Chinese Journal of Chemistry, **2004**, *22*, 585—589

Article

Synthesis of *N*-Squaramidoacids and Their Application in Asymmetric Borane Reduction of Prochiral Ketones

ZHANG, Ji[a](张骥) LI, Lei-Lei[a](李蕾蕾) ZOU, Hai-Hua[a](邹海华)
CHEN, Jun-Jun[a](陈君君) YU, Kai-Bei[b](郁开北) XIE, Ru-Gang*[,a](谢如刚)

[a] *Department of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China*
[b] *Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan 610061, China*

A series of novel *N*-squaramidoacid ligands were prepared conveniently. Without converting to corresponding amino alcohols, these ligands could be used in asymmetric borane reduction of prochiral aromatic ketones to give secondary alcohols in good to excellent enantiomeric excesses. The results showed that *N*-squaramidoacids are more efficient ligands than *N*-sulfonyl amino acids. *N*-Squaryl proline was proved to be an excellent ligand in this catalytic asymmetric process.

Keywords amino acid, squaramidoacid, borane, ketone, asymmetric reduction

Introduction

Asymmetric reduction of prochiral ketones catalyzed by various chiral aminoalcohol ligands has been extensively studied.[1-3] In these studies, excellent results including chemical yields and enantiomeric excesses were achieved and the mechanism of this kind of reaction was studied. However, most aminoalcohol ligands employed were derived from amino acids through multiple-step synthesis including esterification and Grignard addition, with relatively low overall chemical yields. As a commercially available and inexpensive chiral source, amino acids themselves were rarely used as the chiral ligands in asymmetric catalysis,[4,5] especially in asymmetric borane reductions.[6] The most possible reason is that amino acids are insoluble in most common organic solvents, and borane molecule is incompatible with aqueous solutions.

Some ligands[7] with *N*-substituted electron-withdrawing groups such as sulfonamidoalcohols and phosphinamidoalcohols were reported as efficient catalysts for asymmetric borane reduction of prochiral ketones. In our laboratory, squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) derivatives were first used as efficient chiral ligands for enantioselective reduction of prochiral ketones.[8] Among these squaramidoalcohol ligands, *N*-squaryl diphenyl prolinols proved to be the best chiral promoters to achieve high enantioselectivity.[8b] In this paper, we evolve this type of ligands to a new version using amino acids instead of aminoalcohols. We hope that these novel ligands, which were more convenient to prepare, would have similar activities to previous ligands in the asymmetric brone reduction.

Results and discussion

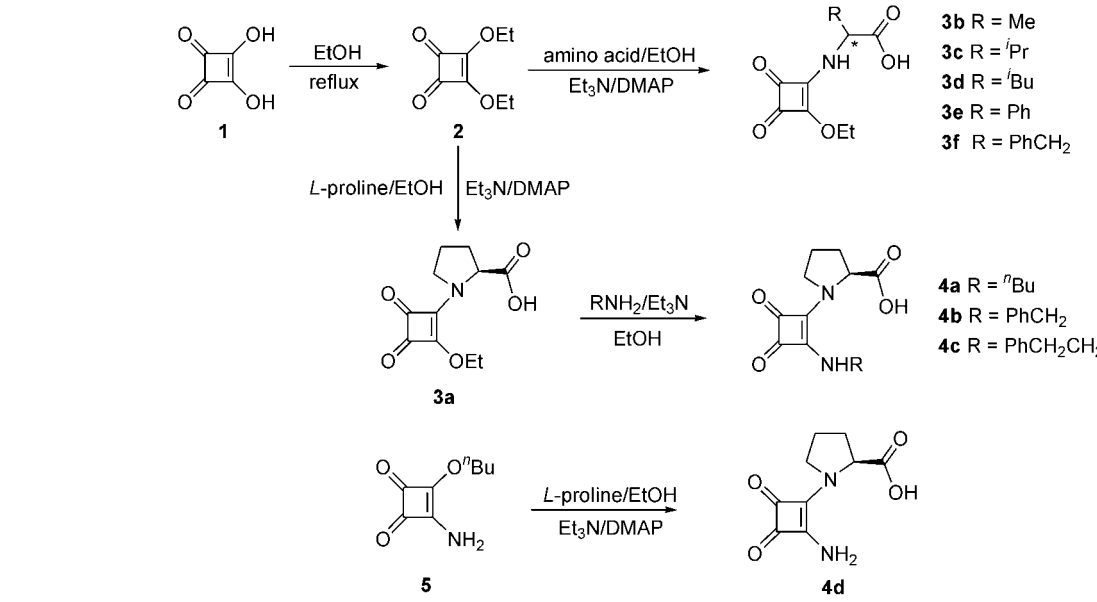
The synthetic route to chiral *N*-squaramidoacids is shown in Scheme 1. Diethyl squarate **2** was formed by refluxing of squaric acid **1** in ethanol. Subsequent treatment of **2** with amino acids in the presence of strong organic base such as DMAP gives corresponding *N*-squaramidoacid products. In order to study the effect of C-3 substituents, we also prepared a series of chiral ligands with different amino group at C-3 position by the reaction of *N*-squaryl proline **3a** with various amines. The synthesis of *N*-squaramidoacids was somewhat more difficult than that of *N*-squaramidoalcohols,[9] since stronger base and higher temperature were crucial in the synthesis of **3**. Reaction of 3-amino-4-butoxy-3-cyclobutene-1,2-dione (**5**) with *L*-proline afforded 3-amino squaryl proline **4d**. Ligands **3** and **4** were characterized by elemental and spectral analyses.

The crystal of ligand **3a** could be obtained by slow evaporation of its dichloromethane and petro ether solution at room temperature. Figure 1 shows the molecular structure and cell packing of **3a**: orthorhombic, space group $P2_12_12_1$ with cell dimensions of $a=0.6900(1)$ nm, $b=0.8752(1)$ nm, $c=2.1050(4)$ nm, $V=1271.2(3)\times10^{-30}$ m^3, $Z=4$, $\mu=11.0$ cm^{-1}. Every three chiral ligand molecules are linked with a water molecule by hydrogen bonds, and one chiral ligand molecule is linked with three water molecules by hydrogen bonds. These hydrogen bonds [O(4)—H···O(6ω), O(6ω)—H_a···O(1) and O(6ω)—H_b···O(2)] construct a rigid three-dimensional structure.

These squaramidoacid ligands were then applied to the asymmetric reduction of prochiral aromatic ketones.

* E-mail: schemorg@mail.sc.cninfo.net
Received December 24, 2002; revised and accepted February 20, 2004.
Project supported by the National Natural Science Foundation of China (No. 20172038) and Youth Science Foundation of Sichuan University.

Scheme 1 Synthesis of *N*-squaramidoacids



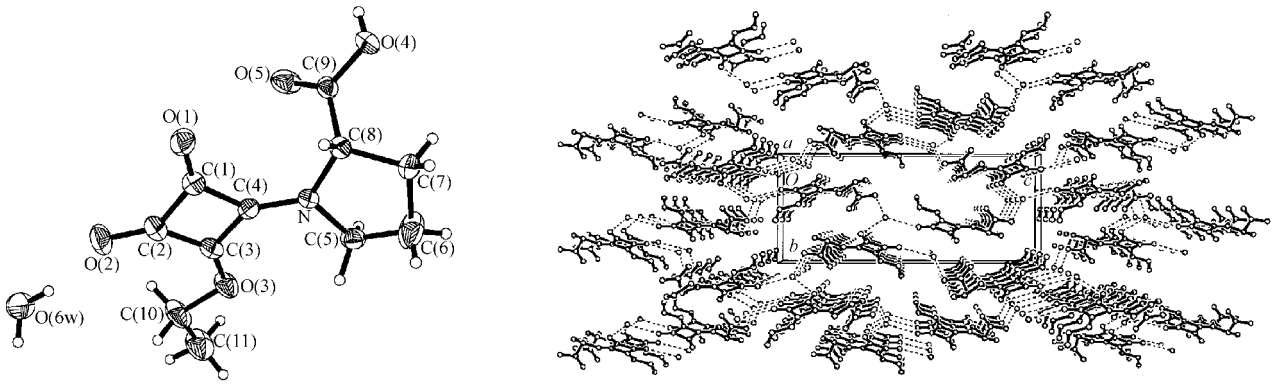


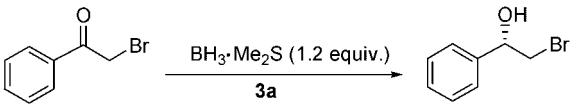
Figure 1 Crystal structure of **3a**.

The reaction conditions were optimized firstly and the results are summarized in Table 1. In the asymmetric reduction of *ω*-bromoacetophenone catalyzed by **3a**, toluene seems to be a better solvent than THF (Entries 1 and 2). The enantioselectivities were obviously affected by temperature, and the best reaction temperature was 50 ℃ in THF and 70 ℃ in toluene, respectively (Entries 1—4). When the reactions were carried out at room temperature, low chemical yields were obtained and no asymmetric induction was observed (Entries 6 and 7). The *ee* values of the produced alcohol increased along with the increasing amount of chiral ligand (Entries 1 and 8, 2 and 9). In toluene at 70 ℃, the reaction using only 10 mol% ligands led to satisfying result (96% *ee*). Controlling the dropping rate is also an important factor in the reaction. Slow addition of substrate led to much better results. This might be explained as that a non-chiral BH_3 reduction process would be dominant when the addition rate of substrate was too fast (Entries 2 and 10).

Then the asymmetric reduction of prochiral ketones catalyzed by *N*-squaramidoacids **3** and **4** were carried out under the optimized conditions. The catalysts were prepared *in situ* by mixing the ligands (0.1 equiv.) and BH_3•Me_2S (1.2 equiv.) at 0 ℃, and the subsequent reduction of prochiral ketones was carried out at 70 ℃ in toluene. The results are summarized in Table 2. Up to 96% *ee* could be obtained when using **3a** as chiral ligand, and this result was much better than non-substituted amino acids.[5] Other ligands led to moderate *ee* values. Ligand **3e**, which was conveniently prepared from industrial product *D*-phenylglycine, catalyzed the reaction to afford the secondary alcohol with *R* configuration (Entry 6). We also tested ligand **4** with amino group at C-3 position and they were proved to be poor catalysts for this kind of reaction.

In order to compare the catalytic activities of these ligands with other similar chiral amino acid derivatives, we applied some *N*-sulfonyl amino acids and squaramidoacid ester (Scheme 2) to the asymmetric reduction of *ω*-bromoacetophenone under the same conditions. It was observed that *N*-tosyl amino acids, **6a—6c**, were poor catalysts for the reduction, which was consistent with literature.[5] For *N*-squaryl proline ethyl ester **7**, only

Table 1 The effects of reaction conditions on the reaction catalyzed by *N*-squaric acid proline [a]



Entry	Solvent	*T*/℃	Cat./mol%	*ee* [b]/%
1	THF	50	10	73
2	Toluene	50	10	87
3	Toluene	70	10	96
4	THF	60—65	10	36
5	THF	50	5	31
6	THF	r.t.	10	0
7	Toluene	r.t.	10	0
8	THF	50	15	80
9	Toluene	50	5	25
10[c]	Toluene	50	10	45

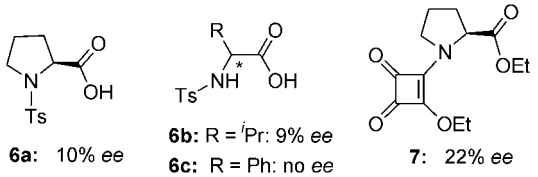
[a] All chemical yields were among 80%—95% except entries 6 (55%) and 7 (61%). [b] Determined by chiral GC analysis, the configuration of all products is *S*. [c] The substrate was added in one portion.

Table 2 Asymmetric reduction of *ω*-bromoacetophenone using chiral *N*-squaramidoacids [a]

Entry	Ligand	Substrate	*ee* [b]/%	Config.[c]
1	**3a**	$PhCOCH_2Br$	96	*S*
2	**3a**	$PhCOCH_3$	92	*R*
3	**3b**	$PhCOCH_2Br$	35	*S*
4	**3c**	$PhCOCH_2Br$	72	*S*
5	**3d**	$PhCOCH_2Br$	52	*S*
6	**3e**	$PhCOCH_2Br$	34	*R*
7	**3f**	$PhCOCH_2Br$	65	*S*

[a] All of the chemical yield were ＞80% (isolated yield). [b] Determined by chiral GC analysis. [c] Determined by comparison with an authentic sample.

Scheme 2 Some *N*-tosyl amino acids and *N*-squaramidoacid ester



22% *ee* was obtained, which indicates that the carboxyl group is somewhat indispensable. In this kind of direct one-pot enantioselective borane reduction, amino acids may be reduced to corresponding aminoalcohols *in situ*, then form oxazaborolidine complexes leading to higher enantioselectivity, whereas amino acid esters are difficult to be reduced by borane, which resulted in poor enantioselectivity. More in-depth studies to elucidate the mechanism of this asymmetric borane reduction are in progress.

Conclusion

In summary, *N*-squaramidoacids, without converting to the corresponding alcohols, can serve as efficient ligands in the catalytic enantioselective borane reduction of prochiral aromatic ketones. The catalytic activities of **3** are higher than its analogs **4**, **6** and **7**. This method provided a convenient way to obtain optically active secondary alcohols.

Experimental

Instruments and materials

Melting points were taken on a micro-melting apparatus and uncorrected. Optical rotations were measured on a WZZ-1 polarimeter. IR spectra were measured on an FT-IR 16PC infrared spectrophotometer with KBr disc. ^{1}H NMR spectra were recorded on Bruker DPX-400 MHz and Bruker AC-E 200 MHz spectrometers with tetramethylsilane as internal standard. Mass spectra data were obtained on a Finnigan MAT 4510 spectrometer. SiO_2 (230—400 mesh) was used in flash chromatography. Elemental analyses were performed with a Carlo Erba 1106 elemental analyzer. GC analyses were carried out through CP-cyclodex (0.25 mm×0.25 m) column. BH_3•Me_2S (10 mol/L) was bought from Aldrich. The solvent (toluene, ethanol) and *ω*-bromoacetophenone were purified before use. Other chemicals were obtained and used without further purification.

Preparation of 3-ethoxy squaramidoacids 3

To a solution of 204 mg (1.2 mmol) diethyl squarate in 10 mL of ethanol was added 0.17 mL (1.2 mmol) of triethylamine, catalytic amount of DMAP and the amino acid (1.0 mmol). The mixture was stirred at 50 ℃ for 24 h. The solvent was removed under reduced pressure. 8 mL of water was added and the solution was acidified with 1 mol•dm^{-3} hydrochloride. Then the water solution was extracted with ethyl acetate three times, and the organic layer was dried with anhydrous $MgSO_4$. The solvent was removed and the residue was purified through column chromatography on silica gel with dichloromethane : acetone, 5∶1 (*V*/*V*).

3-Ethoxy-4-[(2′*S*)-2′-carboxylpyrrolidin-1-yl]-3-cyclobutene-1,2-dione (3a) Colorless flake, 85% yield; $[\alpha]_D^{20}$ −172 (*c* 4, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ: 1.29 (t, J=7.1 Hz, 3H, CH_3), 1.76—1.78 (m, 2H, CH_2), 1.95—2.04 (m, 2H, CH_2), 4.18—4.26 (q, J=7.1 Hz, 2H, OCH_2), 4.49—4.53 (m, 1H, CH), 4.68—4.79 (m, 2H, NCH_2); MS *m*/*z* (%): 240 (M^++1, 100). Anal. calcd for $C_{11}H_{13}NO_5$: C 55.21, H 5.48, N 5.86; found C 55.27, H 5.47, N 5.84.

3-Ethoxy-4-[(1′*S*)-1′-carboxyl-ethylamino]-3-cyclobutene-1,2-dione (3b) Colorless oil, 99% yield; $[\alpha]_D^{20}$ −78.0 (*c* 2, EtOH); ^{1}H NMR ($CDCl_3$) δ: 1.45—1.48 (t, J=6.8 Hz, 3H, CH_3), 1.60—1.62 (m, 3H, CH_3), 4.48 (brs, 1H, NCH), 4.78—4.80 (q, J=6.8 Hz, 2H, OCH_2); MS *m/z* (%): 214 (M^++1, 100). Anal. calcd for $C_9H_{11}NO_5$: C 50.69, H 5.20, N 6.57; found C 50.66, H 5.39, N 6.26.

3-Ethoxy-4-[(1′*S*)-1′-carboxyl-2′-methyl-propylamino]-3-cyclobutene-1,2-dione (3c) Colorless oil, 69% yield; $[\alpha]_D^{20}$ +2.94 (*c* 1.7, EtOH); ^{1}H NMR ($CDCl_3$) δ: 0.91—0.94 (m, 6H, $2CH_3$), 1.33—1.43 (t, J = 6.9 Hz, 3H, CH_3), 2.19—2.23 (m, 1H, CH), 4.36—4.41 (m, 1H, NCH), 4.68 (q, J=6.6 Hz, 2H, OCH_2), 8.47 (d, J=9.2 Hz, 1H, NH); MS *m/z* (%): 242 (M^++1, 100). Anal. calcd for $C_{11}H_{15}NO_5$: C 54.75, H 6.72, N 5.81; found C 54.43, H 6.51, N 5.64.

3-Ethoxy-4-[(1′*S*)-1′-carboxyl-3′-methyl-butylamino]-3-cyclobutene-1,2-dione (3d) Colorless oil, 90% yield; $[\alpha]_D^{20}$ −55.4 (*c* 0.74, EtOH); ^{1}H NMR (CD_3COCD_3) δ: 0.96—0.98 (m, 6H, $2CH_3$), 1.41—1.44 (t, J=6.8 Hz, 3H, CH_3), 1.72—1.76 (m, 1H, CH), 1.78—1.83 (m, 2H, CH_2), 4.41 (m, 1H, NCH), 4.71—4.74 (q, J=6.8 Hz, 2H, OCH_2); MS *m/z* (%): 256 (M^++1, 66). Anal. calcd for $C_{12}H_{17}NO_5$: C 56.45, H 6.72, N 5.49; found C 56.41, H 6.76, N 5.27.

3-Ethoxy-4-[(1′*R*)-1′-carboxyl-1-phenylmethylamino]-3-cyclobutene-1,2-dione (3e) White solid, 90% yield; $[\alpha]_D^{20}$ −169 (*c* 2.4, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ: 1.36 (t, J=6.9 Hz, 3H, CH_3), 4.70 (q, J=7.1 Hz, 2H, OCH_2), 5.45 (d, J=7.0 Hz, 1H, CH), 7.38 (s, 5H, PhH), 7.97 (d, J=5.6 Hz, 1H, NH); MS *m/z* (%): 276 (M^++1, 100). Anal. calcd for $C_{14}H_{13}NO_5$: C 60.09, H 4.73, N 5.09; found C 59.91, H 4.76, N 5.02.

3-Ethoxy-4-[(1′*S*)-1′-carboxyl-2-phenylethylamino]-3-cyclobutene-1,2-dione (3f) Colorless oil, 99% yield; $[\alpha]_D^{20}$ +38.5 (*c* 2.9, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ: 1.43—1.46 (t, J= 6.9 Hz, 3H, CH_3), 2.18 (m, 2H, CH_2), 4.56—4.60 (m, 1H, CH), 4.62—4.67 (m, 2H, OCH_2), 7.30 (m, 5H, PhH), 7.94 (s, 1H, NH); MS *m/z* (%): 290 (M^++1, 100). Anal. calcd for $C_{15}H_{15}NO_5$: C 62.26, H 5.23, N 4.84; found C 62.23, H 5.27, N 4.77.

Preparation of 3-amino squaramidoacids 4

Method 1 General procedure for **4a**—**4c**: To a solution of 100 mg of **3a** (0.418 mmol) in ethanol (10 mL) was added 0.062 mL of *n*-butylamine (0.628 mmol) or corresponding amine (0.46 mmol), and the mixture was stirred at room temperature for 24 h.

Removal of the solvent under reduced pressure afforded yellow solid, which was washed with dichloromethane to give **4a**.

3-*n*-Butylamino-4-[(2′*S*)-2′-carboxylpyrrolidin-1-yl]-3-cyclobutene-1,2-dione (4a) White solid, 31% yield, m.p. 118—120 ℃; ^{1}H NMR (DMSO) δ: 0.85—0.91 (m, 3H, CH_3), 1.27—1.36 (m, 2H, CH_2), 1.45—1.52 (m, 2H, CH_2), 1.79—2.08 (m, 4H, $2CH_2$), 2.71—2.76 (m, 2H, CH_2), 3.45—3.77 (m, 2H, CH_2), 4.61—4.63 (m, 1H, NCH), 8.04 (br, 1H, NH); IR (KBr) *v*: 2954, 1798, 1700 cm^{-1}; MS *m/z* (%): 267 (M^++1, 100). Anal. calcd for $C_{13}H_{18}N_2O_4$: C 58.63, H 6.81, N 10.52; found C 58.47, H 6.84, N 10.45.

Removal of the solvent under reduced pressure afforded yellow solid. Water was added and filtered, then the filtrate was acidified with 1 mol•dm^{-3} hydrochloride to give **4b**.

3-Benzylamino-4-[(2′*S*)-2′-carboxylpyrrolidin-1-yl]-3-cyclobutene-1,2-dione (4b) Colorless needles, 53% yield, m.p. 141—143 ℃; ^{1}H NMR (DMSO) δ: 1.84—1.87 (m, 2H, CH_2), 1.90—1.99 (m, 2H, CH_2), 3.29—3.32 (m, 2H, NCH_2), 3.44—3.65 (m, 2H, CH_2Ph), 4.72—4.77 (m, 1H, NCH), 7.28—7.36 (m, 5H, PhH), 8.16 (brs, 1H, NH), 12.88 (br, 1H, COOH); IR (KBr) *v*: 3418, 2952, 1796, 1701 cm^{-1}; MS *m/z* (%): 299 (M^+−1, 100). Anal. calcd for $C_{16}H_{16}N_2O_4$: C 63.99, H 5.37, N 9.33; found C 63.59, H 5.46, N 9.23.

Removal of the solvent under reduced pressure afforded oil residue. Then water was added and large amount of white solid precipitated. After filtration, the crude product could be recrystallized with ethanol-water to give **4c**.

3-(2-Phenyl)ethylamino-4-[(2′*S*)-2′-carboxylpyrrolidin-1-yl]-3-cyclobutene-1,2-dione (4c) White solid, 51% yield, m.p. 92—94 ℃; ^{1}H NMR (DMSO) δ: 1.75—2.02 (m, 2H, CH_2), 2.11—2.14 (m, 2H, CH_2), 2.84—2.87 (m, 2H, CH_2Ph), 3.73—4.00 (m, 4H, NCH_2), 4.70—4.75 (m, 1H, NCH), 7.22—7.29 (m, 5H, PhH); IR (KBr) *v*: 2984, 1795, 1698 cm^{-1}; MS *m/z* (%): 315 (M^++1, 100). Anal. calcd for $C_{17}H_{18}N_2O_4$: C 64.96, H 5.77, N 8.91; found C 64.78, H 5.80, N 8.84.

Method 2 To a solution of 3-amino-4-butoxy-3-cyclobutene-1,2-dione (**5**, 1 mmol) in ethanol (10 mL) was added 0.17 mL (1.2 mmol) of triethylamine, catalytic amount of DMAP and then *L*-proline (1.0 mmol). The mixture was stirred at 50 ℃ for 24 h. The solvent was removed under reduced pressure, then small amount of water was added and the solution was acidified by 1 mol•dm^{-3} hydrochloride to give **4d**.

3-Amino-4-[(2′*S*)-2′-carboxylpyrrolidin-1-yl]-3-cyclobutene-1,2-dione (4d) Pale yellow solid, 86% yield, m.p. 210—214 ℃; ^{1}H NMR (DMSO) δ: 1.76—2.23 (m, 4H, CH_2), 3.67—3.75 (m, 2H, NCH_2), 4.75 (m, 1H, NCH), 7.65 (s, 2H, NH_2), 12.84 (br, 1H, COOH); IR (KBr) *v*: 3354, 1804, 1720 cm^{-1}; MS *m/z* (%): 211 (M^++1, 100). Anal. calcd for $C_9H_{10}N_2O_4$: C 51.43, H 4.80, N 13.33; found C 51.67, H 4.78, N 13.29.

General procedure for the catalytic reduction of prochiral ketones

0.05 mmol (0.1 equiv) chiral ligand was added to a 25 mL round-bottom flask. Under argon atmosphere, toluene (3 mL) was added to resolve the ligand. BH_3•Me_2S (0.6 mmol, 1.2 equiv.) was then added in ice bath. The mixture was stirred at ambient temperature for 2 h and warmed to 70 ℃ for another 0.5 h. The toluene (2 mL) solution of ketone (0.5 mmol) was added slowly over a period of 1.5 h under the same temperature and stirred for another 1 h. The reaction mixture was cooled

to 0 ℃ and quenched with 8 mL of 1 mol•dm^{-3} HCl solution, then extracted with ethyl acetate (3×10 mL). The combined ethyl acetate solution was washed with brine and dried with anhydrous $MgSO_4$. Then the solvent was removed under reduced pressure. The residue was passed through a short silica column (petroleum ether∶ethyl acetate, 10∶1, *V/V*) to give pure product.

References

1 Zhou, W.-S.; Zhuang, Z.-P. *Asymmetric Synthesis*, Science Press, Beijing, **1997** (in Chinese).

2 (a) Deloux, L.; Srebnik, M. *Chem. Rev.* **1993**, *93*, 763.
(b) Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1986, and the references cited therein.

3 (a) Itsuno, S.; Ito, K.; Hirao, A.; Nakahama, S. *J. Org. Chem.* **1984**, *49*, 555.
(b) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551.

4 Studer, A. *Synthesis* **1996**, 793.

5 Patonay, T.; Hajdu, C.; Jekõ, J.; Lévai, A.; Micskei, K.; Zucchi, C. *Tetrahedron Lett.* **1999**, *40*, 1373.

6 Huang, S.; Wang, B.; Shan, Z.; Zhao, D. *Synth. Commun.* **2000**, *30*, 2423.

7 (a) Zhang, J.; Zhou, H.-B.; Xie, R.-G. *Curr. Org. Chem.* **2002**, *6*, 865.
(b) Yang, G.-S.; Hu, J.-B.; Zhao, G.; Ding, Y.; Tang, M.-H. *Tetrahedron: Asymmetry* **1999**, *10*, 4307.
(c) Hu, J.-B.; Zhao, G.; Yang, G.-S.; Ding, Z.-D. *J. Org. Chem.* **2001**, *66*, 303.
(d) Hu, J.-B.; Zhao, G.; Ding, Z.-D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1109

8 (a) Zhou, H.-B.; Lü, S.-M.; Xie, R.-G.; Chan, A. S. C.; Yang, T.-K. *Tetrahedron Lett.* **2001**, *42*, 1107.
(b) Zhang, J.; Zhou H.-B.; Lü, S.-M.; Luo, M.-M.; Xie, R.-G.; Choi, M. C. K.; Zhou, Z.-Y.; Chan, A. S. C.; Yang, T.-K. *Tetrahedron: Asymmetry* **2001**, *12*, 1907.
(c) Zhou, H.-B.; Zhang, J.; Lü, S.-M.; Xie, R.-G.; Zhou, Z.-Y.; Choi, M. C. K.; Chan, A. S. C.; Yang, T.-K. *Tetrahedron* **2001**, *57*, 9325.
(d) Lü, S.-M.; Zhou, H.-B.; Xie, R.-G.; Zhou, Z.-Y.; Chan, A. S. C.; Yang, T.-K. *Acta Chim. Sinica* **2001**, *59*, 587 (in Chinese).
(e) Lü, S.-M.; Zhou, H.-B.; Zhang, J.; Xie, R.-G.; Zhou, Z.-Y.; Chan, A. S. C.; Yang, T.-K. *Chem. J. Chin. Univ.* **2001**, *22*, 1498 (in Chinese).
(f) Lü, S.-M.; Zhou, H.-B.; Xie, R.-G.; Sun, X.-X. *J. Sichuan Univ., Nat. Sci. Ed.* **2000**, *37*, 736 (in Chinese).

9 Zhang, J. *Ph.D. Thesis*, Sichuan University, Chengdu, **2002** (in Chinese).

10 Quallich, G. J.; Keavey, K. N.; Woodall, T. M. *Tetrahedron Lett*. **1995**, *36*, 4729.

(E0212241 ZHAO, X. J.)