

Memory of Chirality Generated by Spontaneous Crystallization and Asymmetric Synthesis Using the Frozen Chirality

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Asymmetric synthesis using frozen chirality generated by spontaneous crystallization was performed. Achiral asymmetrically substituted imide with a tetrahydronaphthyl group on the nitrogen atom crystallized in a chiral fashion, with space group $P2_12_12_1$. The molecular chirality generated by spontaneous crystallization was retained in cold THF. The half-life determined on the basis of decreasing optical activity followed by CD spectrometer was 7.8, 33.1, and 150.0 min at -20 , -30 , -40 °C, respectively. The energy barrier (ΔG^\ddagger) of racemization was calculated with the temperature dependence of the kinetic constant to be 18.24–18.36 kcal mol⁻¹ at 233–253 K. The memorized frozen chirality was transferred to permanent optically active alcohols by nucleophilic addition with *n*-butyllithium.

Introduction

One of the fundamental and intriguing aspects of life is the homochirality of the essential molecules.^{1–3} The origin of chirality in a biological system has been a challenge to scientists, and novel approaches to absolute asymmetric synthesis are attempted by the photochemical reaction with circular polarized light^{4–6} and conversion in chiral crystals.^{7–15} The spontaneous crystallization is a most attractive phenomenon because achiral molecules are doped in molecular chirality or chiral arrangement in the crystals without any outside chiral source.

A number of apparent achiral organic compounds have been obtained as chiral crystals, and the solid-state photoreaction gave many successive absolute asymmetric syntheses. However, most of them were limited to photochemical reactions, because it is difficult for chemical reagents to react inside the crystals without decomposition of the crystal lattice. Exceptionally, successive examples are reported for heterogeneous reaction involving the bromination of the C=C double bond of chalcone derivatives and the rearrangement of the cyclopropane ring by dried hydrogen chloride; however, regrettably, the maximum ee value was not so high.^{16–18} That is to say, respectable high enantioselectivity has not been achieved in a solid-state reaction using chiral crystals except for the photochemical reaction.

On the other hand, Azumaya et al. reported an interesting example of retention of the molecular chirality when the chiral crystal of 1,2-bis(*N*-benzoyl-*N*-methylamino)benzene **A** was dissolved in a cold solution (Figure 1).¹⁹ Furthermore, Tissot et al. recently reported a fine example of catalytic asymmetric synthesis using chiral ligand **B** prepared by spontaneous resolution.²⁰ Both **A** and **B** exist as mixtures of many conformational isomers or diastereomers in solution at ambient temperature. If the molecular chirality is retained in homogeneous conditions such as these examples, the frozen chirality

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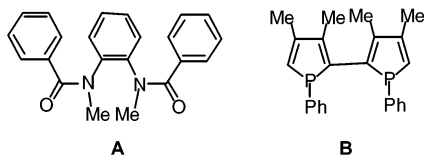
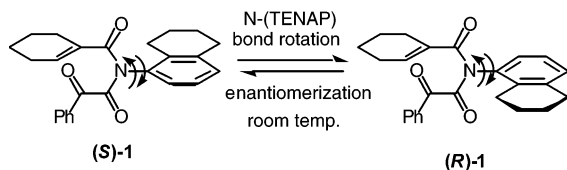


FIGURE 1.

SCHEME 1



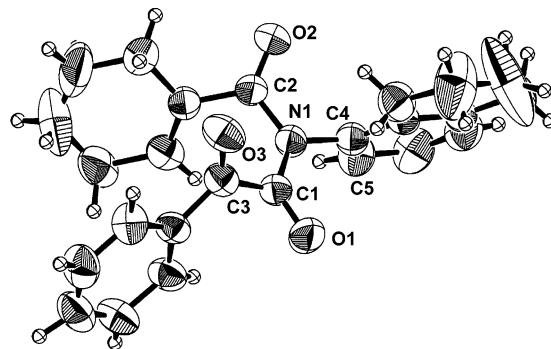
generated by spontaneous crystallization should be effectively transferred to the products by asymmetric reactions.

It is known that the rotational barrier of amides with a bulky substituent has considerably high activation energy for the bond rotation, and some optically active amides with molecular chirality have been isolated.^{21–29} Now, we have found that achiral asymmetrically substituted imide **1**, in which the bond between the nitrogen atom and the tetrahydronaphthyl (TENAP) group rotates freely at room temperature, crystallized in a chiral fashion by spontaneous crystallization, and the enantiomerization owing to the bond rotation was suppressed at low temperature. Furthermore, the frozen molecular chirality could be transferred to optically active compounds in solution media.

Results and Discussion

Acyclic achiral imide **1** was conveniently prepared by benzoylformylation of the corresponding amide in the presence of triethylamine, and recrystallization from the chloroform–hexane solution afforded colorless prisms. The crystal was subjected to X-ray crystallographic analysis to obtain details of the molecular conformation and the architecture in the crystals. To achieve the presented asymmetric synthesis, it was requisite that achiral materials crystallize in a chiral space group. Fortunately, the imide **1** gave a chiral crystal system, the space group $P2_12_12_1$. Each single crystal is chiral and all molecules in one crystal are optically active, offering the same chiral configuration.

Figure 2 shows the Ortep drawing of the imide **1**, in which the imide group has the (*E,E*) conformation. The sp^2 nitrogen atom is slightly twisted from the theoretical imide plane, and the torsional angles of $C1=O1$

FIGURE 2. Ortep drawing of the imide **1**. The space group is chiral $P2_12_12_1$.

and $C2=O2$ from the sp^2 plane of the amide group are 13.2° and 35.0° , respectively. This means that the lone pair electrons on the nitrogen atom conjugate with the $C1=O1$ carbonyl rather than the $C2=O2$ group. The tetrahydronaphthyl group (TENAP) directed to the imide group is almost perpendicular, $C1-N1-C4-C5 = 78^\circ$. The benzoylformyl group ($O1-C1-C3-O3$) is also considerably twisted at 118.2° , and the carbonyl oxygen ($O3$) is placed on the same side of the imide plane as the TENAP group.

The bulk of crystals used for the asymmetric reaction were prepared by stirred crystallization as follows. The crystals of the imides **1** (mp $161–163^\circ\text{C}$) were dissolved in chloroform–hexane solution, and the solvent was removed at 40°C in the open air by stirring with a mechanical stirrer until all the solvent was evaporated off perfectly. In many cases, the first generated enantiomorphic crystal works as a seed in the crystallization step, and all the crystals in the batch can turn out to have the same absolute configuration.^{14,15} On the other hand, once enantiomorphic crystals are formed, a large amount of the desired crystals can be selectively prepared by seeding the desired crystals through recrystallization. In this case, there was no considerable difference in the optical purity of the crystals in each batch between the use of seeding and spontaneous crystallization.³⁰

Can the imide **1** retain the molecular chirality after dissolving crystals into solution? Figure 3 shows the CD spectra of the solution of imide **1** prepared by dissolving chiral crystals into cold THF with use of the cryostat apparatus. When the crystals were dissolved at -10°C , the CD spectrum did not show the Cotton effect. However, optical activity was observed when the crystals were dissolved at -20°C (Figure 3a). The optical activity gradually decreased, and the half-life was 7.8 min. Furthermore, panels b and c in Figure 3 also show the changes in the CD spectra measured at -30 and -40°C , respectively, which were prepared by the same method. The half-life increased according with lower temperatures: $t_{1/2}$ was 31.6 and 150.0 min at temperatures of -30 and -40°C , respectively.

Table 1 shows the kinetic parameters determined on the basis of the rate constant of enantiomerization. The energy barrier (ΔG^\ddagger) of enantiomerization was calculated with the temperature dependence of the kinetic constant

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(30) Direct determination of the enantiomeric purity of the crystal of the imide **1** was difficult; therefore, the ee values of oxetane **2** obtained by the solid-state photochemical reaction were compared.

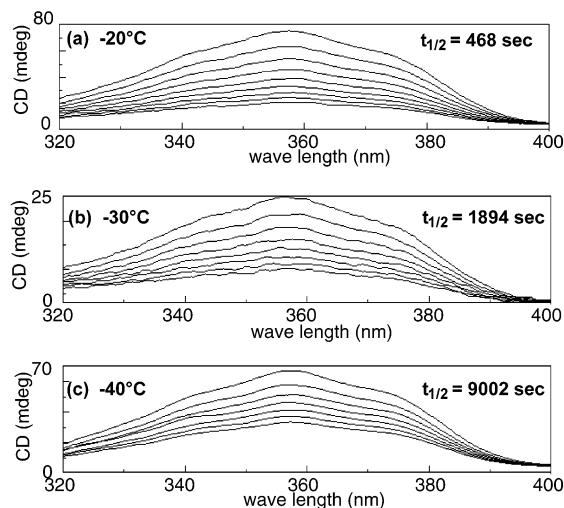


FIGURE 3. CD spectra of **1** at various temperatures.

TABLE 1. Activation Parameters for Enantiomerization of Imide **1**

<i>T</i> (°C)	$10^{-4}k_{\text{rot}}$	$t_{1/2}$ (s)	ΔG° (kcal mol ⁻¹)	ΔH° (kcal mol ⁻¹)	ΔS° (cal mol ⁻¹ deg ⁻¹)
-20	7.40	468	18.36	16.81	-6.14
-25	3.78	917	18.32	16.82	-6.06
-30	1.83	1894	18.29	16.83	-6.02
-35	0.874	3965	18.26	16.84	-5.95
-40	0.385	9002	18.24	16.85	-5.98

(253 K, 7.40×10^{-4} ; 243 K, 1.83×10^{-4} ; 233 K, 3.85×10^{-5}) to be 18.24–18.36 kcal mol⁻¹ at 233–253 K. The enthalpy (ΔH°) factor is 16.81–16.85 kcal mol⁻¹, and the entropy factor was slightly negative, $\Delta S^\circ = -6$ cal mol⁻¹ deg⁻¹ at 233–253 K. These facts indicate that achiral imide **1** can retain the molecular chirality doped in the crystal lattice below -20 °C in homogeneous conditions, and the lifetime is long enough for the next application to asymmetric synthesis.

Before the asymmetric synthesis in solution, the solid-state photoreaction was investigated to determine the enantiomeric purity of the crystals obtained by spontaneous crystallization.³¹ When the bulk of crystals of **1** in a test tube was irradiated at 15 °C under argon atmosphere with an ultra-high-pressure mercury lamp, intramolecular 2+2 cyclization proceeded effectively without melting down.³¹ Separation by column chromatography on silica gel gave two diastereomeric oxetanes, **2** and **3**, in 95 and 5% yield, respectively. The enantiomeric purity of the main product **2** was determined as >99% ee by HPLC, using chiral cell OJ column, whereas the ee value of **3** could not be determined. These results indicate that the bulk of the crystals in one batch are optically pure owing to the same chiral configuration. The structure of **2** was established by X-ray single-crystal analysis. The cyclic imides **2** and **3** were stable at room temperature and bond rotation between the nitrogen atom and the TENAP group did not occur; however, refluxing in a benzene solution of **2** gradually formed the enantiomeric **3** owing to the bond rotation. Many successive asymmetric syn-

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SCHEME 2

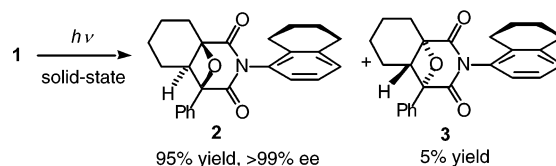


TABLE 2. Reaction of **1** with *n*-BuLi/TMEDA in Various Conditions

entry	solvent	temp (°C)	time (h)	conv (%)	yield (%) of 4 + 5	ee (%)		
						4 : 5	of 4 ^c of 5 ^c	
1 ^a	THF	20	0.5	100	88	90:10	0	0
2 ^b	THF	20	0.5	100	88	90:10	41	5
3 ^b	THF	10	0.5	100	88	91:9	6	4
4 ^b	THF	0	0.5	100	88	88:12	11	8
5 ^b	THF	-10	0.5	100	88	86:12	18	9
6 ^b	THF	-20	0.5	100	87	76:24	40	14
7 ^b	THF	-40	0.5	100	77	66:34	56	29
8 ^b	THF	-60	0.5	100	77	76:24	71	52
9 ^b	THF	-80	2.0	100	70	66:34	83	81
10 ^b	ether	-80	2.0	97	66	92:8	73	56
11 ^b	toluene	-80	2.0	100	78	86:14	52	24
12 ^b	hexane	-80	24.0	0	0			

^a Method A: A solution of *n*-butyllithium was added immediately after dissolving **1** and TMEDA in THF. ^b Method B: Powdered crystals of **1** were added to the THF solution containing *n*-butyllithium and TMEDA. ^c When the crystal exhibiting the (+)-Cotton effect at 358 nm (Figure 3) was used for the reaction, (-)-rotatory **4** and **5** were obtained. The same reaction with use of enantiomeric crystals gave enantiomeric (+)-**4** and (+)-**5**, respectively.

theses with chiral crystals are reported; however, most of them involved solid-state photochemical reactions and, exceptionally, some solid-gas reactions.^{15–17} The molecular chirality generated by spontaneous crystallization should be much more effectively transferred to the products, if the asymmetric synthesis can be promoted in homogeneous media.

To achieve the new asymmetric synthesis, a nucleophilic reaction with *n*-butyllithium was examined. A commercially available hexane solution of *n*-butyllithium (5 mmol) was added to the THF solution immediately after the powdered crystals of **1** (0.5 mmol) were dissolved into the THF solution (5 mL) containing TMEDA (5 mmol) at 20 °C. After 0.5 h of stirring at the same temperature, aq NH₄Cl was added to quench the reaction, and the reaction mixture was extracted with ether in the usual manner. The products were separated by thick-layer chromatography on silica gel. Nucleophilic addition to the benzoyl carbonyl group occurred effectively, the adduct **4** and hydrogenated product **5** were obtained in 88% yield, and the ratio of **4**:**5** was 90:10. As a matter of course, molecules immediately lost chirality on dissolving the chiral crystals in a solvent, and racemic products, **4** and **5**, were obtained (Table 2, entry 1). The structure of adduct **4** was established by X-ray single-crystal analysis.

Surprisingly, when powdered crystals were added to the THF solution containing *n*-butyllithium and TMEDA at 20 °C, optically active products **4** (41% ee) and **5** (5%

ee) were isolated (Table 2, entry 2). The ee value of the products was determined by HPLC by using a chiral cel OJ column. Optically active products were also obtained from the reaction at 10 to -10 °C (entries 3–5); however, the ee value is lower than that of the reaction at 20 °C. Furthermore, according to the decreased temperature, the enantioselectivity increased (entries 6–9), and the maximum ee values, 83% ee for **4** and 81% ee for **5**, were obtained when the reaction temperature was -80 °C (entry 9). There was a solubility problem when diethyl ether was used, and the reaction in toluene resulted in lower ee values (entries 10 and 11). When hexane was used as a solvent, the crystals did not dissolve at all, and the reaction did not proceed even after 24 h (entry 12). Therefore, THF is the most prominent solvent for this asymmetric nucleophilic reaction. Furthermore, the result of the reaction in hexane solution (entry 12) indicates that the nucleophilic reaction does not proceed on the surface of the crystals, but occurred in homogeneous conditions. It is noteworthy that optically active products were obtained at 20 °C, and higher optical purity was observed than in the reaction at 10 to -10 °C (entries 3–5), though the imide **1** racemized in an instant at this temperature. The ee value of the products is influenced by the rate of both enantiomerization of the imide **1** and the reaction with a nucleophile. In the range of 10 to -10 °C, the rate of racemization is superior to the addition of a nucleophile, and low ee values of products were obtained. It seems that the nucleophilic reaction of **1** occurs competitively with racemization at 20 °C; therefore, higher enantioselective reaction is promoted. These results are particularly surprising in view of the fact that optically active materials are obtained by the reaction of frozen chirality with *n*-butyllithium even at 20 °C.

The absolute configuration of neither the imide **1** in chiral crystal nor frozen chiral conformation could be determined. When the crystals, which exhibited the (+)-Cotton effect at 358 nm in the CD spectra (Figure 3), were irradiated in the solid state, (+)-rotatory oxetane **2** was obtained. On the other hand, the reaction with *n*-butyllithium with the same rotatory crystals gave (–)-**4** and (–)-**5**. As a matter of course, the use of enantiomorphic crystals gave (–)-**2** by the solid-state photolysis and (+)-**4** and (+)-**5** by the nucleophilic reaction with *n*-butyllithium in the same chemical and enantiomeric yields.

A mechanistic approach for the asymmetric synthesis cannot be devised without the absolute configuration of both the starting imide **1** and the products; however, the presumed asymmetric induction is outlined as follows. Imide **1** is achiral because the enantiomerization occurs at room temperature, and afforded chiral crystals by spontaneous crystallization. The enantiomeric pure bulk of crystals was obtained without seeding; however, the crystals in each batch have a fifty-fifty chance for the absolute configuration of (*R*)- or (*S*)-**1**. Desired crystals could be easily prepared by the seeding method. When enantiomorphic crystals of (*R*)-**1** were dissolved in a low-temperature solvent, the rotation axis of *N*-(TENAP) was restricted, and the frozen molecular chirality was retained as the same configuration in the crystal lattice. Nucleophiles can react from the uncrowded face by keeping away the cyclohexenecarbonyl group to give optically active products.

In conclusion, we have provided a new asymmetric synthesis by the use of frozen molecular chirality generated by spontaneous resolution of achiral materials.

Experimental Section

General Information. Melting points are uncorrected. FT-IR spectra are reported in cm^{-1} . ^1H and ^{13}C NMR spectra were obtained in CDCl_3 solutions at 300 MHz. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the TMS as internal standard. Both 500-W high-pressure and 250-W ultra-high-pressure mercury lamps were used as irradiation sources.

Preparation of *N*-cyclohexenecarbonyl-*N*-(5,6,7,8-tetrahydronaphthalen-1-yl)benzoylformamide **1:** The asymmetrically substituted imide **1** was prepared by the condensation reaction of *N*-(tetrahydronaphthyl)-1-cyclohexenecarbamide with benzoylformyl chloride in the presence of triethylamine according to the procedure reported in the literature.³¹ The imide **1** was obtained as colorless prismatic crystals from hexane–chloroform: HRMS (FAB), calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_3$ (MH^+) 388.1913, found 388.1887; mp 161–163 °C; IR (cm^{-1} , KBr) 1460, 1668, 1716; ^1H NMR (CDCl_3) δ 1.22–1.24 (m, 2H), 1.41–1.45 (m, 2H), 1.56–1.86 (m, 6H), 2.07 (s, 2H), 2.61–2.85 (m, 4H), 6.45 (t, 1H, $J = 2.0$ Hz), 6.97 (dd, 1H, $J = 2.0$ and 9.0 Hz), 7.15–7.19 (m, 2H), 7.48–7.53 (m, 2H), 7.60–7.63 (m, 2H), 8.02–8.05 (m, 2H); ^{13}C NMR (CDCl_3) δ 20.8, 21.3, 22.5, 22.6, 24.5, 24.7, 25.2, 29.5, 125.6, 126.1, 128.7, 129.9, 130.3, 132.7, 134.3, 135.3, 135.5, 136.3, 139.2, 140.2, 169.5, 172.7, 186.5.

X-ray Crystallographic Analysis of *N*-(1-cyclohexenecarbonyl)-*N*-(5,6,7,8-tetrahydronaphthalen-1-yl)benzoylformamide **1:** Colorless prismatic crystals from hexane–chloroform, orthorhombic space group $P2_12_12_1$, $a = 12.774(3)$ Å, $b = 21.130(5)$ Å, $c = 7.766(3)$ Å, $V = 2096.1(1)$ Å³, $Z = 4$, $\rho = 1.227$ g/cm³, $\mu(\text{CuK}\alpha) = 6.391$ cm^{-1} . The structure was solved by the direct method of full-matrix least-squares, where the final R and R_w were 0.041 and 0.045 for 1035 reflections.

General procedure for the photochemical reaction in the solid state: The solid-state photolysis was done under an atmosphere of dried argon. When the solid samples were irradiated as powders in a Pyrex tube for 1 h, bicyclic oxetanes (**2**, **3**) were obtained quantitatively in a **2**:**3** ratio of 95:5. The major isomer **2** could be isolated by column chromatography on silica gel, and the optical purity was determined by HPLC by using a chiral cel-OJ column as >99% ee, whereas the minor isomer **3** could not be isolated on the pure form. Irradiation of the crystals exhibiting the (+)-Cotton effect at 358 nm gave optically active **2** showing (+)-specific rotation rotatory at the α_D line. Irradiation of the enantiomorphic crystal gave (–)-**2** in >99% ee.

Racemic 5-phenyl-3-(5,6,7,8-tetrahydronaphthalen-1-yl)-11-oxa-3-azatricyclo[4.4.1.1^{5,0}.6^{1,6}]undecane-2,4-diones (2** and **3**)** were obtained quantitatively in the **2**:**3** ratio of 75:25, when a benzene solution of **1** was irradiated in an argon atmosphere. Oxetane **2** was obtained as colorless prismatic crystals from hexane–chloroform: HRMS (FAB), calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_3$ (MH^+) 388.1881, found 388.1905; mp 165–166 °C; IR (cm^{-1} , KBr) 1706, 1754; ^1H NMR (CDCl_3) δ 1.50–1.79 (m, 10H), 2.03–2.13 (m, 2H), 2.43–2.52 (m, 2H), 2.79 (br s, 2H), 3.40 (t, $J = 9.0$ Hz, 1H), 6.7–7.0 (m, 1H), 7.1–7.25 (m, 2H), 7.3–7.45 (m, 5H); ^{13}C NMR (CDCl_3) δ 20.3, 21.7, 22.9, 23.0, 24.3, 24.5, 26.0, 29.9, 51.0, 83.5, 88.8, 126.0, 126.3, 126.4, 128.4, 128.8, 130.8, 132.0, 133.6, 135.6, 139.5, 172.3, 173.8.

The diastereomeric oxetane **3** was obtained as colorless prismatic crystals from hexane–chloroform: HRMS (FAB), calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_3$ (MH^+) 388.1881, found 388.1905; mp 165–170 °C; IR (cm^{-1} , KBr) 1707, 1753; ^1H NMR (CDCl_3) δ 1.5–1.8 (m, 10H), 2.0–2.1 (m, 2H), 2.54 (br s, 2H), 2.83 (br s, 2H), 3.38 (t, $J = 9.0$ Hz, 1H), 6.9–7.0 (m, 1H), 7.1–7.25 (m, 2H), 7.3–7.45 (m, 5H); ^{13}C NMR (CDCl_3) δ 20.3, 21.7, 22.90, 22.98, 24.4, 24.8, 26.0, 29.9, 51.0, 83.5, 88.8, 126.2, 126.3, 126.6, 128.4, 128.7, 130.9, 132.1, 133.6, 135.4, 139.2, 172.0, 173.6.

X-ray crystallographic analysis of racemic 2: monoclinic space group $P2_1/n$, $a = 20.336(4)$ Å, $b = 11.966(2)$ Å, $c = 8.443(2)$ Å, $\beta = 98.32(2)^\circ$, $V = 2032.7(7)$ Å³, $Z = 4$, $\rho = 1.266$ g/cm³, $\mu(\text{CuK}\alpha) = 0.66$ cm⁻¹. The structure was solved by the direct method of full-matrix least-squares, where the final R and R_w were 0.056 and 0.120 for 2040 reflections.

Low-temperature CD spectra of 1 and determination of kinetic data for *N*-aryl bond rotation: A cryostat apparatus was used for measuring CD spectra at low temperature. The powdered crystals of **1** were dissolved into cooled THF in a cryostat apparatus and the CD spectra were monitored. The rate for enantiomerization was determined on the basis of the attenuation of the CD spectra. The activation parameters were obtained from the Eyring equation and Arrhenius plot.

Reaction of **1** with *n*-butyllithium in THF solution. The nucleophilic reactions were promoted following by the two procedures.

Method A: Immediately after the powdered crystals of **1** (0.5 mmol) were added to the THF solution containing TMEDA (5 mmol) at the cited temperature, a hexane solution of *n*-butyllithium (5 mmol) was added. After the reaction mixture was stirred at 0.5 h at the same temperature, sat. NH₄Cl solution was added. Ether and water were added and the organic layer was extracted. The organic layer was washed with water and dried; ether was evaporated off in vacuo, and the residual mixture was subjected to thick-layer chromatography on silica gel.

Method B: To a THF solution containing *n*-butyllithium and TMEDA were added powdered crystals of **1** (0.5 mmol) at the cited temperature. After being stirred at the cited temperature, the reaction mixture was treated the same as method A.

2-Hydroxy-2-phenyl-*N*-(5,6,7,8-tetrahydronaphthalen-1-yl)hexanamide 4 was obtained as colorless prismatic crystals from hexane–chloroform: mp 95–98 °C; HRMS (FAB), calcd for C₂₂H₂₈NO₂ (MH⁺) 338.2120, found 338.2118. IR (cm⁻¹, KBr) 1540, 1662, 3262, 3372; ¹H NMR (CDCl₃) δ

0.89–0.92 (m, 3H), 1.31–1.46 (m, 4H), 1.72–1.80 (m, 4H), 2.09–2.47 (m, 4H), 2.72–2.75 (m, 2H), 3.09 (d, 1H, $J = 2.0$ Hz), 6.86 (d, 1H, $J = 7.0$ Hz), 7.08 (t, 1H, $J = 8.0$ Hz), 7.25–7.32 (m, 1H), 7.35–7.39 (m, 1H), 7.64–7.66 (m, 2H), 7.77 (d, 2H, $J = 5.0$ Hz), 8.31 (s, 1H); ¹³C NMR (CDCl₃) δ 14.3, 22.7, 23.1, 24.3, 25.9, 30.0, 39.5, 79.8, 125.6, 126.10, 126.13, 127.4, 128.1, 128.8, 135.3, 138.2, 142.6, 172.0.

X-ray crystallographic analysis of racemic 4: Colorless prismatic crystals from hexane–chloroform, triclinic space group $P2_1/c$, $a = 9.031(3)$ Å, $b = 10.123(3)$ Å, $c = 21.928(6)$ Å, $\beta = 95.28(3)^\circ$, $V = 1996.1(1)$ Å³, $Z = 4$, $\rho = 1.123$ g/cm³, $\mu(\text{CuK}\alpha) = 0.56$ cm⁻¹. The structure was solved by the direct method of full-matrix least-squares, where the final R and R_w were 0.047 and 0.048 for 1465 reflections.

2-Hydroxy-2-phenyl-*N*-(5,6,7,8-tetrahydronaphthalen-1-yl)ethanamide 5 was obtained as colorless prismatic crystals from hexane–chloroform: mp 137–138 °C; HRMS (FAB), calcd for C₁₈H₂₀NO₂ (MH⁺) 282.1494, found 338.1495; IR (cm⁻¹, KBr) 1519, 1652, 2927, 3224, 3301; ¹H NMR (CDCl₃) δ 1.70–1.77 (m, 4H), 2.34–2.48 (m, 2H), 2.72–2.75 (t, 2H), 3.93 (s, 1H), 5.11 (s, 1H), 6.88 (d, 1H, $J = 8.0$ Hz), 7.05–7.09 (m, 1H), 7.31–7.46 (m, 5H), 7.70 (d, 1H, $J = 8.0$ Hz), 8.02 (s, 1H); ¹³C NMR (CDCl₃) δ 22.3, 22.7, 23.9, 29.7, 74.6, 119.3, 125.7, 126.2, 126.7, 127.5, 128.7, 128.8, 134.5, 138.0, 139.2, 170.1.

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Supporting Information Available: Three X-ray crystallographic files (CIF) and ORTEP drawings for **1**, **2**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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