Asymmetric Hydrogenation of Unfunctionalized Enamines Catalyzed by Iridium Complexes of Chiral Spiro *N*,*N*-Diarylphosphoramidites†

Yan, Pucha(严普查) Xie, Jianhua(谢建华) Zhou, Qilin*(周其林)

State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China

Abstract Chiral spiro *N*,*N*-diarylphosphoramidites were synthesized. These new chiral spiro monophosphoramidites were efficient ligands for iridium-catalyzed asymmetric hydrogenation of unfunctionalized enamines derived from simple alkyl aryl ketones, providing chiral tertiary amines in good enantioselectivities (up to 90% *ee*).

Keywords Iridium, chiral phosphoramidite, enamine, asymmetric catalysis, hydrogenation

Introduction

Chiral tertiary amines are significant compounds which are broadly used in the syntheses of biologically active molecules and natural products. Catalytic asymmetric hydrogenation of *N*,*N*-dialkyl/aryl unfunctionalized enamines provides a direct approach to the preparation of chiral tertiary amines. However, to the best of our knowledge, only a few examples of successful asymmetric hydrogenation of unfunctionalized enamines have been reported so far. In 1994, Buchwald and co-workers reported their pioneering study on the asymmetric hydrogenation of 1-(dialkylamino)-1-arylethenes catalyzed by chiral titanocene complex [(*S*,*S*,*S*)-(EBTHI)TiO_2-binaphtho] with high enantioselectivities (up to 98% *ee*).[1] In 2000, Börner *et al*. used a chiral rhodium-diphosphine complex to catalyze asymmetric hydrogenation of cyclic enamines and obtained moderate enantioselectivities (up to 72% *ee*).[2] Recently, we developed a highly efficient rhodium catalyst with chiral spiro phosphonite ligand (*S*)-**1** for the asymmetric hydrogenation of enamines, (*E*)-1-(1-pyrrolidinyl)-1,2-diarylethenes, providing the corresponding tertiary amines with up to 99.9% *ee*.[3] We also demonstrated that iridium complexes of chiral spiro phosphoramidite ligands (R_a,*S*,*S*) or (S_a,*R*,*R*)-SIPHOS-pe were excellent catalysts for the enantioselective hydrogenation of cyclic enamines such as 1-alkyl-2-arylpyrrolines (up to 97% *ee*)[4] and *N*-alkyl-1-alkylidenetetrahydroisoquinolines (up to 98% *ee*)[5] (Figure 1). Andersson[6] and Pfaltz[7] independently introduced chiral iridium complexes of chiral *P*,*N*-ligands into the asymmetric hydrogenation of enamines, giving the corresponding tertiary amines with up to 87% *ee* and 92.5% *ee*, respectively.

In the study of the asymmetric hydrogenation of simple enamines **3** derived from the alkyl aryl ketones with secondary amines we first employed catalysts Rh-(*S*)-**1** and Ir-(S_a,*R*,*R*)-SIPHOS-pe and obtained low conversions (＜38%) and low enantioselectivities (＜10% *ee*). We then carefully modified the spiro phosphorus ligands and found that the spiro *N*,*N*-diarylphosphoramidite ligands (*R*)-**2** were efficient for the iridium-catalyzed asymmetric hydrogenation of simple enamines **3**. We herein report the detail of iridium-catalyzed asymmetric hydrogenation of simple enamines **3** with chiral spiro *N*,*N*-diarylphosphoramidite ligands, offering the corresponding chiral tertiary amines with high enantioselectivities (up to 90% *ee*, Scheme 1).

Results and discussion

We initially chose the easily prepared 1-(1-phenylvinyl)pyrrolidine **3a** as a model substrate and the hydrogenation reaction was performed under the conditions which are similar to the asymmetric hydrogenation of cyclic enamines.[4,5] By using chiral spiro monophosphoramidite ligand (*R*)-**2a** with two phenyl groups on nitrogen atom, the enamine **3a** was quantitatively hydrogenated under 5×10^6 Pa of hydrogen in THF, and chiral amine (*S*)-**4a** was obtained in 97% yield with 87% *ee* (Table 1, Entry 1). This result was better than those obtained by using Ir catalysts with *P*,*N*-ligands reported in the literatures (33% *ee* and 44% *ee*),[6,7] and encouraged us to study the effect of *N*-aryl group of the ligands on the enantioselectivity of the hydrogenation of enamines **3**. A series of spiro phosphoramidite ligands

* E-mail: qlzhou@nankai.edu.cn; Tel.: (+86)-22-2350-0011; Fax: (+86)-22-2350-6177
Received July 22, 2010; accepted August 11, 2010.
Project supported by the National Nature Science Foundation of China (No. 21032003), National Basic Research Program of China (973 Program, No. 2010CB833300), the "111" project (B06005) of the Ministry of Education of China.
† Dedicated to the 60th Anniversary of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

CHINESE JOURNAL OF CHEMISTRY

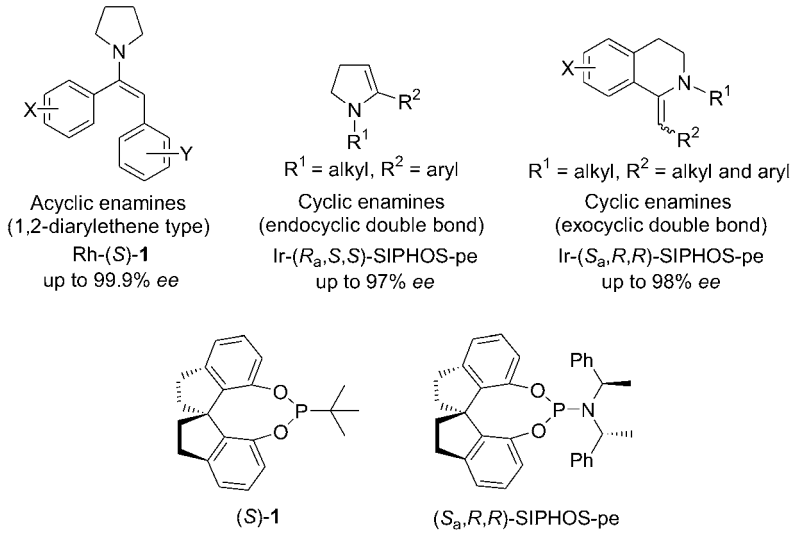
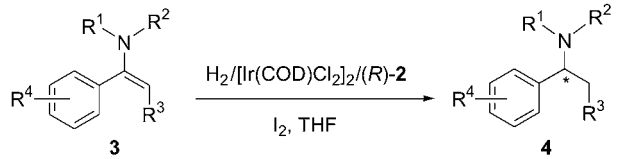
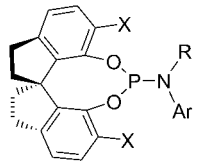


Figure 1 Asymmetric hydrogenation of unfunctionalized enamines with chiral spiro catalysts.

Scheme 1 Asymmetric hydrogenation of *N*,*N*-dialkylenamines with catalysts Ir-(*R*)-**2**





2

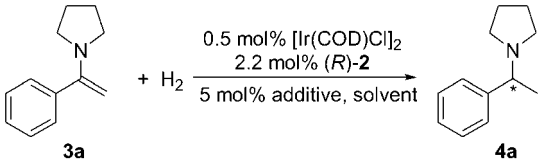
X = H, Ar = R = C_6H_5 ((*R*)-**2a**)
X = H, Ar = R = 4-ClC_6H_4 ((*R*)-**2b**)
X = H, Ar = R = 4-$MeOC_6H_4$ ((*R*)-**2c**)
X = H, Ar = R = 3,5-$Me_2C_6H_3$ ((*R*)-**2d**)
X = H, Ar = C_6H_5, R = 4-MeO-2-MeC_6H_3 ((*R*)-**2e**)
X = H, Ar = C_6H_5, R = 2-Np ((*R*)-**2f**)
X = H, Ar, R = 1,1'-biphenyl ((*R*)-**2g**)
X = H, Ar = C_6H_5, R = H ((*R*)-**2h**)
X = H, Ar = C_6H_5, R = Me ((*R*)-**2i**)
X = Me, Ar = R = C_6H_5 ((*R*)-**2j**)

(*R*)-**2** with different *N*-aryl or *N*,*N*-diaryl groups were synthesized by our previous method.[8] The ligands (*R*)-**2** were compared in the hydrogenation of enamine **3a** and the results were listed in Table 1. Introduction of an electron-withdrawing substituent such as a *para*-chloro (ligand **2b**) into *N*-phenyl groups of the ligand has little effect on the enantioselectivity of the reaction (Table 1, Entry 2). However, the electron-donating group such as a *para*-methoxy on the *N*-phenyl groups (ligand **2c**) led to a small decrease in the enantioselectivity of reaction (Entry 3). The steric effect of ligand **2** was also manifest, for example, the ligand **2d** having 3,5-dimethyl groups on the *N*-phenyl groups yielded product **4a** in low conversion (36%) with very low *ee* value (17% *ee*) (Entry 4). The ligands having different aryl groups on the nitrogen atom such as **2e** and **2f** or connecting a carbazole (ligand **2g**) gave lower enantioselectivity (Entries 5—7). Altering one of the *N*-phenyl groups of ligand **2a** to hydrogen (ligand **2h**) or methyl (ligand **2i**) resulted in very low conversion and enantioselectivities (Entries 8 and 9). Modification of the ligand by adding two methyl groups to the 6,6'-positions of the spirobiindane backbone (ligand **2j**) also led to a very low enantioselectivity (27% *ee*) (Entry 10). Thus, the spiro *N*,*N*-diphenylphosphoramidite **2a** was the choice of ligands for Ir-catalyzed asymmetric hydrogenation of enamine **3a**.

The addition of iodine was crucial for the reaction and no hydrogenation took place without iodine (Entry 11). Although the combination of I_2 with triethylamine or acetic acid has no effect on the reactivity of reaction, it slightly decreased the enantioselectivity of reaction from 87% *ee* to 80% *ee* and 82% *ee*, respectively (Entries 12 and 13). A low conversion was observed by adding KI, it worked effectively in the iridium-catalyzed asymmetric hydrogenation of *N*-alkyl-1-alkylidenetetrahydroisoquinolines[5] (Entry 14). Solvent experiments showed that THF was the best choice of solvent in terms of reactivity and enantioselectivity of reaction (Entry 1 vs. Entries 15—18). The hydrogenation of enamine **3a** can also be carried out at 1×10^6 Pa of hydrogen, giving a comparable result (Entry 19). It is worthy noting that the catalyst loading can be lowered to 0.1 mol% without diminishing the enantioselectivity of reaction (Entry 20).

Under the optimal conditions a variety of *N*,*N*-dialkylenamines **3** have been hydrogenated by the catalyst Ir-(*R*)-**2a**. As shown in Table 2 the alkyl groups at the nitrogen atom of enamine substrates had a manifest effect on both reactivity and enantioselectivity of the reaction. The enamine **3a** with a five-membered cyclic amino group was completely hydrogenated to chiral

Table 1 Optimizing the reaction conditions[a]



Entry	Ligand	Solvent	Additive	Conv.[b]/%	*ee*[c]/%
1	(*R*)-**2a**	THF	I_2	100	87
2	(*R*)-**2b**	THF	I_2	100	87
3	(*R*)-**2c**	THF	I_2	100	78
4	(*R*)-**2d**	THF	I_2	36	17
5	(*R*)-**2e**	THF	I_2	100	75
6	(*R*)-**2f**	THF	I_2	100	85
7	(*R*)-**2g**	THF	I_2	100	70
8	(*R*)-**2h**	THF	I_2	67	7
9	(*R*)-**2i**	THF	I_2	30	15
10	(*R*)-**2j**	THF	I_2	100	27
11	(*R*)-**2a**	THF	no	5	7
12[d]	(*R*)-**2a**	THF	I_2/Et_3N	100	80
13[e]	(*R*)-**2a**	THF	I_2/HOAc	100	82
14	(*R*)-**2a**	THF	KI	23	85
15	(*R*)-**2a**	Et_2O	I_2	10	71
16	(*R*)-**2a**	CH_2Cl_2	I_2	87	84
17	(*R*)-**2a**	toluene	I_2	92	79
18	(*R*)-**2a**	MeOH	I_2	91	69
19[f]	(*R*)-**2a**	THF	I_2	100	87
20[g]	(*R*)-**2a**	THF	I_2	100	86

[a] Recation conditions: Ir/L/add./subs.=1∶2.2∶5∶100, [subs.] =0.1 mol•L^{-1}, 5×10^6 Pa H_2, 0 ℃, 24 h. [b] Determined by GC. [c] Determined by chiral GC. [d] 20 mol% Et_3N. [e] 20 mol% HOAc. [f] 1×10^6 Pa H_2. [g] 0.05 mol% $[Ir(COD)Cl]_2$ (S/C=1000).

amine **4a** within 12 h with 87% *ee* (Table 2, Entry 1). The enamine **3b** with a six-membered piperidine ring needed 24 h for complete hydrogenation, and the enantiomeric excess of amine product became 67% *ee* (Entry 2). However, the enamine **3c** with a morpholine moiety was reluctant to be hydrogenated under standard conditions. It was only hydrogenated under 5×10^6 Pa of hydrogen at 50 ℃, providing chiral amine **4c** with 34% *ee* (Entry 3). The enamines **3d** and **3e**, both having an acyclic amino group, also showed low reactivity in the hydrogenation, requiring 24 h or 40 h at 5×10^6 Pa of hydrogen for full conversion (Entries 4 and 5). The electronic property of substituents on the phenyl ring of the enamines **3** has a visible effect on the enantioselectivity of reaction. The substrates with an electron-donating group at *meta*- or *para*-position of the phenyl ring have high enantioselectivity (Entries 6, 7, 10 and 11). The substrates with an electron-withdrawing group at *para*-position of the phenyl ring gave lower enantioselectivity (Entries 8 and 9). Presumably due to the steric hindrance, a group on the *ortho*-position of the phenyl ring of substrate led to lower enantioselectivities (Entries 12 and 13). Also for the reason of steric hindrance, *β*-substituted *α*-dialkylaminostyrene was not a suitable substrate for this reaction, the asymmetric hydrogenation of 1-(1-phenylprop-1-enyl)pyrrolidine (**3o**) at 5×10^6 Pa of H_2 gave the corresponding amine **4o** in only 43% *ee* (Entry 15). The asymmetric hydrogenation of cyclic enamines **3p**—**3r**, flexibility- restricted substrates, were also examined by using catalyst Ir-(*R*)-**2a**. High enantioselectivities were obtained in the hydrogenation of these cyclic substrates, with the seven-membered cyclic enamine **3r** being the highest enantioselective (Entries 16—18).

Conclusion

In summary, new iridium catalysts based on chiral spiro *N*,*N*-diarylphosphoramidite ligands have been developed for the asymmetric hydrogenation of unfunctionalized enamines derived from alkyl aryl ketones. This reaction provides an efficient method for the synthesis of chiral tertiary amines with good to high enantioselectivities.

Experimental

General

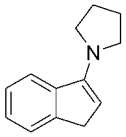
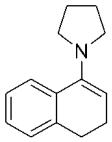
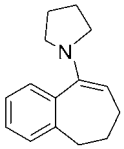
All reactions and manipulations were performed in an argon-filled glovebox (VAC DRI-LAB HE 493) or using standard Schlenk techniques. Melting points were measured on a RY-I apparatus and uncorrected. Et_2O, THF and toluene were distilled from sodium benzophenone ketyl. DCM was distilled from calcium hydride. Anhydrous MeOH was distilled from magnesium. Hydrogen gas (99.999%) was purchased from Boc Gas Inc. NMR spectra were recorded with a Varian spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) or a Bruker AV 300 spectrometer at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR) in $CDCl_3$. Chemical shifts were reported in ppm down field from internal Me_4Si and external 85% H_3PO_4, respectively. Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. HRMS were recorded on IonSpec FT-ICR mass spectrometer with ESI resource. GC analyses were performed using Hewlett Packard Model HP 6890 Series. HPLC analyses were performed using Hewlett Packard Model HP 1100 Series. The enamines were prepared using literature methods.[1,9]

Synthesis of chiral spiro phosphoramidite ligands[8]

***N*,*N*-Diphenyl-[(*R*)-1,1'-spirobiindane-7,7'-diyl]-phosphoramidite ((*R*)-2a)** A solution of (*R*)-1,1'-spirobiindane-7,7'-diol (1.0 g, 4.0 mmol)) and Et_3N (834 mg, 8.2 mmol) in 40 mL THF was cooled to 0 ℃, and a freshly distilled PCl_3 (566 mg, 4.1 mmol) was added. The reaction mixture was stirred at 0 ℃ for 0.5 h, then warmed to room temperature and stirred overnight. The mixture was filtered under nitrogen and the filtrate was

CHINESE JOURNAL OF CHEMISTRY

Table 2 Asymmetric hydrogenation of enamines **3** with catalyst Ir-(*R*)-**2a**[a]

Entry	Substrate			Product	Time/h	*ee*[b]/%
	R^1, R^2	R^3	R^4			
1	$(CH_2)_4$	H	H	**4a**	12	87
2	$(CH_2)_5$	H	H	**4b**	24	67
3[c]	$(CH_2)_2O(CH_2)_2$	H	H	**4c**	48	34
4[d]	Et, Et	H	H	**4d**	24	71
5[d]	Me, Ph	H	H	**4e**	40	57
6	$(CH_2)_4$	H	4-Me	**4f**	12	87
7	$(CH_2)_4$	H	4-MeO	**4g**	12	89
8	$(CH_2)_4$	H	4-Cl	**4h**	12	52
9	$(CH_2)_4$	H	4-F	**4i**	12	67
10	$(CH_2)_4$	H	3-Me	**4j**	12	80
11	$(CH_2)_4$	H	3-MeO	**4k**	12	85
12	$(CH_2)_4$	H	2-Me	**4l**	12	60
13	$(CH_2)_4$	H	2-MeO	**4m**	12	67
14	$(CH_2)_4$	H	3,4-OCH_2O	**4n**	12	76
15[d]	$(CH_2)_4$	Me	H	**4o**	24	43
16				**4p**	12	80
17				**4q**	12	88
18				**4r**	12	90

[a] Recation conditions: Ir/L/add./subs.=1∶2.2∶5∶100, [subs.]=0.1 mol•L^{-1}, 1×10^6 Pa H_2, 0 ℃, 100% conversion, >90% isolated yield. [b] Determined by chiral GC or HPLC. [c] 5×10^6 Pa H_2, 50 ℃. [d] 5×10^6 Pa, 15—18 ℃.

evaporated under reduced pressure. The residue was resolved in 40 mL THF, cooled to −78 ℃, and treated with lithium diphenylamide prepared from diphenylamine (677 mg, 4.0 mmol) and 2.0 mL (4.4 mmol) butyllithium (2.2 mol•L^{-1} solution in hexane) in 10 mL THF at −78 ℃. The resulting solution was warmed to room temperature and stirred for 24 h. The solvent was removed in vacuum and the residue was purified by chromatography on a silica gel column with ethyl acetate/petroleum ether (1/40, *V*/*V*) as eluent to afford (*R*)-**2a** as a white solid (1.4 g, 78%). m.p. 159—161 ℃, $[\alpha]_D^{12}$ +203 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.21—7.13 (m, 5H), 7.10—7.00 (m, 5H), 6.92 (d, *J*=8.0 Hz, 1H), 6.70 (d, *J*=7.6 Hz, 5H), 3.08—2.99 (m, 2H), 2.85—2.71 (m, 2H), 2.22—2.11 (m, 2H), 1.99—1.91 (m, 1H), 1.76—1.69 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 147.3, 147.2, 145.9, 145.5, 145.3, 144.4, 144.3, 141.8, 140.6, 129.3, 128.6, 128.4, 124.9, 123.7, 121.6, 121.0, 117.7, 58.9, 38.1, 37.9, 30.8, 30.4; ^{31}P NMR ($CDCl_3$, 162 MHz) *δ*: 118.1 (s). HRMS (ESI^+) calcd for $C_{29}H_{24}NO_2PH^+$ 450.1617, found 450.1615.

***N*,*N*-Bis(4-chlorophenyl)-[(*R*)-1,1'-spirobiindane-7,7'-diyl]-phosphoramidite ((*R*)-2b)** Ligand (*R*)-**2b** was synthesized by the same procedure as that for (*R*)-**2a**. White solid, 70%, m.p. 152—154 ℃, $[\alpha]_D^{12}$ +127 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.20 (t, *J*=8.0 Hz, 1H), 7.13—7.05 (m, 7H), 6.90 (d, *J*=8.0 Hz, 1H), 6.65—6.59 (m, 5H), 3.09—3.01 (m, 2H), 2.86—2.74 (m, 2H), 2.23—2.15 (m, 2H), 1.98—1.90 (m, 1H), 1.78—1.70 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 146.9, 146.8, 146.0, 145.7, 145.1, 145.0, 142.8, 142.7, 141.7, 140.6, 129.4, 128.8, 128.7, 128.5,

126.0, 121.9, 121.3, 121.2, 120.9, 120.8, 58.9, 38.1, 38.0, 30.8, 30.4; ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 115.7 (s). HRMS (ESI^+) calcd for $C_{29}H_{22}Cl_2NO_2PH^+$ 518.0838, found 518.0837.

***N*,*N*-Bis(4-methoxyphenyl)-[(*R*)-1,1'-spirobiindane-7,7'-diyl]-phosphoramidite ((*R*)-2c)** Ligand (*R*)-**2c** was synthesized by the same procedure as that for (*R*)-**2a**. White solid, 75%, m.p. 146—148 ℃, $[\alpha]_D^{12}$ +234 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.19 (t, *J*=7.6 Hz, 1H), 7.11—7.02 (m, 3H), 6.93 (d, *J*=8.0 Hz, 1H), 6.74—6.64 (m, 9H), 3.75 (s, 6H), 3.09—3.00 (m, 2H), 2.85—2.73 (m, 2H), 2.22—2.14 (m, 2H), 1.99—1.91 (m, 1H), 1.83—1.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.1, 147.6, 147.5, 146.0, 145.6, 145.5, 141.9, 140.7, 138.0, 137.9, 128.6, 128.4, 126.5, 126.4, 121.8, 121.6, 121.2, 121.0, 113.9, 59.0, 55.4, 38.2, 38.1, 30.9, 30.5; ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 117.3 (s). HRMS (ESI^+) calcd for $C_{31}H_{28}NO_4PH^+$ 510.1829, found 510.1834.

***N*,*N*-Bis(3,5-dimethylphenyl)-[(*R*)-1,1'-spirobiindane-7,7'-diyl]-phosphoramidite ((*R*)-2d)** Ligand (*R*)-**2d** was synthesized by the same procedure as that for (*R*)-**2a**. White solid, 76%, m.p. 180—182 ℃, $[\alpha]_D^{12}$ +326 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.19 (t, *J*=7.6 Hz, 1H), 7.13—7.05 (m, 3H), 6.92 (d, *J*=8.0 Hz, 1H), 6.72—6.68 (m, 3H), 6.31 (s, 4H), 3.15—3.02 (m, 2H), 2.87—2.79 (m, 2H), 2.29—2.19 (m, 14H), 2.02—1.94 (m, 1H), 1.91—1.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.6, 147.5, 145.8, 145.7, 145.6, 145.4, 144.2, 144.1, 141.9, 141.8, 140.8, 138.0, 128.5, 125.6, 123.0, 121.9, 121.5, 121.3, 121.2, 121.1, 59.0, 38.1, 30.8, 30.6, 21.2; ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 117.3 (s). HRMS (ESI^+) calcd for $C_{33}H_{32}NO_2PH^+$ 506.2243, found 506.2248.

***N*-(4-Methoxy-2-methylphenyl)-*N*-phenyl-[(*R*)-1,1'-spirobiindane-7,7′-diyl]-phosphoramidite ((*R*)-2e)** Ligand (*R*)-**2e** was synthesized by the same procedure as that for (*R*)-**2a**. White solid, 81%, m.p. 145—147 ℃, $[\alpha]_D^{12}$ +84.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.09 (q, *J*=8.4 Hz, 3H), 7.00—6.93 (m, 3H), 6.84—6.76 (m, 4H), 6.62—6.59 (m, 2H), 6.24 (dd, *J*=1.6, 8.4 Hz, 1H), 5.21 (brs, 1H), 3.62 (s, 3H), 2.98—2.88 (m, 2H), 2.74—2.64 (m, 2H), 2.12—2.08 (m, 1H), 2.10 (s, 3H), 2.01 (dd, *J*=6.0, 11.6 Hz, 1H), 1.89—1.82 (m, 1H), 1.65—1.57 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 157.8, 147.2, 147.1, 146.1, 145.9, 145.7, 145.3, 145.2, 141.8, 140.6, 138.7, 133.1, 133.0, 131.1, 128.9, 128.5, 128.3, 121.6, 121.4, 120.9, 120.7, 116.8, 116.7, 115.2, 111.3, 58.9, 55.1, 38.1, 37.8, 30.8, 30.4, 18.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 118.9 (s). HRMS (ESI^+) calcd for $C_{31}H_{28}NO_3PH^+$ 494.1880, found 494.1875.

***N*-(Naphthalen-2-yl)-*N*-phenyl-[(*R*)-1,1'-spirobiindane-7,7'-diyl]-phosphoramidite ((*R*)-2f)** Ligand (*R*)-**2f** was synthesized by the same procedure as that for (*R*)-**2a**. White solid, 78%, m.p. 142—144 ℃, $[\alpha]_D^{12}$ +285 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.71 (d, *J*=7.6 Hz, 1H), 7.61 (d, *J*=8.8 Hz, 1H), 7.52 (d, *J*=7.6 Hz, 1H), 7.40—7.33 (m, 2H), 7.18 (q, *J*=7.6 Hz, 3H), 7.10—7.01 (m, 4H), 6.93—6.85 (m, 4H), 6.73—6.71 (m, 2H), 3.09—2.98 (m, 2H), 2.84—2.73 (m, 2H), 2.22—2.10 (m, 2H), 2.00—1.92 (m, 1H), 1.77—1.69 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.3, 147.2, 145.9, 145.6, 145.5, 145.4, 144.9, 144.7, 141.8, 141.1, 140.7, 133.7, 130.5, 128.8, 128.6, 128.2, 127.4, 127.3, 125.9, 125.6, 124.9, 124.3, 124.2, 123.5, 122.9, 121.7, 121.6, 121.2, 121.0, 59.0, 38.1, 38.0, 30.8, 30.5; ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 116.5 (s). HRMS (ESI^+) calcd for $C_{33}H_{26}NO_2PH^+$ 500.1774, found 500.1768.

***N*,*N*-Diphenyl-[(*R*)-1,1'-spirobiindane-6,6'-dimethyl-7,7'-diyl]-phosphoramidite ((*R*)-2j)** Ligand (*R*)-**2j** was synthesized by the same procedure as that for (*R*)-**2a**. White solid, 72%, m.p. 136—138 ℃, $[\alpha]_D^{18}$ +240 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.13 (t, *J*=7.6 Hz, 4H), 7.06 (d, *J*=7.6 Hz, 1H), 6.99 (t, *J*=7.2 Hz, 2H), 6.94 (d, *J*=7.2 Hz, 2H), 6.87 (d, *J*=7.2 Hz, 1H), 6.76 (brs, 4H), 2.98—2.90 (m, 2H), 2.78—2.60 (m, 2H), 2.30 (s, 3H), 2.12 (s, 3H), 2.11—2.02 (m, 2H), 1.92—1.85 (m, 1H), 1.70—1.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 145.7, 144.3, 144.2, 142.4, 141.6, 140.3, 129.9, 129.2, 128.5, 128.4, 124.6, 123.6, 121.1, 120.5, 59.4, 38.6, 37.8, 30.2, 29.8, 16.9, 16.4, 16.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 114.0 (s). HRMS (ESI^+) calcd for $C_{31}H_{28}NO_2PH^+$ 478.1930, found 478.1924.

General procedure for asymmetric hydrogenation of enamines and analytical data for the hydrogenation products

To a dry reaction tube equipped with a stirring bar was added $[Ir(COD)Cl]_2$ (1.7 mg, 2.5 μmol), (*R*)-**2a** (4.9 mg, 11 μmol) and anhydrous THF (5.0 mL) under an nitrogen atmosphere. After the mixture was stirred at room temperature for 30 min, iodide (6.4 mg, 25 μmol) and enamines (0.5 mmol) were added. The reaction tube was then put into an autoclave. The nitrogen atmosphere in the tube was replaced by hydrogen three times and the reaction solution was stirred at 0 ℃ under 1×10^6 Pa H_2 pressure for 12 h. After releasing hydrogen, the resulted mixture was filtered through a short silica plug and submitted to analysis for conversion and enantiomeric excess by GC with chiral column. The analytical data for the hydrogenation products are listed below.

(*S*)-1-(1-Phenylethyl)pyrrolidine (4a)[1] Yellow oil, 97% yield, 87% *ee*, $[\alpha]_D^{18}$ −53.4 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 100 ℃ to 120 ℃ at 0.5 ℃/min; t_R=27.55 min (*R*) and t_R=28.00 min (*S*). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.35—7.28 (m, 4H), 7.25—7.21 (m, 1H), 3.17 (q, *J*=6.8 Hz, 1H), 2.58—2.51 (m, 2H), 2.40—2.33 (m, 2H), 1.81—1.71 (m, 4H), 1.41 (d, *J*=6.8 Hz, 3H).

(*S*)-1-(1-Phenylethyl)piperidine (4b)[10] Yellow oil, 98% yield, 67% *ee*, $[\alpha]_D^{18}$ −17.7 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 100 ℃ to 130 ℃ at 0.5 ℃/min; t_R=37.04 min (*R*) and t_R=

CHINESE JOURNAL OF CHEMISTRY

37.55 min (*S*). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.33—7.29 (m, 4H), 7.27—7.21 (m, 1H), 3.40 (q, J=6.8 Hz, 1H), 2.41—2.35 (m, 4H), 1.58—1.53 (m, 4H), 1.41—1.35 (m, 2H), 1.38 (d, J=6.8 Hz, 3H).

(*S*)-4-(1-Phenylethyl)morpholine (4c)[11] Yellow oil, 96% yield, 34% *ee*, $[\alpha]_D^{26}$ −14.2 (*c* 1.0, EtOH), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 105 ℃ to 145 ℃ at 0.5 ℃/min; t_R=40.80 min (*R*) and t_R=41.56 min (*S*). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.32—7.22 (m, 5H), 3.69 (t, J=4.8 Hz, 4H), 3.30 (q, J=6.8 Hz, 1H), 2.50—2.48 (m, 2H), 2.38—2.33 (m, 2H), 1.35 (d, J=6.8 Hz, 3H).

(*S*)-*N*,*N*-Diethyl-1-phenylethanamine (4d)[1] Yellow oil, 94% yield, 71% *ee*, $[\alpha]_D^{18}$ −20.9 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 80 ℃ to 110 ℃ at 0.5 ℃/min; t_R=35.89 min (*S*) and t_R=36.79 min (*R*). ^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.37—7.29 (m, 4H), 7.24—7.21 (m, 1H), 3.79 (q, J=6.8 Hz, 1H), 2.63—2.45 (m, 4H), 1.34 (d, J=6.8 Hz, 3H), 0.99 (t, J=7.2 Hz, 6H).

(−)-*N*-Methyl-*N*-(1-phenylethyl)aniline (4e)[3] Colorless oil, 87% yield, 57% *ee*, $[\alpha]_D^{8}$ −90.6 (*c* 1.0, $CHCl_3$), HPLC condition: Chiralcel OJ-H column (25 cm×0.46 cm ID), *n*-hexane/2-propanol=98∶2, 1.0 mL/min, 254 nm UV detector, t_R=14.58 min (major) and t_R=21.69 min (minor). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.35—7.32 (m, 4H), 7.27—7.23 (m, 3H), 6.84 (d, J=8.0 Hz, 2H), 6.73 (t, J=7.2 Hz, 1H), 5.13 (q, J=6.8 Hz, 1H), 2.68 (s, 3H), 1.55 (d, J=6.8 Hz, 3H).

(−)-1-(1-*p*-Tolylethyl)pyrrolidine (4f) Yellow oil, 95% yield, 87% *ee*, $[\alpha]_D^{18}$ −45.7 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 100 ℃ to 130 ℃ at 0.5 ℃/min; t_R=40.56 min (minor) and t_R=40.97 min (major). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.22 (d, J=7.8 Hz, 2H), 7.11 (d, J=7.8 Hz, 2H), 3.15 (q, J=6.6 Hz, 1H), 2.56—2.51 (m, 2H), 2.39—2.35 (m, 2H), 2.33 (s, 3H), 1.77—1.73 (m, 4H), 1.39 (d, J=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 142.7, 136.3, 128.9, 127.1, 65.6, 53.0, 23.5, 23.2, 21.1. HRMS (ESI^+) calcd for $C_{13}H_{19}NH^+$ 190.1590, found 190.1591.

(−)-1-(1-(4-Methoxyphenyl)ethyl)pyrrolidine (4g)[1] Yellow oil, 92% yield, 89% *ee*, $[\alpha]_D^{18}$ −60.6 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 100 ℃ to 130 ℃ at 0.2 ℃/min; t_R=105.21 min (minor) and t_R=106.00 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.24 (d, J=8.4 Hz, 2H), 6.84 (d, J=8.4 Hz, 2H), 3.79 (s, 3H), 3.13 (q, J=6.4 Hz, 1H), 2.54—2.52 (m, 2H), 2.35—2.33 (m, 2H), 1.77—1.73 (m, 4H), 1.38 (d, J=6.4 Hz, 3H).

(−)-1-(1-(4-Chlorophenyl)ethyl)pyrrolidine (4h)[1] Yellow oil, 94% yield, 52% *ee*, $[\alpha]_D^{25}$ −40.7 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 100 ℃ to 130 ℃ at 0.2 ℃/min; t_R=94.46 min (minor) and t_R=95.67 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.26 (s, 4H), 3.14 (q, J=6.4 Hz, 1H), 2.55—2.48 (m, 2H), 2.36—2.31 (m, 2H), 1.77—1.74 (m, 4H), 1.36 (d, J=6.4 Hz, 3H).

(−)-1-(1-(4-Fluorophenyl)ethyl)pyrrolidine (4i) Yellow oil, 95% yield, 67% *ee*, $[\alpha]_D^{25}$ −46.8 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 100 ℃ to 130 ℃ at 0.5 ℃/min; t_R=32.28 min (minor) and t_R=32.88 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30—7.26 (m, 2H), 6.99—6.95 (m, 2H), 3.15 (q, J=6.4 Hz, 1H), 2.54—2.50 (m, 2H), 2.35—2.30 (m, 2H), 1.76—1.73 (m, 4H), 1.36 (d, J=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 163.3, 160.1, 141.6, 128.5, 128.4, 115.0, 114.8, 65.1, 52.8, 23.4, 23.3. HRMS (ESI^+) calcd for $C_{12}H_{16}FNH^+$ 194.1340, found 194.1346.

(−)-1-(1-*m*-Tolylethyl)pyrrolidine (4j)[1] Yellow oil, 92% yield, 80% *ee*, $[\alpha]_D^{25}$ −40.3 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 90 ℃ to 110 ℃ at 0.2 ℃/min; t_R=69.63 min (minor) and t_R=70.29 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.21—7.11 (m, 3H), 7.05 (d, J=7.2 Hz, 1H), 3.13 (q, J=6.4 Hz, 1H), 2.57—2.53 (m, 2H), 2.38—2.32 (m, 2H), 2.35 (s, 3H), 1.78—1.75 (m, 4H), 1.40 (d, J=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 145.8, 137.7, 128.1, 127.8, 127.6, 124.4, 66.1, 53.1, 23.5, 23.3, 21.5. HRMS (ESI^+) calcd for $C_{13}H_{19}NH^+$ 190.1590, found 190.1591.

(−)-1-(1-(3-Methoxyphenyl)ethyl)pyrrolidine (4k) Yellow oil, 93% yield, 85% *ee*, $[\alpha]_D^{25}$ −56.9 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 90 ℃ to 125 ℃ at 0.2 ℃/min; t_R=125.69 min (minor) and t_R=126.40 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.21 (t, J=7.8 Hz, 1H), 6.93—6.91 (m, 2H), 6.78—6.76 (m, 1H), 3.80 (s, 3H), 3.14 (q, J=6.8 Hz, 1H), 2.57—2.53 (m, 2H), 2.40—2.35 (m, 2H), 1.79—1.72 (m, 4H), 1.39 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.7, 147.6, 129.2, 119.6, 112.7, 112.2, 66.0, 55.2, 52.9, 23.5, 23.2. HRMS (ESI^+) calcd for $C_{13}H_{19}NOH^+$ 206.1539, found 206.1539.

(−)-1-(1-*o*-Tolylethyl)pyrrolidine (4l)[1] Yellow oil, 90% yield, 60% *ee*, $[\alpha]_D^{32}$ −62.1 (*c* 1.0, $CHCl_3$), the enantiomeric excesses of the amine was determined by analysis of ^{1}H NMR spectra of the diastereomeric salts with (*R*)- or (*S*)-*O*-acetylmandelic acid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (d, J=7.6 Hz, 1H), 7.22—7.17 (m, 1H), 7.11 (d, J=4.0 Hz, 2H), 3.46 (q, J=6.4 Hz, 1H), 2.55—2.52 (m, 2H), 2.45—2.42 (m, 2H), 2.36 (s, 3H), 1.79—1.76 (m, 4H), 1.34 (d, J=6.4 Hz, 3H).

(−)-1-(1-(2-Methoxyphenyl)ethyl)pyrrolidine (4m) Yellow oil, 92% yield, 67% *ee*, $[\alpha]_D^{30}$ −32.3 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 100 ℃ to 135 ℃ at 0.2 ℃/min; t_R=128.85 min (minor) and t_R=130.41 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.51 (dd, J=7.6, 1.6 Hz, 1H), 7.21—7.17 (m, 1H), 6.96 (t, J=7.6 Hz, 1H), 6.86 (d, J=8.0 Hz,

1H), 3.81 (q, J=6.8 Hz, 1H), 3.81 (s, 3H), 2.58—2.55 (m, 2H), 2.48—2.45 (m, 2H), 1.78—1.75 (m, 4H), 1.35 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 156.4, 133.4, 127.9, 127.3, 120.8, 110.5, 56.8, 55.4, 52.6, 23.5, 22.1. HRMS (ESI^+) calcd for $C_{13}H_{19}NOH^+$ 206.1539, found 206.1540.

(—)-1-(1-(Benzo[*d*][1,3]dioxol-5-yl)ethyl)pyrrolidine (4n) Yellow oil, 91% yield, 76% *ee*, $[\alpha]_D^{30}$ —49.1 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 100 ℃ to 160 ℃ at 0.5 ℃/min; t_R= 84.05 min (minor) and t_R=84.61 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.88 (d, J=1.2 Hz, 1H), 6.76—6.71 (m, 2H), 5.92 (s, 2H), 3.09 (q, J=6.8 Hz, 1H), 2.54—2.50 (m, 2H), 2.38—2.34 (m, 2H), 1.76—1.73 (m, 4H), 1.35 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 147.6, 146.2, 140.0, 120.1, 107.8, 107.4, 100.8, 65.6, 52.8, 23.4, 23.3. HRMS (ESI^+) calcd for $C_{13}H_{17}NO_2H^+$ 220.1332, found 220.1336.

(—)-1-(1-Phenylpropyl)pyrrolidine (4o) Yellow oil, 93% yield, 43% *ee*, $[\alpha]_D^{18}$ —20.2 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 0.5 mL/min, programmed from 100 ℃ to 110 ℃ at 0.1 ℃/min; t_R=81.20 min (minor) and t_R= 82.24 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.32—7.20 (m, 5H), 2.94 (dd, J=3.6, 10.0 Hz, 1H), 2.57—2.52 (m, 2H), 2.36—2.31 (m, 2H), 2.03—1.93 (m, 1H), 1.78—1.65 (m, 5H), 0.66 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 143.2, 128.2, 128.0, 126.8, 72.8, 52.8, 28.6, 23.3, 10.5. HRMS (ESI^+) calcd for $C_{13}H_{19}NH^+$ 190.1590, found 190.1592.

(+)-1-(2,3-Dihydro-1*H*-inden-1-yl)pyrrolidine (4p) Yellow oil, 90% yield, 80% *ee*, $[\alpha]_D^{30}$ +25.4 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 120 ℃ to 140 ℃ at 0.2 ℃/min; t_R=37.69 min (minor) and t_R=38.61 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37 (d, J=6.8 Hz, 1H), 7.26—7.15 (m, 3H), 4.21 (t, J=5.6 Hz, 1H), 3.09—3.01 (m, 1H), 2.84—2.77 (m, 1H), 2.69—2.56 (m, 4H), 2.19—2.10 (m, 2H), 1.82—1.73 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 144.3, 143.6, 127.4, 125.8, 125.7, 124.8, 67.3, 50.3, 30.9, 28.5, 23.6. HRMS (ESI^+) calcd for $C_{13}H_{17}NH^+$ 188.1434, found 188.1437.

(+)-1-(1,2,3,4-Tetrahydronaphthalen-1-yl)pyrrolidine (4q) Yellow oil, 94% yield, 88% *ee*, $[\alpha]_D^{18}$ +30.2 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 120 ℃ to 160 ℃ at 1.0 ℃/min; t_R =29.86 min (minor) and t_R=30.70 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38 (d, J=7.2 Hz, 1H), 7.18—7.09 (m, 3H), 3.57 (t, J=4.8 Hz, 1H), 2.96—2.89 (m, 1H), 2.80—2.67 (m, 3H), 2.51—2.48 (m, 2H), 2.17—2.08 (m, 1H), 2.01—1.94 (m, 1H), 1.84—1.68 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.7, 137.7, 129.4, 129.1, 126.7, 125.0, 60.8, 50.4, 29.1, 24.8, 23.8, 19.4. HRMS (ESI^+) calcd for $C_{14}H_{19}NH^+$ 202.1590, found 202.1593.

(—)-1-(6,7,8,9-Tetrahydro-5*H*-benzo[7]annulen-5-yl)pyrrolidine (4r) Yellow oil, 96% yield, 90% *ee*, $[\alpha]_D^{25}$ —50.7 (*c* 1.0, $CHCl_3$), GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm), N_2 1.0 mL/min, programmed from 120 ℃ to 170 ℃ at 1.0 ℃/min; t_R=29.49 min (minor) and t_R=30.48 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.15—7.05 (m, 4H), 3.48 (t, J=12.6 Hz, 1H), 3.15 (d, J=6.0 Hz, 1H), 2.57—2.51 (m, 3H), 2.18—2.02 (m, 4H), 1.92—1.88 (m, 1H), 1.79—1.63 (m, 6H), 1.38 (q, J=12.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 144.1, 143.5, 129.7, 129.3, 126.8, 125.4, 71.9, 53.0, 35.4, 32.5, 28.6, 25.9, 23.7. HRMS (ESI^+) calcd for $C_{15}H_{21}NH^+$ 216.1747, found 216.1748.

References

1 Lee, N. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5985.
2 Tararov, V. I.; Kadyrov, R.; Riermeier, T. H.; Holz, J.; Börner, A. *Tetrahedron Lett.* **2000**, *41*, 2351.
3 Hou, G.-H.; Xie, J.-H.; Wang, L.-X.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2006**, *128*, 11774
4 Hou, G.-H.; Xie, J.-H.; Yan, P.-C.; Zhou, Q.-L. *J. Am. Chem. Soc*. **2009**, *131*, 1366.
5 Yan, P.-C.; Xie, J.-H.; Hou, G.-H.; Wang, L.-X.; Zhou, Q.-L. *Adv. Synth. Catal*. **2009**, *351*, 3243.
6 Cheruku, P.; Church, T. L.; Trifonova, A.; Wartmann, T.; Andersson, P. G. *Tetrahedron Lett.* **2008**, *49*, 7290.
7 Baeza, A.; Pfaltz, A. *Chem. Eur. J.* **2009**, *15*, 2266.
8 Qiao, X.-C.; Zhu, S.-F.; Zhou, Q.-L. *Tetrahedron*: *Asymmetry* **2009**, *20*, 1254.
9 Barluenga, J.; Fernández, M. A.; Aznar, F.; Valdés, C. *Chem. Eur. J.* **2004**, *10*, 494.
10 Beaufort-Droal, V.; Pereira, E.; Théry, V.; Aitken, D. J. *Tetrahedron* **2006**, *62*, 11948.
11 Utsunomiya, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 14286.

(E1007222 Cheng, F.)

