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Asymmetric Hydrosilylation of Styrene by Palladium Catalysts Coordinated with Chiral Phosphoramidite Ligands from 3,3'-Disubstituted 1,1'-Binaphthols

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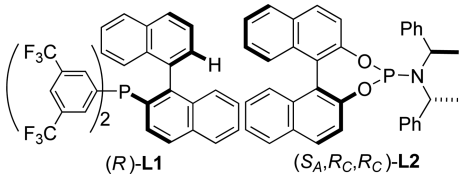
Owing to its high catalytic activity, perfect regioselectivity, and an easy-manipulation without producing any byproduct,[1] palladium-catalyzed asymmetric hydrosilylation of styrene has become a potent methodology to show their efficiencies of newly-developed chiral monodentate phosphorus ligands recently. Ever since a significant improvement for catalytic activity and enantioselectivity in the hydrosilylation of styrenes was achieved by chiral monophosphine (MOP) ligands based on the 2-diphenylphosphino-1,1'-binaphthyl skeleton,[2] several monodentate phosphorus ligands, such as phosphoramidites,[3] planar chiral monophosphines,[4] and helically chiral phosphines[5] have been applied to the hydrosilylation of styrenes to afford moderate to excellent enantioselectivities. Of those monodentate ligands, H-MOP derivative (*R*)-**L1**[2d] lacking a substituent at the 2'-position of the binaphthyl and a phosphoramidite ligand (S_A,R_C,R_C)-**L2**[3a] derived from (*S*)-1,1'-binaphthol and bis((*R*)-1-phenylethyl)amine have been reported to be the most efficient ligands in the hydrosilylation of styrenes (Figure 1). In particular, chiral phosphoramidites have been paid much attention mainly due to their excellent catalytic activities and stereoselectivities in various catalytic reactions and easy accessibility from readily available diols and amines nowadays.[6]

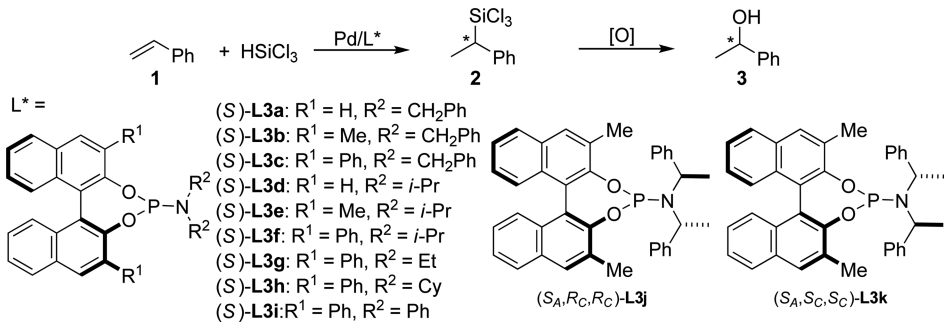


(*R*)-**L1** (S_A,R_C,R_C)-**L2**

Figure 1

On continuous efforts to expand the substrate scope of the hydrosilylation with various ligands,[7] we are interested in the modifications of phosphoramidite ligands based on the 1,1'-binaphthol to evaluate substituent effects on enantioselectivity in the hydrosilylation. Here we wish to report a palladium-catalyzed asymmetric hydrosilylation of styrene (**1**) with trichlorosilane using chiral phosphoramidites **L3** derived from (*S*)-3,3'-disubstituted 1,1'-binaphthols and secondary amines.

In the hydrosilylation of styrene, 1-phenyl-1-(trichlorosilyl)ethane (**2**) was obtained in high yield and the benzylic silane **2** was transformed to optically active 1-phenylethanol (**3**) by a stereospecific oxidative cleavage[8] of the C-Si bond with retention of configuration (Scheme 1). Chiral ligands **L3** were prepared from (*S*)-1,1'-binaphthols having diphenyl[9a] or dimethyl[9b] groups at 3,3'-positions of the binaphthyl according to the known procedure.[10] The hydrosilylation was carried out without solvent in the presence of 1.0 mol % of palladium catalysts generated *in situ* by mixing [PdCl(π-C_3H_5)]$_2$ and **L3** (Pd/P = 1/2). The reactions were completed 20 °C within 20 h to give **2**, whose enantioselectivities were determined after the stereospecific oxidation into **3**. The catalytic activity with the ligands **L3** was high enough with all the ligands except for **L3a** and **L3d**, however, the enantioselectivities varied according to the ligands as shown in Table 1. The enantioselectivities were strongly dependent on the substituents at 3,3'-positions of the binaphthyl in the ligands. It was found that the ligands having diphenyl groups induced the higher enantioselectivities. Thus, the phosphoramidites from 3,3'-diphenylbinaphthol showed the higher



Scheme 1. Pd-catalyzed asymmetric hydrosilylation of styrene using chiral phosphoramidites **L3**.

Table 1. Asymmetric hydrosilylation of styrene using **L3**[a]

Entry	L*	Time (h)	Temp (°C)	Yield[b] (%)	% ee[c]
1	(*S*)-**L3a**	20	20	58	26 (*R*)
2	(*S*)-**L3b**	20	20	99	4 (*R*)
3	(*S*)-**L3c**	20	20	76	64 (*S*)
4	(*S*)-**L3d**	20	20	45	47 (*R*)
5	(*S*)-**L3e**	20	20	88	48 (*S*)
6	(*S*)-**L3f**	20	20	89	78 (*S*)
7	(*S*)-**L3f**	72	-20	99	90 (*S*)
8	(*S*)-**L3g**	20	20	97	64 (*S*)
9	(*S*)-**L3h**	20	20	89	67 (*S*)
10	(*S*)-**L3i**	20	20	99	38 (*S*)
11	(S_A,R_C,R_C)-**L3j**	20	20	96	54 (*R*)
12	(S_A,S_C,S_C)-**L3k**	20	20	94	20 (*R*)

[a]Hydrosilylation was carried out without solvent. The catalyst was generated *in situ* by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and **L3**. The initial ratio of **1**/$HSiCl_3$/Pd/L* was 1.0/1.2/0.010/0.020. [b]Isolated yield of **2** by bulb-to-bulb distillation. [c]Determined by HPLC analyses of **3** with a chiral stationary column (Daicel Chiralpak OD-H).

enantioselectivities than the ligands from 3,3'-dimethylbinaphthol and from binaphthol itself. In both series of the ligands having dibenzylamino part (entries 1-3) and diisopropylamino part (entries 4-6), the order of enantioselectivity was **L3c** (R^1 = Ph, 64% ee) > **L3a** (R^1 = H, 26% ee) > **L3b** (R^1 = Me, 4% ee) and **L3f** (R^1 = Ph, 78% ee) > **L3e** (R^1 = Me, 48% ee) > **L3d** (R^1 = H, 47% ee), respectively. Next, enantioselectivities were also examined changing amino part in the ligands having 3,3'-diphenyl groups on the binaphthyl (entries 8-10). Of those ligands, **L3g** (R^2 = Et, 64% ee) and **L3h** (R^2 = Cy, 67% ee) gave a similar enantioselectivities, but were inferior to **L3f** (R^2 = *i*-Pr, 78% ee). Interestingly, **L3j** (54% ee) induced much lower enantioselectivity with the opposite configuration compared with the mother ligand **L2** (99% ee),[3a] which is one of the best ligands in hydrosilylation of styrene under a similar reaction condition (entry 11). The highest enantioselectivity of 90% ee was obtained with **L3f** at −20 °C in this study (entry 7).

In summary, it is shown that the phosphoramidite ligand from 3,3'-diphenyl-1,1'-binaphthol and diisopropylamine is an effective ligand in palladium-catalyzed asymmetric hydrosilylation of styrene. The hydrosilylation of styrene derivatives with these catalytic systems is on progress.

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Supporting Information. Experimental details and NMR spectra are available in the online version of this paper.

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