Efficient Synthesis of Optically Active 2-*N*-Boc (or Cbz)-amino-1-arylethanols as Key Intermediates for Synthesis of Chiral Drugs *via* Asymmetric Reduction

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Received February 23, 2004

Key Words : Asymmetric reduction, Oxazaborolidine-catalyzed reduction, Chiral drugs, Chiral 2-*N*-Boc-amino-1-arylethanols, (*S*)-CBS-oxazaborolidine

Optically active 2-amino-1-arylethanols are important structural elements in chiral drugs such as α- or β-adrenergic blockers and agonists in the treatment of cardiovascular disease, cardiac failure, asthma and glaucoma.[1] Examples for such chiral drugs include (*R*)-phenylephrine (**1**), (*R*)-norfenifefrine (**2**), (*R*)-synephrine (**3**), (*R*)-octopamine (**4**) and (*R*)-pronethalol (**5**), (*R*)-tembamide (**6**) and (*R*)-aegeline (**7**) (Figure 1). For the synthesis of chiral 2-amino-1-arylethanols, catalytic hydrogenation of optically active 2-azido-1-arylethanols obtained from enzymatic resolution of racemic mixture,[2] enantio- or regioselective azidolysis of chiral aryloxiranes,[3a-f] azidation of chiral 1,2-diol monotosylates and asymmetric reduction of 2-azido-1-arylethanones[4a,b,5,6] have been reported. However, the resolution methods suffer from the fact that the theoretical yields are limited to 50%.[2b] Azidolysis of aryloxiranes are commonly accompanied by the formation of undesired regioisomers with the azido group at the benzylic position.[3b-f] For other synthetic methods of non-racemic β-amino alcohols, reduction of chiral arylcyanonohydrins[7] and aminolysis of chiral 1,2-diol monotosylates have been published.[8] One of the most convenient synthesis is the direct asymmetric reduction of *N*-protected β-amino ketones. For this, there are only two reports including bakers yeast reduction[9] and asymmetric transfer hydrogenation[10] of α-(acyl or alkoxycarbonylamino)-acetophenones. Since Itsuno[11] and Corey[12] reported the first oxazaborolidine-catalyzed asymmetric borane reduction, a number of such reductions of prochiral ketones has been extensively studied. However there are no reports for the asymmetric reduction of α-amino ketone derivatives using these catalytic reducing agents. Recently we reported very effective CBS-oxazaborolidine-catalyzed asymmetric borane reduction of various α-functionalized ketones to give the corresponding alcohols with high enantioselcetivies.[13] On the other hand, it has been known that (–)-*B*-chlorodiisopinocampheylborane (^{d}Ipc$_2$BCl) is a commercially available and highly effective asymmetric reducing agent for the asymmetric reduction of various prochiral ketones to provide high enantioselectivity with predictable stereochemistry.[14] In connection with our continuing efforts toward asymmetric reduction of functionalized ketones, we investigated the asymmetric reduction of 2-*N*-Boc (or Cbz)-amino-1-arylethanones using those chiral reducing agents.

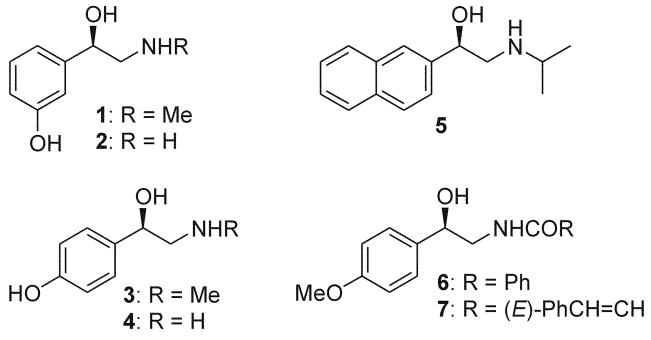
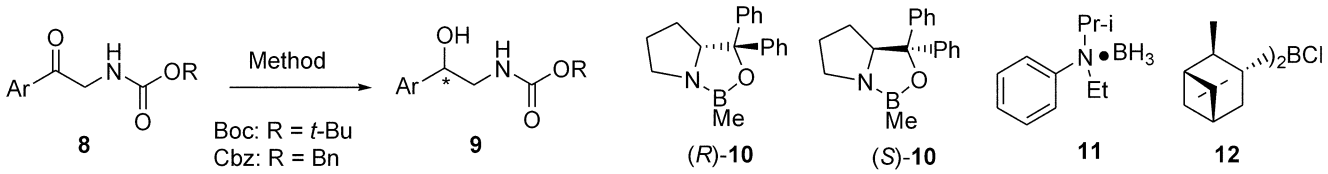


Figure 1.

First, we carried out (*S*)-CBS-oxazaborolidine (**10**)-catalyzed asymmetric borane reduction of 2-*N*-Boc-amino-1-phenylethanone **8a** using environmentally benign borane carrier, *N*-ethyl-*N*-isopropylaniline-borane complex **11**, as the hydride source in THF at 25 °C (Method A). As shown in Table 1, slow addition of **8a** over 1 h to a solution of 0.6 equiv of borane-THF in the presence of 10 mol% of (*S*)-**10** in THF at 25 °C afforded 2-*N*-Boc-amino-1-phenylethanol (**9a**) within 10 min in 93% yield. HPLC analysis of **9a** using a Chiralcel OD-H column (eluent : hexane/*i*-PrOH/Et$_2$NH = 95 : 5 : 0.1) showed it to be 98% ee (entry 1). The reduction of **8b**, protected with Cbz group instead of Boc group of **8a**, provided a similar result under the identical condition (entry 2). Also, we investigated the reduction of **8a** and **8b** with ^{d}Ipc$_2$BCl (**12**). Unfortunately, the reduction using 1.2 equiv of **12** in THF at -25 °C (Method C) afforded **9a** and **9b** in low yields with moderate enantioselectivity (entries 3-4). On the other hand, (*R*)-2-*N*-Boc-amino-1-(3'-benzyloxyphenyl)-ethanol (**9c**), (*R*)-2-*N*-Boc-amino-1-(4'-benzyloxyphenyl)-ethanol (**9d**), (*R*)-2-*N*-Boc-amino-1-(4'-methoxyphenyl)-ethanol (**9e**) and (*R*)-2-*N*-Boc-amino-1-(2-naphthyl)ethanol (**9h**) can be effectively used as key intermediates for the synthesis of chiral drugs **1**-**7**. Therefore we applied the CBS-oxazaborolidine-catalyzed reduction to the synthesis of these intermediates. Thus, the reduction of **8c-e** using (*R*)-**10** as the catalyst (Method B) under the same conditions as those adopted in Method A provided **9c-h** with high enantioselectivities in high yields (entries 5-7 and 10). Similarly, the CBS-oxazaborolidine reduction of other *N*-Boc amino ketones including a heterocyclic analogue provided good enantioselectivities (entry 8-9 and 11). In summary, we have established an efficient synthesis of optically active 2-*N*-

Table 1. Asymmetric Reduction of 2-*N*-Boc (or Cbz)-Amino-1-Arylethanones



8 **9** (*R*)-**10** (*S*)-**10** **11** **12**

No	**1**			**2**[b]				
		Ar	R	Method[a]	Yield (%)	Mp (°C)	$[\alpha]_D^{20}$ (*c*, $CHCl_3$)	% ee	Config.
1	**9a**	C_6H_5	*t*-Bu	A	93	68-69[c]	+54.18 (0.6)[d]	98[e]	S[d]
2	**9b**	C_6H_5	Bn	A	92	106-108	+44.2 (*c* 0.5)	97[f]	*S*[g]
3	**9a**	C_6H_5	*t*-Bu	C	17	h	h	80[e]	*R*[g]
4	**9b**	C_6H_5	Bn	C	20	h	h	48[e]	*R*[g]
5	**9c**	*m*-$BnOC_6H_4$	*t*-Bu	B	93	77-79	–30.6 (*c* 0.5)	88[i]	*R*[g]
6	**9d**	*p*-$BnOC_6H_4$	*t*-Bu	B	96	138-140	–33.74 (*c* 0.7)	93[e]	*R*[g]
7	**9e**	*p*-$MeOC_6H_4$	*t*-Bu	B	95	74-76	–37.2 (*c* 1.0)	81[e]	*R*[g]
8	**9f**	*p*-MeC_6H_4	*t*-Bu	A	96	60-62	+43.8 (*c* 1.0)	87[e]	*S*[g]
9	**9g**	*p*-ClC_6H_4	*t*-Bu	A	95	70-72	+46.3 (*c* 0.5)	89[e]	*S*[g]
10	**9h**	2-Naphthyl	*t*-Bu	B	95	92-94	–46.2 (*c* 0.7)	87[e]	*R*[g]
11	**9i**	2-Thienyl	*t*-Bu	A	94	100-101	+37.3 (*c* 0.9)	82[e]	*R*[g]

[a]Method A = [**8**] : [(*S*)-**10**] : [**11**] = 1 : 0.1 : 1, THF, 25 °C. Method B = [**8**] : [(*R*)-**10**] : [**11**] = 1 : 0.1 : 1, THF, 25 °C. Method C = [**8**] : [**12**] = 1 : 1.2, THF, -25 °C. [b]Fully characterized by ^1H, ^{13}C NMR and IR spectra and elemental analysis. [c]66-68 °C: ref. 10. [d]$[\alpha]_D^{20}$ +3.7 (1.0, EtOH) (lit.[10] +3.5 (1.0, EtOH), 99% ee, *S*. [e]Determined by HPLC analysis using Dairalcel OD-H column; eluent: hexane-EtOH-Et_2NH 95 : 5 : 0.1. [f]Determined by HPLC analysis using Dairalcel OD-H column; eluent: hexane-*i*-PrOH 9 : 1. [g]By analogy based on the sign of optical rotation value and the elution order of HPLC analysis. [h]Not determined. [i]By comparison with optical rotation value of its authentic sample.

Boc-amino-1-arylethanols which can be used as key intermediates for the synthesis of various chiral β-adrenergic drugs by oxazaborolidine-catalyzed reduction using (*R*)-**10** as catalyst.

Experimental Section

General. The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230-400 mesh). NMR spectra were recorded at 300 MHz for ^1H and 75 MHz for ^{13}C using Me_4Si as the internal standard in $CDCl_3$ unless otherwise noted. Optical rotations were measured with a high resolution digital polarimeter. Melting points were uncorrected. Most of organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation when necessary. THF was distilled over sodium benzophenone ketyl and stored in ampules under nitrogen atmosphere. (*R*)- and (*S*)-CBS-oxazaborolidine reagent **10**, *N*-ethyl-*N*-isopropylaniline-borane complex **11** and (–)-*B*-chlorodiisopinocampheylborane **12** were purchased from the Aldrich Chemical Company. Enantiomeric excesses (ees) of the products were determined with a HPLC apparatus fitted with a 25 cm Chiralcel OD-H (Daicel) chiral column using hexane/ethanol/diethylamine 95 : 5 : 0.1 as eluent unless otherwise indicated.

Asymmetric Reduction of 2-*N*-Boc (or Cbz)-amino-1-arylethanones 1.

General Procedure: Method A and B: The reduction was carried out in THF at 25 °C using (*R*)- or (*S*)-**10** and **11** as catalyst and borane carrier, respectively, according to the known procedure.[13] Method C: The reduction was carried out by the literature procedure.[15] The reduction product β-amino alcohol derivatives obtained were further purified by a flash column chromatography on silica gel (230-400 mesh) using EtOAc/hexane 1 : 2 as eluent.

(*S*)-2-*N*-Boc-amino-1-phenylethanol 9a: R_f 0.35; 93% yield; mp 68-69 °C (lit.[10] 66-68 °C); IR (KBr, cm^{-1}) 3371, 3297, 2983, 2927, 1669, 1534, 1269, 1165; ^1H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 3.09 (brs, 1H), 3.19-3.28 (m, 1H), 3.43-3.51 (m, 1H), 4.80 (dd, *J* = 3.44, 7.84 Hz, 1H), 4.93 (brs, 1H), 7.26-7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.72, 48.70, 74.26, 80.12, 126.05, 127.97, 128.66, 141.97; Calcd. for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90. Found: C, 65.65; H, 8.06; N, 6.09; $[\alpha]_D^{20}$ +54.18 (*c* 0.6, $CHCl_3$), +3.7 (*c* 1.0, EtOH) {lit.[10] $[\alpha]_D^{20}$ +3.7 (c 1, EtOH), 99% ee, *S*}; HPLC analysis showed it to be 98% ee, *S* [flow rate = 0.5 mL/min; t_R(*R*) 19.26 min and t_R(*S*) 21.16 min].

(*S*)-2-*N*-Cbz-amino-1-phenylethanol 9b: R_f 0.52; 92% yield; mp 106-108 °C; IR (KBr, cm^{-1}) 313, 3028, 2948, 2893, 1690, 1546, 1452, 1268, 1065; ^1H NMR (300 MHz, $CDCl_3$) δ 3.25-3.34 (m, 1H), 3.51-3.59 (m, 1H), 4.82 (dd, *J* = 3.58, 7.98 Hz, 1H), 5.09 (s, 2H), 5.21 (brs, 1H), 7.25-7.34 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.84, 67.29, 73.93, 126.07, 128.19, 128.35, 128.41, 128.76, 128.78, 136.47, 141.65, 157.30; Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.81; H, 6.30; N, 5.19; $[\alpha]_D^{20}$ +44.2 (*c* 1.0, $CHCl_3$); HPLC analysis determined by a 25 cm Chiralcel OD-H (Daicel) chiral column using hexane/iso-PrOH 9 : 1 as eluent showed it to be 97% ee, *S* [flow rate = 1.0 mL/min; t_R(*R*) 17.42 min and t_R(*S*) 24.67 min].

(*R*)-2-*N*-Boc-amino-1-(3'-benzyloxyphenyl)ethanol 9c: R_f 0.30; 93% yield; mp 77-79 °C; IR (KBr, cm^{-1}) 3467, 3376, 2974, 2934, 1671, 1534, 1368, 1255, 1156; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 3.18-3.27 (m, 1H), 3.43-3.50 (m, 1H), 4.77-4.80 (m, 1H), 4.96 (brs, 1H), 5.04 (s, 2H), 6.86-7.01 (m, 3H), 7.22-7.43 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.74, 48.68, 70.24, 74.22, 80.21, 112.44, 114.41, 118.65, 127.73, 128.19, 128.78, 129.78, 137.04, 143.72, 159.10; Calcd. for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; N, 4.08. Found: C, 69.89; H, 7.41; N, 4.05; $[\alpha]_D^{20}$ -30.6 (*c* 0.5, $CHCl_3$). This value is correspondent to be 88% ee by comparison with optical rotation value of authentic **9c** in 100% ee {$[\alpha]_D^{20}$ -34.8 (*c* 0.3, $CHCl_3$)} obtained from catalytic hydrogenation of the corresponding azido alcohol proven to be 100% ee by HPLC analysis using a Chiralcel OD-H chiral column.

(*R*)-2-*N*-Boc-amino-1-(4'-benzyloxyphenyl)ethanol 9d: R_f 0.29; 96% yield; mp 138-140 °C; IR (KBr, cm^{-1}) 3472, 3424, 2973, 2934, 1676, 1512, 1230, 1165; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 2.85 (brs, 1H), 3.19-3.28 (m, 1H), 3.41-3.43 (m, 1H), 4.75-4.77 (m, 1H), 4.89 (brs, 1H), 5.05 (s, 2H), 6.93-6.96 (m, 2H), 7.24-7.43 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.74, 48.67, 70.34, 73.80, 80.05, 115.08, 107.32, 127.62, 128.14, 128.76, 134.44, 137.12, 158.60; Calcd. for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; N, 4.08. Found: C, 69.86; H, 7.45; N, 4.06; $[\alpha]_D^{20}$ -33.74 (*c* 0.7, $CHCl_3$); HPLC analysis showed it to be 93% ee, *R* [flow rate = 0.5 mL/min; t_R(*R*) 17.02 min and t_R(*S*) 20.46 min].

(*R*)-2-*N*-Boc-amino-1-(4'-methoxyphenyl)ethanol 9e: R_f 0.17; 95% yield; mp 74-76 °C; IR (KBr, cm^{-1}) 3403, 3371, 2977, 2932, 1671, 1512, 1252, 1169; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 3.11 (brs, 1H), 3.19-3.26 (m, 1H), 3.38-3.45 (m, 1H), 3.79 (s, 3H), 4.74-4.76 (m, 1H), 4.98 (brs, 1H), 6.85-6.88 (m, 2H), 7.24-7.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.73, 48.69, 55.60, 73.85, 80.05, 114.13, 127.28, 134.12, 159.42; Calcd. for $C_{14}H_{21}NO_4$: C, 62.90; H, 7.92; N, 5.24. Found: C, 62.93; H, 8.01; N, 5.31; $[\alpha]_D^{20}$ -37.2 (*c* 1.0, $CHCl_3$); HPLC analysis showed it to be 81% ee, *R* [flow rate = 0.5 mL/min; t_R(*R*) 11.07 min and t_R(*S*) 13.27 min].

(*S*)-2-*N*-Boc-amino-1-(4-tolyl)ethanol 9f: R_f 0.29; 96% yield; mp 60-62 °C; IR (KBr, cm^{-1}) 3418, 3370, 2981, 2934, 1691, 1514, 1175; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 2.33 (s, 3H), 2.98 (brs, 1H), 3.17-3.26 (m, 1H), 3.40-3.47 (m, 1H), 4.76 (dd, *J* = 3.30, 7.70 Hz, 1H), 4.93 (brs, 1H), 7.12-7.23 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.77, 29.01, 49.01, 74.39, 80.44, 126.52, 129.86, 138.18, 139.55, 157.57; Calcd. for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57. Found: C, 66.92; H, 8.46; N, 5.58; $[\alpha]_D^{20}$ +43.8 (*c* 1.0, $CHCl_3$); HPLC analysis showed it to be 87% ee, *S* [flow rate = 0.5 mL/min; t_R(*R*) 14.22 min and t_R(*S*) 16.68 min].

(*S*)-2-*N*-Boc-amino-1-(4'-chlorophenyl)ethanol 9g: R_f 0.27; 95% yield; mp 70-72 °C; IR (KBr, cm^{-1}) 3372, 3312, 2976, 2933, 1685, 1534, 1285, 1167, 1091; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 3.16-3.25 (m, 1H), 3.40-3.46 (m, 1H), 4.75-4.81 (m, 1H), 4.93 (brs, 1H), 7.24-7.34 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.68, 48.72, 73.70, 79.96, 127.45, 128.77, 128.83, 133.62, 140.51; Calcd. for $C_{13}H_{18}ClNO_4$: C, 57.46; H, 6.68; N, 5.15. Found: C, 57.44; H, 6.59; N, 5.13; $[\alpha]_D^{20}$ +46.3 (*c* 0.5, $CHCl_3$); HPLC analysis showed it to be 89% ee, *S* [flow rate = 0.5 mL/min; t_R(*R*) 7.82 min and t_R(*S*) 9.97 min].

(*R*)-2-*N*-Boc-amino-1-(2-naphthyl)ethanol 9h: R_f 0.27; 95% yield; mp 92-94 °C; IR (KBr, cm^{-1}) 3403, 3364, 3345, 2981, 1668, 1545, 1295, 1175; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 9H), 3.30-3.35 (m, 1H), 3.50-3.57 (m, 1H), 4.98 (m, 2H), 7.41-7.47 (m, 3H), 7.50-7.87 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.74, 48.66, 74.41, 80.27, 124.10, 124.95, 126.15, 126.43, 127.89, 128.17, 128.47, 133.17, 133.38, 139.37, 157.29; Calcd. for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 71.07; H, 7.32; N, 4.67; $[\alpha]_D^{20}$ -46.2 (*c* 0.7, $CHCl_3$); HPLC analysis showed it to be 87% ee, *R* [flow rate = 0.5 mL/min; t_R(*R*) 13.66 min and t_R(*S*) 15.96 min].

(*R*)-2-*N*-Boc-amino-1-(2-thienyl)ethanol 9i: R_f 0.24; 94% yield; mp 100-101 °C; IR (KBr, cm^{-1}) 3448, 3330, 2979, 1688, 1512, 1367, 1284, 1167; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 3.15-3.25 (m, 1H), 3.33-3.42 (m, 2H), 4.80-4.91 (m, 2H), 7.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.69, 48.76, 73.74, 80.36, 127.43, 128.79, 133.64, 140.48; Calcd. for $C_{11}H_{17}NO_3S$: C, 54.30; H, 7.04; N, 5.76; S, 13.18. Found: C, 54.30; H, 7.22; N, 5.65; S, 13.15; $[\alpha]_D^{20}$ +37.3 (*c* 0.9, $CHCl_3$); HPLC analysis showed it to be 82% ee, *R* [flow rate = 0.5 mL/min; t_R(*S*) 9.97 min and t_R(*R*) 11.00 min].

Acknowledgment. This study was financially supported by the Research Grant from Hallym University, Korea.

References

1. Crossley, R. In *Chirality and the Biological Activity of Drugs*; CRC Press: New York, 1995.
2. (a) Pàmies, O.; Bäckvall, J. E. *J. Org. Chem.* **2001**, *66*, 4022-4025. (b) Foelsche, E.; Hickel, A.; Hönig, H.; Seufer-Wasserthal, P. *J. Org. Chem.* **1990**, *55*, 1749.
3. (a) Lutje Spelberg, J. H.; van Hylckama Vlieg, J. E. T.; Tang, L.; Janssen, D. B.; Kellogg, R. M. *Organic Lett.* **2001**, 41. (b) Kamal, A.; Arifuddin, M.; Rao, M. V. *Tetrahedron: Asymmetry* **1999**, *10*, 4261. (c) Martínez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5897. (d) Megro, M.; Asao, N.; Yamamoto, Y. *J. Chem. Soc. Chem. Commun.* **1995**, 1021. (e) Guy, A.; Doussot, J.; Ferroud, C.; Garreau, A.; Godefroy-Falguieres, A. *Synthesis* **1992**, 821. (f) Guy, A.; Dubuffet, T.; Doussot, J.; Godefroy-Falguieres, A. *Synlett* **1991**, 403.
4. (a) Watanabe, M.; Murata, K.; Ikariya, T. *J. Org. Chem.* **2002**, *67*, 1712. (b) Yadav, J. S.; Reddy, P. T.; Hashim, S. R. *Synlett* **2000**, 1049.
5. Reddy, M. A.; Bhanumathi, N.; Rao, K. R. *J. Chem. Soc. Chem. Commun.* **2001**, 1974.
6. Yadav, J. S.; Reddy, P. T.; Nanda, S.; Rao, A. B. *Tetrahedron: Asymmetry* **2001**, *12*, 63.
7. (a) Ziegler, T.; Hörsch, B.; Effenberger, F. *Synthesis* **1990**, 575. (b) Midland, M. M.; Lee, P. E. *J. Org. Chem.* **1985**, *50*, 3239. (c) Jackson, W. R.; Jacobs, H. A.; Jayatilake, G. S.; Matthews, B. R.; Watson, K. G. *Aust. J. Chem.* **1990**, *43*, 2045. (d) Stork, G.; Worrall, W. S.; Pappas, J. J. *J. Am. Chem. Soc.* **1960**, *82*, 4315.

8. (a) Cho, B. T.; Kang, S. K.; Shin, S. H. *Tetrahedron: Asymmetry* **2002**, *13*, 1209. (b) Cho, B. T.; Kang, S. K.; Yang, W. K. *Bull. Korean Chem. Soc.* **2002**, *23*, 1328. (c) Shin, S. H.; Kang, S. K.; Cho, B. T. *Bull. Korean Chem. Soc.* **2003**, *24*, 1695.
9. (a) Izumi, T.; Fukaya, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1216. (b) Izumi, T.; Satou, K.; Ono, K. *J. Chem. Tech. Biotechnol.* **1996**, *66*, 233.
10. Kawamoto, A. M.; Wills, M. *J. Chem. Soc. Perkin Trans. 1* **2001**, 1916.
11. Itsuno, S.; Ito, K. *J. Org. Chem.* **1984**, *49*, 555. (e) Itsuno, S.; Nakano, M.; Miyazaki, K.; Masuda, H.; Ito, K.; Hirao, A.; Nakahama, S. *J. Chem. Soc. Perkin Trans. 1* **1985**, 2039.
12. (a) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551. (b) Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C.-P.; Singh, V. K. *J. Am. Chem. Soc.* **1987**, *109*, 7925.
13. Cho, B. T. *Aldrichimica Acta* **2002**, *35*, 3 and references cited therein.
14. For a recent review, see: Ramachandran, P. V.; Brown, H. C. in *Reductions in Organic Synthesis (ACS Symposium Series 641)*; Abdel-Magid, A. F., Ed.; American Chemical Society: Washington, DC, 1996; pp 884-897.
15. Cho, B. T.; Choi, O. K *Bull. Korean Chem. Soc.* **2001**, *22*, 443.