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Crystalline inclusion complexes as media of molecular recognitions and selective reactions*

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Abstract: Hexaol host compounds which include guest molecules maximum in 1:6 ratio were prepared. Aromatic hexaol host, hexahydroxytriphenylene, was found to form chiral inclusion crystal by complexation with achiral guest molecules. Some interesting and important optical resolutions of *rac*-guests by inclusion complexation with a chiral host were described. When chemical reaction and the inclusion complexation procedures in a water suspension medium are combined, new economical and ecological method of the preparation of optically active compound can be established. When photochemical reactions are carried out in an inclusion crystal with a chiral host, enantioselective reactions occur, and optically active product can be obtained. Several successful reactions are described.

INTRODUCTION

Cystalline inclusion complexes of guest compounds with various artificial hosts are useful as media for the following molecular recognitions and selective reactions in the solid state.

MOLECULAR RECOGNITIONS IN THE INCLUSION COMPLEXES WITH HEXAOL HOST COMPOUNDS

By our simple principles for design of host molecules [1], we have prepared various kinds of artificial hosts such as alcohols, phenols, amides, amines, alkaloids, hydrocarbons, etc. [2]. Of the alcohol hosts, monool, diol, and tetraol hosts have been well studied [2]. Recently, we prepared hexaol hosts such as **1**–**6**, and found that these show interesting inclusion behaviors for various guests. They include guest maximum in **1**–**6** ratio. In a special case of the inclusion with **1**, both CH_3CN as a polar guest and benzene as a nonpolar guest are included in 1:2:2 ratio [3].

Although **1** includes acetone (1:3), tetrahydrofuran (1:4), and cyclohexanone (1:5) in the ratio less than 1:6 as indicated, **1** includes DMF, DMSO, and γ-butyrolacetone in 1:6 ratio [4]. Chiral derivative [5] of **1** (**2**) also includes some guests in 1:6 ratio, however, its chiral recognition ability is low, although the chiral diol host (**7**) shows high chiral recognition ability for chiral guests [6]. The hexaol host which has naphthalene ring (**3**) also includes some guests in 1:6 ratio. For example, **3** includes dimethyl acetamide in 1:6 ratio through hydrogen-bond formation [7].

Interestingly, **1** includes both polar and nonpolar guests at once. For example, the inclusion complex of **1** with CH_3CN and benzene in 1:2:2 ratio was formed [3]. As we are aware, this is the first example of the inclusion of polar and nonpolar guests at the same time. X-ray analysis of these inclusion crystals shows that two CH_3CN molecules are binding to the hydroxyl group of **1**, but two benzene molecules are accommodating as a spacer in the cavities.

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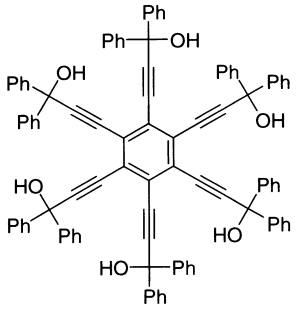

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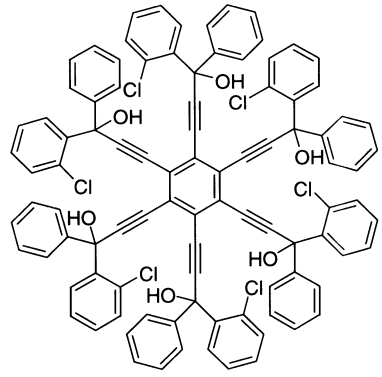

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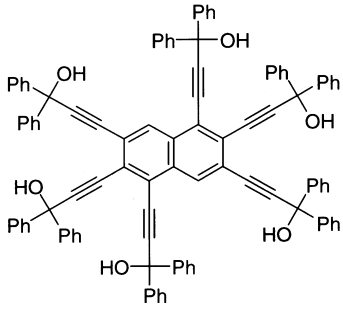

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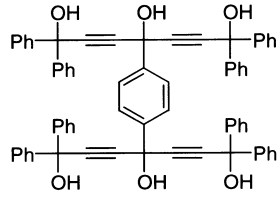

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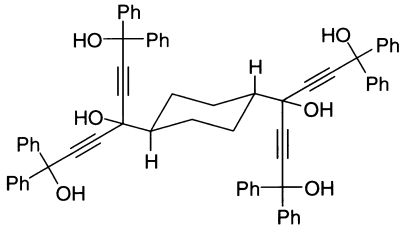

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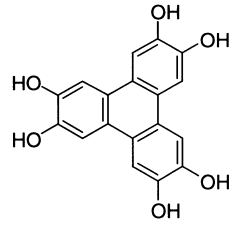

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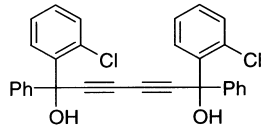

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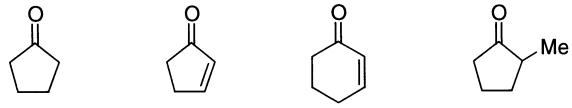
Similar hexaol hosts (**4**, **5**) also include various guests in maximum 1:6 ratio [8]. Aromatic hexaol host, hexahydroxytriphenylene (**6**), also shows interesting inclusion behaviors, although **6** includes most guests in 1:2 or 1:3 ratios but not any in 1:6 ratio (Table 1) [9]. As a special case, **6** includes cyclopentanone and water in 1:4:1 ratio. The interesting thing is, however, that achiral **6** of the planar structure forms chiral inclusion complexes with achiral guest molecules. For example, inclusion complexes of **6** with cyclopentanone (**8**), 2-cyclopentenone (**9**), and 2-cyclohexenone (**10**) are chiral and show CD absorption in Nujol mulls. X-ray analysis of these inclusion crystals shows that achiral molecules of **6** form a chiral helix. To the chiral helix, guest molecules are binding through hydrogen-bond formation. For example, in the 1:4 inclusion complex of **6** with **8**, **6** forms a chiral helix [9].



8 **9** **10** **11**

Table 1 Host-guest ratio of inclusion complexes of **6**.[a]

guest	host/guest[b]
n-PrOH	1:3
i-PrOH	1:2[c]
n-BuOH	1:3
Cyclopentanol	1:3
Cyclohexanol	1:2
Acetone	nc
Acetonylacetone	2:3
Cyclopentanone	1:3[c]
Cyclopentanone	1:4:H_2O
2-Cyclopentenone	1:3[c]
2-Methylcyclopentanone	1:3[c]
3-Methylcyclopentanone	1:3
2-Cyclohexenone	1:3[c]
Cyclohexanone	1:3
2-Methylcyclohexanone	1:3
3-Methylcyclohexanone	1:3
γ-Butyrolactone	1:3
THF	1:2
1,4-dioxane	1:2
DMF	1:2

[a] All melting points are unclear.

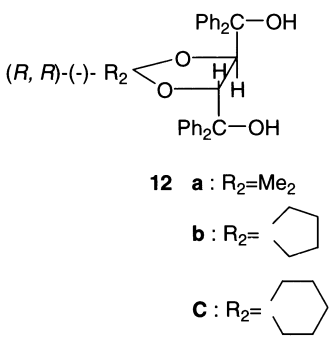
[b] The ratio was determined by ^{1}H-NMR or TG measurement.

[c] Chiral inclusion compound.

By using this phenomena, *rac*-2-methylcyclopentanone (**11**) was resolved by complexation with achiral **6**. Recrystallization of **6** from *rac*-2-methylcyclopentanone (**11**) gave their 1:3 inclusion complex crystal. Heating *in vacuo* of one piece of the crystal which shows a (+)-cotton effect in the region of 300 nm gave (+)-**11** of 34% ee ($[\alpha]_D$ +17.2 (C 0.06 MeOH)) by distillation. Heating *in vacuo* of the other piece of crystal which shows a (–)-cotton effect in the region of 300 nm gave (–)-**11** of 37% ee {$[\alpha]_D$ –18.5 (*c* 0.07, MeOH)} [9].

OPTICAL RESOLUTION BY INCLUSION COMPLEXATION WITH A CHIRAL HOST

The chiral hosts (**12b**) derived from tartaric acid are very useful for optical resolution of various *rac*-guest compounds by their mutual inclusion complexation. We now report optical resolution of hydrocarbons by inclusion complexation with **12b** [10].



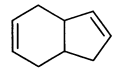
12 **a** : R_2=Me_2

b : R_2=

C : R_2=

13

a : R=3-Me
b : R=4-Me
c : R=4-CH=CH_2



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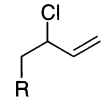

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a : R=H
b : R=Cl

For example, when a solution of *rac*-3-methylcyclohexene (**13a**) (0.58 g, 6.1 mmol) and **12b** (3 g, 6.1 mmol) in ether (15 ml) was kept at room temperature for 12 h, a 2:1 inclusion complex of **12b** and (–)-**13a** (2.5 g, 75% yield) was obtained as colorless prisms. The crystals were purified by two recrystallizations from ether to give the inclusion complex (2.4 g, 71% yield), which upon heating *in vacuo* afforded (–)-**13a** of 75% ee by distillation {0.19 g, 66% yield, $[\alpha]_D$ –66 (*c* 1.0, $CHCl_3$)} [10]. The enantiomeric excess of (–)-**13a** was determined by comparison of its $[\alpha]_D$ value with that reported. It is valuable to be able to separate enantiomers of hydrocarbon by inclusion complexation with simple chiral host compound such as **12b**. By inclusion complexation with (–)-**13a**, νOH of **12b** (3590 and 3400 cm^{-1}) were shifted to lower frequencies (3400 and 3230 cm^{-1}). Since cyclohexane does not form any inclusion complex with **12b**, hydrogen bonding between π-orbital of **13a** and the OH group of **12b** would be important for the inclusion complex formation. Dissociation energies of the 2:1 complex of **12b** and (–)-**13a** were determined by DSC measurement to be 45 kj mol^{-1}. This data shows that the stabilization energy of the complex is quite high. By the same inclusion complexation in a solvent followed by two recrystallizations of the inclusion complex, 4-methyl (**13b**) and 4-vinylcyclohexene (**13c**), bicyclo[4.3]nonane-2,5-diene (**14**), and 3-chloro (**15a**) and 3,4-dichloro-1-butene (**15b**) were also resolved [10] (Table 2). The optical purity of **13b** [11], **13c** [12], and **15a** [13] was determined by the comparison of their $[\alpha]_D$ value with that reported. However, the enantiomeric excess of **14** and **15b** was not determined.

The resolution by inclusion complexation in a water suspension medium is also applicable to hydrocarbons. For example, a suspension of powdered **12b** (3 g, 6.1 mmol) and *rac*-**13a** (0.58 g, 6.1 mmol) in water (20 ml) containing hexadecyltrimethylammonium bromide as a surfactant was stirred for 48 h at room temperature. The inclusion complex formed was filtered and dried to give complex crystal (2.87 g, 87% yield), which upon heating *in vacuo* gave (–)-**13a** of 13% ee (0.25 g, 86% yield). By the same procedure, **13b–c**, **14**, and **15a–b** were also resolved (Table 2) [10].

Table 2 Resolution of **13-15** by complexation with **12** through recrystallization from ether and water suspension methods.

		recrystallization method			water suspension method		
guest	product	yield (%)	$[\alpha]_D$[a]	ee (%)	yield (%)	$[\alpha]_D$[a]	ee (%)
13a	(-)-**13a**	66	-66	75	86	-11	13
13b	(+)-**13b**	55	+31	33	82	+3	3
13c	(-)-**13c**	73	-12	28	64	-3	8
14	(-)-**14**	90	-16	c	53	-2	c
15a	(-)-**15a**	48	-28	56	65	-2	4
15b	(+)-**15b**	42	+15	c	71	+11	c

[a] All $[\alpha]_D$ values of **12a** were measured in $CHCl_3$ at *c* 1.0, and those of **13b-c**, **14**, and **15a-b** were measured in MeOH at *c* 1.0.

[b] Enantiomeric excess of the enantiomer obtained by the inclusion complexation followed by two recrystallizations of the inclusion complex was shown.

[c] Enantiomeric excess was not determined.

The resolution method by fractional distillation in the presence of a chiral host was also found to be applicable to these hydrocarbons. For example, when a mixture of powdered **12b** (12 g, 24 mmol) and *rac*-**13a** (2.23 g, 24 mmol) was distilled at 40 °C/20 mmHg, (+)-**13a** of 9% ee was obtained by volatilization (1.16 g, 100% yield). Further heating of the residue at 120 °C/20 mmHg gave (–)-**13a** of 9% ee (1.16 g, 100% yield) by distillation. By mixing **12b** and *rac*-**13a**, inclusion complexation of **12b** and (–)-**13a** occurs, and the uncomplexed (+)-**13a** volatilizes at 40 °C *in vacuo* and the complex of (–)-**13a** with **12b** decomposes by heating at 120 °C and (–)-**13a** comes out by distillation. By the same distillation method, **13b** and **15a–b** were also resolved (Table 3). However, this method was not applicable to **13c** and **14** [10].

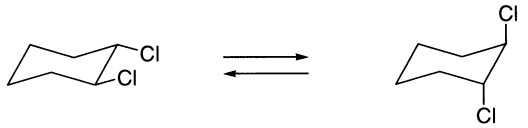
Table 3 Resolution of **13-15** by fractional distillation in the presence of **12**.

	uncomplexed enantiomer				uncomplexed enantiomer			
guest	product	$[\alpha]_D$[a]	yield (%)	ee (%)	product	$[\alpha]_D$[a]	yield (%)	ee (%)
13a	(-)-**13a**	+8	100	9	(-)-**12a**	-8	100	9
13b	(+)-**13b**	-3	100	3	(+)-**12b**	+3	100	3
13c	*rac*-**13c**	0	127	0	*rac*-**12c**	0	82	0
14	*rac*-**14**	0	5	0	*rac*-**13**	0	27	0
15a	(+)-**15a**	+2	105	4	(-)-**14a**	-2	73	4
15b	(-)-**15b**	-9	85	b	(+)-**14b**	+9	86	b

[a] All $[\alpha]_D$ values of **13a** were measured in $CHCl_3$ at *c* 1.0, and those of **13b-c**, **14**, and **15a-b** were measured in MeOH at *c* 1.0.

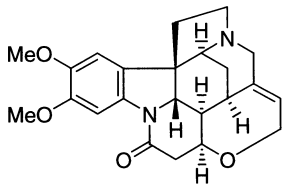
[b] Enantiomeric excess was not determined.

By IR spectroscopy, it has been established that *trans*-1,2-dichlorocyclohexane (**16**) exists mostly as an equatorial form (**16a**) [14]. However, **16** exists as an axial form (**16b**) in an inclusion complex with thiourea [15]. Nevertheless, **16** has been isolated neither in pure equatorial form (**16a**) nor pure optically active form. We prepared 1:2 inclusion complex of (–)-**16a** and **12b**, and determined the absolute configuration of the (–)-**16a** to be (*R*, *R*) by X-ray analysis [16].



16a **16b**

Alkaloid such as brucine (**17**) is also effective for resolution of guest compounds. For example, **17** was found to be effective for resolution of 2-azabicyclo[2.2.1]hept-5-en-3-one (**18**) which is useful synthon for the synthesis of (–)-carbovir (**19**) a chemotherapic agent for AIDS [17].



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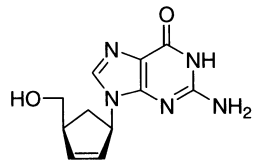

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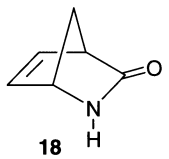

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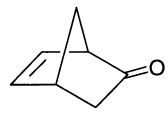

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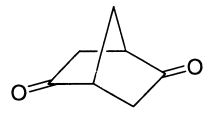

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When a solution of **17** (36 g, 91 mmol) and (±)-**18** (20 g, 183 mmol) in MeOH (50 ml) was kept at room temperature for 6 h, a 1:1 complex of **17** and (–)-**18** was obtained as colorless prisms (31 g) which upon distillation *in vacuo* gave (–)-**18** of 36% ee. Four recrystallizations of the crude complex from MeOH gave the almost pure complex (6.6 g, mp 173–175 ºC) which upon distillation *in vacuo* afforded (–)-**18** of 92% ee {1.3 g, 13%, $[\alpha]_D$ –513 (*c* 0.52, $CHCl_3$)}. Optical purity of (–)-**18** was determined by HPLC analysis [17].

Similar optical resolution of **20** by inclusion complexation with **17** was less efficient. For example, when a solution of **17** (1.8 g, 4.6 mmol) and (±)-**20** (1.0 g, 9.3 mmol) in MeOH (5 ml) was kept at room temperature for 6 h, a 1:1 complex of **17** and (+)-**20** was obtained as colorless prisms (1.22 g, mp 138–151 ºC) which upon distillation *in vacuo* gave (+)-**20** {0.20 g, 40%, $[\alpha]_D$ +274 (*c* 0.55, $CHCl_3$)} of 27% ee. However, the optical purity of (+)-**20** in the inclusion complex was not improved by recrystallization. In the case of bicyclo[2.2.1]heptane-2,5-dione (**21**), **17** could not recognize the chirality of **21** and formed a 1:1 complex with (±)-**21** as colorless prisms (mp 165–168 ºC) in 71% yield [17].

This result suggests that the NH group of **18** plays an important role in the chiral recognition through NH···N hydrogen bonding between NH of (–)-**18** and N atom of brucine (**17**) in the complex. The IR spectrum of the 1:1 complex of (–)-**18** and **17** showed a broad absorption for the νNH of (–)-**18** at lower frequencies, 3300–2700 cm^{-1}. In order to clarify the mechanism of this efficient chiral recognition, the X-ray crystal structure of the 1:1 inclusion complex of (–)-**18** and brucine (**17**) was analyzed [17]. The packing diagram shows that the guest molecules are located in channel-type cavities formed between the hosts, which extend approximately along the *c* axis of the crystal.

ONE-POT PREPARATION OF OPTICALLY ACTIVE COMPOUNDS BY A COMBINATION OF SYNTHESIS AND INCLUSION COMPLEXATION WITH A CHIRAL HOST IN A WATER SUSPENSION MEDIUM

After a *rac*-compound is prepared by carrying out chemical reaction in a water suspension medium, chiral host is added to the medium to give an inclusion complex with one enantiomer of the *rac*-product. From the inclusion complex, optically active compound is obtained. This one-pot method in a water suspension medium is a simple, economical, and clean procedure.

For example, when a suspension of acetophenone (**22a**) and $NaBH_4$ in water was stirred at room temperature for 2 h, *rac*-**23a** was produced. To the water suspension medium of *rac*-**23a** was added the optically active host **12a**, and the mixture was stirred for 3 h to give a 2:1 inclusion complex of **12a** with (–)-**22a**. The inclusion complex was filtered, dried, and distilled *in vacuo* to give (–)-**22a** of 95% ee in 85% yield. From the filtrate, (+)-**22a** of 77% ee was obtained in 70% yield (Table 4) [18].

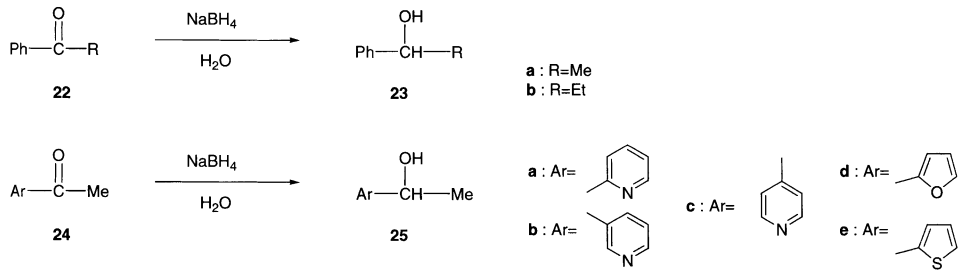

Table 4 One-pot preparation of chiral alcohols in a water suspension medium.

ketone	host	from complex			from filtrate		
		product	yield (%)	optical purity (% ee)	product	yield (%)	optical purity (% ee)
22a	**12a**	(-)-**23a**	85	95	(+)-**23a**	70	77
22b	**12a**	(-)-**23b**	96	62	(+)-**23b**	50	52
24a	**12b**	(-)-**25a**	44	99	(+)-**25a**	134	40
24a	**12c**	(-)-**25a**	92	88	(+)-**25a**	76	62
24b	**12a**	(+)-**25b**	88	>99	(-)-**25b**	86	73
24b	**12b**	(+)-**25b**	86	96	(-)-**25b**	82	66
24c	**12b**	(+)-**25c**	80	77	(-)-**25c**	82	36
24d	**12a**	(+)-**25d**	76	93	(+)-**25d**	96	50
24e	**12a**	(-)-**25e**	84	86	(+)-**25e**	61	43

By the same procedure, optically active alcohols (**23b**, **25a–e**) were obtained (Table 5). When an epoxidation of 2-cyclohexenones (**26**) and an oxidation of sulphides (**28**) in a water suspension media are combined with inclusion complexation with chiral host compounds, optically active epoxides (**27**) (Table 5) and sulfoxides (**29**) (Table 6) were obtained, respectively [18].

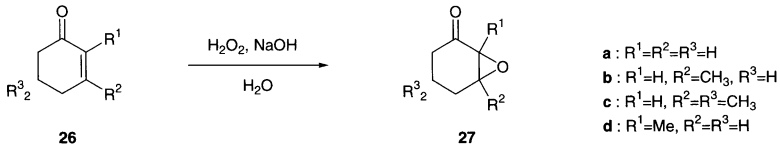

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Table 5 One-pot preparation of chiral epoxycyclohexanone in a water suspension medium.

26	host	from complex			from filtrate		
		product	yield (%)	optical purity (% ee)	product	yield (%)	optical purity (% ee)
26a	**12b**	(+)-**27a**	38	100	(-)-**27a**	78	51
26b	**12c**	(-)-**27b**	61	97	(+)-**27b**	99	48
26b	**12b**	(-)-**27b**	56	97	(+)-**27b**	79	34
26c	**7**	(+)-**27c**	57	100	(-)-**27c**	62	87
26d	**12b**	(-)-**27d**	63	63	(+)-**27d**	96	47

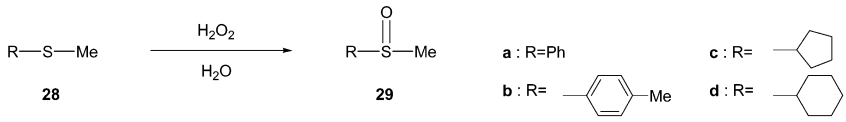

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Table 6 One-pot preparation of chiral sulfoxides in a water suspension medium.

28	host	from complex			from filtrate		
		product	yield (%)	optical purity (% ee)	product	yield (%)	optical purity (% ee)
28a	**12c**	(+)-**29a**	82	57	(-)-**29a**	73	54
28b	**12c**	(+)-**29b**	75	98	(-)-**29b**	89	78
28c	**12c**	(-)-**29c**	70	96	(+)-**29c**	80	55
28d	**12c**	(-)-**29d**	55	49	(+)-**29d**	100	31

ENANTIOSELECTIVE PHOTOREACTIONS IN INCLUSION CRYSTALS

When achiral guest molecules are arranged in a chiral form in their inclusion crystal with a chiral host compound, its chirality can be fixed by thermal and photochemical reactions to give optically active products [19].

Some enantioselective photocyclizations [20–29] and photodimerizations have been studied [30–36].

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