

Modification of Chiral Monodentate Phosphine Ligands (MOP) for Palladium-Catalyzed Asymmetric Hydrosilylation of Cyclic 1,3-Dienes

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Abstract: Several MOP ligands **5** containing aryl groups at 2' position of (*R*)-2-(diphenylphosphino)-1,1'-binaphthyl skeleton were prepared and used for palladium-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes **6** with trichlorosilane. Highest enantioselectivity was observed in the reaction of 1,3-cyclopentadiene (**6a**) catalyzed by a palladium

complex (0.25 mol %) coordinated with (*R*)-2-(diphenylphosphino)-2'-(3,5-dimethyl-4-methoxyphenyl)-1,1'-binaphthyl (**5f**), which gave (*S*)-3-(trichlorosilyl)cyclopentene of 90% ee.

Keywords: allylsilane; asymmetric catalysis; chiral monodentate phosphine ligands; hydrosilylations; palladium

Introduction

Enantiomerically enriched allylic silanes are useful synthetic intermediates that react with electrophiles in an S_E' fashion to give a wide variety of enantiomerically enriched compounds.^[1] We have developed several synthetic methods for their preparation by asymmetric catalysis with chiral phosphine-palladium complexes. These include the asymmetric hydrosilylation of 1,3-dienes,^[2,3,4] cross-coupling of 1-(silyl)-alkyl Grignard reagents with alkenyl halides,^[5] allylic silylation of allyl chlorides with disilanes,^[6] and reduction of 3-(silyl)-2-propenyl carbonates with formic acid.^[7] Of these catalytic asymmetric reactions, the asymmetric hydrosilylation is most promising from the practical point of view, because the hydrosilylation is usually carried out in the presence of not more than 1 mol % of the palladium catalyst and the starting 1,3-dienes are readily accessible. We have also reported the preparation of several chiral monodentate phosphine ligands (MOP) whose chirality is due to the binaphthyl axial chirality^[3] and their successful use for several types of transition metal-catalyzed asymmetric reactions^[3] including palladium-catalyzed hydrosilylation. The MOP ligands have an advantage over others in that their fine tuning is readily made by the introduction of a desired group at the 2' position. In the asymmetric hydrosilylation of simple terminal alkenes^[8] and cyclic alkenes,^[9] high en-

antioselectivity (>90% ee) has been observed by use of 2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl (MeO-MOP, **1**). For styrene derivatives, 2-diphenylphosphino-1,1'-binaphthyl (H-MOP, **2a**)^[10] and its analogue containing the bis[3,5-bis(trifluoromethyl)phenyl]phosphino group (**2b**)^[11] are more effective than MeO-MOP, giving the hydrosilylation products of over 95% ee. However, unfortunately, these MOP ligands are not so effective for the hydrosilylation of 1,3-dienes. The highest enantioselectivity reported so far was 80% ee, which is observed in the hydrosilylation of 1,3-cyclopentadiene in the presence of a palladium catalyst coordinated with 4,4'-biphenanthryl analogue **3** of MeO-MOP (Figure 1).^[12] Here we wish to report that appropriate modification of the MOP ligand by introduction of an aryl group on the 2' position leads to the highest enantioselectivity for 1,3-cyclopentadiene and 1,3-cyclohexadiene.

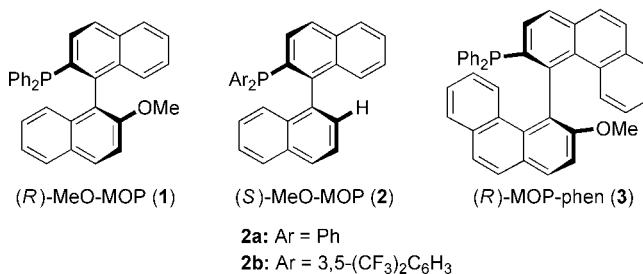
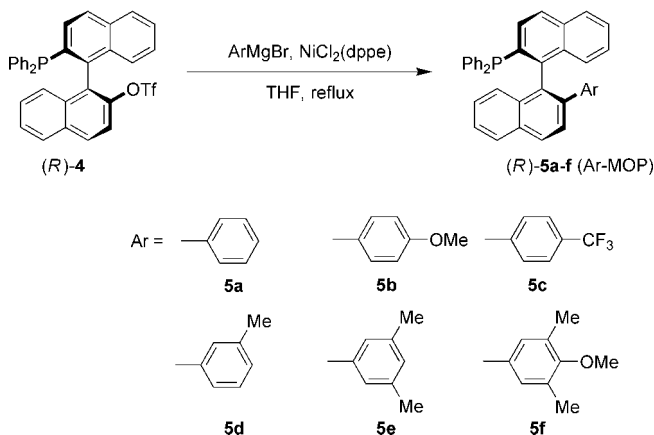


Figure 1. Structures of **1**, **2**, and **3**.

Results and Discussion

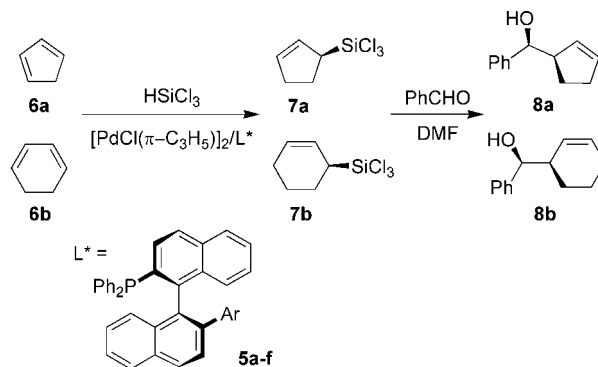
In our previous studies on the palladium-catalyzed asymmetric hydrosilylation of 1,3-dienes, the use of (*R*)-MeO-MOP (**1**) or (*S*)-H-MOP (**2a**) as a chiral ligand resulted in the formation of the corresponding hydrosilylation products of low enantiomeric purity.^[12] Thus, for example, the reaction of 1,3-cyclopentadiene with trichlorosilane in the presence of (*R*)-MeO-MOP (**1**) and (*S*)-H-MOP (**2a**) gave (*R*)-3-(trichlorosilyl)cyclopentene of 39% and 28% ee, respectively. Expecting that a sterically more bulky group at the 2' position of the MOP ligand will bring about higher enantioselectivity, several MOP ligands containing aryl groups at the 2' position were prepared by the nickel-catalyzed cross-coupling of (*R*)-2-(diphenylphosphino)-2'-(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (TfO-MOP, **4**)^[13] with arylmagnesium bromides. Phenyl and substituted phenyl groups were introduced in the presence of a catalytic amount of NiCl₂(dppe) in refluxing THF to give the corresponding (*R*)-2-(diphenylphosphino)-2'-aryl-1,1'-binaphthyls (Ar-MOP, **5a-f**) in around 60% yield (Scheme 1).



Scheme 1. Preparation of chiral monophosphine ligands **5** (Ar-MOP).

The MOP ligands thus obtained were examined for their enantioselectivity in the palladium-catalyzed asymmetric hydrosilylation of 1,3-cyclopentadiene (**6a**) with trichlorosilane. In the presence of 0.25 mol % of the palladium catalyst generated *in situ* from [PdCl(π-C₃H₅)]₂ and the MOP ligand **5** (P/Pd = 2/1), the hydrosilylation was completed at 0 °C in 24 h to give high yields of (*S*)-3-(trichlorosilyl)cyclopentene (**7a**) (Scheme 2). The allyl(trichloro)silane **7a** was allowed to react with benzaldehyde in DMF according to Kobayashi's procedure^[14] to give (3*R*,1'*S*)-(+)-3-[hydroxy(phenyl)methyl]cyclopentene (**8a**), which was subjected to HPLC analysis with a chiral stationary phase column for the determination

of the enantiomeric purity. The results summarized in Table 1 show that the enantioselectivity is generally high with the aryl-substituted MOP ligands compared to that reported with (*R*)-MeO-MOP (**1**) or (*S*)-H-MOP (**2a**)^[12] and that the enantioselectivity is dependent strongly both on the electronic character of the substituents and on the steric bulkiness of the aryl group. The ligand substituted with an electron-donating group at the 4 position showed higher selectivity than that substituted with an electron-withdrawing group. Thus, the order of enantioselectivity is **5b** (Ar = 4-MeOC₆H₄, 76% ee) > **5a** (Ar = C₆H₅, 69% ee) > **5c** (Ar = 4-CF₃C₆H₄, 47% ee) (entries 1–3). Methyl groups at the *meta*-position on the phenyl enhance the enantioselectivity, as indicated by the observation that the order of the selectivity is **5e** (Ar = 3,5-Me₂C₆H₃, 79% ee) > **5d** (Ar = 3-MeC₆H₅, 76% ee) > **5a** (Ar = C₆H₅, 69% ee) (entries 1, 4, and 5). The ligand **5f** which has both the electron-donating methoxy group at the 4 position and the two methyl groups at the 3 and 5 positions was the most enantioselective ligand giving the hydrosilylation product **7a** of 88% ee at 0 °C (entry 6). At a lower reaction temperature, the selectivity was increased to some extent (entries 7 and 8). The enantioselectivity of 90% ee observed at –20 °C is the highest so far reported for the asymmetric hydrosilylation of 1,3-cyclopentadiene.^[15]



Scheme 2. Palladium-catalyzed asymmetric hydrosilylation of cyclic dienes **6a** and **6b**.

It was found that 1,3-cyclohexadiene (**6b**) is a little less reactive than 1,3-cyclopentadiene (**6a**) toward the palladium-catalyzed hydrosilylation, and its reaction was carried out at 20 °C. In the asymmetric hydrosilylation of 1,3-cyclohexadiene (**6b**), the same electronic and steric effects were observed as in the case of 1,3-cyclopentadiene (**6a**) (entries 9–15 in Table 1). Thus, the highest enantioselectivity (76% ee at 20 °C) was obtained with the ligand **5f** that has a 3,5-dimethyl-4-methoxyphenyl group (entry 14), and the order of enantioselectivity of the MOP ligands is **5b** > **5a** > **5c** for the electronic effect of the substituents at the *para*-position (entries 9–11) and **5e** > **5d** > **5a** for

Table 1. Palladium-catalyzed asymmetric hydrosilylation of cyclic dienes with trichlorosilane.^[a]

Entry	Diene	Ligand	T [°C]	Time [h]	Yield [%] ^[b]	% ee ^[c]	Configuration ^[d]
1	6a	5a	0	24	84	69	S
2	6a	5b	0	24	84	76	S
3	6a	5c	0	24	85	47	S
4	6a	5d	0	24	85	76	S
5	6a	5e	0	24	85	79	S
6	6a	5f	0	24	79	88	S
7	6a	5f	–10	72	95	89	S
8	6a	5f	–20	72	89	90	S
9	6b	5a	20	24	74	55	S
10	6b	5b	20	24	75	65	S
11	6b	5c	20	24	90	52	S
12	6b	5d	20	24	78	64	S
13	6b	5e	20	24	82	66	S
14	6b	5f	20	24	74	76	S
15	6b	5f	0	72	75	79	S

^[a] The hydrosilylation was carried out without solvent. The catalyst was generated *in situ* by mixing [PdCl(π -C₃H₅)]₂ and a chiral phosphine ligand 5. The initial ratio of diene/HSiCl₃/Pd/P is 1/1.2/0.0025/0.0050.

^[b] Yield of product isolated by bulb-to-bulb distillation.

^[c] Determined by HPLC analysis of alcohol 8a with a chiral stationary phase column (Daicel Chiralpak OB-H, hexane/2-propanol = 9/1). Determined by GC analysis of alcohol 8b with a chiral stationary phase column (CP-Chirasil-Dex CB).

^[d] Determined by optical rotation of alcohols 8. For entry 8 (8a), [α]_D²⁰: +27.2 (*c* 1.86, chloroform). For entry 15 (8b), [α]_D²⁰: +11.1 (*c* 0.82, benzene).

the steric effect caused by the *meta*-methyl substitution (entries 9, 12, and 13).

The strong dependency of the enantioselectivity on the aryl group at the 2' position of the MOP ligand 5 may suggest that the aryl group is located close to the palladium and that it plays an important role in determining the stereochemical outcome in the present asymmetric hydrosilylation. Structural studies on the MOP-palladium complexes by NMR spectroscopy and X-ray crystal analysis are now in progress.

Conclusions

In summary, we have shown that some of the MOP ligands which contain aryl groups at the 2' position of 2-(diphenylphosphino)-1,1'-binaphthyl skeleton are effective for the palladium-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes with trichlorosilane giving the corresponding allylic silanes of up to 90% ee. The clear relationship between the enantioselectivity and the electronic and steric characters of the aryl group observed here provide us with significant information on the design of more effective chiral ligands.

Experimental Section

General Remarks

All moisture-sensitive manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P₂O₅. Optical rotations were recorded with a JASCO DIP-370 polarimeter. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (500 MHz for ¹H and 202 MHz for ³¹P) in CDCl₃. Chemical shifts are reported in δ ppm referenced to an internal SiMe₄ standard for ¹H NMR and to an external 85% H₃PO₄ standard for ³¹P NMR. HPLC analysis was performed on a JASCO PU-980 liquid chromatograph system with a chiral stationary phase column, Daicel Chiralpak OB-H. GC analysis was carried out on a Hewlett Packard 6890 system with a chiral stationary phase column, CP-Chirasil-Dex CB.

Preparation of (*R*)-2-(Diphenylphosphino)-2'-aryl-1,1'-binaphthyls (Ar-MOP; 5)

A typical procedure is given for the preparation of (*R*)-2-(diphenylphosphino)-2'-(3,5-dimethyl-4-methoxyphenyl)-1,1'-binaphthyl (5f). A mixture of (*R*)-2-(diphenylphosphino)-2'-(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (4) (1.12 g, 1.91 mmol), dichloro[1,3-bis(diphenylphosphino)ethane]-nickel (0.202 g, 0.38 mmol), and 3,5-dimethyl-4-methoxyphenylmagnesium bromide (1.5 M, 9 mL, in tetrahydrofuran) was heated at reflux for 24 h under nitrogen. After cooling to room temperature, the reaction mixture was quenched with saturated ammonium chloride (20 mL) on an ice bath, and extracted with diethyl ether. The extract was dried over anhydrous MgSO₄ and the solvent was evaporated. The residue was chromatographed on silica gel (hexane/ethyl acetate = 5/1) to give 0.634 g (58% yield) as a white solid.

(*R*)-2-(Diphenylphosphino)-2'-(3,5-dimethyl-4-methoxyphenyl)-1,1'-binaphthyl (5f): [α]_D²⁰: +183 (*c* 1.00, chloroform); ¹H NMR (CDCl₃): δ = 1.83 (s, 6H), 3.61 (s, 3H), 6.61 (s, 2H), 6.65 (t, *J* = 6.8 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.90 (t, *J* = 6.8 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.3 Hz, 2H), 7.09 (t, *J* = 6.8 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.9 Hz, 1H), 7.35 (t, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.50 (t, *J* = 6.8 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H); ³¹P{¹H}NMR: δ = –19.5 (s); anal. calcd. for C₄₁H₃₃PO: C, 85.99; H, 5.81; found: C, 85.71; H, 5.91.

(*R*)-2-(Diphenylphosphino)-2'-phenyl-1,1'-binaphthyl (5a): White solid (53% yield); [α]_D²⁰: +143 (*c* 1.00, chloroform); ¹H NMR (CDCl₃): δ = 6.61 (t, *J* = 6.9 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 4H), 6.96 (t, *J* = 8.3 Hz, 1H), 7.00–7.05 (m, 5H), 7.08 (t, *J* = 6.9 Hz, 2H), 7.10 (t, *J* = 8.3 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.21 (dd, *J* = 8.8, 3.0 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 6.9 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H); ³¹P{¹H}NMR: δ = –18.9 (s); anal. calcd. for C₃₈H₂₇P: C, 88.69; H, 5.29; found: C, 88.79; H, 5.49.

(R)-2-(Diphenylphosphino)-2'-(4-methoxyphenyl)-1,1'-binaphthyl (5b): White solid (45% yield); $[\alpha]_{\text{D}}^{20}$: +183 (c 1.00, chloroform); ^1H NMR (CDCl_3): δ = 3.68 (s, 3H), 6.41 (d, J = 8.8 Hz, 2H), 6.63 (t, J = 6.9 Hz, 2H), 6.79 (d, J = 8.3 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.90 (t, J = 7.4 Hz, 2H), 7.03 (t, J = 8.3 Hz, 1H), 7.05 (t, J = 6.9 Hz, 2H), 7.10 (t, J = 7.6 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.24 (dd, J = 8.8, 3.0 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 6.9 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.50 (t, J = 6.9 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = -19.2 (s); anal. calcd. for $\text{C}_{39}\text{H}_{29}\text{PO}$: C, 86.01; H, 5.57; found: C, 86.00; H, 5.59.

(R)-2-(Diphenylphosphino)-2'-(4-trifluoromethylphenyl)-1,1'-binaphthyl (5c): White solid (65% yield); $[\alpha]_{\text{D}}^{20}$: +182 (c 1.20, chloroform); ^1H NMR (CDCl_3): δ = 6.55 (t, J = 7.6 Hz, 2H), 6.84 (d, J = 8.4 Hz, 1H), 6.88 (t, J = 7.5 Hz, 2H), 7.01–7.14 (m, 10H), 7.17 (d, J = 7.9 Hz, 1H), 7.22 (dd, J = 8.4, 2.5 Hz, 1H), 7.35 (t, J = 7.1 Hz, 1H), 7.41 (d, J = 9.8 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.3 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = -14.2 (s); anal. calcd. for $\text{C}_{39}\text{H}_{26}\text{F}_3\text{P}$: C, 80.40; H, 4.50; found: C, 80.67; H, 4.73.

(R)-2-(Diphenylphosphino)-2'-(3-methylphenyl)-1,1'-binaphthyl (5d): White solid (64% yield); $[\alpha]_{\text{D}}^{20}$: +207 (c 0.11, chloroform); ^1H NMR (CDCl_3): δ = 1.93 (s, 3H), 6.61 (t, J = 6.9 Hz, 2H), 6.71 (d, J = 7.7 Hz, 1H), 6.75–6.84 (m, 2H), 6.90–7.12 (m, 10H), 7.17 (t, J = 7.2 Hz, 1H), 7.22 (dd, J = 8.6, 2.7 Hz, 1H), 7.33 (t, J = 7.0 Hz, 1H), 7.36 (t, J = 7.0 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = -14.0 (s); anal. calcd. for $\text{C}_{39}\text{H}_{29}\text{P}$: C, 88.61; H, 5.53; found: C, 88.34; H, 5.69.

(R)-2-(Diphenylphosphino)-2'-(3,5-dimethylphenyl)-1,1'-binaphthyl (5e): White solid (54% yield); $[\alpha]_{\text{D}}^{20}$: +193 (c 1.00, chloroform); ^1H NMR (CDCl_3): δ = 1.87 (s, 6H), 6.61–6.65 (m, 5H), 6.82 (d, J = 8.3 Hz, 1H), 6.92 (t, J = 8.3 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 8.3 Hz, 2H), 7.09 (t, J = 7.4 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.23 (dd, J = 8.8, 3.0 Hz, 1H), 7.33 (t, J = 6.9 Hz, 1H), 7.36 (t, J = 6.9 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.48 (t, J = 6.9 Hz, 1H), 7.64 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = -19.2 (s); anal. calcd. for $\text{C}_{40}\text{H}_{31}\text{P}$: C, 88.53; H, 5.76; found: C, 88.69; H, 5.80.

Palladium-Catalyzed Hydrosilylation of Diene 6

A typical procedure is given for entry 1 in Table 1. To a mixture of $[\text{PdCl}(\pi\text{-C}_5\text{H}_5)]_2$ (0.9 mg, 0.0025 mmol), a chiral ligand **5a** (5.1 mg, 0.0100 mmol), and 1,3-cyclopentadiene (**6a**) (132 mg, 2.0 mmol) was added trichlorosilane (0.24 mL, 2.4 mmol) at 0 °C, and the mixture was kept stirring in a sealed tube at 0 °C for 24 h. The reaction mixture was distilled (bulb-to-bulb) under a reduced pressure (120 °C/15 torr) to give 359 mg (84% yield) of 3-(trichlorosilyl)cyclopentene (**7a**).

3-(Trichlorosilyl)cyclopentene (7a): ^1H NMR (CDCl_3): δ = 2.15–2.25 (m, 2H), 2.45–2.51 (m, 2H), 2.71 (m, 1H), 5.70 (dq, J = 5.5, 2.5 Hz, 1H), 6.00 (dq, J = 5.5, 2.5 Hz, 1H).

3-(Trichlorosilyl)cyclohexene (7b): ^1H NMR (CDCl_3): δ = 1.55–1.59 (m, 1H), 1.78–1.91 (m, 2H), 1.98–2.08 (m, 3H), 2.08–2.32 (m, 1H), 5.71 (dq, J = 7.9, 2.3 Hz, 1H), 5.95 (dq, J = 7.9, 3.0 Hz, 1H).

Reaction of Allylsilane 7 with Benzaldehyde in DMF

A mixture of allyl(trichloro)silane **7** (0.4 mmol) and benzaldehyde (21 μL , 0.2 mmol) in DMF (1 mL) was stirred at 0 °C for 2 h. Saturated aqueous sodium hydrogen carbonate was added to quench the reaction, and the aqueous layer was extracted with diethyl ether. The extract was dried over anhydrous MgSO_4 , and the solvent was evaporated. The crude product was purified by preparative TLC on silica gel (hexane/ethyl acetate = 4/1) to give a high yield of homoallyl alcohol **8**.^[4]

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