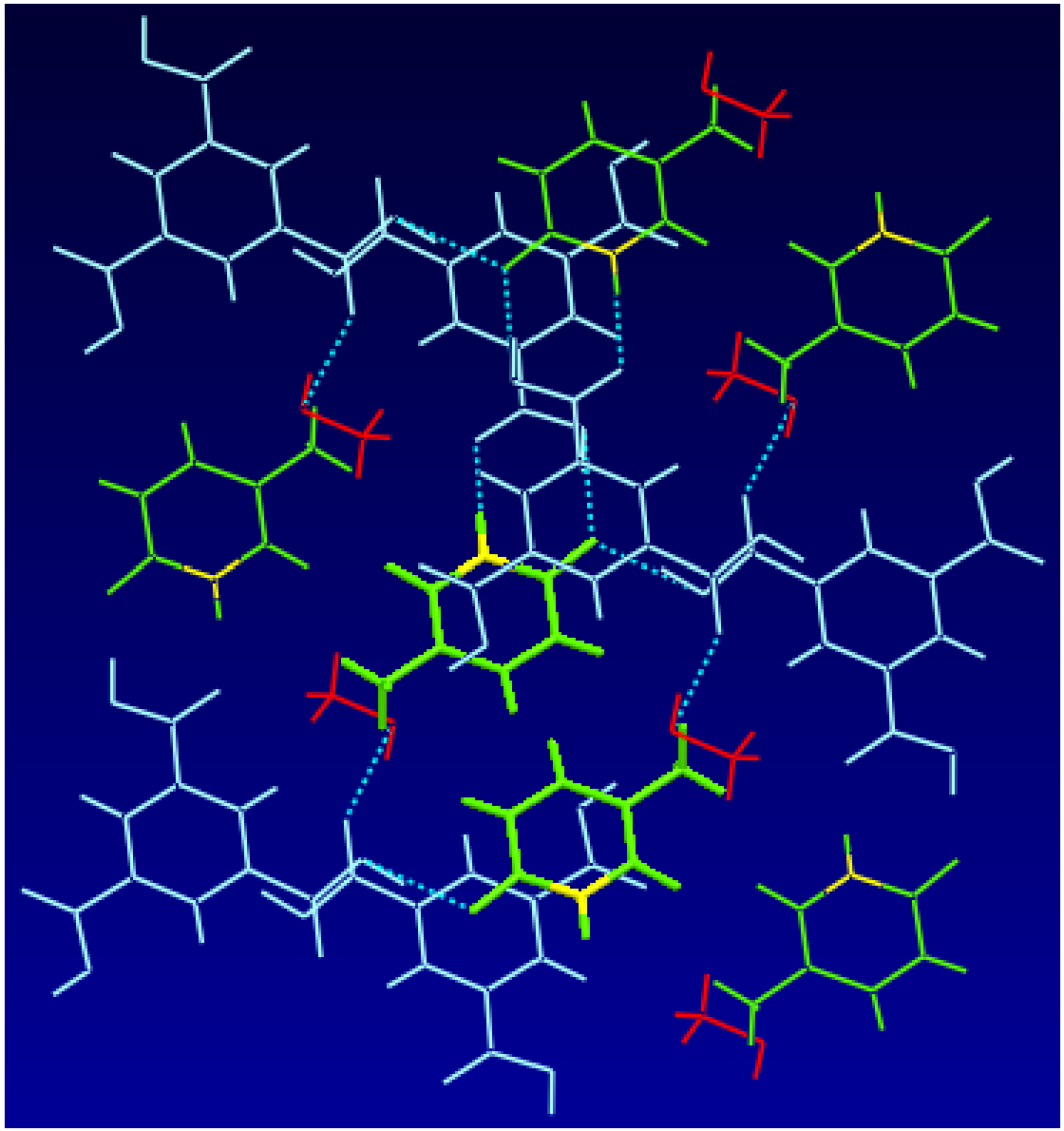


Fig. X-ray structure of the 1:1:1 complex of host:5-methyl-2-pyridone:MeOH (**8**).

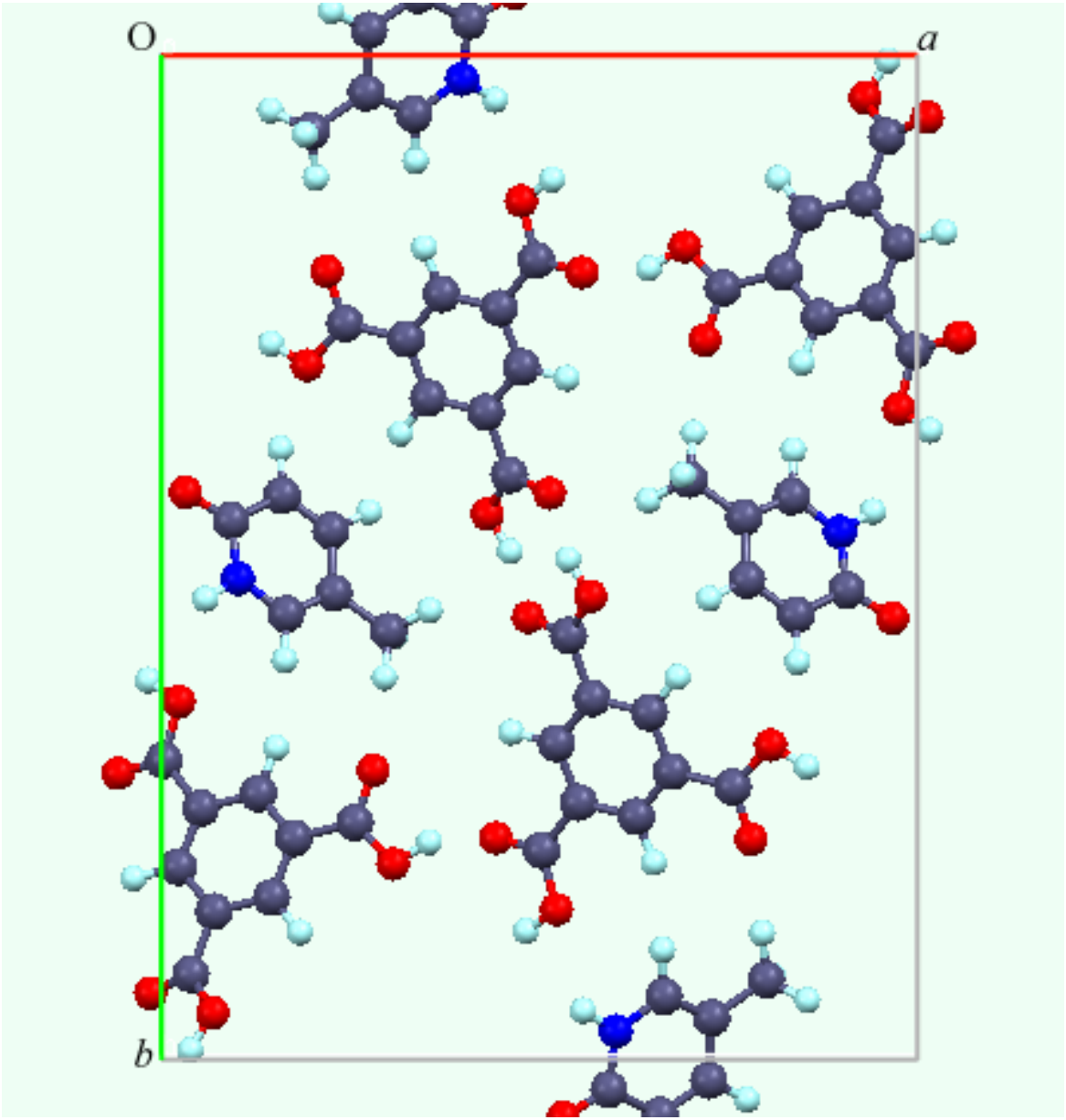


Fig. Packing diagram of **10**.

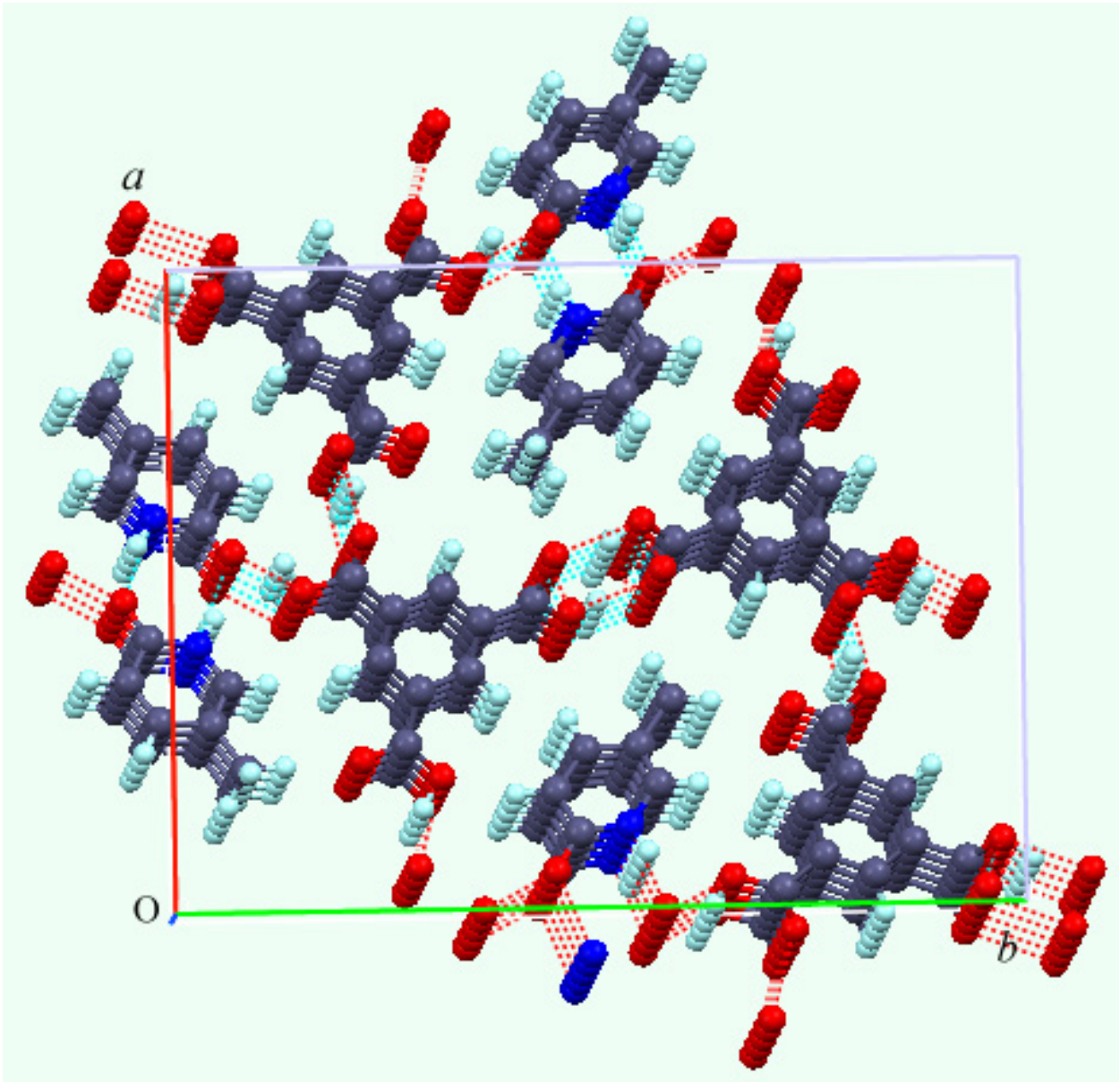


Fig. Packing diagram of **10**.

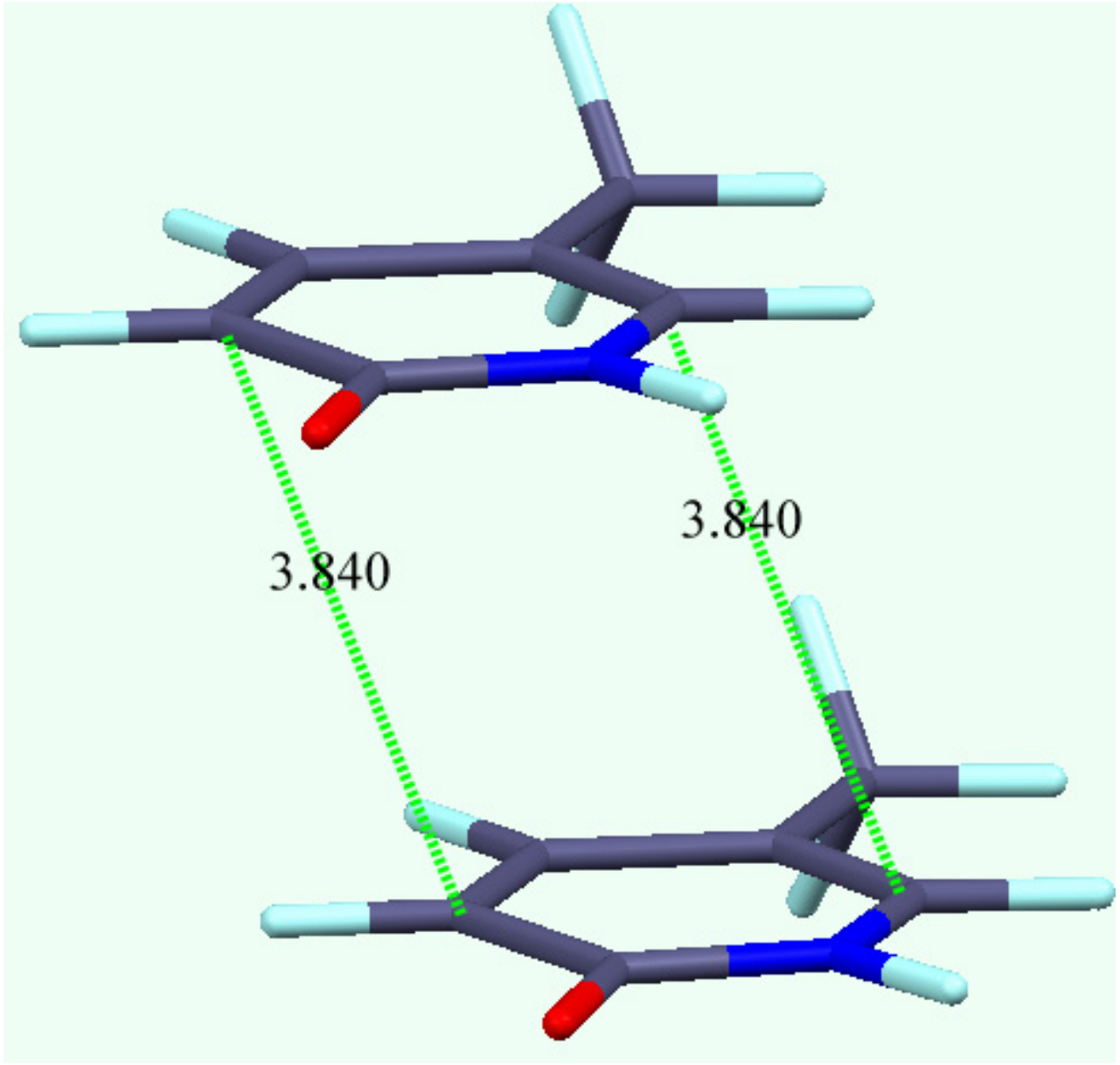
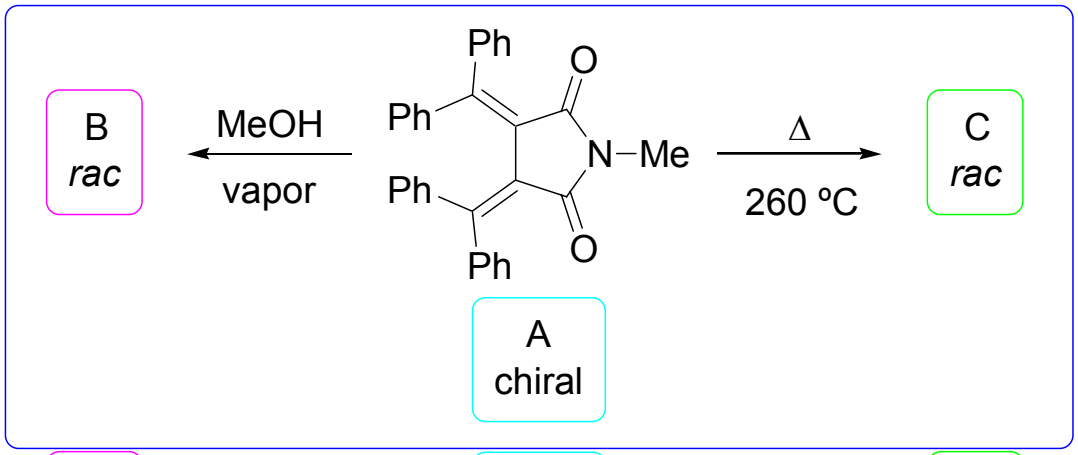
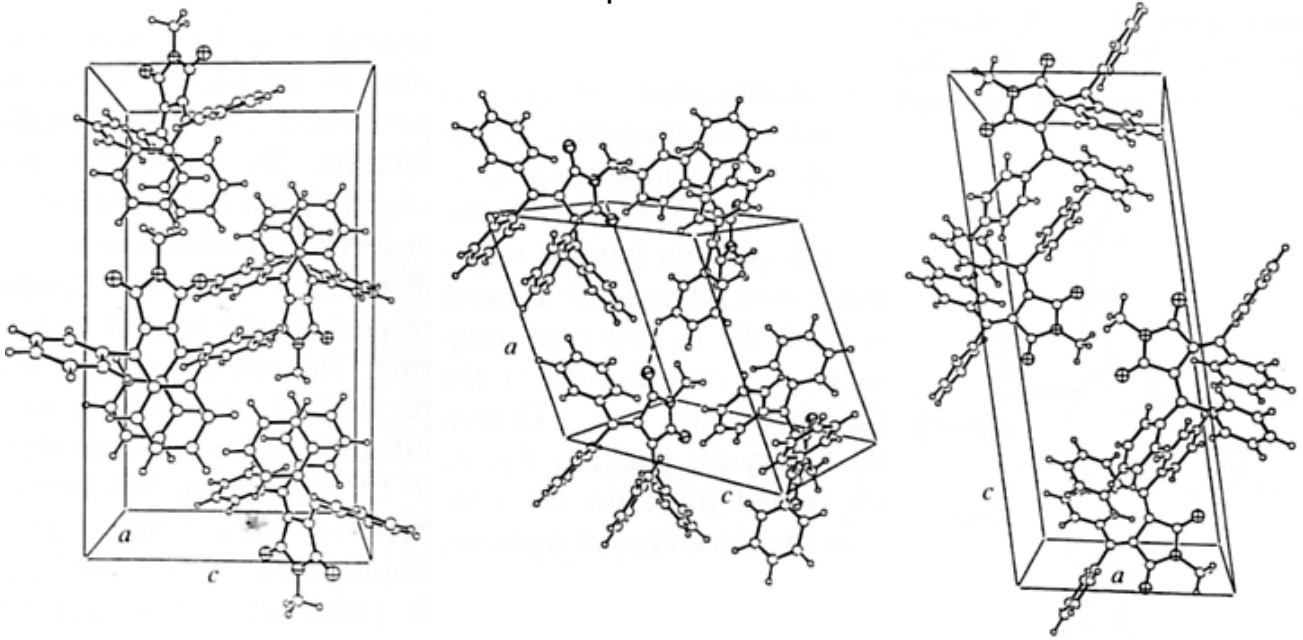


Fig. Distances between 5-methyl-2-pyridone molecules in **10**.

2) succinamide



B *rac*	A chiral	C *rac*
orange plates 302 °C	orange hexagonals mp 260 °C	yellow plates 297 °C



Pbcn	*P2₁*	*P2₁/n*

3) tetraphenylethene

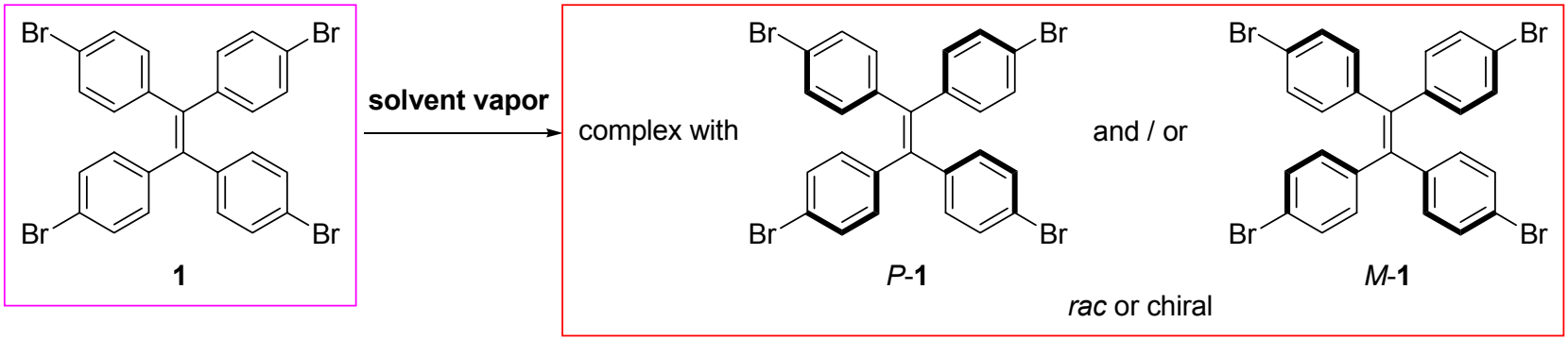


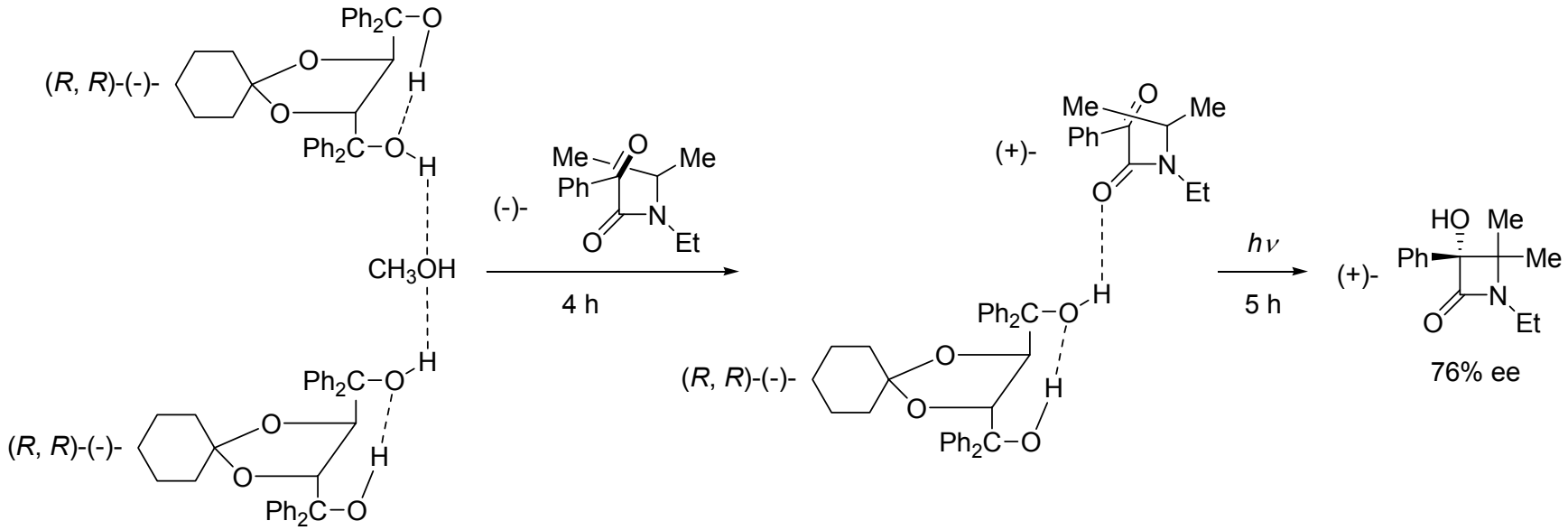
Table 1. Inclusion complexation of **1** with some guest compounds

	Inclusion complex				
	By recrystallization		By gas-solid reaction		
Guest	host : guest		host : guest		*t*/h
Acetone	chiral	1 : 2	—[a]	—[a]	168
Cyclohexanone	*rac*	1 : 1	—[a]	—[a]	168
THF	*rac*	1 : 2	chiral	1 : 2	2
1,4-Dioxane	chiral	1 : 1	chiral	1 : 1	24
Benzene	chiral	1 : 1	chiral	1 : 1	24
Toluene	*rac*	1 : 1	—[a]	—[a]	168
p-Xylene	chiral	1 : 1	chiral	1 : 1	24
β-Picoline	*rac*	1 : 1	chiral	1 : 1	168

[a] No complexation occurred.

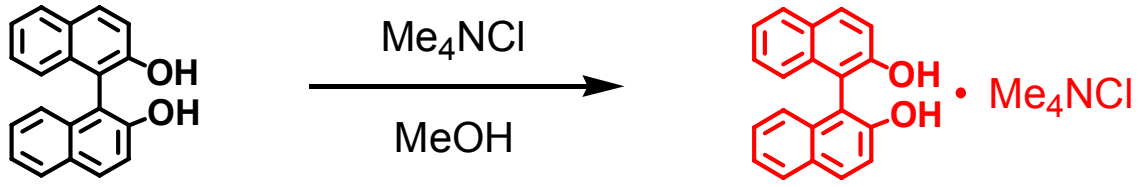
Chem. Comm. **2000**, 413.

4) oxoamide



Chem. Lett. **1995**, 809.

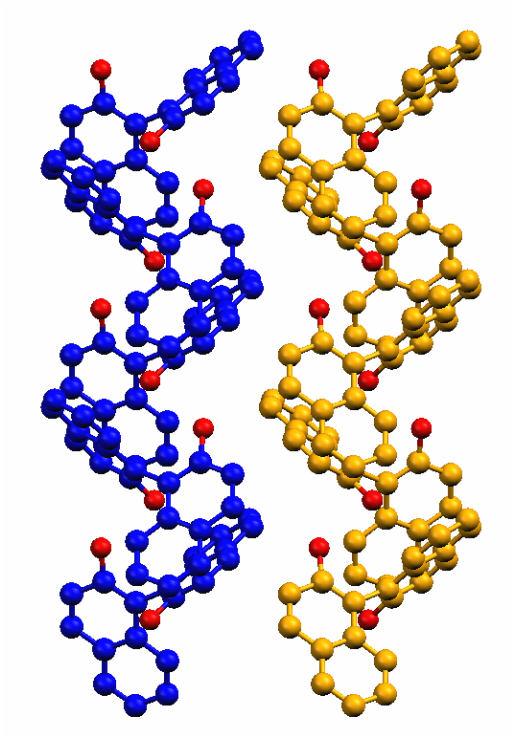
5) BNO

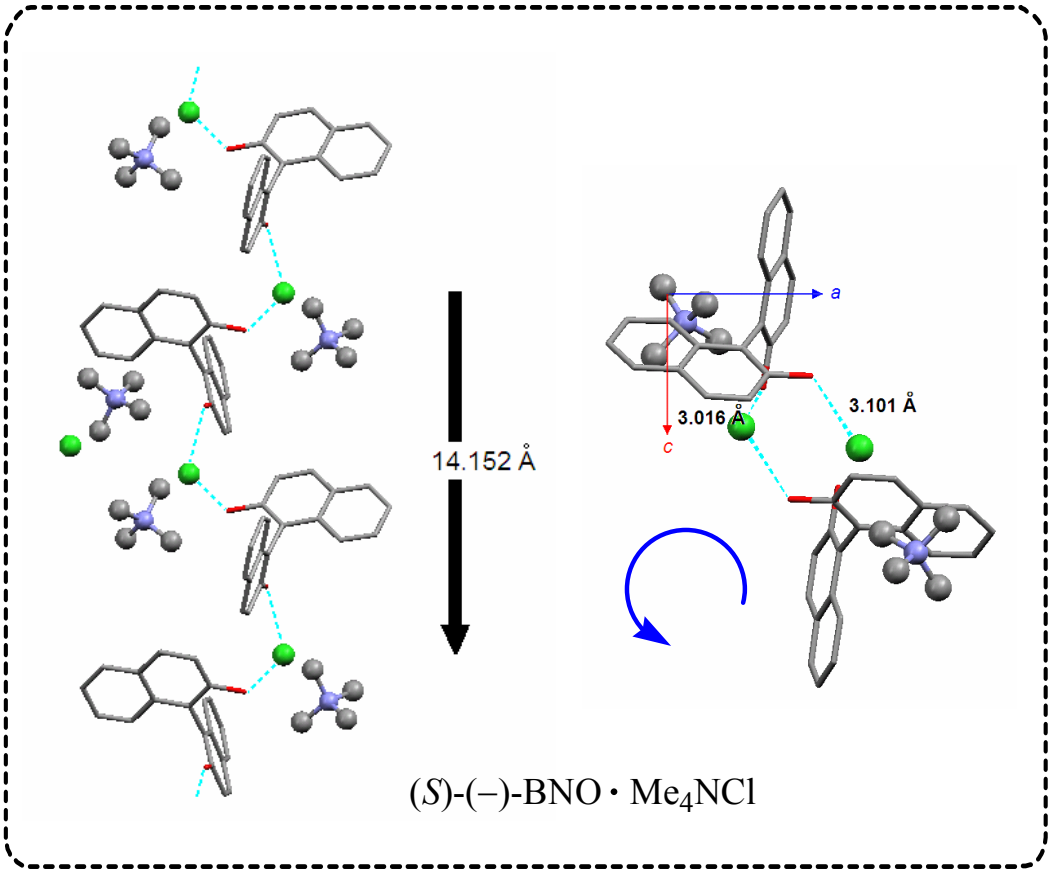


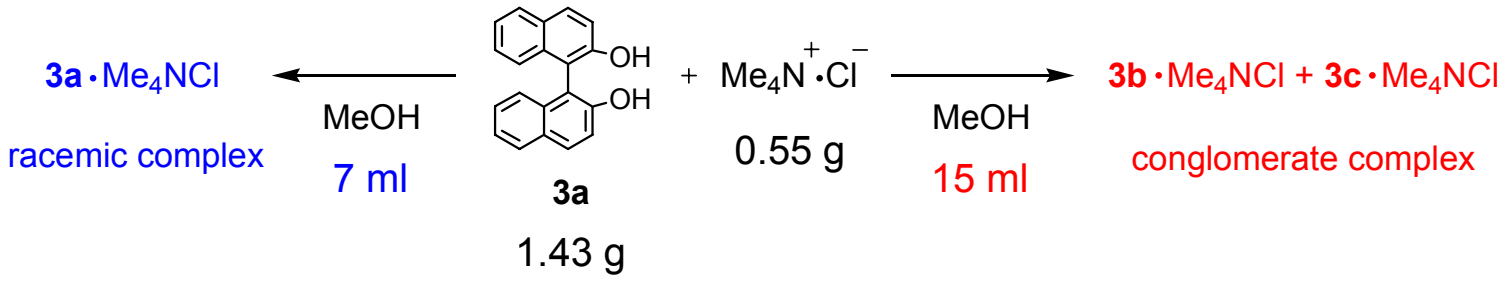
3a

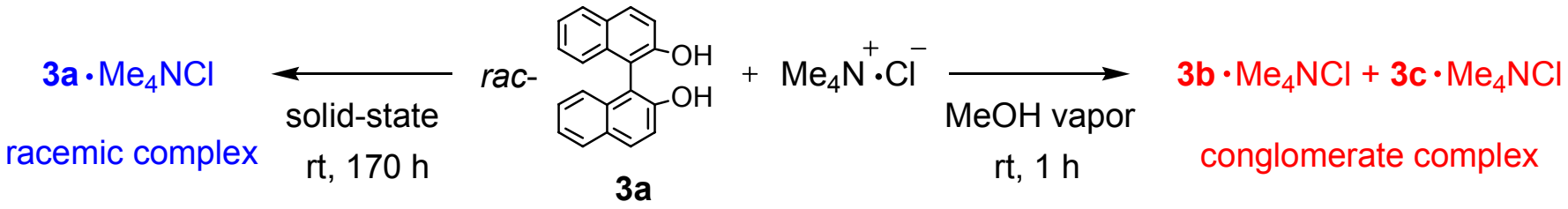
racemate

conglomerate complex

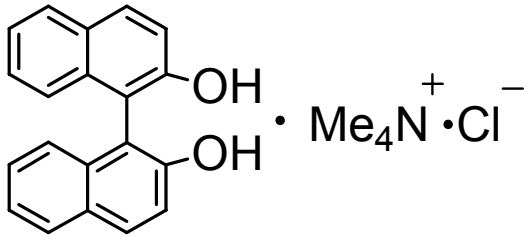





3a · Me4NCl
racemic complex
MeOH
7 ml
OH
OH
3a
1.43 g
+
Me4N+·Cl−
0.55 g
MeOH
15 ml
3b · Me4NCl + 3c · Me4NCl
conglomerate complex


3a · Me4NCl
racemic complex
solid-state
rt, 170 h
rac-
OH
OH
3a
+
Me4N+·Cl−
MeOH vapor
rt, 1 h
3b · Me4NCl + 3c · Me4NCl
conglomerate complex

phase transition



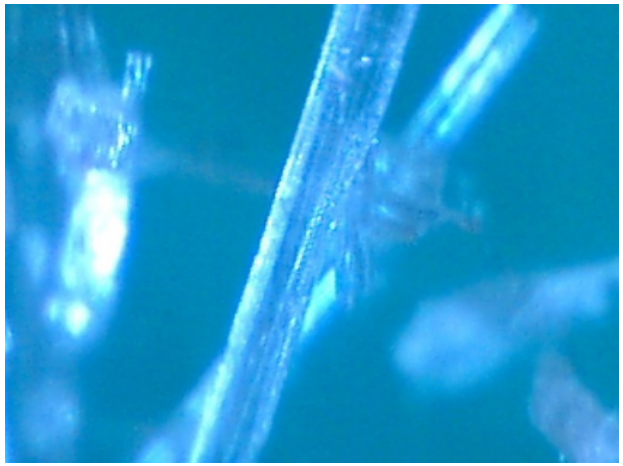
racemate complex

160 °C, 5 min

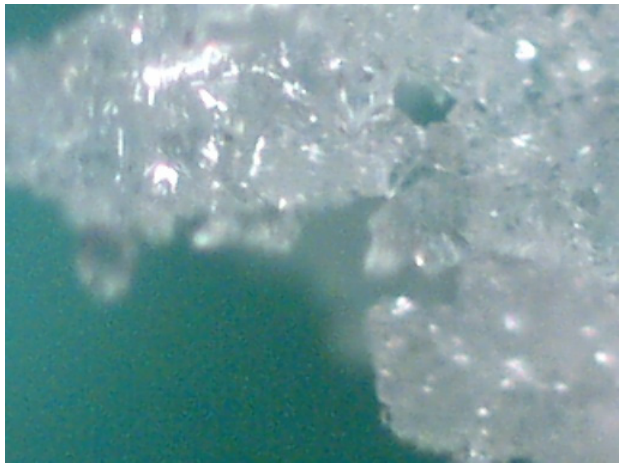
or MeOH vapor

30 min

conglomerate complex

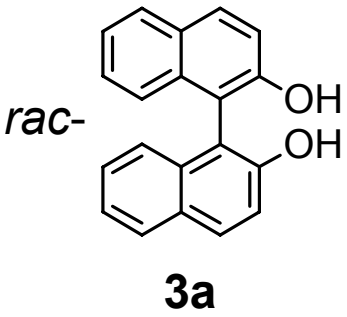


MeOH vapor



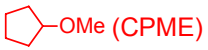
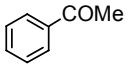
Tetrahedron. **2004**, 7767; *Chem. Comm.* **2004**, 1844.

(III) Seed crystals in the solid state



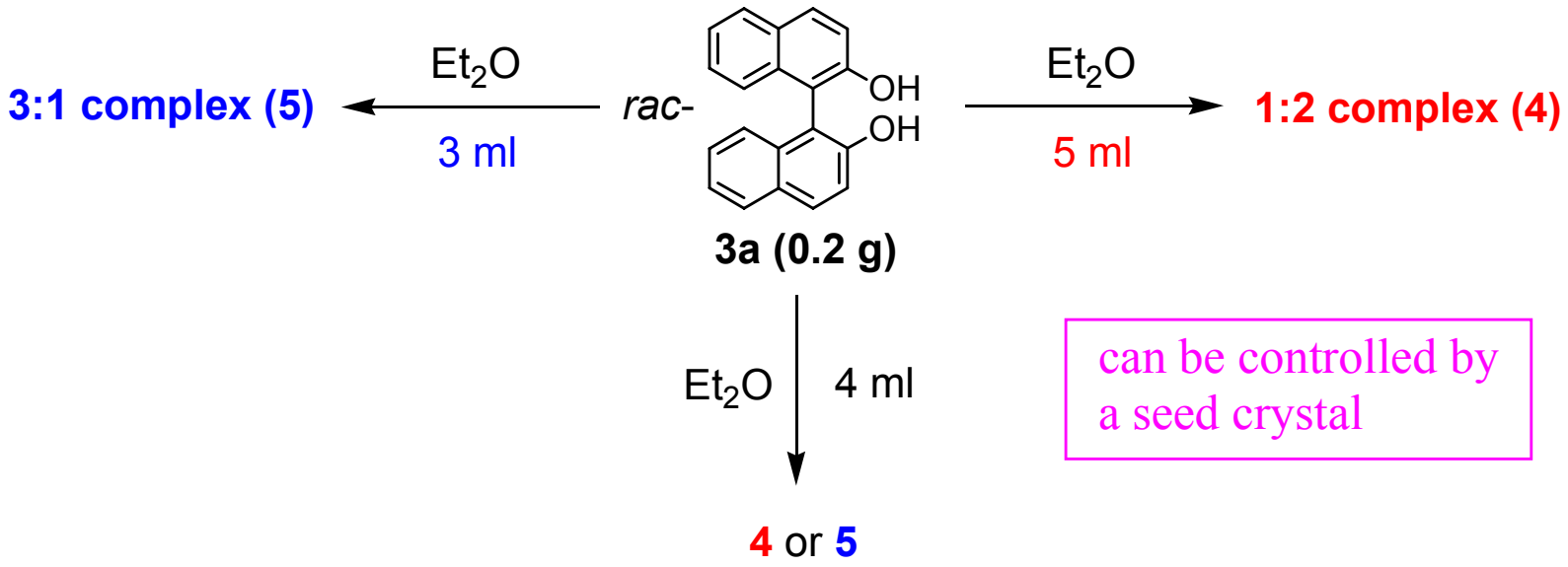
3a

Table 1. Data of inclusion complexes of **3a** with various liquid guests.

guest	complex		
	host : guest ratio[a]	decomp. (°C)	νOH (cm^{-1}) [b]
Et_2O	**3 : 1**	**87-108**	**3419, 3459, 3489**
Et_2O	**1 : 2**	**40-61**	**3198**
	1 : 2	37-74	3198
THF	2 : 3	48-106	3173, 3519
	2 : 3	61-116	3248
AcOMe	3 : 1	83-108	3403, 3463, 3491
AcOEt	3 : 1	75-105	3413, 3464, 3490
	1 : 2	87-128	3366
$Me_2C=O$	1 : 1	70-98	3036, 3404
	1 : 1	79-107	3321, 3419
	1 : 1	87-117	3264, 3417
	1 : 2	94-121	3199
	1 : 2	97-141	3198

[a] The ratio was determined by ^1H NMR spectra and TG analysis.

[b] IR spectra were measured by using the ATR (Attenuated total reflection) method.



Scheme 1. Inclusion complexation of **3a** and Et_2O by recrystallization of **3a** from Et_2O solutions of different concentration.

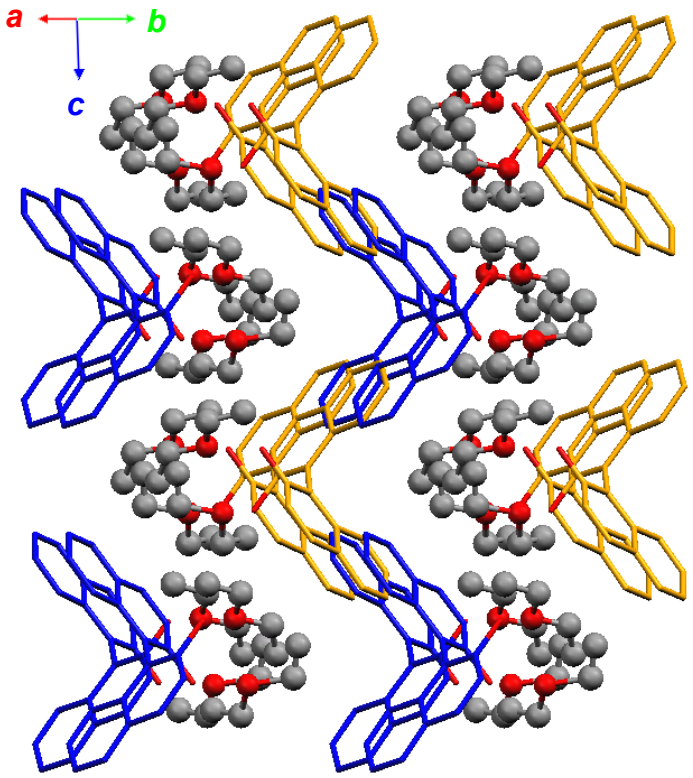


Figure 1. Crystal structure of the 1:2 complex of **3a** and Et_2O (**4**).

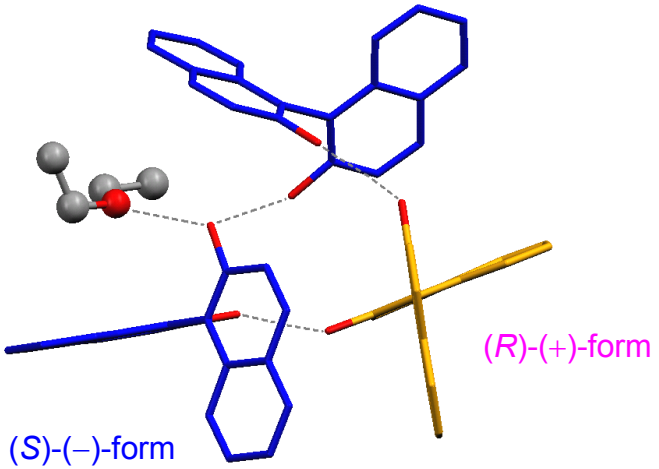
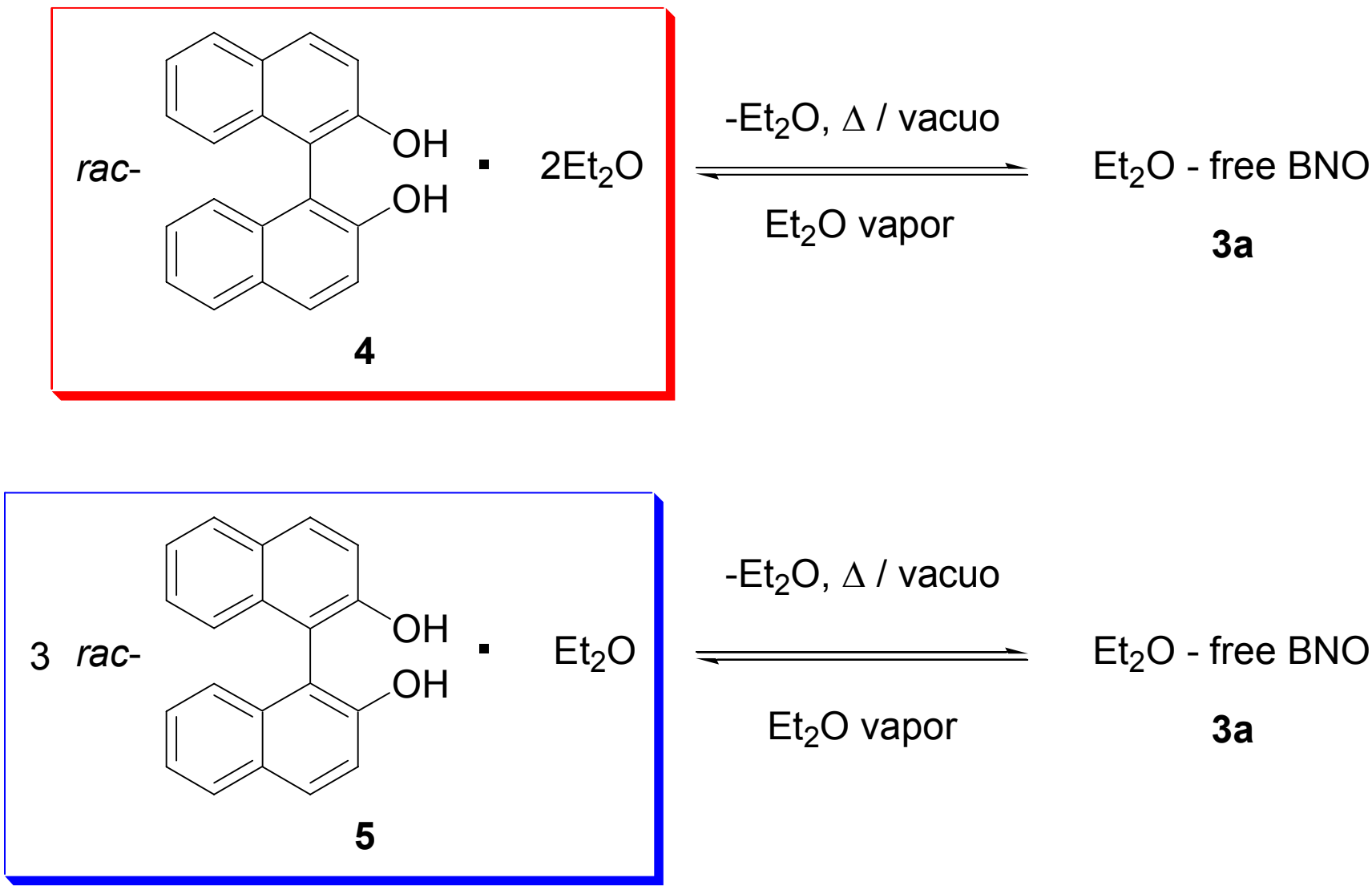
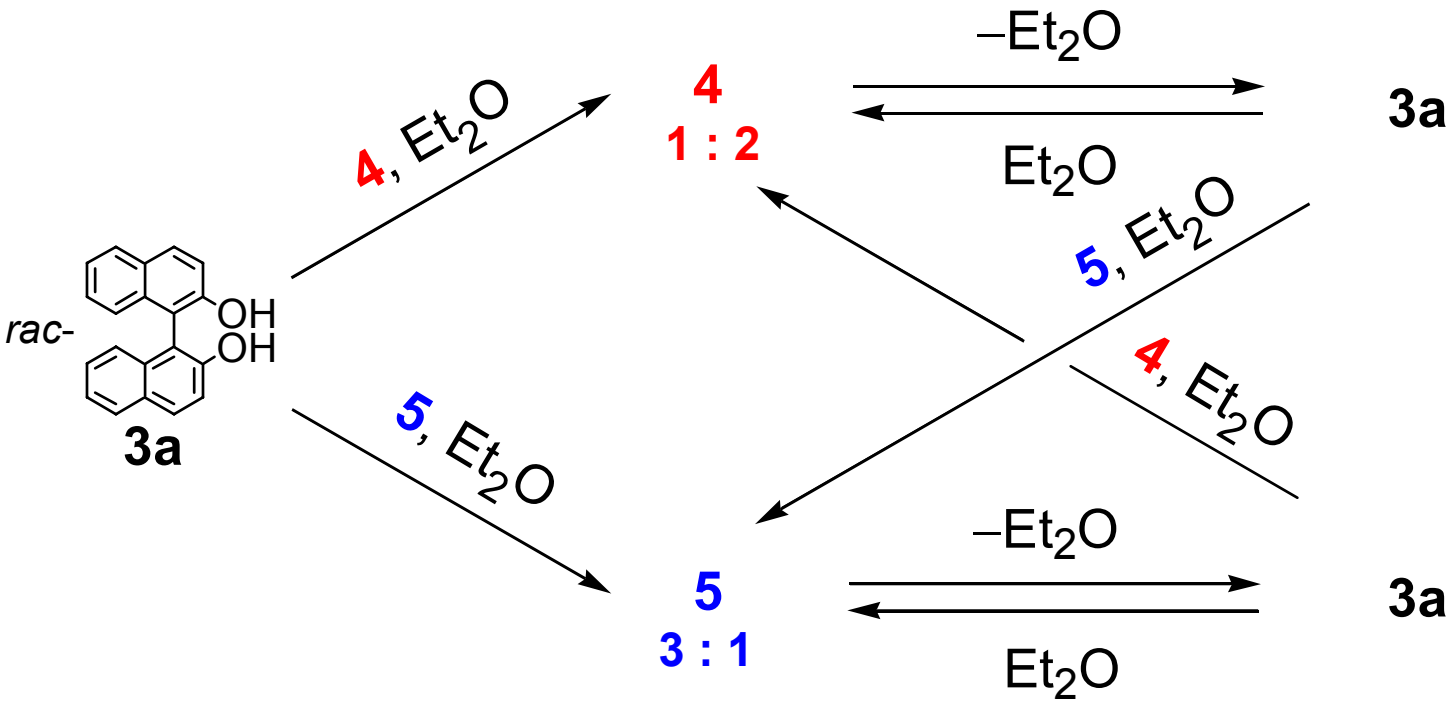


Figure 2. Crystal structure of the 3:1 complex of **3a** and Et_2O (**5**).



Scheme 1. Memory of inclusion pattern.



Scheme 2. Seed crystal experiments in the inclusion complexation between solid host and gaseous Et_2O guest.

Angew. Chem. Int. Ed. **2005**, in press.

Table . Inclusion complexation of powdered *rac*-BNO (**3a**) and gaseous guest in the presence of pseudo seed crystal.

guest (**3a**:guest ratio) in seed crystal	gaseous guest	reaction time (h)	guest (**3a**:guest ratio) in product
AcOMe (3 : 1)	AcOEt	3	AcOEt (3 : 1)
AcOMe (3 : 1)	Et_2O	3	Et_2O (3 : 1)
AcOE t (3 : 1)	AcOMe	3	AcOMe (3 : 1)
AcOEt (3 : 1)	Et_2O	3	Et_2O (3 : 1)
Et_2O (3 : 1)	AcOMe	3	AcOMe (3 : 1)
Et_2O (1 : 2)	CPME	12	CPME (1 : 2)
CPME (1 : 2)	Et_2O	12	Et_2O (1 : 2)
AcOMe (3 : 1)	CPME	12	–
Et_2O (3 : 1)	CPME	12	–