Highly Enantioselective Allylation of Arylaldehydes Catalyzed by a Silver(I)-Chiral Binaphthylthiophosphoramide

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Chiral diphenylthiophosphoramide **L2** prepared from diphenylthiophosphinic chloride and (*R*)-(+)-*N*-ethyl-1,1′-binaphthyl-2,2′-diamine **2** was used as a catalytic chiral ligand in the silver(I)-catalyzed enantioselective allylation reaction of arylaldehydes with allyltributyltin to furnish high *ee* (up to 98%) of the homoallylic alcohols.

Introduction

Catalytic asymmetric synthesis is a valuable method for preparation of optically active substances.[1] In this connection, the stereoselective addition of organometallics to one of the two heterotopic faces of a carbonyl group has been extensively studied. Among them, the enantioselective allylation of carbonyl compounds is of particular importance in organic synthesis. Although significant results have been provided by using a stoichiometric amount of chiral Lewis acids,[2] there are only a few methods available for a catalytic process including chiral (acyloxy)borane (CAB) complex/allylic silanes[3] or allylic stannanes[4] and binaphthol-derived chiral titanium complexes/allylic stannanes[5] and allylation using BINAP, silver(I) complex[6] or chiral phosphoramides[7] as a catalyst. Recently, we reported a new catalytic enantioselective allylation reaction of aldehydes with allyltributyltin promoted by silver(I) (AgOTf)-chiral binaphthylthiophosphoramide **L1** derived from (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine in which good yields (65−84%) and moderate enantioselectivities (54−63% *ee*) have been achieved.[8] In order to get a higher *ee* in this novel Ag^I-binaphthylthiophosphoramide-catalyzed system, we have examined ligands similar to **L1**. Herein, we wish to report a new ligand, binaphthylthiophosphoramide **L2** for AgOTf-catalyzed allylation of arylaldehydes with allyltributyltin, in which a high enantioselectivity (up to 98% *ee*) was attained.

Results and Discussion

The chiral binaphthylthiophosphoramides **L1**−**L7** in Figure 1 were synthesized from the C_2-symmetric chiral scaffold (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine by the procedure shown in Scheme 1. Their structures were determined using spectroscopic data and microanalysis. Those chiral ligands (**L2**−**L7**) were used for the AgOTf-catalyzed asymmetric allylation reactions of 1-naphthaldehyde and benzaldehyde. The *ee*s of the products were determined by HPLC analysis using a chiral stationary-phase column (CHIRALCEL OD and OJ) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation. The results are summarized in Table 1. The table shows that **L2** (20 mol %) as the chiral ligand for the silver(I) (20 mol %)-catalyzed enantioselective allylation reaction of 1-naphthaldehyde with allyltributyltin in THF at −20 °C furnished 76% *ee*, which is higher that that of **L1**, in good yield (Table 1, entry 1).[8] Chiral ligands **L3** and **L4** gave the corresponding allylation products in low *ee* under the same conditions (Table 1, entries 2 and 3). Ligand **L5** showed no activity for this reaction (Table 1, entry 4). Ligands **L6** and **L7** produced the reaction products in moderate *ee* which are very close to that obtained previously with chiral ligand **L1** (Table 1, entries 5 and 6).[8] Among the solvents examined, THF was the best solvent for this silver(I)-chiral ligand-promoted reaction (Table 1, entries 7−9). Chiral ligand **L2** was also examined for the allylation reaction of benzaldehyde with allyltributyltin in the presence of AgOTf. The results are shown in Table 1. With 20 mol % of **L2** and AgOTf (20 mol %), 94% *ee* was attained in 84% yield in THF at −20 °C (Table 1, entry 10). At room temperature (20 °C), the enantioselectivity of allylation product decreased to 73% *ee* in 28% yield (Table 1, entry 13). We also examined the effect of varying the amount of the catalyst system. However, use of **L2** (10 mol %) with AgOTf (10 mol %) or **L2** (5 mol %) with AgOTf (5 mol %) decreased the *ee* to 87% and 68%, respectively (Table 1, entries 11 and 12). In addition, this asymmetric catalytic system was found to be highly sensitive to the amount of chiral ligand and AgOTf: no reaction occurred with **L2** (20 mol %) and AgOTf (10 mol %) (Table 1,

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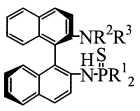
entry 14). This result suggests that the real active species in this asymmetric catalytic reaction is an **L2**:Ag^{I}/1:1 chiral silver complex.



L

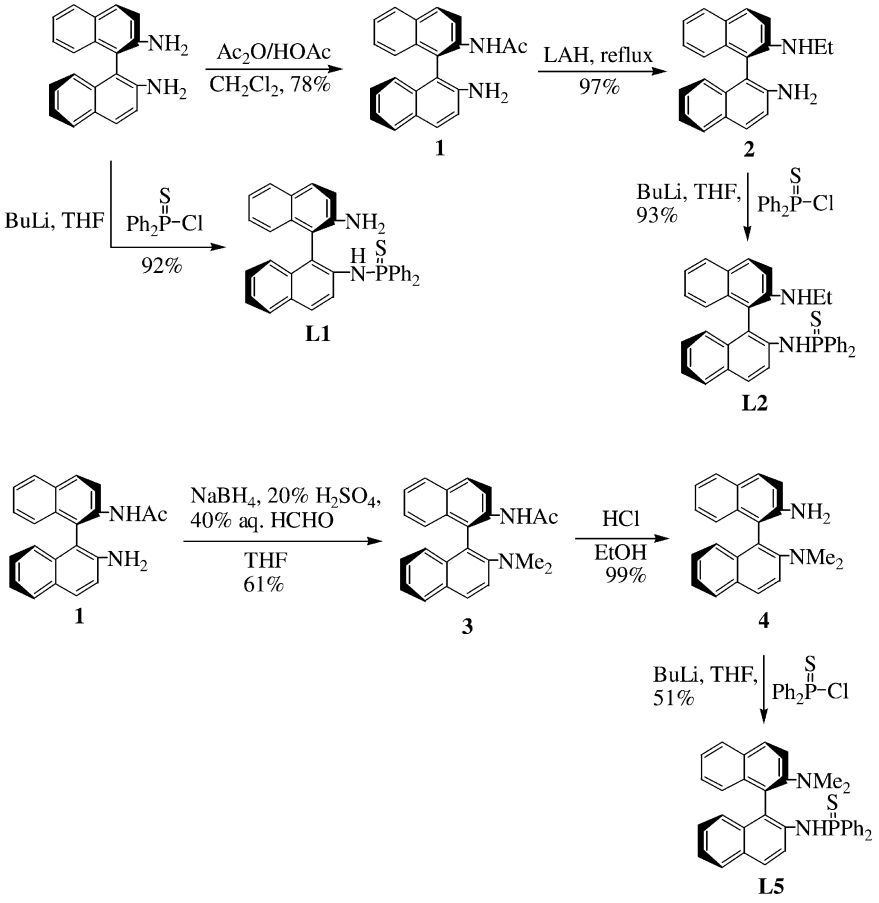
	R^1	R^2	R^3
L1	Ph	H	H
L2	Ph	H	Et
L3	Me	H	Et
L4	Me	H	H
L5	Ph	Me	Me
L6	OEt	H	H
L7	OEt	H	Et

Figure 1. The chiral binaphthylthiophosphoramides

The optimized reaction conditions found for the allylation of 1-naphthaldehyde and benzaldehyde (Table 1, entries 1 and 10) were applied to various arylaldehydes. The corresponding homoallylic alcohols could be obtained in 56−80% yield and 68−98% *ee* with the *S*-configuration.[9] The results are summarized in Table 2. For *p*-methylbenzaldehyde and *p*-chlorobenzaldehyde, 98% and 96% *ee* were obtained, respectively (Table 2, entries 1 and 2), while *trans*-cinnamaldehyde furnished 68% *ee* (Table 2, entry 4).

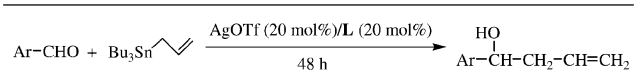
It should be emphasized here that 90% of the chiral phosphoramide ligands **L2**−**L7** could be recovered from the reaction mixture by column chromatography after the usual workup, and could be reused in this asymmetric reaction without loss of enantioselectivity because phosphoramides **L2**−**L7** are quite stable organic compounds (Table 2, entry 5). As for chiral ligand **L2**, we believe that it is a bidentate chiral ligand, with the nitrogen and phosphoryl sulfur atoms coordinated to the silver(I) metal affording a chiral silver(I) Lewis acid.[10,11] In order to get more mechanistic insight into this asymmetric system, we measured the ^{31}P NMR spectrum of ligand **L2** in the absence or presence of AgOTf. The ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) spectrum of **L2** showed a signal at +53.27 ppm (the ^{31}P NMR ($CDCl_3$, 85% H_3PO_4) spectrum of **L2** with AgOTf (molar ratio, 1:1) shows a new signal at +58.05 ppm; see Supporting Information). This chemical shift clearly indicates the formation of a new Ag^{I}-**L2** complex, although at present we do not have a crystal structure for this complex.

In conclusion, the chiral bidentate phosphoramide **L2** prepared from C_2-symmetric (*R*)-(+)-*N*-ethyl-1,1′-binaphthyl-2,2′-diamine was found to be a more effective chiral ligand for the silver(I)-promoted enantioselective allylation reaction of arylaldehydes with allyltributyltin than **L1**.[8] In some cases, the corresponding allylation products were obtained in >90% *ee* by this modified chiral binaphthylthiophosphoramide ligand. These results open a new way to design and synthesize new chiral ligands for asymmetric reactions. We are attempting to elucidate the mechanistic details of this addition reaction and to discover the exact structure of the active species. Moreover we are planning to synthesize similar bidentate chiral phosphoramides embed-



Scheme 1

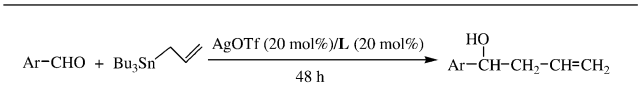
Table 1. Enantioselective allylation reaction of arylaldehyde in the presence of chiral ligands **L2−7** and silver(I) triflate under different reaction conditions

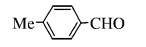
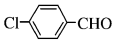
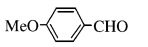
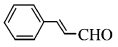
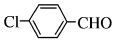


Entry	Ar-CHO	Ligand	Solvent	Temp. [°C]	Yield[a] [%]	*ee*[b] [%]	Config.
1		**L2**	THF	−20	75	76	*S*
2		**L3**	THF	−20	56	31	*S*
3		**L4**	THF	−20	51	~0	–
4		**L5**	THF	−20	no reaction	–	–
5		**L6**	THF	−20	40	61	*S*
6		**L7**	THF	−20	48	70	*S*
7		**L2**	CH_2Cl_2	−20	no reaction	–	–
8		**L2**	Et_2O	–20	23	69	*S*
9		**L2**	toluene	−20	27	76	*S*
10		**L2**	THF	−20	84	94	*S*
11		**L2**	THF	−20	75	87[c]	*S*
12		**L2**	THF	−20	34	68[d]	*S*
13		**L2**	THF	0	28	73	*S*
14		**L2**	THF	−20	no reaction[e]	–	–

[a] Isolated yields. [b] Determined by chiral HPLC. [c] The reaction was carried out in the presence of L2 (10 mol %) and AgOTf (10 mol %). [d] The reaction was carried out in the presence of L2 (5 mol %) and AgOTf (5 mol %). [e] The reaction was carried out in the presence of L2 (20 mol %) and AgOTf (10 mol %).

Table 2. Enantioselective allylation reaction of arylaldehyde in the presence of chiral ligands **L2** and silver(I) triflate under optimized reaction conditions



Entry	Ar-CHO	Ligand	Solvent	Temp. [°C]	Yield[a] [%]	*ee*[b] [%]	Config.
1		**L2**	THF	−20	75	98	*S*
2		**L2**	THF	−20	74	96	*S*
3		**L2**	THF	−20	56	80	*S*
4		**L2**	THF	−20	80	68	*S*
5		**L2**[c]	THF	−20	70	96	*S*

[a] Isolated yields. [b] Determined by chiral HPLC. [c] Recovered **L2** was used as a chiral ligand.

ded in a C_2-symmetric chiral scaffold in order to obtain more effective and stereoselective chiral ligands and to utilize those novel chiral ligands in other catalytic asymmetric reactions. Work along these lines is in progress.

Experimental Section

General Remarks: Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo−Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica-gel coated plates. Flash column chromatography was carried out using 200−300 mesh silica gel at increased pressure. Enantiomeric ratios were determined by chiral HPLC analysis. Racemic products were synthesized by allylation of aldehydes with allylmagnesium bromide (1.0 M in THF) at room temperature.

Synthesis of (*R*)-(+)-*N*-acetyl-1,1′-binaphthyl-2,2′-diamine (1): Acetic anhydride (208 μL, 2.2 mmol) was added to a mixture of (*R*)-(+)-binaphthyldiamine (568 mg, 2 mmol), acetic acid (1.2 mL, 20 mmol) and dichloromethane (20.0 mL) with ice-cooling. The mixture was stirred at room temperature overnight, and 2.0 N NaOH was added until pH > 7. After extraction with dichloromethane, the combined organic layers were dried over $MgSO_4$. The residue obtained upon evaporation was purified by column chromatography to afford 1 as a colorless solid (509 mg, 78%). M.p. 240−241 °C. $[\alpha]_D^{25}$ = +40.0 (*c* = 0.55, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3400, 1675, 1595, 1500, 1445, 1270, 1040, 965, 670 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.85 (s, 3 H, Me), 6.91−7.42 (m, 8 H, ArH and NHCO), 7.81−8.03 (m, 4 H, ArH), 8.58 (d, *J* = 9.0 Hz, 2 H, ArH). ^{13}C NMR [$(CD_3)_2SO$, TMS, 75 MHz]: δ = 23.98, 110.31, 119.39, 121.93, 123.77, 124.48, 125.01, 125.03, 125.68, 126.18, 126.92, 127.91, 128.66, 128.71, 129.97, 130.03, 132.06, 133.14, 134.51, 136.16, 144.98, 169.53. MS (EI): *m*/*z* = 326 (43) [M$^+$], 284 (M$^+$ − 42, 25), 267 (M$^+$ − 59, 100). $C_{22}H_{18}ON_2$ (326.39): calcd. C 80.98, H 5.52, N 8.59; found C 80.66, H 5.61, N 8.48%.

Synthesis of (*R*)-(+)-*N*-Ethyl-1,1′-binaphthyl-2,2′-diamine (2): A solution of **1** (509 mg, 1.56 mmol) in 10.0 mL of THF was added dropwise to a stirred suspension of $LiAlH_4$ (280 mg, 7.37 mmol) in 30.0 mL of anhydrous THF. The mixture was heated under reflux for 4 h. The reaction mixture was cooled in an ice-bath and the remaining hydride was carefully quenched by dropwise addition of water (5.0 mL) and then 10% NaOH (5.0 mL). A white precipitate was filtered off and thoroughly washed with ethyl acetate. The combined filtrate and ethyl acetate washings were washed with brine and dried over $MgSO_4$. After the solvents were evaporated under reduced pressure, the product was purified by flash chromatography to afford product **2** (470 mg, 97%) as a colorless solid. M.p. 123−124 °C. $[\alpha]_D^{25}$ = +175.2 (*c* = 0.63, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3385, 3060, 2985, 2910, 1645, 1598, 1510, 1425, 1350, 1150, 915, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.99 (t, *J* = 7.5 Hz, 3 H, Me), 3.18 (q, *J* = 7.5 Hz, 2 H, CH_2), 3.60 (br., 3 H, amino-H), 6.96−7.25 (m, 8 H, ArH), 7.75−7.87 (m, 4 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 15.57, 39.02, 112.62, 112.84, 114.69, 118.71, 122.28, 122.79, 124.15, 124.36, 127.09, 127.19, 128.03, 128.50, 128.54, 128.80, 129.86, 129.96, 134.01, 134.30, 143.35, 144.73. MS (EI): *m*/*z* = 313 (M$^+$ + 1, 100), 297 (M$^+$ − 15, 34), 280 (M$^+$ − 32, 42), 267 (M$^+$ − 45, 25). $C_{22}H_{20}N_2$ (312.41): calcd. C 84.62, H 6.41, N 8.97; found C 84.53, H 6.56, N 8.95.

Synthesis of (*R*)-(+)-*N*-Acetyl-*N*′,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine (3): A solution of **1** (163 mg, 0.5 mmol) in THF (10 mL)

and $NaBH_4$ (133 mg, 3.5 mmol) were simultaneously added to a stirred solution of 20% H_2SO_4 (0.5 mL) and 40% formaldehyde aqueous solution (0.5 mL, 6.0 mmol) in THF (20 mL) with ice-cooling over a period of 15 min, the mixture was stirred for an additional hour and then 1.0 N NaOH was added until pH > 7. After extraction with ethyl acetate, the combined organic layers were dried over $MgSO_4$. The residue obtained upon evaporation was purified by column chromatography to afford **3** as a colorless solid (108 mg, 61%). M.p. 187−189 °C. $[\alpha]_D^{25} = -244.5$ (c = 0.58, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3402, 1684, 1596, 1501, 1427, 929, 669 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.88 (s, 3 H, Me), 2.58 (s, 6 H, 2Me), 6.95 (d, J = 8.7 Hz, 1 H, ArH), 7.12−7.55 (m, 6 H, ArH), 7.84−7.80 (m, 4 H, ArH), 8.49 (d, J = 9.0 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 24.85, 43.63, 119.02, 121.81, 124.30, 124.62, 125.02, 125.54, 126.64, 126.67, 126.74, 127.04, 128.17, 128.41, 128.84, 129.90, 130.36, 131.30, 133.62, 133.96, 134.12, 149.88, 168.52. MS (EI): m/z = 354 (58) [M^+], 311 (M^+ − 43, 9), 296 (M^+ − 58, 17), 281 (M^+ − 73, 36). $C_{24}H_{22}N_2O$ (354.44): calcd. C 81.36, H 6.21, N 7.91; found C 81.40, H 6.39, N 7.80.

Synthesis of (*R*)-(+)-*N*,*N*-dimethyl-1,1′-binaphthyl-2,2′-diamine (4): (*R*)-(+)-*N*-Acetyl-*N*′,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine **3** (300 mg, 0.85 mmol) was added to a stirred solution of ethanol (25.0 mL) and 4.0 N HCl (9.0 mL), the mixture was heated under reflux for 12 h. After cooling to ambient temperature and removal of the ethanol in vacuo, 2.0 N NaOH was added until pH > 7. After extraction with dichloromethane, the combined organic layers were dried over $MgSO_4$. The residue obtained upon evaporation was purified by column chromatography to afford **4** as a colorless solid (262 mg, 99%). M.p. 116−118 °C. $[\alpha]_D^{25} = +17.4$ (c = 2.0, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3395, 2794, 1621, 1507, 1426, 1380, 1143, 989, 930, 625 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.59 (s, 2Me), 7.0−7.29 (m, 7 H, ArH), 7.47 (d, J = 9.0 Hz, 1 H, ArH), 7.74−7.91 (m, 4 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 38.47, 111.70, 113.46, 114.65, 117.12, 117.17, 118.75, 119.91, 119.99, 121.36, 121.62, 122.98, 123.03, 123.32, 123.91, 124.28, 124.90, 128.71, 129.27, 136.94, 145.23. MS (EI): m/z = 312 (100) [M^+], 297 (M^+ − 15, 4), 280 (M^+ − 32, 38), 267 (M^+ − 45, 47). $C_{22}H_{20}N_2$ (312.41): calcd. C 84.62, H 6.41, N 8.97; found C 84.70, H 6.55, N 8.92.

Representative Experimental Procedure for the Synthesis of Ligands 1−8: *n*-Butyllithium (1.12 mL, 1.8 mmol, 1.6 M solution in hexane) was added dropwise to a solution of (*R*)-(+)-*N*-ethyl-1,1′-binaphthyl-2,2′-diamine **2** (200 mg, 0.64 mmol) in THF (10.0 mL) at −40 °C over 40 min, and the reaction mixture was stirred for 1 h at the same temperature. Then diphenylthiophosphinic chloride (500 mg, 2.0 mmol) in THF (5.0 mL) was added dropwise and the reaction solution was slowly warmed to room temperature. After 2 h, THF was removed in vacuo. The residue was purified by alumina column chromatography to give the ligand **2** (**L2**) as a colorless solid (314 mg, 93%).

Ligand 1 (L1): M.p. 175−177 °C. $[\alpha]_D^{25} = -4.0$ (c = 1.20, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3350, 1625, 1514, 1477, 1438, 1340, 929, 634 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 4.10 (br. s, 2 H, NH), 5.12 (d, J = 7.4 Hz, 1 H, NH), 7.0−7.50 (m, 10 H, ArH), 7.50−7.70 (m, 4 H, ArH), 7.70−8.0 (m, 8 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 110.39, 118.25 (d, J = 4.4 Hz), 119.28 (d, J = 4.8 Hz), 119.84 (d, J = 8.9 Hz), 122.67, 124.00, 124.54 (d, J = 51.7 Hz), 127.12 (d, J = 27.8 Hz), 127.26, 128.28, 128.33, 128.52, 128.71, 128.95, 130.01 (d, J = 27.9 Hz), 130.80, 130.95, 131.62 (d, J = 11.5 Hz), 131.82, 131.86, 131.90, 133.15, 133.41 (d, J = 51.5 Hz), 133.57, 134.52, 134.93, 137.35, 143.16. ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = +53.37. MS (EI): m/z = 500 (3) [M^+]. $C_{32}H_{25}N_2PS$ (500.59): calcd. C 76.78, H 5.03, N 5.60; found C 76.65, H 5.07, N 5.74.

Ligand 2 (L2): M.p. 78−80 °C. $[\alpha]_D^{25} = -47.5$ (c = 0.905, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 1625, 1600, 1515, 1474, 1426, 1055, 898 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.11 (t, J = 7.2 Hz, 3 H, Me), 3.27 (q, J = 7.2 Hz, 2 H, CH_2), 3.78 (br., 1 H, NH), 5.14 (d, J = 7.5 Hz, 1 H, NH), 6.95−7.57 (m, 17 H, ArH), 7.75−7.91 (m, 5 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 15.07, 38.42, 109.85, 113.79, 119.26 (d, J = 4.3 Hz), 119.61 (d, J = 7.8 Hz), 122.01, 123.77, 124.55 (d, J = 57.9 Hz), 126.88, 127.10, 127.45 128.50, 128.51 (d, J = 28.8 Hz), 128.52, 128.67, 128.95, 130.29 (d, J = 51.6 Hz), 130.61 (d, J = 21.4 Hz), 131.63, 131.78, 131.82, 131.84, 131.89, 133.28, 133.46 (d, J = 38.3 Hz), 133.85, 134.83 (d, J = 37.1 Hz), 137.61, 144.51. ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = +53.28. MS (EI): m/z = 528 (2) [M^+], 311 (M^+ − 217, 1), 267 (M^+ − 261, 11). $C_{34}H_{29}N_2PS$ (528.65): calcd. C 77.27, H 5.49, N 5.30; found C 77.52, H 5.89, N 5.17.

Ligand 3 (L3): M.p. 68−70 °C. $[\alpha]_D^{25} = +30.4$ (c = 1.67, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3345, 1620, 1598, 1514, 1427, 1345, 994, 926, 669 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.09 (t, J = 7.2 Hz, 3 H, Me), 1.73 (d, J = 12.9 Hz, 3 H, Me), 1.89 (d, J = 12.9 Hz, 3 H, Me), 3.25 (q, J = 7.2 Hz, 2 H, CH_2), 3.62 (br., 1 H, NH), 4.61 (d, J = 7.2 Hz, 1 H, NH), 6.86 (d, J = 9.3 Hz, 1 H, ArH), 7.01−7.40 (m, 6 H, ArH), 7.79−7.99 (m, 5 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 15.12, 23.96 (d, J = 68.9 Hz), 24.81 (d, J = 68.6 Hz), 38.29, 109.60, 113.68, 118.89, 118.94, 119.61, 121.91, 123.35, 124.22, 124.94, 126.89, 126.94, 127.22, 128.19, 129.13, 129.99, 130.42, 133.26, 133.66, 137.83, 144.34. ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = +56.62. MS (EI): m/z = 404 (100) [M^+], 389 (M^+ − 15, 5), 267 (M^+ − 137, 25). $C_{24}H_{25}N_2PS$ (404.51): calcd. C 71.29, H 6.19, N 6.93; found C 71.65, H 6.57, N 6.49.

Ligand 4 (L4): M.p. 180−182 °C. $[\alpha]_D^{25} = +65.8$ (c = 0.6, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3350, 1620, 1514, 1476, 1422, 927, 626 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.76 (d, J = 13.5 Hz, 3 H, Me), 1.88 (d, J = 13.5 Hz, 3 H, Me), 4.61 (d, J = 6.6 Hz, 1 H, NH), 6.96 (d, J = 8.1 Hz, 1 H, ArH), 7.13−7.40 (m, 6 H, ArH), 7.80−7.99 (m, 5 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 24.01 (d, J = 68.6 Hz), 24.60 (d, J = 68.6 Hz), 110.16, 118.08, 118.97, 119.03, 122.54, 123.57, 124.25, 124.91, 126.95, 127.07, 128.09, 128.19, 128.21, 129.15, 129.97, 130.26, 133.04, 133.58, 137.62, 142.86. ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = +56.96. MS (EI): m/z = 376 (49) [M^+], 284 (M^+ − 92, 16), 267 (M^+ − 109, 100). $C_{22}H_{21}N_2PS$ (376.46): calcd. C 70.19, H 5.62, N 7.44; found C 69.84, H 5.82, N 7.65.

Ligand 5 (L5): M.p. 62−64 °C. $[\alpha]_D^{25} = -180.1$ (c = 1.83, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3350, 3054, 1619, 1595, 1507, 1438, 1422, 1338, 1219, 1153, 896, 817 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.53 (s, 6 H, 2Me), 5.88 (d, J = 9.0 Hz, NH), 7.0 (d, J = 8.7 Hz, 1 H, Ar), 7.14−7.43 (m, 12 H, ArH), 7.56−7.75 (m, 5 H, ArH), 7.79−7.98 (m, 4 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 43.27, 118.47, 120.41 (d, J = 4.8 Hz), 121.81, 123.92 (d, J = 2.6 Hz), 125.75, 126.56 (d, J = 8.3 Hz), 125.97, 128.34 (d, J = 18.6 Hz), 128.36, 128.37 (d, J = 24.0 Hz), 128.38 (d, J = 47.7 Hz), 128.41, 129.67, 129.84 (d, J = 2.8 Hz), 131.04, 131.20, 131.48, 131.52, 131.57, 131.68, 131.72, 132.99, 133.88, 134.03, 134.04 (d, J = 46.1 Hz), 135.25, 136.59, 149.87. ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = +51.47. MS (EI): m/z = 528 (46) [M^+], 311 (M^+ − 217, 35), 267 (M^+ − 261, 100). $C_{34}H_{29}N_2PS$ (528.65): calcd. C 77.27, H 5.49, N 5.30; found C 77.29, H 5.68, N 5.12.

Ligand 6 (L6): M.p. 61−63 °C. $[\alpha]_D^{25}$ = +41.3 (*c* = 2.07, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3020, 1625, 1600, 1521, 1750, 1423, 1030, 929, 895 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.28 (m, 6 H, 2Me), 3.69 (br., 2 H, NH_2), 3.97−4.17 (m, 4 H, $2CH_2$), 5.32 (d, *J* = 14.1 Hz, 1 H, NH), 6.91 (d, *J* = 8.1 Hz, 1 H, ArH), 7.12−7.37 (m, 6 H, ArH), 7.80−7.96 (m, 5 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 15.61 (d, *J* = 8.4 Hz), 15.64 (d, *J* = 7.4 Hz), 63.19 (d, *J* = 4.1 Hz), 63.23 (d, *J* = 4.6 Hz), 110.08, 117.92, 117.96, 118.00, 118.04, 118.07, 122.44, 123.29, 124.12, 124.93, 126.84, 127.90, 128.15, 129.17, 129.75, 130.23, 132.83, 133.48, 136.31, 142.70. ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ +66.63. MS (EI): *m*/*z* = 436 (77) [M^+], 284 (M^+ − 152, 52), 267 (M^+ − 169, 100). $C_{24}H_{25}N_2O_2PS$ (436.51): calcd. C 66.10, H 5.73, N 6.42; found C 65.91, H 6.03, N 6.51.

Ligand 7 (L7): Yellowish oil, $[\alpha]_D^{25}$ = +13.7 (*c* = 2.57, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3360, 3020, 1630, 1598, 1514, 1476, 1427, 1346, 1022, 964, 801 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.06 (t, *J* = 6.9 Hz, Me), 1.28 (m, 6 H, 2Me), 3.24 (q, *J* = 6.9 Hz, CH_2), 3.51 (br., 1 H, NH), 3.95−4.13 (m, 4 H, $2CH_2$), 5.31 (d, *J* = 13.2 Hz, 1 H, NH), 6.81 (d, *J* = 8.4 Hz, 1 H, ArH), 7.08−7.36 (m, 6 H, ArH), 7.78−7.96 (m, 5 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 15.10, 15.73 (d, *J* = 7.9 Hz), 15.77 (d, *J* = 7.9 Hz), 38.32, 63.27 (d, *J* = 4.8 Hz), 63.30 (d, *J* = 4.2 Hz), 109.70, 113.88, 118.10, 118.13, 121.91, 123.20, 124.21, 125.13, 126.80, 126.92, 127.41, 127.99, 128.23, 129.28, 129.92, 130.46, 133.22, 133.65, 136.64, 144.38. ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = +66.57. MS (EI): *m*/*z* = 464 (100) [M^+], 311 (M^+ − 153, 25), 267 (M^+ − 197, 70). HRMS: calcd. for $C_{26}H_{30}N_2O_2PS$ (M^+ +1) 465.1756; found 465.1760.

Ligand 8 (L8): M.p. 57−58 °C. $[\alpha]_D^{25}$ = −149.1 (*c* = 0.9, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3350, 3020, 1619, 1598, 1517, 1475, 1424, 1378, 1216, 1045, 929, 811 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.07 (t, *J* = 7.2 Hz, 3 H, Me), 3.25 (q, *J* = 7.2 Hz, 2 H, CH_2), 3.75 (br., 1 H, NH), 5.46 (d, *J* = 10.8 Hz, 1 H, NH), 6.98−7.49 (m, 15 H, ArH), 7.64−7.94 (m, 7 H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ = 14.77, 38.48, 113.90, 118.40 (d, *J* = 8.7 Hz), 119.13 (d, *J* = 4.4 Hz), 122.16 (d, *J* = 3.3 Hz), 124.11, 124.32 (d, *J* = 84.3 Hz), 126.97 (d, *J* = 5.9 Hz), 127.54, 127.63, 128.25, 128.33, 128.98 (d, *J* = 71.4 Hz), 128.66, 128.68, 129.41, 129.88, 130.35, 130.96, 131.19 (d, *J* = 10.3 Hz), 131.50, 131.89, 131.98, 132.02, 132.68, 133.21, 133.52, 137.66, 144.32 (d, *J* = 2.3 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ = +17.89. MS (EI): *m*/*z* = 512 (53) [M^+], 497 (M^+ − 15, 12), 295 (M^+ − 217, 92), 280 (M^+ − 232, 39). HRMS: calcd. for $C_{34}H_{29}N_2OP$ [M^+] 520.2017; found 520.2061.

General Procedure for the AgOTf-Catalyzed Asymmetric Allylation of Arylaldehydes: Under argon atmosphere and in the dark, AgOTf (26 mg, 0.1 mmol) and **L2** (53 mg, 0.1 mmol) were dissolved in dry THF (2 mL) and stirred for 30 min at 0 °C. Benzaldehyde (51 μL, 0.5 mmol) and allyltributylstannane (186 μL, 0.6 mmol) were added successively to the resulting solution at −20 °C, the mixture was stirred for 48 h at this temperature, then treated with saturated KF solution, and extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by column chromatography to give the homoallylic alcohol (62 mg, 84% yield) as a colorless oil. The enatioselectivity was determined to be 94% *ee* by HPLC analysis. The chiral HPLC charts are given in the Supporting Information (see also the footnote on the first page of this article).

(*S*)-(−)-1-Phenyl-3-buten-1-ol: (Table 1, entry 10) This is a known compound and ^1H NMR spectroscopic data are in agreement with those reported in literature.[6b] ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.36 (br., 1 H, OH), 2.48 (m, 2 H, CH_2), 4.68 (m, 1 H, CH), 5.13 (m, 2 H, vinyl H), 5.78 (m, 1 H, vinyl H), 7.31 (m, 5 H, ArH). $[\alpha]_D^{25}$ = −45.5 (*c* = 2.6, benzene) for 94% *ee* {ref.[6b] $[\alpha]_D^{25}$ = −50.5 (*c* = 1.1, benzene) for 96% *ee*}; Chiralcel OD, hexane/*i*PrOH (95:5), 0.7 mL/min, 254 nm, t_R = 13.44 min, t_S = 15.87 min.

(*S*)-(−)-1-(1-Naphthyl)-3-buten-1-ol: (Table 1, entry 1) This is a known compound and ^1H NMR spectroscopic data are in agreement with those reported in literature.[6b] ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.36 (d, *J* = 3.0 Hz, 1 H, OH), 2.61 (m, 1 H, CH), 2.76 (m, 1 H, CH), 5.21 (m, 2 H, vinyl H), 5.55 (m, 1 H, CH), 5.94 (m, 1 H, vinyl H), 7.52 (m, 3 H, ArH), 7.68 (d, *J* = 7.2 Hz, 1 H, ArH), 7.79 (d, *J* = 8.1 Hz, 1 H, ArH), 7.89 (m, 1 H, ArH), 8.08 (d, *J* = 7.8 Hz, 1 H, ArH). $[\alpha]_D^{25}$ = −69.9 (*c* = 1.7, benzene) for 76% *ee* {ref.[6b] $[\alpha]_D^{25}$ = −96.0 (*c* = 1.1, benzene) for 97% *ee*}; Chiralcel OD, hexane/*i*PrOH (90:10), 0.7 mL/min, 254 nm, t_R = 13.97 min, t_S = 22.50 min.

(*S*)-(−)-1-(*p*-Tolyl)-3-buten-1-ol: (Table 2, entry 1) This is a known compound and ^1H NMR spectroscopic data are in agreement with those reported in literature.[9] ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.0 (br., 1 H, OH), 2.35 (s, 3 H, CH_3), 2.49 (m, 2 H, CH_2), 4.71 (m, 1 H, CH), 5.15 (m, 2 H, vinyl H), 5.81 (m, 1 H, vinyl H), 7.17 (d, *J* = 7.8 Hz, 2 H, ArH), 7.27 (d, *J* = 7.8 Hz, 2 H, ArH). $[\alpha]_D^{25}$ = −47.1 (*c* = 1.5, benzene) for 98% *ee* {ref.[9] $[\alpha]_D^{25}$ = −37.3 (*c* = 2.0, benzene) for 82% *ee*}; Chiralpak AD, hexane/*i*PrOH (98:2), 0.7 mL/min, 254 nm, t_R = 21.12 min, t_S = 23.54 min.

(*S*)-(−)-1-(*p*-Chlorophenyl)-3-buten-1-ol: (Table 2, entry 2) This is a known compound and ^1H NMR spectroscopic data are in agreement with those reported in literature.[9] ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.15 (br., 1 H, OH), 2.47 (m, 2 H, CH_2), 4.72 (m, 1 H, CH), 5.18 (m, 2 H, vinyl H), 5.79 (m, 1 H, vinyl H), 7.31 (m, 4 H, ArH). $[\alpha]_D^{25}$ = −23.5 (*c* = 2.1, benzene) for 96% *ee* {ref.[9] $[\alpha]_D^{23}$ = −28.4 (*c* = 3.03, benzene) for 84% *ee*}; Chiralcel OJ, hexane/*i*PrOH (97.5:2.5), 0.7 mL/min, 254 nm, t_S = 33.40 min, t_R = 36.11 min.

(*S*)-(−)-1-(*p*-Methoxyphenyl)-3-buten-1-ol: (Table 2, entry 3) This is a known compound and ^1H NMR spectroscopic data are in agreement with those reported in literature.[6b] ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.09 (br., 1 H, OH), 2.51 (m, 2 H, CH_2), 3.81 (s, 3 H, CH_3), 4.69 (m, 1 H, CH), 5.14 (m, 2 H, vinyl H), 5.79 (m, 1 H, vinyl H), 6.88 (d, *J* = 8.7 Hz, 2 H, ArH), 7.27 (d, *J* = 8.7 Hz, 2 H, ArH). $[\alpha]_D^{25}$ = −42.5 (*c* = 1.1, $CHCl_3$) for 80% *ee* {ref.[6b] $[\alpha]_D^{25}$ = −40.7 (*c* = 1.1, benzene) for 97% *ee*}; Chiralcel OD, hexane/*i*PrOH (20:1), 0.7 mL/min, 254 nm, t_R = 8.60 min, t_S = 9.11 min.

(*S*), (*E*)-(−)-1-Phenyl-3-buten-1-ol: (Table 2, entry 4) This is a known compound and ^1H NMR spectroscopic data are in agreement with those reported in literature.[6b] ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.92 (br., 1 H, OH), 2.41 (m, 2 H, CH_2), 4.35 (m, 1 H, CH), 5.17 (m, 2 H, vinyl H), 5.83 (m, 1 H, vinyl H), 6.24 (dd, *J* = 6.6, 16.2 Hz, 1 H, vinyl H), 6.60 (d, *J* = 16.2 Hz, 1 H, vinyl H), 7.33 (m, 5 H, ArH). $[\alpha]_D^{25}$ = +10.6 (*c* = 1.3, diethyl ether) for 68% *ee* {ref.[6b] $[\alpha]_D^{25}$ = +15.4 (*c* = 1.1, diethyl ether) for 88% *ee*}; Chiralcel OD, hexane/*i*PrOH (20:1), 0.7 mL/min, 254 nm, t_R = 19.32 min, t_S = 32.73 min.

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