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Palladium-catalyzed asymmetric allylic substitutions by axially chiral P,S-, S,S-, and S,O-heterodonor ligands with a binaphthalene framework

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Abstract—Axially chiral P,S-heterodonor ligand **L1** is effective in the asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate. Its bidentate coordination pattern to a Pd metal center with both P and S atoms has been unambiguously established by X-ray diffraction and NMR spectroscopic analyses. Herein, we further disclose that axially chiral S,S-heterodonor ligands **L2**–**L4** are also effective in the same reaction to give the allylic alkylation product in moderate to good ee. However, the corresponding S,O-heterodonor ligands are not as effective as the corresponding P,S- or S,S-heterodonor ligands in the same asymmetric reaction.

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). Since then, significant effort has been devoted to the design and synthesis of novel binaphthalene-templated ligands. The 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] such as 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 dimethyl malonate in the presence of base.[6] Herein, we report that the P,S-heterodonor ligand **L1** shown in Figure 1 is also fairly effective in the palladium-catalyzed asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate. In the mean time, the details of the investigation on this type of P,S-heterodonor ligand **L1** in the asymmetric allylic substitution of 1,3-diphenylpropenyl acetate are disclosed on the basis of the X-ray crystal structure diffraction and NMR spectroscopic data. We found that this ligand acted as a P,S-bidentate ligand to palladium center and showed no hemilabile character compared to that of BINPO (BINAP monophosphine oxide).[7] In addition, the asymmetric catalysis of several other axially chiral S,S-, S,O-heterodonor ligands in the same reaction has been disclosed in this paper.

2. Results and discussion

2.1. Synthesis of ligands L1–L5

Axially chiral ligands **L1**–**L5** were prepared from *O*-triflated (*R*)-BINOL [(*R*)-(+)-1,1′-bi-2-naphthol] **1** according to the Gladiali's method (Scheme 1).[8] Reduction of compound **4** was carried out by $HSiCl_3$ in the presence of Et_3N in toluene at 120 °C to obtain P,S-heterodonor ligand **L1**. The S,S-heterodonor ligands **L2**–**L4** were easily prepared by heating compounds **9** and **L1** with sulfur at 120 °C. The S,O-heterodonor ligand **L5** was synthesized by reduction of compound **6** with $HSiCl_3$ in the

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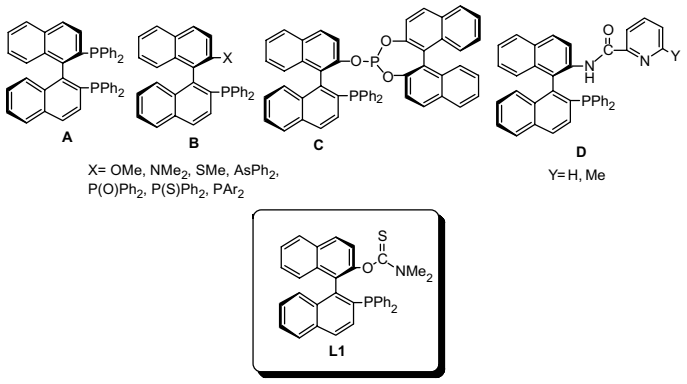
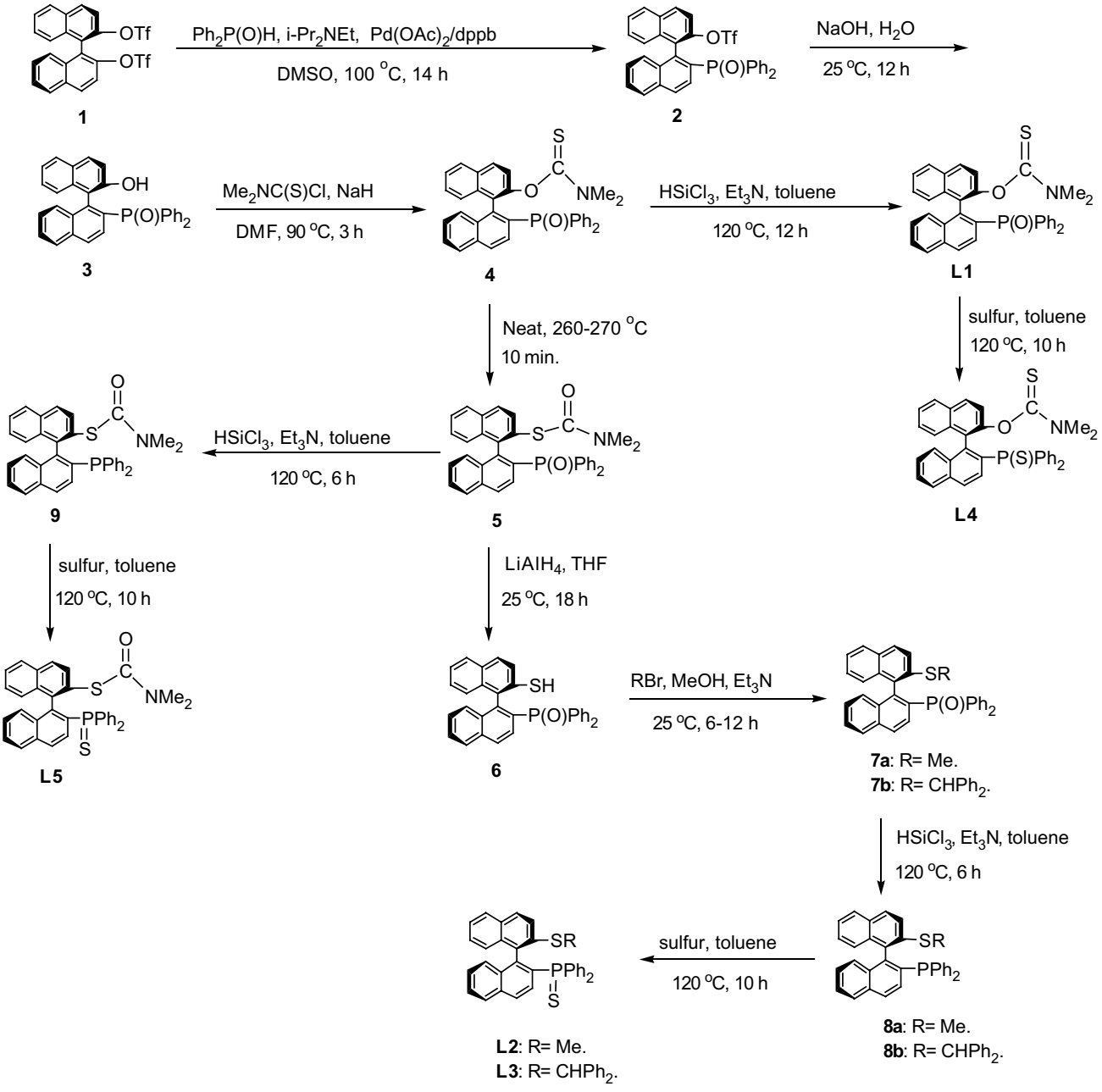


Figure 1. The structure of C_2-symmetric BINAP and C_1-symmetric binaphthyl P,X-heterodonor ligands.



Scheme 1. Synthesis of ligands **L1**–**L5**.

presence of Et_3N and then upon heating with sulfur at 120 °C.

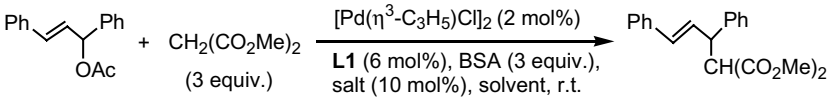
2.2. Catalytic asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate by chiral P,S-heterodonor ligand L1

We found that this novel axially chiral P,S-heterodonor ligand **L1** was quite effective in the Pd(II)-catalyzed asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate. The results are summarized in Table 1. As can be seen from Table 1, the achieved ee was 82% in 75% yield at −20 °C (Table 1, entry 1). At 0 °C, 83% ee was realized in the presence of ammonium salt Bu_4NCl (Table 2, entry 2). At −20 to −30 °C, the use of inorganic salts such as KOAc and LiOAc did not significantly improve the enantioselectivities (Table 1, entries 3–6). In the presence of KOAc, the achieved ee was 80% in 56% yield at −30 °C. In addition, at −20 °C, the achieved ee was 64% in 94% yield in the presence of KOAc and 83% ee in 80% yield in the presence of LiOAc, respectively. On the other hand, the solvent and temperature effects have also been examined under similar conditions with similar results were obtained (Table 1, entries 7–13). When this reaction was carried out in CH_2Cl_2 in the presence of complex **10** (see below) and AgOTf, a comparable result with 75% ee was obtained (Table 1, entry 14). When $NaCH(CO_2Me)_2$, prepared from dimethyl malonates with NaH, was used as a nucleophile in this reaction, the product was obtained with 78% ee in 43% yield (Table 1, entry 15). The best result was obtained in THF in the presence of LiOAc at −20 °C to give the adduct in 80% yield with 83% ee (Table 1, entry 6).

2.3. Other axially chiral S,S- or S,O-heterodonor ligands used in asymmetric allylic alkylation

Asymmetric allylic alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate under the above conditions were carried out in the presence of ligands **L2**–**L5** (Scheme 1). The results are summarized in Table 2. First of all, we found that by using S,S-heterodonor ligand **L2** as a chiral ligand in this reaction, the reaction proceeded smoothly in a variety of solvents and additives (salts) to give the corresponding allylic substitution product in good yields with low to moderate ee (Table 2, entries 1–6). The highest ee was 31% in toluene in the presence of KOAc with an (*S*)-configuration in 77% yield (Table 2, entry 5). Using **L3** as a chiral ligand in this reaction in THF in the presence of either KOAc or LiOAc, the achieved ee could reach 69% and 74% with *R* configuration in 68% and 80% yield, respectively (Table 2, entries 7 and 8). Using **L4** as a chiral ligand under the same conditions, the achieved ee was slightly improved (Table 2, entries 9–14). In THF, the ee was 59% with an (*R*)-configuration in 70% yield in the presence of KOAc (Table 2, entry 9), while using LiOAc as an additive, the ee was increased to 89% in 44% yield (Table 2, entry 14). However, the reaction was sluggish in the presence of axially chiral S,O-heterodonor ligand **L5** under similar conditions (Table 2, entry 15). Thus, the S,S-heterodonor ligands are more effective than S,O-heterodonor ligand in this Pd-catalyzed asymmetric C–C bond forming reaction. Moreover, we also confirmed that other axially chiral compounds **9**, **4**, **5**, and **7a** shown in Scheme 1, did not catalyze the allylic alkylation of 1,3-diphenylpropenyl acetate under the same conditions.

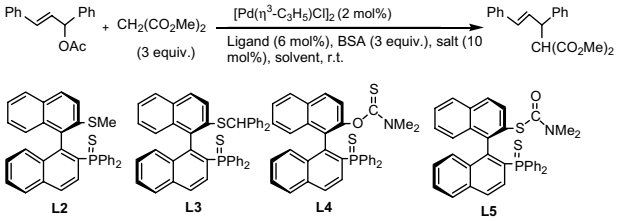
Table 1. The asymmetric allylic substitution catalyzed by Pd(II) in the presence of chiral P,S-ligand **L1**



Entry	Salt	Solvent	Temp. (°C)	Time (h)	Yield[a] (%)	Ee[b]	Absolute configuration[c]
1[d]	—	THF	−20	17	75	82	*R*
2	Bu_4NCl	THF	0	44	74	83	*R*
3	KOAc	THF	0	2	91	45	*R*
4	KOAc	THF	−20	2	94	64	*R*
5	KOAc	THF	−30	68	56	80	*R*
6	**LiOAc**	**THF**	**−20**	**30**	**80**	**83**	***R***
7	Bu_4NCl	$PhCH_3$	0	44	86	80	*R*
8	Bu_4NCl	CH_3CN	0	44	74	83	*R*
9	Bu_4NCl	DMF	0	48	69	75	*R*
10	Bu_4NCl	CH_2Cl_2	0	44	95	76	*R*
11	Bu_4NCl	$CHCl_3$	10	26.5	68	68	*R*
12	Bu_4NCl	$CHCl_3$	0	86	79	71	*R*
13	Bu_4NCl	$CHCl_3$	−20	118	64	72	*R*
14[e]	KOAc	CH_2Cl_2	10	25	12	75	*R*
15[f]	—	THF	10	12	43	78	*R*

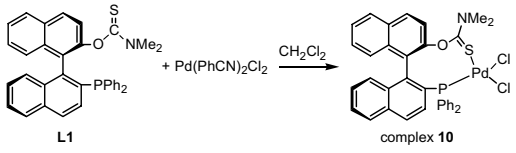
[a] Isolated yields.
[b] Determined by HPLC.
[c] The absolute configuration was determined by comparing the sign of specific rotation with authentic sample reported in the literature.
[d] No additive was used.
[e] The complex **5** derived from **L1** with $Pd(PhCN)_2Cl_2$ and AgOTf was used.
[f] $NaCH(CO_2Me)_2$ was used as an nucleophile.

Table 2. The axially chiral S,S or S,O-heterodonor ligands **L2**–**L5** in asymmetric allylic substitution



Entry	Ligand	Salt	Solvent	Temp. (°C)	Time (h)	Yield[a] (%)	Ee[b](%)	Absolute configuration[c]
1	**L2**	KOAc	THF	10	40	84	23	*S*
2	**L2**	LiOAc	THF	10	40	51	23	*S*
3	**L2**	KOAc	CH_2Cl_2	10	12	86	7	*S*
4	**L2**	KOAc	CH_3CN	10	12	88	4	*S*
5	**L2**	KOAc	$PhCH_3$	10	36	77	31	*S*
6	**L2**	KOAc	DMF	10	36	80	24	*S*
7	**L3**	KOAc	THF	10	26	68	69	*R*
8	**L3**	LiOAc	THF	10	26	80	74	*R*
9	**L4**	KOAc	THF	10	80	70	59	*R*
10	**L4**	KOAc	CH_2Cl_2	10	82	44	27	*R*
11	**L4**	KOAc	CH_3CN	10	82	38	4	*R*
12	**L4**	KOAc	$PhCH_3$	10	168	48	22	*R*
13	**L4**	KOAc	DMF	10	168	17	42	*R*
14	**L4**	LiOAc	THF	10	80	44	89	*R*
15	**L5**	KOAc	THF	5	168	31	9	*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 literature.



^{1}H NMR ($CDCl_3$, TMS) δ2.38, 3.04 (N(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) δ -13.71. ^{13}C NMR ($CDCl_3$, TMS) δ38.07, 42.98 (N(CH_3)$_2$), 166.56 (C=S).

^{1}H NMR ($CDCl_3$, TMS) δ 2.60, 2.70 (N(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) δ 16.21. ^{13}C NMR ($CDCl_3$, TMS) δ39.84, 42.22 (N(CH_3)$_2$), 180.73 (C=S).

Scheme 2. ^{1}H NMR, ^{31}P NMR, and ^{13}C NMR analyses of **L1** and complex **10**.

2.4. Synthesis of complexes Pd(L1)Cl_2, [Pd(η^3-$Ph_2C_3H_3$)(L1)]OTf, and Pd(L2)Cl_2

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 [$Pd(PhCN)_2Cl_2$][9] because it is known that sulfur and phosphorus atom 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**)Cl_2 complex **10** was carried out by the reaction of the appropriate amount of $Pd(PhCN)_2Cl_2$ with 1 equiv of **L1** in CH_2Cl_2 at room temperature under an argon atmosphere (Scheme 2). The ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic investigation on Pd(**L1**)Cl_2 complex **10** and free **L1** in $CDCl_3$ revealed that both phosphorus and sulfur atoms coordinated to the palladium center. For free ligand **L1**, ^{31}P NMR signal appears at −13.71 ppm, while for complex **10** this signal appears at 16.21 ppm. This drastic chemical shift change provides an indication that the phosphorus atom coordinates to the metal center. ^{1}H NMR spectra in $CDCl_3$ show that two methyl signals shift from 2.38 to 3.04 ppm in free ligand **L1** to 2.60 and 2.70 ppm in complex **10**. These facts suggest that the chemical environment surrounding the methyl groups in complex **10** have changed. A similar phenomenon has been observed in ^{13}C NMR spectra in $CDCl_3$ with two methyl signals shifting from 38.07 to 42.98 ppm in free ligand **L1** to 39.84 and 42.22 ppm in complex **10** and the thiocarbonyl signal (C=S group) shifts from 166.56 ppm in free ligand **L1** to 180.73 ppm in complex **10** as well. Thus, we believe that the sulfur atom may coordinate to the palladium metal center as well.

The single crystals suitable for X-ray diffraction were obtained by recrystallization from dichloromethane and toluene (1:4).[10] The ORTEP drawing is shown in Figure 2 in which **L1** acts as a bidentate ligand to Pd(II) center with both sulfur and phosphorus atoms providing a nine-membered chelate ring with an irregular, partially boat-like conformation. The bond distances

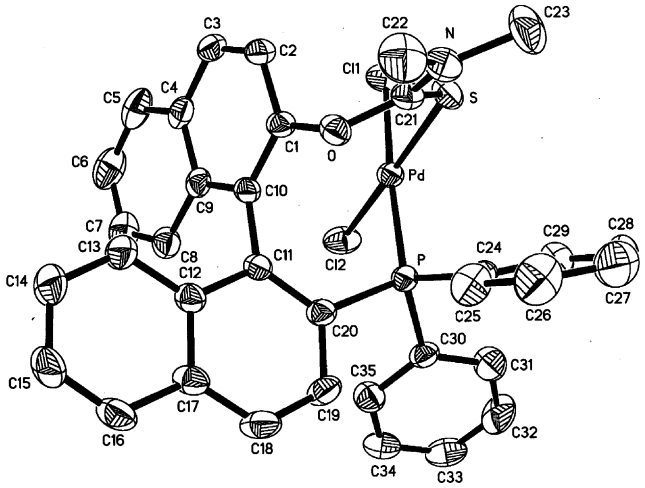


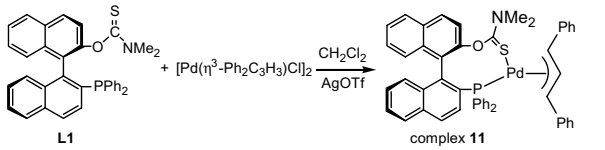
Figure 2. The ORTEP drawing of complex **10**.

Table 3. Selected bond lengths (Å) and bond angles (deg) for $Pd(L1)Cl_2$ complex **10**

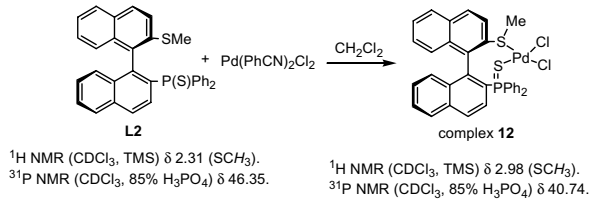
	Bond lengths		Bond angles
Pd–P	2.2585 (10)	P–Pd–S	95.70 (4)
Pd–S	2.3012 (11)	P–Pd–Cl (2)	89.12 (4)
Pd–Cl (1)	2.3539 (12)	S–Pd–Cl (1)	85.33 (4)
Pd–Cl (2)	2.2966 (11)	Cl (2)–Pd–Cl (1)	89.68 (4)

of Pd–S and Pd–P are 2.3012 and 2.2585 Å, respectively, which are in the normal region (Table 3).[11] The stronger *trans* influence[12] of the phosphorus atom (vs the sulfur atom in the thiocarbonyl group) is reflected in the difference of the Pd–Cl bond distances *trans* to the phosphorus atom (2.3539 Å) and *trans* to the sulfur atom (2.2966 Å).

The synthesis of complex **11** was also carried out via reaction of 1,3-diphenylallylpalladium chloride dimmer with **L1** and AgOTf in dichloromethane at room temperature to produce $[Pd(\eta^3\text{-}Ph_2C_3H_3)(\mathbf{L1})]OTf$ (Scheme 3). NMR spectroscopy allowed us to determine the structure of this complex in solution. The ^{31}P NMR spectrum in the $CDCl_3$ of complex **11** showed one signal at 20.66 ppm. This fact suggests that only one isomer of the palladium allyl complex can be obtained in solution. The ^1H NMR spectrum of **11** in $CDCl_3$ solution was also consistent with the existence of one isomer. The signals of two methyl groups were at 2.58 and 2.87 ppm (Scheme 3).



Scheme 3. ^1H NMR and ^{31}P NMR analyses of **L1** and complex **11**.



Scheme 4. ^1H NMR and ^{31}P NMR analyses of **L2** and complex **12**.

The coordination pattern of ligand **L2** to Pd center was investigated by ^1H NMR and ^{31}P NMR spectroscopic studies in $CDCl_3$. The signals of the (*S*)-methyl and phosphorus atom showed significant shifts after the addition of $Pd(PhCN)_2Cl_2$ in $CDCl_3$ as compared with free ligand **L2** (Scheme 4) with complex **12** presumably formed (Scheme 4). These results suggest that the S,S-heterodonor ligand can coordinate to the Pd metal center by two sulfur atoms as a bidentate ligand in a similar way as P,S-heterodonor ligand described above to catalyze the asymmetric C–C bond forming reaction, although in some cases they are not as effective as the P,S-heterodonor ligand.

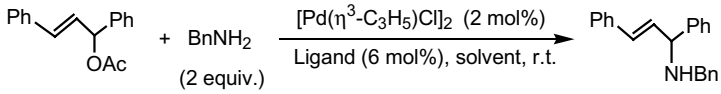
2.5. Axially chiral P,S-heterodonor ligand L1 in asymmetric allylic amination

Asymmetric allylic amination of 1,3-diphenylpropenyl acetate with benzylamine to form carbon–nitrogen bond is a useful method in organic synthesis.[13] However, amines acting as nucleophiles in an asymmetric allylic substitution have proven to be a challenge because the *N*-nucleophiles are less reactive than malonate in the presence of base.[14,15] Thus, the allylic amination of 1,3-diphenylpropenyl acetate with benzylamine was also examined by the axially chiral P,S-heterodonor ligands **L1** under similar conditions. Unfortunately, we found that this chiral ligand is ineffective in allylic amination (Table 4, entries 1–7).

3. Conclusion

We have found a novel axially chiral P,S-heterodonor ligand **L1** is quite effective in an asymmetric C–C bond forming reaction. Their bidentate coordination patterns to the Pd metal center with P and S atoms have been unambiguously established by X-ray diffraction and ^1H NMR, ^{31}P NMR, and ^{13}C NMR analyses. Herein, we have further disclosed that axially chiral S,S-heterodonor ligands **L2**–**L4** are also fairly effective in the same reaction to give the allylic alkylation product in moderate to good ee. While, the corresponding S,O-heterodonor ligands are not as effective as the corresponding P,S- or S,S-heterodonor ligands in this reaction. Based on these results, we are able to plan how to exploit these axially chiral C_1-symmetric P,S- or S,S-heterodonor ligands in other asymmetric catalysis and synthesize further these kinds 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.

Table 4. Allylic amination of 1,3-diphenylpropenyl acetate with benzylamine catalyzed by Pd(II) and chiral ligand **L1**



Entry	Ligand	Solvent	Temp. (°C)	Time (h)	Yield[a] (%)	Ee[b] (%)	Absolute configuration[c]
1	**L1**	CH_2Cl_2	10	48	12	20	*R*
2	**L1**	$ClCH_2CH_2Cl$	10	56	9.4	26	*R*
3	**L1**	CH_3CN	10	56	4	23	*S*
4	**L1**	DMF	10	61	7	0	—
5	**L1**	$CHCl_3$	10	168	NR[d]	—	—
6	**L1**	THF	10	168	NR[d]	—	—
7	**L1**	$PhCH_3$	10	168	NR[d]	—	—

[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 literature.
[d] No reaction took place.

4. Experimental

4.1. General

Melting points were obtained with a micro melting point apparatus and are uncorrected. Optical rotations were determined in a solution of $CHCl_3$ at 20 °C by using a polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Infrared spectra were measured on a spectrometer. ^{1}H NMR spectra were recorded for a solution in $CDCl_3$ with tetramethylsilane (TMS) as the 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 given in Hz. Mass spectra were recorded with an HP-5989 instrument and HRMS was measured by a Finnigan MAT mass spectrometer. The organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper 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 under pressure. All alkylation and amination experiments were performed under an argon atmosphere using standard Schlenk techniques. The enantiomeric excesses of dimethyl(1,3-diphenyl-2-propen-1-yl)malonate and 1-benzylamine-1,3-diphenylprop-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.

4.1.1. (*R*)-2,2′-Bis(trifluoromethanesulfonyl)oxy-1,1′-binaphthyl 1. This is a 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 a 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 a 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 a known compound.[8] $[\alpha]_D^{20} = -142.8$ (*c* 1.155, $CHCl_3$), {lit.[8] $[\alpha]_D^{25} = +149$ (*c* 1, $CHCl_3$) for (*S*)-enantiomer}; ^{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): δ 27.80.

4.1.5. (*R*)-(−)-2-(Diphenylphosphanyl)-1,1′-binaphthyl-2′-ol-*N*,*N*-dimethylthiocarbamate L1. To a solution of (*R*)-(−)-2-(diphenylphosphinyl)-1,1′-binaphthyl-2′-ol-*N*,*N*-dimethylthiocarbamate **4** (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 then added and the reaction mixture stirred at 120 °C for 12 h. After cooling to room temperature, 10% HCl (10 mL) was added and the organic phase was 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 a flash chromatography (eluent: PE/EtOAc = 10:1) to give **L1** as a white solid. 298 mg, yield 55%, mp: 79–81 °C; $[\alpha]_D^{20} = -17.3$ (*c* 0.96, $CHCl_3$); IR (CH_2Cl_2): *v* 1712, 1543, 1436, 1396, 1289, 1219, 1170, 818, 518 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.38 (s, 3H, CH_3), 3.04 (s, 3H, CH_3), 6.85–8.02 (m, 22H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 38.07, 42.98, 123.80, 125.65, 126.37, 126.59 (d, J_{C-P} = 1.3 Hz), 127.52 (d, J_{C-P} = 22.4 Hz), 128.29 (d, J_{C-P} = 2.3 Hz), 128.35 (d, J_{C-P} = 6.6 Hz), 128.46 (d, J_{C-P} = 7.7 Hz), 128.50, 128.52 (d, J_{C-P} = 19.4 Hz), 128.53 (d, J_{C-P} = 6.3 Hz), 128.55 (d, J_{C-P} = 2.5 Hz), 128.61 (d, J_{C-P} = 5.4 Hz), 128.65, 128.73, 130.38 (d, J_{C-P} = 2.0 Hz), 131.55, 133.07 (d, J_{C-P} = 7.1 Hz), 133.71 (d, J_{C-P} = 19.3 Hz), 133.75 (d, J_{C-P} = 0.8 Hz), 133.97 (d, J_{C-P} = 19.6 Hz), 134.15 (d, J_{C-P} = 2.6 Hz), 136.23 (d, J_{C-P} = 11.9 Hz), 138.03 (d, J_{C-P} = 13.1 Hz), 138.26 (d, J_{C-P} = 13.7 Hz), 140.92, 141.38, 149.75, 166.56; ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −13.71; MS (EI)

m/e 541 (M^+, 2.22), 453 (10.74), 437 (100), 268 (9.31), 183 (4.36); HRMS (EI) calcd for $C_{35}H_{28}ONSP$ requires: 541.1629, found: 541.1639.

4.1.6. (*R*)-(+)-2-(Diphenylphosphinyl)-1,1′-binaphthyl-2′-thiol-*N*,*N*-dimethylthiocarbamate 5. This is a known compound.[8] $[\alpha]_D^{20} = +11.3$ (*c* 1.05, $CHCl_3$), {lit.[8] $[\alpha]_D^{25} = -5.7$ (*c* 1, $CHCl_3$) for (*S*)-enantiomer}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.75 (s, 6H, $2CH_3$), 6.80–8.10 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 29.43.

4.1.7. (*R*)-(+)-2-(Diphenylphosphinyl)-1,1′-binaphthyl-2′-thiol 6. This is a known compound.[8] $[\alpha]_D^{20} = +79.9$ (*c* 1.125, $CHCl_3$), {lit.[8] $[\alpha]_D^{25} = -42.3$ (*c* 1, $CHCl_3$) for the (*S*)-enantiomer}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 3.48 (s, 1H, SH), 6.82–8.04 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 28.88.

4.1.8. (*R*)-(+)-2-(Diphenylphosphinoyl)-2′-methylsulfanyl-1,1′-binaphthalenyl 7a. This compound was prepared from **7** as the similar procedure described in the literature.[8] $[\alpha]_D^{20} = +138.1$ (*c* 0.605, $CHCl_3$), {lit.[8] $[\alpha]_D^{25} = -126.2$ (*c* 0.5, $CHCl_3$) for the (*S*)-enantiomer}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.29 (s, 3H, CH_3), 6.86–8.02 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 29.39.

4.1.9. (*R*)-(+)-2-(Diphenylphosphinoyl)-2′-benzhydrylsulfanyl-1,1′-binaphthalenyl 7b. 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 **7b** as a white solid: 294 mg, 45% yield; mp: 119–120 °C; $[\alpha]_D^{20} = +42.7$ (*c* 1.1, $CHCl_3$); IR (CH_2Cl_2) *v* 1422, 1163, 896 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 5.52 (s, 1H, CH), 6.80–8.02 (m, 32H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ 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.

4.1.10. (*R*)-(+)-2-(Diphenylphosphanyl)-2′-methylsulfanyl-1,1′-binaphthalenyl 8a. This compound was prepared from **8a** as described in the literature.[8] $[\alpha]_D^{20} = +49.8$ (*c* 0.535, $CHCl_3$), {lit.[8] $[\alpha]_D^{25} = -52.6$ (*c* 0.5, $CHCl_3$) for the (*S*)-enantiomer}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.31 (s, 3H, CH_3), 6.68–7.99 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ−13.07.

4.1.11. (*R*)-(+)-2-(Diphenylphosphanyl)-2′-benzhydryl-sulfanyl-1,1′-binaphthalenyl 8b. A solution of (*R*)-(+)-2-(diphenylphosphinoyl)-2′-methylsulfanyl-1,1′-binaphthalenyl **7b** (652 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 then 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 **8b** as a white solid. 257 mg, 39% yield. This compound was very sensitive to air and can be easily oxidized to phosphine oxide. Thus, the product always contained some amount of phosphine oxide. ^1H 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.

4.1.12. (*R*)-(+)-2-(Diphenylphosphinothioyl)-2′-methylsulfanyl-1,1′-binaphthalenyl L2. To a solution of (*R*)-(+)-2-(diphenylphosphanyl)-2′-methylsulfanyl-1,1′-binaphthalenyl **8a** (266 mg, 0.55 mmol) in toluene (5 mL) was added sulfur (24.6 mg, 0.77 mmol, 1.4 equiv) and the reaction mixture stirred at room temperature for 1 h and then heated to 120 °C for 10 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue purified by flash chromatography (eluent: PE/EtOAc = 4:1) to give **L2** as a white solid. 218 mg, 77% yield; mp: 98–99 °C; $[\alpha]_D^{20} = +163.7$ (*c* 0.865, $CHCl_3$); IR (CH_2Cl_2): *v* 2685, 2306, 1422, 1162, 896, 403 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.31 (s, 3H, CH_3), 6.88–8.01 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 46.35; MS (EI) *m/e* 517 (M^++1, 1.55), 502 (3.04), 470 (100), 438 (7.78), 282 (16.79), 183 (9.31); HRMS (EI) calcd for: $C_{33}H_{25}PS_2$ requires: 516.1135, found; 516.1152.

4.1.13. (*R*)-(+)-2-(Diphenylphosphinothioyl)-2′-benzhydrylsulfanyl-1,1′-binaphthalenyl L3. This compound was prepared from (*R*)-(+)-2-(diphenylphosphanyl)-2′-benzhydrylsulfanyl-1, 1′-binaphthalenyl **8b** in a similar way to that described above. White solid, yield 87%. Mp: 107–109 °C; $[\alpha]_D^{20} = +42.8$ (*c* 0.835, $CHCl_3$); IR (CH_2Cl_2): *v* 1437, 1161, 896 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 5.40 (s, 1H, CH), 6.81–8.00 (m, 32H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 46.66; MS (ESI) *m/e* 669 (M^++1); HRMS (ESI) calcd for $C_{45}H_{33}PS_2Na$ (M^++Na) requires: 691.1649, found: 691.1654.

4.1.14. (*R*)-(−)-2-(Diphenylphosphinothioyl)-1,1′-binaphthyl-2′-ol-*N*,*N*-dimethylthiocarbamate L4. This compound was prepared from (*R*)-(−)-2-(diphenylphosphanyl)-1,1′-binaphthyl-2′-ol-*N*,*N*-dimethylthiocarbamate **L1** in a similar way to that described above. White solid, yield 88%; mp: 108–109 °C; $[\alpha]_D^{20} = -165.5$ (*c* 0.785, $CHCl_3$); IR (CH_2Cl_2): *v* 1536, 1437, 1220, 1168, 896, 401 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 3.03 (s, 3H, CH_3), 3.06 (s, 3H, CH_3), 6.72–7.90 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 45.75; MS (EI) *m/e* 573 (M^+, 0.99), 501 (100), 485 (31.77), 469 (97.84), 217 (38.87), 88 (43.98);

HRMS (ESI) calcd for $C_{35}H_{28}ONS_2PNa$ (M^++Na) requires: 596.1246, found: 596.1242.

4.1.15. (*R*)-(+)-2-(Diphenylphosphanyl)-1,1′-binaphthyl-2′-thiol-*N*,*N*-dimethylthiocarbamate 9. This compound was prepared from (*R*)-(+)-2-(diphenylphosphinyl)-1,1′-binaphthyl-2′-thiol-*N*,*N*-dimethylthiocarbamate **5** in a similar way to that described above. $[\alpha]_D^{20} = +14.8$ (*c* 0.205, THF), {lit.[8] $[\alpha]_D^{25} = -15$ (*c* 1, THF) for the (*S*)-enantiomer}, ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.66 (s, 6H, $2CH_3$), 6.86–7.98 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ −14.45.

4.1.16. (*R*)-(+)-2-(Diphenylphosphinothioyl)-1,1′-binaphthyl-2′-thiol-*N*,*N*-dimethylthiocarbamate L5. This compound was prepared from (*R*)-(+)-2-(diphenylphosphanyl)-1,1′-binaphthyl-2′-thiol-*N*,*N*-dimethylthiocarbamate **9** in the similar way to that described above. White solid, yield 69%; mp: 206–207 °C; $[\alpha]_D^{20} = +6.4$ (*c* 1.29, $CHCl_3$); IR (CH_2Cl_2): *v* 1664, 1437, 1097 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.76 (s, 6H, $2CH_3$), 6.98–7.96 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 45.85; MS (EI) *m*/*e* 574 (M^++1, 0.88), 501 (100), 469 (97.96), 437 (22.64), 282 (27.16), 217 (23.18); HRMS (EI) calcd for $C_{32}H_{22}S_2P$ ($M^+-C(O)NMe_2$) requires: 501.0901, found: 501.0875.

4.2. The preparation of complex 10 from ligand L1 with $PdCl_2(PhCN)_2$

Ligand **L1** (54 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. Degassed hexane (5.0 mL) was then slowly added at room temperature, which led to the precipitation of the formed complex. The mother liquor was filtered off, and the precipitate washed with hexane (2 × 1.0 mL) to afford complex (*R*)-(+)-**10** as an orange powder; 53 mg, 74% yield. The single crystals for X-ray diffraction were obtained by recrystallization from dichloromethane and toluene (1:4). Mp: >300 °C, $[\alpha]_D^{20} = +206$ (*c* 0.105, $CHCl_3$); IR (neat): *v* 1570, 1434, 1405, 1282, 1212, 1198, 748, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): 2.60 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 6.52–8.27 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 16.04; MS (ESI) *m*/*e* 736.9 (MNH_4^+). Anal. Calcd for $C_{35}H_{28}Cl_2NOPSPd\cdot 1/2C_7H_8\cdot 2/3CH_2CL_2$ requires: C, 57.25; H, 4.09; N, 1.70. Found: C, 56.92; H, 4.12; N, 1.44%.

4.3. The preparation of complex 11

To a Schlenk flask containing **L1** (27 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) was added [(1,3-diphenylpropenyl)PdCl]$_2$ (17 mg, 0.025 mmol), and the reaction allowed to stir for 1 h. The solution was transferred by cannula into a flask containing AgOTf (13 mg, 0.05 mmol) in CH_2Cl_2 (1 mL) and stirred for 1 h in the absence of light. The reaction was filtered and concentrated in vacuo to obtain an orange power. 40 mg, 81% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.37 (d, J = 12.0 Hz, 1H, allyl), 2.58 (s, 3H, Me), 2.87 (s, 3H, Me), 3.36 (dd, J = 11.4, 11.1 Hz, 1H, allyl), 2.37 (dd, J = 12.3, 11.7 Hz, 1H, allyl), 6.39–6.51 (m, 4H, Ar), 6.68–6.78 (m, 5H, Ar), 7.04–7.67 (m, 18H, Ar), 7.88–7.94 (m, 3H, Ar), 8.21 (d, J = 8.1 Hz, 1H, Ar), 8.46 (d, J = 8.7 Hz, 1H, Ar). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 20.66.

4.4. The preparation of complex 12 from ligand L2 with $PdCl_2(PhCN)_2$

This complex was prepared in the similar method as that described above. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.98 (s, 3H, Me), 6.18–8.16 (m, 22H, Ar); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 40.74.

4.5. 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%). The reaction solution was then stirred for a further 5 min under certain temperature (see Tables 1–3). Afterwards, 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 flash chromatography on silica gel (eluent: PE/EtOAc = 20:1) to furnish dimethyl(1,3-diphenyl-2-propen-1-yl)malonate 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,[16] eluent: *n*-hexane/*i*-propanol = 80:20), flow rate: 0.7 mL/min, retention times: 18.0 min (*R*), 19.3 min (*S*).

4.6. Typical reaction procedure of Pd-catalyzed asymmetric allylic amination of 1,3-diphenylpropenyl acetate with benzylamine

To a solution of allyl chloride palladium dimmer [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 and the reaction stirred for a further 5 min at room temperature. Then, benzylamine (0.63 mL, 0.5 mmol, 2 equiv) was added into the reaction mixture and the reaction

monitored by TLC plates until 1,3-diphenylpropenyl acetate was consumed completely or the time as indicated in Table 4. 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 yield 1-benzylamine-1,3-diphenylprop-2-ene as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.65 (br, 1H, NH), 3.79 (dd, $J = 13.5$, 16.2 Hz, 2H, CH_2), 4.40 (d, $J = 7.2$ Hz, 1H, CH), 6.32 (dd, $J = 7.5$, 15.9 Hz, 1H, CH), 6.58 (d, $J = 15.9$ Hz, 1H, CH), 7.21–7.45 (m, 15H, Ar). The enantiomeric excess was determined by HPLC (Chiralcel OJ,[16] eluent: *n*-hexane/*i*-propanol = 90:10), flow rate: 0.7 mL/min, retention times: 14.5 min (*S*), 17.9 min (*R*).

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10. The X-ray crystal data of complex **5**: $C_{43}H_{38}NOPCl_4PdS$, formula weight: 895.97, temperature: 293(2) K, crystal system, space group: Orthorhombic, *P*2(1)2(1)2(1), unit cell dimensions: $a = 11.7766(6)$ Å, $b = 13.7252(7)$ Å, $c = 25.4436(13)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 4112.6(4)$ Å^3, $Z_{value} = 4$, $D_{calc} = 1.447$ g/cm^3, $F_{000} = 1824$. Crystal size: $0.560 \times 0.255 \times 0.136$ mm. Data/restraints/parameters = 9413/6/437. Final *R* indices [$I > 2\sigma(I)$]: $R1 = 0.0442$, $wR2 = 0.1082$, *R* indices (all data): $R1 = 0.0528$; $wR2 = 0.1121$. Its crystal structure has been deposited at the Cambridge Crystallographic Data Center and has been allocated the deposition numbers: CCDC 213072.
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