

A highly efficient and recyclable ligand-free protocol for the Suzuki coupling reaction of potassium aryltrifluoroborates in water†

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Cite this: *Green Chem.*, 2014, **16**, 2185

Received 23rd October 2013,
Accepted 30th December 2013

DOI: 10.1039/c3gc42182a

www.rsc.org/greenchem

A highly efficient, recyclable and ligand-free protocol was developed for the Suzuki coupling of aryl halides with potassium aryltrifluoroborates in water using Pd(OAc)₂ as a catalyst and Na₂CO₃ as a base in air. The presence of poly(ethylene glycol) (PEG) was crucial to the efficiency of the protocol. A wide range of functional groups were tolerated under the optimized conditions. Furthermore, the protocol could be extended to the Suzuki coupling of heteroaryl halides with potassium phenyltrifluoroborate, delivering the desired products in moderate to excellent yields. After simple workup, Pd(OAc)₂-H₂O-PEG could be recycled at least eight times without significant loss in activity.

Introduction

Palladium-catalyzed Suzuki cross-coupling reaction of aryl halides with organoboron nucleophiles has become one of the most powerful and important synthetic methods for carbon-carbon bond formation to construct biaryl compounds,¹ which are found widely in natural products, pharmaceuticals and functional materials.² Since the pioneering studies reported by Genêt *et al.* in 1997,³ potassium organotrifluoroborate salts have emerged as an attractive and promising alternative to organoboronic acids.⁴ These salts exhibit several advantages over organoboronic acids, although organoboronic acids have been used and studied extensively in Suzuki cross-coupling reactions.⁵ Potassium organotrifluoroborates can be easily purified and readily prepared from the corresponding organoboronic acids or esters by treatment with inexpensive KHF₂ in MeOH-H₂O.⁶ They are generally crystalline and monomeric solids, air and water stable and easier to handle. Great efforts have been devoted to the development of an efficient catalytic system for the Suzuki coupling of arylboronic acid in water.^{7,8} However, the Suzuki coupling reaction involving potassium organotrifluoroborates has been underdeveloped compared with organoboronic acids. Recently, efficient catalytic systems have been developed by Molander, Kwong, and many other research groups for the Suzuki coupling of potassium

organotrifluoroborates, by using ligands including phosphine-base and N-containing ligands,⁹ microwave techniques,¹⁰ and some heterogeneous catalysts, such as Pd/C.¹¹

One of the hottest topics in green chemistry is the use of an environmentally benign reaction medium to replace volatile and poisonous organic solvents. Water, the most abundant molecule on Earth, is safe, inexpensive, non-toxic, non-inflammable and environment-friendly.^{8,12} It is an ideal green solvent for use in organic synthesis. The first ligand-free Suzuki coupling reaction of aryl halides with potassium aryltrifluoroborates in water was reported by Molander *et al.*¹³ They found that only water-soluble aryl halides bearing -COOH or -OH could be coupled in pure water using Pd(OAc)₂ as a catalyst and K₂CO₃ as a base. In view of our general interest in palladium-catalyzed cross-coupling reactions and cleaner chemical processes, we herein report a highly efficient, recyclable and ligand-free catalytic system for the Suzuki coupling of aryl halides and heteroaryl halides with potassium aryltrifluoroborates in water. This catalytic system, using Pd(OAc)₂ as a catalyst and Na₂CO₃ as a base with poly(ethylene glycol) (PEG) additive, was shown to be extremely efficient for the Suzuki coupling of aryl and heteroaryl bromides with potassium aryltrifluoroborates. These reactions could be carried out in air under 80 °C without the use of microwaves or protection of inert gases.

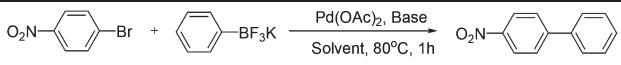
Results and discussion

Optimization of reaction conditions

First, the optimal reaction conditions of this protocol were studied by choosing the Suzuki coupling reaction of 1-bromo-

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† Electronic supplementary information (ESI) available: Experimental details and characterization of the Suzuki coupling products. See DOI: 10.1039/c3gc42182a

Table 1 The effect of a solvent and a base on the Suzuki coupling reaction of 1-bromo-4-nitrobenzene with potassium phenyltrifluoroborate^a


Entry	Solvent	Base	Yield ^b (%)
1	H ₂ O (3 g)	Na ₂ CO ₃	Trace
2	PEG2000–H ₂ O (3 : 3 g)	Na ₂ CO ₃	99
3	PEG2000 (3 g)	Na ₂ CO ₃	42
4	PEG400–H ₂ O (3 : 3 g)	Na ₂ CO ₃	95
5	PEG1000–H ₂ O (3 : 3 g)	Na ₂ CO ₃	98
6	PEG4000–H ₂ O (3 : 3 g)	Na ₂ CO ₃	88
7	PEG6000–H ₂ O (3 : 3 g)	Na ₂ CO ₃	85
8	PEG2000–H ₂ O (3 : 3 g)	No base	35
9	PEG2000–H ₂ O (3 : 3 g)	K ₂ CO ₃	98
10	PEG2000–H ₂ O (3 : 3 g)	NaOH	98
11	PEG2000–H ₂ O (3 : 3 g)	K ₃ PO ₄	98
12	PEG2000–H ₂ O (3 : 3 g)	NaOAc	88
13	PEG2000–H ₂ O (3 : 3 g)	NEt ₃	97
14	PEG2000–H ₂ O (3 : 3 g)	Pyridine	Trace

^a Reaction conditions: 1-bromo-4-nitrobenzene (0.5 mmol), PhBF₃K (0.60 mmol), Pd(OAc)₂ (1 mol%), base (1 mmol), 80 °C, 1 h, in air.
^b Isolated yields.

4-nitrobenzene (0.5 mmol) with potassium phenyltrifluoroborate (0.60 mmol) as the model reaction in terms of solvent and base. Only a trace amount of the desired product was obtained when the reaction was conducted in pure water (3 g) using Pd(OAc)₂ (1 mol%) as a catalyst and Na₂CO₃ (1 mmol) as a base at 80 °C for 1 h (Table 1, entry 1). Poly(ethylene glycol)s (PEGs), being cheap, commercially available, low toxic, inflammable and non-corrosive, are environment-benign polymers and omnipresent in our everyday lives.¹⁴ They can be used as polymeric supports, phase transfer catalysts, and eco-friendly reaction media in modern organic synthesis. Therefore, the effect of addition of PEG to the above system was studied. It is noteworthy that the addition of PEG2000 (3 g) led to a dramatic increase in activity, and 99% isolated yield for the product was achieved (Table 1, entry 2). This result demonstrated that the presence of PEG played a vital role in the efficiency of this ligand-free protocol in water. It was reported in the literature that palladium nanoparticles could be generated in pure PEGs and PEGs–H₂O.^{15,16} In these systems, PEGs acted not only as a reductant but also as a stabilizer of palladium nanoparticles. The high efficiency of our protocol was probably attributed to palladium nanoparticles generated *in situ* during the reaction process.

It was well documented that the chain length of PEGs had a differential influence on the efficiency of metal-catalyzed reactions.^{15a} Therefore the effect of the chain length of PEGs was next investigated. As shown in Table 1, we could see that the chain length range from PEG400 to PEG6000 had a slight effect on the efficiency of the catalytic system, while PEG6000 provided lower efficiency (Table 1, entries 2 and 4–7). PEG2000 was used as an additive in the following experiment.

Further studies exploring the effect of commonly-used bases on the efficiency of the protocol were carried out. Little reaction was observed without a base (Table 1, entry 8).

Inorganic bases, such as Na₂CO₃, K₂CO₃, K₃PO₄, NaOH, and NaOAc, afforded the desired product in good to excellent yields (Table 1, entries 2 and 9–12). The organic base NEt₃ could afford the product in much higher yield than that when pyridine was used (Table 1, entries 13–14). With the consideration of practical application, Na₂CO₃ was chosen as the optimal base for enhancing the efficiency of this protocol.

Scope and limitations of substrates

To explore the scope and limitations of this protocol, the Suzuki coupling reactions of a wide range of aryl bromides with potassium aryltrifluoroborates were studied (Table 2). All reactions were performed in water (3 g) using Pd(OAc)₂ (1 mol%) as a catalyst, Na₂CO₃ (1 mmol) as a base with PEG2000 (3 g) additive at 80 °C in air. It was obvious that the current protocol was applicable to various aryl bromides, and both electron-deficient and electron-rich aryl bromides gave the corresponding products in good to excellent yields (Table 2, entries 1–13). A broad range of functional groups, such as –NH₂, –OH, –NO₂, –CN, –CF₃, –COMe, –Me and –OMe, were tolerated in the catalytic system. Sterically demanding aryl bromide could be coupled with potassium phenyltrifluoroborate to give good yield of product (Table 2, entry 7). For the Suzuki coupling of 1-bromonaphthalene and 2-bromonaphthalene with potassium phenyltrifluoroborate, the desired products were obtained in excellent yields (Table 2, entries 12–13). In addition, the Suzuki coupling of aryl chlorides with potassium phenyltrifluoroborate was also studied. Only a trace amount of the product was found in the Suzuki coupling reaction of 1-chloro-4-nitrobenzene with potassium phenyltrifluoroborate (Table 2, entry 22), while a moderate yield was obtained when only PEG2000 was used as the solvent under enhanced reaction conditions (Table 2, entry 23).

The generality of various potassium aryltrifluoroborate was next investigated. The potassium aryltrifluoroborate bearing an electron-donating group underwent the Suzuki coupling smoothly to afford the desired product in excellent yield (Table 2, entries 14–17 and 19), while potassium aryltrifluoroborate bearing an electron-withdrawing substitution gave a much lower yield (Table 2, entries 18 and 20). Sterically demanding potassium 2-methylphenyltrifluoroborate was also effective in the coupling reaction with 1-bromo-4-nitrobenzene and 2-bromotoluene to generate the corresponding biaryls in moderate to good yields (Table 2, entries 16 and 21).

It was well documented that catalytic systems developed for the Suzuki coupling of arylboronic acids were often limited to the construction of non-heteroaryl–aryl units, and were usually difficult for the synthesis of heterocyclic biaryl derivatives.^{16,17} Therefore, the Suzuki coupling of heteroaryl halides was next investigated with potassium phenyltrifluoroborate in our catalytic system. As shown in Table 3, we found that heteroaryl bromides could be coupled smoothly under the optimized conditions, and moderate to excellent yields of the products were obtained (Table 3, entries 1–10). 2-Bromopyridine and 3-bromopyridine could be coupled smoothly with PhBF₃K to afford the desired products in good yields (Table 3, entries 1

Table 2 Suzuki coupling of aryl halides with potassium aryltrifluoroborates in water^a

Entry	Aryl halides	ArBF ₃ K	Time	Yield ^d (%)
1			1 h	99
2			1 h	98
3			1 h	74 (84) ^b
4			1 h	90 (99) ^b
5			1 h	88 (98) ^b
6			4 h	96
7			4 h	85
8			4 h	95
9			4 h	99
10			4 h	99
11			4 h	98
12			4 h	90
13			4 h	96
14			1 h	99
15			1 h	98
16			1 h	98
17			1 h	96
18			1 h	65
19			4 h	89
20			4 h	70

Table 2 (Contd.)

Entry	Aryl halides	ArBF ₃ K	Time	Yield ^d (%)
21			4 h	60
22			8 h	Trace
23			12 h	48 ^c

^a Reaction conditions: aryl halide (0.5 mmol), ArBF₃K (0.60 mmol), Pd(OAc)₂ (1 mol%), Na₂CO₃ (1 mmol), H₂O-PEG2000 (3 : 3 g), 80 °C. ^b The reaction time was 2 h. ^c The reaction was carried out in pure PEG2000 (3 g) and the temperature is 120 °C. ^d Isolated yields.

Table 3 The Suzuki coupling of heteroaryl halides with potassium phenyltrifluoroborate^a

Entry	Heteroaryl halide	Product	Conditions	Yield ^d (%)
1			4 h	75
2			8 h	87
3			4 h	99
4			4 h	90
5			4 h	No
6			4 h	96
7			4 h, 100 °C 15 h, 100 °C	40 70
8			4 h	25
9			4 h	85
10 ^b			18 h	86
11			15 h, 100 °C	10
12			15 h, 100 °C	35 ^c

^a Reaction conditions: heteroaryl halides (0.5 mmol), PhBF₃K (0.60 mmol), Na₂CO₃ (1 mmol), Pd(OAc)₂ (1 mol%), PEG2000-H₂O (3 : 3 g), 80 °C, 4 h, in air. ^b PhBF₃K (1.2 mmol), Na₂CO₃ (2 mmol), Pd(OAc)₂ (2 mol%). ^c The amount of Pd(OAc)₂ was 3 mol%. ^d Isolated yields.

and 2). Good to excellent yields were achieved in the Suzuki coupling of 5-bromopyrimidine, 2-bromopyrazine (Table 3, entries 3 and 4), and no coupling product was found in the Suzuki coupling of 2-bromopyrimidine (Table 3, entry 5). For the Suzuki coupling of 3-bromoquinoline with PhBF_3K , the desired product was obtained in 96% isolated yield while 4-bromoisoquinoline gave a much lower yield even under enhanced reaction conditions (Table 3, entries 6 and 7). In the Suzuki reaction of chloropyridine, the catalytic system showed poor catalytic efficiency, delivering the desired products in low yields (Table 3, entries 11 and 12). It was reported in the literature that organic materials (conjugated molecules or oligomers) containing the thiophene unit had good optoelectronic properties, and they could be used as organic semiconductors.¹⁸ Therefore, the Suzuki coupling of 2-bromothiophene and 3-bromothiophene with PhBF_3K was also studied in our catalytic system. Under the optimized conditions, 3-bromothiophene gave the desired product in much higher yield than 2-bromothiophene, with the isolated yields 85% and 25%, respectively (Table 3, entries 8 and 9). 2,5-Dibromothiophene could afford the bis-coupling product in good yield (Table 3, entry 10).

The reusability of the catalyst was next investigated using the Suzuki coupling of 1-bromo-4-nitrobenzene with potassium phenyltrifluoroborate in the presence of $\text{Pd}(\text{OAc})_2$ and Na_2CO_3 at 80 °C for 1 h using H_2O -PEG as the medium. After the first cycle, $\text{Pd}(\text{OAc})_2$ - H_2O -PEG was subjected to the next run by charging with 1-bromo-4-nitrobenzene, potassium phenyltrifluoroborate and Na_2CO_3 . The results are shown in Fig. 1. It was clear that the $\text{Pd}(\text{OAc})_2$ - H_2O -PEG catalytic system could be recycled at least eight times without significant loss in activity. It was reported by Joucla *et al.* that a heterogeneous Pd/C catalyst could be used as a recyclable catalyst in the vinylation of aryl bromides, and the stability of the catalyst was dependent on the addition of the base.^{11d} Therefore, we studied the reusability of the catalyst without any addition of Na_2CO_3 . The yields for the first three cycles were 99%, 70% and 45%, respectively. This result demonstrated that the

presence of a base had a prominent effect on the reusability of the catalytic system.

Conclusions

In summary, we have developed a highly efficient and recyclable ligand-free protocol for the Suzuki coupling of aryl halides with potassium aryltrifluoroborates in water using $\text{Pd}(\text{OAc})_2$ and Na_2CO_3 with PEG additive. A wide range of functional groups were tolerated in the catalytic system, and good to excellent yields were obtained under the optimized conditions. Additionally, the catalytic system could be extended to the Suzuki coupling of heteroaryl halides, and moderate to excellent yields of the products were obtained. This methodology offered a green, novel alternative way for the synthesis of both aryl-aryl and heteroaryl-aryl units. What's more, the catalytic system, $\text{Pd}(\text{OAc})_2$ - H_2O -PEG, could be recycled at least eight times without significant loss in activity. The Suzuki coupling involving potassium aryltrifluoroborates in water was performed in our laboratory.

Experimental section

General

All reactions were carried out in air without any protection of inert gases. Potassium aryltrifluoroborates used were prepared by corresponding arylboronic acids following the method reported in the literature.⁶ Other starting materials were purchased from common commercial sources and used without further purification. All products were isolated by chromatography on a silica gel (300–400 mesh) using petroleum ether (60 °C–90 °C) and ethyl acetate.

¹H NMR spectra were recorded on a Bruker Avance 300 MHz or 400 MHz spectrometer using TMS as an internal standard (CDCl_3 : δ 7.26 ppm, *d*-DMSO: δ 2.50 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. Mass spectroscopy data were collected on a Shimadzu GCMS-QP 2010 instrument.

Typical procedure for the product

General procedure for the Suzuki coupling of aryl and heteroaryl halides with potassium aryltrifluoroborates. A 25 mL round-bottom flask was charged with aryl or heteroaryl halide (0.5 mmol), ArBF_3K (0.60 mmol), base (1 mmol), $\text{Pd}(\text{OAc})_2$ (1 mol%), and H_2O -PEG (3 : 3 g) and the mixture was stirred at 80 °C for the indicated time in air. Then the mixture was cooled to room temperature, and extracted using diethyl ether (4 × 10 mL). The combined organic layer was concentrated under reduced pressure. And the residue was isolated by chromatography on a silica gel (300–400 mesh) column using petroleum and ethyl acetate to afford the corresponding biaryl product.

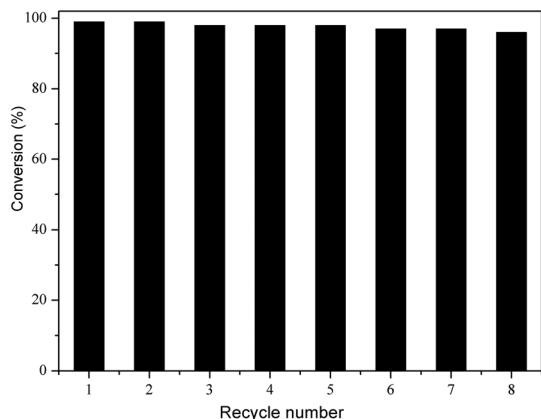


Fig. 1 The reusability of $\text{Pd}(\text{OAc})_2$ - H_2O -PEG in the Suzuki coupling reaction of 1-bromo-4-nitrobenzene with potassium phenyltrifluoroborate.

General procedure for the reusability of Pd(OAc)₂-H₂O-PEG in the Suzuki coupling reaction of 1-bromo-4-nitrobenzene with PhBF₃K. A 25 mL round-bottom flask was charged with 1-bromo-4-nitrobenzene (0.5 mmol), PhBF₃K (0.60 mmol), Na₂CO₃ (1 mmol), Pd(OAc)₂ (1 mol%), and H₂O-PEG (3 : 3 g) and the mixture was stirred at 80 °C for 1 h. Then the mixture was cooled to room temperature, and extracted using diethyl ether (4 × 10 mL). The residue (Pd(OAc)₂-H₂O-PEG) was subjected to the next run of the Suzuki reaction by charging with the same substrates (1-bromo-4-nitrobenzene (0.5 mmol), PhBF₃K (0.60 mmol), Na₂CO₃ (1 mmol)) under the same reaction conditions. Water (0.5 mL) was added to the catalytic system in the third, fifth and seventh runs. The combined organic layer was concentrated under reduced pressure, and the residue was isolated by chromatography on a silica gel (300–400 mesh) column using petroleum and ethyl acetate to afford the product.

Acknowledgements

Financial support from the Natural Science Foundation of Shandong Province (ZR2010BQ022, ZR2010BL015, and J10LB55) and Dezhou University (08RC14) is acknowledged.

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