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Microwave-promoted Palladium Catalyzed Suzuki Cross-coupling Reaction in Water

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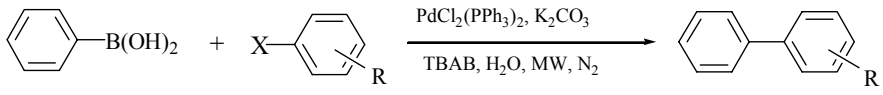
Abstract: A simple, rapid and environmental friendly method for the synthesis of biaryl compounds under microwave irradiation is reported.

Keywords: Suzuki coupling, palladium catalyst, biaryl compounds, microwave irradiation.

Suzuki coupling is probably the most versatile approach among the cross-coupling reactions and the reaction has long been the subject of intensive work in the area of transition-metal chemistry[1]. In recent years, various modifications involving the catalyst, solvents, bases, reaction conditions and synthetic technique have been developed[2].

The Suzuki cross-coupling reaction in water is more safe, economical. It is an environmentally friendly alternative in organic synthesis. The use of water facilitates the catalyst-product separation. We supposed that the combination of metal catalysis and microwave heating in aqueous solvent will facilitate this reaction. The use of microwave irradiation in cross-coupling reaction is well acknowledged[3]. Recently, we have reported the environmental friendly synthesis in water by palladium-catalyzed[4]. The reactions were reviewed by the highlights of *Green Chemistry*[5] . We herein report palladium-catalyzed heterogeneous Suzuki cross-coupling reaction in water using microwave condition. The reactions are shown in the **Scheme 1** and the results are listed in **Table 1**.

Scheme 1



1 **2a-j** **3a-j**

The experimental results showed that the microwave irradiation can shorten the coupling reaction time dramatically (from 6 h to 10 min), the yields of the products are often increased, comparing with the original method[6].

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Table 1 Synthesis of biaryls [a]

Entry	PhX, X=	Product	M.P./°C(Lit.)[7]	Yield(%)[b]
3a				
3b	Br	C_6H_5-C_6H_5	69-70 (71)	90
3c	Br	4-$CH_3C_6H_4$-C_6H_5	46-7 (49-50,47-8[8])	91
3d	Br	4-$CH_3CONHC_6H_4$-C_6H_5	148-9 (149)	92
3e	Br	4-$CH_3COC_6H_4$-C_6H_5	120-1 (121)	93
3f	Br	4-$NO_2C_6H_4$-C_6H_5	112-4 (114)	88
3g	Br	4-$CH_3OC_6H_4$-C_6H_5	88-9 (90)	91
3h	Br	4-$CO_2HC_6H_4$-C_6H_5	227-8 (228)	93
3i	4-BrPhBr	4-C_6H_5-C_6H_4-C_6H_5–4′	212-3 (213)	92
3j	4-ClPhBr	4-ClC_6H_4-C_6H_5	78-9 (77.7)	91
	Br	2-$C_{10}H_7$-C_6H_5	95-6 (103-4,95-6[8])	94

a. All the products gave satisfactory ^{1}HNMR and IR. The reaction were carried out in the presence of K_2CO_3 using $PdCl_2(PPh_3)_2$ as catalyst in water at 750 W for 10 min under nitrogen atmosphere. b. Yield of isolated product.

General prodcedure for the synthesis of biaryls: The aryl bromide (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol), tetrabutylamine bromide (0.3 mmol), H_2O (10 mL) were added in a bottle (50 mL), and irradiated at 750 W for 10 min in microwave oven under nitrogen. After cooling to room temperature, the reaction mixture was extracted with Et_2O (20 mL×3). The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure to afford the biaryls. The product was recrystallized from 95% ethanol or purified by column chromatography on silica gel using petroleum/ethyl acetate (30∶1) as the eluent to give the analytically pure product.

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