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PAPER

A simple and efficient protocol for a palladium-catalyzed ligand-free Suzuki reaction at room temperature in aqueous DMF†

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A convenient, effective and mild protocol has been developed for the palladium-catalyzed ligand-free Suzuki reaction of aryl bromides with arylboronic acids in aqueous *N*,*N*-dimethylformamide (DMF) in the presence of K_2CO_3 and a catalytic amount of $PdCl_2$ in air at room temperature. It is noteworthy that the volume ratio of water–DMF and base play important roles in the reaction, and various functional groups are tolerated under the optimized conditions. Furthermore, this protocol could be extended to the cross-couplings of nitrogen-based heteroaryl halides with arylboronic acids in moderate to excellent yields.

Introduction

The palladium-catalyzed Suzuki cross-coupling reaction of aryl halides with arylboronic acids has become an extremely important method for the construction of carbon–carbon bonds, in particular for the formation of biaryls, due to the broad functional group tolerance and the low toxicity associated with boron compounds.[1,2] The general palladium-catalyzed Suzuki reaction employs phosphine ligands, which are often water- and/or air-sensitive.[3–6] Although some modified ligands could work in water, and even in air, the tedious multi-step synthesis and high cost of these ligands restrict their applications.[7–11] Numerous attempts have been made to develop ligand-free catalytic systems for the Suzuki reaction.[12] However, most systems are operated with the aid of additives, such as surfactants[13–15] or polymers.[12]

With consideration of economy, safety and environment problems, the use of water as a solvent for palladium-catalyzed coupling reactions such as Ullman, Suzuki, Hiyama and Stille couplings in air was first examined by Li and co-workers.[16] The study of Suzuki reactions in water or aqueous–organic mixtures has received much attention since then.[17–23] Due to the ability to dissolve bases in water for activating arylboronic acids, the reaction proceeds much faster in an aqueous medium. Zhang *et al.* reported that the palladium-catalyzed Suzuki reaction of aryl bromides with arylboronic acids occurred smoothly in aqueous acetone[24] or PEG/H_2O[25] in the absence of a ligand. Sajiki and co-workers have described a Pd/C-catalyzed ligand-free system for the Suzuki reaction in a mixture of water and ethanol at room temperature.[26] However, the procedures mentioned above were performed either with heating or over a long reaction time. Very recently, Del Zotto *et al.* developed a fast protocol for the Suzuki reaction in aqueous ethylene glycol monomethyl ether, which is the only example of a highly efficient and ligand-free Suzuki reaction in air at room temperature.[27] There is still considerable room for the development of simple and efficient reaction systems for such transformations.

Water–DMF mixtures are widely used as solvents in organic reactions.[28–33] Artok and co-workers[34,35] have employed aqueous DMF for the Pd(II)-NaY zeolite-catalyzed Suzuki reaction of aryl halides with arylboronic acids using a high palladium loading for a long reaction time at room temperature. We report herein that a fast and efficient Suzuki reaction of aryl bromides with arylboronic acids can be achieved in the presence of $PdCl_2$, K_2CO_3 and aqueous DMF at room temperature in air. Moreover, this simple catalytic system can be applied to the cross-couplings of *N*-heteroaryl halides with arylboronic acids at room temperature after replacing K_2CO_3 with $K_3PO_4 \cdot 7H_2O$.

Results and discussion

Optimization of reaction conditions

As reported in the literature, a suitable amount of water is very important for improving the reactivity of Suzuki reactions.[17,25] We initially studied the impact of the volume ratio of water–DMF on the Suzuki reaction. The coupling of 4-bromoanisole (0.5 mmol) and phenylboronic acid (0.75 mmol) was chosen as the model reaction in 4 mL water–DMF with $PdCl_2$ (0.0025 mmol, 0.44 mg) and K_2CO_3 (1 mmol) at room temperature in air. No coupling took place when just DMF was

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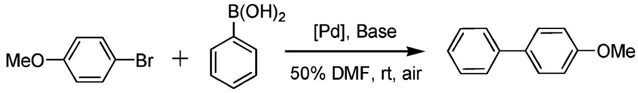
Table 1 Optimization of the reaction conditions for the Suzuki reaction of 4-bromoanisole with phenylboronic acid[a]



Entry	[Pd]	Base	Time/min	Yield (%)[b]
1	$PdCl_2$	K_2CO_3	5	99
2[c]	$PdCl_2$	K_2CO_3	120	84
3	$Pd(OAc)_2$	K_2CO_3	5	94
4	Pd/C	K_2CO_3	5	11
5	$Pd_2(dba)_3$	K_2CO_3	5	trace
6	$PdCl_2$	$K_3PO_4 \cdot 7H_2O$	5	18
7	$PdCl_2$	NaOH	5	17
8	$PdCl_2$	CH_3ONa	5	16
9	$PdCl_2$	$KF \cdot 2H_2O$	5	20

[a] Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), [Pd] (0.0025 mmol), base (1 mmol), DMF–H_2O (2 mL/2 mL), room temperature, in air. The reaction was monitored by TLC. [b] Isolated yield. [c] $PdCl_2$ (0.0005 mmol, 0.088 mg).

used as the solvent. Upon changing the volume ratio of water to DMF from 3 : 1 to 2 : 1, the yield of the product increased from 31 to 81%. A quantitative coupling yield (99%) was obtained when the volume ratio of water–DMF reached 1 : 1. Upon further increasing the water content, the yield dropped sharply to trace in neat water. Hence, the ratio 1 : 1 was the best choice, combined with the maximum water content.

The next investigation in this study was to optimize the conditions of the Suzuki coupling reaction in terms of the palladium species and bases in the same model reaction (see Table 1). The results indicate that $PdCl_2$ (Table 1, entry 1) and $Pd(OAc)_2$ (Table 1, entry 3) have a preferable catalytic activity, while the zero-valent pre-catalysts Pd/C (Table 1, entry 4) and $Pd_2(dba)_3$ (Table 1, entry 5) showed a rather poor catalytic activity under the same reaction conditions. The reason for this might be that both Pd/C and $Pd_2(dba)_3$ are not activated at room temperature, which is consistent with our reported results.[23,36] Besides, the amount of $PdCl_2$ could be decreased even down to 0.0005 mmol, giving an isolated yield of 84% (Table 1, entry 2).

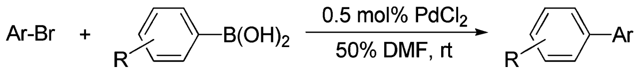
Further studies focused on the effect of bases. The experimental data presented in Table 1, entries 1, 6–9 showed that K_2CO_3 gave the highest yield (99%) in 5 min, resulting in a turnover frequency (TOF) of up to 2400 h^{-1} (Table 1, entry 1). However, the other bases, such as $K_3PO_4 \cdot 7H_2O$, NaOH, CH_3ONa and $KF \cdot 2H_2O$, which are commonly used in Suzuki reactions,[37–39] gave disappointing results (<20%). The results reveal that K_2CO_3 was the exclusive base for activating this catalytic system.

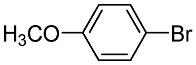
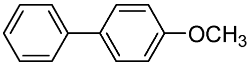
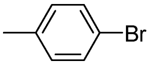
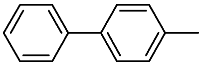
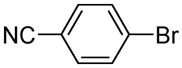
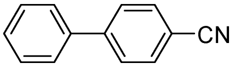
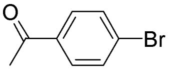
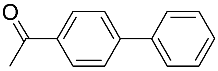
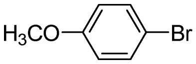
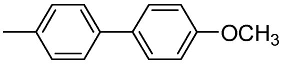
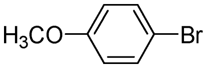
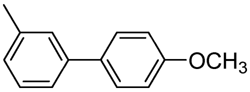
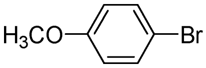
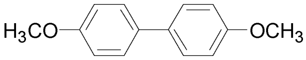
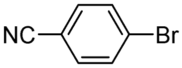
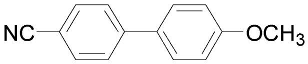
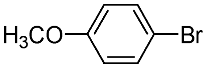
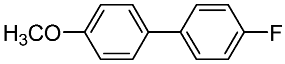
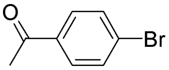
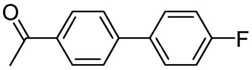
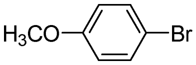
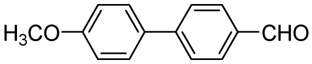
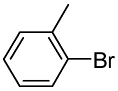
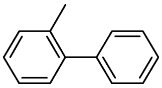
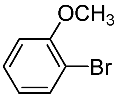
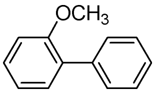
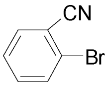
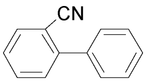
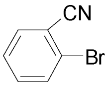
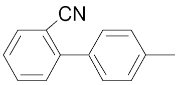
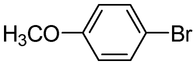
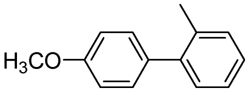
Scope and limitations of substrates

We then explored the scope and limitations of substrates for this protocol under the optimized conditions. As shown in Table 2, in general, all the reactions gave biaryl derivatives in high yield. Various 4-substituted aryl bromides bearing either electron-donating or electron-withdrawing groups, such as methyl, methoxy, cyano and acetyl, provided the corresponding products in good to excellent yields (Table 2, entries 1–4). For example, 4-bromobenzonitrile afforded a quantitative yield in 3 min, resulting in a high TOF of 4000 h^{-1} (Table 2, entry 3). However, substituted arylboronic acids containing electron-withdrawing groups showed a slightly lower reactivity than those containing electron-donating or neutral groups, due to the effect of these substituents on the nucleophilicity on the arylboronic acid. Therefore, 4-fluoro-phenylboronic acid completed the reaction in a longer time than arylboronic acids with electron-donating groups (Table 2, entries 5–7 *vs.* entries 9–11). Besides, the protocol tolerated the presence of functional groups in the *ortho* position of the aryl bromide and arylboronic acid. In comparison to the non-sterically-hindered substrates, the *ortho*-substituted substrates were coupled in good to excellent yields in almost the same reaction time (Table 2, entries 12–15), even sometimes in a shorter reaction time (Table 2, entry 17). The most challenging combination was the cross-coupling of 2-bromoanisole with 2-methoxy-phenylboronic acid, which gave a quantitative yield in 10 min (Table 2, entry 18). To the best of our knowledge, this is the most effective protocol for the synthesis of such products.[40,41] Overall, because of the high activity of this catalytic system, both steric and electronic effects made only a small impact on the reaction rate. Thus, the scope of this protocol is quite broad.

As far as we know, the ligand-free Suzuki reaction of heterocycle-containing substrates usually proceeds with additional heating due to its low reactivity.[42–44] Only one paper,[27] to the best of our knowledge, has reported the cross-coupling of *N*-heteroaryl halides with arylboronic acids at room temperature in aqueous media. However, the limitation was that only a moderate yield of the target product was obtained when 2-bromopyridine reacted with phenylboronic acid. The present protocol was also extended to the synthesis of nitrogen-based heterobiaryls. The results are summarized in Table 3. Noticeably, the Suzuki reaction of 2-bromopyridine with phenylboronic acid using $K_3PO_4 \cdot 7H_2O$ as the base was more effective than using K_2CO_3 under the same conditions (Table 3, entries 1 and 2), affording the product in 81% yield. Thus, the coupling reactions of arylboronic acids containing electron-donating groups, such as methyl or methoxy, afforded a slightly higher yield than that of phenylboronic acid using a $PdCl_2$ loading of 1.5 mol% (0.0075 mmol, 1.32 mg; Table 3, entries 3 and 4), while an arylboronic acid bearing electronic-withdrawing groups, such as a fluoro group, merely converted in a moderate yield (Table 3, entry 5). It is worth noting that the coupling of 5-bromo-2-methoxypyridine with phenylboronic acid gave the product in 98% yield. Compared with the reported methods,[45,46] this is the most efficient catalytic system for such a transformation. In addition, the electronic effect had little influence on the reactivity of the arylboronic acid (Table 3, entry 6). Both electron-rich and electron-deficient arylboronic acids completed the reaction in quantitative yields within 1 h (Table 3, entries 7 and 8). However, the reaction between 5-bromo-2-methoxypyridine and 2-methylphenylboronic acid gave only 52% yield in 3 h due to the effect of steric hindrance (Table 3, entry 9). Another noteworthy result was that the couplings of 2-chloropyrazine with 4-methylphenyl boronic acid or phenylboronic acid afforded high yields (Table 3, entries 10 and 11) after a prolonged period. To the best of our knowledge, this is the first example where a Suzuki reaction of an *N*-heteroaryl chloride could be performed smoothly in an aqueous medium at room temperature in air.

Table 2 Suzuki reactions of aryl bromides with arylboronic acids[a]



Entry	Ar–Br	R	Product	Time/min	Yield (%)[b]
1		H		5	99
2		H		15	85
3		H		3	99
4		H		10	99
5		$4\text{-}CH_3$		6	94
6		$3\text{-}CH_3$		6	99
7		$4\text{-}OCH_3$		15	99
8		$4\text{-}OCH_3$		25	97
9		4-F		25	99
10		4-F		14	99
11		4-CHO		120	76
12		H		15	72
13		H		6	97
14		H		6	99
15		$4\text{-}CH_3$		5	99
16		$2\text{-}CH_3$		12	99

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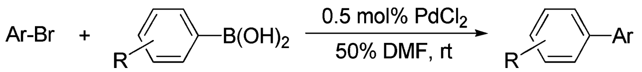
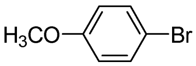
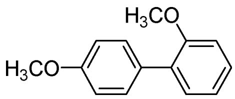
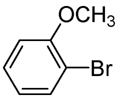
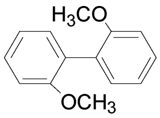
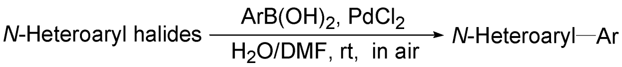


Entry	Ar–Br	R	Product	Time/min	Yield (%)[b]
17		2-OCH$_3$		5	99
18		2-OCH$_3$		10	99

[a] Reaction conditions: aryl bromides (0.5 mmol), arylboronic acids (0.75 mmol), K_2CO_3 (1 mmol), $PdCl_2$ (0.0025 mmol, 0.44 mg), DMF–H_2O (2 mL/2 mL), room temperature, in air. The reaction was monitored by TLC. [b] Isolated yield.

Table 3 The Suzuki reaction of *N*-heteroaryl halides with arylboronic acids[a]



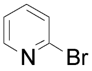
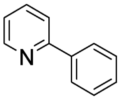
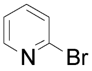
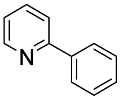
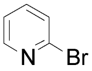
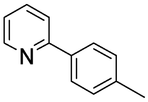
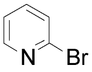
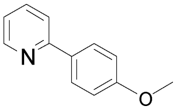
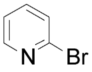
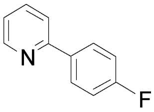
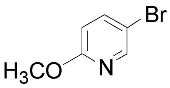
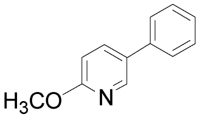
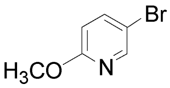
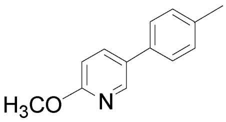
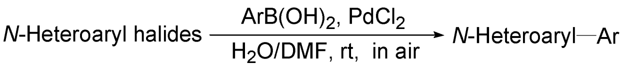
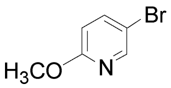
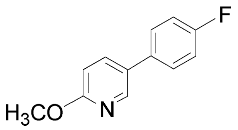
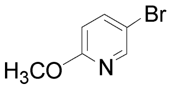
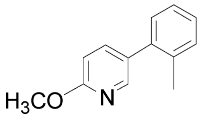
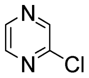
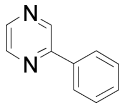
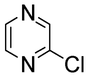
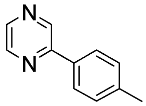
Entry	*N*-Heteroaryl halides	Product	Time/h	Yield (%)[b]
1			12	55[c]
2			12	81
3			12	98
4			12	83
5			12	68
6			1	98
7			0.75	99

Table 3 *(Contd.)*



Entry	*N*-Heteroaryl halides	Product	Time/h	Yield (%)[b]
8			1	95
9			3	52
10			24	83
11			24	88

[a] Reaction conditions: heteroaryl halide (0.5 mmol), arylboronic acid (0.75 mmol), $PdCl_2$ (0.0075 mmol, 1.32 mg), $K_3PO_4 \cdot 7H_2O$ (1 mmol), DMF–H_2O (2 mL/2 mL), rt, in air. The reaction was monitored by TLC. [b] Isolated yield. [c] K_2CO_3 (1 mmol) instead of $K_3PO_4 \cdot 7H_2O$.

The effect of atmosphere on the Suzuki reactions

Inspired by two recently reported oxygen-promoted systems, PEG-400/Pd$(OAc)_2$[36,47] and Pd$(OAc)_2$/*i*-PrOH/H_2O,[44] we further examined the effect of different atmospheres on the Suzuki reaction. The results are illustrated in Table 4. We observed that all the reactions carried out under aerobic conditions worked better than those under nitrogen. However, the atmosphere had a different effect on the Suzuki reaction of different substrates. For example, the cross-coupling of 4-bromobenzonitrile with 4-methoxyphenylboronic acid resulted in a 97% isolated yield in air (Table 4, entry 1a) and 96% isolated yield in nitrogen (Table 4, entry 1b) after the same reaction time (25 min).

Noticeably, the Suzuki reaction between 2-bromopyridine and phenylboronic acid using $K_3PO_4 \cdot 7H_2O$ as the base in open air resulted in an 81% isolated yield in 12 h (Table 4, entry 4a), while the isolated yield decreased to 16% in nitrogen (Table 4, entry 4b). Although the mechanism involving oxygen in the reaction is unclear, we propose that a peroxo-palladium complex might be formed in the presence of oxygen[48,49] that accelerates the oxidative addition step due to the enhanced electron density of the palladium.

Conclusions

In summary, we have developed a simple and highly active ligand-free protocol for the palladium-catalyzed Suzuki coupling of aryl bromides with arylboronic acids in air in aqueous DMF at room temperature. It is noteworthy that a wide range of groups could be tolerated. Moreover, this protocol could be extended to the synthesis of nitrogen-based heterobiaryls. The role of oxygen in the reaction and further applications of this system in other transformations are currently under investigation in our laboratory.

Experimental section

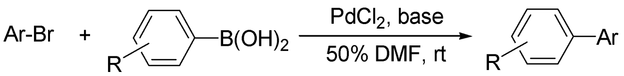
General remarks

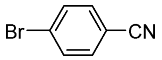
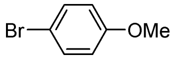
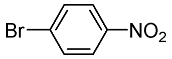
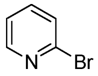
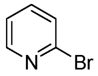
Unless otherwise noted, all the reactions were carried out in air. All aryl halides and arylboronic acids were purchased from Alfa Aesar, Avocado and used without purification. NMR spectra were recorded on a Varian Inova 400 spectrometer. Chemical shifts are reported in ppm relative to TMS. Mass spectroscopy data of the product were collected on an MS-EI instrument. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted. Compounds described in the literature were characterized by ^{1}H NMR spectra and compared to reported data.

General procedure for the Suzuki reaction of aryl bromides with arylboronic acids

A mixture of aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), $PdCl_2$ (0.0025 mmol, 0.44 mg), K_2CO_3 (1 mmol), distilled water (2 mL) and DMF (2 mL) was stirred at room temperature in air for the indicated time. The mixture was added to brine (15 mL) and extracted four times with diethyl ether (4 × 15 mL). The solvent was concentrated under vacuum and the product isolated by short chromatography on a silica gel (200–300 mesh) column.

Table 4 The effect of atmosphere on the Suzuki reaction[a]



Entry	Ar–Br	R	Atmosphere	Time/min	Yield (%)[b]
1a		4-OMe	Air	25	97
1b			N_2	25	96
2a		4-F	Air	25	99
2b			N_2	25	94
3a		H	Air	25	77
3b			N_2	25	37
4a		H	Air	720	81
4b			N_2	720	16
5a		4-OMe	Air	720	83
5b			N_2	720	72

[a] Reaction conditions: aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), K_2CO_3 (1 mmol) (1 mmol K_3PO_4·$7H_2O$ for 4a, 4b, 5a and 5b), $PdCl_2$ (0.0025 mmol, 0.44 mg) (0.0075 mmol, 1.32 mg for 4a, 4b, 5a and 5b), DMF–H_2O (2 mL/2 mL), room temperature. [b] Isolated yield. [c] The DMF and H_2O were de-gassed.

General procedure for the Suzuki Reaction of *N*-heteroaryl halides with arylboronic acids

$PdCl_2$ (0.0075 mmol, 1.32 mg) and K_3PO_4·$7H_2O$ (1 mmol) were used instead of $PdCl_2$ (0.0025 mmol, 0.44 mg) and K_2CO_3 (1 mmol) in the above procedure, respectively.

2-Methoxyl-5-(4-fluorophenyl)pyridine. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.33 (d, J = 2.4 Hz, 1H), 7.74 (dd, J = 8.4, 2.4 Hz), 7.49–7.45 (m, 2H), 7.15–7.11 (m, 2H), 6.81 (d, J = 8.4, 1H), 3.98 (s, 3H); ^{13}C NMR δ 163.6 (d, J = 246.4 Hz), 161.2, 144.8, 137.4, 134.1 (d, J = 3.04 Hz), 129.2, 128.3 (d, J = 8.10 Hz), 115.9 (d, J = 21.25 Hz), 110.9, 53.57; MS (EI) m/z 203 (M$^+$, 100%): 204, 175, 172, 146, 133, 132, 107, 83, 63. Melting point: 75 °C.

2-Methoxyl-5-(*o*-tolyl)pyridine. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.13 (d, J = 2.8 Hz, 1H), 7.54 (dd, J = 8.8, 2.4 Hz, 1H), 7.28–7.19 (m, 4H), 6.79 (d, J = 8.4, 1H), 3.98 (s, 3H), 2.27 (s, 3H); ^{13}C NMR δ 163.3, 146.7, 139.7, 138.3, 135.9, 130.7, 130.6, 130.1, 127.8, 126.2, 110.3, 53.6, 20.6; MS (EI) m/z 199 (M$^+$, 100%): 200, 198, 170, 169, 167, 154, 141, 128, 127, 115, 102, 89, 77, 63, 48, 39.

Acknowledgements

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