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Hydroesterification of Vinylarenes Catalyzed by Palladium Complexes of Dialkylmonoaryl- and Monoalkyldiarylphosphines

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Hydroesterification of vinylarenes using a mixture of $PdCl_2$ and monodentate phosphorus ligands as a catalyst was studied. As ligands, menthyldiphenylphosphine (MDPP), neomenthyldiphenylphosphine (NMDPP), and dicyclohexyl(phenyl)phosphine (Cy_2PPh) were effective to obtain branched esters with high regioselectivity under the moderate reaction conditions without additives such as acids. Not only electronic effects but also steric effects of the cycloalkyl groups were revealed to be significant in order to achieve high catalytic activity. When (*S*)-2-dicyclopentylphosphino-2′-methoxy-1,1′-binaphthyl was used for the asymmetric hydroesterification of 2-methoxy-6-vinylnaphthalene, (*S*)-naproxen methyl ester was obtained with 53% ee.

Profens, 2-arylpropanoic acids, are an important class of non-steroidal anti-inflammatory agents.[1] Intensive efforts have been made for decades to develop various methods for the asymmetric synthesis of profens. Examples are stereospecific 1,2-aryl migration in chiral α-substituted acetals of propiophenones,[2] methylation of arylacetic acids,[3] hydrogenation of 2-arylpropenoic acids,[4] hydroformylation of vinylarenes,[5] hydrocyanation of vinylarene,[6] hydrovinylation of vinylarene,[7] Grignard coupling reaction using chiral transition metal reagent,[8] asymmetric protonation of arylketene bistrimethylsilyl acetal,[9] addition of alchols to ketenes,[10] and enzymatic resolution of 2-arylpropanoic esters.[11] Among these strategies, hydrocarboxylation and hydroesterificatoin of vinylarenes using carbon monoxide are a straightforward and thus practical method because of low cost and ready availability of starting materials.[12]

For the hydroesterification reaction, however, there are the following three problems to be solved. (1) The reaction usually requires rather severe conditions.[13] (2) Extra addition of acids, such as hydrochloric acid or *p*-toluenesulfonic acid, is essential to promote the catalytic activities[14] but the acids often induce corrosion of the high-pressure reactor simultaneously. (3) It is usually hard to control both regio- and enantioselectivities. Control of regioselectivity[15,16] and enantioselectivity is in general a counter balance with a few exceptions.[17] We previously reported highly efficient and regioselective hydroesterification of 6-methoxy-2-vinylnaphthalene using a $Pd(MDPP)Cl_2$ catalyst in the absence of an acid under mild conditions.[18] Here we report further investigation on our system and application to asymmetric hydroesterification.

Results and Discussion

First, hydroesterification of styrene was studied using various monoalkyl-diphenylphosphines as summarized in Table 1. An acetone solution of $PdCl_2$, a ligand, styrene, and methanol was pressurized with CO and stirred at 50 °C for 24 h. Hydroesterification with NMDPP (run 2) was completed within 24 h under the same conditions, as those for MDPP (run 1, 2.0 MPa of CO at 50 °C). The branched ester was isolated in a high yield with perfect regioselectivity. When a cyclohexyl or isopropyl group was employed as the alkyl group of the alkyldiphenylphosphine ligand (runs 3 and 7), the reaction proceeded under 4.0 MPa of CO at 50 °C to afford the branched ester with high regioselectivity. Although the catalytic activities in runs 3 and 7 were lower than those in runs 1 and 2, the longer reaction time gave acceptable isolated yields as demonstrated in runs 4 and 8. On the other hand, use of cyclopentyl, ethyl, and methyl groups (runs 6, 9, and 10) was not effective under these conditions. Thus, the steric influence of an alkyl group seems to play a crucial role: a cyclohexyl group among others allowed us to effect the reaction under milder conditions. Especially, substituents on the six-membered ring appear to accelerate the reaction (compare runs 1, 2, and 5).

Next, we varied the number of the cyclohexyl groups in $(c\text{-}C_6H_{11})_nPPh_{3-n}$. Under 4.0 MPa of CO at 50 °C, the reaction with $PdCl_2$ and a ligand of type $(c\text{-}C_6H_{11})_nPPh_{3-n}$ was further carried out, and the results are compared in Table 2. The reaction with $(c\text{-}C_6H_{11})_2PPh$ (runs 3 and 4) gave the highest yield and was found to proceed smoothly under conditions similar to MDPP and NMDPP (Table 1, runs 1 and 2); other ligands were less. Thus, phenyldicyclohexylphosphine was the best ligand for high activity and good selectivity for the branched isomer.

Based on the results mentioned above, we chose dicycloalkylphosphinobinaphthalene as a chiral ligand and examined the asymmetric hydroesterification of styrene. Dicyclohexylphosphinobinaphthyl derivatives **1a–d** were employed for the chiral ligand, as summarized in Table 3. Remarkably, all li-

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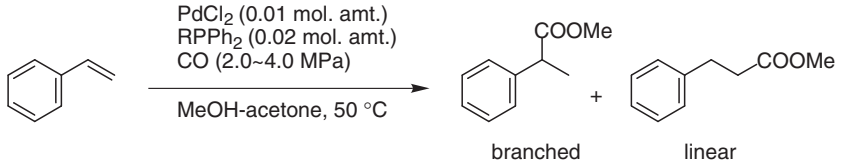
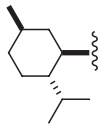
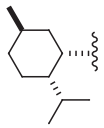
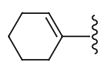
Table 1. Hydroesterification of Styrene Using $PdCl_2$ with $RPPh_2$



Run	R	CO/MPa	Time/h	b : l	Yield/%
1		2.0	24	100 : 0	95[a)]
2		2.0	24	100 : 0	96[a)]
3	*c*-C_6H_{11}	4.0	24	95 : 5	30
4	*c*-C_6H_{11}	4.0	60	95 : 5	80
5	*c*-C_6H_{11}	2.0	65	86 : 14	20
6	*c*-C_5H_9	4.0	40	— : —	<1
7	*i*-Pr	4.0	24	93 : 7	14
8	*i*-Pr	4.0	65	93 : 7	57
9	Et	4.0	40	— : —	<1
10	Me	6.0 (100 °C)	24	— : —	<1
11		2.0	65	79 : 21	15

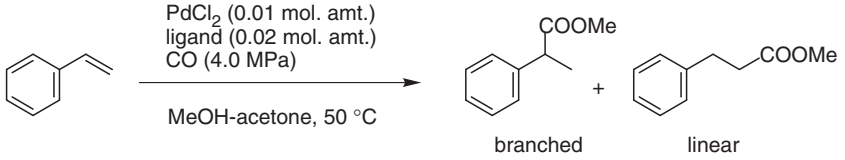
a) <10% ee.

gands gave only the branched ester, and the asymmetric induction using **1a** reached 41% ee. The ee was estimated by chiral HPLC. Next, cyclopentyl (**2a**) and isopropyl (**3a**) on phosphrus were also tested (runs 5 and 6); **2a** in particular ensured good regio- and enantioselectivities.

With dicyclopentylphosphinobinaphthyl **2**, we studied the substituent effect of the alkoxy group; we summarize the results in Table 4. In benzene as a solvent, a *t*-BuO group was found to afford the branched ester with 48% ee (run 8). The branched ester of 51% ee was given using **2a** and styrene in excess with no additional solvents (run 2). Because ee achieved with **2e** (R^2 = H) was lower than those using **2a**, **2c**, or **2g**, weak coordination of the alkoxy oxygen atom might be essential to increase the enantioselectivity. Although the enantiomeric excess values achieved here are lower than the values reported as 86%, 86%, and 99% by Alper,[17b] Inoue,[15b] and Lu,[17c] respectively, we believe the mild conditions employed here have potential synthetic applications.

Asymmetric hydroesterification of 2-methoxy-6-vinylnaphthalene leading to naproxen methyl ester was also studied. Hydroesterification with any ligand prepared proceeded under 3.0 MPa of CO at 40 °C to afford only the branched methyl ester

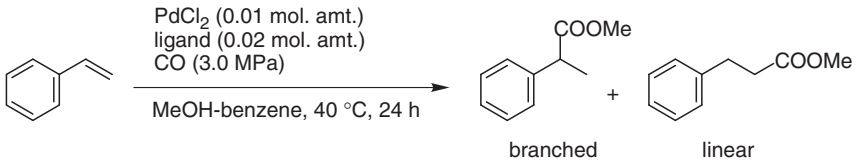
Table 2. Hydroesterification of Styrene Using $PdCl_2$ with $(c\text{-}C_6H_{11})_nPPh_{3-n}$



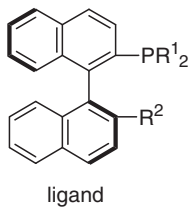
Run	n	Ligand	CO/MPa	Time/h	b:l	Yield/%
1	0	PPh_3	4.0	24	92:8	<4
2[a)]	1	$(c\text{-}C_6H_{11})PPh_2$	4.0	24	95:5	30
3	2	$(c\text{-}C_6H_{11})_2PPh$	4.0	24	99:1	65
4			4.0	50	98:2	86
5			2.0	46	96:4	78
6	3	$(c\text{-}C_6H_{11})_3P$	4.0	24	—:—	<1

a) The same result as run 3 in Table 1.

Table 3. Hydroesterification of Styrene Using $(c\text{-}C_6H_{11})_2PAr$

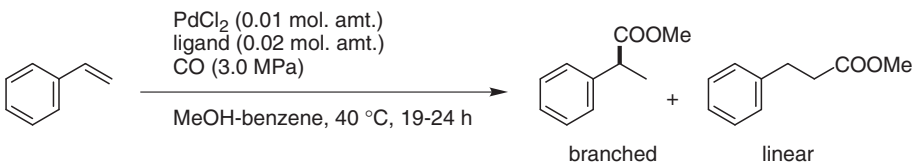


Run	Ligand	R^1	R^2	b : l	Yield/%	ee/%
1	**1a**	$c\text{-}C_6H_{11}$	OMe	100 : 0	41	41
2	**1b**	$c\text{-}C_6H_{11}$	O^{i}Pr	100 : 0	20	37
3	**1c**	$c\text{-}C_6H_{11}$	OBn	100 : 0	28	36
4	**1d**	$c\text{-}C_6H_{11}$	NMe_2	100 : 0	4	47
5	**2a**	$c\text{-}C_5H_9$	OMe	100 : 0	72	46
6	**3a**	*i*-Pr	OMe	100 : 0	28	38

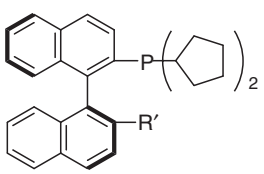


ligand

Table 4. Asymmetric Hydroesterification of Styrene Using $(c\text{-}C_5H_9)_2PAr$



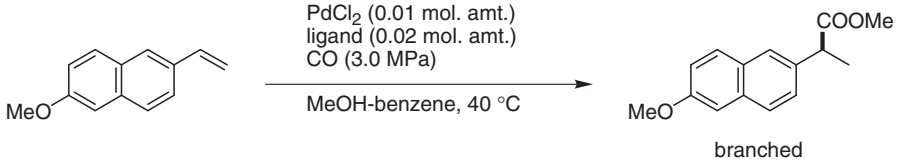
Run	Ligand	R′	b : l	Yield/%	ee/%
1	**2a**	OMe	100 : 0	72	46
2	**2a**	OMe	100 : 0	350[a)]	51
3	**2b**	O^{i}Pr	100 : 0	<1	—
4	**2c**	OBn	100 : 0	49	48
5[b)]	**2d**	OH	100 : 0	85	48
6	**2e**	H	100 : 0	67	28
7	**2f**	OTMS	100 : 0	7	45
8	**2g**	O^{t}Bu	100 : 0	12	48



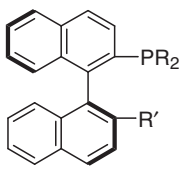
2a-g

a) TON when styrene was used as a solvent. b) THF was used as a solvent.

Table 5. Asymmetric Hydroesterification of 2-Methoxy-6-vinylnaphthalene



Run	Ligand	R	R′	Time/h	Yield/%	ee/%
1[a)]	**1a**	*c*-C_6H_{11}	OMe	24	99	34
2	**1b**	*c*-C_6H_{11}	O*i*Pr	24	17	30
3	**1c**	*c*-C_6H_{11}	OBn	24	23	28
4	**1d**	*c*-C_6H_{11}	NMe_2	24	0	—
5[a)]	**2a**	*c*-C_5H_9	OMe	24	21	53
6	**2a**	*c*-C_5H_9	OMe	144	98	48
7	**2c**	*c*-C_5H_9	OBn	96	93	37
8[a)]	**2d**	*c*-C_5H_9	OH	43	95	37
9	**2f**	*c*-C_5H_9	OTMS	24	15	41
10	**2g**	*c*-C_5H_9	O*t*Bu	24	14	50
11	**2h**	*c*-C_5H_9	NMe_2	144	28	40
12	**3a**	*i*-Pr	OMe	24	29	42
13	**3c**	*i*-Pr	OBn	24	30	33



a) The reaction was carried out at 60 °C.

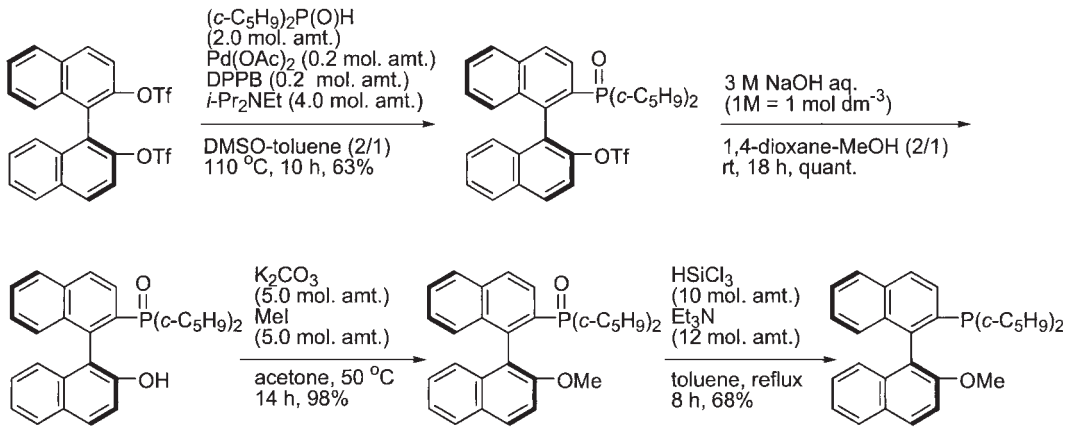
(Table 5); the best enantioselectivity of 53% ee was achieved with MeO-substituted dicyclopentylphosphinobinaphthyl **2a**. The absolute configuration of naproxen methyl ester was *S*. Although even higher enantioselectivity of 85% ee was reported previously, its synthetic application has not yet been explored.[17b]

Ligand Synthesis

The chiral ligand **2a** was prepared according to the sequence of reactions shown in Scheme 1.[19,20] Palladium-catalyzed coupling reaction of (*S*)-1,1′-binaphthyl-2,2′-diyl ditriflate with dicyclopentylphosphine oxide gave (*S*)-2-dicyclopentylphosphinoyl-2′-trifluoromethylsulfonyloxy-1,1′-binaphthyl. Hydrolysis, methylation, and reduction with trichlorosilane afforded (*S*)-2-dicyclopentylphosphino-2′-methoxy-1,1′-binaphthyl (**2a**). Other ligands were prepared in a similar way.

Conclusion

Palladium-catalyzed hydroesterification of vinylarene was studied, using MDPP, NMDPP, and dicyclohexylphenylphosphine. The desired branched esters, 2-arylpropanoic esters, were obtained with excellent regioselectivity in high yields under mild conditions. When (*S*)-2-dicyclopentylphophino-2′-methoxy-1,1′-binaphthyl (**2a**) was used as the ligand, hydroes-



Scheme 1.

terification of 2-methoxy-6-vinylnaphthalene was achieved to give only the branched ester, (*S*)-naproxen methyl ester, of 53% ee.

Experimental

General Remarks. All experiments were carried out using the standard Schlenk technique. TLC analysis was carried out by means of Merck Kieselgel 60 F254. Silica gel column chromatography was performed using Wakogel C-200 or Merck Silica gel 60.

Apparatus. All NMR spectra were recorded at room temperature, unless otherwise stated, on a Varian Mercury 200 spectrometer (^{1}H NMR 200 MHz, ^{13}C NMR 50 MHz, ^{19}F NMR 188 MHz, and ^{31}P NMR 81 MHz), a JEOL EX-270 spectrometer (^{1}H NMR 270 MHz, ^{13}C NMR 68 MHz, and ^{31}P NMR 109 MHz) and a JEOL ECP-500 spectrometer (^{1}H NMR 500 MHz, ^{13}C NMR 126 MHz, and ^{31}P NMR 202 MHz) using tetramethylsilane as an internal standard (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), or 85% phosphoric acid (^{31}P) as an external standard. Optical rotations were measured on a JASCO DIP-360. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer. FAB-MS analyses were obtained with a JEOL JMS-HX110A. Melting points were determined using a YANAKO MP-500D. HPLC analyses were carried out with a TOSOH CCPM equipped with a CO-8000 injection unit and a UV-8000 detector. Elemental analyses were performed at the Microanalytical Center, Kyoto University.

Chemicals. Unless otherwise noted, the reagents were purchased from Wako Pure Chemical Industries Ltd., Tokyo Kasei Kogyo Co., Ltd., Nacalai Tesque, Ltd., Kanto Chemical Co., Ltd. or Aldrich Chemical Co., Inc., and were used without further purification. Solvents and styrene were purified by distillation under argon after drying over suitable drying reagents. Carbon monoxide (99.9%) was purchased from Teisan Co., Ltd., (*S*)-(−)-1,1′-bi-2-naphthol from Sumikin Chemical Co., Ltd.

Preparation of (*S*)-(+)-2-Dicyclopentylphosphino-2′-methoxy-1,1′-binaphthalene-2,2′-diyl (2a) as General Procedure for 2-Dialkylphosphino-2′-alkoxy-1,1′-binaphthalene-2,2′-diyls. An oven-dried Schlenk tube (250 mL) was charged with 1,1′-binaphtyl-2,2′-diyl ditriflate (16.5 g, 30 mmol), (*c*-C_5H_9)$_2$P(O)H (11.2 g, 60 mmol), $Pd(OAc)_2$ (0.68 g, 3.0 mmol), DPPB (1.28 g, 3.0 mmol), dry DMSO (89 mL), distilled toluene (47 mL), and EtN(*i*-Pr)$_2$ (21 mL, 20 mmol) under an atmosphere of argon. The mixture was degassed by 3–5 cycles of freeze–thaw. Then, the mixture was heated at 110 °C and stirred for 10 h. After cooling to room temperature, DMSO, toluene, and excess amine were removed under reduced pressure (13–27 Pa). The residue was diluted with ethyl acetate, and the solution was washed with water and sat. aq. NaCl solution, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (ethyl acetate as an eluent) to give (*S*)-(+)-2-dicyclopentylphosphinoyl-2′-trifluoromethylsulfonyloxy-1,1′-binaphthyl as a colorless powder (11.1 g, 63% yield), mp 96–97 °C, R_f 0.33 (ethyl acetate), $[\alpha]_D^{23}$ +24 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.10–7.92 (m, 4H), 7.68–7.44 (m, 4H), 7.38–7.19 (m, 3H), 7.12 (d, J = 10.0 Hz, 1H), 2.32–1.12 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 145.4, 133.92, 133.87, 133.2, 133.0, 131.9, 130.5, 129.0, 128.8, 128.3, 127.8, 127.7, 127.2, 127.0, 126.9, 126.6, 126.3, 126.2, 125.9, 119.1, 41.2, 40.3, 39.7, 38.8, 27.7, 27.6, 26.4, 26.2, 26.1, 26.0, 25.8, 25.6, 25.5, 25.3 (multiplet due to P–C coupling); ^{19}F NMR (188 MHz, $CDCl_3$) δ −75.52; ^{31}P NMR (81 MHz, $CDCl_3$) δ 47.3; IR (KBr) 3057, 2957, 2912, 2868, 1508, 1452, 1416, 1312, 1248, 1215, 1175, 1140, 1115, 1061, 957, 941, 905, 868, 853, 835, 810, 775, 748, 706, 681, 631, 611, 592, 571, 548, 496 cm^{-1}; HRMS (FAB) Calcd for $C_{31}H_{31}F_3O_4PS$: MH$^+$ 587.1633. Found: m/z 587.1630.

(*S*)-(+)-2-Dicyclopentylphosphinoyl-2′-hydroxy-1,1′-binaphthyl. To a mixture of (*S*)-(+)-2-dicyclopentylphosphinoyl-2′-trifluoromethylsulfonyloxy-1,1′-binaphthyl (2.4 g, 4.2 mmol) in a 2:1 mixture of 1,4-dioxane and MeOH (30 mL) was added 3 M NaOH aq. solution (15 mL). The reaction mixture was stirred for 11 h at room temperature, then acidified (pH = 1) with conc. HCl and extracted with EtOAc. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure to give (*S*)-(+)-2-dicyclopentylphosphinoyl-2′-hydroxy-1,1′-binaphthyl as a pale yellow solid. This was used for the next step without purification, mp 180–181 °C, R_f 0.15 (hexane–ethyl acetate = 1:5), $[\alpha]_D^{22}$ +43 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.36–8.19 (m, 1H), 8.04–7.76 (m, 5H), 7.52–7.01 (m, 5H), 6.71 (d, J = 8.2 Hz, 1H), 3.65 (s, 1H), 2.10–0.80 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 153.2, 134.8, 134.7, 134.4, 133.3, 133.1, 130.4, 128.3, 128.1, 128.04, 127.96, 127.9, 127.84, 127.79, 127.0, 126.9, 126.0, 124.8, 123.0, 118.9, 38.6, 37.9, 37.6, 36.9, 28.1, 27.8, 26.7, 26.4, 25.7, 25.6, 25.2, 25.0 (observed complexity due to P–C splitting); ^{31}P NMR (81 MHz, $CDCl_3$) δ 52.5; IR (KBr) 2949, 2866, 2600, 1622, 1508, 1433, 1346, 1246, 1121, 820, 746, 637 cm^{-1}; HRMS Calcd for $C_{30}H_{32}O_2P$: MH$^+$ 455.2140. Found: m/z 455.2146.

(*S*)-(−)-2-Dicyclopentylphosphinoyl-2′-methoxy-1,1′-binaphthyl. Methyl iodide (0.33 mL, 5.3 mmol) was added to a mixture of (*S*)-(+)-2-dicyclopentylphosphinoyl-2′-hydroxy-1,1′-binaphthyl (0.49 g, 1.07 mmol), and K_2CO_3 (0.74 g, 5.3 mmol), and acetone (15 mL). The resulting mixture was stirred at 50 °C for 12 h, then cooled to room temperature, and filtered through a Celite pad. The insoluble material was washed with Et_2O. The combined organic phase was concentrated under reduced pressure. The residue was purified by silica gel chromatography (ethyl acetate as an eluent) to give 0.49 g (98%) of (*S*)-(−)-2-dicyclopentylphosphinoyl-2′-methoxy-1,1′-binaphthyl, mp 115–116 °C, R_f 0.15 (hexane–ethyl acetate = 1:5), $[\alpha]_D^{24}$ −15 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.40–8.30 (m, 1H), 8.09–7.81 (m, 4H), 7.54–7.08 (m, 6H), 6.86 (d, J = 8.4 Hz, 1H), 3.71 (s, 3H), 2.02–0.81 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 154.5, 137.6, 134.3, 134.2, 129.0, 128.9, 128.3, 128.2, 127.9, 127.4, 127.2, 126.7, 126.6, 126.5, 125.0, 124.6, 122.2, 120.2, 113.2, 110.9, 55.4, 39.6, 38.6, 37.6, 29.7, 28.5, 28.4, 27.8, 26.5, 26.0, 25.8, 24.6 (observed complexity due to P–C splitting); ^{31}P NMR (81 MHz, $CDCl_3$) δ 48.0; IR (KBr) 2951, 2866, 1508, 1269, 1250, 1173, 1148, 1080, 810, 748, 637 cm^{-1}; HRMS Calcd for $C_{31}H_{34}OP$: MH$^+$ 469.2296. Found: m/z 469.2300.

(*S*)-(−)-2-Dicyclopentylphosphino-2′-methoxy-1,1′-binaphthyl (2a). To a mixture of (*S*)-(+)-2-dicyclopentylphosphinoyl-2′-methoxy-1,1′-binaphthyl (0.49 g, 1.05 mmol) and Et_3N (1.76 mL, 12.6 mmol) in toluene (8 mL) was added Cl_3SiH (1.06 mL, 10.6 mmol) at 0 °C. The resulting mixture was stirred at 110 °C for 21 h, cooled to room temperature, diluted with diethyl ether (8 mL), and treated with sat. aq. $NaHCO_3$ (1 mL). The resulting yellow suspension was filtered through a Celite pad, and the insoluble material was washed with diethyl ether. The combined organic phase was dried over magnesium sulfate and concentrated under reduced pressure to give a residue, which was purified by silica gel chromatography (hexane–dichloromethane = 1:1) to give (*S*)-(−)-2-dicyclopentylphosphino-2′-methoxy-1,1′-binaphthyl (**2a**) as a colorless solid (0.31 g, 69%), mp 175–176 °C, R_f 0.85 (hexane–ethyl acetate–CH_2Cl_2 = 1:1:1), $[\alpha]_D^{22}$ −68 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.02–7.79 (m, 5H),

7.46–7.38 (m, 2H), 7.29–7.09 (m, 4H), 6.91 (d, $J = 8.2$ Hz, 1H), 3.73 (s, 3H), 2.26–0.80 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 154.0, 142.0, 141.5, 137.9, 134.1, 133.4, 132.9, 132.8, 129.5, 128.3, 128.2, 127.7, 127.2, 126.9, 126.8, 125.9, 125.7, 123.0, 122.2, 112.2, 55.4, 31.5, 31.2, 30.9, 30.8, 26.8, 26.7, 26.3, 26.2, 26.0, 25.9, 25.6, 25.5 (multiplet due to complex P–C coupling); ^{31}P NMR (81 MHz, $CDCl_3$) δ −8.2; IR (KBr) 2949, 2862, 1510, 1269, 1250, 1082, 806, 743 cm^{-1}; HRMS Calcd for $C_{31}H_{34}P$: MH^+ 453.2347. Found: m/z 453.2350.

(*S*)-2-Dicyclohexylphosphinoyl-2′-trifluoromethylsulfonyloxy-1,1′-binaphthyl. Prepared according to the literature[20] as a colorless solid, R_f 0.29 (ethyl acetate). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.10–7.91 (m, 5H), 7.62–7.42 (m, 4H), 7.39–7.19 (m, 2H), 7.12 (d, $J = 7.9$ Hz, 1H), 2.19–0.80 (m, 22H); ^{31}P NMR (81 MHz, $CDCl_3$) δ 48.7.

(*S*)-2-Dicyclohexylphosphino-2′-methoxy-1,1′-binaphthyl (1a).[20] The prepared sample exhibited ^{31}P NMR (81 MHz, $CDCl_3$) δ −6.7.

Ligands **1a–c**, **2b–d**, and **3a–b** were also prepared according to methods described above:

(*S*)-(−)-2-Dicyclohexylphosphinoyl-2′-isopropoxy-1,1′-binaphthyl. Mp 39–40 °C, $[\alpha]_D^{24}$ −49 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.13–7.81 (m, 5H), 7.54–7.08 (m, 6H), 6.90 (d, $J = 8.1$ Hz, 1H), 4.50 (septet, $J = 6.0$ Hz, 1H), 1.90–0.85 (m, 22H), 1.12 (d, $J = 6.0$ Hz, 3H), 0.74 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 153.5, 134.5, 134.11, 134.08, 133.1, 129.6, 128.6, 128.3, 128.1, 127.7, 127.6, 127.0, 126.8, 126.6, 125.9, 125.6, 123.4, 123.0, 122.9, 116.3, 71.5, 37.9, 37.8, 36.9, 36.8, 26.6, 26.53, 26.47, 26.4, 26.3, 26.2, 26.12, 26.05, 25.8, 25.7, 22.8, 22.1 (multiplet due to complex P–C coupling); ^{31}P NMR (81 MHz, $CDCl_3$) δ 48.9; IR (KBr) 2924, 2849, 1447, 1263, 1242, 1111, 1003, 806, 746 cm^{-1}; HRMS Calcd for $C_{35}H_{42}O_2P$: MH^+ 525.2922. Found: m/z 525.2922.

(*S*)-(−)-2-Dicyclohexylphosphino-2′-isopropoxy-1,1′-binaphthyl (1b). Yield: 11% (2 steps from (*S*)-2-dicyclohexylphosphinoyl-2′-hydroxy-1,1′-binaphthyl) as a colorless solid, mp 117–118 °C, $[\alpha]_D^{22}$ −98 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.97–7.60 (m, 5H), 7.55–6.95 (m, 6H), 6.85 (d, $J = 8.4$ Hz, 1H), 4.45 (sept, $J = 6.0$ Hz, 1H), 1.86–0.60 (m, 22H), 1.03 (d, $J = 6.0$ Hz, 3H), 0.74 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 152.9, 143.7, 143.3, 134.4, 133.2, 133.1, 129.0, 128.9, 128.3, 127.6, 127.4, 127.0, 126.4, 126.3, 126.1, 125.9, 125.4, 125.3, 123.0, 115.3, 70.3, 35.2, 34.8, 30.7, 30.4, 30.2, 30.0, 27.4, 27.2, 26.5, 26.4, 25.8, 22.7, 22.1 (multiplet due to complex P–C coupling); ^{31}P NMR (81 MHz, $CDCl_3$) δ −6.7; IR (KBr) 2924, 2849, 1622, 1591, 1506, 1447, 1369, 1325, 1265, 1244, 1001, 812, 746 cm^{-1}; HRMS Calcd for $C_{35}H_{42}OP$: MH^+ 509.2973. Found: m/z 509.2976.

(*S*)-(−)-2-Dicyclohexylphosphinoyl-2′-benzyloxy-1,1′-binaphthyl. Mp 74–75 °C, $[\alpha]_D^{23}$ −60 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06–7.83 (m, 5H), 7.59–7.02 (m, 9H), 6.95 (d, $J = 8.8$ Hz, 1H), 6.88–6.78 (m, 2H), 5.09 (d, $J = 12.3$ Hz, 1H), 5.01 (d, $J = 12.3$ Hz, 1H), 1.88–0.40 (m, 22H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 153.7, 136.8, 129.8, 128.3, 128.2, 128.1, 127.95, 127.91, 127.86, 127.7, 127.6, 127.22, 127.17, 127.0, 126.9, 126.84, 126.76, 126.7, 126.53, 126.46, 126.3, 126.0, 125.8, 125.6, 123.5, 114.8, 70.7, 38.0, 37.8, 37.1, 36.9, 26.9, 26.8, 26.6, 26.4, 26.3, 26.1, 25.9, 25.8, 25.6, 25.4 (multiplet due to complex P–C coupling); ^{31}P NMR (81 MHz, $CDCl_3$) δ 49.0; IR (KBr) 2926, 2851, 1508, 1448, 1267, 1217, 1148, 1022, 814, 746, 694 cm^{-1}; HRMS Calcd for $C_{39}H_{42}O_2P$: MH^+ 573.2922. Found: m/z 573.2913.

(*S*)-(−)-2-Dicyclohexylphosphino-2′-benzyloxy-1,1′-binaphthyl (1c). Yield: 9% (2 steps from (*S*)-2-dicyclohexylphosphinoyl-2′-hydroxy-1,1′-binaphthyl) as a colorless solid, mp 90–91 °C, $[\alpha]_D^{22}$ −64 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.05–6.73 (m, 17H), 5.05 (s, 2H), 2.07–0.80 (m, 22H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 153.4, 137.3, 134.1, 133.4, 133.2, 133.1, 129.3, 129.0, 128.7, 128.6, 128.3, 127.9, 127.7, 127.6, 127.4, 127.2, 127.0, 126.8, 126.5, 126.3, 126.1, 126.0, 125.7, 123.5, 123.3, 114.1, 70.0, 35.4, 35.1, 34.6, 34.4, 30.6, 30.4, 30.2, 30.0, 29.8, 27.3, 26.9, 26.8, 26.4, 25.8 (observed complexity due to P–C splitting); ^{31}P NMR (81 MHz, $CDCl_3$) δ −6.6; IR (KBr) 2922, 2847, 1622, 1593, 1499, 1447, 1267, 1219, 1070, 1020, 804, 745, 694 cm^{-1}; HRMS Calcd for $C_{39}H_{42}OP$: MH^+ 557.2973. Found: m/z 557.2966.

(*S*)-(−)-2-Dicyclopentylphosphinoyl-2′-isopropoxy-1,1′-binaphthyl. Colorless solid, R_f 0.43 (ethyl acetate). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.90–7.68 (m, 5H), 7.43–7.28 (m, 2H), 7.25–7.02 (m, 4H), 6.86 (d, $J = 8.6$ Hz, 1H), 4.47 (m, $J = 6.0$ Hz), 2.21–1.95 (br, 2H), 1.95–1.62 (br, 2H), 1.60–1.20 (br, 14H), 1.04 (d, $J = 6.0$ Hz, 3H), 0.75 (d, $J = 6.0$ Hz, 3H); ^{31}P NMR (81 MHz, $CDCl_3$) δ 50.5. HRMS (FAB) Calcd for $C_{33}H_{38}O_2P$: MH^+ 497.2609. Found: m/z 497.2610.

(*S*)-(−)-2-Dicyclopentylphosphino-2′-isopropoxy-1,1′-binaphthyl (2b). Yield: 55% (2 steps from (*S*)-2-dicyclopentylphosphinoyl-2′-hydroxy-1,1′-binaphthyl) as a colorless solid, mp 136–137 °C, R_f 0.55 (hexane–ethyl acetate = 10:1), $[\alpha]_D^{22}$ −101 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.96–7.68 (m, 7H), 7.44–7.28 (m, 3H), 7.26–6.98 (m, 5H), 6.86 (d, $J = 8.2$ Hz, 1H), 4.48 (m, 1H), 2.41–1.95 (br, 2H), 1.87–1.62 (br, 2H), 1.60–1.19 (br, 14H), 1.04 (d, $J = 6.0$ Hz, 3H), 0.74 (d, $J = 5.8$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 152.9, 134.5, 129.1, 128.4, 128.2, 127.6, 127.5, 127.1, 126.9, 126.2, 125.9, 125.5, 123.1, 115.5, 79.6, 70.5, 39.1, 31.6, 31.3, 30.9, 26.8, 26.7, 26.3, 26.2, 25.8, 25.74, 25.69, 25.57, 22.6, 22.2; ^{31}P NMR (81 MHz, $CDCl_3$) δ −8.8; IR (KBr) 2950, 2864, 1622, 1591, 1508, 1448, 1265, 1242, 1109, 1001, 806, 746 cm^{-1}; HRMS (FAB) Calcd for $C_{33}H_{38}OP$: MH^+ 481.2660. Found: m/z 481.2662.

(*S*)-(−)-2-Dicyclopentylphosphinoyl-2′-benzyloxy-1,1′-binaphthyl. Colorless solid, R_f 0.17 (hexane–ethyl acetate = 1:9). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06 (dd, $J = 8.6$, 1.3 Hz, 1H), 7.84 (d, $J = 7.9$ Hz, 1H), 7.55 (ddd, $J = 7.9$, 6.5, 1.3 Hz, 1H), 7.45–7.18 (m, 5H), 6.94 (d, $J = 8.6$ Hz, 1H), 6.83 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.2, 153.8, 138.0, 137.9, 136.3, 134.5, 134.4, 134.2, 133.0, 132.8, 130.3, 128.5, 128.4, 128.3, 128.0, 127.8, 127.6, 127.4, 127.3, 126.7, 126.5, 126.4, 126.2, 125.4, 123.8, 121.5, 114.6, 70.6, 38.9 (d, $J = 42$ Hz), 37.8 (d, $J = 42$ Hz), 27.8, 26.6, 26.5, 26.4, 26.2, 26.1, 25.6, 25.4, 25.3, 25.2, 21.3; ^{31}P NMR (81 MHz, $CDCl_3$) δ 50.8. HRMS (FAB) Calcd for $C_{37}H_{38}O_2P$: MH^+ 545.2609. Found: m/z 545.2601.

(*S*)-(−)-2-Dicyclopentylphosphino-2′-benzyloxy-1,1′-binaphthyl (2c). Yield: 58% (2 steps from (*S*)-2-dicyclopentylphosphinoyl-2′-hydroxy-1,1′-binaphthyl) as a colorless solid, mp 154–156 °C, R_f 0.38 (hexane–ethyl acetate = 10:1), $[\alpha]_D^{22}$ −44 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.02–7.63 (m, 3H), 7.50–6.80 (m, 14H), 4.74 (d, $J = 11.9$ Hz, 1H), 4.59 (d, $J = 11.9$ Hz, 1H), 2.18–0.82 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 153.2, 137.3, 135.3, 134.2, 133.4, 131.6, 131.4, 130.3, 129.3, 127.9, 127.7, 127.6, 127.3, 127.1, 127.0, 126.9, 126.3, 126.0, 123.3, 122.3, 70.1, 39.0, 38.9, 31.5, 30.9, 26.6, 26.5, 26.3, 26.2, 25.7; ^{31}P NMR (81 MHz, $CDCl_3$) δ −8.8; IR (KBr) 2960, 2860, 1622, 1591, 1506, 1452, 1417, 1261, 1221, 1020, 802, 744 cm^{-1}; HRMS

(FAB) Calcd for $C_{37}H_{38}OP$: MH^+ 529.2660. Found: m/z 529.2658.

(*S*)-(−)-2-Dicyclopentylphosphino-2′-hydroxy-1,1′-binaphthyl (2d). Prepared in 76% yield from (*S*)-2-dicyclopentylphosphinoyl-2′-hydroxy-1,1′-binaphthyl as a colorless solid, mp 139–141 °C, R_f 0.25 (hexane–dichloromethane = 1:1), $[\alpha]_D^{22}$ −29 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.05–7.82 (m, 4H), 7.56–7.46 (m, 1H), 7.38–7.12 (m, 6H), 6.92 (d, J = 8.2 Hz, 1H), 4.66 (br, 1H), 2.30–2.02 (m, 2H), 2.02–0.84 (m, 16H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 153.1, 147.9, 145.2, 143.6, 141.6, 134.4, 133.9, 129.9, 128.2, 128.1, 127.9, 127.7, 127.5, 126.7, 126.4, 126.2, 123.4, 126.2, 123.5, 122.6, 118.7, 117.4, 41.1, 40.1, 38.5, 38.0, 37.7, 36.8, 27.6, 27.4, 27.2, 26.8, 26.4, 24.7, 25.5 (multiplet due to complex P–C splitting); ^{31}P NMR (81 MHz, $CDCl_3$) δ −10.1; IR (KBr) 3454, 2959, 2862, 1620, 1597, 1346, 1261, 1097, 1022, 815, 744 cm^{-1}; HRMS (FAB) Calcd for $C_{37}H_{38}OP$: MH^+ 439.2191. Found: m/z 439.2201.

(*S*)-(−)-2-Dicyclopentylphosphinoyl-1,1′-binaphthyl. Prepared from (*S*)-(−)-2-trifluoromethylsulfonyloxy-1,1′-binaphthyl in 18% yield as a colorless solid, mp 195–198 °C; R_f 0.10 (hexane–ethyl acetate = 1:4), $[\alpha]_D^{22}$ −2.1 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.39 (dd, J = 8.9, 8.9 Hz, 1H), 8.35–7.84 (m, 4H), 7.57–7.35 (m, 4H), 7.17 (dd, J = 7.1, 7.1 Hz, 2H), 7.04 (dd, J = 8.6 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 140.2, 136.1, 133.1, 132.9, 132.0, 130.8, 129.1, 129.0, 128.2, 127.8, 127.7, 127.5, 127.3, 127.1, 126.5, 126.3, 126.1, 126.0, 124.7, 42.2, 41.2, 39.9, 38.9, 38.7, 37.7, 28.5, 28.4, 27.2, 27.1, 26.6, 26.5, 26.2, 25.3, 25.2; ^{31}P NMR (81 MHz, $CDCl_3$) δ 48.2; IR (KBr) 2950, 2856, 1584, 1552, 1454, 1377, 1307, 1168, 899, 808, 738 cm^{-1}; HRMS (FAB) Calcd for $C_{30}H_{32}OP$: MH^+ 439.2191. Found: m/z 439.2194.

(*S*)-(−)-2-Dicyclopentylphosphino-1,1′-binaphthyl (2e). Yield 85% as a colorless solid, mp 114–116 °C, R_f 0.38 (hexane–dichloromethane–ethyl acetate = 1:1:1), $[\alpha]_D^{22}$ −56 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.57–8.10 (m, 1H), 8.08–7.67 (m, 4H), 7.59–7.23 (m, 4H), 7.23–6.94 (m, 4H), 2.25–0.65 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 133.0, 128.9, 128.7, 128.2, 128.1, 127.7, 127.5, 127.0, 126.8, 126.3, 126.1, 125.9, 125.7, 125.6, 125.4, 124.7, 61.3, 58.4, 57.8, 57.5, 57.0, 55.0, 39.8, 37.6, 33.2, 31.5, 26.9, 26.5, 26.4, 26.0, 25.7, 25.6, 25.1; ^{31}P NMR (81 MHz, $CDCl_3$) δ −9.9; IR (KBr) 2960, 2856, 1654, 1589, 1560, 1461, 1377, 1259, 1112, 1024, 800, 744 cm^{-1}; HRMS (FAB) Calcd for $C_{30}H_{32}P$: MH^+ 423.2242. Found: m/z 423.2242.

Preparation of (*S*)-(+)-2-Dicyclopentylphosphino-2′-trimethylsiloxy-1,1′-binaphthyl (2f). A flame dried Schlenk tube (20 mL) was charged with **2d** (168 mg, 0.38 mmol), THF (2 mL), and triethylamine (0.63 mL, 4.6 mmol) under an argon atmosphere of argon. The solution was degassed 3 times by freeze–thaw. Then trimethylchlorosilane (0.49 mL, 3.8 mmol) was added to the solution at room temperature and the solution was stirred for 11 h. After the solvent and excess amine were removed under reduced pressure, the residue was filtered through a neutral alumina column to afford (*S*)-(−)-2-dicyclopentylphosphino-2′-trimethylsiloxy-1,1′-binaphthyl (**2f**) as a colorless solid (0.158 g, 80% yield), mp 66–67 °C, $[\alpha]_D^{24}$ +28 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.59–8.42 (m, 1H), 8.28–7.98 (m, 4H), 7.80–7.12 (m, 6H), 6.95 (d, J = 8.2 Hz, 1H), 2.52–0.82 (m, 18H), 0.37 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 150.4, 134.6, 130.0, 128.9, 128.6, 128.2, 127.8, 127.7, 127.64, 127.55, 127.3, 127.02, 126.97, 125.9, 125.8, 125.4, 124.9, 123.2, 120.6, 119.2, 31.7, 31.5, 31.3, 31.1, 26.8, 26.6, 26.5, 26.2, 25.84, 25.79, 25.6, 25.5, 2.0, 1.5, 1.0 (multiplet due to complex P–C coupling); ^{31}P NMR (81 MHz, $CDCl_3$) δ −8.7; IR (KBr) 2954, 2866, 1346, 1250, 1121, 1030, 999, 845, 818, 746 cm^{-1}; HRMS (FAB) Calcd for $C_{33}H_{40}OPSi$: MH^+ 511.2586. Found: m/z 511.2588.

(*S*)-(−)-2-Dicyclopentylphosphino-2′-*t*-butoxy-1,1′-binaphthyl (2g). Prepared as above in 21% overall yield as a colorless solid: mp 68–69 °C, $[\alpha]_D^{24}$ −15 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.50–8.41 (m, 1H), 7.99–7.69 (m, 4H), 7.46–6.98 (m, 5H), 6.83 (d, J = 8.2 Hz, 1H), 2.20–0.70 (m, 27H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 149.1, 134.6, 134.0, 133.9, 132.9, 132.8, 129.9, 128.6, 128.4, 128.2, 128.0, 127.9, 127.0, 126.8, 126.7, 125.9, 125.4, 123.7, 122.9, 117.5, 55.5, 38.9, 38.4, 38.2, 37.8, 31.3, 26.5, 26.4, 26.3, 26.1, 25.8, 25.7, 25.6, 25.5 (multiplet due to complex P–C splitting); ^{31}P NMR (81 MHz, $CDCl_3$) δ −8.1; IR (KBr) 2951, 2862, 1433, 1344, 1261, 1097, 1022, 812, 746 cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{40}OP$: MH^+ 495.2817. Found: m/z 495.2802.

Preparation of (*S*)-(+)-2-Dicyclopentylphosphinoyl-2′-dimethylamino-1,1′-binaphthyl. An oven-dried Schrenk tube (20 mL) was charged with **5** (192 mg, 0.51 mmol), (*c*-Pen)$_2$P(O)H (191 mg, 1.02 mmol), $Pd(OAc)_2$ (58 mg, 0.26 mmol), DPPB (111 mg, 0.26 mmol), DMSO (1.5 mL), distilled toluene (0.8 mL), and EtN(*i*-Pr)$_2$ (0.36 mL, 2.0 mmol) under an argon atmosphere. The mixture was degassed 5 times by the freeze–thaw cycles. Then, the mixture was heated at 110 °C and stirred for 19 h at 110 °C. After cooling to room temperature, DMSO, toluene, and excess amine were removed under reduced pressure (13–27 Pa). The residue was diluted with EtOAc, washed with water and brine, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (ethyl acetate as an eluent) to give (*S*)-(+)-2-dicyclopentylphosphinoyl-2′-dimethylamino-1,1′-binaphthyl as a pale yellow powder (170 mg, 69% yield), mp 202–203 °C, R_f 0.30 (ethyl acetate), $[\alpha]_D^{24}$ +10 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.41–8.30 (m, 1H), 8.10–7.89 (m, 2H), 7.82–7.38 (m, 5H), 7.35–7.20 (m, 2H), 7.11–7.01 (m, 1H), 6.73 (d, J = 8.6 Hz, 1H), 2.48 (s, 6H), 2.32–0.74 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 149.4, 134.2, 133.7, 133.6, 133.4, 132.7, 132.4, 129.0, 128.8, 128.6, 128.4, 128.3, 127.7, 127.5, 126.8, 126.4, 125.9, 125.1, 122.9, 118.7, 43.5, 31.1, 30.8, 30.2, 29.9, 27.3, 27.2, 26.4, 26.3, 26.1, 26.0, 25.4, 25.3 (observed complexity due to P–C splitting); ^{31}P NMR (81 MHz, $CDCl_3$) δ 48.5; IR (KBr) 2941, 2866, 1504, 1159, 1128, 826, 814, 750, 552, 507 cm^{-1}; HRMS (FAB) Calcd for $C_{33}H_{37}NOP$: MH^+ 482.2613. Found: m/z 482.2616.

Preparation of (*S*)-(+)-2-Dicyclopentylphosphino-2′-dimethylamino-1,1′-binaphthyl (2h). To a mixture of (*S*)-(+)-2-dicyclopentylphosphinoyl-2′-dimethylamino-1,1′-binaphthyl (266 mg, 0.55 mmol) and Et_3N (0.90 mL, 6.6 mmol) in toluene (9 mL) was added Cl_3SiH (0.56 mL, 5.5 mmol) at 0 °C. The reaction mixture was stirred at 110 °C for 25 h, cooled to room temperature, diluted with Et_2O (8 mL), quenched with 1 M NaOH aq. solution, and extracted with diethyl ether. The combined organic phase was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by Florisil chromatography (CH_2Cl_2 as an eluent) to give (*S*)-(+)-2-dicyclopentylphosphino-2′-dimethylamino-1,1′-binaphthyl (**2h**) as a yellow solid (95 mg, 37% yield), mp 126–128 °C, R_f 0.44 (CH_2Cl_2), $[\alpha]_D^{24}$ +56 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.88–7.63 (m, 4H), 7.45–7.06 (m, 6H), 7.02–6.87 (m, 1H), 6.69 (d, J = 8.6 Hz, 1H), 2.36 (s, 6H), 2.04–0.73 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ (observed complexity due to P–C splitting); ^{31}P NMR (81 MHz, $CDCl_3$) δ −7.4; IR (KBr) 2945, 2860, 1261, 1097,

1024, 991, 812, 748 cm^{-1}; HRMS (FAB) Calcd for $C_{33}H_{37}NP$: MH^+ 466.2663. Found: m/z 466.2665.

General Procedure for Hydroesterification of Styrene. A 50 mL autoclave was charged with $PdCl_2$ (1.8 mg, 0.010 mmol), a phosphine ligand (0.020 mmol), styrene (104 mg, 1.00 mmol), methanol (0.5 mL), and solvent (2.0 mL). The mixture was pressurized with 3.0 MPa of CO and stirred for 24 h at 40 °C. After the pressure was released, the resulting mixture was distilled under 13 Pa to give methyl 2-phenylpropanoate as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37–7.22 (m, 5H), 3.72 (q, 1H, J = 7.1 Hz), 3.65 (s, 3H), 1.50 (d, 3H, J = 7.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 174.5, 140.3, 128.3, 127.1, 126.8, 51.7, 45.2, 18.5. The ee was determined by HPLC using Daicel Chiralpak OJ.

General Procedure for Hydroesterification of 2-Methoxy-6-vinylnaphthalene. A 50 mL autoclave was charged with $PdCl_2$ (1.8 mg, 0.010 mmol), a phosphine ligand (0.020 mmol), 2-methoxy-6-vinylnaphthalene (184 mg, 1.00 mmol), methanol (0.5 mL), and a solvent (2.0 mL). The mixture was pressurized with 3.0 MPa of CO and stirred for 24 h at 40 °C or 60 °C. After the pressure was released, the resulting mixture was purified by silica gel chromatography (hexane–ethyl acetate = 10:1) to give naproxen methyl ester as a colorless solid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75–7.64 (m, 3H), 7.44–7.37 (m, 1H), 7.19–7.10 (m, 2H), 3.91 (s, 3H), 3.86 (q, 1H, J = 7.1 Hz), 3.67 (s, 3H), 1.59 (d, 3H, J = 7.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 174.9, 157.4, 133.6, 129.1, 128.8, 127.1, 126.1, 125.8, 118.9, 105.5, 104.4, 55.3, 52.1, 45.4, 18.7. The ee was estimated by HPLC using Daicel Chiralpak OD.

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References

1 a) H. R. Sonawane, N. S. Bellur, J. R. Ahuja, and D. G. Kulkarni, *Tetrahedron: Asymmetry*, **3**, 163 (1992). b) J.-P. Rieu, A. Boucherle, H. Cousse, and G. Mouzin, *Tetrahedron*, **42**, 4095 (1986). c) C. Botteghi, S. Paganelli, A. Schionato, and M. Marchetti, *Chirality*, **3**, 355 (1991).

2 a) G. Castaldi, S. Cavicchioli, C. Giordano, and F. Uggeri, *J. Org. Chem.*, **52**, 3018 (1987). b) C. Giordano, G. Castaldi, S. Cavicchioli, and M. Villa, *Tetrahedron Lett.*, **45**, 4243 (1989). c) G. Tsuchihashi, *Tetrahedron Lett.*, **23**, 5427 (1982). d) G. Tsuchihashi, A. Ori, and Y. Honda, *Bull. Chem. Soc. Jpn.*, **52**, 10 (1987). e) G. Castaldi, A. Belli, F. Uggeri, and C. Giordano, *J. Org. Chem.*, **48**, 4658 (1983). f) C. Giordano, G. Castaldi, F. Casagrande, and A. Belli, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2575.

3 K. Fuji, M. Node, F. Tanaka, and S. Hosoi, *Tetrahedron Lett.*, **30**, 2825 (1989).

4 a) R. Noyori and S. Hashiguchi, "Applied Homogeneous Catalysis with Organometallic Compounds," ed by B. Cornils and W. A. Herrmann, Wiley-VCH, New York (1996), p. 552. b) T. Ohta, H. Takaya, M. Kitamura, K. Nagai, and R. Noyori, *J. Org. Chem.*, **52**, 3174 (1987). c) R. Noyori and H. Takaya, *Acc. Chem. Res.*, **23**, 345 (1990).

5 a) K. Nozaki, S. Mano, and H. Takaya, *J. Am. Chem. Soc.*, **115**, 7033 (1993). b) N. Sakai, K. Nozaki, and H. Takaya, *J. Chem. Soc., Chem. Commun.*, **1994**, 395. c) T. Higashijima, N. Sakai, K. Nozaki, and H. Takaya, *Tetrahedron Lett.*, **35**, 2023 (1994). d) K. Nozaki, W. G. Li, T. Horiuchi, H. Takaya, T. Saito, A. Yoshida, K. Matsumura, Y. Kato, T. Imai, T. Miura, and H. Kumobayashi, *J. Org. Chem.*, **61**, 7658 (1996). e) K. Nozaki, S. Mano, and H. Takaya, *J. Am. Chem. Soc.*, **119**, 4413 (1997). f) K. Nozaki, T. Nanno, and H. Takaya, *J. Organomet. Chem.*, **527**, 103 (1997). g) T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, and H. Takaya, *Tetrahedron*, **53**, 7795 (1997). h) T. Horiuchi, E. Shirakawa, K. Nozaki, and H. Takaya, *Organometallics*, **16**, 2981 (1997). i) T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, and H. Takaya, *J. Org. Chem.*, **62**, 4285 (1997). j) K. Nozaki, W. G. Li, T. Horiuchi, and H. Takaya, *Tetrahedron Lett.*, **38**, 4611 (1997). k) K. Nozaki, H. Takaya, and T. Hiyama, *Top. Catal.*, **4**, 175 (1997).

6 a) T. V. RajanBabu and A. L. Casalnuovo, *J. Am. Chem. Soc.*, **114**, 6265 (1992). b) A. L. Casalnuovo, T. V. RajanBabu, T. A. Ayers, and T. H. Warren, *J. Am. Chem. Soc.*, **116**, 9869 (1994).

7 a) G. Wilke, J. Monkiewicz, and H. Kuhn, U. S. Patent 4912274 (1990); *Chem. Abstr.*, **114**, 43172 (1991). b) W. Wilke, *Angew. Chem., Int. Ed. Engl.*, **27**, 185 (1988). c) P. W. Jolly and G. Wilke, "Applied Homogeneous Catalysis with Organometallic Compounds," ed by B. Cornils and W. A. Herrmann, Wiley-VCH, New York (1996), p. 1024, and references therein. d) N. Nomura, J. Jin, H. Park, and T. V. RajanBabu, *J. Am. Chem. Soc.*, **120**, 459 (1998). e) T. V. RajanBabu, N. Nomura, J. Jin, B. Radetich, H. Park, and M. Nandi, *Chem.—Eur. J.*, **5**, 1963 (1999).

8 a) T. Hiyama and N. Wakasa, *Tetrahedron Lett.*, **26**, 3259 (1985). b) G. W. Erickson, EP 110671 (1974).

9 a) S. Nakamura, M. Kaneeda, K. Ishihara, and H. Yamamoto, *J. Am. Chem. Soc.*, **122**, 8120 (2000). b) H. Ishibashi, K. Ishihara, and H. Yamamoto, *Chem. Rec.*, **2**, 177 (2002). c) K. Ishihara, S. Nakamura, M. Kaneeda, and. H. Yamamoto, *J. Am. Chem. Soc.*, **118**, 12854 (1996). d) K. Ishihara, D. Nakashima, Y. Hiraiwa, and H. Yamamoto, *J. Am. Chem. Soc.*, **125**, 24 (2003).

10 a) B. L. Hodous, J. C. Ruble, and G. C. Fu, *J. Am. Chem. Soc.*, **121**, 2637 (1999). b) C. Fehr, *Angew. Chem., Int. Ed. Engl.*, **35**, 2567 (1996). c) R. D. Larsen, E. G. Corley, P. Davis, P. J. Reider, and J. J. Grabowski, *J. Am. Chem. Soc.*, **111**, 7650 (1989).

11 a) M. Ahmar, C. Girard, and R. Bloch, *Tetrahedron Lett.*, **30**, 7053 (1989). b) Q.-M. Gu, C.-S. Chen, and C. J. Shi, *Tetrahedron Lett.*, **27**, 1763 (1986).

12 a) K. Nozaki and I. Ojima, "Catalytic Asymmetric Synthesis, Second Edition," ed by I. Ojima, John Wiley & Sons, New York (2000), p. 429. b) B. E. Ali and H. Alper, "Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals," ed by M. Beller and C. Bolm, John Wiley & Sons, New York (1998), p. 49. c) J. F. Knifton, *J. Org. Chem.*, **41**, 2885 (1976). d) G. Gavinator and A. Toniolo, *J. Mol. Catal.*, **10**, 161 (1981).

13 a) D. Thompson, "Comprehensive Organic Synthesis," ed by B. M. Trost, I. Fleming, and G. FRS. Pattenden, Pergamon Press, New York (1991), Vol. 3, p. 1015. b) H. M. Colquhoun, D. J. Thompson, and M. V. Twigg, "Carbonylation; Direct Synthesis of Carbonyl Compounds," Plenum Press, New York (1991). c) J. Tsuji, *Acc. Chem. Res.*, **2**, 96 (1969).

14 a) T. Fuchikami, K. Ohishi, and I. Ojima, *J. Org. Chem.*, **48**, 3803 (1983). b) I. J. B. Lin and H. Alper, *J. Chem. Soc.*, **1989**, 248. c) W. A. Nugent and R. J. McKinnery, *J. Org. Chem.*, **50**, 5370 (1985).

15 a) K. Nozaki, M. L. Kantam, T. Horiuchi, and H. Takaya, *J. Mol. Catal. A: Chem.*, **118**, 247 (1997). b) S. Oi, M. Nomura, T. Aiko, and Y. Inoue, *J. Mol. Catal. A: Chem.*, **115**, 289 (1997). c) T. Fuchikami, K. Ohishi, and I. Ojima, *J. Org. Chem.*, **48**, 3803

(1983).

16 a) K. Bittler, N. V. Kutepow, D. Neubauer, and H. Reis, *Angew. Chem., Int. Ed. Engl.*, **7**, 329 (1968). b) D. M. Fenton, *J. Org. Chem.*, **38**, 3192 (1973). c) Y. Sugi and K. Bando, *Chem. Lett.*, **1976**, 727. d) Y. Sugi, K. Bando, and S. Shin, *Chem. Ind.*, **1975**, 397. e) J. Y. Yoon, E. J. Jang, K. H. Lee, and J. S. Lee, *J. Mol. Catal. A: Chem.*, **118**, 181 (1997). f) A. Seayad, S. Jayasree, and R. V. Chaudhari, *Org. Lett.*, **1**, 459 (1999).

17 a) G. Consiglio and P. Pino, *Chimia*, **30**, 193 (1976). b) H. Alper and N. Hamel, *J. Am. Chem. Soc.*, **112**, 2803 (1990). c) H. Zhou, J. Hou, J. Cheng, S. Lu, H. Fu, and H. Wang, *J. Organomet. Chem.*, **543**, 227 (1997). d) L. Wang, W. H. Kwok, A. S. C. Chan, T. Tu, X. Hou, and L. Dai, *Tetrahedron: Asymmetry*, **14**, 2291 (2003).

18 T. Hiyama, N. Wakasa, and T. Kusumoto, *Synlett*, **1991**, 569.

19 a) T. Hayashi, *Acc. Chem. Res.*, **33**, 354 (2000). b) T. Hayashi, S. Hirate, K. Kitayama, H. Tsuji, A. Torii, and Y. Uozumi, *J. Org. Chem.*, **66**, 1441 (2001). c) Y. Uozumi, N. Suzuki, A. Ogiwara, and T. Hayashi, *Tetrahedron*, **50**, 4293 (1994). d) T. Hayashi, H. Iwamura, M. Naito, Y. Matsumoto, Y. Uozumi, M. Miki, and K. Yanagi, *J. Am. Chem. Soc.*, **116**, 775 (1994). e) Y. Uozumi, A. Tanahashi, S.-Y. Lee, and T. Hayashi, *J. Org. Chem.*, **58**, 1945 (1993).

20 T. Hamada, A. Chieffi, J. Åhman, and S. L. Buchwald, *J. Am. Chem. Soc.*, **124**, 1261 (2002).