4720 *J. Org. Chem.* **1996,** *61,* 4720−4724

Palladium-Catalyzed Cross-Coupling of Organoboron Compounds with Iodonium Salts and Iodanes

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Received January 30, 1996⊗

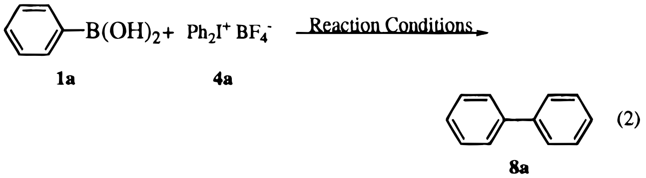
The palladium-catalyzed cross-coupling reaction of iodinanes (iodonium salts and iodanes) with organoboron compounds to form carbon−carbon bonds was achieved at ambient temperature under aqueous conditions in the absence of base. Coupling of phenylboronic acid with diphenyliodonium tetrafluoroborate in the presence of $Pd(PPh_3)_4$ (0.2 mol %) or $Pd(OAc)_2$ (0.2 mol %) under aqueous conditions gave biphenyl in almost quantitative yield. Under the same conditions, substituted boronic acids, boronates, and trialkylboranes were readily coupled with diaryl-, alkenyl-, and alkynyliodonium salts. Finally, the iodanes ArI(OH)OTs underwent cross-coupling with boronic acids, boronates, and trialkylboranes to afford biphenyls and aryl-substituted alkenes.

Introduction

The palladium-catalyzed cross-coupling of organoboranes (boronic acids, boronates, and trialkylboranes) with organic electrophiles (i.e., halides and triflates) in the presence of base is known as the Suzuki reaction[1] and has become an extremely powerful tool in organic synthesis. These coupling reactions tolerate many functional groups, yield easily removable nontoxic byproducts, and use nontoxic and readily available organoboranes. Consequently, they are utilized extensively in the synthesis of natural products. However, coupling with aryl or vinyl halides and triflates usually requires a longer reaction time at a higher temperature.[1,2] These relatively drastic conditions may reduce the yields due to the thermal instability of the substrates, products, or the catalyst itself. In some cases, the use of bases such as TlOH and $Ba(OH)_2$ allows the reaction to proceed at room temperature in biaryl couplings.[3] In connection with our programs to utilize hypervalent iodonium salts[4,5] and iodanes[4,6] as electrophiles for palladium-catalyzed C−C bond formation,[7] we report here the palladium-catalyzed cross-coupling of organoboranes[8] (boronic acids **1** and **3a**, boronates **2** and **3b**, and trialkylboranes **3c**,**d**) with iodonium salts **4**−**6** and iodanes **7** under aqueous conditions at ambient temperature (Scheme 1, eq 1).

Results and Discussion

Cross-Coupling with Iodonium Salts. A. Coupling of Phenylboronic Acid with Diphenyliodonium Tetrafluoroborate. The palladium-catalyzed cross-coupling of arylboronic acids with aryl halides to give unsymmetrical biaryls has been reported previously.[9,10] Snieckus[2c] utilized aryl triflates instead of aryl halides in Pd-catalyzed cross-coupling with arylboronic acids to synthesize unsymmetrical biaryls. In our attempts to find an alternative to halides and triflates for mild conditions, we focused our attention on hypervalent iodine compounds. We found that excellent yields of unsymmetrical biaryls could be obtained under extremely mild conditions when arylboronic acids were reacted with hypervalent iodonium salts using 0.2 mol % $Pd(PPh_3)_4$ or ligand-free $Pd(OAc)_2$ as a catalyst. To determine suitable reaction conditions, a series of experiments were performed on the coupling of phenylboronic acid with diphenyliodonium tetrafluoroborate to form biphenyl (**8a**) (eq 2). The results are summarized in Table 1.



We first coupled phenylboronic acid (**1a**) with diphenyliodonium tetrafluoroborate (**4a**)[11] in the presence of Pd($PPh_3)_4$ (0.2 mol %) and Na_2CO_3 (2 equiv) in DME/H_2O

⊗ Abstract published in *Advance ACS Abstracts,* June 1, 1996.

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Scheme 1

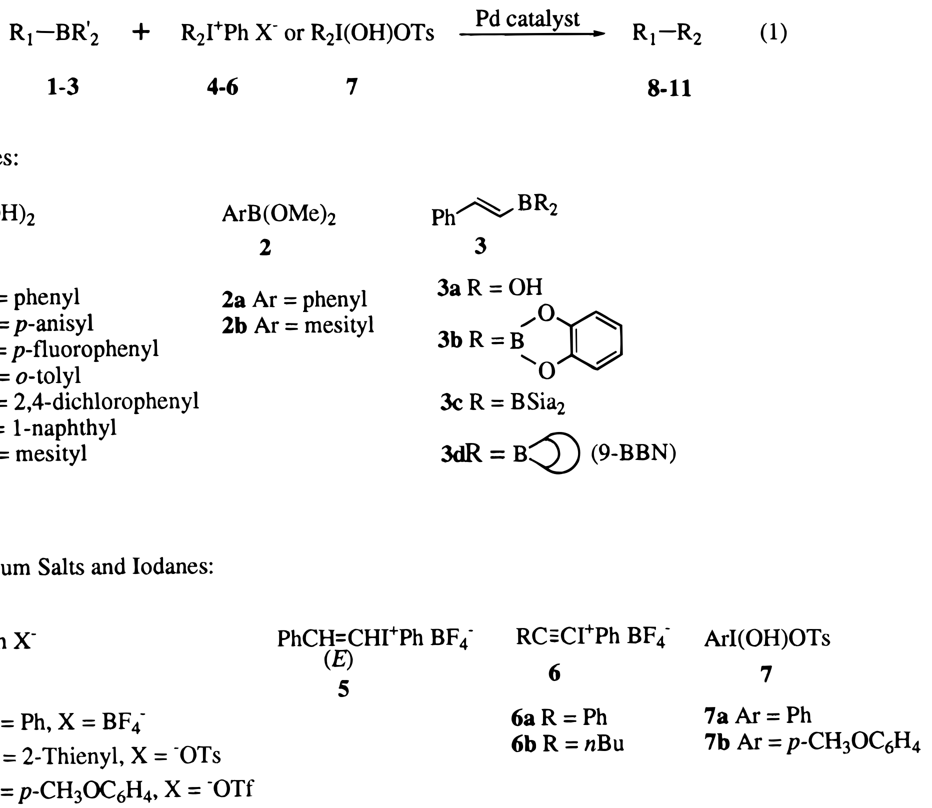

Table 1. Reaction Conditions for Cross-Coupling of Phenylboronic Acid with Diphenyliodonium Tetrafluoroborate

entry	reaction condns[a]	time (min)	yield[c] (%)
1	$Pd(PPh_3)_4$ (0.2 mol %), Na_2CO_3, DME/H_2O (4:1),[b] rt	30	98
2	$Pd(PPh_3)_4$ (0.2 mol %), DME/H_2O (4:1), rt	30	96
3	$Pd(PPh_3)_4$ (0.2 mol %), DME, rt	30	95
4	$Pd(OAc)_2$ (0.2 mol %), Na_2CO_3, DME/H_2O (4:1), rt	1	99
5	$Pd(OAc)_2$ (0.2 mol %), DME/H_2O (4:1), rt	5	97
6	$Pd(OAc)_2$ (0.2 mol %), DME, rt	5	95
7	$Pd(OAc)_2$ (0.2 mol %), H_2O, rt	5	95
8	Pd/C (2 mol %), Na_2CO_3, EtOH, rt[d]	10	94

[a] The amount of palladium catalyst can be reduced to 0.2 mol %. However, the yield decreased with 0.1 mol %. At 80 °C, the reactions were completed within 5 min. Two equiv of base (Na_2CO_3 or K_2CO_3) was used. The coupling reaction did not proceed in the absence of palladium catalysts. [b] Acetone/H_2O (4:4.5) can be used as a solvent with Na_2CO_3 or K_2CO_3, or without base, to give comparable yields. [c] Isolated yields. [d] The addition of Ph_3P to Pd/C decreased the yield.

(4:1) at room temperature to afford biphenyl (**8a**) in 98% yield with high catalytic efficiency (entry 1, Table 1). Cross-coupling was achieved at ambient temperature. Although there are few other examples of Suzuki-type biaryl coupling at ambient temperature, they require the use of water-soluble aryl iodides and catalyst[12] or TlOH as a base.[3] Consistent with the mechanism of the Suzuki reaction, 2 equiv of base is required. However, high yields were obtained in the absence of base, even though base is essential for boron cross-coupling.[1,2] The reaction of phenylboronic acid **1a** with $Ph_2I^+BF_4^-$ (**4a**) in DME/H_2O (4:1) without base gave the coupled product **8a** in 96% yield (entry 2, Table 1). Since H_2O can act as base, H_2O was excluded in the coupling (entry 3, Table 1). It is noteworthy that coupling can occur even in the absence of base, as in tin-mediated coupling (Stille reaction).[13] To explain coupling in the absence of base, it is presumed that $PhPd^+BF_4^-$ is formed as a reactive intermediate in the reaction of the iodonium salt **4a** and Pd(0) species.[7a] The counterion tetrafluoroborate can be used in the formation of phenylboronate with the Lewis acid phenylboronic acid. Thus, the transmetalation reaction of the phenylboronate and $PhPd^+BF_4^-$ is favored even in the absence of base. Comparable yields were achieved when $Pd(PPh_3)_4$ was replaced with $Pd(OAc)_2$, and the reaction proceeded faster (entries 4−7, Table 1). With $Pd(OAc)_2$ as a catalyst in H_2O as a solvent, coupling provided the biphenyl (**8a**) (entry 7, Table 1). Finally, Pd/C (2 mol %) was used effectively as a source of Pd(0) in this cross-coupling (entry 8, Table 1).

B. Coupling of Organoboron Compounds with Iodonium Salts. When we extended this protocol to other arylboronic acids, unsymmetrical biaryls were readily obtained in high yields under the same conditions. The results are summarized in Table 2. Reaction of substituted arylboronic acid **1b** with diphenyliodonium tetrafluoroborate (**4a**) in the presence of Na_2CO_3 with $Pd(PPh_3)_4$ as a catalyst in DME/H_2O (4:1) at room temperature for 30 min gave the unsymmetrical biaryl **8b** (method A in entry 1, Table 2). Without using base, comparable yields of biaryl **8b** were obtained in 95% yield. Under the same conditions but with $Pd(OAc)_2$, the reaction gave the unsymmetrical biaryl **8b** (method B). In the case of $Pd(OAc)_2$, a trace amount of biphenyl (**8a**) was obtained as a side product. In the absence of base, biaryl **8b** was obtained in 93% yield. It is known that

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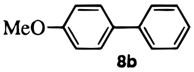
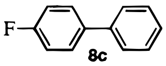
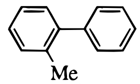
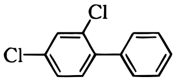
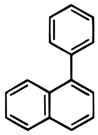
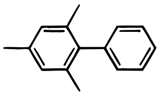
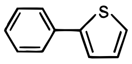
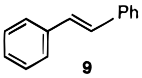
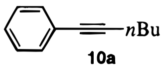
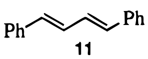
Table 2. Pd-Catalyzed Cross-Coupling of Organic Boron Compounds with Iodonium Salts[a]

Entry	Boranes	Iodonium Salts[b]	Reaction Conditions	Time(min)	Products	Yield(%)[c]
Boronic Acids:						
1	**1b**	**4a**	A B	30(40) 30(45)	 **8b**	99(95) 97(93)
2	**1c**	**4a**	A B	25 5	 **8c**	97 99
3	**1d**	**4a**	A	30	 **8d**	96
4	**1e**	**4a**	A	25	 **8e**	98
5	**1f**	**4a**	A	25	 **8f**	99
6	**1g**	**4a**	A B	25(30) 20(25)	 **8g**	97(94) 98(96)
7	**1a**	**4b**	A	5	 **8h**	99
8	**1a**	**4c**	A	25	**8b**	97
9	**1a**	**5**	A	30	 **9**	87
10	**1a**	**6b**	A	30	 **10a**	86
11	**3a**	**4a**	A	10	**9**	98
Boronates:						
12	**2a**	**5**	A	10(15)	**9**	96(92)
13	**2a**	**6a**	A	10(15)	Ph—≡—Ph **10b**	97(94)
14	**2b**	**4a**	A	10	**8g**	96
15	**3b**	**4a**	A	10	**9**	98
16	**3b**	**5**	A	10	 **11**	98
Trialkylboranes:						
17	**3c**	**4a**	A	10	**9**	80
18	**3d**	**4a**	A	10	**9**	97

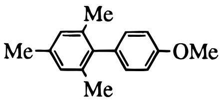
[a] The reactions were run with arylboronic acid (1.1 equiv), iodonium salt (1 equiv), and $Pd(PPh_3)_4$ (0.2 mol %) in the presence of Na_2CO_3 (2 equiv) in DME/H_2O (4:1). The reactions can also be carried out without base. At reflux, the reactions were complete within 5 min. Method A: $Pd(PPh_3)_4$ (0.2 mol %). Method B: $Pd(OAc)_2$ (0.2 mol %). [b] The 2-thienyl(phenyl)iodonium tosylate was prepared according to Koser; see ref 14. [c] Isolated yields. The yields in parentheses are those obtained in the absence of base.

the cross-coupling of sterically hindered arylboronic acids proceeds slowly and gives lower yields due to steric hindrance and competitive hydrolytic deboronation.[10] The reaction of 1-naphthylboronic acid (**1f**) and mesitylboronic acid (**1g**) with iodonium salt **4a** proceeded smoothly to give the coupled biaryls **8f** and **8g**[3b] at ambient temperature in almost quantitative yields (entries 5 and 6, Table 2). Similarly, with 2-thienyl(phenyl)iodonium tosylate

(**4b**),[14] the coupling reaction with phenylboronic acid (**1a**) gave 2-phenylthiophene (**8h**)[15] as the sole product (entry 7, Table 2). *p*-Methoxybiphenyl (**8b**) was obtained (entry 8, Table 2) from (*p*-methoxyphenyl)(phenyl)iodonium triflate (**4c**).[16] These results suggest that, in the catalytic cycle, only electron-donating ArPd$^+$X$^-$ formed after liberation of PhI participates in the coupling. This coupling was also applied to alkenyl- and alkynyliodonium salts[11] to give alkenyl- and alkynyl-substituted aromatic compounds **9** and **10a** (entries 9 and 10, Table 2). Similarly, vinylboronic acid **3a** was also coupled with diphenyliodonium salt **4a** to give **9** (entry 11, Table 2). This method was successfully applied to organic boronates. The results are shown in entries 12–16 of Table 2. Phenylboronate **2a** was treated with alkenyl- and alkynyliodonium salts **5** and **6a** to give *trans*-stilbene (**9**) and disubstituted alkyne **10b** in the presence or absence of base (entries 12 and 13, Table 2).[17a] Sterically hindered arylboronate **2b** was successfully coupled with diphenyliodonium salt **4a** to give **8g**[3b] (entry 14, Table 2). For vinylcatecholboronate **3b**, treatment with diphenyl- and alkenyliodonium salts **4a** and **5** gave the coupled products **9** and **11**, respectively (entries 15 and 16, Table 2). Vinyldisiamylborane **3c** and trialkylborane **3d** were coupled with diphenyliodonium tetrafluoroborate (**4a**) to give **9** (entries 17 and 18, Table 2).[17b]

Coupling of Organoboron Compounds with Iodanes. We examined the reactions of iodanes in palladium-catalyzed coupling. Among hypervalent iodine(III) compounds, readily available hydroxy(tosyloxy)iodobenzene (HTIB) (**7a**), PhI(OH)OTs,[18] referred to as Koser's reagent, has been used in a variety of organic transformations.[6] However, to our knowledge, there have been no reports of transition metal-catalyzed carbon–carbon bond formation with iodanes, although there have been reports of palladium-catalyzed coupling of alkenyliodonium salts with organotin compounds and activated olefins.[7] The palladium-catalyzed C–C coupling of iodanes is summarized in Table 3.[19] Iodane, PhI(OH)OTs, underwent facile coupling with phenylboronic acid (**1a**) in the presence of Pd(PPh$_3$)$_4$ (0.2 mol %) with or without base to give **8a** (entry 1, Table 3). The unsymmetrical biaryls **8b**–**f** were easily synthesized by cross-coupling with iodane **7a** (entries 2–5, Table 3). The sterically hindered mesitylboronic acid (**1g**) coupled smoothly with iodane **7a** in 89% yield (entry 6, Table 3). This coupling was also applied to the substituted iodane *p*-CH$_3$OC$_6$H$_4$I(OH)OTs (**7b**),[20] which was coupled with phenylboronic acid and mesitylboronic acid to yield **8b** and **8i**,[21] respectively (entries 7 and 8, Table 3). The iodane PhI(OH)OTs was also reacted with vinylcatecholboronate **3b** and mesitylboronate **2b** to give the coupled products **9** and **8g** in yields of 98 and 91%, respectively (entries 9 and 10, Table 3). Finally, trialkylboranes were used in cross-coupling to afford *trans*-stilbene (**9**) (entries 11 and 12, Table 3). To explain coupling of iodanes with organoboranes in the absence of base, it is presumed that facile oxidative addition of iodane with the Pd(0) species gives the intermediate PhPdOTs bearing a Pd–O bond. This complex is believed to be polar and more reactive than organopalladium halide[2g] for transmetalation with organoborate. The organoborate is supposed to be formed from boronic acid and counterion hydroxide derived from iodane. It has been known that the cross-coupling of organoboron compounds with 1,3-butadiene monoepoxide[22] and propargylic carbonates[23] occurs under neutral conditions without the need for base.

Table 3. Pd-Catalyzed Cross-Coupling of Organic Boron Compounds with Iodanes[a]

Entry	Boranes	Iodanes[b]	Time(min)	Products	Yield(%)[c]
Boronic Acids:					
1	**1a**	**7a**	35(40)	**8a**	94(92)
2	**1b**	**7a**	30	**8b**	97
3	**1c**	**7a**	25	**8c**	93
4	**1d**	**7a**	35	**8d**	95
5	**1f**	**7a**	30	**8f**	93
6	**1g**	**7a**	25	**8g**	89
7	**1a**	**7b**	30	**8b**	91
8	**1g**	**7b**	30	 **8i**	86
Boronates:					
9	**3b**	**7a**	20	**9**	98
10	**2b**	**7a**	20	**8g**	91
Trialkylboranes:					
11	**3c**	**7a**	20	**9**	95
12	**3d**	**7a**	20	**9**	96

[a] The reactions were run with arylboronic acid (1.1 equiv), iodanes (1 equiv), and Pd(PPh$_3$)$_4$ (0.2 mol %) in the presence of Na$_2$CO$_3$ (2 equiv) in DME/H$_2$O (4:1). The reactions can be carried out without base. Pd(PPh$_3$)$_4$ gave better results than Pd(OAc)$_2$ in terms of reaction time and yield. In the case of Pd(OAc)$_2$, the reaction time was 50–60 min. At reflux, the reactions were complete within 5 min. [b] *p*-CH$_3$OC$_6$H$_4$I(OH)OTs was prepared according to Koser; see ref 20. [c] Isolated yields. The yields in parentheses are those obtained in the absence of base.

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(19) Instead of Koser's reagent, PhI(OH)OTs, Zefirov's reagent, can be used. For the preparation of Zefirov's reagent, see: Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Org. Chem.* **1987**, *52*, 3650.

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(21) (a) Bell, H. C.; Kalman, J. R.; Pinhey, J. T.; Sternhell, S. *Tetrahedron Lett.* **1974**, *15*, 857. (b) Morgan, J.; Parkinson, C. J.; Pinhey, J. T. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3361. (c) Norman, R. O. C.; Thomas, C. B.; Wilson, J. S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 325.

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Conclusion

In conclusion, hypervalent iodonium salts and iodanes can readily undergo palladium-catalyzed cross-coupling with aryl-, alkenyl-, and alkylboranes under extremely mild and aqueous conditions at ambient temperature even in the absence of base. Hypervalent iodine compounds may be soluble in water and act as superior electrophiles which facilitate the oxidative addition with Pd(0) to allow coupling under aqueous and mild conditions. We believe that the method described here may be a valuable alternative to Suzuki and Stille couplings.

Experimental Section

General Procedures. All solvents for reactions were purified before use. IR spectra were recorded on a FT-IR spectrometer. ^{1}H NMR were conducted at 400 MHz in CDCl$_3$, and chemical shifts are reported in δ units relative to the tetramethylsilane (TMS) signal at 0.00 ppm. Coupling constants (J) are reported in Hz. Melting points were determined in unsealed capillary tubes and are uncorrected. For thin-layer chromatography (TLC), Merck precoated plates (silica gel 60 F$_{254}$, 0.25 mm) were used. Silica gel 60 (9385, 230–400 mesh) from Merck was used for column chromatography. The reported yields are for chromatographically pure isolated products.

Boron Reagents. Phenylboronic acid (**1a**) was purchased from Aldrich Chemical Co. *p*-Anisylboronic acid (**1b**), *p*-fluorophenylboronic acid (**1c**), *o*-tosylboronic acid (**1d**), 2,4-dichlorophenylboronic acid (**1e**), and 1-naphthylboronic acid (**1f**) were purchased from Lancaster. Mesitylboronic acid (**1g**) was easily prepared by hydrolysis of **2b**. Mesitylboronate (**2b**) was prepared[24] from 1-bromo-2,4,6-trimethylbenzene by lithiation followed by treatment of trimethylborate according to Pinhey's method. Phenylboronate (**2a**) was prepared[25] from bromobenzene by lithiation followed by treatment with trimethylborate. (*E*)-β-Styrylboronic acid (**3a**) was easily prepared by hydrolysis of **3b**. (*E*)-β-Styrylcatecholborane (**3b**) was prepared[8b] from catecholborane (1,3,2-benzodioxaborole) and phenylacetylene according to Brown's method. (*E*)-β-Styryldisiamylborane (**3c**) was prepared[8a,c] *via* the hydroboration of phenylacetylene with disiamylborane–THF and was used without further purification. (*E*)-1-(9-BBN-9-yl)-2-phenylethene (**3d**) was prepared[26] by hydroboration of phenylacetylene with 9-BBN.

Iodonium Salts and Iodanes. Hydroxy(tosyloxy)iodobenzene (**7a**) was purchased from Aldrich Chemical Co. Diphenyliodonium tetrafluoroborate (**4a**), alkenyliodonium salt (**5**), and alkynyliodonium salts (**6a** and **6b**) were prepared[11] according to Ochiai et al. 2-Thienyl(phenyl)iodonium tosylate (**4b**) was prepared[14] according to Margida and Koser. (*p*-Methoxyphenyl)(phenyl)iodonium triflate (**4c**) was prepared[16] by the method of Kitamura et al. *p*-CH$_3$OC$_6$H$_4$I(OH)OTs (**7b**) was prepared by known procedures.

General Procedure for Cross-Coupling Reactions with Iodonium Salts: Biphenyl (8a). To a mixture of diphenyliodonium tetrafluoroborate (900 mg, 2.45 mmol) and Pd(PPh$_3$)$_4$ (0.2 mol %, 5.70 mg) was added Na$_2$CO$_3$ (518 mg, 2.59 mmol) under nitrogen atmosphere followed by phenylboronic acid (328 mg, 2.69 mmol) in DME/H$_2$O (10 mL, 4:1) at room temperature. The reaction mixture was stirred at room temperature for 30 min and then quenched with saturated aqueous NH$_4$Cl. The reaction mixture was extracted with ether (20 mL × 2), and the organic layer was dried over anhydrous MgSO$_4$ and evaporated *in vacuo*. The crude product was separated by SiO$_2$ column chromatography (hexanes, $R_f = 0.47$) to afford biphenyl (**8a**) (370 mg, 98%): TLC, SiO$_2$, hexanes, $R_f = 0.47$; mp 68.5–69.5 °C (lit.[28] mp 69–72 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (m, 2H), 7.46 (m, 4H), 7.61 (m, 4H); IR (KBr) 3035, 1568, 1480, 730 cm^{-1}; MS (m/e) 154 (M$^+$, base peak), 153, 152, 128, 115, 77, 76, 75. All of the compounds (**8b**, **8c**, **8d**, **8e**,[27] **8f**, **8g**, **8h**, **9**, **10a**, **10b**, and **11** in Table 2) have been previously reported and were prepared according to procedures in the literature.

General Procedure for Cross-Coupling Reactions with Iodanes: Biphenyl (8a). To a mixture of hydroxy(tosyloxy)iodobenzene (HTIB) (960 mg, 2.45 mmol) and Pd(PPh$_3$)$_4$ (0.2 mol %, 5.70 mg) was added Na$_2$CO$_3$ (518 mg, 2.59 mmol) under nitrogen atmosphere followed by phenylboronic acid (328 mg, 2.69 mmol) in DME/H$_2$O (10 mL, 4:1) at room temperature. The reaction mixture was stirred at room temperature for 35 min and then quenched with saturated NH$_4$Cl solution. The reaction mixture was extracted with ether (20 mL × 2), and the organic layer was dried over anhydrous MgSO$_4$ and evaporated *in vacuo*. The crude product was separated by SiO$_2$ column chromatography (hexanes, $R_f = 0.47$) to give biphenyl (**8a**) (355 mg, 94%): TLC, SiO$_2$, hexanes, $R_f = 0.47$; mp 68.5–69.5 °C (lit.[28] mp 69–72 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (m, 2H), 7.46 (m, 4H), 7.61 (m, 4H); IR (KBr) 3035, 1568, 1480, 730 cm^{-1}; MS (m/e) 154 (M$^+$, base peak), 153, 152, 128, 115, 77, 76, 75. All of the compounds (**8a**, **8b**, **8c**, **8d**, **8f**, **8g**, **8i**, and **9** in Table 2) have been previously reported and were prepared according to procedures in the literature.

Acknowledgment. The generous financial support of KOSEF-OCRC and the Ministry of Education (BSRI-95-3420) is gratefully acknowledged.

Supporting Information Available: Experimental procedures and spectral and analytical data for the compounds (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960195M

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