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Efficient Synthesis of Sterically Crowded Biaryls by Palladium-Phosphinous Acid-Catalyzed Cross-Coupling of Aryl Halides and Aryl Grignards

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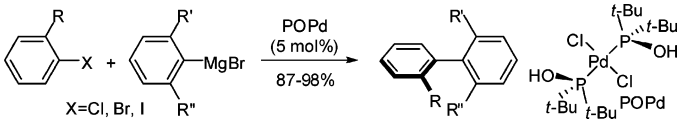
Received August 28, 2007



A series of sterically hindered biaryls have been obtained by palladium- and nickel-phosphinous acid-catalyzed Kumada−Corriu cross-coupling of *ortho*-substituted aryl halides and Grignard reagents. This method allows formation of di- and tri-*ortho*-substituted biaryls in 87−98% yield under mild reaction conditions even when electron-rich aryl chlorides are used. The reaction also proceeds with aryl iodides at −20 °C, and under these conditions, functional groups that are generally not compatible with Grignard reagents are tolerated.

Introduction

The biaryl motif is a ubiquitous building block that determines the properties and applications of many natural products,[1] pharmaceuticals,[2] catalysts,[3] and sensors.[4] It has been established that the dihedral angle between the aryl planes and the barrier to rotation about the pivotal bond of biaryls mainly depend on the number and size of *ortho* substituents, while buttressing effects and electronic contributions from *meta* and *para* substituents, respectively, play a minor role.[5] The synthesis of sterically crowded biaryls by transition-metal-catalyzed cross-coupling is quite challenging because strong repulsion between *ortho* substituents impedes formation of the incipient aryl−aryl bond.[6] Nevertheless, a wide range of congested biaryls has been prepared from aryl halides and boronic acids,[7] stannanes,[8] or organozinc compounds.[9]

Following Kharasch's seminal work on cobalt(II)-catalyzed reactions with organomagnesium compounds,[10] Kumada and Corriu independently reported in 1972 the first cross-coupling of aryl halides and aryl Grignards.[11] Despite these early

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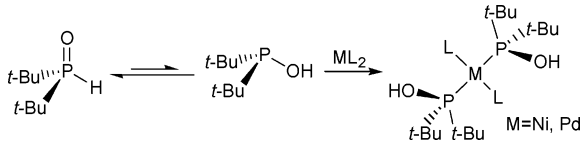
10.1021/jo701893m CCC: $40.75
Published on Web 12/06/2007

discoveries, Suzuki, Stille, and Negishi reactions have been studied in much more detail and gained considerably more popularity due to the inherently superior functional group tolerance. A remaining drawback of these methods is the limited reactivity of aryl boronic acids, stannanes, and zinc compounds which are usually prepared from Grignard or organolithium precursors. The direct use of Grignard reagents therefore remains an attractive alternative that eliminates an unnecessary synthetic step. Since Knochel et al. introduced elegant synthetic entries to organomagnesium compounds which tolerate the presence of ester, nitrile, nitro, and other functional groups at 25 °C or under cryogenic conditions,[12] the Kumada−Corriu reaction has received increasing attention.[13] However, many procedures require high temperatures, and transition-metal-catalyzed coupling of sterically hindered aryl chlorides or bromides with *ortho*-substituted aryl Grignard reagents has not been reported.[14]

Results and Discussion

We and others have introduced palladium-phosphinous acids to Suzuki, Stille, Hiyama, Sonogashira, and other cross-coupling reactions.[15] This class of catalysts enjoys several synthetic applications, and it is stable to air and water, which facilitates operation and catalyst handling and storage (Scheme 1).[16] Since Li demonstrated the feasibility of Kumada−Corriu coupling with

SCHEME 1. Formation of $(t\text{-Bu}_2\text{POH})_2\text{ML}_2$



sterically unhindered aryl chlorides,[17] we decided to explore the possibility of nickel- and palladium-phosphinous acid-catalyzed formation of biaryls exhibiting at least two *ortho* substituents from readily available aryl Grignard reagents. In particular, the development of a mild coupling method that utilizes unactivated, sterically hindered aryl bromides and chlorides would be very useful.

On the basis of our experience with palladium-phosphinous acid-catalyzed Suzuki, Stille, and Hiyama reactions and because of the high nucleophilicity of organomagnesium compounds, we anticipated that transmetalation might readily occur at room temperature while oxidative addition would be the rate-limiting step. We therefore focused our initial efforts on the cross-coupling of Grignard reagents with aryl bromides which are more reactive than chlorides. The effects of palladium precatalyst, ligand, and solvent on the reaction between 2-bromo-1-isopropylbenzene, **1**, and 2-tolylmagnesium bromide, **2**, were systematically examined. Using 5 mol % of a nickel-phosphinous acid prepared in situ from equimolar amounts of $Ni(cod)_2$ and di-*tert*-butylphosphine oxide in tetrahydrofuran, we found that biphenyl **3** can be prepared in 89% yield at room temperature within 15 h. Further studies revealed that 3 mol % of $Pd_2(dba)_3$ provides slightly better results (Table 1, entries 1, 2, and 7−9). We then used this catalyst to evaluate the scope of the reaction. As shown in Table 1, a wide range of sterically hindered biaryls was prepared in up to 96% yield with this procedure.[18]

When we employed aryl chlorides in the Kumada−Corriu reaction, we realized that heating to 50 °C is necessary when the nickel precatalyst is used while the palladium-phosphinous acid affords much better results at room temperature (Table 2, entries 1, 2, 4, and 9). The same yields were obtained by in situ formation of the palladium-phosphinous acid from $Pd_2(dba)_3$ and di-*tert*-butylphosphine oxide and by direct use of POPd which can be conveniently stored at room temperature and under air. This method provides di- and tri-*ortho*-substituted biaryls in excellent yields even when electron-rich chlorides, which are generally reluctant to oxidative addition under mild conditions, are used. For example, coupling of 1-chloro-2-methoxybenzene, **29**, with 2-isopropylphenylmagnesium bromide, **30**, or di-*ortho*-substituted aryl Grignards **13**, **27**, and **38** gave biaryls **31**, **35**, **37**, and **40**, respectively, in 89−93% yield (entries 1, 5, 7, and 10). To the best of our knowledge, the cross-coupling of *ortho*-substituted aryl chlorides with sterically hindered Grignard reagents is unprecedented.

As expected, our POPd-catalyzed coupling procedure is also suitable to aryl iodides. We obtained biaryls **5** and **28** in 90−96% yield from 1-iodonaphthalene, **42**, and Grignards **27** and **30**, even when the temperature was lowered to −20 °C (Scheme 2). Under these conditions, the presence of an ester group is well tolerated. Coupling of **30** and methyl 4-bromo-3-methyl

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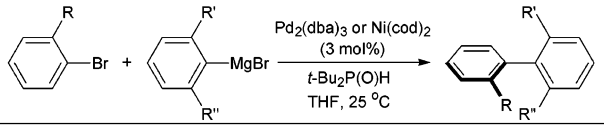
(18) During the preparation of this paper, a Pd-catalyzed Kumada−Corriu coupling providing a 2,2′,6-trimethylbiphenyl derivative in 93% yield from an aryl iodide was reported; see ref 14k.

TABLE 1. Kumada−Corriu Coupling of Aryl Bromides with Palladium- and Nickel-Derived Phosphinous Acids[a]



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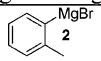
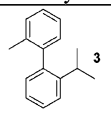
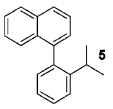
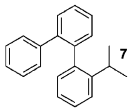
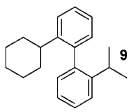
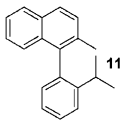
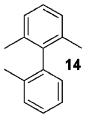
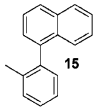
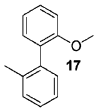
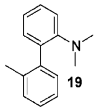
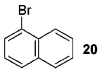
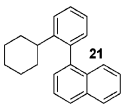
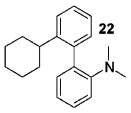
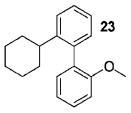
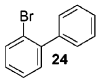
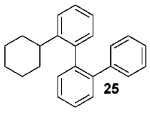
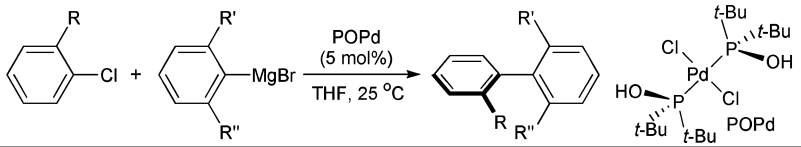
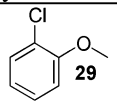
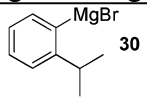
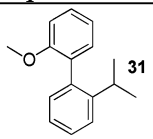
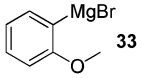
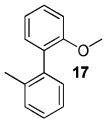
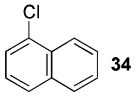
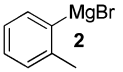
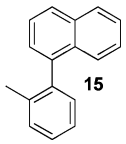
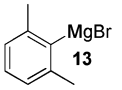
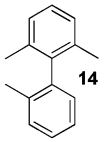
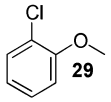
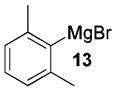
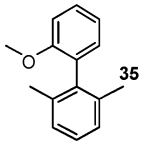
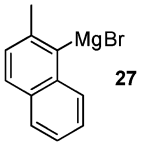
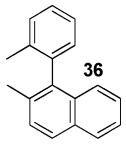
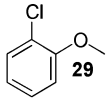
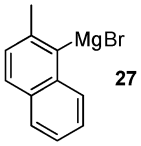
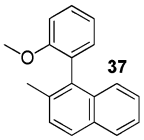
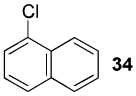
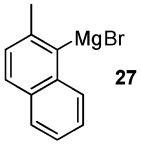
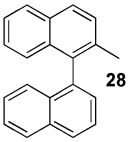
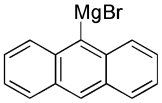
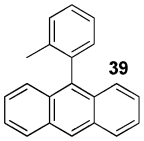
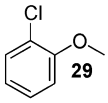
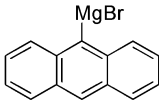
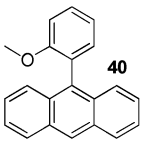
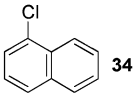
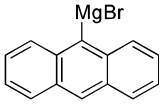
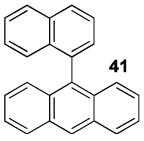
1				90, 89[c]
2				90, 88[c]
3				94
4				95
5				92
6				89
7				96, 90[c]
8				89, 90[c]
9				83, 83[c]
10				94
11				94
12				93
13				96
14				92

[a] Reaction conditions: aryl bromide (1.0 mmol), $Pd_2(dba)_3$ (3 mol %), di(*tert*-butyl)phosphine oxide (6 mol %), arylmagnesium bromide (2.0 mmol) in THF (2.0 M), 25 °C, 15 h. [b] Isolated yields. [c] $Ni(cod)_2$ (5 mol %), di(*tert*-butyl)phosphine oxide (5 mol %).

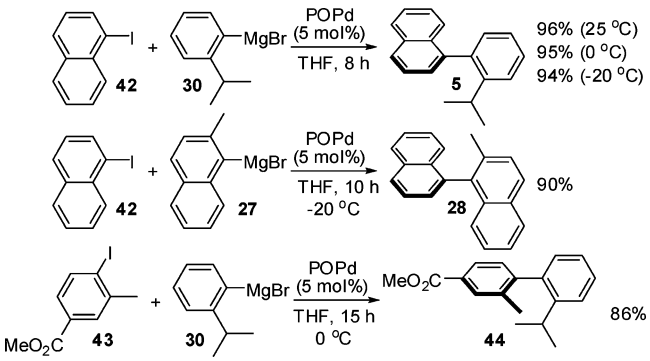
TABLE 2. Cross-Coupling of Aryl Chlorides with Grignard Reagents[a]



entry	aryl chloride	Grignard reagent	product	yield (%)[b]
1				91, 83[d]
2				98, 76[d]
3				85
4				90[c] ,81[d]
5				93[c]
6				89[c]
7				91[c]
8				92
9				90[c], 65[d]
10				89[c]
11				85[c]

[a] Reaction conditions: aryl chloride (1.0 mmol), POPd (5 mol %), arylmagnesium bromide (2.0 mmol) in THF (2.0 M), 25 °C, 15 h. [b] Isolated yields. [c] 24 h. [d] $Ni(cod)_2$ (5 mol %), di(*tert*-butyl)phosphine oxide (5 mol %), 50 °C, 24 h.

SCHEME 2. POPd-Catalyzed Kumada−Corriu Coupling Using Aryl Iodides



benzoate, **43**, gave ester **44** in 86% yield. Our method thus extends the scope of this reaction to sterically hindered substrates bearing functional groups that are usually not compatible with organomagnesium reagents.

Conclusion

In summary, we have developed a broadly applicable palladium-catalyzed Kumada−Corriu cross-coupling method that utilizes sterically hindered substrates under mild reaction conditions. Our procedure furnishes di- and tri-*ortho*-substituted biaryls in 87−98% yield and is suited for a range of aryl halides, including electron-rich aryl chlorides. The reaction proceeds with aryl iodides at −20 °C, and under these conditions, functional groups that are generally not compatible with Grignard reagents are tolerated. The POPd-catalyzed Kumada−Corriu reaction provides efficient access to sterically congested multifunctional biaryls and eliminates the need for conversion of intermediate aryl Grignard reagents to the corresponding boronic acids or stannanes prior to the cross-coupling step.

Experimental Section

All chemicals used were of reagent grade, and reactions were carried out under nitrogen. Flash chromatography was performed on Kieselgel 60, particle size 0.032−0.063 mm. NMR spectra were obtained at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR) using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million relative to TMS.

General Procedure for the Palladium-Phosphinous Acid-Catalyzed Cross-Coupling of Aryl Halides and Aryl Grignard Reagents. A solution of $Pd_2(dba)_3$ (0.03 mmol) and di(*tert*-butyl)-phosphine oxide (0.06 mmol) in anhydrous tetrahydrofuran (1.0 mL) was stirred under nitrogen for 4 h. Then, a solution of the aryl halide (1.00 mmol) in anhydrous tetrahydrofuran (1.0 mL) was added, and the mixture was stirred for another 15 min. This was followed by dropwise addition of the aryl Grignard reagent (2.00 mmol, ∼2 M, prepared prior to use from another aryl halide (2.0 mmol) and magnesium (3.0 mmol) in anhydrous tetrahydrofuran) at room temperature. The mixture was stirred at 25 °C for 15 h, quenched with water, extracted with diethyl ether, and dried over anhydrous $MgSO_4$. The solvents were removed under vacuum, and the crude product was purified by flash chromatography on silica gel.

2-Isopropyl-2′-methylbiphenyl, 3. Purification by flash chromatography (hexanes) gave 0.90 mmol of a colorless oil (90% from bromide): ^{1}H NMR δ 1.07 (d, J = 6.8 Hz, 3H), 1.14 (d, J = 6.8 Hz, 3H), 2.05 (s, 3H), 2.69 (sept, J = 6.8 Hz, 1H), 7.04−7.40 (m, 8H); ^{13}C NMR δ 20.2, 23.2, 24.7, 29.8, 125.3, 125.5, 127.1, 127.6, 129.3, 129.4, 129.6, 129.7, 136.0, 140.3, 141.5, 146.5. Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 90.95; H, 8.41.

1-(2-Isopropylphenyl)naphthalene, 5. Purification by flash chromatography (hexanes) gave 0.90 mmol of a colorless oil (90% from bromide): ^{1}H NMR δ 1.03 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 6.8 Hz, 3H), 2.64 (sept, J = 6.8 Hz, 1H), 7.17−7.50 (m, 9H), 7.82−7.88 (m, 2H); ^{13}C NMR δ 24.1, 25.5, 30.7, 125.9, 126.0, 126.1, 126.4, 126.5, 127.0, 127.5, 128.0, 128.7, 128.8, 131.2, 133.4, 134.1, 139.7, 140.4, 148.3. Anal. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.60; H, 7.23.

2-Isopropyl-2′-phenylbiphenyl, 7. Purification by flash chromatography (hexanes) gave 0.94 mmol of colorless crystals (94% from bromide): ^{1}H NMR δ 0.64 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H), 2.66 (sept, J = 6.8 Hz, 1H), 7.06−7.46 (m, 13H); ^{13}C NMR δ 22.4, 25.6, 30.0, 125.3, 125.5, 126.7, 127.3, 127.8, 127.9, 128.0, 130.0, 131.1, 140.3, 140.6 141.3, 141.6, 146.7. Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.24; H, 7.35.

2-Cyclohexyl-2′-isopropylbiphenyl, 9. Purification by flash chromatography (hexanes) gave 0.95 mmol of a colorless oil (95% from bromide): ^{1}H NMR δ 0.86−1.34 (m, 8H), 1.46−1.74 (m, 8H), 2.29 (m, 1H), 2.70 (sept, J = 6.8 Hz, 1H), 7.03−7.38 (m, 8H); ^{13}C NMR δ 23.8, 25.4, 26.8, 27.4, 30.5, 34.1, 36.0, 41.2, 125.7, 125.8, 126.5, 126.6, 128.0, 128.2, 130.3, 130.4, 140.8, 141.1, 146.4, 147.3. Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.51; H, 9.11.

1-(2-Isopropylphenyl)-2-methylnaphthalene, 11. Purification by flash chromatography (hexanes) gave 0.92 mmol of a colorless oil (92% from bromide): ^{1}H NMR δ 0.95 (d, J = 6.8 Hz, 3H), 1.06 (d, J = 6.8 Hz, 3H), 2.15 (s, 3H), 2.47 (sept, J = 6.8 Hz, 1H), 7.04 (dd, J = 7.6, 1.5 Hz, 1H), 7.20−7.41 (m, 6H), 7.45 (dd, J = 7.8, 1.5 Hz, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ 21.4, 24.6, 25.0, 30.8, 125.4, 126.3, 126.4, 126.9, 127.8, 128.4, 128.6, 128.7, 129.2, 130.8, 132.6, 133.9, 134.0, 138.2, 138.5, 148.2. Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.84; H, 7.41.

2,2′,6-Trimethylbiphenyl, 14.[19] Purification by flash chromatography (hexanes) gave 0.89 mmol of a colorless oil (89% from bromide): ^{1}H NMR δ 1.94 (s, 6H), 1.96 (s, 3H), 7.00−7.27 (m, 7H); ^{13}C NMR δ 20.1, 21.0, 126.7, 127.6, 127.7, 127.9, 129.5, 130.6, 136.2, 136.5, 141.2, 141.7.

1-(2-Tolyl)naphthalene, **15.**[20] Purification by flash chromatography (hexanes) gave 0.96 mmol of colorless crystals (96% from bromide): ^{1}H NMR δ 2.00 (s, 3H), 7.21−7.36 (m, 6H), 7.41−7.51 (m, 3H), 7.83 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H); ^{13}C NMR δ 20.7, 126.0, 126.2, 126.4, 126.6, 126.8, 127.3, 128.1, 128.2, 128.9, 130.5, 131.0, 132.7, 134.2, 137.4, 140.4, 140.9.

2-Methoxy-2′-methylbiphenyl, 17.[21] Purification by flash chromatography (hexanes/CH_2Cl_2 10:1) gave 0.89 mmol of a colorless oil (89% from bromide): ^{1}H NMR δ 2.13 (s, 3H), 3.70 (s, 3H), 6.90−7.33 (m, 8H); ^{13}C NMR δ 20.3, 55.7, 111.1, 120.9, 125.9, 127.7, 129.0, 130.0, 130.4, 131.3, 131.4, 137.2, 139.1, 157.0.

2-Dimethylamino-2′-methylbiphenyl, 19.[22] Purification by flash chromatography (hexanes/CH_2Cl_2 9:1) gave 0.83 mmol of a colorless oil (83% from bromide): ^{1}H NMR δ 2.15 (s, 3H), 2.50 (s, 6H), 6.95−7.30 (m, 8H); ^{13}C NMR δ 20.6, 43.8, 118.1, 121.7, 126.3, 127.4, 128.6, 130.6, 130.7, 132.4, 135.2, 136.8, 142.4, 152.2.

1-(2-Cyclohexylphenyl)naphthalene, 21. Purification by flash chromatography (hexanes) gave 0.94 mmol of a colorless oil (94% from bromide): ^{1}H NMR δ 0.78−1.75 (m, 10H), 2.25 (m, 1H), 7.06−7.41 (m, 7H), 7.45 (t, J = 8.8 Hz, 2H), 7.82 (t, J = 8.8 Hz, 2H); ^{13}C NMR δ 26.7, 27.3, 34.3, 36.0, 41.3, 125.8, 125.9, 126.3, 126.4, 126.8, 127.0, 127.4, 128.0, 128.5, 128.7, 131.2, 133.4, 134.1, 139.8, 140.3, 147.3. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 91.80; H, 7.83.

(19) Ohta, H.; Tokunaga, M.; Obora, Y.; Iwai, T.; Iwasawa, T.; Fujihara, T.; Tsuji, Y. *Org. Lett.* **2007**, *9*, 89−92.
(20) Navarro, O.; Marion, N.; Oonishi, Y.; Kelly, R. A.; Nolan, S. P. *J. Org. Chem.* **2006**, *71*, 685−692.
(21) Dhudshia, B.; Thadani, A. N. *Chem. Commun.* **2006**, 668−670.
(22) Sugasawa, S.; Matsuo, H. *Chem. Pharm. Bull.* **1958**, *6*, 601−607.

2-Cyclohexyl-2′-dimethylaminobiphenyl, 22. Purification by flash chromatography (hexanes/CH_2Cl_2 9:1) gave 0.94 mmol of a colorless oil (94% from bromide): ^{1}H NMR δ 0.83−1.65 (m, 10H), 1.79 (m, 1H), 2.47 (s, 6H), 6.94−7.34 (m, 8H); ^{13}C NMR δ 27.0, 27.7, 34.0, 36.2, 41.4, 43.8, 118.1, 121.8, 126.1, 127.0, 127.7, 128.5, 130.8, 132.6, 135.6, 141.2, 146.4, 152.2. Anal. Calcd for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01. Found: C, 85.71; H, 8.52; N, 4.94.

2-Cyclohexyl-2′-methoxybiphenyl, 23. Purification by flash chromatography (hexanes/CH_2Cl_2 10:1) gave 0.93 mmol of a colorless oil (93% from bromide): ^{1}H NMR δ 1.04−1.87 (m, 10H), 2.36 (m, 1H), 3.68 (s, 3H), 6.90−7.35 (m, 8H); ^{13}C NMR δ 26.9, 27.6, 34.3, 35.6, 41.5, 55.8, 111.0, 121.0, 125.9, 126.4, 128.2, 129.0, 130.8, 131.5, 131.9, 138.2, 147.0, 157.3. Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.75; H, 8.06.

2-Cyclohexyl-2′-phenylbiphenyl, 25. Purification by flash chromatography (hexanes) gave 0.96 mmol of colorless crystals (96% from bromide): ^{1}H NMR δ 0.56 (m, 1H), 0.92−1.23 (m, 5H), 1.43−1.57 (m, 4H), 2.22 (m, 1H), 7.06−7.45 (m, 13H); ^{13}C NMR δ 26.8, 27.6, 32.8, 36.2, 41.1, 125.7, 126.6, 127.1, 127.7, 128.0, 128.1, 128.3, 130.3, 130.4, 131.5, 131.7, 140.9, 150.0, 141.6, 142.0, 146.0. Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 91.98; H, 7.52.

2-Methyl-1,1′-binaphthyl, 28.[23] Purification by flash chromatography (hexanes) gave 0.92 mmol of colorless crystals (92% from bromide): ^{1}H NMR δ 2.07 (s, 3H), 7.06−7.56 (m, 9H), 7.80−7.89 (m, 4H); ^{13}C NMR δ 21.2, 125.5, 126.0, 126.3, 126.5, 126.6, 126.7, 126.8, 126.9, 128.2, 128.3, 128.4, 128.9, 129.3, 132.6, 133.2, 134.1, 134.4, 135.0, 136.7, 138.2.

2-Isopropyl-2′-methoxybiphenyl, 31.[24] Purification by flash chromatography (hexanes/CH_2Cl_2 10:1) gave 0.91 mmol of a colorless oil (91% from chloride): ^{1}H NMR δ 1.04 (d, J = 6.8 Hz, 3H), 1.19 (d, J = 6.8 Hz, 3H), 2.77 (sept, J = 6.8 Hz, 1H), 3.69 (s, 3H), 6.93 (d, J = 8.3 Hz, 1H), 6.98 (ddd, J = 7.3, 7.3, 1.0 Hz, 1H), 7.10−7.15 (m, 2H), 7.19 (ddd, J = 7.6, 7.6, 2.2 Hz, 1H), 7.29−7.38 (m, 3H); ^{13}C NMR δ 23.6, 25.0, 30.5, 55.6, 110.8, 120.7, 125.4, 125.6, 128.1, 128.8, 130.4, 131.2, 131.6, 137.7, 147.8, 157.1.

2-Methoxy-2′,6′-dimethylbiphenyl, 35.[25] Purification by flash chromatography (hexanes/CH_2Cl_2 10:1) gave 0.93 mmol of a colorless oil (93% from chloride): ^{1}H NMR δ 2.00 (s, 6H), 3.65 (s, 3H), 6.93 (d, J = 8.3 Hz, 1H), 6.97−7.02 (m, 2H), 7.06−7.16 (m, 3H), 7.29 (m, 1H); ^{13}C NMR δ 21.1, 55.9, 111.4, 121.3, 127.6, 129.0, 130.1, 131.2, 137.1, 138.8, 157.1.

2-Methyl-1-(2-tolyl)naphthalene, 36.[26] Purification by flash chromatography (hexanes) gave 0.89 mmol of a colorless oil (89% from chloride): ^{1}H NMR δ 1.88 (s, 3H), 2.12 (s, 3H), 7.07 (d, J = 6.6 Hz, 1H), 7.20−7.36 (m, 7H), 7.71 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H); ^{13}C NMR δ 20.2, 21.0, 125.4, 126.4, 126.6, 126.7, 127.8, 128.1, 128.5, 129.2, 130.7, 132.7, 133.2, 133.7, 137.4, 138.1, 139.8.

1-(2-Methoxyphenyl)-2-methylnaphthalene, 37.[27] Purification by flash chromatography (hexanes/CH_2Cl_2 10:1) gave 0.91 mmol of a colorless oil (91% from chloride): ^{1}H NMR δ 2.17 (s, 3H), 3.50 (s, 3H), 6.92 (d, J = 8.3 Hz, 1H), 7.00 (ddd, J = 7.3, 7.3, 1.2 Hz, 1H), 7.10 (dd, J = 7.4, 1.8 Hz, 1H), 7.20−7.38 (m, 5H), 7.69 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 21.1, 56.0, 111.7, 121.3, 125.2, 126.3, 126.5, 127.8, 128.4, 128.8, 129.1, 129.4, 132.4, 132.6, 133.6, 134.4, 135.3, 157.9.

9-(2-Tolyl)anthracene, 39.[28] Purification by flash chromatography (hexanes/CH_2Cl_2 10:1) gave 0.90 mmol of white crystals (90% from chloride): ^{1}H NMR δ 1.84 (s, 3H), 7.21−7.41 (m, 8H), 7.50 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.6 Hz, 2H), 8.42 (s, 1H); ^{13}C NMR δ 20.41, 125.8, 126.1, 126.5, 127.1, 127.2, 128.5, 129.1, 130.6, 130.7, 131.9, 132.1, 137.1, 138.4, 138.8.

9-(2-Methoxyphenyl)anthracene, 40.[29] Purification by flash chromatography (hexanes/CH_2Cl_2 9:1) gave 0.89 mmol of white crystals (89% from chloride): ^{1}H NMR δ 3.53 (s, 3H), 7.08 (d, J = 8.3 Hz, 1H), 7.12 (ddd, J = 7.3, 7.3, 1.0 Hz, 1H), 7.24 (dd, J = 7.5, 1.8 Hz, 1H), 7.26−7.32 (m, 2H), 7.36−7.42 (m, 2H), 7.47 (ddd, J = 7.8, 7.8, 2.0 Hz, 1H), 7.59 (dd, J = 9.8, 1.0 Hz, 2H), 7.97 (d, J = 8.3 Hz, 2H), 8.42 (s, 1H); ^{13}C NMR δ 56.3, 111.9, 121.3, 125.6, 125.8, 126.5, 127.4, 128.0, 129.1, 130.0, 131.0, 132.1, 133.5, 134.4, 158.7.

9-(1-Naphthyl)anthracene, 41.[30] Purification by flash chromatography (hexanes/CH_2Cl_2 9:1) gave 0.85 mmol of white crystals (85% from chloride): ^{1}H NMR δ 7.06−7.09 (m, 2H), 7.11−7.17 (m, 2H), 7.32−7.40 (m, 5H), 7.46 (dd, J = 7.1, 1.2 Hz, 1H), 7.58 (dd, J = 7.6, 7.6 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 7.97 (dd, J = 8.3, 8.3 Hz, 3H), 8.49 (s, 1H); ^{13}C NMR δ 125.8, 126.2, 126.6, 126.9, 127.2, 127.6, 128.7, 128.9, 129.0, 129.7, 131.6, 132.1, 134.2, 134.3, 135.6, 137.2.

Methyl 2-methyl-2′-isopropylbiphenyl-4-carboxylate, 44. Purification by flash chromatography (hexanes/ethyl acetate 50:1) gave 0.86 mmol of a colorless oil (86%): ^{1}H NMR δ 1.06 (d, J = 6.8 Hz, 3H), 1.14 (d, J = 6.8 Hz, 3H), 2.10 (s, 3H), 2.62 (sept, J = 6.8 Hz, 1H), 3.92 (s, 3H), 7.01 (dd, J = 1.1, 7.2 Hz, 1H), 7.17−7.23 (m, 2H), 7.32−7.41 (m, 2H), 7.90 (dd, J = 1.2, 7.8 Hz, 1H), 7.97 (s, 1H); ^{13}C NMR δ 20.7, 23.7, 25.2, 30.5, 52.6, 126.0, 126.1, 127.2, 128.6, 129.4, 129.6, 130.4, 131.5, 137.0, 139.9, 146.7, 147.1, 167.7. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.25; H, 7.31.

Acknowledgment. We thank Combiphos Catalysts, Inc. (www.combiphos.com) for a generous supply of palladium-phosphinous acids.

Supporting Information Available: NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO701893M

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