Direct Palladium-Catalyzed Phosphinylation of Aryl Triflates with Secondary Phosphines. Its Scope and Limitations: The Synthesis of Optically Active Carboxylated 2-(Diphenylphosphino)-1,1′-binaphthalenes

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Introduction

A major objective of modern organic synthesis is improving the efficiency of chemical reactions ("atom economy" as put for by B. M. Trost[1]) and phase-separation as well.[2] The advantages of using water-soluble[3] and/or "fluorous-phase"-soluble reagents or catalysts to this end have been highlighted in the recent literature. We have recently embarked on a program to explore catalytic, enantioselective organometallic chemistry in nonconventional solvents for which we required a flexible, rapid access to a variety of water-soluble (or otherwise) chiral ligands for use as auxiliaries in the synthesis of enantiomerically pure compounds. Herein we report on a simple and reliable methodology for the preparation of carboxylated phosphines and phosphine oxides which bears a close relationship with the recently discovered palladium-catalyzed amination of aromatic halides.[4] We also report on its scope and limitations when applied to the synthesis of chiral, optically active monophosphine **1** (Figure 1), a carboxylated analogue of Hayashi's MOPs.[5] Chiral 2-(diphenylphosphino)-2′-alkoxy-1,1′-binaphthyls (MOPs) have been employed as chiral monodentate ligands in catalytic, enantioselective hydrosylilation[6] and reduction of allylic esters.[7]

The condensation of an aromatic electrophile and a primary or secondary phosphine is arguably the most direct, general route toward carboxylated phosphines. Given the well-known regiochemical limitations of aromatic nucleophillic substitutions we decided to explore the palladium-catalyzed direct phosphination of aromatic triflates as an attractive, presumably general, alternative toward that end. The availability of the required triflates

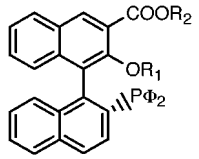

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Figure 1.

and secondary phosphines also added to this decision, as well as the fact that closely related palladium-catalyzed aminations of aromatic halides have been recently achieved using aminostannanes, aminoboranes, or, even simpler, NH compounds in the presence of a strong base.[8] A survey of the literature on transition metal-catalyzed formation of carbon−phosphorus bonds revealed that palladium-catalyzed coupling of aryl halides with stannyl- and silylphosphines had already been recognized as a useful entry to tertiary phosphines back in 1987,[9] but the method has remained largely unexplored since then. Imamoto's phosphine−borane complexes, on the other hand, have been shown to undergo coupling with aryl iodides, but failure has been reported with other aryl halides,[10] as well as with aryl triflates.[11] Special mention, in this regard, merits the recently published BINAP synthesis through nickel(0)-catalyzed C−P(III) formation carried out on the corresponding triflate, where the palladium(0)-catalyzed reaction had previously failed.[12] Formation of C−P(V) bonds mediated by palladium-catalyzed reactions appears to be less problematic as judged by the abundant number of inter- or intramolecular couplings of P(V)-H nucleophiles such as phosphinic esters,[13] secondary phosphine oxides,[14] or phosphonate esters[15] with halides or even triflates[16] in the presence of weak bases. Nevertheless, as demonstrated by Morgans et al., this reaction could not be applied to the

(1) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.

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(3) Herrmann, W. A.; Kohlpaintner, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.

(4) The first publications on the subject are due to the following: Kosugi, M.; Kameyama, M.; Migita, T. *Chem. Lett.* **1983**, 927. Kosugi, M.; Kameyama, M.; Sano, H.; Migita, T. *Nippon Kagaku Kaishi* **1985**, *3*, 547. See ref 8 for more recent work.

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(7) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775. Hayashi, T.; Iwamura, H.; Uozumi, Y.; Matsumoto, Y.; Ozawa, F. *Synthesis* **1994**, 526.

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(9) Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748.

(10) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244. Oshiki, T.; Imamoto, T. *J. Am. Chem. Soc.* **1992**, *114*, 3975. Imamoto, T. *Pure Appl. Chem.* **1993**, *65*, 655.

(11) Horiuchi, T.; Ohta, T.; Stephan, M.; Takaya, H. *Tetrahedron: Asymmetry* **1994**, *5*, 325.

(12) Cai, D.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *J. Org. Chem.* **1994**, *59*, 7180.

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(14) Xu, Y; Xia, J.; Guo, H. *Synthesis* **1986**, 691. Xu, Y.; Li, Z.; Xia, J.; Guo, H.; Huang, Y. *Synthesis* **1984**, 781.

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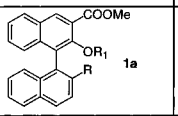
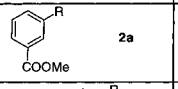
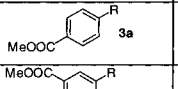
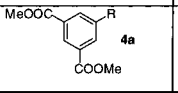
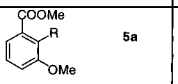
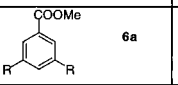
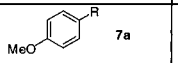
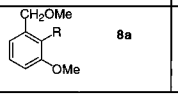
Table 1

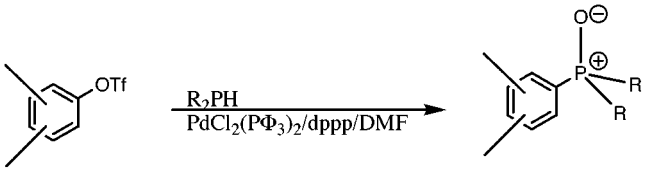
Entry	Starting Triflate (R=OTf)	Product (b R=P(O) PPh_2) (c R=P(O) PEt_2)	Method	Yield %
1	 **1a**	**1b** **1b**	**A** **B**	0 76
2	 **2a**	**2b**	**A**	89
3		**2c**	**A**	21
4	 **3a**	**3b**	**A**	95
5	 **4a**	**4b**	**A**	82
6	 **5a**	**5b**	**A**	62
7	 **6a**	**6b**	**A**	40
8	 **7a**	**7b**	**A**	90
9	 **8a**	**8b**	**A**	71

synthesis of BINAPO as only one triflate moiety was found to undergo coupling.[17]

Results and Discussion

In light of the successful amination of aryl halides promoted by palladium(0),[4,8] the analogous coupling of secondary phosphines with simple aryl triflates in the presence of base appeared to us as the solution of choice for a rapid access to nonsymmetric tertiary phosphines. We were conscious though that complications may appear as a result of competition of the different phosphines for the palladium species present in the catalytic cycle. Accordingly, for our planned access to carboxylated monophosphine **1** we choose to optimize first the reaction with the carboxyl-substituted aryl triflates **2**, **3**, **4**, **5**, and **6** in the presence of an appropriate base (Table 1). For the sake of completeness this methodology was also extended to some extra examples of simple aryl triflates (**7** and **8**) whose results are also included in Table 1. Initial assays immediately showed that only phosphine oxides were obtained instead of the desired tertiary phosphines. Nevertheless, as only one single example of this R_2PH to R_2ArPO transformation had been reported in the literature,[17] we have further pursued the optimization (carried out with triflates **6** and **7**) of such reaction variables as the source of catalyst, the bidentate phosphine ligand added, and base, solvent, and temperature. It is worth remarking at this point that the reaction did not occur if carried out in the absence of the palladium catalyst (triflate **7a** remained unaltered after heating with diphenylphosphine and triethylamine or diisopropylethylamine, for 15 h at 100 °C, as shown by ^{19}F NMR monitoring). In agreement with the recent report of Amatore and Jutand et al.,[18] we found that the presence of a chelating phosphine is also a stringent requirement for the reaction to occur (triflate **7a** remained almost unaltered after heating with diphenylphosphine, $PdCl_2(PPh_3)_2$, and diisopropylethylamine, for several hours at 100 °C, as shown by ^{19}F NMR monitoring). After some experimentation it was found that acceptable-to-good yields of the final phosphine oxide products were obtained when employing a catalytic amount (5−10% mol, per each -OTf rest) of $PdCl_2(PPh_3)_2$ as catalyst precursor (both $Pd(OAc)_2$ and $NiCl_2(PPh_3)_2$ gave somewhat lower yields in most cases), diisopropylethylamine as base (other bases assayed were sodium carbonate, DABCO or sodium *tert*-butoxide, yielding much poorer results in the former two cases and complete destruction in the latter case), and 1,3-bis(diphenylphosphino)propane (nonchelating phosphines or arsines such as PPh_3 or PAs_3 did not work, whereas dppb, dppe, or dppf[19] gave substantially lower yields) in refluxing DMF as solvent (THF and other low-boiling temperature solvents gave recovered starting material) (Scheme 1). Either secondary alkyl or aryl phosphines can be employed as reactants though yields with the former are significantly lower (Table 1, entry 3).

Scheme 1



Although aside from our original objective, a number of experiments have been carried out to shed some light into the mechanism of the reaction[20] and in particular, in an attempt to establish the nature of the phosphorus actual reagent (either a P−H or a P−(O)H species) involved in the coupling step. Extensive ^{31}P NMR monitoring of the phosphinylation reaction under different conditions (both the DMF-d_6 and DMSO-d_6 employed as solvents contained some residual water and were not degassed) has led us to the following observations: (1) in the absence of palladium no significant Ph_2PH to $Ph_2P(O)H$ oxidation was observed even after heating Ph_2PH or a mixture of **7a** + Ph_2PH + R_3N for several hours; (2) when oxygen (air) is introduced on purpose, Ph_2PH is consumed completely even in the absence (slow reaction) of palladium; significantly, in the presence of a palladium(0) species such as $(Ph_3P)_4Pd$, residual oxigen in the medium promotes the instantaneous oxidation of Ph_2PH into $Ph_2P(O)H$; (3) fast oxidation also occurs when the mixture **7a** + Ph_2PH is heated in the presence of the catalytic Pd(II) species being used [$PdCl_2(PPh)_3$ or $Pd(OAc)_2$], either with (faster) or without (slower) added amine; the red-orange (with added amine) or yellowish solutions (without amine) so produced contain both Ph_2PH (rapidly exchanging, broad signal) and $Ph_2P(O)H$ (sharp); these later observations agree well with the occurrence of the well-established redox processes Pd(II)

(17) Kurtz, L.; Lee, G.; Morgans, D., Jr.; Waldyke, M. J.; Ward, T. *Tetrahedron Lett.* **1990**, *31*, 6321. See also: Doucet, H.; Brown, J. M. *Tetrahedron: Asymmetry* **1997**, *8*, 3775.

(18) Amatore, C.; Broeker, G.; Jutand, A.; Khalil F. *J. Am. Chem. Soc.* **1997**, *119*, 5176.

(19) Acronyms dppb, dppe, dppf, and dppp stand for 1,4-bis(diphenylphosphino)butane, 1,2-bis(diphenylphosphino)ethane, 1, 1′-bis(diphenylphosphino)ferrocene, and 1,3-bis(diphenylphosphino)propane, respectively.

(20) Detailed mechanistic studies are in progress.

→ Pd(0)//Ph_2PH → Ph_2PPPh_2,[9] followed by palladium(0)-catalyzed oxidation (see below). In summary, this qualitative study revealed that in our reaction mixtures an excess of rapidly equilibrating Ph_2PH (^{31}P, broad) coexists with a limited amount of free $Ph_2P(O)H$ (^{31}P, narrow) at the outset of the reaction, i.e., prior to the addition of triflates.

In principle, the following crude working hypothesis for the formation of the final $Ph_2P(O)Ar$ products can be considered: (i) Ph_2PH is completely oxidized to $Ph_2P(O)H$ during the initial stages of the reaction by Pd(0)[21]-catalyzed oxidation promoted by oxygen which enters the reaction vessel; the key phosphinylation reagent will thus be $Ph_2P(O)H$; (j) the key coupling step involves Ph_2PH/R_3N attack on the species resulting from oxidative addition [$ArPd(L)_2^+$ TfO^-],[22] followed by oxidation[23] of $ArPd(L)_2PPh_2$ to $ArPd(L)_2P(O)Ph_2$ and, eventually, by reductive elimination; (k) coupling as in (j) leads to phosphines Ph_2PAr which are then oxidized to the final $Ph_2P(O)Ar$ products. The failure to isolate tertiary phosphines Ph_2PAr from the reaction mixtures would suggest that either (i) or (j), or a combination or both, is the actual mechanistic scheme operating in our reactions. Even though we are prone to consider (j) as a less plausible alternative, it is clear that careful mechanistic work is needed to clarify this point.[20]

An unexpected limitation was found for the case of naphthyl triflates. Thus, in striking contrast with our results using common aryl triflates, the application of our optimized palladium-catalyzed methodology (method A) to the preparation of monophosphine oxide **1b** from **1a** (R_1 = H) failed, monotriflate **1a** (R_1 = H) being recovered unchanged. On the other hand, application of Cai's nickel(0) protocol to **1a** (R_1 = H) led to a very complex mixture in which we could not find evidence of the desired phosphine. Eventually, the desired **1a** to **1b** (R_1 = H) conversion could be achieved by using a slightly modified Morgans' phospinylation procedure which employs pure, commercial $Ph_2P(O)H$ as reactant (method B). The unexpected failure of **1a** (2-methyl-1-naphthyl and 2-naphthyl triflate behaved analogously as according to NMR analysis) to undergo coupling with Ph_2PH (method A) was initially taken as a disclaim of mechanism (i) above. However, things turned out to be also complicated for Morgans' phosphinylation reaction as we discovered (^{31}P and ^{19}F NMR monitoring) that Ph_2PH can act as a strong inhibitor for this reaction as applied for naphthyl triflates. In fact, we found that whereas common aryl triflates such as **7a** undergo phosphinylation reaction with either (a) pure $Ph_2P(O)H$ or (b) pure Ph_2PH and (c) a 1:1 mixture of Ph_2PH and $Ph_2P(O)H$, the corresponding reaction carried out with **1a** worked well only with (a) pure $Ph_2P(O)H$ but failed to occur with (b) Ph_2PH or (c) a 1:1 mixture of Ph_2PH and $Ph_2P(O)H$; identical results were found for 2-methyl-1-naphthyl or 2-naphthyl triflate as revealed by NMR. Again, a clear explanation must await a full mechanistic study.

For the sake of completeness we have proceeded to convert a couple of phosphine oxides to the corresponding carboxylated phosphines by recourse to the usual trichlorosilane/triethylamine reduction procedure.[24] Phosphine **2** (R = $P(Ph)_2$) was obtained uneventfully by reduction of **2b**. However, direct reduction of phenol **1b** (R_1 = H, R = $P(O)PPh_2$) was unsuccessful, due to the ease of oxidation of the corresponding phenolic phosphine. Reduction took place as expected on the easily available benzyl derivative **1b** (R_1 = Bz, R = $P(O)PPh_2$), the corresponding phosphine **1** (R_1 = Bz) being thus obtained without difficulty.

Sizable amounts of optically active (R) phosphine **1** (R_1 = Bz) were obtained in this manner, starting with triflate **1a** (R_1 = H), itself obtained from the corresponding optically active phenol, available by resolution of racemic 3-(methoxycarbonyl-2,2′-dihydroxy-1,1′-binaphthalene.[25]

In summary, the palladium-catalyzed coupling of secondary phosphines with aryl triflates is a convenient method for making C−P bonds. Phosphine oxides are obtained instead of the expected phosphines. Even though a wide range of aryl triflates can be used as substrates, the method failed for some naphthalene derivatives, for which Morgans' phosphinylation procedure which uses pure, commercial $Ph_2P(O)H$ worked well. We have also uncovered that Ph_2PH can act as a strong inhibitor of Morgans' phosphinylation, though only for naphthalene derivatives. In light of the much wider availability of secondary phosphines and their being much cheaper (10 times) than the corresponding phosphine oxides, we suggest the use of our method for accessing aryl phosphine oxides. Carboxylated phosphines **1** and related analogues can now be assayed in two-phase organometallic chemistry.

Experimental Section

General. Melting points were taken on a capillary melting point apparatus and are uncorrected. NMR spectra (^1H, ^{13}C, ^{31}P) were obtained on a Bruker AMX-300 spectrometer in $CDCl_3$ or DMSO-d_6. Low- and high-resolution electron impact mass spectra were recorded at 70 eV ionizing energy. Elemental analyses were obtained at the Servicio de Microanalisis de la U. de Zaragoza. Column chromatographies were performed on Merck silica gel (Kieselgel 40). Commercial anhydrous DMF, $NiCl_2(PPh_3)_2$, $PdCl_2(PPh_3)_2$, $Pd(OAc)_2$, $HPPh_2$, and 1,4-diazabicyclo[2.2.2]octane (DABCO) were used as received. Racemic 3-(methoxycarbonyl)-2,2′-dihydroxy-1,1′-binaphthalene was obtained by copper-mediated heterocoupling involving 2-naphthol and 2-hydroxy-3-naphthoic acid as described by Hovorka et al. and eventually resolved into its enantiomers.[26] Phenol triflates **1a**−**8a** and naphthyl triflates were prepared as previously reported from the corresponding phenols.[27] The purity of all compounds for which no elemental analysis is provided was judged to be higher than 95% by ^{13}C and ^1H NMR (see Supporting Information). The NMR samples employed for the mechanistic analysis were prepared using Schlenk tecniques under argon, and eventually the tubes were sealed.

(21) Palladium and platinum(0) possess catalytic activity in the oxidation of phosphines. See: Takahashi, S.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc. Jpn.* **1966**, *87*, 610. Kashiwagi, T.; Yasuoka, N.; Kasai, N.; Kakudo, M. *J. Chem. Soc., Chem. Commun.* **1969**, 743.

(22) Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810.

(23) For a related Re−PPh_2 to Re−$P(O)Ph_2$ oxidation, see: Buhro, W. E.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3346.

(24) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012. Vineyard, B. D.; Knowles, W. S.; Sabacky, S. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.

(25) Hovorka, M.; Scigel, P.; Gunterova, J.; Tichy, M.; Závada, J. *Tetrahedron* **1992**, *48*, 9503.

(26) To be reported in due course. Partially enriched material has been obtained by enantioselective oxidative coupling in the presence of a chiral amine. See: Smrcina, M.; Poláková, J.; Vyskocil, S.; Kocovsky, P. *J. Org. Chem.* **1993**, *58*, 4534.

(27) (a) Saá, J. M.; Martorell, G.; García-Raso, A. *J. Org. Chem.* **1992**, *57*, 678. (b) Martorell, G.; García-Raso, A.; Saá, J. M. *Tetrahedron Lett.* **1990**, *31*, 2357. (c) Saá, J. M.; Dopico, M.; Martorell, G.; García-Raso, A. *J. Org. Chem.* **1990**, *55*, 991. (d) Saá, J. M.; Martorell, G. *J. Org. Chem.* **1993**, *58*, 1963.

General Procedure for the Palladium-Catalyzed Coupling of Secondary Phosphines with Aryl Triflates. Method A. A three-necked round-bottom flask charged with a mixture of 0.2 mmol of triflate, 0.3 mmol of diphenylphosphine (or diethylphosphine), dppp (0.015 mmol), and $PdCl_2(PPh_3)_2$ (0.01 mmol) and diisopropylethylamine (1 mmol) in 2.5 mL of DMF was heated overnight to reflux, under argon. Water and ether (25 mL) were added, and the organic phase was washed with 1.5 N HCl (6 × 20 mL), brine, and water and finally dried over anhydrous sodium sulfate. Evaporation to dryness yielded crude material which was purified by column chromatography (*n*-hexanes−ethyl acetate). Final crystallization or bulb-to-bulb distillation furnished pure products.

(3-Methoxycarbonylphenyl)diphenylphosphine Oxide (2b). Colorless oil, bp 135−140 °C/0.02 mmHg. IR (film) *ν*: 3060, 2950, 1725, 1440, 1295, 1270, 1195, 1130, 1120, 750, 730, 700 cm^{-1}. ^1H NMR *δ*: 8.32 (d, 1H, *J* = 12.1 Hz), 8.18 (dd, 1H, *J* = 7.8 and 1.2 Hz), 7.87 (dd, 1H, *J* = 7.8, and 11.7 Hz), 7.67−7.43 (m, 11H), 3.85 (s, 3H) ppm. ^{31}P NMR *δ*: 26.40 ppm. ^{13}C NMR *δ*: 166.68, 136.84, 136.71 134.69, 133.60, 133.48, 133.46, 133.33, 133.16, 132.78, 132.75, 132.64, 132.51, 131.77, 131.19, 131.03,129.38, 129.29, 129.22, 129.13, 52.90 ppm. EIMS: *m/e* (%) 336 (M^+, 50), 335 (100), 277 (30), 259 (10), 201 (20), 183 (23), 152 (33), 77 (28). HRMS calcd for $C_{20}H_{17}O_3P$: 336.09153. Found: 336.09049.

(4-Methoxycarbonylphenyl)diphenylphosphine Oxide (3b). White solid, mp 104−105 °C. IR (film) *ν*: 3060, 2960, 1730, 1440, 1290, 1280, 1200, 1125, 1110, 740, 730, 710 cm^{-1}. ^1H NMR *δ*: 8.10 (dd, 2H, *J* = 8.4 and 2.4 Hz), 7.75 (dd, 2H, *J* = 11.5 and 8.4 Hz), 7.68−7.45 (m, 10H), 3.93 (s, 3H) ppm. ^{31}P NMR *δ*: 26.65 ppm. ^{13}C NMR *δ*: 166.04, 138.15, 136.81, 132.98, 132.37, 132.01, 131.95, 131.90, 131.82, 131.77, 130.98, 129.28, 129.12, 128.53, 128.36, 52.27 ppm. EIMS: *m/e* (%) 336 (M^+, 40), 335 (100), 278 (6), 277 (18), 201 (11), 199 (8), 152 (10), 77 (15). HRMS calcd for $C_{20}H_{16}O_3P$ ($M^+ - 1$): 335.08370. Found: 335.08415.

[3,5-Bis(methoxycarbonyl)phenyl]diphenylphosphine Oxide (4b). Solid, mp 224−225 °C. IR (film) *ν*: 3060, 2950, 1730, 1440, 1320, 1250, 1200, 1150, 1120, 1000, 750, 725, 700 cm^{-1}. ^1H NMR *δ*: 8.83 (d, 1H, *J* = 1.2 Hz), 8.54 (dd, 2H, *J* = 11.6 and 1.2 Hz), 7.69−7.46 (m, 10H), 3.92 (s, 3H) ppm. ^{31}P NMR *δ*: 25.53 ppm. ^{13}C NMR *δ*: 166.06, 137.59, 137.45, 134.90, 134.50, 133.16, 133.12, 132.79, 132.66, 131.92, 131.77, 131.47, 129.58, 129.42, 53.32 ppm. EIMS: *m/e* (%) 394 (M^+, 55), 393 (100), 379 (32), 363 (15), 335 (18), 201 (24), 199 (7), 183 (12), 152 (8), 77 (20). HRMS calcd for $C_{22}H_{18}O_5P$ ($M^+ - 1$): 393.08918. Found: 393.08931.

[2-Methoxycarbonyl-6-methoxyphenyl]diphenylphosphine Oxide (5b). Solid, mp 123−126 °C. IR (film) *ν*: 3060, 2950, 1730, 1570, 1460, 1440, 1300, 1185, 1120, 1150, 1120, 1060, 760, 730, 700 cm^{-1}. ^1H NMR *δ*: 7.71−7.38 (m, 11H), 7.22 (dd, 1H, *J* = 8.2 and 2.4 Hz), 6.95 (dd, 1H, *J* = 8.2 and 3.6 Hz), 3.79 (s, 3H), 3.34 (s, 3H) ppm. ^{31}P NMR *δ*: 24.90, ppm. ^{13}C NMR *δ*: 170.14, 170.08, 160.77, 160.72, 141.65, 141.59, 135.10, 134.36, 134.34, 133.65, 132.69, 132.56, 132.50, 132.46, 132.07, 131.94, 131.88, 131.84, 129.12, 128.96, 128.62, 128.45, 122.02, 121.90, 120.58, 119.26, 114.09, 114.01, 55.88, 53.20 ppm. EIMS: *m/e* (%) 365 (0.4), 352 (11), 351 (50), 289 (9), 199 (11), 152 (15), 91 (100), 77 (56). Anal. Calcd for $C_{21}H_{19}O_4P$: C, 68.85; H, 5.19. Found: C, 69.04; H, 5.20.

(5-Methoxycarbonylphenyl)-1,3-bisdiphenylphosphine Oxide (6b). Obtained as a solid, mp 224−225 °C. ^1H NMR *δ*: 8.58 (dd, 2H, *J* = 11.1 and 1.4 Hz), 7.93 (t, 1H, *J* = 1.4 Hz), 7.59−7.39 (m, 20H), 3.86 (s, 3H) ppm. ^{31}P NMR *δ*: 25.60 ppm. ^{13}C NMR *δ*: 165.79, 139.67, 139.53, 139.38, 136.82, 136.78, 136.67, 136.63, 135.95, 135.81, 134.62, 134.48, 132.98, 132.96, 132.94, 132.53, 132.46, 132.39, 131.82, 131.67, 131.52, 131.01, 129.39, 129.13, 46.16 ppm. EIMS: *m/e* (%) 536 (M^+, 42), 535 (43), 459 (18), 335 (100), 334 (59), 257 (19), 201 (86), 199 (32), 152 (28), 77 (71). HRMS calcd for $C_{32}H_{26}O_4P_2$: 536.13063. Found: 536.12903.

(4-Methoxyphenyl)diphenylphosphine Oxide (7b). Obtained as a yellow oil, bp 223−225 °C (0.04 mm of Hg). IR (film) *ν*: 3060, 2950, 1600, 1505, 1440, 1290, 1255, 1190, 1180, 1120, 1030, 730, 710, 700 cm^{-1}. ^1H NMR *δ*: 7.67−7.42 (m, 12H), 6.94 (dd, 2H, *J* = 8.8 and 2.2 Hz), 3.81 (s, 3H) ppm. ^{31}P NMR *δ*: 27.12 ppm. ^{13}C NMR *δ*: 163.07, 163.03, 134.58, 134.43, 134.16, 132.78, 132.64, 132.51, 132.39, 132.35, 129.08, 128.92 124.78, 123.32, 114.73, 114.56, 55.90 ppm. EIMS: *m/e* (%) 292 (M^+, 21), 262 (100), 183 (85), 152 (11), 108 (30), 107 (18), 75 (4), 51 (7). HRMS calcd for $C_{19}H_{17}O_2P$: 308.09661. Found: 308.09517.

[2-(Methoxymethyl)-6-methoxyphenyl]diphenylphosphine Oxide (8b). Solid, mp 107−108 °C. IR (film) *ν*: 3060, 2970, 1590, 1570, 1465, 1440, 1270, 1185, 1120, 1070, 755, 725, 700, cm^{-1}. ^1H NMR *δ*: 7.69−7.37 (m, 12H), 6.75 (dd, 1H, *J* = 8 and 4.9 Hz), 5.13 (s, 2H), 3.38 (s, 3H), 3.20 (s, 3H) ppm. ^{31}P NMR *δ*: 29.74 ppm. ^{13}C NMR *δ*: 160.99, 160.93, 148.49, 148.41, 136.41, 134.98, 134.19, 134.16, 132.69, 132.56, 132.48, 132.45, 131.85, 131.71, 131.60, 131.56, 129.11, 128.95, 128.59, 128.43, 121.66, 121.53, 118.37, 117.03, 111.24, 111.16, 72.71, 72.67, 58.99, 55.41 ppm. EIMS: *m/e* (%) 352 (0.4), 351 (2), 278 (22), 277 (52), 201 (12), 199 (12), 183 (11), 149 (82), 86 (64), 84 (100), 77 (15). Anal. Calcd for $C_{21}H_{21}O_3P$: C, 71.59; H, 5.96. Found: C, 71.68; H, 5.95.

[3-Methoxycarbonylphenyl]diethylphosphine Oxide (2c). Obtained as a yellow oil, bp 210−215 °C (0.001 mmHg). IR (film) *ν*: 2980, 1720, 1295, 1270, 1160, 1140, 750 cm^{-1}. ^1H NMR *δ*: 8.26 (ddd, 1H, *J* = 10.9, 1.4 and 1.1 Hz), 8.17 (ddd, 1H, *J* = 7.8, 1.5 and 1.1 Hz), 7.96 (tm, 1H, *J* = 7.6 Hz), 7.58 (tm, 1H, 5.5 Hz), 3.92 (s, 3H), 1.95 (m, 4H), 1.09 (m 6H) ppm. ^{31}P NMR *δ*: 41.77 ppm. ^{13}C NMR *δ*: 166.94, 136.06, 135.96, 133.81, 133.26, 133.22, 132.61, 131.86, 131.73, 131.16, 129.65, 129.51, 53.06, 23.37, 22.45, 6.17, 6.10 ppm. EIMS: *m/e* (%) 240 (M^+, 7), 212 (100), 211 (99), 183 (34), 151 (9), 123 (9), 105 (9), 77 (10). HRMS calcd for $C_{12}H_{17}O_3P$: 240.09153. Found: 240.09169.

(*R*,*S*)-3-Methoxycarbonyl-2-hydroxy-2′-[[(trifluoromethyl)sulfonyl]oxy]-1,1′-binaphthalene. Pale yellow solid, mp 156−160 °C. ^1H NMR: *δ* 10.81 (s, 1H, OH), 8.73 (s, 1H, ArH), 7.91−8.09 (m, 3H, ArH), 7.53−7.60 (m, 2H, ArH), 7.33−7.42 (m, 4H, ArH), 7.04−7.26 (m, 1H, ArH), 4.07 (s, 3H, OCH_3) ppm. ^{13}C NMR: *δ* 171.9, 155.25, 146.54, 137.67, 134.79, 134.08, 133.45, 131.51, 130.54 (2C), 129.19, 128.40, 127.77, 127.67, 127.36, 126.93, 125.45, 124.97, 120.34, 119.04 (q, *J* = 320 Hz, CF_3), 115.12, 114.72, 53.56 ppm. EIMS: *m/z* (%) 476 (M^+, 100), 444 (44), 295 (69), 283 (86). HRMS calcd for $C_{23}H_{15}O_6SF_3$: 476.0530. Found: 476.0541.

Palladium-Catalyzed Coupling of Secondary Phosphine Oxides with Aryl Triflates. Method B. A three-necked round-bottom flask charged with a mixture of 0.2 mmol of triflate, 0.4 mmol of diphenylphosphine oxide, dppp (0.015 mmol), and $Pd(AcO)_2$ (0.01 mmol) and diisopropylethylamine (1 mmol) in 2.5 mL of DMSO was heated overnight to reflux, under argon. The solvent was removed under reduced pressure. To the residue were added water and ether (25 mL), and the organic phase was washed with 1.5 N HCl (6 × 20 mL), brine, and water and finally dried over anhydrous sodium sulfate. Evaporation to dryness yielded a crude material which was purified by column chromatography (*n*-hexanes−ethyl acetate). Final crystallization or bulb-to-bulb distillation furnished pure products.

(*R*,*S*)-3-Methoxycarbonyl-2-hydroxy-2′-(diphenylphosphinyl)-1,1′-binaphthalene (1b) (R_1 = H). The title compound was obtained by treating (*R*,*S*)-3-(methoxycarbonyl)-2-hydroxy-2′-[[(trifluoromethyl)sulfonyl]oxy]-1,1′-binaphthalene as shown above. It was obtained as a yellow solid, mp 178−179 °C. IR (film) *ν*: 3060, 2980, 1740, 1685, 1440, 1350, 1330, 1300, 1215, 1125, 920, 755, 730, 719, 705 cm^{-1}. ^1H NMR *δ*: 10.38 (s, 1H), 8.30 (s, 1H), 7.93 (m, 3H), 7.67 (m, 3H), 7.55 (td, 1H, *J* = 6.6 and 1.1 Hz), 7.41 (td, 1H, *J* = 7.2 and 1.5 Hz), 7.27 (m, 8H), 7.11 (td, 1H, *J* = 7.2 and 1.5 Hz), 6.95 (m, 3H), 3.99 (s, 3H) ppm. ^{31}P NMR *δ*: 25.84 ppm. ^{13}C NMR *δ*: 170.72, 154.19, 140.03, 140.10, 138.19, 135.50, 135.47, 134.69, 133.98, 133.45, 133.32, 133.29, 132.71, 132.51, 131.84, 131.81, 131.76, 131.71, 131.58, 131.15, 131.11, 130.39, 129.71, 129.62, 129.54, 128.81, 128.73, 128.66, 128.56, 128.50, 127.83, 127.66, 127.19, 127.14, 126.17, 124.49, 119.50, 119.43, 113.72, 53.15 ppm. EIMS: *m/e* (%) 528 (M^+, 61), 468 (22), 326 (100), 295 (15), 277 (29), 267 (24), 239 (14), 214 (10), 201 (98), 155 (5), 77 (12). HRMS calcd for $C_{34}H_{25}O_4P$: 528.14904. Found: 528.15063.

(*R*,*S*)-3-Methoxycarbonyl-2-(benzyloxy)-2′-(diphenylphosphinyl)-1,1′-binaphthalene (1b) (R_1 = Bz). To a stirred solution of 528 mg (1 mmol) of **1b** (R_1 = H) and 276 mg of potassium carbonate (2 mmol) in dry DMF (5 mL) was added 257 mg (180 *μ*L, 1.5 mmol) of benzyl bromide via syringe. The mixture was heated at 60−70 °C for 1−2 h, until the yellow color

completely vanished. The solution was cooled to room temperature and was partitioned into ether and 2 N hydrochloric acid. The organic layer was washed with hydrochloric acid and brine, dried over anhydrous sodium sulfate, and evaporated to dryness. The solid residue was purified by column chromatography on silica gel (a 4:1 mixture of ethyl acetate−methylene choride was used as eluant) to yield 575 mg (93% yield) of **1b** (R_1 = Bz) as a white solid. Recrystallization in hexanes−ethyl acetate afforded white needles, mp 122−4 °C. ^{1}H NMR: δ 8.24 (s, 1H, ArH), 7.85−8.01 (m, 3H, ArH), 7.72 (d, J = 8 Hz, 1H, ArH, 7.42−7.56 (m, 3H, ArH), 7.02−7.36 (m, 14 H, ArH), 6.92 (d, J = 8 Hz, 1H, ArH), 6.68−6.82 (m, 2H, ArH), 6.65 (m, 1H, ArH), 5.01 (d, J = 10 Hz, 1H, OCH_2), 4.33 (d, J = 10 Hz, 1H, OCH_2), 3.91 (s, 3H, OCH_3) ppm. ^{13}C NMR: δ 167.18, 153.33, 139.57, 139.46, 137.81, 136.36, 135.27, 135.25, 134.94, 134.38, 133.97, 133.82, 133.68, 133.00, 132.84, 132.76, 132.70, 132.50, 132.29, 132.13, 132.07, 132.00, 131.83, 131.80, 131.39, 131.35, 131.15, 130.02, 129.87, 129.85, 129.28, 129.25, 129.19, 129.00, 128.89, 128.77, 128.73, 128.67, 128.63, 128.57, 128.50, 128.40, 128.12, 127.80, 127.78, 127.73, 127.61, 126.75, 126.03, 124.89, 76.00, 52.90 ppm. ^{31}P NMR: δ 27.94 (s, 1P) ppm. EIMS: m/z (%) 618 (M^+, 19), 527 (45), 416 (20), 201 (100). HRMS calcd for $C_{41}H_{31}O_4P$: 618.1960. Found: 618.1951.

General Procedure for the Reduction of Phosphine Oxides. At 0 °C, trichlorosilane (1 mmol) was carefully added to a mixture of phosphine oxide (0.2 mmol) and triethylamine (4.8 mmol) in xylene (5 mL) in a three-necked round-bottom flask, under argon. The mixture was then heated to reflux overnight. To the cooled mixture were added ether and sodium bicarbonate. Solids were removed by filtration, and the solvent was removed under reduced pressure. The crude phosphine was purified by column chromatography on silica gel using hexane/ethyl acetate as eluant.

***(R,S)*-3-Methoxycarbonyl-2-(benzyloxy)-2′-(diphenylphosphino)-1,1′-binaphthalene (1) (R_1 = Bz).** Obtained by reduction of **1b** (R_1 = Bz) according to the general method above in 73% yield as a colorless solid, mp 184−6 °C. ^{1}H NMR: δ 8.65 (s, 1H, ArH), 7.93−7.97 (m, 3H, ArH), 7.49−7.56 (m, 2H, ArH), 7.33−7.40 (m, 3H, ArH), 7.01−7.24 (m, 14H, ArH), 6.83 (d, J = 8.5 Hz, 1H, ArH), 6.68 (m, 2H, ArH), 5.01 (d, J = 9.9 Hz, 1H, OCH_2), 4.47 (d, J = 9.9 Hz, 1H, OCH_2), 3.95 (s, 3H, OCH_3) ppm. ^{13}C NMR: δ 167.67, 153.12, 153.10, 141.93, 141.47, 138.79, 138.62, 137.96, 137.89, 137.71, 137.45, 137.29, 136.58, 136.55, 134.68, 134.40, 134.27, 134.07, 133.92, 133.82, 133.77, 133.53, 131.57, 131.45, 131.25, 131.22, 130.10, 129.51, 128.94, 128.75, 128.72, 128.67, 128.52, 128.49, 128.38, 127.94, 127.47, 127.42, 127.37, 126.78, 126.02, 125.86, 75.90, 52.95 ppm. ^{31}P NMR: δ −15.26 ppm. EIMS: m/z (%) 602 (M^+, 1), 571 (3), 495 (100). HRMS calcd for $C_{41}H_{31}O_3P$: 602.2011. Found: 602.2008.

Chiral, optically active (*R*)-**1** ($[\alpha]^{20}_D$ = −49.8 °, c = 1, THF) was obtained analogously.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **1**, **1b** (R_1 = H), **1b** (R_1 = Bz), **2b**, **2c**, **3b**, **4b, 5b**, **6b**, **7b**, and **8b** (26 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.

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