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Catalytic Intermolecular Ortho-Arylation of Phenols

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Received May 7, 2003

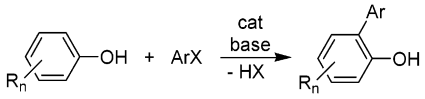
The use of rhodium catalysts such as $[RhCl(PPh_3)_3]$ or $[\{RhCl(COD)\}_2]$ with $PiPr_2(OAr)$ or $P(NMe_2)_3$ co-catalysts allows the ortho-selective intermolecular arylation of phenols. The reaction proceeds via orthometalation of P-OAr groups and then transesterification liberates the product phenol. When 2-substituted phenols are used as substrates, $[RhCl(PPh_3)_3]/iPr_2(OAr)$ mixtures are typically the catalysts of choice, whereas for substrates without 2-substitution $[\{RhCl(COD)\}_2]/P(NMe_2)_3$ mixtures tend to give better results.

Introduction

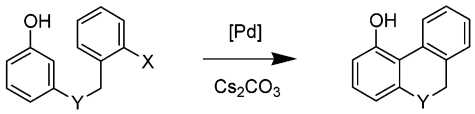
The biaryl subunit is an important structural motif that is found in a wide range of compounds such as natural products, polymers, liquid crystals, and ligands for homogeneous transition metal catalysts.[1] One class of reaction that provides particular challenges for the catalytic chemist is the synthesis of ortho-arylated phenols. Currently the most commonly used catalytic routes to these compounds employ Suzuki or Stille coupling reactions.[2] These require the introduction and subsequent loss of stoichiometric amounts of either boronic acid/ester or organotin functions. In addition it may prove necessary to protect the phenolic hydroxide function during the course of the coupling reactions, and this in turn adds further steps to the synthetic procedure. Regardless, such catalytic routes are often preferential to stoichiometric processes, which tend to require equimolar or greater amounts of reagents such as arylleads[3] or arylbismuths.[4] Therefore the ability to couple an aryl halide *directly* with a phenol (Scheme 1) without the need for either (a) a sacrificial electrophilic boron or tin fragment or (b) the introduction and subsequent removal of a protecting group would be highly desirable from both synthetic and atom-economic points of view.

The transition-metal-catalyzed ortho-selective arylation of phenols has been limited to a few examples of intramolecular couplings of aryl halides that are tethered to the phenolic substrates (Scheme 2)[5] and the reactions of aryl halides with 2-aryl-substituted phenols (Scheme 3) or with 1-naphthol (Scheme 4).[6]

SCHEME 1. Catalytic Ortho-Arylation of Phenols

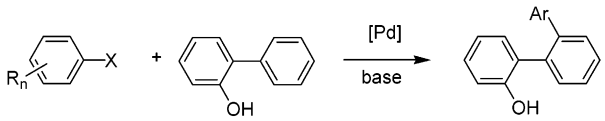


SCHEME 2

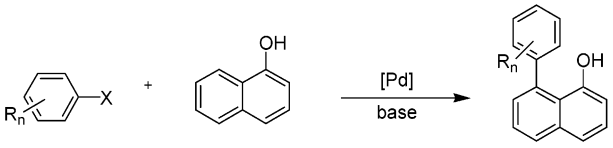


X = Br, I; Y = CH_2, O, NR

SCHEME 3



SCHEME 4



In all of these cases the reactions proceed via the formation of stable five- or six-membered metallacycles. Simple phenols avoid orthometalation reactions with late transition metals, as this would give unfavorably strained, four-membered metallacycles,[7] and therefore these reac-

(1) (a) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263−303. (b) Bringmann, G.; Walter, R.; Weirich, R. *Angew Chem., Int. Ed. Engl.* **1990**, *29*, 977.

(2) For recent examples, see: (a) Zhuravel, M. A.; Nguyen, S. T. *Tetrahedron Lett.* **2001**, *42*, 7925. (b) Kranich, R.; Eis, K.; Geis, O.; Mühle, S.; Bats, J. W.; Schmalz, H.-G. *Chem. Eur. J.* **2000**, *6*, 2874. (c) Simonsen, K. B.; Gothelf, K. V.; Jørgensen, K. A. *J. Org. Chem.* **1998**, *63*, 7536. (d) Zembower, D. E.; Zhang, H. *J. Org. Chem.* **1998**, *63*, 9300. (e) Yonezawa, S.; Komurasaki, T.; Kawada, K.; Tsuri, T.; Fuji, M.; Kugimiya, A.; Haga, N.; Mitsumori, S.; Inagaki, M.; Nakatani, T.; Tamura, Y.; Takechi, S.; Taishi, T.; Ohtani, M. *J. Org. Chem.* **1998**, *63*, 5831.

(3) Saito, S.; Kano, T.; Muto, H.; Nakadai M.; Yamamoto, H. *J. Am. Chem. Soc.* **1999**, *121*, 8943 and references therein.

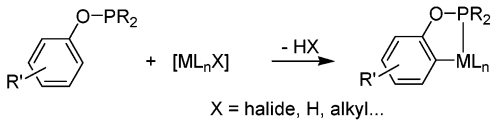
(4) Fedorov, A. Combes S. Finet, J.-P. *Tetrahedron* **1999**, *55*, 1341.

(5) (a) Hennings, D. D.; Iwasa, S.; Rawal, V. H. *J. Org. Chem.* **1997**, *62*, 2. (b). Hennings, D. D.; Iwasa, S.; Rawal, V. H. *Tetrahedron Lett.* **1997**, *38*, 6379.

(6) (a) Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1740. (b) Satoh, T.; Inoh, J.; Kawamura, Y.; Kawamura, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2239.

10.1021/jo030157k CCC: $25.00
Published on Web 10/01/2003

SCHEME 5



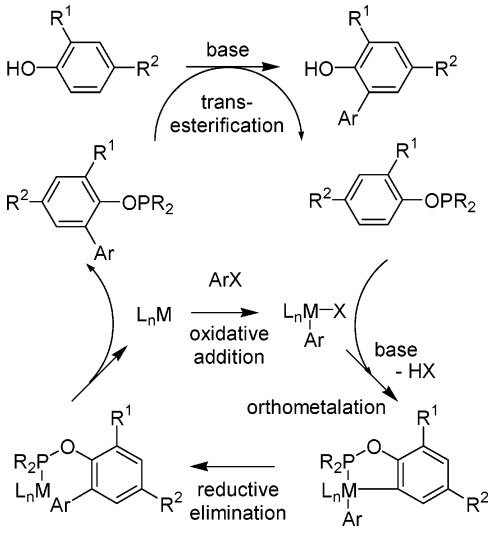
tions cannot be readily extended to such substrates. However when aryloxide groups are incorporated into phosphorus donors such as phosphites, $P(OAr)_3$, or phosphinites, $PR_2(OAr)$, then facile orthometalation can occur to give low-strain, five-membered metallacyles (Scheme 5).

Lewis exploited this phenomenon when he demonstrated that ruthenium triarylphophite complexes catalyze the ortho-specific deuteration and ethylation of phenol.[8,9] These catalytic processes rely on the reversible in situ "transesterification" of catalytic amounts of triaryl phosphite ligands with the substrate phenols. These findings led to the development of a range of new catalytic reactions that proceed via an orthometalation and subsequent insertion of an unsaturated substrate into the new M−C bond.[10] By contrast, intermolecular ortho-selective couplings that proceed via the coupling of an orthometalated carbon with a substrate introduced by oxidative addition of an organic halide remain very rare. Recently Yamaguchi and co-workers demonstrated that phenols can be coupled with haloalkynes in the presence of a gallium catalyst, and Oi and co-workers showed that arylimines can be coupled with aryl bromides in the presence of a ruthenium catalyst.[11,12] We were interested to see whether catalytic transesterification of phenols and their subsequent C−H activation by orthometalation could be used to realize the intermolecular ortho-arylation of these substrates (Scheme 1). It can be envisaged that such a process may proceed via a mechanism related to that shown in Scheme 6, in which two interlinked catalytic pathways lead to the ortho-arylation of the phenol incorporated in a $PR_2(OAr)$ ligand, followed by a transesterification of the modified $PR_2(OAr)$ ligand to liberate the product phenol. If this could be realized, it should allow the synthesis of a wide range of selectively 2-arylated phenols. The results of our study into the inception and development of this new catalytic process are presented below.[13]

Results and Discussion

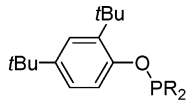
Screening of Catalysts and Optimization using 2-Substituted Phenols. In the first instance, to probe the feasibility of the reaction, we limited our investigation to the potential ortho-arylation of phenols with sterically

SCHEME 6

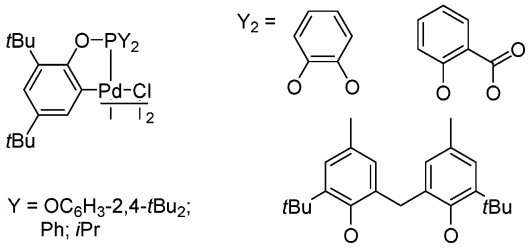


hindered functions in the 2-position, as we anticipated this would give us the greatest chance of success since orthometalation is accelerated by steric bulk. In addition, by blocking off one of the ortho-positions, the number of potential side products that could be formed is reduced. The substrates used in the optimization studies are the bulky phenol 2,4-di-*tert*-butylphenol, since phosphorus donors that incorporate this aryloxide residue have been found to undergo particularly facile orthometalation reactions,[14] and 4-bromoacetophenone, which is electronically activated with respect to oxidative addition.

Initial experiments focused on the use of either (i) palladium catalysts formed in situ from dipalladium tris(dibenzylideneacetone) with the ligands tris(2,4-di-*tert*-butylphenyl)phosphite (**1**), (2,4-di-*tert*-butylphenyl) diphenylphosphinite (**2**), or (2,4-di-*tert*-butylphenyl) diisopropylphosphinite (**3a**) acting as co-catalysts or (ii) preformed palladacyclic catalysts of the type **4** containing these and related ligands.[14b,c,e,15] In all cases we observed either no reaction or the oxidative coupling of the phenol to give 2,2′,4,4′-tetra-*tert*-butylbiphenol, **5**.



1: R = OC_6H_3-2,4-tBu_2
2: R = Ph
3a: R = *i*Pr



4: Y = OC_6H_3-2,4-tBu_2; Ph; *i*Pr

By contrast, when $[RhCl(PPh_3)_3]$, Wilkinson's catalyst, is employed with an appropriate co-catalyst, then the reaction proceeds as shown in Scheme 1 to give the ortho-arylated phenol 2,4-di-*tert*-butyl-6-(4′-acetylphenyl)phenol, **6a**. The choice of co-catalyst is important. The reaction works with the bulky triaryl phosphite ligand **1** only if it is used in 100 mol % loading (i.e., no free phenol

(7) Miura and co-workers have demonstrated the 1-arylation of 2-naphthols. This pattern of reactivity may result from the high susceptibility of the 1-position to electrophilic attack rather than the formation of a highly strained four-membered palladacycle. See ref 6.

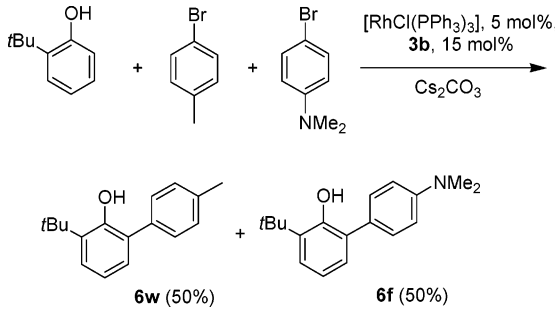
(8) Lewis, L. N. *Inorg. Chem.* **1985**, *24*, 4433.
(9) Lewis L. N.; Smith, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 2728.
(10) For recent reviews, see: (a) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (b) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1699.
(11) Kobayashi, K.; Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2002**, *124*, 8528.
(12) Oi, S.; Ogino, Y.; Fukita, S.; Inoue, Y. *Org. Lett.* **2002**, *4*, 1783.
(13) Aspects of this work have been communicated previously: Bedford, R. B.; Coles, S. J.; Hursthouse, M. B.; Limmert, M. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 112.

is used in the reaction). This implies that transesterification works, at best, only very poorly with this ligand. In addition it is necessary to use 30 mol % of Wilkinson' catalysts and a large excess (3.5 equiv) of aryl bromide is required, otherwise the major product formed is again the homocoupled biphenol, **5**. The triarylphosphinite ligand **2** suffers from most of these limitations as well, although the reaction proceeds when only 1.5 equiv of the aryl bromide are used. However, when it is replaced by the aryl dialkylphosphinite **3a**, then the reaction is far more efficient and transesterification becomes viable; thus high yields of the product **6a** are obtained with 5 mol % Rh, 15 mol % **3a**, and 1.5 equiv of 4-bromoacetophenone (Table 1, entry 1). Although the reaction proceeds well in toluene, the use of 1,4-dioxane leads to complete inactivity. Lowering the catalyst and co-catalyst loadings to 3 mol % rhodium and 10 mol % **3a** leads to a similar yield of product (88%). The catalyst and co-catalyst loadings can be dropped further (vide infra), but for the remainder of the initial coupling reactions the non-optimized levels of 5 mol % Rh and 15 mol % phosphinite co-catalyst were used.

The "standard" loading of aryl bromides was maintained at 1.5 equiv compared with the total phenol content (including that incorporated in the phosphinite co-ligands), because in certain (but no means all) cases hydrodehalogenation of the aryl bromide occurs, thus lowering the amount available for reaction. In principle any OAr function can be incorporated into the phosphinite co-catalyst, but for ease of product identification and purification we typically employed phosphinites that contain the substrate phenol. The data from the catalytic studies with Wilkinson's catalyst and the aryl dialkylphosphinite ligands acting as co-catalysts are summarized in Table 1. The yields quoted are isolated yields based on the amount of free phenol used, since in many cases the hydrolytic workup did not lead to complete or substantial hydrolysis of the phosphinites.

As can be seen from entries 1−8, good to excellent conversions to the ortho-arylated phenols are seen regardless of whether the aryl bromide used is activated, nonactivated, or deactivated with respect to oxidative addition. The reaction also proceeds smoothly when sterically hindered aryl bromide substrates are employed (entries 9−12). Even aryl chlorides can be used as substrates (entries 13 and 14), although much lower yields of coupled products result. The lower activity in the coupling of aryl chlorides compared with aryl bromides is further illustrated by the reaction of 4-chlorobromobenzene with 2-*tert*-butylphenol (entry 14). Here two products are formed: the 1,4-dicoupled product, **9**, and 2-*tert*-butyl-6-(4′-chlorophenyl)phenol, **6n**. No 2-*tert*-butyl-6-(4′-bromophenyl)phenol is observed in the product mix. This product distribution presumably results from the fact that while the C−Cl bond of 4-chlorobromobenzene is deactivated with respect to oxidative addition, arylation of the para-position activates it. This implies that when aryl chlorides are used the rate-determining step is probably oxidative addition.

To establish whether oxidative addition of aryl bromide substrates is also rate-determining, we performed a competitive coupling of 2-*tert*-butylphenol with 1 equiv each of the electronically deactivated (with respect to oxidative addition) aryl bromide 4-bromo-*N*,*N*-dimethylamine and the nonactivated substrate 4-bromotoluene (eq 1). In this case we found that quantitative conversion of the phenol to coupled products occurs with the two possible products **6w** and **6f** formed in identical amounts. This implies that with aryl bromides, unlike with aryl chlorides, oxidative addition is *not* the rate-determining step.



(1)

In all cases where the phenol substrate is unsubstituted at the 4-position only ortho-arylation occurs; a simple electrophilic reaction of these substrates should also lead to the formation of para-arylated products. This demonstrates that the reaction is indeed ortho-selective, which in turn implies that the C−H activation of the phenol occurs *after* it has been incorporated into the phosphinite co-catalyst.

In certain cases the reaction does not stop at the simple ortho-arylated products and arylation of a previously introduced ortho-aryl group occurs (entries 5, 6, 8, 16−18, 21). Such multiple arylation reactions have been observed before and proceed by essentially the same route as shown in Scheme 3 for the arylation of 2-phenylphenol.[6]

As well as simple aryl halides, heteroaryl bromides can be used as coupling partners (entries 15−18). The particularly low yield obtained with 2-bromopyridine maybe be due, in part, to deactivation of the catalyst since both the product phenol and, in particular, the intermediate modified phosphinite can form chelate complexes with the metal center. Both 3-bromo- and 3-bromo-4-methylthiophene couple with 2-*tert*-butylphenol but are then subject to further arylations. 2-Bromothiophene gives only trace amounts of mono- and diarylated products as determined by GC−MS. The poor results here are again presumably due to catalyst inhibition by chelate formation.

It is not necessary to have a bulky *tert*-butyl in the 2-position of the phenol for the reaction to proceed; the incorporation of progressively smaller groups such as isopropyl and ethyl still gives reasonable yields of the products (entries 19 and 20). Coupling is even seen with 2-methylphenol (entry 21); however, in this case the yield

(14) (a) Bedford, R. B.; Castillon, S.; Chaloner, P. A.; Claver, C.; Fernandez, E.; Hitchcock, P. B.; Ruiz, A. *Organometallics* **1996**, *15*, 3990. (b) Albisson, D. A.; Bedford, R. B.; Lawrence, S. E.; Scully, P. N. *Chem. Commun.* **1998**, 2095. (c) Bedford, R. B.; Welch, S. L. *Chem. Commun.* **2001**, 129. (d) Bedford, R. B.; Hazelwood, S. L. *Organometallics* **2002**, *21*, 2599. (e) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E.; Brown, J. M.; Ramdeehul, S.; Cowley, A. R.; Coles S. J.; Hursthouse, M. B. *Organometallics* **2003**, *22*, 1364. (f) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E.; Albisson, D. A.; Draper, S. M.; Scully, P. N.; Coles S. J.; Hursthouse, M. B. *Chem. Eur. J.* **2003**, *9*, 3216.

(15) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E. *Chem. Commun.* **2002**, 2610.

TABLE 1. Catalytic Ortho-Arylation of Phenols with 2-Substituents[a]

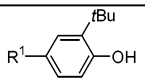
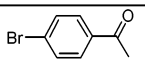
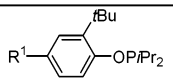
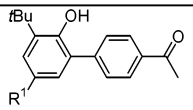
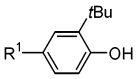
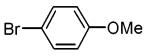
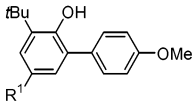
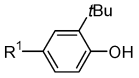
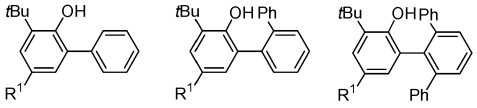
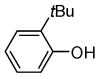
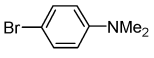
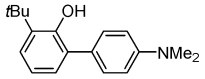
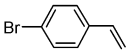
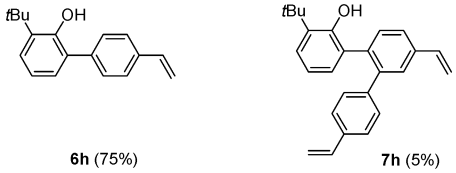
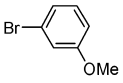
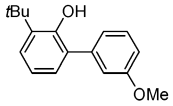
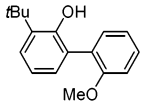
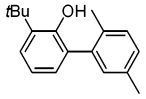
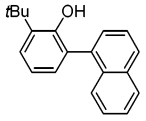
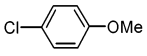
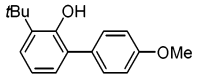
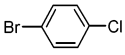
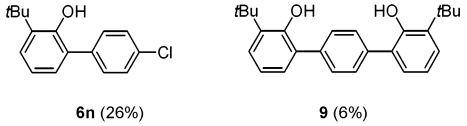
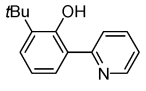
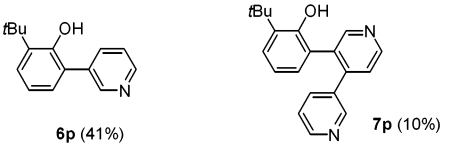
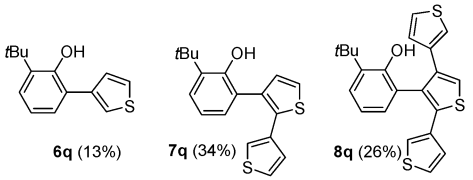
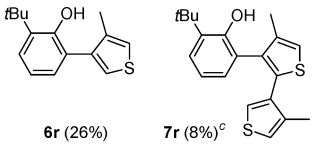
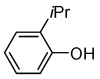
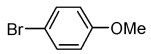
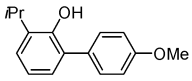
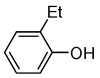
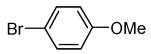
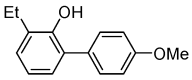
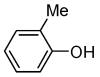
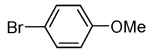
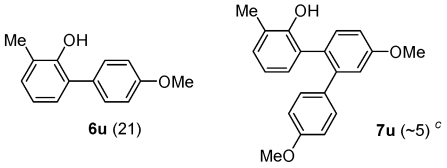
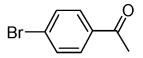
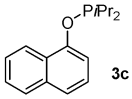
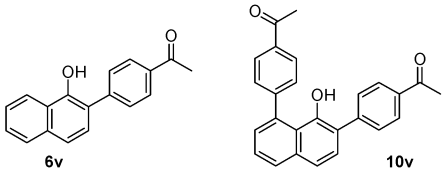
Entry	Phenol	Aryl halide	Phosphinite co-catalyst	Product (yield, %)[b]
1 (R^1 = *t*Bu) 2 (R^1 = H)			 **3a:** R^1 = *t*Bu **b:** R^1 = H	 **6a:** R^1 = *t*Bu, (96) **b:** R^1 = H, (96)
3 (R^1 = *t*Bu) 4 (R^1 = H)			**3a** **3b**	 **6c:** R^1 = *t*Bu, (86) **d:** R^1 = H, (79)
5 (R^1 = *t*Bu) 6 (R^1 = H)			**3a** **3b**	 **6e:** R^1 = *t*Bu, (81) **f:** R^1 =, H (84) **7e:** R^1 = *t*Bu, (6) **f:** R^1 = H, (8) **8e:** R^1 = *t*Bu (5)
7			**3b**	 **6g** (86%)
8	"		"	 **6h** (75%) **7h** (5%)
9	"		"	 **6i** (100%)
10	"		"	 **6j** (100%)
11	"		"	 **6k** (100)
12	"		"	 **6m** (92%)
13	"		"	 **6d** (15)
14	"		"	 **6n** (26%) **9** (6%)
15	"		"	 **6o** (23%)
16	"		"	 **6p** (41%) **7p** (10%)

TABLE 1 (Continued)

Entry	Phenol	Aryl halide	Phosphinite co-catalyst	Product (yield, %)[b]
17	"		"	 **6q** (13%) **7q** (34%) **8q** (26%)
18			"	 **6r** (26%) **7r** (8%)[c]
19			"	 **6s** (68)
20			"	 **6t** (53)
21			"	 **6u** (21) **7u** (~5)[c]
22			 **3c**	 **6v** **10v** ~4 : 1[c] combined yield 67%[d]

[a] Conditions: 2-substituted phenol (or naphthol) (1.0 mmol), aryl halide (1.5 mmol), Cs_2CO_3 (1.7 mmol), [$RhCl(PPh_3)_3$] (5 mol %), $PR_2(OAr)$, (15 mol %), toluene, reflux, 18 h. [b] Isolated yields after chromatography, not optimized. [c] Estimated by ^1H NMR spectroscopy. [d] Isolated yield of microanlaytically pure **6v**, 39%.

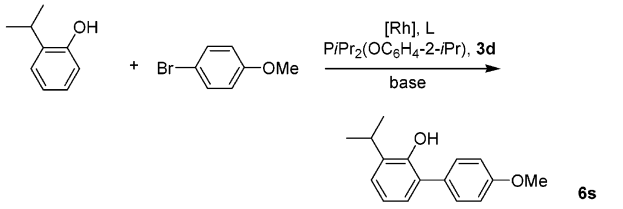
is significantly lower. It is not necessary to have an alkyl group in the 2-position to facilitate the coupling reaction; 1-naphthol can also be used as a substrate to good effect (entry 22). In this case a small amount of the 2,8-diarylated product, **10v**, is observed. Presumably the 8-arylation occurs after the 2-arylation as there is no evidence for the formation of the 8-monoarylated naphthol. It is possible that the 8-arylation does not proceed via the orthometalation of a phosphinite intermediate, since 1-naphthol itself has been shown to undergo 8-arylation in the presence of a palladium catalyst as shown in Scheme 4.[6]

No activity is observed with unsubstituted phenol. The observed reduction in catalytic activity with decreasing steric bulk implies that, with aryl bromide substrates, the rate-determining step is probably the orthometalation of the phosphinite ligand.

Having established a protocol for the ortho-arylation of phenols with 2-substitution, we wished to see whether it was possible to refine the process to be able to (i) reduce the amount of rhodium needed, (ii) reduce the loading of co-catalyst, (iii) employ a cheaper base, (iv) establish the role of the phosphine co-ligands, and (v) extend the reaction to phenols without 2-substitution. The latter point will be discussed later. To address points i−iv we chose the coupling of 2-isopropylphenol with 4-bromoanisole as a standard reaction, as it proceeds reasonably well (Table 1, entry 19) but has scope for improvement, making it ideal for optimization studies. The results from this study are summarized in Table 2.

In all cases [{$Rh(\mu\text{-}Cl)(COD)\}_2$] was used as the rhodium source. As can be seen in entry 1, the use of a catalyst formed in situ from this dimer and 2 equiv per Rh of PPh_3 gives a performance very similar to that of the catalyst formed from Wilkinson's catalyst and the phosphinite co-catalyst (Table 1, entry 19). Reducing the number of equivalents of co-ligand from 2 to 1 per rhodium does not perturb the system too greatly (Table 2, entry 2), nor does halving the rhodium loading while increasing the co-catalyst:Rh ratio to 3:1 (entry 3). However, when the

TABLE 2. Effect of Varying Conditions and Ligands on the Ortho-Arylation Reaction[a]



entry	mol % Rh	phosphinite loading (equiv per Rh)	added ligand L (equiv per Rh)	base	conv (%)[b]
1	5.0	2	PPh_3 (2)	Cs_2CO_3	68
2	5.0	1	PPh_3 (2)	Cs_2CO_3	62
3	2.5	3	PPh_3 (2)	Cs_2CO_3	62
4	1.0	3	PPh_3 (2)	Cs_2CO_3	43
5	5.0	3	PPh_3 (2)	K_2CO_3	22
6	5.0	3	PPh_3 (2)	K_3PO_4	88
7	5.0	3	PPh_3 (4)	Cs_2CO_3	76
8	5.0	3	PPh_3 (3)	Cs_2CO_3	78
9	5.0	3	PPh_3 (2)	Cs_2CO_3	74
10	5.0	3	PPh_3 (1)	Cs_2CO_3	72
11	5.0	3	0	Cs_2CO_3	74
12	5.0	3	PCy_3 (3)	Cs_2CO_3	45
13	5.0	3	P*t*Bu_3 (3)	Cs_2CO_3	34

[a] Conditions: 2-isopropylphenol (1.0 mmol), 4-bromoanisole (1.5 mmol), base (1.7 mmol) [{RhCl(COD)}$_2$] (1−5 mol %), **3d** (1−3 equiv per Rh), toluene (10 mL), reflux temperature, 18 h. [b] Conversion determined by ^{1}H NMR using 1,3,5-trimethoxybenzene in $CDCl_3$ as an internal standard.

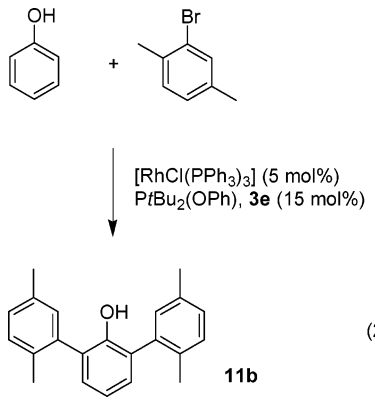
rhodium loading is reduced further to 1 mol %, some loss in performance is observed.

We were keen to find if it is possible to replace the rather expensive base, cesium carbonate, with a cheaper alternative. While potassium carbonate does not seem to be particularly useful, changing to potassium phosphate actually appears to be beneficial to catalyst performance, with a substantial increase in conversion observed (entry 6).

To address the role played by the supporting ligands in the catalysis we studied the effect of changing the relative amounts and type of added phosphines. We were very surprised to find that when the ratio of PPh_3:Rh is varied from 4:1 to 0:1 there is essentially no difference in conversion (compare entries 7−11). This implies that the triphenylphosphine does not play any particular role and can be omitted from the reaction. Thus when Wilkinson's catalyst is used, it is presumably only acting as a soluble source of rhodium(I) for the reaction. It is possible that if, as discussed earlier, the rate-determining step is indeed orthometalation, there is insufficient difference in the donor properties of the PPh_3 co-ligand and the P*i*Pr_2(OAr) co-catalyst to effect the rate regardless of the number of each type of ligand on the metal center. To increase the rate of orthometalation, assuming it occurs via oxidative addition of the C−H bond rather than by electrophilic displacement,[16] it would be necessary to increase the electron density on the rhodium center. The use of trialkylphosphine co-ligands would be expected to do this. However, as can be seen in entries 12 and 13 the use of either PCy_3 or P*t*Bu_3 leads to a substantial decrease in activity. This may imply that the mechanism for orthometalation is in fact electrophilic displacement. However, if this was the case, it would be anticipated that the use of co-catalysts that are poorer σ-donors and better π-acids than P*i*Pr_2(OAr) would give better results, but as discussed in the initial optimization studies, PPh_2(OAr) and P(OAr)$_3$ ligands make progressively poorer co-catalysts while their net donation of electron-density to the rhodium center decreases. Alternative explanations are that the catalysts formed in situ with PCy_3 or P*t*Bu_3 are too crowded to facilitate orthometalation or that the rhodium center is now too electron-rich and the rate-determining step is shifted to reductive elimination.

Screening of Catalysts and Optimization for Phenols without 2-Substitution. Obviously it would be highly desirable if the catalytic methodology could be modified to allow facile and clean ortho-arylation of phenols without 2-substitution. It appears as if the rate-determining step with small phenols is orthometalation, and therefore we wondered whether the use of iridium-based catalysts may prove advantageous since bulky phosphite ligands undergo particularly facile orthometalation reactions with this metal.[14a] Unfortunately when either a mixture of [{IrCl(COD)}$_2$]/2 PPh_3/P*i*Pr_2(OAr) or [{IrCl(COE)$_2$}$_2$]/2 PPh_3/P*i*Pr_2(OAr) were used as precatalysts in the coupling of the small substrate 2-methylphenol with 4-bromoanisole, no reaction was observed. Therefore we concentrated instead on rhodium-based systems with a range of co-catalysts with variable steric and electronic properties. For the optimization we focused on the coupling of phenol with 4-bromoanisole in toluene with cesium carbonate as base, and the results of this study are summarized in Figure 1.

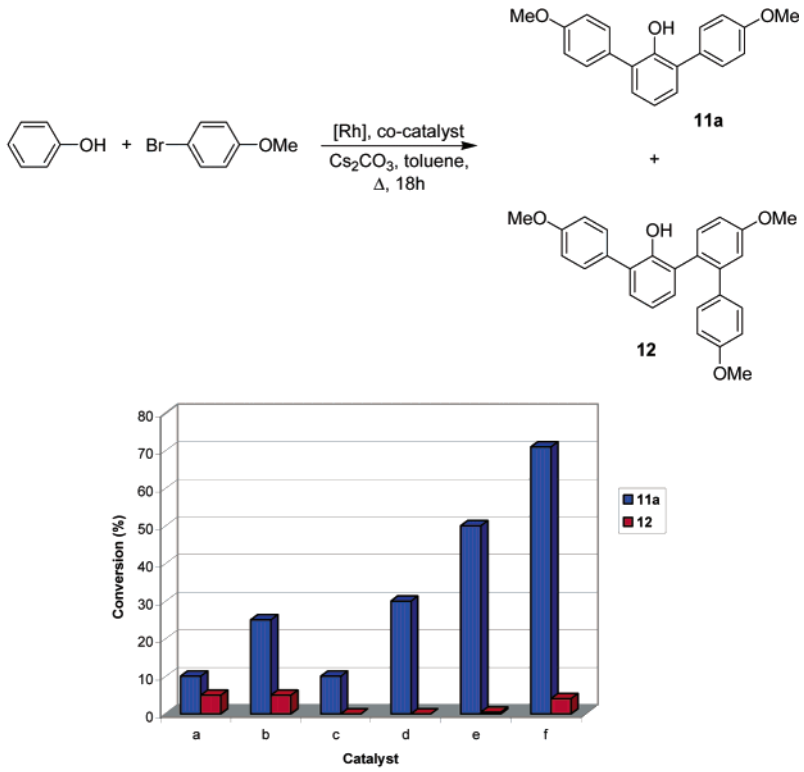
In an attempt to accelerate the orthometalation process we initially investigated the application of the bulkier phosphinite co-catalyst P*t*Bu_2(OPh), **3e**, formed by reaction of P*t*Bu_2Cl with sodium phenoxide. We were pleased to see that at 15 mol % loading of **3e**, some conversion to the diarylated product, **11a**, and the triarylated product, **12**, occurred, and even greater conversion was obtained with 30 mol % loading of the co-catalyst (Figure 1, catalysts **a** and **b** respectively). When the aryl bromide is changed to 2-bromo-*p*-xylene, the diarylated product 2,5,2″,5″-tetramethyl-[1,1′;3′,1″]terphenyl-2′-ol, **11b**, is obtained in 34% yield (eq 2).



(2)

The product distribution in both of these reactions implies that the rate-determining step with phenol is

(16) For a discussion on the mechanisms of cyclometalation, see: Ryabov; A. D. *Chem. Rev.* **1990**, *90*, 403.



Catalyst:	a	b	c	d	e	f
	$[RhCl(PPh_3)_3]$	$[RhCl(PPh_3)_3]$	$[\{RhCl(COD)\}_2]$	$[\{RhCl(COD)\}_2]$	$[\{RhCl(COD)\}_2]$	$[\{RhCl(COD)\}_2]$
(mol%)	(5)	(5)	(5)	(5)	(5)	(5)
	+ $PrBu_2(OPh)$	+ $PrBu_2(OPh)$	+ $P(OPh)_3$	+ $P(NMe_2)(OPh)_2$	+ $(NMe_2)_2(OPh)$	+ $P(NMe_2)_3$
	(15)	(30)	(30)	(30)	(30)	(30)

FIGURE 1. Coupling of phenol with 2-bromoanisole with varying catalysts/co-catalysts.

again probably orthometalation. The absence of monoarylated phenol means the rate of arylation of the 2-arylated phenol must be much higher than that for the arylation of phenol. This is presumably because the larger size of the intermediate phosphinite leads to a greater rate of orthometalation.

While increasing the steric bulk of the alkyl substituents on the phosphinite co-catalyst does indeed appear to open up the possibility of using phenols without 2-substitution as substrates, the overall yield and selectivity is too low to be of use. Therefore we next decided to investigate the effect of changing the electronics of the co-ligand. We were surprised to find that the small, π-acidic ligand triphenyl phosphite could be used as a co-catalyst (Figure 1, catalyst **c**). Although the conversion to coupled products observed is poor, the selectivity for diarylation rather than triarylation is high with only trace amounts of **12** observed. When first one and then two of the OPh residues are replaced by NMe_2 in the co-catalyst, the conversion increases. Since the co-catalysts $P(NMe_2)(OPh)_2$ and $P(NMe_2)_2(OPh)$ are readily prepared by reaction of appropriate amounts of phenol with $P(NMe_2)_3$ in toluene at reflux temperature, we wondered whether $P(NMe_2)_3$ itself would act as a useful co-catalyst. This indeed proves to be the case, with a respectable conversion to the diarylated product **11a** of 71% and good selectivity observed. During the course of this work we became aware that Oi and co-workers have independently found this Rh-$P(NMe_2)_3$-based system to be active for the ortho-arylation of phenols; these results were presented at the 81st annual meeting of the Japanese Chemical Society.[17]

These optimization results seem a little surprising in the sense that, under the conditions we are employing, it would be expected that all of the $P(NMe_2)_3$ would be converted to $P(OPh)_3$ and yet the results obtained with these two ligands are quite different. One possible explanation for this observation is that the transesterification does not happen on the free ligands but rather is mediated by the rhodium. Given that the ratio of $P(NMe_2)_3$ to rhodium is 3:1, it is highly likely that all of the co-catalyst is coordinated to the rhodium and that transesterification may indeed occur in the coordination sphere.

Having established that mixtures of $[\{RhCl(COD)\}_2]$ and $P(NMe_2)_3$ can be used to good effect for the coupling of unsubstituted phenol, we then investigated the application of this catalyst system to a range of coupling reactions. The results of this study are summarized in Table 3. In some cases the isolated yields are low; this is due to the fact that isolation of the pure compounds by

(17) Fukita, S.; Watanabe, S.; Oi, S.; Inoue, Y. *Abstracts of the 81st Annual Meeting of Japan Chemical Society*, 2002; p 1108, 1G5−40.

TABLE 3. Catalytic Ortho-Arylation of Phenols without 2-Substituents[a]

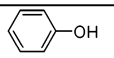
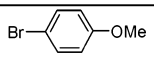
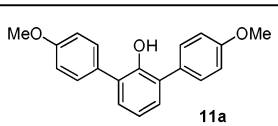
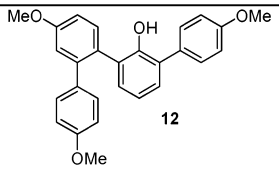
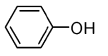
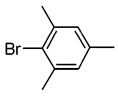
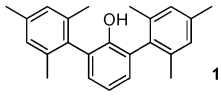
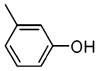
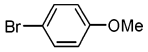
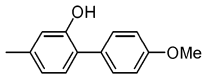
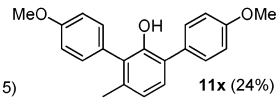
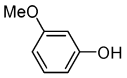
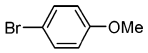
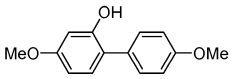
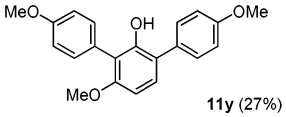
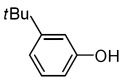
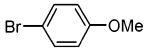
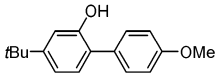
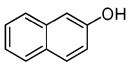
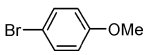
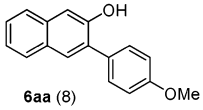
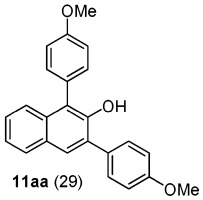
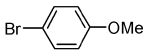
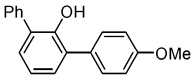
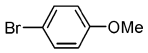
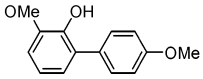
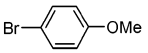
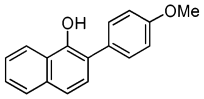
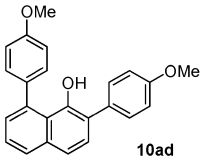
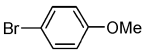
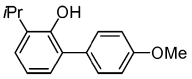
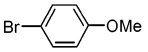
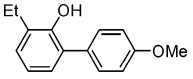
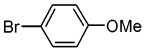
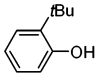
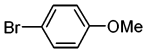
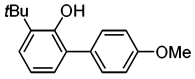
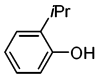
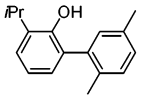
Entry	Phenol	Aryl halide	Product (yield, %)[b]
1			 **11a**  **12** 50 : 3[c] combined yield = 62%[d]
2			 **11c** (16%)
3			 **6x** (15)  **11x** (24%)
4			 **6y** (24%)  **11y** (27%)
5			 **6z** (39%)
6			 **6aa** (8)  **11aa** (29)
7			 **6ab** (53)
8			 **6ac** (71)
9			 **6ad**  **10ad** ~4 : 1[c] combined yield ca. 70%[e]
10			 **6s** (69)
11			 **6t** (77)
12			**6u** (28%) **7u** (34%)

TABLE 3 (Continued)

Entry	Phenol	Aryl halide	Product (yield, %)[b]
13			 **6d** (29)
14			 **6ae** (27)

[a] Conditions: phenol (or naphthol) (1.0 mmol), aryl halide (1.5 mmol), Cs_2CO_3 (1.7 mmol), [{RhCl(COD)}$_2$] (10 mol % Rh), $P(NMe_2)_3$, (30 mol %), toluene, reflux, 18 h. [b] Isolated yields of microanalytically pure product after chromatography, not optimized. [c] Determined by ^{1}H NMR spectroscopy. [d] Isolated yield of microanlaytically pure **11a**, 31%. [e] Isolated yield of microanalytically pure **6ad**, 38%.

chromatography, particularly when large amounts of secondary coupled products are present, proved problematic. The yields refer only to the amount of product isolated microanalytically pure, unless otherwise indicated.

As well as reacting with the electronically deactivated substrate 4-bromoanisole (entry 1), phenol can be coupled with the hindered aryl bromide bromomesitylene; however, the yield of the dicoupled product **11c** obtained after 18 h is poor (entry 2). When 3-substituted phenols are used as substrates, monosubstituted phenols **6** are also produced in which the arylation occurs solely in the 6-position, presumably because of the steric bulk of the 3-subsituent. Thus both 3-methylphenol and 3-methoxyphenol react to give the 6-monoarylated species **6x** and **6y**, respectively, as well as the 2,6-diarylated species **11x** and **11y** (entries 3 and 4). The absence of any 2-monoarylated products indicates that the 6-arylation occurs first. It is particularly interesting to note that no 2-monoarylation occurs with 3-methoxyphenol, as this indicates that the selectivity is purely steric in basis with no acceleration of 2-arylation by precoordination of the methoxy group to the rhodium center. When the size of the 3-substituent is increased, e.g., in the case of 3-*tert*-butylphenol (entry 5), no 2-aryation is observed and the 6-monoarylated phenol, **6z**, is obtained as the sole product. 2-Naphthol can also be used as a substrate, again giving a mixture of the mono- and diarylated compounds **6aa** and **11aa** (entry 6).

Neither 2-phenylphenol nor 2-methoxyphenol are ortho-arylated effectively when using the protocol outlined in Table 1. However, the use of $P(NMe_2)_3$ as a co-catalyst allows both to be ortho-arylated in the 6-position to give **6ab** and **6ac**, respectively (entries 7 and 8). This methodology can also be used to couple 1-naphthol with 4-bromoanisole (entry 9), a reaction that fails with the earlier methodology.

By comparing the formation of **6s** under these conditions (entry 10) with those used in Table 1 (entry 19), it can be seen that there is not any significant increase in conversion, despite the fact that the loading of rhodium is double that used in the earlier method. The yields from the reactions of 4-bromoanisole with 2-ethylphenol and 2-methylphenol are significantly and marginally better, respectively, under the conditions used in Table 3 (entries 11 and 12) compared with the same couplings in Table 1 (entries 20 and 21), although in the latter case the second, diarylated product **7u** is formed in far greater amounts than when using the phosphinite-based protocol. Therefore although the latter method is useful for phenols without 2-substitution, the lower rhodium loading means that the earlier method is more applicable for most 2-substituted phenols. Even more striking is the poor yield obtained in the coupling of 2-*tert*-butylphenol with 4-bromoanisole (entry 13) compared with that obtained using the earlier method (Table 1, entry 4). It seems that in most cases where the phenol is 2-substituted the method outlined in Table 1 gives superior yields. However, if a reaction with a 2-susbtituted phenol fails using the phosphinite-based method, e.g., when using 2-phenylphenol or 2-methoxyphenol as substrates or when coupling 1-naphthol with 4-bromoanisole, it is worth trying the second, complementary $P(NMe_2)_3$-based protocol.

Summary

In summary, we have developed the catalytic ortho-arylation of phenols as a viable process. In many cases high yields and high selectivity result. It appears that the precise nature of the P-OAr-containing co-catalyst is highly important, and as yet, one class of ligand does not work in all cases. For most phenol substrates with 2-substituents the diisopropylphosphinite, P*i*Pr$_2$(OAr), ligands are the best tested, whereas for substrates without 2-substituents tris(dimethylamino)phosphine, $P(NMe_2)_3$, is a much better choice. Obviously it is still necessary to work on the systems in order to bring down further the catalyst loading and, in certain cases, increase the yield and/or the product selectivity of the reactions. This work is currently ongoing in our group.

Experimental Section

Synthesis of Phosphinite Ligands 3c and 3d. The ligands **3c** and **3d** were prepared using an analogous method to that described peviously for the synthesis of **3a** and **b**.[18]

Data for 3c. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (m, 12 H), 2.06 (apparent d of sept., J = 7.2, 2.8 Hz, 2H), 7.36 (m, 2H), 7.47 (m, 3H), 7.80 (m, 1H), 8.25 (m, 1H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 147.

Data for 3d. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (m, 12 H), 1.24 (d, J = 6.9 Hz, 6H), 1.98 (apparent d of sept., J = 7.0, 2.0 Hz, 2H), 3.0 (sept., J = 6.9 Hz, 1H), 6.93 (ddd, J = 7.4, 7.3, 0.8 Hz, 1H), 7.03 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 7.11 (dd, J = 7.4, 1.6 Hz, 1H), 7.25 (ddd, J = 8.1, 0.8 Hz, J(H, P) = 4.7 Hz, 1H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 143.

(18) Bedford, R. B.; Hazelwood, S. L.; Horton, P. N.; Hursthouse, M. B. *Dalton Trans.* **2003**, in press.

General Catalytic Methodology using Wilkinson's Catalysts and Arylphosphinite Co-catalysts (Table 1). In a Radleys reaction tube under nitrogen were added [RhCl(PPh$_3$)$_3$] (46 mg, 0.05 mmol), toluene (10 mL), the appropriate aryl halide (1.5 mmol), phosphinite (0.15 mmol), 2-substituted phenol (or 1-naphthol) (1.0 mmol), and Cs_2CO_3 (0.550 g, 1.70 mmol). The mixture was heated at reflux temperature for 18 h and allowed to cool, and then HCl (aq) (2 M, 5 mL) was added. The organic phase was extracted with dichloromethane (3 × 25 mL), dried ($MgSO_4$), and filtered, and the solvent removed under reduced pressure. The crude mixture was then subjected to column chromatography (silica).

Coupling of 2,4-Di-*tert*-butylphenol with 4-Bromoacetophenone (Table 1, entry 1). Phosphinite ligand **3a** used.

3,5-Di-*tert*-butyl-4′-acetyl-biphenyl-2-ol (6a). Colorless solid, 313 mg (96%); R_f 0.11 ($CHCl_3$/hexane, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 9H), 1.46 (s, 9H), 2.66 (s, 3H), 5.22 (s, 1H), 7.08 (d, J = 2.5 Hz, 1H), 7.38 (d, J = 2.5 Hz, 1H), 7.60 (d, J = 8.1 Hz, 2H), 8.08 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.6, 28.7, 30.6, 33.3, 34.1, 123.5, 123.5, 126.0, 128.3, 128.8, 134.9, 135.2, 141.5, 142.2, 147.5, 196.5; HRMS (CI) calcd for $C_{22}H_{29}O_2$ [M$^+$ + H] 325.2167, found 325.2156. Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.28; H 8.62.

Coupling of 2-*tert*-Butylphenol with 4-Bromoacetophenone (Table 1, entry 2). Phosphinite ligand **3b** used.

3-*tert*-Butyl-4′-acetyl-biphenyl-2-ol (6b). Colorless solid, 257 mg (96%); R_f 0.11 ($CHCl_3$/hexane, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9H), 2.65 (s, 3H), 5.37 (s, 1H), 6.95 (apparent t (dd), J = 7.6 Hz, 1H), 7.09 (dd, J = 7.5, 1.7 Hz, 1H), 7.34 (dd, J = 7.7, 1.7 Hz, 1H), 7.58 (d, J = 8.6 Hz, 2H), 8.08 (d, J = 8.6 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.7, 29.6, 34.9, 120.2, 127.3, 127.8, 127.8, 129.3, 129.8, 136.3, 136.7, 142.5, 150.9, 197.6; HRMS (CI) calcd for $C_{18}H_{21}O_2$ [M$^+$ + H] 269.1541, found 269.1543. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.26; H, 7.31.

Coupling of 2,4-Di-*tert*-butylphenol with 4-Bromoanisole (Table 1, entry 3). Phosphinite ligand **3a** used.

3,5-Di-*tert*-butyl-4′-methoxy-biphenyl-2-ol (6c). Colorless solid, 270 mg (87%); R_f 0.27 ($CHCl_3$/hexane, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 9H), 1.47 (s, 9H), 3.88 (s, 3H), 5.32 (s, 1H), 7.05 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 2.3 Hz, 1H), 7.34 (d, J = 2.3 Hz, 1H), 7.41 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 28.3, 30.2, 32.9, 33.7, 53.9, 113.4, 122.1, 123.4, 126.2, 128.4, 129.4, 133.8, 140.5, 147.4, 157.9; HRMS (CI) calcd for $C_{21}H_{29}O_2$ [M$^+$ + H] 313.2167, found 313.2161. Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.53; H, 8.98.

Coupling of 2-*tert*-Butylphenol with 4-Bromoanisole (Table 1, entry 4). Phosphinite ligand **3b** used.

3-*tert*-Butyl-4′-methoxy-biphenyl-2-ol (6d). Colorless solid, 202 mg (78%); R_f 0.41 ($CHCl_3$/hexane, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 9H), 3.88 (s, 3H), 5.46 (s, 1H), 6.92 (apparent t (dd), J = 7.6 Hz, 1H), 7.05 (d, J = 8.6 Hz, 2H), 7.08 (dd, J = 7.5, 1.7 Hz, 1H), 7.34 (dd, J = 7.8, 1.7 Hz, 1H), 7.40 (d, J = 8.6 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.6, 34.9, 55.3, 114.8, 119.7, 126.3, 128.0, 128.4, 129.2, 130.7, 136.0, 151.1, 159.4; HRMS (CI) calcd for $C_{17}H_{21}O_2$ [M$^+$ + H] 257.1541, found 257.1527. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.42; H, 7.62.

Coupling of 2,4-Di-*tert*-butylphenol with Bromobenzene (Table 1, entry 5). Phosphinite ligand **3a** used. Column chromatography ($CHCl_3$/hexane, 1:3) gave **6e** (228 mg, 80%), **7e** (21 mg, 6%, impure), and **8e** (22 mg, 5%, impure).

3,5-Di-*tert*-butyl-biphenyl-2-ol (6e). Colorless oil; R_f 0.68 ($CHCl_3$/hexane, 1:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 9H), 1.54 (s, 9H), 5.39 (s, 1H), 7.17 (d, J = 2.4 Hz, 1H), 7.43 (d, J = 2.4 Hz, 1H), 7.52 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 30.2, 32.1, 34.6, 35.4, 124.6, 125.2, 128.3, 128.5, 129.9, 130.1, 135.8, 138.5, 142.5, 149.1; HRMS (CI) calcd for $C_{20}H_{27}O$ [M$^+$ + H] 283.2062, found 283.2061. Anal. Calcd for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found C, 84.70; H, 9.73.

3,5-Di-*tert*-butyl-[1,1′;2′,1″]terphenyl-2-ol (7e). Colorless oil; R_f 0.50 ($CHCl_3$/hexane, 1:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 9H), 1.29 (s, 9H), 4.92 (s, 1H), 6.84 (d, J = 2.4 Hz, 1H), 7.09 (m, 2H), 7.16 (m, 4H), 7.50 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.5, 31.5, 34.1, 34.8, 122.9, 126.0, 126.7, 127.2, 127.8, 128.1, 128.5, 129.1, 130.5, 131.2, 135.0, 136.0, 140.5, 141.8, 142.3, 148.6; HRMS (CI) calcd for $C_{26}H_{31}O$ [M$^+$ + H] 359.2375, found 359.2321.

2,4-Di-*tert*-butyl-6-[1,1′;3′,1″]terphenyl-2′-yl-phenol (8e). Colorless oil; R_f 0.38 ($CHCl_3$/hexane, 1:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (s, 9H), 1.12 (s, 9H), 4.64 (s, 1H), 6.55 (d, J = 2.3 Hz, 1H), 6.91 (d, J = 2.3 Hz, 1H), 7.12 (m, 10H), 7.52 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.3, 31.3, 33.8, 34.5, 121.9, 121.9, 125.6, 126.5, 127.3, 127.5, 128.4, 129.2, 129.7, 134.5, 141.0, 141.4, 143.3, 148.7; HRMS (CI) calcd for $C_{32}H_{35}O$ [M$^+$ + H] 435.2688, found 435.2650.

Coupling of 2-*tert*-Butylphenol with Bromobenzene (Table 1, entry 6). Phosphinite ligand **3b** used. Column chromatography ($CHCl_3$/hexane, 1:3) gave **6f** (189 mg, 84%) and **7f** (24 mg, 8%, impure).

3-*tert*-Butyl-biphenyl-2-ol (6f). Colorless oil; R_f 0.62 ($CHCl_3$/hexane, 1:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.49 (s, 9H), 5.48 (s, 1H), 6.96 (apparent t (dd), J = 7.7 Hz, 1H), 7.12 (dd, J = 7.5, 1.7 Hz, 1H), 7.34 (dd, J = 7.8 Hz, 1.7 Hz, 1H), 7.49 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.6, 34.9, 119.8, 126.6, 127.9, 128.0, 128.8, 129.4, 129.5, 136.2, 137.2, 150.1; HRMS (CI) calcd for $C_{16}H_{19}O$ [M$^+$ + H] 227.1436, found 227.1425. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.29; H, 7.70.

3-*tert*-Butyl-[1,1′;2′,1″]terphenyl-2-ol (7f). Colorless oil; R_f 0.46 ($CHCl_3$/hexane, 1:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 9H), 4.95 (s, 1H), 6.81 (apparent t (dd), J = 7.6 Hz, 1H), 6.96 (dd, J = 7.5, 1.7 Hz, 1H), 7.17 (m, 5H), 7.50 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 29.3, 34.6, 119.6, 126.1, 126.9, 127.9, 128.2, 128.3, 128.6, 128.7, 128.9, 130.6, 131.7, 135.3, 136.0, 140.2, 141.8, 150.8; HRMS (CI) calcd for $C_{22}H_{23}O$ [M$^+$ + H] 303.1749, found 303.1744.

Coupling of 2-Butylphenol with 4-Bromo-*N*,*N*-dimethylaniline (Table 1, entry 7). Phosphinite ligand **3b** used.

3-*tert*-Butyl-4′-(dimethylamino)-biphenyl-2-ol (6g). Light-sensitive, colorless oil, 232 mg (86%); R_f 0.35 ($CHCl_3$/hexane, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 9H), 3.07 (s, 6H), 5.67 (s, 1H), 6.90 (d, J = 8.9 Hz, 2H), 6.93 (apparent t (dd), J = 7.7 Hz, 1H), 7.15 (dd, J = 7.5, 1.7 Hz, 1H), 7.34 (dd, J = 7.8, 1.7 Hz, 1H), 7.40 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.6, 34.9, 40.4, 113.1, 119.6, 124.3, 125.8, 128.0, 129.0, 130.2, 135.7, 150.1, 151.3; HRMS (CI) calcd for $C_{18}H_{24}NO$ [M$^+$ + H] 270.1858, found 270.1852. Anal. Calcd for $C_{18}H_{23}NO$: C, 80.26; H, 8.61; N, 5.21. Found: C, 80.36; H, 9.21; N, 5.07.

Coupling of 2-*tert*-Butylphenol with 4-Bromostyrene (Table 1, entry 8). Phosphinite ligand **3b** used. Column chromatography ($CHCl_3$/hexane, 1:4) gave **6h** (194 mg, 75%) and **7h** (18 mg, 5%, impure).

3-*tert*-Butyl-4′-vinyl-biphenyl-2-ol (6h). Colorless solid; R_f 0.58 ($CHCl_3$/hexane, 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9H), 5.33 (dd, J = 10.9, 0.8 Hz, 1H), 5.44 (d, J = 0.5 Hz, 1H), 5.83 (dd, J = 17.7, 0.8 Hz, 1H), 6.78 (dd, J = 17.7, 10.9 Hz, 1H), 6.93 (apparent t (dd), J = 7.7 Hz, 1H), 7.09 (dd, J = 7.5, 1.7 Hz, 1H), 7.31 (ddd, J = 7.8, 1.7, 0.5 Hz, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.6, 34.9, 114.6, 119.9, 126.6, 127.2, 127.9, 128.4, 129.7, 136.1, 136.2, 136.6, 137.2, 151.1; HRMS (CI) calcd for $C_{18}H_{21}O$ [M$^+$ + H] 253.1592, found 253.1583. Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.84; H 8.27.

3-*tert*-Butyl-4′,4″-divinyl-[1,1′;2′,1″]terphenyl-2-ol (7h). Colorless solid; R_f 0.32 ($CHCl_3$/hexane, 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 9H), 4.95 (d, J = 0.6 Hz, 1H), 5.20 (dd, J = 10.9, 0.9 Hz, 1H), 5.36 (dd, J = 10.9, 0.8 Hz, 1H), 5.69 (dd, J = 17.6, 0.9 Hz, 1H), 5.87 (dd, J = 17.6, 0.8 Hz, 1H), 6.64 (dd, J = 17.6, 10.9 Hz, 1H), 6.80 (apparent t (dd), J = 7.7 Hz, 1H), 6.81 (ddd, J = 17.6, 10.9, 0.3 Hz, 1H), 6.94 (dd, J =

7.5, 1.7 Hz, 1H), 7.10 (d, J = 8.2 Hz, 2H), 7.18 (ddd, J = 7.7, 1.7, 0.6 Hz, 1H), 7.24 (dd, J = 8.2, 0.5 Hz, 2H), 7.42 (ddd, J = 7.7, 0.5, 0.3 Hz, 1H), 7.52 (dd, J = 7.7, 1.8 Hz, 1H), 7.42 (ddd, J = 1.8, 0.5, 0.5 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.3, 34.6, 113.8, 115.0, 119.7, 125.8, 125.8, 126.2, 128.0, 128.4, 128.5, 129.0, 131.9, 134.7, 136.1, 136.1, 136.3, 136.4, 138.0, 139.6, 141.6, 150.9; HRMS (CI) calcd for $C_{26}H_{27}O$ [M^+ + H] 355.2062, found 355.2055.

Coupling of 2-*tert*-Butylphenol with 3-Bromoanisole (Table 1, entry 9). Phosphinite ligand **3b** used.

3-*tert*-Butyl-3′-methoxy-biphenyl-2-ol (6i). Colorless oil, 256 mg (100%); R_f 0.39 ($CHCl_3$/hexane, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 9H), 3.86 (s, 3H), 5.59 (d, J = 0.5 Hz, 1H), 6.94 (dd, J = 7.8, 7.5 Hz, 1H), 6.97 (ddd, J = 8.1, 2.6, 0.9 Hz, 1H), 6.99 (ddd, J = 2.6, 0.9, 0.8 Hz, 1H), 7.05 (ddd, J = 7.5, 1.5, 0.9 Hz, 1H), 7.11 (dd, J = 7.5, 1.7 Hz, 1H), 7.32 (ddd, J = 7.8, 1.7, 0.5 Hz, 1H), 7.43 (ddd, J = 8.1, 7.5, 0.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.6, 34.9, 55.3, 113.7, 114.9, 119.8, 121.5, 126.6, 127.7, 128.6, 130.5, 136.2, 138.6, 151.0, 160.4; HRMS (CI) calcd for $C_{17}H_{21}O_2$ [M^+ + H] 257.1541, found 257.1535. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.47; H, 8.19.

Coupling of 2-*tert*-Butylphenol with 2-Bromoanisole (Table 1, entry 10). Phosphinite ligand **3b** used.

3-*tert*-Butyl-2′-methoxy-biphenyl-2-ol (6j). Colorless oil, 256 mg (100%); R_f 0.40 ($CHCl_3$/hexane, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 (s, 9H), 3.90 (s, 3H), 6.16 (d, J = 0.5 Hz, 1H), 6.98 (apparent t (dd), J = 7.7 Hz, 1H), 7.07 (ddd, J = 8.2, 1.1, 0.3 Hz, 1H), 7.13 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 7.14 (dd, J = 7.5, 1.6 Hz, 1H), 7.36 (ddd, J = 7.5, 1.8, 0.3 Hz, 1H), 7.36 (ddd, J = 7.8, 1.6, 0.5 Hz, 1H), 7.42 (ddd, J = 8.2, 7.5, 1.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.7, 35.0, 56.0, 111.4, 120.1, 122.0, 126.5, 127.0, 127.1, 129.2, 129.3, 132.7, 137.4, 152.3, 155.7; HRMS (CI) calcd for $C_{17}H_{21}O_2$ [M^+ + H] 257.1541, found 257.1522. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.55; H, 8.23.

Coupling of 2-*tert*-Butylphenol with 2-Bromo-*p*-xylene (Table 1, entry 11). Phosphinite ligand **3b** used.

3-*tert*-Butyl-2′,5′-dimethyl-biphenyl-2-ol (6k). Colorless oil, 254 mg (100%); ($CHCl_3$/hexane, 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.49 (s, 9H), 2.15 (s, 3H), 2.40 (s, 3H), 5.02 (d, J_{HH} = 0.6 Hz, 1H), 6.94 (apparent t (dd), J = 7.5 Hz, 1H), 7.01 (dd, J = 7.4, 1.9 Hz, 1H), 7.14 (d, J = 1.9 Hz, 1H), 7.18 (dd, J = 7.7, 1.9 Hz, 1H), 7.27 (d, J = 7.7 Hz, 1H), 7.34 (ddd, J = 7.6, 1.9, 0.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 19.2, 20.9, 29.56, 34.5, 119.5, 126.2, 127.6, 128.4, 129.3, 130.6, 131.4, 134.4, 135.6, 135.8, 136.2, 151.0; HRMS (CI) calcd for $C_{18}H_{23}O$ [M^+ + H] 255.1749, found 255.1750 Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.69; H, 9.01.

Coupling of 2-*tert*-Butylphenol with 1-Bromonaphthalene (Table 1, entry 12). Phosphinite ligand **3b** used.

2-*tert*-Butyl-6-naphthalene-1-yl-phenol (6m). Light-sensitive, colorless oil, 255 mg (92%); R_f 0.51 ($CHCl_3$/hexane, 1:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (s, 9H), 5.01 (d, J = 0.6 Hz, 1H), 7.00 (dd, J = 7.8, 7.4 Hz, 1H), 7.13 (dd, J = 7.4, 1.7 Hz, 1H), 7.41 (ddd, J = 7.8, 1.7, 0.6 Hz, 1H), 7.47 (ddd, J = 8.2, 7.0, 1.4 Hz, 1H), 7.54 (dd, J = 6.9, 1.4 Hz, 1H), 7.55 (ddd, J = 8.0, 6.8, 1.4 Hz, 1H), 7.60 (dd, J = 8.2, 7.0 Hz), 1H, 7.66 (d, br, J = 8.2 Hz, 1H), 7.95 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 29.6, 34.9, 119.6, 125.2, 125.8, 126.4, 126.7, 126.7, 126.7, 128.4, 128.6, 128.8, 128.9, 132.1, 134.0, 134.1, 136.2, 151.7; HRMS (CI) calcd for $C_{22}H_{21}O$ [M^+ + H] 277.1592, found 277.1587. Anal. Calcd for $C_{22}H_{20}O$: C, 86.92; H 7.29. Found: C, 86.85; H 7.71.

Coupling of 2-*tert*-Butylphenol with 4-Chloroanisole (Table 1, entry 13). Phosphinite ligand **3b** used. Compound **6d**, 38 mg (15%). Data as above.

Coupling of 2-*tert*-Butylphenol with 4-Chlorobromobenzene (Table 1, entry 14). Phosphinite ligand **3b** used. Column chromatography ($CHCl_3$/hexane, 1:5) gave **6n** (68 mg, 26%) and **9** (22 mg, 6%, impure).

3-*tert*-Butyl-4′-chloro-biphenyl-2-ol (6n). Colorless solid; R_f 0.61 ($CHCl_3$/hexane, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9H), 5.27 (d, J = 0.5 Hz, 1H), 6.93 (apparent t (dd), J = 7.7 Hz, 1H), 7.05 (dd, J = 7.5, 1.7 Hz, 1H), 7.32 (ddd, J = 7.8, 1.7, 0.6 Hz, 1H), 7.40 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.6, 34.9, 120.1, 126.9, 127.6, 127.9, 129.6, 130.9, 134.1, 135.7, 136.4, 150.9; HRMS (CI) calcd for $C_{16}H_{18}ClO$ [M^+ ($^{37/35}$Cl) + H] 263.1038/261.1046, found 263.1038/261.1038. Anal. Calcd for $C_{16}H_{17}ClO$: C, 73.70; H, 6.57. Found: C, 73.79; H, 6.66.

3,3″-Di-*tert*-butyl-[1,1′;4′,1″]terphenyl-2,2″-diol (9). Colorless solid; R_f 0.23 ($CHCl_3$/hexane, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.46 (s, 18H), 5.44 (s, 2H), 6.96 (apparent t (dd), J = 7.7 Hz, 2H), 7.13 (dd, J = 7.5, 1.7 Hz, 2H), 7.32 (dd, J = 7.7, 1.7 Hz, 2H), 7.60 (s, 4H); ^{13}CNMR (75.5 MHz, $CDCl_3$) δ 29.6, 34.7, 120.1, 126.9, 128.0, 128.1, 130.6, 136.4, 137.0, 151.0; HRMS (CI) calcd for $C_{26}H_{31}O_2$ [M^+ + H] 375.2324, found 375.2309.

Coupling of 2-*tert*-Butylphenol with 2-Bromopyridine (Table 1, entry 15). Phosphinite ligand **3b** used.

2-*tert*-Butyl-6-pyridine-2-yl-phenol (6o). Sticky, pale yellow solid, 52 mg (23%); R_f 0.53 ($CHCl_3$/hexane, 1:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (s, 9H), 6.87 (apparent t (dd), J = 7.9 Hz, 1H), 7.22 (ddd, J = 7.4, 5.0, 1.1 Hz, 1H), 7.36 (dd, J = 7.7, 1.6 Hz, 1H), 7.70 (ddd, J = 8.0, 1.6, 0.4 Hz, 1H), 7.81 (ddd, J = 8.4, 7.4, 1.9 Hz, 1H), 7.92 (dddd, J = 8.4, 1.1, 1.0, 0.4 Hz, 1H), 8.39 (ddd, J = 5.0, 1.9, 1.0 Hz, 1H), 15.01 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.5, 35.0, 117.8, 118.6; 119.6, 121.1, 124.4, 128.6, 137.7, 138.4, 145.2, 158.5, 159.3; HRMS (CI) calcd for $C_{15}H_{18}NO$ [M^+ + H] 228.1388, found 228.1386.

Coupling of 2-*tert*-Butylphenol with 3-Bromopyridine (Table 1, entry 16). Phosphinite ligand **3b** used. Column chromatography (NEt_3/ethyl acetate/hexane, 1:4:5) gave **6p** (93 mg, 41%) and **7p** (33 mg, 11%, impure).

2-*tert*-Butyl-6-pyridine-3-yl-phenol (6p). Yellow solid; R_f 0.83 (NEt_3/ethyl acetate/hexane, 1:4:5; recrystallized from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 9H), 6.29 (s, br, 1H), 6.96 (apparent t (dd), J = 7.6 Hz, 1H), 7.03 (dd, J = 7.5, 1.9 Hz, 1H), 7.35 (ddd, J = 7.9, 4.9, 0.9 Hz, 1H), 7.36 (dd, J = 7.7, 1.9 Hz, 1H), 7.82 (ddd, J = 7.9, 2.3, 1.7 Hz, 1H), 8.43 (dd, J = 4.9, 1.9 Hz, 1H), 8.50 (dd, J = 2.3, 0.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.7, 35.0, 120.3, 123.6, 126.0, 127.4, 128.2, 134.2, 137.5, 137.6, 148.2, 150.0, 151.8; HRMS (CI) calcd for $C_{15}H_{18}NO$ [M^+ + H] 228.1388, found 228.1389. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.32; H, 7.76; N, 5.96.

2-[3,4′]-Bipyridinyl-3′-yl-6-*tert*-butyl-phenol (7p). Pale yellow oil; R_f 0.24 (NEt_3/ethyl acetate/hexane, 1:4:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 9H), 5.80 (d, br, 1H), 6.89 (apparent t (dd), J = 7.6 Hz, 1H), 6.97 (dd, J = 7.5, 1.7 Hz, 1H), 7.11 (ddd, J = 7.9, 4.9, 0.8 Hz, 1H), 7.25 (dd, J = 7.7, 1.7 Hz, 1H), 7.38 (dd, J = 5.0, 0.7 Hz, 1H), 7.39 (ddd, J = 7.9, 2.3, 1.6 Hz, 1H), 8.40 (dd, J = 2.3, 0.8 Hz, 1H), 8.45 (dd, J = 4.9, 1.6 Hz, 1H), 8.56 (m, br, 1H), 8.61 (m, br, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.3, 34.6, 120.5, 122.8, 123.9, 124.4, 127.4, 128.6, 133.8, 135.6, 137.4, 146.1, 149.0, 149.1, 149.6, 151.3, 151.9; HRMS (CI) calcd for $C_{20}H_{21}N_2O$ [M^+ + H] 305.1654, found 305.1646.

Coupling of 2-*tert*-Butylphenol with 3-Bromothiophene (Table 1, entry 17). Phosphinite ligand **3b** used. Column chromatography ($CHCl_3$/hexane, 1:4) gave **6q** (30 mg, 13%, impure), **7q** (108 mg, 34%), and **8q** (102 mg, 26%).

2-*tert*-Butyl-6-thiophene-3-yl-phenol (6q). Colorless oil; R_f 0.60 ($CHCl_3$/hexane, 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 5.62 (s, 1H), 6.90 (dd, J = 7.9, 7.5 Hz, 1H), 7.13 (dd, J = 7.5, 1.7 Hz, 1H), 7.21 (dd, J = 4.9, 1.3 Hz, 1H), 7.28 (dd, J = 7.9, 1.7 Hz, 1H), 7.42 (dd, J = 3.0, 1.3 Hz, 1H), 7.52 (dd, J = 4.9, 3.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.5, 34.9, 119.8, 123.3, 123.6, 126.6, 127.5, 127.7, 128.7, 136.2, 137.6, 151.4; HRMS (CI) calcd for $C_{14}H_{17}OS$ [M^+ + H] 233.1000, found 233.1009.

2-[2,3′]Bithiophenyl-3-yl-6-*tert*-butyl-phenol (7q). Yellow oil; R_f 0.49 ($CHCl_3$/hexane, 1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9H), 5.30 (s, 1H), 6.92 (dd, J = 7.8, 7.5 Hz, 1H), 6.97 (dd, J = 5.0, 1.4 Hz, 1H), 7.04 (d, J = 5.1 Hz, 1H), 7.07 (dd, J = 3.0, 1.4 Hz, 1H), 7.08 (dd, J = 7.5, 1.7 Hz, 1H), 7.20 (dd, J = 5.0, 3.0 Hz, 1H), 7.32 (dd, J = 7.8, 1.7 Hz, 1H), 7.35 (d, J = 5.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.5, 34.9, 120.0, 121.7, 123.6, 124.5, 125.8, 126.8, 126.8, 128.0, 131.3, 132.1, 133.6, 135.9, 136.3, 151.5; HRMS (CI) calcd for $C_{18}H_{19}OS_2$ [M^+ + H] 315.0877, found 315.0857. Anal. Calcd for $C_{18}H_{18}OS_2$: C, 68.75; H, 5.77. Found: C, 68.71; H 5.98.

2-*tert*-Butyl-6-[3,2′;4′,3″]terthiophene-3′-yl-phenol (8q). Yellow solid; R_f 0.33 ($CHCl_3$/hexane, 1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9H), 5.22 (d, J = 0.5 Hz, 1H), 6.80 (dd, J = 3.0, 1.3 Hz, 1H), 6.88 (apparent t (dd), J = 7.4 Hz, 1H), 6.93 (dd, J = 7.4, 2.0 Hz, 1H), 6.99 (dd, J = 5.0, 1.4 Hz, 1H), 7.00 (dd, J = 5.0, 1.3 Hz, 1H), 7.01 (dd, J = 3.0, 1.4 Hz, 1H), 7.18 (dd, J = 5.0, 3.0 Hz, 1H), 7.20 (dd, J = 5.0, 3.0 Hz, 1H), 7.35 (ddd, J = 7.4, 2.0, 0.5 Hz, 1H), 7.42 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.3, 34.7, 120.4, 120.7, 121.3, 121.8, 123.4, 125.0, 125.6, 126.9, 127.1, 127.2, 128.7, 130.2, 133.9, 135.9, 136.5, 138.2, 138.4, 152.2; HRMS (CI) calcd for $C_{22}H_{21}OS_3$ [M^+ + H] 397.0754, found 397.0727. Anal. Calcd for $C_{22}H_{20}OS_3$: C, 66.63; H, 5.08. Found: C, 66.82; H 4.96.

Coupling of 2-*tert*-Butylphenol with 3-Bromo-4-methylthiophene (Table 1, entry 18). Phosphinite ligand **3b** used. Column chromatography ($CHCl_3$/hexane, 1:4) gave **6r** (65 mg, 26%, impure) and **7r** (mixture with **6r**, ~8%).

2-*tert*-Butyl-6-(4-methyl-thiophene-3-yl)-phenol (6r). Colorless oil; R_f 0.59 ($CHCl_3$/hexane, 1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9H), 2.11 (dd, J = 1.0, 0.3 Hz, 3H), 5.28 (s, br, 1H), 6.90 (apparent t (dd); J = 7.7 Hz, 1H), 7.01 (dd, J = 7.5, 1.8 Hz, 1H), 7.15 (dq, J = 3.2, 1.0 Hz, 1H), 7.30 (dd, J = 3.2, 0.3 Hz, 1H), 7.31 (dd, J = 7.8, 1.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.6, 29.5, 34.8, 119.4, 123.0, 123.4, 125.1, 126.7, 128.1, 136.0, 137.3, 137.7, 151.8; HRMS (CI) calcd for $C_{15}H_{19}OS$ [M^+ + H] 247.1156, found 247.1154.

2-*tert*-Butyl-6-(4,4′-dimethyl-[2,3′]bithiophenyl-3-yl)-phenol (7r). Colorless oil; R_f 0.50 ($CHCl_3$/hexane, 1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.03 (dd, J = 1.1, 0.4 Hz, 3H), 2.10 (d, J = 1.0 Hz, 3H), 5.18 (d, J = 0.6 Hz, 1H), 6.80 (apparent t (dd), J = 7.5 Hz, 1H), 6.84 (dq, J = 3.3, 1.0 Hz, 1H), 6.86 (dd, J = 6.86, 2.0 Hz, 1H), 7.05 (dd, J = 3.3, 0.4 Hz, 1H), 7.12 (q, J = 1.1 Hz, 1H), (ddd, J = 7.5, 2.0, 0.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 15.3, 15.4, 29.3, 34.6, 119.6, 121.5, 121.5, 123.0, 125.4, 126.4, 128.5, 134.0, 134.8, 136.0, 136.4, 136.7, 138.1, 151.7; HRMS (CI) calcd for $C_{20}H_{23}OS_2$ [M^+ + H] 343.1190, found 343.1187.

Coupling of 2-Isopropylphenol with 4-Bromoanisole (Table 1, entry 19). Phosphinite ligand **3b** used.

3-Isopropyl-4′-methoxy-biphenyl-2-ol (6s). Colorless solid, 165/166 mg (68%); R_f 0.65 ($CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (d, J = 6.9 Hz, 6H), 3.37 (sept., J = 6.9 Hz, 1H), 3.88 (s, 3H), 5.30 (s, 1H), 6.97 (apparent t (dd), J = 7.6 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 7.07 (dd, J = 7.5, 1.7 Hz, 1H), 7.24 (dd, J = 7.7, 1.7 Hz, 1H), 7.41 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.6, 27.2, 55.3, 114.8, 120.3, 125.5, 127.5, 127.5, 129.4, 130.4, 134.8, 149.7, 159.3; HRMS (CI) calcd for $C_{16}H_{19}O_2$ [M^+ + H] 243.1380, found 243.1383. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.41; H, 7.72.

Coupling of 2-Ethylphenol with 4-Bromoanisole (Table 1, entry 20). Phosphinite ligand **3b** used.

3-Ethyl-4′-methoxy-biphenyl-2-ol (6t). Colorless solid, 121/176 mg (53%); R_f 0.56 ($CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, J = 7.5 Hz, 3H), 3.37 (q, J = 7.5 Hz, 2H), 3.87 (s, 3H), 5.25 (s, 1H), 6.92 (apparent t (dd), J = 7.5 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 7.07 (dd, J = 7.6, 1.6 Hz, 1H), 7.24 (dd, J = 7.4, 1.6 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 14.0, 23.4, 55.3, 114.7, 120.2, 127.4, 127.7, 128.4, 129.4, 130.4, 130.5, 150.3, 159.3; HRMS (CI) calcd for $C_{15}H_{17}O_2$ [M^+ + H] 229.1228, found 229.1223. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.01; H, 7.15.

Coupling of 2-Methylphenol with 4-Bromoanisole (Table 1, entry 21). Phosphinite ligand **3b** used. Column chromatography (MeOH/$CHCl_3$/hexane, 0.1:1:4) gave **6u** (21%). Compound **7u** observed in impure product mixture (~5% by ^1H NMR, not isolated; see below for data, Table 3, entry 12).

4′-Methoxy-3-methyl-biphenyl-2-ol (6u). Colorless solid; R_f 0.50 (MeOH/$CHCl_3$/hexane, 0.1:1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.87 (s, 3H), 5.25 (s, 1H), 6.89 (apparent t (dd), J = 7.4 Hz, 1H), 7.03 (d, J = 8.9 Hz, 2H), 7.06 (dd, J = 7.6, 1.7 Hz, 1H), 7.16 (dd, J = 7.3, 1.7 Hz, 1H), 7.39 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 16.2, 55.3, 114.7, 120.1, 124.4, 127.3, 127.7, 129.3, 130.1, 130.3, 150.6, 159.3; HRMS (CI) calcd for $C_{14}H_{15}O_2$ [M^+ + H] 215.1072, found 215.1087. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.56; H, 6.50.

Coupling of 2-Naphthol with 4-Bromoacetophenone (Table 1, entry 22). Phosphinite ligand **3c** used. Column chromatography ((MeOH/$CHCl_3$, 1:99) gave **6v** (102 mg, 39%) and **10v** (~1:1 mixture with **6v**, ~13%).

2-(4-Acetyl-phenyl)-naphthalene-1-ol (6v). Light-sensitive, colorless solid; R_f 0.33 (MeOH/$CHCl_3$, 1:99); ^1H NMR (300 MHz, $CDCl_3$) δ 2.67 (s, 3H), 5.83 (s, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.52 (d, br, J = 8.4 Hz,1H), 7.53 (m, 1H), 7.54 (m, 1H), 7.68 (d, J = 8.6 Hz, 2H), 7.54 (m, 1H), 8.12 (d, J = 8.6 Hz, 2H), 8.30 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.7, 120.2, 120.6 122.3, 124.4, 125.8, 126.9, 127.0, 127.6, 129.5, 129.5, 134.4, 136.2, 142.6, 147.9, 197.6; HRMS (CI) calcd for $C_{18}H_{15}O_2$ [M^+ + H] 263.1072, found 263.1067. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.50; H, 5.25.

2,8-Bis(4-acetyl-phenyl)-1-naphthalene-1-ol (10v). Light-sensitive, red substance; R_f 0.33 (MeOH/$CHCl_3$, 1:99); ^1H NMR (300 MHz, $CDCl_3$) δ 2.61 (s, 3H), 2.65 (s, 3H), 5.46 (s, 1H), 7.26 (dd, 1H, J = ~7, 1.2 Hz), 7.46 (d, 1H, J = 8.4 Hz), 7.52 (m, 1H), 7.60 (d, 2H, J = 8.6 Hz), 7.61 (d, 2H, $^3J_{HH}$ = 8.4 Hz), 7.62 (d, 2H, J = 8.7 Hz), 7.91 (dd, 1H, J = 8.4, 1.2 Hz), 8.01 (d, 2H, J = 8.7 Hz), 8.04 (d, 2H, J = 8.6 Hz); HRMS (CI) calcd for $C_{26}H_{20}O_3$ [M^+ + H] 381.1490, found 381.1477.

Competitive Coupling of 4-*tert*-Butylphenol with 4-Bromotoluene and 4-Bromo-*N*, *N*-dimethylaniline (eq 1). In a Radleys reaction tube under nitrogen were added [RhCl(PPh_3)$_3$] (46 mg, 0.05 mmol), toluene (10 mL), 4-bromotoluene (0.255 g, 1.5 mmol), 4-bromo-*N*,*N*-dimethylaniline (0.3000 g, 1.5 mmol), **3b** (0.037 g, 0.15 mmol), 2-*tert*-butylphenol (0.150 g, 1.0 mmol), and Cs_2CO_3 (0.550 g, 1.70 mmol). The mixture was heated at reflux temperature for 18 h and allowed to cool, and then HCl (aq) (2 M, 5 mL) was added. The organic phase was extracted with dichloromethane (3 × 25 mL), and a solution of 1,3,5-trimethoxybenzene (0.333 M in toluene, 1.00 mL, ^1H NMR standard) was added. The solution was dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. A sample in $CDCl_3$ was taken without further treatment from the crude reaction mixture, and the conversion to **6w** and **6f** was determined by ^1H NMR spectroscopy.

Effect of Varying Conditions and Ligands on the Ortho-Arylation Reaction (Table 2). In a Radleys reaction tube under nitrogen were added the appropriate amount of [{RhCl(COD)}$_2$], toluene (10 mL), the 4-bromoanisole (0.19 mL, 1.5 mmol), the appropriate amount of **3d**, the appropriate amount of phosphine co-ligand, 2-isoproylphenol (0.136 g, 1.0 mmol), and base (1.70 mmol). The mixture was heated at reflux temperature for 18 h and allowed to cool, and then HCl (aq) (2 M, 5 mL) was added. The organic phase was extracted with dichloromethane (3 × 25 mL), and a solution of 1,3,5-trimethoxybenzene (0.333 M in toluene, 1.00 mL, ^1H NMR standard) was added. The solution was dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. A sample in $CDCl_3$ was taken without further treatment from the crude reaction mixture, and the conversion to **6s** was determined by ^1H NMR spectroscopy.

General Method for Coupling of Phenol with 2-Bromoanisole with Varying Catalysts/Co-catalysts (Figure

1). In a Radleys reaction tube under nitrogen were added the rhodium precursor (either $[RhCl(PPh_3)_3]$ or $[\{RhCl(COD)\}_2]$ (5 mol % Rh), toluene (10 mL), phenol (0.094 g, 1.0 mmol), 4-bromoanisole (0.19 mL, 1.5 mmol), and the appropriate ligand (see Figure 1) (0.15 or 0.30 mmol). The mixture was heated at reflux temperature for 18 h and allowed to cool, and then HCl (aq) (2 M, 5 mL) was added. The organic phase was extracted with dichloromethane (3 × 25 mL), and a solution of 1,3,5-trimethoxybenzene (0.333 M in toluene, 1.00 mL, ^{1}H NMR standard) was added. The solution was dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. A sample in $CDCl_3$ was taken without further treatment from the crude reaction mixture, and the conversions to **11a** and **12** were determined by ^{1}H NMR spectroscopy. See below for data for these compounds.

Coupling of Phenol with 2-Bromo-*p*-xylene (eq 2). As above with $[RhCl(PPh_3)_3]$ (5 mol %) and phosphinite **3d** (15 mol %).

2,5,2″,5″-Tetramethyl-[1,1′;3′,1″]terphenyl-2′-ol (11b). Colorless oil, 103 mg (34%); R_f 0.54 ($CHCl_3$/hexane, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20 (s, 6H), 2.37 (s, 6H), 4.85 (s, 1H), 7.07 (m, 1H), 7.14 (m, br, 6H), 7.22 (m, br, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.8, 21.4, 120.0, 128.4, 128.8, 129.7, 130.1, 130.9, 133.9, 135.5, 136.6, 149.4; HRMS (CI) calcd for $C_{22}H_{23}O$ [M^+ + H] 303.1749, found 303.1740. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.28; H, 7.51.

General Catalytic Methodology for Arylation of Phenols without 2-Substitution and Related Reactions (Table 3). In a Radleys reaction tube under nitrogen were added the $[\{RhCl(COD)\}_2]$ (25 mg, 0.05 mmol), toluene (10 mL), the appropriate aryl halide (1.5 mmol), $P(NMe_2)_3$ (0.049 g, 0.30 mmol), the appropriate phenol (1.0 mmol), and Cs_2CO_3 (0.550 g, 1.70 mmol). The mixture was heated at reflux temperature for 18 h and allowed to cool, and HCl (aq) (2 M, 5 mL) was added. The organic phase was extracted with dichloromethane (3 × 25 mL), dried ($MgSO_4$), and filtered, and the solvent was removed under reduced pressure. The crude mixture was then subjected to column chromatography (silica).

Coupling of Phenol with 4-Bromoanisole (Table 3, entry 1). Column chromatography (MeOH/$CHCl_3$/hexane, 0.1:1:4) gave **11a** (94 mg, 31%) and **12** (~3%, impure, contains substantial amounts of **11a)**.

4,4″-Dimethoxy-[1,1′;3′,1″]terphenyl-2′-ol (11a). Colorless solid; R_f 0.23 (MeOH/$CHCl_3$/hexane, 0.1:1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.97 (s, 6H), 5.40 (s, 1H), 7.02 (d, J = 8.8 Hz, 4H), 7.04 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 7.4 Hz, 2H), 7.50 (d, J = 8.8 Hz, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.3, 114.2, 120.5, 128.3, 129.5, 129.8, 130.4, 149.4, 159.1; HRMS (CI) calcd for $C_{20}H_{19}O_3$ [M^+ + H] 307.1334, found 307.1338. Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.14; H, 5.74.

4,4″,4‴-Trimethoxy-[1,1′;3′,1″;2″,1‴]quaterphenyl-2′-ol (12). Colorless oil; R_f 0.10 (MeOH/$CHCl_3$/hexane, 0.1:1:4); ^{1}H NMR (300 MHz, $CDCl_3$) (some signals obscured by **11a** impurity) δ 3.77 (s, 3H), 3.83 (s, 3H), 3.89 (s, 3H), 5.01 (s, 1H), 6.77 (d, J = 8.8 Hz, 2H), 6.89 (apparent t (dd), J = 7.6 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 7.16 (dd, J = 7.5, 1.8 Hz, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.4 Hz, 1H); HRMS (CI) calcd for $C_{27}H_{25}O_4$ [M^+ + H] 413.1753, found 413.1741.

Coupling of Phenol with Bromomesitylene (Table 3, entry 2). 2,4,6,2″,4″,6″-Hexamethyl-[1,1′;3′,1″]terphenyl-2′-ol (11c). Colorless solid, 52 mg (16%); R_f 0.50 ($CHCl_3$/hexane, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (s, 12H), 2.34 (s, 6H), 4.55 (s, 1H), 6.99 (s, br, 4H), 7.04 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.2, 21.1, 120.6, 126.8, 128.4, 129.5, 133.2, 137.1, 137.4, 149.4; HRMS (CI) calcd for $C_{24}H_{27}O$ [M^+ + H] 331.2062, found 331.2054. Anal. Calcd for $C_{24}H_{26}O$: C, 87.23; H, 7.93. Found: C, 86.99; H, 8.01.

Coupling of 3-Methylphenol with 4-Bromoanisole (Table 3, entry 3). Column chromatography (MeOH/$CHCl_3$, 1:99) gave **6x** (32 mg, 15%, impure) and **11x** (76 mg, 24%).

4′-Methoxy-4-methyl-biphenyl-2-ol (6x). Colorless solid; R_f 0.42 (MeOH/$CHCl_3$, 1:99); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.86 (s, 3H), 5.13 (s, 1H), 6.79 (dd, J = 8.1, 1.6 Hz, 1H), 6.81 (d, J = 1.6 Hz, 1H), 7.01 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 8.1 Hz, 1H), 7.38 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.2, 55.3, 114.7, 116.2, 121.6, 124.9, 129.2, 130.0, 130.2, 139.0, 152.2, 159.1; HRMS (CI) calcd for $C_{14}H_{15}O_2$ [M^+ + H] 215.1072, found 215.1073.

4,4″-Dimethoxy-4′-methyl-[1,1′;3′,1″]terphenyl-2′-ol (11x). Colorless solid; R_f 0.64 (MeOH/$CHCl_3$, 1:99); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.84 (s, 3H), 3.87 (s, 3H), 5.02 (s, 1H), 6.91 (d, J = 7.7 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 7.7 Hz, 1H), 7.26 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.4, 55.3, 55.3, 113.9, 114.7, 121.9, 125.2, 127.5, 128.1, 129.1, 130.3, 130.4, 131.4, 136.7, 149.9, 158.7, 159.3; HRMS (CI) calcd for $C_{21}H_{21}O_3$ [M^+ + H] 321.1491, found 321.1484. Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.96; H, 6.35.

Coupling of 3-Methoxyphenol with 4-Bromoanisole (Table 3, entry 4). Column chromatography (MeOH/$CHCl_3$, 1:99) gave **6y** (156 mg, 68%) and **11y** (92 mg, 27%).

4,4′-Dimethoxy-biphenyl-2-ol (6y). Colorless solid; R_f 0.21 (MeOH/$CHCl_3$, 1:99); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.85 (s, 3H), 5.29 (s, 1H), 6.56 (d, J = 2.4 Hz, 1H), 6.56 (dd, J = 9.1, 2.4 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 9.1 Hz, 1H), 7.35 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.3, 55.3, 101.1, 106.8, 114.7, 120.5, 129.0, 130.2, 130.7, 153.4, 159.0, 160.2; HRMS (CI) calcd for $C_{14}H_{15}O_3$ [M^+ + H] 231.1021, found 231.1030. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.34; H, 6.10.

4,4′,4″-Trimethoxy-[1,1′;3′,1″]terphenyl-2′-ol (11y). Colorless solid; R_f 0.56 (MeOH/$CHCl_3$, 1:99); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 5.24 (s, 1H), 6.67 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.6 Hz, 1H), 7.36 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.2, 55.3, 55.8, 103.2, 113.9, 114.4, 116.9, 121.2, 124.6, 129.5, 130.2, 130.3, 132.0, 150.5, 156.7, 158.6, 159.2; HRMS (CI) calcd for $C_{21}H_{21}O_4$ [M^+ + H] 337.1440, found 337.1432. Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 75.20; H, 6.03.

Coupling of 3-*tert*-Butylphenol with 4-Bromoanisole (Table 3, entry 5). 4-*tert*-Butyl-4′-methoxy-biphenyl-2-ol (6z). Colorless solid, 100 mg (39%); R_f 0.54 (MeOH/$CHCl_3$, 1:99); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 9H), 3.86 (s, 3H), 5.15 (s, 1H), 7.01 (dd, J = 8.5, 1.9 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 1.9 Hz, 1H), 7.16 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 31.3, 34.6, 55.3, 112.8, 114.7, 117.8, 124.8, 129.2, 129.7, 130.2, 152.0, 152.5, 159.1; HRMS (CI) calcd for $C_{17}H_{21}O_2$ [M^+ + H] 257.1542, found 257.1540. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.48; H, 8.02.

Coupling of 2-Naphthol with 4-Bromoanisole (Table 3, entry 6). Column chromatography (MeOH/$CHCl_3$, 1:99) gave **6aa** (20 mg, 8%, impure) and **11aa** (102 mg, 29%).

3-(4-Methoxy-phenyl)-naphthalene-2-ol (6aa). Light-sensitive, colorless solid; R_f 0.31 (MeOH/$CHCl_3$, 1:99); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.89 (s, 3H), 5.32 (s, 1H), 7.06 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 0.6 Hz, 1H), 7.35 (m, 1H), 7.43 (m, 1H), 7.50 (d, J = 8.9 Hz, 2H), 7.71 (d, J = 0.6 Hz, 1H), 7.73 (m, 1H), 7.78 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.4, 110.0, 114.6, 123.8, 126.2, 126.3, 127.6, 128.8, 128.8, 129.3, 130.1, 130.5, 134.1, 150.9, 159.5; HRMS (CI) calcd for $C_{17}H_{15}O_2$ [M^+ + H] 251.1072, found 251.1073.

1,3-Bis(4-methoxy-phenyl)-naphthalene-2-ol (11aa). Light-sensitive, colorless solid; R_f 0.50 (MeOH/$CHCl_3$, 1:99); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3H), 3.92 (s, 3H), 5.36 (s, 1H), 7.03 (d, J = 8.9 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 7.38 (m, 3H), 7.40 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H), 7.80 (s, 1H), 7.82 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.3, 55.3, 113.9, 114.9, 121.3, 123.5, 124.6, 126.1, 126.3, 127.9, 128.8, 129.1, 129.8, 130.2, 130.7, 132.4, 133.0, 148.0, 159.1, 159.5; HRMS (CI) calcd for $C_{24}H_{21}O_3$ [M^+ + H] 357.1490, found

357.1490. Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 81.08; H, 5.53.

Coupling of 2-Phenylphenol with 4-Bromoanisole (Table 3, entry 7). 4-Methoxy-[1,1′;3′,1″]terphenyl-2′-ol (6ab). Colorless solid, 147 mg (53%); R_f 0.57 ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.87 (s, 3H), 5.40 (s, 1H), 7.02 (d, J = 8.4 Hz, 2H), 7.05 (apparent t (dd), J = 7.5 Hz, 1H), 7.26 (d, J = 7.5 Hz, 2H), 7.39 (m, 1H), 7.47 (m, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.57 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.3, 114.3, 120.6, 127.6, 128.4, 128.6, 128.8, 129.3, 129.6, 129.6, 129.9, 130.5, 137.6, 149.3, 159.1; HRMS (CI) calcd for $C_{19}H_{17}O_2$ [M^+ + H] 1229, found 277.1222. Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.90; H, 5.76.

Coupling of 2-Methoxyphenol with 4-Bromoanisole (Table 3, entry 8). 3,4′-Dimethoxy-biphenyl-2-ol (6ac). Colorless solid, 164 mg (71%); R_f 0.30 ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.94 (s, 3H), 5.88 (s, 1H), 6.86 (dd, J = 7.7, 2.0 Hz, 1H), 6.92 (apparent t (dd), J = 7.7 Hz, 1H), 7.16 (dd, J = 7.7, 2.0 Hz, 1H), 6.99 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.1, 55.2, 109.2, 113.6, 119.6, 122.5, 127.3, 130.0, 130.2, 142.6, 146.8, 158.7; HRMS (CI) calcd for $C_{14}H_{15}O_3$ [M^+ + H] 231.1021, found 231.1016. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.20; H, 6.13.

Coupling of 1-Naphthol with 4-Bromoanisole (Table 3, entry 9). Column chromatography ($CHCl_3$) gave **6ad** (96 mg, 38%) and **10ad** (11 mg, 3%, impure).

2-(4-Methoxy-phenyl)-naphthalene-1-ol (6ad). Light-sensitive, colorless solid; R_f 0.55 ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.89 (s, 3H), 5.86 (s, 1H), 7.08 (d, 2H, J = 8.9 Hz), 7.34 (d, 1H, J = 8.4 Hz), 7.47 (d, 2H, J = 8.9 Hz), 7.49 (m, 3H), 7.83 (m, 1H), 8.32 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.3, 115.0, 120.0, 120.9, 122.3, 124.2, 125.4, 126.2, 127.4, 127.7, 129.3, 130.5, 133.9, 147.7, 159.2; HRMS (CI) calcd for $C_{17}H_{15}O_2$ [M^+ + H] 251.1072, found 251.1070. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.58; H, 5.47.

2,8-Bis(4-methoxy-phenyl)-naphthalene-1-ol (10ad). Light-sensitive, pale yellow oil; R_f 0.55 ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 3.86 (s, 3H), 5.95 (s, 1H), 6.95 (d, 2H, J = 8.9 Hz), 7.00 (d, 2H, J = 8.8 Hz), 7.21 (dd, 1H, J = 7.0, 1.4 Hz), 7.43 (dd, 1H, J = 8.2, 7.0 Hz), 7.44 (d, 2H, J = 8.8 Hz), 7.45 (d, 1H, J = 8.4 Hz), 7.48 (d, 2H, J = 8.9 Hz), 7.54 (d, 1H, J = 8.4 Hz), 7.84 (dd, 1H, J = 8.2, 1.4 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.3, 55.4, 113.7, 114.1, 120.6, 121.7, 123.6, 124.8, 128.4, 129.0, 129.4, 130.7, 130.8, 131.0, 133.5, 134.9, 136.4, 149.3, 158.5, 158.6; HRMS (CI) calcd for $C_{24}H_{21}O_3$ [M^+ + H] 357.1490, found 357.1491.

Coupling of 2-Isopropylphenol with 4-Bromoanisole (Table 3, entry 10). Compound **6s**, 166 mg, (69%). Data as above.

Coupling of 2-Ethylphenol with 4-Bromoanisole (Table 3, entry 11). Compound **6t**, 176 mg (77%). Data as above.

Coupling of 2-Methylphenol with 4-Bromoanisole (Table 3, entry 12). Column chromatography (MeOH/$CHCl_3$/hexane, 0.1:1:4);) gave **6u** (60 mg, 28%) and **7u** (73 mg, 34%, impure). Data for **6u** as above.

3-*tert*-Butyl-4′,4″-dimethoxy-[1,1′;2′,1″]terphenyl-2-ol (7u). Colorless oil; R_f 0.07 (MeOH/$CHCl_3$/hexane, 0.1:1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (s, 3H), 3.76 (s, 3H), 3.89 (s, 3H), 4.89 (s, 1H), 6.73 (dd, J = 7.8, 7.2 Hz, 1H), 6.75 (d, J = 8.7 Hz, 2H), 6.84 (dd, J = 7.8, 1.5 Hz, 1H), 6.97 (dd, J = 8.4, 2.6 Hz, 1H), 7.01 (m, 1H), 7.03 (d, J = 2.6 Hz, 1H), 7.10 (d, J = 8.7 Hz, 2H), 7.38 (d, 1H, J = 8.4 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 16.2, 55.1, 55.4, 113.2, 113.4, 115.9, 119.8, 124.2, 127.0, 127.2, 128.8, 129.9, 130.1, 132.6, 132.7, 142.6, 150.8, 158.7, 159.6; HRMS (CI) calcd for $C_{21}H_{21}O_3$ [M^+ + H] 321.1490, found 321.1489.

Coupling of 2-*tert*-Butylphenol with 4-Bromoanisole (Table 3, entry 13). Compound **6d**, 75 mg (29%). Data as above.

Coupling of 2-Isopropyl Phenol with 2-Bromo-*p*-xylene (Table 3, entry 14). 3-Isopropyl-2′,5′-dimethyl-biphenyl-2-ol (6ae). Colorless oil, 64 mg (27%); R_f 0.44 ($CHCl_3$/hexane, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (d, 6H, J = 6.9 Hz), 2.12 (s, 3H), 2.25 (s, 3H), 3.33 (sept., 1H, J = 6.9 Hz), 4.82 (s, 1H), 6.92 (m, 2H), 7.08 (d, br, 1H, J = 1,9 Hz), 7.14 (dd, br, 1H, J = 8.1, 1.9 Hz), 7.22 (dd, 1H, J = 7.7, 1.8 Hz), 7.28 (d, br, 1H, J = 8.1 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.2, 20.9, 22.5, 22.6, 27.2, 120.0, 125.6, 127.2, 127.4, 129.2, 130.6, 131.2, 134.2, 134.6, 135.8, 136.1, 149.6; HRMS (CI) calcd for $C_{17}H_{21}O$ [M^+ + H] 241.1592, found 241.1605. Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.47; H, 8.58.

Acknowledgment. We thank the EPSRC for funding (PDRA for M.E.L.).

Supporting Information Available: General experimental section and ^{1}H and ^{13}C NMR spectra of the coupled products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO030157K