Transition-Metal-Catalyzed Asymmetric Organic Synthesis via Polymer-Attached Optically Active Phosphine Ligands. 13. Asymmetric Hydrogenation with Polymer Catalysts Containing Primary and Chiral Secondary Pendant Alcohols

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The copolymerizations of (4*S*,5*S*)-2-*p*-styryl-4,5-bis[(diphenylphosphino)methyl]-1,3-dioxolane [(*S*,*S*)-**5**] with a cross-linking monomer, ethylene 1,2-dimethacrylate (**7**), and methacrylates bearing both a primary alcohol function and a chiral secondary alcohol function, (2*S*)-, (2*RS*)-, or (2*R*)-2,3-dihydroxypropyl methacrylate [(*S*)-**2**, (*RS*)-**2**, and (*R*)-**2**, respectively], gave polymers (**6a–c**, respectively) onto which rhodium was exchanged via the chloro(1,5-cyclooctadiene)rhodium(I) dimer. The resulting insoluble polymers containing chiral rhodium centers and the ancillary alcohol sites catalyzed the hydrogenation of olefins in ethanol to yield chiral *N*-acylamino acids and hydratropic acid. The catalyst containing the *R* alcohol (**6a**) gave amino acids in an optical yield that was 6% higher than that obtained from polymer (**6b**) bearing the racemic alcohol and 8% higher than that obtained from the catalyst with the *S* alcohol when the reactions were performed in THF.

Asymmetric hydrogenation and hydroformylation reactions of olefins can be carried out efficiently by the use of a chiral transition-metal catalyst bound to a polymer support. Although initial attempts to effect asymmetric hydrogenation reactions with chiral catalysts supported on polymers were not particularly successful (high enantiomeric excesses were not realized),[1-7] the meticulous design of the polymer support and the careful introduction of the chiral site in the polymer allowed the same high enantiomeric excesses (ee) to be achieved as were attained in the analogous homogeneous reactions.[8-17] An important consideration in designing such a supported homogeneous catalyst is the architecture of the polymer to which the catalyst is attached. To this end, the solvent for the reaction and thus the compatibility of the polymer with the solvent must be considered. For most asymmetric hydrogenations that are carried out in polar solvents, the cross-linked polymer bearing the catalyst should also be polar and therefore swell in the reaction medium, such that all the catalyst sites become accessible to the substrate.

Some of the most suitable polymers as supports for asymmetric hydrogenations have been those carrying pendent alcohol groups.[8-16] In principle, the interaction between chiral pendent alcohol units on the polymer support and the catalyst may lead to an enhanced ee in the asymmetric synthesis. This effect, in fact, has been demonstrated both with polymers containing 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane[9,12,15,16] (DIOP) and (2*S*,4*S*)-*N*-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BPPM).[12,15,16] Thus, with a DIOP- or BPPM-like attached ligand of one configuration, the presence of one enantiomeric pendent alcohol could increase the ee of the product, while the presence of the other enantiomer could diminish the ee.

In the case of a polymer-supported (*R*,*R*)-DIOP ligand, a 9–15% difference in the optical yield was observed in hydrogenation reactions when a catalyst containing a secondary *S* alcohol and a catalyst containing a secondary *R* alcohol were used.[9-12] Similar effects were noted with a catalyst consisting of an (*S*,*S*)-BPPM ligand attached to a polymer containing pendent secondary *S* alcohol functions and one containing secondary *R* alcohol groups (Δee = 11%).[12] Surprisingly, in all of these examples, a primary alcohol obtained from the incorporation of hydroxyethyl acrylate into the polymer gave higher ee's than

Scheme I

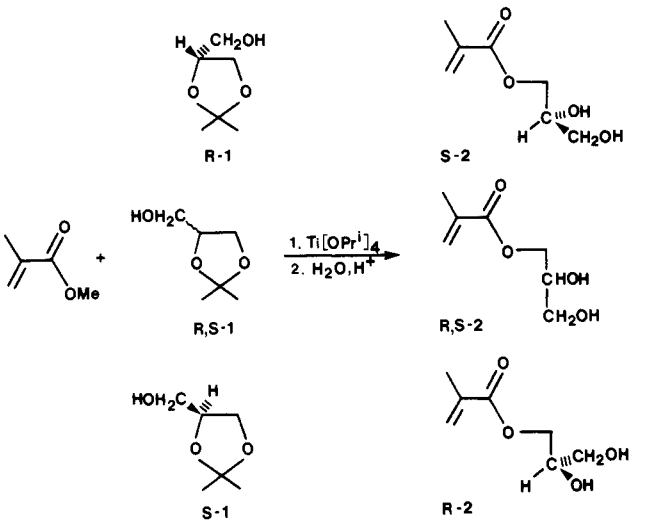

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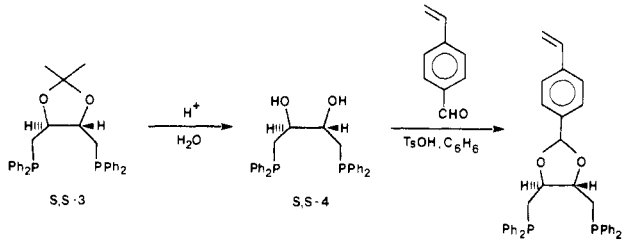
Table I. Asymmetric Hydrogenation with Rh(I)-6 Catalysts[a]

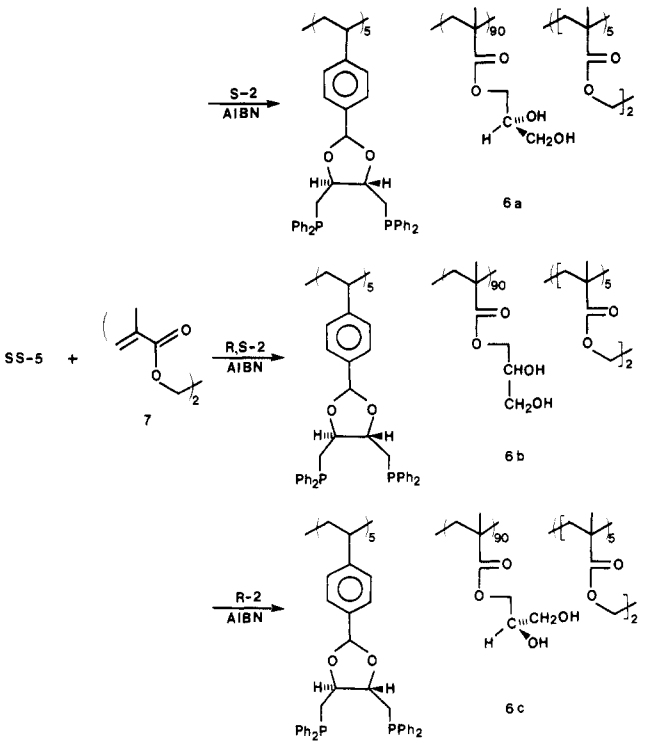
run	R	R′	polymer support	alcohol config	solv	time, h	yield,[b] %	optical yield,[c] %	config	DIOP[d]
1	H	NHAc	**6b**	rac	EtOH	10	93	64	*S*	73
2[e]	H	NHAc	**6b**	rac	EtOH	10	88	60	*S*	
3	Ph	NHAc	**6b**	rac	EtOH	24	83	77	*S*	81
4	H	Ph	**6b**	rac	EtOH	24	89	56	*R*	63
5	H	NHAc	**6c**	*R*	THF	15	36[f]	27	*S*	59
6	H	NHAc	**6b**	rac	THF	15	31[f]	21	*S*	
7	H	NHAc	**6a**	*S*	THF	15	32[f]	19	*S*	
8	H	NHAc	**6c**	*R*	EtOH	10	90	63	*S*	

[a] Ratio of substrate/Rh(I) = 50. [b] Determined by ^{1}H NMR. [c] Optical yields were calculated with the following values for optically pure compounds. (*R*)-*N*-Acetylalanine, $[\alpha]_D$ +66.5° (*c* 2, H_2O) [Birbaum, S. H.; Levintow, L.; Kingsley, R. B.; Greenstein, J. P. *J. Biol. Chem.* **1952**, *194*, 455]. (R)-*N*-Acetylphenylalanine, $[\alpha]^{26}_D$ +46.0° (*c* 1, EtOH) [Dang, T. P.; Paulin, J. C.; Kagan, H. R. *J. Organomet. Chem.* **1975**, *91*, 105]. (*S*)-Hydratropic acid, $[\alpha]^{25}_D$ +76.3° (*c* 1.6, $CHCl_3$) [Bakshi, S. P.; Turner, E. E. *J. Chem. Soc.* **1961**, 171]. [d] Optical yields reported with the homogeneous Rh(I)-DIOP catalyst.[12,16] [e] After three previous hydrogenations with this catalyst. [f] Rates in THF are slower than rates in alcohol; conversions >90% required 2 days under these reaction conditions.

Scheme II



Scheme III



any of the chiral secondary alcohol containing polymers. This difference was attributed to the ability of a less sterically hindered primary alcohol to interact more effectively with the catalyst. Consequently, we undertook the task of synthesizing interacting supports for catalysts that had both a primary alcohol and a chiral secondary alcohol in the pendent group.

Results and Discussion

Monomer and Polymer Synthesis. For the alcohol-containing monomer a methacrylate ester was chosen in which the alcohol portion of the ester was glycerin-derived. Thus, the synthesis of a methacrylate containing both a primary alcohol and a chiral secondary alcohol was undertaken. The methacrylate esters (*R*)-**2**, (*R*,*S*)-**2**, (*S*)-**2** were prepared from the glycerol 1,2-acetonides (*R*)-**1**, (*R*,*S*)-**1**, (*S*)-**1** by transesterification with methyl methacrylate in the presence of catalytic titanium tetraisopropoxide followed by deacetalization (Scheme I). The (*R*)- and (*S*)-glycerol 1,2-acetonides (*R*)-**1**, (*S*)-**1** are available from L-serine[18] and D-mannitol,[19,20] respectively.

The phosphine-bearing monomer [(*S*,*S*)-**5**] was obtained from the hydrolysis of (*S*,*S*)-DIOP (**3**) to the diphosphine diol **4** in dilute acid followed by acetalization with *p*-vinylbenzaldehyde (Scheme II). Although this monomer could be purified by column chromatography, it did not crystallize at any time in the course of this research.

An analogous phosphine containing a phenyl substituent (derived from benzaldehyde) instead of the *p*-vinylbenzyl group has been shown to give the same optical yield of *N*-acetylphenylalanine from *N*-acetylcinnamic acid as DIOP in hydrogenations utilizing a rhodium catalyst.[21]

Polymers **6a–c** containing about 5 mol % of the DIOP-type phosphine ligand, 90 mol % of the acrylate ester bearing both primary and secondary alcohol functions, and 5 mol % of the cross-linking unit (introduced via ethylene dimethacrylate (**7**)) were prepared by a free radical copolymerization in benzene (Scheme III). Phosphorus analysis on the polymers verified that the mole percent of phosphorus monomer (*S*,*S*)-**5** charged to the polymerization reaction resulted in its incorporation in the same mole percent. Thus, cross-linked polymers containing the (*S*,*S*)-DIOP ligand and a pendent primary alcohol in combination with an *R*, *S*, or a racemic pendent secondary alcohol function could be prepared for use as a supporting ligand for asymmetric hydrogenation reactions.

Hydrogenation Reactions. The polymer-attached catalysts were prepared by stirring the polymer and dichlorobis(1,5-cyclooctadiene)dirhodium(I) in ethanol for 36 h. After filtration the catalyst was transferred under argon to a Fischer–Porter tube containing the substrate. Solvent was added via a syringe and the hydrogenation reactions of the acrylic acid derivatives were allowed to proceed at ambient temperature under 1 atm of H_2.

The hydrogenation reactions were performed in ethanol or tetrahydrofuran (THF), because the polymers **6a–c** swelled in both solvents. In ethanol, the polymer-sup-

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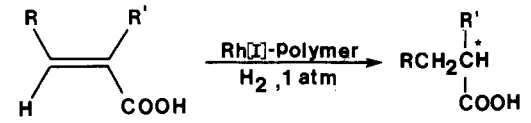

ported catalyst containing racemic alcohol and (*S,S*)-DIOP hydrogenated the acrylic acid derivatives to give the chiral products in slightly lower optical yields than observed with a homogeneous rhodium–DIOP catalyst (Table I, runs 1–4). Hydrogenation of (*N*-acylamino)acrylic acid in ethanol with **6c** containing the *R* ancillary alcohol gave (*S*)-*N*-acylalanine in the same optical yield as **6b** containing racemic ancillary alcohol (run 8). Because ethanol appeared to compete with the polymer-bound alcohol sites, THF was utilized to distinguish the effects of the ancillary chiral alcohol site on the stereospecificity of the reaction. In THF, an 8% difference in optical yield was observed with catalysts derived from polymers **6a** and **6c**, containing the pendent optically active alcohols of opposite configuration (runs 5 and 7). Hydrogenation with catalyst derived from **6b** containing racemic pendent alcohol gave an intermediate optical yield (run 6).

The optical yields obtained with catalysts derived from polymer **6** in THF are not surprising in view of previous results,[12,16] A (*R,R*)-DIOP-containing polymer with a chiral secondary alcohol derived from (*R,R*)- or (*S,S*)-2,3-butanediol hydrogenated (*N*-acetylamino)acrylic acid in 1% *R* and 10% *S* ee (Δee = 11%), and a (*R,R*)-DIOP-containing polymer with primary alcohol functions derived from hydroxyethyl acrylate hydrogenated the same substrate in 26% ee.[12,16] Thus, the 19% and 27% optical yields obtained with **6a** and **6c** are approximately those expected in the presence of a primary alcohol ancillary group, and the difference in optical yield is that expected from the respective chiral secondary alcohol pendent groups.

Experimental Section

^1H and ^{13}C NMR spectra (270 and 68 MHz, respectively) were recorded on an IBM WP 270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard for ^1H NMR. ^{31}P NMR spectra (81 MHz) were recorded on an IBM WP 200 spectrometer in $CDCl_3$ with 85% H_3PO_4 as external reference. Infrared spectra were recorded on a Beckman 4250 spectrometer. Mass spectra were recorded on a VG-Micromass 16^F spectrometer. Optical rotations were measured on a Autopol III automatic polarimeter. Conversions of hydrogenation reactions were determined by ^1H NMR on a Varian EM 360 spectrometer in Me_2SO-d_6 with tetramethylsilane as internal standard.

Filtrations involving polymer-supported catalyst were performed under an inert atmosphere in a glovebag. The polymerization and hydrogenation reactions were carried out in solvents that were freshly distilled and deoxygenated by three freeze–pump–thaw cycles. Benzene and tetrahydrofuran were distilled from sodium–benzophenone ketyl, and ethanol was distilled from magnesium ethoxide.

(2*S*,3*S*)-2,3-Dihydroxy-1,4-bis(diphenylphosphino)butane (4). Under a stream of nitrogen, 3 g (6 mmol) of (*S,S*)-DIOP (**3**),[22] 150 mL of methanol, 3 mL of concentrated hydrochloric acid, and 10 mL of water were heated at reflux for 3 h. The solution was cooled to room temperature, and the solvents were removed under reduced pressure. Water (20 mL) was added to the yellowish oil, and the mixture was allowed to stand overnight at 0 °C. The resulting solids were removed by filtration and dried under 0.05 mmHg to yield 2.26 g (64%) of a white powder: mp >75 °C dec; $[\alpha]^{23}_D$ +35.2° (*c* 1.0, $CHCl_3$); ^1H NMR δ 2.1–2.3 (br s, 2 H, disappeared by shaking with D_2O), 2.2–2.3 (d, *J* = 4.8 Hz, 4 H), 3.6–3.7 (t, *J* = 4.9 Hz, 2 H), 7.1–7.4 (m, 20 H); ^{31}P NMR δ −23 (s, 2 P); IR (KBr) 3300, 3030, 2850, 1480, 1430, 1030, 730, 690 cm^{-1}; MS, *m/e* (relative intensity) 458 (1 M^+). Anal. Calcd for $C_{28}H_{28}O_2P_2$: C, 73.40; H, 6.12; P, 13.50. Found: C, 73.85; H, 6.20; P, 12.90.

(4*S*,5*S*)-2-*p*-Styryl-4,5-bis[(diphenylphosphino)methyl]-1,3-dioxolane (5). Under a stream of nitrogen, 0.087 g (0.66 mmol) of *p*-vinylbenzaldehyde,[23] 0.34 g (0.74 mmol) of **4**, 30 mg of *p*-toluenesulfonic acid, and a small amount of *p*-*tert*-butylcatechol were heated at reflux for 10 h in 30 mL of benzene. The water was continuously extracted by distillation over 4-Å molecular sieves. The solution was cooled to room temperature and the reaction mixture was purified by flash chromatography[24] with benzene/tetrahydrofuran (90/10, v/v). The solvents were removed under reduced pressure to afford 0.2 g (60%) of an oil. The product did not crystallize from ethanol or methanol: $[\alpha]^{25}_D$ +29.2° (*c* 0.12, C_6H_6); ^1H NMR δ 2.4 (d, *J* = 4.6 Hz, 4 H), 4.10 (t, *J* = 4.5 Hz, 2 H), 5.1–5.2 (d, *J* = 11.2 Hz, 1 H), 5.5–5.7 (d, *J* = 17.6 Hz, 1 H), 5.77 (s, 1 H), 6.5–6.7 (dd, *J* = 17.6, 11.2 Hz, 1 H), 7.2–7.4 (m, 24 H); ^{31}P NMR δ −21.8 (s, 1 P), −23.0 (s, 1 P); IR (KBr) 3030, 1560, 1470, 1200, 1070, 980, 910, 780 cm^{-1}. Anal. Calcd for $C_{37}H_{34}O_2P_2$: C, 77.65; H, 5.94; P, 10.82. Found: C, 77.34; H, 6.09; P, 10.71. R_f 0.91 (benzene/tetrahydrofuran (10/1, v/v), silica gel 60 F-254).

(2*S*)-2,3-(Isopropylidenedioxy)propyl Methacrylate. Under a stream of nitrogen, 26.4 g (0.2 mol) of (*R*)-**1**,[18] 40.0 g (0.4 mol) of methyl methacrylate, 2.8 g (0.01 mol) of titanium tetraisopropoxide,[25] and a small amount of *p*-phenylenediamine inhibitor were heated at reflux for 15 h in 400 mL of cyclohexane. The methanol formed during the transesterification was continuously removed by distillation over 100 g of 3-Å molecular sieves.[26] The solution was then cooled to room temperature and a solution of hydrochloric acid (3.2 mL of 6 N HCl) added. The reaction mixture was filtered, and the layers were separated. The organic layer was washed with a saturated solution of aqueous sodium bicarbonate and with water and then dried over sodium sulfate. The solvent was removed under reduced pressure. Distillation of the residue under reduced pressure gave 31.6 g (79%) of product: bp 51–53 °C (0.15 mmHg); $[\alpha]^{22}_D$ −8.38° (*c* 1.91, $CHCl_3$); ^1H NMR δ 1.37 (s, 3 H), 1.96 (dd, *J* = 1.0, 1.6 Hz, 3 H), 3.80 (dd, *J* = 6.1, 8.5 Hz, 1 H), 4.10 (dd, *J* = 6.3, 8.5 Hz, 1 H), 4.22 (d, *J* = 6.1 Hz, 1 H), 4.36 (m, *J* = 6.2 Hz, 1 H), 5.60 (dd, *J* = 1.0, 1.5 Hz, 1 H), 6.15 (dd, *J* = 1.5, 1.5 Hz, 1 H); ^{13}C NMR δ 18.2, 26.6, 64.5, 66.4, 73.8, 109.7, 125.9, 136.0, 167.1; IR (neat) 3290, 2880, 1725, 1640, 1455, 1385, 1375, 1320, 1300, 1165, 1050, 940, 845 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.03; H, 8.00. Found: C, 59.72; H, 8.03.

(2*RS*)-2,3-(Isopropylidenedioxy)propyl Methacrylate. The racemic isomer was prepared in 67% yield from (*RS*)-**1**[27] as described for the *S* isomer: bp 70–72 °C (0.14 mmHg). Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.03; H, 8.00. Found: C, 60.10; H, 7.85. The spectroscopic data were identical with those reported for the *S* isomer.

(2*R*)-2,3-(Isopropylidenedioxy)propyl Methacrylate. The *R* isomer was prepared in 70% yield from (*S*)-**1**[19,20] as described for the *S* isomer: bp 55–57 °C (0.2 mmHg); $[\alpha]^{22}_D$ +8.30° (*c* 1.58, $CHCl_3$). Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.03; H, 8.00. Found: C, 59.85; H, 7.91. The spectroscopic data were identical with those reported for the *S* isomer.

(2*S*)-2,3-Dihydroxypropyl Methacrylate [(*S*)-2]. A mixture of 10 g (50 mmol) of (2*S*)-(2,3-isopropylidenedioxy)propyl methacrylate, 25 mL of glacial acetic acid, 75 mL of water, and a small amount of *p*-methoxyphenol were introduced into a flask that was placed in an oil bath preheated to 80 °C. The solution was stirred for 10 min, cooled to room temperature, and concentrated. Distillation of the residue under reduced pressure gave 6.4 g (80%) of (*S*)-**2**: bp 92–93 °C (0.04 mmHg); $[\alpha]^{22}_D$ −11.83° (*c* 1.97, CH_3OH); ^1H NMR δ 1.94 (dd, *J* = 1.0, 1.5 Hz, 3 H), 2.25 (br s, 1 H, disappeared by shaking with D_2O), 2.75 (br s, 1 H,

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Table II. Phosphorus Analyses

polymer	% P	% 5 in 6
6a	1.59	4.67
6b	1.83	5.38
6c	1.55	4.56

disappeared by shaking with D_2O), 3.60 (m, 3 H), 4.25 (d, J = 5.5 Hz, 2 H), 5.62 (dd, J = 1.4, 1.4 Hz, 1 H), 6.17 (dd, J = 1.0, 1.3 Hz, 1 H); ^{13}C NMR δ 18.1, 63.5, 65.4, 70.3, 126.2, 135.9, 166.7; IR (neat) 3400, 2960, 2890, 1720, 1645, 1335, 1300, 1175, 1050, 945, 820 cm^{-1}. Anal. Calcd for $C_7H_{12}O_4$: C, 52.53; H, 7.50. Found: C, 52.50; H, 7.52.

(2*RS*)-2,3-Dihydroxypropyl Methacrylate [(*R*,*S*)-2]. The racemic isomer was prepared in 80% yield from (2*RS*)-(2,3-isopropylidenedioxy)propyl methacrylate as described for the *S* isomer: bp 95–97 °C (0.05 mmHg). Anal. Calcd for $C_7H_{12}O_4$: C, 52.53; H, 7.50. Found: C, 52.45; H, 7.45. The spectroscopic data were identical with those reported for the *S* isomer.

(2*R*)-2,3-Dihydroxypropyl Methacrylate [(*R*)-2]. The *R* isomer was prepared in 69% yield from (2*R*)-(2,3-isopropylidenedioxy)propyl methacrylate as described for the *S* isomer: bp 85–86 °C (0.025 mmHg); $[\alpha]^{22}_D$ +11.91° (*c* 2.15, CH_3OH). Anal. Calcd for $C_7H_{12}O_4$: C, 52.53; H, 7.50. Found: C, 52.70; H, 7.60. The spectroscopic data were identical with those reported for the *S* isomer.

Preparation of Copolymer 6a. To a resin kettle equipped with an efficient overhead stirrer, a condenser, and a nitrogen inlet was added 5 mL of benzene, which was then heated to 65 °C. The monomers (*S*,*S*)-5 (0.18 g, 0.32 mmol), (*S*)-2 (0.93 g, 5.80 mmol), and ethylene dimethacrylate (0.064 g, 0.32 mmol) and AIBN (20 mg) were dissolved in 5 mL of benzene, and this solution was added to the resin kettle. The mixture was stirred at 65 °C for 15 h, cooled to room temperature, and filtered. The copolymer was washed with (5 × 10 mL) benzene and dried overnight at 0.10 mmHg to yield 0.99 g (85%) of **6a** as a white powder.

The above procedure was used for the preparation of **6b** and **6c**. The elemental analyses of copolymers **6a–c** are reported in Table II.

General Procedure for Asymmetric Hydrogenation Using Polymer-Supported Catalysts. To an argon-filled flask were added 68 mg (0.018 mequiv of diphosphine) of **6a**, 3.0 mg (0.012 mequiv of Rh) of chloro(1,5-cyclooctadiene)rhodium(I) dimer, and 10 mL of ethanol. The mixture was stirred for 36 h and then filtered. The copolymer was washed with 10 mL of ethanol and dried overnight under 0.05 mmHg to give the light yellow polymer-bound catalyst. The catalyst was transferred to a Fischer–Porter tube containing 0.6 mmol of substrate, and 10 mL of solvent was added via a syringe. The apparatus was then pressurized to 1 atm with hydrogen, and the mixture was stirred at room temperature. The workup consisted of filtration to remove the catalyst and evaporation of the solvet under reduced pressure. The ratio of *N*-acylamino acid to unsaturated *N*-acylamino acid was determined by NMR, and the enantiomeric excess was determined by optical rotation on the basis of the mole percent amino acid as described previously.[12,13]

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Palladium-Catalyzed Olefination of Vinyl Triflates

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The olefination of vinyl trifluoromethanesulfonates (triflates) takes place under mild reaction conditions in polar solvents to give high yields of conjugated dienes. The reaction of 4-*tert*-butylcyclohexenyl triflate with Michael acceptors in the presence of a catalytic amount of bis(triphenylphosphine)dichloropalladium(II) and an excess of triethylamine gave high yields of the expected regioisomer. The reaction conditions are sufficiently mild that acrolein gave (*E*)-3-(4-*tert*-butylcyclohexenyl)propenal in 86% yield without appreciable polymerization. Acetylenes also undergo the reaction to give high yields of enynes. Less reactive olefins may be employed with the use of palladium(0) catalysts and, in some cases, added lithium salts.

The palladium-catalyzed olefination of organic halides with alkenes (the Heck reaction) is a unique method of carbon–carbon bond formation in which the organic halide is homologated by two or more carbons.[1,2] The alkene insertion is largely regiospecific with the organic halide adding to the least hindered position of the alkene. The organic halides are limited mostly to aryl, vinyl, and benzyl halides, since alkyl halides containing an sp^3 hydrogen β to the carbon bearing the halogen undergo a facile β-hydride elimination in preference to alkene insertion.

The palladium-catalyzed reaction of alkenes with vinyl halides has been practically limited to the reactions of vinyl bromides and iodides. While the synthesis of acyclic vinyl halides from alkynes has been well worked out,[3-7] the generation of cyclic vinyl iodides from cyclic ketones[8-10] proceeds with variable regioselectivity. In general, 2-substituted cyclic vinyl iodides are unavailable from the corresponding 2-substituted ketone or enone.

The ease of preparation of vinyl trifluoromethanesulfonates (triflates) in high regioselective purity from ketones[11,12] and enones[12,13] and the availability of the starting materials have expanded their use as vinyl cation synthons. For example, organocopper reagents react with vinyl triflates to yield coupled products.[14-16] More re-

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