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Efficient P,N,N-type ligands for Ru(II)-catalyzed asymmetric cyclopropanations

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Abstract

Novel chiral P,N,N-type ligands (**4**) derived from (*R*)-(*S*)-PPFNH$_2$-R (**6**) and 2-pyridinecarboxaldehydes were employed in Ru(II)-catalyzed asymmetric cyclopropanation of styrene with ethyl diazoacetate. Up to 99% yield with 95% e.e. for *cis*-isomer and 90% e.e. for *trans*-isomer was obtained on Ru(II)/**4a**.

Keywords: Ligand; Isomer; Asymmetric cyclopropanations

1. Introduction

Catalytic asymmetric cyclopropanation of olefins with diazoacetates is an important method for the production of chiral cyclopropane compounds [1,2]. Different methods have been developed for the asymmetric synthesis of cyclopropanes. The metal-catalyzed decomposition of diazoacetate derivatives in the presence of alkenes is one of the most efficient procedures. The transition metal catalysts containing copper, cobalt, rhodium, and palladium have been proved to be the most efficient in terms of both activity and chemoselectivity or stereoselectivity [3–8]. Recently, ruthenium based catalysts have been developed for the asymmetric cyclopropanation, excellent catalytic activity and stereoselectivity for the cyclopropanation were obtained [9]. Ligands containing N and N, O-donor atom are employed in the asymmetric cyclopropanation with high enantioselectivity, however, few ligands with P-donor atom are reported to be active for the cyclopropanation reactions [9a,b]. More recently, Mezzetti described a cationic ruthenium system of PNNP type, this PNNP–chelate ruthenium complex exhibits higher activity and enantioselectivity than its analogues [9e]. Ligand **1** reported by Ahn and coworkers was used in asymmetric cyclopropanation of styrene, however, only 7% e.e. was obtained when ethyl diazoacetate was used [9b]. Ligand **2** was also tried in the catalytic asymmetric cyclopropanation of styrene with ethyl diazoacetate, and 93% e.e. for *trans*-isomer was obtained on C_2-symmetrical copper(I)–PNNP complexes [10].

Since Hayashi et al.'s pioneer work [11], we have developed various ferrocenephosphine-imine (P,N type) ligands **3** which were successfully employed in allylic alkylation [12]. Herein, we report the synthesis of new ferrocenephosphine-imine (P,N,N type) ligands **4** from (*R*)-(*S*)-PPFNH$_2$-R (**6**) and 2-pyridinecarboxaldehydes and their application in Ru(II)-catalyzed asymmetric cyclopropanation of styrene with ethyl diazoacetate. Compared with ligand **1**, the new ligand has both central and planar chirality and thus, would exhibit different behavior in the catalytic reactions. As expected, high *trans*:*cis* selectivity (up to 81:19) and high enantioselectivity (up to 95% for *cis*-isomer) were obtained on **4a** with ethyl diazoacetate. As far as we know, this is the most efficient catalytic system ever reported for the asymmetric cyclopropanation of styrene with ethyl diazoacetate using ligands containing P-donor atom (Fig. 1).

2. Experiment

2.1. General methods

All experiments were carried out under argon atmosphere using Schlenk and syringe techniques. All solvents were

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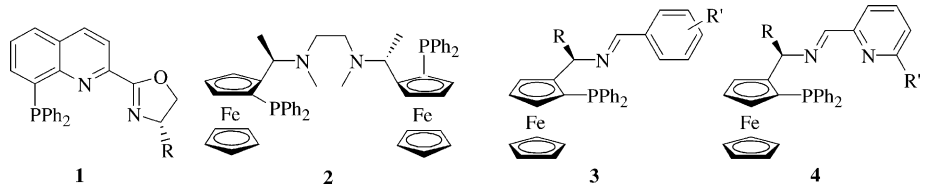


1 2 3 4

Fig. 1. Chemical structures of ligands **1**–**4**.

dried and purified according to standard methods. Optical rotations were measured on a HORIBA SEPA-200 high sensitive polarimeter. ^{1}H NMR spectra were recorded on Bruker DRX-400 NMR spectrometer with TMS as an internal standard. ^{31}P NMR spectra were referenced to external 85% H_3PO_4. The yields and e.e. values were determined by GC analysis with a chiral capillary column (cyclodex-β, 2,3,6-methylated, 30 m × 0.25 mm (i.d.)). Configurations of phenylcyclopropanecarboxylate were determined by GC, the GC elution order of the enantiomers was compared with an authentic sample prepared according to the literature [2f,g]. The starting materials PPFA-R **5** and PPFNH$_2$-R **6** were prepared according to literature procedures [12].

2.2. General procedure for the synthesis of ligands *4a–d*

A mixture of 2-pyridinecarboxaldehyde (118 mg, 1.1 mmol), (*R*)-(*S*)-PPFNH$_2$-Me (413 mg, 1.0 mmol), and $MgSO_4$ (500 mg) in absolute ethanol was stirred at refluxing temperature for 2 h. The solid was removed by filtration and the resulting orange solution was evaporated to dryness. The residue was recrystallized from hexane to afford 500 mg of **4a** (yield 92%). Ligands **4b**–**d** were prepared using the same method.

2.2.1. (R)-N-(Pyridin-2-methylene)-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine (4a)

Orange crystals; mp 185–187 °C. $[\alpha]_{20}^{D}$ −378(*c* 0.15, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 1.67 (d, J = 6.4 Hz, 3H), 3.75 (s, 1H), 4.07 (s, 5H), 4.32 (s, 1H), 4.64 (s, 1H), 4.94–4.95 (m, 1H), 6.72–8.12 (m, 14H), 8.41(d, J = 4.4 Hz, 1H); ^{31}P NMR δ −24.1. Anal. Calcd. for $C_{30}H_{27}FeN_2P$. C, 71.71; H, 5.38; N, 5.58. Found: C, 71.52; H, 5.36; N, 5.61.

2.2.2. (R)-N-(6-Methylpyridin-2-methylene)-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine (4b)

Brown crystals; 90% yield; mp 162–163 °C. $[\alpha]_{D}^{20}$ −336(*c* 0.12, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 1.57 (d, J = 6.0 Hz, 3H), 2.38 (s, 3H), 3.72 (s, 1H), 4.04 (s, 5H), 4.41 (s, 1H), 4.66 (s, 1H), 4.84–4.85 (m, 1H), 6.82–7.49 (m, 13H), 8.00 (s, 1H); ^{31}P NMR δ −25.5. Anal. Calcd. for $C_{31}H_{29}FeN_2P$. C, 72.09; H, 5.62; N, 5.43. Found: C, 72.18; H, 5.57; N,5.68.

2.2.3. (R)-N-(Pyridin-2-methylene)-1-[(S)-2-(diphenylphosphino)ferrocenyl]propylamine (4c)

Orange solid; 51% yield; mp 177–179 °C; $[\alpha]_{D}^{25}$ −390 (*c* 0.60, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 0.85 (t, J = 7.0 Hz, 3H), 1.81–1.88 (m, 1H), 2.22–2.28 (m, 1H), 3.69 (s, 1H), 4.04 (s, 5H), 4.39–4.45 (m, 2H), 4.65 (s, 1H), 6.77–8.04 (m, 14H), 8.41 (m, 1H); ^{31}P NMR δ −19.8. Anal. Calcd. for $C_{31}H_{29}FeN_2P$. C, 72.09; H, 5.62; N, 5.43. Found: C, 72.22; H, 5.77; N, 5.53.

2.2.4. (R)-N-(Pyridin-2-methylene)-1-[(S)-2-(diphenylphosphino)ferrocenyl]phenylmethylamine (4d)

Brown solid; 47% yield; mp 187–189 °C; $[\alpha]_{D}^{25}$ −306 (*c* 0.67, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 3.81 (s, 1H), 3.83 (s, 5H), 4.28 (s, 1H), 4.39 (s, 1H), 5.87–5.88 (m, 1H), 6.94–7.62 (m, 19H), 8.42 (d, J = 4.4 Hz, 1H); ^{31}P NMR δ −19.9. Anal. Calcd for $C_{35}H_{29}FeN_2P$. C, 74.47; H, 5.18; N, 4.96. Found: C, 74.62; H, 5.27; N, 4.68.

2.3. General procedure for asymmetric intermolecular cyclopropanation

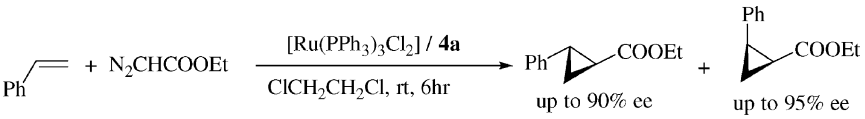
In 25 ml Schlenk tube, $Ru(PPh_3)_3Cl_2$ (19.1 mg, 0.020 mmol) was mixed with ligand **4a** (10.5 mg, 0.021 mmol) in 2.0 ml of CH_2Cl_2 under argon atmosphere. The solution was refluxed for 2 h, and then concentrated in vacuo. The residue was washed with Et_2O (3 × 1.0 ml) and vacuum dried. The solid was dissolved in 2.0 ml of $ClCH_2CH_2Cl$, followed by addition of 2.0 ml styrene. The mixture was stirred for 0.5 h at 60 °C, and then a solution of ethyl diazoacetate (114 mg, 1.00 mmol) in 6.0 ml of $ClCH_2CH_2Cl$ was added through a syringe pump over a period of 6 h. The resulting mixture was stirred for another 2 h. The catalyst-free sample was analyzed as described in the footnotes in Table 1.

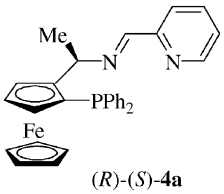
3. Results and discussion

3.1. Synthesis of ferrocenyl P,N,N ligands

The synthesis of the chiral P,N,N-ligand **4** is shown in Scheme 1. The initial step involved ferrocenylphosphine-amines **5** with Ac_2O at 100 °C followed by the treatment with a large excess of ammonia in methanol in an autoclave at 80 °C. The dimethylamino group of **5** was substituted by a primary amino group to form the key intermediate, (*R*)-(*S*)-PPFNH$_2$-R (**6**) [11]. Nucleophilic substitution on the ferrocenylmethyl position was demonstrated to occur with retention of configuration of the stereogenic carbon center [13]. The target ligands **4** were prepared with high yields by Schiff base condensation of (*R*)-(*S*)-PPFNH$_2$-R

Table 1
Catalytic asymmetric cyclopropanation of styrene with ethyl diazoacetate[a]





(*R*)-(*S*)-**4a**

Entry	Ligand	Yield (%)[b]	*cis*:*trans*[c]	% e.e. (*cis*)[c]	% e.e. (*trans*)[c]
1	**4a**	93	25:75	85 (1*S*,2*R*)	83 (1*S*,2*S*)
2	**4b**	90	20:80	64 (1*S*,2*R*)	50 (1*S*,2*S*)
3	**4c**	52	20:80	50 (1*S*,2*R*)	45 (1*S*,2*S*)
4	**4d**	32	20:80	3 (1*R*,2*S*)	10 (1*R*,2*R*)
5[d]	**4a**	81	4:96	50 (1*S*,2*R*)	61 (1*S*,2*S*)
6[e]	**4a**	86	3:97	90 (1*R*,2*S*)	62 (1*R*,2*R*)
7[f]	**4a**	80	5:95	60 (1*S*,2*R*)	66 (1*S*,2*S*)

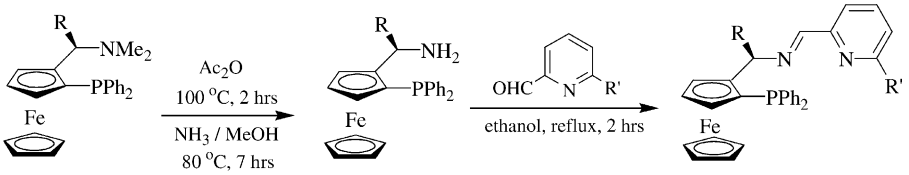
[a] Reaction conditions: 1.0 mmol of ethyl diazoacetate, 2.0 ml of styrene, 2.0 mol% catalyst generated in situ (based on the diazoacetate), 3.0 ml of 1,2-dichloroethane, room temperature.
[b] Determined by GC with diethyl adipate as an internal standard.
[c] The e.e. of the cyclopropanation products and the ratio of *trans*- and *cis*-isomers were determined by a chiral capillary GC column (cyclodex-β, 2,3,6-methylated, 30 m × 0.25 mm (i.d.)), and the configuration of the four isomers were determined by comparing the GC elution order with the authentic samples prepared according to the known the literature.
[d] L-Menthyl diazoacetate was used as substrate.
[e] D-Menthyl diazoacetate was used as substrate.
[f] *t*-Butyl diazoacetate was used as substrate.

(**6**) and 2-pyridine carboxaldehyde in ethanol in the presence of anhydrous $MgSO_4$ as dehydrating agent. Orange crystals of **4a** were obtained in 92% yield. The ^{1}H NMR spectra of ligand **4a** are consistent with the title molecule structure, and the ^{31}P NMR spectrum shows the expected signal ($\delta = -24.1$ ppm). Ligand **4b** was obtained as a brown crystal (90% yield) by treating PPFNH$_2$-Me with 6-methyl-2-pyridinecarboxaldehyde. The resonance of $-CH_3$ protons connected with pyridine ring was observed at 2.38 ppm in ^{1}H NMR spectrum of **4b**, which evidenced the difference between **4a** and **4b**. The ^{31}P NMR spectrum presented a singlet at −25.5 ppm, which could be assigned to the phosphino group.

To examine the substituent effects on the asymmetric cyclopropanation, ligands **4c** and **4d** were also prepared with (*R*)-(*S*)-PPFNH$_2$-Et and (*R*)-(*S*)-PPFNH$_2$-Ph as the chiral building block in a similar way, respectively (Scheme 1).

3.2. Catalytic asymmetric cyclopropanaiton of styrene using P,N,N ligand–Ru(II) complexes

The catalytic properties of the above ligands were investigated in Ru(II)-catalyzed asymmetric cyclopropanation of styrene with ethyl diazoacetate. The catalyst was generated in situ by mixing the ligand and [Ru(PPh$_3$)$_3$Cl$_2$] together in CH_2Cl_2. The results of cyclopropanation were listed in Table 1. Both **4a** and **4b** gave the major cyclopropane products with (1*S*,2*R*) configuration. Ligand **4a** exhibited higher catalytic activity and enantioselectivity than ligand **4b**. The **4b**–Ru complex has more sterically hindered structure, thus



(*R*)-(*S*)-PPFA-R, **5** (*R*)-(*S*)-PPFNH$_2$-R, **6**

4a: R=Me, R'=H
4b: R=Me, R'=Me
4c: R=Et, R'=H
4d: R=Ph, R'=H

Scheme 1.

perhaps cause poor chiral induction. Surprisingly, replacing of the aminoethyl group of **4a** with aminopropyl group (**4c**) and aminobenzyl group (**4d**) led to dramatic decreasing of activity and enantioselectivity. Fifty percent e.e. for *cis*-isomer and 45% e.e. for *trans*-isomer with 52% yield was obtained using **4c** as ligand (entry 3, Table 1), while only 3% e.e. for *cis*-isomer and 10% e.e. for *trans*-isomer with 32% yield were obtained using **4d** as ligand (entry 4, Table 1). Interestingly, the product formed on ligand **4d** showed the reverse configuration.

In most cases of cyclopropanation with diazoacetates, *trans*:*cis* selectivity and stereoselectivity are strongly related to the bulkiness and the shapes of the ester moiety of the diazoacetates, in general, bulky ester groups (such as *t*-butyl and *t*-menthyl) favor high *trans*:*cis* selectivity and enantioselectivity [14]. To examine the influence of the bulkiness of the ester group on the diastereoselectivity and enantioselectivity, the asymmetric cyclopropanation of styrene with bulkier ester (L-menthyl, D-menthyl and *t*-butyl diazoacetate) on ligand **4a** was investigated. The great increase of diastereoselectivities was observed (from 97/3 to 95/5 of *trans*:*cis* ratio, respectively, entries 5–7, Table 1), D-menthyl showed expected higher enantioselectivities and higher *trans*:*cis* ratio, however, L-menthyl and *t*-butyl diazoacetate only gave moderate e.e. (entry 5, Table 1), the unexpected decreasing of e.e. value may be due to the mismatching of the stereotopic situation [15].

To optimize the reaction condition, solvent and temperature effect on cyclopropanation of styrene with ethyl diazoacetate were examined using Ru(II)–**4a** complex. In protonic solvents such as ethanol and 2-propanol, the major products are diethyl maleate and diethyl fumarate accompanied by a small amount of the cyclopropanes with poor e.e. (entries 1 and 2, Table 2). These results indicate that protonic solvent inhibits the interaction between Ru-carbene and styrene, and thus dimmers are formed. Using hydrocarbon as solvent, the catalytic system exhibits lower catalytic activity and enantioselectivity (entries 3–5, Table 2). This is probably due to the fact that the catalyst is not very soluble in hydrocarbons under the catalytic reaction condition. When the reaction was performed in THF and MTBE (entries 6 and 7, Table 2), the catalyst shows higher activity and moderate e.e. value (92% yield with 70% e.e. of *cis*-isomer and 68% e.e. of *trans*-isomer in THF; 90% yield with 75% e.e. of *cis*-isomer and 72% e.e. of *trans*-isomer in MTBE). The highest enantioselectivity is obtained by using 1,2-dichloroethane as solvent (93% yield with 83% e.e. for *cis*-isomer and 83% e.e. for *trans*-isomer, entry 9, Table 2).

Interestingly, the same catalytic results can still be obtained when the reaction was performed under air atmosphere (entry 10, Table 2). The result indicates that the ruthenium catalytic system is not very air-sensitive, which would be a good merit for the practical applications.

The cyclopropanation was performed at different reaction temperatures, the results were summarized in Table 3. With increasing reaction temperature, the activity and enantioselectivty increased. The highest activity and enantioselectivity were obtained when the reaction was carried out at 60 °C (99% yield with 95% e.e. of *cis*-isomer and 90% e.e. of *trans*-isomer, entry 7, Table 3). Further, increasing the reaction temperature above 60 °C led to decreasing of the activity and enantioselectivity. These results show that the reaction temperature plays an important role on the catalytic property of Ru(II) catalysts.

Table 2
The influence of solvent on the asymmetric cyclopropanation of styrene with ethyl diazoacetate using **4a** as ligand[a]

Entry	Solvent	Yield (%)[b]	*cis*:*trans*[c]	% e.e. (*cis*)[c,d]	% e.e. (*trans*)[c,e]
1	Ethanol	8	20:80	1	2
2	2-Propanol	10	20:80	5	8
3	Hexane	52	16:84	31	24
4	Benzene	50	20:80	35	28
5	Toluene	58	25:75	29	22
6	THF	92	14:86	70	68
7	MTBE	90	18:82	75	72
8	Dichloromethane	92	20:80	81	80
9	1,2-Dichloroethane	93	25:75	83	83
10[f]	1,2-Dichloroethane	91	20:80	80	78

[a] Reaction conditions: 1.0 mmol of ethyl diazoacetate, 2.0 ml of styrene, 2.0 mol% catalyst, generated in situ (based on the diazoacetate), 3.0 ml of solvent, room temperature.
[b] Determined by GC with diethyl adipate as a internal standard.
[c] The e.e. of the cyclopropanation product and the ratio of *trans*- and *cis*-isomers were determined by a chiral capillary GC column (cyclodex-β, 2,3,6-methylated, 30 m × 0.25 mm (i.d.)), and the configurations of the four isomers were determined by comparing the GC elution order with the authentic samples prepared according to the literature.
[d] (1*S*,2*R*) as the major enantiomer.
[e] (1*S*,2*S*) as the major enantiomer.
[f] The reaction was performed in air.

Table 3
The influence of reaction temperature on the asymmetric cyclopropanation of styrene with ethyl diazoacetate using **4a** as ligand[a]

Entry	*T* (°C)	Yield (%)[b]	*cis*:*trans*[c]	% e.e. (*cis*)[c,d]	% e.e. (*trans*)[c,e]
1	0	30	25:75	27	75
2	10	86	25:75	75	76
3	20	93	25:75	85	83
4	30	94	19:81	87	82
5	40	95	20:80	89	87
6	50	95	20:80	92	88
7	60	99	19:81	95	90
8	70	89	27:73	89	87
9	80	87	26:74	77	76

[a] Reaction conditions: 1.0 mmol of ethyl diazoacetate, 2.0 ml of styrene, 2.0 mol% catalyst prepared in situ (based on the diazoacetate), 3.0 ml of 1,2-dichloroethane.
[b] Determined by GC with diethyl adipate as internal standard.
[c] The e.e. of the cyclopropanation product and the ratio of *trans*- and *cis*-isomers were determined by a chiral capillary GC column (cyclodex-β, 2,3,6-methylated, 30 m × 0.25 mm (i.d.)), and the configurations of the four isomers were determined by comparing the GC elution order with the authentic sample prepared according to the literature.
[d] (1*S*,2*R*) as the major enantiomer.
[e] (1*S*,2*S*) as the major enantiomer.

4. Conclusion

In conclusion, a new type of chiral ferrocenylphophine-imine ligands **4a–d** were synthesized and these new P,N,N-type ligands are proved to be efficient in ruthenium catalyzed asymmetric cyclopropanation of styrene with ethyl diazoacetate. 95% e.e. of *cis*-isomer and 90% e.e. of *trans*-isomer were achieved using $[Ru(PPh_3)_3Cl_2]$–**4a** as catalyst in cyclopropanation of styrene.

Acknowledgements

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References

[1] (a) For recent reviews: (a) M.P. Doyle, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, vol. 191, VCH, New York, 1999;
(b) M.P. Doyle, D.C. Forbes, Chem. Rev. 98 (1998) 911;
(c) V.K. Singh, A.D. Gupta, G. Sekar, Synthesis (1997) 137;
(d) M.P. Doyle, M.N. Protopova, Tetrahedron 54 (1998) 7919.

[2] (a) P. Liu, E.N. Jacobsen, J. Am. Chem. Soc. 123 (2001) 10772;
(b) A. Srikrishna, K.J. Anebouselvy, J. Org. Chem. 66 (2001) 7102;
(c) B. Charette, E. Jolicoeur, G.A.S. Bydlinski, Org. Lett. 3 (2001) 3293;
(d) T. Abellan, B. Mancheno, C. Najera, J.M. Sansano, Tetrahedron 57 (2001) 6627;
(e) M.P. Doyle, W. Hu, Adv. Synth. Catal. 343 (2001) 299;
(f) T. Aratani, Y. Yoneyoshi, T. Nagase, Tetrahedron Lett. (1975) 1707;
(g) T. Aratani, Pure Appl. Chem. 57 (1985) 1839.

[3] (a) J. Krysiak, T. Kato, H. Gornitzka, A. Baceiredo, M. Mikolajczyk, G. Bertrand, J. Org. Chem. 66 (2001) 8240;
(b) J.M. Fraile, J.I. Garcia, C.I. Herrerias, J.A. Mayoral, D. Carrie, M. Vaultier, Tetrahedron Asymm. 12 (2001) 1891;
(c) H.M.L. Davies, R.J. Townsend, J. Org. Chem. 66 (2001) 6595;
(d) V.K. Aggarwal, E. Alonso, G. Fang, M. Ferrara, G. Hynd, M. Porcelloni, Angew. Chem. Int. Ed. Engl. 40 (2001) 1433;
(e) T. Uchida, B. Saha, T. Katsuki, Tetrahedron Lett. 42 (2001) 2521;
(f) C.-M. Che, J.-S. Huang, F.-W. Lee, Y. Li, T.-S. Lai, H.-L. Kwong, P.-F. Teng, W.-S. Lee, W.-C. Lo, S.-M. Peng, Z.-Y. Zhou, J. Am. Chem. Soc. 123 (2001) 4119;
(g) G. Chelucci, A. Saba, D. Vignola, C. Solinas, Tetrahedron 57 (2001) 1099;
(h) S. Iwasa, F. Takezawa, Y. Tuchiya, H. Nishiyama, Chem. Commun. 59 (2001) 59;
(i) D.C. Wynne, M.M. Olmstead, P.G. Jessop, J. Am. Chem. Soc. 122 (2000) 7638;
(j) S.K. Bertilsson, P.G. Andersson, J. Organomet. Chem. 603 (2000) 13;
(k) J. Balsells, P.J. Walsh, J. Org. Chem. 65 (2000) 5005;
(l) M. Glos, O. Reiser, Org. Lett. 2 (2000) 2045;
(m) Y. Imai, W. Zhang, T. Kida, Y. Nakatsuji, I. Ikeda, J. Org. Chem. 65 (2000) 3326;
(n) R. Boulch, A. Scheurer, P. Mosset, R.W. Saalfrank, Tetrahedron Lett. 41 (2000) 1023;
(o) A.B. Charette, C. Molinaro, C. Brochu, J. Am. Chem. Soc. 123 (2001) 12168.

[4] (a) T. Aratani, Y. Yoneyoshi, T. Nagase, Tetrahedron Lett. (1977) 2599;
(b) T. Aratani, Y. Yoneyoshi, T. Nagase, Tetrahedron Lett. 23 (1982) 685.

[5] A. Nakamura, A. Honishi, Y. Tassuno, S. Otsuka, J. Am. Chem. Soc. 100 (1978) 3443.

[6] (a) H. Fritsuchhi, U. Leutenegger, A. Pfaltz, Angew. Chem. Int. Ed. Engl. 25 (1986) 1005;
(b) A. Pfaltz, Acc. Chem. Res. 26 (1993) 339.

[7] (a) R.E. Lowenthal, A. Abiko, S. Masamune, Tetrahedron Lett. 31 (1990) 6005;
(b) D.A. Evans, K.A. Woerpal, M.M. Hinman, M.M. Faul, J. Am. Chem. Soc. 113 (1991) 726;
(c) R.E. Lowenthal, A. Abiko, S. Masamune, Tetrahedron Lett. 32 (1991) 7373;
(d) D. Muller, G. Umbricht, B. Weber, A. Pfaltz, Helv. Chim. Acta 74 (1991) 232;
(e) Y. Uozumi, H. Kyota, E. Kishi, K. Kitayama, T. Hayashi, Tetrahedron Asymm. 7 (1996) 1603;
(f) A.V. Bedekar, E.B. Koroleva, P.C. Anderson, J. Org. Chem. 62 (1997) 2518.

[8] (a) K. Ito, T. Katsuki, Tetrahedron Lett. 34 (1993) 2661;
(b) K. Itoh, M. Yoshitake, T. Katsuki, Heterocycles 42 (1996) 305;
(c) M.P. Doyle, B.D. Brandes, A.P. Kazala, R.J. Pirters, M.B. Jarstfer, L.M. Watkins, C.T.J. Eagle, Tetrahedron Lett. 31 (1990) 6613;
(d) H.M.L. Davies, P.R. Bruzinski, D.H. Lake, N. Kong, M.J. Fall, J. Am. Chem. Soc. 118 (1996) 6897;
(e) Z. Li, Z. Zheng, H. Chen, Tetrahedron Asymm. 11 (2000) 1157;
(f) Z. Li, Z. Zheng, H. Chen, Tetrahedron 56 (2000) 7187;
(g) X. Yao, M. Qiu, W. Lu, H. Chen, Z. Zheng, Tetrahedron Asymm. 12 (2001) 197;
(h) L. Cai, H. Mahmoud, Y. Han, Tetrahedron Asymm. 10 (1999) 411.

[9] (a) H.M. Lee, C. Bianchini, G. Jia, P. Barbaro, Organometallics 18 (1999) 1961;
(b) S.W. Park, J.H. Son, S.G. Kim, K.H. Ahn, Tetrahedron Asymm. 10 (1999) 1903;
(c) W. Tang, X. Hu, X. Zhang, Tetrahedron Lett. 43 (2002) 3075;
(d) H. Nishiyama, Y. Itoh, H. Matsumoto, S.-B. Park, K. Itoh, J. Am. Chem. Soc. 116 (1994) 2223;
(e) C. Bonaccorsi, S. Bachmann, A. Mezzetti, Tetrahedron Asymm. 14 (2003) 845, and the references cited therein;
(f) J.A. Miller, W. Jin, S.T. Nguyen, Angew. Chem. Int. Ed. Engl. 41 (2002) 2953.

[10] D.-J. Cho, S.-J. Jeon, H.-S. Kim, C.-S. Cho, S.-C. Shim, T.-J. Kim, Tetrahedron Asymm. 10 (1999) 3833.

[11] T. Hayashi, C.J. Hayashi, Y. Uozumi, Tetrahedron Asymm. 6 (1995) 2503.

[12] X. Hu, H. Dai, X. Hu, H. Chen, J. Wang, C. Bai, Z. Zheng, Tetrahedron Asymm. 13 (2002) 1687.

[13] (a) G.W. Gokel, D. Maequarding, I.K. Ugi, J. Org. Chem. 37 (1972) 3052;
(b) T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, Bull. Chem. Soc. Jpn. 53 (1980) 1138.

[14] H. Nishiyama, Y. Itoh, Y. Sugawara, A. Matsumoto, K. Aoki, K. Itoh, Bull. Chem. Soc. Jpn. 68 (1995) 1247, and the references cited therein.

[15] H. Nishiyama, N. Soeda, T. Naito, Y. Motoyama, Tetrahedron Asymm. 9 (1998) 2865.