Pergamon

Tetrahedron, Vol. 53, No. 10, pp. 3513-3526, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00084-7

Asymmetric Allylation of Aromatic Aldehydes Catalyzed by Chiral Phosphoramides Prepared from (*S*)-Proline

Katsuhiko Iseki,* Yoshichika Kuroki, Mie Takahashi, Satoshi Kishimoto and Yoshiro Kobayashi

MEC Laboratory, Daikin Industries, Ltd., Miyukigaoka, Tsukuba, Ibaraki 305, Japan

Abstract: Chiral phosphoramides prepared from (*S*)-proline were used to catalyze the allylation and crotylation of aromatic aldehydes with allylic trichlorosilanes in good enantioselective yields. Phosphoramides **4d** and **4m** gave chiral homoallylic alcohols and their enantiomers, respectively, with similar levels of enantioselectivity. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

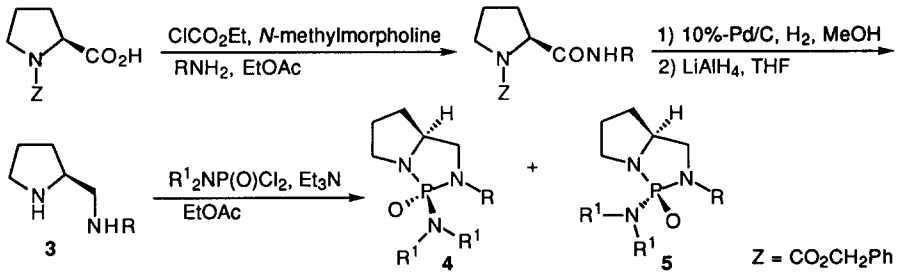
The asymmetric addition of allylmetal reagents to aldehydes has been found very effective for synthesizing chiral homoallylic alcohols.[1] Catalytic asymmetric allylation with allylsilanes[2] and -stannanes[2c,3] using chiral Lewis acids has been reported. Though good to excellent enantioselectivity was achieved, these transformations, which proceed through open transition structures,[2b,4] provide *syn* homoallylic alcohols with high diastereoselectivity from either stereoisomer of crotylsilanes and -stannanes.

Kobayashi *et al.* successfully carried out the addition of allyl- (**1**) and crotyltrichlorosilanes (**2**) to aldehydes in *N,N*-dimethylformamide (DMF) and stereoselectively obtained *syn* and *anti* homoallylic alcohols from (*Z*)- and (*E*)-crotyltrichlorosilanes, respectively.[5] They consider DMF as a Lewis base to form the requisite siliconate complex, and allylation and crotylation in DMF to proceed through associated cyclic transition structures.[6] Denmark *et al.* noted the asymmetric allylation and crotylation of aromatic aldehydes with allylic trichlorosilanes to be promoted by chiral phosphoramides as Lewis bases in high yield and modest enantiomeric excess.[7,8] We wish to report herein that the asymmetric allylation and crotylation of aromatic aldehydes with allylic trichlorosilanes can be catalyzed by chiral phosphoramides prepared from (*S*)-proline in a good enantioselective manner.[9]

RESULTS AND DISCUSSION

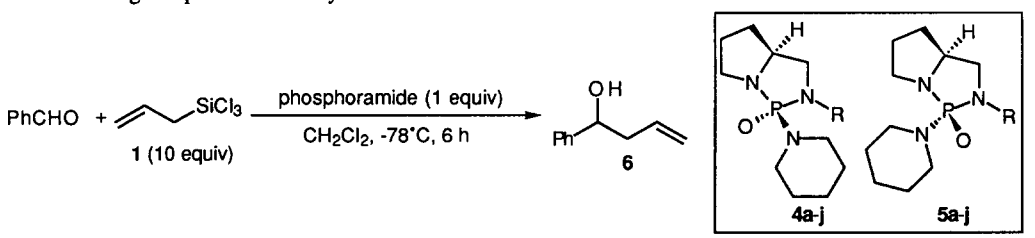
Asymmetric allylation with stoichiometric quantities of chiral phosphoramides. Various phosphoramides as stoichiometric reagents were examined for their ability to function as catalysts for mediating asymmetric allylation. Phosphoramides were prepared from (*S*)-proline as shown in Scheme 1. (*S*)-*N*-Carbobenzyloxyproline was effectively converted to (*S*)-diamine **3** according to the literature.[10] Diamine **3** was treated with *N,N*-disubstituted phosphoramidic dichlorides as described by Peyronel *et al.*[11] to give the (*R*P)-phosphoramide **4** and (*S*P)-isomer **5**. The absolute configuration at phosphorus in **4** and **5** was determined by ^{31}P NMR[11] and X-ray crystallography.[12] Phosphoramides having a piperidine moiety were then evaluated for their usefulness in the allylation of benzaldehyde using 10 equiv of allyltrichlorosilane (**1**) at -78°C for 6 h (Table 1). All reactions were carried out by simply adding benzaldehyde and then **1** to a solution of phosphoramide in dichloromethane. The corresponding product, 1-phenyl-3-buten-1-ol (**6**), was

purified by flash chromatography and the enantiomeric excess was determined by HPLC using a Daicel Chiralcel OD-H column. In most cases, chemical and optical yields were found strongly dependent on the phosphorus configuration in the phosphoramides. Phosphoramide **4d** promoted allylation in 74% yield and 71% ee, while only 5% yield and 29% ee were obtained with phosphoramide **5d** (entries 7 and 8). Enantioselectivity [81% (*R*)] was the highest with phosphoramide **4f** (entry 11).



Scheme 1

Table 1. Asymmetric Allylation of Benzaldehyde Catalyzed by Stoichiometric Amounts of Phosphoramides Each Possessing a Piperidine Moiety

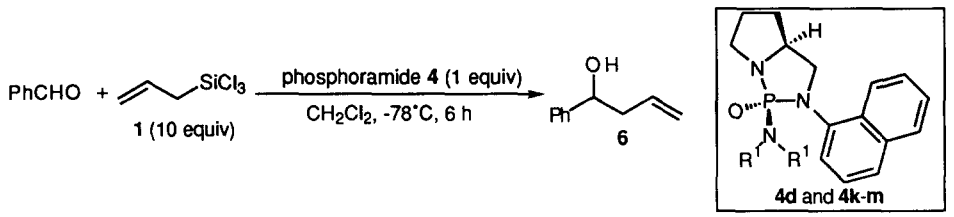


Entry	Phosphoramide		Product **6**	
		R	Yield[a] %	ee[b] % (config)[c]
1	**4a**	Me	16	12 (*S*)
2	**5a**	Me	85	35 (*R*)
3	**4b**	CH_2Ph	73	32 (*R*)
4	**5b**	CH_2Ph	80	1 (*S*)
5	**4c**	Ph	74	49 (*R*)
6	**5c**	Ph	28	12 (*R*)
7	**4d**	1-naphthyl	74	71 (*R*)
8	**5d**	1-naphthyl	5	29 (*R*)
9	**4e**	2-naphthyl	78	33 (*R*)
10	**5e**	2-naphthyl	14	34 (*R*)
11	**4f**	1-anthranyl	57	81 (*R*)
12	**4g**	4-$CH_3OC_6H_4$	99	56 (*R*)
13	**5g**	4-$CH_3OC_6H_4$	71	2 (*S*)
14	**4h**	4-$CF_3C_6H_4$	70	2 (*S*)
15	**5h**	4-$CF_3C_6H_4$	8	48 (*R*)
16	**4i**	5,6,7,8-tetrahydro-1-naphthyl	81	80 (*R*)
17	**5i**	5,6,7,8-tetrahydro-1-naphthyl	15	36 (*R*)
18	**4j**	cyclohexyl	97	69 (*R*)

a) Isolated yields based on benzaldehyde; b) Determined by HPLC using a Daicel Chiralcel OD-H column; c) The absolute configuration of the major enantiomer was established by comparison with rotation reported in the literature. See ref. 7.

After phosphoramides **4** (R_P) having a piperidine moiety (**4d, 4f** and **4i**) had been shown capable of serving as allylation mediators, attempts were made to replace the piperidino group of **4d** with other dialkylamino groups. The results for the allylation of benzaldehyde are summarized in Table 2. Phosphoramide **4d** gave (*R*)-**6** with 71% ee, while phosphoramides **4l-m** rather interestingly provided (*S*)-**6** with essentially the same or greater enantioselectivity (entries 3-5).

Table 2. Asymmetric Allylation of Benzaldehyde Catalyzed by Stoichiometric Amounts of Phosphoramides **4** Each Having a 1-Naphthyl Group

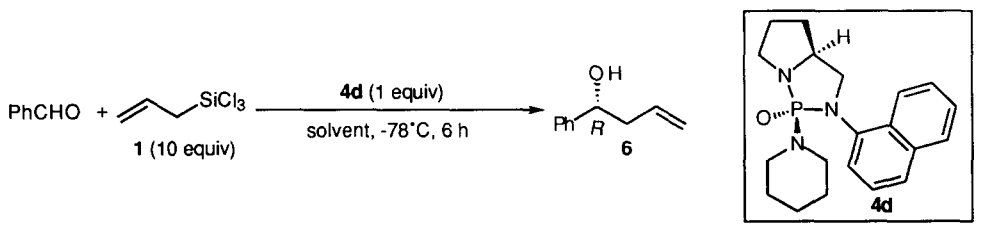


Entry	Phosphoramide		Product **6**	
		R^1	Yield[a] %	ee[b] % (config)[c]
1	**4d**	-$(CH_2)_5$	74	71 (*R*)
2	**4k**	-$(CH_2)_4$	88	2 (*S*)
3	**4l**	Et	83	73 (*S*)
4	**4m**	Pr	84	85 (*S*)
5	**4n**	*i*-Bu	21	90 (*S*)

a) Isolated yields based on benzaldehyde; b) Determined by HPLC using a Daicel Chiralcel OD-H column; c) The absolute configuration of the major enantiomer was established by comparison with reported rotation. See ref. 7.

Examination was made of solvent effects during the allylation of benzaldehyde with allyltrichlorosilane mediated by phosphoramide **4d**. As shown in Table 3, toluene, propionitrile, ethyl acetate and acetone gave enantioselectivity similar to that in dichloromethane. Tetrahydrofuran provided the highest optical yield (82% ee, entry 2). The chemical yield was highest with propionitrile (90%, entry 4).

Table 3. Asymmetric Allylation of Benzaldehyde Catalyzed by Stoichiometric Amounts of Phosphoramide **4d** in Various Solvents

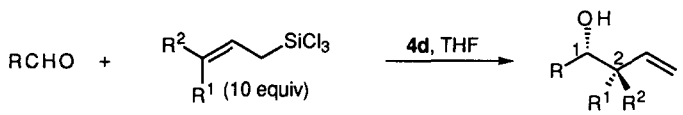


Entry	Solvent	Product **6**	
		Yield[a] %	ee[b] %
1	CH_2Cl_2	74	71
2	THF	79	82
3	toluene	63	69
4	C_2H_5CN	90	71
5	EtOAc	55	72
6	acetone	81	73

a) Isolated yields based on benzaldehyde; b) Determined by HPLC using a Daicel Chiralcel OD-H column.

Asymmetric allylation and crotylation with catalytic amounts of chiral phosphoramides. After the (R_P)-phosphoramides **4** had been shown to be effective stoichiometric reagents, **4d** and **4m** in substoichiometric quantities were evaluated for their use as catalysts. Allylic trichlorosilane (**1** or **2**) was added dropwise to a solution of aromatic aldehyde and phosphoramide (**4d** or **4m**, 10-20 mol%) in tetrahydrofuran at -60 or -78°C. The reaction mixture was stirred at -60 or -78°C for 72-168 h followed by the usual work-up. The products thus obtained, homoallylic alcohols **6-11**, were purified by flash chromatography and the enantiomeric excess was determined by HPLC using a chiral column or ^{1}H NMR of the corresponding (*R*)-MTPA ester. The absolute configurations of homoallylic alcohols **6** and **9** were established based on comparison with literature values.[7,13,14] The results with **4d** are summarized in Table 4. The allylation of benzaldehyde and *o*-tolualdehyde with allyltrichlorosilane (**1**) was promoted in good enantiomeric excess, while α,α,α-trifluoro-*p*-tolualdehyde, an aldehyde having an electron-withdrawing group, was shown less effective with respect to its chemical and optical yields (entries 1-3). Crotylation of benzaldehyde and 4-*tert*-butylbenzaldehyde with (*Z*)-crotyltrichlorosilane [(*Z*)-**2**] proceeded at -60°C to afford homoallylic alcohols *syn*-**9** and -**10**, respectively, with excellent diastereoselectivity and good enantiomeric excess (entries 4 and 6). The reaction of benzaldehyde with (*E*)-crotyltrichlorosilane [(*E*)-**2**] gave *anti*-**9** in high diastereoselective and good enantioselective yields (entry 5).

Table 4. Asymmetric Allylation and Crotylation of Aromatic Aldehydes Catalyzed by Substoichiometric Amounts of Phosphoramide **4d**



1 $R^1 = R^2 = H$
(*Z*)-**2** R^1 = Me, R^2 = H (>99/1)
(*E*)-**2** R^1 = H, R^2 = Me (>99/1)

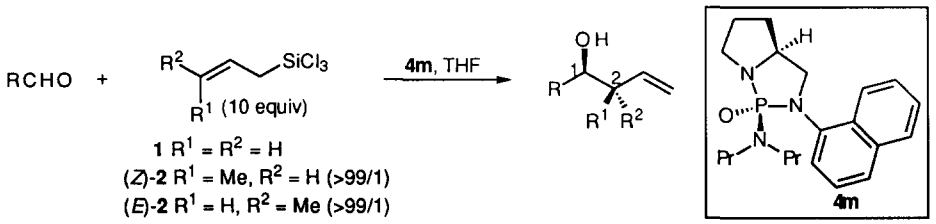
Entry	Aldehyde	Silane	Catalyst	Temp.	Time	Product		
	R		(mol%)	(°C)	(h)		Yield[a] % (*syn*/*anti*)[b]	ee[c] % (config)[d]
1	C_6H_5	**1**	10	-78	168	**6**	67	85 (*R*)[7,13]
2	2-MeC_6H_4	**1**	20	-60	72	**7**	89	80
3	4-$CF_3C_6H_4$	**1**	20	-60	72	**8**	47	72
4	C_6H_5	(*Z*)-**2**	20	-60	96	*syn*-**9**	95 (98/2)	76 (1*R*,2*S*)[14]
5	C_6H_5	(*E*)-**2**	20	-60	96	*anti*-**9**	68 (3/97)	73 (1*R*,2*R*)[14]
6	4-*t*-BuC_6H_4	(*Z*)-**2**	20	-60	120	*syn*-**10**	52 (>99/1)	82

a) Isolated yields based on starting aldehydes; b) Determined by ^{1}H NMR; c) Determined by HPLC using a Daicel Chiralcel OD-H or AD column and by ^{1}H NMR of the corresponding (*R*)-MTPA ester; d) Absolute configuration of the major enantiomer was established by comparison with the literature.

As shown in Table 5, allylation and crotylation catalyzed by 10-20 mol% of phosphoramide **4m** were carried out with good enantioselectivity. The allylation of benzaldehyde with allylsilane **1** at -78°C for 168 h gave the highest optical yield (88% ee, entry 1). The crotylation of benzaldehyde, 4-*tert*-butylbenzaldehyde and *o*-tolualdehyde with crotylsilane (*Z*)-**2** proceeded at -60°C to give *syn*-homoallylic alcohols **9-11**, respectively, with high diastereoselectivity and good enantiomeric excess (entries 3, 5 and 6). The reaction of benzaldehyde with crotylsilane (*E*)-**2** at -60°C for 96 h gave (1*S*,2*S*)-*anti*-**9** in 90% yield and with 98/2 diastereoselectivity and 83% enantiomeric excess (entry 4). The use of substoichiometric amounts of phosphoramides **4d** and **4m** essentially showed the same enantioselectivity compared to the stoichiometric quantities, though additional reaction time was required. A point of particular interest was that phosphoramide

4m provided the enantiomers of the homoallylic alcohols obtained by phosphoramide **4d** with similar levels of enantioselectivity in all cases (**6**, **7**, *syn*-**9**, *anti*-**9** and *syn*-**10**).

Table 5. Asymmetric Allylation and Crotylation of Aromatic Aldehydes Catalyzed by Substoichiometric Amounts of Phosphoramide **4m**

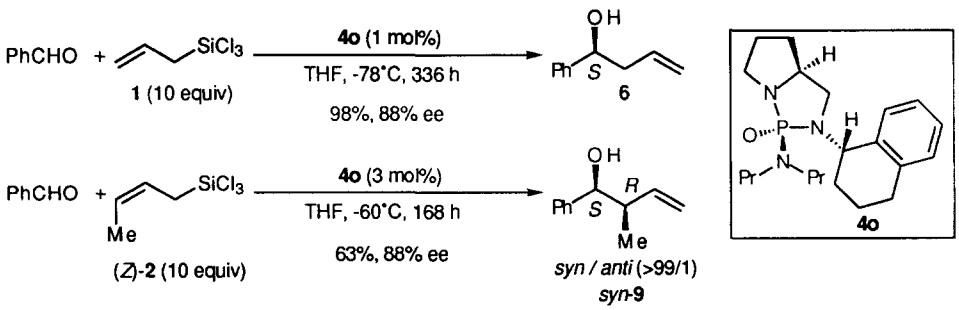


1 $R^1 = R^2 = H$
(*Z*)-**2** R^1 = Me, R^2 = H (>99/1)
(*E*)-**2** R^1 = H, R^2 = Me (>99/1)

Entry	Aldehyde R	Silane	Catalyst (mol%)	Temp. (°C)	Time (h)	Product	Yield[a] % (*syn*/*anti*)[b]	ee[c] % (config)[d]
1	C_6H_5	**1**	10	-78	168	**6**	83	88 (*S*)[7,13]
2	2-MeC_6H_4	**1**	20	-60	72	**7**	86	81
3	C_6H_5	(*Z*)-**2**	20	-60	96	*syn*-**9**	80 (98/2)	77 (1*S*,2*R*)[14]
4	C_6H_5	(*E*)-**2**	20	-60	96	*anti*-**9**	90 (2/98)	83 (1*S*,2*S*)[14]
5	2-MeC_6H_4	(*Z*)-**2**	20	-60	120	*syn*-**11**	78 (>99/1)	83
6	4-*t*-BuC_6H_4	(*Z*)-**2**	20	-60	120	*syn*-**10**	72 (95/5)	82

a) Isolated yields based on starting aldehydes; b) Determined by ^{1}H NMR; c) Determined by HPLC using a Daicel Chiralcel OD-H or AD column and by ^{1}H NMR of the corresponding (*R*)-MTPA ester; d) Absolute configuration of the major enantiomer was established by comparison with the literature.

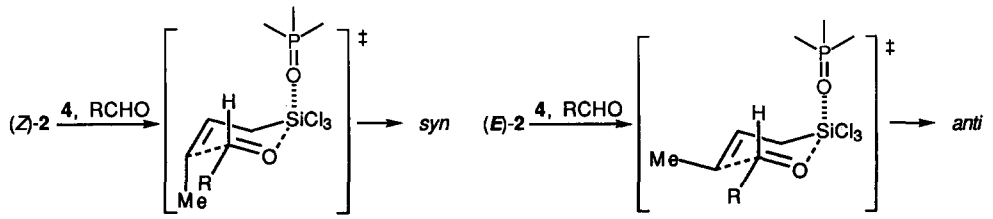
Finally, 1-3 mol% of phosphoramide **4o** having an (*S*)-1,2,3,4-tetrahydro-1-naphthyl group was also examined for potential catalytic use in reactions run for 7-14 days at -60 or -78°C. At only 1 mol% did the allylation of benzaldehyde proceeded at -78°C for 14 days to give the (*S*)-enriched homoallylic alcohol **6** in 98% yield with 88% ee. Treatment of benzaldehyde with (*Z*)-crotyltrichlorosilane [(*Z*)-**2**] and **4o** (3 mol%) at -60°C for 7 days gave (1*S*,2*R*)-**9** in 63% yield with high diastereo- and good enantioselectivities (Scheme 2).



Scheme 2

Mechanism. The stereochemical outcome in all crotylations with (*Z*)- and (*E*)-**2** has been shown consistent with a common cyclic chair siliconate transition structure[5a,6] (Scheme 3). Phosphoramide **4** coordinates with the silicon atom of crotylsilanes to give pentacoordinate allylic tricholorosilicates which possess sufficient Lewis acidity to form hexacoordinate silicates with the carbonyl oxygen of the aldehyde

and greater nucleophlicity of the γ-carbon due to enhanced σ-π conjugation.[15] Consequently, crotylations are capable of stereoselectively proceeding via the cyclic chair transition states shown in Scheme 3.



Scheme 3

The structures of pentacoordinate silicates formed during the crotylations with (*Z*)-crotyltrichlorosilane [(*Z*)-**2**] mediated by phosphoramides **4d** and **4m** were calculated with the PM-3 Hamiltonian[16] in the MOPAC 93 program.[17] As stated above, enantioselectivity with **4d** was opposite to that with **4m** in all allylations and crotylations. The PM-3 calculation was started by approaching the silicon atom of (*Z*)-**2** to the oxygen of **4d** or **4m**,[18] and the reaction coordinate (RC) calculation gave a pentacoordinate allylic silicate. The following clarification of the geometry of the silicate provided several conformers with minimal heats of formation. Five conformers were obtained from **4d**. Since energy barriers between the conformers are less than 2 kcal/mol, the rate of interconversion is supposed to be rather high even at -60°C, thus allowing equilibration of the conformers. The presence of conformer **A** having the lowest energy is thought to be predominant.[19] In the same manner, six conformers were attained from **4m**, and barriers for interconversion are also low enough to allow the equilibration. Conformer **B** possessing the second lowest energy of the six conformers bears comparison with the stablest conformer in concentration.[20,21] The geometry around the silicon atom was approximated by a trigonal bipyramidal arrangement for conformers **A** and **B**. Their structures support the presence of enhanced σ-π conjugation.

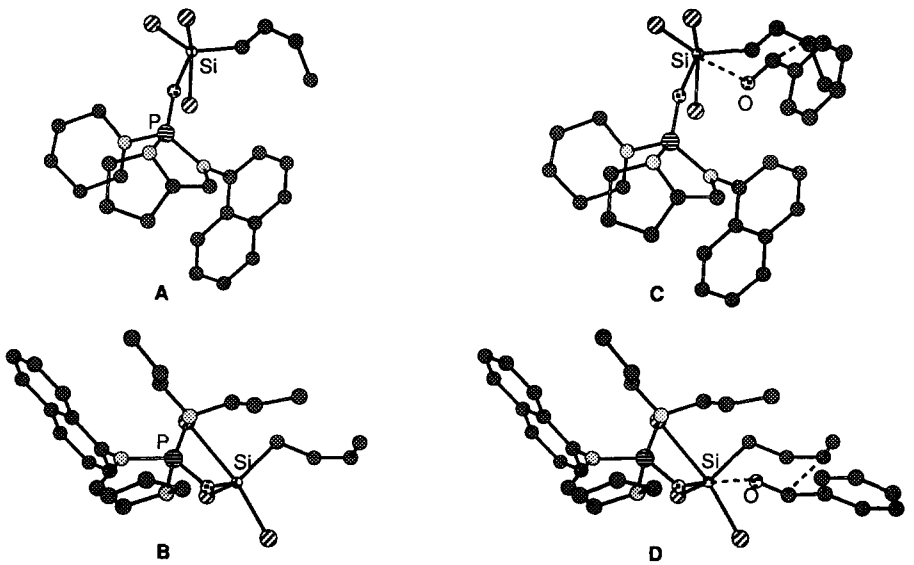


Fig. 1

We propose that (1*R*,2*S*)-homoallylic alcohol **9** would be selectively derived via transition state **C** formed from benzaldehyde and the pentacoordinate silicate **A**. The reaction of benzaldehyde with **B** may possibly lead to (1*S*,2*R*)-**9** via transition state **D**. These considerations are consistent with the experimental results.

However, this proposal only indicates a part of the possible reaction courses for the crotylations catalyzed by phosphoramides **4d** and **4m**. Further consideration for the reaction mechanism requires the calculation of not only transition states **C** and **D** but also the cyclic chair transition states formed from the minor conformers except for **A** and **B** to find activation energies, reaction rates and so on.

CONCLUSION

Chiral phosphoramides prepared from (*S*)-proline, **4d**, **4m** and **4o**, were found to effectively function as catalysts for the allylation and crotylation of aromatic aldehydes with allylic trichlorosilanes. The means for enhancing the chemical and optical yields are presently under investigation.

EXPERIMENTAL

General. Reactions were run under an argon atmosphere with magnetic stirring in oven-dried glassware. Tetrahydrofuran was distilled from sodium benzophenone kethyl immediately before use. Dichloromethane, toluene and propionitrile were freshly distilled from CaH_2. Other solvents and reagents were used as supplied or purified. Anhydrous magnesium sulfate was used as the drying agent. Silica gel 60 (Merck, 230-400 mesh) was used for column chromatography. Melting points are uncorrected. Liquid chromatographic analysis was conducted at 254 nm using a chiral column (Daicel Chiralcel OD-H and AD columns). Optical rotations were measured at 589 nm using a 1.0-dm cell with a total volume of 1 ml. Infrared spectra were taken either neat or in KBr pellets. Absorption was expressed in reciprocal centimeters (cm^{-1}). ^1H NMR spectra were recorded at 200 MHz and expressed in parts per million (ppm) downfield from TMS as the internal standard (δ). Coupling constants are in hertz. ^{31}P NMR spectra were measured at 200 MHz and given in parts per million (ppm) downfield from 85% aqueous H_3PO_4 as the internal reference. $CDCl_3$ and DMSO-d_6 served as solvents for the ^1H and ^{31}P NMR, respectively. Low- and high-resolution mass spectral analyses were performed at 70 eV electron-impact (EI). Elemental and X-ray structure analyses were carried out at the Toray Research Center Inc., Tokyo.

Preparation of crotyltrichlorosilane (2) according to the literature:[6a,22] **(Z)-Crotyltrichlorosilane [(*Z*)-2].** Trichlorosilane (25.0 g, 185 mmol), 1,3-butadiene (9.5 g, 176 mmol) and $Pd(PPh_3)_4$ (578 mg) were charged in a sealed tube and stirred at 20°C for 14 h. After the reaction, the mixture was distilled to give (*Z*)-**2** (24.5 g, 74%, *E*/*Z* = 0.3/99.7) at 145-148°C/760 Torr: IR (neat) 1442, 1394, 990, 784, 578; ^1H NMR 1.60-1.73 (m, 3H), 2.29-2.42 (m, 2H), 5.31-5.82 (m, 2H); MS *m*/*z* 192, 190, 188 [M^+], 152, 137, 135, 133, 116, 98.

(*E*)-Crotyltrichlorosilane [(*E*)-2]. A mixture of (*E*)-crotyl chloride (6 g, 66.3 mmol), trichlorosilane (12.9 g, 95.2 mmol) and ether (40 ml) was added dropwise to a suspension of CuCl (217 mg, 2.19 mmol) and Et_3N (10.1 ml, 72.5 mmol) in ether (50 ml) at room temperature. After 20 min at this temperature, the reaction mixture was filtered. Distillation of the filtrate gave (*E*)-**2** (11.2 g, 89%, *E*/*Z* = 99.6/0.4) at 142-143°C/760 Torr: IR (neat) 1453, 1391, 964, 765, 573; ^1H NMR 1.68-1.78 (m, 3H), 2.21-2.31 (m, 2H), 5.28-5.70 (m, 2H); MS *m*/*z* 192, 190 188 [M^+], 152, 137, 135, 133, 116, 98.

(*E*)-Crotyl chloride.[22a] The alcohol obtained by the reduction of crotonaldehyde with $LiAlH_4$ was treated with 3,5-dinitrobenzoyl chloride followed by recrystallization of the resulting benzoate in acetone and ethanol. The benzoate purified by repeating the recrystallization was hydrolyzed with aqueous NaOH-THF to

give pure (*E*)-crotyl alcohol (*E*/*Z* = >99/1). (*E*)-crotyl chloride was obtained by the reaction of the (*E*)-crotyl alcohol with PCl_3-pyridine.

Preparation of (S)-diamine 3: (*S*)-Diamine was prepared from (*S*)-*N*-carbobenzyloxyproline and the corresponding primary amines (methylamine, benzylamine, aniline, 1-aminonaphthalene, 2-aminonaphthalene, 1-aminoanthracene, *p*-anisidine, 4-(trifluoromethyl)aniline, 1-amino-5,6,7,8-tetrahydronaphthalene, cyclohexylamine and (*S*)-1,2,3,4-tetrahydro-1-naphthylamine[23]) according to *Asami et al.*[10]

Preparation of Phosphoramides 4 and 5 from (S)-diamine 3 according to the literature:[11] **(3*R*,7a*S*)- and (3*S*,7a*S*)-1,2,5,7,7a-Hexahydro-2-methyl-3-piperidinopyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4a and 5a).** *N*-(Dichlorophosphinyl)piperidine (4.68 g, 23.2 mmol) was added dropwise into a solution of (*S*)-2-(*N*-methylaminomethyl)pyrrolidine (2.65 g, 23.2 mmol) and Et_3N (7.3 ml, 52.4 mmol) in EtOAc (80 ml) at 0°C and the mixture was warmed to room temperature. After stirring at this temperature for 18 h, the reaction mixture was filtered. The filtrate was evaporated and chromatography of the residue with EtOAc-methanol as the eluent gave the less polar isomer (**5a**, 678 mg, 12%) and more polar isomer (**4a**, 508 mg, 9%): **4a** a colorless oil; $[\alpha]_D^{24}$ -14.6° (*c* 1.31, $CHCl_3$); IR (neat) 2931, 1449, 1166, 1069, 960, 742; ^1H NMR 1.40-2.05 (m, 10H), 2.53 (s, 1.5H), 2.57 (s, 1.5H), 2.90-3.35 (m, 8H), 3.75-3.93 (m, 1H); ^{31}P NMR 22.11 (s); MS *m*/*z* 243 [M$^+$], 159, 84; HRMS Calcd for $C_{11}H_{22}N_3OP$ [M$^+$] 243.150, found 243.149; **5a** a colorless oil; $[\alpha]_D^{24}$ +4.8° (*c* 1.45, $CHCl_3$); IR (neat) 2930, 1449, 1166, 1070, 960, 741; ^1H NMR 1.38-2.02 (m, 10H), 2.53 (s, 1.5H), 2.57 (s, 1.5H), 2.70-3.21 (m, 7H), 3.40-3.60 (m, 1H), 3.66-3.85 (m, 1H); ^{31}P NMR 28.68 (s); MS *m*/*z* 243 [M$^+$], 159, 84; HRMS Calcd for $C_{11}H_{22}N_3OP$ [M$^+$] 243.150, found 243.151.

(3*R*,7a*S*)- and (3*S*,7a*S*)-2-Benzyl-1,2,5,7,7a-hexahydro-3-piperidinopyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4b and 5b) The general procedure for phosphoramides was followed using (*S*)-2-(*N*-benzylaminomethyl)pyrrolidine and *N*-(dichlorophosphinyl)piperidine. Chromatography of the residue with *n*-hexane-EtOAc and EtOAc-methanol gave the less polar isomer (**5b**, 36%) and more polar isomer (**4b**, 40%): **4b** colorless needles; mp 81.9-82.8°C (*n*-hexane-ether); $[\alpha]_D^{25}$ -14.1° (*c* 1.02, $CHCl_3$); IR (KBr) 2934, 1457, 1221, 1065, 953, 735; ^1H NMR 1.30-1.68 (m, 6H), 1.77-2.05 (m, 4H), 2.83-3.28 (m, 8H), 3.70-4.00 (m, 2H), 4.11-4.24 (m, 1H), 7.19-7.41 (m, 5H); ^{31}P NMR 22.24 (s); MS *m*/*z* 319 [M$^+$], 235, 84; Anal. Calcd for $C_{17}H_{26}N_3OP$: C, 63.9; H, 8.2; N, 13.2; P, 9.7. Found: C, 63.6; H, 8.3; N, 13.1; P, 9.8; **5b** colorless needles; mp 87.7-89.5°C (*n*-hexane-EtOAc); $[\alpha]_D^{24}$ -26.1° (*c* 1.01, $CHCl_3$); IR (KBr) 2917, 1215, 1074, 957, 738; ^1H NMR 1.40-1.65 (m, 6H), 1.75-2.02 (m, 4H), 2.68-3.21 (m, 7H), 3.45-3.62 (m, 1H), 3.65-3.84 (m, 1H), 3.91-4.16 (m, 2H), 7.18-7.40 (m, 5H); ^{31}P NMR 28.22 (s); MS *m*/*z* 319 [M$^+$], 235, 84; Anal. Calcd for $C_{17}H_{26}N_3OP$: C, 63.9; H, 8.2; N, 13.2; P, 9.7. Found: C, 63.8; H, 8.2; N, 13.4; P, 10.1.

(3*R*,7a*S*)- and (3*S*,7a*S*)-1,2,5,7,7a-Hexahydro-2-phenyl-3-piperidinopyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4c and 5c) The general procedure for phosphoramides was followed using (*S*)-2-(*N*-phenylaminomethyl)pyrrolidine and *N*-(dichlorophosphinyl)piperidine. Chromatography of the residue with *n*-hexane-EtOAc and EtOAc-methanol gave the less polar isomer (**5c**, 46%) and more polar isomer (**4c**, 47%): **4c** colorless needles; mp 128.5-130.3°C (EtOAc); $[\alpha]_D^{25}$ +66.5° (*c* 1.91, $CHCl_3$); IR (KBr) 2932, 1600, 1496, 1304, 968, 762; ^1H NMR 1.14-1.50 (m, 6H), 1.52-1.73 (m, 1H), 1.90-2.22 (m, 3H), 2.85-3.37 (m, 7H), 3.60-3.80 (m, 1H), 3.98-4.18 (m, 1H), 6.82-6.97 (m, 1H), 7.08-7.33 (m, 4H); ^{31}P NMR 15.84 (s); MS *m*/*z* 305 [M$^+$], 221, 84; Anal. Calcd for $C_{16}H_{24}N_3OP$: C, 63.0; H, 7.9; N, 13.8; P, 10.2. Found: C, 63.0; H, 8.0; N, 14.1; P, 10.1; **5c** colorless needles; mp 117.6-118.3°C (*n*-hexane-EtOAc); $[\alpha]_D^{26}$ -21.8° (*c* 1.10, $CHCl_3$); IR (KBr) 2933, 1602, 1502, 1305, 959, 754; ^1H NMR 1.20-2.15 (m, 10H), 2.80-3.18 (m, 6H), 3.30-3.48 (m, 1H), 3.58-3.90 (m, 2H), 6.88-7.00 (m, 1H), 7.02-7.17 (m, 2H), 7.20-7.38 (m, 2H); ^{31}P NMR 22.30 (s); MS *m*/*z* 305 [M$^+$], 221, 84; Anal. Calcd for $C_{16}H_{24}N_3OP$: C, 63.0; H, 7.9; N, 13.8; P, 10.2. Found: C, 62.9; H, 7.9; N, 14.0; P, 10.4.

((3*R*,7a*S*)- and (3*S*,7a*S*)-1,2,5,7,7a-Hexahydro-2-(1'-naphthyl)-3-piperidinopyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4d and 5d) The general procedure for phosphoramides was followed using (*S*)-2-[*N*-(1'-naphthyl)aminomethyl]pyrrolidine and *N*-(dichlorophosphinyl)piperidine. Chromatography of the residue with *n*-hexane-EtOAc and EtOAc-methanol gave the less polar isomer (**5d**, 45%) and more polar isomer (**4d**, 42%): **4d** colorless needles; mp 143.0-144.1°C (ether); $[\alpha]_D^{25}$ -22.9° (*c* 1.93, $CHCl_3$); IR (KBr) 2934, 1592, 1509, 1232, 959, 780; ^1H NMR 1.25-2.20 (m, 10H), 3.30-3.42 (m, 6H), 3.58-3.80 (m, 2H), 4.01-4.20 (m, 1H), 7.39-8.30 (m, 7H); ^{31}P NMR 16.71 (s); MS *m/z* 355 [M+], 271, 84; Anal. Calcd for $C_{20}H_{26}N_3OP$: C, 67.6; H, 7.4; N, 11.8; P, 8.7. Found: C, 67.6; H, 7.5; N, 11.8; P, 8.6; **5d** colorless needles; mp 126.3-127.6°C (ether); $[\alpha]_D^{26}$ +44.6° (*c* 1.21, $CHCl_3$); IR (KBr) 2926, 1590, 1508, 957, 780; ^1H NMR 1.05-2.18 (m, 10H), 2.81-3.14 (m, 5H), 3.21-3.40 (m, 1H), 3.58-3.94 (m, 2H), 4.11-4.31 (m, 1H), 7.31-8.22 (m, 7H); ^{31}P NMR 23.37 (s); MS *m/z* 305 [M+], 221, 84; Anal. Calcd for $C_{20}H_{26}N_3OP$: C, 67.6; H, 7.4; N, 11.8; P, 8.7. Found: C, 67.7; H, 7.6; N, 11.8; P, 9.1.

(3*R*,7a*S*)- and (3*S*,7a*S*)-1,2,5,7,7a-Hexahydro-2-(2'-naphthyl)-3-piperidinopyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4e and 5e) The general procedure for phosphoramides was followed using (*S*)-2-[*N*-(2'-naphthyl)aminomethyl]pyrrolidine and *N*-(dichlorophosphinyl)piperidine. Chromatography of the residue with *n*-hexane-EtOAc and EtOAc-methanol gave the less polar isomer (**5e**, 45%) and more polar isomer (**4e**, 36%): **4e** colorless needles; mp 206.3-206.5°C (ether); $[\alpha]_D^{25}$ +4.3° (*c* 1.03, $CHCl_3$); IR (KBr) 2936, 1631, 1302, 961, 760; ^1H NMR 1.12-2.25 (m, 10H), 2.88-3.46 (m, 7H), 3.74-3.92 (m, 1H), 4.02-4.22 (m, 1H), 7.11-7.81 (m, 7H); ^{31}P NMR 15.89 (s); MS *m/z* 355 [M+], 271, 84; Anal. Calcd for $C_{20}H_{26}N_3OP$: C, 67.6; H, 7.4; N, 11.8; P, 8.7. Found: C, 67.6; H, 7.3; N, 11.9; P, 8.8; **5e** colorless needles; mp 134.5-135.5°C (ether); $[\alpha]_D^{25}$ -36.9° (*c* 1.17, $CHCl_3$); IR (KBr) 2936, 1631, 1298, 961, 754; ^1H NMR 1.20-2.20 (m, 10H), 2.82-3.28 (m, 5H), 3.41-4.01 (m, 4H), 7.16-7.81 (m, 7H); ^{31}P NMR 22.07 (s); MS *m/z* 355 [M+], 271, 84; Anal. Calcd for $C_{20}H_{26}N_3OP$: C, 67.6; H, 7.4; N, 11.8; P, 8.7. Found: C, 67.6; H, 7.4; N, 11.9; P, 8.6.

(3*R*,7a*S*)-2-(1'-Anthranyl)-1,2,5,7,7a-hexahydro-3-piperidinopyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4f) The general procedure for phosphoramides was followed using (*S*)-2-[*N*-(1'-anthranyl)aminomethyl]pyrrolidine and *N*-(dichlorophosphinyl)piperidine. Chromatography of the residue with EtOAc-methanol gave **4f** (22%) as the more polar isomer: **4f** pale yellow prisms; mp 154.5-155.9°C (*n*-hexane-EtOAc); $[\alpha]_D^{23}$ +24.7° (*c* 0.90, $CHCl_3$); IR (KBr) 2942, 1594, 1304, 962, 754; ^1H NMR 1.30-2.25 (m, 10H), 2.92-3.65 (m, 6H), 3.88-4.25 (m, 3H), 7.08-7.45 (m, 9H); ^{31}P NMR 16.83 (s); MS *m/z* 405 [M+], 321, 84; Anal. Calcd for $C_{24}H_{28}N_3OP$: C, 71.1; H, 7.0; N, 10.4; P, 7.6. Found: C, 70.9; H, 7.4; N, 10.3; P, 7.6.

(3*R*,7a*S*)- and (3*S*,7a*S*)-1,2,5,7,7a-Hexahydro-2-(4'-methoxyphenyl)-3-piperidinopyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4g and 5g) The general procedure for phosphoramides was followed using (*S*)-2-[*N*-(4'-methoxyphenyl)aminomethyl]pyrrolidine and *N*-(dichlorophosphinyl)piperidine. Chromatography of the residue with *n*-hexane-EtOAc and EtOAc-methanol gave the less polar isomer (**5g**, 43%) and more polar isomer (**4g**, 43%): **4g** colorless needles; mp 206.3-206.5°C (ether); $[\alpha]_D^{22}$ +61.1° (*c* 1.43, $CHCl_3$); IR (KBr) 2932, 1517, 1246, 966, 710; ^1H NMR 1.20-2.13 (m, 10H), 2.79-3.12 (m, 5H), 3.28-3.42 (m, 1H), 3.58-3.90 (m, 3H), 3.77 (s, 3H), 6.84 (d, J = 9.0, 2H), 7.06 (d, J = 9.0, 2H); ^{31}P NMR 16.04 (s); MS *m/z* 335 [M+], 251, 84; Anal. Calcd for $C_{17}H_{26}N_3O_2P$: C, 60.9; H, 7.8; N, 12.5; P, 9.2. Found: C, 60.9; H, 7.8; N, 12.6; P, 9.1; **5g** a colorless oil; $[\alpha]_D^{23}$ -18.9° (*c* 1.27, $CHCl_3$); IR (neat) 2939, 1516, 1249, 965, 713; ^1H NMR 1.12-2.22 (m, 10H), 2.83-3.35 (m, 7H), 3.57-3.72 (m, 1H), 3.77 (s, 3H), 3.98-4.13 (m, 1H), 6.83 (d, J = 9.1, 2H), 7.09 (d, J = 9.1, 2H); ^{31}P NMR 22.50 (s); MS *m/z* 335 [M+], 251, 84; HRMS Calcd for $C_{17}H_{26}N_3O_2P$ [M+] 335.176, found 335.176.

(3*R*,7a*S*)- and (3*S*,7a*S*)-1,2,5,7,7a-Hexahydro-3-piperidino-2-(α,α,α-trifluoro-*p*-tolyl)pyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4h and 5h) The general procedure for phosphoramides was followed using (*S*)-2-[*N*-(α,α,α-trifluoro-*p*-tolyl)aminomethyl]pyrrolidine and *N*-(dichlorophosphinyl)piperidine.

Chromatography of the residue with *n*-hexane-EtOAc and EtOAc-methanol gave the less polar isomer (**5h**, 48%) and more polar isomer (**4h**, 40%): **4h** colorless needles; mp 182.1-183.3°C (*n*-hexane-EtOAc); $[\alpha]_D^{24}$ +63.6° (*c* 1.28, $CHCl_3$); IR (KBr) 2938, 1617, 1312, 962, 719; ^1H NMR 1.19-2.31 (m, 10H), 2.90-3.38 (m, 7H), 3.66-3.83 (m, 1H), 4.00-4.18 (m, 1H), 7.13 (d, *J* = 9.0, 2H), 7.51 (d, *J* = 9.0, 2H); ^{31}P NMR 15.38 (s); MS *m/z* 373 [M+], 289, 84; Anal. Calcd for $C_{17}H_{23}F_3N_3OP$: C, 54.7; H, 6.2; N, 11.3; P, 8.3. Found: C, 55.0; H, 6.2; N, 11.3; P, 8.4; **5h** colorless needles; mp 119.1-120.7°C (*n*-hexane-EtOAc); $[\alpha]_D^{24}$ -29.4° (*c* 1.43, $CHCl_3$); IR (KBr) 2965, 1621, 1221, 957, 717; ^1H NMR 1.21-2.20 (m, 10H), 2.81-3.18 (m, 6H), 3.30-3.48 (m, 1H), 3.58-3.92 (m, 2H), 7.14 (d, *J* = 8.9, 2H), 7.54 (d, *J* = 8.9, 2H); ^{31}P NMR 21.90 (s); MS *m/z* 373 [M+], 289 84; Anal. Calcd for $C_{17}H_{23}F_3N_3OP$: C, 54.7; H, 6.2; N, 11.3; P, 8.3. Found: C, 54.9 H, 6.2; N, 11.3; P, 8.3.

(3*R*,7a*S*)- and (3*S*,7a*S*)-1,2,5,7,7a-Hexahydro-3-piperidino-2-(5',6',7',8'-tetrahydro-1'-naphthyl)pyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4i and 5i) The general procedure for phosphoramides was followed using (*S*)-2-[*N*-(5',6',7',8'-tetrahydro-1'-naphthyl)aminomethyl]pyrrolidine and *N*-(dichlorophosphinyl)piperidine. Chromatography of the residue with *n*-hexane-EtOAc and EtOAc-methanol gave the less polar isomer (**5i**, 20%) and more polar isomer (**4i**, 23%): **4i** a colorless oil; $[\alpha]_D^{25}$ +13.7° (*c* 1.46, $CHCl_3$); IR (neat) 2930, 1581, 1463, 1235, 959, 719; ^1H NMR 1.36-2.15 (m, 14H), 2.58-2.89 (m, 2H), 2.91-3.55 (m, 10H), 3.99-4.15 (m, 1H), 6.89-7.30 (m, 3H); ^{31}P NMR 16.67 (s); MS *m/z* 359 [M+], 275, 84; HRMS Calcd for $C_{20}H_{30}N_3OP$ [M+] 359.213, found 359.213; **5i** a colorless oil; $[\alpha]_D^{25}$ +0.3° (*c* 1.03, $CHCl_3$); IR (neat) 2933, 1583, 1464, 1225, 962, 720; ^1H NMR 1.18-2.20 (m, 14H), 2.68-3.22 (m, 11H), 3.41-3.68 (m, 2H), 3.88-4.08 (m, 1H), 6.90-7.45 (m, 3H); ^{31}P NMR 22.93 (s); MS *m/z* 359 [M+], 275, 84; HRMS Calcd for $C_{20}H_{30}N_3OP$ [M+] 359.213, found 359.212.

(3*R*,7a*S*)-2-Cyclohexyl-1,2,5,7,7a-hexahydro-3-piperidinopyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4j) The general procedure for phosphoramides was followed using (*S*)-2-(cyclohexylaminomethyl)pyrrolidine and *N*-(dichlorophosphinyl)piperidine. Chromatography of the residue with EtOAc-methanol gave **4j** (25%) as the more polar isomer: **4j** a colorless oil; $[\alpha]_D^{26}$ +7.6° (*c* 1.59, $CHCl_3$); IR (neat) 2930, 1450, 1224, 959, 769; ^1H NMR 0.90-2.20 (m, 20H), 2.81-3.21 (m, 8H), 3.22-3.41 (m, 1H), 3.71-3.90 (m, 1H); ^{31}P NMR 19.60 (s); MS *m/z* 311 [M+], 227, 84; HRMS Calcd for $C_{16}H_{30}N_3OP$ [M+] 311.213, found 311.214.

(3*R*,7a*S*)-1,2,5,7,7a-Hexahydro-2-(1'-naphthyl)-3-pyrrolidinopyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4k) The general procedure for phosphoramides was followed using (*S*)-2-[(1'-naphthyl)aminomethyl]pyrrolidine and *N*-(dichlorophosphinyl)pyrrolidine. Chromatography of the residue with EtOAc-methanol gave **4k** (37%) as the more polar isomer: **4k** colorless needles; mp 100.7-101.7°C (*n*-hexane-EtOAc); $[\alpha]_D^{26}$ -17.4° (*c* 1.07, $CHCl_3$); IR (KBr) 2966, 1591, 1278, 921, 776; ^1H NMR 1.49-2.20 (m, 8H), 2.86-3.35 (m, 6H), 3.62-3.92 (m, 2H), 4.15-4.33 (m, 1H), 7.36-8.20 (m, 7H); ^{31}P NMR 14.63 (s); MS *m/z* 341 [M+], 271, 70; Anal. Calcd for $C_{19}H_{24}N_3OP$: C, 66.9; H, 7.1; N, 12.3; P, 9.1. Found: C, 66.9 H, 7.1; N, 12.3; P, 9.0.

(3*R*,7a*S*)-3-(*N*,*N*-Diethylamino)-1,2,5,7,7a-hexahydro-2-(1'-naphthyl)pyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4l) The general procedure for phosphoramides was followed using (*S*)-2-[(1'-naphthyl)aminomethyl]pyrrolidine and *N*,*N*-diethylphosphoramidic dichloride. Chromatography of the residue with EtOAc-methanol gave **4l** (54%) as the more polar isomer: **4l** colorless needles; mp 90.1-91.5°C (*n*-hexane-EtOAc); $[\alpha]_D^{23}$ -31.5° (*c* 1.04, $CHCl_3$); IR (KBr) 2967, 1590, 1210, 950, 780; ^1H NMR 0.89 (t, *J* = 7.0, 6H), 1.60-2.20 (m, 3H), 2.98-3.41 (m, 7H), 3.57-3.83 (m, 2H), 4.00-4.20 (m, 1H), 7.39-8.21 (m, 7H); ^{31}P NMR 18.55 (s); MS *m/z* 343 [M+], 271, 72; Anal. Calcd for $C_{19}H_{26}N_3OP$: C, 66.5; H, 7.6; N, 12.2; P, 9.1. Found: C, 66.5 H, 7.6; N, 12.3; P, 9.0.

(3*R*,7a*S*)-3-(*N*,*N*-Dipropylamino)-1,2,5,7,7a-hexahydro-2-(1'-naphthyl)-pyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4m) The general procedure for phosphoramides was followed using (*S*)-2-[(1'-naphthyl)aminomethyl]pyrrolidine and *N*,*N*-dipropylphosphoramidic dichloride. Chromatography of the residue with EtOAc-methanol gave **4m** (35%) as the more polar isomer: **4m** colorless needles; mp 58.0-59.4°C (*n*-hexane-EtOAc); $[\alpha]_D^{24}$ -15.0° (*c* 1.08, $CHCl_3$); IR (KBr) 2962, 1592, 1281, 988, 780; ^1H NMR 0.76 (t, *J* = 7.2, 6H), 1.20-2.21 (m, 8H), 2.83-3.08 (m, 4H), 3.10-3.42 (m, 2H), 3.58-3.84 (m, 2H), 4.01-4.18 (m, 1H), 7.38-8.23 (m, 7H); ^{31}P NMR 18.45 (s); MS *m/z* 371 [M+], 271, 100; Anal. Calcd for $C_{21}H_{30}N_3OP$: C, 67.9 H, 8.1; N, 11.3; P, 8.3. Found: C, 67.9 H, 8.1; N, 11.3; P, 8.4.

(3*R*,7a*S*)-3-(*N*,*N*-Diisobutylamino)-1,2,5,7,7a-hexahydro-2-(1'-naphthyl)-pyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4n) The general procedure for phosphoramides was followed using (*S*)-2-[(1'-naphthyl)aminomethyl]pyrrolidine and *N*,*N*-diisobutylphosphoramidic dichloride. Chromatography of the residue with EtOAc-methanol gave **4n** (15%) as the more polar isomer: **4n** colorless needles; mp 85.2-86.5°C (*n*-hexane-EtOAc); $[\alpha]_D^{23}$ -9.5° (*c* 0.99, $CHCl_3$); IR (KBr) 2956, 1595, 1219, 1019, 772; ^1H NMR 0.72 (d, *J* = 8.8, 6H), 0.75 (d *J* = 8.9, 6H), 1.50-2.28 (m, 6H), 2.72-3.03 (m, 4H), 3.10-3.48 (m, 2H), 3.50-3.65 (m, 1H), 3.75-3.88 (m, 1H), 4.01-4.20 (m, 1H), 7.35-8.28 (m, 7H); ^{31}P NMR 17.48 (s); MS *m/z* 399 [M+], 271; Anal. Calcd for $C_{23}H_{34}N_3OP$: C, 69.2 H, 8.6; N, 10.5; P, 7.8. Found: C, 69.1 H, 8.6; N, 10.5; P, 7.8.

(1'*S*,3*R*,7a*S*)-3-(*N*,*N*-Dipropylamino)-1,2,5,7,7a-hexahydro-2-(1',2',3',4'-tetrahydro-1'-naphthyl)pyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (4o) The general procedure for phosphoramides was followed using (1'*S*,2*S*)-2-[(1',2',3',4'-tetrahydro-1'-naphthyl)aminomethyl]pyrrolidine and *N*,*N*-dipropylphosphoramidic dichloride. Chromatography of the residue with EtOAc-methanol gave **4o** (48%) as the more polar isomer: **4o** colorless needles; mp 62.8-63.7°C (petroleum ether); $[\alpha]_D^{27}$ +40.1° (*c* 0.99, $CHCl_3$); IR (KBr) 2953, 1485, 1223, 920, 752; ^1H NMR 0.91 (t, *J* = 7.3, 6H), 1.38-2.10 (m, 11H), 2.38-2.51 (m, 1H), 2.67-3.32 (m, 10H), 3.70-3.90 (m, 1H), 4.35-4.50 (m, 1H), 7.06-7.31 (m, 4H); ^{31}P NMR 24.45 (s); MS *m/z* 375 [M+], 275, 100; Anal. Calcd for $C_{21}H_{34}N_3OP$: C, 67.2 H, 9.1; N, 11.2; P, 8.3. Found: C, 67.2 H, 9.1; N, 11.2; P, 8.3.

General Procedure for Allylations with Allyltrichlorosilane (1): To a solution of aldehyde (1 mmol) and phosphoramide (**4** or **5**, 0.01-1 mmol) in solvent (2 ml) was added dropwise allyltrichlorosilane (**1**, 10 mmol) at -60 or -78°C. After stirring for 6-336 h at this temperature, the reaction mixture was treated with saturated aqueous $NaHCO_3$ solution and extracted with ether. The combined extracts were washed with brine, dried and filtered. After evaporation of the solvent, chromatography of the residue with *n*-hexane-EtOAc as the eluent gave the corresponding homoallylic alcohol.

1-Phenyl-3-buten-1-ol (6). a colorless oil; $[\alpha]_D^{24}$ +41.1° (*c* 1.05, benzene) (85% ee using **4m**); IR (neat) 3370, 1641, 1454, 700; ^1H NMR 2.42-2.58 (m, 2H), 4.72 (t, *J* = 5.9, 1H), 5.09-5.23 (m, 2H), 5.68-5.92 (m, 1H), 7.21-7.40 (m, 5H); MS *m/z* 148 [M+], 107, 79; HRMS Calcd for $C_{10}H_{12}O$ [M+] 148.089, found 148.089.

1-*o*-Tolyl-3-buten-1-ol (7): a colorless oil; $[\alpha]_D^{23}$ +35.1° (*c* 1.55, ethanol) (80% ee using **4d**); IR (neat) 3372, 1640, 1488, 1052; ^1H NMR 2.35 (s, 3H), 2.40-2.65 (m, 2H), 4.92-5.03 (m, 1H), 5.14-5.28 (m, 2H), 5.77-5.98 (m, 1H), 7.10 (m, 4H); MS *m/z* 162 [M+], 129, 91; HRMS Calcd for $C_{11}H_{14}O$ [M+] 162.104, found 162.105.

1-(α,α,α-Trifluoro-*p*-tolyl)-3-buten-1-ol (8): a colorless oil; $[\alpha]_D^{26}$ +36.5° (*c* 1.36, $CHCl_3$) (72% ee using **4d**); IR (neat) 3372, 1621, 1327, 843; ^1H NMR 2.38-2.65 (m, 2H), 4.79 (dd, *J* = 5.3, 5.1, 1H), 5.12-5.26 (m, 2H), 5.69-5.91 (m, 1H), 7.43-7.68 (m, 4H); MS *m/z* 197 [M-19], 175, 127; HRMS Calcd for $C_{11}H_{11}F_3O$ [M+] 216.076, found 216.076.

General Procedure for Crotylation with crotyltrichlorosilane (2): To a solution of aldehyde (1 mmol) and phosphoramide (**4** , 0.03-0.2 mmol) in tetrahydrofuran (2 ml) was added dropwise crotyltrichlorosilane (**2**, 10 mmol) at -60 or -78°C. After stirring for 96-336 h at this temperature, the reaction mixture was treated with saturated aqueous $NaHCO_3$ solution and extracted with ether. The combined extracts were washed with brine, dried and filtered. After evaporation of the solvent, chromatography of the residue with *n*-hexane-EtOAc as the eluent gave the corresponding homoallylic alcohol.

***syn*-2-Methyl-1-phenyl-3-buten-1-ol (*syn*-9):** a colorless oil; $[\alpha]_D^{25}$ +15.2° (*c* 1.00, $CHCl_3$) (76% ee using **4d**); IR (neat) 3404, 1639, 1454, 701; ^1H NMR 1.02 (d, J = 6.8, 3H), 2.51-2.70 (m, 1H), 4.63 (d, J = 5.5, 1H), 5.01-5.12 (m, 2H), 5.69-5.87 (m, 1H), 7.20-7.45 (m, 5H); MS *m/z* 162 [M^+], 107, 79; HRMS Calcd for $C_{11}H_{14}O$ [M^+] 162.104, found 162.105.

***anti*-2-Methyl-1-phenyl-3-buten-1-ol (*anti*-9):** a colorless oil; $[\alpha]_D^{25}$ +80.6° (*c* 1.05, $CHCl_3$) (73% ee using **4d**); IR (neat) 3402, 1640, 1022, 701; ^1H NMR 0.89 (d, J = 6.9, 3H), 2.40-2.60 (m, 1H), 4.37 (d, J = 7.0, 1H), 5.16-5.26 (m, 2H), 5.72-5.91 (m, 1H), 7.22-7.38 (m, 5H); MS *m/z* 162 [M^+], 107, 79; HRMS Calcd for $C_{11}H_{14}O$ [M^+] 162.104, found 162.104.

***syn*-1-(4-*tert*-Butylphenyl)-2-methyl-3-buten-1-ol (*syn*-10):** a colorless oil; $[\alpha]_D^{26}$ -15.8° (*c* 1.03, $CHCl_3$) (82% ee using **4m**); IR (neat) 3396, 1639, 1363, 913; ^1H NMR 1.02 (d, J = 6.9, 3H), 1.32 (s, 9H), 2.50-2.66 (m, 1H), 4.56-4.63 (m, 1H), 5.03-5.14 (m, 2H), 5.69-5.88 (m, 1H), 7.20-7.40 (m, 4H); MS *m/z* 218 [M^+], 163, 91; HRMS Calcd for $C_{15}H_{22}O$ [M^+] 218.167, found 218.167.

***syn*-2-Methyl-1-*o*-tolyl-1-buten-1-ol (*syn*-11):** a colorless oil; $[\alpha]_D^{26}$ -14.4° (*c* 1.00, $CHCl_3$) (83% ee using **4m**); IR (neat) 3414, 1638, 1461, 1006; ^1H NMR 1.06 (d, J = 6.8, 3H), 2.32 (s, 3H), 2.48-2.65 (m, 1H), 4.83-4.91 (m, 1H), 5.01-5.13 (m, 2H), 5.72-5.92 (m, 1H), 7.09-7.50 (m, 4H); MS *m/z* 176 [M^+], 121, 93, 77; HRMS Calcd for $C_{12}H_{16}O$ [M^+] 176.120, found 176.120.

REFERENCES AND NOTES

1. a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207-2293. b) Hoffmann, R.W. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 489-503.
2. a) Furuta, K.; Mouri, M.; Yamamoto, H. *Synlett* **1991**, 561-562. b) Ishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 11490-11495. c) Aoki, S.; Mikami, K.; Terada, M.; Nakai, T. *Tetrahedron* **1993**, *49*, 1783-1792. d) Gauthier, Jr., D.R.; Carreira, E.M. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2363-2365.
3. a) Keck, G.E.; Tarbet, K.H.; Geraci, L.S. *J. Am. Chem. Soc.* **1993**, *115*, 8467-8468. b) Keck, G.E.; Krishnamurthy, D.; Grier, M.C. *J. Org. Chem.* **1993**, *58*, 6543-6544. c) Keck, G.E.; Geraci, L.S. *Tetrahedron Lett.* **1993**, *34*, 7827-7828. d) Costa, A.L.; Piazza, M.G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001-7002. e) Marshall, J.A.; Tang, Y. *Synlett* **1992**, 653-654. f) Bedeschi, P.; Casolari, S.; Costa, A.L.; Tagliavini, E.; Umani-Ronchi, A. *Tetrahedron Lett.* **1995**, *36*, 7897-7900. g) Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 4723-4724. h) Faller, J.W.; Sams, D.W.I.; Liu, X. *J. Am. Chem. Soc.* **1996**, *118*, 1217-1218. i) Weigand, S.; Brückner, R. *Chem. Eur. J.* **1996**, *2*, 1077-1084. j) Yu, C.-M.; Choi, H.-S.; Jung, W.-H.; Lee, S.-S. *Tetrahedron Lett.* **1996**, *37*, 7095-7098.
4. a) Denmark, S.E.; Almstead, N.G. *J. Org. Chem.* **1994**, *59*, 5130-5132. b) Denmark, S.E.; Hosoi, S. *J. Org. Chem.* **1994**, *59*, 5133-5135.
5. a) Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453-3456. b) Kobayashi, S.; Nishio, K. *Synthesis* **1994**, 457-459. c) Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620-6628. d) See also: Wang, Z.; Wang, D.; Sui, X. *J. Chem. Soc., Chem. Commun.* **1996**, 2261-2262.

6. a) Kira, M.; Kobayashi, M.; Sakurai, H. *Tetrahedron Lett.* **1987**, *28*, 4081-4084. b) Hosomi, A.; Kohra, S.; Tominaga, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1517-1518. c) Hayashi, T.; Matsumoto, Y.; Kiyoi, T.; Ito, Y.; Kohra, S.; Tominaga, Y.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 5667-5670. d) Hosomi, A.; Kohra, S.; Ogata, T.; Yanagi, T.; Tominaga, Y. *J. Org. Chem.* **1990**, *55*, 2415-2420.
7. Denmark, S.E.; Coe, D.M.; Pratt, N.E.; Griedel, B.D. *J. Org. Chem.* **1994**, *59*, 6161-6163.
8. Asymmetric allylations of aldehydes mediated by chiral diamines: Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1995**, *36*, 6729-6732.
9. For preliminary communications, see: Iseki, K.; Kuroki, M.; Takahashi, M.; Kobayashi, Y. *Tetrahedron Lett.* **1996**, *37*, 5149-5150.
10. Asami, M.; Ohno, H.; Kobayashi, S.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1869-1873.
11. Peyronel, J.-F.; Samuel, O.; Fiaud, J.-C. *J. Org. Chem.* **1987**, *52*, 5320-5325.
12. X-ray structure analyses of **4c**, **4d**, **4l** and **4m** were conducted at the Toray Research Center Inc., Tokyo. Crystal data for **4c**: $C_{16}H_{24}N_3OP$, 305.36, colorless prism, 0.30 x 0.40 x 0.25 mm, orthorhombic, space group $P2_12_12_1$ (#19); a = 9.881 (1) Å, b = 17.806 (1) Å, c = 8.903 (1) Å; V = 1566.6 (2) Å^3; Z = 4; D_{calc} = 1.295 g/cm^3; F (000) = 656.00. The diffraction data were obtained using a Rigaku AFC7R diffractometer at 26°C in the ω-2θ mode using Cu-K$_\alpha$ radiation (μ = 15.73 cm^{-1}, λ = 1.54178 Å) to a maximum 2θ value of 150.1°. The structure was solved by direct methods (MITHRIL84). The final cycle of full-matrix least squares refinement was based on 3129 unique reflections ($I > 3.00\ \sigma(I)$) and 287 variable parameters and converged with an unweighted and weighted agreement factor of R = 0.032 (R_w = 0.038). Crystal data for **4d**: $C_{20}H_{26}N_3OP$, 355.42, colorless prism, 0.20 x 0.25 x 0.40 mm, orthorhombic, space group $P2_12_12_1$ (#19); a = 11.075 (3) Å, b = 16.241 (3) Å, c = 10.373 (2) Å; V = 1865.8 (6) Å^3; Z = 4; D_{calc} = 1.265 g/cm^3; F (000) = 760.00. The diffraction data were collected at 26°C in the ω-2θ mode using Cu-K$_\alpha$ radiation (μ = 13.99 cm^{-1}, λ = 1.54178 Å) to a maximum 2θ value of 150.5°. The structure was solved by direct methods (SHELXS86). The final cycle of full-matrix least squares refinement was based on 1657 unique reflections ($I > 3.00\ \sigma(I)$) and 216 variable parameters and converged with an unweighted and weighted agreement factor of R = 0.076 (R_w = 0.077). Crystal data for **4l**: $C_{19}H_{26}N_3OP$, 343.41, colorless plate, 0.50 x 0.40 x 0.20 mm, orthorhombic, space group $P2_12_12_1$ (#19); a = 16.784 (5) Å, b = 17.540 (4) Å, c = 12.899 (6) Å; V = 3797 (1) Å^3; Z = 8; D_{calc} = 1.201 g/cm^3; F (000) = 1472.00. The diffraction data were collected at 26°C in the ω-2θ mode using Mo-K$_\alpha$ radiation (μ = 1.55 cm^{-1}, λ = 0.71069 Å) to a maximum 2θ value of 50.0°. The structure was solved by direct methods (DIRDIF92 PATTY). The final cycle of full-matrix least squares refinement was based on 1895 unique reflections ($I > 1.00\ \sigma(I)$) and 433 variable parameters and converged with an unweighted and weighted agreement factor of R = 0.062 (R_w = 0.064). Crystal data for **4m**: $C_{21}H_{30}N_3OP$, 371.46, colorless plate, 0.40 x 0.30 x 0.10 mm, orthorhombic, space group $P2_12_12_1$ (#19); a = 8.035 (1) Å, b = 33.060 (1) Å, c = 7.785 (1) Å; V = 2068.0 (4) Å^3; Z = 4; D_{calc} = 1.193 g/cm^3; F (000) = 800.00. The diffraction data were collected at 26°C in the ω-2θ mode using Cu-K$_\alpha$ radiation (μ = 12.80 cm^{-1}, λ = 1.54178 Å) to a maximum 2θ value of 120.1°. The structure was solved by direct methods (SAPI91). The final cycle of full-matrix least squares refinement was based on 1520 unique reflections ($I > 1.50\ \sigma(I)$) and 236 variable parameters and converged with an unweighted and weighted agreement factor of R = 0.035 (R_w = 0.036).
13. Minowa, N.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3697-3704.
14. Roush, W.R.; Ando, K.; Powers, D.B.; Palkowitz, A.D.; Halterman, R.L. *J. Am. Chem. Soc.* **1990**, *112*, 6339-6348.
15. a) Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1988**, *110*, 4599-4602. b) Kira, M.; Sato, K.; Sakurai, H.; Hada, M.; Izawa, M.; Ushio, J. *Chem. Lett.* **1991**, 387-390.
16. Stewart, J.J.P *J. Comput. Chem.* **1989**, *10*, 209-220.
17. MOPAC 93 Rev. 2 (JCPE P081): Stewart, J.J.P. Stewart Computational Chemistry, Colorado Springs, CO, USA and Fujitsu, Ltd., Tokyo, Japan, 1993.

18. The geometry optimized structures of **4d** and **4m**, based on X-ray crystallography, were used for the PM-3 calculations.
19. Conformer **A** was calculated to account for 69% of all conformer concentrations from **4d** at -60°C.
20. The ratio of conformer **B** and the stablest conformer at -60°C was calculated to be approximately 49:51.
21. The stablest conformer obtained from **4m** appears not to have sufficient space to form a cyclic chair transition structure with benzaldehyde.
22. a) Kira, M.; Hino, T.; Sakurai, H. *Tetrahedron Lett.* **1989**, *30*, 1099-1102. b) Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1973**, *30*, 2143-2146. c) Takahashi, S.; Shibano, T.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1969**, 161.
23. Smith, R.A.; White, R.L.; Krantz, A. *J. Med. Chem.* **1988**, *31*, 1558-1566.

(*Received in Japan* 18 *November* 1996; *accepted* 16 *January* 1997)