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**Citation:**

A Modified *in Situ* Suzuki Cross-Coupling of Haloarenes for the Preparation of $C_2$-Symmetric Biaryls
Neil G. Andersen, Shawn P. Maddaford, and Brian A. Keay
pp 9556 – 9559.

**Tables:**

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

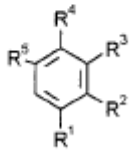
| entry[a] | halide | base | product (% yield)[b] |
|---|---|---|---|
| 1 | iodobenzene | 2 M $Na_2CO_3$ | biphenyl (73) |
| 2 | iodobenzene | $Ba(OH)_2$ | biphenyl (80) |
| 3 | bromobenzene | $Ba(OH)_2$ | biphenyl (85) |
| 4 | 2-bromotoluene | 2 M $Na_2CO_3$ | 2,2′-dimethyl-biphenyl (40) |
| 5 | 2-bromoanisole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

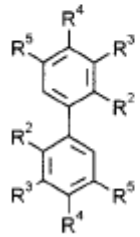
[a] All reactions done in toluene with $Pd(PPh_3)_4$ and 12 h reflux time. [b] Isolated yields.

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

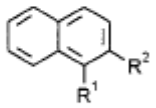
**4f** $R^2$=$CO_2$(*i*-Pr), $R^3$-$R^5$=H

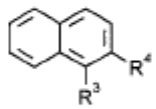
**4g** $R^2$=CON(*i*-Pr)$_2$, $R^3$-$R^5$=H

**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

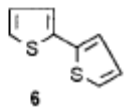
**2c** $R^1$=H, $R^2$=Br

**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

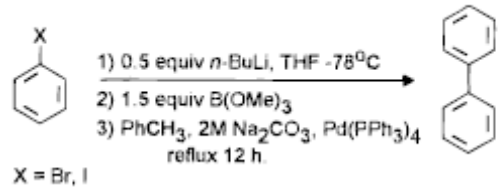
**3**



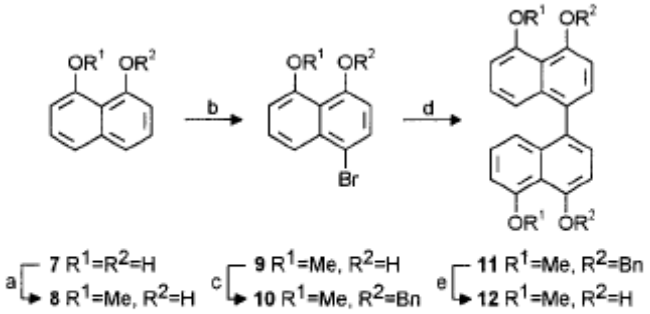
**6**

**Schemes:**

Scheme 1




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%).

**DOI:** 10.1021/jo9617880