

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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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*)-norfenefrine (**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-arylethanols^{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 arylicyanonohydrins⁷ 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 baker's yeast reduction⁹ and asymmetric transfer hydrogenation¹⁰ of α -(acyl or alkoxy-carbonylamino)-acetophenones. Since Itsuno¹¹ and Corey¹² 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 enantioselectivities.¹³ On the other hand, it has been known that (*-*)-*B*-chlorodisopinocampheylborane (^dIpc₂BCl) 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.

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/Et₃NH = 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 ^dIpc₂BCl (**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*-

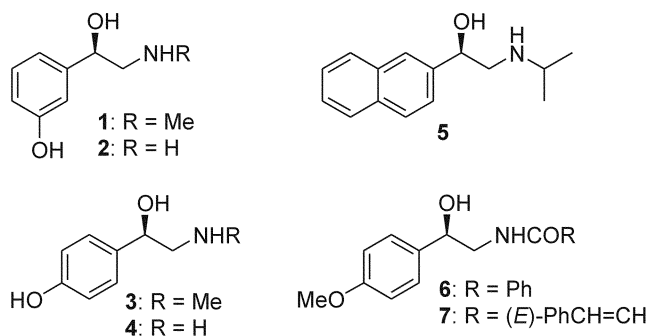


Figure 1.

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

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

^aMethod 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. ^bFully characterized by ¹H, ¹³C NMR and IR spectra and elemental analysis. ^c66-68 °C; rel. 10. ^d $[\alpha]_D^{20}$: +3.7 (1.0, EtOH) (lit.¹⁰ -3.5 (1.0, EtOH), 99% ee, *S*). ^eDetermined by HPLC analysis using Daicelcel OD-H column; eluent: hexane-EtOH-Et₃NH 95:5:0.1. ^fDetermined by HPLC analysis using Daicelcel OD-H column; eluent: hexane-*i*-PrOH 9:1. ^gBy analogy based on the sign of optical rotation value and the elution order of HPLC analysis. ^hNot determined. ⁱBy comparison with optical rotation value of its authentic sample.

Boc-amino-1-arylethanol 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 ¹³C using Me₄Si as the internal standard in CDCl₃ 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 or 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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) δ 28.72, 48.70, 74.26, 80.12, 126.05, 127.97, 128.66, 141.97; Calcd. for C₁₃H₁₉NO₃: 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, CHCl₃), -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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₆H₁₇NO₃: 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, CHCl₃); 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; ^1H 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 $\text{C}_{20}\text{H}_{25}\text{NO}_4$: 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; ^1H 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 $\text{C}_{20}\text{H}_{25}\text{NO}_4$: 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; ^1H 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 $\text{C}_{14}\text{H}_{21}\text{NO}_4$: 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; ^1H 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 $\text{C}_{14}\text{H}_{21}\text{NO}_3$: 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; ^1H 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 $\text{C}_{13}\text{H}_{18}\text{ClNO}_4$: 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; ^1H 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 $\text{C}_{17}\text{H}_{21}\text{NO}_3$: 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; ^1H 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 $\text{C}_{11}\text{H}_{17}\text{NO}_3\text{S}$: 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].

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