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New Chiral Sulfoxide Ligands Possessing a Phosphano or Phosphanoamino Functionality in Palladium-Catalyzed Asymmetric Allylic Nucleophilic Substitution Reactions

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Abstract—New chiral sulfoxide ligands possessing a phosphano or phosphanoamino functionality as an alternative coordinating element were developed, and their usefulness was demonstrated by applying them to palladium-catalyzed asymmetric allylic nucleophilic substitution reactions. The structure of the catalyst precursor coordinated by the chiral phosphino sulfoxide was determined by X-ray crystallographic analysis. The possible mechanism for the asymmetric induction using these chiral ligands was proposed on the basis of the stereochemical outcome obtained.

Introduction

The increasing practical usefulness of catalytic asymmetric synthesis has received much attention in recent years,[1] especially in the pharmaceutical field, for the preparation of biologically active chiral compounds. Currently, much interest is being focused on new efficient chiral ligands. Hitherto, various types of chiral ligands, possessing stereocontrollable coordinating elements such as phosphane,[2] phosphite,[3] amine,[4] oxygen (alcohol or ether),[5] sulfenyl functions,[6] and so on, have been developed. The design and development of new chiral ligands that effect bond formation in a highly enantioselective fashion stand as important and challenging tasks in modern asymmetric synthesis. There have been some issues published related to asymmetric synthesis with chiral ligands bearing organosulfur functions; however, few reports have appeared concerning asymmetric synthesis with chiral ligands bearing chiral organosulfur groups such as sulfinyl[7] and sulfoximine functions[8] as sole chiral sources.

We have taken much interest in the participation of chirality in a chiral sulfinyl function in transition metal-catalyzed reactions, and extensive efforts have been made for the development of asymmetric synthetic methodologies with chiral organosulfur compounds such as cyclopropane–cyclobutane[9] and -cyclopentene rearrangements,[10] intramolecular ene reactions,[11] nucleophilic substitutions of π-allylpalladium complexes,[12] [3+2] cycloaddition reactions,[13] and allene formation with chiral sulfinates.[14] Several years ago, we extended our project to catalytic asymmetric synthesis with chiral ligands focused on chiral organosulfur functionality, and developed new chiral ligands bearing chiral organosulfur groups.[15] We describe in this report details of our recent work on asymmetric synthesis with chiral sulfoxide ligands bearing a β-phosphano or phosphanoamino function as another coordinating element.[16]

Results and Discussion

Synthesis of chiral sulfoxide ligands

Chiral β-phosphanoethyl *p*-tolyl sulfoxide (*R*)-**1** was prepared by a Michael addition of lithium diphenylphosphide to (*R*)-*p*-tolyl vinyl sulfoxide,[17] however, the β-phosphano sulfoxide was too labile at room temperature to be isolated in complete purity, presumably due to the facile conversion into the corresponding phosphane oxide **1b** by the intramolecular redox reaction via **1a** (Scheme 1).

Chiral *o*-phosphanophenyl sulfoxides (*S*)-**5a**,**b** were obtainable from 2-fluoroiodobenzene (**2**) and readily available chiral sulfinates. Lithiation of **2** with *n*-butyllithium followed by sulfinylation with (*Ss*)-**3a**[18] or -**3b**[19] produced (*S*)-**4a** or -**4b**, respectively. Phosphanylation of (*S*)-**4a** or -**4b** with potassium diphenylphosphide ($KPPh_2$)[20] gave (*S*)-**5a**,**b**. Other chiral (3, 4, or 5-substituted-2-phosphano)phenyl sulfoxides (*S*)-**8a**–**d** were prepared from **6a**–**d** in a similar procedure to that mentioned above. Chiral sulfoxides (*S*)-**10a** and (*R*)-**10b** were readily obtained starting from

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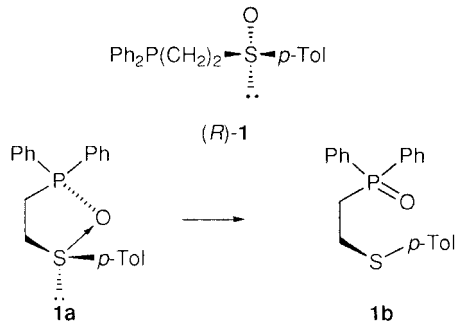


Scheme 1.

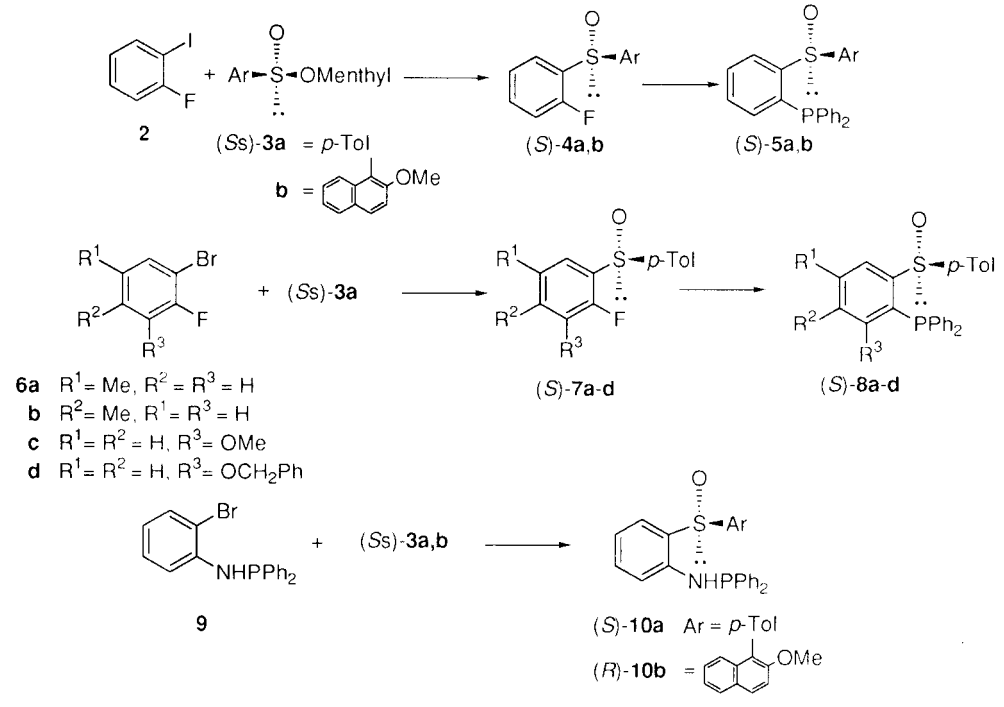
2-bromoaniline. The reaction of 2-bromoaniline with chlorodiphenylphosphane was carried out in refluxing benzene in the presence of triethylamine to give **9**. Treatment of **9** with *n*-butyllithium followed by sulfinylation with (*Ss*)-**3a** or -**3b** produced (*S*)-**10a** or (*R*)-**10b** in good yields, respectively (Scheme 2).

In contrast to (*R*)-**1**, chiral *o*-phosphanophenyl sulfoxides were obtained with retention of the chirality on the sulfinyl functions. The reason for this unexpected stability of the chirality is rationalised by the lower reactivity of the aromatic phosphano functions compared with that of the aforementioned phosphanoethyl group in (*R*)-**1**.

Thus, we executed detailed studies on the thermal stability of chiral *o*-phosphanophenyl sulfoxides. The chiral sulfoxide (*S*)-**5a** was extremely stable at room temperature, however under heating in THF it was partially converted into the corresponding phosphane oxide **11a**. The time-course of the conversion of (*S*)-**5a** into **11a** was listed in Table 1. Comparatively, the chiral sulfoxide (*S*)-**5b** was concluded to be very stable in THF at room temperature with compete retention of the chirality without conversion into the phosphane oxide (only quite a small amount of the corresponding phosphane oxide (**11b**) was detected by HPLC analysis). However, upon heating in refluxing THF a more rapid irreversible transformation of (*S*)-**5b** into **11b** was observed with almost complete retention of the enantiomeric excess value as shown in Fig. 1, plotted by HPLC analysis with Chiralpak AD in accordance with elapse of reaction time. The complete retention of the enantiomeric excess value under the thermal condition means that the transformation reaction should be irreversible. Thus, with chiral *o*-phosphinophenyl sulfoxides as ligands, it should be desirable to perform the reactions at rather low temperature, at least below 50°C (Scheme 3).

Palladium-catalyzed asymmetric reactions with chiral β-phosphano or -phospanoamino sulfoxide ligands

The palladium-catalyzed asymmetric allylic alkylations of (±)-1,3-diphenyl-2-propenyl acetate (**13**) with dimethyl malonate sodium enolate (generated by treating with NaH) were studied using (*S*)-**5a**,**b** and (*S*)-**8a-d** as chiral ligands. The reactions of (±)-**13** with sodium malonate were carried out in THF, DME, CH_3CN, or DMSO at room temperature for 6–10 h in the presence of $[PdCl(\pi\text{-allyl})]_2$, $Pd(OAc)_2$, $Pd(dba)_2$, or $Pd_2(dba)_3{\cdot}CHC1_3$ (0.06 equiv.) and (*S*)-**5a** (0.12 equiv.), producing (*S*)-**14a** in good yields with moderate enantiomeric excess (e.e.) (22–46%). The reaction of (±)-**13** with dimethyl malonate was also accomplished by using *N*,*O*-bis(trimethylsilyl)acetamide (BSA)[21] (3.0 equiv.) and a catalytic amount of sodium acetate, instead of sodium hydride, giving (*S*)-**14a** in 81% yield with 44% e.e. The palladium-catalyzed reactions of (±)-**13** with dimethyl malonate using (*S*)-**8a–d** as a ligand gave (*S*)-**14a** with rather low e.e., similar to the results obtained with (*S*)-**5a**. These results show, not as expected, that the marked electronic and steric



Scheme 2.

Table 1. The thermal conversion of sulfoxide (*S*)-**5a** into phosphane oxide **11a** (a solution of (*S*)-**5a** in THF was heated under reflux)

Reaction time (h)	2	4	18	20	24	30	40	50	70	90	130	150
Product **11a**[a] ratio (%)	–	–	3.2	3.5	3.7	4.3	4.5	4.6	5.0	5.7	7.5	9.6
e.e. (%)[a] of (*S*)-**5a**	100	99	96	95	96	98	96	96	96	96	96	96

[a] The product **11a** ratio and the e.e. of (*S*)-**5a** obtained were determined by HPLC analysis with Chiralpak OJ (^{i}PrOH/hexane 1:9) (the retention time of (*R*)-**5a**, (*S*)-**5a**, and **11a**; 14, 18 and 34 min, respectively, flow rate 0.5 ml/min.) in accordance with elapse of the reaction time.

effects of the methyl or vicinal alkoxy groups could not be detected. However, a chiral sulfinyl compound (*S*)-**5b** with a bulky substituent was demonstrated to serve as a highly efficient chiral ligand in the palladium-catalyzed reactions, providing an extremely high degree of asymmetric induction. The reactions of (±)-**13** with sodium malonate were carried out in THF at −20 or −40°C in the presence of $[PdCl(\pi\text{-allyl})]_2$ (0.03 equiv.) and (*S*)-**5b** (0.06 equiv.) to afford (*S*)-**14a** in good yields with 75% e.e. The use of $PdC1_2(CH_3CN)_2$ (0.03 equiv.) and (*S*)-**5b** (0.06 equiv.) in the reaction at −20°C in THF improved the e.e. (82%) of the product (*S*)-**14a**. The e.e. and the absolute configuration of the product **14a** were determined by HPLC analysis with Chiralpak AD.[22] The results obtained under other various reaction conditions are summarized in Table 2 (Scheme 4).

The asymmetric allylic amination of (±)-**13** under palladium catalysis with (*S*)-**5b** provided a high degree of asymmetric induction. Enantioselectivity of (*R*)-**14b** as high as 85% e.e. was observed when the reactions of (±)-**13** with benzylamine were carried out in toluene at 0°C in the presence of $[PdCl(\pi\text{-allyl})]_2$ (0.06 equiv.) and (*S*)-**5b** (0.12 equiv.). The e.e. and the absolute configuration of the product **14b** were determined by HPLC analysis with Chiralcel OD.[23] The results obtained under other various reaction conditions are summarized in Table 3. As shown in Table 3, unequivocal solvent effects on the asymmetric induction were observed; with DMSO, DMF, or acetonitrile as solvent, a very poor e.e. of (*R*)-**14b** was obtained.

The catalyst precursor (**12**) derived from (*S*)-**5b** and $PdC1_2(CH_3CN)_2$ was isolated by recrystallization from CH_2Cl_2-Et_2O. The structure was determined by X-ray crystallographic analysis as shown in Fig. 2. The palladium-catalyzed reactions of (±)-**13** with sodium malonate using the isolated palladium complex **12** as a catalyst gave the same result as that obtained under the normal reaction conditions with $PdCl_2(CH_3CN)_2$ and (*S*)-**5b**.

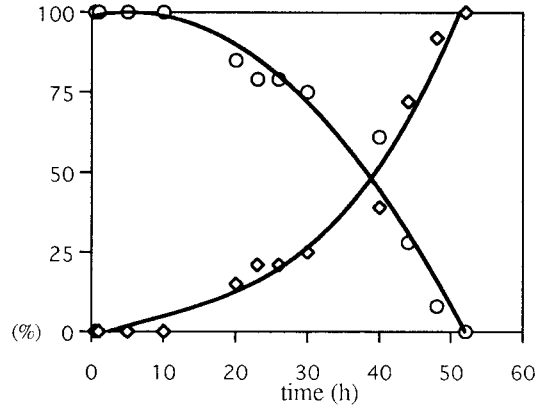
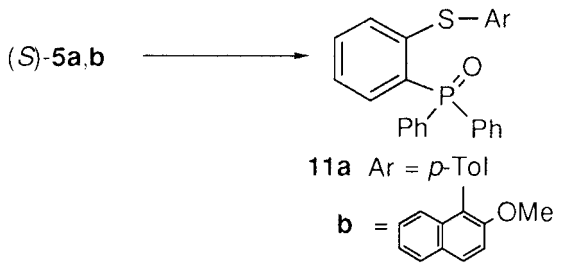


Figure 1. Convertion ratio of (*S*)-**5b** to **11b** upon heating in refluxing THF. (○)(*S*)-**5b**; (◇) **11b**.

With chiral β-phosphanoamino sulfoxides as chiral ligands, marked stereoelectronic effects were observed. The palladium-catalyzed reactions of (±)-**13** with dimethyl malonate sodium enolate were carried out in the presence of $[PdCl(\pi\text{-allyl})]_2$ (0.06 equiv.) and the chiral ligand (*S*)-**10a** (0.12 equiv.) in THF at room temperature to give (*S*)-**14a** with 45% e.e. Use of other palladium catalysts such as $Pd(OAc)_2$, $Pd(dba)_2$, and $Pd_2(dba)_3{\cdot}CHCl_3$ gave (*S*)-**14a** with rather low e.e. (24, 31, and 39%, respectively). Rather unequivocal solvent effects were observed in this catalytic reaction. The above reactions of (±)-**13** with sodium malonate catalyzed by $[PdCl(\pi\text{-allyl})]_2$ were carried out in DME, toluene, benzene, acetonitrile, or DMSO to give (*S*)-**14a** with 44, 28, 23, 19, or 8% e.e., respectively, as listed in Table 4. The effect of the molar ratio of $[PdCl(\pi\text{-allyl})]_2$ to (*S*)-**10a** was studied in the reaction of (±)-**13** with sodium malonate in THF at room temperature. The 1:4 to 1:8 molar ratios of $[PdCl(\pi\text{-allyl})]_2$ to (*S*)-**10a** provided higher enantioselectivity (43 and 49%, respectively) of (*S*)-**14a**.

The higher enantioselectivity was obtained by using 2-methoxy-1-naphthyl sulfoxide (*R*)-**10b**, and the results are summarized in Table 4. The reaction of (±)-**13** with sodium malonate catalyzed by $[PdCl(\pi\text{-allyl})]_2$ and (*R*)-**10b** produced (*R*)-**14a** with 97% e.e. The effects of the molar ratio of the palladium catalyst to the ligand used were extremely remarkable. In particular, the 1:8 molar ratio of $[PdCl(\pi\text{-allyl})]_2$ to (*R*)-**10b** resulted in the highest enantioselectivity of (*R*)-**14a**. The reason for this high efficiency is not clear at the present time. It should also be remarked that the absolute configuration of the product **14a** obtained by the palladium-catalyzed reaction of (±)-**13** with dimethyl malonate using (*R*)-**10b** was inversed from that obtained with (*S*)-**10a**. However, the reaction in DMSO gave (*S*)-**14a** with low e.e. This indicates that the sulfinyl functionality would participate in this palladium-catalyzed reaction via coordination to the catalyst to result in the stereocontrol of the product. The result of this high enantioselectivity was the most highly selective example among the asymmetric

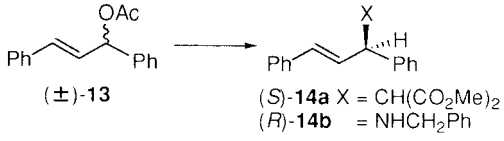


Scheme 3.

Table 2. Palladium-catalyzed asymmetric allylic alkylation of **13** with dimethyl malonate using (*S*)-**5a**,**b** or **8a**–**d** (the reactions of **13** with carbanion of dimethyl malonate (generated by treating with NaH (1.2 equiv.)) were carried out in the presence of a palladium catalyst (0.06 equiv.) and chiral ligands (*S*)-**5a**,**b** or **8a**-**d** (0.12 equiv.))

Entry	Ligand	Catalyst	Solvent	Reaction temp. (°C)	Reaction time (h)	Yield (%) of (*S*)-**14a**	e.e (%) of (*S*)-**14a**[a]
1	(*S*)-**5a**	$[PdCl(\pi\text{-allyl})]_2$	THF	rt	10	70	34
2		$Pd(OAc)_2$	THF	rt	10	75	15
3		$Pd(dba)_2$	THF	rt	10	73	38
4		$Pd_2(dba)_3{\cdot}CHCl_3$	THF	rt	6	72	24
5		$[PdCl(\pi\text{-allyl})]_2$	DME	rt	10	77	22
6		$[PdCl(\pi\text{-allyl})]_2$	CH_3CN	rt	10	84	39
7		$[PdCl(\pi\text{-allyl})]_2$	DMSO	rt	10	39	46
8		$[PdCl(\pi\text{-allyl})]_2$	CH_2Cl_2	rt	6	81[b]	44
9	(*S*)-**5b**	$[PdCl(\pi\text{-allyl})]_2$	THF	0	10 min	73	65
10		$[PdCl(\pi\text{-allyl})]_2$	THF	−20	3	75	75
11		$[PdCl(\pi\text{-allyl})]_2$	THF	−20	4	72[c]	75
12		$[PdCl(\pi\text{-allyl})]_2$	THF	−20	8	72[d]	70
13		$PdCl_2(CH_3CN)_2$	THF	−20	8	71[e]	82
14		$[PdCl(\pi\text{-allyl})]_2$	THF	−45	72	59	75
15		$[PdCl(\pi\text{-allyl})]_2$	DME	−20	8	74	75
16		$[PdCl(\pi\text{-allyl})]_2$	Toluene	−20	3	73	52
17		$[PdCl(\pi\text{-allyl})]_2$	DMSO	rt	30 min	64	13
18		$[PdCl(\pi\text{-allyl})]_2$	CH_3CN	0	10 min	70	15
19		$[PdCl(\pi\text{-allyl})]_2$	THF	rt	12	61	21
20	(*S*)-**8a**	$[PdCl(\pi\text{-allyl})]_2$	CH_2Cl_2	rt	12	89[c]	36
21		$[PdCl(\pi\text{-allyl})]_2$	CH_2Cl_2	rt	12	58[c]	22
22	(*S*)-**8b**	$[PdCl(\pi\text{-allyl})]_2$	CH_2Cl_2	0	12	73[b]	36
23		$[PdCl(\pi\text{-allyl})]_2$	THF	rt	12	67	36
24	(*S*)-**8c**	$[PdCl(\pi\text{-allyl})]_2$	CH_2Cl_2	rt	4	83[b]	20
25		$[PdCl(\pi\text{-allyl})]_2$	THF	rt	24	53	38
26	(*S*)-**8d**	$[PdCl(\pi\text{-allyl})]_2$	CH_2Cl_2	rt	12	92[b]	28

[a] The enantiomeric excess (e.e.) of (*S*)-**14a** was calculated by HPLC analysis with Chiralpak AD.[22]
[b] Reacted in the presence of BSA (3.0 equiv.) and a catalytic amount of NaOAc.
[c] The catalyst $[PdCl(\pi\text{-allyl})]_2$ (0.01 equiv.) was used.
[d] The catalyst $[PdCl(\pi\text{-allyl})]_2$ (0.005 equiv.) was used.
[e] The catalyst $PdCl_2(CH_3CN)_2$ (0.03 equiv.) was used.



Scheme 4.

synthetic reactions reported previouly, by means of chiral organosulfur ligands as the sole chiral sources.

The mechanism for the asymmetric induction with chiral β-phosphano and β-phosphanoamino sulfoxides as chiral ligands

The mechanism for the asymmetric induction with chiral *o*-phosphanophenyl sulfoxide ligands is proposed on the basis of the stereochemical results obtained. A five-membered chelated π-allylpalladium complex would be formed by

Table 3. Palladium-catalyzed asymmetric allylic amination of **13** with benzylamine using chiral sulfoxide ligands (*S*)-**5a**,**b** (the reactions of **13** with benzylamine (2.0 equiv.) were carried out in THF in the presence of a catalyst (0.06 equiv.) and chiral ligands (*S*)-**5a**,**b** (0.12 equiv.))

Entry	Ligand	Catalyst	Solvent	Reaction temp. (°C)	Reaction time (h)	Yield (%) of (*R*)-**14b**	e.e.(%) of (*R*)-**14b**[a]
1	(*S*)-**5a**	$[PdCl(\pi\text{-allyl})]_2$	THF	50	37	56	30
2	(*S*)-**5b**	$PdCl(\pi\text{-allyl})]_2$	THF	50	24	84	74
3		$PdCl(\pi\text{-allyl})]_2$	THF	rt	96	55	75
4		$Pd_2(dba)_3{\cdot}CHCl_3$	THF	50	65	59	66
5		$Pd(dba)_2$	THF	50	98	37	79
6		$Pd(OAc)_2$	THF	50	144	20	76
7		$PdCl_2(CH_3CN)_2$	THF	50	168	29	72
8		$PdCl(\pi\text{-allyl})]_2$	DMSO	50	65	85	10
9		$PdCl(\pi\text{-allyl})]_2$	DMF	50	38	64	12
10		$PdCl(\pi\text{-allyl})]_2$	CH_3CN	50	16	72	3
11		$PdCl(\pi\text{-allyl})]_2$	DME	50	23	66	74
12		$PdCl(\pi\text{-allyl})]_2$	Toluene	50	20	91	50
13		$PdCl(\pi\text{-allyl})]_2$	Toluene	rt	20	85	70
14		$PdCl(\pi\text{-allyl})]_2$	Toluene	0	92	51	85

[a] The enantiomeric excess (e.e.) of (*R*)-**14b** was calculated by HPLC analysis with Chiralcel OD.[23]

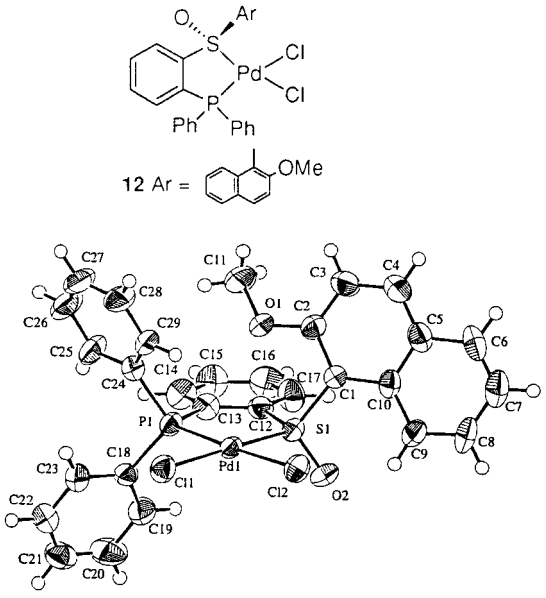


Figure 2. Molecular structure (ORTEP drawing) of **12** with the omission of two molecules of CH_2Cl_2 included.

coordination of the phosphano group and the sulfinyl sulfur function to palladium. In the conformational equilibrium of the five-membered chelate, the conformer **15b** would be preferred to **15a** because of the existence of steric interference between the large substituent (*p*-toly or 2-methoxy-1-naphthyl) on the chiral sulfoxide and the phenyl group in the allyl terminus in **15a**. The nucleophile (sodium malonate or benzylamine) attacks preferentially the allyl terminus *trans* to the better π-acceptor,[24] which is the phosphane group in the current case, despite the steric effect by the bulky substituent (2-methoxy-1-naphthyl), affording (*S*)-**14a** or (*R*)-**14b**, respectively (Scheme 5).

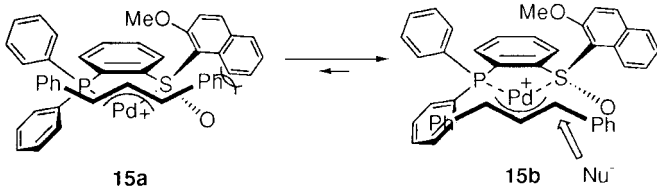
Furthermore, the existence of the vicinal phosphanoamino functions in the chiral sulfinyl ligands was demonstrated to be most essential for the improvement of the enantioselectivity, in comparison with the cases of the vicinal amino and phosphano sulfinyl ligands. This high enantioselectivity arises presumably from the formation of a sterically controllable six-membered transition state as described below.

The mechanism of this asymmetric synthesis induced by the chirality of the chiral sulfinyl group is rationalized as follows. The phosphorus and sulfur atoms in the chiral phosphanoamino ligand (*S*)-**10a** have rather strong coordination ability to palladium catalysts, forming six-membered π-allylpalladium intermediates **16a**–**d**, in which **16a**,**b** would be more sterically preferred to **16c**,**d**, because of the existence of 1,3-diaxial steric interference between the tolyl group and the phenyl group in **16c**,**d**. In the conformational equilibrium between **16a** and **16b**, **16b** would be preferred to **16a** which has steric interference between the

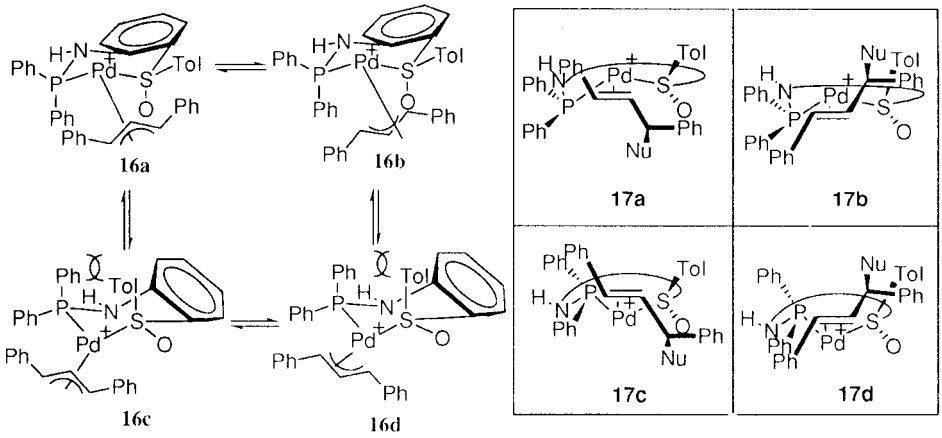
Table 4. The palladium-catalyzed asymmetric alkylation of **13** with (*S*)-**10a** or (*R*)-**10b** (the reaction of **13** with dimethyl malonate sodium enolate (generated by treating with NaH (1.2 equiv.)) were carried out in the presence of $[PdCl(\pi\text{-allyl})]_2$ (0.06 equiv.) and chiral ligands (*S*)-**10a** or (*R*)-**10b**)

Entry	Ligand	Ratio of Pd/ligand	Solvent	Reaction temp. (°C)	Reaction time (h)	Yield (%) of **14a**[a]	e.e.(%) of **14a**[b] (Abs. confign.)
1	(*S*)-**10a**	1:1	THF	rt	55	26 (39)	39 (*S*)
2		1:2	THF	rt	24	22 (70)	45 (*S*)
3		1:4	THF	rt	55	18 (51)	43 (*S*)
4		1:8	THF	rt	62	27 (42)	49 (*S*)
5		1:2	DME	rt	47	33 (72)	44 (*S*)
6		1:2	Toluene	rt	40	12 (75)	28 (*S*)
7		1:2	CH_3CN	rt	17	59 (87)	19 (*S*)
8		1:2	DMSO	rt	17	50 (90)	8 (*S*)
9	(*R*)-**10b**	1:1	THF	0	110	26 (59)	67 (*R*)
10		1:2	THF	0	110	29 (82)	73 (*R*)
11		1:2	THF	rt	48	41 (87)	53 (*R*)
12		1:4	THF	0	110	33 (94)	70 (*R*)
13		1:8	THF	0	132	49 (90)	97 (*R*)
14		1:2	DME	0	40	41 (92)	75 (*R*)
15		1:2	DME	rt	76	46 (80)	71 (*R*)
16		1:4	Toluene	0	110	26 (67)	81 (*R*)
17		1:4	Toluene	rt	35	34 (51)	67 (*R*)
18		1:2	DMSO	rt	3	83	11 (*S*)

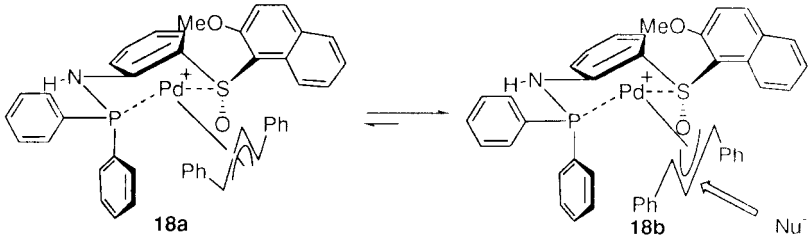
[a] The corrected yields of **14a** based on the recovered starting material are described in parentheses.
[b] The enantiomeric excess (e.e.) of **14a** was calculated by HPLC analysis with Chiralpak AD.[22]



Scheme 5.



Scheme 6.



Scheme 7.

tolyl group and the phenyl substituent in the allylic system. In general, nucleophilic attack would be preferred at the allyl terminus in **16a–d** *trans* to the better π-acceptor,[24] which is the phosphorus group in the current case, resulting in the formation of the corresponding intermediates **17a–d**, respectively. The nucleophile (malonate carbanion) would attack preferentially the allylic site *trans* to the phosphorus group in the sterically most preferred π-allylpalladium complex **16b**, producing (*S*)-**14a** via **17b** (Scheme 6).

Surprisingly, the ligand (*R*)-**10b** with the larger substituent, the 2-methoxy-1-naphthyl group, was highly effective in the asymmetric induction via the π-allylpalladium complex, controlling the stereochemistry of the product. Since, presumably, the steric crowding by the large naphthyl group would disturb the alkylation at the allylic site *trans* to the phosphorus group in the sterically preferred **18b**, similarly as mentioned above, in the equilibrium of **18a**,**b**, the preferential alkylation at the allylic site *syn* to the phosphorus group in **18b** would occur to give (*R*)-**14a** (Scheme 7).

Conclusion

Thus, chiral *o*-phosphanophenyl sulfoxides and 2-(phosphanoamino)phenyl sulfoxides were demonstrated to serve as efficient chiral ligands in the palladium-catalyzed allylic nucleophilic substitution reactions. It should be noted that chiral 2-(diphenylphosphanoamino)phenyl 2-methoxy-1-naphthyl sulfoxide was the most efficient ligand among the known ligands bearing a chiral organosulfur functionality as the sole chiral source. Our present work is the first report related to asymmetric synthesis with high efficiency using chiral sulfoxides as the sole chiral sources, involving studies on the thermal stability of chiral β-phosphano sulfoxides with the elapse of the reaction time and the structural determination of an intermediary palladium complex with a chiral β-phosphano sulfoxide.

Experimental

Infrared (IR) spectra were obtained in the indicated state with a JASCO DR-81 Fourier-Transform IR spectrometer. NMR spectra were determined in the indicated solvent with a JEOL JNM-LA 400 (^{1}H NMR; 400 MHz) and JEOL EX-270 (^{1}H NMR; 270 MHz) high-resolution NMR spectrometer; chemical shifts are given in ppm from tetramethylsilane as an internal standard. Splitting patterns are designated as s, singlet; bs, broad singlet; d, doublet; dd, doublet of doublets; ddd, double doublet of doublets; t, triplet; dt, triplet of doublets; td, doublet of triplets; m, multiplet. Mass spectra were taken on a JEOL JMS-DX 303/JMA-DA 5000 system. High performance liquid chromatography (HPLC) was performed with a Tosoh UV-8010 CCPM (column: Dicel Chiralpak AD (hexane/*i*-PrOH 20:1) or Chiralcel OD (hexane/*i*-PrOH 200:1), 0.5 ml/min, 254 nm). Optical rotations were measured at 24°C with a JASCO DIP-370 polarimeter. X-Ray diffraction analysis was carried out on a Rigaku RAXIS-IV diffractometer. Flash column chromatography was performed with Merck Silica gel 60 (230–400 mesh). Thin layer or thick layer plates (preparative TLC) were made of Merck Silica gel 60PF-254 activated by drying at 140°C for 3.5 h.

(*S*)-2-Fluorophenyl *p*-tolyl sulfoxide (4a). A 1.06 M cyclohexane solution of *sec*-butyllithium (*sec*-BuLi) (3 ml,

2.70 mmol) was added at −78°C to a solution of 2-fluoroiodobenzene (**2**) (500 mg, 2.25 mmol) in THF (4 ml), and the reaction mixture was stirred at −78°C for 1 h. A solution of (−)-menthyl (*Ss*)-*p*-toluenesulfinate (**3a**)[18] (728 mg, 2.47 mmol) in THF (8 ml) was added to the above solution, and the reaction mixture was stirred at room temperature for 3 h. The reaction solution was diluted with ether and the solution was washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was subjected to preparative TLC (ether/hexane=3:1) to give (*S*)-**4a** (353 mg, 67% yield).

The sulfinylations of **2**, 3-bromo-4-fluorotoluene (**6a**) or 4-bromo-3-fluorotoluene (**6b**) with (*Ss*)-**3a** or (−)-menthyl (*Ss*)-2-methoxy-1-naphthalenesulfinate (**3b**)[19] were carried out in the same way as described above to give (*S*)-2-fluorophenyl 2-methoxy-1-naphthyl sulfoxide (**4b**), (*S*)-2-fluoro-3-tolyl *p*-tolyl sulfoxide (**7a**) or (*S*)-2-fluoro-4-tolyl *p*-tolyl sulfoxide (**7b**), respectively.

(*S*)-4a. $[\alpha]_D=-77°$ (*c*=1.2, acetone). IR ν_{max}^{film} cm^{-1}: 1595 (aromatic), 1040 (SO). NMR (400 MHz; $CDCl_3$) δ: 2.36 (s, 3H, CH_3), 7.00–7.05 (m, 1H, ArH), 7.25–7.27 (m, 2H, ArH), 7.31–7.44 (m, 2H, ArH), 7.59–7.60 (m, 2H, ArH), 7.91–7.95 (m, 1H, ArH). MS *m/z*: 234 (M^+). HRMS: 234.0515 (Calcd $C_{13}H_{11}OFS$: 234.0527).

(*S*)-4b. 74% yield. $[\alpha]_D=+176°$ (*c*=6.5, acetone). IR ν_{max}^{film} cm^{-1}: 1595 (aromatic), 1035 (SO). NMR (270 MHz; $CDCl_3$) δ: 3.87 (s, 3H, CH_3), 6.84–6.94 (m, 1H, ArH), 7.21 (d, *J*=9.1 Hz, 1H, ArH), 7.30–7.40 (m, 3H, ArH), 7.48–7.54 (m, 1H, ArH), 7.76 (dt, *J*=8.2, 0.7 Hz, 1H, ArH), 7.94 (d, *J*=9.1 Hz, 1H, ArH), 8.14–8.24 (m,1H, ArH), 8.66 (d, *J*=8.6 Hz, 1H, ArH). MS *m/z*: 300 (M^+). HRMS: 300.0620 (Calcd $C_{17}H_{13}O_2FS$: 300.0640).

(*S*)-7a. 79% yield. $[\alpha]_D=-22°$ (*c*=1.1, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1595 (aromatic), 1040 (SO). NMR (270 MHz; $CDCl_3$) δ: 2.329 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 6.82 (dd, *J*=10.6, 0.7 Hz, 1H, ArH), 7.09 (dd, *J*=1.5, 0.6 Hz, 1H, ArH), 7.23 (dd, *J*=8.6, 0.6 Hz, 2H, ArH), 7.55–7.58 (m, 2H, ArH), 7.73–7.78 (m, 1H, ArH). MS *m/z*: 248 (M^+). HRMS: 248.0652 (Calcd $C_{14}H_{13}OFS$: 248.0671).

(*S*)-7b. 49% yield. $[\alpha]_D=+26°$ (*c*=1.4, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1590 (aromatic), 1042 (SO). NMR (270 MHz; $CDCl_3$) δ: 2.37 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 6.87–6.94 (m, 1H, ArH), 7.15–7.21 (m, 1H, ArH), 7.26 (t, *J*=4.0 Hz, 2H, ArH), 7.57–7.60 (m, 2H, ArH), 7.67–7.70 (m, 1H, ArH). MS *m/z*: 248 (M^+). HRMS: 248.0721 (Calcd $C_{14}H_{13}OFS$: 248.0671).

(*S*)-2-Fluoro-3-methoxyphenyl *p*-tolyl sulfoxide (7c). A solution of 2-fluoroanisole (200 mg, 1.59 mmol) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDTA) (329 mg, 1.90 mmol) in THF (5 ml) was added at −78°C to a 1.56 M hexane solution of *n*-butyllithium (*n*-BuLi) (1 ml, 1.90 mmol), and the reaction mixture was stirred at −78°C for 2 h. A solution of (*Ss*)-**3a** (559 mg, 1.90 mmol) in THF (5 ml) was added to the above solution, and the reaction mixture was stirred at room temperature for 12 h. The reaction solution was diluted with ether, and the solution was washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$, and saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was subjected to preparative TLC (ether/hexane=1:1) to give (*S*)-**7c** (502 mg, 74% yield).

The sulfinations of 2-fluoro-1-benzyloxybenzene were carried out in the same way as described above to give (*S*)-2-fluoro-3-benzyloxyphenyl *p*-tolyl sulfoxide (**7d**).

(*S*)-7c. $[\alpha]_D=-31°$ (*c*=1.5, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1600 (aromatic), 1020 (SO). NMR (270 MHz; $CDCl_3$) δ: 2.36 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.98–7.05 (m, 7H, ArH), 7.23–7.28 (m, 3H, ArH), 7.44 (dd, *J*=5.6, 1.6 Hz, 1H, ArH), 7.58–7.61 (m, 2H, ArH). MS *m/z*: 264 (M^+). HRMS: 264.0582 (Calcd $C_{25}H_{21}OPS$: 264.0620).

(*S*)-7d. 37% yield. $[\alpha]_D=-71°$ (*c*=6.5, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1600 (aromatic), 1040 (SO). NMR (270 MHz; $CDCl_3$) δ: 2.36 (s, 3H, CH_3), 5.08 (d, *J*=1.3 Hz, 2H, CH_2), 7.03–7.09 (m, 1H, ArH), 7.17–7.50 (m, 9H, ArH), 7.60 (d, *J*=7.6 Hz, 2H, ArH). MS *m/z*: 340 (M^+). HRMS: 340.0975 (Calcd $C_{25}H_{21}OPS$: 340.0934).

(*S*)-(Diphenylphosphano)phenyl *p*-tolyl sulfoxide (5a). A 0.5 M THF solution of potassium diphenylphosphide ($KPPh_2$)[20] (commercially available) (2 ml, 1.16 ml) was added at room temperature to a solution of (*S*)-**4a** (181 mg, 0.77 mmol) in THF (4 ml), and the reaction mixture was stirred at room temperature for 30 min. The reaction solution was diluted with ether and filtered through Celite. The filtrate was concentrated in vacuo and the residue was subjected to preparative TLC (ether/hexane=3:1) to give (*S*)-**5a** (268 mg, 87% yield).

The phosphanations of (*S*)-**4** or **7a**–**d**, were carried out in the same way as described above to give (*S*)-2-(diphenylphosphano)phenyl 2-methoxy-1-naphthyl sulfoxide (**5b**), (*S*)-2-(diphenylphosphano)-3-tolyl *p*-tolyl sulfoxide (**8a**), (*S*)-2-(diphenylphosphano)-4-tolyl *p*-tolyl sulfoxide (**8b**), (*S*)-2-(diphenylphosphano)-3-methoxyphenyl *p*-tolyl sulfoxide (**8c**), (*S*)-3-benzyloxy-2-(diphenylphosphano)phenyl *p*-tolyl sulfoxide (**8d**), respectively.

(*S*)-5a. Mp 124°C (colorless prisms; recrystallized from $CHCl_3$/hexane). $[\alpha]_D=-138°$ (*c*=1.1, acetone). IR ν_{max}^{film} cm^{-1}: 1595 (aromatic), 1040 (SO). ^1H NMR (270 MHz; $CDCl_3$) δ: 2.24 (s, 3H, CH_3), 6.93–7.06 (m, 5H, ArH), 7.14–7.37 (m, 9H, ArH), 7.44 (d, *J*=8.2 Hz, 2H, ArH), 7.55–7.61 (m, 1H, ArH), 8.14–8.18 (m, 1H, ArH). ^{13}C NMR (67.8 MHz; $CDCl_3$) δ: 21.3, 124.1, 124.3, 126.3, 126.4, 128.1, 128.2, 128.4, 128.5, 128.8, 129.4, 130.5, 132.0, 133.1, 133.3, 133.4, 133.6, 134.3, 134.4, 135.0, 135.3, 135.5, 135.6, 141.0, 141.8. MS *m/z*: 400 (M^+). HRMS: 400.1051 (Calcd $C_{25}H_{21}OPS$: 400.1043).

(*S*)-5b. Mp 203°C (colorless prisms; recrystallized from $CHCl_3$/hexane). 73% yield. $[\alpha]_D=+130°$ (*c*=1.9, acetone). IR ν_{max}^{film} cm^{-1}: 1595 (aromatic), 1035 (SO). NMR (270 MHz; $CDCl_3$) δ: 3.48 (s, 3H, CH_3), 6.16–6.23 (m, 2H, ArH), 6.63 (d, *J*=9.2 Hz, 1H, ArH), 6.76–6.82 (m, 2H, ArH), 6.93–7.04 (m, 4H, ArH), 7.17–7.26 (m, 3H, ArH), 7.32–7.39 (m, 2H, ArH), 7.47 (d, *J*=9.1 Hz, 1H,

ArH), 7.55–7.70 (m, 3H, ArH), 8.47–8.52 (m, 1H, ArH), 8.88 (dd, J=7.7, 0.8 Hz, 1H, ArH). ^{13}C NMR (67.8 MHz; $CDCl_3$) δ: 56.6, 110.7, 113.1, 113.7, 120.5, 123.3, 123.9, 124.0, 127.1, 127.4, 127.5, 127.6, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 129.0, 129.2, 131.0, 132.3, 132.4, 132.6, 132.8, 133.1, 134.1, 134.6, 134.9. MS m/z: 466 (M^+). HRMS: 466.1156 (Calcd $C_{29}H_{23}O_2PS$: 466.1191).

(*S*)-8a. 50% yield. $[\alpha]_D$=−56° (c=3.1, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1591 (aromatic), 1024 (SO). NMR (400 MHz; $CDCl_3$) δ: 2.24 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 6.89–7.01 (m, 5H, ArH), 7.14–7.34 (m, 9H, ArH), 7.44–7.46 (m, 2H, ArH), 7.98–7.99 (m, 1H, ArH). MS m/z: 414 (M^+). HRMS: 414.1223 (Calcd $C_{26}H_{23}O_4PS$: 414.1207).

(*S*)-8b. 51% yield. $[\alpha]_D$=−72° (c=2.3, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1584 (aromatic), 1026 (SO). NMR (400 MHz; $CDCl_3$) δ: 2.24 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 6.78–6.79 (m, 1H, ArH), 6.97–7.01 (m, 4H, ArH), 7.18–7.44 (m, 11H, ArH), 8.02 (dd, J=8.1, 3.7 Hz, 1H, ArH). MS m/z: 414 (M^+). HRMS: 414.1200 (Calcd $C_{26}H_{23}OPS$: 414.1207).

(*S*)-8c. 71% yield. $[\alpha]_D$=−11° (c=1.2, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1580 (aromatic), 1020 (SO). NMR (400 MHz; $CDCl_3$) d: 2.22 (s, 3H, CH_3), 3.27 (s, 3H, CH_3), 6.81–6.89 (m, 2H, ArH), 6.91 (d, J=0.7 Hz, 1H, ArH), 6.98 (d, J=7.8 Hz, 2H, ArH), 7.04–7.08 (m, 2H, ArH), 7.14–7.18 (m, 1H, ArH), 7.24–7.35 (m, 5H, ArH), 7.52 (d, J=8.1 Hz, 2H, ArH), 7.68 (t, J=8.1 Hz, 1H, ArH), 7.97 (ddd, J=7.8, 3.2, 1.0 Hz, 1H, ArH). MS m/z: 430 (M^+). HRMS: 430.1187 (Calcd $C_{26}H_{23}O_2SP$: 430.1156).

(*S*)-8d. 48% yield. $[\alpha]_D$=−58° (c=1.3, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1580 (aromatic), 1030 (SO). NMR (270 MHz; $CDCl_3$) δ: 2.29 (s, 3H, CH_3), 4.68 (d, J=1.5 Hz, 2H, CH_2), 6.65–6.68 (m, 2H, ArH), 6.92–7.39 (m, 13H, ArH), 7.47–7.58 (m, 3H, ArH), 7.67 (dd, J=6.4, 1.8 Hz, 2H, ArH), 7.74–7.80 (m, 1H, ArH), 8.36 (ddd, J=8.0, 2.7, 0.8 Hz, 1H, ArH). MS m/z: 506 (M^+). HRMS: 506.1443 (Calcd $C_{32}H_{27}O_2SP$: 506.1469).

(*S*)-*N*-(Diphenylphosphano)-2-(*p*-toluenesulfinyl)aniline (10a). A 1.08 M cyclohexane solution of *sec*-BuLi (2 ml, 1.85 mmol) was added at −78°C to a solution of 2-bromo-*N*-(diphenylphosphano)aniline (**9**) (300 mg, 0.84 mmol) in THF (3 ml), and the reaction mixture was stirred at −78°C for 1 h. A solution of (*Ss*)-**3a** (372 mg, 1.26 mmol) in THF (3 ml) was added to the above solution, and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with ether, and the solution was filtered through Celite. The filtrate was concentrated in vacuo and the residue was subjected to preparative TLC (ethyl acetate/hexane=3:1) to give (*S*)-**10a** (601 mg, 52% yield). The sulfinylation of **9** with (*Ss*)-**3b** was carried out in the same way as described above to give (*R*)-*N*-(diphenylphosphano)-2-(2-methoxy-1-naphthylsulfinyl)aniline (**10b**).

(*S*)-10a. Mp 205°C (colorless prisms; recrystallized from $CHCl_3$/hexane). $[\alpha]_D$=−54° (c=0.7, acetone). IR ν_{max}^{film} cm^{-1}:1600 (aromatic), 1020 (SO). NMR (400 MHz; $CDCl_3$) δ: 1.65 (bs, 1H, NH), 2.44 (s, 3H, CH_3), 6.96 (td, J=7.5, 1.0 Hz, 1H, ArH), 7.19–7.56 (m, 14H, ArH), 7.75 (ddd, J=12.7, 6.8, 1.5 Hz, 2H, ArH), 8.44 (d, J=12.0 Hz, 1H, ArH). MS m/z: 415 (M^+). ^{13}C NMR (100 MHz; $CDCl_3$) δ: 21.3, 120.4, 120.5, 124.7, 126.1, 126.3, 128.1, 128.2, 128.3, 128.4, 128.6, 129.5, 130.8, 131.1, 131.2, 131.7, 131.8, 131.9, 132.0, 132.1, 132.6, 132.8, 139.6, 140.8, 142.8. HRMS: 415.1160 (Calcd $C_{25}H_{22}NOPS$: 415.1107).

(*R*)-10b. Mp 143°C (colorless prisms; recrystallized from $CHCl_3$/hexane). 33% yield. $[\alpha]_D$=+147° (c=1.1, acetone). IR ν_{max}^{film} cm^{-1}: 1590 (aromatic), 1020 (SO). NMR (400 MHz; $CDCl_3$) δ: 1.41 (bs, H, NH), 3.77 (s, 3H, CH_3), 6.76–6.89 (m, 1H, ArH), 6.96–7.22 (m, 6H, ArH), 7.34–7.56 (m, 7H, ArH), 7.81–8.00 (m, 5H, ArH), 8.67–8.74 (m, 1H, ArH). ^{1}C NMR (100 MHz; $CDCl_3$) δ: 56.7, 112.2, 113.3, 114.1, 120.0, 120.1, 121.0, 122.6, 123.0, 124.7, 125.5, 127.2, 127.3, 127.8, 128.6, 128.7, 128.8, 128.9, 129.0, 129.3, 130.8, 131.3, 131.4, 132.0, 132.1, 132.2, 132.3, 132.4, 135.4. MS m/z: 481 (M^+). HRMS: 481.1266 (Calcd $C_{29}H_{24}O_2PNS$: 481.1279).

2-(2-Methoxy-1-naphthylsulfanyl)phenyl diphenylphosphane oxide (11b). A solution of (*S*)-**5b** (30 mg, 0.08 mmol) in THF (8 ml) was stirred under heating at reflux. The reaction solution was concentrated in vacuo and the residue was subjected to preparative TLC (ethyl acetate/hexane=5:1) to give **11b** (3.0 mg, 10% yield).

11a. IR ν_{max}^{film} cm^{-1}: 1600 (aromatic). NMR (270 MHz; $CDCl_3$) δ: 2.31 (s, 3H, CH_3), 7.03–7.16 (m, 6H, ArH), 7.28–7.38 (m, 2H, ArH), 7.44–7.57 (m, 6H, ArH), 7.73–7.79 (m, 4H, ArH). MS m/z: 400 (M^+). HRMS: 400.1011 (Calcd $C_{25}H_{21}OPS$: 400.1051).

11b. 88% yield. IR ν_{max}^{film} cm^{-1}: 1601 (aromatic). NMR (270 MHz; $CDCl_3$) δ: 3.31 (s, 3H, CH_3), 6.52 (d, J=9.0 Hz, 1H, ArH), 6.68 (dd, J=6.8, 1.2 Hz, 2H, ArH), 6.94–7.00 (m, 2H, ArH), 7.04–7.08 (m, 1H, ArH), 7.20–7.49 (m, 9H, ArH), 7.52–7.65 (m, 2H, ArH), 7.84 (dt, J=16.8, 1.5 Hz, 1H, ArH), 8.75–8.78 (m, 1H, ArH), 8.95 (d, J=8.5 Hz, 1H, ArH). MS m/z: 467 (M^++1). HRMS: 466.1146 (Calcd $C_{29}H_{23}O_2PS$: 466.1156).

The chelate of palladium with (*S*)-5b

(*S*)-**5b** (30 mg, 0.06 mmol) and bis(acetonitrile)dichloropalladium [$PdCl_2(CH_3CN)_2$] (18 mg, 0.06 mmol) were dissolved in CH_2Cl_2 (3 ml) at room temperature by stirring for 10 min, and the solution was concentrated in vacuo, yielding a product, [$PdCl_2$-(*S*)-**5b**]·$2CH_2Cl_2$ (42 mg, 40% yield), which was recrystallized from ether-dichloromethane (5:1). The structure of the chelate obtained was determined by X-ray crystallographic analysis. The principal crystallographic parameters of the product are as follows: $C_{31}H_{27}O_2PSCl_6Pd$; Fw=813.70; monoclinic; space group $P2_1$(#4); a=9.466(1) Å, b=17.136(2)Å, c=11.180(1)Å, β=107.99(1)°; V=1724.9(3) Å^3; Z=2; D_c=1.567 g/cm$_3$; Mo Kα; λ=0.71070 Å, μ=11.37 cm^{-1}; F(000)=816. The colorless prismatic crystal with dimensions of 0.15×0.10×0.10 mm was used for data collection. The structure was refined to a final R=0.038, Rw=0.049 for 2985 reflections, $I>3\sigma(I)$.

Palladium-catalyzed asymmetric nucleophilic substitution reactions of 1,3-diphenyl-2-propenyl acetate (13) with chiral sulfoxide ligands.

General procedure A. A 25 ml two-necked flask equipped with a septem inlet and a magnetic stirring bar, and containing sodium hydride (50% oil dispersion, 23 mg, 0.48 mmol), was flushed with argon, and maintained under a positive pressure of argon. A solution of dimethyl malonate (63 mg, 0.48 mmol) in THF (3 ml) was added at 0°C to the above flask. Another 25 ml two-necked flask equipped with a septem inlet and a magnetic stirring bar, and containing di-μ-chlorobis-(π-allyl)dipalladium ($[PdCl(CH_2{=}CHCH_2)]_2$) (4 mg, 0.01 mmol) and chiral sulfoxide ligands (0.02 mmol), was flushed with argon, and maintained under a posstive pressure of argon. A solution of (±)-1,3-diphenyl-2-propenyl acetate (13) (100 mg, 0.40 mmol) in THF (3 ml) was added at room temperature to the above solution, and the mixture was stirred at room temperature for 30 min. The solution was added to the above solution including sodium dimethyl malonate, and the reaction mixture was stirred under the conditions listed in Tables 2 and 4. The reaction solution was diluted with ether, and the solution was washed with saturated aqueous NH_4Cl and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was subjected to preparative TLC (ethyl acetate/hexane=1:7) to give optically active diethyl (1,3-diphenyl-2-propenyl) propanedioate (**14**).[22] The e.e. and the absolute configuration of the product were determined by HPLC analysis with a chiral column, Chiralpak AD (hexane/*i*-propanol=20:1).[22] The results obtained are listed in Tables 2 and 4.

General procedure B. A solution of chiral sulfoxide ligands (0.02 mmol) and $[PdCl(CH_2{=}CHCH_2)]_2$ (4 mg, 0.01 mmol) in CH_2Cl_2 (2 ml) was stirred under argon for 30 min, and then a solution of (±)-**13** (100 mg, 0.40 mmol) in THF (1 ml), dimethyl malonate (157 mg, 1.19 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (BSA)[21] (0.3 ml, 1.19 mmol), and a catalytic amount of anhydrous sodium acetate was added to the above solution. The reaction mixture was stirred at 0°C-room temperature for 4–12 h. The reaction mixture was diluted with ether. The organic layer was washed 10% aqueous sodium hydroxide and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was subjected to preparative TLC (ethyl acetate/hexane=1:7) to give **14a**.[22] The results obtained are listed in Table 2.

General procedure C. To a solution of chiral sulfoxide ligands (0.02 mmol) and $[PdCl(CH_2{=}CHCH_2)]_2$ (5 mg, 0.02 mmol) in THF(1 ml), which had been prestirred for 30 min, were added successively a solution of (±)-**13** (80 mg, 0.32 mmol) in THF (3 ml) and a solution of benzylamine (68 mg, 0.64 mmol) in THF (3 ml). The reaction mixture was stirred at room temperature −50°C for 16–168 h. After the mixture had been concentrated *in vacuo*, the crude product obtained was subjected to preparative TLC (ether/hexane=1:4) to give optically active *N*-benzyl-1,3-diphenyl-2-propenylamine (**14b**).[23] The e.e. and the absolute configuration of the product were determined by HPLC analysis with a chiral column, Chiralcel OD (hexane/*i*-propanol=200:1).[23] The results obtained are listed in Table 3.

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