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Syntheses and Applications of 2-Phosphino-2′-alkoxy-1,1′-binaphthyl Ligands. Development of a Working Model for Asymmetric Induction in Hydrovinylation Reactions

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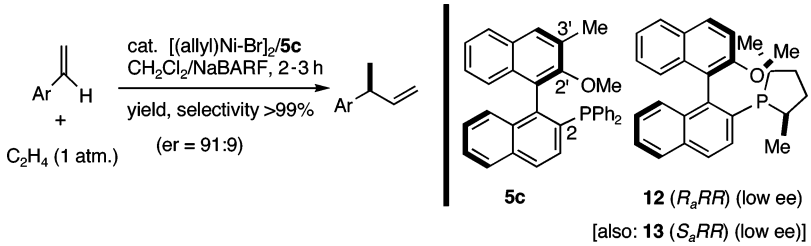
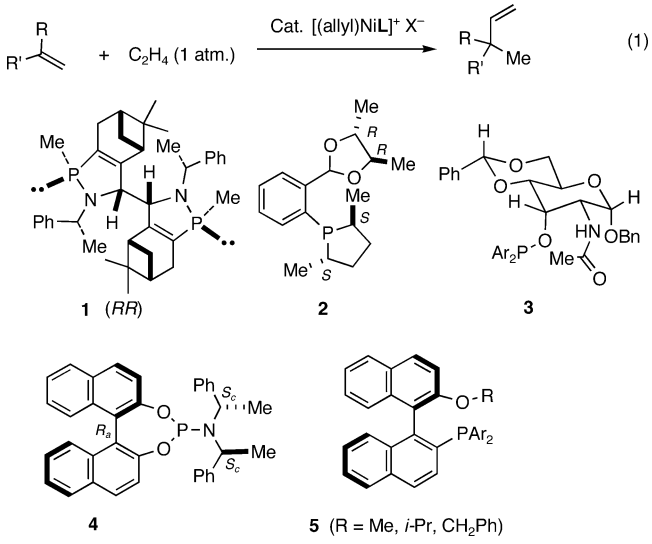


Among the handful of monophosphine ligands that effect asymmetric hydrovinylation of vinylarenes, 2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl (**MOP**) is among the most accessible. Addition of a methyl group at the 3′-position of this ligand significantly improves the enantioselectivity of hydrovinylation of prototypical alkenes. Introduction of a chiral phospholane at the C_2 position of this scaffolding has no effect on the enantioselectivity. These results are consistent with a model proposed for the asymmetric induction for this exacting reaction.

Introduction

The nickel-catalyzed hydrovinylation of olefins (heterodimerization of ethylene and other olefins, eq 1)[1] has recently received considerable attention, and the scope of the substrates and list of ligands that give high yields and selectivities continue to grow. In addition to Wilke's original azaphospholene system (**1**),[2] 2,5-dialkyl-1-arylphospholanes (**2**),[3] β-acetamido-diarylphosphinites (**3**),[4] phosphoramidites (**4**),[5] and 2-diarylphosphino-2′-alkoxy-1,1′-binaphthyl(**5**)[6] have been found to give good to excellent selectivities for this exacting reaction.



As a group, the 2′-alkoxybinaphthyl-2-phosphines (**5**) belonged to one of the first general classes of ligands that gave nearly quantitative yields and high selectivities for the 3-arylbutenes. Ancillary studies using this ligand system also established the crucial role played by counterions and their synergistic

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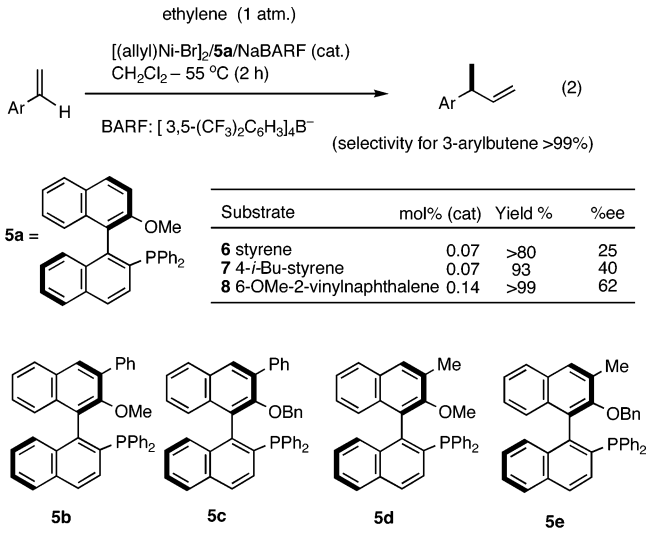
relationship to hemilabile groups in a ligand system.[6] Thus, hydrovinylation of 6-methoxy-2-vinylnaphthalene **8** (MVN), a potential precursor for naproxen, using the **MOP** ligand (**5a**, R = Me) gave >95% yield of the product in 62% ee when the reaction was carried out at −55 °C in the presence of Na^+-$\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}^-$ (eq 2). Under identical conditions, styrene (**6**) and 4-isobutylstyrene (**7**) gave 25 and 40% ee, respectively. Substitution of the methoxy group in the **MOP** ligand by a benzyloxy group (**5**, R = CH_2Ph) improved the ee of MVN up to 73%. Variation of the P-aryl substituent and/or other changes in the O-alkyl group in **5** had only marginal effects on selectivity.[6b] Among the viable ligands for hydrovinylation, the binaphthyl phosphines are the most air-stable and easiest to handle. Thus there may be practical advantages if a better ligand with this scaffolding can be found. In this paper, we report the synthesis and applications of such ligands. In addition, synthesis of a hybrid ligand system that incorporates the chiral C_2-symmetric 1,5-dialkyl phospholane and binaphthyl moieties (vide infra, **12** and **13**) is also reported since these ligands provide an opportunity to test the validity of a model transition state that was successfully used in the design of ligands for asymmetric hydrovinylation.



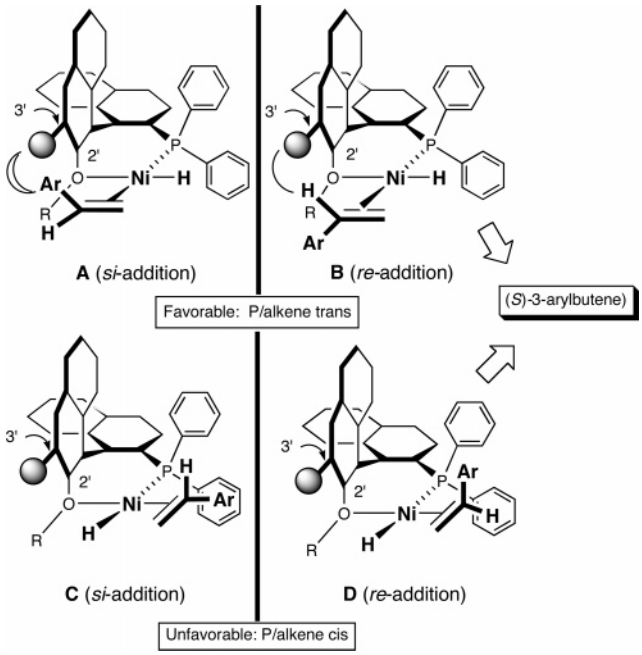


FIGURE 1. A model for asymmetric induction in the hydrovinylation of vinylarenes.

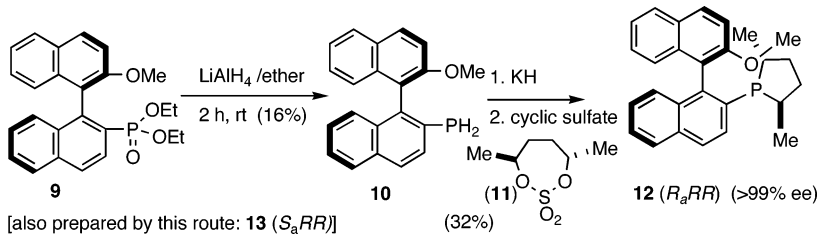
Results and Discussion

Shown in Figure 1 is a working model for the asymmetric induction in the (**5**)-Ni(II)-catalyzed asymmetric hydrovinylation of a vinylarene. In this model, the favorable transition states **A** and **B** are characterized by a square planar geometry for [**L**(alkene)Ni^+-H], in which the alkene and the **P** moiety are trans to each other. The corresponding transition states in which the phosphorus and the alkene are cis to each other (**C** and **D**) would be precluded (vide infra) because of the steric repulsion between the aryl group of the substrate and the aryl substituents on the phosphorus. Note that these TS's will lead to the Ni being placed in the benzylic position, which could be stabilized by η^3-coordination.

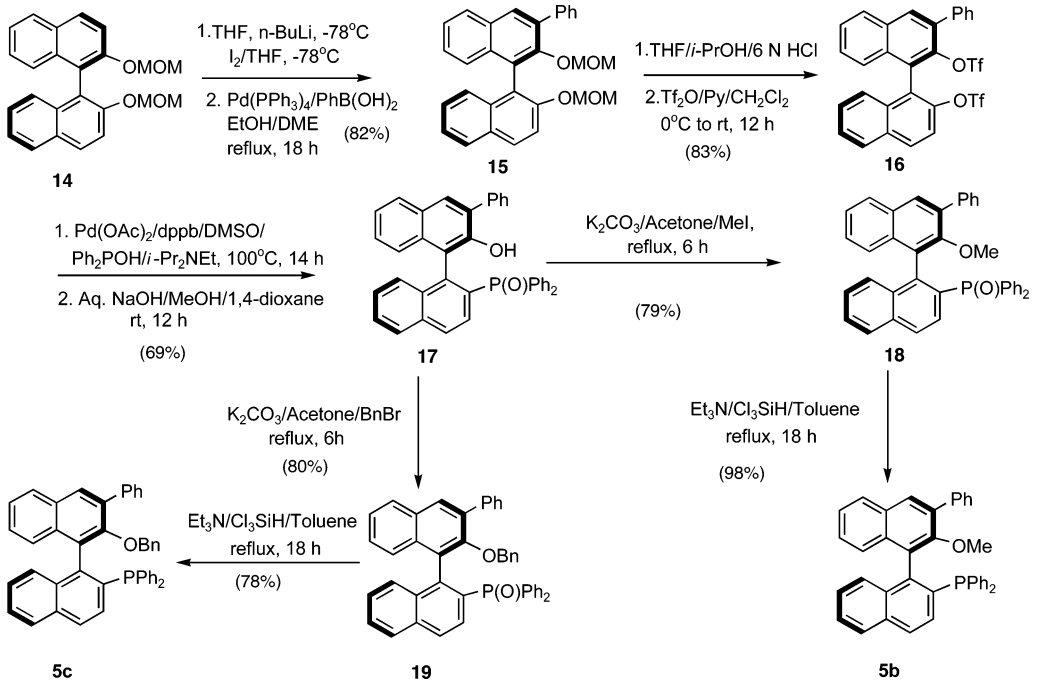
Before one can invoke the transition states (TS) in which alkene/phosphorus groups are trans (**A** and **B**), others in which these groups are cis (**C** and **D**) should be explicitly considered. To this end, diastereomeric 2,5-dimethyl-1-[2-(1,1′-binaphthyl)]-phospholano ligands **12** and **13** were synthesized (Scheme 1) and tested in the hydrovinylation of **8** (6-methoxy-2-vinylnaphthalene, MVN). The known BINAP−phosphonate derivative[7a] **9** was reduced with LAH to get the corresponding phosphine **10**. This phosphine was coupled to the cyclic sulfate **11** derived from (*SS*)-hexane-2,5-diol along the lines described for the synthesis of similar phospholanes.[7b] Starting with (*R*)-binaphthol phosphonate derivative **9**, the phospholane **12** (R_aRR) was synthesized in ∼5% yield. The ee of this ligand is assumed to be the same as that of the diol from which the cyclic sulfate and the binaphthol was derived (>99.5%). Synthesis of the diastereomer **13** (S_aRR) (∼5% yield) is described in the Supporting Information. These yields have not been optimized.

These ligands **12** and **13** were found to give very low ee's [∼17% (*R*) and <5% (*R*), respectively] in the hydrovinylation of MVN, even though the yields and selectivities for the formation of the 3-arylbutene were nearly perfect (>97%). Such phospholano ligands are known to exercise excellent control in

SCHEME 1. Synthesis of 2-Phospholano-2′-methoxy-1,1′-binaphthyl Ligands



SCHEME 2. Synthesis of 2-Diphenylphosphino-2′-alkoxy-3′-phenyl-1,1′-binaphthyl (5b and 5c)



other situations where alkene/P-cis intermediates are possible (see refs 3b and 3c). In keeping with the previous results, in the present context, a cis (alkene/P) transition state such as **F** (Figure 2) would be expected to give significant selectivity if such transition states were to be involved. The observation that there is no enantiocontrol by these phospholane ligands structurally similar to **MOP** provides some support for the lack of involvement of TS (e.g., **E** or **F**) in which the phosphorus and alkene are cis to each other.

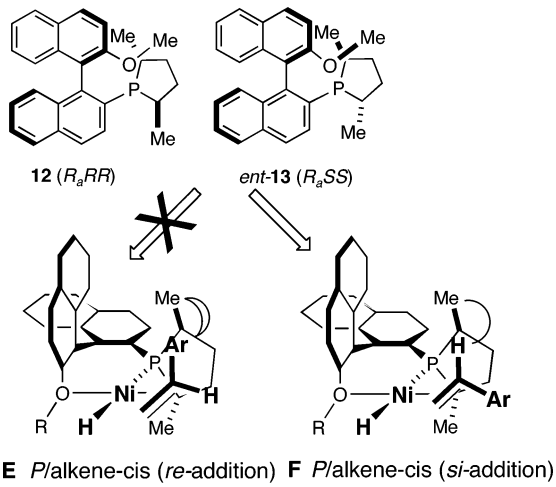


FIGURE 2. A model for asymmetric induction using phospholano−BINAP ligands.

As shown in Figure 1, the stereo-differentiating nickel hydride addition to the vinylarene takes place from the *re*-face (**B**) because, in the alternate *si*-face addition (**A**), there is an unfavorable interaction between the Ar group of the vinylarene and the 3′-substituent on the alkoxy−BINAP fragment. Thus if the aryl group avoids steric interactions with the 3′-substituent of the BINAP, a *re*-face addition (**B**) would be preferred, giving the (*S*)-3-arylbutene as the major product. Indeed, the major product from hydrovinylation using (*R*)-BINAP derivatives as ligands has the *S* configuration.[6] Additionally, this model correctly predicts the increase in enantioselectivity with an increase in the size of the vinyl substituent (phenyl, 25%; 4-isobutylphenyl, 40%; 6-methoxy-2-naphthyl, 62%) (eq 2). Conversely, an increase in the size of the BINAP-3′-substituent should also lead to better enantioselectivity. We have prepared 3′-substituted ligands **5b**, **5c**, **5d**, and **5e** to examine the effect of 3′-substitution on the reactivity and selectivity of the hydrovinylation reaction. The details of the synthesis and applications of these phosphines for asymmetric hydrovinylation of prototypical vinylarenes are reported in this paper.

Initially, the 3′-phenyl derivatives **5b** and **5c** were targeted, and the syntheses of these compounds are shown in Scheme 2. Thus the known 2,2′-bismethoxymethyl-1,1′-binaphthol **14** was subjected to directed metalation and iodination. Subsequent Suzuki coupling and exchange of the phenolic protecting group provided the bistriflate **16**. Palladium(0)-catalyzed cross-coupling with diphenylphosphineoxide[8] gave a monotriflate which was hydrolyzed to the phenolic phosphineoxide, **17**. Reaction of this phenol with appropriate alkylating agent (BnBr or MeI) followed by deoxygenation with trichlorosilane and triethylamine gave the ligands **5b** and **5c**.

Syntheses of the corresponding 3-methyl derivatives **5d** and **5e** were accomplished by a similar route, starting with **14**.

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SCHEME 3. Synthesis of 2-Diphenylphosphino-2′-alkoxy-3′-methyl-1,1′-binaphthyl (5d and 5e)

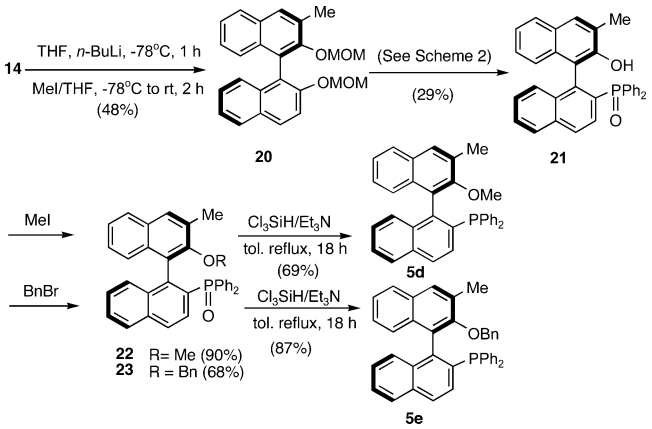

TABLE 1. Asymmetric Hydrovinylation of Vinylarenes[a]

entry	vinylarene[b]	ligand	temp (°C)	conv (%)	ee (%)[c]
1[d]	MVN	**5a**	−55	>98	62
2	MVN	**12**	−45	>99	17 (*R*)
3	MVN	**13**	−45	97	4 (*R*)
4	MVN	**5b**	−55	90	65
5	MVN	**5c**	−55	84	<5
6	MVN	**5d**	−55	>99	81
7	MVN	**5e**	−55	>98	75
8	IBS	**5a**	−55	93	40
9	IBS	**5b**	−30	70	13
10	IBS	**5c**	−55	91	<5
11	IBS	**5d**	−55	33	50
12	IBS	**5d**	−30	70	47
13	IBS	**5e**	−55	68	24
14	4-methylstyrene	**5c**	−55	75	<5
15	4-methylstyrene	**5d**	−55	75	60
16	4-methylstyrene	**5e**	−55	50	60

[a] See eq 2 for procedure. [b] MVN: 6-OMe-2-vinylnaphthalene; IBS 4-*i*-Bu-styrene. [c] Determined by HPLC or GC (refs 3b, 6a); see Supporting Information. [d] Data from ref 6b.

Monomethylation of **14** at the ortho position (Scheme 3) after directed metalation gave **20**, which was transformed into **21** using chemistry used for the synthesis of **17**. The phenol **21** was alkylated with either benzyl bromide (68%) or methyl iodide (90%) to get the corresponding phosphineoxides (**22** and **23**), which were deoxygenated with trichlorosilane as before to complete the synthesis of **5d** and **5e**.

Hydrovinylations of the prototypical substrate 6-methoxy-2-vinylnaphthalene (MVN) were examined using the newly synthesized ligands **5b**, **5c**, **5d**, **5e**, **12**, and **13** under our standard protocols,[6] and the results are shown in Table 1. No isomerization of the double bond to the more stable 2-arylbutenes, nor dimerization of the vinylarenes, two common side reactions under hydrovinylation conditions, were observed under these conditions. A careful examination of the results suggests that, as predicted by the models, the ligand **5d** with a methyl substituent at the 3′-position is clearly superior to the unsubstituted **MOP** ligand **5a**. The enantioselectivity for MVN at −55 °C using the unsubstituted **MOP** ligand was only 62% ee, while that using the 3′-methyl-substituted ligand **5d** is 81%, both giving nearly quantitative yields (entries 1 and 6). *This represents one of the highest overall yield and selectivity reported to date for this important substrate.* The 3′-phenyl **MOP** ligand (**5b**) gave 90% conversion and 65% ee (entry 4). Similar ligand with a 2′-benzyloxy substituent **5c** gave an acceptable conversion (84%) but very poor ee (<5%, entry 5). Presence of two sterically encumbering groups in the ortho position thus has a detrimental effect on the selectivity of the reaction. The corresponding benzyloxy ligand **5e** with a 3′-Me substituent also gave a high ee of 75%. The enantioselectivity for hydrovinylation of 4-isobutylstyrene using ligand **5d**, even at −30 °C, is superior (entry 12) to what is observed with the simple **MOP** ligand at −55 °C (entry 8). As in the case of MVN, the ligands **5b** and **5c** were found to be unsatisfactory for the hydrovinylation of this substrate. Note that surprisingly low selectivities were observed for all substrates using the 3-phenyl ligands, **5b**, and especially for **5c** (<5%). It is tempting to speculate that an optimum size for the 3′-group may be required for the best selectivity. For example, reducing the size of the 3′-substituent by switching to the methyl group in the 2′-benzyloxy ligand returns reasonable selectivity. For example, compare the benzyl ether ligands **5c** and **5e**: ee's for MVN, 4-isobutylstyrene, and 4-methylstyrene improve from <5% in each case to 75, 24, and 60%, respectively. Clearly, the Ph substituent is detrimental to selectivity when there is a bulky ether at position 2′.

Conclusion

Addition of a methyl group at the 3′-position of the well-known **MOP** ligand (2-diarylphosphino-2′-alkoxy-1,1′-binaphthyl) significantly improves the enantioselectivity of hydrovinylation of prototypical alkenes. Introduction of further chirality at the 2-position in structurally related BINAP−phospholane scaffolding has no effect on the enantioselectivity as shown by incorporation of the chiral 1-(2,5-dimethylphospholano) substituent at this position. These results are consistent with a model proposed for the asymmetric induction for this exacting reaction.

Experimental Section

Preparation of (*R*)-2,2′-Bis(methoxymethoxy)-3′-phenyl-1,1′-binaphthyl (15). To a suspension of $Pd(PPh_3)_4$ (0.095 g, 0.083 mmol) in anhydrous DME (5 mL) was added (*R*)-2,2′-bis-(methoxymethoxy)-3′-iodo-1,1′-binaphthyl (1.3 g 2.77 mmol).[9] The mixture was stirred for 10 min at room temperature. To this solution were added sequentially phenyl boronic acid (0.506 g, 4.15 mmol) in a minimum volume of EtOH (4 mL) and aq Na_2CO_3 (2 M solution), and the mixture was refluxed for 18 h, cooled, and subjected to filtration. The filtrate was evaporated to dryness and dissolved into ethyl acetate (50 mL) and washed with brine (1 × 10 mL) and water (1 × 10 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (elution with hexane/EtOAc, 9/1) to afford the title compound in 82% yield (1.02 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.95−7.87 (m, 3H), 7.70 (d, J = 7.88 Hz, 1H), 7.58 (d, J = 9.06 Hz, 1H), 7.43−7.33 (m, 5H), 7.27−7.20 (m, 5H), 5.16 (d, J = 6.86 Hz, 1H), 5.05 (d, J = 6.87 Hz, 1H), 4.33 (d, J = 5.81 Hz, 1H), 4.27 (d, J = 5.82 Hz, 1H), 3.20 (s, 3H), 2.27 (s, 3H). IR (KBr): ν 1620, 1593, 1507, 1468, 1424, 1390, 1354, 1332, 1296, 1260, 1238 (C−O), 1139, 1152, 1071, 1033 (C−O), 1010, 985, 963, 922, 900, 802, 755, and 697 cm^{-1}. The high-resolution mass for the corresponding deprotected derivative (a bisphenol) is reported in the next experiment.

Preparation of (*R*)-2,2′-Bis(hydroxy)-3′-phenyl-1,1′-binaphthyl. A mixture of (*R*)-2,2′-bis(methoxymethoxy)-3′-phenyl-1,1′-binaphthyl (**15**, 0.6 g, 1.33 mmol), 25 mL of aq HCl (6 N) in THF (75 mL), and isopropanol (25 mL) was stirred at room temperature

(9) For a recent comprehensive review of BINAP derivatives, see: Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.* **2005**, *105*, 1801.

overnight. The solvents were removed, and the crude residue was extracted with CH_2Cl_2 (2 × 25 mL). The solvent was collected together and dried over $MgSO_4$, evaporated, and purified through column chromatography (elution with hexane/EtOAc, 4/1) to afford the title compound in 83% yield (0.4 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.00−7.87 (m, 4H), 7.73−7.69 (m, 2H), 7.50−7.23 (m, 9H), 7.14 (d, J = 8.25 Hz, 1H), 5.26 (s, 1H), 5.09 (s, 1H). IR (KBr): ν 3421, 3437, 1618, 1599, 1502, 1424, 1302, 1334, 1315, 1269, 1240, 1182, 1128, 963, 810, 782, 750, 702, and 495 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{18}O_2Na^+$: 385.1198. Found: 385.1195.

Preparation of (*R*)-2,2′-Bis[(trifluromethanesulfonyl)oxy]-3′-phenyl-1,1′-binaphthyl (16). To a solution of (*R*)-2,2′-bis(hydroxy)-3′-phenyl-1,1′-binaphthyl (0.4 g, 1.09 mmol) and pyridine (0.43 mL, 2.59 mmol) in CH_2Cl_2 (5 mL) was added triflic anhydride (0.26 mL, 3.22 mmol) at 0 °C, and the mixture was stirred for 12 h. After removal of solvent, the residue was diluted with 25 mL of EtOAc and washed with 5% aq HCl, saturated $NaHCO_3$, and brine (1 × 10 mL for each). The organic layer was dried and concentrated under reduced pressure. The residue was purified via column chromatography (elution with CH_2Cl_2/hexane, 7/3) to afford the title compound in 87% yield (0.59 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.05−7.98 (m, 2H), 7.88 (d, J = 8.25 Hz, 2H), 7.53−7.23 (m, 10H), 7.15−7.08 (m, 2H). IR (KBr): ν 1507, 1419, 1211, 1135, 1067, 939, 851, 831, 808, 776, 748, 700, 675, 627, 602, and 494 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{28}H_{16}F_6O_6S_2Na^+$: 649.0184. Found: 649.0193.

Preparation of (*R*)-2-(Diphenylphosphinyl)-2′-[(trifluromethanesulfonyl)oxy]-3′-phenyl-1,1′-binaphthyl. To a mixture of (*R*)-2,2′-bis[(trifluromethanesulfonyl)oxy]-3′-phenyl-1,1′-binaphthyl (0.37 g, 0.59 mmol), diphenylphosphineoxide (0.24 g, 1.18 mmol), Pd(OAc)$_2$ (0.007 g, 0.03 mmol), and dppb (0.013 g, 0.03 mmol) were added dry DMSO (3 mL) and diisopropyl ethyl amine (0.4 mL, 2.35 mmol). The mixture was heated with stirring for 14 h at 100 °C. Then the reaction mixture was cooled to room temperature and diluted with EtOAc and washed twice with water. The organic layer was dried and concentrated. The residue was purified by column chromatography (elution with hexane/EtOAc, 3/2) to afford the title compound in 59% yield (0.234 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.99−7.97 (m, 1H), 7.92 (d, J = 8.40 Hz, 1H), 7.86 (s, 1H), 7.77 (d, J = 8 Hz, 1H), 7.73−7.68 (m, 2H), 7.60−7.53 (m, 4H), 7.48−7.29 (m, 11H), 7.22−7.20 (m, 1H), 7.11−7.05 (m, 3H), 6.85 (d, J = 8 Hz, 1H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ 27.90. IR (KBr): ν 1497, 1435, 1411, 1202, 1133, 969, 937, 851, 814, 779, 744, 723, 701, 624, 592, 541, 519, and 495 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{39}H_{26}F_3O_4PSNa^+$: 701.1133. Found: 701.1122.

Preparation of (*R*)-2-(Diphenylphosphinyl)-2′-hydroxy-3′-phenyl-1,1′-binaphthyl (17). To a solution of (*R*)-2-(diphenylphosphinyl)-2′-[(trifluromethanesulfonyl)oxy]-3′-phenyl-1,1′-binaphthyl (0.33 g, 0.49 mmol) in 1,4-dioxane (2 mL) and MeOH (1 mL) was added aq NaOH solution (3 N) (0.5 mL) at room temperature. The reaction mixture was stirred for 12 h and acidified (pH = 1) by addition of concentrated HCl and then extracted twice with EtOAc. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the title compound in 69% yield (0.18 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (s, 1H), 7.92−7.87 (m, 4H), 7.80 (d, J = 7.61 Hz, 2H), 7.64 (s, 1H), 7.58−7.33 (m, 9H), 7.27−7.22 (m, 3H), 7.10 (t, J = 7.60 Hz, 1H), 6.91 (t, J = 8.4 Hz, 1H), 6.81 (t, J = 7.60 Hz, 1H), 6.73−6.68 (m, 2H), 6.43 (d, J = 8.40 Hz, 1H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ 31.09. IR (KBr): ν 3050, 1587, 1533, 1495, 1435, 1383, 1249, 1151, 1111, 816, 747, 721, 6098, 549, and 526 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{38}H_{27}O_2PNa^+$: 569.1640. Found: 569.1619.

Preparation of (*R*)-2-(Diphenylphosphinyl)-2′-methoxy-3′-phenyl-1,1′-binaphthyl (18). To a mixture of (*R*)-3-phenyl-2′-(diphenylphosphinyl)-2′-hydroxy-1,1′-binaphthyl (0.18 g, 0.33 mmol) and K_2CO_3 (0.19 g, 1.41 mmol) in acetone (2 mL) was added MeI (0.2 g, 1.41 mmol). The mixture was refluxed for 6 h. After being cooled to room temperature, the mixture was filtered through Celite and the solid was washed with Et_2O. The combined organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (elution with hexane/EtOAc, 1/9) to afford the title compound in 79% yield (0.14 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.99−7.90 (m, 3H), 7.66−7.36 (m, 12H), 7.26−6.95 (m, 10H), 6.76 (d, J = 8.48 Hz, 1H), 2.96 (s, 3H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ 29.70. IR (KBr): ν 1496, 1459, 1435, 1403, 1382, 1348, 1247 (C−O), 1197, 1107, 1067, 1038, 1017, 748, 716, 697, 644, 589, 541, and 517 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{39}H_{29}O_2PNa^+$: 583.1797. Found: 583.1763.

Preparation of (*R*)-2-(Diphenylphosphino)-2′-methoxy-3′-phenyl-1,1′-binaphthyl (5b). To a mixture of (*R*)-2-(diphenylphosphinyl)-2′-methoxy-3′-phenyl-1,1′-binaphthyl (0.1 g, 0.18 mmol) and Et_3N (0.54 mL, 3.56 mmol in dry toluene (4.5 mL)) was added trichlorosilane (0.1 mL, 0.89 mmol) at 0 °C. The reaction mixture was refluxed for 18 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with small amount of aq $NaHCO_3$. The resulting suspension was filtered through Celite, and the solid was washed with Et_2O. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by column chromatography using Et_2O to afford the title compound in 98% yield (0.095 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (s, 1H), 7.88−7.84 (m, 3H), 7.62 (d, J = 7.35 Hz, 2H), 7.49 (d, J = 2.69 Hz, 1H), 7.46 (d, J = 2.40 Hz, 1H), 7.40−7.26 (m, 12H), 7.16−6.99 (m, 6H), 6.83 (d, J = 8 Hz, 1H), 2.92 (s, 3H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ −12.42. IR (KBr): ν 1492, 1435, 1402, 1301, 1250 (C−O), 1200, 1716, 1116, 1015, 746, 720, and 699 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{39}H_{29}O_2PNa^+$: 583.1797. Found: 583.1793.

Preparation of (*R*)-2,2′-Bis(methoxymethoxy)-3′-methyl-1,1′-binaphthyl (20). (*R*)-2,2′-Bis(methoxymethoxy)-1,1′-binaphthyl (**14**, 1.11 g, 2.98 mmol) was dissolved into THF (10 mL) under N_2 and cooled to −78 °C. To this solution was added *t*-BuLi (1.7 M in pentane, 3.85 mL, 6.55 mmol) slowly, and the mixture was stirred at the same temperature for 1 h, and methyl iodide (0.8 mL, 13.02 mmol) in THF (10 mL) was added dropwise to the reaction mixture. The reaction mixture was allowed to room temperature and stirred for another 1 h and quenched with aq NH_4Cl. The whole mixture was extracted with EtOAc (2 × 25 mL), solvent was removed under reduced pressure, and the residue was purified by column chromatography (elution with hexane/EtOAc, 19/1 to 6/1) to afford the title compound in 48% yield (0.56 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 9.04 Hz, 1H), 7.78 (d, J = 8.10 Hz, 1H), 7.72 (d, J = 8.73 Hz, 2H), 7.50 (d, J = 9.05 Hz, 1H), 7.27 (t, J = 7.94 Hz, 2H), 7.20−7.07 (m, 4H), 5.04 (d, J = 6.91 Hz, 1H), 4.94 (d, J = 6.91 Hz, 1H), 4.56 (d, J = 5.56 Hz, 1H), 4.48 (d, J = 5.57 Hz, 1H), 3.06 (s, 3H), 2.82 (s, 3H), 2.50 (s, 3H). IR (KBr): ν 1614, 1594, 1505, 1462, 1429, 1378, 1355, 1330, 1256, 1234 (C−O), 1201, 1144, 1094, 1083, 1058, 1027, 1015, 957, 802, and 749 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{25}H_{24}O_4Na^+$: 411.1566. Found: 411.1570.

Preparation of (*R*)-2,2′-Bis(hydroxy)-3′-methyl-1,1′-binaphthyl. A mixture of (*R*)-2,2′-bis(methoxymethoxy)-3′-methyl-1,1′-binaphthyl (0.92 g, 2.37 mmol), 50 mL of aq HCl (6 N) in THF (147 mL), and isopropanol (50 mL) was stirred at room temperature overnight. The solvents were removed, and the crude residue was extracted with CH_2Cl_2 (2 × 50 mL). The solvent was collected together and dried over $MgSO_4$, evaporated, and purified through column chromatography (elution with hexane/EtOAc, 4/1) to afford the title compound in 84% yield (0.6 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.85 (d, J = 9.0 Hz, 1H), 7.79−7.68 (m, 3H), 7.28−6.95 (m, 7H), 4.99 (s, 1H), 4.92 (s, 1H), 2.40 (s, 3H). IR (KBr): ν 3500, 3446, 1616, 1591, 1505, 1462, 1300, 1312, 1215, 1187, 1147, 1129, 1094, 1047, 810, and 750 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{21}H_{16}O_2Na^+$: 323.1042. Found: 323.1032.

Preparation of (*R*)-2,2′-Bis[(triflurometh anesulfonyl)oxy]-3′-methyl-1,1′-binaphthyl. To a solution of (*R*)-2,2′-bis(hydroxy)-3′-methyl-1,1′-binaphthyl (0.58 g, 1.92 mmol) and pyridine (0.46 mL, 5.7 mmol) in CH_2Cl_2 (10 mL) was added triflic anhydride (0.77 mL, 4.6 mmol) at 0 °C, and the mixture was stirred for 12 h. After removal of solvent, the residue was diluted with 40 mL of EtOAc and washed with 5% aq HCl, saturated $NaHCO_3$, and brine (1 × 15 mL for each). The organic layer was dried and concentrated under reduced pressure. The residue was purified via column chromatography (elution with CH_2Cl_2/hexane, 7/3) to afford the title compound in 76% yield (0.82 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.10 (d, J = 9.0 Hz, 1H), 7.99 (s, 1H), 7.96 (s, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.60−7.25 (m, 6H), 7.10 (d, J = 8.5 Hz, 1H), 2.65 (s, 3H). IR (KBr): ν 1508, 1415, 1214, 1136, 1075, 1045, 937, 886, 820, 748, 628, and 490 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{23}H_{14}F_6O_6S_2Na^+$: 587.0028. Found: 587.0015.

Preparation of (*R*)-2-(Diphenylphosphinyl)-2′-[(triflurometh anesulfonyl)oxy]-3′-methyl-1,1′-binaphthyl. To a mixture of (*R*)-2,2′-bis[(triflurometh anesulfonyl)oxy]-3′-methyl-1,1′-binaphthyl (0.74 g 1.3 mmol), diphenylphosphineoxide (0.52 g, 2.6 mmol), $Pd(OAc)_2$ (0.02 g, 0.098 mmol), and dppb (0.04 g, 0.098 mmol) were added dry DMSO (5.5 mL) and diisopropyl ethyl amine (0.89 mL). The mixture was heated with stirring for 14 h at 100 °C. Then the reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL), and washed twice with water (2 × 2 mL). The organic layer was dried and concentrated. The residue was purified by column chromatography (elution with hexane/EtOAc, 3/2) to afford the title compound in 59% yield (0.47 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.93−7.83 (m, 2H), 7.67−6.95 (m, 18H), 6.78 (d, J = 12.8 Hz, 1H), 2.41 (s, 3H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ 27.8. HRMS (ESI) *m*/*z* calcd for $C_{34}H_{24}F_3O_4PSNa^+$: 639.0977. Found 639.0958.

Preparation of (*R*)-2-(Diphenylphosphinyl)-2′-hydroxy-3′-methyl-1,1′-binaphthyl (21). To a solution of (*R*)-2-(diphenylphosphinyl)-2′-[(triflurometh anesulfonyl)oxy]-3′-methyl-1,1′-binaphthyl (0.115 g, 0.186 mmol) in 1,4-dioxane (0.6 mL) and MeOH (0.3 mL) was added aq NaOH solution (3 N) (0.2 mL) at room temperature. The reaction mixture was stirred for 12 h and acidified (pH = 1) by the addition of concentrated HCl and then extracted twice with EtOAc (2 × 5 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the title compound in 78% yield (0.07 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92−7.87 (m, 4H), 7.58−7.48 (m, 4H), 7.44 (s, 1H), 7.39−7.34 (m, 2H), 7.22−7.12 (m, 5H), 7.04 (t, J = 7.2 Hz, 1H), 6.85−6.77 (m, 2H), 6.70−6.65 (m, 2H), 6.36 (d, J = 8.4 Hz, 1H), 2.52 (s, 3H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ 30.70. IR (KBr): ν 2912, 1533, 1500, 1438, 1385, 1352, 1237, 1152, 1113, 998, 939, 815, 744, 720, 697, 655, 632, 540, 525, and 519 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{33}H_{25}O_2PNa^+$: 507.1484. Found: 507.1490.

Preparation of (*R*)-2-(Diphenylphosphinyl)-2′-methoxy-3′-methyl-1,1′-binaphthyl (22). To a mixture of (*R*)-3′-methyl-2-(diphenylphosphinyl)-2′-hydroxy-1,1′-binaphthyl (0.065 g, 0.134 mmol) and K_2CO_3 (0.08 g, 0.58 mmol) in acetone (1 mL) was added MeI (0.082 g, 0.58 mmol). The mixture was refluxed for 6 h. After being cooled to room temperature, the mixture was filtered through Celite and the solid was washed with Et_2O. The combined organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (elution with hexane/EtOAc, 1/9) to afford the title compound in 90% yield (0.06 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.96−7.85 (m, 3H), 7.54−7.02 (m, 16H), 7.02−6.88 (m, 1H), 6.73 (d, J = 8.25 Hz, 1H), 3.30 (s, 3H), 2.30 (s, 3H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ 28.95. IR (KBr): ν 1503, 1437, 1383, 1242 (C−O), 1173, 1158, 1116, 1104, 1009, 817, 748, 724, 697, 634, 544, 526, and 505 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{34}H_{27}O_2PNa^+$: 521.1640. Found 521.1637.

Preparation of (*R*)-2-(Diphenylphosphino)-2′-methoxy-3′-methyl-1,1′-binaphthyl (5d). To a mixture of (*R*)-2-(diphenylphosphinyl)-2′-methoxy-3′-methyl-1,1′-binaphthyl (0.06 g, 0.12 mmol) and Et_3N (0.334 mL, 2.40 mmol) in dry toluene (3 mL) was added trichlorosilane (0.06 mL, 0.53 mmol) at 0 °C. The reaction mixture was refluxed for 18 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with small amount of aq $NaHCO_3$. The resulting suspension was filtered through Celite, and the solid was washed with Et_2O. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by column chromatography (elution with hexane/Et_2O, 1/4) to afford the title compound in 69% yield (0.04 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.84 (d, J = 8.5 Hz, 2H), 7.75 (s, 1H), 7.70 (d, J = 8.25 Hz, 1H), 7.49 (d, J = 2.75 Hz, 1H), 7.46−7.43 (m, 1H), 7.26−7.0 (m, 13H), 6.87−6.79 (m, 1H), 6.64 (d, J = 7.5 Hz, 1H), 3.26 (s, 3H), 2.48 (s, 3H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ −13.33. IR (KBr): ν 1498, 1431, 1404, 1302, 1351, 1238 (C−O), 1099, 1005, 813, 741, 696, 515, and 489 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{34}H_{27}O_2PNa^+$: 521.1640. Found: 521.1623.

Preparation of (*R*)-2-(Diphenylphosphinyl)-2′-benzyloxy-3′-methyl-1,1′-binaphthyl (23). To a mixture of (*R*)-3′-methyl-2-(diphenylphosphinyl)-2-hydroxy-1,1′-binaphthyl (0.13 g, 0.27 mmol) and K_2CO_3 (0.15 g, 1.07 mmol) in acetone (4 mL) was added benzyl bromide (0.182 g, 1.07 mmol). The mixture was refluxed for 6 h. After being cooled to room temperature, the mixture was filtered through Celite and the solid was washed with Et_2O. The combined organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (elution with hexane/EtOAc, 1/9) to afford the title compound in 68% yield (0.105 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98−7.88 (m, 3H), 7.56−7.41 (m, 5H), 7.29−6.99 (m, 13H), 6.87−6.84 (m, 3H), 6.69 (d, J = 6.8 Hz, 2H), 4.70 (d, J = 10.8 Hz, 1H), 4.23 (d, J = 10.8 Hz, 1H), 2.35 (s, 3H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ 30.12. IR (KBr): ν 3410, 3041, 2940, 1618, 1590, 1552, 1499, 1482, 1436, 1419, 1384, 1370, 1238, 1200, 1146, 1114, 1100, 1049, 1027, 981, 878, 822, 746, 721, 696, 657, and 637 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{40}H_{31}O_2PNa^+$: 597.1959. Found 597.1959.

Preparation of (*R*)-2-(Diphenylphosphino)-2′-methoxy-3′-methyl-1,1′-binaphthyl (5e). To a mixture of (*R*)-2-(diphenylphosphinyl)-2′-benzyloxy-3′-methyl-1,1′-binaphthyl (0.085 g, 0.147 mmol) and Et_3N (0.445 mL, 2.94 mmol) in dry toluene (4.5 mL) was added trichlorosilane (0.085 mL, 0.735 mmol) at 0 °C. The reaction mixture was refluxed for 18 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with small amount of aq $NaHCO_3$. The resulting suspension was filtered through Celite, and the solid was washed with Et_2O. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by column chromatography (elution with hexane/Et_2O, 1/4) to afford the title compound in 87% yield (0.072 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 8.4 Hz, 2H), 7.82 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.49−7.46 (m, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.29−7.00 (m, 15H), 6.92 (t, J = 8.4 Hz, 1H), 6.8 (d, J = 8.4 Hz, 1H), 6.63 (d, J = 7.2 Hz, 2H), 4.61 (d, J = 10.8 Hz, 1H), 4.28 (d, J = 10.8 Hz, 1H), 2.53 (s, 3 H). ^{31}P NMR ($CDCl_3$, 101.25 MHz): δ −13.26. IR (KBr): ν 1580, 1493, 1472, 1429, 1381, 1347, 1312, 1239, 1213, 1183, 1166, 1144, 1097, 1045, 1024, 994, 929, 907, 886, 864, 856, 817, 748, and 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{40}H_{32}OP^+$ (M + H): 559.2191. Found: 559.2191.

Asymmetric Hydrovinylation Reactions of Vinyl Arenes. General Procedure for Asymmetric Hydrovinylation Reaction of Vinylarenes Using [(Allyl)NiBr]$_2$ and Ligand (5b−5e, 12, and 13) in the Presence of NaBARF in CH_2Cl_2. To a solution of [(allyl)NiBr]$_2$ in CH_2Cl_2 (1.5 mL) at room temperature was added a solution of ligand in CH_2Cl_2 (1.5 mL) in drybox. The resulting solution was added to a suspension of NaBARF in CH_2Cl_2 (1 mL). After stirring at room temperature for 1.5 h, the mixture was filtered through a small plug of Celite and the precipitate was rinsed with CH_2Cl_2 (1 mL). The filtrate was collected in a Schlenk flask and was taken out of the drybox. The catalyst solution was cooled to the designated temperature in the table. Under 1 atm of ethylene,

the solution of vinylarenes in CH_2Cl_2 (3 mL) was added dropwise to the catalyst solution. After stirring for 3 h at this temperature, the mixture was quenched with saturated aq NH_4Cl solution and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and passed through a small plug of silica gel. The filtrate was concentrated to afford the crude products which were analyzed by GC. The enantiomeric excess of the alkene products was determined by HPLC on a Daicel Chiralcel OJ column using a hexane/isopropanol mixture as solvent or Chiral GC using a cyclodex-B column. See refs 3b, 4, and 6 for chromatographic separation of the enantiomers of the hydrovinylation products.

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Supporting Information Available: General experimental methods, full experimental details of synthesis of ligands **12** and **13**, ^{1}H and ^{13}P spectra for key intermediates and ligands listed. This material is available free of charge via the Internet at http://pubs.acs.org.

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