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Axially chiral P,S-heterodonor ligands with a binaphthalene framework for palladium-catalyzed asymmetric allylic substitutions: experimental investigation on the reversal of enantioselectivity between different alkyl groups on sulfur atom

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Abstract—The enantioselectivity in the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate using axially chiral P,S-heterodonor ligands BINAPS with different alkyl groups on sulfur atom has been investigated. Their bidentate coordination patterns to a Pd metal center with both P and S atoms have been unambiguously disclosed by X-ray diffraction. The reaction mechanism and the investigation on the reversal of enantioselectivity between different alkyl groups on sulfur atom have been discussed on the basis of the X-ray crystal structure and NMR spectroscopic data.

1. Introduction

Chiral C_2-symmetric ligand 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) **A**[1] and C_1-symmetric ligand 2-(diphenylphosphino)-1,1′-binaphthyl (MOP) **B** (X = OMe)[2] 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 **B** where X is a different heteroatom (X = NMe_2, SMe, $AsPh_2$, $P(O)Ph_2$, $P(S)Ph_2$, PAr_2),[3] phosphane–phosphite ligand BINAPHOS **C**,[4] and phosphine–pyridine ligand **D**,[5] 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 $CH_2(CO_2Me)_2$ in the presence of a base, which has become a famous asymmetric C–C bonding formation reaction.[6] So far, it is already known that MOP or MAP (X = NMe_2) ligands actually act as a monophosphine or P,C-bidentate ligand in a Pd(0)-catalyzed asymmetric allylic substitution.[7] Thus, it is interesting to know the coordination fashion of an axially chiral P,S-heterodonor ligand (**B**, X = SMe, BINAPS) to a Pd metal center. Previously, Kang et al. and Gladiali et al. independently reported BINAPS ligands **L1** and **L2** in the asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with $CH_2(CO_2Me)_2$ to achieve 91% and 60% ee, respectively.[8] Moreover, Gladiali et al. suggested that the BINAPS **L1** would be a bidentate ligand in this Pd-catalyzed asymmetric C–C bond forming reaction, namely, both sulfur and phosphorus atoms coordinate to the Pd metal center, on the basis of the ^{1}H NMR and ^{31}P NMR spectroscopic investigations.[8b] Herein, we report the further details of the investigation on this type of P,S-heterodonor ligands in the asymmetric allylic substitution of 1,3-diphenylpropenyl acetate on the basis of the X-ray crystal structure diffraction and NMR spectroscopic data. We found that BINAPS **L1**, **L2**, **L3**, and **L4** (Fig. 1) produced the allylic substitution products with opposite absolute configurations. The reaction mechanism and the reversal of enantioselectivity between different alkyl groups on a sulfur atom have been discussed on the basis of the X-ray crystal structures and NMR spectroscopic data.

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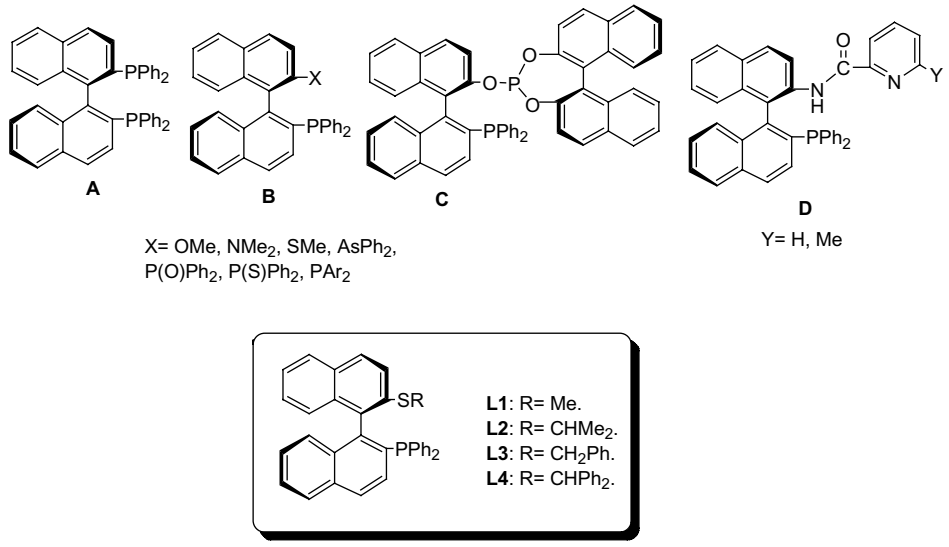


Figure 1. The structure of C_2-symmetric BINAP and C_1-symmetric binaphthyl P,X-heterodonor ligand.

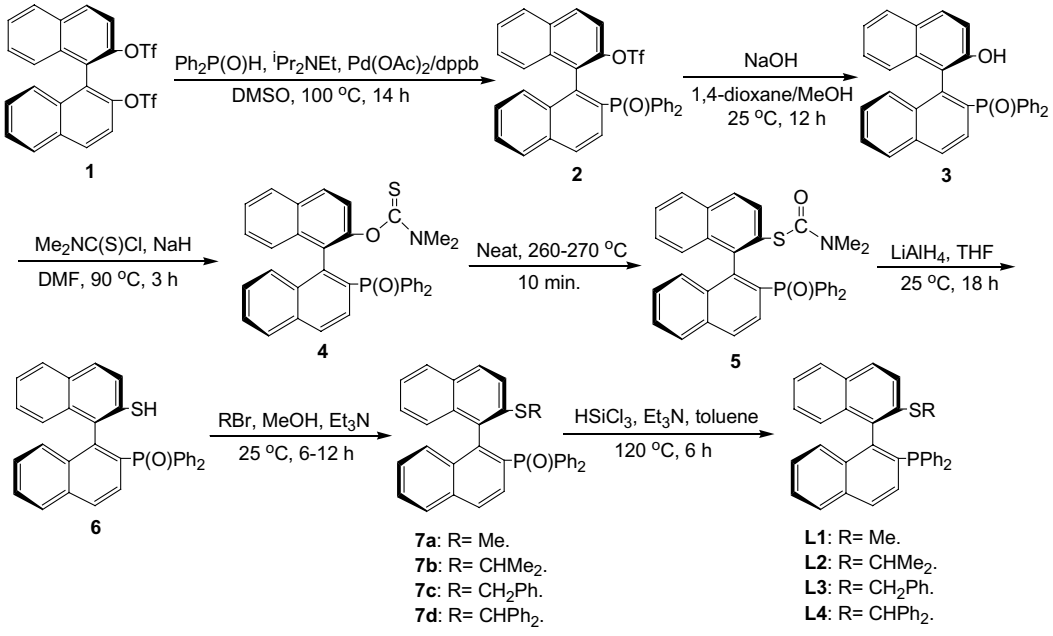
2. Results and discussion

2.1. Synthesis of ligands L1–L4

The axially chiral P,S-heterodonor ligands **L1**–**L4** were prepared according to the previously reported procedure (Scheme 1).[8b]

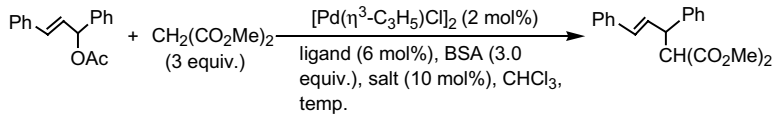
2.2. Palladium-catalyzed allylic alkylation

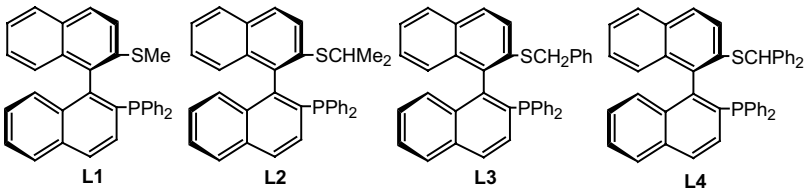
The obtained ligands **L1**–**L4** were used in the asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate in the presence of an organic base [bis(trimethylsilyl)acetamide: BSA]. The reaction was carried out in $CHCl_3$ or THF with a molar ratio of palladium catalyst:ligand:additive (salt):1,3-diphenylpropenyl acetate:$CH_2(CO_2Me)_2$:BSA of 0.02:0.06:0.1:1:3:3. The ee of the product was determined by chiral HPLC analysis using a chiral stationary phase column (CHIRALCEL OD).[9] The absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation. The results are summarized in Table 1. Using **L1** or **L2** as a ligand in $CHCl_3$, the obtained ees and chemical yields are very similar as those reported previously.[8] The presence of salts, such as Bu_4NX (X = Cl, Br) or KOAc improved the chemical yields of the allylic alkylation product, but in general did not significantly alter the



Scheme 1. The preparation of chiral P,S-heterodonor ligands **L1**–**L4**.

Table 1. The effects of salt and temperature on allylic alkylation by (*S*)-alkyl BINAPS ligands





Entry	Ligand	Salt	Temp (°C)	Time (h)	Yield[a] (%)	Ee[b] (%)	Absolute configuration[c]
1	**L1**	—[d]	10	16	78	75	*S*
2	**L1**	Bu_4NCl	10	11.5	86	77	*S*
3	**L1**	Bu_4NBr	10	20	95	75	*S*
4	**L1**	Bu_4NI	10	11.5	53	77	*S*
5	**L1**	KOAc	10	11.5	89	75	*S*
6	**L1**	Bu_4NCl	0	17	59	78	*S*
7	**L1**	Bu_4NCl	−20	17	58	82	*S*
8	**L1**	Bu_4NCl	−78	168	NR[e]	—	—
9	**L1**	LiOAc	10	11.5	96	96	*S*
10	**L2**	Bu_4NCl	10	24	95	65	*R*
11	**L2**	KOAc	10	24	95	72	*R*
12	**L2**	LiOAc	10	24	95	7	*R*
13	**L3**	Bu_4NCl	10	24	94	44	*S*
14	**L3**	LiOAc	10	24	90	77	*S*
15	**L4**	LiOAc[f]	−20	26	68	33	*R*

[a] Isolated yields.
[b] Determined by HPLC.
[c] The absolute configuration was determined by comparing the sign of specific rotation with authentic sample reported in the previous literature.
[d] No salt was added.
[e] No reaction took place.
[f] THF was used as a solvent.

ees in this reaction (Table 1, entries 1–3, 5).[10,11] In addition, Bu_4NI showed no improvement for this reaction (Table 1, entry 4). At lower reaction temperatures, we found that the ees of the reaction product was slightly improved but at the expense of the chemical yields (Table 1, entries 6 and 7). At −78 °C, no reaction occurred (Table 3, entry 8). Recently, Furukawa and co-workers disclosed that using BSA as a base in the presence of lithium acetate (LiOAc) in this reaction, the enantioselectivity of the reaction product in the palladium-catalyzed asymmetric reaction could be greatly improved.[12] On the basis of this result, we examined the effect of lithium acetate in this reaction using **L1** as a ligand and found that the achieved ee reached 96% under identical conditions (Table 1, entry 9). However, using **L2** as a ligand under similar conditions, we obtained the product in 65% and 72% ee in the presence of Bu_4NCl and KOAc, respectively, and a lower ee (7%) in the presence of LiOAc (Table 1, entries 10–12). This result suggests that LiOAc is not suitable for all ligands in this reaction. We unexpectedly found that chiral ligands **L1** and **L2** produced the allylic substitution products with opposite absolute configurations (Table 1, entries 1–8 and 10–12). This phenomenon has not been realized before.[8] Using **L3** or **L4** as a chiral ligand in this reaction, the same phenomenon was observed, but in relatively low ee (44% or 77% and 33% ee, respectively) (Table 1, entries 13–15). Therefore, it is necessary to clarify the mechanistic details of this reversal of enantioselectivity between chiral ligands **L1**, **L3** and **L2**, **L4**.

Table 2. Selected bond lengths and bond angles for complex **E**

	Bond length (Å)		Bond angle (deg)
Pd–P	2.258 (2)	P–Pd–S	89.83 (8)
Pd–S	2.298 (2)	P–Pd–Cl (2)	85.90 (8)
Pd–Cl (2)	2.305 (2)	S–Pd–Cl (1)	93.44 (8)
Pd–Cl (1)	2.350 (2)	Cl (2)–Pd–Cl (1)	90.93 (8)

Table 3. Selected bond lengths and bond angles for complex **G**

	Bond length (Å)		Bond angle (deg)
Pd–P	2.360 (3)	P–Pd–S	90.61 (11)
Pd–S	2.379 (3)	C (44)–Pd–C (42)	66.9 (5)
Pd–C (42)	2.311 (12)	C (44)–Pd–P	98.6 (3)
Pd–C (43)	2.153 (11)	C (42)–Pd–S	103.1 (4)
Pd–C (44)	2.289 (12)		

2.3. Mechanistic considerations

The coordination patterns of **L1**–**L4** with a Pd metal center were determined by NMR spectroscopic investigation of the ligand–metal complexes and X-ray crystallographic analysis. The complexes **E** and **F** were prepared from the reaction of **L1** and **L2** with $Pd(PhCN)_2Cl_2$[13] in CH_2Cl_2, respectively. ^1H NMR and ^{31}P NMR spectroscopic studies on complex **E** [(**L1**)$PdCl_2$] in $CDCl_3$ showed significant chemical shifts of (*S*)-methyl and phosphorus atom when compared with **L1** (Scheme 2). Similar chemical shifts of (*S*)-isopropyl and a phosphorus atom on complex **F** [(**L2**)$PdCl_2$] in $CDCl_3$ were also observed when compared with **L2** (Scheme 2).

The X-ray diffraction analysis of a single crystal of complex **E** obtained by recrystallization from CH_2Cl_2/toluene (1/4) gave the structure shown in Figure 2 (ORTEP draw).[14] As can be seen from Figure 2, axially chiral P,S-heterodonor ligand **L1** is a P,S-bidentate ligand to Pd metal center in this catalytic reaction system. In this structure, the palladium atom shows a distorted-square-planar coordination, bonded to sulfur, phosphorus, and two chloride atoms (Table 2). The bond distances of Pd–S and Pd–P are 2.298 and 2.258 Å, respectively, which are with in the normal region.[15] The stronger *trans* influence[16] of the phosphine (vs the thioether group) is reflected in the difference in Pd–Cl bond distances *trans* to the phosphorus atom (2.350 Å) and *trans* to the sulfur atom (2.305 Å). For complex **E**, the metallacycle takes a boat-like seven-membered configuration.

2.4. Palladium allylic complexes and NMR spectroscopic studies

Ionic palladium complexes containing the 1,3-diphenylallyl group were prepared from the corresponding [(1,3-diphenylpropenyl)$PdCl]_2$[17] and the appropriate chiral ligand **L1** or **L2** in the presence of silver hexafluoroantimonate ($AgSbF_6$). These compounds were obtained as monometallic complexes of the general formula [Pd(**L**)(1,3-diphenylpropenyl)](SbF_6), where **L** acted as a P,S-bidentate ligand. Crystals suitable complex **G** for X-ray diffraction were obtained after recrystallization from CH_2Cl_2/toluene (1/4). A view of the allylic cation and the most representative parameters of the structure are reported in Figure 3 and Table 3.[18]

The structure shows that the diphenylallyl group adopts a *syn*/*syn* configuration and that the phenyl groups of the allylic ligand and the naphthyl groups of the ligand are located at the opposite side of the coordination plane as shown in Figure 3. The bond lengths are within the normal region, but the Pd–P bond is longer than reported for similar complexes with P,S-ligands.[15] Furthermore, the longer Pd–C bond *trans* to the phosphorus atom (Pd–C_{42} = 2.311 Å) when compared to the Pd–C bond *trans* to sulfur atom (Pd–C_{44} = 2.289 Å) reflects the stronger *trans* influence of the phosphine ligand and a more electrophilic π-allyl terminus at C_{42}.[19] Based on the orientation of the π-allyl moiety in the crystal structure, the observed stereochemical outcome of the reaction can be rationalized by envisioning a nucleophilic addition *trans* to the phosphine ligand. Although the X-ray structure of complex **G**

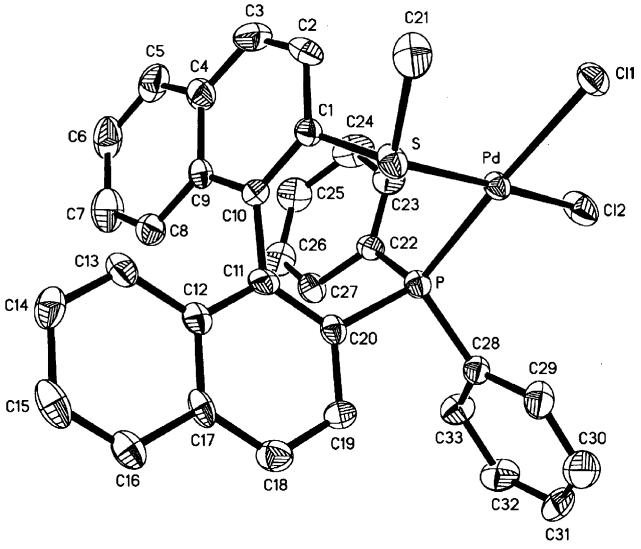
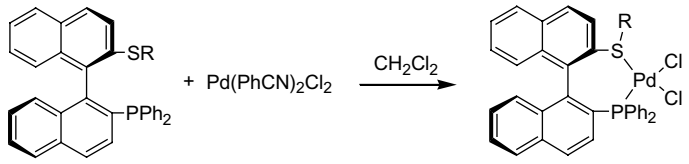


Figure 2. The ORTEP draw of complex **E**.



L1: R = CH_3

^1H NMR ($CDCl_3$, TMS) δ 2.31 (SC*H*$_3$).
^{31}P NMR ($CDCl_3$, 85% H_3PO_4) δ -13.07.

complex **E**: R = CH_3

^1H NMR ($CDCl_3$, TMS) δ 2.92 (SC*H*$_3$).
^{31}P NMR ($CDCl_3$, 85% H_3PO_4) δ +27.52.

L2: R = $CH(CH_3)_2$

^1H NMR ($CDCl_3$, TMS) δ 3.58 (SC*H*$(CH_3)_2$).
^{31}P NMR ($CDCl_3$, 85% H_3PO_4) δ -13.49 .

complex **F**: R = $CH(CH_3)_2$

^1H NMR ($CDCl_3$, TMS) δ 4.67 (SC*H*$(CH_3)_2$).
^{31}P NMR ($CDCl_3$, 85% H_3PO_4) δ +28.20.

Scheme 2. ^1H NMR and ^{31}P NMR analyses of **L1**/**L2** and complexes **E**/**F**.

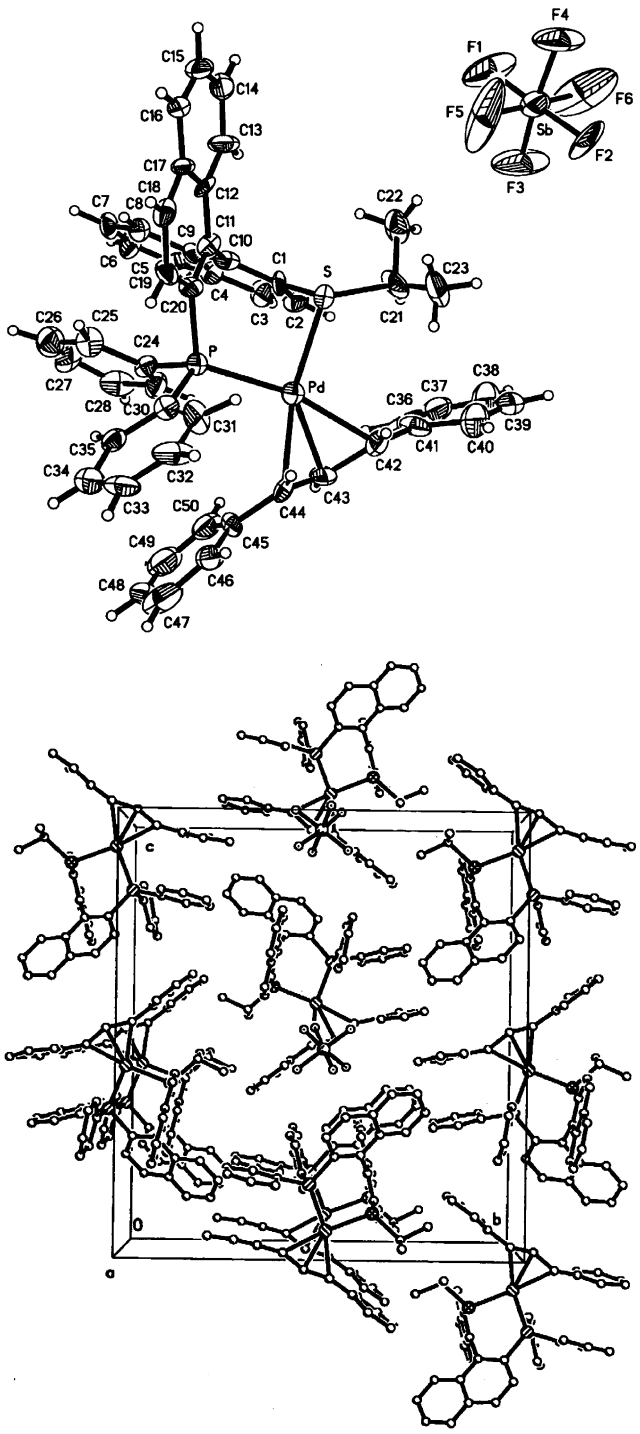


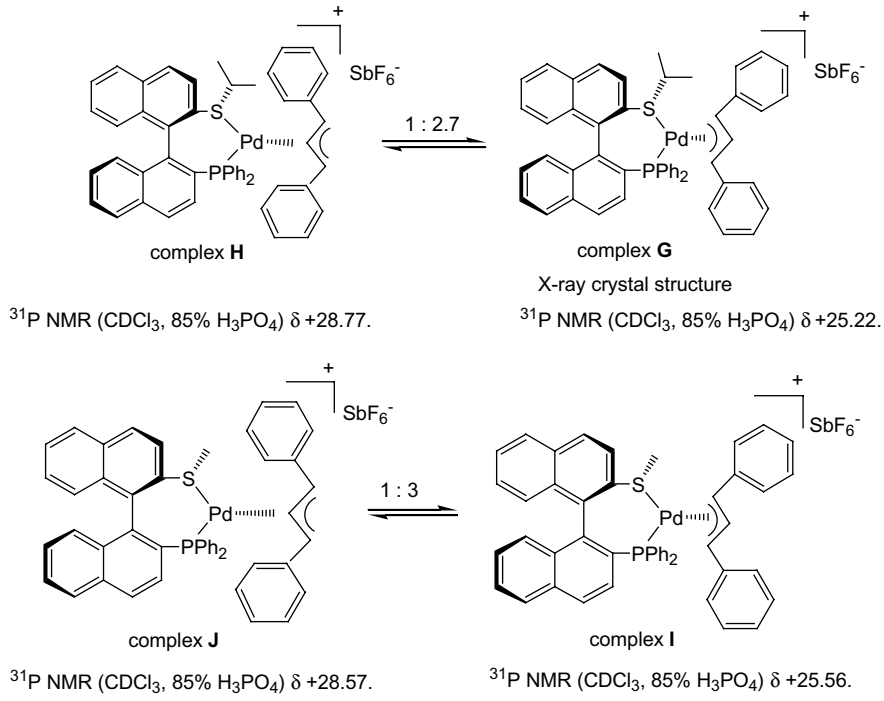
Figure 3. The ORTEP draw of complex **G** [Pd(**L2**)(1,3-diphenylpropenyl)](SbF_6).

shows only one diastereomeric π-allyl complex, it is well known that palladium π-allyl isomerization is a facile process in solution.[20] ^{1}H NMR and ^{31}P NMR studies of complex **G** derived from **L2** with [(1,3-diphenylpropenyl)PdCl]$_2$ in the presence of silver hexafluoroantimonate ($AgSbF_6$) in $CDCl_3$ showed a 2.7:1 mixtures of diastereomeric complexes in a rapid equilibrium with complex **H** (Scheme 3). Similarly, ^{1}H NMR and ^{31}P NMR studies of complex **I** derived from **L1** with [(1,3-diphenylpropenyl)PdCl]$_2$ in the presence of silver hexafluoroantimonate ($AgSbF_6$) in $CDCl_3$ indicated a 3:1 mixture of diastereomeric complexes in a rapid equilibrium with complex **J**.

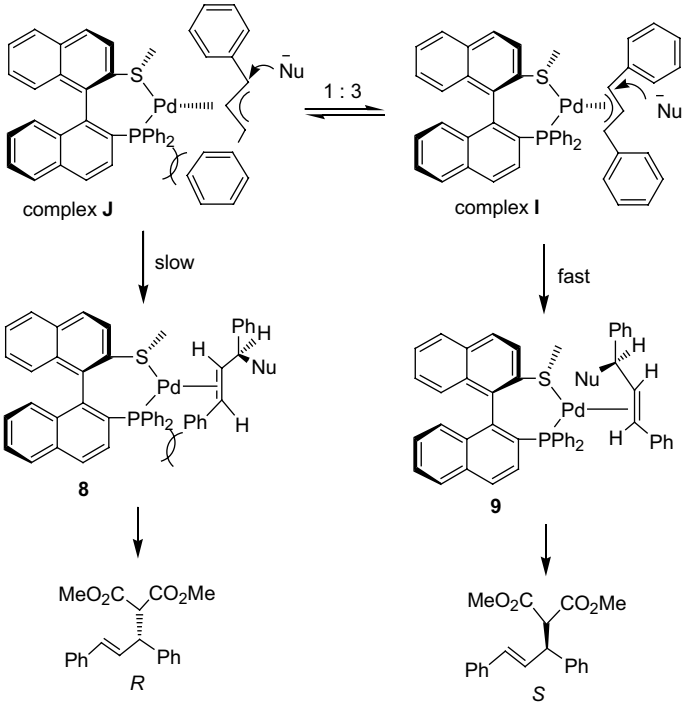
2.5. Explanation on the reversal of enantioselectivity

According to the X-ray structure and the proposed model by Evans et al. in a mixed phosphorus/sulfur ligand,[15] the mechanistic explanation of the opposite configuration between ligands **L1** and **L2** are shown in Schemes 4 and 5, respectively. Evans et al. has suggested that the greater π-accepting ability of the phosphinite when compared to the thioether supports the nucleophilic substitution *trans* to the phosphorus atom. The NMR spectroscopic data and X-ray structure suggest that the achieved ee and the opposite absolute configuration for this reaction by **L1** and **L2** are the results of a Curtin–Hammett condition in which the nucleophilic addition *trans* to phosphorus atom proceeds faster in the major diastereomeric π-allyl complex **I**.[21] In π-allyl complex **J**, the non-bonding interaction between the phenyl group on the phosphorus atom and the proximal phenyl substituent on the π-allyl moiety is larger than that between (*S*)-methyl substituent on the ligand and the proximal phenyl substituent on the π-allyl moiety. Upon nucleophilic addition, this strain still occurs, affording the staggered palladium–olefin complex **8**. However, the major diastereomeric intermediate **I**, upon nucleophilic addition, formed the less steric strain olefinic complex **9** (Scheme 4). Therefore, the formation of (*S*)-configuration enriched product is favored and is a faster reaction process. This is the result of the major π-allyl diastereomeric intermediate producing the major product enantiomer in the allylic substitution of aromatic substrates.[22]

On the other hand, in the case of ligand **L2**, the (*S*)-isopropyl group is a more sterically hindered bulky group than the (*S*)-methyl group in ligand **L1** controlling the nucleophilic addition process. In fact, Togni et al.[10e] has similarly reported in the allylic amination that the configuration of the π-allylpalladium intermediate can effectively be controlled by the steric nature of the ligand. The π-allyl complex **G**, which is a major diastereoisomer in solution and its structure, which was determined by X-ray diffraction, is more stable in any sense. In reaction solution, the transformation of complex **G** to complex **H** occurs, which has been observed by ^{31}P NMR spectroscopic analysis.[23] The steric strain was developed upon nucleophilic addition to complex **G** to form the olefinic complex **11** (Scheme 5). Therefore, the π-allylpalladium complex **G** is less reactive in this reaction. In the minor diastereomeric complex **H**, the non-bonding interaction between the (*S*)-isopropyl substituent on ligand **L2** and the proximal phenyl substituent on the π-allyl moiety is larger than that between the phenyl group on the phosphorus and the proximal phenyl substituent on the π-allyl moiety. Upon nucleophilic addition, this strain is released, to afford palladium–olefin complex **10**. Thus, the product is given in an (*R*-enriched configuration. The driving force is the formation of a less sterically strained complex **10** (Scheme 5). This result is in contrast to that described

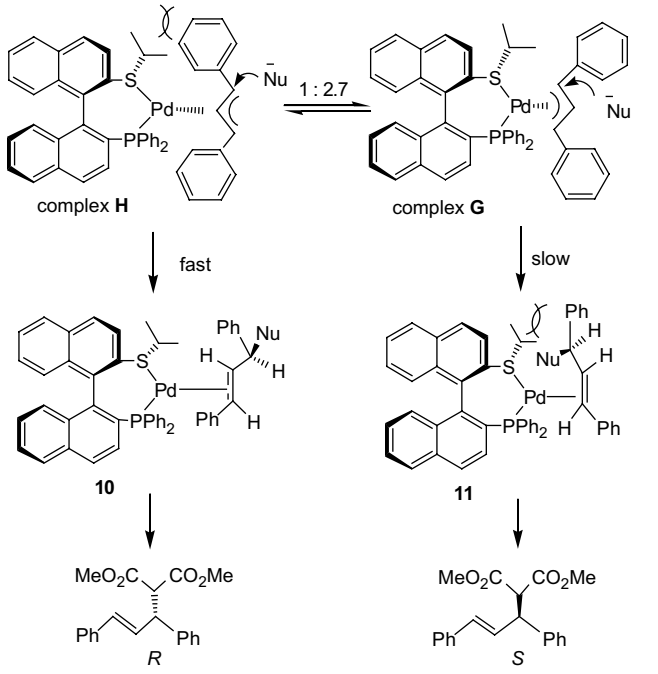


Scheme 3. ^{31}P NMR studies of complexes **L1** and **L2** with [(1,3-diphenylpropenyl)PdCl]$_2$.



Scheme 4. Proposed model for allylic substitution in the presence of chiral ligand **L1**.

in the case of ligand **L1**, that is, the minor diastereomeric π-allyl complex is more reactive. The above-proposed mechanism can also explain the different ee value by using LiOAc as an additive with **L1** and **L2** (Table 1, entries 9 and 12). The lithium cation chelates to the sulfur atom of **L1** and oxygen atom of the dimethyl malonate anion to stabilize the transition state of the intermediate **9**. However, this chelation is difficult to form in the case of intermediate **11** because of the steric hindrance of the (*S*)-isopropyl group, leading to



Scheme 5. Proposed model for allylic substitution in the presence of chiral ligand **L2**.

low ee in this reaction. It is also well known that the cation (K^+, Li^+, Bu_4N^+) acts differently in this reaction because of the steric nature of the employed ligands.[24]

Herein, we observed an interesting reversal of the absolute configuration in the asymmetric allylic alkylation by changing the steric bulkiness of the (*S*)-alkyl group in the P,S-heterodonor ligands **L1**, **L3** and **L2**, **L4** having the same axially chiral binaphthalene framework.

3. Conclusion

Palladium catalytic system with ligands chiral ligands **L1**–**L4** has been tested in the allylic alkylation of 1,3-diphenylpropenyl acetate using dimethyl malonate as the nucleophile. We have found that these axially chiral P,S-heterodonor ligands **L1** and **L2** gave the corresponding reaction products in the opposite absolute configuration with 96% and 72% ee in good yields in the presence of LiOAc and KOAc, respectively. A similar phenomenon appears between chiral ligands **L3** and **L4**. Their bidentate coordination patterns to the Pd metal center with both P and S atoms have been unambiguously disclosed by X-ray diffraction and NMR spectroscopic data. In addition, the X-ray crystallographic analysis and NMR spectroscopic studied indicate that the metallacycle is a pseudo-boat-seven-membered arrangement, in which the alkyl group on the sulfur atom acts as a key effect in forming the reversal of the enantioselectivity. We have determined that the steric bulkiness of (*S*)-alkyl group in BINAPS is sufficient enough to control the orientation of the nucleophilic attacks to give the product with a different absolute configuration. Based on these results, we are currently planning to utilize these axially chiral C_1-symmetric P,S-heterodonor ligands in other asymmetric catalysis and synthesize further such types of ligands in order to seek out more effective and stereoselective chiral ligands in catalytic asymmetric reactions. Work along this line is currently in progress.

4. Experimental

4.1. General

Melting points were obtained with a micromelting point apparatus and are uncorrected. Optical rotations were determined in a solution of $CHCl_3$ at 20 °C; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Infra-red spectra were measured on a spectrometer. ^{1}H NMR spectra were recorded for a solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. ^{31}P NMR spectra were recorded at 121 MHz for a solution in $CDCl_3$ with 85% H_3PO_4 as the external reference. *J*-values are in hertz. Mass spectra were recorded with an HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. The organic solvents used, were dried by standard methods when necessary. All solid compounds reported herein gave satisfactory CHN microanalyses and HRMS values. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC. Flash column chromatography was carried out using silica gel at increased pressure. All alkylation and amination experiments were performed under an argon atmosphere using standard Schlenk techniques. The enantiomeric excesses of 1,3-diphenyl-1-(2-dimethylmalonyl)prop-2-ene and 1,3-diphenyl-1-(2-benzylamine)prop-2-ene were determined by chiral HPLC analyses and the absolute configuration of the major enantiomer assigned according to the sign of the specific rotation. (*R*)-(+)-1,1′-bi-2-naphthol was purchased from Aldrich Co.

Compounds **1**–**6** were prepared in the same manner as those described in the literature.[2b,8b]

4.1.1. (*R*)-2,2′-Bis(trifluoromethanesulfonyl)oxy-1,1′-binaphthyl 1. This is an already known compound.[2b] ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 7.24–8.16 (m, 12H, Ar).

4.1.2. (*R*)-(+)-2-(Diphenylphosphinyl)-2′-[(trifluoromethanesulfonyl)oxy]-1,1′-binaphthyl 2. This is an already known compound.[2b] ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 6.98–8.02 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = 29.60.

4.1.3. (*R*)-(−)-2-(Diphenylphosphinyl)-2′-hydroxybinaphthyl 3. This is an already known compound.[2b] ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 6.41–7.95 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = 31.97.

4.1.4. (*R*)-(−)-2-(Diphenylphosphinyl)-1,1′-binaphthyl-2′-ol-*N*,*N*-dimethylthiocarbamate 4. This is an already known compound.[8b] $[\alpha]_D^{20} = -142.8$ (*c* 1.155, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.97 (s, 3H,

CH_3), 3.05 (s, 3H, CH_3), 6.83–8.05 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): $\delta = 27.80$.

4.1.5. (*R*)-(+)-2-(Diphenylphosphinyl)-1,1′-binaphthyl-2′-thiol-*N*,*N*-dimethylthiocarbamate 5. This is an already known compound.[8b] $[\alpha]_D^{20} = +11.3$ (*c* 1.05, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 2.75$ (s, 6H, $2CH_3$), 6.80–8.10 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): $\delta = 29.43$.

4.1.6. (*R*)-(+)-2-(Diphenylphosphinyl)-1,1′-binaphthyl-2′-thiol 6. This is an already known compound.[8b] $[\alpha]_D^{20} = +79.9$ (*c* 1.125, $CHCl_3$), ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 3.48$ (s, 1H, SH), 6.82–8.04 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): $\delta = 28.88$.

4.2. Representative experimental details for the synthesis of compounds 7a–d

Compound (*R*)-(+)-2-(diphenylphosphinoyl)-2′-methylsulfanyl-1,1′-binaphthalenyl **7a** was prepared from **6** as the similar procedure described in the literature:[8b] To a solution of (*R*)-(+)-2-(diphenylphosphinyl)-1,1′-binaphthyl-2′-thiol **6** (900 mg, 1.85 mmol) in methanol (10 mL), Et_3N (6 mL) with methyl iodide (0.12 mL, 2 mmol) was added. The reaction mixture was stirred for 5 h at room temperature. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 (10 mL). The organic phase was washed with water (3×10 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give a crude product, which was purified by a flash chromatography (eluent: PE/EtOAc = 2/1) to give **7a** as a white solid: 757 mg, 82% yield. $[\alpha]_D^{20} = +138.1$ (*c* 0.605, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 2.29$ (s, 3H, CH_3), 6.86–8.02 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): $\delta = 29.39$.

4.2.1. (*R*)-(+)-2-(Diphenylphosphinoyl)-2′-isopropylsulfanyl-1,1′-binaphthalenyl 7b. This compound was prepared in a similar way to that described above to give a white solid, 92% yield; $[\alpha]_D^{20} = +124.4$ (*c* 1.105, $CHCl_3$), {lit.:[8b] $[\alpha]_D^{20} = -117.8$ (*c* 0.5, $CHCl_3$) for (*S*)-enantiomer}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 1.08$ (d, $J = 6.3$ Hz, 3H, CH_3), 1.16 (d, $J = 6.6$ Hz, 3H, CH_3), 3.43 (m, 1H, CH), 6.83–8.03 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): $\delta = 29.93$.

4.2.2. (*R*)-(+)-2-(Diphenylphosphinoyl)-2′-benzylsulfanyl-1,1′-binaphthalenyl 7c. This compound was prepared in a similar way to that described above. A white solid, 93% yield; mp: 86–87 °C; $[\alpha]_D^{20} = +87.2$ (*c* 1.01, $CHCl_3$); IR (CH_2Cl_2): $\nu = 2685, 2306, 1437, 1422, 1163, 896, 540, 524, 405\ cm^{-1}$; ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 4.01$ (dd, $J = 12.9, 13.2$ Hz, 2H, CH_2), 6.84–8.01 (m, 27H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): $\delta = 29.40$; MS (EI): *m/e* 576 (M^+, 12.96), 453 (100), 374 (41.17), 282 (28.69), 268 (38.24), 201 (65.91); HRMS (EI) calcd for $C_{39}H_{29}OPS$ requires: 576.1677, found: 576.1675.

4.2.3. (*R*)-(+)-2-(Diphenylphosphinoyl)-2′-benzhydrylsulfanyl-1,1′-binaphthalenyl 7d. This compound was prepared in a similar way to that described above. A white solid, 45% yield; mp: 119–120 °C; $[\alpha]_D^{20} = +42.7$ (*c* 1.1, $CHCl_3$); IR (CH_2Cl_2): $\nu = 1422, 1163, 896\ cm^{-1}$; ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 5.52$ (s, 1H, CH), 6.80–8.02 (m, 32H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): $\delta = 30.11$; MS (EI): *m/e* 652 (M^+, 12.57), 485 (30.68), 453 (18.26), 282 (21.22), 201 (100), 167 (77.42); HRMS (ESI) calcd for $C_{48}H_{33}OPSNa$ (M^++Na) requires: 675.1852, found: 675.1882.

4.3. Representative experimental details for the synthesis of ligands L1–L4

4.3.1. (*R*)-(+)-2-(Diphenylphosphanyl)-2′-methylsulfanyl-1,1′-binaphthalenyl L1. This compound was prepared from **7a** as described in the literature.[8b] A solution of (*R*)-(+)-2-(diphenylphosphinoyl)-2′-methylsulfanyl-1,1′-binaphthalenyl **7a** (500 mg, 1.0 mmol) in toluene (10 mL) containing Et_3N (8.4 mL) was stirred at 0 °C. $HSiCl_3$ (0.85 mL, 6.2 mmol) was added and the reaction mixture stirred at 120 °C for 6 h. After cooling to room temperature, 10% HCl (10 mL) was added and the organic phase separated. The aqueous layer was extracted with ether (3×20 mL), the combined organic phase dried over anhydrous Na_2SO_4, and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography (eluent: PE/EtOAc = 10/1) to give **L1** as a white solid. 430 mg, 89% yield. $[\alpha]_D^{20} = +49.8$ (*c* 0.535, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 2.31$ (s, 3H, CH_3), 6.68–7.99 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): $\delta = -13.07$.

4.3.2. (*R*)-(+)-2-(Diphenylphosphanyl)-2′-isopropylsulfanyl-1,1′-binaphthalenyl L2. This compound was prepared from (*R*)-(+)-2-(diphenylphosphinoyl)-2′-isopropylsulfanyl-1,1′-binaphthalenyl **7b** in a similar way to that described above. A white solid, 68% yield; $[\alpha]_D^{20} = +84.1$ (*c* 0.53, $CHCl_3$), [lit.:[8b] $[\alpha]_D^{20} = -81.2$ (*c* 0.5, $CHCl_3$) for (*S*)-enantiomer]; ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 1.07$ (d, $J = 7.2$ Hz, 3H, CH_3), 1.18 (d, $J = 6.3$ Hz, 3H, CH_3), 3.58 (m, 1H, CH), 6.65–7.95 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): $\delta = -13.49$.

4.3.3. (*R*)-(+)-2-(Diphenylphosphanyl)-2′-benzylsulfanyl-1,1′-binaphthalenyl L3. This compound was prepared from (*R*)-(+)-2-(diphenylphosphinoyl)-2′-benzylsulfanyl-1,1′-binaphthalenyl **7c** in a similar way to that described above. A white solid, 49% yield; mp: 83–84 °C, $[\alpha]_D^{20} = +54.2$ (*c* 0.55, $CHCl_3$); IR (CH_2Cl_2): $\nu = 2306, 1436, 896, 422, 414\ cm^{-1}$; ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 4.05$ (dd, $J = 13.2, 13.2$ Hz, 2H, CH_2), 6.66–7.92 (m, 27H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): $\delta = 37.84, 124.93, 125.30, 126.26, 126.46, 126.72$ (d, $J_{C-P} = 2.7$ Hz), 126.86, 127.14, 127.30, 128.06 (d, $J_{C-P} = 1.3$ Hz), 128.26, 128.42, 128.44 (d, $J_{C-P} = 8.0$ Hz), 128.54 (d, $J_{C-P} = 8.0$ Hz), 128.60, 128.66 (d, $J_{C-P} = 24.8$ Hz), 129.22, 130.90 (d, $J_{C-P} = 18.0$ Hz), 131.43, 132.74 (d, $J_{C-P} = 7.6$ Hz), 133.28 (d, $J_{C-P} = 18.0$ Hz), 133.86 (d, $J_{C-P} = 2.7$ Hz), 134.17 (d, $J_{C-P} = 20.8$ Hz), 135.42 (d, $J_{C-P} = 3.0$ Hz), 136.35 (d, $J_{C-P} = 10.4$ Hz),

137.29 (d, J_{C-P} = 7.9 Hz), 138.55 (d, J_{C-P} = 12.4 Hz), 143.73, 144.19; ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = −13.42; MS (EI): *m/e* 561 (M^++1, 1.68), 469 (100), 437 (45.96), 282 (12.54), 183 (12.07); HRMS (EI) calcd for $C_{39}H_{29}PS$ requires: 560.1728, found: 560.1777.

4.3.4. (*R*)-(+)-2-(Diphenylphosphanyl)-2′-benzhydrylsulfanyl-1,1′-binaphthalenyl L4. This compound was prepared from (*R*)-(+)-2-(diphenylphosphinoyl)-2′-benzhydrylsulfanyl-1,1′-binaphthalenyl **7d** in a similar way to that described above. A white solid, 39% yield. This compound is very sensitive to air and can be easily oxidized to the phosphine oxide. Thus, it always contains some amount of phosphine oxide. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 5.52 (s, 0.77H, CH), 5.70 (s, 1H, CH), 6.61–8.01 (m, 57H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = −13.30, 30.14.

4.3.5. The preparation of complex E from ligand L1 with $PdCl_2(PhCN)_2$. Ligand **L1** (48 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 (53 mg, 80%). The single crystals for X-ray diffraction were obtained by recrystallization from dichloromethane and toluene (1/4). Mp: 281–282 °C, $[\alpha]_D^{20}$ = +176.9 (*c* 0.0567, $CHCl_3$); IR (CH_2Cl_2): ν = 3019, 2992, 1438, 1216, 1099, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.92 (s, 3H, CH_3), 6.52–8.01 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = 27.52; Anal. Calcd for $C_{33}H_{25}Cl_2PSPd{\cdot}CH_2Cl_2$ requires: C, 54.68; H, 3.64. Found: C, 54.74; H, 3.79%.

4.3.6. The preparation of complex F from Ligand L2 with $PdCl_2(PhCN)_2$. This complex was prepared in a similar method to that described above. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.08 (s, 3H, Me), 1.47 (s, 3H, Me), 4.67 (m, 1H, CH), 5.42–8.01 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = 28.20.

4.3.7. The preparation of complexes I and J [Pd(L1)(1,3-diphenylpropenyl)](SbF_6). To a Schlenk tube containing **L1** (24.2 mg, 0.05 mmol) in CH_2Cl_2 (1 mL) was added [(1,3-diphenylpropenyl)PdCl]$_2$ (16.7 mg, 0.025 mmol), and the reaction mixture stirred for 1 h at room temperature. The solution was transferred by cannula into a flask containing $AgSbF_6$ (17.2 mg, 0.05 mmol) in CH_2Cl_2 (1 mL) and stirred for 1 h in the absence of light. The reaction was cannula filtered into a Schlenk tube and concentrated in vacuo to yield a 3:1 mixture of diastereomeric π-allyl complexes **I** and **J**. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): minor: δ = 2.85 (s, 1H, Me), 3.56 (d, *J* = 8.7 Hz, 0.3H, CH), 4.13 (t, *J* = 8.7 Hz, 9.0 Hz, 0.3H, CH), 4.95 (d, *J* = 9.0 Hz, 0.3H, CH), 6.61–7.94 (m, 12H, Ar); major: δ = 3.49 (s, 3H, Me), 3.68 (d, *J* = 9.0 Hz, 1H, CH), 4.38 (t, *J* = 9.0 Hz, 9.3 Hz, 1H, CH), 5.04 (d, *J* = 9.3 Hz, 1H, CH), 6.61–7.94 (m, 32H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = 28.57 (minor), 25.56 (major).

4.3.8. The preparation of complexes G and H [Pd(L2)(1,3-diphenylpropenyl)](SbF_6). This complex was prepared in a similar method to that described above. The single crystals for X-ray diffraction were obtained by recrystallization from dichloromethane and toluene (1/4). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): minor: δ = 1.13 (d, *J* = 6.6 Hz, 1.1H, Me), 1.17 (d, *J* = 6.3 Hz, 1.1H, Me), 3.81–3.91 (m, 0.3H, CH), 4.93 (d, *J* = 8.7 Hz, 0.3H, CH), 5.41 (t, *J* = 8.4 Hz, 8.7 Hz, 0.3H, CH), 5.95 (d, *J* = 8.4 Hz, 0.3H, CH), 6.62–8.04 (m, 12H, Ar); major: δ = 0.83 (d, *J* = 6.0 Hz, 3H, Me), 0.91 (d, *J* = 6.6 Hz, 3H, Me), 3.57–3.68 (m, 1H, CH), 5.06 (d, *J* = 8.7 Hz, 1H, CH), 5.51 (t, *J* = 8.4 Hz, 8.7 Hz, 1H, CH), 6.17 (d, *J* = 8.4 Hz, 1H, CH), 6.62–8.04 (m, 32H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = 28.77 (minor), 25.22 (major).

4.3.9. Typical reaction procedure of Pd-catalyzed asymmetric allylation of 1,3-diphenylpropenyl acetate with dimethyl malonate. To a solution of allyl chloride palladium dimer [Pd(η^3-C_3H_5)Cl]$_2$ (1.8 mg, 0.005 mmol, 2 mol%) in solvent (1.0 mL) was added enantiomerically pure ligand **L1** (0.015 mmol, 6 mol%) under an argon atmosphere, and the reaction mixture 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%) and the reaction solution stirred for a further 5 min under a certain temperature (see Tables 1–3. Then, dimethyl malonate (0.09 mL, 0.75 mmol, 3 equiv) and *N,O*-bis(trimethylsilyl)acetamide (BSA) (0.19 mL, 0.75 mmol, 3 equiv) were added and the reaction 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 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 a flash chromatography on silica gel (eluent: PE/EtOAc = 20/1) to furnish 1,3-diphenyl-1-(2-dimethylmalonyl)prop-2-ene as a colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.52 (s, 3H, Me), 3.70 (s, 3H, Me), 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 OD, eluent: *n*-hexane/*i*-propanol = 80/20), Flow rate: 0.7 mL/min, retention times: 18.0 min (*R*), 19.3 min (*S*).

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