A Modified *in Situ* Suzuki Cross-Coupling of Haloarenes for the Preparation of C_2-Symmetric Biaryls

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Palladium-catalyzed cross-coupling between aryl boronic acids and haloarenes or aryl triflates has been shown to be a versatile method for the preparation of biaryls.[1] The original procedure developed by Suzuki[2] has achieved widespread popularity in organic synthesis since it is compatible with a large variety of functional groups and the conditions tolerate aqueous reaction media. Moreover, the inorganic byproduct of the reaction is nontoxic and easily removed from the reaction mixture thereby making the Suzuki protocol suitable for industrial processes. Moreno-Mañas *et al.*[3] have recently reported a palladium-catalyzed Suzuki type self-coupling of arylboronic acids for the preparation of symmetrical biaryls. The initial findings for this method are promising; however, the versatility of the reaction with respect to various functional groups and the effect of steric hinderance at the *ortho* positions has not been fully investigated. Moreover, the self-coupling method requires the isolation of the organoboronic acid precursor. Although these compounds are generally quite thermally stable and not air-sensitive, their high solubility in aqueous media often complicates their isolation and purification procedures. We have recently reported an efficient method for the cross-coupling of aryl, furyl, primary, and benzylic boranes with aryl or vinyl bromides and iodides without the need for isolation of the organoboronic acid.[4] We herein report a method for the preparation of C_2-symmetric biaryls via a modified *in situ* Suzuki cross-coupling reaction.[5]

Our interests in natural product synthesis and chiral auxiliary design prompted us to develop an *in situ* Suzuki coupling method for synthesizing C_2-symmetric biaryls which obviates the need for boronic acid isolation. By treating the starting haloarene with only 0.5 equiv of *n*-butyllithium followed by an excess of trimethoxyborate, we felt that it would be possible to generate the needed 1:1 molar ratio of haloarene and arylboronic acid *in situ* which could subsequently be coupled under modified Suzuki conditions (Scheme 1).

Treatment of a solution of iodobenzene in THF under the above conditions afforded biphenyl in 73% yield. Unfortunately, haloarenes possessing one or more *ortho* substituents afforded the respective biaryls in disappointing yield (Table 1). Suzuki and co-workers have demonstrated that the cross-coupling of sterically hindered boronic acids with haloarenes is greatly enhanced by use of stronger bases such as $Ba(OH)_2$, NaOH, and TlOH.[6] In our hands, use of a saturated aqueous solution of $Ba(OH)_2$ in place of the 2 M Na_2CO_3 had little effect on the reaction outcome. When 1-iodo-2-methoxynaphthalene (entry 6) was treated under our initial reaction conditions, less than 10% of the desired binaphthyl product was formed. The remainder of the reaction mixture was determined to be a 2:1:1 mixture of the starting haloarene, 2-methoxy-1-naphthylboronic acid, and 2-methoxynaphthalene, respectively. Increasing the reaction time did not significantly increase the yield of the desired binaphthyl but rather resulted in increased amounts of the hydrolytic deboration product, 2-methoxynaphthalene, being isolated from the reaction mixture.

Scheme 1

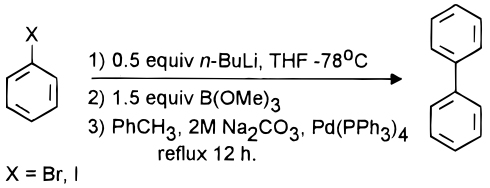

Table 1. Initial Attempts to Prepare C_2-Symmetric Biaryls via the *in Situ* Suzuki Reaction

entry[a]	halide	base	product (% yield)[b]
1	iodobenzene	2 M Na_2CO_3	biphenyl (73)
2	iodobenzene	$Ba(OH)_2$	biphenyl (80)
3	bromobenzene	$Ba(OH)_2$	biphenyl (85)
4	2-bromotoluene	2 M Na_2CO_3	2,2′-dimethylbiphenyl (40)
5	2-bromoanisole	$Ba(OH)_2$	2,2′-dimethoxybiphenyl (56)
6	1-iodo-2-methoxynaphthalene	2 M Na_2CO_3	2,2′-dimethoxy-1,1′-binaphthyl (<10)

[a] All reactions done in toluene with $Pd(PPh_3)_4$ and 12 h reflux time. [b] Isolated yields.

In order to optimize the reaction conditions, we decided to investigate the role of different solvent mixtures on the *in situ* cross-coupling of 1-iodo-2-methoxynaphthalene. We were pleased to find that the 3:3:1 mixture of toluene, ethanol, and water reported by Grahn *et al.*[7] afforded a 96% yield of the desired binaphthyl (**5b**) (Table 2, entry 12). This solvent mixture was not limited to this one example, and Table 2 summarizes the scope and limitations of the optimized reaction conditions. In general, the developed *in situ* method affords C_2-symmetric biaryls in moderate to excellent yield and tolerates a wide range of functionalities including esters, amides, acetals, and nitriles (entries 6−9, respectively). The reaction was limited by the presence of a phenolic TBDPS group which was cleaved under the reaction conditions (entry 10).

The synthetic value of this method could be realized for the production of many C_2-symmetric biaryls needed for chiral ligand development and natural product synthesis. To demonstrate the latter, we endeavored to synthesize the recently discovered 4,4′-dihydroxy-5,5′-

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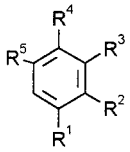
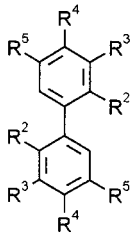
Table 2. Results from the Preparation of C_2-Symmetric Biaryls Using the Optimized *in Situ* Suzuki Coupling Conditions

entry	halide	product (% Yield)[a]	entry	halide	product (% Yield)[a]
1	**1a**	**4a** (85)	8	**1h**	**4h** (91)
2	**1b**	**4b** (73)	9	**1i**	**4i** (68)
3	**1c**	**4c** (79)	10	**1j**	**4j** (92)[b]
4	**1d**	**4d** (95)	11	**2a**	**5a** (86)
5	**1e**	**4e** (89)	12	**2b**	**5b** (96)
6	**1f**	**4f** (32)	13	**2c**	**5c** (84)
7	**1g**	**4g** (79)	14	**3**	**6** (73)

[a] Isolated yield. [b] Hydrolysis of the TBDPS ether takes place under the reaction conditions.





1a R^1=Br, R^2-R^5=H

1b R^1=Br, R^2=CH_3, R^3-R^5=H

1c R^1=Br, R^2=R^4=R^5=H, R^3=CF_3

1d R^1=Br, R^2=OMe, R^3-R^5=H

1e R^1=Br, R^2=R^5=OMe, R^3=R^4=H

1f R^1=I, R^2=CO_2(*i*-Pr), R^3-R^5=H

1g R^1=I, R^2=CON(*i*-Pr)$_2$, R^3-R^5=H

1h R^1=Br,R^3-R^5=H, R^2= 

1i R^1=Br, R^2=R^4=R^5=H, R^3=CN

1j R^1=Br, R^2=R^3=R^5=H, R^4=OTBDPS

4a R^2-R^5=H

4b R^2=CH_3, R^3-R^5=H

4c R^2=R^4=R^5=H, R^3=CF_3

4d R^2=OMe, R^3-R^5=H

4e R^2=R^5=OMe, R^3=R^4=H

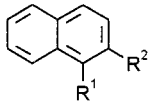
4f R^2=CO_2(*i*-Pr), R^3-R^5=H

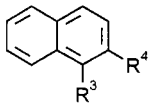
4g R^2=CON(*i*-Pr)$_2$, R^3-R^5=H

4h R^3-R^5=H, R^2= 

4i R^2=R^4=R^5=H, R^3=CN

4j R^2=R^3=R^5=H, R^4=OH





2a R^1=Br, R^2=H

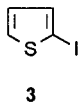
2b R^1=I, R^2=OMe

2c R^1=H, R^2=Br

5a R^3=naphth-1-yl, R^4=H

5b R^3=(2-methoxynaphth-1-yl), R^4=OMe

5c R^3=H, R^4=naphth-2-yl



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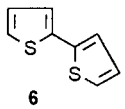

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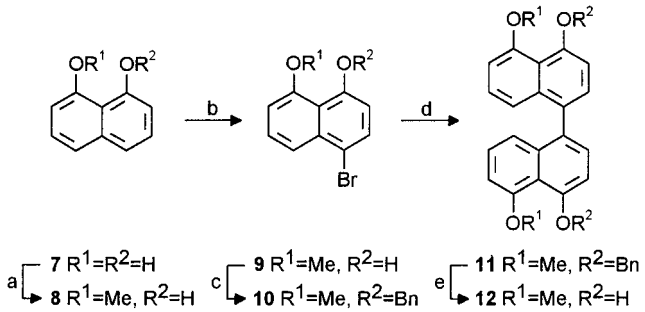
dimethoxy-1,1′-binaphthyl (**12**) isolated from the fungus (Ascomycetes*) Daldinia concentrica*[8] (Scheme 2). 1,8-Dihydroxynaphthalene (**7**) was chosen as a suitable starting material and prepared from 1,8-naphthosultone according to literature procedure.[9] Monomethylation of the starting diol under standard conditions gave methyl ether **8** in 95% yield. The corresponding sodium phenoxide was brominated in CCl_4 to afford a mixture of regioisomers in which the desired bromide **9** was the major component. Protection of the remaining hydroxyl group in **9** with benzyl bromide in DMF and subsequent treatment of the resulting benzyl ether with our modified *in situ* Suzuki coupling protocol afforded coupled product **11** in 72% yield. Removal of the benzyl groups via hydrogenolysis yielded the natural product **12** in an overall yield of 41% (five steps).

Scheme 2[a]



[a] (a) 1 equiv of NaH, DMF, 5 equiv of MeI (95%); (b) NaH, CCl_4, 1 equiv of Br_2 (60%); (c) NaH, DMF, BnBr, (100%); (d) 0.5 equiv of *n*-BuLi, THF −78 °C then $B(OMe)_3$ rt 12 h and then $PhCH_3$, EtOH, H_2O, Na_2CO_3, $Pd(PPh_3)_4$ reflux 12 h (72%); (e) H_2, Pd/C, $EtOH/CH_2Cl_2$ (100%).

In summary, we have developed a one step modified *in situ* Suzuki coupling method for the production of C_2-symmetric biaryls which eliminates the need for boronic acid isolation. Moderate to excellent yields are obtained and a wide variety of functional groups are tolerated. Moreover, our *in situ* method is synthetically useful for the synthesis of natural products and the preparation of C_2-symmetric biaryl ligands.

Experimental Section

General Comments. All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. All chemicals were reagent grade and used without purification. Ether refers to diethyl ether. THF was distilled from Na/benzophenone ketyl immediately prior to use. Merck silica gel 60 (230−400 mesh) was used for chromatography, which was carried out by using the flash technique.[10] Radial chromatography was accomplished using a model 7924T chromatotron. Thin-layer chromatography (TLC) was done on Merck 60F-254 silica gel plates. Detection of TLC components was accomplished using either a 254/366 nm UV lamp or developing with an acidic solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Melting points are uncorrected. Elemental and MS analyses were performed by D. Fox and Q. Wu at The University of Calgary. Starting materials **1g**,[11] **1h**,[12] and **7**[9] were synthesized according to standard literature procedures with minor modification.

General Procedure for the Coupling of Haloarenes. To a solution of the haloarene (1 mmol) in dry THF (10 mL) at −78 °C was added 0.5 equiv of *n*-BuLi followed by 1.5 equiv of $B(OMe)_3$. The resulting solution was warmed to rt over a 4 h period and subsequently stirred overnight under an inert atmosphere. To the solution were then added toluene (10 mL), ethanol (10 mL), water (4 mL), Na_2CO_3 (1.5 mmol), and $Pd(PPh_3)_4$ (0.01 mmol). The resulting mixture was refluxed under a N_2 atmosphere for 24 h. The reaction contents were then cooled to rt and extracted with CH_2Cl_2. The organic phases were combined, washed with H_2O, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford the crude biaryl which was

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further purified by a suitable method. Coupled products **4a**,**b**,[13] **4c**,[14] **4d**,**e**,[1] **4h**,[15] **4i**,[16] **4j**,[17] **5a**,[18] **5b**,[19] **5c**,[1] and **6**[20] exhibited spectral data and physical properties consistent to those reported in the literature.

Isopropyl 2-Iodobenzoate (1f). To a solution of 2-iodobenzoic acid (2.49 g, 10.0 mmol) in DMF (80 mL) were added K_2CO_3 (3.47 g, 25.1 mmol) and isopropyl iodide (1.0 mL, 10.0 mmol). The resulting mixture was stirred at room temperature for 24 h after which time the solution was diluted with ether (300mL) and washed with 10% NaOH and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated *in vacuo* to afford an orange oil. The crude material was purified by distillation under reduced pressure to give 2.76 g of **1f** (95%): bp 60−65 °C (0.1 mmHg); IR (neat) 1724, 1291, 1254, 1101, 1016 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.39 (d, J = 6.2 Hz, 6H), 5.28 (sept, J = 6.2 Hz, 1H), 7.14 (td, J = 7.6 and 1.8 Hz, 1H), 7.4 (td, J = 7.6 and 1.2 Hz, 1H), 7.76, (dd, J = 7.7 and 1.7 Hz, 1H), 7.97 (dd, J = 7.9 and 1.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.8, 69.5, 93.8, 127.8, 130.6, 132.3, 136.0, 141.1, 166.2; MS (EI, m/z) 290 (29, M^+), 248 (58, $M^+ - C_3H_6$), 76 (100, $M^+ - C_4H_7IO_2$); HRMS calcd for $C_{10}H_{11}IO_2$ 289.9800, found 289.9786. Anal. Calcd for $C_{10}H_{11}IO_2$: C, 41.40; H, 3.82. Found: C, 41.28, H, 3.72.

***N*,*N*-Diisopropyl-2-bromobenzamide (1g):** mp 147−149 °C (lit.[4] 141−145 °C); IR (CCl_4) 1628, 1440, 1341 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.06 (d, J = 6.7 Hz, 3H), 1.23 (d, J = 6.7 Hz, 3H), 1.56 (d, J = 6.8 Hz, 3H), 1.58 (d, J = 6.8 Hz, 3H), 3.56 (sept, J = 6.8 Hz, 2H), 7.35 (m, 3H), 7.55 (d, J = 7.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) ppm 20.1 (q), 20.5 (q), 20.6 (q), 20.7 (q), 46.0 (d), 51.1 (d), 119.0 (s), 126.6 (d), 127.5 (d), 129.4 (d), 140.2 (s), 168.1 (s); MS (EI, m/z) 283/285 (15, M^+), 282/284 (15, $M^+ - H$), 240/242 (43, $M^+ - C_3H_7$), 183/185 (100, $M^+ - N(C_3H_7)_2$). Anal. Calcd for $C_{13}H_{18}BrNO$: C, 54.94; H, 6.38; N, 4.93. Found: C, 55.02; H, 6.45; N, 4.91.

1-[(*tert*-Butyldiphenylsilyl)oxy]-4-bromobenzene (1j). To a solution of 4-bromophenol (3.96 g, 22.9 mmol) in DMF (50 mL) were added *tert*-butyldiphenylsilyl chloride (4.82 mL, 27.5 mmol) and imidazole (3.90 g, 57.2 mmol). The resulting solution was stirred for 2 d at rt, quenched with H_2O (50 mL), and stirred for a further 30 min. The mixture was then diluted with ether (150 mL) and washed with 10% HCl and brine solution. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to afford a light yellow oil. The crude silane was distilled under reduced pressure to afford a clear, colorless oil which later solidified (9.10 g, 96.7%): mp 43.5−45 °C; bp 130−150 °C (0.1 mmHg); IR (NaCl) 1486, 1272, 1251, 1113 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.12 (s, 9 H), 6.66 (d, 2H, J = 8.8 Hz), 7.20 (d, 2H, J = 8.7 Hz), 7.41 (m, 6 H), 7.72 (dd, 4H, J = 7.4 and 1.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.4, 26.5, 113.4, 121.5, 127.9, 130.1, 132.1, 132.5, 135.5, 154.8; MS (EI, m/z) 105 (56), 152 (54), 181 (31), 197 (39), 273 (52), 353/355 (100, $M^+ - C_4H_9$), 410/412 (4, M^+); Anal. Calcd for $C_{22}H_{23}BrOSi$: C, 64.23; H, 5.64. Found: C, 64.23; H, 5.55.

1-Iodo-2-methoxynaphthalene (2b). To a solution of 1-bromo-2-methoxynaphthalene (3.03 g, 12.8 mmol) in THF (150 mL) was added *n*-BuLi (2.5 M solution in hexanes, 5.6 mL, 14.1 mmol, 1.1 equiv) at −78 °C. To the cooled solution was then added I_2 (0.3 M solution in THF, 50 mL, 15.3 mmol, 1.3 equiv). The vessel was then warmed to rt and stirred 1 h under an N_2 atmosphere. The reaction contents were then diluted with water (150 mL) and ether (250 mL). The organic phase was washed with a saturated solution of $Na_2S_2O_3$, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to afford a red oil which later solidified. The crude material was recrystallized from hexanes to afford the title compound (3.63 g) in quantitative yield: mp 86−87 °C (lit.[21] mp 88.5−89 °C); ^1H NMR (200 MHz, $CDCl_3$) δ 4.04 (s, 3H), 7.22 (d, J = 9.0 Hz, 1H), 7.39 (td, J = 7.4 and 1.0 Hz, 1H), 7.56 (td, J = 7.7 and 1.2 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) ppm 57.2 (q), 87.78 (s), 113.0 (d), 124.3 (d), 128.1 (d), 128.2 (d), 129.9 (s), 130.3 (d), 131.2 (d), 135.7 (s), 156.7 (s); MS (EI, m/z) 284 (100, M^+), 269 (14, $M^+ - CH_3$), 241 (45), 142 (69, $M^+ - CH_3I$).

Diisopropyl 2,2′-biphenyldicarboxylate (4f): mp 68−70 °C; IR (KBr) 1699, 1267, 1097 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (d, 6H, J = 6.2 Hz) 1.00 (d, 6H, J = 6.2 Hz), 4.92 (sept, 2H, J = 6.2 Hz), 7.19 (dd, 2H, J = 4.0 and 1.3 Hz), 7.46 (m, 4H), 8.02 (dd, 2H, J = 4.1 and 1.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.3, 67.9, 126.9, 129.9, 130.1, 130.4, 130.9, 143.3, 166.7; MS (EI, m/z) 197 (100, M^+-$C_7H_{13}O_2$), 239 (23, $M^+ - CO_2C_3H_7$), 326 (1, M^+). HRMS calcd for $C_{20}H_{22}O_4$ 326.1518, found 326.1540; Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.60; H, 6.80.

***N*,*N*,*N*′,*N*′-Tetraisopropyl-2,2′-biphenyldicarboxamide (4g):** mp 167−168 °C; IR (KBr) 1614, 1429, 1342, 1330 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.79 (d, 6H, J = 6.5 Hz), 1.07 (d, 6H, 6.6 Hz), 1.33 (d, 6H, 6.8 Hz), 1.49 (d, 6H, 6.8 Hz), 3.37 (sept, 2H, J = 6.8 Hz), 3.96 (sept, 2H, 6.5 Hz), 7.28 (m, 6H), 7.50 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.7, 20.2, 20.6, 21.0, 45.6, 50.4, 126.4, 127.3, 127.7, 130.3, 136.3, 138.4, 169.8; MS (EI, m/z) 308 (100, $M^+ - C_6H_{14}N$), 408 (19, M^+); HRMS calcd for $C_{26}H_{36}N_2O_2$, 408.2777, found 408.2777. Anal. Calcd for $C_{26}H_{36}N_2O_2$: C, 76.43; H, 8.88; N, 6.86. Found: C, 76.26; H, 9.17; N, 6.86.

4-Bromo-1-hydroxy-8-methoxynaphthalene (9). 1-Hydroxy-2-methoxynaphthalene (1.03 g, 5.9 mmol) was dissolved in CCl_4 (50mL). To the solution was added sodium hydride (142 mg, 5.9 mmol) followed by bromine (304 μL, 5.9 mmol). After 15 min at rt, the solution was diluted with ether and washed with water followed by saturated $Na_2S_2O_3$ solution. The ether layer was dried (Na_2SO_4) and filtered, and the solvent was evaporated to afford a blue oil. The crude material was recrystallized from CH_2Cl_2/hexanes to give 0.98 g (67%) light blue crystals which were determined by ^1H NMR spectroscopy to be a 9:1 mixture of **9** and 2-bromo-1-hydroxy-8-methoxynaphthalene. This mixture was used without further purification in the subsequent benzylation step. An analytical sample of **9** was obtained by radial chromatrography [elution with hexanes/ethyl acetate (9:1)]: mp 111.5−113.5 °C; IR (KBr) 1392, 1260, 1080 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.08 (s, 3H), 6.77 (d, 1H, J = 8.3 Hz), 6.86 (d, 1H, J = 7.8 Hz), 7.44 (t, 1H, J = 8.5 Hz), 7.65 (d, 1H, J = 8.3 Hz), 7.84 (d, 1H, J = 8.7 Hz), 9.48 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 56.4, 104.9, 111.1, 111.3, 116.2, 121.3, 127.0, 131.7, 134.3, 154.6, 156.2; MS (EI, m/z) 102 (100), 173 (11, $M^+ - Br$), 209/211 (58), 237/239 (25, $M^+ - CH_3$), 252/254 (35, M^+); HRMS calcd for $C_{11}H_9BrO_2$ 251.9786/253.9767, found 251.9763/253.9755.

1-(Benzyloxy)-4-bromo-8-methoxynaphthalene (10). To a solution of the starting naphthol (1.02 g, 4.04 mmol) in DMF (25 mL) was added NaH (107 mg, 4.44 mmol) followed by benzyl bromide (528 μL, 4.44 mmol). The resulting solution was stirred at rt for a 36 h period, quenched with H_2O, and diluted with ether (100 mL). The organic layer was washed with 10% NaOH and saturated brine solution. After the mixture was dried over Na_2SO_4, the solvent was removed *in vacuo* to afford a yellow solid. The two isomeric products were seperated by fractional recrystalization from CH_2Cl_2/hexanes to afford the title compound in quantitative yield (1.25 g): mp 95−96 °C; IR (KBr) 1582, 1568, 1364, 1268, 1051 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.97 (s, 3H), 5.20 (s, 2H), 6.80 (d, 1H, J = 8.4 Hz), 6.96 (d, 1H, J = 7.8 Hz), 7.28−7.75 (m, 7H), 7.86 (dd, 1H, J = 8.5 Hz and 1.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 56.4, 71.7, 107.2, 109.0, 114.3, 119.4, 120.1, 127.0, 127.7, 127.8, 128.4, 130.3, 135.0, 137.3, 156.2, 157.5; MS (EI, m/z) 91 (100), 114 (26), 193/195 (25), 263 (3, $M^+ - Br$), 342/344 (15, M^+); HRMS calcd for $C_{18}H_{15}BrO_2$ 342.0256/344.0236, found 342.0238/344.0217. Anal. Calcd for $C_{18}H_{15}BrO_2$: C, 62.99; H, 4.40. Found: C, 62.89; H, 4.40.

4,4′-(Dibenzyloxy)-5,5′-dimethoxy-1,1′-binaphthyl (11): mp 243−245 °C; IR (KBr) 1586, 1277, 1103, 1054, 1033 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.00 (s, 6H), 5.30 (s, 4H), 6.9 (m, 4H), 7.05 (d, 2H, J = 8.0 Hz), 7.14−7.50 (m, 10H), 7.68 (d, 4H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.4, 71.6, 106.3, 108.2, 118.1, 119.7, 126.3, 127.1, 127.5, 128.4, 132.0, 136.9, 137.8,

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155.8, 157.4; MS (EI, *m*/z) 91 (100), 345 (20), 435 (36, $M^+ - C_7H_7$), 526 (28, M^+); HRMS calcd for $C_{36}H_{30}O_4$ 526.2144, found 526.2124.

4,4′-Dihydroxy-5,5′-dimethoxy-1,1′-binaphthyl (12). To a solution of coupled product **11** (68.5 mg, 0.130 mmol) in CH_2Cl_2 (3 mL) and EtOH (1 mL) was added 10% wt/wt Pd/C (100 mg). The reaction vessel was purged with H_2 and subsequently stirred for 12 h under a hydrogen atmosphere. The reaction contents were then filtered, and the filterings were washed with CH_2Cl_2 (25 mL). The filtrate was concentrated *in vacuo* to afford a clean white solid in quantitative yield: mp 269−271 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.11 (s, 6H), 6.79 (dd, 2H, J = 7.6 and 0.8 Hz), 7.05 (m, 6H), 7.33 (d, 2H, J = 7.8 Hz), 9.54 (s, 2H) (lit.[8] ^{1}H NMR ($CDCl_3$) δ 4.10 (s, 6H), 9.53 (s, 2H)); ^{13}C NMR (50 MHz, $CDCl_3$) δ 56.3, 104.0, 110.1, 115.1, 120.8, 125.5, 129.6, 130.2, 136.1, 154.2, 156.4; MS (EI, *m*/z) 300 (14, $M^+ - C_2H_6O$) 316 (10, $M^+ - C_2H_6$), 331 (6, $M^+ - CH_3$), 346 (100, M^+); HRMS calcd for $C_{22}H_{18}O_4$ 346.1205, found 346.1188.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra are availiable for compunds **9, 11,** and **12** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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