Transition-Metal-Catalyzed Asymmetric Organic Synthesis via Polymer-Attached Optically Active Phosphine Ligands. 5.[1] Preparation of Amino Acids in High Optical Yield via Catalytic Hydrogenation

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Two new optically active phosphinopyrrolidine monomers were prepared by the reaction of (2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine and (2*R*,4*R*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine with acryloyl chloride to give *N*-acryloyl-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (1) and *N*-acryloyl-(2*R*,4*R*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (2). Copolymerization of 1 and 2 with hydrophilic comonomers and a divinyl monomer provided cross-linked insoluble polymers containing 3–5% of 1 or 2 that would swell in polar solvents. Exchange of rhodium(I) onto the polymer gave catalysts which were active for the asymmetric hydrogenation of *N*-acyl α-amino acids in high optical yields, the phosphine derived from the enantiomer of the naturally occurring 4-hydroxyproline giving (*S*)-amino acids. The catalysts could be reused with no loss in selectivity by simple filtration.

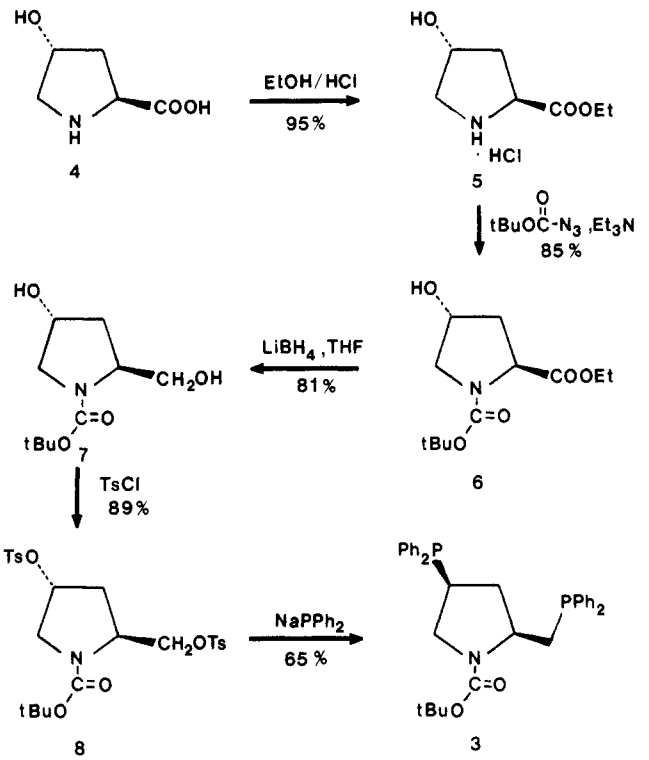
Phosphinopyrrolidine–rhodium catalysts have proven to be useful for the hydrogenation of many unsaturated substrates[2] and especially for the reduction of dehydroamino acids in optical yields exceeding 90%. Unfortunately, the predominant enantiomer formed has the *R* configuration rather than the *S* configuration of naturally occurring amino acids, and enantiomeric phosphinopyrrolidines whose use would result in the production of *S* amino acids are not readily available.

In previous papers[3,4] we described an optically active monomer, 2-*p*-styryl-4,5-bis[(tosyloxy)methyl]-1,3-dioxolane, which could be polymerized with a variety of comonomers to provide polymer-attached optically active ligands for rhodium-catalyzed hydroformylation[1] and hydrogenation[3,4] reactions that gave optically active aldehydes and amino acids. The polymer-supported catalysts achieved the same enantioselectivity as their homogeneous counterparts, were able to be recycled by simple filtration, and were reused without a significant loss of activity.

At the time that the work reported in this paper was being completed, another polymer-supported optically active phosphine catalyst,[5] prepared by the copolymerization of 1-(4-vinylbenzoyl)-(2*S*,4*S*)-2-(diphenylphosphino)-4-[(diphenylphosphino)methyl]-pyrrolidine with hydroxyethyl methacrylate, was described. While this system was able to catalyze the reduction of itaconic acid to methyl succinic acid in about the same optical yield as the homogeneous analogue (82% vs. 89% optical yield), the reduction of (*Z*)-acetamidocinnamic acid to *N*-acetylphenylalanine proceeded in far lower optical yield (23% vs. 91% optical yield) with the polymer-supported catalyst. When the rhodium(I) species bound to the polymer was changed from a neutral to a cationic species, the optical yield for the cinnamic acid hydrogenation was raised to 70%, still far below the results obtained with the homogeneous catalyst.

We report here the preparation of optically active phosphinopyrrolidine monomers of both *S,S* and *R,R* chirality, whose copolymers are active catalysts for the asymmetric hydrogenation of *N*-acyl-α-aminocinnamic acids to produce *N*-acyl-α-amino acids of both *R* and *S* configurations, respectively, in high optical yields.

Scheme I. Synthesis of *N*-(*tert*-Butoxycarbonyl)-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (3)



Results and Discussion

Synthesis of Phosphinopyrrolidenes. The optically active diphosphine *N*-(*tert*-butoxycarbonyl)-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]-pyrrolidine (3) was synthesized from 4-hydroxy-L-proline by a modification of a previous procedure[6] (Scheme I). Standard esterification and N-protection were followed by reduction of ester 6 with lithium borohydride in tetra-

(1) Part 4: Fritschel, S. J.; Ackerman, J. J. H.; Keyser, T.; Stille, J. K. *J. Org. Chem.* **1979**, *44*, 3152.
(2) For a review see: Achiwa, K. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum: New York, 1979; Vol. III, p 549.
(3) Takaishi, N.; Imai, H.; Bertelo, C. A.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 264.
(4) Masuda, T.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 268.
(5) Achiwa, K. *Chem. Lett.* **1978**, 905.
(6) Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8265.

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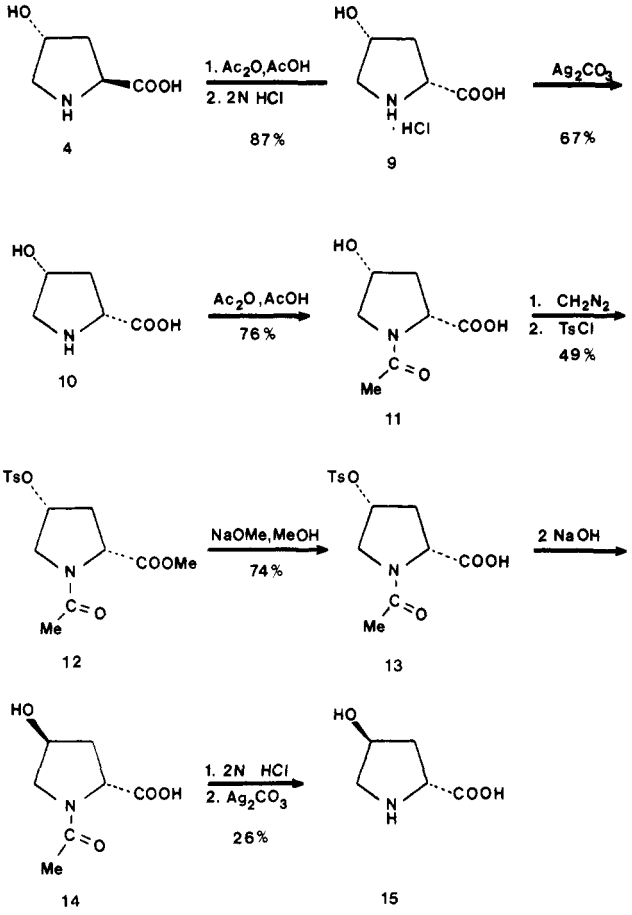
Scheme II. Synthesis of 4-Hydroxy-D-prolene (15)



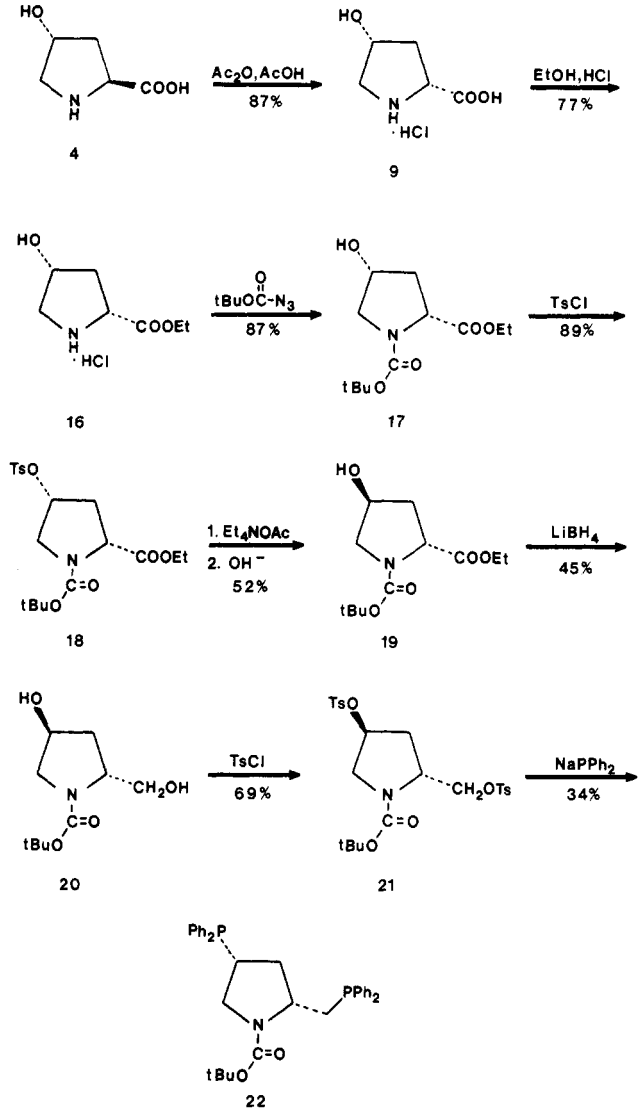
hydrofuran to produce diol **7** in good yield. Attempts to reduce ester **6** with lithium aluminum hydride as reported[6] failed to provide **7** in synthetically useful amounts. Tosylation and subsequent phosphination proceeded to give diphosphine **3**.

Since 4-hydroxy-D-proline is not naturally available, the enantiomer of **3** is more difficult to obtain. Initially the synthetic strategy was to convert 4-hydroxy-L-proline to 4-hydroxy-D-proline by the published procedure (Scheme II),[7,8] and then to prepare **22** by the steps outlined for its enantiomer in Scheme I. This procedure is long, tedious, and expensive; the overall yield for the conversion of the L to D isomer was only 4.2%.

The epimerization of 4-hydroxy-L-proline (**4**) proceeds in high yield to the cis or allo isomer **9**. This product was purified as the hydrochloride, free from the trans starting material. Removal of the hydrochloride by silver carbonate and acylation of the free amine gave the protected amine **11** in moderate yield. The methyl ester **12** was prepared with diazomethane, and the alcohol was converted to tosylate **12**. After hydrolysis of the methyl ester, the tosylate was displaced with hot base to give **14** with the desired stereochemistry. Olefin byproducts arising from elimination of the tosylate complicated the purification steps. Ultimately, 4-hydroxy-D-proline was isolated in 26% yield.

To obtain synthetically useful amounts of the D isomer **15**, large amounts of 4-hydroxy-L-proline must be used. The use of stoichiometric amounts of silver carbonate in the second and final steps makes this procedure quite expensive. In addition, molar amounts of diazomethane

Scheme III. Synthesis of *N*-(*tert*-Butoxycarbonyl)-(2*R*,4*R*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (22)



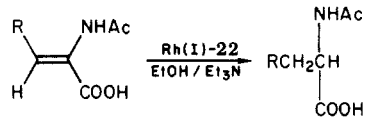
are employed. Despite these limitations, a small amount of 4-hydroxy-D-proline prepared as shown in Scheme II was ultimately carried on to the desired diphosphine **22** by the steps outlined in Scheme I for is enantiomer, albeit in only a 0.2% overall yield.

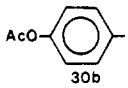
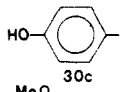
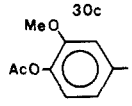
A revision of our approach to the synthesis of **22** to a more direct synthetic route (Scheme III) eliminated several problems associated with the former synthetic schemes (Schemes I and II). The hydrochloride salt **9** was directly esterified with ethanol and the amine blocked with the *tert*-butoxycarbonyl groups to give **17**. Tosylation of the free alcohol gave an intermediate which could be converted to the enantiomer (**19**) of **6** in Scheme I. Tetraethylammonium acetate was used as described for an analogous conversion[9] to displace the tosylate. After the acetate was hydrolyzed, the free alcohol **19** was easily isolated by distillation. By using the methods developed for the synthesis of **3**, its enantiomer **22** was prepared in useful amounts.

The purified phosphine **22** was used in the Rh(I)-catalyzed asymmetric hydrogenation of dehydroamino acids to demonstrate its utility for the production of *S* amino acids. All reductions were carried out at 800 psig of hy-

(7) Greenstein, J. P.; Winitz, M. "Chemistry of the Amino Acids"; Wiley: New York, 1961; p 2037.
(8) Robinson, D. S.; Greenstein, J. P. *J. Biol. Chem.* **1952**, *195*, 383.
(9) Kende, A. S.; Demuth, T. P. *Tetrahedron Lett.* **1980**, *21*, 715.

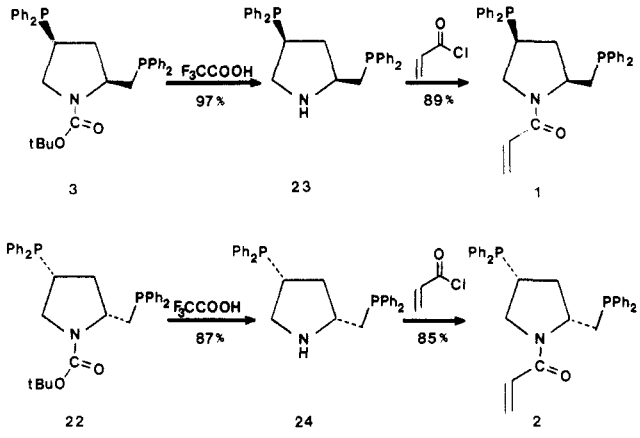
Table I. Hydrogenation of Dehydroamino Acids with Rh(I)-22[a]



R	optical yield,[b] % (config)	lit.[c]
 30a	90 (S)	91 (R)
 30b	87 (S)	87 (R)
 30c	93 (S)	
 30d	88 (S)	86 (R)

[a] All reactions were run using a diphosphine/rhodium ratio of 1.4:1, a substrate/rhodium ratio of 50:1, 15 mL of ethanol, 800 psig of H_2, 20 °C, and an Et_3N/Rh ratio of 4. [b] Optical yields are calculated with respect to the following values for optically pure compounds: (S)-30a, $[\alpha]_D$ +46.0° (c 1, EtOH);[13] (S)-30b, $[\alpha]_D$ +40.4° (c 0.5, H_2O);[14] (R)-30c, $[\alpha]_D$ 48.3° (H_2O);[15] (S)-30d, $[\alpha]_D$ 40.8° (c 1, MeOH).[16] [c] Reference 6.

Scheme IV. Synthesis of (2R,4R)- and (2S,4S)-N-Acryloyl-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidines (1 and 2)



drogen at 20 °C by using neutral catalysts so that meaningful comparisons could be made with previously reported results.[6] In the cases examined, comparable results were obtained, but the predominant configuration of the product was S, as expected (Table I).

Polymer Synthesis. Acryloyl derivatives of 3 and 22 were readily prepared by removal of the protecting group with cold trifluoroacetic acid and subsequent acylation of the free amines (Scheme IV). By use of Schotten–Bauman conditions, the acrylamides were prepared in nearly 90% yield. Purification of the acryloyl derivatives proved difficult as extensive decomposition was noted on silica, alumina, and Florisil. Recrystallization from toluene/hexane gave pure monomers as white crystalline monohexanates.

Diphosphine monomer 1 was copolymerized with hydroxyethyl methacrylate or N,N-dimethylacrylamide by free-radical initiators using ethylene dimethacrylate as a cross-linking agent (Scheme V). In a similar fashion, polymer 29 was prepared by copolymerizing 2 with hydroxyethyl methacrylate and ethylene dimethacrylate. Elemental analyses of the resulting copolymers showed incorporation of the diphosphine monomer corresponding to the monomer feed ratio of 3–5%. This relatively low percentage incorporation coupled with a cross-link density of 10% was maintained in order to ensure the isolation of

Scheme V. Polymers Containing (2R,4R)- and (2S,4S)-Phosphines

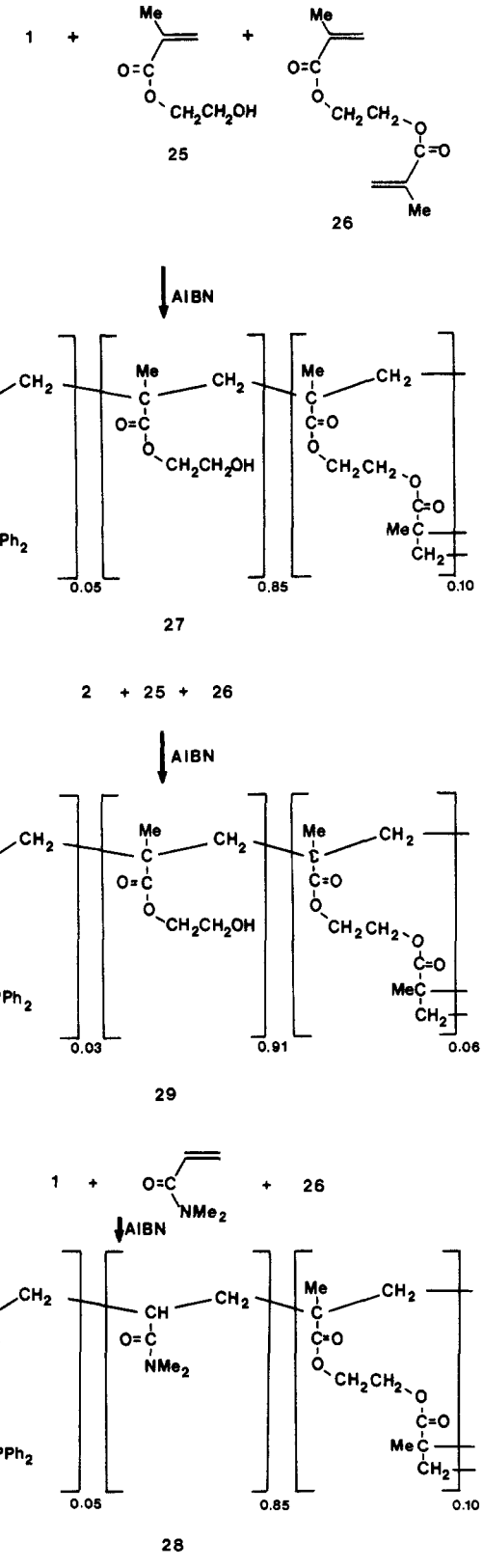
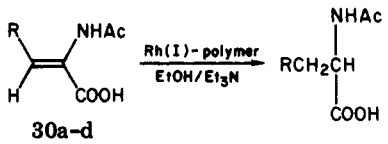
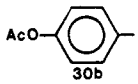
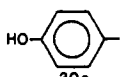
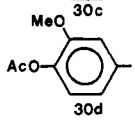


Table II. Hydrogenation of Dehydroamino Acids with Polymer Bound Catalysts[a]



30a–d

R	polymer	optical yield,[b] (config)	lit.[c]
 30a	27	91 (*R*)	
	28	64 (*R*)	91 (*R*)
	29	90 (*S*)	
 30b	27	83 (*R*)	87 (*R*)
	29	87 (*S*)	
 30c	27	33 (*R*)	
	28	35 (*R*)	
 30d	27	88 (*R*)	86 (*R*)
	29	88 (*S*)	

[a] All reactions were run by using 0.02 mequiv of diphosphine, 0.01 mequiv of Rh, 0.5 mmol of substrate in 15 mL of EtOH, 800 psig of H_2, 20 °C, and Et_3N/Rh ratio of 4. [b] See note *b* of Table I. [c] See ref 6 for homogeneous hydrogenation using *N*-(*tert*-butoxycarbonyl)-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]-pyrrolidine (3).

the catalyst sites on the polymer backbone. Polymers **27** and **29** were white free-flowing powders that swelled in polar solvents such as ethanol. Polymer **28** was obtained as a pale yellow powder which swelled in solvents ranging in polarity from benzene to ethanol.

The reaction between polymers **27–29** and rhodium(I) in the form of $[Rh(biallyl)Cl]_2$ or $[Rh(COD)Cl]_2$ gave light yellow polymer-bound catalysts which were used for the hydrogenation of olefins **30a–d** (Table II). All reactions were run at 800 psig of hydrogen at 20 °C with a rhodium/diphosphine site ratio of 0.5 and a substrate/rhodium ratio of 50. The excess of phosphine sites over rhodium was maintained to ensure that any phosphine sites which may have been oxidized during handling would not complex rhodium. The addition of triethylamine (6 mol % based on substrate) was essential for high optical yields. The reductions catalyzed by both polymers **27** and **29** gave the same optical yields as could be obtained with the homogeneous analogues, except that the reduction of **30c** to give the tyrosine derivative did not provide high optical yields. The course of this anomoly is not understood. The reduction of **30a** with the polymer **28** rhodium(I) catalyst proceeded to give a lower optical yield than that obtained with polymer **27**. It is likely that the pendent amide groups, present in large excess compared to the phosphine sites, are able to compete with phosphine sites for rhodium, thereby producing some catalytic sites which are not chiral.

Conclusions

As a result of practical synthetic routes for the production of phosphinopyrrolidines of both *R,R* and *S,S* chirality, both *R* and *S* amino acids can be synthesized. Polymer-bound phosphinopyrrolidines were equivalent to their homogeneous analogues (with one exception) in the ability to yield amino acid derivatives in high optical yields. Unlike homogeneous catalysts, the polymer-bound catalysts could be easily separated from the reaction mixture by filtration and could then be reused without a significant loss in selectivity.

The choice of the proper type of polymer backbone is vital. The swelling characteristics of the polymer must be matched to the solvent system of interest so that the catalytic sites are accessible to the substrate. In order to mimic the homogeneous reaction, the polymer backbone should not interfere with the catalytic site. The use of polymers **27** and **29** with pendent alcohols showed no detectable interaction, at least as judged by optical yields. The use of polymer **28** with pendent amides led to an overall drop in enantioselectivity due to the competition of the amides for the rhodium.

Experimental Section

All reactions were routinely performed under an inert atmosphere of nitrogen or argon. Manipulations involving phosphines dissolved in solvents were carried out in a drybox or by Schlenk techniques. Inert gases were dried and deoxygenated by successive passage through a train of BASF De-ox catalyst and 4A molecular sieves. ^1H NMR spectra were obtained on a Varian EM360 or on a JEOL FX-100 spectrometer with tetramethylsilane as the internal standard. ^{13}C NMR spectra were obtained on a JEOL FX-100 instrument with tetramethylsilane as the internal standard. ^{31}P NMR spectra were obtained on a Nicolet NT-150 instrument or on a Bruker HX-90E spectrometer with an SPX high-power amplifier, a broad-band decoupler, and a Model B-NC 12 computer with 85% H_3PO_4 as the external reference. Infrared spectra were obtained on a Beckman Acculab 3 or on a Perkin-Elmer 267 instrument as neat samples or potassium bromide pellets. Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter. Melting points are uncorrected. Elemental analyses were determined by Micro-Tech Laboratories.

4-Hydroxy-L-proline Ethyl Ester Hydrochloride (5). A slurry of 100 g (760 mmol) of 4-hydroxy-L-proline in 600 mL of absolute ethanol was treated with dry hydrogen chloride until homogeneous. The solution was heated to the reflux temperature for 2 h. Upon being cooled in the refrigerator, the product was obtained as white needles which were filtered, washed well with ether, and dried under reduced pressure to yield 141 g (95%) of **5**: mp 153–153.5 °C (lit.[10] mp 147–148 °C); ^1H NMR (Me_2SO-d_6) δ 1.25 (t, 3 H, J = 7 Hz), 4.20 (q, 2 H, J = 7 Hz); ^{13}C NMR (D_2O) 24.1, 47.1, 63.6, 68.7, 73.8, 79.1, 177.5; IR (KBr) 3320, 1735 cm^{-1}.

***N*-(*tert*-Butoxycarbonyl)-4-hydroxy-L-proline Ethyl Ester (6).** A stirred mixture of 100 g (510 mmol) of **5**, 75.0 mL (540 mmol) of *tert*-butoxycarbonyl azide, 150 mL of triethylamine, 500 mL of water, and 500 mL of *p*-dioxane was heated under nitrogen to 50 °C for 15 h. The mixture was reduced in volume by half on a rotary evaporator and extracted with four 100-mL portions of ether. The combined extracts were washed with brine, dried over magnesium sulfate, and concentrated to a yellow oil under reduced pressure. Distillation of the oil under reduced pressure gave 97.5 g (69.6%) of **6** as a pale yellow oil: bp 126–128 °C (0.05 mm); ^1H NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 7 Hz), 1.45 (s, 9 H), 1.8–2.4 (m), 3.4–3.7 (m), 4.2 (q, 2 H, J = 7 Hz), 4.4–4.6 (m); ^{13}C NMR ($CDCl_3$) δ 14.2, 28.2, 28.3, 38.2, 39.0, 54.4, 57.7, 58.0, 60.9, 68.7, 69.4, 79.9, 80.1, 153.8, 154.3, 172.7, 173.0; IR (neat) 3450, 1735, 1680 cm^{-1}; $[\alpha]^{20}_D$ –68.3° (*c* 2, EtOH) (lit.[6] $[\alpha]^{20}_D$ –67.8° (*c* 1.75, EtOH)).

***N*-(*tert*-Butoxycarbonyl)-4-hydroxy-L-prolinol (7).** To an ice-cold solution of 50.0 g (190 mmol) of **6** in 600 mL of tetrahydrofuran was added 15.0 g (690 mmol) of lithium borohydride in one portion. The mixture was stirred at 0 °C for 1 h followed by 15 h at room temperature. The solution was cooled to 0 °C with stirring and 255 mL of water and 100 mL of 1:1 water/concentrated hydrochloric acid were added carefully. The solution was warmed until an organic phase separated. The organic phase was withdrawn, and the aqueous layer was extracted with three 150-mL portions of ethyl acetate. The combined organic layers were washed with 100 mL each of 2 N sodium hydroxide, 2 N hydrochloric acid, and brine. The organic layers were dried over magnesium sulfate and evaporated under reduced pressure to an

(10) Kapfhammer, J.; Matthes, K. *Z. Physiol. Chem.* **1934**, *223*, 43.

oil. The oil was kept at 0.05 mm for 24 h and then used without further purification. The yield of **7** was 33.9 g (81%): ^{1}H NMR ($CDCl_3$) δ 1.1–2.0 (m), 1.48 (s, 9 H), 3.3–4.2 (m), 4.4 (s); ^{13}C NMR ($CDCl_3$) δ 28.4, 37.2, 54.9, 55.4, 57.7, 58.4, 63.5, 65.9, 68.6, 80.2, 154.8, 156.5; IR (neat) 3400, 1670, 1420 cm^{-1}.

***N*-(*tert*-Butoxycarbonyl)-4-hydroxy-L-prolinol Di-*p*-toluenesulfonate (8).** To a stirred solution of 11.3 g (52.0 mmol) of **7** in 300 mL of dry pyridine at 0 °C under nitrogen was added 29.7 g (156 mmol) of recrystallized *p*-toluenesulfonyl chloride in one portion. The mixture was stored in the refrigerator for 5 days. The mixture was then cooled to 0 °C, and 600 mL of water was added dropwise with stirring to precipitate a white powder which was filtered, washed with water, and dried under reduced pressure to yield 24.4 g (89%) of crude product. Recrystallization from 95% ethanol produced white needles of **8**: mp 105–106 °C (lit.[6] mp 155–156 °C?); ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 9 H), 2.2 (m), 2.5 (s, 6 H), 3.2–3.8 (m), 3.9–4.4 (m), 4.9–5.2 (m), 7.3–7.9 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 27.7, 33.5, 34.1, 51.4, 53.4, 68.4, 79.0, 125.4, 127.6, 130.2, 131.1, 142.4, 150.8; IR (KBr) 1690, 1600, 1450, 1360, 685, 672, 658, 620 cm^{-1}; $[\alpha]^{25}_D$ −25.9° (*c* 0.6, benzene) [lit.[6] $[\alpha]^{20}_D$ −23° (*c* 0.4, benzene)]. Anal. Calcd for $C_{24}H_{31}NO_8S_2$: C, 54.63; H, 6.30; N, 2.65. Found: C, 54.68; H, 5.92; N, 2.62.

***N*-(*tert*-Butoxycarbonyl)-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (3).** To 50 mL of liquid ammonia was added 1.15 g (50.0 mmol) of sodium cut into small pieces. Upon completion of the addition, 8.47 mL (50.0 mmol) of diphenylphosphine dissolved in 20 mL of dry tetrahydrofuran was added dropwise over 20 min. The ammonia was allowed to evaporate from the clear orange solution under a steam of nitrogen. When the solution had reached room temperature, a solution of 10.0 g (18.9 mmol) of **8** in 20 mL of dry tetrahydrofuran was added dropwise over 30 min. The mixture was allowed to stir at room temperature for 18 h. The solution was treated with methanol to destroy the excess anion and filtered. The filter cake was washed with benzene, and the filtrate was concentrated under reduced pressure. The remaining oil was crystallized from 100 mL of absolute ethanol after standing in the refrigerator for 48 h. The reaction yielded 6.15 g (59%) of white crystalline **3**. An additional 0.47 g (4.5%) was obtained through concentration of the solution and further cooling: mp 103.5–105 °C (lit.[6] mp 104–105 °C); ^{1}H NMR ($CDCl_3$) δ 1.2–1.6 (m), 1.4 (s, 9 H), 1.8–2.2 (m), 2.7–3.2 (m), 7.2–7.4 (br s, 20 H); ^{13}C NMR ($CDCl_3$) δ 28.4 (s), 35.0 (d, J = 9 Hz), 37.5 (d, J = 15 Hz), 49.7 (s), 50.7 (s), 55.8 (dd, J = 22, 7 Hz), 79.4 (s), 128.0–129.4 (4 peaks), 131.5–133.3 (9 peaks), 136.0–136.8 (4 peaks), 138.3 (s), 138.7 (s), 153.5 (s); IR (KBr) 1680, 1480, 1435, 1395, 1175, 1125, 1100, 740, 695 cm^{-1}; $[\alpha]^{25}_D$ −38.9° (*c* 0.6, benzene) [lit.[6] $[\alpha]^{20}_D$ −36° (*c* 0.6, benzene)]. Anal. Calcd for $C_{34}H_{37}NO_2P_2$: C, 73.76; H, 6.73; N, 2.53; P, 11.19. Found: C, 73.44; H, 6.76; N, 2.41; P, 10.49.

Allo-4-hydroxy-D-proline Hydrochloride (9). A solution of 1020 g (10 mol) of acetic anhydride in 3 L of glacial acetic acid was heated to 50 °C, and 247 g (1.89 mol) of 4-hydroxy-L-proline was added in one portion. Heating was continued until the reflux temperature was reached, and the solution was held at reflux for 5.5 h. After the mixture cooled, the solvent was removed in vacuo, giving a thick oil. The oil was dissolved in 3.5 L of 2 N hydrochloric acid and was then heated to reflux temperature for 3 h. The solution was treated with charcoal while hot and then filtered through Celite. As the solution was concentrated by rotary evaporation, white needles formed that were collected by suction filtration. The needles were dried under reduced pressure to give 240 g (1.4 mol, 75%) of the hydrochloride salt: mp 161–163 °C; ^{1}H NMR (D_2O, external Me_4Si) δ 2.3–3.0 (m, 2 H), 3.5 (d, 2 H, J = 2.5 Hz), 4.4–4.8 (m, 2 H); ^{13}C NMR (Me_2SO-d_6) δ 171.0, 68.9, 58.3, 53.7, 37.9; IR (KBr) 3430, 3240, 3020, 1710, 1585, 1380, 1280, 1260, 965, 720, 665 cm^{-1}. The filtrate was further concentrated to give an additional 39 g (0.22 mol, 12%) of **9**.

Allo-4-hydroxy-D-proline (10). The free amine was prepared from the hydrochloride salt as described[8] to yield 140 g (1.13 mol, 67%) of **10**: mp 252–257 °C dec; ^{1}H NMR (D_2O) δ 2.4–3.1 (m, 2 H), 3.4 (d, 2 H, J = 2.5 Hz), 3.9–4.7 (m, 2 H); $[\alpha]^{25}_D$ +60.3° (*c* 2.6, H_2O) [lit.[8] $[\alpha]_D$ +59.5° (*c* 2, H_2O)].

***N*-Acetyl-allo-4-hydroxy-D-proline (11).** The amine was protected as described[8] to yield 26 g (0.15 mol, 76%) of pure **11**: mp 145.5–147 °C (lit.[8] 145.5 °C); ^{1}H NMR (D_2O, external Me_4Si) δ 2.0 (s, 3 H), 2.1–2.6 (m, 2 H), 4.2–2.7 (m, 2 H); $[\alpha]^{22}_D$ +91.0° (*c* 9.7, H_2O) [lit.[8] $[\alpha]^{25}_D$ +91.0° (*c* 2, H_2O)].

***N*-Acetyl-allo-4-(*p*-toluenesulfonyloxy)-D-proline Methyl Ester (12).** The methyl ester was prepared as described[8] to yield 130 g (0.38 mol, 49%) of white needles: mp 150–152 °C (lit.[8] mp 143.5 °C); ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 2.2–2.8 (m, 5 H), 3.5–3.8 (m, 5 H), 4.2–4.7 (m, 1 H), 7.1–7.7 (m, 4 H); $[\alpha]^{22}_D$ +36.7° (*c* 3.1, EtOH) [lit.[8] $[\alpha]^{25}_D$ +32.0° (*c* 1, EtOH)].

***N*-Acetyl-allo-4-(*p*-toluenesulfonyloxy)-D-proline (13).** The ester was hydrolyzed as described[8] to give 67.2 g (0.20 mol, 74%) of the free acid **13**: mp 149–151 °C (lit.[8] mp 153.5 °C); ^{1}H NMR ($CDCl_3$) δ 2.1 (s, 3 H), 2.2–2.7 (m, 2 H), 2.4 (s, 3 H), 3.6–3.6 (m, 2 H), 4.3–4.7 (m, 1 H), 4.8–5.2 (m, 1 H), 7.1–7.8 (m, 4 H); $[\alpha]^{20}_D$ +30.5° (*c* 0.8, EtOH) [(lit.[7] $[\alpha]^{25}_D$ +30.5° (EtOH)].

4-Hydroxy-D-proline (15). The amino acid was prepared as described[8] from **14** to give 5.1 g (39 mmol, 26%) of 4-hydroxy-D-proline as white crystals: ^{1}H NMR (D_2O, external Me_4Si) δ 1.7–2.6 (m, 2 H), 3.3 (m, 2 H), 4.1–4.7 (m, 2 H); $[\alpha]^{21}_D$ +79.3° (*c* 2, H_2O) [lit.[8] $[\alpha]^{25}_D$ +76° (*c* 2, H_2O)].

4-Hydroxy-D-proline Ethyl Ester Hydrochloride. The ester was prepared as described for the L isomer **5**: yield 3.6 g (19 mmol, 57%); mp 157–158.5 °C; ^{1}H NMR (Me_2SO) δ 1.25 (t, 3 H, J = 7 Hz), 4.20 (q, 2 H, J = 7 Hz).

***N*-(*tert*-Butoxycarbonyl)-4-hydroxy-D-proline Ethyl Ester (19). (a) From 4-Hydroxy-D-proline Ethyl Ester Hydrochloride.** The *t*-Boc derivative was prepared as described for the corresponding L isomer: yield 4.0 g (15 mmol, 81%); bp 130 °C (0.05 mm); ^{1}H NMR ($CDCl_3$) δ 1.2 (t, 3 H, J = 7 Hz), 1.5 (s, 9 H), 1.8–2.5 (m, 2 H), 3.4–3.7 (m, 2 H), 4.1 (q, 2 H, J = 7 Hz), 4.3–4.5 (m, 2 H); $[\alpha]^{20}_D$ +70.4° (*c* 2, ethanol).

(b) From 18. To 200 mL of benzene was added 28.7 g (110 mmol) of tetraethylammonium acetate tetrahydrate. The water was azeotropically removed overnight. To the mixture at the reflux temperature was added 39.7 g (100 mmol) of tosylate **18**. After 1.5 h, the reaction was cooled to room temperature. Platelets of tetraethylammonium tosylate formed and were removed by suction filtration. The benzene portions were evaporated to dryness, giving an oil. The oil was dissolved in 200 mL of methanol and cooled to 0 °C. To the ice-cold solution was carefully added 160 mL of 1 N sodium hydroxide. The mixture was stirred for 75 min, and the pH was adjusted to 7 by using concentrated hydrochloric acid dropwise. The solution volume was reduced by half by rotary evaporation and was then extracted with three 100-mL portions of chloroform. The combined extracts were dried over magnesium sulfate, filtered, and evaporated to dryness. The resulting yellow oil was distilled under reduced pressure [147–148 °C (0.15 mm)] to give 13 g (52 mmol, 52%) of **19** as a thick, pale yellow oil identical with that obtained by method a. The forerun in the distillation contained olefin products corresponding to acetate or tosylate elimination.

***N*-(*tert*-Butoxycarbonyl)-4-hydroxy-D-prolinol (20).** The diol was prepared by the same procedure used to prepare the L isomer **7**: yield 4.8 g (22 mmol, 45%); ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 9 H), 1.8–2.3 (m, 1 H), 3.2–4.3 (m, 8 H), 4.7 (br, OH).

***N*-(*tert*-Butoxycarbonyl)-4-hydroxy-D-prolinol Di-*p*-toluenesulfonate (21).** The ditosylate was prepared by the method used for the L isomer **8**: yield 8.0 g (15 mmol, 69%); mp 104–106 °C; ^{1}H NMR ($CDCl_3$) δ 1.3 (s, 9 H), 2.2 (m, 2 H), 2.4 (s, 6 H), 3.1–3.7 (m, 2 H), 3.9–4.4 (m, 3 H), 4.8–5.1 (m, 1 H), 6.9–7.7 (m, 8 H); $[\alpha]^{22}_D$ +27.2° (*c* 1.94, benzene).

***N*-(*tert*-Butoxycarbonyl)-(2*R*,4*R*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (22).** The diphosphine was prepared as described for the *S*,*S* isomer **3**: yield 3.6 g (6.5 mmol, 34%); mp 103–104 °C; ^{1}H NMR ($CDCl_3$) δ 1.2–1.6 (m, 1 H), 1.4 (s, 9 H), 1.8–2.2 (m, 4 H), 2.7–3.2 (m, 3 H), 7.2–7.4 (br s, 20 H); ^{31}P NMR ($CDCl_3$) δ −7.3, −21.8; $[\alpha]^{20}_D$ −36.5° (*c* 0.6, benzene). Anal. Calcd for $C_{34}H_{37}NO_2P_2$: C, 73.76; H, 6.73; N, 2.53; P, 11.19. Found: C, 74.06; H, 6.87; N, 2.65; P, 11.12.

Allo-4-hydroxy-D-proline Ethyl Ester Hydrochloride (16). A slurry of 100 g (0.6 mol) of **9** in 500 mL of absolute ethanol was treated with dry hydrochloric acid gas until complete dissolution of the acid had occurred. The solution was then heated to reflux temperature for 5 h and then was slowly cooled. The white needles which formed were collected by suction filtration and dried under reduced pressure to give 90 g (0.46 mol, 77%) of ester **16**: mp 155–156 °C; ^{1}H NMR (Me_2SO-d_6) δ 1.2 (t, 3 H, J = 7 Hz), 1.8–2.6 (m, 3 H), 3.15 (d, 2 H, J = 3 Hz), 4.1 (q, 2 H, J = 7 Hz), 4.1–4.5

(m, 2 H); ^{13}C NMR (Me_2SO-d_6) δ 169.2, 68.6, 62.5, 57.9, 53.3, 38.3, 14.4; IR (KBr) 3250, 1715 cm^{-1}.

***N*-(*tert*-Butoxycarbonyl)-allo-4-hydroxy-D-proline Ethyl Ester (17).** To a solution of 89 g (0.46 mol) of **16** in 600 mL of a 1:1 mixture of dioxane/water were added 150 mL of triethylamine and 68 mL of *tert*-butoxycarbonyl azide. The mixture was heated to 50 °C for 15 h. The volume of solvent was reduced by half by rotary evaporation, and the resulting solution was extracted with four 100-mL portions of ether. The combined ether layers were washed with saturated sodium chloride solution and then dried over magnesium sulfate. The solution was filtered and evaporated to give a thick oil, which after distillation [118–119 °C (0.15 mm)] gave 103 g (0.40 mol, 87%) of **17** as a thick, pale yellow oil: ^1H NMR ($CDCl_3$) δ 1.2 (t, 3 H, J = 7 Hz), 1.4 (s, 9 H), 1.9–2.4 (m, 2 H), 3.4 (m, 2 H), 3.7–4.3 (m, 2 H), 4.1 (q, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 173.9, 154.1, 153.6, 80.1, 70.6, 69.6, 61.4, 58.0, 55.3, 54.9, 38.6, 37.8, 28.3, 14.1; IR (neat) 3450, 1745, 1700 cm^{-1}; $[\alpha]^{22}_D$ +15.4° (*c* 3.3, ethanol). Anal. Calcd for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40. Found: C, 55.53; H, 8.40; N, 5.34.

***N*-(*tert*-Butoxycarbonyl)-allo-4-hydroxy-D-proline Ethyl Ester *p*-Toluenesulfonate (18).** To a solution of 80 g (0.31 mol) of alcohol **17** in 300 mL of dry pyridine at 0 °C was added 65.2 g (0.34 mol) of *p*-toluenesulfonyl chloride in three portions. After an additional hour at 0 °C, the solution was allowed to warm to room temperature. After 48 h, the tosylate was precipitated by slowly adding 1 L of water to the pyridine solution at 0 °C over 4 h. The solid was collected by suction filtration, washed well with water, and dried under reduced pressure. The solid was recrystallized from 300 mL of absolute ethanol to give 110 g (0.28 mol, 89%) of **18** as white crystals: mp 74–75.5 °C; ^1H NMR ($CDCl_3$) δ 1.25 (t, 3 H, J = 7 Hz), 1.4 (s, 9 H), 2.2–2.4 (m, 2 H), 2.4 (s, 3 H), 3.6 (m, 2 H), 4.2–4.4 (m, 1 H), 4.1 (q, 2 H, J = 7 Hz), 4.8–5.2 (m, 1 H), 7.1–7.8 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 170.1, 170.6, 153.3, 153.0, 144.9, 133.4, 129.8, 127.3, 79.9, 79.3, 78.1, 61.0, 57.4, 52.0, 51.7, 36.8, 35.9, 28.1, 21.4, 14.1; IR (KBr) 1760, 1700, 1605, 1400, 1375, 900, 740, 660 cm^{-1}; $[\alpha]^{22}_D$ +17.8° (*c* 2.35, ethanol). Anal. Calcd for $C_{19}H_{27}NO_7S$: C, 55.19; H, 6.58; N, 3.39. Found: C, 55.20; H, 6.64; N, 3.33.

(2*S*,4*S*)-4-(Diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (23). To 100 mL of ice-cold trifluoroacetic acid under nitrogen was added 12.1 g (21.8 mmol) of **3** in one portion. The mixture was stirred at 0 °C for 30 min, and the trifluoroacetic acid was removed under reduced pressure. The residue was taken up in 100 mL of dichloromethane and washed with 100 mL of water, two 100-mL portions of 2 N sodium hydroxide, and two 50-mL portions of brine. The organic layer was dried over potassium carbonate and evaporated under reduced pressure to yield 9.87 g (99.6%) of **23** as a pale yellow oil which crystallized after 20 h at 0.5 mm: mp 73–75 °C (lit.[11] mp 103–104 °C?); ^1H NMR ($CDCl_3$) δ 1.2–1.6 (m), 2.0–2.5 (m), 2.7–3.2 (m), 7.2–7.6 (m); ^{13}C NMR ($CDCl_3$) δ 35.0 (d, J = 13 Hz), 36.5 (dd, J = 10, 1.5 Hz), 38.9 (dd, J = 18, 7 Hz), 50.4 (d, J = 24 Hz), 57.7 (dd, J = 16, 7 Hz), 127.9–128.8 (8 peaks), 131.9–133.2 (8 peaks), 137.4–138.4 (7 peaks); IR (KBr) 1480, 1430, 740, 695 cm^{-1}; $[\alpha]^{25}_D$ −15.65° (*c* 1.08, benzene) [(lit.[11] $[\alpha]^{20}_D$ −7° (*c* 1.84, benzene)]. Anal. Calcd for $C_{29}H_{29}NP_2$: C, 76.80; H, 6.44; N, 3.09; P, 13.66. Found: C, 76.23; H, 6.21; N, 2.91; P, 13.73.

(2*R*,4*R*)-4-(Diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (24). The *R,R* isomer **24** was prepared as described for the *S,S* isomer **23**: yield 2.1 g (4.7 mmol, 87%); ^1H NMR ($CDCl_3$) δ 1.2–1.6 (m, 1 H), 2.0–2.5 (m, 4 H), 2.7–3.2 (m, 3 H), 7.0–7.5 (m, 20 H); IR (neat) 3300, 1655, 1585, 1480, 1430, 725, 690 cm^{-1}.

***N*-Acryloyl-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (1).** To a well-stirred, two-phase mixture of 7.20 g (15.8 mmol) of **23** in 100 mL of toluene and 100 mL of 2 N sodium hydroxide at 0 °C was added 1.87 g (20.6 mmol) of acryloyl chloride in 50 mL of toluene dropwise over 30 min. The mixture was stirred for an additional 15 min at 0 °C, and the layers were separated. The aqueous phase was extracted with two 100-mL portions of benzene, and the combined organic layers were washed with 50 mL of 2 N hydrochloric acid and two 50-mL portions of brine. The solution was dried over magnesium sulfate and concentrated under reduced pressure to a pale yellow oil which solidified at 0.5 mm to yield 7.20 g (89%) of crude **1**. Recrystallization from toluene/hexane (1:10) gave white needles of **1** as the mono hexane solvate (by NMR). Dissolution in chloroform and reevaporation provided solvent free material: the melting point was broad with extensive decomposition; ^1H NMR ($CDCl_3$) δ 1.9–2.5 (m), 3.2–3.7 (m), 5.5–5.9 (m), 6.0–6.3 (m), 7.2–7.7 (m); ^{13}C NMR ($CDCl_3$) δ 33.1 (d, J = 14 Hz), 35.7 (d, J = 9 Hz), 36.8 (m, not well resolved), 51.1 (d, J = 28 Hz), 56.2 (dd, J = 20, 4 Hz), 127.1, 127.7–129.2 (11 peaks), 131.4–133.6 (9 peaks), 135.4–136.8 (5 peaks), 138.4, 138.9, 163.2, 163.8; IR (KBr) 1650, 1610, 1480, 1430, 740, 695 cm^{-1}; $[\alpha]^{20}_D$ −25.7° (*c* 1.04, benzene). Anal. Calcd for $C_{32}H_{31}NOP_2$: C, 75.72; H, 6.16; P, 12.21. Found: C, 75.43; H, 6.09; P, 11.89.

***N*-Acryloyl-(2*R*,4*R*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (2).** The *R,R*-acrylamide was prepared as described for the *S,S* isomer **1**: yield 0.54 g (1.1 mmol, 28%); ^1H NMR ($CDCl_3$) δ 1.9–2.5 (m, 4 H), 3.2–3.7 (m, 4 H), 5.5–5.9 (m, 1 H), 6.0–6.3 (m, 2 H), 7.2–7.7 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 163.9, 163.4, 139.0, 138.5, 137.4, 135.6 (5 peaks), 133.6–130.3 (8 peaks), 128.9–127.0 (6 peaks), 56.9–55.8 (4 peaks), 51.8–48.6 (4 peaks), 38.0–32.9 (9 peaks); ^{31}P NMR ($CDCl_3$) δ −6.4, −8.5, −21.9, −22.3; IR (KBr) 1650, 1615, 1480, 1430, 735, 690 cm^{-1}; $[\alpha]^{22}_D$ +26.1° (*c* 1.04, benzene). Anal. Calcd for $C_{32}H_{31}NOP_2$: C, 75.72; H, 6.16. Found: C, 75.91; H, 6.33.

Materials for Hydrogenation Reactions. Ethanol was dried and degassed by distillation from magnesium ethoxide under argon. Triethylamine was dried and degassed by distillation from calcium hydride under argon. Tetrahydrofuran was distilled from sodium–benzophenone ketyl under argon. Hydrogen was purchased from Airco and used as received. α-Acetoamidocinnamic acid (**30a**) was prepared by a published procedure.[12] Substituted cinnamic acids **30b–d** were prepared in a similar fashion from the appropriate aldehydes.

Copolymerization of 1 and 2 with Hydroxyethyl Methacrylate and Ethylene Dimethacrylate. Preparation of 27 and 29. The following procedure illustrated for the preparation of polymer **27** was also used for the preparation of **29**.

To a resin kettle equipped with an efficient overhead stirrer, condenser, and nitrogen inlet was added 50 mL of distilled, thiophene-free benzene which was heated to 65 °C. An additional 10 mL of benzene was used to dissolve 2.179 g (16.75 mmol) of freshly distilled hydroxyethyl methacrylate, 0.390 g (1.97 mmol) of ethylene dimethacrylate, and 0.500 g (0.985 mmol) of **1**. The monomer solution was degassed via two freeze–pump–thaw cycles and added to the resin kettle. The polymerization was initiated by the addition of 50 mg of azobis(isobutyronitrile) (AIBN). The mixture was stirred at 65 °C for 12 h and filtered under argon in a drybox, and the filter cake was dried under reduced pressure to yield 2.62 g (85%) of **27** as a white powder. The elemental analyses for polymers **27** and **29** appear in Table III.

Table III. Elemental Analyses of Polymers 27–29

polymer	% P	mol % of P_2	mmol of P_2/g
27	1.59	3.75	0.25
28	2.14	4.48	0.29
29	1.04	2.45	0.17

Copolymerization of 1 with *N,N*-Dimethylacrylamide and Ethylene Dimethacrylate. Preparation of 28. To a resin kettle equipped with an efficient stirrer, condenser, and nitrogen inlet was added 30 mL of distilled, thiophene-free benzene which was heated to 70 °C. An additional 10 mL of benzene was used to dissolve 1.660 g (16.75 mmol) of *N,N*-dimethylacrylamide, 0.390 g (1.97 mmol) of ethylene dimethacrylate, and 0.500 g (0.985 mmol) of **1**. The solution was degassed via two freeze–pump–thaw cycles and added to the resin kettle. The polymerization was initiated by the addition of 100 mg of AIBN. After 2.5 h at 70 °C, the

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mixture set to a yellow gel. The mixture was cooled and treated with 100 mL of degassed hexane to shrink the gel. The insoluble material was filtered in the drybox and dried under reduced pressure to yield 2.36 g (92%) of **28** as a yellow powder. The elemental analysis for polymer **28** appears in Table III.

General Procedure for Asymmetric Hydrogenation Using Homogeneous Phosphinopyrrolidine–Rhodium(I) Catalysts. A typical hydrogenation was carried out as follows. To a glass-lined bomb were added 4 mg (0.01 mmol) of μ-dichloro-bis(1,5-hexadiene)dirhodium(I), 12 mg (0.022 mmol) of **22**, and 2 mmol of substrate. The bomb was brought into the drybox, and 15 mL of absolute ethanol and 8.3 μL of triethylamine were added. The bomb was sealed under argon and then pressurized to 800 psig with hydrogen. The bomb was placed in a constant-temperature bath maintained at 20 °C and stirred magnetically. The reactions were worked up as described previously.[15] The product was analyzed by ^{1}H NMR. The integration between product and starting material *N*-acetyl peaks was used to determine conversion. The optical yield was determined by polarimetry. Results are reported in Table I.

General Procedure for Asymmetric Hydrogenation Using Polymer-Supported Catalysts. A typical hydrogenation was carried out as follows. To an argon filled flask were added 68 mg (0.018 mequiv of diphosphine) of **27**, 2 mg (0.01 mmol of Rh) of μ-dichloro-bis(1,5-hexadiene)dirhodium(I), and 15 mL of ethanol. The mixture was stirred for 1 h and then filtered under argon to give the yellow polymer-bound catalyst. The catalyst was transferred under argon to a glass-lined bomb equipped with magnetic stirring. After addition of 0.5 mmol of substrate, 15 mL of ethanol, and 5.0 μL of triethylamine, the bomb was pressurized to 800 psig with hydrogen and stirred at 20 °C. The workup consisted of filtration to remove the catalyst and evaporation of the solvent. When the reaction solvent was ethanol, the residue was taken up in 10 mL of nitromethane and reevaporated. This removes the last trace of ethanol. The products were analyzed by ^{1}H NMR. The integration between product and starting material *N*-acetyl peaks was used to determine conversion. The optical yields were determined by polarimetry. The results are listed in Table II.

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Registry No. **1**, 73300-49-9; **2**, 77429-64-2; **3**, 61478-28-2; **4**, 51-35-4; **5**, 33996-30-4; **6**, 37813-30-2; **7**, 61478-26-0; **8**, 61478-27-1; **9**, 77449-94-6; **10**, 2584-71-6; **11**, 37712-75-7; **12**, 77449-95-7; **13**, 77449-96-8; **14**, 77449-97-9; **15**, 3398-22-9; **15** ethyl ester HCl, 77449-98-0; **16**, 77449-99-1; **17**, 77450-00-1; **18**, 77450-01-2; **19**, 77450-02-3; **20**, 77450-03-4; **21**, 77450-04-5; **22**, 72598-03-9; **23**, 61478-29-3; **24**, 77450-05-6; **25**, 868-77-9; **26**, 97-90-5; **27**, 77429-62-0; **28**, 77429-63-1; **29**, 77429-65-3; (*R*)-**30a**, 10172-89-1; (*S*)-**30a**, 2018-61-3; (*R*)-**30b**, 61478-30-6; (*S*)-**30b**, 17355-23-6; (*R*)-**30c**, 19764-32-0; (*S*)-**30c**, 537-55-3; (*R*)-**30d**, 33043-31-1; (*S*)-**30d**, 31269-52-0; (*Z*)-α-acetamidocinnamic acid, 55065-02-6; (*Z*)-α-acetamido-*p*-acetyloxycinnamic acid, 64896-34-0; (*Z*)-α-acetamido-*p*-hydroxycinnamic acid, 64896-33-9; (*Z*)-α-acetamido-4-acetoxy-3-methoxycinnamic acid, 55739-56-5; μ-dichloro-bis(1,5-hexadiene)dirhodium(I), 12092-47-6; acryloyl chloride, 814-68-6; *N*,*N*-dimethylacrylamide, 2680-03-7.

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Transition-Metal-Catalyzed Asymmetric Organic Synthesis via Polymer-Attached Optically Active Phosphine Ligands. 6.[1] Asymmetric Hydrogenation with Polymer Catalysts Containing Optically Active Pendent Alcohols

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Three acrylate comonomers, (*S*,*S*), (*R*,*R*) and racemic 1-methyl-2-hydroxypropyl acrylate (**7a–c**), were prepared from the corresponding isomers of 2,3-butanediol. The acrylates were copolymerized with ethylene dimethacrylate and *N*-acryloyl-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (**8**) to give cross-linked resins containing phosphinopyrrolidines and optically active alcohols. Polymers containing the 4,5-bis[(diphenylphosphino)methyl]-1,3-dioxolane unit (DIOP) were prepared by copolymerizing acrylates **7a–c** with ethylene dimethacrylate and 2-*p*-styryl-4,5-bis[(tosyloxy)methyl]-1,3-dioxolane (**1**) and treating the polymers with an excess of sodium diphenylphosphide. Exchange of Rh(I) onto these polymers provided catalysts that hydrogenated 2-acetamidoacrylic acid in tetrahydrofuran. The enantiomeric excesses obtained with the polymer-bound catalysts varied with the structure of the pendent alcohol, suggesting the participation of the polymer-bound alcohol at the catalyst site to provide an alcohol-like environment. A difference in enantiomeric excess (ee) was noted when catalysts containing either *R* or *S* alcohols were used.

One of the most challenging problems in preparing polymer-bound catalysts is the proper design of the polymer support. Previously we had prepared polymer-bound catalysts for asymmetric hydrogenation[2,3] and hydroformylation;[4] each catalyst was prepared with the solvent requirements of the reaction in mind. For the reduction of dehydroamino acids, a polar support obtained from copolymerization with hydroxyethyl methacrylate was synthesized, thus allowing the polymer-bound catalyst

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