# Derivatives of 2-Amino-2′-diphenylphosphino-1,1′-binaphthyl (MAP) and Their Application in Asymmetric Palladium(0)-Catalyzed Allylic Substitution†

Štěpán Vyskočil,*[,‡,§] Martin Smrčina,[‡] Vladimír Hanuš,[||] Miroslav Polášek,[||] and Pavel Kočovský*[,§,⊥]

*Department of Organic Chemistry, Charles University, 128 40, Prague 2, Czech Republic, Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K., and J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic*

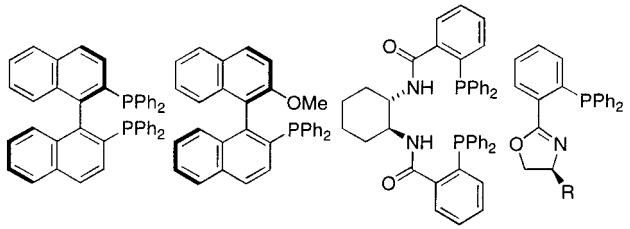
*Received April 21, 1998*

(*R*)-(+)-2-Amino-2′-hydroxy-1,1′-binaphthyl (NOBIN, **5**) can be readily converted into a series of novel *N*,*N*-disubstituted aminophosphines **9** and **23**−**25**. The *N*,*N*-dimethyl derivative (*R*)-**9** (MAP) was prepared via a sequence involving reductive alkylation with $CH_2O$ and $NaBH_4$ (**5** → **6**), Pd(0)-catalyzed coupling of the corresponding triflate with $Ph_2P(O)H$ (**7** → **8**), and reduction of the resulting phosphine oxide with $Cl_3SiH$ (**8** → **9**). Variation of this scheme was required for the preparation of **23**−**25** as the phosphinylation failed in the presence of bulky *N* substituents; the *N*-protected triflate **17** was first coupled with $Ph_2P(O)H$, and the resulting phosphine oxide **18** was reduced with $Cl_3SiH$ to give the aminophosphine **19**, which was then subjected to reductive alkylation with individual ketones and $NaBH_4$. The new *P*,*N*-binaphthyls thus obtained (**23**−**25** and **9**) were utilized as chiral ligands in Pd(0)-catalyzed allylic substitution. The enantioselectivites obtained for racemic 1,3-diphenylprop-2-en-1-yl acetate (±)-**26** and malonate nucleophiles, which gave (*S*)-(−)-**28**, (*R*)-(+)-**29**, and (*R*)-(+)-**30** as the respective products (in up to 71−73% ee at room temperature with $Cs_2CO_3$ in $CH_2Cl_2$ and **9** or **23** as a ligand), are interpreted in terms of the chelated transition state **37** and preferential attack at the allylic terminus that is trans with respect to the phosphorus acceptor atom.

## Introduction

Chiral phosphines are ligands par excellence in asymmetric catalysis,[1] and among them, the prime role is played by those possessing the binaphthyl scaffold.[1,2] Both $C_2$-symmetrical (e.g., Noyori's BINAP[3]) and unsymmetrical (e.g., Hayashi's MOP[4]) representatives of this class (Chart 1) often give levels of asymmetric induction previously reserved to enzymes. Thus, for instance, the bidentate diphosphine ligand BINAP (**1**) has been utilized in Rh(I)- or Ru(I)-catalyzed asymmetric hydrogenation,[5] double bond isomerization,[6] Heck addition (both inter-[7] and intramolecular[8]), and numerous other reactions.[1,3]

**Chart 1**




**1** **2** **3** **4**

The monophosphine MOP (**2**) has been found to be the ligand of choice in Pd(0)-catalyzed hydrosilylations[4,9] and in Pd(0)-catalyzed reduction of allylic esters with formic acid.[4,10]

† In memoriam Miroslav Protiva.
‡ Charles University.
§ University of Leicester.
|| J. Heyrovský Institute.
⊥ E-mail: PK10@Le.ac.uk.

(1) (a) Morrison, J. D. *Asymmetric Synthesis*; Academic Press: New York, 1983−1985; Vols. 1−5. (b) Kočovský, P.; Tureček, F.; Hájíček, J. *Synthesis of Natural Products: Problems of Stereoselectivity*; CRC Press: Boca Raton, FL, 1986; Vols. 1 and 2. (c) Nogrady, M. *Stereoselective Synthesis*; VCH: Weinheim, 1987. (d) Ojima, I. *Asymmetric Catalysis*; VCH: New York, 1993. (e) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley & Sons: New York, 1994. (f) Dawson, G. J.; Bower, J. F.; Williams, J. M. J. *Contemp. Org. Synth.* **1996**, *3*, 277. (g) Tonks, L.; Williams, J. M. J. *Contemp. Org. Synth.* **1997**, *4*, 353.

(2) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503.

(3) (a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. (b) Miyashita, A.; Takaya, H.; Souchi, T.; Noyori, R. *Tetrahedron* **1984**, *40*, 1245. (c) Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* **1986**, *51*, 629. (d) Takaya, H.; Akutagawa, S.; Noyori, R. *Org. Synth.* **1988**, *67*, 20. (e) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345.

(4) (a) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887. (b) For a review, see: Hayashi, T. *Acta Chem. Scand.* **1996**, *50*, 259.

(5) Olefines: (a) Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. *J. Org. Chem.* **1987**, *52*, 3174. (b) Kawano, H.; Ikariya, T.; Ishii, Y.; Saburi, M.; Yoshikawa, S.; Uchida, Y.; Kumobayashi, H. *J. Chem. Soc., Perkin Trans.* **1989**, 1571. (c) Noyori, R.; Ikeda, T.; Ohkuma, T.; Widhalm, M.; Kitamura, M.; Takaya, H.; Akutagawa, S.; Sayo, N.; Saito, T.; Taketomi, T.; Kumobayashi, H. *J. Am. Chem. Soc.* **1989**, *111*, 9134. (d) Noyori, R.; Ohta, M.; Hsiao, Y.; Kitamura, M.; Ohta, T.; Takaya, H. *J. Am. Chem. Soc.* **1986**, *108*, 7117. Ketones: (e) Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1987**, *109*, 5856. (f) Kitamura, M.; Ohkuma, T.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1988**, *29*, 1555.

(6) (a) Tani, K.; Yamagata, T.; Otsuka, S.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R. *J. Chem. Soc., Chem. Commun.* **1982**, 600. (b) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208.

(7) (a) Ozawa, F.; Kubo, A.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 1417. (b) Ozawa, F.; Kubo, A.; Hayashi, T. *Tetrahedron Lett.* **1992**, *33*, 1485. (c) Hayashi, T.; Uozumi, Y. *Pure Appl. Chem.* **1992**, *64*, 1911.

(8) Sato, Y.; Watanabe, S.; Shibasaki, M. *Tetrahedron Lett.* **1992**, *33*, 2589. Sato, Y.; Honda, T.; Shibasaki, M. *Tetrahedron Lett.* **1992**, *33*, 2593.

10.1021/jo980757x CCC: $15.00 
Published on Web 10/16/1998

Despite the great success that the BINAP-type ligands have enjoyed over the years, less satisfactory or even poor results have been reported for their application in the Rh(I)-catalyzed asymmetric hydrosilylations of ketones,[11] Heck addition in certain instances,[12,13] and in several other cases.[1] One of the most important areas where BINAP and its congeners had generally failed to exhibit impressively high enantioselectivity is palladium(0)-catalyzed allylic substitution.[14] The first substantial progress here was made by Ito and Hayashi,[15] who designed bidentate, ferrocene-based diphosphine ligands equipped with a hydroxyl arm and demonstrated a relatively high asymmetric induction.[16] However, it was not until this decade got into full swing that the focused efforts by several groups brought a breakthrough into this long-standing problem. Notably, the bidentate phosphine ligands, derived from *trans*-1,2-diamino-cyclohexane (**3**) and related diamines, have been shown by Trost[17,18] to be very efficient in a number of examples, due to their unique, dome-type architecture, which controls the stereochemistry of the reaction primarily by steric effects. A conceptually different approach was based on the idea that a bidentate ligand with two electronically different ligating groups should encourage a preferential attack at one of the two termini of the $\pi$-allyl complex owing to the trans effect of the acceptor center relayed through the metal. While the present work was in progress, Pfaltz,[19] Helmchen,[20] and Williams[21] have independently introduced P,N ligands capable of chelation of Pd between a traditionally arylated phosphorus atom and an imine-type nitrogen contained in an oxazoline ring (**4**);[22,23] analogues, containing other heteroatoms in lieu of the phosphorus (S, Se, O, or N),[24] were reported subsequently. Several other types of ligands have more recently been reported to also exhibit

(9) Uozumi, Y.; Kitayama, K.; Hayashi, T.; Yanagi, K.; Fukuyo, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 713.

(10) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775.

(11) Zhang, X. Y.; Kumobayashi, H.; Takaya, H. *Tetrahedron: Asymmetry* **1994**, *5*, 1179.

(12) For a recent review on Heck addition, see: de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2379.

(13) Some of the low enantioselectivities reported in the earlier studies on Heck addition[12] are due to the use of aryl halides rather than triflates; for mechanistic rationale, see ref 7. Other effects can also take part, namely the in situ partial oxidation of BINAP by traces of water to the corresponding phosphine oxide, which gives low asymmetric induction, thereby distorting the overall picture. For mechanistic considerations, see ref 7 and the following: (a) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009. (b) Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc.* **1993**, *115*, 9531. (c) Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176.

(14) For overviews on Pd(0)-catalyzed allylic substitution, see: (a) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (b) Starý, I.; Zajíček, J.; Kočovský, P. *Tetrahedron* **1992**, *48*, 7229. (c) Williams, J. M. J. *Synlett* **1996**, 705. (d) Trost, B. M. *Acc. Chem. Res.* **1996**, *29*, 355.

(15) (a) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 191. For an overview, see: (b) Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857.

(16) Chiraphos gave a lower level of asymmetric induction than Ito's ligands: (a) Auburn, P. R.; MacKenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033. (b) MacKenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046. By contrast, ligands such as DIOP failed completely.[15a]

(17) Pd: (a) Trost, B. M.; Van Vranken, D. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 228. (b) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327. (c) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 4089. (d) Trost, B. M.; Breit, B.; Organ, M. M. *Tetrahedron Lett.* **1994**, *35*, 5817. (e) Trost, B. M.; Breit, B.; Peukert, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2386. (f) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 235. (g) Trost, B. M.; Bunt, R. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 99. (h) Trost, B. M.; Kirsche, M. J.; Radinov, R.; Zanoni, G. *J. Am. Chem. Soc.* **1996**, *118*, 6297. (i) Trost, B. M.; Krueger, A. C.; Bunt, R. C.; Zambrano, J. *J. Am. Chem. Soc.* **1996**, *118*, 6520. (j) Trost, B. M.; Madsen, R.; Guile, S. G.; Elia, A. E. H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1569. (k) Trost, B. M.; Radinov, R. *J. Am. Chem. Soc.* **1997**, *119*, 5962. (l) Trost, B. M.; Radinov, R.; Grenzer, E. M. *J. Am. Chem. Soc.* **1997**, *119*, 7879. (m) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1998**, *120*, 815. Mo: (n) Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104.

(18) (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Trost, B. M. *Science* **1991**, *254*, 1471. (c) Trost, B. M. *Pure Appl. Chem.* **1992**, *64*, 315. (d) Trost, B. M. *Pure Appl. Chem.* **1996**, *68*, 779. (e) Trost, B. M.; Marschner, C. *Bull. Soc. Chim. Fr.* **1977**, *134*, 263.

(19) Pd: (a) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. (b) von Matt, P.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T.; Helmchen, G. *Terahedron: Asymmetry* **1994**, *5*, 573. (c) Koch, G.; Lloyd-Jones, G. C.; Loiselleur, O.; Pfaltz, A.; Prétôt, R.; Schaffner, S.; Schneider, P.; von Matt, P. *Recueil Pays-Bas* **1995**, *114*, 206. (d) Pfaltz, A. *Acta Chim. Scand.* **1996**, *50*, 189. (e) Koch, G.; Pfaltz, A. *Tetrahedron: Asymmetry* **1996**, *7*, 2213. (f) Loiseleur, O.; Meier, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Eng.* **1996**, *35*, 200. (g) Loiseleur, O.; Hayashi, M.; Schmees, N.; Pfaltz, A. *Synthesis* **1997**, 1338. (h) Prétôt, R.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 323. W: (i) Lloyd-Jones, G. C.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 462. (j) Lloyd-Jones, G. C.; Pfaltz, A. *Z. Natuforsch. B* **1995**, *50*, 361. Ir: (k) Schnider, P.; Koch, G.; Prétôt, R.; Wang, G. Z.; Bohnen, F. M.; Kruger, C.; Pfaltz, A. *Chem.—Eur. J.* **1997**, *3*, 887. For a recent review, see: (l) Ghosh, A. K.; Mathiyanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1.

(20) Pd: (a) Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769. (b) Sprinz, J.; Kiefer, M.; Helmchen, G.; Huttner, G.; Walter, O.; Zsonai, L.; Reggelin, M. *Tetrahedron Lett.* **1994**, *35*, 1523. (c) Sennhenn, P.; Gabler, B.; Helmchen, G. *Tetrahedron Lett.* **1994**, *35*, 8595. (d) Rieck, H.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2687. (e) Peer, M.; Dejong, J. C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P. *Tetrahedron* **1996**, *52*, 7547. (f) Steinhagen, H.; Reggelin, M.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2108. Rh: (g) Langer, T.; Janssen, J.; Helmchen, G. *Tetrahedron: Asymmetry* **1996**, *7*, 1599. Cu: (h) Sagasser, I.; Helmchen, G. *Tetrahedron Lett.* **1998**, *39*, 261. For overviews, see: (i) Steinhagen, H.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2339. (j) Helmchen, G.; Kudis, S.; Sennhenn, P.; Steinhagen, H. *Pure Appl. Chem.* **1997**, *69*, 513. Ir: (k) Janssen, J. P.; Helmchen, G. *Tetrahedron Lett.* **1997**, *38*, 8025.

(21) Pd: (a) Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 2015. (b) Dawson, G. J.; Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 3149. (c) Jumnah, R.; Williams, J. M. J.; Williams, A. C. *Tetrahedron Lett.* **1993**, *34*, 6619. (d) Dawson, G. J.; Frost, C. G.; Martin, C. J.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 7793. (e) Allen, J. V.; Dawson, G. J.; Frost, C. G.; Williams, J. M. J.; Coote, S. J. *Tetrahedron* **1994**, *50*, 779. (f) Allen, J. V.; Coote, S. J.; Dawson, G. J.; Frost, C. G.; Martin, C. J.; Williams, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2065. (g) Allen, J. V.; Bower, J. F.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1994**, *5*, 1895. (h) Dawson, G. J.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1995**, *36*, 461. (i) Baldwin, I. C.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1995**, *6*, 679. (j) Jumnah, R.; Williams, A. C.; Williams, J. M. J. *Synlett* **1995**, 821. (k) Baldwin, I. C.; Williams, J. M. J.; Beckett, R. P. *Tetrahedron: Asymmetry* **1995**, *6*, 1515. (l) Dawson, G. J.; Williams, J. M. J.; Coote, S. J. *Tetrahedron: Asymmetry* **1995**, *6*, 2535. (m) Bower, J. F.; Williams, J. M. J. *Synlett* **1996**, 685. (n) Bower, J. F.; Jumnah, R.; Williams, A. C.; Williams, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1411. Rh: (o) Newman, L. M.; Williams, J. M. J.; McCague, R.; Potter, G. A. *Tetrahedron: Asymmetry* **1996**, *7*, 1597.

(22) Priority issue has little consequence in the case of phosphinoxazoline ligands **4**, for the first papers by each of these groups were submitted within the span of one month (in the chronological order indicated). However, Williams spelled out some of his ideas a year earlier in a review[14a] and was the most prolific member of this triumvirate.

(23) For the closely related P,N ligands with the nitrogen constituting part of an oxazine ring, see: Evans, P. A.; Brandt, T. A. *Tetrahedron Lett.* **1996**, *37*, 9143.

(24) S: Reference 20b,e and the following: (a) Frost, C. G.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1993**, *4*, 1785. (b) Morimoto, T.; Tachibana, K.; Achiwa, K. *Synlett* **1997**, 783. (c) Chelucci, G.; Berta, D.; Saba, A. *Tetrahedron* **1997**, *53*, 3843. Se: References 20b,e. (d) Chesney, A.; Bryce, M. R.; Chubb, R. W. J.; Batsanov, A. S.; Howard, J. A. K. *Tetrahedron: Asymmetry* **1997**, *8*, 2337. O: (e) Allen, J. V.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1994**, *5*, 277. Acetals: (f) Frost, C. G.; Williams, J. M. J. *Synlett* **1994**, 551. N: (g) Muller, D.; Umbricht, G.; Weber, B.; Pfaltz, A. *Helv. Chim. Acta* **1991**, *74*, 232. (h) von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rüegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265. (i) Zehnder, M.; Neuburger, M.; von Matt, P.; Pfaltz, A. *Acta Crystallogr., Sect. C* **1995**, *51*, 1109. (j) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339. (k) Nordstrom, K.; Macedo, E.; Moberg, C. *J. Org. Chem.* **1997**, *62*, 1604. (l) Hoarau, O.; Ait-Haddou, H.; Castro, M.; Balavoine, G. G. A. *Tetrahedron: Asymmetry* **1997**, *8*, 3755.

high enantioselectivity in at least one if not more cases of allylic substitution.[25−27]

A majority of these ligands are characterized by the phosphine moiety ($PAr_2$) adjacent to an aromatic ring that constitutes part of the scaffold. The synthesis of this class of compounds relies on the pioneering work of Noyori, who employed the lithiation of racemic 2,2′-dibromo-1,1′-binaphthyl with *t*-BuLi followed by addition of $Ph_2PCl$.[3a] Racemic BINAP (**1**) thus formed was then resolved via a complex with Pd(II) and an enantiopure amine.[3a] In a later version, the C−P bond was constructed by reaction of the corresponding Grignard reagent with $Ph_2P(O)Cl$, followed by reduction of the P−O bond with trichlorosilane.[3c,d] Recently, (*R*)-**1** was prepared by coupling of the enantiopure bistriflate derived from BINOL with $Ph_2PH$ or $Ph_2PCl$ in the presence of a Ni catalyst.[28] Another approach relies on the coupling of an aromatic triflate with $Ph_2P(O)H$ in the presence of a Pd(0) catalyst, followed by reduction of the resulting phosphine oxide with $Cl_3SiH$.[29] The latter method constitutes the key step in the synthesis of MOP (**2**).[30] 2-Diphenylphosphinobenzoic acid, required for the synthesis of **3**, was prepared by the reaction of *o*-chlorobenzoic acid with $Ph_2PNa$ or $Ph_2PLi$.[31] The key step in the preparation of phosphooxazolines **4** was the substitution of the fluorine in 2-fluorobenzonitrile by $Ph_2PK$.[19−21]

We have recently demonstrated that our binaphthyl derivative NOBIN (**5**), readily available by direct, Cu(II)-mediated oxidative coupling of 2-naphthol with 2-naphthylamine,[32] undergoes reductive *N*-alkylation with a variety of aldehydes and ketones to give the corresponding mono- or dialkylated amino alcohols.[33] Thus, treatment of NOBIN (**5**) with aqueous formaldehyde and $NaBH_4$ in the presence of $H_2SO_4$ afforded the *N*,*N*-dimethyl derivative **6** in 84% yield (Scheme 1). We envisaged that triflates, derived from **6** and its congeners, could undergo catalytic coupling with either $Ph_2P(O)H$ or $Ph_2PH$. If successful, this approach would access a series of binaphthyl-type phosphines, analogous to Hayashi's MOP (**2**), but having a nitrogen atom in place of oxygen.

Herein, we report on preparation of the aminophosphine **9** and its congeners **19**−**25** and their application in asymmetric, Pd(0)-catalyzed allylic substitution. For this new class of P,N-type binaphthyl ligands we propose the acronym MAP ("A" standing for "amino") in analogy to MOP.

(25) For P,$CO_2H$-type ligands, see: (a) Okada, Y.; Minami, T.; Sasaki, Y.; Umezu, Y.; Yamaguchi, M. *Tetrahedron Lett.* **1990**, *31*, 3905. (b) Okada, Y.; Minami, T.; Umezu, Y.; Nishikawa, S.; Mori, R.; Nakayama, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 667. (c) Knühl, G.; Sennhenn, P.; Helmchen, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1845.

(26) For bisaziridine ligands, see: (a) Tanner, D.; Andersson, P. G.; Harden, A.; Somfai, P. *Tetrahedron Lett.* **1994**, *35*, 4631. (b) Andersson, P. G.; Harden, A.; Tanner, D.; Nordby, P. O. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 12. (c) Andersson, P. G.; Harden, A.; Tanner, D.; Nordby, P. O. *Chem.—Eur. J.* **1995**, *1*, 12. For an overview, see: (d) Tanner, D.; Harden, A.; Johansson, F.; Wyatt, P.; Andersson, P. G. *Acta Chem. Scand.* **1996**, *50*, 361.

(27) Other ligands recently employed in Pd(0)-catalyzed allylic substitution are the following. Monophosphines: (a) Chen, Z. G.; Jiang, Q, Z.; Zhu, G. X.; Xiao, D. M.; Cao, P.; Guo, C.; Zhang, X. M. *J. Org. Chem.* **1997**, *62*, 4521. (b) Tye, H.; Smyth, D.; Eldred, C.; Wills, M. *Chem. Commun.* **1997**, 1053. Bisphosphines: (c) Yamaguchi, N.; Shima, T.; Yamagishi, T.; Hida, M. *Tetrahedron Lett.* **1990**, *31*, 5049. (d) Yamazaki, A.; Achiwa, K. *Tetrahedron: Asymmetry* **1995**, *6*, 51. Bisphosphines chiral at phosphorus: (e) Zhu, G.; Terry, M.; Zhang, X. *Tetrahedron Lett.* **1996**, *37*, 4475. (f) Nettekoven, U.; Widhalm, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1997**, *8*, 3185. Phosphinites: (g) Seebach, D.; Devaquet, E.; Ernst, A.; Hayakawa, M.; Kuhnle, F. N. M.; Schweizer, W. B.; Weber, B. *Helv. Chim. Acta* **1995**, *78*, 1636. P,N ligands with an $sp^2$ nitrogen: (h) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493. (i) Pregosin, P. S.; Salzmann, R.; Togni, A. *Organometallics* **1995**, *14*, 842. (j) Togni, A.; Bruckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. (k) Bruckhardt, U.; Gramlich, V.; Hofmann, P.; Nesper, R.; Pregosin, P. S.; Salzmann, R.; Togni, A. *Organometallics* **1996**, *15*, 3496. (l) Zhang, W.; Hirao, T.; Ikeda, I. *Tetrahedron Lett.* **1996**, *37*, 4545. (m) Burckhardt, U.; Baumann, M.; Togni, A. *Tetrahedron: Asymmetry* **1997**, *8*, 155. (n) Burckhardt, U.; Baumann, M.; Trabesinger, G.; Gramlich, V.; Togni, A. *Organometallics* **1997**, *16*, 5252. (o) Mino, T.; Imiya, W.; Yamashita, M. *Synlett* **1997**, 583. (p) Saitoh, A.; Morimoto, T.; Achiwa, K. *Tetrahedron: Asymmetry* **1977**, *8*, 3565. (q) Ahn, K. H.; Cho, C. W.; Park, J. W.; Lee, S. W. *Tetrahedron: Asymmetry* **1997**, *8*, 1179. (r) Brunel, J. M.; Constantieux, T.; Labande, A.; Lubatti, F.; Buono, G. *Tetrahedron Lett* **1997**, *38*, 5971. (s) Ahn, K. H.; Cho, C. W.; Park, J.; Lee, S. *Bull Korean Chem. Soc.* **1997**, *18*, 789. (t) Chelucci, G. *Tetrahedron: Asymmetry* **1997**, *8*, 2667. (u) Chelucci, G.; Medici, S.; Saba, A. *Tetrahedron: Asymmetry* **1997**, *8*, 3183. (v) Claridge, T. D. W.; Long, J. M.; Brown, J. M.; Hibbs, D.; Hursthouse, M. B. *Tetrahedron* **1997**, *53*, 4035. (w) Saitoh, A.; Achiwa, K.; Morimoto, T. *Tetrahedron: Asymmetry* **1998**, *9*, 741. (x) Saitoh, A.; Morimoto, T.; Achiwa, K. *Tetrahedron: Asymmetry* **1997**, *8*, 3567. (y) Gais, H.-J.; Eichelman, H.; Spalthoff, N.; Gerhards, F.; Frank, M.; Raabe, G. *Tetrahedron: Asymmetry* **1998**, *9*, 235. P,N ligands with an $sp^3$ nitrogen: (z) Brenchley, G.; Merifield, E.; Wills, M.; Fedouloff, M. *Tetrahedron Lett.* **1994**, *35*, 2791. (aa) Kubota, H.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 6689. (bb) Wimmer, P.; Widhalm, M. *Tetrahedron: Asymmetry* **1995**, *6*, 657. (cc) Hattori, T.; Komuro, Y.; Hayashizaka, N.; Takahashi, H.; Miyano, S. *Enantiomer* **1997**, *2*, 203. (dd) Bourghida, M.; Widhalm, M. *Tetrahedron: Asymmetry* **1998**, *9*, 1073. (ee) Vasconcelos, I. C. F.; Rath, N. P.; Spilling, C. D. *Tetrahedron: Asymmetry* **1998**, *9*, 937. N,N ligands: (ff) Imai, Y.; Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron Lett.* **1998**, *39*, 4343. (gg) Ogasawara, M.; Yoshida, K.; Kamei, H.; Kato, K.; Uozumi, Y.; Hayashi, T. *Tetrahedron: Asymmetry* **1998**, *9*, 1779. (hh) Imai, Y.; Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron Lett.* **1998**, *39*, 4343. (ii) Togni, A. *Tetrahedron: Asymmetry* **1991**, *2*, 683. (jj) Kubota, H.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1993**, *34*, 8135. (kk) Chelucci, G.; Gerard, A. P. B.; Saba, A. *Tetrahedron: Asymmetry* **1997**, *8*, 2571. (ll) Chelucci, G.; Pinna, G. A.; Saba, A. *Tetrahedron: Asymmetry* **1998**, *9*, 531. S,N ligands: (mm) Anderson, J. S.; James, D. S.; Mathias, J. P. *Tetrahedron: Asymmetry* **1998**, *9*, 753. For further examples, see ref 14a and the following overviews: (nn) Reiser, O. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 547. (oo) Moberg, C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 248. P,O ligand (isomer of MOP): (pp) Fuji, K.; Sakurai, M.; Kinoshita, T.; Kawabata, T. *Tetrahedron Lett.* **1998**, *39*, 6323. (qq) Fuji, K.; Sakurai, M.; Tohkai, N.; Kuroda, A.; Kawabata, T.; Fukazawa, Y.; Kinoshita, T.; Tada, T. *J. Chem. Soc., Chem. Commun.* **1996**, 1609.

(28) (a) Cai, D.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *J. Org. Chem.* **1994**, *59*, 7180. (b) Ager, D. J.; East, M. B.; Eisenstadt, A.; Laneman, S. A. *Chem. Commun.* **1997**, 2359.

(29) Kurz, L.; Lee, G.; Morgans, D., Jr.; Waldyke, M. J.; Wars, T. *Tetrahedron Lett.* **1990**, *31*, 6321.

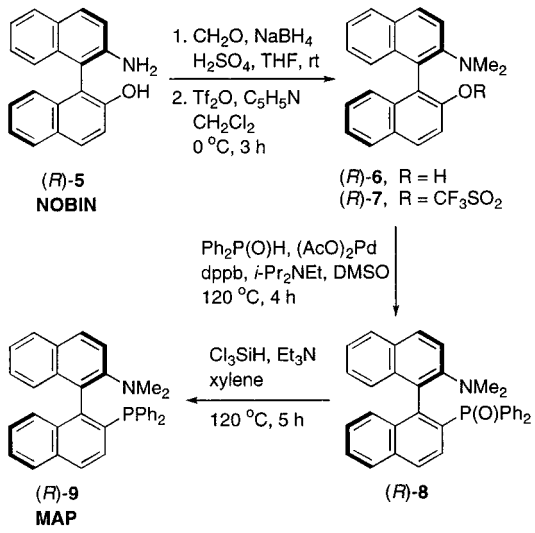
(30) (a) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945. (b) Uozumi, Y.; Suzuki, N.; Ogiwara, A.; Hayashi, T. *Tetrahedron* **1994**, *50*, 4293. (c) Hayashi, T.; Iwamura, H.; Uozumi, Y.; Matsumoto, Y.; Ozawa, F. *Synthesis* **1994**, 526.

(31) (a) Issleib, K.; Zimmerman, H. *Z. Allg. Chem.* **1967**, *353*, 197. (b) Hoots, J. E.; Rauchfuss, T. B.; Wrobleski, D. A. *Inorg. Synth.* **1982**, *21*, 175. (c) Wrobleski, D. A.; Rauchfuss, T. B.; Rheingold, A. L.; Lewis, K. A. *Inorg. Chem.* **1984**, *23*, 3124. (d) Refusco, F.; Tisato, F.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1993**, 2901. An alternative route to 2-diphenylphosphinobenzoic acid relies on the reaction of *o*-lithiated triphenylphosphine with $CO_2$: (e) Ravindar, V.; Hemling, H.; Schumann, H.; Blum, J. *Synth. Commun.* **1992**, *22*, 1453. Palladium-catalyzed coupling of ArBr with $Ph_2PH$ has also been used: (f) Herd, O.; Hessler, A.; Hingst, M.; Tepper, M.; Stelzer, O. *J. Organomet. Chem.* **1996**, *552*, 69.

(32) (a) Smrčina, M.; Lorenc, M.; Hanuš, V.; Kočovský, P. *Synlett* **1991**, 231. (b) Smrčina, M.; Lorenc, M.; Hanuš, V.; Sedmera, P.; Kočovský, P. *J. Org. Chem.* **1992**, *57*, 1917. (c) Smrčina, M.; Poláková, J.; Vyskočil, Š.; Kočovský, P. *J. Org. Chem.* **1993**, *58*, 4534. (d) Smrčina, M.; Vyskočil, Š.; Polívková, J.; Poláková, J.; Kočovský, P. *Collect. Czech. Chem. Commun.* **1996**, *61*, 1520. For the analogous Fe(III)-mediated coupling, see: (e) Ding, K.; Xu, Q.; Wang, Y.; Liu, J.; Yu, Z.; Du, B.; Wu, Y.; Koshima, Y.; Matsuura, T. *Chem. Commun.* **1997**, 693. (f) Vyskočil, Š.; Smrčina, M.; Hanuš, V.; Polášek, M.; Kočovský, P. *Chem. Commun.* **1998**, 585.

(33) (a) Smrčina, M.; Vyskočil, Š.; Polívková, J.; Poláková, J.; Sejbal, J.; Hanuš, V.; Polášek, M.; Verrier, H.; Kočovský, P. *Tetrahedron: Asymmetry* **1997**, *8*, 537. (b) Vyskočil, Š.; Jaracz, S.; Smrčina, M.; Štícha, M.; Hanuš, V.; Polášek, M.; Kočovský P. *J. Org. Chem.* **1998**, *63*, adjacent paper.

**Scheme 1**

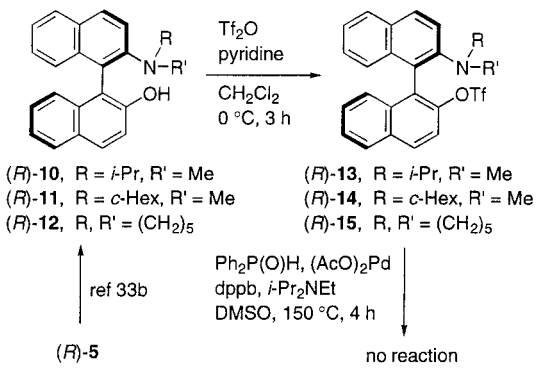



## Results and Discussion

**Synthesis of the Binaphthyl P,N Ligands.** Two methods have been reported for the conversion of aryl triflates into the corresponding aryl phosphines: (1) the Ni-catalyzed insertion of $Ph_2PH$[28] and (2) the Pd-catalyzed coupling with $Ph_2P(O)H$, followed by reduction.[29] To identify a protocol suitable to our system, we set out to investigate the reactivity of the triflate (*R*)-**7**, readily obtained from (*R*)-**6** in 96% yield (Scheme 1), as a prototype substrate. The reaction with $Ph_2PH$ in the presence of $NiCl_2$ and dppe failed under various conditions, and the starting triflate (*R*)-**7** was always recovered in high yield. The attempted Pd-catalyzed reaction of (*R*)-**7** with $Ph_2P(O)H$, carried out under the same conditions as those previously used for the synthesis of **2**,[29,30] also gave only the unreacted starting triflate. However, elevating the temperature (from 100 °C to 120 °C) led to the formation of the desired phosphine oxide (*R*)-**8** in 82% yield. Subsequent reduction of the latter product with trichlorosilane gave rise to the required aminophosphine (*R*)-**9** (**MAP**) in 86% isolated yield.

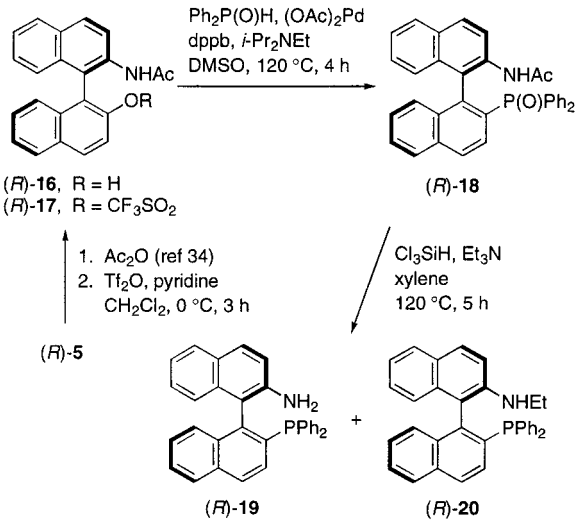
Preparation of analogues of the amino phosphine (*R*)-**9**, bearing bulkier N substituents, proved to be less straightforward. Thus, although the amino alcohols **10**−**12**, obtained via the reductive *N*-alkylation of (*R*)-**5** with the corresponding carbonyl compound, $NaBH_4$, and $H_2SO_4$ in THF−$H_2O$,[33b] were readily converted into the respective triflates **13**−**15** (Scheme 2), all attempts at their phosphinoylation failed even at a much higher temperature (150 °C), and the unreacted triflates were recovered in high yield. This lack of reactivity apparently reflects the further increased steric hindrance, which was already apparent in the case of the dimethylamino triflate (*R*)-**7** (compared to the less hindered bistriflate derived from BINOL). A change in the dihedral angle about the chiral axis may be another contributing factor.

**Scheme 2**




To mitigate the effects of steric hindrance, we changed the order of the reactions above, i.e., by first preparing the N-unsubstituted amino phosphine (*R*)-**19** and then introducing the bulky substituents onto its $NH_2$ group in the next step, using reductive alkylation[33b] (Scheme 3). Thus, the N-protected triflate (*R*)-**17** (91%) was first prepared from the hydroxy amide (*R*)-**16**,[33a] which in turn, was obtained by acetylation of NOBIN (*R*)-**5** in 95% yield.[34] Palladium(0)-catalyzed phosphinoylation of the triflate (*R*)-**17** proceeded smoothly at 120 °C, affording the *N*-acetylphosphine oxide (*R*)-**18** (84%), whose reduction with trichlorosilane produced amino phosphine (*R*)-**19** (75%) contaminated with a small amount of *N*-ethyl derivative **20** (8%), arising from the concomitant reduction of the carbonyl of the amide group. The latter byproduct was removed by flash chromatography on silica gel.

**Scheme 3**



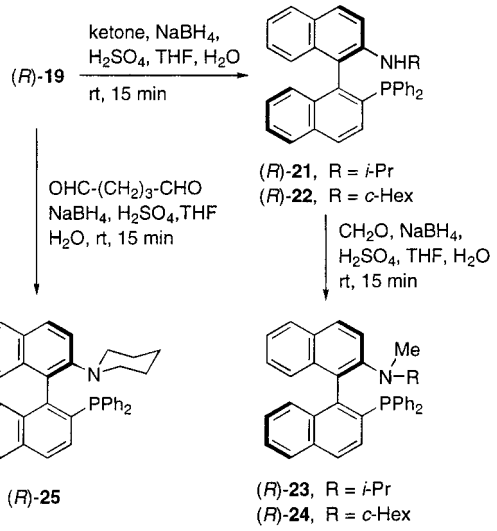

The amino phosphine (*R*)-**19** was submitted to the $NaBH_4$-mediated reductive alkylation with acetone and cyclohexanone, respectively (Scheme 4); both reactions proceeded readily under our standard conditions to afford the respective *N*-monoalkylated amino phosphines (*R*)-**21** (81%) and (*R*)-**22** (63%).[35] Each of the latter products was then methylated ($CH_2O$, $NaBH_4$) to give the respective *N*-isopropyl-*N*-methyl and *N*-cyclohexyl-*N*-methylamino phosphines (*R*)-**23** (85%) and (*R*)-**24** (44%). Similarly, reaction of the amino phosphine (*R*)-**19** with glutaric dialdehyde and $NaBH_4$ furnished the piperidinyl derivative (*R*)-**25** (91%).

**Enantiopurity of the Binaphthyl P,N Ligands.** Since some of the reaction conditions employed in our synthetic routes were rather harsh, we were anxious to

(34) The acetylation of (*R*)-**5** with just 1 equiv of $Ac_2O$ (rt, 8 h) gave a mixture of the acetamide (*R*)-**16** (67%) and the corresponding *N,O*-bisacetylated product (16%).[33a] However, completed bisacetylation of (*R*)-**5** with excess $Ac_2O$ (rt, 8 h), followed by Zemplén hydrolysis of the OAc group (dry MeOH, cat. sodium) improved the overall yield of the "monoacetate" (*R*)-**16** to 95%.

(35) Unlike for (*R*)-**5**, attempted alkylation with 2-adamantanone failed, demonstrating the steric limitations of this protocol.

**Scheme 4**[a]



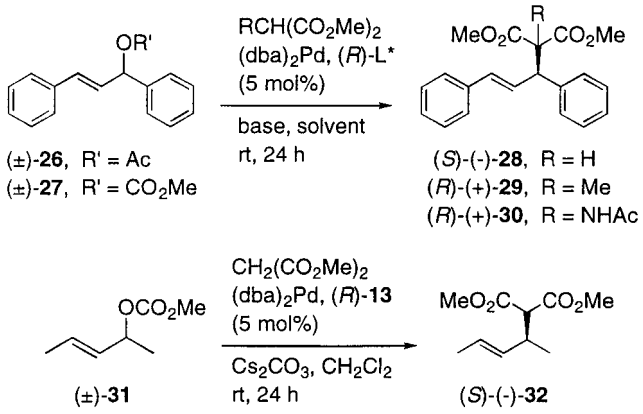

[a] Ketone = acetone or cyclohexanone.

check the extent of retention of the enantiopurity of the final products (note that the starting NOBIN was of ≥99% ee[32]). To this end, we first prepared racemic aminophosphine (±)-**9** from (±)-**5** for comparison, using the same technology as that employed for its optically active form. Unfortunately, chiral HPLC proved to be of little use, as none of the available columns (Chiralpak AD, Chiracel OJ, or Chiralcel OD-H) could separate the enantiomers of **9**.

In view of the failure of HPLC, we considered another option, namely to adopt the method originally developed by Noyori[3b] and Murdoch[36] for the resolution of BINAP into enantiomers that relies on the preparation of a stoichiometric complex of the racemic phosphine with an enantiomerically pure palladacyle generated from *N*,*N*-dimethyl-α-methylbenzylamine and Pd(II). Since this procedure would have required a synthesis of the latter palladacycle, we resolved to first explore a simpler alternative, namely generating a complex of the cheaper (*R*)-(+)-α-methylbenzylamine and Pd(II) with the ligand in question and recording the corresponding NMR spectra. However, this method proved fruitless for **9** as the required signal resolution could be obtained neither in the $^1$H NMR (at 400 MHz) nor in the $^{31}$P NMR spectrum. Finally, we found that a 1:1:1 complex of $Pd(dba)_2$, (*R*)-(+)-α-methylbenzylamine, and the racemic phosphine oxide (±)-**8**, prepared from (±)-**5**, showed splitting of the phosphorus signal in the $^{31}$P NMR spectrum, whereas the free **8** exhibited one signal at 28.39 ppm; two signals in a 1:1 ratio were observed for the latter complex, namely at 28.21 and 28.60 ppm. Repeating the same experiment with the optically active (*R*)-**8** gave a $^{31}$P NMR spectrum that exhibited only the signal at 28.21 ppm, whereas no trace of the signal at 28.60 ppm could be detected, indicating ≥97% ee.

Since reduction of the latter phosphine oxide (*R*)-**8** to the phosphine (*R*)-**9** in the final step of the whole synthetic sequence (Scheme 1) required heating at 120 °C with $Cl_3SiH$ for 5 h, partial racemization in the final step could not be ruled out. Although Noyori has demonstrated that BINAP does not racemize under these conditions,[3c,d,37] Fuji has reported racemization in the synthesis of the 8,8′-isomer of MOP (**2**)[27] so that we endeavored to exclude this possibility in the case of **9**. To this end, a sample of (*R*)-**8** was prepared by air oxidation of (*R*)-**9** (air, rt, 10 h in THF, followed by flash chromatography). The $^{31}$P NMR spectrum of a complex of the phosphine oxide (*R*)-**8** thus obtained with $(dba)_2Pd$ and (*R*)-(+)-α-methylbenzylamine was identical to that recorded previously for (*R*)-**8**; no trace of the other enantiomer could be detected. Analogous experiments were carried out for the phosphine oxide (*R*)-**8**, generated by reductive methylation of (*R*)-**19** ($CH_2O$, $NaBH_4$) followed by air oxidation. Since neither of these experiments could reveal the presence of the opposite enantiomer and with the view that the reductive amination is known to occur without racemization,[33] we can conclude that our aminophosphines (*R*)-**9** and (*R*)-**23**−**25** are of ≥97% ee.

**Scheme 5**




**Asymmetric Pd(0)-Catalyzed Allylic Substitution.** Being the first representatives of the *P*,*N*-binaphthyl class where both heteroatoms are directly adjacent to the aromatic scaffold, the amino phosphines **9** and **23**−**25** called for application in the Pd(0)-catalyzed allylic substitution.[38] We set out to examine the reaction of racemic 1,3-diphenylprop-2-en-1-yl acetate (±)-**26**, the golden standard[18−21,23−27] in allylic chemistry, with malonate-type nucleophiles (Scheme 5). The advantage of this system is that (±)-**26** generates a meso $\pi$-allyl fragment whose symmetry is perturbed only by the chiral ligand coordinated to the palladium so that the ligand effect is free of regioselectivity problems and can be observed directly.

In a typical run, the allylic substrate was treated with a malonate-derived nucleophile (vide infra) in the presence of a catalyst (5 mol %), generated in situ from $(dba)_2Pd$ and the chiral ligand **9**, **23**, **24**, or **25** (typically in a 1:1.5 ratio). The effects of the base, counterion, solvent, and the metal/ligand ratio were also investigated, and the results are summarized in Table 1.

With (±)-**26** as a prototype allylic substrate, (*R*)-**9** as a chiral ligand, and dimethyl sodiomalonate, generated in situ from $CH_2(CO_2Me)_2$ and NaH, as a nucleophile, the

(36) (a) Brown, K. J.; Berry, M. S.; Waterman, K. C.; Lingenfelter, D.; Murdoch, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4717. For a recent application of an analogous naphthalene-derived palladacycle, see: (b) Gladialli, S.; Pilacchini, S.; Fabbri, D.; Menassero, M.; Sansoni, M. *Tetrahedron: Asymmetry* **1998**, *9*, 391.

(37) Zhang, X.; Masima, K.; Koyano, K.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Takaya, H. *Tetrahedron Lett.* **1991**, *32*, 7283.

(38) Note that the few binaphthyl ligands of the P,N-type, previously employed in the Pd(0)-catalyzed allylic substitution,[19h,27y,z,30b] did not have the ligating groups directly connected with the aromatic system.

**Table 1. Asymmetric, Pd(0)-Catalyzed Substitution of Racemic Allylic Substrates 26, 27, and 31 with Malonate Nucleophiles and (*R*)-9 and 23−25 as Ligands (Scheme 5)[a]**

| entry | allylic substrate | ligand[b] | nucleophile | base | solvent | product | yield (%) | ee[c] (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | (±)-**26** | (*R*)-**9** | $CH_2(CO_2Me)_2$ | NaH | THF | (*S*)-(−)-**28** | 91 | 53 |
| 2 | (±)-**26** | (*R*)-**9** | $CH_2(CO_2Me)_2$ | NaH | $CH_2Cl_2$ | (*S*)-(−)-**28** | 86 | 64 |
| 3 | (±)-**26** | (*R*)-**9** | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | THF | (*S*)-(−)-**28** | 90 | 64 |
| 4 | (±)-**26** | (*R*)-**9** | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**28** | 87 | 71 |
| 5 | (±)-**26** | (*R*)-**9** | $CH_2(CO_2Me)_2$ | BSA | THF | (*S*)-(−)-**28** | 95 | 62 |
| 6 | (±)-**26** | (*R*)-**9** | $CH_2(CO_2Me)_2$ | BSA | $CH_2Cl_2$ | (*S*)-(−)-**28** | 87 | 64 |
| 7 | (±)-**26** | (*R*)-**9**[d] | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**28** | 91 | 69 |
| 8 | (±)-**26** | (*R*)-**9**[e] | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**28** | 88 | 69 |
| 9 | (±)-**26** | (*R*)-**9**[f] | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**28** | 85 | 71 |
| 10 | (±)-**26** | (*R*)-**9**[g] | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**28** | 85 | 70 |
| 11 | (±)-**26** | (*R*)-**9** | $MeCH(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*R*)-(+)-**29**[h] | 85 | 70[i] |
| 12 | (±)-**27** | (*R*)-**9** | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**28** | 95 | 68 |
| 13 | (±)-**26** | (*R*)-**9** | $AcNHCH(CO_2Me)_2$ | NaH | $CH_2Cl_2$ | (*R*)-(+)-**30**[h] | 91 | 59[j] |
| 14 | (±)-**26** | (*R*)-**9** | $AcNHCH(CO_2Me)_2$ | BSA | $CH_2Cl_2$ | (*R*)-(+)-**30**[h] | 93 | 56[j] |
| 15 | (±)-**26** | (*R*)-**9** | $AcNHCH(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*R*)-(+)-**30**[h] | 85 | 68[j] |
| 16 | (±)-**31** | (*R*)-**9** | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**32**[k] | 93 | 40[i] |
| 17 | (±)-**26** | (*R*)-**23** | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**28** | 85 | 73 |
| 18 | (±)-**26** | (*R*)-**24** | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**28** | 80 | 69 |
| 19 | (±)-**26** | (*R*)-**25** | $CH_2(CO_2Me)_2$ | $Cs_2CO_3$ | $CH_2Cl_2$ | (*S*)-(−)-**28** | 77 | 68 |

[a] Reactions were carried out at room temperature for 24 h; the catalyst was generated in situ from $(dba)_2Pd$ and the chiral ligand. [b] Pd/ligand ratio 1:1.5 unless stated otherwise. [c] Determined by HPLC on Chiralpak AD (see the Experimental Section) unless stated otherwise. [d] Pd/ligand ratio 1:4. [e] Pd/ligand ratio 1:2. [f] Pd/ligand ratio 1:1. [g] Pd/ligand ratio 1:0.5. [h] The seemingly inverted configuration here is actually due to the change in priority of the substituents in the Cahn−Ingold−Prelog notation. [i] Determined by the $^1H$ NMR spectra taken in the presence of $Eu(hfc)_3$ in $CDCl_3$. [j] Determined by HPLC on Chiralcel OJ (see the Experimental Section). [k] Regarding the absolute configuration of **32**, see ref 43.

Pd(0)-catalyzed reaction afforded (*S*)-(−)-**28**[39] in 53% ee when carried out in THF at room temperature over 24 h (Table 1, entry 1). Running the same reaction in $CH_2Cl_2$ increased the enantioselectivity to 64% ee (Table 1, entry 2). Using $Cs_2CO_3$ as a base,[17i] instead of NaH, led to 64% ee in THF (Table 1, entry 3) and 71% ee in $CH_2Cl_2$ (entry 4). The silyl enol ether, generated from dimethyl malonate by an in situ reaction with *N*,*O*-bis(trimethylsilyl)acetamide (BSA) in the presence of AcOK, afforded (*S*)-(−)-**28** in 62% ee and 64% ee, respectively (entries 5 and 6). Clearly, these results demonstrate the superiority of $Cs_2CO_3$ as a base and $CH_2Cl_2$ as a solvent, in agreement with an earlier observation by Trost.[17i,18]

The influence of the metal/ligand ratio was investigated for the range of 1:4, 1:2, 1:1.5, 1:1, and 1:0.5 (with the amount of Pd held constantly at 5 mol %), but as Table 1 shows, practically no effect was observed (entries 4 and 7−10). The actual catalyst loading also proved to be unimportant; thus, while 5 mol % of the catalyst led to 71% ee (entry 4), reactions run with 3 and 10 mol % (all at the 1:1.5 Pd/ligand ratio) gave 70% ee each.

The reaction of (±)-**26** with dimethyl methylmalonate and $Cs_2CO_3$, carried out in $CH_2Cl_2$ at room temperature for 24 h, produced (*R*)-(+)-**29**[40] in 70% ee (entry 11), which is essentially identical with the result obtained for dimethyl malonate (entry 4). Replacing acetate as the leaving group by carbonate also had little effect, as documented by the reaction of methyl carbonate (±)-**27** with dimethyl malonate and $Cs_2CO_3$ (rt, 24 h), that afforded (*S*)-(−)-**28** in 68% ee (entry 12).

Dimethyl acetamidomalonate gave the substitution product (*R*)-(+)-**30** with slightly reduced enantioselectivity (entries 13−15) compared to that for dimethyl malonate.[41] Lower enantioselectivity was attained for the sterically less demanding methyl (3-penten-2-yl) carbonate (±)-**31** as the allylic substrate (entry 16), which is in line with the reports by other groups.[17e,18a,19a,b,21f,42,43]

The ligands carrying bulkier N substituents, namely (*R*)-**23**, (*R*)-**24**, and (*R*)-**25**, exhibited similar asymmetric induction as the *N*,*N*-dimethylamino derivative (*R*)-**9** (entries 17−19), with the maximum of 73% ee attained in the case of (*R*)-**23** (entry 17).

**Memory Effect.** During the preparation of this manuscript, Hayashi[46] has demonstrated an interesting "memory effect" (Scheme 6);[47] whereas cinnamyl acetate **33** reacted with $NaCMe(CO_2Me)_2$ in the presence of the

(39) The absolute configuration of **28** has previously been established via a chemical correlation of its (*S*)-(−)-enantiomer with (*S*)-(+)-2-phenylsuccinate: Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143.

(40) Interestingly, the absolute configuration of **29** has never been rigorously established. Authors, who prepared this compound via the Pd(0)-catalyzed allylic substitution,[17,21,39] have arbitrarily assigned its configuration in analogy to **28**; we thank Professors Trost and Williams for this personal communication. We have now confirmed the assignment by chemical correlation: methylation of the sodium salt of (*S*)-(−)-**28** with $CH_3I$ afforded (*R*)-(+)-**29**. Note the pseudoinversion of configuration of **29** vs **28** due to the change in the substituent priorities.

(41) The absolute configuration of **30** has been established previously via a chemical correlation with (*R*)-(+)-**28**, which was converted into (*S*)-(−)-**30** in three steps.[27c]

(42) Kang, J.; Cho, W. O.; Cho, H. G. *Tetrahedron: Asymmetry* **1994**, *5*, 1347.

(43) To our knowledge, the absolute configuration of **32** has never been established. Pfaltz obtained its (−)-enantiomer and only reported the ee, whereas others[18a,21f,27q] *assumed* the configuration in view of the results of the Pd(0)-catalyzed allylic substitution obtained for **26** and related allylic substrates. We thank Professors Pfaltz and Ahn for this personal communications. In principle, the absolute configuration of **32** could be established via saponification and decarboxylation to the known 3-methyl-4-hexenoic acid. However, there is a disagreement on the configuration of the latter acid:[44,45] whereas the recent source claims that the (R,E) isomer is levorotatory,[44] this configuration was assigned to the dextrorotatory enantiomer in an earlier paper, based on an extensive correlation with several compounds of known configuration.[45] Unfortunately, we have not been able to communicate with the senior author of the recent paper. As a result, the assignment of (S) configuration to (−)-**32** indicated in Schemes 5 and 7 has to be treated as tentative (and very likely) but not rigorously proven.

(44) McKew, J. C.; Kurth, M. J. *J. Org. Chem.* **1993**, *58*, 4589.

(45) Hill, R. K.; Soman, R.; Sawada, S. *J. Org. Chem.* **1972**, *37*, 3737.

(46) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681.

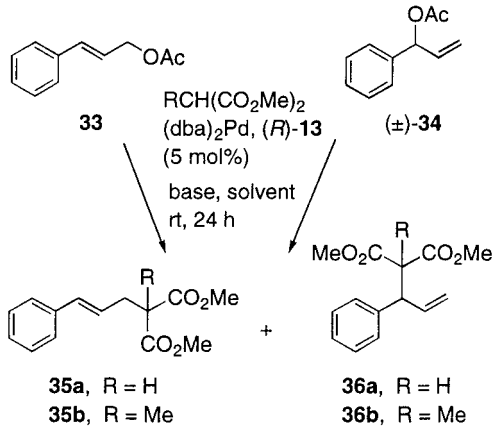
(47) For the original reports on the "memory effect" in the Pd(0)-catalyzed allylic substitution, see: (a) Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* **1981**, *22*, 1399. (b) Trost, B. M.; Schmuff, N. R. *Tetrahedron Lett.* **1981**, *22*, 2999. (c) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 235. For the most recent insight, see: (d) Lloyd-Jones, G. C.; Stephen, S. C. *Chem.−Eur. J.*, in press.

**Table 2. Memory Effect in the Pd(0)-Catalyzed Reaction of 33 and 34 with Malonate Nucleophiles (Scheme 6)[a]**

| entry | allylic substrate | malonate nucleophile | base[b] | solvent | ligand | ratio[c] **35**/**36** | yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | **33** | $MeCH(CO_2Me)_2$ | NaH | THF | **2** | 72:21[d] | 99[d] |
| 2 | **34** | $MeCH(CO_2Me)_2$ | NaH | THF | **2** | 23:77[d] | 96[d] |
| 3 | **33** | $CH_2(CO_2Me)_2$ | BSA | $CH_2Cl_2$ | P,N[e,f] | 24:76 | 86[e] |
| 4 | **33** | $CH_2(CO_2Me)_2$ | NaH | THF | **9** | >200:1 | 96 |
| 5 | **33** | $CH_2(CO_2Me)_2$ | BSA | $CH_2Cl_2$ | **9** | >200:1 | 94 |
| 6 | **33** | $MeCH(CO_2Me)_2$ | NaH | THF | **9** | >200:1 | 96 |
| 7 | **33** | $MeCH(CO_2Me)_2$ | BSA | $CH_2Cl_2$ | **9** | >200:1 | 92 |
| 8 | **34** | $CH_2(CO_2Me)_2$ | NaH | THF | **9** | 95:5 | 94 |
| 9 | **34** | $CH_2(CO_2Me)_2$ | BSA | $CH_2Cl_2$ | **9** | 97:3 | 91 |
| 10 | **34** | $MeCH(CO_2Me)_2$ | NaH | THF | **9** | 91:9 | 92 |
| 11 | **34** | $MeCH(CO_2Me)_2$ | BSA | $CH_2Cl_2$ | **9** | 95:5 | 91 |

[a] Reactions were carried out at room temperature for 24 h; the catalyst was generated in situ from $(dba)_2Pd$ and the chiral ligand; the Pd/ligand ratio was 1:1.5. [b] BSA = *N*,*O*-bis(trimethylsilyl)acetamide. [c] Determined by HPLC. [d] Reference 46. [e] Reference 19h. [f] A *P*,*N*-oxazoline-type ligand (ref 19h).

**Scheme 6**




complex of Pd(0) and MOP **2** (in THF at 20 °C) to give mainly the expected product **35b** (Table 2, entry 1), its allylic isomer **34** preferentially produced the regioisomer **36b** (entry 2).[46] Apparently, in this instance, the nucleophile tends to attack the carbon that originally carried the leaving group. Interestingly, in his earlier preliminary communication,[48] Hayashi reported 68−86% ee for the resulting branched isomer **36b**, whereas his recent full paper[46] lacked this information. In addition to Hayashi's work, Pfaltz has now reported on a new series of oxazoline-type P,N ligands, whose Pd(0) complexes converted cinnamyl acetate **33** preferentially into the branched product **36a** on reaction with $CH_2(CO_2Me)_2$ and BSA in $CH_2Cl_2$ (entry 3) with the maximum of 90% ee.[19h,49]

In view of the similarity between MOP (**2**) and MAP (**9**), these reports could hardly fail to stir our group into action. We have first studied the reactivity of cinnamyl acetate **33** to malonate nucleophiles. When carried out in the presence of 5 mol % of the complex of Pd(0) and (*R*)-**9** (in a 1:1.5 Pd/ligand ratio), the reaction with $NaCH(CO_2Me)_2$ in THF (Hayashi's conditions)[46] turned out to give exclusively the linear product **35a** (entry 4); no trace of **36a** was detected in the $^1H$ NMR spectrum of the crude product. Similarly, the reaction of **33** with $NaCMe(CO_2Me)_2$, carried out under the same conditions, afforded **35b** as the sole product (entry 6). Racemic isocinnamyl acetate (±)-**34** also furnished mainly the linear products; while $NaCH(CO_2Me)_2$ yielded **35a** and **36a** in a 95:5 ratio (entry 8), $NaCMe(CO_2Me)_2$ gave a 91:9 mixture of **35b** and **36b** (entry 10).[50] Under the Pfaltz conditions,[19h] i.e., with $CH_2(CO_2Me)_2$ or $MeCH(CO_2Me)_2$ and BSA in $CH_2Cl_2$, cinnamyl acetate **33** was again converted solely to the respective linear products **35a** and **35b** (entries 5 and 7), whereas isocinnamyl acetate (±)-**34** yielded **35a** and **36a** in a 97:3 ratio with $CH_2(CO_2Me)_2$ (entry 9) and a 95:5 mixture of **35b** and **36b** with $MeCH(CO_2Me)_2$ (entry 11).[50] Clearly, the "memory effect" has been substantially reduced with our MAP ligand **9** as compared to MOP (**2**). We have now realized that this is not the only fundamental difference between MAP and MOP. Thus, for instance, the Pd−MAP complexes failed, under various conditions, to catalyze hydrosilylation, for which MOP is the champion ligand(!).[4,9]

**Mechanistic Considerations.** The sense of asymmetric induction observed in the above Pd(0)-catalyzed allylic substitution reactions is, as expected, consistent with the transition state **37**, in which the nucleophilic attack occurs preferentially at the carbon trans related[16b,19−21,27h,i] (via Pd) to the phosphorus acceptor (Scheme 7). The latter transition state **37** is assumed to contain only one molecule of the ligand. In fact, an intermediate coordinating two molecules of MAP (monodentate rather than bidentate), i.e., $(\pi\text{-allyl})Pd^+(MAP)_2$, would seem to be too crowded and, therefore, less likely. This hypothesis is supported by the experiments carried out with various Pd/**9** ratios (1:4 to 1:0.5; Table 1, entries 4, 7−10), where practically no effect on the level of the enantioselectivity has been observed.

In the transition state **37**, MAP is postulated to serve as a bidentate P,N ligand, which may appear to be at odds with the behavior of Hayashi's MOP (**2**), shown to act as a monodentate ligand by a single-crystal X-ray analysis of *trans*-$(\mathbf{2})_2PdCl_2$[9] and believed to involve coordination of Pd to the naphthyl aromatic system rather than to the MeO group in an $\eta^2$-complex, intercepted as the prime product of allylic substitution.[51,52] However, in the case of our MAP, it is hard to imagine that the palladium, being positively charged (in the transient $\pi$-allyl complex), would not interact, at least weakly, with the nearby amino group. In fact, a weak

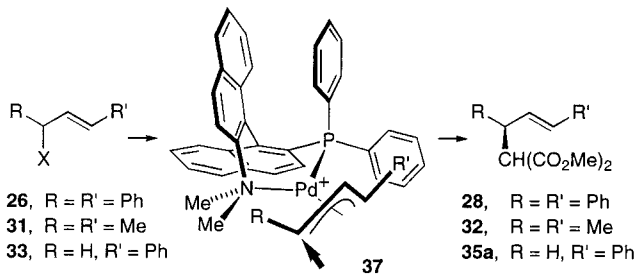
(48) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *Chem. Commun.* **1997**, 561.

(49) An even higher ratio favoring the branched isomer (5:95) was found for the analogous substrate possessing 1-naphthyl in place of phenyl.[19h]

(50) The enantiomeric excess has not been determined for either **36a** or **36b** in view of the very low yield.

(51) This unusual coordination was suggested in ref 46 and is supported by $^1H$ NMR data. The $\eta^2$-complex in question was generated by a stoichiometric reaction of dimethyl sodiomalonate with the ($\pi$-cyclohexenyl)Pd(**2**) complex and found to be stable at room temperature for several days.

**Scheme 7**




coordination of the metal to an *O*-alkyl group has recently been proposed by RajanBabu as the crucial factor controlling the Ni/MOP-catalyzed hydrovinylation.[53,54] Since the coordination to nitrogen in amine-$Pd^{2+}$ complexes is known to be relatively strong (stronger than that to neutral oxygen ligands, such as $R_2O$, due to the difference in Lewis basicity), the transition state **37** does not appear to be unrealistic.

The very weak "memory effect" exhibited by our MAP **9**, as opposed to a strong one demonstrated for MOP **2**,[46] is indicative of a further difference between these two ligands (vide supra). The factors that can tip the balance in favor of the attack at the less substituted terminus (**33** → **35a**) apparently are the different steric bulk and Lewis basicity of the $Me_2N$ group vs those of MeO, presumably resulting in a different way of coordination (vide supra).

## Conclusions

We have demonstrated that (*R*)-(+)-2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN, **5**) can be readily converted into a series of N,N-disubstituted aminophosphines **9**, **23**−**25**; **9** was prepared by employing a sequence of reductive alkylation ($CH_2O$, $NaBH_4$, $H_2SO_4$, aq THF; **5** → **6**) and Pd(0)-catalyzed phosphinoylation of the corresponding triflate, followed by reduction with $Cl_3SiH$ (**7** → **8** → **9**). Variation of this scheme was required for the preparation of **23**−**25** possessing bulkier N substituents. These *P,N*-binaphthyls, for which we propose the acronym MAP, constitute a new, promising class of chiral ligands to be used, e.g., in Pd(0)-catalyzed allylic substitution. The enantioselectivites obtained for (±)-**26**, a prototype allylic substrate, and malonate nucleophiles (up to 73% ee with $Cs_2CO_3$ in $CH_2Cl_2$) can be interpreted in terms of the transition state **37** and preferential attack at the allylic terminus that is trans with respect to the phosphorus acceptor center. Fundamental differences have been observed between MAP and its oxygen congener MOP.

## Experimental Section

**General Methods.** Melting points were determined on a Kofler block and are uncorrected. The optical rotations were measured in THF (unless stated otherwise) with an error of $<\pm 0.1$. The $^1H$ NMR spectra were recorded on 250, 300, or 400 MHz instruments (FT mode) for $CDCl_3$ solutions at 25 °C with TMS as the internal reference. The $^{13}C$ NMR spectra were recorded on a 63 MHz instrument (FT mode) for $CDCl_3$ solutions at 25 °C. The $^{31}P$ NMR spectra were recorded on a 101 MHz instrument (FT mode) for $CDCl_3$ solutions at 25 °C with $H_3PO_4$ as the external reference. The IR spectra were measured in dichloromethane, chloroform, or Nujol. The high-resolution mass spectra were measured on a double focusing spectrometer (70 eV, 50 $\mu$A) using direct inlet and the lowest temperature enabling evaporation; the accuracy was ≤5 ppm. Yields are given in milligrams of isolated product, showing one spot on a chromatographic plate and no impurities detectable in the NMR spectrum. Semipreparative HPLC analyses were carried out on a Magnum 9 column (Partisil 10, Whatman) using petroleum ether−ethyl acetate mixtures and RI detection. Chiral HPLC analyses were carried out on Chiralpak AD (Daicel) and Chiracel OJ (Daicel) columns with a 10 mm guard column (silica) using hexanes−ethanol mixtures and UV detection at 254 nm.

**(*R*)-(−)-2-(Dimethylamino)-2′-(trifluoromethylsulfonyloxy)-1,1′-binaphthyl, (*R*)-(−)-7.** Trifluoromethanesulfonic anhydride (1.96 mL, 11 mmol) was slowly added to a solution of (*R*)-(+)-**6**[33a] (3.13 g, 10 mmol) in dichloromethane (50 mL) and pyridine (2.4 mL, 30 mmol) at 0 °C, and the mixture was stirred for 3 h. The reaction mixture was then diluted with dichloromethane (100 mL) and washed with 5% HCl (2 × 30 mL), saturated $NaHCO_3$ (25 mL), and water (25 mL). The organic phase was dried over $MgSO_4$, concentrated under reduced pressure, and chromatographed on silica gel (50 g, elution with toluene) to give (*R*)-(−)-**7** as a light-yellow solid (4.17 g, 96%): $[\alpha]_D$ −142.6 (*c* 0.5, THF); $^1H$ NMR (400 MHz) $\delta$ 2.48 (s, 6 H), 6.93 (d, $J$ = 8.5 Hz, 1 H), 7.15 (td, $J$ = 9.2 Hz, $J$ = 1.6 Hz, 1 H), 7.29 (td, $J$ = 7.4 Hz, $J$ = 1.2 Hz, 1 H), 7.35 (td, $J$ = 7.8 Hz, $J$ = 1.2 Hz, 1 H), 7.42 (d, $J$ = 8.4 Hz, 1 H), 7.49 (d, $J$ = 8.8 Hz, 1 H), 7.52 (td, $J$ = 7.4 Hz, $J$ = 1.2 Hz, 1 H), 7.56 (d, $J$ = 9.2 Hz, 1 H), 7.82 (d, $J$ = 8.0 Hz, 1 H), 7.96−8.00 (m, 2 H), 8.00 (d, $J$ = 9.2 Hz, 1 H); $^{13}C$ NMR $\delta$ 43.52 (q), 117.92 (q, $J_{C-F}$ = 323 Hz, $CF_3$), 119.37 (d), 119.78 (s), 119.86 (d), 123.68 (d), 125.15 (d), 126.27 (d), 126.72 (d), 127.27 (d), 127.50 (d), 127.89 (d), 128.29 (d), 129.48 (s), 129.52 (s), 129.89 (d), 130.20 (d), 132.44 (s), 133.65 (s), 134.20 (s), 145.34 (s), 150.85 (s); IR ($CHCl_3$) $\nu$ 1621 and 1596 (C=C arom), 1224 and 1142 (S=O) $cm^{-1}$; MS *m/z* (%) 445 ($M^{\bullet+}$, 24), 296 (100).

**(*R*)-(−)-2-(Dimethylamino)-2′-(diphenylphosphinoyl)-1,1′-binaphthyl, (*R*)-(−)-8. a. Method A.** To a mixture of (*R*)-(−)-**7** (1.02 g, 2.3 mmol), diphenylphosphine oxide (1 g, 4.9 mmol), palladium(II) acetate (112 mg, 0.5 mmol), and 1,4-bis(diphenylphosphino)butane (dppb, 213 mg, 0.5 mmol) were added dimethyl sulfoxide (50 mL) and diisopropylethylamine (1.5 mL, 1.11 g, 8.6 mmol), and the mixture was stirred at 120 °C for 4 h. After cooling to room temperature, the mixture was poured into 5% aqueous HCl (300 mL) and the product was extracted with dichloromethane (3 × 50 mL). The combined extracts were washed twice with 1% aqueous HCl, 5% ammonia, and water, dried with $MgSO_4$, and concentrated under reduced pressure. Chromatography of the crude product on silica gel (100 g, elution with a 7:2:1 toluene−dichloromethane−methanol mixture) gave (*R*)-(−)-**8** as a yellow solid (937 mg, 82%): $[\alpha]_D$ −12.5 (*c* 0.3, $CH_3OH$); $^1H$ NMR (400 MHz) $\delta$ 2.38 (s, 6 H), 6.72 (d, $J$ = 8.5 Hz, 1 H), 6.96−7.08 (m, 3 H), 7.12−7.38 (m, 10 H), 7.51−7.63 (m, 5 H), 7.77−7.83 (m, 1 H), 7.90−7.96 (m, 2 H); $^{31}P$ NMR $\delta$ 28.39 (s); IR ($CHCl_3$) $\nu$ 1620 and 1591 (C=C arom) $cm^{-1}$; MS *m/z* (%) 497 ($M^{\bullet+}$, 23), 341 (100).

**b. Method B.** A solution of (*R*)-(−)-**9** (48 mg, 0.1 mmol) in THF (10 mL) was stirred in the presence of air for 10 h. The solvent was evaporated, and the residue was chromatographed on silica gel (10 g; elution with a 7:2:1 toluene−dichloromethane−methanol mixture) to give the pure phosphine oxide (*R*)-**12** (31 mg, 62%).

**c. Method C.** A solution of (*R*)-(−)-**19** (45 mg, 0.1 mmol) in THF (2 mL) and solid $NaBH_4$ (53 mg, 1.4 mmol) were slowly added (simultaneously) to a solution of 40% aqueous formal-

(52) Similar bonding to the aryl unit has been identified for [(MeO−Biphen)Ru($\eta^5$-$C_8H_{11}$)]$^+$ and [(BINAP)RuCp]$^+$ as follows: (a) Pathak, D. D.; Adams, H.; Bailey, N. A.; King, P. J.; White, C. *J. Organomet. Chem.* **1994**, *479*, 237. (b) Feiken, N.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1997**, *16*, 537. (c) Feiken, N.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1998**, *17*, 5756. For an overview, see: (d) Pregosin, P. S.; Trabesinger, G. *J. Chem. Soc., Dalton Trans.* **1998**, 727.

(53) Nomura, N.; Jin, J.; Park, H.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 459.

(54) In light of the recent Hayashi's report,[46] this effect can now also be viewed as originating from the coordination of Ni to the aromatic naphthyl nucleus rather than to the MeO group. Application of MAP to hydrovinylation would certainly be interesting as it may shed more light on this mechanistic issue.

dehyde (0.12 mL; 1.4 mmol) and 20% aqueous $H_2SO_4$ (0.2 mL) in THF (1 mL) over a period of 15 min. The reaction mixture was stirred for an additional 15 min and then poured into a 2% aqueous KOH solution (10 mL). The resulting suspension was extracted with dichloromethane (2 × 5 mL), and the extract was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel (10 g) with toluene to give (*R*)-(−)-**9** (38 mg, 79%). The (*R*)-(−)-**9** was then oxidized to (*R*)-**8** by method B (see above).

**(*R*)-(−)-2-(Dimethylamino)-2′-(diphenylphosphino)-1,1′-binaphthyl, (*R*)-(−)-9.** Trichlorosilane (1.35 g, 10 mmol) was added to a mixture of (*R*)-(−)-**8** (840 mg, 1.7 mmol) and triethylamine (4.5 mL, 3.27 g, 32 mmol) in xylene (40 mL) at 0 °C, and the mixture was stirred at 120 °C for 5 h. After being cooled to room temperature, the mixture was diluted with dichloromethane and quenched with a small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite, and the solid was washed with dichloromethane. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure and the residue was chromatographed on silica gel (50 g, elution with a 1:1 toluene−hexane mixture) to give (*R*)-(−)-**9** as a white solid (703 mg, 86%): $[\alpha]_D$ −19.0 (*c* 1, THF); $^1$H NMR (250 MHz) $\delta$ 2.12 (s, 6 H), 6.68 (d, $J$ = 8.8 Hz, 1 H), 6.82−7.43 (m, 17 H), 7.67−7.84 (m, 4 H); $^{31}$P NMR $\delta$ −13.14 (s); IR ($CHCl_3$) $\nu$ 1620 and 1596 (C═C arom) cm$^{-1}$; MS *m*/*z* (%) 481 (M$^{\bullet+}$, 19), 437 (100).

**(*R*)-(−)-2-(*N*-Isopropyl-*N*-methylamino)-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl, (*R*)-(−)-13.** (*R*)-(+)-**10**[33b] (341 mg, 1 mmol) was submitted to the same reaction conditions as those described for the preparation of (*R*)-(−)-**7**. A standard workup, followed by column chromatography on silica gel (50 g, elution with toluene), gave (*R*)-(−)-**13** as a yellow oil (416 mg, 88%): $[\alpha]_D$ −121 (*c* 0.4, THF); $^1$H NMR (400 MHz) $\delta$ 0.49 (d, $J$ = 6.6 Hz, 3 H), 0.79 (d, $J$ = 6.6 Hz, 3 H), 2.56 (s, 3 H), 2.92−3.03 (m, 1 H), 7.01 (d, $J$ = 8.5 Hz, 1 H), 7.14−7.23 (m, 1 H), 7.28−7.39 (m, 3 H), 7.48−7.58 (m, 3 H), 7.83 (d, $J$ = 8.2 Hz, 1 H), 7.92−8.03 (m, 3 H); $^{13}$C NMR $\delta$ 17.20 (q), 19.73 (q), 31.81 (q), 53.80 (d), 118.13 (q, $J_{C-F}$ = 320.1 Hz, $CF_3$), 119.82 (d), 121.48 (d), 121.90 (s), 123.84 (d), 125.46 (d), 126.14 (d), 126.62 (d), 127.16 (d), 127.42 (d), 127.80 (d), 128.30 (d), 129.71 (d), 129.81 (d), 129.66 (s), 132.46 (2 × s), 133.73 (s), 134.04 (s), 145.19 (s), 151.26 (s); IR ($CHCl_3$) $\nu$ 1621 and 1594 (C═C arom), 1220 and 1142 (S═O) cm$^{-1}$; MS *m*/*z* (%) 473 (M$^{\bullet+}$, 56), 458 (100).

**(*R*)-(−)-2-(*N*-Cyclohexyl-*N*-methylamino)-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl, (*R*)-(−)-14.** (*R*)-(+)-**11**[33b] (381 mg, 1 mmol) was submitted to the same reaction conditions as those described for the preparation of (*R*)-(−)-**7**. A standard workup, followed by column chromatography on silica gel (50 g, elution with toluene), furnished (*R*)-(−)-**14** as a yellow oil (436 mg, 85%): $[\alpha]_D$ −90.6 (*c* 0.65, THF); $^1$H NMR (400 MHz) $\delta$ −0.20−(−0.01) (m, 1 H), 0.49−0.61 (m, 2 H), 0.64−0.76 (m, 1 H), 0.96−1.10 (m, 1 H), 1.14−1.26 (m, 3 H), 1.32−1.36 (m, 1 H), 1.41−1.49 (m, 1 H), 2.41−2.53 (m, 1 H), 2.65 (s, 3 H), 7.02 (d, $J$ = 8.5 Hz, 1 H), 7.15−7.57 (m, 7 H), 7.83 (d, $J$ = 8.2 Hz, 1 H), 7.92−8.02 (m, 3 H); $^{13}$C NMR $\delta$ 25.64 (2 × t), 25.87 (t), 27.90 (t), 30.62 (t), 32.65 (q), 62.99 (d), 118.14 (q, $J_{C-F}$ = 319.8 Hz, $CF_3$), 119.00 (d), 121.18 (d), 123.65 (d), 125.27 (d), 126.14 (d), 126.67 (d), 127.21 (d), 127.41 (d), 127.80 (d), 128.31 (d), 129.40 (s), 129.61 (d), 129.68 (d), 129.85 (s), 132.48 (s), 133.73 (2 × s), 134.19 (s), 145.14 (s), 151.33 (s); IR ($CHCl_3$) $\nu$ 1621 and 1594 (C═C arom), 1223 and 1143 (S═O) cm$^{-1}$; MS *m*/*z* (%) 513 (M$^{\bullet+}$, 68), 470 (100).

**(*R*)-(−)-2-(*N*-Piperidinyl)-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl, (*R*)-(−)-15.** (*R*)-(+)-**12**[33b] (353 mg, 1 mmol) was submitted to the same reaction conditions as those described for the preparation of (*R*)-(−)-**7**. A standard workup, followed by column chromatography on silica gel (50 g, elution with toluene), afforded (*R*)-(−)-**15** as a yellow oil (417 mg, 86%): $[\alpha]_D$ −117 (*c* 1.5, THF); $^1$H NMR (400 MHz) $\delta$ 1.00−1.32 (m, 6 H), 2.65−2.83 (m, 4 H), 6.99−7.05 (m, 1 H), 7.16−7.22 (m, 2 H), 7.30−7.35 (m, 2 H), 7.42−7.55 (m, 2 H), 7.58 (d, $J$ = 9.1 Hz, 1 H), 7.81−7.85 (m, 1 H), 7.89−8.01 (m, 3 H); $^{13}$C NMR $\delta$ 24.09 (t), 26.09 (t), 53.01 (d), 118.18 (q, $J_{C-F}$ = 316.0 Hz, $CF_3$), 119.76 (d), 120.34 (d), 122.84 (s), 124.10 (d), 125.57 (d), 126.15 (d), 126.56 (d), 127.10 (d), 127.34 (d), 127.86 (d), 128.26 (d), 129.12 (s), 129.67 (d), 130.16 (s), 130.32 (d), 132.40 (s), 133.48 (s), 133.90 (s), 145.09 (s), 151.19 (s); IR ($CHCl_3$) $\nu$ 1621 and 1594 (C═C arom), 1221 and 1142 (S═O) cm$^{-1}$; MS *m*/*z* (%) 485 (M$^{\bullet+}$, 36), 352 (100).

**(*R*)-(+)-2-(Acetamido)-2′-hydroxy-1,1-binaphthyl, (*R*)-(+)-16.**[33a] Acetyl chloride (1.6 mL, 11 mmol) was slowly added to a solution of (*R*)-(+)-**5** (2.85 g, 10 mmol) in dry pyridine (40 mL) at 0 °C, and the mixture was then kept at room temperature for 8 h. The mixture was poured onto ice and water and extracted with dichloromethane. The extract was successively washed with water, 5% aqueous HCl, water, sat. aqueous $NaHCO_3$, and water and dried with $Na_2SO_4$. The solvent was evaporated, and the residue was chromatographed on silica gel (50 g) with a 2:1 toluene−ethyl acetate mixture to give the *N*,*O*-diacetate[33a] (3.58 g, 97%). The diacetate was dissolved in dry methanol (250 mL), a catalytic amount of MeONa (20 mg) was added, and the mixture was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel (50 g) with a 2:1 toluene−ethyl acetate mixture to give crystalline (*R*)-(+)-**16** (3.17 g, 98%):[33a] mp 208−209 °C (EtOH); $[\alpha]_D$ +79 (*c* 0.5, $CHCl_3$) [an authentic sample of (*S*)-(−)-**16**[33a] had mp 208−209 °C; $[\alpha]_D$ −79].

**(*R*)-(+)-2-(Acetamido)-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl, (*R*)-(+)-17.** (*R*)-(+)-**16**[33a] (3.27 g, 10 mmol) was submitted to the same reaction conditions as those described for the preparation of (*R*)-(−)-**7**. A standard workup, followed by column chromatography on silica gel (50 g, elution with toluene−ethyl acetate 19:1), produced (*R*)-(+)-**17** as a yellow oil (4.17 g, 91%): $[\alpha]_D$ +26.6 (*c* 0.66, THF); $^1$H NMR (400 MHz) $\delta$ 1.78 (s, 3 H), 6.88 (bs, 1 H), 7.00 (d, $J$ = 8.5 Hz, 1 H), 7.23−7.45 (m, 4 H), 7.58−7.64 (m, 2 H), 7.92 (d, $J$ = 8.2 Hz, 1 H), 8.00−8.07 (m, 2 H), 8.15 (d, $J$ = 9.1 Hz, 1 H), 8.36 (d, $J$ = 8.8 Hz, 1 H); $^{13}$C NMR $\delta$ 24.09 (q), 118.12 (q, $J_{C-F}$ = 316.0 Hz, $CF_3$), 119.00 (s), 119.49 (d), 122.17 (d), 124.69 (d), 125.36 (d), 126.15 (d), 126.51 (s), 126.92 (d), 127.71 (d), 128.20 (d), 128.39 (d), 128.53 (d), 130.17 (d), 131.12 (s), 131.73 (d), 132.24 (s), 132.77 (s), 132.80 (s), 135.06 (s), 145.27 (s), 168.48 (s); IR ($CHCl_3$) $\nu$ 3425 (NH), 1694 (C═O), 1624 and 1602 (C═C arom), 1223 and 1140 (S═O) cm$^{-1}$; MS *m*/*z* (%) 459 (M$^{\bullet+}$, 52), 284 (100).

**(*R*)-(−)-2-(Acetamido)-2′-(diphenylphosphinoyl)-1,1′-binaphthyl, (*R*)-(−)-18.** To a mixture of (*R*)-(+)-**17** (1.05 g, 2.3 mmol), diphenylphosphine oxide (1 g, 4.9 mmol), palladium(II) acetate (112 mg, 0.5 mmol), and 1,4-bis(diphenylphosphino)butane (dppb, 213 mg, 0.5 mmol) were added dimethyl sulfoxide (50 mL) and diisopropylethylamine (1.5 mL, 1.11 g, 8.6 mmol), and the mixture was stirred at 120 °C for 4 h. After cooling to room temperature, the reaction mixture was poured into 5% aqueous HCl (300 mL) and the product was extracted with dichloromethane (3 × 50 mL). The combined extracts were washed twice with 1% aqueous HCl and water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (100 g, elution with a 15:4:1 toluene−dichloromethane−methanol mixture) to afford (*R*)-(−)-**18** as a colorless solid (1.12 g, 84%): $[\alpha]_D$ −143 (*c* 0.5, THF); $^1$H NMR (400 MHz) $\delta$ 1.92 (s, 3 H), 6.52 (d, $J$ = 8.5 Hz, 1 H), 6.60−6.65 (m, 2 H), 6.73−6.77 (m, 1 H), 6.92−6.99 (m, 1 H), 7.01−7.22 (m, 6 H), 7.45−7.55 (m, 4 H), 7.63−7.74 (m, 4 H), 7.88−7.99 (m, 3 H), 9.73 (bs, 1 H); $^{31}$P NMR $\delta$ 28.66 (s); IR (Nujol) $\nu$ 3511 (NH), 1684 (C═O), 1519, and 1499 (C═C arom) cm$^{-1}$; MS *m*/*z* (%) 511 (M$^{\bullet+}$, 41), 267 (110).

**(*R*)-(−)-2-Amino-2′-(diphenylphosphino)-1,1′-binaphthyl, (*R*)-(−)-19.** Trichlorosilane (2.7 g, 20 mmol) was added to a mixture of (*R*)-(−)-**18** (868 mg, 1.7 mmol) and triethylamine (4.5 mL, 3.27 g, 32 mmol) in xylene (40 mL) at 0 °C, and the mixture was stirred at 120 °C for 5 h. After being cooled to room temperature, the mixture was diluted with dichloromethane and quenched with a small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite, and the solid was washed with dichloromethane. The combined organic extracts were dried over

$MgSO_4$ and concentrated under reduced pressure and the residue was chromatographed on silica gel (50 g, elution with toluene) to provide (*R*)-(−)-**19** as a white solid (577 mg, 75%): $[\alpha]_D$ −20.5 (*c* 0.6, THF); $^1$H NMR (400 MHz) $\delta$ 3.28 (bs, 2 H), 6.67 (d, $J$ = 8.5 Hz, 1 H), 6.91−7.15 (m, 9 H), 7.23−7.31 (m, 6 H), 7.44−7.51 (m, 2 H), 7.71−7.81 (m, 2 H), 7.86−7.90 (m, 2 H); $^{31}$P NMR $\delta$ −13.47 (s); IR ($CHCl_3$) $\nu$ 3489 ($NH_2$ asym), 3393 ($NH_2$ sym), 1622 and 1586 (C=C arom) cm$^{-1}$; MS *m*/*z* (%) 453 (M$^{\bullet+}$, 91), 437 (100).

**(*R*)-(−)-2-(Ethylamino)-2′-(diphenylphosphino)-1,1′-binaphthyl, (*R*)-(−)-20.** (*R*)-(−)-**20** was isolated as a faster moving byproduct in the previous experiment (65 mg, 8%): $[\alpha]_D$ −30.1 (*c* 0.3, THF); $^1$H NMR (400 MHz) $\delta$ 0.77 (t, $J$ = 7.1 Hz, 3 H), 2.75−2.88 (m, 1 H), 3.00−3.14 (m, 1 H), 6.59 (d, $J$ = 8.2 Hz, 1 H), 6.91−7.33 (m, 17 H), 7.43−7.51 (m, 2 H), 7.73 (d, $J$ = 7.9 Hz, 1 H), 7.86−7.91 (m, 2 H); $^{31}$P NMR $\delta$ −14.22 (s); IR ($CH_2Cl_2$) $\nu$ 3403 (NH), 1621 and 1599 (C=C arom) cm$^{-1}$; MS *m*/*z* (%) 481 (M$^{\bullet+}$, 62), 437 (100).

**(*R*)-(−)-2-(Isopropylamino)-2′-(diphenylphosphino)-1,1′-binaphthyl, (*R*)-(−)-21.** A solution of (*R*)-(−)-**19** (453 mg, 1 mmol) in THF (10 mL) and solid $NaBH_4$ (378 mg, 10 mmol) were slowly added (simultaneously) to a solution of acetone (1.5 mL, 20 mmol) and a 20% aqueous $H_2SO_4$ (2 mL) in THF (5 mL) over a period of 15 min. Then, the next portion of solid $NaBH_4$ (378 mg, 10 mmol) was slowly added, and the mixture was stirred for an additional 15 min and then poured into a 2% aqueous KOH (100 mL). The resulting suspension was extracted with dichloromethane (3 × 20 mL), and the extract was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel (20 g) using a 1:1 toluene−hexane mixture as eluent to furnish (*R*)-(−)-**25** as a white solid (401 mg, 81%): $[\alpha]_D$ −13.7 (*c* 0.42, THF); $^1$H NMR (250 MHz) $\delta$ 0.77 (d, $J$ = 6.3 Hz, 3 H), 0.88 (d, $J$ = 6.3 Hz, 3 H), 3.07 (bs, 1 H), 3.58−3.79 (m, 1 H), 6.50 (d, $J$ = 9.9 Hz, 1 H), 6.85−6.95 (m, 1 H), 6.98−7.27 (m, 14 H), 7.48 (dd, $J$ = 8.5 Hz, $J$ = 2.5 Hz, 2 H), 7.72 (d, $J$ = 7.9 Hz, 1 H), 7.86−7.91 (m, 3 H); $^{31}$P NMR $\delta$ −14.37 (s); IR ($CHCl_3$) $\nu$ 3418 (NH), 1621 and 1600 (C=C arom cm$^{-1}$); MS *m*/*z* (%) 495 (M$^{\bullet+}$, 100).

**(*R*)-(−)-2-(Cyclohexylamino)-2′-(diphenylphosphino)-1,1′-binaphthyl, (*R*)-(−)-22.** A solution of (*R*)-(−)-**19** (453 mg, 1 mmol) in THF (10 mL) and solid $NaBH_4$ (378 mg, 10 mmol) were slowly added (simultaneously) to a solution of cyclohexanone (2 mL, 20 mmol) and 20% aqueous $H_2SO_4$ (2 mL) in THF (5 mL) over a period of 15 min. Then, the next portion of solid $NaBH_4$ (378 mg, 10 mmol) was slowly added, and the mixture was stirred for an additional 15 min and then poured into a 2% aqueous KOH (100 mL). The resulting suspension was extracted with dichloromethane (3 × 20 mL), and the extract was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel (20 g) with a 1:1 toluene−hexane mixture to yield (*R*)-(−)-**22** as a white solid (337 mg, 63%): $[\alpha]_D$ −17 (*c* 0.28, THF); $^1$H NMR (400 MHz) $\delta$ 0.39−0.50 (m, 1 H), 0.59−0.69 (m, 1 H), 0.80−0.93 (m, 2 H), 1.11−1.28 (m, 2 H), 1.42−1.57 (m, 2 H), 1.63−1.82 (m, 2 H), 3.14 (bs, 1 H), 3.23−3.34 (m, 1 H), 6.50 (d, $J$ = 8.5 Hz, 1 H), 6.88 (dt, $J$ = 7.5 Hz, $J$ = 1.3 Hz, 1 H), 7.02−7.29 (m, 15 H), 7.43−7.51 (m, 2 H), 7.70 (d, $J$ = 8.2 Hz, 1 H), 7.83−7.89 (m, 2 H); $^{31}$P NMR $\delta$ −14.25 (s); IR ($CH_2Cl_2$) $\nu$ 3409 (NH), 1622 and 1601 (C=C arom cm$^{-1}$); MS *m*/*z* (%) 535 (M$^{\bullet+}$, 99), 437 (100).

**(*R*)-(−)-2-(*N*-Isopropyl-*N*-methylamino)-2′-(diphenylphosphino)-1,1′-binaphthyl, (*R*)-(−)-23.** A solution of (*R*)-(−)-**21** (248 mg, 0.5 mmol) in THF (5 mL) and solid $NaBH_4$ (189 mg, 5 mmol) were slowly added (simultaneously) to a solution of 40% aqueous formaldehyde (1 mL, 12 mmol) and 20% aqueous $H_2SO_4$ (1 mL) in THF (5 mL) over a period of 15 min. Then, the next portion of solid $NaBH_4$ (189 mg, 5 mmol) was slowly added, and the mixture was stirred for an additional 15 min and then poured into a 2% aqueous KOH (50 mL). The resulting suspension was extracted with dichloromethane (3 × 20 mL), and the extract was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel (20 g) with a 1:1 toluene−hexane mixture to give (*R*)-(−)-**23** as a white solid (216 mg, 85%): $[\alpha]_D$ −77 (*c* 0.1, THF); $^1$H NMR (400 MHz) $\delta$ 0.37 (d, $J$ = 6.6 Hz, 3 H), 0.68 (d, $J$ = 6.6 Hz, 3 H), 2.39 (s, 3 H), 3.08−3.14 (m, 1 H), 6.69 (d, $J$ = 8.5 Hz, 1 H), 6.86−6.93 (m, 3 H), 6.99−7.05 (m, 3 H), 7.20−7.32 (m, 8 H), 7.43−7.52 (m, 3 H), 7.75−7.93 (m, 4 H); $^{31}$P NMR $\delta$ −12.89 (s); IR ($CHCl_3$) $\nu$ 1620 and 1594 (C=C arom cm$^{-1}$); MS *m*/*z* (%) 509 (M$^{\bullet+}$, 27), 326 (100).

**(*R*)-(−)-2-(*N*-Cyclohexyl-*N*-methylamino)-2′-(diphenylphosphino)-1,1′-binaphthyl, (*R*)-(−)-24.** A solution of (*R*)-(−)-**22** (267 mg, 0.5 mmol) in THF (5 mL) and solid $NaBH_4$ (189 mg, 5 mmol) were slowly added (simultaneously) to a solution of 40% aqueous formaldehyde (1 mL, 12 mmol) and 20% aqueous $H_2SO_4$ (1 mL) in THF (5 mL) over a period of 15 min. Then, the next portion of solid $NaBH_4$ (189 mg, 5 mmol) was slowly added, and the mixture was stirred for an additional 15 min and then poured into a 2% aqueous KOH (50 mL). The resulting suspension was extracted with dichloromethane (3 × 20 mL), and the extract was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel (20 g) with a 1:1 toluene−hexane mixture to afford (*R*)-(−)-**24** as a white solid (131 mg, 44%): $[\alpha]_D$ −85 (*c* 0.12, THF); $^1$H NMR (250 MHz) $\delta$ −0.36−(−0.20) (m, 1 H), 0.31−0.37 (m, 1 H), 0.54−0.72 (m, 2 H), 0.85−1.01 (m, 2 H), 1.10−1.25 (m, 2 H), 1.43−1.49 (m, 2 H), 2.34 (s, 3 H), 2.53−2.64 (m, 1 H), 6.74 (d, $J$ = 8.8 Hz, 1 H), 6.82−6.91 (m, 2 H), 6.93−7.07 (m, 4 H), 7.15−7.22 (m, 2 H), 7.25−7.32 (m, 5 H), 7.40−7.49 (m, 4 H), 7.75−7.92 (m, 4 H); $^{31}$P NMR $\delta$ −12.66 (s); IR ($CHCl_3$) $\nu$ 1619 and 1592 (C=C arom) cm$^{-1}$; MS *m*/*z* (%) 594 (M$^{\bullet+}$, 28), 326 (100).

**(*R*)-(−)-2-(*N*-Piperidyl)-2′-(diphenylphosphino)-1,1′-binaphthyl, (*R*)-(−)-25.** A solution of (*R*)-(−)-**19** (226 mg, 0.5 mmol) in THF (5 mL) and solid $NaBH_4$ (378 mg, 10 mmol) were slowly added (simultaneously) to a solution of 25% aqueous glutaric dialdehyde (2.2 mL, 6 mmol) and 20% aqueous $H_2SO_4$ (1 mL) in THF (5 mL) over a period of 15 min. Then, the next portion of solid $NaBH_4$ (189 mg, 5 mmol) was slowly added, and the mixture was stirred for an additional 15 min and then poured into a 2% aqueous KOH (50 mL). The resulting suspension was extracted with dichloromethane (3 × 20 mL), and the extract was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel (20 g) with toluene as eluent to produce (*R*)-(−)-**25** as a white solid (237 mg, 91%): $[\alpha]_D$ − 87 (*c* 1.0, THF); $^1$H NMR (400 MHz) $\delta$ 0.99−1.09 (m, 4 H), 1.18−1.29 (m, 2 H), 2.78 (t, $J$ = 5.2 Hz, 4 H), 6.58 (d, $J$ = 8.5 Hz, 1 H), 6.79−6.85 (m, 1 H), 6.87−6.93 (m, 2 H), 6.98−7.03 (m, 2 H), 7.06−7.12 (m, 1 H), 7.18−7.30 (m, 8 H), 7.41−7.49 (m, 1 H), 7.51−7.59 (m, 2 H), 7.77 (d, $J$ = 8.0 Hz, 1 H), 7.82−7.89 (m, 2 H), 7.96 (d, $J$ = 9.2 Hz, 1 H); $^{31}$P NMR $\delta$ −12.50 (s); IR ($CHCl_3$) $\nu$ 1620 and 1592 (C=C arom) cm$^{-1}$; MS *m*/*z* (%) 521 (M$^{\bullet+}$, 37), 335 (100).

**General Procedure for the Pd(0)-Catalyzed Allylic Substitution.** In a Schlenk tube, $(dba)_2Pd$ (0.050 mmol, 5 mol %) and the (R) ligand (0.075 mmol) were dissolved in a solvent (2 mL, Table 1) and stirred at room temperature for 10 min. A solution of the allylic substrate (acetate **26**, or carbonate **27**, or **31**; 1 mmol) in a solvent (2 mL, Table 1) was then added, and the mixture was stirred at room temperature for an additional 10 min. Then, a solution of the nucleophile, generated in situ from the corresponding malonate (2 mmol) and the base (2 mmol) (see Table 1), in a solvent (3 mL, Table 1) was slowly added, and the reaction mixture then was stirred at room temperature for 24 h. The reaction mixture was quenched by adding 5% aqueous HCl (20 mL), and the product was extracted into ethyl acetate (3 × 10 mL). The combined extracts were washed successively with water, 5% aqueous $KHCO_3$, and water and dried with $MgSO_4$, and the solvent was evaporated in vacuo. The crude product was purified by a semipreparative HPLC (silica gel; Magnum 9 Whatman column; a 4:1 hexanes−ethyl acetate mixture as eluent) to give the pure respective products **28**−**30**, **32** as colorless oils. The enantiomeric purities were determined by chiral HPLC (vide infra) or by the $^1$H NMR spectra measured in the presence of $Eu(hfc)_3$. The yields and enantioselectivities are given in Table 1. The same protocol was used for the preparation of **35a**,**b** and **36a**,**b** (Table 2).

**(*S*)-(−)-Dimethyl (1,3-Diphenylprop-2-en-1-yl)malonate, (*S*)-(−)-28.** $[\alpha]_D$ −12.7 (*c* 1, EtOH [lit.[19a] −18.4 (*c* 1.1, EtOH)]. $^1$H NMR (250 MHz) $\delta$ 3.53 (s, 3 H), 3.70 (s, 3 H), 3.95 (d, $J$ = 11 Hz, 1 H), 4.27 (dd, $J$ = 11 Hz, $J$ = 8 Hz, 1 H), 6.32 (dd, $J$ = 15 Hz, $J$ = 8 Hz, 1 H), 6.48 (d, $J$ = 15 Hz, 1 H), 7.15−7.44 (m, 10 H). Chromatography on Daicel Chiralpak AD (elution hexane−2-propanol 19:1, flow rate 1 mL/min, UV detection at 254 nm) showed 71% ee ($t_R$ = 15 min, $t_S$ = 20 min).

**(*R*)-(+)-Dimethyl (1,3-Diphenylprop-2-en-1-yl)methylmalonate, (*R*)-(+)-29. a. Method A (from the Allylic Substitution).** $[\alpha]_D$ +30 (*c* 0.7, EtOH). $^1$H NMR (250 MHz) $\delta$ 1.36 (s, 3 H), 3.51 (s, 3 H), 3.59 (s, 3 H), 4.30 (d, $J$ = 9 Hz, 1 H), 6.46 (d, $J$ = 16 Hz, 1 H), 6.68 (dd, $J$ = 16 Hz, $J$ = 9 Hz, 1 H), 7.27−7.35 (m, 10 H). The $^1$H NMR spectrum measured in the presence of Eu(hfc)$_3$ showed 70% ee.

**b. Method B [from (*S*)-(−)-28].** Sodium hydride (55% in mineral oil, 48 mg, 1.1 mmol) was added to a solution of (*S*)-(−)-**28** (324 mg, 1 mmol), obtained from the Pd(0)-catalyzed experiment [entry 4 in Table 1; $[\alpha]_D$ −12.7 (*c* 1, EtOH), which corresponds to 71% ee] in dry dichloromethane (10 mL). After the mixture was stirred at room temperature for 10 min, iodomethane (170 mg, 1.2 mmol) was added and the mixture was stirred at room temperature for 24 h. A standard workup followed by flash chromatography on silica gel with a 4:1 hexanes−ethyl acetate mixture afforded (*R*)-(+)-**29** (310 mg, 92%), whose spectral characteristics were identical with those of the product obtained by the allylic substitution (see above); $[\alpha]_D$ +31 (*c* 0.8, EtOH).

**(*R*)-(+)-Dimethyl (1,3-Diphenylprop-2-en-1-yl)(acetamido)malonate, (*R*)-(+)-30.** $[\alpha]_D$ +35 (*c* 0.7, EtOH [lit.[27c] −54 (*c* 0.6, EtOH) for the (S) enantiomer]. $^1$H NMR (400 MHz) $\delta$ 1.98 (s, 3 H), 3.63 (s, 3 H), 3.79 (s, 3 H), 4.75 (d, $J$ = 7.2 Hz, 1 H), 6.33 (d, $J$ = 16 Hz, 1 H), 6.58 (bs, 1 H), 6.73 (dd, $J$ = 16 Hz, $J$ = 7.2 Hz, 1 H), 7.24−7.33 (m, 10 H). Chromatography on Daicel Chiralcel OJ (elution hexanes−ethanol−diethylamine 800:200:1, flow rate 1 mL/min, UV detection at 254 nm) showed 68% ee ($t_S$ = 10 min, $t_R$ = 21 min).

**(*S*)-(−)-Dimethyl (Pent-3-en-2-yl)malonate, (*S*)-(−)-32.**[43] $[\alpha]_D$ −8.6 (*c* 0.5, $CHCl_3$ [lit.[42] +15.4 (*c* 0.9, $CHCl_3$ for a sample of 69% ee]. $^1$H NMR (400 MHz) $\delta$ 1.06 (d, $J$ = 6.8 Hz, 3 H), 1.63 (dd, $J$ = 6 Hz, $J$ = 1.2 Hz, 3 H), 2.85−2.93 (m, 1 H), 3.26 (d, $J$ = 9.2 Hz, 1 H), 3.69 (s, 3 H), 3.73 (s, 3 H), 5.30−5.38 (m, 1 H), 5.47−5.57 (m, 1 H). The $^1$H NMR spectrum recorded in the presence of Eu(hfc)$_3$ showed 40% ee.

**Acknowledgment.** We thank the GAČR for Grants 203/97/1009, 203/97/0351, and 203/98/1185, GAUK for Grants 86/95 and 18/98, British Council and the University of Leicester for additional support. We also thank Johnson-Matthey for the loan of $(dba)_2Pd$.

**Supporting Information Available:** $^1$H NMR spectra of the new compounds prepared, **8**, **13**−**15**, **17**−**25**, their MS and HRMS spectral characteristics, and NMR characterization of **35a**,**b** and **36a**,**b** (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO980757X