Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 665 (2003) 122–126
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Palladium-catalyzed asymmetric allylic substitution using planar chiral hydrazone ligands

Takashi Mino [a,*], Teruhiro Ogawa [b], Masakazu Yamashita [b]

[a] Department of Materials Technology, Faculty of Engineering, Chiba University, Inage-ku, Chiba 263-8522 Japan
[b] Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0394, Japan

Received 10 October 2002; received in revised form 1 November 2002; accepted 5 November 2002

Abstract

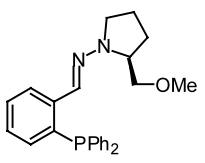
Palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate (**3**) with a dimethyl malonate–BSA–LiOAc system has been successfully carried out in the presence of planar chiral phosphine-hydrazone ligands such as **2a** in good yields with good enantioselectivities (up to 96% ee).

Keywords: Palladium; Ferrocene; Hydrazone; Asymmetric catalysis; Allylic alkylation; Allylic amination

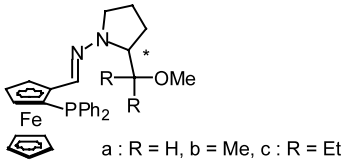
1. Introduction

Synthesis of chiral ferrocene derivatives has attracted much interest in various research fields [1]. Planar chiral ferrocenes have shown efficiency as catalysts for asymmetric synthesis. Palladium-catalyzed allylic substitution is a versatile and widely used process in organic synthesis [2], and the development of efficient enantioselective catalysis for this reaction is an important goal of current research in this area [3]. So chiral ferrocene ligands with planar chirality began to be used in palladium-catalyzed allylic substitution [4].

We previously described the palladium-catalyzed asymmetric allylic substitution of using 2-diphenylphosphinobenzaldehyde SAMP hydrazone (DPPB-SAMP) (**1**) as a chiral ligand [5]. On the other hand, Enders recently described the synthesis of planar chiral ferrocenyl ketone hydrazone [6]. We here report the synthesis of phosphine-hydrazone ligands **2** with planar chirality and palladium catalyzed asymmetric allylic alkylation [7] and amination using ligands **2**.



1



2

2. Results and discussion

2.1. Synthesis of the planar chiral hydrazone ligands

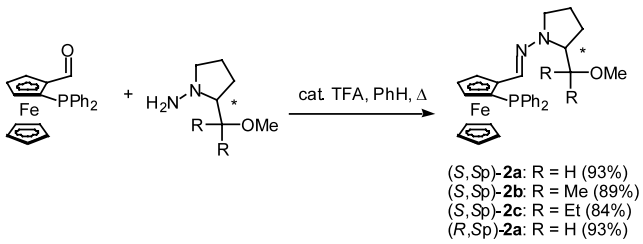
Phosphine-hydrazone ligands **2** were easily prepared from (*S*)-α-(diphenylphosphino)ferrocenecarboxaldehyde [4c] with (*S*)-1-amino-2-(methoxymethyl)pyrrolidine (SAMP), (*S*)-amino-2-(1′-methoxy-1′-methylethyl)-pyrrolidine (SADP), (*S*)-amino-2-(1′-methoxy-1′-ethylpropyl)pyrrolidine (SAEP), and (*R*)-1-amino-2-(methoxymethyl)pyrrolidine (RAMP) in good yields (Scheme 1).

2.2. Palladium-catalyzed asymmetric allylic alkylation

These ligands were examined in the palladium-catalyzed asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate (**3**) [8] with dimethyl mal-

* Corresponding author. Tel.: +81-43-290-3385; fax: +81-43-290-3401
E-mail address: tmino@planet.tc.chiba-u.ac.jp (T. Mino).

0022-328X/02/$ - see front matter
PII: S0022-328X(02)02102-2



Scheme 1.

onate in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) [9] at room temperature (Scheme 2 in Table 1). Using 1 mol% of SAMP hydrazone, (*S*,*S*p)-**2a**, and lithium acetate in CH_2Cl_2 (Entry 1), the product **4** was obtained in 86% yield and 92% ee. When toluene was used instead of CH_2Cl_2, the enantioselectivity of **4** was increased to 96% ee (Entry 4). Sodium acetate or potassium acetate was used instead of lithium acetate in toluene, the yield and/or enantioselectivity of **4** was decreased (Entries 6 and 7 vs. 4 in Table 1). Thus, the optimized result was realized when the reaction was carried out in the presence of lithium acetate in toluene.

In this condition, SADP hydrazone ((*S*,*S*p)-**2b**) and SAEP hydrazone ((*S*,*S*p)-**2c**) were used instead of (*S*,*S*p)-**2a**, and the enantioselectivity of **4** decreased (Entries 8 and 9 vs. 4 in Table 1). Product **4** was formed with the (*R*)-(+)-enantiomer predominating, as determined from the sign of the optical rotation [10]. We next investigated the asymmetric allylic alkylation using the diastereomer of (*S*,*S*p)-**2a** as ligand. The enantioselectivity of **4** decreased and the configuration of **4** was inverted using (*R*,*S*p)-**2a** which was prepared from (*S*p)-α-(diphenylphosphino)ferrocenecarboxaldehyde and RAMP (Entry 4 vs. 10 in Table 1).

This observation indicates that the central chirality in the hydrazone unit is more influential factor determining the stereochemical outcome in the allylic alkylation than the planar chirality. We next investigated the effect of temperature on this reaction (Table 2). The enantioselectivity and yield were dependent on the reaction temperature, the best result was obtained at room temperature (Entry 2 in Table 2).

Table 2
Effect of reaction temperature on asymmetric allylic alkylation using (*S*,*S*p)-**2a** in PhMe [a]

Entry	Temperature	Time (h)	Yield of **4** (%) [b]	Ee of **4** (%) [c]
1	50 °C	3	89	89
2	r.t.	20	93	96
3	4 °C	48	95	95
4	−20 °C	198	78	95

[a] Molar ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.005 equivalent), ligand (0.01 equivalent), dimethyl malonate (3.0 equivalent), BSA (3.0 equivalent), MOAc (0.01 equivalent).
[b] Isolated yields.
[c] The ee values were determined by HPLC analysis using a chiral column (Chiralcel OD (hexane:*i*-PrOH = 99:1)).

We next investigated the effect of amount of Pd catalyst on this reaction (Table 3). When only 0.5 mol% of Pd was used (Entry 3 in Table 3), the product **4** was obtained in 90% yield and 94% ee. The palladium complex of hydrazone ligand **2a** is highly reactive in this reaction.

2.3. Palladium-catalyzed asymmetric allylic amination

We next investigated the palladium-catalyzed asymmetric allylic amination of racemic acetate **3** with benzylamine using **2** (Scheme 2, Table 4). The reaction proceeded slowly to give the product **5** with 88% ee at room temperature by using (*S*,*S*p)-**2a** as ligand (Entry 1). When the reaction was carried out at 50 °C, the product **5** was obtained in 99% yield and 88% ee. Using hydrazone (*S*,*S*p)-**2b** instead of (*S*,*S*p)-**2a,** the product **5** was obtained in 79% yield and 93% ee at 50 °C (Entry 3). The ee value of **5** was decreased if (*R*,*S*p)-**2a** was

Table 1
Asymmetric allylic alkylation catalyzed by palladium complexes with chiral hydrazone ligands **2** [a]

Entry	Ligand	Solvent	M	Yield of **4** (%) [b]	Ee of **4** (%) [c]	Configuration of **4**
1	(*S*,*S*p)-**2a**	DCM	Li	86	92	*R*
2	(*S*,*S*p)-**2a**	THF	Li	88	92	*R*
3	(*S*,*S*p)-**2a**	MeCN	Li	90	90	*R*
4	(*S*,*S*p)-**2a**	PhMe	Li	93	96	*R*
5	(*S*,*S*p)-**2a**	Ether	Li	90	92	*R*
6	(*S*,*S*p)-**2a**	PhMe	Na	87	95	*R*
7	(*S*,*S*p)-**2a**	PhMe	K	82	89	*R*
8	(*S*,*S*p)-**2b**	PhMe	Li	90	90	*R*
9	(*S*,*S*p)-**2c**	PhMe	Li	88	74	*R*
10	(*R*,*S*p)-**2a**	PhMe	Li	94	46	*S*

[a] Molar ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.005 equivalent), ligand (0.01 equivalent), dimethyl malonate (3.0 equivalent), BSA (3.0 equivalent), MOAc (0.01 equivalent).
[b] Isolated yields.
[c] The ee values were determined by HPLC analysis using a chiral column (Chiralcel OD (hexane:*i*-PrOH = 99:1)).

Table 3
Effect of amount of palladium complexes on asymmetric allylic alkylation using (*S*,*S*p)-**2a** in PhMe [a]

Entry	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (equivalent)	(*S*,*S*p)-**2a** (equivalent)	Yield of **4** (%) [b]	Ee of **4** (%) [c]
1	0.02	0.04	98	96
2	0.005	0.01	93	96
3	0.0025	0.005	90	94
4	0.00125	0.0025	34	82

[a] Molar ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.005 equivalent), ligand (0.01 equivalent), dimethyl malonate (3.0 equivalent), BSA (3.0 equivalent), MOAc (0.01 equivalent).
[b] Isolated yields.
[c] The ee values were determined by HPLC analysis using a chiral column (Chiralcel OD (hexane:*i*-PrOH = 99:1)).

used (Entry 2 vs. 5 in Table 4). The product **5** was formed with the (*S*)-(+)-enantiomer predominating, as determined from the sign of the optical rotation [11]. This observation indicates that the planar chirality is more influential factor determining the stereochemical outcome in the allylic amination than the central chirality in the hydrazone unit (Scheme 3).

3. Conclusion

We have prepared new chiral planar phosphine-hydrazone ligands easily from (*S*)-α-(diphenylphosphino)ferrocenecarboxaldehyde and chiral hydrazines such as SAMP. These ligands such as (*S*,*S*p)-**2a** can be used in palladium-catalyzed asymmetric allylic substitution with high enantiomeric excess.

4. Experimental

4.1. General methods

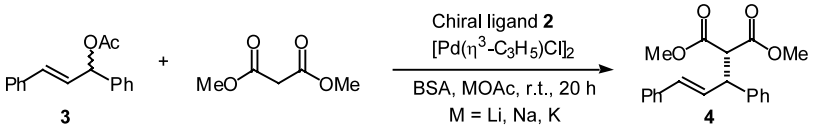
All the experiments were carried out under an argon atmosphere. IR spectra were taken on a Hitachi 260-10 spectrometer or a JASCO FTIR-230 spectrometer. NMR spectra were recorded on a JEOL A-400 spectrometer or a Bruker DPX-300 spectrometer. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H- and ^{13}C-NMR. ^{31}P-NMR spectra were obtained using 85% H_3PO_4 as an external reference. Mass spectra were recorded on a JEOL JMS-HX110 or a JMS-700 or a Shimadzu GCMS-QP2000A or a Hitachi M-80B. Optical rotations were measured on a JASCO DIP-370 or a HORIBA SEPA-200. Chiral HPLC analyses were performed on a Shimadzu LC-6A system using a Chiralcel OD column (25 × 0.46 cm) by Daicel Chemical Ind., Ltd.

4.2. Typical procedure for the preparation of **2**

A mixture of (*S*)-α-(diphenylphosphino)-ferrocenecarboxaldehyde (0.38 mmol), chiral hydrazine (0.46 mmol), and benzene (10 ml) was heated at 100 °C for 6 h under an argon atmosphere, and then cooled to room temperature (r.t.). The reaction mixture was diluted with ether and water. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated with a rotary evaporator and the residue was purified by column chromatography.

4.2.1. (*S*)-α-(Diphenylphosphino)ferrocenecarboxaldehyde SAMP hydrazone ((*S*,*S*p)-**2a**)

(*S*)-α-(Diphenylphosphino)ferrocenecarboxaldehyde SAMP hydrazone ((*S*,*S*p)-**2a**): 99%; $[\alpha]_{25}^{D} = +138.0^{\circ}$ (*c* 0.50, $CHCl_3$); ^{1}H-NMR (300 Mz, $CDCl_3$) δ 1.72–1.99 (m, 4H), 2.73 (dd, 8.0 and 16.8 Hz, 1H), 3.14–3.30 (m, 2H), 3.25 (s, 3H), 3.31–3.39 (m, 1H), 3.39–3.45 (m, 1H), 3.65–3.71 (m, 1H), 4.07 (s, 5H), 4.31 (t, 2.4 Hz, 1H), 4.75–4.86 (m, 1H), 7.13–7.25 (m, 6H), 7.32–7.43 (m, 3H), 7.48–7.48 (m, 2H); ^{13}C-NMR (75 Mz, $CDCl_3$) δ 21.98, 26.41, 49.41, 59.06, 63.01, 68.41 (d, 3.1 Hz), 69.79, 70.12, 72.05 (d, 3.8 Hz), 74.08, 74.36 (d, 10.0 Hz), 88.73 (d, 17.7 Hz), 127.50, 127.96 (d, 6.0 Hz), 128.08 (d, 7.7 Hz), 129.01, 131.50 (d, 7.0 Hz), 132.16 (d, 17.8 Hz), 135.26 (d, 21.1 Hz), 137.92 (d, 10.2 Hz), 140.33 (d, 11.1 Hz); ^{31}P-NMR (121 Mz, $CDCl_3$) δ −19.80; FABMS *m*/*z* 510 [M^+, 30]; HRMS (FAB) Calc. for $C_{29}H_{31}N_2OPFe$ [M^+]: 510.1523. Found: 510.1499.



Scheme 2.

Table 4
Asymmetric allylic amination catalyzed by palladium complexes with chiral hydrazone ligands **2** [a]

Entry	Ligand	Temperature	Yield of **5** (%) [b]	Ee of **5** (%) [c]	Configuration of **5**
1	(*S*,*S*p)-**2a**	r.t.	21	88	*S*
2	(*S*,*S*p)-**2a**	50 °C	99	88	*S*
3	(*S*,*S*p)-**2b**	50 °C	79	93	*S*
4	(*S*,*S*p)-**2c**	50 °C	71	74	*S*
5	(*R*,*S*p)-**2a**	50 °C	99	51	*S*

[a] Molar ratio: $Pd_2(dba)_3$ (0.02 equivalent), ligand (0.04 equivalent), benzylamine (3.0 equivalent), BSA (3.0 equivalent).
[b] Isolated yields.
[c] The ee values were determined by HPLC analysis using a chiral column (Chiralcel OD (hexane:*i*-PrOH = 199:1)).

4.2.2. (*S*)-α-(Diphenylphosphino)ferrocenecarboxaldehyde SADP hydrazone ((*S*,*S*p)-**2b**)

(*S*)-α-(Diphenylphosphino)ferrocenecarboxaldehyde SADP hydrazone ((*S*,*S*p)-**2b**): 89%; $[\alpha]_{25}^{D} = +576.0^{\circ}$ (*c* 0.50, $CHCl_3$); ^{1}H-NMR (400 Mz, $CDCl_3$) δ 1.11 (s, 3H), 1.17 (s, 3H), 1.77–1.98 (m, 4H), 2.63 (dd, 8.5 and 15.9 Hz, 1H), 3.22 (s, 3H), 3.40–3.49 (m, 2H), 3.71–3.72 (m, 1H), 4.04 (s, 5H), 4.33 (t, 2.4 Hz, 1H), 4.89–4.91 (m, 1H), 7.12–7.23 (m, 5H), 7.25 (s, 1H), 7.36–7.39 (m, 3H), 7.50–7.58 (m, 2H); ^{13}C-NMR (75 Mz, $CDCl_3$) δ 21.03, 23.07, 23.69, 24.64, 49.59, 51.12, 67.71 (d, 3.5 Hz), 69.96, 70.06, 71.17, 71.76 (d, 3.5 Hz), 74.31 (d, 9.4 Hz), 77.69, 89.09 (d, 18.5 Hz), 127.62, 128.06, 127.07 (d, 13.4 Hz), 129.08, 130.22 (d, 9.7 Hz), 132.16 (d, 17.7 Hz), 135.16 (d, 21.0 Hz), 137.53 (d, 9.4 Hz), 140.00 (d, 10.5 Hz); ^{31}P-NMR (121 Mz, $CDCl_3$) δ −20.84; FABMS *m*/*z* 538 [M^+, 38]; HRMS (FAB) Calc. for $C_{31}H_{35}N_2OPFe$ [M^+]: 538.1836. Found: 538.1852.

4.2.3. (*S*)-α-(Diphenylphosphino)ferrocenecarboxaldehyde SAEP hydrazone ((*S*,*S*p)-**2c**)

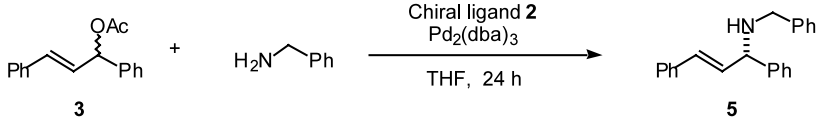
(*S*)-α-(Diphenylphosphino)ferrocenecarboxaldehyde SAEP hydrazone ((*S*,*S*p)-**2c**): 84%; $[\alpha]_{25}^{D} = +526.0^{\circ}$ (*c* 0.50, $CHCl_3$); ^{1}H-NMR (400 Mz, $CDCl_3$) δ 0.88 (t, 7.5 Hz, 3H), 0.90 (t, 7.1 Hz, 3H), 1.42–2.05 (m, 8H), 2.64 (dd, 9.5 and 17.5 Hz, 1H), 3.26 (s, 3H), 3.33–3.42 (m, 1H), 3.64 (dd, 2.5 and 8.5 Hz, 1H), 3.71 (dt, 1.2 and 2.3 Hz, 1H), 4.03 (s, 5H), 4.33 (t, 2.5 Hz, 1H), 4.94 (dt, 1.2 and 2.3 Hz, 1H), 7.13–7.24 (m, 5H), 7.25 (s, 1H), 7.36–7.40 (m, 3H), 7.51–7.58 (m, 2H); ^{13}C-NMR (75 Mz, $CDCl_3$) δ 7.89, 8.62, 23.55, 23.69, 24.38, 26.25, 50.36, 50.66, 67.50 (d, 3.5 Hz), 69.97, 70.09, 70.34, 71.75 (d, 3.6 Hz), 74.19 (d, 9.2 Hz), 80.40, 89.22 (d, 18.6 Hz), 127.68, 128.09, 127.10 (d, 12.8 Hz), 129.05 (d, 9.9 Hz), 129.12, 132.15 (d, 17.6 Hz), 135.15 (d, 20.9 Hz), 137.44 (d, 9.2 Hz), 139.93 (d, 10.3 Hz); ^{31}P-NMR (121 Mz, $CDCl_3$) δ −20.99; FABMS *m*/*z* 566 [M^+, 22]; HRMS (FAB) Calc. for $C_{33}H_{39}N_2OPFe$ [M^+]: 566.2150. Found: 566.2157.

4.2.4. (*S*)-α-(Diphenylphosphino)ferrocenecarboxaldehyde RAMP hydrazone ((*R*,*S*p)-**2a**)

(*S*)-α-(Diphenylphosphino)ferrocenecarboxaldehyde RAMP hydrazone ((*R*,*S*p)-**2a**): 93%; $[\alpha]_{25}^{D} = +282.0^{\circ}$ (*c* 0.50, $CHCl_3$); ^{1}H-NMR (400 Mz, $CDCl_3$) δ 1.71–2.05 (m, 4H), 2.84 (dd, 8.1 and 16.6 Hz, 1H), 3.21–3.41 (m, 3H), 3.33 (s, 3H), 3.54 (dd, 5.6 and 9.2 Hz, 1H), 3.71 (t, 1.1 Hz, 1H), 4.04 (s, 5H), 4.33 (t, 2.4 Hz, 1H), 4.87 (t, 1.0 Hz, 1H), 7.11–7.24 (m, 5H), 7.29 (s, 1H), 7.36–7.40 (m, 3H), 7.50-7.59 (m, 2H); ^{13}C-NMR (75 Mz, $CDCl_3$) δ 22.01, 26.58, 49.73, 59.15, 63.23, 68.76 (d, 3.2 Hz), 70.03, 70.24, 72.00 (d, 4.0 Hz), 74.36, 74.49, 88.60 (d, 18.3 Hz), 127.56, 127.92 (d, 5.8 Hz), 128.08 (d, 7.6 Hz), 129.04, 132.12 (d, 9.9 Hz), 132.17 (d, 17.6 Hz), 135.26 (d, 21.1 Hz), 137.81 (d, 9.9 Hz), 139.99 (d, 10.5 Hz); ^{31}P-NMR (121 Mz, $CDCl_3$) δ −20.99; FABMS *m*/*z* 510 [M^+, 61]; HRMS (FAB) Calc. for $C_{29}H_{31}N_2OPFe$ [M^+]: 510.1523. Found: 510.1542.

4.3. General procedure for the palladium-catalyzed allylic alkylation

To mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 μmol, 0.9 mg), chiral hydrazone **2** (5.0 μmol), and metal acetate (10 μmol) in a solvent (1 ml) was added BSA (1.5 mmol, 0.37 ml), racemic 1,3-diphenyl-2-propenyl acetate (**3**) (0.5 mmol, 0.126 g), and dimethyl malonate (1.5 mmol, 0.17 ml) at r.t. under an argon atmosphere. After being stirred for 20 h, the reaction mixture was diluted with ether and water. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated with a rotary evaporator and the residue was purified by column chromatography.



Scheme 3.

4.3.1. (*R*)-**4**

Yield 93% (Table 1, Entry 4); 96% ee; $[\alpha]_D^{25} = 18.8^\circ$ (*c* 1.01, EtOH); ^{1}H-NMR (400 Mz, $CDCl_3$) δ 3.51 (s, 3H), 3.70 (s, 3H), 3.95 (d, 11.0 Hz, 1H), 4.27 (dd, 8.5 and 11.0 Hz, 1H), 6.44 (dd, 8.5 and 15.8 Hz, 1H), 6.71 (d, 15.8 Hz, 1H), 7.19–7.33 (m, 10H); ^{13}C-NMR (100 Mz, $CDCl_3$) δ 49.20, 52.45, 52.63, 57.66, 126.40, 127.18, 127.58, 127.86, 128.48, 128.73, 129.12, 131.85, 136.83, 140.18, 167.79, 168.21; MS (EI) *m*/*z* 324 [M^+, 30].

4.4. General procedure for the palladium-catalyzed allylic amination

To mixture of $Pd_2(dba)_3$ (0.01 mmol, 0.01 g), chiral hydrazone **2** (0.02 mmol), in a solvent (1 ml) was added racemic 1,3-diphenyl-2-propenyl acetate (**3**) (0.5 mmol, 0.126 g), and benzylamine (1.5 mmol, 0.26 g) at r.t. under an argon atmosphere. After being stirred for 24 h at 50 °C, the reaction mixture was diluted with ether and sat. $NaHCO_3$. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated with a rotary evaporator and the residue was purified by column chromatography.

4.4.1. (*S*)-**5**

Yield 99% (Table 4, Entry 2); 88% ee; $[\alpha]_D^{25} = 20.0^\circ$ (*c* 1.0, $CHCl_3$); ^{1}H-NMR (400 Mz, $CDCl_3$) δ 1.81 (br-s, 1H), 3.78 (d, 13.3 Hz, 1H), 3.82 (d, 13.3 Hz, 1H), 4.39 (d, 7.4 Hz, 1H), 6.31 (dd, 7.9 and 15.9 Hz, 1H), 6.58 (d, 15.9 Hz, 1H), 7.20–7.44 (m, 15H); ^{13}C-NMR (100 Mz, $CDCl_3$) δ 15.27, 51.36, 64.57, 65.86, 126.40, 126.93, 127.29, 127.36, 127.44, 128.17, 128.41, 128.50, 128.61, 130.35, 132.56, 136.90, 140.36, 142.84; MS (EI) *m*/*z* 299 [M^+, 11].

References

[1] For leading references, see; (a) A. Togni, T. Hayashi (Eds.), Ferrocenes, VCH, Weinheim, 1995.(b) C.J. Richards, A.J. Locke, Tetrahedron: Asymmetry 9 (1998) 2377.

[2] (a) J. Tsuji, I. Minami, Acc. Chem. Res. 20 (1987) 140;
(b) B.M. Trost, T.R. Verhoeven, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon, Oxford, 1982, p. 799;
(c) B.M. Trost, Acc. Chem. Res. 13 (1980) 385.

[3] (a) B.M. Trost, Chem. Pharm. Bull. 50 (2002) 1;
(b) G. Helmchen, J. Oraganomet. Chem. 576 (1999) 203;
(c) A. Pfaltz, M. Lautens, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vol. 2, Springer, Tokyo, 1999, p. 833;
(d) B.M. Trost, D.L. Van Vranken, Chem. Rev. 96 (1996) 395;
(e) J.M.J. Williams, Synlett (1996) 705.;
(f) A. Pfaltz, Acc. Chem. Res. 26 (1993) 339;
(g) T. Hayashi, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH Publishers, New York, 1993;
(h) G. Consiglio, R.M. Waymouth, Chem. Rev. 89 (1989) 257 (and references cited therein).

[4] For some recent papers on palladium catalyzed allylic substitution, see; (a) S.L. You, X.L. Hou, L.X. Dai, Y.H. Yu, W. Xia, J. Org. Chem. 67 (2002) 4684.(b) W.P. Deng, S.L. You, X.L. Hou, L.X. Dai, Y.H. Yu, W. Xia, J. Sun, J. Am. Chem. Soc. 123 (2001) 6508.(c) W.P. Deng, X.L. Hou, L.X. Dai, L.X. Yu, W. Xia, Chem. Commun. (2000) 285.(d) S.L. You, X.L. Hou, L.X. Dai, Tetrahedron: Asymmetry 11 (2000) 1495.(e) D. Enders, R. Peters, J. Runsink, J.W. Bats, Org. Lett. 1 (1999) 1863.(f) W. Zhang, T. Shimanuki, T. Kida, Y. Nakatsuji, I. Ikeda, J. Org. Chem. 64 (1999) 6247.(g) S.L. You, Y.G. Zhou, X.L. Hou, L.X. Dai, Chem. Commun. (1998) 2765.(h) K.H. Ahn, C.W. Cho, J. Park, S. Lee, Bull. Korean Chem. Soc. 18 (1997) 789.(i) O. Riant, O. Samuel, T. Flessner, S. Taudien, H.B. Kagan, J. Org. Chem. 62 (1997) 6733.

[5] (a) T. Mino, W. Imiya, M. Yamashita, Synlett (1997) 583.;
(b) T. Mino, M. Shiotsuki, N. Yamamoto, T. Suenaga, M. Sakamoto, T. Fujita, M. Yamashita, J. Org. Chem. 66 (2001) 1795.

[6] D. Enders, R. Peters, R. Lochtman, J. Runsink, Eur. J. Org. Chem. (2000) 2839.

[7] T. Mino, T. Ogawa, M. Yamashita, Heterocycles 55 (2001) 453.

[8] P.R. Auburn, P.B. Mackenzie, B. Bosnich, J. Am. Chem. Soc. 107 (1985) 2033.

[9] B.M. Trost, D.J. Murphy, Organometallics 4 (1985) 1143.

[10] T. Hayashi, A. Yamamoto, T. Hagihara, Y. Ito, Tetrahedron Lett. 27 (1986) 191.

[11] T. Hayashi, A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, J. Am. Chem. Soc. 111 (1989) 6301.