Synthesis of (β-*N*-Sulfonylaminoalkyl)phosphines and Their Use in Palladium-Mediated Asymmetric Synthesis[1)]

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A series of (β-*N*-sulfonylaminoalkyl)phosphine ligands has been developed and employed for asymmetric palladium-catalyzed hydrosilylation and Heck-type hydroarylation, affording up to 72% ee and 90% yield.

Key words catalytic asymmetric hydrosilylation; catalytic asymmetric Heck-type hydroarylation; palladium complex; aminophosphine

Chiral phosphines have been widely used as ligands for transition metal complexes. The main asymmetric catalytic systems are based on the complexes of chiral phosphines and transition metals such as nickel, cobalt, rhodium, ruthenium, platinum and palladium.[2)] Most of the chiral phosphine ligands so far devised are bisphosphines,[3)] because the steric interactions which mediate the chiral recognition in the bisphosphine ligand–metal complexes are expected to be higher than in the case of monophosphine ligands. Recently, however, the development of monophosphine ligands has gained considerable attention due to the fact that the bisphosphine–metal complexes are ineffective for some transition-metal catalyzed reactions such as nickel-catalyzed cross coupling and palladium-catalyzed hydrosilylation of olefins.[4)] In this paper we report the development of chiral (β-aminoalkyl)phosphine derivatives bearing *N*-sulfonyl groups and their use in palladium-catalyzed asymmetric hydrosilylation[5)] and Heck-type hydroarylation.[6)]

Chiral (*S*)-(*N*-sulfonylaminoalkyl)phosphines (**3a—g**, **4** and **6**) were prepared simply by both *N*- and *O*-sulfonylations of (*S*)-chiral amino alcohol with sulfonyl chlorides, followed by phosphination with lithium diarylphosphides.

Asymmetric hydrosilylation of cyclopentadiene with dichloromethylsilane[7)] was carried out under an argon atmosphere in the presence of 0.1 mol% of chiral phosphines–palladium complexes prepared *in situ* by mixing the ligand and dichlorobis(acetonitrile)palladium. The results are summarized in Table 1. The palladium complexes of **3a—e** and **4** were catalytically active even at 0 °C, giving (*S*)-3-(dichloromethylsilyl)cyclopentene (**11**) in high yields. In the case of **3a** the enantioselectivities were higher at lower temperatures and at −20 °C the highest optical yield (71% ee) was obtained. The substituents on each phenyl group of **3b—e** did not have a dramatic influence on the enantioselection. Since an *N*-methyl-*N*-methylsulfonyl derivative (NMe-Ms-Valphos) (**6**) showed much lower selectivity than **3a**, the NH group

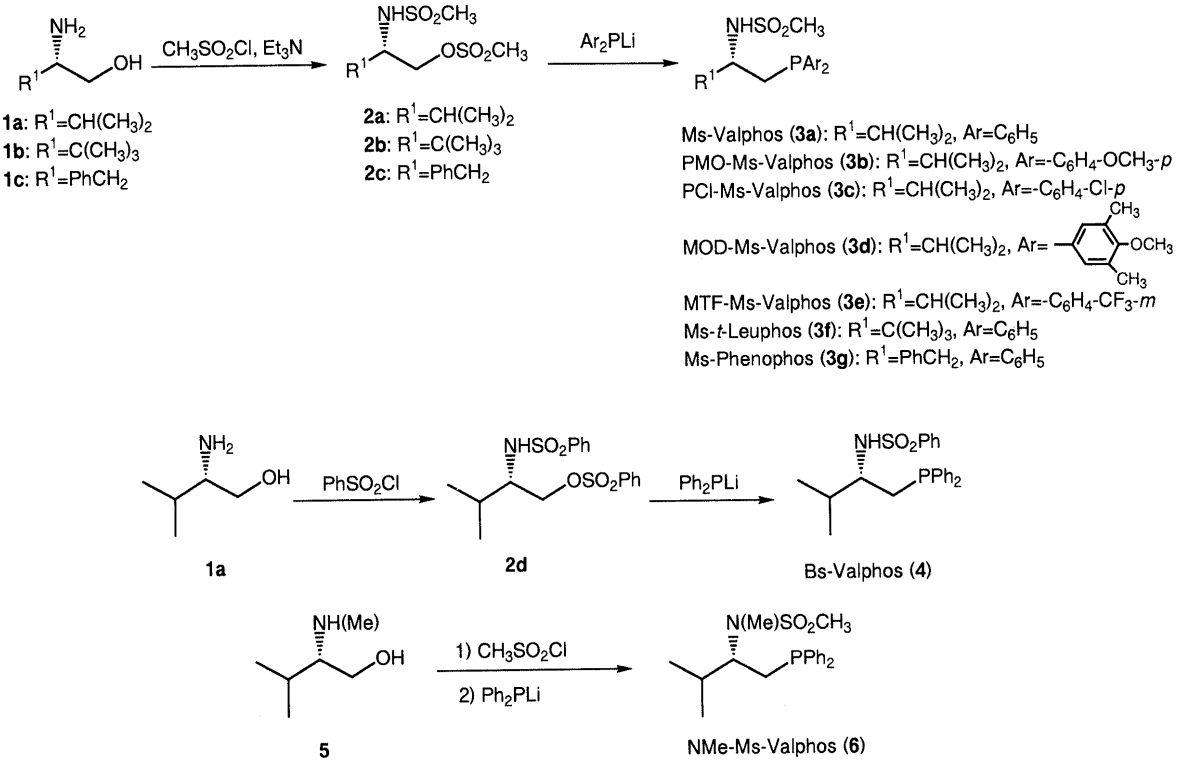

Chart 1

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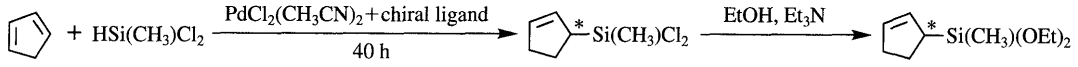
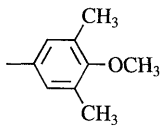
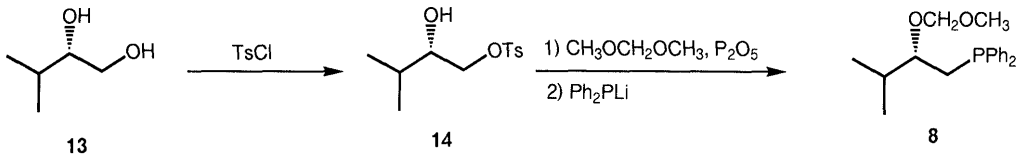
Table 1. Asymmetric Hydrosilylation of Cyclopentadiene with Dichloromethylsilane Catalyzed by Chiral Phosphine–Pd(II) Complexes[a]



9 10 11 12

	Chiral ligand: R	Ar	Temp. (°C)	Yield of **11** (%)[b]	$[\alpha]_D^{18-24}$ of **12** (°) (benzene)	% ee[c]	(Confign.)
3a	$-NHSO_2CH_3$	$-C_6H_5$	r.t.	83	−64.2	48	(*S*)
			0	82 (84)[d]	−80.8 (−82.5)[d]	61 (62)[d]	(*S*)
			−20	35	−93.8	71	(*S*)
3b	$-NHSO_2CH_3$	$-C_6H_4OCH_3$-*p*	0	74	−82.9	62	(*S*)
3c	$-NHSO_2CH_3$	$-C_6H_4Cl$-*p*	0	88	−67.9	51	(*S*)
3d	$-NHSO_2CH_3$		0	11	−61.9	47	(*S*)
3e	$-NHSO_2CH_3$	$-C_6H_4CF_3$-*m*	0	87	−64.1	48	(*S*)
4	$-NHSO_2C_6H_5$	$-C_6H_5$	0	93	−70.9	53	(*S*)
6	$-N(CH_3)SO_2CH_3$	$-C_6H_5$	0	84	−9.0	7	(*S*)
7a	$-N(CH_3)_2$	$-C_6H_5$	r.t.	60	+0.9		(*R*)
7b	$-N(CH_3)_2$	$-C_6H_4OCH_3$-*p*	r.t.	37	+1.1		(*R*)
7c	$-N(CH_3)_2$	$-C_6H_4Cl$-*p*	r.t.	78	+1.0		(*R*)
8	$-OCH_2OCH_3$	$-C_6H_5$	0	87	+48.7	37	(*R*)

a) [**9**]/[**10**]/[Pd] = 1/2/10^{-3}, palladium catalysts were prepared *in situ* by mixing dichlorobis(acetonitrile)palladium(II) with 1 eq of ligands. *b*) Yield based on **9**. *c*) The enantiomeric purity of **12** was calculated on the basis of the reported value (ref. 19). *d*) The isolated palladium complex catalyst was used. Temp. = temperature. r.t. = room temperature.



13 14 8

Chart 2

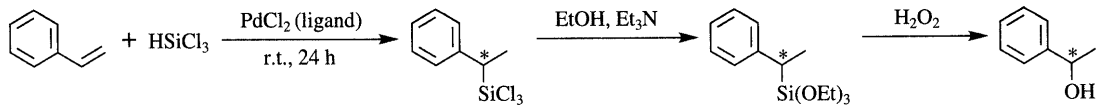
of the sulfonamide was considered to be important for giving high selectivity. On the other hand, both Valphos (**7a**)[8] itself and its derivatives (**7b**, **c**) showed catalytic activity at room temperature, but the selectivity was very low. Then, in order to clarify the role of the substituted amino groups, we prepared another analogue (**8**) bearing a methoxymethyloxy group in place of the substituted amino group (Chart 2). It was of interest that the palladium complex of this ligand showed the reverse enantioselectivity in comparison with the sulfonamide derivatives under the same reaction conditions, giving the (*R*)-product in 37% ee. These results may imply that the β-substituents of the alkylphosphine ligands play much more important roles than the phosphino groups in the enantioselectivities.

Asymmetric hydrosilylation of styrene was also examined. Treatment of styrene (**15**) with trichlorosilane (**16**)[9] in the presence of 0.1 mol% of palladium complex gave 1-phenyl-1-(trichlorosilyl)ethane (**17**) as a single isomer, which was converted quantitatively into 1-phenyl-1-(triethoxysilyl)ethane (**18**) by treatment with ethanol and triethylamine. Oxidation of **18** according to the reported procedure[10] gave *sec*-phenyl alcohol (**19**). The results are summarized in Table 2. In these cases, as well as the hydrosilylation of **9**, the substituents on each phenyl group of the phosphino group did not have a dramatic effect on the selectivity. Further, in order to obtain more efficient catalysts, we designed and prepared new chiral ligands, (*S*)-(*N*-sulfonylaminoalkyl)phosphines (**3f** and **25**); the former bearing a *tert*-butyl group as a sterically bulkier moiety and the latter bearing a trifluoromethylsulfonyl group as a more electron-withdrawing group (Charts 1 and 3). Hydrosilylations of cyclopentadiene and styrene were carried out under the same conditions as shown in Tables 1 and 2. The results, summarized in Table 3, show that the palladium complex of **3f** and **25** gave higher selectivity than that of **3a** in the hydrosilylation of **9**, but the selectivity of the complex of **25** decreased in the hydrosilylation of **15**. Electronic effects of the sulfonamide groups were considered to play important roles in the enantioselections.

Recently the preparation of chiral compounds containing fluorine atoms has gained considerable attention due to their importance and increasing range of application.[11] We next turned our attention to the asymmetric hydrosilylation of trifluoromethyl- and fluorostyrene. The results are summarized in Table 4. The best optical purity (75.7% ee) was obtained when 3-(trifluoromethyl)styrene (**26a**) and $PdCl_2$(Ms-*t*-Leuphos) (**20e**) were used as the substrate and the catalyst, respectively. Unfortunately, the hydrosilylation of 2-(trifluoromethyl)styrene, 4-(trifluoromethyl)styrene and 2,3,4,5,6-pentafluorostyrene did not proceed under the same conditions.

Palladium-catalyzed arylation and alkenylation of

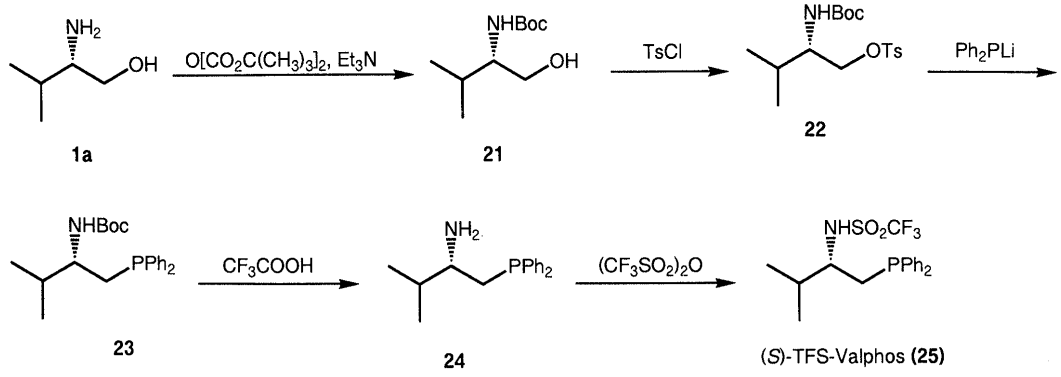
Table 2. Asymmetric Hydrosilylation of Styrene with Trichlorosilane Catalyzed by Chiral Phosphine–Pd(II) Complexes[a]



15 16 17 18 19

Catalyst	Yield of **17** (%)[b]	% ee[c]	(Confign.)
$PdCl_2$(Ms-Valphos) (**20a**)	57[d]	64.8	(*S*)
$PdCl_2$(PMO-Ms-Valphos) (**20b**)	60	51.8	(*S*)
$PdCl_2$(PCl-Ms-Valphos) (**20c**)	88	58.9	(*S*)
$PdCl_2$(Bs-Valphos) (**20d**)	81	50.7	(*S*)

a) [**15**]/[**16**]/[Pd] = 1/2/10^{-3}. *b*) Yield based on **15**. *c*) Determined by HPLC analysis of **19** (Daicel Chiralcel OB, *n*-hexane/2-propanol = 9/1). *d*) Overall yield of **18** from **15**.



1a **21** **22** **23** **24** (*S*)-TFS-Valphos (**25**)

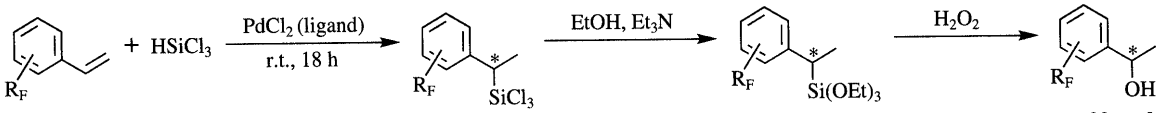
Chart 3

Table 3. Asymmetric Hydrosilylation of Cyclopentadiene and Styrene Catalyzed by Chiral Phosphine–Pd(II) Complexes[a]

Substrate	Catalyst	Temp. (°C)	Time (h)	Yield (%)[b]	$[\alpha]_D^{22}$ (°) (benzene)	% ee	(Confign.)
9	$PdCl_2(CH_3CN)_2$ + Ms-*t*-Leuphos (**3f**)	0	40	84 (**11**)	−96.0 (**12**)	72[c]	(*S*)
9	$PdCl_2(CH_3CN)_2$ + TFS-Valphos (**25**)	0	40	84 (**11**)	−90.7 (**12**)	68[c]	(*S*)
15	$PdCl_2$(Ms-*t*-Leuphos) (**20e**)	r.t	24	63 (**18**)		16.3[d]	(*S*)
15	$PdCl_2$(TFS-Valphos) (**20f**)	r.t	24	90 (**18**)		63.0[d]	(*S*)

a) [**9**]/[**10**]/[Pd] = 1/2/10^{-3}, [**15**]/[**16**]/[Pd] = 1/2/10^{-3}. The isolated palladium complex catalyst was used. *b*) Yield based on **9** or **15**. *c*) Calculated on the basis of the reported value (ref. 19). *d*) Determined by HPLC analysis of **19** (Daicel Chiralcel OB, *n*-hexane/2-propanol = 9/1). Temp. = temperature. r.t. = room temperature.

Table 4. Asymmetric Hydrosilylation of Fluorinated Styrene Catalyzed by Chiral Phosphine–Pd(II) Complexes[a]

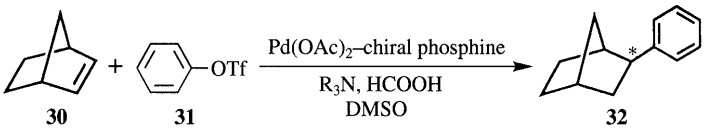


26a: R_F = 3-CF_3 **16** **27a—d** **28a—d** **29a—d**
26b: R_F = 2-F
26c: R_F = 3-F
26d: R_F = 4-F

Substrate R_F	Catalyst	Yield of **27a—d** (%)[b]	% ee[c]	(Confign.)
3-CF_3	$PdCl_2$(Ms-Valphos) (**20a**)	72.2	60.6	(*S*)[d]
	$PdCl_2$(Ms-*t*-Leuphos) (**20e**)	86.7	75.7	(*S*)[d]
2-F	$PdCl_2$(Ms-Valphos) (**20a**)	58.0	51.1	(*S*)[d]
3-F	$PdCl_2$(Ms-Valphos) (**20a**)	54.0	51.1	(*S*)[d]
4-F	$PdCl_2$(Ms-Valphos) (**20a**)	86.2	58.8	*S*
	$PdCl_2$(Ms-*t*-Leuphos) (**20e**)	76.1	63.4	*S*[e]

a) [**26**]/[**16**]/[Pd] = 1/2/5 × 10^{-3}. *b*) Yield based on **26**. *c*) Determined by HPLC analysis of **29**. *d*) By analogy with the hydrosilylation of styrene. *e*) $[\alpha]_D^{22}$ −26.5° (*c* = 3.3, methanol) [lit. (*R*)-**29d**: $[\alpha]_D^{21}$ +38.7° (*c* = 1.309, methanol) reported for 97.8% ee (ref. 21)].

Table 5. Asymmetric Hydrophenylation of Norbornene with Phenyl Triflate Catalyzed by $Pd(OAc)_2$–Chiral Phosphine Complexes[a]



30 31 32

Entry	Ligand (Pd/ligand)	Yield (%)[b]	% ee[c]
1	Ms-Valphos (**3a**) (1/1)	61.9	70.2 (−)
2	Ms-Valphos (**3a**) (1/2)	73.6	71.4 (−)[d]
3	Ms-Phenophos (**3g**) (1/2)	89.0	59.6 (−)
4	Ms-*t*-Leuphos (**3f**) (1/2)	75.2	61.8 (−)
5	PMO-Ms-Valphos (**3b**) (1/2)	85.1	62.7 (−)
6	PCl-Ms-Valphos (**3c**) (1/2)	80.5	67.6 (−)
7	Bs-Valphos (**4**) (1/2)	65.9	61.0 (−)
8	NMe-Ms-Valphos (**6**) (1/2)	62.0	5.0 (−)
9	(*S*)-BINAP (**33**) (1/2)	70.0	10.8 (−)
10	(+)-Norphos (**34**) (1/2)	94.2	43.0 (−)
11	(−)-MOD-DIOP (**35**) (1/2)	54.2	7.1 (+)
12	(2*S*,4*S*)-BPPM (**36**) (1/2)	63.1	23.4 (−)

a) The reaction was carried out in DMSO at 65 °C for 20 h under an argon atmosphere in the presence of triethylamine as a base. [**30**]/[**31**]/[Pd]/[ligand]/[Et_3N]/[HCOOH] = 1.5/1/0.012/0.024/3.5/3. *b*) Isolated yield. *c*) Determined by HPLC. *d*) $[\alpha]_D^{22}$ −29.6° (*c* = 1.0, $CHCl_3$).

olefins (Heck reaction)[12] is one of the most significant carbon–carbon bond-forming reactions in organic synthesis and its enantioselective control[13] has been a challenging subject in recent asymmetric synthesis. We found that the palladium complexes of **3a**—**g** and **4** were efficient catalysts for asymmetric Heck-type hydroarylation of norbornene (**30**) with phenyl triflate (phenyl trifluoromethanesulfonate) (**31**).[14] The results of the asymmetric hydroarylation of norbornene are summarized in Table 5. In our initial attempts, we applied chiral bisphosphine ligands (**33**—**36**) to Brunner's arylation system using phenyl triflate instead of phenyl iodide, but the chiral bisphosphine–palladium complex did not give satisfactory results. For example, when the reaction was carried out using 1.2 mol% of $Pd(OAc)_2$–(+)-Norphos[15] complex as a catalyst, the optical purity was 43% ee (entry 10). The ligands, (*S*)-BINAP (**33**),[16] which has been successfully used for other asymmetric Heck-reactions, (−)-MOD-DIOP (**35**)[17] and (2*S*,4*S*)-BPPM (**36**)[18] were far less effective for our present asymmetric hydroarylation. The best optical purity (71.4% ee) was obtained when the Ms-Valphos (**3a**)–$Pd(OAc)_2$ complex and triethylamine were used as the catalyst and the base, respectively (entry 2). Table 5 contains the following significant features. 1) Both PMO-Ms-Valphos (**3b**) bearing a di(*p*-methoxyphenyl)phosphino group and PCl-Ms-Valphos (**3c**) bearing a di(*p*-chlorophenyl)phosphino group showed somewhat lower selectivity than Ms-Valphos; these results may imply that the electronic effect of the substituent on the phosphino group is small. 2) The enantioselectivity was not greatly affected by the ratio of chiral ligand to palladium (entries 1 and 2). 3) Since the *N*-methyl-*N*-methylsulfonyl derivative (**6**) showed much lower selectivity than **3a**—**g** and **4**, the NH group of the sulfonamide was considered to be important for giving high selectivity.

Table 6 showed the effects of base on the asymmetric hydroarylation. It was reported that the enantiomeric purity of the product was greatly affected by the base in palladium-catalyzed asymmetric arylation of 2,3-dihydrofuran, and Proton–Sponge (1,8-bis(dimethylamino)naphthalene) gave the best result.[13k] In our present work, however, *N*,*N*-diisopropylethylamine was found to be the most efficient base in terms of enantioselectivity. The use of other solvents, such as *N*,*N*-dimethylformamide (DMF) and hexamethylphosphoramide (HMPA), gave less satisfactory results.

Table 6. Effect of Base on the Asymmetric Hydrophenylation of Norbornene (**30**) with Phenyl Triflate (**31**) Catalyzed by $Pd(OAc)_2$-Ms-Valphos (**3a**)[a]

Entry	Base	Yield (%)[b]	% ee[c]
1	Et_3N	73.6	71.4 (−)
2	iso-Pr_2NEt	80.5	73.6 (−)
3	Proton-Sponge[d]	38.8	70.5 (−)
4	DABCO	85.2	67.9 (−)

a) The reaction was carried out in DMSO at 65 °C under an argon atmosphere for 20 h. [**30**]/[**31**]/[**3a**]/[base]/[HCOOH] = 1.5/1/0.0012/0.0024/3.5/3. *b*) Isolated yield. *c*) Determined by HPLC. *d*) Proton-Sponge: 1,8-bis(dimethylamino)naphthalene.

In conclusion, we have synthesized new chiral (*β*-*N*-sulfonylaminoalkyl)phosphines and found that their palladium complexes were efficient catalysts for asymmetric hydrosilylation and Heck-type hydroarylation of olefins.

Experimental

General Procedures All melting points were determined with a micro-melting point apparatus (Yazawa) and are uncorrected. Optical rotations were measured on a JASCO DIP-140 digital polarimeter. Infrared (IR) spectra were measured on a JASCO A-202 IR spectrophotometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on JEOL-EX 270 spectrometers using tetramethylsilane (TMS) as an internal standard, and the chemical shifts are given in δ values. The abbreviations of signal patterns are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Column chromatography was carried out on Silica gel 60 (70—230 mesh, Merck).

(*S*)-3-Methyl-2-methylsulfonylamino-1-butyl Methylsulfonate (2a) A solution of methanesulfonyl chloride (8.25 g, 72 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a mixture of (*S*)-2-amino-3-methyl-1-

butanol (L-valinol) (**1a**) (3.09 g, 30 mmol) and triethylamine (7.59 g, 75 mmol) in CH_2Cl_2 (50 ml) at 0 °C, and the mixture was stirred at room temperature for 18 h, then concentrated *in vacuo*. Saturated aqueous $NaHCO_3$ (30 ml) was added to the residue, and the mixture was extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography on silica gel with toluene/ethyl acetate (6/1) as an eluent to give **2a** (5.29 g, 68%). ^{1}H-NMR ($CDCl_3$) δ: 1.03 (3H and 3H, br d, J=8 Hz, $(C\underline{H}_3)_2CH$), 1.85—2.02 (1H, m, $(CH_3)_2C\underline{H}$), 3.04 and 3.08 (3H and 3H, s and s, $SO_2CH_3 \times 2$), 3.42—3.53 (1H, m, C<u>H</u>N), 4.23—4.35 (2H, m, CH_2O), 4.50—4.74 (1H, m, NH).

[(2*S*)-3-Methyl-2-(methylsulfonylamino)butyl]diarylphosphine (3a—e) A typical procedure is given for the preparation of [(2*S*)-3-methyl-2-(methylsulfonylamino)butyl]diphenylphosphine ((*S*)-Ms-Valphos, **3a**). Under an argon atmosphere, *n*-BuLi (1.57 M in *n*-hexane, 4.5 ml, 7.1 mmol) was added to a solution of diphenylphosphine (1.2 ml, 6.5 mmol) in tetrahydrofuran (THF) (7 ml) at −30 °C and the mixture was stirred at −30 °C for 30 min. A solution of **2a** (663 mg, 2.6 mmol) in THF (3 ml) was added to the stirred lithium phosphide at −30 °C, and the whole was stirred at −30 °C for 18 h, then concentrated *in vacuo*. Saturated aqueous $NaHCO_3$ (20 ml) was added to the residue, and the mixture was extracted with degassed toluene. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography on silica gel with toluene/ethyl acetate (6/1) as an eluent to give **3a** (790 mg, 87%), mp 67—68 °C, $[\alpha]_D^{20}$ +8.4° (c=0.92, benzene). IR (KBr): 1320, 1150 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.89 and 0.93 (3H and 3H, d and d, J=7 Hz, $(C\underline{H}_3)_2CH$), 2.05—2.37 (3H, m, $CHCCH_2P$), 2.89 (3H, s, CH_3SO_2), 3.27—3.37 (1H, m, CHN), 4.41 (1H, br d, J=7 Hz, NH), 7.15—7.44 (10 H, m, Ar-H). *Anal.* Calcd for $C_{18}H_{24}NO_2PS$: C, 61.87; H, 6.92; N, 4.01. Found: C, 62.26; H, 6.84; N, 3.92.

[(2*S*)-3-Methyl-2-(methylsulfonylamino)butyl]bis(4-methoxyphenyl)-phosphine ((*S*)-PMO-Ms-Valphos, **3b**): 62% yield, $[\alpha]_D^{23}$ +8.0° (c=0.35, benzene). IR (KBr): 1320, 1150 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 and 0.92 (3H and 3H, d and d, J=7 Hz, $(C\underline{H}_3)_2CH$), 2.04—2.29 (3H, m, $CHCCH_2P$), 2.90 (3H, s, CH_3SO_2), 3.26—3.33 (1H, m, CHN), 3.80 and 3.81 (3H and 3H, s and s, $CH_3O \times 2$), 4.30 (1H, br d, J=7 Hz, NH), 6.87—6.91 (4H, m, Ar-H). *Anal.* Calcd for $C_{20}H_{28}NO_4PS$: C, 58.66; H, 6.89; N, 3.42. Found: C, 58.72; H, 6.89; N, 3.44.

[(2*S*)-3-Methyl-2-(methylsulfonylamino)butyl]bis(4-chlorophenyl)-phosphine ((*S*)-PCl-Ms-Valphos, **3c**): 86% yield, $[\alpha]_D^{23}$ +3.1° (c=0.33, benzene). IR (KBr): 1320, 1150 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 and 0.93 (3H and 3H, d and d, J=7 Hz, $(C\underline{H}_3)_2CH$), 2.04—2.28 (3H, m, $CHCCH_2P$), 2.93 (3H, s, CH_3SO_2), 3.29—3.34 (1H, m, CHN), 4.33 (1H, br d, J=7 Hz, NH), 7.13—7.37 (8H, m, Ar-H). *Anal.* Calcd for $C_{18}H_{22}Cl_2NO_2PS$: C, 51.68; H, 5.30; N, 3.35. Found: C, 54.01; H, 5.32; N, 2.99.

[(2*S*)-3-Methyl-2-(methylsulfonylamino)butyl]bis(4-methoxy-3,5-dimethylphenyl)phosphine ((*S*)-MOD-Ms-Valphos, **3d**): 56% yield, $[\alpha]_D^{23}$ −7.2° (c=0.25, benzene). IR (KBr): 1329, 1150 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.90 and 0.94 (3H and 3H, d and d, J=7 Hz, $(C\underline{H}_3)_2CH$), 2.02—2.23 (3H, m, $CHCCH_2P$), 2.26 (12H, s, Ar-$(C\underline{H}_3)_2 \times 2$), 2.86 (3H, s, CH_3SO_2), 3.25—3.32 (1H, m, CHN), 3.71 and 3.72 (3H and 3H, s and s, $CH_3O \times 2$), 4.25 (1H, br d, J=7 Hz, NH), 7.06—7.28 (4H, m, Ar-H). *Anal.* Calcd for $C_{24}H_{36}NO_4PS$: C, 61.91; H, 7.79; N, 3.01. Found: C, 62.97; H, 7.83; N, 2.90.

[(2*S*)-3-Methyl-2-(methylsulfonylamino)butyl]bis[3-(trifluoromethyl)phenyl]phosphine ((*S*)-MTF-Ms-Valphos, **3e**): 55% yield, $[\alpha]_D^{23}$ +13.2° (c=0.48, benzene). IR (KBr): 1320, 1150 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.90 and 0.95 (3H and 3H, d and d, J=7 Hz, $(C\underline{H}_3)_2CH$), 2.04—2.38 (3H, m, $CHCCH_2P$), 2.94 (3H, s, CH_3SO_2), 3.28—3.34 (1H, m, CHN), 4.40 (1H, br d, J=7 Hz, NH), 7.13—7.70 (8H, m, Ar-H). *Anal.* Calcd for $C_{20}H_{22}F_6NO_2PS$: C, 49.49; H, 4.57; N, 2.89. Found: C, 48.11; H, 5.20; N, 4.29.

(*S*)-3-Methyl-2-phenylsulfonylamino-1-butyl Phenylsulfonate (2d) Benzenesulfonyl chloride (2.8 ml, 22 mmol) was added to a solution of **1a** (1.03 g, 10 mmol) in pyridine (30 ml) at 0 °C and the mixture was stirred at room temperature for 18 h. After evaporation of the pyridine under reduced pressure, the residue was acidified to pH 2 by addition of 10% HCl and extracted with ethyl acetate. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with toluene/ethyl acetate (6/1) as an eluent to give **2d** as a colorless oil (2.30 g, 60%). ^{1}H-NMR ($CDCl_3$) δ: 0.74 and 0.76 (3H and 3H, d and d, J=7 Hz, $(C\underline{H}_3)_2CH$), 1.78—2.01 (1H, m, $(CH_3)_2CH$), 3.13—3.22 (1H, m, CHN), 3.81—4.04 (2H, m, CH_2P), 5.12 (1H, br d, NH), 7.43—7.84 (10H, m, $SO_2C_6H_5 \times 2$).

[(2*S*)-3-Methyl-2-(phenylsulfonylamino)butyl]diphenylphosphine (4) The title compound was prepared by using the same procedure as for the preparation of **3a**, from diphenylphosphine (327 mg, 2 mmol), *n*-BuLi (1.57 M in *n*-hexane, 3.5 ml, 5.5 mmol), and **2d** (615 mg, 1.6 mmol). The reaction product was purified by column chromatography on silica gel with toluene/ethyl acetate (6/1) as an eluent to give **4** as white crystals (350 mg, 53%), mp 101—103 °C, $[\alpha]_D^{20}$ −46.6° (c=0.92, benzene). IR (KBr): 1330, 1155 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.71 and 0.78 (3H and 3H, d and d, J=7 Hz, $(C\underline{H}_3)_2CH$), 2.08—2.23 (3H, m, $CHCCH_2P$), 3.10—3.17 (1H, m, CHN), 4.62 (1H, br d, J=7 Hz, NH), 7.19—7.75 (15H, m, Ar-H). *Anal.* Calcd for $C_{23}H_{26}NO_2PS$: C, 67.13; H, 6.37; N, 3.40. Found: C, 66.83; H, 6.39; N, 3.41.

(*S*)-3,3-Dimethyl-2-methylsulfonylamino-1-butyl Methylsulfonate (2b) The title compound was prepared from (*S*)-2-amino-3,3-dimethyl-1-butanol (**1b**) by using the same procedure as for the preparation of **2a**, from **1b** (500 mg, 4.3 mmol), methanesulfonyl chloride (1.15 g, 10 mmol) and triethylamine (1.52 g, 15 mmol). The reaction product was purified by column chromatography on silica gel with toluene/ethyl acetate (4/1) as an eluent to give **2b** (280 mg, 24%), mp 82—85 °C, $[\alpha]_D^{22}$ −8.5° (c=0.43, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.03 (9H, s, $(CH_3)_3$), 3.07 and 3.09 (3H and 3H, s and s, $SO_2CH_3 \times 2$), 3.50 (1H, m, C<u>H</u>N), 4.21 (1H, dd, J=7.9, 10.6 Hz, H_a of CCH_2P), 4.42 (1H, dd, J=3.6, 10.6 Hz, H_b of CCH_2P), 4.90 (1H, br d, NH). FAB-MS m/z: 274 $(M+H)^+$.

(*S*)-2-Methylsulfonylamino-3-phenyl-1-propyl Methylsulfonate (2c) The title compound was prepared from (*S*)-2-amino-3-phenyl-1-propanol (**1c**) by using the same procedure as for the preparation of **2a**, from **1c** (1.00 g, 6.6 mmol), methanesulfonyl chloride (2.7 g, 23.8 mmol) and triethylamine (2.5 g, 24.8 mmol). The reaction product was recrystallized from ethyl acetate-isopropyl alcohol to give **2c** (1.8 g, 59.2%), mp 87—88 °C, $[\alpha]_D^{22}$ −40.6° (c=1.04, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 2.48 (3H, s, $NHSO_2C\underline{H}_3$), 2.82 (1H, dd, J=8.9, 13.9 Hz, H_a of $PhC\underline{H}_2$), 3.00 (1H, dd, J=5.9, 8.9 Hz, H_b of $PhC\underline{H}_2$), 3.09 (3H, s, OSO_2CH_3), 3.88 (1H, m, CHN), 4.24 (1H, dd, J=4.3, 10.2 Hz, H_a of CH_2OSO_2), 4.30 (1H, dd, J=4.6, 10.2 Hz, H_b of CH_2OSO_2), 5.06 (1H, br d, NH), 7.30 (5H, m, Ar-H). FAB-MS m/z: 308 $(M+H)^+$.

[(2*S*)-3,3-Dimethyl-2-(methylsulfonylamino)butyl]diphenylphosphine (3f) The title compound was prepared from **2b** by using the same procedure as for the preparation of **3a**, from **2b** (500 mg, 1.8 mmol), diphenylphosphine (0.87 ml, 5 mmol) and *n*-BuLi (1.57 M in *n*-hexane, 3.5 ml, 5.5 mmol). The reaction product was purified by column chromatography on silica gel with toluene/ethyl acetate (4/1) as an eluent to give **3f** (620 mg, 94.8%), mp 143—145 °C, $[\alpha]_D^{22}$ +108.4° (c=0.42, $CHCl_3$). IR (KBr): 1300, 1140 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.91 (9H, s, $(CH_3)_3$), 1.96 and 2.47 (2H, m, $C\underline{H}_2P$), 3.13 (3H, s, SO_2CH_3), 3.31 (1H, m, CHN), 4.36 (1H, br s, NH), 7.14—7.48 (10H, m, Ar-H). *Anal.* Calcd for $C_{19}H_{26}NO_2PS$: C, 62.79; H, 7.20; N, 3.85. Found: C, 62.71, H, 7.09; N, 3.82.

[(2*S*)-2-(Methylsulfonylamino)-3-phenylpropyl]diphenylphosphine (3g) The title compound was prepared from **2c** by using the same procedure as for the preparation of **3a**, from **2c** (800 mg, 2.6 mmol), diphenylphosphine (1 ml, 5.7 mmol) and *n*-BuLi (1.57 M in *n*-hexane, 3.8 ml, 6 mmol). The reaction product was purified by column chromatography on silica gel with toluene/ethyl acetate (4/1) as an eluent to give **3g** (940 mg, 91%), mp 127—129 °C, $[\alpha]_D^{22}$ −26.0° (c=0.54, $CHCl_3$). IR (KBr): 1305, 1140 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.37 (2H, m, CH_2P), 2.47 (3H, s, SO_2CH_3), 2.85 (1H, dd, J=7.3, 13.6 Hz, H_a of $PhC\underline{H}_2$), 3.07 (1H, dd, J=5.9, 13.6 Hz, H_b of $PhC\underline{H}_2$), 3.65 (1H, m, CHN), 4.39 (1H, br d, NH), 7.14—7.48 (15H, m, Ar-H). *Anal.* Calcd. for $C_{22}H_{24}NO_2PS$: C, 66.48; H, 6.09; N, 3.52. Found: C, 66.58: H, 5.89; N, 3.51.

[(2*S*)-3-Methyl-2-(*N*-methyl-*N*-methylsulfonylamino)butyl]diphenylphosphine (6) (*S*)-3-Methyl-2-(*N*-methyl-*N*-methylsulfonylamino)-1-butyl methylsulfonate (**2d**) was prepared from (*S*)-3-methyl-2-(*N*-methylamino)-1-butanol (**5**)[20] by using the same procedure as for the preparation of **2a**, from **5** (433 mg, 3.7 mmol), methanesulfonyl chloride (1.09 g, 8.9 mmol) and triethylamine (941 mg, 9.3 mmol). The reaction product was purified by column chromatography on silica gel with toluene/ethyl acetate (6/1) as an eluent to give the corresponding methanesulfonate **2d** (600 mg, 60%). A solution of **2d** (546 mg, 2 mmol) in dry, degassed THF (5 ml) was added to a suspension of lithium diphenylphosphide, which was prepared from diphenylphosphine

(560 mg, 3 mmol) and *n*-BuLi (1.57 M in *n*-hexane, 2.1 ml, 3.3 mmol) in dry, degassed THF (10 ml) as described above. The mixture was stirred at −20 °C for 18 h, then concentrated *in vacuo*. Saturated aqueous $NaHCO_3$ was added to the residue, and the mixture was extracted with degassed toluene. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography on silica gel with toluene/ethyl acetate (9/1) as an eluent to give **6** (327 mg, 45%), mp 80—82 °C, $[\alpha]_D^{22}$ +72.4° (c=0.43, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.93 and 0.96 (3H and 3H, d and d, J=6.9 Hz, $(C\underline{H}_3)_2CH$), 1.75—2.11, 2.49—2.58 (3H, m, $(CH_3)_2C\underline{H}$, $C\underline{H}_2P$), 2.78 (3H, s, SO_2CH_3), 2.93 (3H, s, CH_3N), 7.32—7.50 (10H, m, Ar-H). *Anal.* Calcd for $C_{19}H_{26}NO_2PS$: C, 62.79; H, 7.21; N, 3.85. Found: C, 62.55; H, 7.04; N, 3.82.

(*S*)-2-Hydroxy-3-methyl-1-butyl *p*-Toluenesulfonate (14) A mixture of (*S*)-3-methyl-1,2-butanediol (**13**) (1.04 g, 10 mmol) and *p*-toluenesulfonyl chloride (2.29 g, 12 mmol) in pyridine (10 ml) was stirred at −50 °C for 15 h. The reaction mixture was diluted with H_2O (20 ml) and extracted with ethyl acetate. The organic layer was washed with 10% HCl and brine, and then dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with toluene/ethyl acetate (3/1) as an eluent to give **14** (1.59 g, 61.5%) as an oil, $[\alpha]_D^{22}$ −23.4° (c=0.80, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.78 (6H, d, J=6.9 Hz, $(C\underline{H}_3)_2CH$), 1.78 (1H, m, $(CH_3)_2C\underline{H}$), 2.42 (3H, s, Ar-CH_3), 3.04 (1H, m, $C\underline{H}(OH)$), 3.57 (2H, m, CH_2OSO_2), 7.30 (2H, d, J=8.3 Hz, Ar-H), 7.79 (2H, d, J=8.3 Hz, Ar-H).

[(2*S*)-2-(Methoxymethyloxy)-3-methylbutyl]diphenylphosphine (8) A mixture of **14** (1.29 g, 5 mmol), dimethoxymethane (3.81 g, 50 mmol) and phosphorus pentoxide (0.5 g, 3.5 mmol) in CH_2Cl_2 (5 ml) was refluxed for 15 h. Then 15% aqueous K_2CO_3 (25 ml) was added, and the whole was extracted with isopropyl ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel with toluene/ethyl acetate (4/1) as an eluent to give the corresponding *O*-methoxymethyl ether as an oil (1.26 g, 83.3%). A solution of this compound (604 mg, 2 mmol) in dry, degassed THF (3 ml) was added to a suspension of lithium diphenylphosphide, which was prepared from diphenylphosphine (0.56 ml, 3 mmol) and *n*-BuLi (1.57 M in *n*-hexane, 2.1 ml, 3.3 mmol) in dry, degassed THF (5 ml) as described above. Saturated aqueous $NaHCO_3$ (15 ml) was added, and the mixture was extracted with toluene. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel with toluene as an eluent to give **8** as an oil (327 mg, 51.7%), $[\alpha]_D^{22}$ +1.6° (c=0.45, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.86 and 0.93 (3H and 3H, d and d, J=6.8 Hz, $(C\underline{H}_3)_2CH$), 2.03 (1H, m, $(CH_3)_2C\underline{H}$), 3.35 (3H, s, OCH_3), 3.47 (1H, m, $C\underline{H}OCH_2$), 4.56 and 4.61 (2H, d and d, J=13.7 Hz, OCH_2O), 7.18—7.46 (10H, m, Ar-H). *Anal.* Calcd for $C_{19}H_{25}O_2P$: C, 72.13; H, 7.96. Found: C, 71.87; H, 7.89.

(2*S*)-*N*-(*tert*-Butoxycarbonyl)-3-methyl-1-butanol (21) A solution of di-*tert*-butyl dicarbonate (5.24 g, 24 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a solution of L-valinol (**1a**) (2.4 g, 23.3 mmol) and triethylamine (2.43 g, 24 mmol) in CH_2Cl_2 (15 ml) at room temperature, and the whole was stirred at the same temperature for 2 h. After evaporation of the solvent, the residue was distilled to give **21** as a colorless oil (4.34 g, 90%), bp 180 °C (2 mmHg), $[\alpha]_D^{22}$ −20.7° (c=1.35, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.93 and 0.96 (3H and 3H, d and d, J=6.9 Hz, $(C\underline{H}_3)_2CH$), 1.45 (9H, s, $(CH_3)_3$), 1.81 (1H, m, $(CH_3)_2C\underline{H}$), 3.43—3.68 (3H, m, $CHC\underline{H}_2OH$). FAB-MS m/z: 204 $(M+H)^+$.

(2*S*)-*N*-(*tert*-Butoxycarbonyl)-3-methyl-1-butyl *p*-Toluenesulfonate (22) *p*-Toluenesulfonyl chloride (3.30 g, 17 mmol) was added to a solution of **21** (3.11 g, 15 mmol) in pyridine (20 ml) at 0 °C, and the mixture was stirred at room temperature for 18 h. After evaporation of the solvent, the residue was acidified to pH 2 by addition of 10% HCl and extracted with ethyl acetate. The organic layer was washed with 10% HCl, saturated aqueous $NaHCO_3$ and brine, and then dried over anhydrous $MgSO_4$. Concentration *in vacuo* and chromatography on silica gel with *n*-hexane/ethyl acetate (1/1) as an eluent gave **22** (4.57 g, 85%). mp 64—65 °C, $[\alpha]_D^{22}$ −20.8° (c=3.50, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.86 and 0.90 (3H and 3H, d and d, J=6.9 Hz, $(C\underline{H}_3)_2CH$), 1.41 (9H, s, $(CH_3)_3$), 1.80 (3H, s, Ar-CH_3), 3.48 (1H, m, CHN), 4.06 (2H, m, CH_2OSO_2). *Anal.* Calcd for $C_{17}H_{27}NO_5S$: C, 57.12; H, 7.61; N, 3.92. Found: C, 57.84; H, 7.56; N, 4.00.

[(2*S*)-*N*-(*tert*-Butoxycarbonyl)-3-methylbutyl]diphenylphosphine (23) A solution of **22** (3.67 g, 10.3 mmol) in THF (20 ml) was added at −40 °C to a suspension of lithium diphenylphosphide, which was prepared from diphenylphosphine (2.87 g, 15.4 mmol) and *n*-BuLi (1.57 M in *n*-hexane, 10.8 ml, 17 mmol) in dry, degassed THF (30 ml) as described above, and the mixture was stirred at −30 °C for 12 h. After evaporation of the solvent, saturated aqueous $NaHCO_3$ (40 ml) was added to the residue, and the mixture was extracted with toluene. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with toluene as an eluent to give **23** (2.61 g, 68%). ^{1}H-NMR ($CDCl_3$) δ: 0.85 and 0.87 (3H and 3H, d and d, J=6.6 Hz, $(C\underline{H}_3)_2CH$), 1.40 (9H, s, $(CH_3)_3$), 1.87—2.25 (3H, m, $(CH_3)_2C\underline{H}$, $C\underline{H}_2P$), 3.58 (1H, m, CHN), 4.40 (1H, br d, NH), 7.32—7.50 (10H, m, Ar-H). FAB-MS m/z: 372 $(M+H)^+$.

[(2*S*)-2-Amino-3-methylbutyl]diphenylphosphine (24) A mixture of **23** (2.00 g, 5.4 mmol) and trifluoroacetic acid (15 ml) was stirred at 0 °C under an argon atmosphere for 1 h. After evaporation of the solvent, saturated aqueous $NaHCO_3$ (30 ml) was added to the residue, and the mixture was extracted with toluene. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. Concentration *in vacuo* gave **24** (1.01 g, 69%), which was spectroscopically pure and used without further purification. ^{1}H-NMR ($CDCl_3$) δ: 0.88 and 0.90 (3H and 3H, d and d, J=6.6 Hz, $(C\underline{H}_3)_2CH$), 1.79 (1H, m, $(CH_3)_2C\underline{H}$), 2.43 (2H, m, CH_2P), 3.08 (1H, m, $C\underline{H}NH_2$), 7.40—7.80 (10H, m, Ar-H). FAB-MS m/z: 272 $(M+H)^+$.

[(2*S*)-3-Methyl-2-(trifluoromethylsulfonylamino)butyl]diphenylphosphine ((*S*)-TFS-Valphos, 25) A solution of trifluoromethanesulfonic anhydride (119 mg, 0.42 mmol) in CH_2Cl_2 (0.5 ml) was added to a mixture of **24** (95 mg, 0.35 mmol) and triethylamine (71 mg, 0.7 mmol) in CH_2Cl_2 (0.5 ml) at −70 °C. The mixture was stirred at the same temperature for 3 h, then concentrated *in vacuo*, and saturated aqueous $NaHCO_3$ (5 ml) was added to the residue. The mixture was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography on silica gel with toluene as an eluent to give **25** (76 mg, 53.8%), mp 112—114 °C, $[\alpha]_D^{22}$ −18.4° (c=0.5, benzene). ^{1}H-NMR ($CDCl_3$) δ: 0.90 and 0.92 (3H and 3H, d and d, J=6.6 Hz, $(C\underline{H}_3)_2CH$), 2.20 (1H, m, $(CH_3)_2C\underline{H}$), 2.38 (2H, m, CH_2P), 3.51 (1H, m, CHN), 4.83 (1H, br d, J=9.2 Hz, NH), 7.34—7.49 (10H, m, Ar-H). FAB-MS m/z: 404 $(M+H)^+$.

Dichloro[(*S*)-*N*-sulfonylaminophosphine]palladium(II) (20a—e) A typical procedure is given for the preparation of dichloro[(*S*)-Ms-Valphos]palladium ($PdCl_2$[(*S*)-Ms-Valphos], **20a**). A solution of Ms-Valphos (**3a**) (67 mg, 0.19 mmol) in benzene (2 ml) was added to a suspension of dichlorobis(acetonitrile)palladium(II) (50 mg, 0.19 mmol) in benzene (2 ml). After stirring at room temperature for 18 h, the reaction mixture was evaporated and the residue was dissolved in a mixed solvent of CH_2Cl_2 (1 ml) and benzene (1 ml). *n*-Hexane was added to the solution until a precipitate formed. The precipitate was collected by filtration and dried *in vacuo* to give **20a** as red crystals (60 mg, 60.0%), mp 137—139 °C, $[\alpha]_D^{22}$ +83.6° (c=0.41, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.73 and 0.94 (3H and 3H, d and d, J=6.9 Hz, $(C\underline{H}_3)_2CH$), 1.84—2.18, 3.22—3.45 (4H, m, $(CH_3)_2C\underline{H}$, $C\underline{H}N$, $C\underline{H}_2P$), 3.31 (3H, br s, SO_2CH_3), 5.83 (1H, br s, NH), 7.43—7.85 (10H, m, Ar-H). *Anal.* Calcd for $C_{18}H_{24}Cl_2NO_2PPdS$: C, 41.04; H, 4.59; N, 2.66. Found: C, 40.65; H, 4.64; N, 2.46.

$PdCl_2$[(*S*)-PMO-Ms-Valphos] (**20b**): 82% yield, mp 140—143 °C, $[\alpha]_D^{22}$ +163.2° (c=0.31, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.73 and 0.94 (3H and 3H, d and d, J=6.6 Hz, $(C\underline{H}_3)_2CH$), 1.74—2.18, 3.04—3.28 (4H, m, $(CH_3)_2C\underline{H}$, $C\underline{H}N$, $C\underline{H}_2P$), 3.37 (3H, br s, SO_2CH_3), 3.85 and 3.88 (3H and 3H, s and s, $OCH_3\times2$), 5.88 (1H, br d, NH), 6.93—7.03, 7.52—7.77 (8H, m, Ar-H). *Anal.* Calcd for $C_{20}H_{28}Cl_2NO_4PPdS$: C, 40.94; H, 4.81; N, 2.39. Found: C, 41.11; H, 4.53; N, 2.27.

$PdCl_2$[(*S*)-PCl-Ms-Valphos] (**20c**): 67.2% yield, mp 153—155 °C, $[\alpha]_D^{22}$ +97.2° (c=0.30, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.78 and 0.96 (3H and 3H, d and d, J=6.9 Hz, $(C\underline{H}_3)_2CH$), 1.8—2.19 (4H, m, $(CH_3)_2C\underline{H}$, $C\underline{H}_2P$, $C\underline{H}N$), 3.29 (3H, br s, SO_2CH_3), 7.37—7.77 (8H, m, Ar-H). *Anal.* Calcd for $C_{18}H_{22}Cl_4NO_2PPdS$: C, 36.30; H, 3.72; N, 2.35. Found: C, 36.20; H, 3.50; N, 2.04.

$PdCl_2$[(*S*)-BS-Valphos] (**20d**): 89% yield, mp 140—142 °C, $[\alpha]_D^{22}$ +51.8° (c=0.25, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.44 and 0.71 (3H and 3H, d and d, J=6.6 Hz, $(C\underline{H}_3)_2CH$), 1.72—2.30, 3.00 (4H, m, $(CH_3)_2C\underline{H}$, $C\underline{H}_2P$, $C\underline{H}N$), 6.34 (2H, br s, NH), 7.20—7.52 (15H, m, Ar-H). *Anal.* Calcd for $C_{23}H_{26}Cl_2NO_2PPdS$: C, 46.92; H, 4.45; N, 2.38. Found: C, 46.22; H, 4.23; N, 2.35.

$PdCl_2$[(*S*)-Ms-*t*-Leuphos] (**20e**): 79% yield, mp 160—163 °C, $[\alpha]_D^{22}$

+52.0° (c=0.21, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.85 (9H, s, $(CH_3)_3$), 2.10—2.18, 3.07—3.35 (3H, m, CHN, CH_2P), 5.83 (1H, d, J=8.6 Hz, NH), 7.26—7.58 (10H, m, Ar-H). *Anal.* Calcd for $C_{19}H_{26}Cl_2NO_2PPdS$: C, 42.20; H, 4.85; N, 2.59. Found: C, 40.45; H, 4.58; N, 2.43.

$PdCl_2$[(*S*)-TFS-Valphos] (**20f**): 57.3% yield, mp 135—137 °C. ^{1}H-NMR ($CDCl_3$) δ: 0.68 and 0.94 (3H and 3H, d and d, J=6.9 Hz, $(CH_3)_2CH$), 1.90—2.18, 3.26 (4H, m, $(CH_3)_2CH$, CHN, CH_2P), 7.50—7.90 (10H, m, Ar-H). *Anal.* Calcd for $C_{18}H_{21}Cl_2F_3NO_2PPdS$: C, 37.23; H, 3.64; N, 2.41. Found: C, 37.90; H, 3.29; N, 2.25.

Asymmetric Hydrosilylation of Cyclopentadiene (General Procedure) All the reactions were carried out under an argon atmosphere. A mixture of dichlorobis(acetonitrile)palladium(II) (2.6 mg, 0.01 mmol), chiral ligand (0.01 mmol) and cyclopentadiene (**9**) (661 mg, 10 mmol) was stirred at 0 °C for 10 min. Dichloromethylsilane (**10**) (2.1 ml) was added to the mixture, and the whole was stirred at 0 °C for 40 h. Distillation gave 3-(trichlorosilyl)cyclopentene (**11**) (bp 120 °C (20 mmHg, bulb to bulb)). Compound **11** was added to a mixture of ethanol (10 ml) and triethylamine (4.5 g) at 0 °C and the whole was stirred at room temperature for 1 h. The precipitate was filtered off and the filtrate was evaporated. The residue was distilled to give 3-(diethoxymethylsilyl)cyclopentene (**12**), bp 110 °C [20 mmHg, bulb to bulb (lit. bp 92—96 °C (25 mmHg)[19]]. ^{1}H-NMR ($CDCl_3$) δ: 0.06 (3H, s, $SiCH_3$), 1.20 (6H, t, J=7 Hz, CH_2CH_3 ×2), 1.73—2.60 (5H, m, CH_2CH_2CHSi), 3.73 (4H, q, J=7 Hz, CH_2CH_3 ×2), 5.30—5.80 (2H, m, CH=CH).

Asymmetric Hydrosilylation of Styrene Derivatives (General Procedure) All the reactions were carried out under an argon atmosphere. A mixture of $PdCl_2$[(*S*)-*N*-sulfonylaminophosphine] (5.3×10^{-3} mmol or 0.027 mmol) and a substrate (**15**, **26a—d**) (5.3 mmol) was stirred at room temperature for 10 min. Trichlorosilane (**16**) (2.1 ml) was added to the mixture, and the whole was stirred at room temperature for 18 h. Distillation gave 1-aryl-1-trichlorosilylethane (**17**, **27a—d**) as an oil. This compound (**17**, **27a—d**) was added to a mixture of ethanol (10 ml) and triethylamine (4.5 g) at 0 °C and the mixture was stirred at room temperature for 1 h. The precipitate was filtered off and the filtrate was evaporated. The residue was distilled to give 1-aryl-1-triethoxyethane (**18** and **28a—d**) as an oil. $KHCO_3$ (330 mg, 3.3 mmol) and 30% H_2O_2 (2.0 ml) were added to this compound (**18**, **28a—d**) in a mixture of THF (10 ml) and methanol (10 ml) at room temperature, then the whole was refluxed for 6 h. After ice-cooling of the resultant suspension, dilute aqueous $NaHCO_3$ (10 ml) was added and the mixture was extracted with ether. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the alcohol (**19** and **29a—d**) as an oil. The enantiomeric purity was determined by HPLC analysis with a chiral stationary phase (**19**: Daicel Chiralcel OB, *n*-hexane/2-propanol=9/1; **29a**: Daicel Chiralcel OJ, *n*-hexane/2-propanol=9/1; **29b—d**: Daicel Chiralcel OB-H, *n*-hexane/2-propanol=9/1). ^{1}H-NMR ($CDCl_3$) spectra for the products are shown below. 1-[3-(Trifluoromethyl)phenyl]ethanol (**29a**): 1.47 (3H, d, J=6.3 Hz, CH_3), 2.55 (1H, br s, CH(OH)), 4.91 (1H, q, J=6.3 Hz, CH(OH)), 7.41—7.62 (4H, m, Ar-H). 1-(2-Fluorophenyl)ethanol (**29b**): 1.48 (3H, d, J=6.6 Hz, CH_3), 2.75 (1H, br s, CH(OH)), 5.16 (1H, q, J=6.6 Hz, CH(OH)), 6.95—7.50 (4H, m, Ar-H). 1-(3-Fluorophenyl)ethanol (**29c**): 1.43 (3H, d, J=6.6 Hz, CH_3), 4.83 (1H, q, J=6.6 Hz, CH(OH)), 6.89—7.31 (4H, m, Ar-H). 1-(4-Fluorophenyl)ethanol (**29d**): 1.42 (3H, d, J=6.3 Hz, CH_3), 2.60 (1H, br s, CH(OH)), 4.81 (1H, q, J=6.3 Hz, CH(OH)), 6.96—7.02 (2H, m, Ar-H), 7.26—7.31 (2H, m, Ar-H).

Asymmetric Hydrophenylation of Norbornene (General Procedure) All the reactions were carried out under an argon atmosphere. Phenyl triflate (**31**) (339 mg, 1.5 mmol) was added to a solution of palladium(II) acetate (4.0 mg, 0.018 mmol), chiral ligand (0.036 mmol) and norbornene (**30**) (188 mg, 2.0 mmol) in dry dimethyl sulfoxide (3 ml). After addition of triethylamine (536 mg, 5.3 mmol) and formic acid (207 mg, 4.5 mmol), the mixture was stirred at 65 °C for 20 h. H_2O (5 ml) was added, and the whole was extracted with ethyl acetate. The organic layer was washed with H_2O and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by short column chromatography on silica gel with *n*-hexane/ethyl acetate (5/1) as an eluent to give *exo*-2-phenylbicyclo[2.2.2]heptane (**32**). The enantiomeric purity was determined by HPLC analysis with a chiral stationary phase (Daicel Chiralcel OJ, *n*-hexane/2-propanol=9/1). ^{1}H-NMR spectral data were in fair agreement with the reported values.[14] ^{1}H-NMR ($CDCl_3$) δ: 1.15—1.39 (3H, m), 1.52—1.80 (5H, m), 2.35 (2H, m), 2.73 (1H, dd), 7.11—7.30 (5H, m).

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