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Enhanced catalytic activity in asymmetric hydrosilylation of 1,3-dienes with a soluble palladium catalyst

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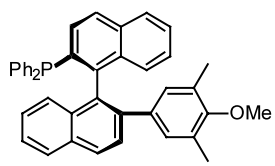
Abstract—A new MOP ligand **8** containing two *n*-octyl groups at the 6 and 6′ positions of the (*R*)-2-(diphenylphosphino)-2′-aryl-1,1′-binaphthyl skeleton was prepared and used for the palladium-catalyzed asymmetric hydrosilylation of 1,3-dienes with trichlorosilane. The introduction of the *n*-octyl groups made the palladium–phosphine catalyst soluble in the reaction system, realizing high catalytic activity at a low reaction temperature. As a result, ligand **8** showed highest enantioselectivity for both cyclic and linear 1,3-dienes.

1. Introduction

Enantiomerically enriched allylsilanes are useful chiral reagents for organic synthesis and their preparation by asymmetric catalysis attracts increasing attention.[1] They have been prepared by one of the four types of palladium-catalyzed asymmetric reactions, i.e. (1) asymmetric cross-coupling of 1-silylalkyl Grignard reagents with alkenyl bromides,[2] (2) asymmetric reduction of silyl-substituted allylic carbonates with formic acid,[3] (3) asymmetric silylation of allylic chlorides with a disilane,[4] and (4) asymmetric hydrosilylation of 1,3-dienes.[5–8] Of these catalytic methods, asymmetric hydrosilylation has advantages over the others in that (a) the starting materials, hydrosilane and 1,3-dienes, are readily accessible, (b) the hydrosilylation does not require any solvents, (c) it proceeds with a low catalyst loading, and (d) silafunctional allylsilanes can be obtained. The development of palladium-catalyzed asymmetric hydrosilylation has been dependent upon the development of chiral monophosphine ligands with higher enantioselectivity. No chelating bisphosphine–palladium complexes can be used because of their low catalytic activity. The most enantioselective ligand so far reported for the palladium-catalyzed hydrosilylation of 1,3-dienes is (*R*)-2-(diphenylphosphino)-2′-(3,5-dimethyl-4-methoxyphenyl)-1,1′-binaphthyl (Ar-MOP, **1**),[7c,9] which gave the corresponding allylsilane of 90% ee in the hydrosilylation of cyclopentadiene with trichlorosilane.[7c] However, the catalytic activity of the palladium complex coordinated with the Ar-MOP ligand is not high enough due mainly to the low solubility of its palladium complex in the reaction media consisting of a diene and trichlorosilane. Although the concept of introducing a long-chain alkyl group to increase solubility has often appeared in polymer chemistry,[10,11] there have been few reports in the field of homogeneous asymmetric catalysis.[12] Here we wish to report that appropriate modification of the Ar-MOP ligand by introducing a long-chain alkyl group at the 6 and 6′ positions of binaphthyl leads to the higher catalytic activity and enantioselectivity for 1,3-dienes.[13]



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2. Results and discussion

A synthetic route to the Ar-MOP ligand which contains *n*-octyl groups at the 6 and 6′ positions of 1,1′-binaphthyl is outlined in Scheme 1. The *n*-octyl group was introduced by the palladium-catalyzed Grignard cross-coupling of (*R*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthyl[14] **2**. Thus, the reaction of **2** with an excess of *n*-octylmagnesium bromide in the presence of $PdCl_2$(dppf)[15] as a catalyst in ether gave 91% yield of (*R*)-2,2′-diethoxy-6,6′-dioctyl-1,1′-binaphthyl **3**, which

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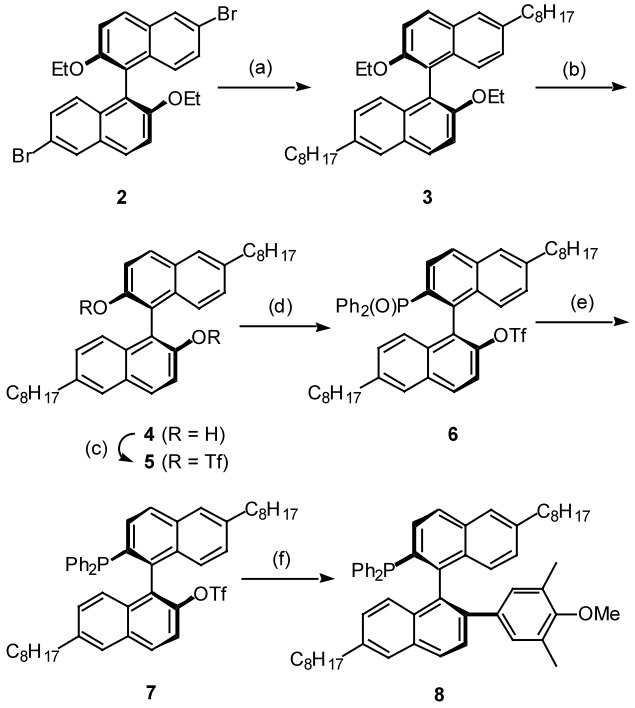
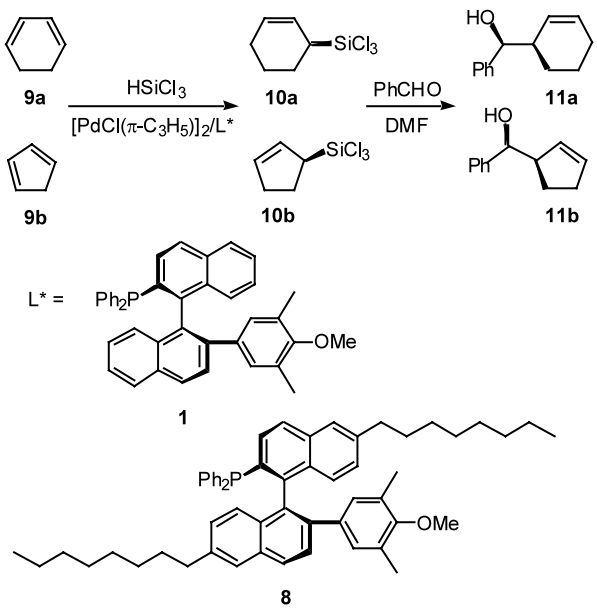


Scheme 1. Preparation of ligand **8** containing *n*-octyl groups at the 6 and 6′ positions of binaphthyl. (a) *n*-$C_8H_{17}MgBr$, $PdCl_2$(dpp), ether, 50°C, 20 h, 91%; (b) BBr_3, CH_2Cl_2, 12 h, 95%; (c) Tf_2O, py, CH_2Cl_2, 2 h, 95%; (d) Ph_2POH, $Pd(OAc)_2$, dppb, *i*-Pr_2NEt, DMSO, 130°C, 18 h, 78%; (e) $HSiCl_3$, Et_3N, xylene, 100°C, 12 h, 93%; (f) 3,5-Me_2-4-$MeOC_6H_2MgBr$, $NiCl_2(PPh_3)_2$, THF, 80°C, 24 h, 80%.

was treated with BBr_3 for the deprotection of ethyl ether to give (*R*)-6,6′-dioctyl-2,2′-dihydroxy-1,1′-naphthyl[11] **4** in 95% yield. Friedel–Crafts acylation followed by reduction of carbonyl is also a useful method for this transformation.[11] The conversion of **4** into (*R*)-2-diphenylphosphino-2′-(3,5-dimethyl-4-methoxyphenyl)-6,6′-dioctyl-1,1′-binaphthyl **8** was achieved in a high yield by the four-step reactions according to the procedures reported for Ar-MOP ligand **1**.[7c,16] In the course of the transformations, the *n*-octyl group on the binaphthyl skeleton did not interfere with the reactions. Thus, the selective monophosphinylation of the ditriflate **5**, readily obtained by treatment of **4** with Tf_2O, with diphenylphosphine oxide in the presence of a palladium catalyst at 130°C gave 78% yield of (*R*)-2-diphenylphosphinyl-6,6′-dioctyl-2′-trifluoromethanesulfonyloxy-1,1′-binaphthyl **6**. The reduction of phosphine oxide in **6** with trichlorosilane followed by substitution of the remaining triflate of **7** with 3,5-dimethyl-4-methoxyphenyl group by the nickel-catalyzed Grignard cross-coupling gave the *n*-octylated Ar-MOP ligand **8**. As expected, the introduction of two *n*-octyl groups made ligand **8** much more soluble in non-polar solvents such as hexane and diethyl ether than the original Ar-MOP ligand **1**.[7c]

A palladium catalyst coordinated with the *n*-octylated Ar-MOP ligand **8**, which is more soluble in the reaction media than with Ar-MOP ligand **1**, was examined for its catalytic activity and enantioselectivity in the asymmetric hydrosilylation of cyclic 1,3-dienes **9a** and **9b** with trichlorosilane (Scheme 2). The reaction was carried out without solvent in the presence of 0.25 mol% of the palladium catalyst generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ with 2 equiv. (to palladium) of chiral ligand **8**. The hydrosilylation products, allyl(trichloro)silanes **10a** and **10b**, were allowed to react with benzaldehyde in DMF according to Kobayashi's procedure[17] to give the corresponding homoallylic alcohols **11**, which were subjected to the HPLC analysis with a chiral stationary phase column for determination of the enantioselectivity. The results are summarized in Table 1, which also contains the data obtained[7c] with (*R*)-Ar-MOP **1** for comparison. In the reaction of 1,3-cyclohexadiene **9a**, the highest enantioselectivity so far recorded was 79% ee, which was observed with Ar-MOP ligand **1** at 0°C (entry 1 in Table 1). At a lower temperature, the hydrosilylation of **9a** did not proceed at all even if the reaction time was prolonged, due to the insolubility of the palladium catalyst coordinated with ligand **1** in the reaction media consisting of 1,3-cyclohexadiene **9a** and trichlorosilane (entry 3 in Table 1). As shown in Fig. 1, considerable amounts of off-white precipitates were observed in the reaction flask containing the palladium catalyst coordinated with the Ar-MOP ligand **1**. On the other hand, the palladium catalyst of the new ligand **8** was soluble in the reaction media, forming a clear solution even at –10°C. As a result, the hydrosilylation of **9a** was catalyzed by the palladium/**8** at −10°C to give (*S*)-3-trichlorosilylcyclohexene **10a** with 83% ee, which is the highest value for the reaction of **9a** (entry 4 in Table 1). The enantioselectivity of the Ar-MOP ligands was not influenced greatly by introduction of the *n*-octyl group, which is shown by essentially the same stereochemical outcome obtained in the hydrosilylation at 0°C (entries 1 and 2 in Table 1). The highest enantioselectivity was



Scheme 2. Pd-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes.

Table 1. Pd-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes with $HSiCl_3$[a]

Entry	Diene	Ligand (L*)	Temp. (°C)	Time (h)	Yield[b] (%)	Ee[c] (%)	Config.[d]
1	**9a**	**1**	0	72	75	79	*S*
2	**9a**	**8**	0	72	80	80	*S*
3	**9a**	**1**	−10	168	0	–	–
4	**9a**	**8**	−10	168	70	83	*S*
5	**9b**	**1**	−20	72	89	90	*S*
6	**9b**	**8**	−20	72	86	90	*S*
7	**9b**	**1**	−30	168	0	–	–
8	**9b**	**8**	−30	168	75	91	*S*

[a] The hydrosilylation was carried out without solvent. The catalyst was generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and a chiral ligand **1** or **8**. The initial ratio of diene/$HSiCl_3$/Pd/L* was 1.0/1.2/0.0025/0.0050.
[b] Isolated yield by bulb-to-bulb distillation.
[c] Determined by HPLC analysis of alcohol **11** with a chiral stationary column (Daicel Chiralpak OB-H) for **10**.
[d] Determined by optical rotation of alcohols **11**. For entry 2 (**11a**), $[\alpha]_D^{20}$ +11.1 (*c* 0.82, benzene). For entry 6 (**11b**), $[\alpha]_D^{20}$ +27.2 (*c* 1.86, chloroform).

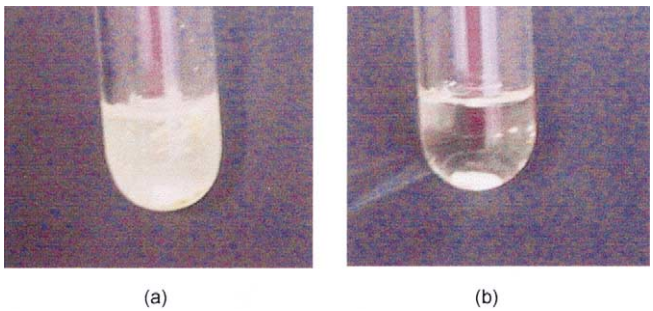
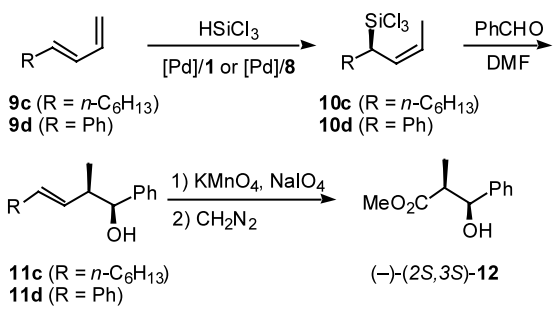


Figure 1. The solubility of palladium catalysts coordinated with ligand **1** (a) and ligand **8** (b).

also observed in the hydrosilylation of cyclopentadiene **9b** by use of the *n*-octylated MOP ligand **8**. Thus, the reaction of **9b** proceeded at –30°C in the presence of the palladium/**8** as a catalyst, to give (*S*)-3-trichlorosilylcyclopentene **10b** of 91% ee (entry 8 in Table 1). Here again, the reaction with ligand **1** did not take place at the same temperature (entry 7 in Table 1).

The palladium catalysts coordinated with ligand **1** and **8** were also effective for the asymmetric hydrosilylation of linear 1,3-dienes, (*E*)-1,3-decadiene **9c** and (*E*)-1-phenyl-1,3-butadiene **9d**, with trichlorosilane (Scheme 3). The hydrosilylation took place in an exclusive 1,4-fashion where the hydrogen and the silyl group are attached to the 1 and 4 positions of diene, respectively, to give (*Z*)-allyl(trichloro)silanes **10c** and **10d** with perfect regioselectivity. The results are summarized in Table 2. The reaction of (*E*)-1,3-decadiene **9c** with trichlorosilane in the presence of palladium/**1** catalyst at 20°C gave (*R*)-(*Z*)-4-(trichlorosilyl)-2-decene **10c** in 81% isolated yield as a single regioisomer (entry 1 in Table 2). The allylsilane, (*R*)-(*Z*)-**10c**, was allowed to react with benzaldehyde in DMF to give (1*S*,2*R*)-(*E*)-2-methyl-1-phenyl-3-decen-1-ol **11c** {$[\alpha]_D^{20}$ –12.6 (*c* 1.1, $CHCl_3$), 69% ee}, of which enantiomeric purity was determined by HPLC analysis with a chiral stationary phase column. The relative and absolute stereochemistry of the homoallylic alcohol **11c** was correlated with that of known methyl 3-hydroxy-2-methyl-3-phenylpropanoate[18] **12**. Thus, oxidative cleavage of **11c** with $KMnO_4$ and $NaIO_4$ followed by esterification with diazomethane gave 48% yield of (–)-methyl (2*S*,3*S*)-3-hydroxy-2-methyl-3-phenylpropanoate **12** {$[\alpha]_D^{20}$ –16.4 (*c* 1.0, $CHCl_3$)}, indicating that **11c** has (1*S*,2*R*) configuration. The *R* configuration of allylsilane **10c** was deduced from the assumption that the reaction of allyl(trichloro)silane with aldehyde proceeds via a cyclic transition state.[17] At –10°C, the hydrosilylation of **9c** by palladium/**1** was very slow, giving only 9% yield of the product with 77% ee, which is also due to the insolubility of the palladium catalyst coordinated with ligand **1** in the reaction media (entry 3 in Table 2). The higher catalytic activity of the palladium catalyst of the *n*-octylated Ar-MOP ligand **8** is clearly demonstrated by monitoring the reaction progress in the reaction of 1,3-decadiene with the palladium catalysts of ligand **1** and **8** (Fig. 2). With all other variables being constant, hydrosilylation with ligand **8** was completed within 4 h, while it took longer than 24 h with ligand **1**. This dramatic enhancement of catalytic reactivity with ligand **8** is attributed to the increased solubility of the complex in the reaction media. Enantioselectivities for linear 1,3-dienes appeared to show the same trend as for cyclic dienes. That is, *n*-octyl group on the ligand did not influence the stereochemical outcome in the hydrosilylation of linear 1,3-dienes (entries 1 and 2, entries 5 and 6 in Table 2). At a lower temperature, higher enantioselectivities were observed with ligand **8** (entries 4 and 8 in Table 2). Notably, use of hexane as solvent gave better results than without solvent in the hydrosilylation[6b] of 1-phenyl-1,3-butadiene (**9d**) with ligand **8** (entry 9 in Table 2).



Scheme 3. Pd-catalyzed asymmetric hydrosilylation of linear 1,3-dienes.

Table 2. Pd-catalyzed asymmetric hydrosilylation of linear 1,3-dienes with $HSiCl_3$[a]

Entry	Diene	Ligand (L*)	Temp. (°C)	Time (h)	Yield[b] (%)	Ee[c] (%)	Config.[d]
1	**9c**	**1**	20	24	81	69	*R*
2	**9c**	**8**	20	4	91	68	*R*
3	**9c**	**1**	−10	168	9	77	*R*
4	**9c**	**8**	−10	168	76	77	*R*
5	**9d**	**1**	20	22	85	62	*S*
6	**9d**	**8**	20	22	95	63	*S*
7	**9d**	**1**	0	168	14	71	*S*
8	**9d**	**8**	0	168	52	72	*S*
9[e]	**9d**	**8**	0	168	53	79	*S*

[a] The hydrosilylation was carried out without solvent. The catalyst was generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and a chiral ligand **1** or **8**. The initial ratio of diene/$HSiCl_3$/Pd/L* was 1.0/1.2/0.0025/0.0050.

[b] Isolated yield by bulb-to-bulb distillation.

[c] Determined by HPLC analysis of alcohol **11c** and **11d** with a chiral stationary column (Daicel Chiralpak AD and Daicel Chiralcel OD-H) for **10c** and **10d**, respectively.

[d] Determined by optical rotation of alcohols **11**. For entry 1 (**11c**), $[\alpha]_D^{20}$ −12.6 (*c* 1.1, chloroform). For entry 8 (**11d**), $[\alpha]_D^{20}$ +15.0 (*c* 1.1, chloroform).[14]

[e] In hexane solvent.

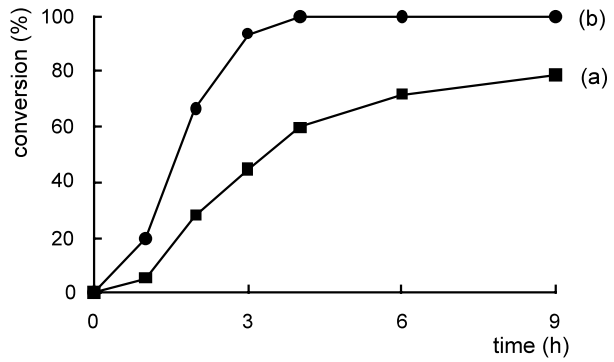


Figure 2. Reaction profile in the hydrosilylation of **9c** with ligand **1** (a) and ligand **8** (b).

3. Conclusion

We have shown that the palladium-catalyzed Grignard cross-coupling is a useful method for introducing an alkyl group onto the binaphthyl skeleton. The Ar-MOP ligand **8** which contains two *n*-octyl groups at the 6 and 6′ positions of binaphthyl was prepared and used for the palladium-catalyzed asymmetric hydrosilylation of 1,3-dienes. The introduction of two *n*-octyl groups made the palladium catalyst soluble in the hydrosilylation media. The high solubility of the chiral palladium catalyst realized the hydrosilylation at a lower reaction temperature, resulting in the higher enantioselectivity in the asymmetric hydrosilylation of 1,3-dienes with trichlorosilane.

4. Experimental

All moisture-sensitive manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. Optical rotations were measured with a Jasco DIP-370 polarimeter. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^1H NMR, residual chloroform (δ 77.00) for ^{13}C, and external 85% H_3PO_4 standard for ^{31}P NMR. HPLC analysis was performed on a Jasco PU-980 liquid chromatograph system with a chiral stationary phase column, Daicel Chiralpak OB-H, Chiralpak AD, or Chiralcel OD-H. (*R*)-2-(Diphenylphosphino)-2′-(3,5-dimethyl-4-methoxyphenyl)-1,1′-binaphthyl[7c] **1** and (*R*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthyl[14] **2** was prepared according to the reported procedure.

4.1. (*R*)-2,2′-Diethoxy-6,6′-dioctyl-1,1′-binaphthyl 3

A mixture of (*R*)-2,2′-dibromo-6,6′-diethoxy-1,1′-binaphthyl **2** (1.1 g, 2.1 mmol), $PdCl_2$(dppf) (0.032 g, 0.04 mmol), and *n*-octylmagnesium bromide (1.0 M, 7 mL, in diethyl ether) in 5 mL of diethyl ether was refluxed for 20 h. After cooling to room temperature, the reaction mixture was quenched with saturated ammonium chloride and extracted with ethyl acetate. The extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel (hexane/ethyl acetate = 30/1) to give 1.1 g (91% yield) of the titled compound as colorless oil. ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 6.1 Hz, 6H), 1.04 (t, J = 7.0 Hz, 6H), 1.20–1.43 (m, 20H), 1.62–1.68 (m, 4H), 2.69 (t, J = 7.8 Hz, 4H), 3.98–4.03 (m, 4H), 7.04 (s, 4H), 7.37 (d, J = 8.9 Hz, 2H), 7.60 (s, 2H), 7.84 (d, J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.04, 15.00, 22.61, 29.39, 29.46, 31.26, 31.84, 35.81, 65.31, 116.04, 120.90, 125.44, 126.03, 127.63, 128.34, 129.42, 132.59, 137.81, 153.71. Anal. calcd for $C_{40}H_{54}O_2$: C, 84.75; H, 9.60. Found: C, 84.56; H, 9.74. $[\alpha]_D^{20}$ +0.4 (*c* 1.3, $CHCl_3$).

4.2. (*R*)-6,6′-Dioctyl-1,1′-bi-2-naphthol 4

A solution of (*R*)-2,2′-diethoxy-6,6′-dioctyl-1,1′-binaphthyl **3** in 5 mL of methylene chloride was added dropwise to a BBr_3 solution (1.0 M, 6.0 mL, in methylene chloride) at 0°C. The reaction mixture was stirred for 12 h, treated with water, and extracted with methylene chloride. The extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel (hexane/ethyl acetate = 5/1) to give 0.8 g (95% yield) of the titled compound as colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 7.1 Hz, 6H), 1.21–1.38 (m, 20H), 1.63–1.69 (m, 4H), 2.71 (t, J = 7.8 Hz, 4H), 4.97 (s, 2H), 7.07 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 9.0 Hz, 2H), 7.65 (s, 2H), 7.88 (d, J = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.03, 22.60, 29.20, 29.34, 29.44, 31.35, 31.84, 35.74, 110.85, 117.56, 124.11, 126.81, 128.94, 129.57, 130.72, 131.67, 138.58, 152.02. Anal. calcd for $C_{36}H_{46}O_2$: C, 84.66; H, 9.08. Found: C, 84.41; H, 9.28. $[\alpha]_D^{20}$ –66 (*c* 1.4, $CHCl_3$).

4.3. (*R*)-2,2′-Bis(trifluoromethanesulfonyloxy)-6,6′-dioctyl-1,1′-binaphthyl 5

Trifluoromethanesulfonic anhydride (2.7 mL, 16.2 mmol) was added dropwise to a solution of (*R*)-6,6′-dioctyl-1,1′-bi-2-naphthol **4** (3.5 g, 6.8 mmol) and pyridine (1.6 mL, 20.4 mmol) in 15 mL of methylene chloride at 0°C. After stirring at 0°C for 1 h, the reaction mixture was concentrated under reduced pressure. The residue was diluted with ethyl acetate and washed with 5% hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel (hexane) to give 5.0 g (95% yield) of the titled compound as colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 6H), 1.21–1.39 (m, 20H), 1.54–1.72 (m, 4H), 2.76 (t, J = 7.6 Hz, 4H), 7.16 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 9.1 Hz, 2H), 7.75 (s, 2H), 8.04 (d, J = 9.1 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.01, 22.59, 29.16, 29.31, 29.37, 30.93, 31.79, 35.85, 118.10 (q, J_{C-F} = 319.9 Hz), 119.10, 123.29, 126.53, 126.57, 129.49, 131.16, 131.52, 132.54, 142.11, 144.74. Anal. calcd for $C_{38}H_{44}F_6O_6S_2$: C, 58.90; H, 5.72. Found: C, 58.79; H, 5.78. $[\alpha]_D^{20}$ –108 (*c* 1.3, $CHCl_3$).

4.4. (*R*)-2-Diphenylphosphinyl-6,6′-dioctyl-2′-trifluoromethanesulfonyloxy-1,1′-binaphthyl 6

A mixture of (*R*)-2,2′-bis(trifluoromethanesulfonyloxy)-6,6′-dioctyl-1,1′-binaphthyl **5** (1.8 g, 2.4 mmol), diphenylphosphine oxide (1.0 g, 4.7 mmol), $Pd(OAc)_2$ (0.054 g, 0.24 mmol), 1,4-bis(diphenylphosphino)butane (0.1 g, 0.24 mmol), and diisopropylethylamine (1.6 mL, 9.4 mmol) in 20 mL of DMSO was heated with stirring at 130°C for 18 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was diluted with ethyl acetate and washed with water, 5% hydrochloric acid, and saturated sodium chloride, successively. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel (hexane/ethyl acetate = 5/1) to give 1.5 g (78% yield) of the titled compound as colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.85–0.89 (m, 6H), 1.19–1.43 (m, 20H), 1.62–1.73 (m, 4H), 2.69 (t, J = 8.0 Hz, 2H), 2.74 (t, J = 8.0 Hz, 2H), 6.89 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 8.7 Hz, 1H), 7.07 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 8.9 Hz, 1H), 7.20–7.27 (m, 5H), 7.33–7.38 (m, 2H), 7.40–7.48 (m, 4H), 7.57 (s, 1H), 7.62 (dd, J = 11.5, 8.6 Hz, 1H), 7.69 (s, 1H), 7.79 (d, J = 9.1 Hz, 1H), 7.92 (d, J = 8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.05, 14.08, 22.62, 22.65, 29.18, 29.26, 29.29, 29.40, 29.47, 30.89, 31.81, 31.88, 35.88, 35.96, 117.60 (q, J_{C-F} = 313.5 Hz), assignment of all peaks of ^{13}C NMR was difficult owing to the ^{13}C–^{31}P coupling and the overlapping of peaks; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 28.9 (s). Anal. calcd for $C_{49}H_{54}F_3O_4PS$: C, 71.17; H, 6.58. Found: C, 71.44; H, 6.72. $[\alpha]_D^{20}$ +30 (*c* 1.3, $CHCl_3$).

4.5. (*R*)-2-Diphenylphosphino-6,6′-dioctyl-2′-trifluoromethanesulfonyloxy-1,1′-binaphthyl 7

Trichlorosilane (0.36 mL, 3.6 mmol) was added dropwise to a solution of (*R*)-2-diphenylphosphinyl-6,6′-dioctyl-2′-trifluoromethanesulfonyloxy-1,1′-binaphthyl **6** (1.1 g, 1.3 mmol), and triethylamine (0.61 mL, 4.4 mmol) in 10 mL of xylene. The reaction mixture was heated with stirring at 100°C for 12 h. After cooling to room temperature, the mixture was diluted with diethyl ether and quenched with small amount of saturated sodium bicarbonate. The resulting suspension was filtered through Celite and the Celite was washed with diethyl ether. The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel (hexane/ethyl acetate = 40/1) to give 1.0 g (93% yield) of the titled compound as colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.84–0.88 (m, 6H), 1.23–1.32 (m, 20H), 1.62–1.73 (m, 4H), 2.68 (t, J = 7.8 Hz, 2H), 2.71 (t, J = 7.9 Hz, 2H), 6.81 (d, J = 8.8 Hz, 1H), 6.90 (d, J = 8.8 Hz, 1H), 6.98–7.01 (m, 2H), 7.05–7.17 (m, 5H), 7.22–7.29 (m, 5H), 7.39 (dd, J = 8.8, 3.0 Hz, 1H), 7.47 (d, J = 9.3 Hz, 1H), 7.64 (s, 1H), 7.67 (s, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.95 (d, J = 9.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.06, 14.09, 22.62, 22.64, 29.19, 29.24, 29.32, 29.33, 29.42, 29.45, 31.04, 31.09, 31.82, 31.86, 35.85, 35.95, 118.00 (q, J_{C-F} = 319.9 Hz), assignment of all peaks of ^{13}C NMR was difficult owing to the ^{13}C–^{31}P coupling and the overlapping of peaks; ^{31}P{^{1}H} NMR ($CDCl_3$) δ –12.07 (s). FAB MS m/z (M^++H) calcd for $C_{49}H_{55}F_3O_3PS$: 811.36. Found: 811.39. $[\alpha]_D^{20}$ –11 (*c* 1.3, $CHCl_3$).

4.6. (*R*)-2-Diphenylphosphino-2′-(3,5-dimethyl-4-methoxyphenyl)-6,6′-dioctyl-1,1′-binaphthyl 8

A mixture of (*R*)-2-diphenylphosphino-6,6′-dioctyl-2′-trifluoromethanesulfonyloxy-1,1′-binaphthyl **7** (0.45 g, 0.55 mmol), $NiCl_2(PPh_3)_2$ (0.072 g, 0.11 mmol), and 3,5-dimethyl-4-methoxyphenylmagnesium bromide (0.6 M, 2 mL, in tetrahydrofuran) was refluxed for 24 h. The mixture was quenched with saturated ammonium chloride on an ice bath and was extracted with diethyl

ether. The extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel (hexane/ethyl acetate = 30/1) to give 0.35 g (80% yield) of the titled compound as colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.85–0.90 (m, 6H), 1.20–1.33 (m, 20H), 1.64–1.69 (m, 4H), 1.83 (s, 6H), 2.69 (t, J = 8.0 Hz, 2H), 2.73 (t, J = 8.0 Hz, 2H), 3.60 (s, 3H), 6.61 (s, 2H), 6.66 (t, J = 7.1 Hz, 2H), 6.74 (d, J = 8.7 Hz, 1H), 6.82 (dd, J = 8.7, 1.6 Hz, 1H), 6.90 (t, J = 7.4 Hz, 2H), 7.01–7.23 (m, 8H), 7.37 (d, J = 8.7 Hz, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.60 (s, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.66 (s, 1H), 7.93 (d, J = 8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.07, 14.10, 15.70, 22.64, 22.67, 29.23, 29.25, 29.29, 29.38, 29.48, 29.53, 31.19, 31.24, 31.91, 35.91, 35.94, 59.54, assignment of all peaks of ^{13}C NMR was difficult owing to the ^{13}C–^{31}P coupling and the overlapping of peaks; ^{31}P{^{1}H} NMR ($CDCl_3$) δ –14.20 (s). FAB MS m/z (M^++H) calcd for $C_{57}H_{66}OP$: 797.48. Found: 797.51. $[\alpha]_D^{20}$ +130 (c 0.3, $CHCl_3$).

4.7. Palladium-catalyzed asymmetric hydrosilylation of 1,3-dienes

The reaction conditions and results are summarized in Tables 1 and 2. A typical procedure is given for the preparation of 3-(trichlorosilyl)cyclohexene **10a** (entry 2, Table 1). To a mixture of $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.9 mg, 0.0025 mmol), the *n*-octylated MOP ligand **8** (8.0 mg, 0.0100 mmol), and 1,3-cyclohexadiene (277 mg, 2.0 mmol) was added dropwise trichlorosilane (0.24 mL, 2.4 mmol) at 0°C. The reaction mixture was stirred in a sealed tube at 0°C for 72 h, and then distilled (bulb-to-bulb) under a reduced pressure (170°C/20 torr) to give 345 mg (80% yield) of 3-(trichlorosilyl)cyclohexene **10a**. ^{1}H NMR spectra for allylsilanes, 3-(trichlorosilyl)-cyclohexene **10a** and 3-(trichlorosilyl)cyclopentene **10b**, have been reported in Ref. 7c.

4.7.1. (*Z*)-4-(Trichlorosilyl)-2-decene 10c. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 3H), 1.24–1.34 (m, 8H), 1.45–1.53 (m, 1H), 1.66 (dd, J = 6.9, 1.9 Hz, 3H), 1.78–1.81 (m, 1H), 2.53 (td, J = 11.0, 2.1 Hz, 1H), 5.15 (tq, J = 10.9, 1.9 Hz, 1H), 5.76 (dq, J = 10.8, 6.9 Hz, 1H).

4.7.2. (*Z*)-4-Phenyl-4-(trichlorosilyl)-2-butene 10d. H NMR ($CDCl_3$) δ 1.74 (d, J = 5.9 Hz, 3H), 3.94 (d, J = 9.8 Hz, 1H), 5.81–5.85 (m, 2H), 7.25–7.34 (m, 5H).

4.8. Reaction of (*Z*)-4-(trichlorosilyl)-2-decene 10c with benzaldehyde in DMF

A mixture of **10c** (109 mg, 0.4 mmol) and benzaldehyde (21 μL, 0.2 mmol) in 1 mL of DMF 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 45 mg (91% yield) of (1*S*,2*R*)-(*E*)-2-methyl-1-phenyl-3-decen-1-ol **11c**. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H), 1.21–1.30 (m, 8H), 1.92 (d, J = 3.9 Hz, 1H), 1.97 (q, J = 6.9 Hz, 2H), 2.53 (m, 1H), 4.58 (dd, J = 5.4, 3.9 Hz, 1H), 5.30 (dd, J = 15.4, 7.4 Hz, 1H), 5.44 (dt, J = 15.4, 6.9 Hz, 1H), 7.23–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.09, 14.82, 22.61, 28.74, 29.39, 31.70, 32.63, 43.76, 77.49, 126.54, 127.17, 127.94, 131.46, 132.20, 142.67. Anal. calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.94; H, 10.91. $[\alpha]_D^{20}$ –12.6 (c 1.1, $CHCl_3$) for 69% ee.

4.9. Oxidation of (1*S*,2*R*)-(*E*)-2-methyl-1-phenyl-3-decen-1-ol 11c with $KMnO_4$ and $NaIO_4$

To a solution of (1*S*,2*R*)-(*E*)-2-methyl-1-phenyl-3-decen-1-ol **11c** (125 mg, 0.51 mmol) in 14 mL of *t*-butyl alcohol was added a solution of K_2CO_3 (213 mg, 1.54 mmol) in 10 mL of water. A solution of $NaIO_4$ (883 mg, 4.13 mmol) and $KMnO_4$ (108 mg, 0.69 mmol) in 10 mL of water was added and the resulting solution was adjusted to pH 8.5 with 2N NaOH. After stirring for 24 h, *t*-butyl alcohol was evaporated. The residue was acidified with concentrated HCl, and 10% aqueous solution of $NaHSO_3$ was added to destroy the MnO_2. The solution was made basic with 2N NaOH. The mixture was extracted with diethyl ether and washed with water. The extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated. A solution of the crude acid in diethyl ether was treated with diazomethane at 0°C for 1 h. Acetic acid was added to quench excess diazomethane and the mixture was extracted with diethyl ether. The extract was washed with saturated aqueous sodium hydrogen carbonate, and dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by preparative TLC on silica gel (hexane/ethyl acetate = 4/1) gave 48 mg (48% yield) of methyl (2*S*,3*S*)-3-hydroxy-2-methyl-3-phenylpropanoate[18] **12**. $[\alpha]_D^{20}$ –16.4 (c 1.0, $CHCl_3$) for 69% ee.

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