# Enantioselective Photocyclization of *N*-Alkylfuran-2-carboxyanilides to *trans*-Dihydrofuran Derivatives in Inclusion Crystals with Optically Active Host Compounds Derived from Tartaric Acid

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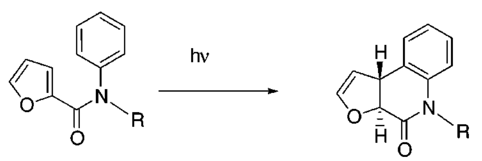
*Received October 19, 1998*

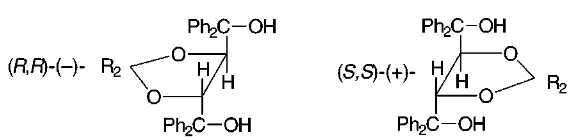
The steric course of the photocyclization reaction of the title achiral compounds (**1**) to optically active *trans*-dihydrofuran derivatives (**2**) was controlled by carrying out the reaction in inclusion crystals (**4**) with optically active hosts (**3**) derived from tartaric acid. The mechanism of the enantioselective reaction of **1** in **4** was studied by X-ray structural analysis of **4**. In some cases, the steric course of the photoreaction was different depending on whether **4** was prepared by recrystallization or by mixing of **1** and **3**.

Although the very useful synthetic route to *trans*-dihydrofuran derivatives (**2**) by photoreaction of the title carboamides (**1**) in MeOH has been established, the reaction gives *rac*-**2** together with some other byproducts.[1] To control the reaction to produce optically active **2** rather than both enantiomers, the photoreaction of **1** was carried out in an inclusion crystal with the optically active host compounds (**3**)[2] derived from tartaric acid.[3]




**1** **2**

**a**: R=H
**b**: R=Me
**c**: R=Et
**d**: R=iPr
**e**: R=CH$_2$CH=CH$_2$
**f**: R=CH$_2$Ph




**3** **5**

**a**: R$_2$=Me$_2$
**b**: R$_2$= -(CH$_2$)$_4$-
**c**: R$_2$= -(CH$_2$)$_5$-

Although **1a** did not form an inclusion crystal with **3a**−**c**, **1b**−**f** formed inclusion crystals **4** in the ratios indicated in Table 1. Irradiation of these powdered inclusion crystals **4** in a water suspension gave optically active **2b**−**f** in the chemical and optical yields summarized in Table 2.

**Table 1. Inclusion Compounds 4 of 3 and 1 Prepared by Recrystallization**

| host **3** | guest **1** | inclusion compd **4** | host:guest | mp (°C) |
|---|---|---|---|---|
| **3a** | **1a** | *a* | | |
| **3b** | **1a** | *a* | | |
| **3c** | **1a** | *a* | | |
| **3a** | **1b** | *a* | | |
| **3b** | **1b** | **4bb** | 1:1 | 122−123 |
| **3c** | **1b** | **4cb** | 1:1 | 149−151 |
| **3a** | **1c** | *a* | | |
| **3b** | **1c** | *a* | | |
| **3c** | **1c** | **4cc** | 2:1 | 117−124 |
| **3a** | **1d** | **4ad** | 1:1 | 130−133 |
| **3b** | **1d** | **4bd** | 1:1 | 137−139 |
| **3c** | **1d** | **4cd** | 1:1 | 126−133 |
| **3a** | **1e** | **4ae** | 1:1 | 130−132 |
| **3b** | **1e** | **4be(1:1)** | 1:1 | 100−101 |
| **3b** | **1e** | **4be(2:1)** | 2:1 | 79−82 |
| **3c** | **1e** | **4ce(2:1)** | 2:1 | 112−115 |
| **3a** | **1f** | *a* | | |
| **3b** | **1f** | *a* | | |
| **3c** | **1f** | **4cf** | 1:1 | 127−131 |

[a] Inclusion compound was not formed.

In the case of **1e**, two kinds of inclusion compounds with the host **3b**, **4be(1:1)** and **4be(2:1)**, were formed with the different host:guest ratios indicated (Table 1). Interestingly, photolysis of **4be(1:1)** and **4be(2:1)** gave (−)-**3e** and (+)-**3e**, respectively (Table 2). This is the first example of the formation of different enantiomers from a prochiral guest included by the same host in different ratios. To clarify the reasons, the crystal structures of **4be(1:1)** and **4be(2:1)** were studied by X-ray analysis. It was found that **1e** was arranged in a chiral form in **4be(1:1)**. The structure of the guest molecule **1e** is shown in Figure 1. C38 and N lie almost on the mean plane of the furan ring, and the distances between these atoms and the plane are less than 0.06 Å. O6 and C39 lie apart

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(1) Bates, R. B.; Kane, V. V.; Martin, A. R.; Mujumdar, R. B.; Ortega, R.; Hatanaka, Y.; San-nohe, K.; Kanaoka, Y. *J. Org. Chem.* **1987**, *52*, 3178.
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(3) A preliminary report on the present work has appeared: Toda, F.; Miyamoto, H.; Kanemoto, K. *J. Org. Chem.* **1996**, *61*, 6490.

10.1021/jo982099m CCC: $18.00 
Published on Web 02/23/1999

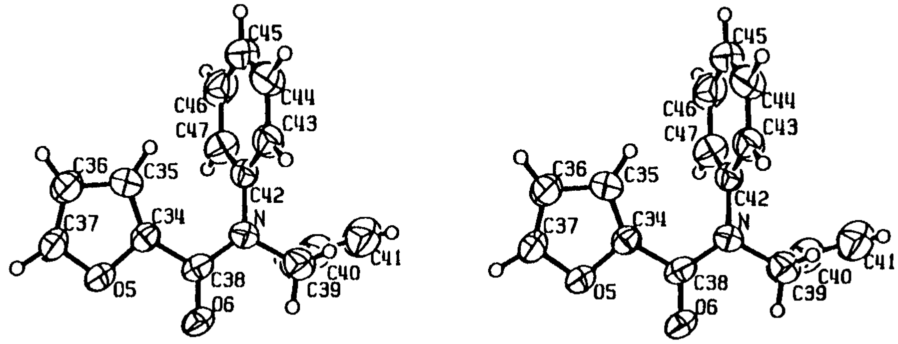



**Figure 1.** ORTEP stereodrawing of the crystal structure of guest molecule **1e** in **4be(1:1)**.

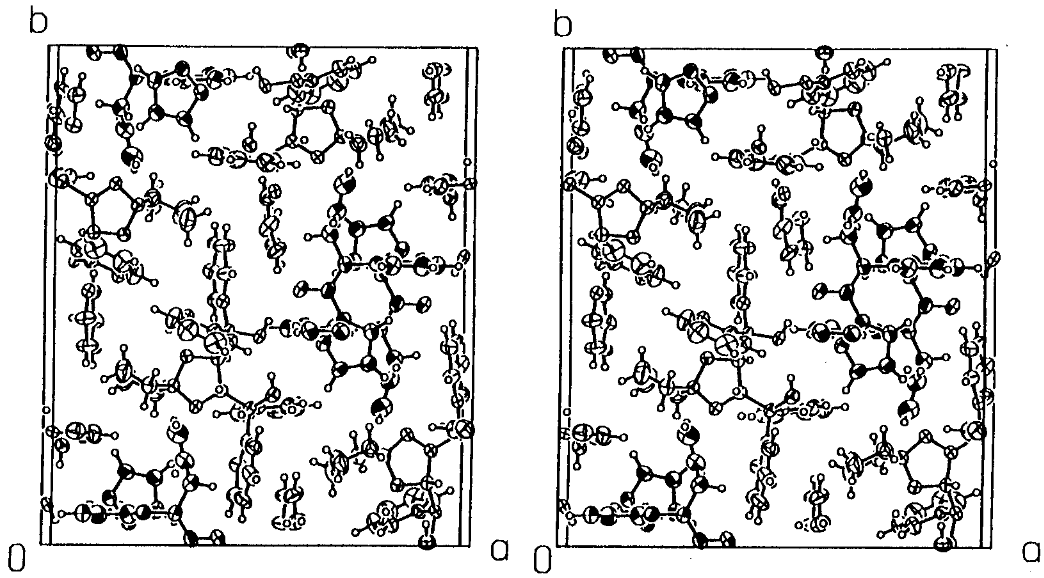



**Figure 2.** ORTEP stereodrawing of the crystal structure of **4be(1:1)** projected onto the crystallographic *ab* plane.

**Table 2. Photoreaction of 4 Prepared by Recrystallization**

| inclusion compds | irradiation time (h) | product 2 | yield (%)[b] | optical purity (% ee) |
|---|---|---|---|---|
| **4bb** | 40 | (−)-**2b** | 25 | 8 |
| **4cb** | *a* | | | |
| **4cc** | 120 | (+)-**2c** | 41 | 99 |
| **4ad** | *a* | | | |
| **4bd** | *a* | | | |
| **4cd** | 143 | (+)-**2d** | 16 | 52 |
| **4ae** | 96 | (+)-**2e** | 20 | 93 |
| **4be(1:1)** | 77 | (−)-**2e** | 50 | 96 |
| **4be(2:1)** | 48 | (+)-**2e** | 86 | 98 |
| **4ce(1:1)** | 50 | (+)-**2e** | 77 | 98 |
| **4cf** | 120 | (−)-**2f** | 72 | 98 |

[a] No reaction occurred. [b] Other product was not determined.

from the plane to the C43 side about 0.18 Å, whereas C42 is apart on the opposite side about 0.2 Å. The interatomic bond angles are C38−N−C39 = 119.7(3), C39−N−C42 = 116.4(3), and C42−N−C38 = 123.9(3) deg, respectively. The angle between the normals to the mean planes of the furan and phenyl groups is 82.3 deg. This slight inclination from the rectangular is reflected in the difference between the interatomic distances of C35−C43 = 3.405(6) and C35−C47 = 3.260(7) Å, respectively. The crystal structure projected onto the crystallographic *ab* plane is shown in Figure 2. No hydrogen bond was seen. During the process of the solid-state photoreaction, C35 becomes bonded to C43 or C47. If C35 and C43 are involved, the (*R*,*S*) form of **2e** is produced. On the other hand, the (*S*,*R*) form is created by the C35 and C47 connection. According to the reaction mechanism reported previously[1] and the structure determined in this study, the photoreaction is thought to be initiated by the rotation of the phenyl group around the N−C42 bond. Therefore, the environment in the vicinity of the phenyl group was examined precisely. The structure around the phenyl group is shown stereographically in Figure 3, which is the projection in the direction from C45 to C42 with the horizontal axis along C43−C47. If the phenyl group rotates to make a C35−C43 bond, H atoms bonded to C25 and C30 hinder the rotation. On the other hand, if the phenyl group rotates to the opposite direction to make a C35−C47 bond, although there is a slight interference from the H atom bonded to C10, there is enough space in the upper right region in Figure 3. So it seems easier for the phenyl group to rotate this way than the former. Furthermore, the initial distance of C35−C47 is shorter than that of C35−C43 by 0.145 Å. It can be concluded that **1e** is arranged in a chiral form in **4be-(1:1)** to produce the (*S*,*R*)-(−) form by the [4 + 2] conrotatory photocyclization reaction between the furan and phenyl rings. Once the reaction is complete on the center molecule in Figure 3, the reaction of the left molecule is accelerated by the vacancy of C43 of the center molecule, and C43 of the right molecule is pushed by the steric repulsion, which promotes the further

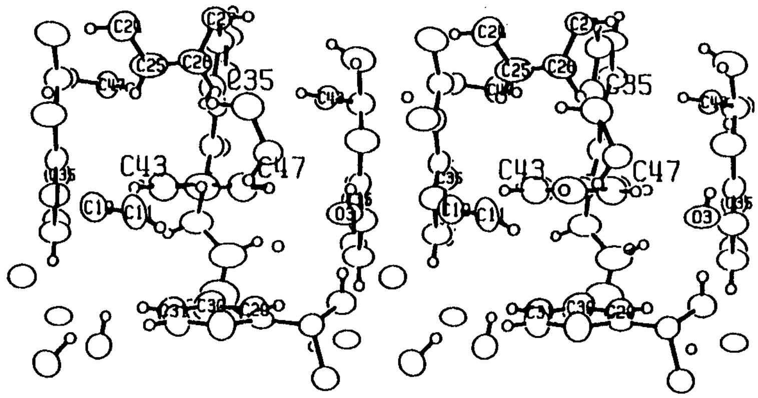



**Figure 3.** ORTEP stereodrawing of the crystal structure around the phenyl group in **4be(1:1)**.

reaction. Unfortunately, however, the molecular and crystal structure of **4be(2:1)** was not studied, because no suitable crystal for analysis was obtained.

One other interesting finding in this study is that the complexation between **3** and **1** gave different inclusion compounds depending on whether the inclusion experiment is carried out by recrystallization from solvent or by mixing in the solid state. Finally, photolysis of these different inclusion compounds gave different photoreaction products.

Recrystallization of **1a** and the same molar amount of **3b** from ether gave a mixture of the two inclusion crystals **4be(1:1)** and **4be(2:1)** as colorless prisms and needles, respectively. These were separated mechanically. When a piece of **4be(1:1)** crystal is added as a seed crystal during the inclusion complexation of **1a** and the same molar amount of **3b**, **4be(1:1)** was obtained in a large quantity. Contrarily, when a piece of **4be(2:1)** crystal is added as a seed crystal during the inclusion complexation of **1a** and two molar amounts of **3b**, **4be(2:1)** was obtained in a large quantity.

Photolysis in a water suspension of **4be(1:1)** and **4be-(2:1)** gave (−)- and (+)-**2e**, respectively, in the chemical and optical yields indicated in Table 2. Chiral arrangement of the prochiral **1e** in **4be(1:1)** was clarified by measurement of CD spectra in the solid state.[3,4] A 1:1 inclusion compound (**6be(1:1)**) prepared from the (*S*,*R*)-(−) enantiomer of **3b** (**5b**) with **1e** showed the mirror imaged CD spectra (Figure 4). The molecular and crystal structure of **4be(1:1)** were studied by X-ray analysis (Figures 1−3). The data suggest that the [4 + 2] conrotatory photocyclization of **4be(1:1)** should give (*S*,*R*)-(−)-**2e**. Unfortunately, however, absolute configuration of the (*S*,*R*)-(−)-**2e** was not confirmed by X-ray analysis, because no suitable crystal for analysis was obtained. Contrarily, photolysis of **4be(2:1)** gave (+)-**2e**. In **4be-(2:1)**, **1e** molecules are probably arranged in the form enantiomerically opposite to **1e** in **4be(1:1)**, and photocyclization of **1e** in **4be(2:1)** should produce (*R*,*S*)-(+)-**2e**. However, the structure of **4be(2:1)** and (+)-**2e** was again not analyzed, because no suitable crystal for analysis was obtained. In the CD spectra in Nujol mull, **4be(2:1)** and **6be(2:1)** prepared from **5b** and **1e** showed mirror imaged absorptions (Figure 5). Similarly, photolysis of **4cc**, **4cd**, **4ce**, and **4cf** gave optically active photocyclization products of high optical purity in good yield (Table 2). It is clear that the photoreaction of **1** in inclusion crystals with **3** or **5** is useful for the preparation of optically active dihydrofuran derivatives **2**.

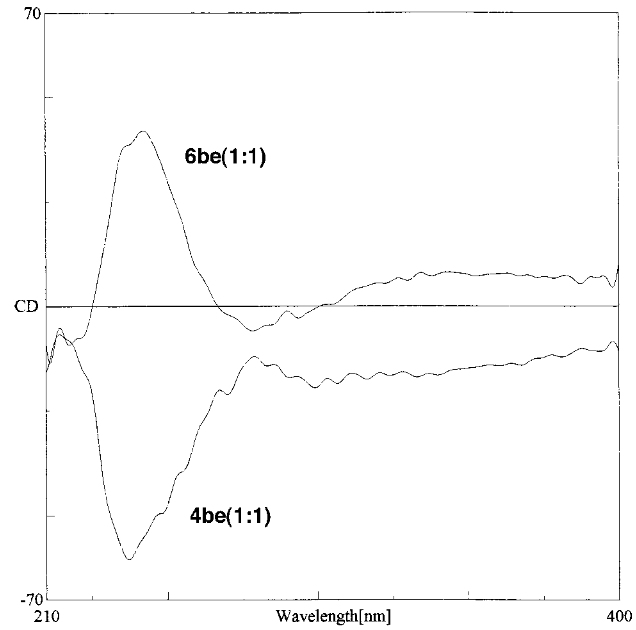



**Figure 4.** CD spectra of **4be(1:1)** and **6be(1:1)** in Nujol mull.

Inclusion complexation of **1** with **3** occurs also by mixing these in the solid state. For example, mixing powdered **3a** and **1e**, using an agate mortar and pestle or a planetary micro mill for 2 h, gave their 1:1 complex **4ae**, which upon irradiation produced (+)-**2e** of high optical purity (Table 3). The data are comparable to those of the photoreaction of **4ae** prepared by recrystallization from solvent (Table 3). Interestingly, however, both the 1:1 and 2:1 inclusion compounds **4be(1:1)** and **4be(2:1)** prepared by mixing of powdered **3b** and **1e** in 1:1 and 2:1 ratios, respectively, gave the same product (−)-**2e** upon irradiation, although the **4be(1:1)** and **4be(2:1)** prepared by recrystallization gave the different products (−)- and (+)-**2e**, respectively (Table 2). In the case of the inclusion complexation between **3c** and **1e**, the two inclusion compounds **4ce(1:1)** and **4ce(2:1)** were formed by mixing of **3c** and **1e** in 1:1 and 2:1 ratios, respectively. Irradiation of **4ce(1:1)** and **4ce(2:1)** gave the same product (−)-**2e** (Table 3). However, recrystallization of **3c** and **1e** from toluene gave only **4ce(2:1)**, and its photoreaction gave (+)-**2e** but not (−)-**2e** (Table 2). In the CD spectral measurement, **4ce(2:1)** and **6ce(2:1)**

(4) Toda, F.; Miyamoto, H.; Kikuchi, S.; Kuroda, R.; Nagami, F. *J. Am. Chem. Soc.* **1996**, *118*, 11315.

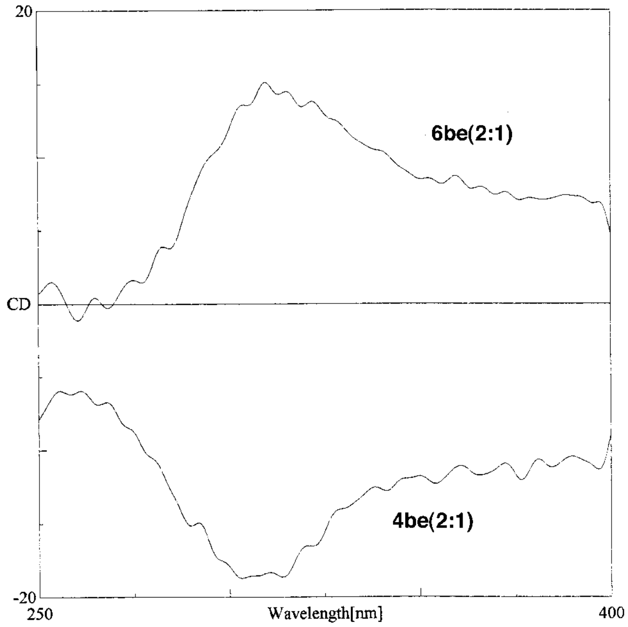



**Figure 5.** CD spectra of **4be(2:1)** and **6be(2:1)** in Nujol mull.

**Table 3. Photocyclization of 1e in the Inclusion Compounds with 3 Prepared by Mixing**[a]

| inclusion compd | irradiation time (h) | **2e** (% yield,[b] % ee) |
|---|---|---|
| **4ae** | 89 | (+)-**2e** (14, 98) |
| **4be(1:1)** | 75 | (−)-**2e** (10, 98) |
| **4be(2:1)** | 82 | (−)-**2e** (16, 97) |
| **4ce(1:1)** | 40 | (−)-**2e** (16, 49) |
| **4ce(2:1)** | 90 | (−)-**2e** (11, 54) |

[a] Liquid paraffin added to the solid state. [b] Other product was not determined.

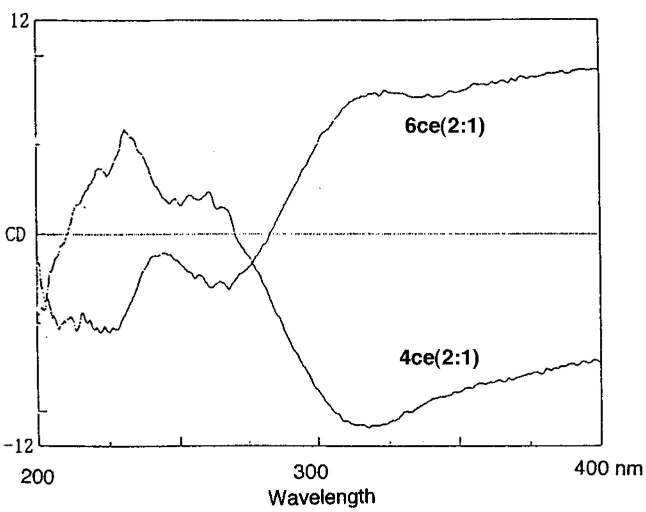



**Figure 6.** CD spectra of **4ce(2:1)** and **6ce(2:1)** in Nujol mull.

prepared by recrystallization of **5c** and **1e** in 2:1 ratio showed mirror imaged absorptions (Figure 6). Similarly, **4ce(1:1)** and **6ce(1:1)** prepared by mixing of **6c** and **1e** in 1:1 ratio showed mirror imaged CD spectral absorptions (Figure 7). Another example of the formation of different inclusion compounds, depending on experimental conditions, has been reported. For example, recrystallization from solvent and mixing in the solid state of **3c** and *N*,*N*-dimethylphenylglyoxamide gave different 1:1 inclusion compounds that gave (+)- and (−)-$\beta$-lactam derivatives, respectively, by photolysis.[5] In this case, however, the inclusion complexation of **1e** with **3** is seriously affected by the experimental conditions. The reason for the difference is not clear, although this is one of the most important keys to resolving molecular motion in the solid state.

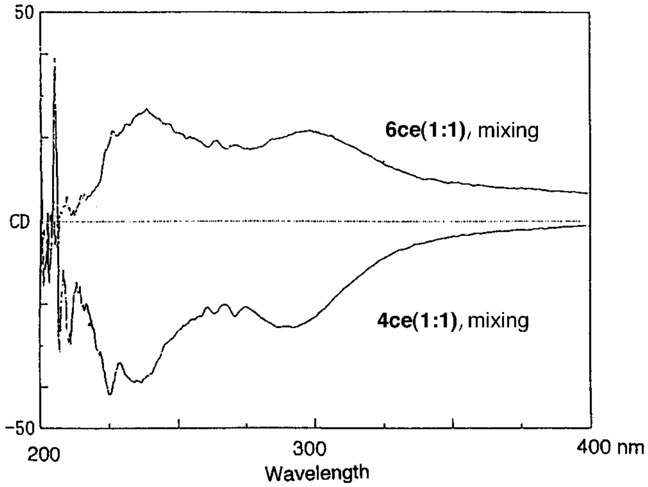



**Figure 7.** CD spectra of **4ce(1:1)** and **6ce(1:1)** prepared by mixing in Nujol.

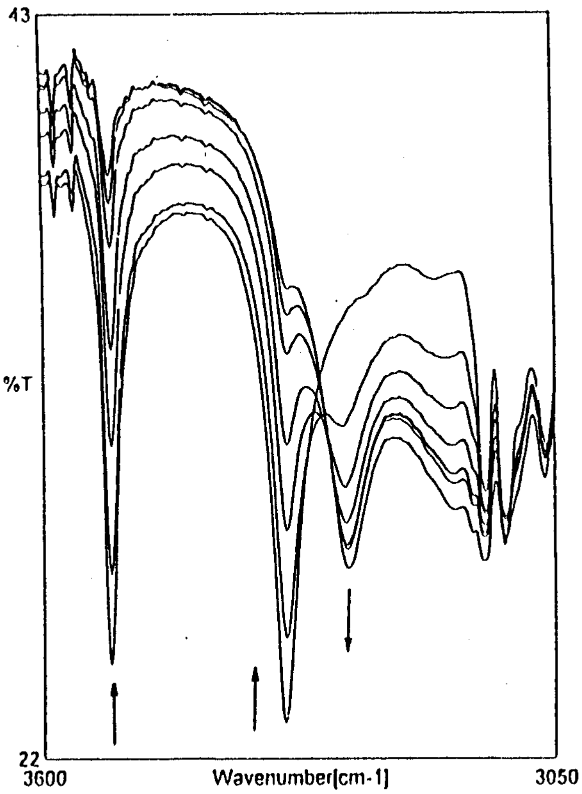
Inclusion complexation of **1e** with **3c** in the solid state was followed by successive measurement of IR and CD spectra as Nujol mulls. In the IR spectral measurement, OH absorptions of **3c** at 3529 and 3340 cm$^{-1}$ decreased and a new one at 3275 cm$^{-1}$ appeared. In addition, the C═O absorption of **1e** at 1634 cm$^{-1}$ decreased, and a new one at 1637 cm$^{-1}$ appeared as the complexation proceeded (Figure 8). After 2 h, the inclusion complexation was complete, and only the new OH and C═O absorptions remained (Figure 8). The complexation can also be followed by measurement of CD spectra in the Nujol mull. As the complexation of **1e** with **3c** and **5c** proceeded, CD spectra due to a chiral arrangement of **1e** molecules increased and mirror imaged CD absorptions are completed (Figure 9).

Photoconversion of **4be(1:1)** and **6be(1:1)** prepared by mixing in the solid state was followed by successive measurement of CD spectra as Nujol mulls. In the CD spectra in Nujol, (−)- and (+)-**2e** showed mirror imaged absorptions (Figure 10). As shown in Figure 11, the CD spectra of **4be(1:1)** and **6be(1:1)** prepared by mixing in Nujol turned to (−)- and (+)-**2e** as the photoreaction proceeded.

## Experimental Section

**General Methods.** Preparation of inclusion compounds (**4**) of **1** with the host **3a** and **3c** and with **3b** was carried out by recrystallization from toluene and ether, respectively. The host:guest ratio of all inclusion compounds was determined by elemental analysis and measurement of $^1$H NMR spectra. Photolysis in a water suspension at room temperature of the inclusion compounds was carried out through a Pyrex filter by using a 100-W high-pressure Hg lamp. IR spectra were measured with an IR spectrometer, JASCO FT/IR-350, in Nujol mull. $^1$H NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-LA300 (300 MHz) spectrometer. All $[\alpha]_D$ values were measured with a digital polarimeter, JASCO DIP-1000S.

(5) Toda, F.; Miyamoto, H.; Kanemoto, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1719.



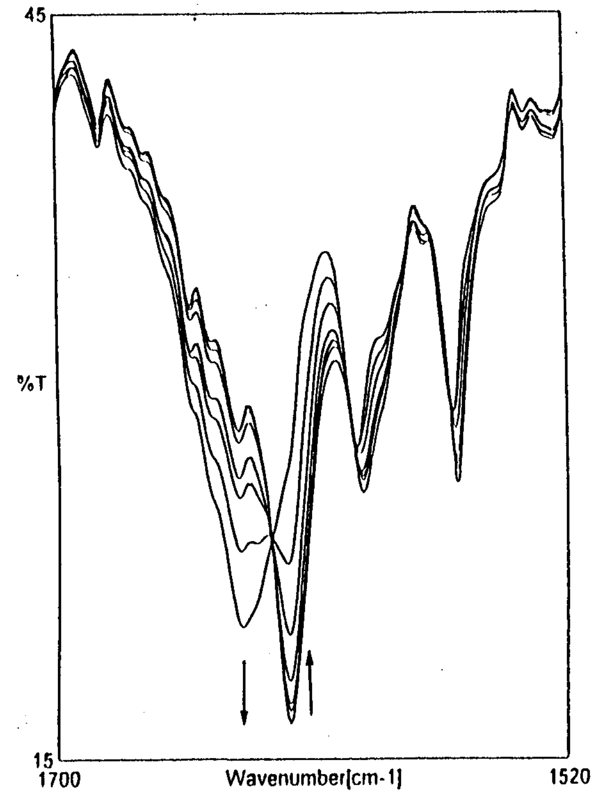




**Figure 8.** IR spectra of inclusion complexation of **1e** with **3c** in Nujol mull.

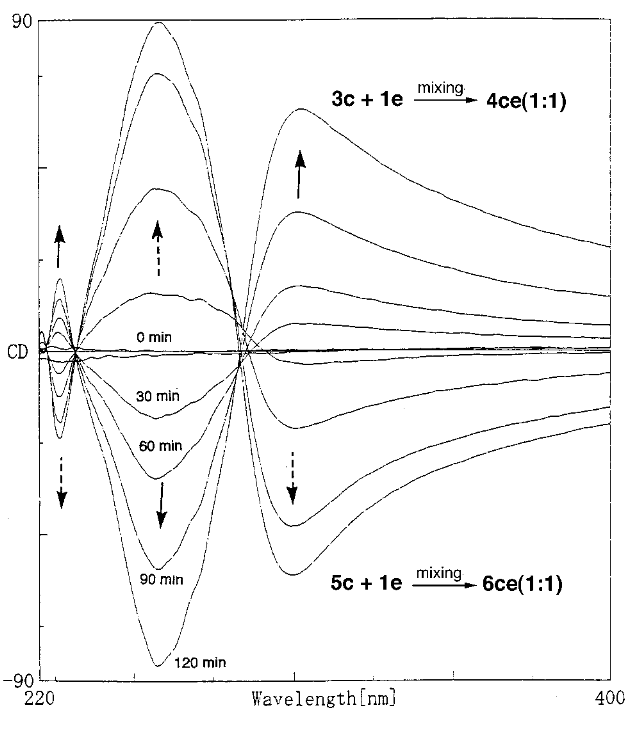



**Figure 9.** CD spectra of inclusion complexation of **1e** with **3c** in Nujol mull.

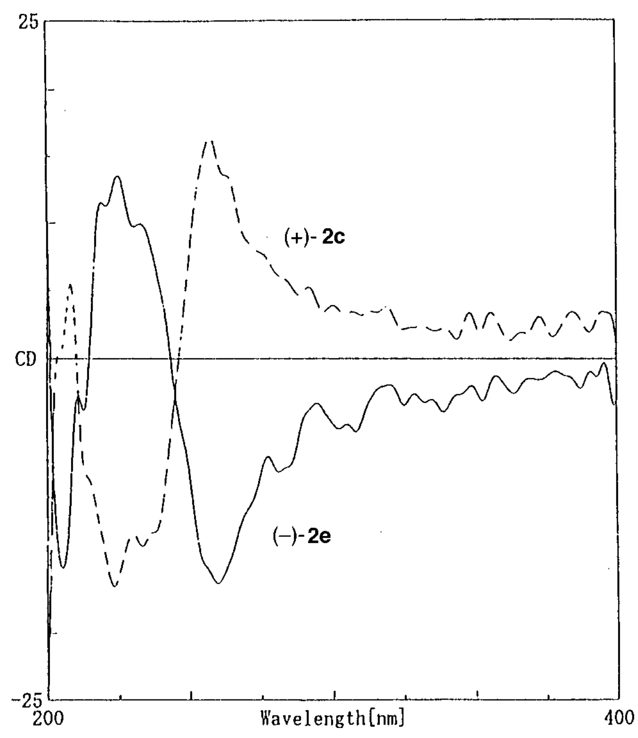



**Figure 10.** CD spectra of (−)- and (+)-**2e** in Nujol mull.

Optical purities were determined by HPLC using hexane/2-propanol (9:1) or hexanes/ethanol (95:5) solvent unless otherwise stated (flow rate, 1.0 mL/min) and a column (0.46 cm × 25 cm) containing the chiral solid phase, Chiralcel OD or Chiralpak AS, which are commercially available from Daicel Chemical Industries Ltd., Himeji, Japan.

**Preparation of 1a−f.** Compounds **1a**−**f** were prepared by a literature procedure.[1] **Furan-2-carboxyanilide (1a)** (colorless needles, mp 125−126 °C): IR (Nujol) $\nu_{max}$ 1650 cm$^{-1}$; $^{1}$H NMR $\delta$ 6.56 (s, 1H), 7.20−7.66 (m, 6 H), 8.06 (s, 1 H). Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.58; N, 7.48. Found: C, 70.52; H, 4.85; N, 7.22. ***N*-Methylfuran-2-carboxyanilide (1b)** (colorless prisms, mp 125−126 °C): IR (Nujol) $\nu_{max}$ 1638 cm$^{-1}$; $^{1}$H NMR $\delta$ 3.44 (s, 3H), 5.42 (d, 1H), 6.19 (d, 1H), 7.20−7.41 (m, 6 H). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.49; H, 5.68; N, 7.22. ***N*-Ethylfuran-2-carboxyanilide (1c)** (colorless prisms, mp 126−127 °C): IR (Nujol) $\nu_{max}$ 1627 cm$^{-1}$; $^{1}$H NMR $\delta$ 1.21 (t, 1H), 3.91 (q, 2H),

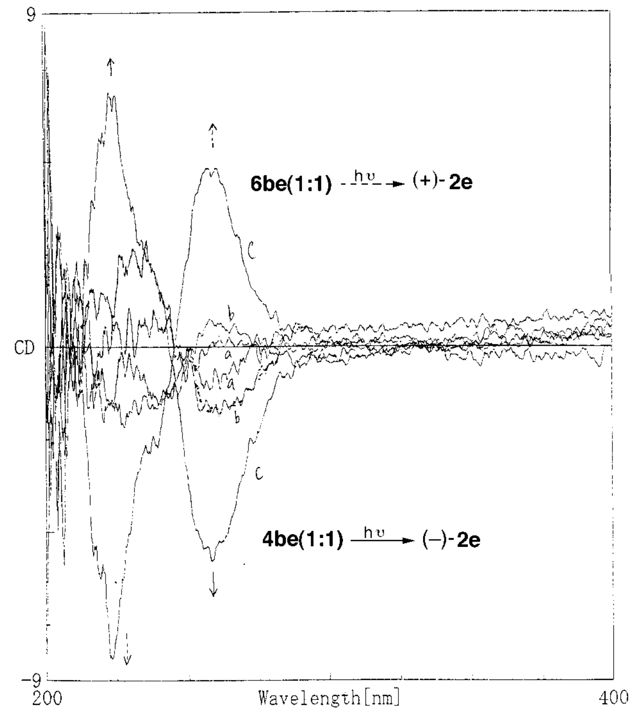



**Figure 11.** Photoconversion of **4be(1:1)** and **6be(1:1)** to (−)- and (+)-**2e**, respectively, by continuous measurements of CD spectra in Nujol mull, after (a) 0 min, (b) 2 min, and (c) 4 min of irradiation.

5.71 (d, 1H), 6.18 (q, 1H), 7.18−7.42 (m, 6H). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.45; H, 6.23; N, 6.51. ***N*-Isopropylfuran-2-carboxyanilide (1d)** (colorless prisms, mp 114−115 °C): IR (Nujol) $\nu_{max}$ 1631 cm$^{-1}$; $^1$H NMR $\delta$ 1.11 (d, 6H), 5.12 (m, 1H), 5.36 (d, 1H), 6.09 (q, 1H), 7.28 (t, 1H), 7.12−7.33 (m, 9H). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.42; H, 6.67; N, 6.13. ***N*-Allylfuran-2-carboxyanilide (1e)** (colorless prisms, mp 58−59 °C): IR (Nujol) $\nu_{max}$ 1634 cm$^{-1}$; $^1$H NMR $\delta$ 1.11 (d, 6H), 5.12 (m, 1H), 5.36 (d, 1H), 6.09 (q, 1H), 7.28 (t, 1H), 7.12−7.33 (m, 9H). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.92; H, 5.98; N, 6.29. ***N*-Benzylfuran-2-carboxyanilide (1f)** (colorless prisms, mp 109−111 °C): IR (Nujol) $\nu_{max}$ 1637 cm$^{-1}$; $^1$H NMR $\delta$ 5.05 (s, 2H), 5.71 (d, 1H), 6.18 (q, 1H), 7.02 (q, 1H), 7.26−7.33 (m, 9H). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.86; H, 5.68; N, 5.22.

**Preparation of Inclusion Compounds (4) by Recrystallization Method.** When a solution of **3b** (2.0 g, 4.0 mmol) and **1b** (0.8 g, 4.0 mmol) in ether (20 mL) was kept at room temperature for 12 h, their 1:1 inclusion compound (**4bb**) was obtained as colorless plates (2.1 g, 72% yield, mp 122−123 °C): IR (Nujol) $\nu_{max}$ 3280 and 1620 cm$^{-1}$. Anal. Calcd for $C_{45}H_{43}NO_6$: C, 77.90; H, 6.52; N, 2.02. Found: C, 78.16; H, 6.30; N, 1.96. By the same procedure, the following inclusion compounds were prepared. A 1:1 inclusion compound (**4cb**) (colorless needles, 76% yield, mp 149−151 °C): IR (Nujol) $\nu_{max}$ 3280, 3190, and 1620 cm$^{-1}$. Anal. Calcd for $C_{46}H_{45}NO_6$: C, 78.05; H, 6.41; N, 1.98. Found: C, 77.91; H, 6.53; N, 1.99. A 2:1 inclusion compound (**4cc**) (colorless needles, 91% yield, mp 117−124 °C): IR (Nujol) $\nu_{max}$ 3630, 3400, 3270, and 1550 cm$^{-1}$. Anal. Calcd for $C_{81}H_{81}NO_{10}$: C, 79.91; H, 6.65; N, 1.14. Found: C, 77.91; H, 6.87; N, 1.31. A 1:1 inclusion compound (**4ad**) (colorless needles, 71% yield, mp 130−133 °C): IR (Nujol) $\nu_{max}$ 3240 and 1626 cm$^{-1}$. Anal. Calcd for $C_{45}H_{45}NO_6$: C, 77.67; H, 6.52; N, 2.02. Found: C, 77.81; H, 6.57; N, 1.99. A 1:1 inclusion compound (**4bd**) (colorless needles, 79% yield, mp 137−139 °C): IR (Nujol) $\nu_{max}$ 3247, 3167, and 1613 cm$^{-1}$. Anal. Calcd for $C_{47}H_{47}NO_6$: C, 78.20; H, 6.56; N, 1.94. Found: C, 78.27; H, 6.65; N, 1.91. A 1:1 inclusion compound (**4cd**) (colorless needles, 88% yield, mp 126−133 °C): IR (Nujol) $\nu_{max}$ 3637, 3414, 3268, and 1550 cm$^{-1}$. Anal. Calcd for $C_{48}H_{49}NO_6$: C, 78.34; H, 6.71; N, 1.90. Found: C, 77.81; H, 6.94; N, 1.68. A 1:1 inclusion compound (**4ae**) (colorless prisms, 61% yield, mp 130−132 °C): IR (Nujol) $\nu_{max}$ 3200 and 1625 cm$^{-1}$. Anal. Calcd for $C_{49}H_{41}NO_6$: C, 77.90; H, 6.24; N, 2.02. Found: C, 78.15; H, 6.41; N, 2.01. A 1:1 inclusion compound (**4be(1:1)**) (colorless prisms, 79% yield, mp 100−101 °C): IR (Nujol) $\nu_{max}$ 3222 and 1620 cm$^{-1}$. Anal. Calcd for $C_{47}H_{45}NO_6$: C, 78.42; H, 6.30; N, 1.95. Found: C, 78.27; H, 6.59; N, 1.78. A 2:1 inclusion compound (**4be(2:1)**) (colorless needles, 83% yield, mp 79−82 °C): IR (Nujol) $\nu_{max}$ 3628, 3414, 3275, and 1551 cm$^{-1}$. Anal. Calcd for $C_{80}H_{77}NO_{10}$: C, 79.25; H, 6.40; N, 1.16. Found: C, 77.78; H, 6.56; N, 1.23. A 2:1 inclusion compound (**4ce(2:1)**) (colorless needles, 79% yield, mp 112−115 °C): IR (Nujol) $\nu_{max}$ 3629, 3414, 3280, and 1550 cm$^{-1}$. Anal. Calcd for $C_{82}H_{81}NO_{10}$: C, 79.39; H, 6.58; N, 1.13. Found: C, 77.20; H, 6.70; N, 1.03. A 1:1 inclusion compound (**4cf**) (colorless needles, 77% yield, mp 112−115 °C): IR (Nujol) $\nu_{max}$ 3256, 3148, and 1621 cm$^{-1}$. Anal. Calcd for $C_{52}H_{49}NO_6$: C, 79.67; H, 6.30; N, 1.79. Found: C, 79.82; H, 6.50; N, 1.76.

**Photocyclization of 1 to *N*-Alkyl-1,2,3,4-tetrahydro-2-oxoquinolino[2,1-*b*]-*trans*-dihydrofuran (2) in 4.** A suspension of powdered **4bb** (1.70 g, 2.45 mmol) in water (120 mL) containing hexadecyltrimethylammonium bromide (0.1 g) as a surfactant was irradiated under stirring for 40 h with a 100-W high-pressure Hg lamp. The reaction mixture was filtered, dried, and chromatographed on silica gel, using AcOEt/toluene (1:10) as an eluent to give **(3*S*,4*R*)-(−)-*N*-methyl-1,2,3,4-tetrahydro-2-oxoquinolino[2,1-*b*]-*trans*-dihydrofuran (2b)** in 8% ee as a colorless oil (0.123 g, 25% yield, $[\alpha]_D$ −30° (*c* 0.7, MeOH)): IR (Nujol) $\nu_{max}$ 1710 cm$^{-1}$; $^1$H NMR $\delta$ 3.41 (s, 3H), 4.18 (d, $J$ = 18.6 Hz, 1H), 4.28 (d, $J$ = 18.6 Hz, 1H), 5.68 (q, 1H), 6.67 (t, 1H), 7.05−7.34 (m, 4H). The optical purity of (−)-**2b** was determined by HPLC on the chiral solid phase, Chiralcel OD. By the same procedure, irradiation of **4cc** for 120 h gave **(3*R*,4*S*)-(+)-*N*-ethyl-1,2,3,4-tetrahydro-2-oxoquinolino[2,1-*b*]-*trans*-dihydrofuran (2c)** in 99% ee as a colorless oil (41% yield, $[\alpha]_D$ +232° (*c* 0.4, MeOH)): IR (Nujol) $\nu_{max}$ 1700 cm$^{-1}$; $^1$H NMR $\delta$ 1.27 (t, 3H), 4.03 (m, 2H), 4.15 (d, $J$ = 18 Hz, 1H), 4.27 (d, $J$ = 18 Hz, 1H), 5.67 (q, 1H), 7.08−7.33 (m, 4H). The optical purity of (+)-**2c** was determined by HPLC on the chiral solid phase, Chiralcel OD. Irradiation of **4cd** for 143 h gave **(3*R*,4*S*)-(+)-*N*-Isopropyl-1,2,3,4-tetrahydro-2-oxoquinolino[3,1-*b*]-*trans*-dihydrofuran (2d)** in 52% ee as a colorless oil (16% yield, $[\alpha]_D$ +99° (*c* 0.5, MeOH)): IR (Nujol) $\nu_{max}$ 1706 cm$^{-1}$; $^1$H NMR $\delta$ 1.49 (d, 3H), 1.61 (d, 3H), 4.14 (s, 2H), 4.70 (m, 1H), 5.64 (d, 1H), 6.66 (q, 1H), 7.08−7.30 (m, 4H). The optical purity of (+)-**2c** was determined by HPLC on the chiral solid phase, Chiralcel OD. Irradiation of **4ae** for 96 h gave **(3*R*,4*S*)-(+)-*N*-allyl-1,2,3,4-tetrahydro-2-oxoquinolino[2,1-*b*]-*trans*-dihydrofuran (2e)** in 93% ee as colorless crystals (20% yield, $[\alpha]_D$ +275° (*c* 0.8, MeOH)): IR (Nujol) $\nu_{max}$ 1706 cm$^{-1}$; $^1$H NMR $\delta$ 4.21 (d, $J$ = 18.3 Hz, 1H), 4.34 (d, $J$ = 18.3 Hz, 1H), 4.37 (m, 1H), 4.81 (m, 1H), 5.18 (m, 1H), 5.69 (m, 1H), 5.88 (m, 1H), 6.68 (t, 1H), 7.09 (m, 2H), 7.27 (m, 2H). The optical purity of (+)-**2e** was determined by HPLC on the chiral solid phase, Chiracel OD. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.74; H, 5.86; N, 5.88. Irradiation of **4be(1:1)** for 77 h gave (−)-**2e** in 96% ee as colorless crystals (50% yield, $[\alpha]_D$ −283° (*c* 0.5, MeOH)). Irradiation of **4be(2:1)** for 48 h gave (+)-**2e** in 98% ee as colorless crystals (86% yield, $[\alpha]_D$ +314° (*c* 0.4, MeOH)). Irradiation of **4ce** for 50 h gave (+)-**2e** in 98% ee as colorless crystals (77% yield, $[\alpha]_D$ −283° (*c* 0.5, MeOH)). Irradiation of **4cf** for 120 h gave **(3*S*,4*R*)-(−)-*N*-benzyl-1,2,3,4-tetrahydro-2-oxoquinolino[2,1-*b*]-*trans*-dihydrofuran (2f)** in 98% ee as colorless crystals (72% yield, $[\alpha]_D$ −230° (*c* 0.6, MeOH)): IR (Nujol) $\nu_{max}$ 1696 cm$^{-1}$; $^1$H NMR $\delta$ 4.28 (d, $J$ = 18.3 Hz, 1H), 4.46 (d, $J$ = 18.3 Hz, 1H), 5.06 (d, $J$ = 16.1 Hz, 1H), 5.35 (d, $J$ = 16.1 Hz, 1H), 5.70 (m, 1H), 6.71 (d, 1H), 6.97−7.33 (m, 9H). The optical purity of (−)-**2f** was determined by HPLC on the chiral solid phase, Chiralpak AS. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.10; H, 5.58; N, 4.71.

**Preparation of 4 by Mixing Method.** As an example, **4ce(1:1)** was prepared by mixing powdered **3c** (1.38 g, 2.73 mmol) and **1e** (0.62 g, 2.73 mmol) and liquid paraffin (0.1 g) for 1 h at room temperature, using a planetary micro mill, Fritsch pulverizette 7.

**Photoreaction of 4ce(1:1) Prepared by Mixing Method.** A suspension of powdered **4ce** (2.00 g, 2.73 mmol) in water (120 mL) containing hexadecyltrimethylammonium bromide (0.1 g) as a surfactant was irradiated under stirring for 40 h with 100-W high-pressure Hg lamp. The reaction mixture was filtered, dried, and chromatographed on silica gel using AcOEt/toluene (1:10) as an eluent to give (−)-**2e** in 49% ee as colorless crystals (0.09 g, 16% yield, $[\alpha]_D$ −135° (c 0.4, MeOH)). Photoreaction of **4ce(1:1)** prepared by mixing in the absence of liquid paraffin also gave an identical (−)-**2e**.

**Structure Determination of 4be(1:1).** The integrated X-ray diffraction intensity from the single crystal of **4be(1:1)** was collected by a four-circle diffractometer. The crystal structure was solved by direct methods, SIR92,[6] and refined by the full matrix least-squares method, SHELX-97.[7] Molecular and crystal structures were plotted by ORTEP-III.[8]

**Supporting Information Available:** Tables of data and details of crystal structure determinations, anisotropic displacement parameters, and bond lengths and angles.

JO982099M

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