JOC*Note*

Catalytic Asymmetric Synthesis of Optically Active Atropisomeric Anilides through Enantioselective *N*-Allylation with Chiral Pd-tol-BINAP Catalyst

Osamu Kitagawa, Mitsuteru Kohriyama, and Takeo Taguchi*

Tokyo University of Pharmacy and Life Science, 1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan

taguchi@ps.toyaku.ac.jp

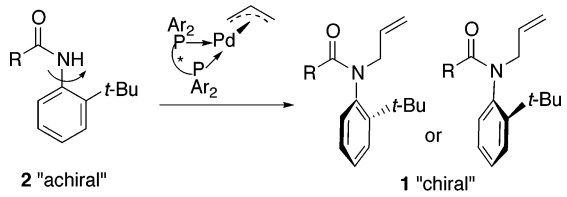
Received September 10, 2002

Abstract: Catalytic asymmetric *N*-allylation reaction of *ortho*-*tert*-butylanilide derivatives with diallyl carbonate proceeds in the presence of tol-BINAP−Pd catalyst to give chiral *N*-allyl *ortho*-*tert*-butylanilides of 32−44%ee in excellent chemical yields (≥ 90%).

N-Substituted *o*-*tert*-butylanilide derivatives are well-known to exist as stable atropisomeric compounds at room temperature due to restriction of free rotation around the N−Ar bond.[1,2] Application of such *o*-*tert*-butylanilides to organic reactions, especially stereoselective reaction, was reported initially by Curran and coworker,[3] followed by several other groups.[4] However, in these reactions, since racemic atropisomeric anilides were used, application to asymmetric reaction had to wait until optically pure compounds were available.

In 1997, we succeeded in the first synthesis of such an atropisomeric *o*-*tert*-butylanilide **1a** with high optical purity and definite absolute configuration.[5] Following this publication, syntheses of various optically active atropisomeric anilides through optical resolution by the formation of diastereomeric derivative or HPLC separation using a chiral column have been reported by other groups,[6,7] while there is no report on syntheses through an asymmetric reaction except for only one example. As the first enantioselective synthesis of atropisomeric compounds having an N−C chiral axis, Uemura et al. have recently reported a method based on enantiotopic selective lithiation of a prochiral 2,6-disubstituted arene chromium complex with chiral bases.[8] Although various

SCHEME 1



N-methyl 2-methyl-6-alkylated-anilides were obtained in high enantiomeric excess, this method cannot be applied to the synthesis of atropisomeric *o*-*tert*-butylanilides which can effectively shield one diastereoface of a reaction part. In addition, this method using stoichiometric chiral lithium amide is effective for the direct synthesis of benzamides and pivalamides, while further transformation involving several steps is required to obtain α,*β*-unsaturated amides and propanamide having a reaction site.

In this paper, we would like to propose a possibile method for catalytic enantioselective synthesis of various optically active atropisomeric *o*-*tert*-butylanilides which can be utilized for asymmetric reaction. Our method is asymmetric *N*-allylation of *N*-nonsubstitued *o*-*tert*-butylanilides using a chiral palladium catalyst (Scheme 1). Although the enantioselectivities are not high (32−44% ee), the present reaction, as far as we know, is the first example of catalytic asymmetric synthesis of nonbiaryl atropisomeric compounds.[9]

As mentioned above, we have succeeded in the synthesis of various atropisomeric *N*-allylated *o*-*tert*-butylanilides with high optical purity (96−98% ee).[7] These anilides have a rotational barrier of more than 28.3 kcal/mol and can be at least stored without racemization for

* Address correspondence to this author. FAX and phone: +81-426-76-3257.

(1) (a) Bock, L. H.; Adams, R. *J. Am. Chem. Soc.* **1931**, *53*, 374. (b) Kashima, C.; Katoh, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1599. (c) Roussel, C.; Adjimi, M.; Chemlal, A.; Djafri, A. *J. Org. Chem*. **1988**, *53*, 5076. (d) Kawamoto, T.; Tomishima, M.; Yoneda, F.; Hayami, J. *Tetrahedron Lett*. **1992**, *33*, 3169. (e) Mannschreck, A.; Koller, H.; Stuhler, G.; Davies, M. A.; Traber, J. *Eur. J. Med. Chem. Chim. Ther*. **1984**, *19*, 381.

(2) Curran, D. P.; Hale, G. R.; Geib, S. J.; Balog, A.; Cass, Q. B.; Degani, A. L. G.; Hernandes, M. Z.; Freitas, L. C. G. *Tetrahedron: Asymmetry* **1997**, *8*, 3955.

(3) Curran, D. P.; Qi, H.; Geib, S. J.; DeMello, N. C. *J. Am. Chem. Soc*. **1994**, *116*, 3131.

(4) (a) Kishikawa, K.; Tsuru, I.; Kohomoto, S.; Yamamoto, M.; Yamada, K. *Chem. Lett*. **1994**, 1605. (b) Hughes, A. D.; Price, D. A.; Shishkin, O.; Simpkins, N. S. *Tetrahedron Lett*. **1996**, *37*, 7607. (c) Bach, T.; Schröder, J.; Harms, K. *Tetrahedron Lett*. **1999**, *40*, 9003.

(5) Kitagawa, O.; Izawa, H.; Taguchi, T.; Shiro, M. *Tetrahedron Lett*. **1997**, *38*, 4447.

(6) (a) Hughes, A. D.; Simpkins, N. S. *Synlett* **1998**, 967. (b) Hughes, A. D.; Price, D. A.; Simpkins, N. S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1295. (c) Kondo, K.; Fujita, H.; Suzuki, T.; Murakami, Y. *Tetrahedron Lett*. **1999**, *40*, 5577. (d) Curran, D. P.; Liu, W.; Chen, C. H. *J. Am. Chem. Soc*. **1999**, *121*, 11012. (e) Shimizu, K. D.; Freyer, H. O.; Adams, R. D. *Tetrahedron Lett*. **2000**, *41*, 5431. (f) Kondo, K.; Iida, T.; Fujita, H.; Suzuki, T.; Yamaguchi, K.; Murakami, Y. *Tetrahedron* **2000**, *56*, 8883. (g) Godfrey, C. R. A.; Simpkins, N. S.; Walker, M. D. *Synlett* **2000**, 388. (h) Ates, A.; Curran, D. P. *J. Am. Chem. Soc*. **2001**, *123*, 5130.

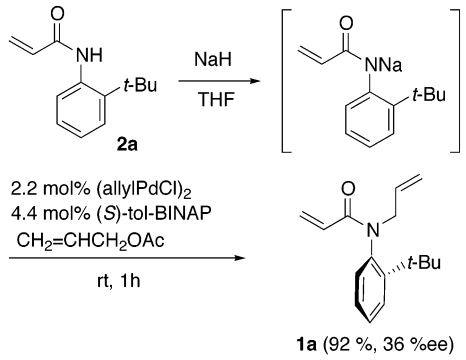
(7) Our papers on the preparation of optically active atropisomeric anilides through other methods: (a) Kitagawa, O.; Izawa, H.; Sato, K.; Dobashi, A.; Taguchi, T.; Shiro, M. *J. Org. Chem*. **1998**, *63*, 2634. (b) Fujita, M.; Kitagawa, O.; Izawa, H.; Dobashi, A.; Fukaya, H.; Taguchi, T. *Tetrahedron Lett*. **1999**, *40*, 1949 (Corrigendum: Fujita, M.; Kitagawa, O.; Izawa, H.; Dobashi, A.; Fukaya, H.; Taguchi, T. *Tetrahedron Lett*. **2000**, *41*, 4997). (c) Kitagawa, O.; Momose, S.; Fushimi, Y.; Taguchi, T. *Tetrahedron Lett*. **1999**, *40*, 8827. (d) Fujita, M.; Kitagawa, O.; Yamada, Y.; Izawa, H.; Hasegawa, H.; Taguchi, T. *J. Org. Chem*. **2000**, *65*, 1108. (e) Kitagawa, O.; Fujita, M.; Kohriyama, M.; Hasegawa, H.; Taguchi, T. *Tetrahedron Lett*. **2000**, *41*, 8539.

(8) (a) Hata, T.; Koide, H.; Taniguchi, N.; Uemura, M. *Org. Lett*. **2000**, *2*, 1907. (b) Koide, H.; Hata, T.; Uemura, H. *J. Org. Chem*. **2002**, *67*, 1929.

(9) *N*,*N*-Dialkyl 2,6-disubstituted aromatic amides are also known to exist as stable nonbiaryl atropisomeric compounds at room temperature. Recently, the synthesis of optically active forms of these compounds has been reported by several groups, while there is no report on their catalytic asymmetric synthesis except for kinetic resolution. (a) Thayumanavan, S.; Beak, P.; Curran, D. P. *Tetrahedron Lett*. **1996**, *37*, 2899. (b) Clayden, J.; Lai, L. W. *Angew. Chem., Int. Ed*. **1999**, *38*, 2556. (c) Clayden, J.; Mitjans, D.; Youssef, L. H. *J. Am. Chem. Soc*. **2002**, *124*, 5266. (d) Rios, R.; Jimeno, C.; Carrol, P. J.; Walsh, P. J. *J. Am. Chem. Soc*. **2002**, *124*, 10272.

10.1021/jo0264271 CCC: $22.00
Published on Web 10/31/2002

SCHEME 2



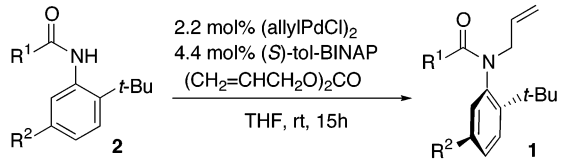
1 week at 25 °C. In contrast, *N*-nonsubstitued *o-tert*-butylanilides are nonatropisomeric compounds, because free rotation around the N−Ar bond from the amide hydrogen site easily occurs at room temperature. We expected that catalytic asymmetric synthesis of atropisomeric anilides may be possible by enantioselective *N*-allylation of *N*-nonsubstitued *o-tert*-butylanilides with a chiral π-allyl palladium complex (Scheme 1).[10]

On the basis of this concept, in the presence of a chiral phosphine−palladium catalyst (chiral phosphine 0.044 equiv; allyl palladium chloride dimer 0.022 equiv) and allyl acetate (1.5 equiv), *N*-allylation of Na amide prepared from *N*-2-(*tert*-butyl)phenyl propenamide **2a** and NaH (1.0 equiv) was examined in THF at room temperature. Although a survey of various representative chiral phosphine ligands was performed [(*R*,*R*)-DIOP, (*R*,*R*)-CHIRAPHOS, (*S*,*S*)-NORPHOS, (*S*,*S*)-BCPMA, (*S*)-PHANEPHOS, (*S*)-xyl-BINAP, (*S*)-BINAPO, (−)-DTMB-SEGPHOS, (*R*,*R*)-Trost ligand,[11] (*R*)-(*S*)-BPPFA, (*R*)-(*S*)-BPPFAOAc, (*R*)-(*S*)-BPPFNMe$(CH_2)_2$OH,[12] (*R*)-N,P-ligand[13]], in most cases, *N*-allyl anilide **1a** was obtained as a racemic form or in poor enantioselectivity (≤20% ee). The best enantioselectivity was observed in the reaction with (*S*)-tol-BINAP;[14] in this case, **1a** of 36% ee was obtained in excellent chemical yield (92%) (Scheme 2).[15]

For further improvement of the enantioselectivity, the solvent (THF, toluene, DMF, CH_2Cl_2), base (NaH, KH, *tert*-BuOK, *n*-BuLi, Et_2Zn, NaH-15-crown-5, NaH-*n*-Bu_4NBr), Pd-catalyst [allylpalladium chloride dimer, Cl_2Pd$(PhCN)_2$, Pd$(OOCCF_3)_2$], and reaction temperature (−15 °C, 0 °C, rt) were investigated in the presence of (*S*)-tol-BINAP catalyst. However, in all cases, an optical yield of more than 36% ee could not be observed.

Allylation reagents such as cinnamyl acetate, prenyl acetate, 2-benzyloxy-2-propenyl acetate, and diallyl carbonate were also investigated, while a better result than that using allyl acetate was not obtained except for the use of diallyl carbonate. A slight increase in the enantioselectivity (40% ee) was observed in the reaction with diallyl carbonate without the use of a base such as NaH (Table 1, entry 1).

TABLE 1. Catalytic Asymmetric *N*-Allylation of Various *N*-Nonsubstituted Amides 2



entry	**2**	R^1	R^2	**1**	yield (%)[a]	ee (%)[b]	$[\alpha]_D$[c] S or R
1	**2a**	CH_2=CH	H	**1a**	94	40	+74.9 (*S*)
2	**2b**	MeO_2C	H	**1b**	92	44	+55.0 (*S*)
3	**2c**	*trans*-CH_3CH=CH	H	**1c**	93	36	+71.8 (*S*)
4	**2d**	*trans*-PhCH=CH	H	**1d**	96	37	+75.1 (*S*)
5	**2e**	PhC=O	H	**1e**	95	35	+72.1 (*S*)
6	**2f**	CH_3CH_2	H	**1f**	90	32	+44.2[d]
7	**2g**	CH_3	H	**1g**	93	36	+48.3[d]
8	**2h**	CH_2=CH	*t*-Bu	**1h**	92	35	+54.7[d]
9	**2i**	2-furyl	H	**1i**	96	34	+35.7[d]
10[e]	**2j**	C_6H_5	H	**1j**	96	33	+20.4[d]

[a] Isolated yield. [b] The ee was determined by HPLC analysis using a chiral column (CHIRALPAK AS or CHIRALCEL OD).[c] $[\alpha]_D$ value in $CHCl_3$ (c = 1). [d] The absolute stereochemistry was not determined. [e] The reaction was carried out in the presence of allyl acetate and NaH.

The asymmetric *N*-allylation of various *N*-nonsubstitued *o-tert*-butylanilides **2b**−**j** was further examined under the optimized conditions [(*S*)-tol-BINAP (0.044 equiv), allyl palladium chloride dimer (0.022 equiv), diallyl carbonate (1.5 equiv) in THF at room temperature for 15 h] (Table 1). All reactions proceeded smoothly to give the products **1b**−**j** in excellent yields (≥90%), but in moderate enantioselectivity (32−44% ee) (entries 2−10). For example, the reaction of amide ester **2b** gave *N*-allyl anilide **1b** in 44% ee (Entry 2). In reactions with other amides such as α,β-unsaturated amides **2c**,**d**,**h**, ketoamide **2e**, saturated amides **2f**,**g**, and aromatic amides **2i**,**j**, products **1c**−**j** were obtained in an enantiomeric excess of less than 40% (32−37% ee) (entries 3−10). In the case of benzamide **2j**, the reaction was carried out under basic conditions using NaH and allyl acetate (entry 10), while formation of product **1j** was not detected using diallyl carbonate.

The absolute stereochemistries of *N*-allyl amides **1a**−**e** (entries 1−5) obtained by the use of (*S*)-tol-BINAP were confirmed to be the *S*-configuration on the basis of our previous reports.[7a,c] The stereochemistries of amides **1f**−**j** (entries 6−10), which have positive $[\alpha]_D$ values like **1a**−**e**, were also tentatively predicted to be the *S*-configuration.

An attempt to improve the enantiomeric excess of the anilide through recrystallization was next investigated. We already found that amide ester **1b** is an important intermediate for the preparation of various atropisomeric anilides.[7c] Unfortunately, since **1b** having low optical purity is an oil, recrystallization was performed by using a crystalline derivative from **1b** (Scheme 3). After condensation of **1b** (37%ee) and *p*-nitroaniline (89% yield), the resulting bisanilide **3b** was successively recrystallized

(10) For reviews on catalytic asymmetric allylation with a chiral π-allylpalladium complex see: (a) Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH Publishers: New York, 1994; pp 325−365. (b) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (c) Williams, J. M. *Synlett* **1996**, 705.

(11) (a) Trost, B. M.; Radinov, R.; Grenzer, E. M. *J. Am. Chem. Soc.* **1997**, *119*, 7879. (b) Trost, B. M.; Schroeder, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 6759.

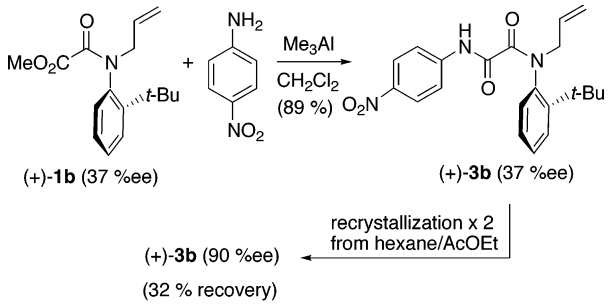
(12) Hayashi, T.; Kanehira, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1988**, *53*, 113.

(13) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336.

(14) (a) Noyori, Y.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (b) Mashima, K.; Kusano, K.; Sato, N.; Matsumura, Y.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizuka, T.; Akutagawa, S.; Takaya, H. *J. Org. Chem.* **1994**, *59*, 3064.

(15) The reaction with (*S*)-BINAP gave the **1a** of 33% ee.

SCHEME 3



from hexane and AcOEt (3:1) twice. The ee of **3b** obtained from the supernatant liquor was found to increase to 90% (32% recovery).

In conclusion, we have found catalytic asymmetric *N*-allylation of *N*-nonsubstituted *o*-*tert*-butylanilides with a tol-BINAP-palladium catalyst. Although the enantioselectivities are low (32−44% ee), the present reaction is the first example of catalytic enantioselective synthesis of nonbiaryl atropisomeric compounds and should provide a new possible method for the catalytic asymmetric synthesis of optically active atropisomeric anilde having an N−C chiral axis.

Experimental Section

Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 300- or 400-MHz spectrometer. In ^{1}H and ^{13}C NMR spectra, chemical shifts were expressed in δ (ppm) downfield from $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm), respectively. Mass spectra were recorded by electron impact or chemical ionization. Column chromatography was performed on silica gel (75−150 μm). Medium-pressure liquid chromatography (MPLC) was performed on a 30 × 4 cm i.d. prepacked column (silica gel, 50 μm) with a UV detector. High-performance liquid chromatography (HPLC) was performed on a 25 × 0.4 cm i.d. chiral column with a UV detector.

General Procedure of Asymmetric Allylation Using tol-BINAP-Pd Complex. Under Ar atmosphere, to a solution of allylpalladium chloride dimer (4 mg, 0.011 mmol) and (*S*)-tol-BINAP (15 mg, 0.022 mmol) in THF (3 mL) was added diallyl carbonate (108 μL, 0.75 mmol), and then the reaction mixture was stirred for 10 min at room temperature. Subsequently, acryl amide **2a** (102 mg, 0.5 mmol) was added to the mixture. After being stirred for 15 h at room temperature, the mixture was poured into 2% HCl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 20) gave (+)-**1a** (114 mg, 94%).

(*S*)-*N*-Allyl-*N*-2-(*tert*-Butyl)phenyl Propeamide [(+)-1a]. The ee (40% ee) of (+)-**1a** was determined by HPLC analysis using a CHIRALPACK AS column [25 cm × 0.46 cm i.d.; 0.1% *i*-PrOH in hexane; flow rate, 1.0 mL/min; (−)-**1a** (minor); t_R = 15.5 min, (+)-**1a** (major); t_R = 20.6 min]. (+)-**1a**: $[\alpha]_D$ +74.9 (*c* 0.9, $CHCl_3$, 40% ee). ^{1}H NMR data of **1a** coincided with those reported in our previous literature.[7a]

(*S*)-Methyl 2-[Allyl-2-(*tert*-butyl)anilino]-2-oxoacetate [(+)-1b]. (+)-**1b** was prepared from **2b** (118 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of (+)-**1a**. Purification by column chromatography (hexane/AcOEt = 12) gave (+)-**1b** (127 mg, 92%). The ee (44% ee) of (+)-**1b** was determined by HPLC analysis using a CHIRALPACK AS column [25 cm × 0.46 cm i.d.; 1% *i*-PrOH in hexane; flow rate, 0.5 mL/min; (−)-**1b** (minor); t_R = 16.3 min, (+)-**1b** (major); t_R = 18.9 min]. (+)-**1b**: colorless oil; $[\alpha]_D$ +55.0 (*c* 1.0, $CHCl_3$, 44% ee); IR (neat) 1740, 1663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55 (1H, dd, *J* = 1.3, 8.2 Hz), 7.32 (1H, dt, *J* = 1.3, 8.0 Hz), 7.12 (1H, dt, *J* = 1.3, 8.0 Hz), 6.96 (1H, dd, *J* = 1.3, 7.8 Hz), 5.93 (1H, dddd, *J* = 5.4, 8.1, 10.2, 17.3 Hz), 5.21 (1H, d, *J* = 10.0 Hz), 5.15 (1H, dd, *J* = 1.0, 17.3 Hz), 4.93 (1H, dd, *J* = 5.4, 14.1 Hz), 3.53 (3H, s), 3.45 (1H, dd, *J* = 8.1, 14.1 Hz), 1.42 (9H, s); ^{13}C NMR ($CDCl_3$) δ 162.3, 161.0, 147.3, 135.9, 132.2, 130.7, 130.4, 129.1, 126.0, 119.9, 53.5, 51.9, 36.3, 32.2; MS (*m*/*z*) 275 (M^+). Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.76; N, 5.04. Found: C, 69.79; H, 7.69; N, 5.09. In ^{1}H and ^{13}C NMR spectra of **1b**, the minor signals on the basis of the existence of the amide C−N rotamer were also observed in a ratio of 8.2:1.

(*S*)-*N*-Allyl-*N*-(2-*tert*-butylphenyl)-*N*′-(4-nitrophenyl)oxalamide [(+)-3b]. Under Ar atmosphere, to a solution of *p*-nitroaniline (2.07 g, 15 mmol) in CH_2Cl_2 (120 mL) was added a 1 M hexane solution of Me_3Al (18 mL, 18.0 mmol) at 0 °C, and then the reaction mixture was stirred for 20 min at room temperature. Subsequently, (+)-**1b** (1.38 g, 5 mmol, 37% ee) was added to the mixture. After being stirred for 1 h at room temperature, the mixture was poured into 10% HCl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave (+)-**3b** (1.70 g, 89%, 37% ee). The ee (37% ee) of (+)-**3b** was determined by HPLC analysis using a CHIRALPACK AS column [25 cm × 0.46 cm i.d.; 5% *i*-PrOH in hexane; flow rate, 1.0 mL/min; (−)-**3b** (minor); t_R = 10.2 min, (+)-**3b** (major); t_R = 14.9 min]. (+)-**3b**: white solid; mp 165−167 °C; $[\alpha]_D$ +52.1 (*c* 1.0, $CHCl_3$, 37% ee); IR (KBr) 3290, 1704, 1644 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.79 (1H, br s), 8.14 (2H, d, *J* = 9.4 Hz), 7.66 (2H, *J* = 9.4 Hz), 7.60 (1H, dd, *J* = 1.5, 8.0 Hz), 7.37 (1H, dt, *J* = 1.5, 8.0 Hz), 7.19 (1H, dt, *J* = 1.5, 8.0 Hz), 6.93 (1H, dd, *J* = 1.5, 8.0 Hz), 6.00 (1H, dddd, *J* = 5.6, 7.6, 10.0, 17.0 Hz), 5.28 (1H, d, *J* = 10.0 Hz), 5.21 (1H, dd, *J* = 1.2, 17.0 Hz), 4.96 (1H, dd, *J* = 5.6, 14.1 Hz), 3.52 (1H, dd, *J* = 7.6, 14.1 Hz), 1.39 (9H, s); ^{13}C NMR ($CDCl_3$) δ 160.0, 157.0, 144.7, 143.9, 142.4, 139.4, 130.5, 130.0, 129.9, 128.6, 126.4, 124.9, 120.4, 119.2, 57.3, 36.2, 32.3; MS (*m*/*z*) 381 (M^+). Anal. Calcd for $C_{21}H_{23}N_3O_4$: C, 66.13; H, 6.08; N, 11.02. Found: C, 66.33; H, 6.18; N, 10.98. In ^{1}H and ^{13}C NMR spectra of **3b**, the minor signals on the basis of the existence of the amide C−N rotamer were also observed in a ratio of 4.5:1.

Improvement of Enantiomeric Excess by Recrystallization. After diamide **3b** (1.70 g, 4.46 mmol, 37%ee) was dissolved in AcOEt (17 mL), to this solution was added hexane (51 mL), and then the mixture was left for 24 h at room temperature. The supernatant liquor and the precipitated crystal were separated by decantation. Evaporation of the filtrate gave **3b** (800 mg, 47% recovery) of 69% ee. Repeatedly, a solution of **3b** of 69% ee (800 mg) in AcOEt (8.0 mL) and hexane (32 mL) was left to stand for 24 h at room temperature, and then the precipitates were removed by decantation. Evaporation of the filtrate gave **3b** of 90% ee (549 mg, total 32% recovery). (+)-**3b**: white solid; mp 65−68 °C; $[\alpha]_D$ +126.8 (*c* 1.0, $CHCl_3$, 90% ee).

Acknowledgment. We gratefully thank the Takasago International Corporation for our supply of chiral phosphine ligands [(−)-DTBM-SEGPHOS and (*S*)-xyl-BINAP].

Supporting Information Available: Experimental procedures for the preparation and characterization data of products **1c**−**j**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0264271