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ORIGINAL PAPER

POPd/TBAB co-catalyzed Suzuki cross-coupling reaction of heteroaryl chlorides/bromides with 4-fluorophenylboronic acid in water

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Abstract An organic solvent free and efficient heterogeneous synthesis for bridging heteroaryl halides and 4-fluorophenylboronic acid was studied in aqueous media according to the Suzuki cross-coupling protocol. High yields of heteroaryl-aryl fluorides were successfully obtained with: chloro-/bromo-substituted pyridine, thiophene, indole, and inzole in neat water using palladium phosphinous acid complexes (POPd)/tetrabutylammonium bromide (TBAB) as co-catalysts. A possible mechanism for the heterogeneous coupling reaction is proposed and discussed according to the function of the TBAB interphases. The notable properties of the reported method are highly co-catalytic activity, hetero-atom tolerance, simple separating procedure and little environmental disposal impact.

Keywords POPd/TBAB co-catalysis · Heterogeneous Suzuki cross-coupling reaction · Heteroaryl-aryl fluorides · Green chemistry

Introduction

Fluorinated aromatic compounds are of increasing interest due to their ability to provide functional synthetic intermediates, medicinal agents, and organic materials, e.g., the fluorinated heteroaryl-aryl group is found in many natural products that exhibit remarkable biological activities [1, 2]. Fluorinated heteroaryl-aryl compounds are also deemed as the effective structural moieties for the manufacture of pharmaceutical [3–6] and agrochemical products [7–9]. Advantageously, fluorine substituents can enhance the lifetime and activity of pharmaceutical and agrochemical chemicals in a multitude of approaches [10]. The introduction of fluorine into heteroaryl-aryl molecules can significantly improve molecular properties and electronic stabilities [5, 11, 12], but the synthesis of C–F bond within heteroaromatic compounds still remains challenging. Since fluorinated polycyclic aromatic hydrocarbons (FPAHs) are not naturally occurring, these compounds are synthesized according to the specific synthetic routes such as Balz–Schiemann reaction [7, 13, 14] or transition-metal-mediated fluorination [9, 15], which is still a significant challenge for aryl C–F bond formation [8, 16, 17].

In an alternative approach, Pd-catalyzed Suzuki cross-coupling reactions [18, 19] of heteroaryl halides and fluorinated arylboronic acid leading to the coupling of heteroaryl-aryl compounds is another proposed efficient indirect synthetic route for C–F aromatic compound formation. It has also been demonstrated that with this approach, Suzuki cross-coupling reactions can be performed using environmentally friendly aqueous solvent systems [20]. The formation of the $C(sp_2)$–$C(sp_2)$, $C(sp_2)$–$C(sp_3)$ and $C(sp_3)$–$C(sp_3)$ bonds involves the nucleophilic aromatic substitution reactions between electron-deficient organic halides and organoboronic reagents [21, 22]. Both coupling components must be functionalized on the noble metal sites following oxidative-transmetallic-reductive cycling steps, and the required organometallic nucleophilic reagents should be highly efficient. The use of water provides an environmentally and economically more attractive method compared with the use of traditional organic reaction solvents. Water is generally regarded as the ultimate green solvent for

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organic synthesis. Hence, water based heterogeneous Suzuki cross-coupling reactions represent an attractive, simple, flexible, and robust alternative to the traditional organic solvent-catalyzed route especially when used to synthesize FPAHs.

Phosphinous acid complex [(*t*-Bu)$_2$P(OH)]$_2$PdCl$_2$ (POPd) was reported as a highly effective and environmental friendly Pd-catalyst for Suzuki cross-coupling reaction of (hetero) aryl halides and arylboronic acids [23–25]. POPd and its family derivatives [[(*t*-Bu)$_2$P-(OH)(*t*-Bu)$_2$PO)]PdCl]$_2$ (POPd1) and [(*t*-Bu)$_2$P(OH)PdCl$_2$]$_2$ (POPd2) are typically characterized as air-stable, with good water solubility, high reactivity, and easy separation from the organic mixtures, their steric molecular frameworks are depicted in Fig. 1 [23].

The properties of the heteroaryl-aryl structural unit in biologically and synthetically important molecules have attracted considerable attention in the development of novel methods for C_{Ar}–C_{Ar} bond formation. Traditional methods [26, 27] for making fluoro-aromatics, use expensive reagents and produce a large amount of undesired by-products. In contrast, the synthetic procedure described in this report using inexpensive water as the liquid phase allows the production of fluoroaromatics by an efficient, cost-effective, and environmentally friendly heterogeneous process. This study describes the further development of the efficient synthetic procedures to prepare biologically relevant heterocyclic compounds. In particular, these recent studies have been directed towards the heterogeneous preparative synthesis of a diverse range of heteroaryl-aryl fluorides using POPd/TBAB co-catalyzed Suzuki cross-coupling reactions in a water based solvent system. The TBAB served to function as a phase transfer catalyst (PTC) in these reactions.

Experimental

General remarks

Synthesis of heteroaryl-aryl fluorides was performed in a Schlenk glass tube under nitrogen atmosphere. Flash column chromatography was performed using silica gel (pore size 60 Å, standard grade) and 0.65–0.85 mm particle size sand. Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 200–300 mesh silica gel impregnated with a fluorescent indicator (silica gel 60 F254, Sinopharm Chemical Reagent Co., Ltd). Thin layer chromatography plates were illuminated at 254 nm by exposure to UV light to monitor the coupling reaction process. Organic solutions were concentrated using a rotary evaporator operated at low vacuum conditions at the temperature below 40 °C. Commercial A.R. grade reagents (Sinopharm Chemical Reagent Co., Ltd.) and solvents were used as received. ^{1}H NMR (500 MHz) spectra were recorded using CDCl$_3$ as solvent on a Bruker Avance (AV500) spectrometer with tetramethylsilane (TMS) acting as the internal standard substance. Mass spectra were obtained using an Agilent 1100 LC–MS system equipped with electrospray and atmospheric pressure chemical ionization sources.

A general procedure for C_{Ar}–C_{Ar} Suzuki cross-coupling reaction of 4-fluoro-phenyl boronic acid with heteroaryl halides is demonstrated in Scheme 1.

With reference to Scheme 1: in a 15 ml Schlenk bottle pre-filled with nitrogen, a mixture of 4-fluorophenylboronic acid 1a (1.2 mmol), heteroaryl bromides 2a (1.0 mmol, 1.0 equiv), KOH (3.0 mmol, 3.0 equiv), TBAB (0.3 mmol) and POPd (0.005 mmol) in water (2 ml) was magnetically stirred and refluxed for 1-24 h. After completion of the reaction as indicated by TLC analysis, the mixture was

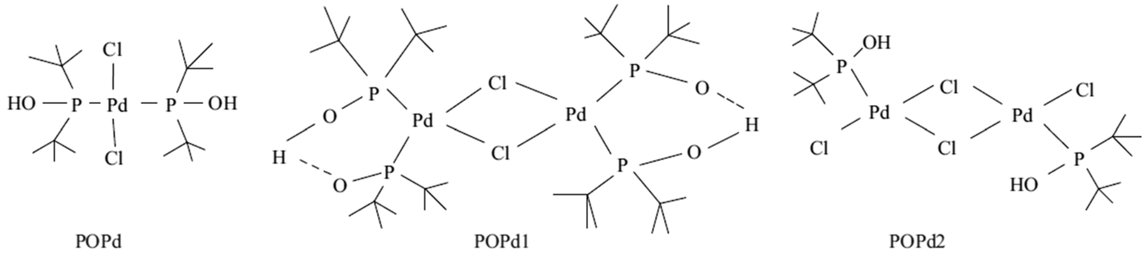
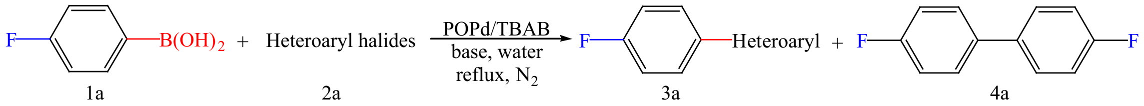


Fig. 1 Highly active and air-stable (di)palladium phosphinous acid complexes, steric framework of POPd, POPd1 and POPd2



Scheme 1 Typically performed heterogenous Suzuki cross-coupling reaction in water

gradually cooled to room temperature. The resulting mixture was extracted with ethyl acetate (3 × 20 ml aliquots) and dried using magnesium sulfate powder. The combined ethyl acetate extracts were then subjected to evaporation under vacuum resulting in the isolation of a dense oily liquid. This oil was purified by flash column chromatography using petroleum ether and ethyl acetate as the eluting phase to isolate the corresponding product 3a and by-product 4a (4,4′-difluorobiphenyl).

Summary of structural analysis results

2-(4-fluorophenyl)-thiophene: yellow powder; mp 48.2–49.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (m, 3H), 7.36 (s, 1H), 7.44 (s, 1H), 7.72 (t, $J = 7.80$ Hz, 2H); MS (ESI): *m/z* $[M+H]^+$ calculated for $C_{10}H_7FS$: 179.0; found: 179.1.

2-(4-fluorophenyl)-pyridine: white powder; mp 39.9–40.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 2H), 7.33 (m, 1H), 7.87 (m, 1H), 7.92 (d, $J = 7.90$ Hz, 1H), 8.17 (m, 2H), 8.66 (d, $J = 4.61$ Hz, 1H); MS (ESI): *m/z* $[M+H]^+$ calculated for $C_{11}H_8FN$: 174.0; found: 173.9 *m/z*.

4-(4-fluorophenyl)-pyridine: white powder; mp 47.1–48.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (t, $J = 7.23$ Hz, 2H), 7.26 (s, 1H), 7.57 (dd, $J1 = 4.37$ Hz, $J2 = 5.42$ Hz, 2H), 7.65 (d, $J = 4.68$ Hz, 2H), 7.92 (s, 1H), 8.20 (s, 1H); MS (ESI): *m/z* $[M+H]^+$ calculated for $C_{11}H_8FN$: 174.0; found: 173.9.

2-amino-5-(4-fluorophenyl)-pyridine: light yellow powder; mp 126.8–127.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 4.77 (d, $J = 6.50$ Hz, 2H), 6.61 (d, $J = 6.50$ Hz, 1H), 7.09 (t, $J = 7.36$ Hz, 2H), 7.44 (t, $J = 7.80$ Hz, 2H), 7.65 (d, $J = 4.40$ Hz, 1H), 8.37 (s, 1H); MS (ESI): *m/z* $[M+H]^+$ calculated for $C_{11}H_9FN_2$: 189.0; found: 188.9.

2-fluoro-5-(4-fluorophenyl)-pyridine: white powder; mp 99.1–100.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (m, 1H), 7.20 (m, 2H), 7.74 (m, 2H), 8.21 (m, 1H), 8.48 (d, $J = 2.33$ Hz, 1H); MS (ESI): *m/z* $[M+H]^+$ calculated for $C_{11}H_7F_2N$: 192.0; found: 191.9.

3-fluoro-4-(4-fluorophenyl)-pyridine: white powder; mp 89.1–90.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 2H), 7.61 (m, 1H), 7.77 (m, 2H), 8.51 (d, $J = 4.94$ Hz, 1H), 8.59 (d, $J = 2.61$ Hz, 1H); MS (ESI): *m/z* $[M+H]^+$ calculated for $C_{11}H_7F_2N$: 192.0; found: 191.9.

2,5-di-(4-fluorophenyl)-pyridine: white powder; mp 188.4–189.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.97 (s, 1H), 7.41 (m, 4H), 7.79 (t, $J = 7.36$ Hz, 2H), 7.94 (s, 1H), 8.21 (d, $J = 5.40$ Hz, 1H), 8.47 (m, 2H), 8.89 (s, 1H); MS (ESI): *m/z* $[M+H]^+$ calculated for $C_{17}H_{11}F_2N$: 268.0; found: 267.9.

5-(4-fluorophenyl)-inzole: white powder; mp 237.8–238.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.99 (s, 1H), 7.29 (dd, $J1 = 8.86$ Hz, $J2 = 6.93$ Hz, 2H), 7.65 (dd, $J1 = 1.66$ Hz, $J2 = 1.56$ Hz, 2H), 7.84 (m, 2H), 8.63 (d, $J = 5.92$ Hz, 2H); MS (ESI): *m/z* $[M+H]^+$ calculated for $C_{13}H_9FN_2$: 213.0; found: 213.0.

5-(4-fluorophenyl)-1H-indole: white powder; mp 81.8–82.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.96 (s, 1H), 6.42 (s, 1H), 7.19 (s, 2H), 7.37 (d, $J = 3.25$ Hz, 2H), 7.67 (s, 1H), 7.69 (d, $J = 5.47$ Hz, 2H), 7.81 (s, 1H); MS (ESI): *m/z* $[M+H]^+$ calculated for $C_{14}H_{10}FN$: 212.0; found: 212.0 m/z.

Results and discussion

Initially, to optimize the experimental conditions for the heterogeneous Suzuki coupling reaction in water, the reaction shown in Scheme 1 was studied. In the presence of POPd/TBAB the heterogeneous Suzuki cross-coupling of 4-fluorophenylboronic acid (1a) with 2-bromopyridine (2a) occurred to afford (3a) in an aqueous reaction mixture. The effects of different Pd-catalysts, phase transfer catalysts, alkalis, and solvents were experimentally investigated. Experimental cross-coupling results in both water and other different organic solvents were initially compared using the same experimental conditions.

The results are summarized in Table 1, entries 1–8. With respect to the seven organic solvents, the 3a yield of 55 % obtained in neat water compared to: (1) a corresponding 54 % yield in DMSO and, (2) between the highest yield in toluene and the lowest yield in THF. The yield of 2-phenylpyridine in water is moderate compared with other organic solvents. Therefore, it was established that water provides considerable potential to act as a highly effective reaction solvent for Suzuki cross-coupling reaction of aromatic halides.

In comparison, using $Pd_2(dba)_3$ and $Pd(PPh_3)_4$ as Pd-catalyst results in 49 and 11 % respective yields of the target 3a 2-(4-fluorophenyl-pyridine) in water, and a trace of 4,4′-difluorobyphenyl 4a via the inter-coupling reaction of 1a. In contrast POPd serials afforded 3a in an encouraging 82–85 % yield (Table 1, entries 11, 17, 18). A further study demonstrated that increasing the amount of POPd from 0.25 to 2.0 % mmol led to a faster coupling rate, but the coupling yield of 3a still remained less than 90 %. Examination of the amount of phase transfer catalysts revealed that the yield was found to increase with increasing PTC/POPd ratio. A lower yield was obtained using the combination of POPd with TMAB acting as the PTC (Table 1, entry 21). No reaction occurred in the absence of Pd-catalysts or PTCs.

The results shown in Table 1 indicate an "alkaline effect" whereby the strong bases give rise to the high yields, whereas the low yields were obtained using the weak bases (Table 1, entries 8–16). When weak inorganic bases were exchanged for the weak organic bases such as

Table 1 Optimization of reaction conditions for the reaction shown in Scheme 1

Entry	Time (h)	Pd catalyst	Solvent	Base	PTC	Yield (%)[b]
1	6	POPd	Toluene	K_2CO_3	TBAB	67
2	4	POPd	DMF	K_2CO_3	TBAB	66
3	4	POPd	C_2H_5OH	K_2CO_3	TBAB	63
4	5	POPd	Dioxane	K_2CO_3	TBAB	63
5	6	POPd	THF	K_2CO_3	TBAB	37
6	3	POPd	DMSO	K_2CO_3	TBAB	54
7	6	POPd	2-Propanol	K_2CO_3	TBAB	48
8	5	POPd	H_2O	K_2CO_3	TBAB	55
9	2.5	POPd	H_2O	KOtBu	TBAB	87
10	2.5	POPd	H_2O	NaOtBu	TBAB	86
11	2.5	POPd	H_2O	KOH	TBAB	85
12	2.5	POPd	H_2O	NaOH	TBAB	65
13	4	POPd	H_2O	Na_2CO_3	TBAB	48
14	6	POPd	H_2O	$NaHCO_3$	TBAB	11
15	8	POPd	H_2O	Et_3N	TBAB	6
16	2.5	POPd	H_2O	NaOAc	TBAB	4
17	2.5	POPd1	H_2O	KOH	TBAB	85
18	2.5	POPd2	H_2O	KOH	TBAB	82
19	2.5	$Pd_2(dba)_3$	H_2O	KOH	TBAB	49
20	2.5	$Pd(PPh_3)_4$	H_2O	KOH	TBAB	11
21	2.5	POPd	H_2O	KOH	TMAB[c]	66

[a] Reaction conditions: 2-bromopyridine 2a (1.0 mmol), 4-fluorophenylboronic acid 1a (1.2 mmol, 1.2 equiv), base (3.0 mmol), PTC (0.3 mmol), water 3 ml, 4 h

[b] Isolated yield based of 2-bromopyridine 1a

[c] Tetramethylamine bromide

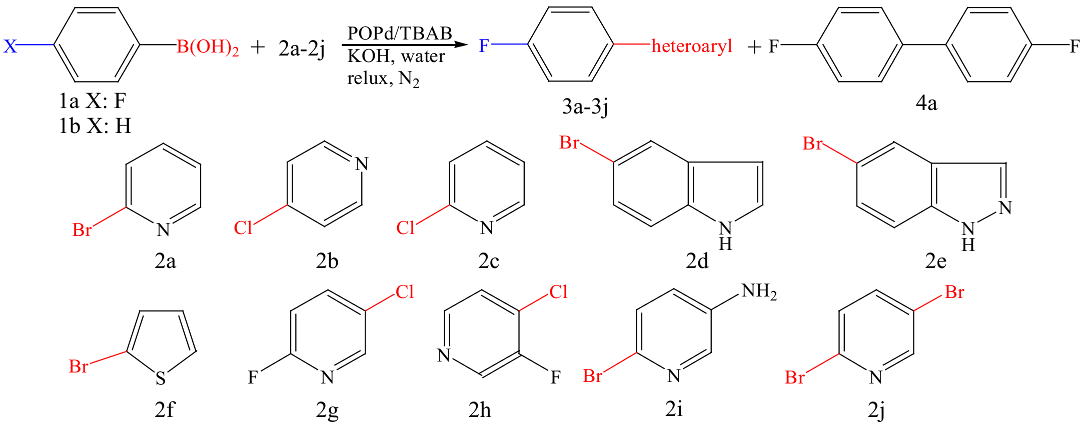
Et_3N or NaOAc, only trace levels of the desired product were synthesized (Table 1, entries 15 and 16). However, using the strong bases NaOtBu, KOtBu or KOH, the corresponding yields of 3a are between 85 and 87 %. Hence, under optimized conditions [using: POPd (0.5 mmol %), TBAB (3.0 equiv), KOH, water], the 2-(4-fluorophenyl-pyridine) product 3a, was obtained in 85 % isolated yield by flash column chromatography as well as 5.0 % yield of 4,4′-difluorobyphenyl (4a).

After obtaining the results summarized in Table 1, the study involving the use of water as reaction solvent was extended to a second series of synthetic reactions. This involved the C_{Ar}–C_{Ar} bond coupling formation/arylation of 4-fluorophenylboronic acid 1a with hetero-aryl bromides and chlorides according to Table 2. Using the optimized conditions established for the reactions shown in Table 1, a range of various substrates were subjected to Suzuki cross-coupling reactions as summarized in Table 2.

The results of the second series of synthetic experiments are provided in Table 2, bromide or chloride directed C_{Ar}–C_{Ar} Suzuki cross-coupling formation can be further applied to a wide variety of substrates. Thus, 4-fluorophenylboronic acid 1a/phenylboronic acid 1b coupled with a range of heteroaryl bromides or chlorides to give the corresponding arylated products in moderate to good yields in water using POPd/TBAB as co-catalyst.

It has been previously established that the POPd/TBAB catalytic complex can tolerate a wide range of functional groups, such as NO_2, OMe, CN, OH, Cl, and NH_2 [22]. As shown in Table 2, a series of heteroaryl halides underwent efficient Suzuki cross-coupling reaction with *p*-fluorophenylboronic acid when the reaction was performed in water with POPd/TBAB. Heteroaryl halides containing electron-withdrawing groups afforded higher yields than those containing electron-donating groups, especially for pyridine chlorides (Table 2, Entries 1–3 & 7–8). Pyridine halides also afforded moderate yields between 39 and 79 %. It was observed that the coupling yield of 3-chloropyridine (77 %) is almost twice compared with 2-chloropyridine (39 %), indicating the pronounced steric hindrance of the chloride atom with the nitrogen atom during the coupling reaction. Unexpected high yield (98 %) of 4-fluoro-5-phenylindole and low yield (10 %) of 4-fluoro-5-phenylindazole was, respectively obtained (Entries 4 & 5 in Table 2). The enormous cross-coupling divergence for these two aza-polycyclic compounds in water could be plausibly caused by the neighbour nitrogen atoms conjugating interaction and electron pair overlapping each other to strengthen the

Table 2 C_{Ar}–C_{Ar} bond coupling formation/arylation of 4-fluorophenylboronic acid 1a and phenylboronic acid 1b with heteroaryl bromides and chlorides



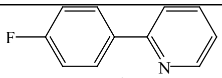
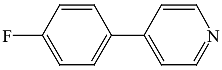
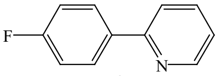
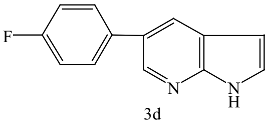
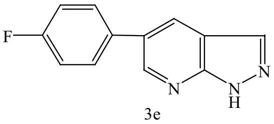
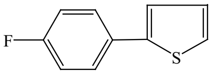
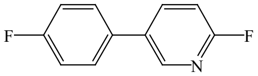
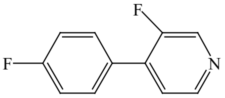
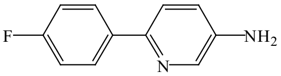
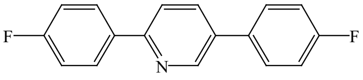
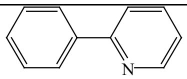
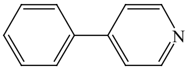
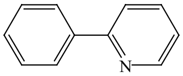
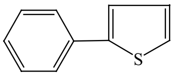
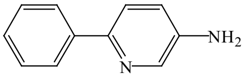
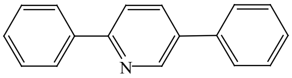
Entry	Boronic acid 1a/1b	2	Time [h]	3	Yield (%)[a]
1	1a	2a	6	 3a	55.0
2	1a	2b	6.5	 3b	77.0
3	1a	2c	7.5	 3a	39.0
4	1a	2d	8	 3d	98.0
5	1a	2e	21	 3e	10.0
6	1a	2f	2	 3f	79.0
7	1a	2g	4	 3g	79.0
8	1a	2h	6	 3h	73.0
9	1a	2i	2	 3i	57.0

Table 2 continued

10	1a	2j	6.5	 3j	18.5
11	1b	2a	6.0	 3k	32.0
12	1b	2b	8	 3l	-
13	1b	2c	8	 3k	-
14	1b	2f	3.5	 3m	82.4
15	1b	2i	8	 3n	35.2
16	1b	2j	6.5	 3 o	35.5

Reaction conditions: 4-fluorophenylboronic acid 1a (1.2 mmol), heteroaryl bromides 2a–2j (1.0 mmol), PTC (0.3 mmol), base (3 mmol), water (3 ml), reflux, 2–21 h

[a] Isolated yield based on heteroaryl bromides

electrovalent bond with bromine atom which is deemed as an electrostatic hindrance for the C_{Ar}–Br oxidative addition with POPd in water.

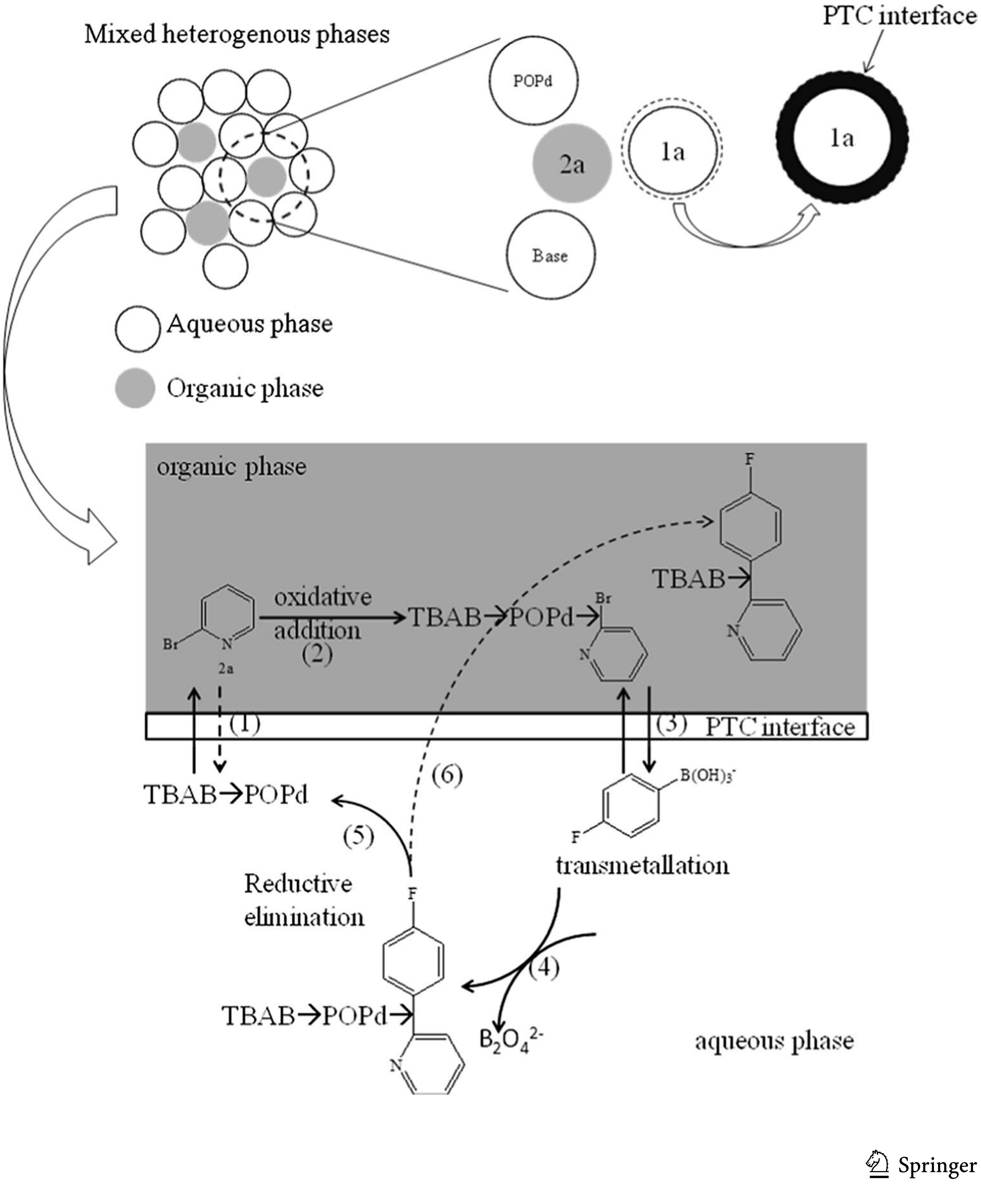
To investigate the real influence of the fluorine atom for the coupling reaction of arylboronic acid and heteroaryl halides, phenylboronic acid was chosen as a reference to reaction with 2a–2c, 2f, 2i and 2j under the same experimental conditions (Table 2, Entries 11–16). It was found that the C–X (X: Br or Cl) bond strength and steric hindrance of the nitrogen lone electron pair determined the reactivity of the substrates. Pyridine bromide substrates could tolerate several functional groups such as NH_2 or F atom (actually F atom is not a group but is the strongest electron withdrawing atom). 2-bromopyridine (2a) was experimentally determined to provide a higher yield than 2-chloropyridine (2c), but for the isomer of 3-chloropyridine (2b), 2b gives even higher yield (77 %) than its counterpart bromide 2a (55 %), which could be explained according to the steric effect of the nitrogen single electron pair imposed on the C_{Ar}–C_{Ar} bond formation. For 2c, the chlorine atom is in the *para*-position to the nitrogen atom leading to a low hindrance for bond formation. In contrast, for 2b the chlorine atom is in close vicinity to the nitrogen, and part of electron cloud on these two atoms would be overlaid and could cause interference to disturb new bond formation of the C_{Ar}–C_{Ar}. Improved results were obtained when heteroaryl chlorides containing a moderately electron-withdrawing group 2 g/2 h or electron-neutral group (H atom) 2a/2f were employed.

Based on known metal-catalyzed directing-group-assisted C–C bond coupling reactions [28–32] and an analogy for the reaction of 4-fluorophenylboronic acid, a proposed reaction scheme for the Suzuki cross-coupling for arylboronic acid and heteroaryl haloride (2a–2j) is provided in Scheme 2. As reported in literature [16], the roles of TBAB are categorized as facilitating solvation of the organic substrates in aqueous mixture and activating the arylboronic acid via the intermediate formation of $[ArB(OH)_3]^-[Bu_4N]^+$. Additionally, TBAB molecules simultaneously form an interface between arylboronic acid/POPd and heteroaryl haloride in the liquid mixture, resulting in the POPd active sites becoming associated with the heteroaryl haloride in the organic phase, that returns after oxidation to the aqueous phase, with subsequent transfer of the target coupling products to the organic phase.

The proposed catalytic coupling process involves the following steps: (1)–(2), the cyclo-palladation of heteroaryl haloride via C_{Ar}-haloride bond activation (TBAB→POPd→2a). The Pd atom is temporarily oxidized by the addition of 2a; (3)–(4), the TBAB transports [POPd→2a] oxidative complex back to the alkaline aqueous mixture, and the [TBAB→ POPd→2a] transition complex continues to undergo transmetallation with 4-fluorophenylboronic acid, cross-coupling of these two molecules by switching halide atom with borates; (5)–(6), the reductive elimination of Pd atom affords the cross-coupling product and returns to the organic phase with respect to the transportation of TBAB. The fluoro-substituted biphenyl product was formed during the decomposition of 4-fluorophenylboronic acid becoming self-coupled together to form the corresponding biphenyl fluoride compound (4a).

Conclusions

In a summary, we have described a combined and efficient method for the arylation of heteroaryl halides via C_{Ar}–C_{Ar} Suzuki coupling method using POPd/TBAB in water. A combination of POPd and TBAB, greatly accelerated the rate of the coupling reaction and effectively bridged the gap between two immiscible phases by binary activity at the interphases. The desired C_{Ar}–C_{Ar} bond formation proceeded efficiently with good functional-group tolerance



Scheme 2 Proposed mechanism for POPd/TBAB co-catalyzed heterogeneous Suzuki cross-coupling reaction in water

and high selectivity. The proposed mechanism for the arylation of heteroaryl bromides and chlorides is consistent with the experimental results that have been obtained. We are currently conducting a series of further studies involving the application of the heterogeneous couplings in water between C atom and hetero-atoms such as N or S to synthesize C_{Ar}-heteroatom bonds.

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