Some Enantioselective Photocyclization Reactions in Inclusion Crystals with Optically Active Host Compounds

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Photoirradiation of inclusion crystals of 2-[*N*-(2-propenyl)amino]cyclohex-2-enones, 3-oxo-2-cyclohexenecarboxamides, and 4-(3-butenyl)cyclohexa-2,5-dien-1-ones with the optically active host compound (*R,R*)-(−)-*trans*-4,5-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane or (*R,R*)-(−)-*trans*-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[5.4]decane in the solid state gave optically active 9-azatricyclo[5.2.1.$0^{1,6}$]decan-2-ones, 2-aza-1,5-dioxospiro[3.5]nonanes, and 1-carbomethoxytricyclo[4.3.1.$0^{7,10}$]dec-2-en-4-ones, respectively.

It has been reported that the photoreaction of the 2-[*N*-(2-propenyl)amino]cyclohex-2-enone derivatives **1**, 3-oxo-2-cyclohexenecarboxamides **7**, and 4-carbomethoxy-4-(3-butenyl)cyclohexa-2,5-dien-1-ones **12** in solution gives the racemic photocyclization products 9-azatricyclo[5.2.1.$0^{1,6}$]-decan-2-ones **2**,[1-3] 2-aza-1,5-dioxaspiro[3.5]nonanes **9**,[4] and 1-carbomethoxytricyclo[4.3.1.$0^{7,10}$]dec-2-en-4-ones **13**,[5] respectively. In order to synthesize the optically active photocyclization products (**2**, **9**, and **13**) selectively, we studied solid-state photoreactions of **1**, **7**, and **12** in their inclusion crystals with the optically active host compound such as (*R,R*)-(−)-*trans*-4,5-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane (**3a**) or (*R,R*)-(−)-*trans*-2,3-bis-(hydroxydiphenylmethyl)-1,4-dioxaspiro[5.4]decane (**3b**).[6,7]

Recrystallization of **3a** or **3b** and 2-[*N*-benzoyl-*N*-(2-propenyl)amino]cyclohex-2-enone (**1a**) from ether or toluene–hexane gave a 2:1 inclusion crystal of **3a** or **3b** with **1a**. Photoirradiation of a suspension of a powdered 2:1 inclusion crystal of **3a** with **1a** in water containing sodium alkylsulfate as a surfactant for 17 h under stirring gave (+)-**2a** in 64% yield, after purification by column chromatography on silica gel. However, an accurate $[\alpha]_D$ value of the (+)-**2a** was not determined because (+)-**2a** forms hydrate **4a** and hemiacetal **5a** in the presence of water and alcohol, respectively, and then (+)-**2a** shows mutarotations in the measurement of $[\alpha]_D$ value. Easy formation of a hydrate of *rac*-**2a** has been reported.[3] Since formation of the hydrate of **2** is relatively slower in dry CCl_4, the $[\alpha]_D$ values of **2** measured in that solvent are shown in Table I. Furthermore, optical purity of (+)-**2a** is not determined by ^1H NMR spectral measurement in the presence of a chiral shift reagent and by HPLC analysis on a chiral solid phase because the mutarotation occurs by the formation of the hydrate of hemiacetal during the measurement or analysis. Finally, the optical purity of the (+)-**2a** was determined to be 99% ee for its ethylene glycol acetal, 2,2-(ethylenedioxy)-9-benzoyl-9-azatricyclo[5.3.1.$0^{1,6}$]-decane ((−)-**6a**), by HPLC analysis on the chiral solid phase, Chiralcel OJ (Table II).

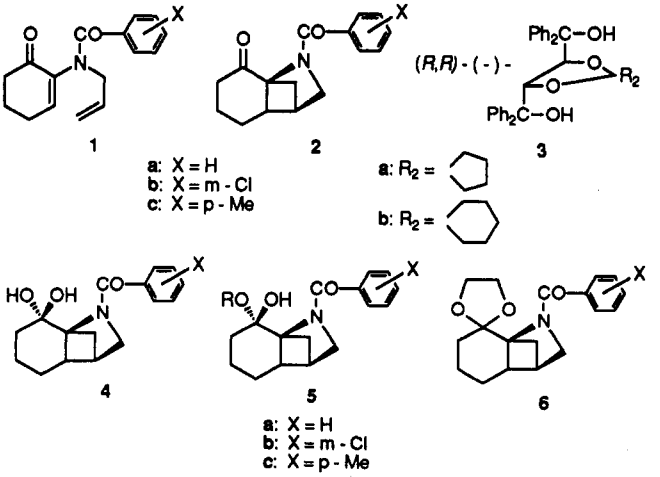
Table I. Photocyclization of 1 in a 2:1 Inclusion Compound with 3 in a Water Suspension

host–guest compd				photocyclizn product			
host	guest	mp (°C)	irradn time (h)	product	yield (%)	mp (°C)	$[\alpha]_D$ (deg) (*c* in CCl_4)[b]
3a	**1a**	118–119	17	(+)-**2a**	64	106–107	+70 (0.10)
3b	**1a**	139.5–142	15	(+)-**2a**	81	106–107	+90 (1.32)
3b	**1b**	nc[a]	36	(+)-**2b**	71	116.5–118	+77 (0.85)
3b	**1c**	nc[a]	43	(+)-**2c**	65	162–163	+61 (0.53)

[a] Not clear. [b] Since **2** shows mutarotation in the $[\alpha]_D$ measurement in protic and wet solvent by formation of acetal, hemiacetal, and hydrate, the $[\alpha]_D$ value was measured in dry CCl_4 in which the mutarotation occurs relatively slower.

Table II. Yield, Melting Point, and $[\alpha]_D$ Value of (−)-6

6	yield (%)	mp (°C)	$[\alpha]_D$ (deg) (*c* in CCl_4)	optical purity (% ee)
6a	72	108–110	−166 (2.53)	99
6b	76	143–145	−144 (1.38)	>99.9
6c	68	115–116	−151 (1.43)	99



Photoirradiation of a 2:1 inclusion crystal of **1a** with **3b** by the same procedure described above gave (+)-**2a** in 81% yield, from which (−)-**6a** of 99% ee was derived in 45% yield (Tables I and II). Since the host **3b** was more effective than **3a** for the enantioselective photocyclization of **1a**, the photocyclization of **1b** and **1c** was carried out by using the host **3b**, and (+)-**2b** and (+)-**2c** were obtained

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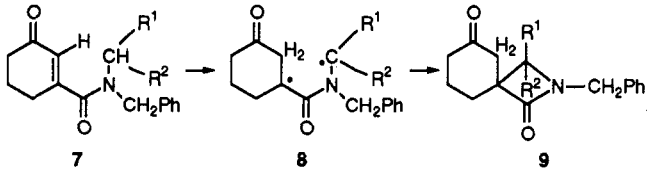
in 71 and 65% yields, respectively (Table I). The optical purity of (+)-**2b** and (+)-**2c** was determined to be >99.9 and 99% ee, respectively, by HPLC analysis of their acetal derivatives, (−)-**6b** and (−)-**6c** (Table II).

There is a possibility that the optical purity of the acetal (−)-**6** was raised up to 99–>99.9% ee by an optical resolution during the course of acetalization of the (+)-**2** and purification of the resulted (−)-**6**. Therefore, enantioselectivity of the photocyclization of **1** in the inclusion crystal with **3** cannot simply be determined to be 99–>99.9%. Nevertheless, it is very possible to be able to obtain (−)-**6** of 99–>99.9% ee from **1** by a combination of the two processes, the photoreaction of **1** in an inclusion crystal with **3** and the acetalization of the resulted optically active ketone (+)-**2**.

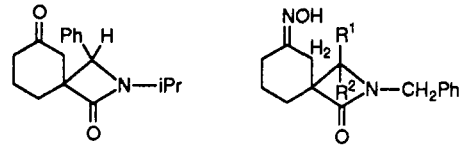
Some other highly enantioselective [2 + 2] photocyclization reactions of enone derivatives in an inclusion complex with optically active host compound have also been reported for tropolone alkyl ether,[8] pyridone,[9] cycloocta-2,4,6-trien-1-one,[10,11] cycloocta-2,4-dien-1-one,[10,11] and coumarin.[12]

By the same procedure applied to **1**, 2:1 inclusion crystals of **3** with **7** were prepared. Photoirradiation of a 2:1 inclusion crystal of *N*-benzyl-*N*-isopropyl-3-oxo-2-cyclohexanecarboxamide (**7d**) with **3b** in a water suspension for 4 h gave optically pure (−)-*N*-benzyl-2-aza-3,3-dimethyl-1,5-dioxospiro[3.5]nonane (**9d**) as an oil in 53% yield.



7 **8** **9**

a: $R^1 = R^2 = H$
b: $R^1 = H$; $R^2 = Me$
c: $R^1 = H$; $R^2 = Et$
d: $R^1 = R^2 = Me$
e: $R^1 = H$; $R^2 = Ph$
f: $R^1 = H$; $R^2 = nPr$



10 **11**

When a 2:1 inclusion crystal of **7d** with **3a** is irradiated, optically pure (−)-**9d** was obtained in 51% yield (Table III). It has been known that the photoirradiation of **7d** in MeCN for 1.5 h gives *rac*-*N*-isopropyl-2-aza-3-phenyl-1,5-dioxospiro[3.5]nonane (**10**) in 14% yield, although the stereochemistry on the benzyl carbon is not determined.[4] The reason why the isopropyl group but not the benzyl group of **7d** reacts with the cyclohexenone group in the inclusion crystal with **3** is not clear; however, it is believed that the isopropyl group attacks the cyclohexenone plane from one side selectively in the inclusion crystal. Furthermore, the stereochemistry on the chiral carbon at position 3 of **9b** and **9c** was also controlled in the photoreactions. The irradiation of a 2:1 inclusion crystal of **7c** with **3b** gave (−)-**9c** which upon treatment with hydroxylamine gave the optically pure (−)-oxime derivative (**11c**) of (−)-**9c** in 67% yield. Hydrolysis of **11c** with 10% H_2SO_4 gave optically pure (−)-**9c** (Table III). By the same method, **7b** gave the optically pure (−)-oxime derivative (**11b**) of (−)-**9c** (Table III).

Table III. Photocyclization of 7 in a 2:1 Inclusion Compound with 3 in a Water Suspension

host–guest compd			product						
			11			9			
host 3	guest 7	mp (°C)		yield (%)	mp (°C)		yield (%)	$[\alpha]_D$ (deg) (c $CHCl_3$)	optical purity (% ee)
a	**a**	165–167				**9a**	*a*		
b	**a**	193–195				**9a**	*a*		
a	**b**	154–157	**11b**	27	173–175	**9b**	18	−20 (0.6)	>99.9
b	**b**	188–190	**11b**	30		**9b**	20		
a	**c**	123–124	**11c**	60	168–170	**9c**	41	−22 (1.3)	>99.9
b	**c**	158–160	**11c**	67		**9c**	46		
a	**d**	107–109				**9d**	51	−31 (1.3)	>99.9
b	**d**	159–163				**9d**	53	−33 (1.6)	>99.9
b	**e**	133–140				**9e**	46	0	
a	**f**	95–97				**9f**	*a*		
b	**f**	not clear				**9f**	*a*		

[a] No reaction occurred.

It is difficult to evaluate the efficiency of the enantioselectivity on the carbon-3 of **9** from the data shown in Table III because the possibility of purification of **11** by an optical resolution during its preparation and isolation cannot be neglected. In any way, optically pure **9b** and **9c** can be prepared by the combination of photoirradiation of **7b** and **7c**, respectively, in their inclusion crystals with **3** and purification of the reaction product via oxime derivatives. Nevertheless, **7a** and **7f** were inert to the photoirradiation in 2:1 inclusion crystals with **3**, although **7a** gives *rac*-**9a** by an irradiation in MeCN.[4] In the case of **7e**, irradiation of a 2:1 inclusion crystal gave an optically inactive single product (**9e**) which consisted of two enantiomeric isomers on the spiro carbon, and the photoreaction of **7e** in MeCN gives the same product in 70% yield.[4] On the reaction in MeCN, stereochemistry on the benzylcarbon of **7e** is well controlled and only the stereoisomer which has the phenyl group on the azetidinone ring and the cyclohexanone carbonyl group in an anti-position is formed, although the stereochemistry on the spirocarbon is, of course, not controlled.[4]

In the inclusion crystal of **7a** and **7f** with **3**, the methyl of **7a** and the propyl group of **7f** might be located at the position apart from the cyclohexenone moiety which abstracts hydrogen from these alkyl groups, and then **7a** and **7f** in the inclusion crystal might be inert to the photoreaction. In the inclusion crystal of **7e** with **3b**, the methyl group is located at a close position by the cyclohexenone moiety, and the diradical intermediate (**8e**) is formed by a hydrogen abstraction. However, the stereochemistry on the spiro-carbon of **9e** was not controlled by the host **3b** during the cyclization of **8e** to **9e**. Two reasons are considerable for the nonstereoselective photocyclization of **7e**. One reason is that the generation of **8e** from **7e** in the inclusion crystal is followed by decomposition of the inclusion compound, and the cyclization of **8e** to **9e** occurs out of the inclusion crystalline lattice. Another reason is that the steric course of the cyclization of the initially formed **8e** to **9e** in the inclusion crystal with **3b** is simply not affected by the chirality of the host **3b**.

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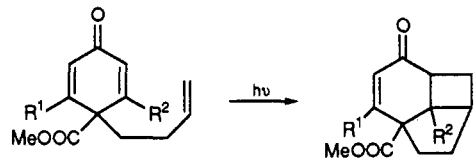
Photocyclization reaction of 4-cabomethoxy-4-(3-butenyl)cyclohexa-2,5-dien-1-one derivatives such as **12** to *rac*-1-cabomethoxytricyclo[4.3.1.0^{7,10}]dec-2-en-4-one (**13**) has been reported.[5] Enantioselective photocyclization of **12** to **13** was also achieved by irradiation of an inclusion crystal of **12** with **3** in the solid state. For example, reaction of



12 **13**

a: $R^1 = R^2 = OMe$
b: $R^1 = OMe$; $R^2 = H$

a powdered 2:1 inclusion crystal of 3,5-dimethoxy derivative **12a** with **3a** in a water suspension for 5 h gave (+)-**13b** of 73% ee in 50% yield. In the case of 3-methoxy derivative **12b**, enantioselective inclusion complexation occurred to give a 1:1 complex of optically pure (−)-**12b** with **3a**, and its irradiation in a water suspension gave optically pure (+)-**13b** in 57% yield. From the inclusion complex, optically pure (−)-**12b** was isolated. Although photoreaction in solution of the optically pure enantiomer of **12b**, which had been prepared by a classical and complex resolution method, to the optically pure **13b** has also been reported,[5] the inclusion complexation method is a much simpler and easier preparation method of the optically active **13b**.

Experimental Section

Preparation of inclusion compounds with the host **3a** and **3b** was carried out in the solvents ether and toluene–hexane (1:1), respectively, unless otherwise stated. Photoirradiations were carried out through a Pyrex filter by using a 100-W Hg lamp at room temperature (25 °C). IR spectra were measured with an IR spectrometer, Hitachi 260–10. All $[\alpha]_D$ values were measured with a digital polarimeter, JASCO DIP-140. Optical purities were determined by HPLC using hexane–2-propanol (9:1) solvent unless otherwise stated (flow rate: 1.0 mL/min) and a column (0.46 cm × 25 cm) containing the chiral solid phase, Chiralcel OJ or OD and Chiralpak AS which are commercially available from Daicel Chemical Industries Ltd., Himeji, Japan.

Preparation of 1. The following compounds were prepared by a known literature procedure.[3] **2-(*N*-benzoyl-*N*-allylamino)-cyclohex-2-enone (1a)** (IR (neat) ν_{max} 1690 and 1660 cm^{-1}); **2-(*N*-(*m*-chlorobenzoyl)-*N*-allylamino)cyclohex-2-enone (1b)** (IR (neat) ν_{max} 1690 and 1655 cm^{-1}); and **2-(*N*-(*p*-methylbenzoyl)-*N*-allylamino)cyclohex-2-enone (1c)** (IR (neat) ν_{max} 1690 and 1650 cm^{-1}). Since **1a–c** were obtained as an oily material, they were identified by IR and ^{1}H NMR spectra and elemental analysis of their inclusion compounds with the host **3**.

Preparation of Inclusion Compounds of 1 with 3. When a solution of **3a** (1 g, 2 mmol) and **1a** (0.27 g, 1 mmol) in ether (10 mL) was kept at room temperature for 2 h, a 2:1 inclusion compound of **3a** and **1a** was obtained as colorless needles (1.2 g, 93% yield, mp 118–119 °C): IR (Nujol) ν_{max} 3300, 1685, and 1615 cm^{-1}. Anal. Calcd for $C_{82}H_{81}NO_{10}$: C, 79.40; H, 6.58; N, 1.13. Found: C, 79.50; H, 6.63; N, 1.02. By the same procedure, the following inclusion compounds were prepared. A 2:1 inclusion compound of **3b** with **1a** (95% yield, mp 139.5–142 °C): IR (Nujol) ν_{max} 3300, 1690, and 1610 cm^{-1}. Anal. Calcd for $C_{84}H_{85}NO_{10}$: C, 79.53; H, 6.75; N, 1.10. Found: C, 79.42; H, 6.68; N, 1.05. A 2:1 inclusion compound of **3b** with **1b** (mp is not clear, 96% yield): IR (neat) ν_{max} 3330, 1690, and 1620 cm^{-1}. Anal. Calcd for $C_{84}H_{84}NO_{10}Cl$: C, 77.43; H, 6.50; N, 1.07. Found: C, 77.56; H, 6.69; N, 1.07. A 2:1 inclusion compound of **3b** with **1c** (mp is not clear, 95% yield): IR (Nujol) ν_{max} 3350, 1690, and 1615 cm^{-1}. Anal. Calcd for $C_{85}H_{87}NO_{10}$: C, 79.60; H, 6.84; N, 1.09. Found: C, 79.32, H, 7.10; N, 1.03.

Photocyclization of 1 to 2. A suspension of a powdered 2:1 inclusion compound of **3a** with **1a** (1.2 g, 0.97 mmol) in water (120 mL) containing sodium alkylsulfate (0.1 g) as a surfactant was irradiated under stirring for 17 h. The reaction product was filtered, dried, and chromatographed on silica gel using AcOEt–hexane (1:1) as an eluent to give (+)-**2a** (0.16 g, 0.62 mmol, 64% yield, mp 106–107 °C): IR (Nujol) ν_{max} 1720 and 1650 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.25; H, 6.79; N, 5.28. By the same procedure, 2:1 inclusion compounds of **3b** with **1a**, **3b** with **1b**, and **3b** with **1c** gave (+)-**2a**, (+)-**2b**, and (+)-**2c**, respectively, in the yields shown in Table I. IR and analytical data of **2b** and **2c** are as follows. **2b**: IR (Nujol) ν_{max} 1725 and 1660 cm^{-1}. Anal. Calcd for $C_{16}H_{16}NO_2Cl$: C, 66.32; H, 5.57; N, 4.83. Found: C, 66.47; H, 5.60; N, 4.69. **2c**: IR (Nujol) ν_{max} 1720 and 1640 cm^{-1}. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 76.01; H, 7.27; N, 5.01.

(−)-2,2-(Ethylenedioxy)-9-benzoyl-9-azatricyclo[5.2.1.0^{1,5}]-decane ((−)-6a) and Its Derivatives (−)-6b and (−)-6c. A solution of **2a** (0.38 g, 1.49 mmol) and ethylene glycol (0.23 g, 3.71 mmol) in benzene (20 mL) containing a catalytic amount of TsOH was refluxed for 12 h under continuous removing of water by azeotropic distillation with benzene. The benzene solution was washed with water and dried over $MgSO_4$. The residue left after evaporation of the solvent was chromatographed on silica gel using AcOEt–hexane (1:1) as an eluent to give the acetal (−)-**6a** of 99% ee as colorless needles (0.32 g, 1.07 mmol, 72% yield, mp 108–110 °C): IR (Nujol) ν_{max} 1650 cm^{-1}. Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.02; H, 7.22; N, 4.61. By the same procedure, the acetals (−)-**6b** of >99.9% ee and (−)-**6c** of 99% ee were obtained from the ketones (+)-**2b** and (+)-**2c**, respectively, in the yields shown in Table II. IR and analytical data are as follows. (−)-**6b**: IR (Nujol) ν_{max} 1670 and 1660 cm^{-1}. Anal. Calcd for $C_{18}H_{20}NO_3Cl$: C, 64.77; H, 6.04; N, 4.20. Found: C, 64.87, H, 6.14; N, 4.03. (−)-**6c**: IR (Nujol) ν_{max} 1660 and 1650 cm^{-1}. Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 73.02; H, 7.57; N, 4.26.

Preparation of 7. The following compounds were prepared by a modified condensation method of unsaturated oxoacid and amines using diethylphosphoryl cyanide (DEPC) instead of dicyclohexylcarbodiimide (DCC) in the reported method.[4] *N*-(benzyl-*N*-methyl-3-oxo-3-cyclohexenecarboxamide (**7a**) (IR (neat) ν_{max} 1680 and 1640 cm^{-1}); *N*-benzyl-*N*-ethyl-3-oxo-2-cyclohexenecarboxamide (**7b**) (IR (neat) ν_{max} 1680 and 1640 cm^{-1}); *N*-benzyl-*N*-*n*-propyl-3-oxo-2-cyclohexenecarboxamide (**7c**) (IR (neat) ν_{max} 1680 and 1640 cm^{-1}); *N*-benzyl-*N*-isopropyl-3-oxo-2-cyclohexenecarboxamide (**7d**) (IR (neat) ν_{max} 1680 and 1635 cm^{-1}); *N*-dibenzyl-3-oxo-2-cyclohexenecarboxamide (**7e**) (IR (Nujol) ν_{max} 1680 and 1640 cm^{-1}); and *N*-benzyl-*N*-*n*-butyl-3-oxo-2-cyclohexenecarboxamide (**7f**) (IR (neat) ν_{max} 1685 and 1640 cm^{-1}). Since **7a–7d,f** were obtained as oily materials, they were identified by their IR spectra and elemental analysis of their inclusion compounds with the host **3**.

Preparation of Inclusion Compounds of 7 with 3. When a solution of **3a** (1.34 g, 2.71 mmol) and **7a** (0.33 g, 1.36 mmol) in ether (50 mL) was kept at room temperature for 0.5 h, a 2:1 inclusion compound of **3a** and **7a** was obtained as colorless crystals (1.5 g, 90% yield, mp 165–167 °C): IR (Nujol) ν_{max} 3300, 1665, and 1615 cm^{-1}. Anal. Calcd for $C_{81}H_{81}NO_{10}$: C, 79.19; H, 6.65; N, 1.14. Found: C, 79.01; H, 6.84; N, 1.26. By the same procedure, the following inclusion compounds were prepared. A 2:1 inclusion compound of **3b** with **7a** (92% yield, mp 193–195 °C): IR (Nujol) ν_{max} 3300, 1665, and 1615 cm^{-1}. Anal. Calcd for $C_{83}H_{85}NO_{10}$: C, 79.33; H, 6.82; N, 1.11. Found: C, 79.34; H, 7.06; N, 1.23. A 2:1 inclusion compound of **3a** with **7b** (91% yield, mp 154–157 °C): IR (Nujol) ν_{max} 3300, 1670, and 1610 cm^{-1}. Anal. Calcd for $C_{82}H_{83}NO_{10}$: C, 79.26; H, 6.73; N, 1.13. Found: C, 79.30; H, 6.99; N, 1.09. A 2:1 inclusion compound of **3b** with **7b** (91% yield, mp 188–190 °C): IR (Nujol) ν_{max} 3300, 1670, and 1610 cm^{-1}. Anal. Calcd for $C_{84}H_{87}NO_{10}$: C, 79.40; H, 6.90; N, 1.10. Found: C, 79.46; H, 7.06: N, 1.17. A 2:1 inclusion compound of **3a** with **7c** (88% yield, mp 123–124 °C): IR (Nujol) ν_{max} 3300, 1670, and 1610 cm^{-1}. Anal. Calcd for $C_{83}H_{85}NO_{10}$: C, 79.33; H, 6.82; N, 1.11. Found: C, 79.14; H, 6.96; N, 1.31. A 2:1 inclusion compound of **3b** with **7c** (85% yield, mp 158–160 °C): IR (Nujol) ν_{max} 3300,

1670, and 1610 cm^{-1}. Anal. Calcd for $C_{85}H_{89}NO_{10}$: C, 79.47; H, 6.98; N, 1.09. Found: C, 79.32; H, 7.09; N, 1.26. A 2:1 inclusion compound of **3a** with **7d** (72% yield, mp 107–109 °C): IR (Nujol) ν_{max} 3350, 1670, and 1610 cm^{-1}. Anal. Calcd for $C_{83}H_{85}NO_{10}$: C, 79.33; H, 6.82; N, 1.11. Found: C, 79.53; H, 6.70; N, 1.26. A 2:1 inclusion compound of **3b** with **7d** (80% yield, mp 159–163 °C): IR (Nujol) ν_{max} 3350, 1670, and 1610 cm^{-1}. Anal. Calcd for $C_{85}H_{89}NO_{10}$: C, 79.47; H, 6.98; N, 1.09. Found: C, 79.24; H, 7.28; N, 0.95. A 2:1 inclusion compound of **3b** with **7e** (75% yield, mp 133–140 °C): IR (Nujol) ν_{max} 3300, 1670, and 1620 cm^{-1}. Anal. Calcd for $C_{89}H_{89}NO_{10}$: C, 80.21; H, 6.73; N, 1.05. Found: C, 79.92; H, 6.96; N, 1.10. A 2:1 inclusion compound of **3a** with **7f** (50% yield, mp 95–97 °C): IR (Nujol) ν_{max} 3300, 1670, and 1610 cm^{-1}. Anal. Calcd for $C_{84}H_{87}NO_{10}$: C, 79.40; H, 6.90; N, 1.10. Found: C, 79.39; H, 7.06; N, 0.94. A 2:1 inclusion compound of **3b** with **7f** (62% yield, mp is not clear): IR (Nujol) ν_{max} 3300, 1670, and 1610 cm^{-1}. Anal. Calcd for $C_{86}H_{91}NO_{10}$: C, 79.54; H, 7.06; N, 1.08. Found: C, 79.68; H, 7.19; N, 0.77.

Photocyclization of 7 to 9. A suspension of a powdered 2:1 inclusion compound of **3b** with **7b** (6.72 g, 5.29 mmol) in water (120 mL) containing sodium alkylsulfate (0.1 g) as a surfactant was irradiated under stirring for 4 h. The reaction mixture was filtered, dried, and chromatographed on silica gel using AcOEt–hexane (1:2) as an eluent to give crude (–)-**9b** (1.18 g, 87% yield). Treatment of the crude (–)-**9b** (1.18 g) with NH_2OH·HCl (0.32 g) and AcONa (0.66 g) in 50% aqueous EtOH (20 mL) gave the oxime **11b** as colorless prisms (0.43 g, 34% yield, mp 173–175 °C): IR (Nujol) ν_{max} 3340 and 1730 cm^{-1}. Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.49; H, 7.58; N, 10.55. The overall yield of **11b** from the 2:1 inclusion compound of **3b** with **7b** was 30%. After a mixture of **11b** (0.43 g), 10% H_2SO_4 (10 mL), and toluene (10 mL) was heated under reflux for 6 h, the toluene layer was separated, washed with water, and dried over $MgSO_4$. The toluene solution was evaporated, and the residue was chromatographed on silica gel using AcOEt–hexane (1:2) as an eluent to give (–)-**9b** of >99.9% ee (0.27 g, 67% yield, $[\alpha]_D$ –20° (*c* 0.6, $CHCl_3$)): IR (neat) ν_{max} 1740 cm^{-1}. The overall yield of (–)-**9b** from the 2:1 inclusion compound of **3b** with **7b** was 20%. The optical purity of (–)-**9b** was determined by HPLC on the chiral solid phase, Chiralcel OJ. By the same method, (–)-**11b** was obtained from a 2:1 inclusion compound of **3a** with **7b** in 27% yield. Hydrolysis of the **11b** gave (–)-**9b** of >99.9% ee in 18% overall yield from the inclusion compound. By the same procedure, a 2:1 inclusion compound of **3b** with **7c** gave **11c** as colorless needles (67% yield from the inclusion compound, mp 168–170 °C): IR (Nujol) ν_{max} 3300 and 1735 cm^{-1}. Anal. Calcd for $C_{17}H_{22}N_2O_2$: C, 71.30; H, 7.95; N, 9.78. Found: C, 71.53; H, 7.95; N, 9.60. Hydrolysis of **11c** gave (–)-**9c** of >99.9% ee (46% yield from the inclusion compound, $[\alpha]_D$ –22° (*c* 1.3, $CHCl_3$)). From the 2:1 inclusion compound of **3a** with **7c** were obtained **11c** and **9c** in 60% and 41% overall yields, respectively. Similar photoirradiation of a 2:1 inclusion compound of **3b** with **7d** followed by similar workup as above gave (–)-**7d** of >99.9% ee as an oil (53% yield, $[\alpha]_D$ –33° (*c* 1.6, $CHCl_3$)): IR (neat) ν_{max} 1730 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.46; H, 7.99; N, 5.03. From a 2:1 inclusion compound of **3a** with **7d**, (–)-**9d** of >99.9% ee was obtained in 51% yield $[\alpha]_D$ –31° (*c* 1.3, $CHCl_3$)). The optical purity of **9c** and **9d** was also determined by HPLC on the chiral solid phase, Chiralcel OJ. By the same procedure, a 2:1 inclusion compound of **3b** with **7e** gave optically inactive **9e** in 46% yield as colorless needles (mp 155–159 °C): IR (Nujol) ν_{max} 1750 and 1720 cm^{-1}. Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 79.02; H, 6.75; N, 4.18. However, 2:1 inclusion compounds of **3a** or **3b** with **7a** and **7f** are inert to the photoirradiation, and inclusion compounds were recovered unchanged.

Preparation of Inclusion Compounds of 12 with 3 and Optical Resolution of 12b. When a solution of **3a** (0.47 g, 0.95 mmol) and **12a** (0.13 g, 0.49 mmol) in ether–hexane (1:1, 10 mL) was kept at room temperature for 10 h, a 2:1 inclusion compound of **3a** with **12a** was obtained as colorless needles (0.36, g, 60% yield, mp not clear): IR (Nujol) ν_{max} 3240, 1730, 1655, 1610, and 1600 cm^{-1}. Anal. Calcd for $C_{80}H_{82}O_{13}$: C, 76.78; H, 6.60. Found: C, 77.00; H, 6.59. When a solution of **3a** (1.4 g, 2.9 mmol) and **12b** (1.4 g, 5.9 mmol) in ether–hexane (1:1, 50 mL) was kept at room temperature for 10 h, a 1:1 inclusion compound of **3a** with (–)-**12b** was obtained as colorless prisms (1.4 g, 74% yield). Optical purity of the (–)-**12b** in the inclusion compound was found to be 66.4% ee by HPLC analysis on the chiral solid-phase Chiralcel OD. Three recrystallizations of the inclusion compound from ether–hexane (1:1) gave pure inclusion compound (0.95 g, 46% yield, mp 91–95 °C): IR (Nujol) ν_{max} 3270, 1760, 1735, 1655, and 1595 cm^{-1}. Anal. Calcd for $C_{46}H_{47}O_8$: C, 75.91; H, 6.51. Found: C, 75.88; H, 6.62. Chromatography of the pure inclusion compound on silica gel using AcOEt–toluene (1:9) as an eluent gave (–)-**12b** of >99.9% ee in quantitative yield ($[\alpha]_D$ –76.0° (*c* 0.325, $CHCl_3$) (lit.[5] $[\alpha]_D$ –75.3° (*c* 0.17, $CHCl_3$)).

However, neither **12a** nor **12b** formed an inclusion compound with the host **3b**.

Photocyclization of 12 to 13. A suspension of powdered 2:1 inclusion compound of **3a** with **12a** (0.36 g) in water (100 mL) containing sodium alkylsulfate (0.1 g) as a surfactant was irradiated under stirring for 5 h. The reaction mixture was filtered, dried, and chromatographed on silica gel using AcOEt–hexane (1:1) as an eluent gave to give (+)-**13a** of 73% ee (0.04 g, 50% yield, $[\alpha]_D$ +5.7°, mp 110–113 °C (lit.[5] mp for *rac*-**13a** 140–141 °C)). The structure of **13a** was determined by comparison of its IR and ^1H NMR spectra with those reported.[5] The optical purity of the (+)-**13a** was determined by HPLC on the chiral solid phase, Chiralcel OJ. By the same photoirradiation procedure, a 1:1 inclusion compound of **3a** with **12b** of >99.9% ee gave (+)-**13b** of >99.9% ee in 57% yield ($[\alpha]_D$ +45° (*c* 0.70, MeOH), +36.4° (*c* 0.686, $CHCl_3$) (lit.[5] $[\alpha]_D$ +30.2° (*c*, 0.625, $CHCl_3$), mp 110–111 °C (lit.[5] mp for *rac*-**13b** 76–78 °C)). The optical purity of (+)-**13b** was determined by HPLC on the chiral solid phase, Chiralpak As, using hexane–EtOH (95:5) as solvent.

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Supplementary Material Available: IR spectral data for inclusion compounds of **3a** and **3b** with **7a–f** shown in Table III, inclusion compounds of **3a** with **12a** and **12b**, and photocyclization products **9b–e** and their oxime derivatives **11b** and **11c** and ^1H NMR spectral data measured with a JEOL JNM-PMX 60 spectrometer in $CDCl_3$ for inclusion compounds of **3a** and **3b** with **7a–f** shown in Table III, photocyclization products **9b–e** and their oxime derivatives **11b** and **11c**, and inclusion compounds of **3a** with **12a** and **12b** (38 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.