

Catalytic asymmetric hydrosilylation of 1,3-dienes with difluoro(phenyl)silane [☆]

Hideaki Ohmura ^a, Hayao Matsubashi ^a, Makoto Tanaka ^a, Manabu Kuroboshi ^a,
Tamejiro Hiyama ^{a,*}, Yasuo Hatanaka ^b, Ken-ichi Goda ^b

^a Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

^b Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229, Japan

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Abstract

A palladium complex with an optically active ligand catalyzes asymmetric hydrosilylation of 1,3-dienes using difluoro(phenyl)silane to give optically active allyl difluoro(phenyl)silanes in good enantiomeric excess.

Keywords: Chirality; Fluorine; Silane; Ferrocene; Silicon; Palladium

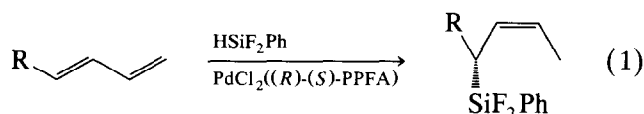
1. Introduction

Asymmetric hydrosilylation of olefins using a transition metal catalyst with a chiral ligand is a straightforward approach to the synthesis of optically active organosilicon compounds. In particular, optically active allylsilanes, available by asymmetric hydrosilylation of conjugated dienes, are useful synthetic intermediates for various carbon–carbon bond forming reactions such as cross-coupling [1]. Asymmetric hydrosilylation has been partly successful with acyclic dienes [2], but cyclic conjugated dienes, e.g. 1,3-cyclohexadiene, rarely give high enantiomeric excess (ee) [3].

2. Results and discussion

Recently, we have been studying asymmetric hydrosilylation of 1,3-dienes with organofluorosilanes using a palladium catalyst. Asymmetric hydrosilylation of 1,3-pentadiene, 1,3-hexadiene and 1-phenyl-1,3-butadiene with difluoro(phenyl)silane in the presence of PdCl₂((R)-(S)-PPFA) ((R)-(S)-PPFA refers to (R)-

N,N-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine) [2] afforded, respectively, (*Z*)-4-difluoro(phenyl)silyl-2-pentene, -2-hexene, and (*Z*)-1-phenyl-1-difluoro(phenyl)silyl-2-butene in 69% ee. Hence, both fluorine and phenyl group appear to induce high ee [4].



R = Me 69% ee

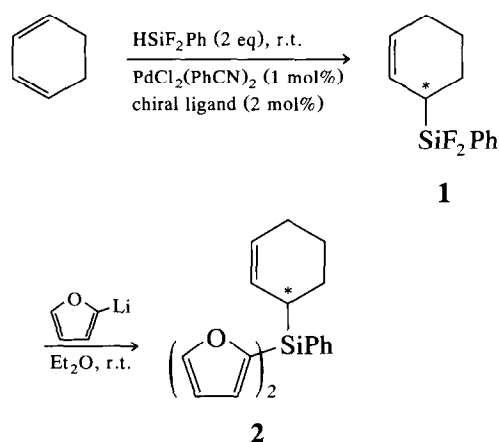
R = Et 69% ee

R = Ph 69% ee

We applied similar conditions to 1,3-cyclohexadiene in an attempt to achieve high ee in a cyclic diene system. We first examined the reaction using difluoro(phenyl)silane in the presence of bis(benzonitrile)palladium(II) chloride (1 mol%) and a chiral phosphine ligand (2 mol%). The major product of this reaction was 3-[difluoro(phenyl)silyl]cyclohexene (**1**). To determine the ee of the product, we treated **1** with 2-furyllithium to isolate 3-[di(2-furyl)(phenyl)silyl]cyclohexene (**2**) (Scheme 1) which was assayed by HPLC. The experimental results are summarized in Table 1. The chiral ligands we used were PPFA and its derivatives (runs 2–6), (*R*)-2-(diphenylphosphino)-2'-hydroxy-1,1'-binaphthyl (BINP-OH) and its derivatives (runs 7–11), (+)-neomenthyldiphenylphosphine

[☆] Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

* Corresponding author.



Scheme 1.

(NMDPP) and (*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP).

In contrast to acyclic dienes, hydrosilylation of 1,3-cyclohexadiene with the Pd–PPFA catalyst resulted in low ee (run 1). Substitution of an alkoxy group for the dimethylamino group improved the ee. For example, PPF–OMe [5] and PPF–OEt gave **2** with 54% ee (runs 2 and 3). Moreover, PPF–OCH₂CF₃, PPF–OAc [5] and PPF–OH [5] gave **2** with 65%, 62% and 72% ee, respectively (runs 4–6). These results indicate that the role of the functional side chain of PPFA is extremely important.

The lone pair of nitrogen atom in PPFA does not appear to produce a favorable asymmetric environment. BINP–OH and its derivatives attained at best 39% ee (run 9). Both the monophosphine ligand NMDPP and the diphosphine ligand BINAP gave inferior ee's (runs 12 and 13).

We next studied the contribution of the palladium catalyst using (*R*)-(*S*)-PPF–OAc as the chiral ligand. We observed 62% ee with a molar ratio of PdCl₂(PhCN)₂:ligand = 1:2. Reactions with a molar ratio of Pd:ligand = 1:1 or 1:3 gave **2** with only 28% or 45% ee, respectively. We used the 1:2 ratio with Pd(OAc)₂, Pd₂(dba)₃·CHCl₃ and [PdCl(η³-C₃H₅)₂]₂ and observed 57%, 40%, and 77% ee, respectively. Thus, [PdCl(η³-C₃H₅)₂]₂ gave the highest ee.

With a 1:1 molar ratio of difluoro(phenyl)silane and 1,3-cyclohexadiene, a fair amount of the by-product 1,1,2,2-tetrafluoro-1,2-diphenyldisilane was formed. Thus, optimum conditions were concluded to be [PdCl(η³-C₃H₅)₂]₂ and (*R*)-(*S*)-PPF–OAc with a molar ratio of silane:diene = 2:1.

The ee of **2** was affected remarkably by the substituents of hydrosilanes as summarized in Table 2. When dihalosilanes such as HSiF₂Ph or HSiCl₂Ph were employed, high ee's resulted (runs 1 and 2). HSiCl₃ gave a lower ee (run 8). However, substitution of a cyclohexyl group for the phenyl group reversed the asymmetric induction (runs 3 and 4). Triorganosilane HSiMe₂Ph did not exhibit satisfactory reactivity (run 5). In addition, monohalosilanes such as HSiFPh₂ or HSiClPh₂ totally failed to effect hydrosilylation (runs 6 and 7). These results indicate that both electronic and steric effects of the phenyl group on the silicon atom are crucial.

3. Conclusion

We have demonstrated that 77% ee is achieved in the asymmetric hydrosilylation of 1,3-cyclohexadiene using difluoro(phenyl)silane and (*R*)-(*S*)-PPF–OAc. The opti-

Table 1
Effect of chiral phosphine ligand in the hydrosilylation of 1,3-cyclohexadiene ^a

Run	Chiral ligand	Time (h)	2			
			Yield (%) ^b	% ee ^c	Configuration ^d	[α] _D ³⁰ ^e
1	(<i>R</i>)-(<i>S</i>)-PPF–NMe ₂	62	45 (48)	9	<i>S</i>	–4.9
2	(<i>R</i>)-(<i>S</i>)-PPF–OMe	20	50 (51)	54	<i>S</i>	–23.5
3	(<i>R</i>)-(<i>S</i>)-PPF–OEt	46	54	54	<i>S</i>	–20.9
4	(<i>R</i>)-(<i>S</i>)-PPF–OCH ₂ CF ₃	42	57	65	<i>S</i>	–33.5
5	(<i>R</i>)-(<i>S</i>)-PPF–OAc	20	31 (74)	62	<i>S</i>	–30.8
6	(<i>R</i>)-(<i>S</i>)-PPF–OH	42	63	72	<i>S</i>	–41.2
7	(<i>R</i>)-BINP–OH	60	65	2	<i>S</i>	–
8	(<i>R</i>)-BINP–OMe	62	73 (80)	18	<i>R</i>	+8.8
9	(<i>R</i>)-BINP–OSiMe ₂ <i>t</i> -Bu	62	50	39	<i>R</i>	+17.7
10	(<i>R</i>)-BINP–OSiPh ₃	62	42	5	<i>S</i>	–4.9
11	(<i>R</i>)-BINP–OSi <i>i</i> -Pr ₃	62	42	2	<i>S</i>	–
12	(+)-NMDPP	66	57 (63)	30	<i>S</i>	–10.9
13	(<i>R</i>)-BINAP ^f	37	13	3	<i>S</i>	–

^a All reactions were carried out as follows: difluoro(phenyl)silane was added slowly to a mixture of 1,3-cyclohexadiene, PdCl₂(PhCN)₂ and the chiral ligand. The molar ratio of diene:silane: Pd:ligand was 1.0:2.0:1.0 × 10^{–2}:2.0 × 10^{–2}. ^b Overall yields based on 1,3-cyclohexadiene are given. Isolated yield of **1** is shown in parenthesis. ^c Determined by HPLC analysis (Daicel, CHIRALCEL OD-H, hexane). ^d Judged from the sign of [α]_D³¹ of 2-cyclohexenol obtained after oxidation. ^e Measured in CHCl₃ with *c* 0.13–0.59. ^f Ligand was 1 mol%.

Table 2
Substituent effect of hydrosilane ^a

Run	Hydrosilane	Time (h)	Product		
			Yield (%)	%ee	Config-uration ^c
1	HSiF ₂ Ph	20	58 ^b	77 ^d	<i>S</i>
2	HSiCl ₂ Ph	69	75 ^b	71 ^d	<i>S</i>
3	HSiCl ₂ c-Hex	61	48 ^b	15 ^e	<i>R</i>
4	HSiCl ₂ c-Hex	63	59 ^c	14 ^e	<i>R</i>
5	HSiMe ₂ Ph	no reaction			
6	HSiFPh ₂	111	~ 10 ^c	2 ^e	—
7	HSiClPh ₂	111	trace	—	—
8	HSiCl ₃	39	44 ^c	38 ^e	<i>S</i>

^a A molar ratio of 1,3-cyclohexadiene : silane : [PdCl(η³-C₃H₅)₂·PPF-OAc] was 1.0:2.0:0.5 × 10⁻²:2.0 × 10⁻². ^b Yield of 2 based on 1,3-cyclohexadiene. ^c Yield of 2-cyclohexenol based on 1,3-cyclohexadiene. ^d Determined by HPLC analyses (Daicel Chiralcel OD-H, hexane). ^e Determined after oxidation to 2-cyclohexenol.

cally active allylsilane should find many applications in various carbon–carbon bond forming reactions.

4. Experimental details

All temperatures are uncorrected. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker AC-200 spectrometer in CDCl₃ with tetramethylsilane as an internal standard. IR spectra were obtained on a Hitachi 260-10 spectrometer in neat liquid. MS were recorded with a Hitachi M-80A spectrometer with ionization voltage 70 eV. Optical rotations were measured on a JASCO DIP-370 instrument. Elemental analyses were carried out with a Yanako MT2 CHN Corder. Analytical TLC was performed using Merck Silica Gel 60 F-254 TLC plates. Column chromatography was carried out with Merck Silica Gel 60 (230–400 mesh).

4.1. Difluoro(phenyl)silane

A mixture of dichloro(phenyl)silane (10.0 g, 57 mmol) and 48% hydrofluoric acid (4.9 ml, 0.28 mol) was stirred for 40 min at –40°C in a polyethylene flask. The organic layer was separated and treated with trichlorosilane (2.0 ml) to quench any excess HF. After 30 min calcium hydride was added, and the mixture was stirred for 20 min. Distillation at 85°C/100 mm Hg (or 110–114°C at atmospheric pressure) afforded difluoro(phenyl)silane (7.1 g, 87% yield) as a colorless oil. ¹H NMR: δ 5.19 (t, *J* = 69 Hz, 1H), 7.48–7.72 (m, 5H); ¹⁹F NMR: δ –141.63 (d, *J* = 69 Hz); IR: 3095, 3070, 2240, 1600, 1430, 1135, 920, 870, 830, 740, 695, 490 cm⁻¹.

4.2. Fluoro(diphenyl)silane

To a solution of ammonium hexafluorosilicate (7.6 g, 42 mmol) in 1,2-dimethoxyethane (0.20 l) was added chloro(diphenyl)silane (5.0 g, 23 mmol) at room tem-

perature under argon. The resulting mixture was heated under reflux for 30 min, cooled to room temperature, diluted with dry hexane, and filtered through Celite. The solvents were evaporated under reduced pressure, and the residue was distilled at 95°C/2 mm Hg to give fluoro(diphenyl)silane (4.8 g, 90% yield) as a colorless oil. ¹H NMR: δ 5.64 (d, *J* = 54 Hz, 1H), 7.49–7.71 (m, 10H); ¹⁹F NMR: δ –175.67 (d, *J* = 54 Hz). Found: C, 70.99; H, 5.43%. Calc. for C₁₂H₁₁FSi: C, 71.25; H, 5.48%.

4.3. Asymmetric hydrosilylation of 1,3-hexadiene

A mixture of PdCl₂((*R*)-(*S*)-PPFA) (13 mg, 0.021 mmol, 0.5 mol%) and 1,3-hexadiene (0.70 g, 8.5 mmol) was stirred at room temperature under argon for 1 h. To this mixture was added dropwise difluoro(phenyl)silane (0.61 g, 4.3 mmol). The reaction mixture was stirred for 9 h, diluted with hexane (20 ml), filtered to remove the catalyst, and concentrated under reduced pressure. The residue was distilled with Kugelrohr at 100–120°C/1–2 mm Hg to give (*R*)-(*Z*)-4-difluoro(phenyl)silyl-2-hexene (0.72 g, 75% yield) as a colorless oil. [α]_D²⁰ –40.4° (c 1.05, CHCl₃), 69% ee. ¹H NMR: δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.48 (m, 1H), 1.52 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.78 (m, 1H), 2.25 (m, 1H), 5.20 (ddq, *J* = 10.7, 10.7, 1.6 Hz, 1H), 5.60 (dq, *J* = 6.4, 10.7, 0.9 Hz, 1H), 7.36–7.58 (m, 3H), 7.62–7.73 (m, 2H); IR: 3019, 2964, 1595, 1431, 902, 854, 740, 711, 695 cm⁻¹. HRMS: Found M⁺, 226.0966; Calc. for C₁₂H₁₆SiF₂, 226.0988. Found: C, 63.76; H, 7.34%. Calc. for C₁₂H₁₆SiF₂: C, 63.68; H, 7.13%.

4.4. Asymmetric hydrosilylation of 1,3-pentadiene

A mixture of 1,3-pentadiene (0.27 g, 4.0 mmol) and PdCl₂((*R*)-(*S*)-PPFA) (6.2 mg, 0.010 mol%) was stirred at room temperature for 1 h under argon. To this mixture was added dropwise difluoro(phenyl)silane (0.62 g, 2.0 mmol) and the mixture was stirred at room temperature for 9 h before dilution with hexane. Filtration of the catalyst followed by distillation at 120°C/1 mm Hg gave (*R*)-(*Z*)-4-difluoro(phenyl)silyl-2-pentene (0.17 g, 82% yield). [α]_D²⁰ –45.19° (c 1.00, CHCl₃), 69% ee. ¹H NMR: δ 1.21 (d, *J* = 7.3 Hz, 3H), 1.52 (dd, *J* = 6.4, 1.4 Hz, 3H), 2.42 (m, 1H), 5.25 (ddq, *J* = 10.7, 10.7, 1.4 Hz, 1H), 5.52 (dq, *J* = 10.7, 6.7, 0.9 Hz, 1H), 7.32–7.59 (m, 3H), 7.62–7.72 (m, 2H); IR: 3100, 2960, 1592, 1427, 900, 845, 738, 710, 695 cm⁻¹; HRMS: Found M⁺, 212.0823; Calc. for C₁₁H₁₄F₂Si, 212.0831.

4.5. Oxidation of (*R*)-(*Z*)-4-difluoro(phenyl)silyl-2-pentene

A mixture of (*R*)-(*Z*)-4-difluoro(phenyl)silyl-2-pentene (0.42 g, 2.0 mmol), 5% Pd–C (0.17 g) and

ethanol (6 ml) was agitated under hydrogen (1 atm) for 5 h at room temperature. Filtration followed by distillation with Kugelrohr gave 2-[difluoro(phenyl)silyl]pentane, 0.15 g of which was treated with potassium fluoride (5 mg, 0.086 mmol) suspended in dimethylformamide (4 ml). *meta*-Chloroperbenzoic acid (*m*-CPBA, 0.69 g, 4.0 mmol) was then added, and the resulting mixture was stirred at room temperature for 9 h and at 60°C for 1 h. To this reaction mixture were added at 0°C pyridine (1 ml) and benzoyl chloride (0.14 g, 1.0 mmol), and the whole was stirred at room temperature for 9 h before quenching with saturated aqueous NaCl. Extraction with diethyl ether, washing with saturated aqueous sodium hydrogencarbonate, 10% hydrochloric acid, and then with saturated aqueous NaCl drying (Na_2SO_4), concentration, followed by column chromatography (silica gel, hexane) afforded 1-methylbutyl 3-chlorobenzoate (0.14 g, 89% yield) in place of an expected benzoate. ^1H NMR: δ 0.96 (t, $J = 6.0$ Hz, 3H), 1.35 (d, $J = 6.0$ Hz, 3H), 1.51 (m, 4H), 5.20 (m, 1H), 7.70 (m, 4H); IR: 1719, 1575, 1285, 1255, 1132, 1118, 1080, 1070, 745 cm^{-1} ; MS: m/z 226 (M^+), 157, 139, 87, 77, 50, 43. Absolute configuration was determined by comparing the retention time of HPLC (Chiralcel AD, hexane) of authentic sample prepared alternatively from racemic and (*S*)-(+)-2-pentanol.

4.6. Asymmetric hydrosilylation of 1-phenyl-1,3-butadiene

A mixture of 1-phenyl-1,3-butadiene (1.30 g, 9.8 mmol) and $\text{PdCl}_2((R)\text{-}(S)\text{-PPFA})$ (25 mg, 0.040 mmol) was stirred at room temperature for 1 h under argon before addition of difluoro(phenyl)silane (1.40 g, 9.7 mmol). The mixture was stirred at room temperature for 22 h and diluted with hexane. Filtration of precipitated material followed by concentration and distillation with Kugelrohr at 140°C/0.9 mm Hg gave (*S*)-(*Z*)-1-phenyl-1-[difluoro(phenyl)silyl]-2-butene (1.40 g, 53% yield). ^1H NMR: δ 1.56 (d, $J = 5.0$ Hz, 3H), 2.87 (m, 1H), 5.83 (m, 2H), 7.33 (m, 10H); IR: 3030, 1595, 1495, 1425, 1125, 910, 870, 840, 740, 710, 695, 520 cm^{-1} .

4.7. 1-Phenyl-1-butanol

A mixture of (*S*)-(*Z*)-1-phenyl-1-[difluoro(phenyl)silyl]-2-butene (0.25 g, 0.91 mmol), 5% Pd-C (76 mg) and ethanol (5 ml) was stirred vigorously under hydrogen (1 atm) at room temperature overnight. Filtration followed by concentration gave a residue which was dissolved in DMF (3 ml) and treated with KF (5 mg) and *m*-CPBA (80%, 0.52 g, 3.0 mmol) at room temperature for 18 h. Workup and purification by TLC (hexane) afforded the desired alcohol in 36% yield. ^1H NMR: δ

0.94 (t, $J = 7.3$ Hz, 3H), 1.29–1.96 (m, 7H), 4.67 (t, $J = 6.5$ Hz, 1H), 7.34 (m, 5H); IR: 3370, 2950, 2930, 2870, 1740, 1450, 1380, 1245, 1100, 1015, 760, 700 cm^{-1} . HPLC (Chiralcel OB, hexane-isopropyl alcohol 40:1) revealed 69% ee and (*S*)-configuration upon comparison with an authentic sample.

4.8. Asymmetric hydrosilylation of 1,3-cyclohexadiene

A mixture of 1,3-cyclohexadiene (40 mg, 0.50 mmol), $\text{PdCl}_2(\text{PhCN})_2$ (1.9 mg, 0.005 mmol) and (*R*)-(*S*)-PPF-OAc (4.6 mg, 0.010 mmol) was stirred at room temperature for 30 min. To this mixture was added difluoro(phenyl)silane (72 mg, 0.50 mmol) at 0°C, and the resulting mixture was stirred at room temperature for 14 h before dilution with hexane. Insoluble material was filtered, and the filtrate was concentrated in vacuo. Distillation with Kugelrohr at 100–120°C/4–6 mm Hg afforded 3-[difluoro(phenyl)silyl]cyclohexene (**1**, 82 mg, 74% yield). ^1H NMR: δ 1.35–2.40 (m, 7H), 5.72 (m, 2H), 7.24–7.82 (m, 5H); ^{19}F NMR: δ 145.53 (d, $J = 20$ Hz, 1F), –146.75 (d, $J = 20$ Hz, 1F); IR: 3090, 3070, 3040, 2940, 2870, 2850, 1600, 1450, 1440, 1210, 1170, 1130, 1070, 1040, 1000, 900, 850, 770, 740, 710 cm^{-1} ; MS: m/z (rel. intensity) 224 (M^+ , 50), 146 (65), 81 (100), 51 (18).

4.9. 3-[Di(2-furyl)(phenyl)silyl]cyclohexene (2)

A hexane solution of butyllithium (1.60 M, 5.9 ml, 8.8 mmol) was added to a solution of furan (0.95 ml, 12 mmol) in diethyl ether (5 ml) at room temperature under argon, and the mixture was stirred for 1 h. To this solution of 2-furyllithium was added **1** (0.33 g, 1.5 mmol) dissolved in diethyl ether (5 ml) at 0°C temperature, and the whole mixture was stirred at room temperature for 1 h before dilution with diethyl ether. All insoluble material was filtered through a short Celite-silica gel column, and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (hexane-ethyl acetate 10:1, R_f 0.5) to give **2** (0.44 g, 94% yield). ^1H NMR: δ 1.48–2.10 (m, 7H), 5.66–5.78 (m, 2H), 6.36–6.40 (m, 2H), 6.74–6.84 (m, 2H), 7.28–7.42 (m, 3H), 7.48–7.66 (m, 2H), 7.68–7.86 (m, 2H); ^{13}C NMR: δ 22.39, 23.66, 24.21, 24.91, 109.59, 124.00, 126.23, 127.18, 127.85, 129.92, 135.37, 147.82; IR: 3015, 2920, 2850, 2830, 1540, 1445, 1425, 1200, 1140, 1110, 1000, 890, 740 cm^{-1} ; MS m/z (rel. intensity) 320 (M^+ , 1), 239 (100), 213 (7), 165 (12), 105 (18). Found: C, 74.50; H, 6.33%. Calc. for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{Si}$: C, 74.74; H, 6.30%.

4.10. Determination of absolute configuration of **1**

To a solution of **1** (0.40 g, 1.79 mmol) in THF (7 ml) and methanol (7 ml) was added dropwise a mixture of

30% aqueous hydrogen peroxide (1.21 g, 10.7 mmol), potassium fluoride (0.104 g, 1.79 mmol) and sodium hydrogencarbonate (0.150 g, 1.79 mmol) at 0°C, and the resulting mixture was stirred for 6 h at 60°C. Excess hydrogen peroxide was quenched by aqueous sodium hydrogen sulfite at 0°C. The reaction mixture was extracted with diethyl ether. The organic layer was separated, dried (MgSO₄), filtered, and concentrated under reduced pressure. Silica gel column chromatography afforded (*S*)-2-cyclohexenol (0.112 g, 64% yield) as a colorless oil, $[\alpha]_D^{31} - 8.6^\circ$ (*c* 0.33, CHCl₃); (*S*)-enantiomer is reported to have $[\alpha]_D^{20} - 112.0^\circ$ (*c* 0.6, CHCl₃) [6].

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References and notes

- [1] (a) Y. Hatanaka, K. Goda and T. Hiyama, *Tetrahedron Lett.*, 35, (1994) 1279; (b) T. Hiyama and Y. Hatanaka, *Pure Appl. Chem.*, 66 (1994) 1471.
- [2] (a) Asymmetric hydrosilylation of 1-phenyl-1,3-butadiene with trichlorosilane in the presence of PdCl₂((*R*)-(*S*)-PPFA) is reported by Hayashi and coworkers to give (*Z*)-1-phenyl-1-trichlorosilyl-2-butene with 64% ee: T. Hayashi, and K. Kabeta, *Tetrahedron Lett.*, 26, (1985) 3023; (b) T. Hayashi, S. Hengrasmee and Y. Matsumoto, *Chem. Lett.*, (1990) 1377; (c) Y. Uozumi and T. Hayashi, *J. Am. Chem. Soc.*, 113 (1991) 9887.
- [3] (a) T. Hayashi, K. Kabeta, T. Yamamoto, K. Tamao and M. Kumada, *Tetrahedron Lett.*, 24 (1983) 5661; (b) T. Hayashi, Y. Matsumoto, I. Morikawa and Y. Ito, *Tetrahedron: Asymmetry*, 1 (1990) 151; (c) T. Okada, T. Morimoto and K. Achiwa, *Chem. Lett.*, (1990) 999.
- [4] Y. Hatanaka, F. Yamashita, K. Goda and T. Hiyama, *Tetrahedron Lett.*, 35 (1994) 7981.
- [5] T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawamoto, M. Konishi, K. Yamamoto and M. Kumada, *Bull. Chem. Soc. Jpn.*, 53, (1980) 1138.
- [6] S. Yamada, N. Takamura and T. Mizoguchi, *Chem. Pharm. Bull.*, 23, (1975) 2539.