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Synthesis of Biaryls by Intramolecular Radical Transfer in Phosphinates

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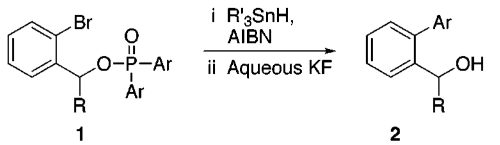
Phosphinates **20a**−**35a** give biaryls **20b**−**35b** on heating with stannanes in the presence of AIBN. The process involves a radical ipso substitution on the migrating aryl ring.

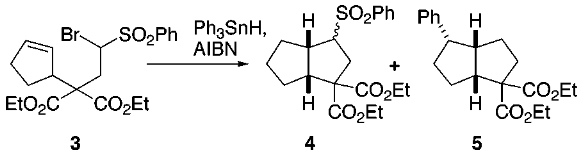
In a preliminary communication,[1] we reported several examples of the radical aryl transfer summarized in eq 1 (R = H, Me; Ar = aromatic or heteroaromatic). Here



(1)

we describe full details of that work, provide additional examples, and give the results of a brief mechanistic study, but we have not made a comparison with standard organometallic routes[2] to biaryls.

The first instance of a radical aryl transfer observed in this laboratory was met during the cyclization of **3** to **4**.[3] One of the byproducts (18%) was compound **5**, the result of intramolecular phenyl transfer and loss of SO$_2$.



(2)

At that time, a number of radical aryl transfers were already known, and more have since been reported. The transfers involve migration of the aryl group (or, in a few cases, of a vinyl unit, ArC=C) from carbon to carbon,[3,4] from carbon to silicon,[5] from carbon to oxygen,[6] or from a heteroatom to carbon: O → C,[7] N → C,[8] Si → C,[9] S(VI) → C,[10] or Sn → C.[11] When the initial radical is carbon-centered, it can be a vinyl,[10g,h] aryl,[4f,g,k,7e,9f,10f,i,j,k,m] or alkyl radical.[3,4a−e,h−j,7a−d,8,9a−e,10a−e,l,11] In the latter case, it can even be stabilized by a heteroatom,[7a] or be adjacent to an electron-withdrawing group[4e,h] or an aromatic ring,[7b] and still engage in satisfactory transfer.

The transfer of aryl groups involves ipso attack of a radical on the aromatic ring, and transition state sizes for the intermediate cyclization adduct (see **8**, Scheme 1) are usually five- or six-membered (X−Y represents a chain of two or three atoms). If the transfer involves the generation of a new stereogenic center, then in some cases the process is stereoselective, either by reason of enforced delivery across one face of a cyclic structure[3,7d] or because the chain connecting the initial radical with the acceptor aryl group adopts a chair transition state[9d,e,10l] or otherwise avoids unfavorable nonbonded interac-

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(2) Synthetic methods for biaryls. See, for example: (a) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263−303. (b) Knight, D. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ed.; Pergamon Press: Oxford, 1991; Vol. 3, p 499. (c) Bringmann, G.; Breuning, M.; Tasler, S. *Synthesis* **1999**, 525−558.

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(4) Transfer from carbon to carbon: (a) Urry, W. H.; Kharasch, M. S. *J. Am. Chem. Soc.* **1944**, *66*, 1438−1440. (b) Winstein, S.; Heck, R.; Lapporte, S.; Baird, R. *Experientia* **1956**, *12*, 138−141. (c) Wilt, J. W.; Dabeck, R. A.; Welzel, K. C. *J. Org. Chem.* **1972**, *37*, 425−430. (d) Lindsay, D. A.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 7087−7093. (e) Ishibashi, H.; Nakamura, N.; Ito, K.; Kitayama, S.; Ikeda, M. *Heterocycles* **1990**, *31*, 1781−1784. (f) Giraud, L.; Lacôte, E.; Renaud, P. *Helv. Chim. Acta* **1997**, *80*, 2148−2156. (g) Alcaide, B.; Rodríguez-Vincente, A. *Tetrahedron Lett.* **1998**, *39*, 6589−6592. (h) Amii, H.; Kondo, S.; Uneyama, K. *J. Chem. Soc., Chem. Commun.* **1998**, 1845−1846. (i) Wang, S.-F.; Chuang, C.-P.; Lee, J. H.; Liu, S.-T. *Tetrahedron* **1999**, *55*, 2273−2228. (j) Senboku, H.; Hasegawa, H.; Orito, K.; Tokuda, M. *Tetrahedron Lett.* **2000**, *41*, 5699−5703. (k) Harrowven, D. C.; Nunn, M. I. T.; Newman, N. A.; Fenwick, D. R. *Tetrahedron Lett.* **2001**, *42*, 961−964.

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(6) For example, see: (a) Kharasch, M. S.; Poshkus, A. C.; Fono, A.; Nudenberg, W. *J. Org. Chem.* **1951**, *16*, 1458−1479. (b) Starnes, W. H., Jr. *J. Am Chem. Soc.* **1963**, *85*, 3708−3709. (c) Starnes, W. H., Jr. *J. Am Chem. Soc.* **1968**, *90*, 1807−1815.

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(10) Transfer from sulfur(VI) to carbon: (a) Loven, R.; Speckamp, W. N. *Tetrahedron Lett.* **1972**, 1567−1570. (b) Köhler, J. J.; Speckamp, W. N. *Tetrahedron Lett.* **1977**, 631−634. (c) Köhler, J. J.; Speckamp, W. N. *Tetrahedron Lett.* **1977**, 635−637. (d) Speckamp, W. N.; Köhler, J. J. *J. Chem. Soc., Chem. Commun.* **1978**, 166−167. (e) Köhler, H. J.; Speckamp, W. N. *J. Chem. Soc., Chem. Commun.* **1980**, 142−143. (f) Motherwell, W. B.; Pennell, A. M. K. *J. Chem. Soc., Chem. Commun.* **1991**, 877−879. (g) Motherwell, W. B.; Pennell, A. M. K.; Ujjainwalla, F. *J. Chem. Soc., Chem. Commun.* **1992**, 1067−1068. (h) Bonfand, E.; Motherwell, W. B.; Pennell, A. M. K.; Uddin, M. K.; Ujjainwalla, F. *Heterocycles* **1997**, *46*, 523−534. (i) da Mata, M. L. E. N.; Motherwell, W. B.; Ujjainwalla, F. *Tetrahedron Lett.* **1997**, *38*, 137−140. (j) da Mata, M. L. E. N.; Motherwell, W. B.; Ujjainwalla, F. *Tetrahedron Lett.* **1997**, *38*, 141−144. (k) Godfrey, C. R. A.; Hegarty, P.; Motherwell, W. B.; Uddin, M. K. *Tetrahedron Lett.* **1998**, *39*, 723−726. (l) Studer, A.; Bossart, M. *J. Chem. Soc., Chem. Commun.* **1998**, 2127−2128. (m) Bonfand, E.; Forslund, L.; Motherwell, W. B.; Vázquez, S. *Synlett* **2000**, 475−478.

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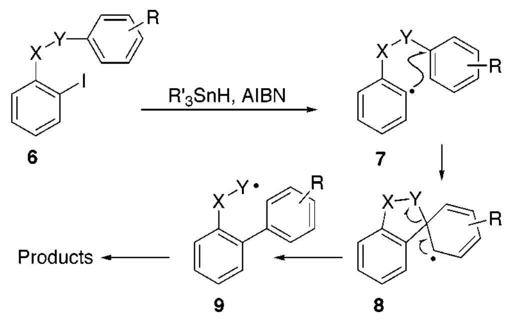
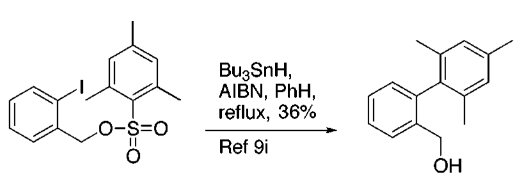
10.1021/jo010371d CCC: $20.00

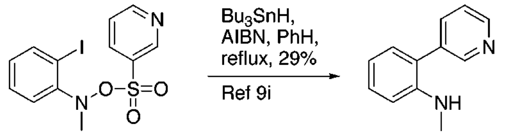
Scheme 1



tions.[4j,10e] Much of the published work has involved tethering two units, the radical center and the aryl acceptor, by means of an SO$_2$-containing linkage.[3,10a−m] Some of the aryl transfers generate biaryls,[4f,g,k,7e,9f,10f,i,j,m] and typical examples are those shown in eqs 3−9. Some of the reports describe the preparation of quite hindered biaryls.[4g,10i,m]



(3)



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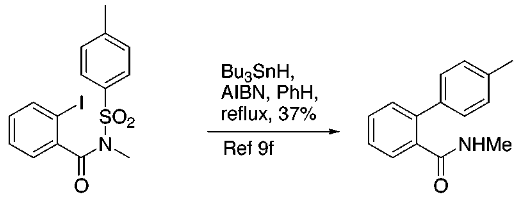
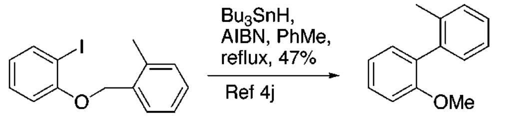
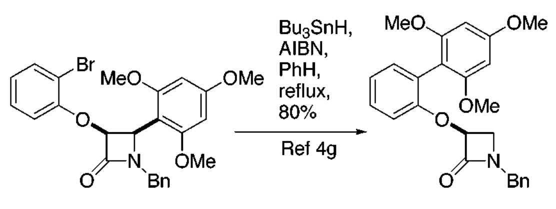


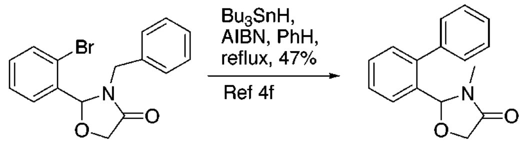
(5)



(6)



(7)



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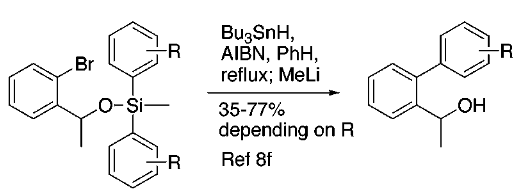
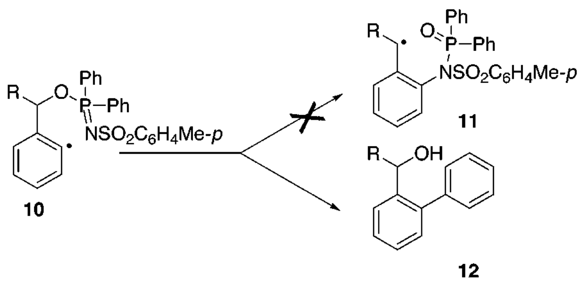


(9)

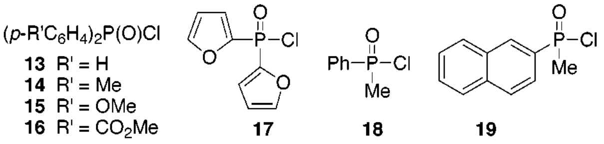
Scheme 2



The starting point for our own work was an unsuccessful attempt to effect the transformation **10** → **11**, shown in Scheme 2. However, as indicated, the actual product was biphenyl **12** (R = H, 45%; R = Me, 50%; R = Ph, ~15%). As soon as this trend was established, it was clear that the nitrogen subunit of **10** might play little role on the course of the reaction, and it was indeed quickly established that the nitrogen subunit is unnecessary and that the aryl transfer is a characteristic of phosphinates, as summarized in eq 1. We have studied a number of examples and have established the generality of the process (Table 1), as well as part of the mechanism.

Preparation of Phosphinates

The starting phosphinates were made by acylation of the parent alcohol with the appropriate phosphinic chloride, under standard conditions (Et$_3$N, DMAP, CH$_2$Cl$_2$, room temperature, ~1 h), and the reactions usually proceeded in good yield (see Table 1). The phosphinic chlorides we used are **13**−**19**. Of these, **13**, **14**,[12] and **18**[13] were known compounds, and the first (**13**) is commercially available; the other two were prepared by the literature methods. The remaining phosphinic chlorides were made by the action of SOCl$_2$ on the corresponding phosphinic acids, the latter being obtained by standard methods (see Experimental Section). The enol phosphinates **34a** and **35a** were prepared from the corresponding lithium enolates.



Radical Rearrangement of Phosphinates

Each of the phosphinates **20a**−**35a** (Table 1) was treated with a stannane and AIBN in a refluxing hydrocarbon, the stannane and initiator being added in a single solution by syringe pump over about 10 h. Usually, xylene was used as the solvent, because early experiments with **21a** suggested that higher yields were obtained with xylene than with PhMe or PhH. Standard high dilution conditions were employed, with the reagent solution being 0.03−0.06 M in stannane and 0.006−0.016 M in initiator. The amounts of stannane and initiator were 2 mol per mole of substrate and 0.5 mol per mole of substrate, respectively. The amount of AIBN was arbi-

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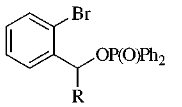
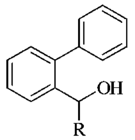
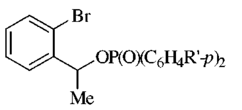
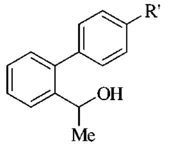
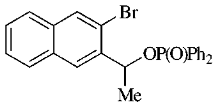
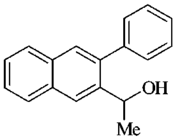
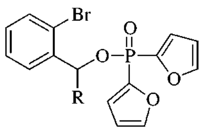
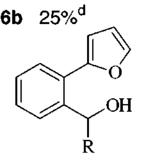
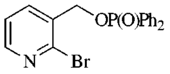
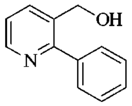
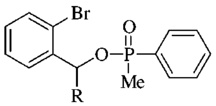
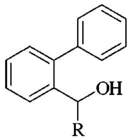
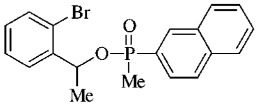
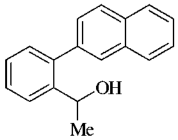
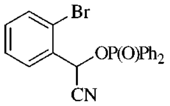
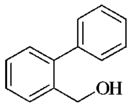
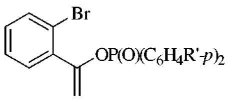
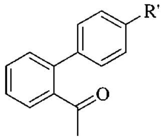
(12) Harger, M. J. P. *J. Chem. Soc., Perkin Trans. 2* **1980**, 154−160.

(13) Korpiun, O.; Lewis, R. A.; Chickos, J.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4842−4846.

Table 1.

Starting phosphinate	Conditions[a]	Aryl transfer product
	→	
20a R = H, 85%[b]	Ph_3SnH, xylene	**20b** R = H, 58%[c]
21a R = Me, 88%	Ph_3SnH, xylene	**21b** R = Me, 64%[c]
22a R = Ph, 59%	Ph_3SnH, xylene	**22b** R = Ph, 46%[c]
	→	
23a R' = Me, 84%	Ph_3SnH, xylene	**23b** R' = Me, 63%[d]
24a R' = OMe, 96%	Ph_3SnH, xylene	**24b** R' = OMe, 52%[d]
25a R' = CO_2Me, 67%	Bu_3SnH, PhMe	**25b** R' = CO_2Me, 54%[d]
	→	
26a 94%	Ph_3SnH, PhH	**26b** 25%[d]
	→	
27a R = H, 94%	Ph_3SnH, xylene	**27b** R = H, 44%[e]
28a R = Me, 67%	Ph_3SnH, xylene	**28b** R = Me, 17%[e]
	→	
29a 76%	Bu_3SnH, xylene	**29b** 41%[d]
	→	
30a R = H, 91%	Bu_3SnH, PhMe	**30b** (= **20b**) R = H, 27%[d]
31a, 31a' R = Me, 79%[f]	Bu_3SnH, PhMe	**31b** (= **21b**) R = Me, 73%[d]
	→	
32a, 32a' 57%[f]	Ph_3SnH, xylene	**32b** 70%[d]
	→	
33a 90%	Ph_3SnH, xylene	**33b** (= **20b**) 28%[d]
	→	
34a R' = H, 80%	Ph_3SnH, xylene	**34b** R' = H, 70%[d]
35a R' = OMe, 63%	Ph_3SnH, xylene	**35b** R' = OMe, 68%[d]

[a] AIBN used as initiator in all cases. [b] Yield from the parent alcohol. [c] Workup with K_2CO_3, MeOH. [d] Workup with aqueous KF. [e] Workup with $NaCNBH_3$, *t*-BuOH. [f] Two diastereoisomers.

trary, but more than 1.5 equiv (and probably 2 equiv) of stannane is required (see later).

In early experiments, using **20a**, **21a**, and **22a**, the crude reaction product was stirred with methanolic K_2CO_3, in the mistaken belief that the isolated alcohol was the product of hydrolysis occurring during workup. We soon gained the impression, however, that the isolated alcohols were already present in the xylene solution before workup, and so we used KF[14] in most subsequent work to help in the removal of tin species. In the case of **27b** and **28b**, however, the yield was higher when the workup was done with $NaCNBH_3$[15] rather than KF (44% versus 6% for **27b** and 17% versus 7% for **28b**).

We generally used Ph_3SnH, but in a few experiments (preparation of **25b** and **31b**), Bu_3SnH was arbitrarily tried. With **29b** and **30b** the aliphatic stannane gave slightly better yields (41% versus 36% and 27% versus 17%, respectively). However, we did not carry out a systematic survey of the relative merits of the two stannanes.

As shown in the table, electron-withdrawing (CO_2Me) and electron-donating (Me, OMe) groups on the migrating aryl ring are tolerated. Heteroaromatic (2-furanyl) and polycyclic aromatic (2-naphthalenyl) groups can be transferred, and the accepting aryl unit can be a benzene, naphthalene, or pyridine unit. Only one aryl group of the phosphinate migrates, and aryl alkyl phosphinates such as **30a**, **31a**,**a′**, and **32a**,**a′** are at least equally suitable starting materials as diarylphosphinates.

When the cyano-substituted derivative **33a** was subjected to the reaction, the intermediate alcohol, which is a cyanohydrin, evidently lost HCN to afford the corresponding aldehyde; this was then reduced by the stannane to **33b**, which was the product actually isolated.[16]

The enol phosphinates **34a** and **35a** underwent the aryl transfer smoothly.

We met a few cases where the radical rearrangement did not work. With bromonaphthalene **36**, only the reduction product (replacement of Br by H) was isolated (74%). For **37**−**40**, complex mixtures of unidentified products were obtained. Stannane addition to **38** is expected to give a vinyl radical, and the fact that aryl transfer was not observed might be a consequence of the fact that such a transfer would involve initial 5-exo cyclization, whereas all our successful examples involve a 6-exo process. The case of **40** is another one where an alkyl radical would have to undergo 5-exo cyclization. Because the primary alkyl radical derived from **39** did not undergo the aryl transfer, even though the normal 6-exo cyclization would be involved, we conclude that

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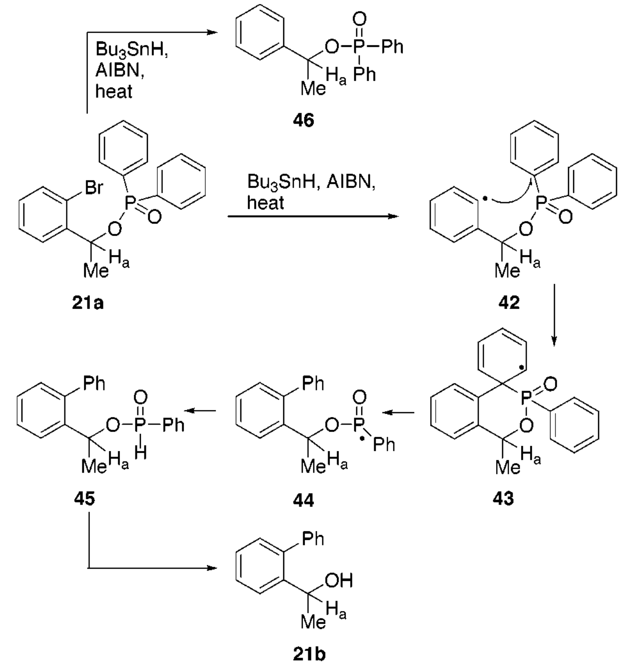
(14) Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449−450.

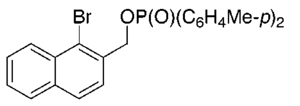
(15) Crich, D.; Sun, S. *J. Org. Chem.* **1996**, *61*, 7200−7201.

(16) In this experiment, 2.4 equiv of stannane was used; possibly, a higher yield might be obtained with 3 equiv.

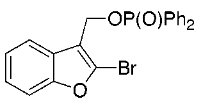
Scheme 3



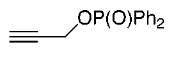
alkyl radicals are unsuitable. An attempt to extend the transfer to the nitrogen series by treatment of **41** under our standard conditions gave a complex mixture.



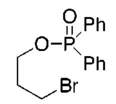
36



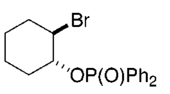
37



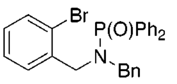
38



39



40



41

Mechanistic Considerations

The expected mechanism of the radical rearrangement for the case of **21a** → **21b** is summarized in Scheme 3 and is supported by experimental evidence. The ipso nature of the initial radical attack (see **42** → **43**) follows from examination of those cases (Table 1, **23a** → **23b**, **24a** → **24b**, **25a** → **25b**, **35a** → **35b**) where the substituent on the migrating ring serves as a positional marker. The intermediacy of phosphinate **45** (at least on one pathway) was confirmed by isolation and comparison with an authentic sample and by following the reaction spectroscopically, as follows.

When the rearrangement of **21a** in PhMe was monitored by ^{1}H NMR, a clear sequence of changes was observed. The NMR spectra were measured after the addition of 0.5, 1.0, 1.5, and 2.0 mol of Ph$_3$SnH per mole of **21a**. The signal corresponding to H$_a$ in the starting material **21a**, a multiplet centered at δ 5.84, decayed and was replaced by multiplets centered at δ 5.04, 5.50, 5.74, and 5.47. The pair of multiplets at δ 5.50 and 5.74 represents H$_a$ of **45**, the multiplet at δ 5.04 is characteristic of H$_a$ in the final product **21b**, and the multiplet at δ 5.47 represents H$_a$ of the simple reduction product[17] **46**. After the addition of 0.5 or 1.0 equiv of stannane, all four species, starting material **21a**, final product **21b**, intermediate phosphinate **45**, and reduction product **46**, were present. When 1.5 equiv had been added, all of **21a** had reacted; **21b**, **45**, and **46** were present. When 2.0 equiv had been added, **45** was absent, but of course, the signals for **21b** and **46** remained. These observations are consistent with the sequence **21a** → **42** → **43** → **44** → **45** → **21b** and the simultaneous operation of a competitive process **21a** → **46**, but they do not identify the mechanism(s) by which **45** (or **44**) affords the observed alcohol **21b**.

Samples from the same ^{1}H NMR experiment were also examined by ^{31}P NMR, and signals for the starting material **21a** (δ 31.5), for the intermediate **45**, which exists as two diastereoisomers (δ 22.5 and 23.0), and for the reduction product **46** (δ 31.2) were monitored. We observed exactly the same sequence as with the ^{1}H NMR spectra. Thus, the intermediate **45** was still present after the addition of 1.5 equiv of Ph$_3$SnH but had disappeared after the addition of 2.0 equiv. We did not observe a ^{31}P signal at δ 23, which would be characteristic[18] of PhPH(O)OH, the expected hydrolysis product of **45**.

At the beginning of this work, we suspected that the isolated alcohol is formed by simple hydrolysis during workup, and this view prompted the use of methanolic K$_2$CO$_3$ in the early experiments (see Table 1). However, such a pathway is ruled out by the subsequent NMR experiments, which show that the final alcohol is present before workup. An authentic sample of **45** was found to be stable to the aqueous KF workup conditions. On heating in xylene overnight, **45** affords alcohol **21b** (~42%), which can be detected (TLC) before workup. In refluxing PhH or PhMe (~12 h), **45** is stable but gives **21b** (~46%) in PhH (PhMe was not tested) in the presence of Bu$_3$SnH and AIBN. Heating of **45** in PhH overnight in the presence of a large excess (24 equiv) of Bu$_3$SnCl resulted in no change. Finally, attempts to trap PhP=O,[19] a possible byproduct in the thermal release of **21b** from **45**, using EtOH[20] or benzil,[21] were unsuccessful, and we did not make any further attempts to identify the later stages of the mechanistic pathway(s).

Conclusion

Our results show that phosphinates are convenient starting materials for the preparation of biaryls by intramolecular radical aryl transfer. The average yield for 16 examples is 50%; in some cases, yields of about 70% are obtained, and the reaction appears to work especially well with enol phosphinates (at least as judged by the two examples studied), giving biaryl ketones. The present experiments extend the range of available linkers

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(17) Noyce, D. S.; Virgilio, J. A. *J. Org. Chem.* **1972**, *37*, 2643−2647.

(18) Values in the range δ 18−20 have been reported (we found δ 22.7): Quin, L. D.; Jankowski, S.; Rudzinski, J.; Sommese, A. G.; Wu, X.-P. *J. Org. Chem.* **1993**, *58*, 6212−6216.

(19) Cf.: Quin, L. D.; Szewczyk, J. In *Multiple Bonds and Low Coordination in Phosphorous Chemistry*; Regitz, M., Schere, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; p 352.

(20) Compound **45** was heated overnight in refluxing EtOH. Cf.: Stille, J. K.; Eichelberger, J. L.; Higgins, J.; Freeburger, M. E. *J. Am. Chem. Soc.* **1972**, *94*, 4761−4763.

(21) Compound **45** was heated overnight in refluxing xylene in the presence of 1 equiv of benzil. Cf.: Nakayama, S.; Yoshifuji, M.; Okazaki, R.; Inamoto, N. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2069−2071.

(see eqs 3−9) between aryl groups that are to be joined by intramolecular ipso radical transfer.

Experimental Section

General Procedures. Unless stated to the contrary, the general experimental procedures used previously[22] were followed. The symbols s′, d′, t′, and q′ used for ^{13}C NMR signals indicate zero, one, two, or three attached hydrogens, respectively. ^{31}P NMR chemical shifts refer to external H_3PO_4 (1% in D_2O).

General Procedure for the Preparation of Diarylphosphinic Chlorides. An excess of $SOCl_2$ (2−3 mL) was added to the diarylphosphinic acid [$Ar_2P(O)OH$] (∼300 mg), and the mixture was refluxed for 2 h and then cooled. The excess $SOCl_2$ was distilled off under water-pump vacuum (protection from moisture, oil bath taken up to 80 °C), and the residual diarylphosphinic chloride [$Ar_2P(O)Cl$] was used without purification.

General Procedure for Acylation of Alcohols with Diarylphosphinic Chlorides. The crude diarylphosphinic chloride, usually in a little CH_2Cl_2, was added over ∼10 min to a stirred solution of the alcohol, Et_3N, and DMAP in freshly distilled CH_2Cl_2. Stirring was continued until all the starting alcohol had been consumed (∼1 h, TLC control, silica gel, EtOAc−hexane). Evaporation of the solvent and flash chromatography of the residue over silica gel, using EtOAc−hexane, gave the required phosphinate.

2-(Bromophenyl)methyl Diphenylphosphinate (20a). The general procedure for acylation was followed, using neat $Ph_2P(O)Cl$[23] (0.237 g, 0.19 mL, 1.0 mmol), (2-bromophenyl)methanol[23] (0.187 g, 1.0 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:2 EtOAc−hexane, gave **20a** (0.329 g, 85%) as a white solid: mp 65−66 °C. FTIR (CH_2Cl_2 cast): 3057, 1439, 1229 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.14 (d, J = 7.0 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.36−7.57 (m, 8H), 7.75−7.95 (m, 4H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 65.7 (t′), 65.8 (t′), 122.7 (s′), 127.6 (d′), 128.6 (d′), 128.7 (d′), 129.5 (d′), 129.7 (d′), 130.5 (s′), 131.7 (d′), 131.8 (d′), 131.9 (s′), 132.4 (d′), 132.7 (d′), 135.76 (s′), 135.84 (s′). Exact mass m/z calcd for $C_{19}H_{16}{}^{79}BrO_2P$, 386.00714; found, 386.00330.

1-(2-Bromophenyl)ethyl Diphenylphosphinate (21a). The general procedure for acylation was followed, using neat $Ph_2P(O)Cl$[23] (0.237 g, 0.19 mL), 2-bromo-α-methylbenzenemethanol[24] (0.201 g, 1.0 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:2 EtOAc−hexane, gave **21a** (0.353 g, 88%) as a colorless oil.

(2-Bromophenyl)phenylmethyl Diphenylphosphinate (22a). The general procedure for acylation was followed, using neat $Ph_2P(O)Cl$[23] (0.237 g, 0.19 mL, 1.0 mmol), 2-bromo-α-phenylbenzenemethanol[25] (0.263 g, 1.0 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:1 EtOAc−hexane, gave **22a** (0.273 g, 59%) as a colorless oil.

1-(2-Bromophenyl)ethyl Bis(4-methylphenyl)phosphinate (23a). The general procedure for making phosphinic chlorides was followed, using bis(4-methylphenyl)phosphinic acid[12] (0.246 g, 1.0 mmol) and $SOCl_2$ (2 mL). The general procedure for acylation was then followed, using the resulting bis(4-methylphenyl)phosphinic chloride, 2-bromo-α-methylbenzenemethanol[24] (0.201 g, 1.0 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:2 EtOAc−hexane, gave **23a** (0.360 g, 84%) as a pale yellow oil. FTIR (CH_2Cl_2 cast): 3022, 2980, 2923, 2866, 1603, 1232 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.62 (d, J = 6.5 Hz, 3H), 2.36 (d, J = 23.2 Hz, 6H), 5.79 (dq, J = 9.4, 6.5 Hz, 1H), 7.09−7.16 (m, 3H), 7.24−7.29 (m, 2H), 7.35 (dt, J = 7.2, 1.5 Hz, 1H), 7.44 (dd, J = 7.8, 1.5 Hz, 1H), 7.51−7.58 (m, 2H), 7.66 (dd, J = 8.0, 2.0 Hz, 1H), 7.71−7.77 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 21.59 (q′), 21.64 (q′), 24.4 (q′), 73.3 (d′), 73.4 (d′), 121.0 (s′), 127.4 (d′), 127.5 (s′), 127.8 (d′), 128.5 (s′), 128.8 (s′), 129.01 (d′), 129.03 (d′), 129.1 (d′), 129.2 (d′), 129.3 (d′), 129.9 (s′), 131.5 (d′), 131.6 (d′), 131.8 (d′), 131.9 (d′), 132.6 (d′), 142.05 (s′), 142.10 (s′), 142.45 (s′), 142.49 (s′), 142.53 (s′). Exact mass m/z calcd for $C_{22}H_{22}O_2P$ (M − Br), 349.13574; found, 349.13555.

1-(2-Bromophenyl)ethyl Bis(4-methoxyphenyl)phosphinate (24a). The general procedure for making phosphinic chlorides was followed, using bis(4-methoxyphenyl)phosphinic acid[23] (0.278 g, 1.0 mmol) and $SOCl_2$ (2 mL). The general procedure for acylation was then followed, using the resulting bis(4-methoxyphenyl)phosphinic chloride, 2-bromo-α-methylbenzenemethanol[24] (0.201 g, 1.0 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 3:2 EtOAc−hexane, gave **24a** (0.443 g, 96%) as a pale yellow oil. FTIR (CH_2Cl_2 cast): 3066, 2977, 2932, 2838, 1598, 1570, 1503, 1255, 1226 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.55 (d, J = 6.5 Hz, 3H), 3.68 (d, J = 14.5 Hz, 6H), 5.72 (dq, J = 9.5, 6.5 Hz, 1H), 6.74 (dd, J = 8.5, 2.5 Hz, 2H), 6.87 (dd, J = 8.5, 2.5 Hz, 2H), 7.00 (dt, J = 7.5, 1.5 Hz, 1H), 7.25 (dt, J = 7.5, 1.0 Hz, 1H), 7.33 (dd, J = 8.0, 1.0 Hz, 1H), 7.52 (dd, J = 11.5, 8.5 Hz, 2H), 7.58 (dd, J = 8.0, 1.5 Hz, 1H), 7.72 (dd, J = 11.5, 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 24.30 (q′), 24.34 (q′), 55.22 (q′), 55.25 (q′), 73.0 (d′), 73.1 (d′), 113.8 (d′), 113.9 (d′), 114.0 (d′), 114.1 (d′), 120.9 (s′), 121.9 (s′), 122.8 (s′), 123.7 (s′), 124.8 (s′), 127.4 (d′), 127.8 (d′), 129.0 (d′), 132.5 (d′), 133.2 (d′), 133.4 (d′), 133.5 (d′), 133.6 (d′), 141.98 (s′), 142.04 (s′), 162.44 (s′), 162.49 (s′), 162.54 (s′). Exact mass m/z calcd for $C_{22}H_{22}O_4P$ (M − Br), 381.12558; found, 381.12497.

4,4′-[[1-(2-Bromophenyl)ethoxy]phosphinylidene]bisbenzoic Acid Dimethyl Ester (25a). The general procedure for making phosphinic chlorides was followed, using 4,4′-phosphinicobisbenzoic acid dimethyl ester[26] [$(p\text{-}MeO_2CC_6H_4)_2P(O)OH$] (0.651 g, 1.95 mmol) and $SOCl_2$ (2 mL). The general procedure for acylation was then followed, using the resulting phosphinic chloride, 2-bromo-α-methylbenzenemethanol[24] (0.382 g, 1.90 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2. Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:2 EtOAc−hexane, gave **25a** (0.658 g, 67%) as a white solid: mp 115−116 °C. FTIR (CH_2Cl_2 cast): 2984, 2951, 1727, 1435, 1278 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.65 (d, J = 6.5 Hz, 3H), 3.91 (d, J = 8.2 Hz, 6H), 5.86 (dt, J = 9.2, 6.5 Hz, 1H), 7.10 (dt, J = 7.8, 1.8 Hz, 1H), 7.34 (dt, J = 7.8, 1.5 Hz, 1H), 7.41 (dd, J = 8.0, 1.5 Hz, 1H), 7.61 (dd, J = 8.0, 1.8 Hz, 1H), 7.67−7.76 (m, 2H), 7.87−8.00 (m, 4H), 8.08−8.15 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 24.23 (q′), 24.26 (q′), 52.41 (q′), 52.46 (q′), 74.2 (d′), 74.3 (d′), 121.1 (s′), 127.3 (d′), 127.9 (d′), 129.3 (d′), 129.4 (d′), 129.5 (d′), 129.7 (d′), 131.5 (d′), 131.6 (d′), 131.8 (d′), 131.9 (d′), 132.8 (d′), 133.5 (s′), 133.60 (s′), 133.63 (s′), 134.6 (s′), 135.3 (s′), 136.3 (s′), 137.2 (s′), 141.0 (s′), 141.1 (s′), 166.1 (s′). Exact mass m/z calcd for $C_{24}H_{22}O_6P$ (M − Br), 437.11539; found, 437.11533.

1-(3-Bromo-2-naphthalenyl)ethyl Diphenylphosphinate (26a). (a) α-Methyl(3-bromo-2-naphthalene)methanol. PCC (0.162 g, 0.75 mmol) was added to a stirred solution of 3-bromo-2-naphthalenemethanol[27] [made from the bis-

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[22] Clive, D. L. J.; Wickens, P. L.; Sgarbi, P. W. M. *J. Org. Chem.* **1996**, *61*, 7426−7437.

[23] Commercial material.

[24] Although it is commercially available, we prepared this alcohol: Marvel, C. S.; Moon, N. S. *J. Am. Chem. Soc.* **1940**, *62*, 45−49.

[25] Brown, E.; Lézé, A.; Touet, J. *Tetrahedron: Asymmetry* **1992**, *3*, 841−844.

[26] Petrov, K. A.; Parshina, V. A.; Daruze, G. L. *J. Gen. Chem. USSR* **1960**, *30*, 2972−2975.

[27] Smith, J. G.; Dibble, P. W.; Sandborn, R. E. *J. Org. Chem.* **1986**, *51*, 3762−3768.

(hexachlorocyclopentadiene) adduct of 2-methylnaphthalene[27,28]] (0.119 g, 0.50 mmol) in CH_2Cl_2 (10 mL). Stirring was continued for 2 h, and the mixture was filtered. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:10 EtOAc−hexane, gave 3-bromo-2-naphthaldehyde[29] as a white solid (0.1128 g, 96%), which was used directly in the next step.

MeMgBr (3.0 M in Et_2O, 0.20 mL) was injected over ∼10 min into a stirred and cooled (0 °C) solution of 3-bromo-2-naphthaldehyde (0.113 g, 0.48 mmol) in dry Et_2O (10 mL). The ice bath was left in place, but not recharged, and stirring was continued for 1 h. The mixture was then quenched at 0 °C with hydrochloric acid (2 M, 10 mL) and extracted with Et_2O. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:4 EtOAc−hexane, gave α-methyl(3-bromo-2-naphthalene)methanol (0.117 g, 97%) as a white solid: mp 86−87 °C. FTIR (CH_2Cl_2 cast): 3600−3100 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.59 (d, $J = 6.5$ Hz, 3H), 2.11 (s, 1H), 5.35 (q, $J = 6.5$ Hz, 1H), 7.44−7.53 (m, 2H), 7.69−7.76 (m, 1H), 7.79−7.86 (m, 1H), 8.05 (s, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 24.0 (q′), 69.3 (d′), 119.9 (s′), 125.5 (d′), 126.5 (d′), 126.6 (d′), 126.7 (d′), 128.0 (d′), 131.4 (d′), 132.5 (s′), 133.6 (s′), 142.0 (s′). Exact mass *m/z* calcd for $C_{12}H_{11}{}^{79}BrO$, 249.99933; found, 249.99872.

(b) 1-(3-Bromo-2-naphthalenyl)ethyl Diphenylphosphinate (26a). The general procedure for acylation was followed, using neat $Ph_2P(O)Cl$[23] (0.129 g, 0.55 mmol, 0.10 mL), α-methyl(3-bromo-2-naphthalene)methanol (0.115 g, 0.46 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in dry CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:1 EtOAc−hexane, gave **26a** (0.195 g, 94%) as a colorless oil. FTIR (CH_2Cl_2 cast): 3056, 2981, 2929, 1439, 1230 cm^{-1}. ^1H NMR ($CDCl_3$, 360 MHz): δ 1.75 (d, $J = 6.2$ Hz, 3H), 5.97 (dq, $J = 9.5$, 6.2 Hz, 1H), 7.25−7.33 (m, 2H), 7.37−7.44 (m, 1H), 7.44−7.57 (m, 5H), 7.67−7.76 (m, 3H), 7.79−7.86 (m, 1H), 7.88−7.96 (m, 2H), 7.98 (s, 1H), 8.09 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 24.9 (q′), 73.7 (d′), 73.8 (d′), 118.8 (s′), 126.57 (d′), 126.60 (d′), 126.62 (d′), 127.0 (d′), 128.0 (d′), 128.3 (d′), 128.5 (d′), 128.6 (d′), 130.4 (s′), 131.3 (s′), 131.4 (d′), 131.5 (d′), 131.6 (d′), 131.7 (d′), 131.9 (d′), 132.09 (d′), 132.11 (d′), 132.2 (d′), 132.3 (s′), 133.1 (s′), 133.7 (s′), 139.08 (s′), 139.15 (s′). Exact mass *m/z* calcd for $C_{24}H_{20}O_2P$ (M − Br), 371.12009; found, 371.12191.

(2-Bromophenyl)methyl Di-2-furanylphosphinate (27a). The general procedure for making phosphinic chlorides was followed, using di-2-furanylphosphinic acid[30] (prepared by alkaline hydrolysis[30] of tri(2-furyl)phosphine oxide)[31] (0.387 g, 1.95 mmol) and $SOCl_2$ (2 mL). The general procedure for acylation was then followed, using the resulting di-2-furanylphosphinic chloride, 2-bromobenzenemethanol[23] (0.355 g, 1.90 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:2 EtOAc−hexane, gave **27a** (0.655 g, 94%) as a pale yellow oil. FTIR (CH_2Cl_2 cast): 3127, 2954, 1555, 1460, 1251 cm^{-1}. ^1H NMR (300 MHz): δ 5.12 (d, $J = 8.0$ Hz, 2H), 6.37−6.42 (m, 2H), 7.06 (dt, $J = 7.2$, 1.7 Hz, 1H), 7.14−7.27 (m, 3H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.54−7.61 (m, 2H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 66.3 (t′), 66.4 (t′), 110.6 (d′), 110.8 (d′), 122.2 (s′), 123.0 (d′), 123.5 (d′), 127.4 (d′), 129.1 (d′), 129.6 (d′), 132.4 (d′), 134.8 (s′), 134.9 (s′), 143.2 (s′), 147.1 (s′), 148.4 (d′), 148.6 (d′). Exact mass *m/z* calcd for $C_{15}H_{12}O_4P$ [M − Br], 287.04733; found, 287.04710.

1-(2-Bromophenyl)ethyl Di-2-furanylphosphinate (28a). The general procedure for making phosphinic chlorides was followed, using di-2-furanylphosphinic acid[30] (0.387 g, 1.95 mmol) and $SOCl_2$ (2 mL). The general procedure for acylation was then followed, using the resulting di-2-furanylphosphinic chloride, 2-bromo-α-methylbenzenemethanol[24] (0.382 g, 1.90 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2. Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:2 EtOAc−hexane, gave **28a** (0.487 g, 67%) as a light yellow oil.

(2-Bromo-3-pyridinyl)methyl Diphenylphosphinate (29a). The general procedure for acylation was followed, using neat $Ph_2P(O)Cl$[23] (0.237 g, 1.0 mmol, 0.19 mL), 2-bromo-3-pyridinemethanol[32,33] (0.188 g, 1.0 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 2:1 EtOAc−hexane, gave **29a** (0.295 g, 76%) as a white solid: mp 101−102 °C. FTIR (CH_2Cl_2 cast): 3055, 1410, 1228 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 5.11 (d, $J = 7.5$ Hz, 2H), 7.27 (dd, $J = 7.0$, 4.8 Hz, 1H), 7.44−7.50 (m, 4H), 7.52−7.58 (m, 2H), 7.81−7.89 (m, 5H), 8.29 (dd, $J = 4.8$, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 64.37 (t′), 64.42 (t′), 123.0 (d′), 128.68 (d′), 128.75 (d′), 128.77 (d′), 128.81 (d′), 130.1 (s′), 131.4 (s′), 131.58 (d′), 131.62 (d′), 131.64 (d′), 131.68 (d′), 132.56 (d′), 132.59 (d′), 133.5 (s′), 133.6 (s′), 137.4 (d′), 141.8 (s′), 149.4 (d′). Exact mass *m/z* calcd for $C_{18}H_{15}{}^{79}BrNO_2P$, 387.00238; found, 387.00245.

(2-Bromophenyl)methyl Methylphenylphosphinate (30a). The general procedure for acylation was followed, using 2-bromobenzenemethanol[23] (0.187 g, 1.0 mmol), methylphenylphosphinic chloride[13] (**18**) (0.209 g, 1.2 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 2:1 EtOAc−hexane, gave **30a** (0.296 g, 91%) as a colorless oil. FTIR (CH_2Cl_2 cast): 3058, 2988, 2916, 1439, 1224 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.72 (d, $J = 14.5$ Hz, 3H), 4.97 [AB q, $J_{AB} = 12.5$ Hz, $\Delta_{AB} = 80.8$ Hz, 2H, each signal of the AB q is split into a d ($J = 6.8$ Hz) by coupling to ^{31}P], 7.11 (dt, $J = 7.5$, 1.8 Hz, 1H), 7.26 (dt, $J = 7.5$, 1.2 Hz, 1H), 7.39−7.56 (m, 5H), 7.74−7.85 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 15.2 (q′), 16.6 (q′), 65.28 (t′), 65.34 (t′), 122.6 (s′), 127.4 (d′), 128.5 (d′), 128.6 (d′), 129.3 (d′), 129.5 (d′), 130.3 (s′), 131.0 (d′), 131.2 (d′), 132.0 (s′), 132.29 (d′), 132.32 (d′), 132.5 (d′), 135.6 (s′), 135.7 (s′). Exact mass *m/z* calcd for $C_{14}H_{14}{}^{79}BrO_2P$, 323.999149; found, 323.98968.

1-(2-Bromophenyl)ethyl Methylphenylphosphinate (31a, 31a′). The general procedure for acylation was followed, using 2-bromo-α-methylbenzenemethanol[23,24] (0.201 g, 1.0 mmol), methylphenylphosphinic chloride[13] (**18**) (0.209 g, 1.2 mmol), Et_3N (1 mL), and DMAP (∼6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 2:1 EtOAc−hexane, gave a mixture of the two diastereoisomers **31a** and **31a′** (0.268 g in all, 79%) as a colorless oil. Small samples of the individual isomers were obtained by flash chromatography, using the above system.

1-(2-Bromophenyl)ethyl Methyl-2-naphthalenylphosphinate (32a, 32a′). (a) Methyl methyl-2-naphthalenephosphinate [$2\text{-}C_{10}H_7P(O)(Me)OMe$] was made by first preparing 2-naphthalenylphosphonous dichloride[34] [$2\text{-}C_{10}H_7PCl_2$] and then following a procedure reported[13] for the corresponding phenylphosphinate.

2-Bromonaphthalene (4.858 g, 23.5 mmol) in Et_2O (10 mL) was added dropwise to a stirred suspension of Mg (0.676 g, 27.8 mmol) in Et_2O (30 mL) to which a crystal of I_2 had been added. After ∼4 mL had been added, the mixture began to

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(33) 2-Bromo-3-(bromomethyl)pyridine was prepared by bromination of commercial 2-bromo-3-methylpyridine, using *N*-bromosuccinimide. The bromination method was based on that described in ref 27. 2-Bromo-3-pyridinemethanol (ref 32) was obtained from 2-bromo-3-(bromomethyl)pyridine, using water and $CaCO_3$ in 1,4-dioxane. The hydrolysis method was based on that described in ref 27.

(34) Sakaki, J.; Schweizer, W. B.; Seebach, D. *Helv. Chim. Acta* **1993**, *76*, 2654−2665.

reflux gently, and the rate of addition was controlled to maintain gentle reflux. At the end of the addition, refluxing was continued for 4 h, and the mixture was then cooled to room temperature and added over 1.5 h to a stirred and cooled (−78 °C) solution of chlorobis(diethylamino)phosphine[34] (4.938 g, 23.5 mmol) in Et_2O (50 mL). The mixture was stirred overnight with the ice bath being left in place but not recharged. The mixture was then refluxed for 30 min, cooled (ice bath), and stirred while HCl was bubbled into it for ~1 h. The cold bath was removed, and the mixture was stirred for 2 h and then filtered. The filtrate was concentrated (rotary evaporator, water-pump, protection from moisture) and distilled under reduced pressure (110°/0.2 mmHg) to give 2-naphthalenylphosphonous dichloride [2-$C_{10}H_7PCl_2$] as a yellow oil. A mixture of dry MeOH (25 mL) and hexane (10 mL) was added slowly (~2 h) under N_2 to a stirred and cooled (0 °C) solution of the oil in hexane (30 mL) (N_2 atmosphere). Stirring was continued for 1 h, at which stage the ice bath was removed. When the mixture had attained room temperature, it was evaporated on a rotary evaporator (protection from moisture), and the residual dimethyl 2-naphthalenylphosphonite [2-$C_{10}H_7P(OMe)_2$] was used in the next step without further purification.

(b) Methyl Methyl-2-naphthalenylphosphinate. The crude phosphonite was added to stirred MeI (3 mL) under N_2 at room temperature, and the mixture was refluxed overnight. The mixture was cooled, and flash chromatography over silica gel (3.5 cm × 25 cm), using 10:1 EtOAc−hexane, gave methyl methyl-2-naphthalenylphosphinate as a colorless oil (1.057 g, 20% overall from 2-bromonaphthalene). FTIR (CH_2Cl_2 cast): 3453, 3054, 2986, 2946, 2917, 2843, 1223 cm^{-1}. ^1H NMR ($CDCl_3$, 360 MHz): δ 1.72 (d, $J = 14.8$ Hz, 3H), 3.62 (d, $J = 11.5$ Hz, 3H), 7.57 (ddq, $J = 7.5, 7.5, 2.0$ Hz, 2H), 7.65−7.72 (m, 1H), 7.84−7.89 (m, 1H), 7.89−7.96 (m, 2H), 8.42 (d, $J = 14.2$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 14.6 (q′), 16.0 (q′), 50.8 (q′), 50.9 (q′), 125.5 (d′), 125.7 (d′), 126.79 (d′), 126.81 (d′), 126.82 (d′), 127.0 (s′), 127.62 (d′), 127.64 (d′), 127.65 (d′), 128.1 (d′), 128.4 (d′), 128.5 (d′), 128.70 (s′), 128.72 (d′), 132.2 (s′), 132.4 (s′), 133.5 (d′), 133.6 (d′), 134.74 (s′), 134.77 (s′). Exact mass *m/z* for $C_{12}H_{13}O_2P$, 220.06532; found, 220.06515.

(c) 1-(2-Bromophenyl)ethyl Methyl-2-naphthalenylphosphinate (32a, 32a′). Methyl-2-naphthalenylphosphinic chloride [2-$C_{10}H_7P(O)(Me)Cl$] was made from methyl methyl-2-naphthalenylphosphinate (0.364 g, 1.65 mmol) by treatment with PCl_5, according to a procedure reported[13] for the corresponding phenylphosphinate, and the compound was used directly, without characterization.

The general procedure for acylation was followed, using the above methyl-2-naphthalenylphosphinic chloride, 2-bromo-α-methylbenzenemethanol[23,24] (0.362 g, 1.80 mmol), Et_3N (1 mL), and DMAP (~6 mg, 0.05 mmol) in dry CH_2Cl_2 (20 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (3 cm × 20 cm), using 1:1 EtOAc−hexane, gave a mixture of the two diastereoisomers **32a** and **32a′** (0.365 g in all, 57%) as a colorless liquid. Small amounts of the individual isomers were obtained by flash chromatography. Compound **32a** FTIR (CH_2Cl_2 cast): 3055, 2981, 2929, 1224 cm^{-1}. ^1H NMR ($CDCl_3$, 360 MHz): δ 1.46 (d, $J = 6.5$ Hz, 3H), 1.69 (d, $J = 14.5$ Hz, 3H), 5.87 (dq, $J = 10.0, 6.5$ Hz, 1H), 7.08−7.18 (m, 1H), 7.32−7.42 (m, 1H), 7.46−7.68 (m, 4H), 7.72−8.00 (m, 4H), 8.48 (d, $J = 13.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 15.4 (q′), 16.7 (q′), 23.95 (q′), 24.00 (q′), 72.7 (d′), 72.8 (d′), 121.0 (s′), 125.6 (d′), 125.7 (d′), 127.0 (d′), 127.2 (d′), 127.86 (d′), 127.89 (d′), 128.3 (d′), 128.4 (d′), 128.6 (d′), 128.7 (s′), 129.0 (d′), 129.2 (d′), 130.4 (s′), 132.4 (s′), 132.6 (s′), 132.8 (d′), 133.2 (d′), 133.3 (d′), 134.9 (s′), 142.0 (s′), 142.1 (s′). Exact mass *m/z* calcd for $C_{19}H_{18}{}^{79}BrO_2P$, 388.02277; found, 388.02228.

Compound **32a′** FTIR (CH_2Cl_2 cast): 3055, 2981, 2928, 1223 cm^{-1}. ^1H NMR ($CDCl_3$, 360 MHz): δ 1.63 (d, $J = 6.2$ Hz, 3H), 1.79 (d, $J = 14.5$ Hz, 3H), 5.67 (dq, $J = 10.0, 6.2$ Hz, 1H), 6.98−7.04 (m, 1H), 7.28−7.31 (m, 2H), 7.38−7.59 (m, 4H), 7.68−7.84 (m, 3H), 8.28 (d, $J = 13.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 15.5 (q′), 16.9 (q′), 24.43 (q′), 24.46 (q′), 73.0 (d′), 73.1 (d′), 121.0 (s′), 125.6 (d′), 125.8 (d′), 126.8 (d′), 127.5 (d′), 127.65 (d′), 127.71 (d′), 128.1 (d′), 128.3 (d′), 128.9 (d′), 129.0 (d′), 129.1 (s′), 132.3 (s′), 132.4 (d′), 133.7 (d′), 133.8 (d′), 141.6 (s′), 141.7 (s′). Exact mass *m/z* calcd for $C_{19}H_{18}{}^{79}BrO_2P$, 388.02277; found, 388.02250.

(2-Bromophenyl)cyanomethyl Diphenylphospinate (33a). The general procedure for acylation was followed, using neat $Ph_2P(O)Cl$[23] (0.180 g, 0.15 mL, 0.76 mmol), α-hydroxy-(2-bromobenzene)acetonitrile[35] (0.161 g, 0.76 mmol), Et_3N (1 mL), and DMAP (~6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:2 EtOAc−hexane, gave **33a** (0.283 g, 90%) as a thick, yellow oil. FTIR (CH_2Cl_2 cast): 3059, 1959, 1439, 1232 cm^{-1}. ^1H NMR ($CDCl_3$, 360 MHz): δ 6.46 (d, $J = 10.0$ Hz, 1H), 7.25 (dt, $J = 7.8, 1.8$ Hz, 1H), 7.33−7.44 (m, 3H), 7.47−7.56 (m, 4H), 7.56−7.64 (m, 1H), 7.67−7.77 (m, 3H), 7.86−7.95 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 63.2 (d′), 63.3 (d′), 115.6 (s′), 115.7 (s′), 122.3 (s′), 128.3 (d′), 128.6 (d′), 128.8 (d′), 128.9 (d′), 129.1 (s′), 129.4 (d′), 130.5 (s′), 130.9 (s′), 131.5 (d′), 131.6 (d′), 131.76 (d′), 131.79 (d′), 131.9 (d′), 132.42 (s′), 132.48 (s′), 132.89 (d′), 132.92 (d′), 133.15 (d′), 133.19 (d′), 133.5 (d′). Exact mass *m/z* calcd for $C_{20}H_{15}NO_2P$ (M − Br), 332.08405; found, 332.08417.

1-(2-Bromophenyl)ethenyl Diphenylphosphinate (34a). A solution of LDA was prepared by dropwise addition of *n*-BuLi (2.5 M in hexane, 1.44 mL) to a stirred and cooled (0 °C) solution of *i*-Pr_2NH (0.364 g, 0.50 mL, 3.60 mmol) in THF (10 mL). Stirring at 0 °C was continued for 20 min, and a solution of 1-(2-bromophenyl)ethanone[37] [(0.597 g, 3.00 mmol), made from 2-bromo-α-methylbenzenemethanol[23,24] by PCC oxidation] in THF (20 mL) was added dropwise. Stirring at 0 °C was continued for 1 h, and neat $Ph_2P(O)Cl$[23] (0.851 g, 0.69 mL, 3.6 mmol) was then injected. Stirring was continued for 30 min at 0 °C, and the mixture was then quenched with water at 0 °C and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 cm × 25 cm), using 1:1 EtOAc−hexane, gave **34a** (0.958 g, 80%) as a colorless liquid. FTIR (CH_2Cl_2 cast): 3057, 1646, 1439, 1290, 1233 cm^{-1}. ^1H NMR ($CDCl_3$, 360 MHz): δ 4.87−4.92 (m, 1H), 5.35−5.40 (m, 1H), 7.09−7.27 (m, 3H), 7.34−7.43 (m, 4H), 7.44−7.55 (m, 3H), 7.78−7.88 (m, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 104.12 (t′), 104.19 (t′), 121.8 (s′), 127.1 (d′), 128.3 (d′), 128.5 (d′), 130.1 (s′), 130.2 (d′), 131.0 (d′), 131.7 (d′), 131.8 (d′), 132.0 (s′), 132.3 (d′), 133.1 (d′), 137.16 (s′), 137.23 (s′), 151.6 (s′), 151.7 (s′). Exact mass *m/z* calcd for $C_{20}H_{16}{}^{79}BrO_2P$, 398.00714; found, 398.00693.

1-(2-Bromophenyl)ethenyl Bis(4-methoxyphenyl)phosphinate (35a). A solution of LDA was prepared by dropwise addition of *n*-BuLi (2.5 M in hexane, 0.66 mL) to a stirred and cooled (0 °C) solution of *i*-Pr_2NH (0.167 g, 0.23 mL, 1.65 mmol) in THF. Stirring at 0 °C was continued for 10 min, and then 1-(2-bromophenyl)ethanone[37] [(0.272 g, 1.37 mmol) made from 2-bromo-α-methylbenzenemethanol[23,24] by PCC oxidation] in THF (10 mL) was added. Stirring was continued at 0 °C for 1 h. Bis(4-methoxyphenyl)phosphinic chloride [made from bis-(4-methoxyphenyl)phosphinic acid[23] (0.419 g, 1.51 mmol) and $SOCl_2$ (3 mL), as described above (see preparation of **24a**)] in THF (5 mL) was then injected dropwise, and stirring was continued for 30 min at 0 °C. The mixture was quenched with water at 0 °C and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.5 cm × 20 cm), using 1:1 EtOAc−hexane, gave **35a** (0.395 g, 63%) as a light brown oil. FTIR (CH_2Cl_2 cast): 1645, 1598, 1503 cm^{-1}. ^1H NMR ($CDCl_3$, 360 MHz): δ 3.80 (s, 6H), 4.86−4.89 (m, 1H), 5.32−5.36 (m, 1H), 6.85−6.92 (m, 4H), 7.09−7.25 (m, 3H), 7.52 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.69−7.79 (m, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 55.3 (q′), 103.76 (t′), 103.83 (t′), 113.8 (d′), 114.0 (d′),

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(35) (a) van Almsick, A.; Buddrus, J.; Hönicke-Schmidt, P.; Laumen, K.; Schneider, M. P. *J. Chem. Soc., Chem. Commun.* **1989**, 1391−1393. (b) We prepared α-hydroxy(2-bromobenzene)acetonitrile from 2-bromobenzaldehyde and KCN at pH 4.0, by the method given in ref 36.

(36) Solís, A.; Luna, H.; Pérez, H. I.; Manjarrez, N.; Sánchez, R. *Tetrahedron Lett.* **1998**, *39*, 8759−8762.

(37) Fleming, I.; Woolias, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 829−837.

121.8 (s′), 123.8 (s′), 127.1 (d′), 130.0 (d′), 131.1 (d′), 133.1 (d′), 133.6 (d′), 133.7 (d′), 137.47 (s′), 137.53 (s′), 151.7 (s′), 151.8 (s′), 162.6 (s′). Exact mass *m/z* calcd for $C_{22}H_{20}{}^{79}BrO_4P$, 458.02826; found, 458.02871.

General Procedure for Radical Aryl Transfer. Departures from the usual procedure are specifically indicated in the appropriate experimental procedures.

The substrate (0.2−0.5 mmol) was placed in a 100-mL oven-dried round-bottomed flask equipped with a Teflon-coated stirring bar and a reflux condenser sealed with a rubber septum. The system was flushed with argon for 5−10 min, and dry xylene (20−40 mL) was injected. (In a few experiments, PhH or PhMe was used.) The flask was lowered into an oil bath that had been preheated to 120 °C (85 °C for PhH, 110 °C for PhMe), and a solution of Ph_3SnH (2 equiv, 0.03−0.06 M) and AIBN (0.5 equiv, 0.006−0.016 M) in xylene was injected over 10 h with a syringe pump. (In a few experiments, Bu_3SnH was used instead of Ph_3SnH.) Refluxing was continued for an arbitrary period of 2 h after the end of the addition, and the mixture was then cooled and evaporated. The residue was taken up in Et_2O (∼20 mL) and stirred with saturated aqueous KF (10 mL) for ∼30 min. The precipitated triphenyltin fluoride was removed by filtration, and the ether layer was dried ($MgSO_4$) and evaporated. The residue was then processed as described for the individual examples.

In several cases, KF was not used; the original xylene solution was evaporated, and the residue was stirred with K_2CO_3−MeOH. In two experiments, the original xylene solution was evaporated, and the residue was dissolved in *t*-BuOH. $NaCNBH_3$ was added, and the mixture was refluxed for 1 h.

[1,1′-Biphenyl]-2-methanol (20b). The general procedure for radical aryl transfer was followed, using phosphinate **20a** (0.116 g, 0.30 mmol) in xylene (30 mL), and Ph_3SnH (0.210 g, 0.60 mmol) and AIBN (0.025 g, 0.15 mmol) in xylene (20 mL). The xylene was evaporated, the residue was covered with MeOH (50 mL), and K_2CO_3 (∼0.2 g) was added. The mixture was stirred for 30 min and then filtered. Evaporation of the solvent and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **20b**[38] (0.032 g, 58%) as a colorless oil. FTIR (CH_2Cl_2 cast): 3500−3100 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.55 (s, 1H), 4.63 (s, 2H), 7.23−7.64 (m, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 63.2 (t′), 127.3 (d′), 127.70 (d′), 127.74 (d′), 128.3 (d′), 128.4 (d′), 129.1 (d′), 130.1 (d′), 138.1 (s′), 140.7 (s′), 141.4 (s′). Exact mass *m/z* calcd for $C_{13}H_{12}O$, 184.08882; found, 184.08936.

α-Methyl[1,1′-biphenyl]-2-methanol (21b). The general procedure for radical aryl transfer was followed, using phosphinate **21a** (0.140 g, 0.35 mmol) in xylene (30 mL), and Ph_3SnH (0.246 g, 0.70 mmol) and AIBN (0.029 g, 0.18 mmol) in xylene (20 mL). The xylene was evaporated, the residue was covered with MeOH (50 mL), and K_2CO_3 (∼0.2 g) was added. The mixture was stirred for 30 min and then filtered. Evaporation of the solvent and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **21b**[39] (0.044 g, 64%) as a white solid.

α-Phenyl[1,1′-biphenyl]-2-methanol (22b). The general procedure for radical aryl transfer was followed, using phosphinate **22a** (0.187 g, 0.40 mmol) in xylene (30 mL), and Ph_3SnH (0.281 g, 0.80 mmol) and AIBN (0.033 g, 0.20 mmol) in xylene (20 mL). The xylene was evaporated, the residue was covered with MeOH (50 mL), and K_2CO_3 (∼0.2 g) was added. The mixture was stirred for 30 min and then filtered. Evaporation of the solvent and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **22b**[40] (0.048 g, 46%) as a white solid.

α,4′-Dimethyl[1,1′-biphenyl]-2-methanol (23b). The general procedure for radical aryl transfer was followed, using phosphinate **23a** (0.183 g, 0.43 mmol) in xylene (30 mL), and Ph_3SnH (0.302 g, 0.86 mmol) and AIBN (0.035 g, 0.21 mmol) in xylene (20 mL). Evaporation of the solvent after KF treatment and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **23b**[41] (0.057 g, 63%) as a white solid: mp 83−84 °C (lit.[41] 84−85 °C). FTIR (CH_2Cl_2 cast): 3500−3200 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.42 (d, $J = 6.5$ Hz, 3H), 1.71 (s, 1H), 2.42 (s, 3H), 5.01 (q, $J = 6.5$ Hz, 1H), 7.19−7.27 (m, 5H), 7.31 (dt, $J = 7.5$, 1.5 Hz, 1H), 7.41 (dt, $J = 7.5$, 1.5 Hz, 1H), 7.77 (dd, $J = 8.0$, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.2 (q′), 24.9 (q′), 66.5 (d′), 125.4 (d′), 127.1 (d′), 127.9 (d′), 128.9 (d′), 129.2 (d′), 130.1 (d′), 136.8 (s′), 138.0 (s′), 140.4 (s′), 141.2 (s′). Exact mass *m/z* calcd for $C_{15}H_{16}O$, 212.12012; found, 212.12000.

4′-Methoxy-α-methyl[1,1′-biphenyl]-2-methanol (24b). The general procedure for radical aryl transfer was followed, using phosphinate **24a** (0.146 g, 0.32 mmol) in xylene (20 mL), and Ph_3SnH (0.225 g, 0.64 mmol) and AIBN (0.026 g, 0.16 mmol) in xylene (20 mL). Evaporation of the solvent after KF treatment and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:8 EtOAc−hexane, gave **24b** (0.038 g, 52%) as a colorless oil. FTIR (CH_2Cl_2 cast): 3600−3200 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.42 (d, $J = 6.5$ Hz, 3H), 1.66 (s, 1H), 3.71 (s, 3H), 5.01 (q, $J = 6.5$ Hz, 1H), 6.93−6.99 (m, 2H), 7.18−7.27 (m, 3H), 7.30 (dt, $J = 7.2$, 1.2 Hz, 1H), 7.40 (dt, $J = 7.2$, 1.5 Hz, 1H), 7.66 (dd, $J = 7.8$, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 24.8 (q′), 55.3 (q′), 66.5 (d′), 113.6 (d′), 125.3 (d′), 127.1 (d′), 127.8 (d′), 130.2 (d′), 130.4 (d′), 133.3 (s′), 140.1 (s′), 143.3 (s′), 158.8 (s′). Exact mass *m/z* calcd for $C_{15}H_{16}O_2$, 228.11504; found, 228.11520.

Methyl 2′-(1-Hydroxyethyl)[1,1′-biphenyl]-4-carboxylate (25b). The general procedure for radical aryl transfer was followed, using phosphinate **25a** (0.183 g, 0.35 mmol) in PhMe (20 mL), and Bu_3SnH (0.206 g, 0.71 mmol) and AIBN (0.029 g, 0.18 mmol) in PhMe (15 mL). Evaporation of the solvent after KF treatment and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **25b** (0.049 g, 54%) as a white solid: mp 97−98 °C. FTIR (CH_2Cl_2 cast): 3600−3100, 1724 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.39 (d, $J = 6.5$ Hz, 3H), 1.89 (s, 1H), 3.94 (s, 3H), 4.93 (q, $J = 6.5$ Hz, 1H), 7.16−7.21 (m, 1H), 7.29−7.48 (m, 4H), 7.69 (dd, $J = 7.8$, 1.8 Hz, 1H), 8.04−8.11 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 25.0 (q′), 52.2 (q′), 66.4 (d′), 125.5 (d′), 127.3 (d′), 128.5 (d′), 129.0 (s′), 129.4 (d′), 129.5 (d′), 129.6 (d′), 139.3 (s′), 143.0 (s′), 145.8 (s′), 167.0 (s′). Exact mass *m/z* calcd for $C_{16}H_{16}O_3$, 256.10995; found, 256.11049.

α-Methyl(3-phenyl-2-naphthalene)methanol (26b). The general procedure for radical aryl transfer was followed, using phosphinate **26a** (0.189 g, 0.42 mmol) in PhH (20 mL), and Ph_3SnH (0.294 g, 0.84 mmol) and AIBN (0.034 g, 0.21 mmol) in PhH (20 mL). Evaporation of the solvent after KF treatment and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **26b** (0.026 g, 25%) as a light yellow solid: mp 100−101 °C. FTIR (CH_2Cl_2 cast): 3500−3100 cm^{-1}. ^1H NMR ($CDCl_3$, 360 MHz): δ 1.45 (d, $J = 6.5$ Hz, 3H), 1.70 (s, 1H), 5.14 (q, $J = 6.5$ Hz, 1H), 7.37−7.53 (m, 7H), 7.68 (s, 1H), 7.79−7.85 (m, 1H), 7.88−7.93 (m, 1H), 8.12 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 25.0 (q′), 66.8 (d′), 124.1 (d′), 126.1 (d′), 126.2 (d′), 127.2 (d′), 127.6 (d′), 127.8 (d′), 128.2 (d′), 128.9 (d′), 129.5 (d′), 132.4 (s′), 132.9 (s′), 139.0 (s′), 140.9 (s′), 141.9 (s′). Exact mass *m/z* calcd for $C_{18}H_{16}O$, 248.12012; found, 248.12020.

2-(2-Furanyl)benzenemethanol (27b). The general procedure for radical aryl transfer was followed, using phosphinate **27a** (0.227 g, 0.62 mmol) in xylene (30 mL), and Ph_3SnH (0.435, 1.24 mmol) and AIBN (0.051 g, 0.31 mmol) in xylene (20 mL). The solvent was evaporated, and the residue was dissolved in *t*-BuOH (∼10 mL). $NaCNBH_3$ (0.081 g, 1.29 mmol) was added, and the mixture was refluxed for 1 h.[15] Evaporation of the solvent and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave

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27b[42] (0.048 g, 44%) as a white solid: mp 68−69 °C. FTIR (CH_2Cl_2 cast): 3500−3000 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.77 (s, 1H), 4.79 (s, 2H), 6.52 and 6.54 (apparent doublets, J = 1.8 Hz, 1H in all), 6.67 and 6.69 (apparent doublets, J = 0.9 Hz, 1H in all) (the signals at 6.52 and 6.54, and at 6.67 and 6.69 correspond to part of an ABX system), 7.29−7.42 (m, 2H), 7.46−7.57 (m, 2H), 7.62−7.70 (m, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 64.3 (t′), 108.7 (d′), 111.7 (d′), 127.8 (d′), 128.1 (d′), 128.1 (d′), 129.4 (d′), 129.7 (s′), 137.2 (s′), 142.5 (d′), 153.2 (s′). Exact mass m/z calcd for $C_{11}H_{10}O_2$, 174.06808; found, 174.06788.

2-(2-Furanyl)-α-methylbenzenemethanol (28b). The general procedure for radical aryl transfer was followed, using phosphinate **28a** (0.125 g, 0.33 mmol) in xylene (20 mL), and Ph_3SnH (0.232 g, 0.66 mmol) and AIBN (0.027 g, 0.16 mmol) in xylene (15 mL). The solvent was evaporated, and the residue was dissolved in *t*-BuOH (∼10 mL). $NaCNBH_3$ (0.058 g, 0.92 mmol) was added, and the mixture was refluxed for 1 h.[15] Evaporation of the solvent and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **28b**[43] (0.0105 g, 17%) as a colorless oil.

2-Phenyl-3-pyridinemethanol (29b). The general procedure for radical aryl transfer was followed, using phosphinate **29a** (0.194 g, 0.50 mmol) in xylene (20 mL), and Bu_3SnH (0.316 g, 1.09 mmol) and AIBN (0.045 g, 0.27 mmol) in xylene (20 mL). Evaporation of the solvent after KF treatment, and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 2:3 EtOAc−hexane, gave **29b** (0.038 g, 41%) as a colorless oil. FTIR (CH_2Cl_2 cast): 3500−3000 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.08 (s, 1H), 4.69 (s, 2H), 7.34 (dd, J = 7.5, 4.5 Hz, 1H), 7.40−7.50 (m, 3H), 7.52−7.56 (m, 2H), 7.42−7.88 (m, 1H), 8.63 (dd, J = 5.0, 2.0 Hz, 1H). ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 62.4 (t′), 122.7 (d′), 128.5 (d′), 128.6 (d′), 129.3 (d′), 134.3 (s′), 136.7 (d′), 140.2 (s′), 148.7 (d′), 158.2 (s′). Exact mass m/z calcd for $C_{12}H_{11}NO$, 185.08406; found, 185.08402.

[1,1′-Biphenyl]-2-methanol (30b) [=(20b)]. The general procedure for radical aryl transfer was followed, using phosphinate **30a** (0.173 g, 0.53 mmol) in PhMe (30 mL), and Bu_3SnH (0.310 g, 1.06 mmol) and AIBN (0.044 g, 0.27 mmol) in PhMe (20 mL). Evaporation of the solvent after KF treatment and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **30b** [=(**20b**)] (0.027 g, 27%) as a colorless oil, identical to material obtained from **20a**.

α-Methyl[1,1′-biphenyl]-2-methanol (31b) [=(21b)]. The general procedure for radical aryl transfer was followed, using phosphinates **31a**,**a′** (0.174 g, 0.51 mmol) in PhMe (30 mL), and Bu_3SnH (0.299 g, 1.03 mmol) and AIBN (0.042 g, 0.26 mmol) in PhMe (20 mL). Evaporation of the solvent after KF treatment, and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **31b** [=(**21b**)] (0.074 g, 73%) as a white solid (mp 109−110 °C), identical to material obtained from **21a**.

α-Methyl[2-(2-naphthalenyl)phenyl]methanol (32b). The general procedure for radical aryl transfer was followed, using phosphinates **32a**,**a′** (0.136 g, 0.35 mmol) in xylene (20 mL), and Ph_3SnH (0.245 g, 0.70 mmol) and AIBN (0.028 g, 0.17 mmol) in xylene (20 mL). Evaporation of the solvent after KF treatment and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **32b** (0.061 g, 70%) as a white solid: mp 145−146 °C. FTIR (CH_2Cl_2 cast): 3500−3100 cm^{-1}. ^{1}H NMR ($CDCl_3$, 360 MHz): δ 1.43 (d, J = 6.5 Hz, 3H), 1.72 (s, 1H), 5.05 (q, J = 6.5 Hz, 1H), 7.29−7.39 (m, 2H), 7.43−7.57 (m, 2H), 7.70−7.80 (m, 4H), 7.84−7.94 (m, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 25.0 (q′), 66.6 (d′), 125.4 (d′), 126.1 (d′), 126.4 (d′), 127.2 (d′), 127.69 (d′), 127.73 (d′), 127.99 (d′), 128.02 (d′), 128.1 (d′), 130.2 (d′), 132.4 (s′), 133.2 (s′), 138.5 (s′), 140.3 (s′), 143.3 (s′). Exact mass m/z calcd for $C_{18}H_{16}O$, 248.12012; found, 248.11999.

[1,1′-Biphenyl]-2-methanol (33b) [=(20b)]. The general procedure for radical aryl transfer was followed, using phosphinate **33a** (0.134 g, 0.33 mmol) in xylene (20 mL), and Ph_3SnH (0.231 g, 0.66 mmol) and AIBN (0.028 g, 0.17 mmol) in xylene (20 mL). Evaporation of the solvent after KF treatment and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave (**33b**) [=(**20b**)] (0.017 g, 28%) as a colorless oil, identical to material obtained from **20a**. A small amount (13%) of simple reduction product (replacement of Br by H in **33a**) was also isolated. ^{1}H NMR ($CDCl_3$, 360 MHz): δ 6.21 (d, J = 10.0 Hz, 1H), 7.35−7.45 (m, 5H), 7.48−7.58 (m, 5H), 7.58−7.74 (m, 3H), 7.87−7.95 (m, 2H).

1-([1,1′-Biphenyl]-2-yl)ethanone (34b). The general procedure for radical aryl transfer was followed, using phosphinate **34a** (0.185 g, 0.46 mmol) in xylene (20 mL), and Ph_3SnH (0.325 g, 0.93 mmol) and AIBN (0.038 g, 0.23 mmol) in xylene (20 mL). Evaporation of the solvent after KF treatment and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **34b**[39] (0.064 g, 70%) as a light yellow liquid. FTIR (CH_2Cl_2 cast): 1687 cm^{-1}. ^{1}H NMR ($CDCl_3$, 360 MHz): δ 2.01 (s, 3H), 7.32−7.58 (m, 9H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 30.4 (q′), 127.5 (d′), 127.9 (d′), 128.7 (d′), 128.9 (d′), 130.3 (d′), 130.7 (d′), 140.5 (s′), 140.8 (s′), 140.9 (s′). Exact mass m/z calcd for $C_{14}H_{12}O$, 196.08882; found, 196.08879.

1-(4′-Methoxy[1,1′-biphenyl]-2-yl)ethanone (35b). The general procedure for radical aryl transfer was followed, using phosphinate **35a** (0.193 g, 0.42 mmol) in xylene (20 mL), and Ph_3SnH (0.295 g, 0.84 mmol) and AIBN (0.028, 0.17 mmol) in xylene (20 mL). Evaporation of the solvent after KF treatment and flash chromatography of the residue over silica gel (1.8 cm × 25 cm), using 1:10 EtOAc−hexane, gave **35b**[44] (0.065 g, 68%) as a light yellow liquid. FTIR (CH_2Cl_2 cast): 1686 cm^{-1}. ^{1}H NMR ($CDCl_3$, 360 MHz): δ 2.01 (s, 3H), 3.83 (s, 3H), 6.94−7.00 (m, 2H), 7.24−7.30 (m, 2H), 7.35−7.42 (m, 2H), 7.46−7.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 36.5 (q′), 58.1 (q′), 109.2 (d′), 120.4 (d′), 121.1 (d′), 123.0 (d′), 123.1 (d′), 123.6 (d′), 125.6 (s′), 131.8 (s′), 132.5 (s′), 148.7 (s′), 188.4 (s′). Exact mass m/z calcd for $C_{15}H_{14}O_2$, 226.09938; found, 226.10004.

1-([1,1′-Biphenyl]-2-yl)ethyl Phenylphosphinate (45). Solid PhPH(O)OH[45] (0.037 g, 0.26 mmol) was added to a stirred solution of α-methyl[1,1′-biphenyl]-2-methanol (**21b**) (0.026 g, 0.13 mmol) and DMAP (∼6 mg, 0.05 mmol) in THF (10 mL). Stirring was continued for ∼10 min, and then DCC (0.054 g, 0.26 mmol) was added. After 1 h, the mixture was filtered, and the filtrate was evaporated. Flash chromatography of the residue over silica gel (1.3 cm × 20 cm), using 1:1 EtOAc−hexane, gave a mixture of two diastereoisomers of 1-([1,1′-biphenyl]-2-yl)ethyl phenylphosphinate (**45**) (0.025 g, 60%) as a colorless oil. FTIR (CH_2Cl_2 cast): 3058, 3025, 2980, 2929, 1236 cm^{-1}. ^{1}H NMR ($CDCl_3$, 360 MHz): δ 1.58 (d, J = 6.5 Hz, 3H), 5.50 (dq, J = 10.0, 6.5 Hz, 0.45H), 5.71 (dq, J = 10.0, 6.5 Hz, 0.52H), 7.35 (d, J = 556 Hz, 0.52H), 7.54 (d, J = 569 Hz, 0.46H), 6.94−7.61 (m, 12H), 7.66−7.75 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 25.0 (q′), 25.1 (q′), 25.18 (q′), 25.23 (q′), 72.0 (d′), 72.1 (d′), 72.9 (d′), 73.0 (d′), 126.1 (d′), 127.2 (d′), 127.5 (d′), 127.7 (d′), 127.9 (d′), 128.1 (d′), 128.2 (d′), 128.5 (d′), 128.67 (d′), 128.71 (d′), 129.0 (d′), 129.1 (d′), 129.8 (d′), 130.1 (d′), 130.7 (d′), 130.9 (d′), 131.0 (d′), 131.2 (d′), 132.81 (d′), 132.84 (d′), 132.87 (d′), 132.90 (d′), 138.93 (s′), 138.98 (s′), 139.40 (s′), 139.47 (s′), 139.9 (s′), 140.0 (s′), 140.1 (s′), 140.6 (s′). Exact mass m/z calcd for $C_{20}H_{19}O_2P$, 322.11227; found, 322.11183.

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Supporting Information Available: NMR spectra of new compounds and characterization data for **21a**, **22a**, **28a**, **31a**, **31a′**, **21b**, **22b**, and **28b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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