Application of SDP Ligands for Pd-Catalyzed Allylic Alkylation

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Abstract: Chiral spiro diphosphines (SDP) are efficient ligands for the Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate and related nucleophiles. The newly synthesized ligand DMM-SDP (**1e**) with 3,5-dimethyl-4-methoxy groups on the *P*-phenyl rings of the phosphine shows the highest enantioselectivity (up to 99.1% ee). Diethylzinc as a base is critical for obtaining high enantioselectivity in the allylic alkylation using β-dicarbonyl nucleophiles. The structure of catalyst [PdCl$_2$((*S*)-SDP)] was determined by single crystal X-ray diffraction. The SDP ligands create an effective asymmetric environment around the palladium, resulting in high enantioselectivities for the asymmetric allylic alkylation reaction

Keywords: allylic alkylation; asymmetric catalysis; diphosphine ligands; palladium; spirobiindane

Introduction

In the last few decades, tremendous progress has been made in the design of new chiral ligands for the development of efficient metal-catalyzed asymmetric transformations.[1] Of the various chiral ligands reported, diphosphines are the most popular in asymmetric catalysis, due mainly to their stability and outstanding ability to form highly active and selective complexes with transition metals.[2] A large number of efficient catalysts with chiral diphosphine ligands has been reported for the different asymmetric reactions. Since the development of DIOP ligand by Kagan[3] and co-workers in 1971, the design of chiral phosphines has for a long period been dominated by chelating diphosphine derivatives possessing a chiral scaffold. Prominent examples are the atropisomeric C_2-symmetric diphosphines with a biaryl scaffold (such as BINAP,[4] BIPHEMP,[5] Bitianp,[6] P-Phos,[7] and Segphos[8]), the planar chiral diphosphines based on ferrocene or paracyclophane backbones (such as Josiphos[9] and Phanephos[10]), and the central chiral diphosphines (such as Duphos[11] and Tangphos[12]). Although these chiral diphosphines have been widely used as ligands for many asymmetric catalytic reactions, the reaction enantioselectivites are highly substrate-dependent. Therefore, the development of new efficient chiral ligands, especially those with new chiral scaffolds remains an important goal in asymmetric catalysis.

Recently, we have developed a new type of axially chiral diphosphine ligands, SDP (**1a–d**), based on the chiral 1,1′-spirobiindane scaffold[13] and found their Ru(II)-diphosphine-diamine complexes to be very effective in the ruthenium-catalyzed asymmetric hydrogenation of simple ketones (S/C up to 100,000 and ee up to 99.5%). This type of ligand has a rigid spiro backbone. As Noyori and co-workers suggested that the highly skew position of the naphthyl rings in BINAP was the determining factor for the ligand to be effective in asymmetric catalytic reaction,[14] the rigid spiro structure would reduce the conformational obscurity of catalyst and create an effective asymmetric environment around the central metal, which subsequently leads to high enantioselectivities in asymmetric reactions.[15] Thus we characterized the structure of our SDP ligands by X-ray crystallography of [PdCl$_2$((*S*)-SDP)], tuned the electronic and steric properties by further synthesis of a new member of the SDP ligands, viz. 7,7′-bis[di-(3,5-dimethyl-4-methoxyphenyl)phosphino]-1,1′-spirobiindane (DMM-SDP, **1e**) with 3,5-dimethyl-4-methoxy groups on the phenyl rings of the phosphine, as well as evaluated SDP ligands in Pd-catalyzed asymmetric allylic alkylations. The results revealed that SDP ligands are effective in the Pd-catalyzed asymmetric allylic alkylation of *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate and related nucleophiles providing the alkylation products in high enantioselectivities (up to 99.1% ee), and the newly synthesized ligand DMM-SDP (**1e**) is the most selective. In this paper, we report the synthesis of the ligand DMM-SDP (**1e**), the molecular structure of the complexes of [PdCl$_2$((*S*)-SDP)] and the application of SDP ligands in asymmetric allylic alkylation reactions.

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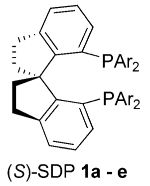


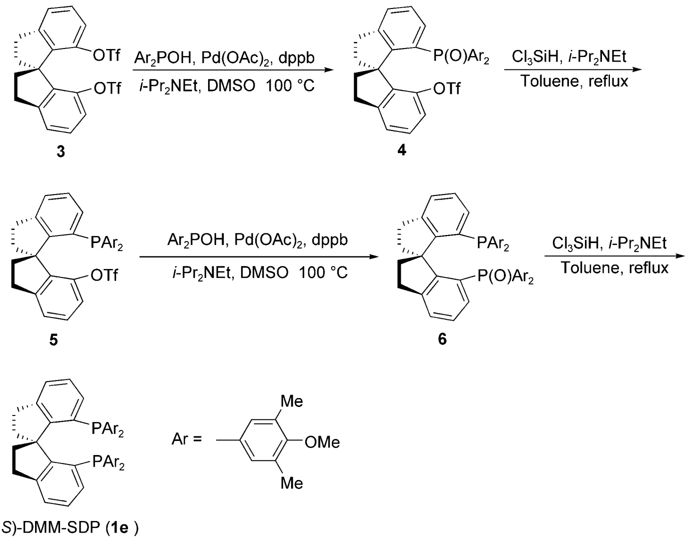
1a Ar = C_6H_5	(SDP)
1b Ar = p-$CH_3C_6H_4$	(Tol-SDP)
1c Ar = p-$CH_3OC_6H_4$	(An-SDP)
1d Ar = 3,5-$(CH_3)_2C_6H_3$	(Xyl-SDP)
1e Ar = 4-MeO-3,5-$(CH_3)_2C_6H_2$	(DMM-SDP)

Scheme 1. SDP ligands.

Results and Discussion

Synthesis of the SDP Ligand DMM-SDP

The new SDP ligand DMM-SDP (**1e**) is prepared from enantiomerically pure 1,1′-spirobiindane-7,7′-diol [(*R*)- or (*S*)-**2**] by a procedure similar to the synthesis of SDP ligands **1a–d** (Scheme 1).[13] Monophosphinylation of ditriflate (*S*)-**3** was carried out in the presence of $Pd(OAc)_2$/dppb [dppb = 1,4-bis(diphenylphosphino)-butane] and diisopropylethylamine at 100 °C for 6 hours to produce compound (*S*)-**4** in 98% yield. The compound (*S*)-**4** was reduced using $HSiCl_3$ in the presence of diisopropylethylamine in toluene at 110 °C for 5 days, giving phosphine monotriflate (*S*)-**5** in 76% yield. The second phosphine group was introduced into compound (*S*)-**5** by using the same conditions as for the first monophosphinylation of (*S*)-**3**, and the compound (*S*)-**6** was obtained in 85% yield. By reducing (*S*)-**6** with $HSiCl_3$, the final spiro diphosphine ligand (*S*)-**1e** was prepared in 85% yield. Using the same procedure, the ligand (*R*)-**1e** was also synthesized from (*R*)-1,1′-spirobiindane-7,7′-diol. The total yield of this procedure is 52% and the purified spiro diphosphine ligand **1e** is obtained as a white solid (Scheme 2). The ^{31}P NMR spectrum of ligand **1e** has a single resonance at − 17.95 ppm.



Scheme 2. Synthesis of DMM-SDP (**1e**).

X-Ray Structure of the Palladium Complex of SDP

Reaction of (*S*)-SDP [(*S*)-**1a**] with a stoichiometric amount of $[PdCl_2(CH_3CN)_2]$ yields {$PdCl_2$ [(*S*)-SDP]} (**7**). A suitable crystal of **7**, obtained from CH_2Cl_2-hexane, was analyzed by single crystal X-ray diffraction. As can be seen from the ORTEP diagrams in Figure 1, the eight-membered heterometallocyclic ring formed by the chelate coordination of SDP to palladium is highly rigid. Two of the phenyl groups are oriented axially and the other two phenyl groups directed equatorially to the P–Pd–P plane. The axial *P*-phenyls are parallel to the phenyl rings of biindane, and the central distances between axial *P*-phenyls and the phenyl rings of biindane are 3.46 and 4.21 Å, respectively. This structural feature is similar to that in the $PdCl_2$[(*R*)-BINAP] complex.[16] In the 1,1′-spirobiindane backbone, the plane of C(2)-C(1)-C(9) is perpendicular to the plane of C(10)-C(1)-C(17) (the dihedral angle of these two planes is nearly 90°). The bond angle of P–Pd–P is 96.01°, which is greater than that of $PdCl_2$[(*R*)-BINAP] (92.69°),[16] and smaller than that of $PdCl_2$(PhanePhos) (103.69°).[17] The Pd–P distances (2.241 and 2.282 Å) and Pd–Cl distances (2.330 and 2.351 Å) are in the typical ranges for dichloropalladium complexes bearing diphosphine ligands.[18]

Asymmetric Allylic Alkylation

Palladium-catalyzed asymmetric C–C bond forming reactions with allylic compounds have been extensively investigated,[19] especially the palladium-catalyzed allylic alkylation of *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate. Excellent enantioselectivities have been documented with N,N- and P,N-chelating ligands.[20] Although chiral diphosphine ligands have proved to be efficient in asymmetric hydrogenation and other catalytic reactions, only a few of them gave high enantioselectivity in asymmetric allylic alkylation.[21] It was exceptional that Trost's ligands provided excellent results in various allylic alkylations.[22] To evaluate the asymmetric induction efficiency of the spiro diphosphine (SDP) ligands in this reaction, we studied the enantioselective allylic alkylation of *rac*-1,3-diphenyl-2-propenyl acetate catalyzed by palladium complexes of SDP.

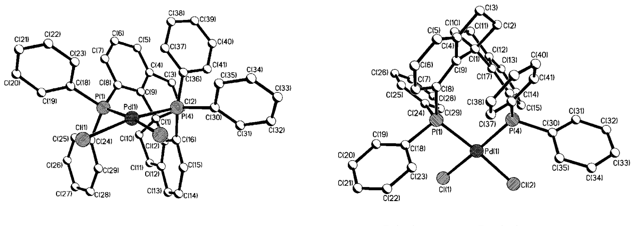
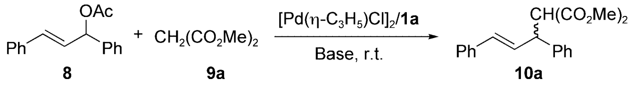


Figure 1. ORTEP diagrams of $PdCl_2$[(*S*)-SDP] (**7**).

Table 1. Asymmetric allylic alkylation of **8** with dimethyl malonate (**9a**) catalyzed by the Pd-complex of ligand **1a**.[a]



Entry	Base	Solvent	Time [h]	Yield [%][b]	ee [%][c]
1	BSA	CH_2Cl_2	1.5	96	73 (*S*)
2	BSA	Toluene	2.5	98	72 (*S*)
3	BSA	DMF	2.5	97	70 (*S*)
4	BSA	CH_3CN	2.5	95	73 (*S*)
5	BSA	THF	2.5	92	57 (*S*)
6	BSA	Dioxane	6.0	91	73 (*S*)
7	NaH	Dioxane	3.0	97	48 (S)
8	Cs_2CO_3	Dioxane	3.0	96	61 (S)
9	Et_2Zn	CH_2Cl_2	15	90	50 (*S*)
10	Et_2Zn	Toluene	5	91	53 (*S*)
11	Et_2Zn	DMF	60	70	65 (*S*)
12	Et_2Zn	Et_2O	3	86	90 (*S*)
13	Et_2Zn	THF	6	89	94 (*S*)
14	Et_2Zn	Dioxane	2.5	96	97 (*S*)
15[d]	Et_2Zn	Dioxane	2.5	98	97 (*S*)
16[e]	Et_2Zn	Dioxane	2.5	97	97 (*S*)

[a] Reaction conditions: $[Pd(\eta\text{-}C_3H_5)Cl]_2$ (0.01 mmol), **1a** (0.024 mmol), **8** (0.4 mmol), **9a** (0.8 mmol), base (1.2 mmol BSA or 0.8 mmol Et_2Zn), at room temperature.

[b] Isolated yield after flash chromatography on silica gel.

[c] Determined by chiral HPLC using Chiralcel OD or Chiralpak AD-H column. The absolute configuration was determined by comparison of the sign of optical rotation or retention time with literature data.

[d] [Pd]/**1a** = 1:2.

[e] [Pd]/**1a** = 1:3.

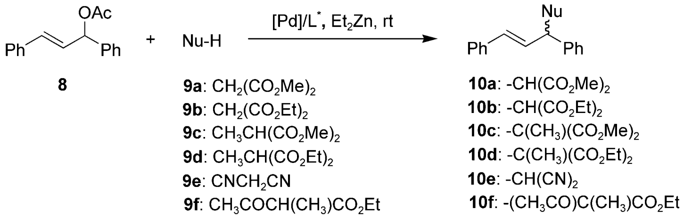
Initially, the reaction of *rac*-1,3-diphenyl-2-propenyl acetate (**8**) with dimethyl malonate (**9a**) was performed at room temperature in the presence of the catalyst formed *in situ* from 2.5 mol % of $[Pd(\eta\text{-}C_3H_5)Cl]_2$ and 6 mol % of ligand **1a**. The nucleophile was generated from dimethyl malonate in the presence of *N,O*-bis(trimethylsilyl)acetamide (BSA). When the reaction was carried out in dichloromethane at room temperature, the allylic alkylation product (*S*)-**10a** was isolated in 96% yield with 73% ee (Table 1, entry 1). Changing solvent to toluene, DMF, CH_3CN or dioxane also gave high yield (>91%) and moderate enantioselectivity (70–73% ee), while the reaction in THF provided a lower enantioselectivity (57% ee) (entry 5). In order to improve the enantioselectivity of the reaction, we further studied the influence of the base used to generate the nucleophile. Using NaH or Cs_2CO_3, instead of BSA, led to decreases in the enantiomeric excesses of **10a** to 48% ee and 61% ee, respectively. A significant improvement in the enantioselectivity was achieved by using Et_2Zn as base, especially in the reactions carried out in dioxane, providing the allylic alkylation product in high yield and excellent enantiomeric excess (97% ee). Increasing the ratio of ligand to Pd precursor has a negligible effect on the yield and enantiomeric excess of alkylation product (entries 14–16).

In the catalyst loading experiments, we found that 2.5 mol % $[Pd(\eta\text{-}C_3H_5)Cl]_2$ is suitable for obtaining a satisfactory result. Lowering the catalyst loading reduced both the rate and enantioselectivity of the alkylation reaction (Table 2, entries 2 and 3). Using $Pd(OAc)_2$, $Pd_2(dba)_3 \cdot dba$ or $Pd_2(dba)_3 \cdot CHCl_3$ as palladium precursors to replace $[Pd(\eta\text{-}C_3H_5)Cl]_2$ also led to lower enantioselectivities (entries 4–6). Under the optimum reaction conditions (**8**/**9a**/[Pd]/**1** = 1/2/0.05/0.06, in dioxane at r.t.), spiro diphosphine ligands **1a–e** were compared. The ligands bearing electron-donating or sterically hindered groups on the *P*-phenyl rings of the phosphine provided higher enantioselectivities. The best enantioselectivity (99.1% ee) was achieved by using the ligand DMM-SDP (**1e**) which has 4-methoxy and 3,5-dimethyls on the *P*-phenyl rings of the phosphine (entry 10).

The results of the allylic alkylation with various nucleophiles using the ligand DMM-SDP (**1e**) are listed in Table 2. When diethyl malonate (**9b**), instead of dimethyl malonate (**9a**), was used the enantiomeric excess of the alkylation product was slightly decreased to 98.6% (entry 11). By introducing an α-methyl group into **9a** or **9b** to increase the hindrance of the nucleophiles, the ees of products were decreased to 97.1% and 97.7%, respectively. These results show that increasing the hindrance of the nucleophile is unfavorable to the enantioselectivity of the reaction. The diastereoselectivity in the alkylation using 2-methyl-3-oxobutyric acid ethyl ester (**9f**) amounted to only 37% de, but the optical purities of the two diastereoisomeric products were still high (91% ee and 97% ee, respectively) (entry 15). A quite low enantioselectivity (56% ee) was obtained in the alkylation reaction with malononitrile (**9e**) (entry 14), indicating that β-dicarbonyl functional groups in the nucleophile are necessary to achieve high enantioselectivity in the Pd-catalyzed allylic alkylation using Et_2Zn as base.

To extend the scope of substrate of the allylic alkylation catalyzed by the Pd-complex of DMM-SDP (**1e**), we next investigated the allylic alkylation of more challenging substrates, such as 2-cyclohexenyl acetate and cinnamyl acetate. The allylic alkylation of 2-cyclohexenyl acetate with dimethyl malonate in the standard conditions for 24 hours provided dimethyl 2-(3-cyclohexenyl)malonate in 95% yield and with only 38% ee. The allylic alkylation of cinnamyl acetate with diethyl 2-methylacetoacetate in the same conditions for 14 hours gave the corresponding allylic alkylation product, ethyl 2-methyl-2-(3-phenylprop-2-enyl)acetoacetate, in 89% yield, but the enantioselectivity (23% ee) was disappointing.

Table 2. Pd-catalyzed asymmetric allylic alkylation of **8** in the presence of SDP ligands **1a–e** using Et_2Zn as base.[a]



Entry	L*	[Pd]	Nu-H	Time [h]	Yield [%][b]	ee [%][c]
1	(*S*)-**1a**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9a**	2.5	98	97 (*S*)
2[d]	(*S*)-**1a**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9a**	8	93	94 (*S*)
3[e]	(*S*)-**1a**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9a**	6	96	95 (*S*)
4	(*S*)-**1a**	$Pd(OAc)_2$	**9a**	2.5	95	83 (*S*)
5	(*S*)-**1a**	$Pd_2(dba)_3.dba$	**9a**	8	93	78 (*S*)
6	(*S*)-**1a**	$Pd(dba)_3.CHCl_3$	**9a**	6	97	87 (*S*)
7	(*S*)-**1b**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9a**	2.5	95	97.3 (*S*)
8	(*S*)-**1c**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9a**	3	95	97.6 (*S*)
9	(*S*)-**1d**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9a**	2.5	97	98.8 (*S*)
10	(*S*)-**1e**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9a**	3	96	99.1 (*S*)
11	(*S*)-**1e**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9b**	4	91	98.6 (*S*)
12	(*S*)-**1e**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9c**	3	93	97.1 (*S*)
13	(*S*)-**1e**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9d**	3	96	97.7 (*S*)
14	(*S*)-**1e**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9e**	3	87	56 (*S*)
15	(*S*)-**1e**	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	**9f**	36	90	91 & 97 (37% de)

[a] Reaction conditions: [Pd] (0.02 mmol), **1** (0.024 mmol), **8** (0.4 mmol), **9** (0.8 mmol), Et_2Zn (0.8 mmol), in dioxane at room temperature.

[b] Isolated yield after flash chromatography on silica gel.

[c] Determined by chiral HPLC using a Chiralcel OD or Chiralpak AD-H column. The absolute configurations were determined by comparison of the sign of optical rotations or retention times with literature data.

[d] 1 mol% [Pd].

[e] 2 mol% [Pd].

Conclusion

An X-ray analysis of the crystal structure of the Pd-SDP complex showed that the SDP ligand created an effective asymmetric environment around the palladium. Spiro diphosphines (SDP) are highly efficient ligands in the palladium-catalyzed asymmetric allylic alkylation of *rac*-1,3-diphenyl-2-propenyl acetate. Introduction of electron-donating or sterically hindered groups into the *P*-phenyls of SDP enhanced the enantioselectivity of the alkylation reaction. Diethylzinc as a base is critical for obtaining high enantioselectivity in the allylic alkylation using β-dicarbonyl nucleophiles. Further efforts are on-going to extend the scope of application of these chiral spiro diphosphine ligands in transition metal-catalyzed asymmetric reactions.

Experimental Section

All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glove box or using standard Schlenk techniques. Commercial reagents were used as received without further purification unless otherwise noted. Toluene, tetrahydrofuran, dioxane and diethyl ether were freshly distilled over sodium benzophenone ketyl under nitrogen. Dichloromethane, DMF and DMSO were distilled from calcium hydride. (*S*)-1,1′-Spirobiindane-7,7′-diol [(*S*)-**2**],[23] (*S*)-7,7′-bis(trifluoromethanesulfonyloxy)-1,1′-spirobiindane [(*S*)-**3**][24] and $Ar_2P(O)H$[25] were prepared according to reported methods. NMR spectra were recorded with a Bruker spectrometer at 300 (^{1}H NMR), 75 (^{13}C NMR) and 121.5 (^{31}P NMR) MHz. Chemical shifts are reported as δ values downfield from tetramethylsilane and external 85% H_3PO_4, respectively. Optical rotations were recorded using a Perkin Elmer Model 341 polarimeter. Elemental analyses were performed on Yanaca CDRDER MT-3 instrument. IR spectra were recorded on Bio-Rad FTS 135 spectrometer. Mass spectra were recorded on a VG-7070E spectrometer. Enantiomeric excesses were determined by chiral HPLC performed using a Hewlett Packard Model HP 1100 Series with a Chiralcel OD or a Chiralpak AD-H column.

(*S*)-7-Di(3,5-dimethyl-4-methoxyphenyl)phosphinyl-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane [(*S*)-4]

To a mixture of (*S*)-7,7′-bis(trifluoromethanesulfonyloxy)-1,1′-spirobiindane [(*S*)-**3**] (4.13 g, 8.0 mmol), di(3,5-dimethyl-4-

methoxylphenyl)phosphine oxide (5.09 g, 16.0 mmol), palladium acetate (90.8 mg, 0.40 mmol) and 1,4-bis(diphenylphosphino)butane (dppb, 170.3 mg, 0.40 mmol) were added 25 mL degassed DMSO and diisopropylethylamine (4.25 g, 33.2 mmol), and the mixture was heated with stirring at 100 °C for 6 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc, washed with 5% hydrochloric acid and saturated $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on a silica gel column with petroleum ether/EtOAc (7:1 v/v) as eluent to give (*S*)-7-di(3,5-dimethyl-4-methoxyphenyl)phosphinyl-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane [(*S*)-**4**] as a white solid; yield: 5.4 g (7.8 mmol, 98%); mp 90–92 °C; $[\alpha]_D^{20}$: −200 (*c* 0.5, CH_2Cl_2); ^1H NMR ($CDCl_3$): δ = 1.60–2.12 (2H, m, CH_2), 2.18 (6H, s, CH_3), 2.21 (6H, s, CH_3), 2.28–2.35 (2H, m, CH_2), 2.95–3.11 (2H, m, CH_2), 3.27–3.35 (2H, m, CH_2), 3.68 (3H, s, OCH_3), 3.79 (3H, s, OCH_3), 6.30 (1H, d, *J* = 7.8 Hz, Ar-H), 6.86 (2H, d, *J* = 11.7 Hz, Ar-H), 7.00–7.08 (4H, m, Ar-H), 7.15–7.21 (2H, m, Ar-H), 7.40 (1H, d, *J* = 7.5 Hz, Ar-H); ^{31}P NMR ($CDCl_3$): δ = 30.58 (s); ^{13}C NMR ($CDCl_3$): δ = 16.3, 30.9, 32.1, 39.6, 40.3, 59.7, 62.0, 115.7, 117.0, 119.4, 123.8, 125.3, 126.1, 126.5, 127.6, 127.8, 128.0, 129.0, 130.4, 130.9, 131.2, 131.8, 132.3, 132.6, 132.7, 133.6, 140.5, 145.0, 145.9, 146.1, 153.1, 153.2, 159.6, 159.9; IR (KBr): ν = 2942, 2364, 1647, 1471, 1406, 1326, 1283, 1217, 1112, 1006, 845 cm^{-1}; MS (FAB): *m/z* = 685 ($M+1^+$); anal. calcd. for $C_{36}H_{36}F_3O_6PS$: C 63.15, H 5.30; found: C 63.01, H 5.50.

(*S*)-7-Di(3,5-dimethyl-4-methoxyphenyl)phosphino-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane [(*S*)-5]

To a mixture of (*S*)-7-di(3,5-dimethyl-4-methoxyphenyl)phosphinyl-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane [(*S*)-**4**] (1.71 g, 2.5 mmol) and diisopropylethylamine (13.2 g, 102 mmol) in toluene (25 mL) was added Cl_3SiH (4.0 mL, 39 mmol) at 0 °C. The reaction mixture was stirred at 110 °C for 5 days. After cooling to room temperature, the mixture was diluted with Et_2O and quenched with small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite and the solid was washed with Et_2O. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude phosphine monotriflate was purified by silica gel column chromatography with petroleum ether/EtOAc (40:1 v/v) as eluent to give (*S*)-7-di(3,5-dimethyl-4-methoxyphenyl)phosphino-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane [(*S*)-**5**] as a white solid; yield: 1.3 g (1.9 mmol, 76%); mp 73–75 °C; $[\alpha]_D^{20}$: −160 (*c* 0.5, CH_2Cl_2); ^1H NMR ($CDCl_3$): δ = 2.14 (6H, s, CH_3), 2.16 (6H, s, CH_3), 2.20–2.37 (4H, m, CH_2), 3.01–3.10 (4H, m, CH_2), 3.67 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 6.60–6.66 (4H, m, Ar-H), 7.13–7.25 (6H, s, OCH_3); ^{31}P NMR ($CDCl_3$): δ = −22.53 (s); ^{13}C NMR ($CDCl_3$): δ = 16.3, 30.9, 32.1, 39.6, 40.3, 59.7, 62.0, 115.7, 117.0, 118.0, 120.1, 123.8, 124.1, 125.3, 127.5, 128.0, 128.4, 130.2, 130.5, 130.7, 130.8, 132.3, 132.5, 133.7, 134.0, 134.3, 134.6, 134.9, 142.1, 143.6, 143.8, 145.6, 148.3, 152.3, 152.6, 157.2,157.8; IR (KBr): ν = 2944, 1647, 1471, 1394, 1279, 1215, 1113, 1112, 930, 852, 780, 610 cm^{-1}; MS (FAB): *m/z* = 669.0 ($M+1^+$); anal. calcd. for $C_{36}H_{36}F_3O_5PS$: C 64.66, H 5.40; found: C 64.90, H 5.25.

(*S*)-7-Di(3,5-dimethyl-4-methoxy-phenyl)phosphino-7′-di(3,5-dimethyl-4-methoxyphenyl)-phosphinyl-1,1′-spirobiindane [(*S*)-6]

To a mixture of (*S*)-7-di(3,5-dimethyl-4-methoxyphenyl)phosphino-7′-trifluoromethanesulfonyloxy-1,1′-spirobiindane [(*S*)-**5**] (1.47 g, 2.2 mmol), di(3,5-dimethyl-4-methoxylphenyl)phosphine oxide (1.37 g, 4.3 mmol), palladium acetate (22.4 mg, 0.1 mmol) and dppb (42.6 mg, 0.1 mmol) were added 15 mL degassed DMSO and diisopropylethylamine (1.0 g, 8.7 mmol), and the mixture was heated with stirring at 100 °C for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc, washed with 5% hydrochloric acid and saturated $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel column with petroleum ether/EtOAc (7:1 v/v) as eluent to give (*S*)-7-di(3,5-dimethyl-4-methoxy-phenyl)phosphino-7′-di(3,5-dimethyl-4-methoxyphenyl)-phospinyl-1,1′-spirobiindane [(*S*)-**6**] as a white solid; yield: 1.6 g (1.9 mmol, 85%); mp 143–145 °C; $[\alpha]_D^{20}$: −100 (*c* 0.5, CH_2Cl_2); ^1H NMR ($CDCl_3$): δ = 1.08–1.32 (2H, m, CH_2), 1.64–1.68 (2H, m, CH_2), 1.78 (6H, s, CH_3), 2.00 (6H, m, CH_3), 2.20 (6H, s, CH_3), 2.23 (6H, s, CH_3), 2.43–2.60 (2H, m, CH_2), 2.78–2.95 (2H, m, CH_3), 3.65 (3H, s, OCH_3), 3.66 (3H, s, OCH_3), 3.70 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 6.64 (2H, d, *J* = 5.7 Hz, Ar-H), 6.88 (2H, d, *J* = 7.5 Hz, Ar-H), 7.07–7.22 (10H, m, Ar-H), 7.31 (1H, d, *J* = 4.5 Hz, Ar-H); ^{31}P NMR ($CDCl_3$): δ = −19.19 (s), 29.35 (s); ^{13}C NMR ($CDCl_3$): δ = 16.3, 30.8, 31.0, 39.8, 39.9, 59.8, 64.6, 125.1, 125.7, 126.3, 129.9, 130.5, 130.8, 131.1, 132.2, 132.5, 132.7, 132.8, 133.2, 133.5, 133.6, 134.5, 135.9, 136.3, 142.2, 142.3, 147.0, 147.2, 154.3, 156.3, 157.8, 158.0, 159.4; IR (KBr): ν = 3050, 2930, 2364, 1643, 1548, 1487, 1408, 1280, 1182, 1114, 1010, 905, 873 cm^{-1}; MS (FAB): *m/z* = 837 ($M+1^+$); anal. calcd. for $C_{53}H_{58}O_5P_2$: C 76.05, H 6.98; found: C 75.96, H 6.72.

(*S*)-7,7′-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphino]-1,1′-spirobiindane [(*S*)-1e]

To a mixture of (*S*)-7-di(3,5-dimethyl-4-methoxy-phenyl)-phosphino-7′-di(3,5-dimethyl-4-methoxyphenyl)-phospinyl-1,1′-spirobiindane [(*S*)-**6**] (1.5 g, 1.8 mmol) and diisopropylethylamine (9.3 g, 72 mmol) in toluene (30 mL) was added Cl_3SiH (2.7 mL, 27 mmol) at 0 °C. The reaction mixture was stirred at 110 °C for 3 days. After cooling to room temperature, the mixture was diluted with Et_2O and quenched with a small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite and the solid was washed with Et_2O. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude phosphine was purified by silica gel column chromatography with petroleum ether/EtOAc (40:1 v/v) as eluent to give (*S*)-7,7′-bis[di(3,5-dimethyl-4-methoxyphenyl)phosphino]-1,1′-spirobiindane [(*S*)-**1e**] as a white solid; yield: 1.23 g (1.5 mmol, 85%); mp 217–219 °C; $[\alpha]_D^{20}$: −80 (*c* 0.5, CH_2Cl_2); ^1H NMR ($CDCl_3$): δ = 1.59–1.66 (2H, m, CH_2), 1.75–1.82 (2H, m, CH_2), 2.01 (12H, s, CH_3), 2.20 (12H, s, CH_3), 2.50–2.60 (2H, m, CH_2), 2.75–2.87 (2H, m, CH_2), 3.66 (6H, s, OCH_3), 2.43–2.60 (2H, m, CH_2), 2.78–2.95 (2H, m, CH_3), 3.65 (3H, s, OCH_3), 3.66 (3H, s, OCH_3), 3.70 (3H, s, OCH_3), 3.72 (6H, s, OCH_3), 6.73–6.75 (3H, m, Ar-H), 6.88–6.90 (3H, m, Ar-H), 7.11–7.23 (8H, m, Ar-H); ^{31}P NMR (CDCl$_3$): δ = −17.95 (s); ^{13}C NMR (CDCl$_3$): δ = 16.1, 16.3, 30.8, 39.2, 59.7, 59.8, 64.3, 109.9, 125.1, 126.8, 130.2, 130.6, 132.6, 133.5, 133.7, 136.0, 136.2, 136.4, 144.2, 153.2,156.5,157.9; IR (KBr): ν = 3056, 2930, 2360, 1643, 1474, 1276, 1216, 1113, 1012, 876, 776, 668, 617 cm^{-1}; MS (FAB): *m/z* = 820 (M$^+$); anal. calcd. for $C_{53}H_{58}P_2O_4$: C 77.53, H 7.12; found: C 77.40, H 6.96.

X-Ray Diffraction Study of {PdCl$_2$[(*S*)-SDP]} (7).

Preparation {PdCl$_2$[(*S*)-SDP]} (7): A solution of (*S*)-SDP (**1a**) (52 mg, 0.09 mmol) in 1.0 mL of benzene was added with stirring to a mixture of $PdCl_2(CH_3CN)_2$ (23 mg, 0.09 mmol) in 2.0 mL of benzene, and the mixture was stirred overnight. The pale yellow precipitate formed was collected by filtration, washed with benzene, dried under vacuum to provide the yellow solid **7**; yield: 68 mg (90%); ^{1}H NMR (CDCl$_3$): δ = 1.51 (2H, m, CH$_2$), 1.76 (2H, m, CH$_2$), 2.03 (2H, m, CH$_2$), 2.61 (2H, m, CH$_2$), 6.89 (2H, d, Ar-H), 6.91–7.20 (9H, m, Ar-H), 7.38–7.50 (11H, m, Ar-H), 7.85–7.93 (4H, m, Ar-H); ^{31}P NMR (CDCl$_3$): δ = 35.26 (s).

The crude product was dissolved in acetone and CH$_2$Cl$_2$, layered with hexane, and allowed to stand at room temperature to give pale red crystals of the title compound, suitable for X-ray study.

Crystal data for [PdCl$_2$((*S*)-SDP)] (7): $C_{41}H_{38}C_{l2}O_2P_{0.67}Pd_{0.33}$, $M_r = 689.73$, hexagonal, P6(3), $a = 19.320(3)$, $b = 19.320(3)$, $c = 18.217(6)$, Å, a = 90°, β = 90°, γ = 120°, $V = 5889(2)$ Å^3, $Z = 6$, $D_{calc} = 1.167$ Mg m^{-3}, λ(MoKα) = 0.71073 Å, F (000) = 2156, T = 293(2) K, Crystal dimensions 0.30 × 0.25 × 0.20 mm, 17439 reflections measured, 5404 unique [R(int) = 0.0511]. R1 [for 5404 reflections with $I > 2\sigma(I)$] = 0.0493, ωR2 (all data) = 0.1077, 433 parameters. Absolute structure parameter χ = 0.00(4). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-239201. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336–033; E-mail: deposit@ccdc.cam.ac.uk].

Asymmetric Allylic Alkylation Catalyzed by Pd-SDP Complexes

Method A: *General.* To a Schlenk tube containing [Pd(η-C$_3$H$_5$)Cl]$_2$ (3.6 mg, 0.01 mmol) and chiral spiro diphosphine ligands **1** (0.024 mmol) was added dry CH$_2$Cl$_2$ (2 mL), and the mixture was stirred at room temperature for 1 hour. Then 1,3-diphenyl-2-propyl acetate (**8**) (101 mg, 0.4 mmol) in CH$_2$Cl$_2$ (3.0 mL) was added and the mixture was stirred for 10 min, dimethyl malonate (158 mg, 1.2 mmol) was added to the reaction mixture followed by BSA (0.30 mL, 1.2 mmol). The resultant mixture was stirred for an appropriate time until conversion was complete, and then was diluted with ether (25 mL), washed with saturated aqueous ammonium chloride. The organic phase was separated and dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography with petroleum ether/EtOAc (5:1 v/v) to afford dimethyl 1,3-diphenyl-2-propenylmalonate **10a** as a colorless oil; The yield and enantiomeric excess are given in Table 1; ^{1}H NMR (CDCl$_3$): δ = 3.52 (3H, s), 3.71 (3H, s), 3.95 (1H, d, *J* = 10.7 Hz), 4.23–4.30 (1H, m), 6.44 (1H, *J* = 15.8 Hz, d), 7.20–7.32 (10H, m); The enantiomeric excess of **10a** was determined by chiral HPLC [Chiralcel OD column, *n*-hexane/2-PrOH 99:1, 0.7 mL/min, t_R = 14.9 min (*R*), t_R = 16.4 min (*S*)].

Method B: *General.* A solution of ligand **1** (0.024 mmol), and [Pd(η-C$_3$H$_5$)Cl]$_2$ (3.6 mg, 0.01 mmol) in dry dioxane (2 mL) was stirred at room temperature for 1 hour, and a solution of 1,3-diphenyl-2-propyl acetate (**8**) (101 mg, 0.4 mmol) in dioxane (3.0 mL) was added. After 10 min, dimethyl malonate (106 mg, 0.8 mmol) in dioxane (5.0 mL) and Et$_2$Zn (1 M in hexane, 0.8 mL, 0.8 mmol) were added to the mixture and stirring was continued at room temperature for the appropriate time. The reaction mixture was treated as in method A. The yields and enantiomeric excesses are given in Tables 1 and 2.

Diethyl 1,3-diphenyl-2-propenyl malonate (10b): Colorless oil, yield: 96%; ^{1}H NMR (CDCl$_3$): δ = 0.94 (3H, t, *J* = 11.6 Hz), 1.15 (3H, t, *J* = 9 Hz), 3.87 (1H, dd, *J* = 12.6, 21.0 Hz), 4.05–4.25 (4H, m), 6.29–6.39 (1H, m), 6.42 (1H, d, *J* = 12 Hz), 7.15–7.21 (10H, m); chiral HPLC conditions: Chiralcel OJ column, *n*-hexane/2-PrOH 95:5, 0.7 mL/min, t_R = 14.5 min (*R*), t_R = 18.9 min (*S*).

Dimethyl 1,3-diphenyl-2-propenyl α-methylmalonate (10c): Colorless oil, yield: 93%; ^{1}H NMR (CDCl$_3$): δ = 1.48 (3H, s), 3.62 (3H, s), 3.69 (3H, s), 4.29(1H, d, *J* = 9 Hz), 6.46 (1H, d, *J* = 15.9 Hz), 6.68 (1H, dd, *J* = 9.1, 15.9 Hz), 7.18–7.34 (10H, m); chiral HPLC conditions: Chiralpak AD-H column, *n*-hexane/2-PrOH 98:2, 0.5 mL/min, t_R = 27.4 min (*S*), t_R = 28.9 min (*R*).

Diethyl 1,3-diphenyl-2-propenyl α-methylmalonate (10d): Colorless oil, yield: 96%; ^{1}H NMR (CDCl$_3$): δ = 1.14–1.27 (6H, m), 1.47 (3H, s), 4.04–4.20 (4H, m), 4.29 (1H, d, *J* = 9 Hz), 6.64 (1H, d, *J* = 15.6 Hz), 6.70 (1H, dd, *J* = 8.1, 15.0 Hz), 7.18–7.34 (10H, m); chiral HPLC conditions: Chiralpak AD-H column, *n*-hexane/2-PrOH 98:2, 0.5 mL/min, t_R = 21.1 min (*S*), t_R = 22.8 min (*R*).

1,3-Diphenyl-2-propenylmalononitrile (10e): Colorless oil, yield: 87%; ^{1}H NMR (CDCl$_3$): δ = 4.05–4.13 (2H, m), 6.35 (1H, m), 6.71(1H, d, *J* = 23.7 Hz), 7.16–7.39 (10H, m); chiral HPLC conditions: Chiralpak AD-H, *n*-hexane/2-PrOH 90:10, 1.0 mL/min, t_R = 15.3 min (*S*), t_R = 16.3 min (*R*).

2-Acetyl-2-methyl-3,5-diphenylpent-4-enoic acid ethyl ester (10f): Colorless oil, yield: 90%; ^{1}H NMR (CDCl$_3$): δ = 1.07–1.25 (3H, m), 1.36 (3H, s), 2.07–2.15 (3H, m), 3.97–4.20 (2H, m), 4.27 (1H, d, *J* = 8.2 Hz), 6.32–6.48 (1H, m), 6.59–6.80 (1H, m), 7.16–7.38 (10H, m); GC conditions: Chiralcel HP-5 (Agilent technologies), carrier gas, N$_2$ (flow 2 mL/min); injection temp, 230 °C; column temp, initial temperature 80 °C, rate 0.6 °C/min, final temperature 200 °C, t_R = 138.1 min (diastereomer A), t_R = 139.3 min (diastereomer B); chiral HPLC conditions: Chiralpak. AD-H, *n*-hexane/2-PrOH 98:2, 0.4 mL/min, diastereomer A: t_R = 23.1 min (major), t_R = 27.2 min (minor); diastereomer B: t_R = 24.3 min (major), t_R = 25.1 min (minor).

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