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Chiral Imidazoline–Phosphine Ligands for Palladium-Catalyzed Asymmetric Allylic Substitutions

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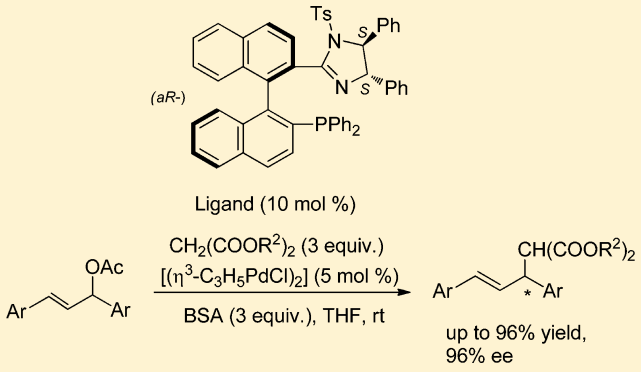
Supporting Information

ABSTRACT: Chiral imidazoline–phosphine ligands with a 1,1′-binaphthalene framework have been developed as new types of N,P ligands. The chiral ligand **L1** prepared from (*R*)-(−)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-acid efficiently affects the palladium-catalyzed enantioselective allylic alkylation of 1,3-diarylpropenyl acetate with dimethyl malonate to give the corresponding adducts in excellent yields and enantioselectivities (up to 96% ee), and chiral ligand **L9** can be used for the palladium-catalyzed asymmetric allylic monofluoromethylation of 1,3-diphenylpropenyl acetate with 1-fluorobis(phenylsulfonyl)methane to afford the corresponding product in excellent enantioselectivities (up to 98% ee) and moderate yields under mild conditions. The bidentate N,P-coordination pattern to the Pd atom with ligand **L1** has been unambiguously confirmed by X-ray diffraction.



INTRODUCTION

With the dramatic growth of chiral compounds in the development of pharmaceuticals, agrochemicals, and materials, the development of attractive asymmetric methodologies for producing enantiomerically pure products is of great value. One of the most important methods to attain chiral substances is homogeneous enantioselective catalysis with chiral transition metal complexes derived from transition metals and chiral ligands, where a small amount of chiral materials can produce a large amount of chiral products. Chiral ligands such as 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) (**LA**)[1] possessing C_2 symmetry and 2-(diphenylphosphino)-1,1′-binaphthyl (MOP) (**LB**) (X = OMe)[2] possessing C_1 symmetry with the axial chiral 1,1′-binaphthalene framework have attracted much attention in asymmetric catalysis and have been widely used in a variety of asymmetric transformations (Figure 1). Thus far, extensive efforts have been devoted to the design and synthesis of new binaphthalene-templated ligands. For example, the binaphthyl P,X-heterodonor ligands **LB**–**LD** are representative examples where X is different heteroatoms (X = NMe_2, SMe, $AsPh_2$, $P(O)Ph_2$, $P(S)Ph_2$, PAr_2),[3] such as the phosphine–phosphoramidite ligand **LC**,[4] derived from a phosphane–phosphite ligand (BINAPHOS),[5] and phosphine–oxazoline ligands **LD**,[6] prepared from (*R*)-(−)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-acid (BINDPCA).[6] Most of these axial chiral ligands having bidentate nitrogen and phosphorus donors (both homo- and heterodonors) have been successfully applied to the palladium-catalyzed asymmetric allylic substitutions of 1,3-diarylpropenyl acetate with dimethyl malonate in the presence of a base, which has become a versatile process that is widely used in organic synthesis for the enantioselective formation of carbon–carbon bonds.[7] With regard to the phosphine–oxazoline ligands **LD**, these interesting ligands were initially explored by Hayashi, Uozumi, and their co-workers[6b] and have been applied in the palladium-catalyzed asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate with the sodium salt of dimethyl malonate, affording the corresponding product in quantitative yield along with up to 91% ee value. On the other hand, as a structural analogue of 2-oxazolines,[8] chiral 2-imidazolines[9] have recently attracted much attention in asymmetric catalysis and have been utilized as ligands in various asymmetric transformations. In this case, the different substitutions on the nitrogen atom can exert diverse electronic effects in catalytic asymmetric reactions. A typical example is the interesting Boehringer–Ingelheim phosphinoimidazoline (BIPI) ligands developed by Busacca and his co-workers.[10] These ligands have been used to catalyze the asymmetric Heck reaction to give the desired products in moderate yields along with moderate ee values. Both of these findings arouse our interest in the design and synthesis of new chiral imidazoline–phosphine-type ligands with an axial chiral 1,1′-binaphthalene framework.

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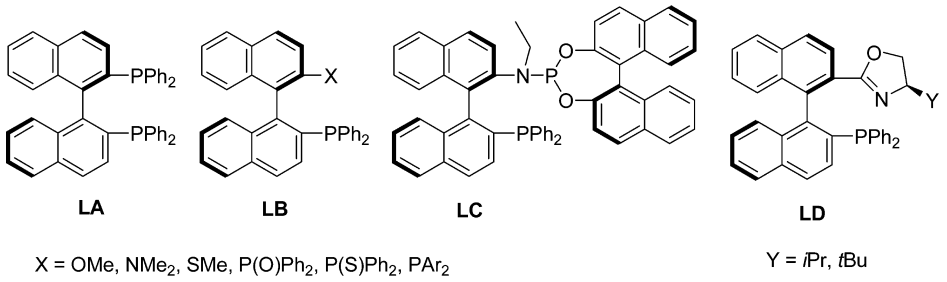

Figure 1. Structure of C_2-symmetric **BINAP** and C_1-symmetric binaphthyl P,X-heterodonor ligands.

Scheme 1. Preparation of Imidazoline−Phosphine-Type Ligands L1−L10

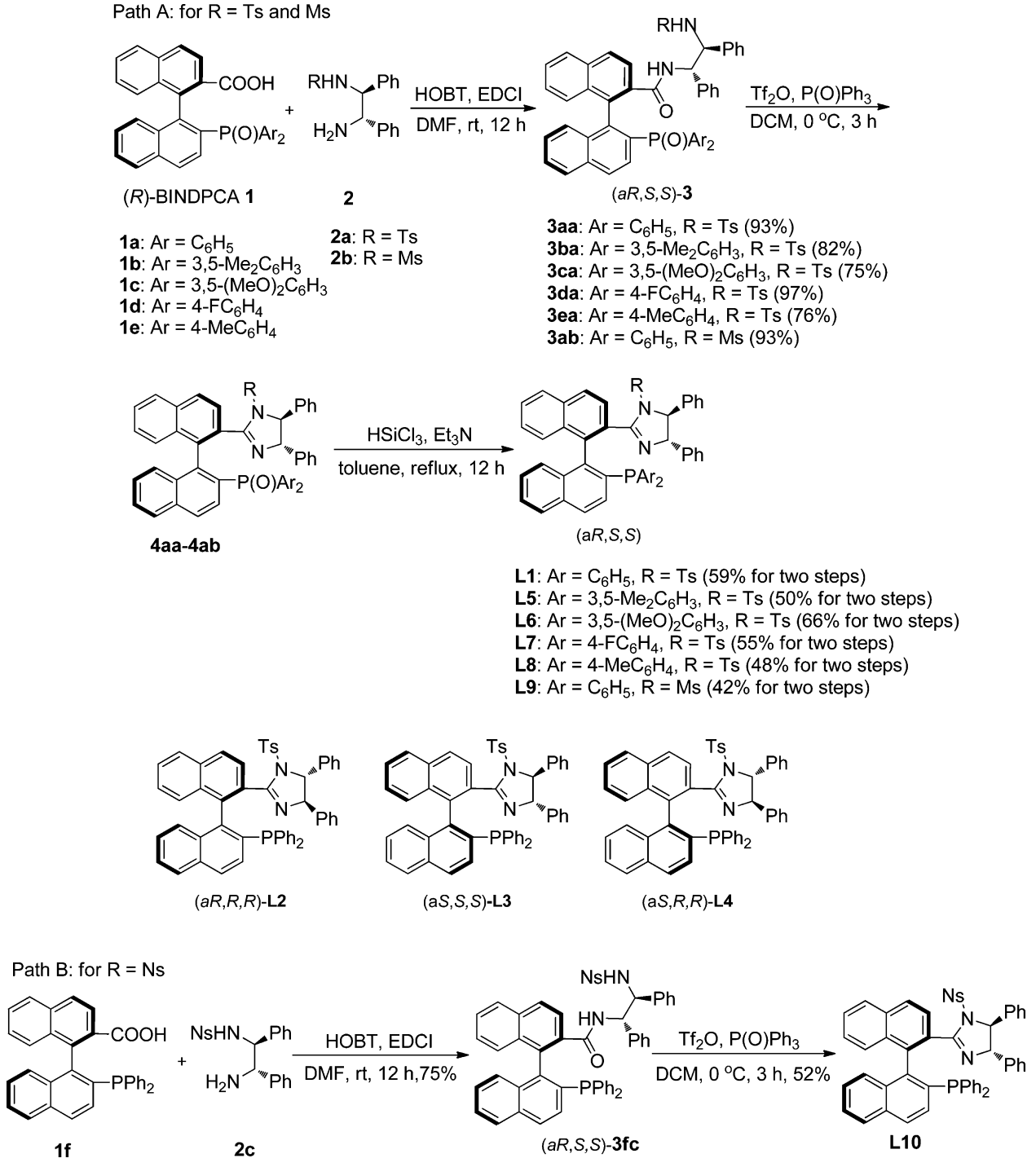

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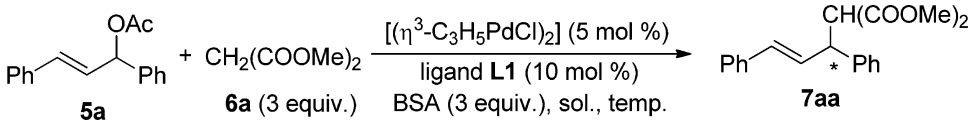
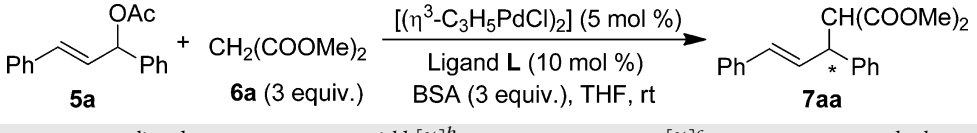
Table 1. Screening of Concentration, Solvents, Temperature, and Additives in Asymmetric Allylic Alkylation Reactions



entry[a]	solvent	temp [°C]	time [h]	additive	yield [%][b]	ee [%][c]	absolute configuration[d]
1[e]	THF	rt	36		31	96	*R*
2	THF	rt	24		96	95	*R*
3	toluene	rt	24		93	94	*R*
4	DCM	rt	24		74	95	*R*
5	DMA	rt	24		74	96	*R*
6	dioxane	rt	24		40	95	*R*
7	THF	0	36		96	96	*R*
8	DME	0	36		31	97	*R*
9	THF	rt	24	LiCl	90	93	*R*
10	THF	rt	24	CH_3COOK	90	86	*R*

[a]The reaction was conducted with allyl acetate (0.1 mmol) and malonic ester (0.1 mmol) in solvent (0.5 mL). [b]Isolated yield. [c]The ee values were determined by chiral HPLC on Chiralcel AD. [d]The absolute configuration was determined by comparing the sign of specific rotation with authentic sample reported in ref 12. [e]The reaction was conducted with allyl acetate (0.1 mmol) and malonic ester (0.1 mmol) in solvent (1.0 mL).

Table 2. Catalytic Behavior of Ligands L2−L10 in Asymmetric Allylic Alkylation Reaction



entry[a]	ligand	yield [%][b]	ee [%][c]	absolute configuration[d]
1	**L2**	65	80	*R*
2	**L3**	62	80	*S*
3	**L4**	86	95	*S*
4	**L5**	83	93	*R*
5	**L6**	81	91	*R*
6	**L7**	90	95	*R*
7	**L8**	93	94	*R*
8	**L9**	88	96	*R*
9	**L10**	90	96	*R*

[a]The reaction was conducted with allyl acetate (0.1 mmol) and malonic ester (0.1 mmol) in solvent (0.5 mL). [b]Isolated yield. [c]The ee values were determined by chiral HPLC on Chiralcel AD. [d]The absolute configuration was determined by comparing the sign of specific rotation with authentic sample reported in ref 12.

On the basis of the above analysis on combining an axial chiral 1,1′-binaphthalene framework with 2-imidazoline, we attempted to explore novel chiral imidazoline−phosphine-type ligands for asymmetric reactions under mild conditions. In this paper, we wish to report that chiral ligand **L1** prepared from (*R*)-(−)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-acid can efficiently affect the palladium-catalyzed enantioselective allylic substitution reaction of 1,3-diarylpropenyl acetate with dimethyl malonate to give the corresponding adducts in excellent yields and enantioselectivities (up to 96% ee), and chiral ligand **L9** could be used for the palladium-catalyzed asymmetric allylic monofluoromethylation of 1,3-diphenylpropenyl acetate with 1-fluoro-bis(phenylsulfonyl)methane to afford the corresponding product in excellent enantioselectivities (up to 98% ee) and moderate to good yields under mild conditions. The bidentate N,P-coordination pattern to the Pd center by ligand **L1** has been unambiguously confirmed by X-ray diffraction.

RESULTS AND DISCUSSION

1. Synthesis of Chiral Ligands L1−L10. Chiral imidazoline−phosphine-type ligands **L1−L10** were synthesized from (*R*)-BINDPCA **1a−1e** or **1f**, as illustrated in Scheme 1. Bisphenyl *N*-tosyl chiral ethylene diamines **2a**, bisphenyl *N*-mesyl chiral ethylene diamines **2b**, and bisphenyl *N*-nosyl chiral ethylene diamines **2c** were synthesized from the corresponding (1*S*,2*S*)-(−)-1,2-diphenylethylenediamine or (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine. Precursors **3aa−3fc** were obtained in good yields from the condensation of **2** with (*R*)-BINDPCA **1a−1e** or **1f** in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (1.0 mmol) and 1-hydroxybenzotriazole (1.5 mmol) in *N*,*N*-dimethylformamide (DMF). Then precatalysts **4aa−4ab** were synthesized from **3aa−3ab** through imidazoline formation using the Hendrickson's reagent,[11] while ligand **L10** was obtained directly from **3fc** in this way in moderate yield. After reduction of **4** with $HSiCl_3$ and Et_3N in toluene under reflux, the desired ligands **L1−L9** could be obtained in moderate yields in two steps. Chiral ligand (a*R*,*R*,*R*)-**L2** was prepared from (*R*)-BINDPCA with (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine, and chiral ligands (a*S*,*S*,*S*)-**L3** and (a*S*,*R*,*R*)-**L4** were prepared from (*S*)-BINDPCA with (1*S*,2*S*)-(−)-1,2-diphenylethylenediamine and (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine, respectively, under identical conditions (Scheme 1).

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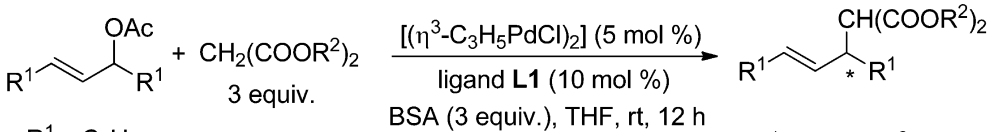
Scheme 2. Scope of Substrates for Pd/L1-Catalyzed Asymmetric Allylic Alkylations

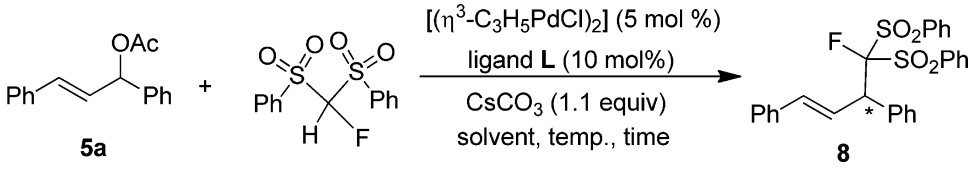


5a: $R^1 = C_6H_5$
5b: $R^1 = 4\text{-}MeC_6H_4$
5c: $R^1 = 4\text{-}ClC_6H_4$
5d: $R^1 = 4\text{-}BrC_6H_4$

6a: $R^2 = Me$
6b: $R^2 = Et$

7ab: $R^1 = C_6H_5$, $R^2 = Et$ (94% yield, 94% ee, *R*)
7ba: $R^1 = 4\text{-}MeC_6H_4$, $R^2 = Me$ (91% yield, 94% ee, *R*)
7ca: $R^1 = 4\text{-}ClC_6H_4$, $R^2 = Me$ (91% yield, 94% ee, *R*)
7da: $R^1 = 4\text{-}BrC_6H_4$, $R^2 = Me$ (83 % yield, 96% ee, *R*)

Table 3. Optimization of the Pd-Catalyzed Enantioselective Allylic Fluorobis(phenylsulfonyl)methylation of Allylic Acetate



entry[a]	ligand	solvent	temp [°C]	time [h]	yield [%][b]	ee [%][c] (abs. config.)[d]
1	**L1**	DCM	0	36	12	80 (*S*)
2	**L2**	DCM	0	36	53	80 (*S*)
3	**L3**	DCM	0	36	63	71 (*R*)
4	**L4**	DCM	0	36	22	88 (*R*)
5	**L5**	DCM	0	36	16	76 (*S*)
6	**L6**	DCM	0	36	30	19 (*S*)
7	**L7**	DCM	0	36	24	92 (*S*)
8	**L8**	DCM	0	36	20	56 (*S*)
9	**L7**	DCM	rt	12	73	88 (*S*)
10	**L7**	DMF	rt	12	trace	ND
11	**L7**	CH_3CN	rt	12	86	95 (*S*)
12	**L7**	toluene	rt	12	80	97 (*S*)
13	**L7**	THF	rt	12	78	84 (*S*)

[a]The reaction was conducted with allyl acetate (0.1 mmol) and $CHF(SO_2Ph)_2$ (0.11 mmol) in DCM (0.5 mL) at 0 °C for 12 h. [b]Isolated yield. [c]The ee values were determined by chiral HPLC on Chiralcel AD. [d]The absolute configuration was determined by comparing the sign of specific rotation with authentic sample reported in ref 7f.

2. Catalytic Asymmetric Allylic Alkylation of 1,3-Diphenyl-2-propenyl Acetate in the Presence of Imidazoline–Phosphine-Type Ligands. Initial examinations using 1,3-diphenylpropenyl acetate **5a** and dimethyl malonate **6a** as the model substrates in the presence of chiral imidazoline–phosphine-type ligand **L1** and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ were aimed at screening the optimal conditions, and the results of these experiments are summarized in Table 1. Using bis(trimethylsilyl)acetamide as an organic base, the yield was much higher when the concentration of reaction mixtures was raised from 0.1 to 0.2 M in tetrahydrofuran (THF) at room temperature (Table 1, entries 1 and 2). By screening different solvents such as toluene, dichloromethane (DCM), dimethyl acetamide (DMA), and 1,4-dioxane, we found that THF was the best one for this asymmetric allylic alkylation, affording the corresponding product **7aa** in 95% ee and 96% yield at room temperature within 24 h (Table 1, entries 3–6). Upon lowering the reaction temperature to 0 °C, no evident improvement of ee and yield could be observed after 36 h (Table 1, entries 7 and 8). The presence of salt additives, such as LiCl or KOAc, did not improve the ee values in this reaction, and the products were obtained in relatively lower yields (Table 1, entries 9 and 10). The absolute configuration of the products was assigned as *R* by comparison of the optical rotation of the products with that in the previous literature and their retention time on HPLC with the literature value.[12]

Ligands **L2**–**L10** were also examined in the asymmetric allylic alkylation under the optimized conditions, and the results are summarized in Table 2. The corresponding products **7aa** were obtained in good to high ee values and moderate to good yields, and ligand **L1** gave the best result (Table 2, entries 1–9). In addition, as expected, we found that ligands **L3** and **L4** derived from (*S*)-BINDPCA produced the corresponding products with opposite absolute configuration (Table 2, entries 2 and 3).

To illustrate the generality of the high catalytic ability of ligand **L1**, other substrates were also tested under optimized conditions, and the results are shown in Scheme 2. Replacing dimethyl malonate **6a** with diethyl malonate **6b** gave the corresponding adduct **7ab** in excellent yield and 94% ee value. At the same time, using **5b**, having a moderately electron-donating group on the benzene ring, or **5c**, having an electron-withdrawing group on the benzene ring, as the substrate also gave the corresponding products **7ba** and **7ca** in high yields and 94% ee values, suggesting that the electronic property of the substrate did not have a significant impact on the reaction outcome. Moreover, product **7da** was obtained in 83% yield and up to 96% ee value using **5d** as the substrate, which has a Br atom on the benzene ring. Their absolute configurations

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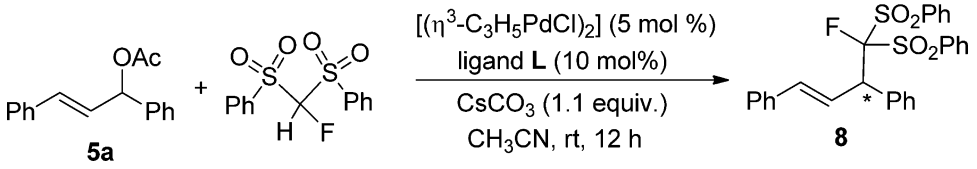
Table 4. Catalytic Behavior of Ligands L1−L10 in Allylic Fluorobis(phenylsulfonyl)methylation of Allylic Acetate under Optimized Conditions



entry[a]	ligand	yield [%][b]	ee [%][c]	absolute configuration[d]
1	**L1**	81	94	*S*
2	**L2**	75	74	*S*
3	**L3**	71	74	*R*
4	**L4**	81	95	*R*
5	**L5**	75	88	*S*
6	**L6**	73	88	*S*
7	**L8**	71	95	*S*
8	**L9**	81	98	*S*
9	**L10**	83	97	*S*

[a]The reaction was conducted with allyl acetate (0.1 mmol) and $CHF(SO_2Ph)_2$ (0.11 mmol) in CH_3CN (0.5 mL) at rt for 12 h. [b]Isolated yield. [c]The ee values were determined by chiral HPLC on Chiralcel AD. [d]The absolute configuration was determined by comparing the sign of specific rotation with authentic sample reported in ref 7f.

were also determined to be *R* by comparison of the optical rotation of the products and their retention time on HPLC with the previous literature value.[13,14]

3. Catalytic Asymmetric Allylic Monofluoromethylation of 1,3-Diphenyl-2-propenyl Acetate in the Presence of Imidazoline−Phosphine-Type Ligands. Initial examinations of allylic monofluoromethylation of 1,3-diphenylpropenyl acetate **5a** with 1-fluoro-bis(phenylsulfonyl)methane were examined in DCM using **L1−L8** as the chiral ligands in the presence of cesium carbonate at 0 °C,[7f] and the results of these experiments are summarized in Table 3. However, we found that the yields of the corresponding product **8** were rather low even though the ee values were moderate to good after 36 h, and using **L7** as the chiral ligand afforded the corresponding product **8** in 24% yield and 94% ee (Table 3, entries 1−8). By conducting the experiment at room temperature using **L7** as the ligand, product **8** was obtained in 73% yield and 88% ee (Table 4, entry 9). By screening different solvents at room temperature using **L7** as the ligand, we found that CH_3CN was the solvent of choice for this asymmetric allylic monofluoromethylation, affording the corresponding product **8** in 95% ee and 86% yield at room temperature (Table 4, entries 10−13). The absolute configuration of the product was determined to be *S* by comparison of the optical rotation of the product and its retention time on HPLC with the literature data (Table 4, entry 11).[7f]

Ligands **L1−L6** and **L8−L10** were also tested in the asymmetric allylic monofluoromethylation under the optimized conditions, and the results are summarized in Table 4. The corresponding product **8** was obtained in 71−83% yields and 74−98% ee values (Table 4, entries 1−9). As for **L9** and **L10**, the corresponding product was obtained in moderate yield and up to 98% ee value, presumably due to the electronic effect caused by the different substitution on the nitrogen atom (Table 4, entries 8 and 9). In addition, as expected, ligands **L3** and **L4** derived from (*S*)-BINDPCA produced the corresponding product **8** with opposite absolute configuration (Table 4, entries 3 and 4).

4. Synthesis of Pd(L1)Cl_2 Complex A. In order to get direct evidence of N,P-coordination to the Pd center, we decided to prepare a Pd(II) complex from **L1** with bis(benzonitrile)palladium dichloride [$Pd(PhCN)_2Cl_2$] because it has been known that nitrogen and phosphorus atoms can coordinate to the Pd(II) atom to give a stable Pd(II) complex, which can be confirmed by X-ray diffraction.[15] The synthesis of the Pd(**L1**)Cl_2 complex was carried out by the reaction of $Pd(PhCN)_2Cl_2$ (19 mg, 0.05 mmol) with 1.0 equiv of **L1** (41 mg, 0.05 mmol) in CH_2Cl_2 at room temperature for 1 h under an argon atmosphere. Degassed hexane (5.0 mL) was then slowly added, which led to the precipitation of the formed complex. The mother liquor was filtered off, and the precipitate was washed with hexane (2 × 1.0 mL) to afford the (*R*)-(+)-complex **A** as a yellow powder (41 mg, 91% yield). Single crystals suitable for X-ray diffraction were obtained by recrystallization from chloroform. The ORTEP drawing of the Pd(**L1**)Cl_2 complex is shown in Figure 2, and the corresponding CIF data are presented in the Supporting Information.[16] From Figure 2, it can be seen that **L1** acts as a *cis*-bidentate ligand to the Pd(II) center in a slightly distorted planar geometry with both nitrogen and phosphorus atoms providing an eight-membered chelate ring. The angle of the N(1)−Pd(1)−P(1) plane is 92.65°, and the bond lengths of N(1)−Pd(1) and Pd(1)−P(1) are 2.051 and 2.2416 Å, respectively.

To gain more detailed information on the difference of our imidazoline−phosphine ligands with phosphine−oxazoline ligands **LD**, the comparison of structures between our Pd complex with the Pd(**LD**)Cl_2 (Y = *i*Pr) complex[6g] has been carried out. We found that the Pd−P and Pd−N bond lengths as well as the N−Pd−P bond angles are very similar in the two Pd complexes, and the main difference lies in the different substitution on the nitrogen atom in our imidazoline−phosphine ligand system, which can exert different electronic effects in catalytic asymmetric reactions. A typical example is that in the Pd-catalyzed asymmetric allylic monofluoromethylation, we found that replacing Ts with Ms or Ns on the nitrogen atom gave the corresponding product in higher ee value (Table 4, entries 1, 8, 9). On the other hand, as for these asymmetric allylic substitutions, our imidazoline−phosphine ligands gave relatively better yields and ee values even under

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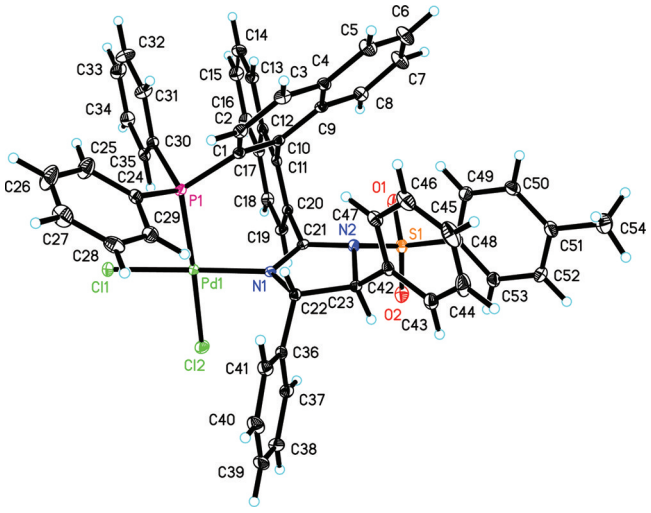

Figure 2. ORTEP drawing of Pd(**L1**)Cl_2 complex **A** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd1−P1 = 2.2416(7), Pd1−N1 = 2.051(2), N1−C21 = 1.272(3), Cl1−Pd1 = 2.2920(6), Cl2−Pd1 = 2.3447(7), N1−Pd1−P1 = 92.65(6), C1−P1−Pd1 = 117.72(8), N1−Pd1−Cl2 = 91.53(6), Cl1−Pd1−Cl2 = 89.43(2), Cl1−Pd1−P1 = 86.65(2), C11−C20−C21 = 117.5(2).

milder conditions as compared with phosphine−oxazoline ligands **LD** reported before.[6b,f]

In summary, a series of novel chiral imidazoline−phosphine ligands **L1**−**L10** has been successfully synthesized and used for the Pd-catalyzed allylic substitution reactions. Ligand **L1**, prepared from (*R*)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-acid (BINDPCA), was found to be a very effective chiral ligand for Pd-catalyzed asymmetric allylic alkylation to give the corresponding products in excellent enantioselectivities (up to 96% ee) and good yields under mild conditions, while ligand **L9** could be used as an effective chiral ligand for Pd-catalyzed asymmetric allylic monofluoromethylation to give the corresponding products in excellent enantioselectivities (up to 98% ee) and moderate yields under mild conditions. Its bidentate coordination pattern to a Pd metal center with both P and N atoms has been unambiguously established by X-ray diffraction. Efforts to use these novel chiral imidazoline−phosphine-type ligands for other asymmetric reactions are under way.

EXPERIMENTAL SECTION

General Methods. Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined in a solution of $CHCl_3$ or CH_2Cl_2 at 20 °C by using a Perkin-Elmer-241 MC polarimeter; $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. Infrared spectra were measured on a spectrometer. ^1H NMR spectra were recorded for solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; ^{31}P NMR spectra were recorded for a solution in $CDCl_3$ with 85% H_3PO_4 as the external reference. *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument, and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300−400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques. The optical purities of products were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. Chiralcel AD), and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation. In addition, chiral 2-(diphenylphosphino)-1,1′-binaphthyl-2′-acids (BINDPCA) were synthesized from the corresponding (*R*)-(+)-1,1′-bi-2-naphthol and (*S*)-(−)-1,1′-bi-2-naphthol, respectively (for more detailed information, please see ref 6).

Typical Procedure of the Preparation of Chiral Imidazoline-Phosphine-Type Ligands L1−L10. *Synthesis of the Precatalysts* ***3****.* A solution of (*R*)-BINDPCA **1a**−**1e** or **1f** (0.5 mmol) in DMF (5.0 mL) with 1-ethyl-3-(3-dimethyllaminopropyl)carbodiimide hydrochloride (EDCI) (1.0 mmol) and 1-hydroxybenzotriazole (1.5 mmol) was stirred at 0 °C for 10 min. Then a solution of **2** (0.75 mmol) in 2.0 mL of DMF was added into the solution by syringe at 0 °C. The reaction mixture was stirred at room temperature for 5 h. The reaction mixture was diluted by the addition of 10 mL of EtOAc, then washed with H_2O and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (PE/EA = 1.5:1) to give the desired product **3** as a pale yellow solid.

(R)-2-(Diphenylphosphoryl)-N-((1S,2S)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)-1,1′-binaphthyl-2-carboxamide, ***3aa****.* Yield: 392 mg, 93%; pale yellow solid, mp 133−136 °C; IR (CH_2Cl_2) ν 3209, 3059, 2924, 1659, 1566, 1497, 1453, 1439, 1373, 1332, 1262, 1202, 1158, 1114, 1090, 1071, 1029, 1000, 972, 952 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.24 (s, 3H, CH_3), 5.04 (dd, 1H, J_1 = 3.6 Hz, J_2 = 9.6 Hz, CH), 5.27 (dd, 1H, J_1 = 3.6 Hz, J_2 = 8.7 Hz, CH), 6.04 (br, 2H, ArH), 6.36 (d, 2H, *J* = 7.8 Hz, ArH), 6.45 (d, 1H, *J* = 8.4 Hz, ArH), 6.76−6.86 (m, 5H, ArH), 6.94−6.99 (m, 2H, ArH), 7.09−7.22 (m, 7H, ArH), 7.24−7.33 (m, 4H, ArH), 7.44−7.50 (m, 4H, ArH), 7.57 (t, 4H, *J* = 5.4 Hz, ArH), 7.76−7.83 (m, 3H, ArH), 7.88 (d, 1H, *J* = 8.1 Hz, ArH), 7.98 (d, 1H, *J* = 6.9 Hz, ArH), 10.29 (d, 1H, *J* = 8.7 Hz, NH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ 31.92; MS (ESI) *m*/*z* (%) 847.7 (100) [M^+ + 1]; HRMS (MALDI) calcd for $C_{54}H_{44}N_2O_4PS^{+1}$($M^+$ + 1) requires 847.2755, found 847.2753. $[\alpha]^{20}_D$ = +108.6 (*c* 0.40, $CHCl_3$).

(R)-2-(Bis(3,5-dimethylphenyl)phosphoryl)-N-((1S,2S)-2-((4-methylphenylsulfonamido)-1,2-diphenylethyl)-1,1′-binaphthyl-2-carboxamide, ***3ba****.* Yield: 297 mg, 78%; pale yellow solid, mp 130−133 °C; IR (CH_2Cl_2) ν 3201, 3059, 3031, 2922, 1725, 1660, 1620, 1566, 1498, 1452, 1422, 1375, 1334, 1305, 1272, 1224, 1203, 1159, 1122, 1092, 1065, 1007, 973, 953 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.97 (s, 6H, CH_3), 2.25 (s, 3H, CH_3), 2.40 (s, 6H, CH_3), 4.97 (dd, 1H, J_1 = 3.6 Hz, J_2 = 10.2 Hz, CH), 5.28 (dd, 1H, J_1 = 3.6 Hz, J_2 = 9.3 Hz, CH), 6.23 (d, 2H, *J* = 7.8 Hz, ArH), 6.47 (s, 1H, ArH), 6.57 (d, 1H, *J* = 8.4 Hz, ArH), 6.70−6.84 (m, 5H, ArH), 6.88−6.91 (m, 1H, ArH), 6.97−7.02 (m, 2H, ArH), 7.04−7.26 (m, 9H, ArH), 7.45−7.49 (m, 4H, ArH), 7.58−7.73 (m, 4H, ArH), 7.90 (d, 1H, *J* = 8.4 Hz, ArH), 8.05 (dd, 1H, J_1 = 2.1 Hz, J_2 = 8.4 Hz, ArH), 8.22 (d, 1H, *J* = 10.2 Hz, ArH), 10.28 (d, 1H, *J* = 9.3 Hz, NH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ 30.39; MS (ESI) *m*/*z* (%) 903.7 (100) [M^+ + 1]; HRMS (MALDI) calcd for $C_{58}H_{52}N_2O_4PS^+$ (M^+ + 1) requires 903.3388, found 903.3380. $[\alpha]^{20}_D$ = +48.0 (*c* 0.15, $CHCl_3$).

(R)-2-(Bis(3,5-dimethoxyphenyl)phosphoryl)-N-((1S,2S)-2-((4-methylphenylsulfonamido)-1,2-diphenylethyl)-1,1′-binaphthyl-2-carboxamide, ***3ca****.* Yield: 319 mg, 75%; pale yellow solid, mp 137−139 °C; IR (CH_2Cl_2) ν 3210, 3060, 3002, 2933, 2838, 1723, 1660, 1585, 1498, 1453, 1419, 1373, 1335, 1303, 1289, 1257, 1206, 1161, 1091, 1063, 973, 953, 925 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.23 (s, 3H, CH_3), 3.56 (s, 6H, OCH_3), 3.77 (s, 6H, OCH_3), 4.99 (dd, 1H, J_1 = 3.0 Hz, J_2 = 9.9 Hz, CH), 5.31 (dd, 1H, J_1 = 3.0 Hz, J_2 = 9.0 Hz, CH), 5.89 (s, 1H, ArH), 6.25 (d, 4H, *J* = 6.9 Hz, ArH), 6.54 (d, 1H, *J* = 8.1 Hz, ArH), 6.67 (s, 1H, ArH), 6.74−6.82 (m, 4H, ArH), 6.89−7.04 (m, 3H, ArH), 7.11−7.20 (m, 9H, ArH), 7.38−7.47 (m, 3H, ArH), 7.54 (d, 1H, *J* = 8.1 Hz, ArH), 7.65−7.75 (m, 2H, ArH), 7.88 (d, 1H, *J* = 8.4 Hz, ArH), 7.97−8.06 (m, 2H, ArH), 10.13 (d, 1H, *J* = 9.0 Hz, NH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ 31.98; MS (ESI) *m*/*z* (%) 967.9 (100) [M^+ + 1]; HRMS (MALDI) calcd for $C_{58}H_{52}N_2O_8PS^+$ (M^+ + 1) requires 967.3192, found 967.3177. $[\alpha]^{20}_D$ = +58.3 (*c* 0.40, $CHCl_3$).

(R)-2-((4-Fluorophenyl)phosphoryl)-N-((1S,2S)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)-1,1′-binaphthyl-2-carboxamide, ***3da****.* Yield: 428 mg, 97%; pale yellow solid, mp 168−170 °C;

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IR (CH_2Cl_2) ν 3206, 3060, 1657, 1592, 1498, 1399, 1331, 1304, 1265, 1233, 1159, 1114, 1090, 1071, 1013, 973, 953, 908, 873, 825, 736, 700, 677, 650 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.25 (s, 3H, CH_3), 5.02 (dd, 1H, J_1 = 3.9 Hz, J_2 = 9.6 Hz, CH), 5.25 (dd, 1H, J_1 = 3.9 Hz, J_2 = 8.7 Hz, CH), 6.36 (d, 2H, J = 7.5 Hz, ArH), 6.40−6.49 (m, 3H, ArH), 6.82−6.87 (m, 5H, ArH), 6.98 (t, 1H, J = 7.5 Hz, ArH), 7.09−7.23 (m, 12H, ArH), 7.29−7.31 (m, 2H, ArH), 7.36−7.44 (m, 1H, ArH), 7.49 (t, 1H, J = 7.5 Hz, ArH), 7.57 (d, 1H, J = 8.1 Hz, ArH), 7.64−7.78 (m, 4H, ArH), 7.90 (d, 1H, J = 8.1 Hz, ArH), 7.99 (dd, 1H, J_1 = 1.8 Hz, J_2 = 8.4 Hz, ArH), 9.99 (d, 1H, J = 8.7 Hz, NH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ 30.76; ^{19}F NMR (CDCl3, 282 MHz, $CFCl_3$) δ −105.97, −107.67; MS (ESI) m/z (%) 883.7 (100) $[M^+ + 1]$; HRMS (ESI) calcd for $C_{54}H_{42}N_2O_4F_2PS^+$ (M^+ + 1) requires 883.2560, found 883.2566. $[\alpha]^{20}_D$ = +104.2 (c 0.90, $CHCl_3$).

(R)-2-((4-Methylphenyl)phosphoryl)-N-((1S,2S)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)-1,1′-binaphthyl-2-carboxamide, ***3ea****.* Yield: 332 mg, 76%; pale yellow solid, mp 178−180 °C; IR (CH_2Cl_2) ν 3193, 3030, 2245, 1917, 1656, 1600, 1559, 1497, 1451, 1399, 1330, 1156, 1113, 1089, 1065, 1020, 971, 952, 911, 872, 851, 811, 762, 698, 676, 662, 648, 618 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.01 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 5.02 (dd, 1H, J_1 = 3.9 Hz, J_2 = 9.9 Hz, CH), 5.28 (dd, 1H, J_1 = 3.9 Hz, J_2 = 9.9 Hz, CH), 6.33 (d, 2H, J = 7.2 Hz, ArH), 6.44−6.52 (m, 3H, ArH), 6.78−6.85 (m, 5H, ArH), 6.95−7.07 (m, 4H, ArH), 7.14−7.21 (m, 7H, ArH), 7.27−7.31 (m, 2H, ArH), 7.39−7.55 (m, 5H, ArH), 7.62 (d, 1H, J = 8.7 Hz, ArH), 7.76 (dd, 1H, J_1 = 8.1 Hz, J_2= 11.4 Hz, ArH), 7.86 (d, 1H, J = 8.1 Hz, ArH), 7.95−8.01 (m, 1H, ArH), 10.22 (d, 1H, J = 9.3 Hz, NH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ 31.72; MS (ESI) m/z (%) 875.7 (100) $[M^+ + 1]$; HRMS (ESI) calcd for $C_{56}H_{48}N_2O_4PS^+$ (M^+ + 1) requires 875.3085, found 875.3067. $[\alpha]^{20}_D$ = +90.7 (c 0.90, $CHCl_3$).

(R)-2-(Diphenylphosphoryl)-N-((1S,2S)-2-(methylsulfonamido)-1,2-diphenylethyl)-1,1′-binaphthyl-2-carboxamide, ***3ab****.* Yield: 316 mg, 82%; pale yellow solid, mp 143−145 °C; IR (CH_2Cl_2) ν 3202, 3058, 1659, 1567, 1438, 1326, 1148, 1119, 1092, 983, 818, 749, 723, 699, 540, 524, 515 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.13 (s, 3H, CH_3), 5.07 (dd, 1H, J_1 = 3.6 Hz, J_2 = 9.9 Hz, CH), 5.46 (dd, 1H, J_1 = 3.6 Hz, J_2 = 8.7 Hz, CH), 6.42 (d, 2H, J = 8.1 Hz, ArH), 6.52 (d, 1H, J = 8.1 Hz, ArH), 6.69 (dt, 2H, J_1 = 2.7 Hz, J_2 = 7.5 Hz, ArH), 6.89 (t, 4H, J = 7.5 Hz, ArH), 6.96−6.99 (m, 1H, ArH), 7.06−7.18 (m, 5H, ArH), 7.33−7.50 (m, 8H, ArH), 7.56−7.68 (m, 5H, ArH), 7.83−7.90 (m, 4H, ArH), 8.02 (d, 1H, J = 9.9 Hz, NH), 10.17 (d, 1H, J = 8.7 Hz, NH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ 31.42; MS (MALDI) m/z (%) 771.3 (100) $[M^+ + 1]$; HRMS (MALDI) calcd for $C_{48}H_{40}N_2O_4PS^+$ (M^+ + 1) requires 771.2441, found 771.2441. $[\alpha]^{20}_D$ = +79.1 (c 0.70, $CHCl_3$).

(R)-2-((4-Methylphenylphosphino)-N-((1S,2S)-2-(4-nitrophenylsulfonamido)-1,2-diphenylethyl)-1,1′-binaphthyl-2-carboxamide, ***3fc****.* Yield: 323 mg, 75%; pale yellow solid, mp 139−141 °C; IR (CH_2Cl_2) ν 3388, 3058, 2956, 2925, 2855, 1633, 1529, 1496, 1348, 1311, 1265, 1166, 1091, 937, 854, 737, 518 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.51 (dd, 1H, J_1 = 5.1 Hz, J_2 = 10.5 Hz, CH), 4.64 (dd, 1H, J_1 = 7.2 Hz, J_2 = 10.5 Hz, CH), 5.87 (d, 2H, J = 8.1 Hz, ArH), 6.10 (d, 1H, J = 6.3 Hz, ArH), 6.63 (d, 2H, J = 8.1 Hz, ArH), 6.68−6.90 (m, 7H, ArH), 6.97−7.05 (m, 3H, ArH), 7.09−7.24 (m, 5H, ArH), 7.28−7.37 (m, 6H, ArH), 7.48−7.51 (m, 4H, ArH), 7.55−7.64 (m, 3H, ArH), 7.87−7.93 (m, 3H, ArH), 8.14 (d, 1H, J = 9.0 Hz, NH), 8.30 (d, 1H, J = 8.1 Hz, NH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −14.34; MS (MALDI) m/z (%) 862.5 (100) $[M^+ + 1]$; HRMS (MALDI) calcd for $C_{53}H_{41}N_3O_5PS^+$ (M^+ + 1) requires 862.2475, found 862.2499. $[\alpha]^{20}_D$ = +38.3 (c 2.00, $CHCl_3$).

Synthesis of the Precatalysts ***4*** *and Ligand* ***L10*** *(ref 11).* To a dried Schlenk tube were added triphenylphosphine oxide (1.5 mmol) and trifluoromethanesulfonic anhydride (1.5 mmol) in CH_2Cl_2 (5.0 mL) at 0 °C, and the reaction mixture was stirred at 0 °C for 0.5 h. Then the solution of precatalyst **3** (0.50 mmol) in CH_2Cl_2 (5.0 mL) was added slowly via syringe. After the completion of the addition, the mixture was stirred at 0 °C for 3 h. The reaction was quenched with saturated $NaHCO_3$(aq), and the aqueous layer was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 1:1) to give crude product **4** (mixed with triphenylphosphine oxide) or ligand **L10**.

(4S,5S)-2-((R)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-nosyl-4,5-dihydro-1H-imidazoline, ***L10****.* Yield: 160 mg, 52%; pale yellow solid, mp 151−154 °C; IR (CH_2Cl_2) ν 3165, 3060, 2915, 1661, 1567, 1529, 1439, 1348, 1311, 1263, 1165, 1113, 1190, 847, 736, 700, 540, 525 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.59 (d, 1H, J = 6.0 Hz, CH), 4.66 (d, 1H, J = 6.0 Hz, CH), 5.88 (d, 2H, J = 6.3 Hz, ArH), 6.69 (d, 1H, J = 8.7 Hz, ArH), 6.86 (dd, 5H, J_1 = 6.6 Hz, J_2 = 13.2 Hz, ArH), 7.01−7.04 (m, 7H, ArH), 7.09−7.25 (m, 8H, ArH), 7.30−7.40 (m, 3H, ArH), 7.54−7.60 (m, 2H, ArH), 7.67 (d, 1H, J = 8.7 Hz, ArH), 7.74 (d, 2H, J = 8.4 Hz, ArH), 7.93−7.99 (m, 2H, ArH), 8.06 (dd, 2H, J_1 = 3.0 Hz, J_2 = 8.4 Hz, ArH), 8.18 (d, 1H, J = 8.7 Hz, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −14.33; MS (MALDI) m/z (%): 844.5 (100) $[M^+ + 1]$; HRMS (MALDI) calcd for $C_{53}H_{39}N_3O_4PS^+$ (M^+ + 1) requires 844.2409, found 844.2393. $[\alpha]^{20}_D$ = +57.0 (c 2.00 $CHCl_3$).

Synthesis of the Chiral Imidazoline−Phosphine Ligands ***L1****−****L9****.* To a dried Schlenk tube filled with argon was added crude precatalyst **4** with Et_3N (10.0 equiv) in 15 mL of anhydrous toluene. The mixture was stirred at 0 °C for 10 min, 10.0 equiv of $HSiCl_3$ was added at 0 °C, and the mixture was stirred at that temperature for 0.5 h. Then the mixture was allowed to warm to room temperature and stirred under reflux overnight. After cooling to room temperature, the reaction was quenched with saturated $NaHCO_3$(aq), the precipitates settled out, and the aqueous layer was extracted with EtOAc. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 5:1) to give the desired product as a pale yellow solid.

(4S,5S)-2-((R)-2′-(Diphenylphosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-tosyl-4,5-dihydro-1H-imidazoline, ***L1****.* Yield: 110 mg, 55% for two steps; pale yellow solid, mp 150−153 °C; IR (CH_2Cl_2) ν 3397, 3055, 2973, 2925, 1725, 1642, 1595, 1479, 1433, 1371, 1306, 1277, 1247, 1205, 1185, 1167, 1089, 1026, 963 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.25 (s, 3H, CH_3), 4.49 (d, 1H, J = 6.0 Hz, CH), 4.54 (d, 1H, J = 6.0 Hz, CH), 5.84 (d, 2H, J = 7.8 Hz, ArH), 6.68 (d, 1H, J = 8.7 Hz, ArH), 6.77−6.92 (m, 9H, ArH), 6.95−7.04 (m, 5H, ArH), 7.07−7.13 (m, 4H, ArH), 7.16−7.22 (m, 5H, ArH), 7.33 (q, 2H, J = 6.9 Hz, ArH), 7.50−7.57 (m, 2H, ArH), 7.81 (d, 1H, J = 8.4 Hz, ArH), 7.91 (d, 1H, J = 7.8 Hz, ArH), 7.98−8.04 (m, 3H, ArH), 8.16 (d, 1H, J = 8.4 Hz, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −13.79; MS (ESI) m/z (%) 813.6 (100) $[M^+ + 1]$; HRMS (MALDI) calcd for $C_{54}H_{42}N_2O_2PS^+$ (M^+ + 1) requires 817.2702, found 817.2699. $[\alpha]^{20}_D$ = +36.5 (c 0.45, $CHCl_3$).

(4R,5R)-2-((R)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-tosyl-4,5-dihydro-1H-imidazoline, ***L2****.* Yield: 199 mg, 63% for two steps; pale yellow solid, mp 147−150 °C; IR (CH_2Cl_2) ν 3401, 3055, 2970, 2925, 1725, 1655, 1590, 1479, 1433, 1389, 1306, 1271, 1239, 1198, 1185, 1165, 1089, 1026, 969 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.18 (s, 3H, CH_3), 4.48 (d, 1H, J = 4.2 Hz, CH), 4.94 (d, 1H, J = 4.2 Hz, CH), 5.97 (d, 2H, J = 7.5 Hz, ArH), 6.61−6.72 (m, 4H, ArH), 6.79−6.87 (m, 4H, ArH), 6.95−7.05 (m, 10H, ArH), 7.14−7.25 (m, 4H, ArH), 7.28−7.40 (m, 5H, ArH), 7.48 (dd, 1H, J_1 = 2.7 Hz, J_2 = 8.4 Hz, ArH), 7.58 (d, 1H, J = 7.2 Hz, ArH), 7.70 (d, 1H, J = 8.7 Hz, ArH), 7.91 (d, 1H, J = 8.4 Hz, ArH), 8.01−8.08 (m, 3H, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −11.64; MS (ESI) m/z (%) 813.6 (100) $[M^+ + 1]$; HRMS (MALDI) calcd for $C_{54}H_{42}N_2O_2PS^+$ (M^+ + 1) requires 817.2702, found: 817.2698. $[\alpha]^{20}_D$ = −19.5 (c 0.35, $CHCl_3$).

(4S,5S)-2-((S)-2′-(Diphenylphosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-tosyl-4,5-dihydro-1H-imidazoline, ***L3****.* Yield: 237 mg, 49% for two steps; pale yellow solid, mp 151−153 °C; IR (CH_2Cl_2) ν 3358, 3075, 2900, 1755, 1642, 1602, 1598, 1459, 1430, 1361, 1300, 1277, 1247, 1215, 1195, 1165, 1089, 1007, 960 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.19 (s, 3H, CH_3), 4.48 (d, 1H, J = 4.2 Hz, CH), 4.94 (d, 1H, J = 4.2 Hz, CH), 5.97 (d, 2H, J = 7.8 Hz, ArH), 6.62−6.75 (m, 4H, ArH), 6.80−6.87 (m, 4H, ArH), 6.95−7.08 (m,

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10H, ArH), 7.15−7.25 (m, 3H, ArH), 7.28−7.40 (m, 5H, ArH), 7.48 (dd, J_1 = 3.0 Hz, J_2 = 8.4 Hz 1H, ArH), 7.58 (t, 1H, J = 7.2 Hz, ArH), 7.70 (d, 1H, J = 7.8 Hz, ArH), 7.92 (d, 2H, J = 8.4 Hz, ArH), 8.01−8.08 (m, 3H, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −11.65; MS (ESI) m/z (%) 813.6 (100) [M^+ + 1]; HRMS (MALDI) calcd for $C_{54}H_{42}N_2O_2PS^+$ (M^+ + 1) requires 817.2702, found 817.2698. $[\alpha]^{20}_D$ = +16.8 (c 0.45, $CHCl_3$).

(4R,5R)-2-((S)-2′-(Diphenylphosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-tosyl-4,5-dihydro-1H-imidazoline, ***L4.*** Yield: 186 mg, 59% for two steps; pale yellow solid, mp 155−158 °C; IR (CH_2Cl_2) ν 3411, 3380, 3055, 3020, 2973, 2925, 1725, 1642, 1608, 1479, 1433, 1371, 1300, 1277, 1247, 1205, 1175, 1157, 1089, 1026, 960, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.28 (s, 3H, CH_3), 4.49 (d, 1H, J = 5.7 Hz, CH), 4.54 (d, 1H, J = 5.7 Hz, CH), 5.85 (d, 2H, J = 7.5 Hz, ArH), 6.68 (d, 1H, J = 8.4 Hz, ArH), 6.78−6.94 (m, 9H, ArH), 6.96−7.02 (m, 5H, ArH), 7.07−7.12 (m, 4H, ArH), 7.19 (d, 5H, J = 8.1 Hz, ArH), 7.31−7.38 (m, 2H, ArH), 7.49−7.58 (m, 2H, ArH), 7.80 (d, 1H, J = 8.1 Hz, ArH), 7.93 (d, 1H, J = 8.1 Hz, ArH), 7.97−8.05 (m, 3H, ArH), 8.17 (d, 1H, J = 8.4 Hz, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −13.81; MS (ESI) m/z (%) 813.6 (100) [M^+ + 1]; HRMS (MALDI) calcd for $C_{54}H_{42}N_2O_2PS^+$ (M^+ + 1) requires 817.2702, found 817.2700. $[\alpha]^{20}_D$ = −36.1 (c 0.40, $CHCl_3$).

(4S,5S)-2-((R)-2′-(Bis(3,5-dimethylphenyl)phosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-tosyl-4,5-dihydro-1H-imidazoline, ***L5.*** Yield: 138 mg, 50% for two steps; pale yellow solid, mp 150−153 °C; IR (CH_2Cl_2) ν 3395, 3152, 2958, 2925, 1886, 1725, 1642, 1590, 1485, 1433, 1371, 1316, 1277, 1207, 1185, 1167, 1075, 1029, 1001, 903 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.88 (s, 6H, CH_3), 2.02 (s, 6H, CH_3), 2.26 (s, 3H, CH_3), 4.47 (d, 1H, J = 5.7 Hz, CH), 4.49 (d, 1H, J = 5.7 Hz, CH), 5.84 (d, 2H, J = 7.8 Hz, ArH), 6.43 (d, 2H, J = 7.8 Hz, ArH), 6.68−6.78 (m, 5H, ArH), 6.81 (d, 2H, J = 6.9 Hz, ArH), 6.85−6.93 (m, 5H, ArH), 7.02 (t, 1H, J = 7.2 Hz, ArH), 7.15−7.19 (m, 5H, ArH), 7.31−7.42 (m, 2H, ArH), 7.53 (t, 1H, J = 7.5 Hz, ArH), 7.67 (d, 1H, J = 8.4 Hz, ArH), 7.83 (d, 1H, J = 8.4 Hz, ArH), 7.95−8.02 (m, 3H, ArH), 8.05 (d, 1H, J = 8.4 Hz, ArH), 8.18 (d, 1H, J = 8.4 Hz, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −12.78; MS (ESI) m/z (%) 869.7 (100) [M^+ + 1]; HRMS (MALDI) calcd for $C_{58}H_{50}N_2O_2PS^+$ (M^+ + 1) requires 869.3357, found 869.3325. $[\alpha]^{20}_D$ = +45.8 (c 0.40, $CHCl_3$).

(4S,5S)-2-((R)-2′-(Bis(3,5-dimethoxyphenyl)phosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-tosyl-4,5-dihydro-1H-imidazoline, ***L6.*** Yield: 185 mg, 66% for two steps; pale yellow solid, mp 156−159 °C; IR (CH_2Cl_2) ν 3403, 3295, 3155, 2993, 2725, 1825, 1769, 1642, 1595, 1479, 1333, 1306, 1277, 1219, 1205, 1185, 1167, 1009, 958, 858 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.27 (s, 3H, CH_3), 3.37 (s, 6H, OCH_3), 3.49 (s, 6H, OCH_3), 4.46 (d, 1H, J = 6.0 Hz, CH), 4.58 (d, 1H, J = 6.0 Hz, CH), 5.79 (d, 2H, J = 7.8 Hz, ArH), 6.00 (dd, 2H, J_1 = 2.4 Hz, J_2 = 8.4 Hz, ArH), 6.18−6.24 (m, 2H, ArH), 6.33 (dd, 2H, J_1 = 2.4 Hz, J_2 = 7.5 Hz, ArH), 6.62 (d, 1H, J = 8.1 Hz, ArH), 6.76−6.93 (m, 7H, ArH), 7.00 (t, 1H, J = 7.5 Hz, ArH), 7.14−7.20 (m, 5H, ArH), 7.30−7.37 (m, 2H, ArH), 7.51−7.60 (m, 2H, ArH), 7.82 (d, 1H, J = 8.7 Hz, ArH), 7.91 (d, 1H, J = 8.1 Hz, ArH), 7.97−8.08 (m, 3H, ArH), 8.16 (d, 1H, J = 8.1 Hz, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −8.80; MS (ESI) m/z (%) 934.0 (100) [M^+ + 1]; HRMS (MALDI) calcd for $C_{58}H_{50}N_2O_6PS^+$ (M^+ + 1) requires 933.3131, found 933.3122. $[\alpha]_D^{20}$ = +47.0 (c 0.20, $CHCl_3$).

(4S,5S)-2-((R)-2′-(Bis(4-fluorophenyl)phosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-tosyl-4,5-dihydro-1H-imidazoline, ***L7.*** Yield: 226 mg, 55% for two steps; pale yellow solid, mp 141−143 °C; IR (CH_2Cl_2) ν 3060, 2926, 1640, 1587, 1493, 1454, 1371, 1341, 1306, 1266, 1227, 1161, 1088, 1058, 1016, 963, 816, 775, 739, 699, 668, 638, 611 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.28 (s, 3H, CH_3), 4.45 (d, 1H, J = 6.4 Hz, CH), 4.54 (d, 1H, J = 6.4 Hz, CH), 5.84 (d, 2H, J = 7.2 Hz, ArH), 6.61 (d, 1H, J = 7.2 Hz, ArH), 6.67−6.73 (m, 4H, ArH), 6.77−6.94 (m, 9H, ArH), 7.00−7.08 (m, 3H, ArH), 7.18−7.22 (m, 5H, ArH), 7.34−7.38 (m, 2H, ArH), 7.43 (dd, 1H, J_1 = 2.4 Hz, J_2 = 8.4 Hz, ArH), 7.55−7.60 (m, 1H, ArH), 7.79 (d, 1H, J = 8.4 Hz, ArH), 7.93 (d, 1H, J = 8.4 Hz, ArH), 7.98−8.06 (m, 3H, ArH), 8.17 (d, 1H, J = 8.4 Hz, ArH); ^{31}P NMR ($CDCl_3$, 162 MHz, 85% H_3PO_4) δ −16.76; ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ −112.92, −114.30; MS (ESI) m/z (%) 849.6 (100) [M^+ + 1]; HRMS (ESI) calcd for $C_{54}H_{40}N_2O_2F_2PS^+$ (M^+ + 1) requires 849.2504, found 849.2511. $[\alpha]^{20}_D$ = +44.1 (c 0.55, $CHCl_3$).

(4S,5S)-2-((R)-2′-(Bis(4-methylphenyl)phosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-tosyl-4,5-dihydro-1H-imidazoline, ***L8.*** Yield: 153 mg, 48% for two steps; pale yellow solid, mp 150−152 °C; IR (CH_2Cl_2) ν 3051, 2920, 2855, 2304, 1913, 1641, 1598, 1495, 1454, 1370, 1339, 1307, 1265, 1186, 1170, 1088, 1057, 1020, 963, 869, 808, 775, 736, 698, 667, 627, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.20 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 4.49 (d, 1H, J = 2.7 Hz, CH), 4.52 (d, 1H, J = 2.7 Hz, CH), 5.83 (d, 2H, J = 7.8 Hz, ArH), 6.68−6.91 (m, 14H, ArH), 7.01 (t, 3H, J = 7.5 Hz, ArH), 7.14−7.23 (m, 5H, ArH), 7.29−7.37 (m, 2H, ArH), 7.49−7.55 (m, 2H, ArH), 7.79 (d, 1H, J = 8.7 Hz, ArH), 7.91 (d, 1H, J = 8.7 Hz, ArH), 8.00 (t, 3H, J = 8.1 Hz, ArH), 8.15 (d, 1H, J = 8.1 Hz, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −15.42; MS (ESI) m/z (%) 841.6 (100) [M^+ + 1]; HRMS (ESI) calcd for $C_{56}H_{46}N_2O_2PS^+$ (M^+ + 1) requires 841.2992, found 841.3012. $[\alpha]^{20}_D$ = +11.3 (c 0.40, $CHCl_3$).

(4S,5S)-2-((R)-2′-(Diphenylphosphino)-1,1′-binaphthyl-2-yl)-4,5-diphenyl-1-mesyl-4,5-dihydro-1H-imidazoline, ***L9.*** Yield: 130 mg, 42% for two steps; pale yellow solid, mp 146−149 °C; IR (CH_2Cl_2) ν 3271, 3043, 2915, 2846, 2346, 1668, 1652, 1634, 1489, 1456, 1434, 1311, 1151, 1051, 1058, 972, 821, 695, 515, 490 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.76 (s, 3H, CH_3), 4.56 (d, 1H, J = 6.6 Hz, CH), 4.94 (d, 1H, J = 6.6 Hz, CH), 6.19 (d, 2H, J = 7.8 Hz, ArH), 6.64 (d, 1H, J = 8.7 Hz, ArH), 6.78 (t, 1H, J = 7.8 Hz, ArH), 6.87 (t, 2H, J = 7.5 Hz, ArH), 6.98−7.06 (m, 5H, ArH), 7.08−7.13 (m, 3H, ArH), 7.15−7.24 (m, 6H, ArH), 7.29−7.37 (m, 4H, ArH), 7.46 (t, 1H, J = 7.5 Hz, ArH), 7.56−7.64 (m, 2H, ArH), 7.88−8.01 (m, 3H, ArH), 8.09 (dd, 2H, J_1 = 3.6 Hz, J_2 = 8.7 Hz, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −14.28; MS (MALDI) m/z (%) 737.5 (100) [M^++1]; HRMS (MALDI) calcd for $C_{48}H_{38}N_2O_2PS^+$ (M^+ + 1) requires 737.2382, found 737.2386. $[\alpha]^{20}_D$ = +49.4 (c 0.90, $CHCl_3$).

Preparation of Palladium Complex A from Ligand L1 with $PdCl_2(PhCN)_2$. Ligand **L1** (41 mg, 0.05 mmol) and bis(benzonitrile) palladium dichloride (19 mg, 0.05 mmol) were dissolved in dichloromethane (1.0 mL) under an argon atmosphere, and the reaction mixture was stirred for 1 h at room temperature. Degassed hexane (5.0 mL) was then slowly added, which led to the precipitation of the formed complex. The mother liquor was filtered off, and the precipitate was washed with hexane (2 × 1.0 mL) to afford the (*R*)-(+)-complex **A** as an orange powder (41 mg, 91% yield). The single crystal for X-ray diffraction was obtained by recrystallization from chloroform.

Pd(L1)Cl$_2$. Yield: 41 mg, 91%; yellow powder, mp 310−312 °C; IR (CH_2Cl_2) ν 3059, 2968, 2904, 2362, 1622, 1585, 1484, 1438, 1354, 1268, 1172, 1130, 1084, 999, 967, 866, 818, 757, 712, 699, 594, 573, 533, 490 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.46 (s, 3H, CH_3), 4.25 (d, 1H, J = 10.4 Hz, CH), 4.57 (d, 1H, J = 10.4 Hz, CH), 5.58 (d, 2H, J = 6.8 Hz, ArH), 6.11 (d, 1H, J = 8.4 Hz, ArH), 6.67−6.74 (m, 3H, ArH), 6.86−6.92 (m, 3H, ArH), 7.10 (t, 1H, J = 7.6 Hz, ArH), 7.15 (dd, 2H, J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 7.19−7.25 (m, 2H, ArH), 7.27−7.36 (m, 6H, ArH), 7.38−7.50 (m, 7H, ArH), 7.60 (d, 1H, J = 8.4 Hz, ArH), 7.63−7.73 (m, 3H, ArH), 7.91 (d, 1H, J = 8.0 Hz, ArH), 8.11 (t, 2H, J = 9.6 Hz, ArH), 8.34 (dd, 2H, J_1 = 8.4 Hz, J_2 = 14.4 Hz, ArH); ^{31}P NMR ($CDCl_3$, 162 MHz, 85% H_3PO_4) δ 22.94; MS (MALDI) m/z (%) 953.1 (98.10) [M^+ + 1]; HRMS (MALDI) calcd for $C_{54}H_{41}N_2O_2PSCl^{102}Pd^+$ (M^+ + 1) requires 949.1379, found 949.1366. $[\alpha]^{20}_D$ = +402.7 (c 1.00, $CHCl_3$).

General Procedure for the Reaction of 1,3-Diphenylpropenyl Acetate with Dimethyl Malonate in the Presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and Chiral Imidazoline−Phosphine Ligand L1. A solution of 1,3-diphenylpropenyl acetate (25 mg, 0.1 mmol), enantiomerically pure ligand **L1** (8.1 mg, 0.01 mmol, 10 mol %), and allyl chloride palladium dimer $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.8 mg, 0.005 mmol, 5 mol %) in solvent (0.5 mL) was stirred at room temperature for 30 min. To the solution were added dimethyl malonate (35 μL, 0.3 mmol, 3 equiv) and bis(trimethylsilyl)acetamide (73 μL, 0.3 mmol, 3 equiv), and the reaction was monitored by TLC plates until 1,3-diphenylpropenyl acetate was consumed completely. The reaction

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was quenched by the addition of a saturated NH_4Cl aqueous solution, and the product was extracted with CH_2Cl_2 (3 × 4 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to yield the crude product, which was purified by flash chromatography on silica gel (eluent: PE/EtOAc = 20:1) to furnish dimethyl(1,3-diphenyl-2-propen-1-yl)malonate as a colorless oil.

*(E)-Dimethyl 2-(1,3-diphenylallyl)malonate (**7aa**).* The ee was determined by chiral HPLC (Daicel CHIRALPACK AD-H, hexane/*i*PrOH = 90:10, 0.7 mL/min, 254 nm): t_{minor} = 25.8 min, t_{major} = 18.5 min. $[\alpha]^{20}_D$ = +14.0 (*c* 1.00, $CHCl_3$) {ref 12 $[\alpha]^{20}_D$ = +19.2; *c* = 1.30, $CHCl_3$; 95% ee}. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.51 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 3.95 (d, 1H, *J* = 10.8 Hz, CH), 4.27 (dd, 1H, J_1 = 8.8 Hz, J_2 = 10.8 Hz, CH), 6.33 (dd, 1H, J_1 = 8.8 Hz, J_2 = 15.6 Hz, =CH), 6.48 (d, 1H, *J* = 15.6 Hz, =CH), 7.17−7.25 (m, 3H, ArH), 7.26−7.34 (m, 7H, ArH).

*(E)-Diethyl 2-(1,3-diphenylallyl)malonate (**7ab**).* The ee was determined by chiral HPLC (Daicel CHIRALPACK IA-H, hexane/*i*PrOH = 90:10, 0.5 mL/min, 254 nm): t_{minor} = 20.4 min, t_{major} = 16.1 min. $[\alpha]^{20}_D$ = +17.2 (*c* 1.40, $CHCl_3$) {ref 13 $[\alpha]^{25}_D$ = −17.2; *c* = 1.02, $CHCl_3$; 97% ee}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.06 (t, 3H, *J* = 7.2 Hz, CH_3), 1.20 (t, 3H, *J* = 7.2 Hz, CH_3), 3.85 (d, 1H, *J* = 11.1 Hz, CH), 4.13−4.25 (m, 5H, CH_2, CH), 6.28 (dd, 1H, J_1 = 8.1 Hz, J_2 =15.6 Hz, =CH), 6.39 (d, 1H, *J* = 15.6 Hz, =CH), 7.15−7.19 (m, 5H, ArH), 7.37−7.46 (m, 5H, ArH).

*(E)-Dimethyl(1,3-bis(4-methylphenyl)-2-propen-1-yl)malonate (**7ba**).* The ee was determined by chiral HPLC (Daicel CHIRALPACK AD-H, hexane/*i*PrOH = 94:6, 0.5 mL/min, 254 nm): t_{minor} = 50.0 min, t_{major}= 34.5 min. $[\alpha]^{20}_D$ = +13.0 (*c* 1.50, $CHCl_3$) {ref 14 $[\alpha]^{20}_D$ = −13.4; *c* = 1.0, $CHCl_3$; 80% ee}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.30 (s, 6H, CH_3), 3.52 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 3.92 (d, 1H, *J* = 10.8 Hz, CH), 4.21 (dd, 1H, J_1 = 8.7 Hz, J_2 = 10.8 Hz, CH), 6.25 (dd, 1H, J_1 = 8.7 Hz, J_2 = 15.9 Hz, =CH), 6.43 (d, 1H, *J* = 15.9 Hz, =CH), 7.05−7.13 (m, 4H, ArH), 7.16−7.25 (m, 4H, ArH).

*(E)-Dimethyl(1,3-bis(4-chlorophenyl)-2-propen-1-yl)malonate (**7ca**).* The ee was determined by chiral HPLC (Daicel CHIRALPACK AD-H, hexane/*i*PrOH = 85:15, 0.8 mL/min, 254 nm): t_{minor} = 36.5 min, t_{major} = 23.4 min. $[\alpha]^{20}_D$ = +1.4 (*c* 1.65, $CHCl_3$) {ref 14 $[\alpha]^{20}_D$ = −3.1; *c* = 1.0, $CHCl_3$; 97% ee}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.55 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 3.90 (d, 1H, *J* = 10.8 Hz, CH), 4.24 (dd, 1H, J_1 = 8.4 Hz, J_2 = 10.8 Hz, CH), 6.26 (dd, 1H, J_1 = 8.4 Hz, J_2 = 15.9 Hz, =CH), 6.41 (d, 1H, *J* = 15.9 Hz, =CH), 7.21−7.32 (m, 8H, ArH).

*(E)-Dimethyl(1,3-bis(4-bromophenyl)-2-propen-1-yl)malonate (**7da**).* The ee was determined by chiral HPLC (Daicel CHIRALPACK IA-H, hexane/*i*PrOH = 90:10, 0.7 mL/min, 254 nm): t_{minor} = 28.1 min, t_{major} = 18.2 min. $[\alpha]^{20}_D$ = −1.1 (*c* = 0.4, $CHCl_3$) {ref 14 $[\alpha]^{20}_D$ = +3.0; *c* 1.0, $CHCl_3$; 97% ee}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.55 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 3.89 (d, 1H, *J* = 10.8 Hz, CH), 4.22 (dd, 1H, J_1 = 8.1 Hz, J_2 = 10.8 Hz, CH), 6.27 (dd, 1H, J_1 = 8.1 Hz, J_2 = 15.9 Hz, =CH), 6.39 (d, 1H, *J* = 15.9 Hz, =CH), 7.15−7.18 (m, 4H, ArH), 7.38−7.47 (m, 4H, ArH).

General Procedure for the Reaction of 1,3-Diphenylpropenyl Acetate with 1-Fluorobis(phenylsulfonyl)methane in the Presence of [Pd(η^3-C_3H_5)Cl]$_2$ and Chiral Imidazoline−Phosphine Ligand L7. A solution of 1,3-diphenylpropenyl acetate (25 mg, 0.1 mmol), enantiomerically pure ligand **L7** (8.5 mg, 0.01 mmol, 10 mol %), and allyl chloride palladium dimer [Pd(η^3-C_3H_5)Cl]$_2$ (1.8 mg, 0.005 mmol, 5 mol %) in solvent (0.5 mL) was stirred at room temperature for 5 min. To the solution were added 1-fluorobis(phenylsulfonyl)methane (35 mg, 0.11 mmol) and Cs_2CO_3 (36 mg, 0.11 mmol). The resulting solution was stirred at room temperature for 12 h, when 1,3-diphenylpropenyl acetate was completely consumed, as indicated by TLC analysis. The reaction mixture was poured into saturated NH_4Cl, and it was extracted with CH_2Cl_2. The organic phase was dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the product was purified by silica gel column chromatography to give **8** as a colorless solid.

*(E)-4-Fluoro-1,3-diphenyl-4,4-bis(phenylsulfonyl)but-1-ene (**8**).* The ee was determined by chiral HPLC (Daicel CHIRALPACK AD-H, hexane/*i*PrOH = 80:20, 1.0 mL/min, 254 nm): t_{major} = 27.1 min, t_{minor} = 20.1 min. $[\alpha]^{20}_D$ = −6.6 (*c* 1.30, $CHCl_3$) {ref 7f $[\alpha]^{20}_D$ = +13.8; *c* 1.54, $CHCl_3$; 96% ee}. Colorless solid, mp 126−128 °C; ^{1}H NMR($CDCl_3$, TMS, 300 MHz) δ 4.66 (dd, 1H, J_1 = 7.2 Hz, J_2 = 11.1 Hz, CH), 6.43 (d, 1H, *J* = 12.0 Hz, =CH), 7.01 (dd, 1H, J_1 = 7.2 Hz, J_2 = 12.0 Hz, =CH), 7.06−7.12 (m, 3H, ArH), 7.17−7.28 (m, 7H, ArH), 7.36−7.50 (m, 7H, ArH), 7.56−7.66 (m, 1H, ArH), 7.78−7.95 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 29.7, 122.8, 122.9, 126.8, 128.0, 128.1, 128.4, 128.5, 128.6, 129.0, 130.4, 130.5, 130.9, 131.0, 134.4, 134.8, 135.3, 136.0, 136.7, 136.9; ^{19}F NMR ($CDCl_3$, 212 MHz, $CFCl_3$) δ −129.2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic charts and chiral HPLC traces of the products shown in Tables 1−4, X-ray crystal data of palladium complex **A** as well as detailed descriptions of experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Miyashita, A.; Yasuda, H.; Takaya, K.; Toriumi, T.; Ito, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932−7934. (b) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345−350. (c) Noyori, R.; Suga, S.; Kawai, K.; Okada, S.; Kitamura, M. *Pure Appl. Chem.* **1988**, *60*, 1597−1606. (d) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187−208.

(2) (a) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887−9888. (b) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945−1948. (c) Uozumi, Y.; Kitayama, K.; Hayashi, T.; Yanagi, K.; Fukuyo, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 713−722.

(3) (a) MOP (X = OMe) was developed by Hayashi and coworkers; see ref 2. (b) MAP (X = NMe_2): Vyskočil, S.; Smrčina, M.; Hanus, V.; Polasek, M.; Kočovský, P. *J. Org. Chem.* **1998**, *63*, 7738−7748. Ding, K.-L.; Wang, Y.; Yun, H.; Liu, J.; Wu, Y.; Terada, M.; Okubo, Y.; Mikami, K. *Chem.—Eur. J.* **1999**, *5*, 1734−1737. (c) BINAPS (X = SMe): Kang, J.; Yu, S.-H.; Kim, J. I.; Cho, H. G. *Bull. Korean Chem. Soc.* **1995**, *16*, 439−443. Gladiali, S.; Medici, S.; Pirri, G.; Pulacchini, S.; Fabbri, D. *Can. J. Chem.* **2001**, *79*, 670−678. (d) Ligand **LB** in which X = $AsPh_2$: Cho, S. Y.; Shibasaki, M. *Tetrahedron Lett.* **1998**, *13*, 1773−1776. Ligand **LB** in which X = $P(O)Ph_2$: (e) Gladiali, S.; Pulacchini, S.; Fabbri, D.; Manassero, M.; Sansoni, M. *Tetrahedron: Asymmetry* **1998**, *9*, 391−395. Ligand **LB** in which X = $P(S)Ph_2$: (f) Faller, J. W.; Wilt, J. C.; Parr, J. *Org. Lett.* **2004**, *6*, 1301−1304. TolBINAP: (g) Gladiali, S.; Dore, A.; Fabbri, D.; Medici, S.; Pirri, G.; Pulacchini, S. *Eur. J. Org. Chem.* **2000**, *16*, 2861−2865.

(4) Yan, Y.-J.; Zhang, X. -M. *J. Am. Chem. Soc.* **2006**, *128*, 7198−7202.

(5) (a) Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033−7034. (b) Nozaki, K.; Sakai, N.; Nanno, T.; Higashijima, T.; Mano, S.; Horiuchi, T.; Takaya, H. *J. Am. Chem. Soc.* **1997**, *119*, 4413−4423. (c) Horiuchi, T.; Takaya, H. *J. Org. Chem.*

1997, *62*, 4285−4292. (d) Nozaki, K.; Kawashima, Y.; Hiyama, T.; Matsubara, T. *J. Am. Chem. Soc.* **2001**, *23*, 534−544. (e) Solinas, M.; Marchetti, M. *J. Mol. Catal. A: Chem.* **2005**, *226*, 141−147. (f) Nozaki, K.; Hiyama, T. *Adv. Synth. Catal.* **2001**, *343*, 61−63. (g) Horiuchi, T.; Takaya, H. *Organometallics* **1997**, *16*, 2981−2986. (h) Nozaki, K.; Li, W.-G.; Takaya, H. *Tetrahedron Lett.* **1997**, *38*, 4611−4614. (i) Nozaki, K.; Li, W.-G.; Miura, T.; Kumobayashi, H. *J. Org. Chem.* **1996**, *61*, 7658−7659. (j) Nanno, T.; Sakai, N.; Nozaki, K.; Takaya, H. *Tetrahedron: Asymmetry* **1995**, *6*, 2583−2591.

(6) (a) Deng, H.-P.; Wei, Y.; Shi, M. *Adv. Synth. Catal.* **2009**, *351*, 2897−2902. (b) Ogasawara, M.; Yoshida, K.; Kamei, H.; Kato, K.; Uozumi, Y.; Hayashi, T. *Tetrahedron: Asymmetry* **1998**, *9*, 1779−1787. (c) Hatano, M.; Yamanaka, M.; Mikami, K. *Eur. J. Org. Chem.* **2003**, 2552−2555. (d) Uozumi, Y.; Suzuki, N.; Ogiwara, A.; Hayashi, T. *Tetrahedron* **1994**, *50*, 4293−4302. (e) Zhao, Q.-Y.; Yuan, Z.-L.; Shi, M. *Tetrahedron: Asymmetry* **2010**, *21*, 943−951. (f) Imai, Y.; Zhang, W.-B.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron Lett.* **1998**, *39*, 4343−4346. (g) Selvakumar, K.; Valentini, M.; Pregosin, P. S.; Albinati, A. *Organometallics* **1999**, *18*, 1207−1215. (h) Zhao, Q.-Y.; Shi, M. *Tetrahedron* **2011**, *67*, 3724−3732.

(7) For recent reviews, see: (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395−422. (b) Pfaltz, A.; Lautens, M. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999; Vol. *2*, Chapter 24. (c) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336−345. (d) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921−2944. (e) Lu, Z.; Ma, S.-M. *Angew. Chem., Int. Ed.* **2008**, *47*, 258−297. (f) Fukuzumi, T.; Shibata, N.; Sugiura, M.; Yasui, H.; Nakamura, S.; Toru, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 4973−4977. (g) Liu, W.-B.; Zheng, S.-C.; He, H.; Zhao, X.-M.; Dai, L.-X.; You, S.-L. *Chem. Commun.* **2009**, 6604−6606.

(8) (a) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1−45. (b) Gómez, M.; Muller, G.; Rocamora, M. *Coord. Chem. Rev.* **1999**, *193*−*195*, 769. (c) McManus, H. A.; Guiry, P. J. *Chem. Rev.* **2004**, *104*, 4151−4202. (d) Zhou, J.; Tang, Y. *Chem. Soc. Rev.* **2005**, *34*, 664−676. (e) Desimoni, G.; Faita, G.; JΦrgensen, K. A. *Chem. Rev.* **2006**, *106*, 3561−3651.

(9) Liu, H.; Du, D.-M. *Adv. Synth. Catal.* **2009**, *351*, 489−519.

(10) For selected examples, see: (a) Busacca, C. A.; Grossbach, D.; So, R. C.; O'Brien, E. M.; Spinelli, E. M. *Org. Lett.* **2003**, *5*, 595−598. (b) Bastero, A.; Ruiz, A.; Claver, C.; Castillón, S. *Eur. J. Inorg. Chem.* **2001**, 3009−3011. (c) Bastero, A.; Ruiz, A.; Claver, C.; Milani, B.; Zangrando, E. *Organometallics* **2002**, *21*, 5820−5829. (d) Bastero, A.; Claver, C.; Ruiz, A.; Castillón, S.; Daura, E.; Bo, C.; Zangrando, E. *Chem.—Eur. J.* **2004**, *10*, 3747−3760. (e) Casey, M.; Smyth, M. P. *Synlett* **2003**, 102−106. (f) Du, X.; Liu, H.; Du, D.-M. *Eur. J. Org. Chem.* **2011**, 786−793.

(11) (a) You, S.-L.; Kelly, J. W. *Org. Lett.* **2004**, *6*, 1681−1683. (b) Liu, H.; Du, D.-M. *Adv. Synth. Catal.* **2010**, *353*, 1113−1118. (c) Wang, X.-Q.; Xia, J.-B.; Dai, X.-Y.; You, S.-L. *Sci. China, Ser. B: Chem.* **2009**, *52*, 1331−1336.

(12) Leutenegger, U.; Umbricht, G.; Fahrni, C.; Matt, P. V.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143−2156.

(13) Tanaka, Y.; Mino, T.; Akita, K.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2004**, *69*, 6679−6687.

(14) Kinoshita, N.; Kawabata, T.; Tsubaki, K.; Bando, M.; Fuji, K. *Tetrahedron* **2006**, *62*, 1756−1763.

(15) For selected examples, see: (a) Sun, Y.-W.; Jiang, J.-J.; Zhao, M.-X.; Wang, F.-J.; Shi, M. *J. Organomet. Chem.* **2011**, *696*, 2850−2856. (b) Chiang, W.-Y.; Hong, F.-E. *J. Organomet. Chem.* **2009**, *694*, 1473−1481. (c) Thiesen, K. E.; Maitra, K.; Olmstead, M. M.; Attar, S. *Organometallics* **2010**, *29*, 6334−6342. (d) Dyer, P. W.; Fawcett, J.; Hanton, M. J. *J. Organomet. Chem.* **2005**, *690*, 5264−5281.

(16) The crystal data of Pd(**L1**)Cl_2 have been deposited in the CCDC with number 826453. Empirical formula: $C_{57}H_{44}Cl_{11}N_2O_2PPdS$; formula weight: 1348.32; crystal color, habit: colorless; crystal dimensions: 0.22 × 0.15 × 0.12 mm; crystal system: orthorhombic; lattice type: primitive; lattice parameters: a = 10.6194(9) Å, b = 19.4491(16) Å, c = 27.882(2) Å, α = 90°, β = 90°, γ = 90°, V = 5758.8(8) Å^3; space group: P2(1)2(1)2(1); Z = 4; D_{calc} = 1.555 g/cm^3; F_{000} = 2720; final R indices [$I > 2\sigma(I)$] R1 = 0.0281, wR2 = 0.653.