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Note

Palladium-catalyzed asymmetric allylic substitutions in the presence of chiral phosphine-imine type ligands

Yin-Wei Sun [a], Jia-Jun Jiang [a], Mei-Xin Zhao [a], Fei-Jun Wang [a], Min Shi [a,b,*]

[a] Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Mei Long Lu, Shanghai 200237, China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

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ABSTRACT

Chiral bidentate phosphine-imine type ligand **L9** is fairly effective in the asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate to give the corresponding adduct in moderate yield and good ee.

1. Introduction

Homogeneous enantioselective catalysis with chiral transition metal complexes is an attractive synthetic methodology, where a small amount of chiral materials can produce a large amount of chiral products [1–3]. Chiral C_2-symmetric ligand 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (**BINAP**) **LA** [4–7] and C_1-symmetric ligand 2-(diphenylphosphino)-1,1′-binaphthyl (**MOP**) **LB** (X = OMe) [8–10] possessing the axially chiral 1,1′-binaphthalene framework have been widely utilized in asymmetric catalysis (Fig. 1). Significant efforts have been devoted to the design and synthesis of novel binaphthalene-templated ligands. Representative examples are the binaphthyl P,*X*-heterodonor ligands **LB** where X is a variety of heteroatoms (X = NMe_2, SMe, $AsPh_2$, $P(O)Ph_2$, $P(S)Ph_2$, PAr_2) [11–18], phosphane–phosphite ligand **BINAPHOS LC** [19–21], and phosphine–pyridine ligand **LD** [22], derived from 2-amino-2′-hydroxy-1,1'binaphthyl (**NOBIN**). Most of these axially chiral ligands are effective in the palladium-catalyzed asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate in the presence of a base, which has become a famous and fundamental asymmetric C–C bonding formation reaction [23]. On the other hand, recently, phosphine-imine type (salen-type) chiral ligands have attracted much attention because they can coordinate with a variety of transition metal ions to afford the corresponding stable chiral metal complexes in good yields and these chiral metal complexes are in general quite efficient in many asymmetric reactions including asymmetric allylic alkylation [24].

These results have promoted us to explore new chiral phosphine-imine type ligands for asymmetric reactions since we envisioned that these chiral ligands can also coordinate with a variety of metal ions under mild conditions. In this paper we wish to report that the chiral phosphine-imine type ligand **L9** prepared from (*R*)-(−)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-amine is fairly effective in the asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate to give the corresponding adduct in moderate yield and good ee. In the mean time, its bidentate coordination pattern to the Pd metal center with both P and N atoms has been unambiguously established by X-ray diffraction.

2. Results and discussion

2.1. Synthesis of ligands *L1–L13*

Chiral phosphine-imine type ligands **L1–L13** were synthesized from the reaction of salicylaldehydes as well as its analogs with (*R*)-(−)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-amine in absolute ethanol under reflux for 12 h, respectively (Scheme 1). After usual workup, these ligands can be obtained in good yields.

* Corresponding author. State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China. Fax: +86 21 64166128.
E-mail address: Mshi@mail.sioc.ac.cn (M. Shi).

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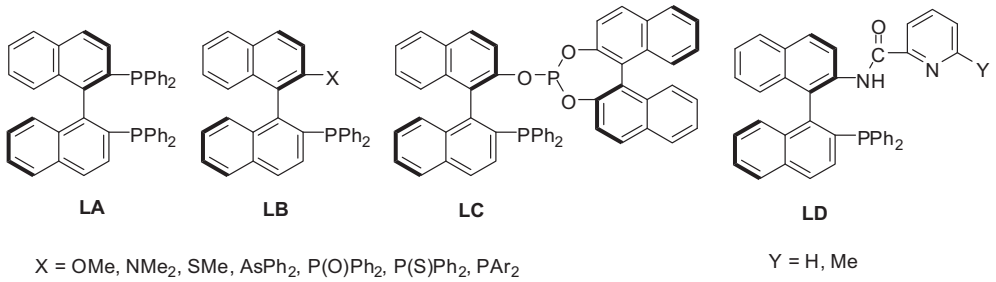
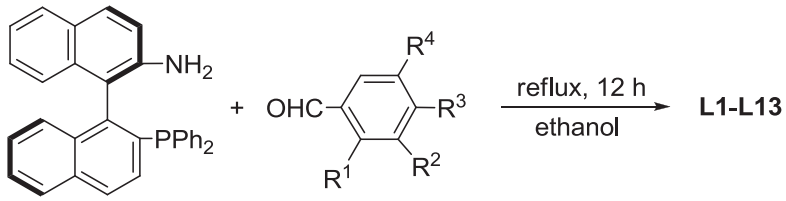
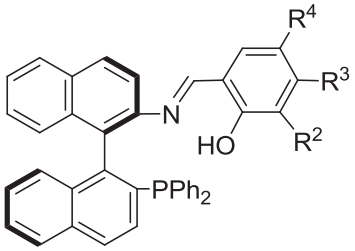


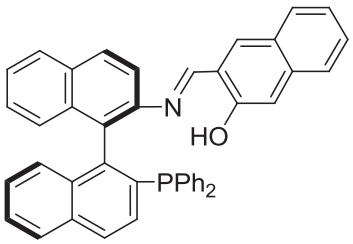
Fig. 1. The structure of C_2-symmetric BINAP and C_1-symmetric binaphthyl P,X-heterodonor ligands.

2.2. Catalytic asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate in the presence of chiral phosphine-imine type ligands

Initial examinations using 1,3-diphenylpropenyl acetate and dimethyl malonate as the substrates in the presence of chiral phosphine-imine type ligand **L1** and Pd(II) salt were aimed at determining the optimal conditions and the results of these experiments are summarized in Table 1. We found that using bis(trimethylsilyl)acetamide (BSA) as an organic base, the corresponding product was obtained in moderate to good yields in a variety of solvents in the presence of **L1** (15 mol %) and palladium salt (5 mol %) at room temperature and up to 35% ee was achieved using tetrahydrofuran (THF) as a solvent (Table 1, entries 1–3). By screening chiral phosphine-imine type ligands **L1**–**L13** in THF and some salt additives, we found that **L9** was the best chiral phosphine-imine type ligand for this asymmetric allylic alkylation,

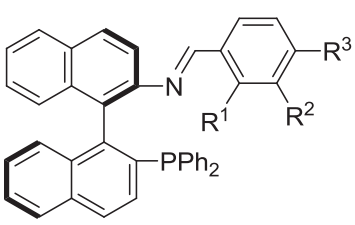


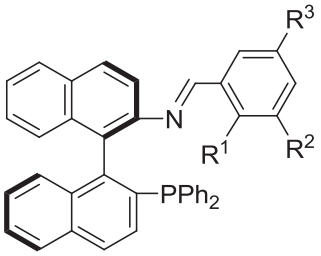




L6

L1: R^2 = H, R^3 = H, R^4 = Me
L2: R^2 = Cl, R^3 = H, R^4 = Cl
L3: R^2 = H, R^3 = H, R^4 = H
L4: R^2 = H, R^3 = OMe, R^4 = H
L5: R^2 = ^{t}Bu, R^3 = H, R^4 = ^{t}Bu



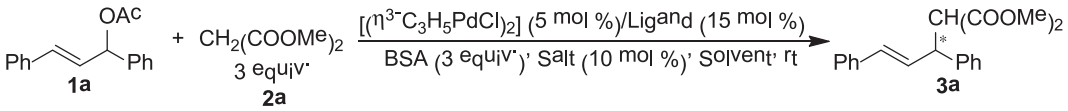


L7: R^1 = Cl, R^2 = Cl, R^3 = H
L8: R^1 = OH, R^2 = OH, R^3 = H
L9: R^1 = OH, R^2 = OH, R^3 = NO_2
L10: R^1 = OMe, R^2 = OMe, R^3 = NO_2

L11: R^1 = OH, R^2 = H, R^3 = NO_2
L12: R^1 = OH, R^2 = OH, R^3 = NO_2
L13: R^1 = OMe, R^2 = OMe, R^3 = NO_2

Scheme 1. Preparation of phosphine-imine type ligands **L1**–**L13**.

Table 1
The asymmetric allylic alkylation catalyzed by Pd(II) in the presence of chiral phosphine-imine type ligands **L1**–**L13**.



Entry	Ligand	Salt	Solvent	Yield(%)[a]	ee(%)[b]	Absolute configuration[c]
1	**L1**	–	CH_2Cl_2	38	0	S
2	**L1**	–	$PhCH_3$	95	20	S
3	**L1**	–	THF	95	35	S
4	**L2**	–	THF	87	0	S
5	**L3**	–	THF	90	12	S
6	**L4**	–	THF	95	18	S
7	**L5**	–	THF	67	35	S
8	**L6**	–	THF	59	33	R
9	**L7**	–	THF	37	20	S
10	**L8**	–	THF	84	20	S
11	**L9**	–	THF	79	47	S
12	**L10**	–	THF	95	25	S
13	**L11**	–	THF	99	7	S
14	**L12**	–	THF	67	4	S
15	**L13**	–	THF	95	5	S
16	**L1**	KOAc	THF	50	37	S
17	**L1**	$LiOAc\cdot 2H_2O$	THF	81	47	S
18	**L1**	Bu_4NBr	THF	64	33	S
19	**L1**	Bu_4NI	THF	23	33	S
20[d]	**L1**	$LiOAc\cdot 2H_2O$	THF	99	33	S
21	**L8**	$LiOAc\cdot 2H_2O$	THF	64	44	S
22	**L9**	$LiOAc\cdot 2H_2O$	THF	62	67	S
23[e]	**L9**	$LiOAc\cdot 2H_2O$	THF	31	76	S
24	**L9**	$LiCl\cdot H_2O$	THF	*63*	*71*	S
25[f]	**L9**	$LiOAc\cdot 2H_2O$	THF	47	70	S
26	**L10**	$LiCl\cdot H_2O$	THF	63	44	S
27	**L11**	$LiCl\cdot H_2O$	THF	99	59	S
28	**L12**	$LiCl\cdot H_2O$	THF	61	55	S
29	**L13**	$LiCl\cdot H_2O$	THF	77	60	S

[a] Isolated yields.
[b] Determined by chiral HPLC analysis.
[c] The absolute configuration was determined by comparing the sign of specific rotation with authentic sample reported in the literature.
[d] 1.0 equiv of salt was added.
[e] The reaction was performed at 0 °C.
[f] 0.2 equiv of salt was added.

affording the corresponding product in 71% ee and 63% yield at room temperature in the presence of $LiCl\cdot H_2O$ (10 mol%) (Table 1, entries 4–29). It should be noted that chiral phosphine-imine type ligand **L2** showed no enantioselectivity for this asymmetric allylic alkylation under identical conditions (Table 1, entry 4). In addition, we unexpectedly found that chiral ligands **L6** and **L9** produced the corresponding products with opposite absolute configuration (Table 1, entries 8 and 11). These results suggested that the substituent on the benzene ring in the chiral phosphine-imine type ligands played a very important role in chiral induction in this asymmetric allylic alkylation reaction. The presence of salt additives, such as Bu_4NX (X = Br, I) or KOAc did not improve the ees in this reaction and the products were obtained in relatively lower yields (Table 1, entries 16, 18 and 19). Recently, Furukawa and coworkers disclosed that using BSA as a base in the presence of lithium salt in this reaction, the enantioselectivity of the reaction product in the palladium-catalyzed asymmetric reaction could be greatly improved [25]. On the basis of this result, we examined the effect of lithium salt such as LiCl or LiOAc (10 mol%) and found that the achieved ee reached 71% under similar conditions (Table 1, entries 22 and 24). We found that these factors such as the amount of lithium salt loading and reaction temperature had little effect on the improvement of enantioselectivity (Table 1, entries 20, 23 and 25). Comparing the reaction outcomes with **L9** and **L11**–**L13**, it can be seen that the nitro group at the 4-position of the benzene ring is crucial to get the corresponding product in good ee value (Table 1, entries 11, 13–15). Moreover, the hydroxyl group was also important in ligand **L9** bearing a nitro group on the 4-position of the benzene ring, giving the corresponding product in higher ee value under identical conditions (Table 1, entries 11 and 12, 24 and 26). On the other hand, when the nitro group was introduced on the 5-position of the benzene ring and OH groups were methylated, the corresponding product was given in similar yield and ee value under identical conditions (for example, using **L12** and **L13** as the ligands) (Table 1, entries 14 and 15, 28 and 29). The best result was obtained if using **L9** as a ligand in THF in the presence of LiCl (10 mol%) at room temperature to give the corresponding product in 63% yield and 71% ee (Table 1, entry 24). The opposite absolute configuration was obtained if using **L6** as a ligand which contains a α-naphthol group, presumably due to the steric effect since naphthyl group is a sterically larger substituent than that of the corresponding phenyl group (Table 1, entry 8).

Furthermore, when diethyl malonate was used as the substrate, the corresponding product **3b** was obtained in 21% yield along with 73% ee value (Scheme 3). As for the allylation substrate having a chlorine atom at the 4-position of the benzene ring, the corresponding product **3c** was formed in 56% yield and 40% ee in the reaction with dimethyl malonate (Scheme 3).

On the other hand, using benzyl amine or morpholine instead of dimethyl malonate as the nucelophile, the corresponding asymmetric

amination products **3d** and **3e** were obtained in 50% yield along with 48% ee and 69% yield along with 40% ee, respectively (Scheme 4).

2.3. Synthesis of complex *E*

In order to get straightforward evidence of the coordination pattern of **L1** to Pd center, we decided to prepare a Pd(II) complex from **L1** with bis(benzonitrile)palladium dichloride [Pd(PhCN)2Cl2] because it is known that nitrogen and phosphorus atoms can coordinate to Pd(II) center to give a stable Pd(II) complex, which can be subjected to the X-ray diffraction. The synthesis of the Pd(**L1**)Cl2 complex E was carried out by the reaction of the appropriate amount of Pd(PhCN)2Cl2 with 1.0 equiv of **L1** in CH2Cl2 at room temperature under an argon atmosphere (Scheme 2). The single crystal suitable for X-ray diffraction was obtained by recrystallization from dichloromethane and petroleum ether (1:4). The ORTEP drawing of Pd complex E is shown in Fig. 2 in which **L1** acts as a cis-bidentate ligand to Pd(II) center in a slightly distorted planar geometry with both nitrogen and phosphorus atoms providing a seven-membered chelate ring. The angle of N(1)-Pd-P(1) plane is 89.55°, and the bond lengths of N(1)-Pd and Pd-P(1) are 2.021 Å and 2.2559 Å, respectively.

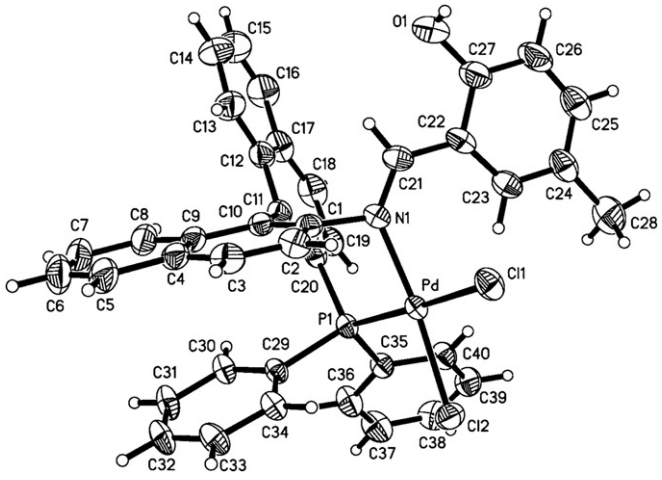
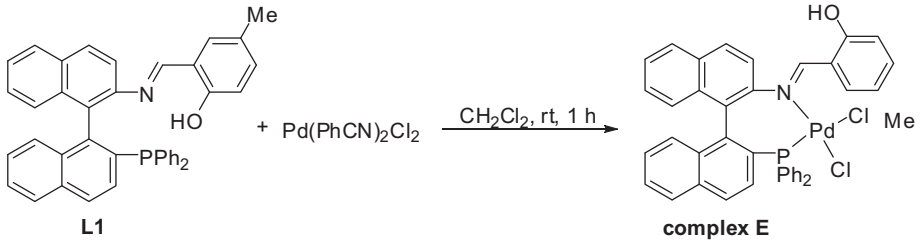


Fig. 2. ORTEP drawing of Pd(**L1**)Cl_2 complex **E** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd-P1 = 2.2559(12), Pd-N1 = 2.021(4), N1-C21 = 1.277(6), Cl1-Pd = 2.3438(13), Cl2-Pd = 2.2954(14), N1-Pd-P1 = 89.55(11), Pd-N1-C1 = 105.8(3), N1-Pd-Cl1 = 87.98(11), Cl1-Pd-Cl2 = 93.25(5), Cl2-Pd-P1 = 88.85(5), C12-C11-C10-C9 = 74.3(6).

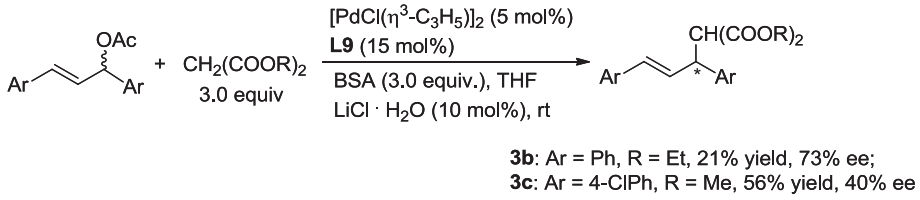
3. Experimental

3.1. Instrumentation

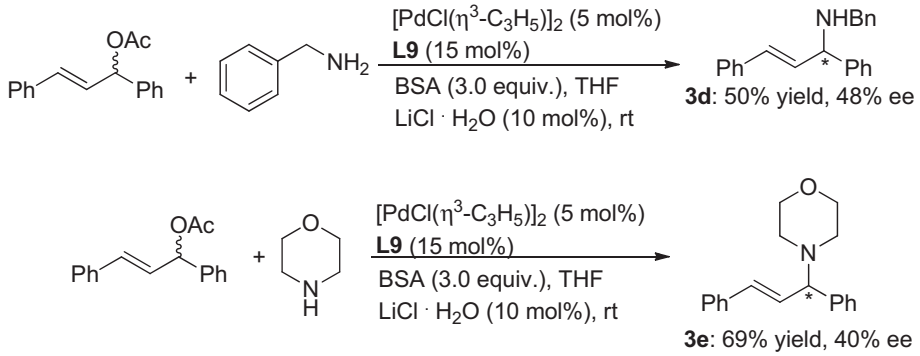
MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. Optical rotations were determined in a solution of $CHCl_3$ or CH_2Cl_2 at 20 °C by using a Perkin–Elmer-241 MC polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Infra-red spectra were measured on a spectrometer. ^1H NMR spectra were recorded for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; ^{31}P NMR spectra were



Scheme 2. Synthesis of the phosphine-imine type-Pd(II) complex **E**.



Scheme 3. Asymmetric Alkylations Catalyzed by Pd/**L9**.



Scheme 4. Asymmetric Aminations Catalyzed by Pd/**L9**.

recorded at 121 MHz 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 an 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 OD) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation.

3.2. Typical procedure for the preparation of chiral phosphine-imine type ligands **L1**–**L13**

To a solution of (*R*)-(−)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-amine [26,27] (227 mg, 0.5 mmol) in absolute ethanol (4.0 mL) was added salicylaldehyde (68 mg, 0.5 mmol) at room temperature and the reaction mixture was stirred under reflux for 12 h. After cooling to room temperature, yellow precipitates settled out, which were filtered to give the corresponding phosphine-imine type ligand **L3** as a yellow solid (208 mg, 75% yield).

3.2.1. (R)-(+)-2–((2-(Diphenylphosphino)-1,1′-binaphthyl-2′-ylimino) methyl)-4-methylphenol **L1**

This is a known compound [28]. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.23 (s, 3H, CH_3), 6.68 (d, *J* = 8.4 Hz, 1H, Ar), 6.82–7.52 (m, 20H, Ar), 7.94–7.96 (m, 3H, Ar), 8.06 (d, *J* = 9 Hz, 1H, Ar), 8.24 (s, 1H, CH=N), 11.55 (s, 1H, OH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −12.52.

3.2.2. (R)-(+)-2,4-dichloro-6–((2-(diphenylphosphino)-1,1′-binaphthyl-2′-ylimino)methyl) phenol **L2**

This is a known compound [28]. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 6.85–7.54 (m, 20H, Ar), 7.94 (d, *J* = 8.4 Hz, 3H, Ar), 8.07 (d, *J* = 9.3 Hz, 1H, Ar), 8.15 (s, 1H, CH=N), 12.48 (s, 1H, OH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −12.90.

3.2.3. (R)-(+)-2–((2-(Diphenylphosphino)-1,1′-binaphthyl-2′-ylimino) methyl)phenol **L3**

This is a known compound [28]. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 6.70 (d, *J* = 8.4 Hz, 1H, Ar), 6.77 (t, *J* = 7.8 Hz, 1H, Ar), 6.85 (t, *J* = 8.1 Hz, 2H, Ar), 6.92–7.50 (m, 18H, Ar), 7.94 (d, *J* = 8.4 Hz, 3H, Ar), 8.06 (d, *J* = 9 Hz, 1H, Ar), 8.29 (s, 1H, CH=N), 11.77 (s, 1H, OH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −12.58.

3.2.4. (R)-(+)-2–((2-(Diphenylphosphino)-1,1′-binaphthyl-2′-ylimino)methyl)-5-methoxyphenol **L4**

This is a known compound [28]. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.74 (s, 3H, CH_3), 6.21 (s, 1H, Ar), 6.34 (d, *J* = 8.4 Hz, 1H, Ar), 6.89–7.28 (m, 15H, Ar), 7.38–7.51 (m, 4H, Ar), 7.91–7.95 (m, 3H, Ar), 8.05 (d, *J* = 8.7 Hz, 1H, Ar), 8.21 (s, 1H, CH=N), 12.30 (s, 1H, OH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −12.59.

3.2.5. (R)-(+)-2,4-di-tert-butyl-6–((2-(diphenylphosphino)-1,1′-binaphthyl-2′-ylimino)methyl) phenol **L5**

This is a known compound [28]. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.22 (s, 9H, $3CH_3$), 1.26 (s, 9H, $3CH_3$), 6.83–7.58 (m, 20H, Ar), 7.88–7.91 (m, 3H, Ar), 8.05 (d, *J* = 8.7 Hz, 1H, Ar), 8.39 (s, 1H, CH=N), 12.64 (s, 1H, OH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −12.32.

3.2.6. (R)-(+)-1–((2-(Diphenylphosphino)-1,1′-binaphthyl-2′-ylimino)methyl)naphthalen-2-ol **L6**

This is a known compound [28]. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 6.60 (t, *J* = 7.2 Hz, 1H, Ar), 6.75 (t, *J* = 7.2 Hz, 2H, Ar), 6.89 (d, *J* = 9 Hz, 1H, Ar), 7.00–7.31 (m, 12H, Ar), 7.43–7.53 (m, 4H, Ar), 7.62–7.73 (m, 4H, Ar), 7.97–8.10 (m, 3H, Ar), 8.12 (d, *J* = 9 Hz, 1H, Ar), 8.95 (s, 1H, CH=N), 13.93 (s, 1H, OH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −12.74.

3.2.7. (R)-(+)-N-(2,3-Dichlorobenzylidene)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-amine **L7**

This is a known compound [28]. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 6.92–7.51 (m, 19H, Ar), 7.69–7.93 (m, 5H, Ar), 8.04 (d, *J* = 8.7 Hz, 1H, Ar), 8.50 (s, 1H, CH=N); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −12.95.

3.2.8. (R,E)-3-((2′-(diphenylphosphino)-1,1′-binaphthyl-2-ylimino) methyl)benzene-1,2-diol **L8**

Yield: (215 mg, 75%). A red solid. Mp: 156–158 °C; IR (CH_2Cl_2) ν 3533, 3044, 2911, 1611, 1582, 1462, 1218, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 5.53 (s, 1H, OH), 6.61–6.70 (m, 2H, Ar), 6.87–7.28 (m, 15H, Ar), 7.38–7.55 (m, 4H, Ar), 7.94 (d, *J* = 8.1 Hz, 3H, Ar), 8.07 (d, *J* = 9.0 Hz, 1H, Ar), 8.29 (s, 1H, CH=N), 12.39 (s, 1H, OH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −12.66; MS (ESI) *m/e* 574 (M^++1, 100); HRMS (ESI) Calcd. For $C_{39}H_{28}NO_2P$ (M + H^+): 574.1936, found: 574.1920; $[\alpha]^{20}_D$ = +108 (*c* 0.4, $CHCl_3$).

3.2.9. (R,E)-3-((2′-(diphenylphosphino)-1,1′-binaphthyl-2-ylimino) methyl)-6-nitrobenzene-1,2-diol **L9**

Yield: (170 mg, 55%). A red solid. Mp: 165–167 °C; IR (CH_2Cl_2) ν 3054, 2333, 1741, 1601, 1509, 1280, 1217, 1089, 818, 745, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 6.72 (d, *J* = 8.7 Hz, 1H, Ar), 6.89–6.99 (m, 5H, Ar), 7.04–7.33 (m, 9H, Ar), 7.44–7.54 (m, 4H, Ar), 7.67 (d, *J* = 9.0 Hz, 1H, Ar), 7.97–8.03 (m, 3H, Ar), 8.15 (d, *J* = 8.4 Hz, 1H, Ar), 9.17 (s, 1H, CH=N), 15.22 (s, 1H, OH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −13.11; MS (ESI) *m/e* 619 (M^++1, 100); HRMS (ESI) Calcd. For $C_{39}H_{27}N_2O_4P$ (M + H^+): 619.1787, found: 619.1792; $[\alpha]^{20}_D$ = −221 (*c* 0.4, $CHCl_3$).

3.2.10. (R,E)-3-((2′-(diphenylphosphino)-1,1′-binaphthyl-2-ylimino)methyl)-6-nitrobenzene-1,2-dimethoxy **L10**

Yield: (30 mg, 47%). A yellow soild. Mp: 133–135 °C; IR (CH_2Cl_2) ν 2927, 1713, 1618, 1575, 1515, 1341, 1279, 1080, 961, 743, 701 cm^{-1}; 1H NMR (CDCl3, TMS, 400 MHz) δ 2.72 (s, 3H, OMe), 3.88 (s, 3H, OMe), 6.89–6.95 (m, 4H, Ar), 7.00–7.06 (m, 4H, Ar), 7.09–7.16 (m, 5H, Ar), 7.24–7.46 (m, 5H, Ar), 7.54 (d, *J* = 8.8 Hz, 1H, Ar), 7.71 (d, *J* = 8.8 Hz, 1H, Ar), 7.84–7.90 (m, 3H, Ar), 8.05 (d, *J* = 8.8 Hz, 1H, Ar), 8.48 (s, 1H, CH=N); 31P NMR (CDCl3, 121 MHz, 85% H3PO4) δ −13.42; MS (EI) *m/z* (%): 646 [M+] (13.0), 469 (48.4), 453 (40.0), 452 (48.0), 451 (100), 437 (52.4), 429 (24.9), 267 (62.8), 201 (34.1); HRMS (EI) Calcd. For C41H31N2O4P (M+): 646.2021, found: 646.2020; $[\alpha]^{20}$D = +75 (c 2.5, CHCl3).

3.2.11. (R,E)-2-((2′-(diphenylphosphino)-1,1′-binaphthyl-2-ylimino)methyl)-4-nitrobenzene-1-ol **L11**

Yield: (36 mg, 53%). A red solid. Mp: 278–280 °C; IR (CH_2Cl_2) ν 3054, 2962, 1612, 1481, 1340, 1295, 1263, 1096, 805, 743, 699 cm^{-1}; 1H NMR (CDCl3, TMS, 400 MHz) δ 6.71 (d, *J* = 9.2 Hz, 1H, Ar), 6.86–6.93 (m, 3H, Ar), 6.98 (td, *J* = 1.2, 8.0 Hz, 2H, Ar), 7.04–7.08 (m, 2H, Ar), 7.13–7.19 (m, 4H, Ar), 7.22–7.30 (m, 3H, Ar), 7.41–7.53 (m, 4H, Ar), 7.94–7.98 (m, 4H, Ar), 8.05–8.09 (m, 2H, Ar), 8.28 (s, 1H, CH=N), 12.93 (s, 1H, OH); 31P NMR (CDCl3, 121 MHz, 85% H3PO4) δ −13.79; MS (EI) *m/z* (%): 602 [M+] (26.0), 603 (10.1), 572 (8.8), 453 (5.7), 438 (33.3), 437 (100), 417 (7.3), 386 (6.1), 281 (8.6); HRMS (EI)

Calcd. For C39H27N2O4P [M+]: 602.1759, found: 602.1757; $[\alpha]^{20}D = +230$ (c 1.8, CHCl3).

3.2.12. (R,E)-3-((2′-(diphenylphosphino)-1,1′-binaphthyl-2-ylimino)methyl)-5-nitrobenzene-1,2-diol **L12**

Yield: (96 mg, 74%). A red solid. Mp: 199–201 °C; IR (CH_2Cl_2) ν 2925, 2855, 1744, 1626, 1463, 1338, 1272, 1170, 951, 844, 743, 702 cm^{-1}; 1H NMR (CDCl3, TMS, 400 MHz) δ 6.07 (br, 1H, OH), 6.92–7.01 (m, 4H, Ar), 7.04–7.08 (m, 2H, Ar), 7.19–7.21 (m, 5H, Ar), 7.26–7.32 (m, 3H, Ar), 7.45–7.56 (m, 3H, Ar), 7.57–7.59 (m, 2H, Ar), 7.64 (d, $J = 2.8$ Hz, 1H, Ar), 7.97–8.03 (m, 3H, Ar), 8.14 (d, $J = 8.8$ Hz, 1H, Ar), 8.19 (s, 1H, CH=N), 14.27 (br, 1H, OH); 31P NMR (CDCl3, 121 MHz, 85% H3PO4) δ −13.86; MS (EI) *m/z* (%): 618 [M+] (22.2), 453 (15.1), 452 (14.9), 451 (22.8), 450 (8.7), 438 (22.5), 437 (100), 268 (9.8), 44 (16.7); HRMS (EI) Calcd. For C39H27N2O4P (M+): 618.1708, found: 618.1708; $[\alpha]^{20}D = -6$ (c 0.9, CHCl3).

3.2.13. (R,E)-3-((2′-(diphenylphosphino)-1,1′-binaphthyl-2-ylimino)methyl)-5-nitrobenzene-1,2-dimethoxy **L13**

Yield: (80 mg, 56%). A yellow solid. Mp: 156–158 °C; IR (CH_2Cl_2) ν 2928, 2856, 1583, 1526, 1479, 1432, 1342, 1286, 997, 743, 701 cm^{-1}; 1H NMR (CDCl3, TMS, 400 MHz) δ 3.60 (s, 3H, CH3), 3.91 (s, 3H, CH3), 6.97–7.06 (m, 6H, Ar), 7.10–7.18 (m, 6H, Ar), 7.26–7.28 (m, 2H, Ar), 7.36–7.47 (m, 4H, Ar), 7.68 (d, $J = 2.4$ Hz, 1H, Ar), 7.83–7.93 (m, 4H, Ar), 8.04 (d, $J = 8.4$ Hz, 1H, Ar), 8.53 (s, 1H, CH=N); 31P NMR (CDCl3, 121 MHz, 85% H3PO4) δ −13.58; MS (EI) *m/z* (%): 646 [M+] (5.2), 469 (6.6), 453 (15.1), 452 (11.4), 451 (6.1), 438 (24.2), 437 (100), 268 (5.6), 267 (14.5); HRMS (EI) Calcd. For C41H31N2O4P (M +): 646.2021, found: 646.2023; $[\alpha]^{20}D = +58$ (c 1.4, CHCl3).

3.3. The preparation of complex **E** from ligand **L1** with PdCl2(PhCN)2

Ligand **L1** (57 mg, 0.1 mmol) and bis(benzonitrile)palladium dichloride (38 mg, 0.1 mmol) were dissolved in dichloromethane (1.0 mL) under an argon atmosphere and the reaction mixture 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 **E** as an orange powder. Yield (60 mg, 80%). The single crystals for X-ray diffraction were obtained by recrystallization from dichloromethane and PE (1/4). Mp: >300 °C; IR (CH_2Cl_2) ν 3216, 2928, 2856, 1810, 1662, 1506, 1436, 1274, 753 cm^{-1} ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.43 (s, 3H, CH_3), 6.41–6.53 (m, 2H, Ar), 6.73–6.85 (m, 4H, Ar), 6.97–7.10 (m, 4H, Ar), 7.31–7.36 (m, 1H, Ar), 7.46–7.74 (m, 11H, Ar), 7.80–7.85 (m, 2H, Ar), 7.91–7.98 (m, 1H, Ar), 8.07 (s, 1H, CH=N), 9.81 (s, 1H, OH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ +25.23; $[\alpha]^{20}_D = +138$ (*c* 0.25, $CHCl_3$). MS (ESI): *m/z* 1427.1 (M^+); HRMS (ESI) Calcd. for $C_{80}H_{60}Cl_2N_2O_2P_2Pd_2$: 1427.1614, Found: 1427.1619.

3.4. Typical reaction procedure

To a solution of allyl chloride palladium dimmer [Pd(η^3–C_3H_5)Cl]$_2$ (4.5 mg, 0.0125 mmol, 5 mol %) in solvent (1.0 mL) was added enantiomerically pure ligand **L1** (0.0375 mmol, 15 mol %) under an argon atmosphere, and the reaction mixture was stirred at room temperature for 30 min. A solution of 1,3-diphenylpropenyl acetate (63 mg, 0.25 mmol) in solvent (0.5 mL) was added, followed by the addition of salt (0.025 mmol, 10 mol %). The reaction solution was then stirred for a further 5 min at room temperature. Afterward, dimethyl malonate (0.09 mL, 0.75 mmol, 3 equiv) and bis(trimethylsilyl)acetamide (BSA) (0.19 mL, 0.75 mmol, 3 equiv) were added and the reaction was monitored by TLC plates until 1,3-diphenylpropenyl acetate was consumed completely. The reaction was quenched by the addition of saturated NH_4Cl aqueous solution and the product was extracted with CH_2Cl_2 (3 × 10 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 (**3a**) as a colorless solid. This is a known compound [29]. ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.52 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 3.94 (d, $J = 16.5$ Hz, 1H, CH), 4.27 (dd, $J = 8.4$, 16.8 Hz, 1H, CH), 6.32 (dd, $J = 8.4$, 15.6 Hz, 1H, = CH), 6.48 (d, $J = 15.6$ Hz, 1H, = CH), 7.19–7.33 (m, 10H, Ar). The enantiomeric excess was determined by HPLC (Chiralcel AD, eluent: *n*-hexane/*i*-propanol = 90:10), flow rate: 0.7 mL/min, retention times: 18.26 min (*R*), 26.19 min (*S*).

3.4.1. Diethyl(1,3-diphenyl-2-propen-1-yl)malonate (**3b**) colorless oil. This is a known compound [29]

^1H NMR (CDCl3, TMS, 400 MHz) δ 0.94 (t, $J = 7.2$ Hz, 3H, CH3), 1.14 (t, $J = 7.2$ Hz, 3H, CH3), 3.84 (d, $J = 10.8$ Hz, 1H, CH), 3.90 (qd, $J = 2.0$, 7.2 Hz, 2H, CH2), 4.10 (q, $J = 7.2$ Hz, 2H, CH2), 4.19 (dd, $J = 8.4$, 10.8 Hz, 1H, CH), 6.26 (dd, $J = 8.4$, 15.6 Hz, 1H, = CH), 6.40 (d, $J = 15.6$ Hz, 1H, = CH), 7.12–7.25 (m, 10H, Ar). The enantiomeric excess was determined by HPLC (Chiralcel AD, eluent: n-hexane/i-propanol = 90:10), flow rate: 0.7 mL/min, retention times: 13.07 min (*R*), 17.40 min (*S*).

3.4.2. (E)-Dimethyl(1,3-bis(4-chlorophenyl)-2-propen-1-yl) malonate (**3c**) colorless oil. This is a known compound [30]

^1H NMR (CDCl3, TMS, 400 MHz) δ 3.54 (s, 3H, CH3), 3.70 (s, 3H, CH3), 3.90 (d, $J = 10.4$ Hz, 1H, CH), 4.24 (dd, $J = 8.4$, 10.4 Hz, 1H, CH), 6.27 (dd, $J = 8.4$, 15.6 Hz, 1H, = CH), 6.41 (d, $J = 15.6$ Hz, 1H, = CH), 7.21–7.30 (m, 8H, Ar). The enantiomeric excess was determined by HPLC (Chiralcel AD, eluent: n-hexane/i-propanol = 85:15), flow rate: 0.8 mL/min, retention times: 15.60 min (*R*), 24.25 min (*S*).

3.4.3. (E)-N-benzyl-1,3-diphenylprop-2-en-1-amine (**3d**) yellow oil. This is a known compound [29]

^1H NMR (CDCl3, TMS, 400 MHz) δ 3.76 (d, $J = 13.2$ Hz, 1H, CH), 3.81 (d, $J = 13.2$ Hz, 1H, CH), 4.40 (d, $J = 7.2$ Hz, 1H, CH), 6.32 (dd, $J = 7.2$, 15.6 Hz, 1H, = CH), 6.58 (d, $J = 15.6$ Hz, 1H, = CH), 7.19–7.44 (m, 15H, Ar). The enantiomeric excess was determined by HPLC (Chiralcel AD, eluent: n-hexane/i-propanol = 199:1), flow rate: 0.5 mL/min, retention times: 41.03 min (*R*), 47.23 min (*S*).

3.4.4. (E)-4-(1,3-Diphenylallyl)morpholine (**3e**) pale siold. This is a known compound [29]

^1H NMR (CDCl3, TMS, 400 MHz) δ 2.36–2.41 (m, 2H, CH2), 2.53 (br, 2H, CH2), 3.69–3.71 (m, 4H, CH2), 3.78 (d, $J = 9.2$ Hz, 1H, CH), 6.28 (dd, $J = 9.2$, 16.0 Hz, 1H, = CH), 6.56 (d, $J = 16.0$ Hz, 1H, = CH), 7.18–7.41 (m, 10H, Ar). The enantiomeric excess was determined by HPLC (Chiralcel OD, eluent: n-hexane/i-propanol = 90:10), flow rate: 1.0 mL/min, retention times: 6.36 min (*R*), 13.54 min (*S*).

4. Conclusions

In conclusion, chiral phosphine-imine type ligand **L9** prepared from (*R*)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-amine was found to be a fairly effective chiral ligand for Pd(II)-catalyzed asymmetric allylic alkylation to give the corresponding product in moderate enantioselectivity and moderate yield under mild conditions. In the mean time, its bidentate coordination pattern to the Pd metal center with both P and N atoms has been unambiguously established by X-ray diffraction. The result will promote us to design and synthesize more new effective chiral

phosphine-imine type ligands for asymmetric reactions. Efforts are underway to elucidate the mechanistic details of this asymmetric allylic alkylation.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.04.036.

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