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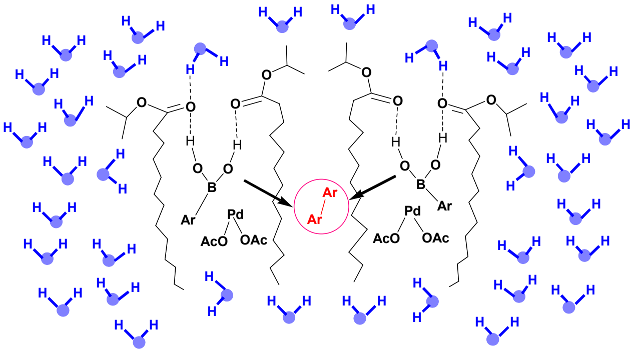

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A green etiquette for Pd catalyzed ligand free homocoupling reaction of arylboronic acids at ambient conditions

Seema Dwivedi, Soumik Bardhan, Prasanjit Ghosh and Sajal Das*

A simple, competent, green etiquette has been developed for Pd catalyzed ligand free homocoupling reaction of aryl boronicacids in water at ambient conditions. An efficient reaction environment is generated in combination of $Pd(OAc)_2$ and 'green additives' which exhibited excellent activity and results in the high yields of the desired coupled products within 15 minutes.

Introduction

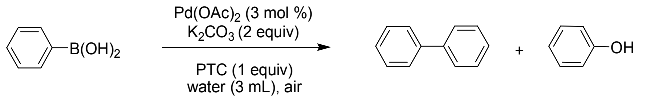
Owing to accelerating environmental concerns, the present era is inducing search of greener alternatives of chemical processes both for academic and industrial purposes. The idea of green technology is hence, receiving momentous thought. Minimization in use of organic solvents and subsequent exploration of aqueous biphase catalysis, supercritical fluids as well as ionic liquids as reaction media are emerging areas of research.[1] However, selection of water as a reaction medium is undoubtedly the best option as it is amply available, cost effective and most importantly environmental benign. Few major drawbacks of this approach are poor substrates solubility, poor yield, side products and prolong reaction time. These predicaments are often solved either by using water soluble reagents or additives and/or phase transfer catalysts (PTC) which are not green itself.[2]

Our main effort was directed toward C-C bond forming reactions.[3] Without deviating from the main objective of green protocol, herein we disclose a new class of green additives that effectively enhances the yield and reaction rate of homocoupling reaction of arylboronic acids in water. Biaryl compounds serve as imperative motifs in natural, biologically active, pharmaceutically and agrochemically efficient moieties. In addition, the widespread application of biaryls as ligands and components in new resources make these compounds attractive man-made targets. Several synthetic means have been developed so far for the construction of biaryl skeletons through C_{sp2}–C_{sp2} bond forming reactions.[4] For synthesis of symmetrical biaryls, the Pd catalyzed Suzuki type homocoupling of arylboronic acids is known to be an indispensible tool.[5] Besides the palladium catalyst, Au,[6] Rh,[7] Cu[8] and Mn[9] catalysts have also been reported to catalyze C-C coupling reactions. Attempts to conduct this reaction in water reports use of PTC,[10] added oxidant,[11] sulphonyl chloride additives,[12] ligands[13] etc. Recently, Wu *et al*. reported the reaction with 6 mol% $Pd(OAc)_2$ simply in presence of K_2CO_3 (base) and water (solvent). However, it required a long time span of 24 hrs.[14] In contrast, our newly developed protocol requires only 1 mol% of $Pd(OAc)_2$ for the effective transformation of aryboronic acids to corresponding biaryls within 15 minutes at ambient condition.

Result and Discussion

We started our investigation to know the effect of phase transfer catalysts on the homocoupling of phenylboronic acid in water. In a typical reaction, equivalent mixture of phenylboronic acid and PTC was treated with 2 equiv potassium carbonate (K_2CO_3) and 3 mol % of $Pd(OAc)_2$ in water for 5 h at ambient condition (scheme 1).

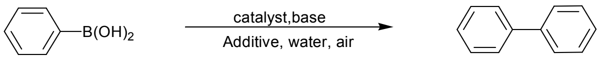
Scheme 1: Homocoupling of phenylboronic acid in presence of PTC.



Both TBAB (tetrabutylammonium bromide) and TBAHS (tetrabutylammoniumhydrogen sulphate) gave disappointing results as only 31% and 35% yields of biphenyl were obtained. Moreover, equivalent amount of phenol, common side product was isolated after the reaction.[15] Then we moved to improve the reaction condition and explore the possibility to substitute the PTC with long chain esters. A variety of long chain esters are commonly used as cosolvent to enhance the solubility of many drugs in dermal and transdermal drug delivery process.[16] We have brought the concept here for the fabrication biaryls motifs.

We tried the model reaction with equivalent amount (160 μL) of IPM (isopropyl myristate) in place of the phase transfer

Table 1: Optimization of homocoupling reaction



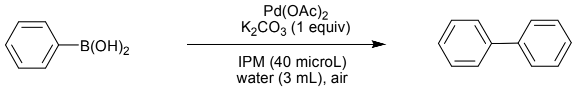
Entry	Catalyst	Base	Additive	Time (min)	Yield[b] (%)
1	Pd(OAc)$_2$	K_2CO_3	IPM (160 µL)	15	83
2	Pd(OAc)$_2$	K_2CO_3	IPM (40 µL)	15	100
3	Pd(OAc)$_2$	K_2CO_3	IPM (30 µL)	15	99
4	Pd(OAc)$_2$	K_2CO_3	IPM (20 µL)	15	97
5	Pd(OAc)$_2$	K_2CO_3	IPM (10 µL)	15	98
6	Pd(OAc)$_2$	K_2CO_3	EM (40 µL)	15	99
7	Pd(OAc)$_2$	K_2CO_3	EO (40 µL)	15	98
8	Pd(OAc)$_2$	K_2CO_3	EP (40 µL)	15	99
9	Pd(OAc)$_2$	K_2CO_3	Stearic acid (0.25 equiv)	60	88
10	Pd(OAc)$_2$	K_2CO_3	Sodium myristate (0.25 equiv)	60	72
11	Pd(OAc)$_2$	K_2CO_3	Ethyl acetate (0.25 equiv)	60	10
12	$PdCl_2$	K_2CO_3	IPM (40 µL)	60	94
13	Pd/C	K_2CO_3	IPM (40 µL)	60	58
14	$CuSO_4.5H_2O$[c]	K_2CO_3	IPM (40 µL)	60	14
15	Ni(OAc)$_2$.4H_2O	K_2CO_3	IPM (40 µL)	60	-
16	Fe(III)acetylacetonate[c]	K_2CO_3	IPM (40 µL)	60	-
17	Fe(II)trifluoromethene-sulphonate	K_2CO_3	IPM (40 µL)	60	51
18	**Pd(OAc)$_2$**	**K_2CO_3[d]**	**IPM (40 µL)**	**15**	**100**
19	Pd(OAc)$_2$	Cs_2CO_3[d]	IPM (40 µL)	15	99
20	Pd(OAc)$_2$	Nil	IPM (40 µL)	180	53
21	Pd(OAc)$_2$	Nil	IPM (160 µL)	180	81

[a]Reaction conditions: Phenylboronic acid (0.5 mmol), catalyst (3 mol%), base (2 equiv), water (3mL), room temperature. [b]HPLC yields, [c]10 mol% catalyst used, [d]1 equivalent base was used.

catalyst (table 1). The reaction completed within 15 minutes and resulted in 83% yield of biphenyl (table 1, entry 1). We then varied the loading of additive and observed that catalytic amount of IPM (10 µL = 0.06 mol %) was sufficient for the effective transformation (table 1, entry 5). However, 40 μL of IPM (0.25 equiv) showed the highest yield 100% (table 1, entry 2). Further we checked some other similar naturally occurring long chain green esters *viz*; ethyl palmitate (EP), ethyl myristate (EM) and ethyl oleate (EO) in place of IPM under same reaction conditions. All these esters showed excellent activity and provided rather synergistic results with slight variations of yields (table 1, entry 6-8). This indicates that long chain ester molecules in some way stabilize the system and facilitate the reaction. We then performed the reaction in neat IPM and observed that no reaction occurred in 15 minutes. The higher yield (100%) with 40 μL of IPM as compared to 160 μL of IPM (83%), suggested the optimum amount of the additive required for effective transformation of arylboronic acid to corresponding biphenyl. Subsequently we performed the reaction in the presence of long chain acid, stearic acid and obtained 88% yield in 1 hour (Table 1, entry 9). Sodium salt of myristic acid was found some less effective and furnishing 72% yield in 1 hour (Table1, entry 10). To assure the requirement of long hydrocarbon chain containing moiety as additive we performed the reaction with ethyl acetate as additive. A poor conversion 10% was observed in 1 hour (Table 1, entry 11).

With this development in hand, we proceeded to navigate the standard conditions for this reaction by varying the reaction parameters like catalyst and base (table 1). Among the various catalysts used for the reaction, $Pd(OAc)_2$ provided best results with complete conversion within 15 minutes (table 1, entry 2). Copper and iron based catalysts were also found active, however, providing lower yields (table 1, entry 14-17). Further, an optimization of base showed that the reaction was not much dependent on the nature of the base. Since, both Cs_2CO_3 and K_2CO_3 were equally effective for the reaction (table 1, entry 18-19). Only one equivalent of base was sufficient for the efficient transformation. The reaction also occurred in the absence of base however, large amount of phenylboronic acid left unreacted providing a low yield (53%) in 3 h (table 1, entry 20). Gradual addition of IPM increased the substrate to product ratio. With equivalent amount of IPM 81% yield of biphenyl product was obtained in 3 hrs in absence of base. It was observed that decreasing the amount of Pd catalyst to 1 mol% did not record any effect on the reaction performance (table 2). $Pd(OAc)_2$ recorded excellent activity reporting 85% yield with just 0.1 mol% catalytic loading (table 2, entry 5).

Table 2: Optimization of catalyst loading[a]



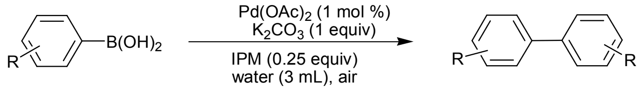
Entry	$Pd(OAc)_2$	Base (1 equiv)	Time (min)	Yield[b] (%)
1	3 mol%	K_2CO_3	15	100
2	2 mol%	K_2CO_3	15	100
3	**1 mol%**	**K_2CO_3**	**15**	**99**
4	0.5 mol%	K_2CO_3	15	87
5	0.1 mol%	K_2CO_3	15	85

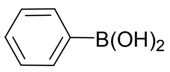
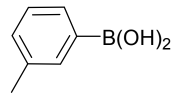
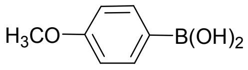
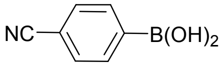
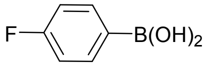
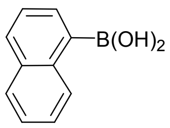
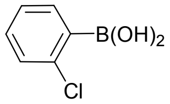
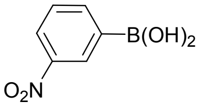
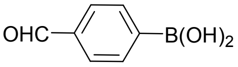
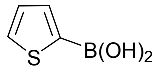
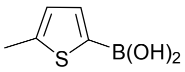
[a]Reaction conditions: Phenylboronic acid (0.5 mmol), $Pd(OAc)_2$, Base (1 euiv), IPM (40μL), room temperature. [b]HPLC Yields

Subsequently, we performed the homocoupling reaction of various arylboronic acids under the optimized conditions (table 3). All the arylboronic acids smoothly reacted to provide the desired homocoupling products. Arylboronic acids with electron donating groups gave considerably good results. 4-methoxyphenylboronic acid and 3-methylphenylboronic acid provided the corresponding coupling products in 93% and 95% yields respectively (table 3, entry 2-3). Unsubstituted phenylboronic acid and napthylboronic acid also ended with high yields of 94% and 97% respectively upon isolation (table 3, entry 1,6). Again, electron deficient substrates like 4-fluorophenylboronic acid, 2-chlorophenylboronic acid and 3-nitrophenylboronic acid also performed very well and accomplished 77%, 74% and 73% yields respectively (table 3, entry 5,7,8). However, 4-cyanophenylboronic acid and 4-formylphenylboronic acid provided the corresponding products 4,4'-dicyanobiphenyl and 1,1´-biphenyl-4,4´-dicarbaldehyde in only 47% and 49% yields respectively (table 3, entry 4 and 9).

Very low yield in case of 4,4´-dicyanobiphenyl and 1,1´-biphenyl-4,4´-dicarbaldehyde may be attributed to the *para* positioning of the cyano and formyl groups respectively which have strong negative mesomeric effect. To test the application of our reaction system for heteroaryl substrates we conducted the homocoupling reaction of 2-thienylboronic acid and 5-methyl-2-thienylboronic acid. They also underwent smooth coupling to accomplish 57% and 59% yields respectively of the desired products (table 3, entry 10, 11). Hence our developed protocol is equally effective for heteroaryl systems as well.

Table 3: Homocoupling of arylboronic acids[a]

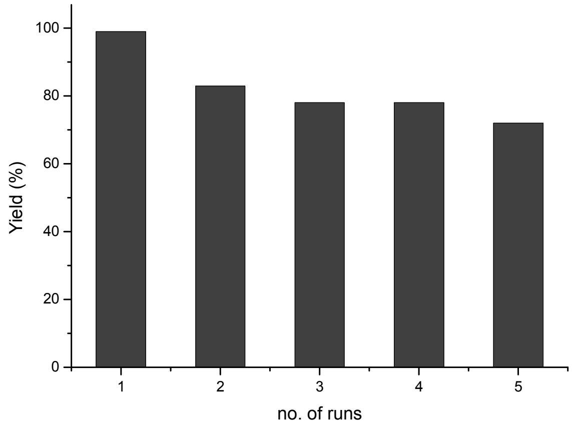


Entry	Aryl boronic acid	Yield (%)
1		94
2		95
3		93
4		47
5		77
6		97
7		74
8		73
9		49
10		57
11		59

[a] Phenylboronic acid (1 mmol), Pd(OAc)$_2$ (1 mol%), K$_2$CO$_3$ (1 equiv), IPM (0.25 equiv), water (3 mL), [b] isolated yields (column chromatography)

The recycling experiment has been done by taking the model homocoupling reaction of phenylboronic acid to ensure the reusability of reaction medium. The reaction has been performed under the optimized condition. After the first run, the product was isolated by the solvent extraction method and the reaction media was used directly for the next run. No other reagents except the phenylboronic acid were added for the subsequent runs. Consecutive five runs were tested and the corresponding results are given in (Figure 1). The reaction system was found to be efficient and a little decrease in yields was observed from the second run onwards. IPM is immiscible in water but it remains in reaction medium after extraction of product. Presence of IPM in the reaction media was detected by the spectroscopic techniques. FTIR analysis of the reaction media after the first run showed the presence of >C=O at 1729 cm^{-1}. The fact was further supported by the NMR analysis. Most plausibly, the IPM molecules are attached with the other reagents present in the system *via* several of use interaction and thus remain in medium after solvent extraction.

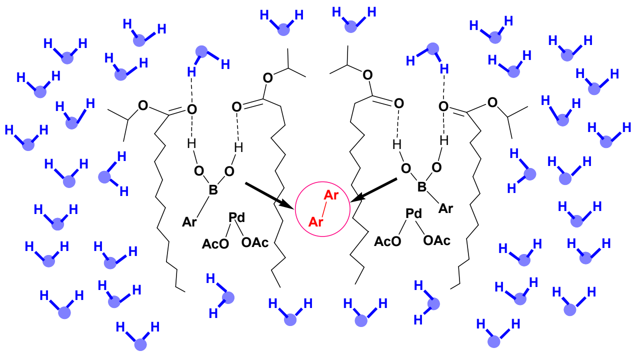
Figure 1: Recycling experiment of the reaction medium



Observed HPLC yield of the biphenyl after each run

In pithy, an in situ generated stimulant combining Pd(OAc)$_2$ and green additives exceptionally promotes the homocoupling reactions of arylboronic acids in water. Further, these additives are capable to endorse the reaction in no base condition and are much effective than the traditional PTC. This scenario prompts us to investigate the role and significance of green additives in this homocoupling reaction. The homocoupling reaction of arylboronic acids is playing well in water in absence of additives after producing their water soluble 'trihydroxyborate salts'. However, relatively low yield (62%) and a comparatively longer time span of 1 hour was required in that case.

Scheme 2: Schematic representation of homocoupling reaction in the presence IPM.



We surmise that the presence of small amount of long chain ester not only resolved the solubility problem of phenylboronic acid in water rather, it encourages the substrate-catalyst communication. The reaction is considered to be homogeneously proceeding around the long chain ester molecules of IPM (Scheme 2). Plausibly, the long chain ester molecules grasp the substrates and bring it to the proximity of the catalyst. The hydrophobic and multiple hydrogen bonding interactions[17] between hydrophobic and hydrophilic branch of esters and complementary modules of substrates might be responsible for such type of special arrangement.

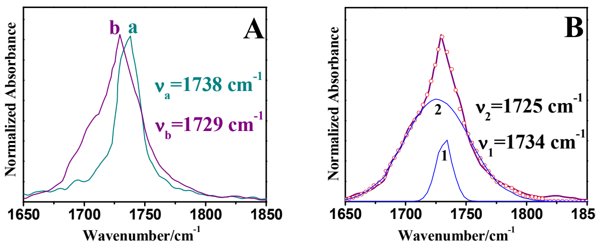


Figure. 2. (A) Shifting of C=O stretching band of ester group in IPM (Specification: a; neat IPM, b; IPM in presence of PhB(OH)$_2$) (1:1)). (B) Gaussian deconvolution of C=O stretching band of IPM in presence PhB(OH)$_2$) (1:1) (Specification: Experimental spectra, overall fitted point (open circle) and deconvoluted curves, 1: free C=O stretching band ; 2: bound C=O stretching

Presence of H-bonding interaction has further been supported by the FTIR spectroscopic analysis. IPM exhibits a sharp peak of >C=O stretching frequency at 1738 cm^{-1} (Figure 2A and SA). But in the presence of phenylboronic acid the peak becomes broader and appearing at1729 cm^{-1}. This downward shifting and the broadening nature indicates the formation of intermolecular H-bonding between >C=O and the complementary module of phenylboronic acid. [18] Then, the observed broad band has been fitted as a sum of Gaussian with the help of Gaussian curve fitting program, and the vibrational characteristics has been analyzed further. Upon deconvolution, it has been found that the broad peak is a combination of two different peaks (Figure 2B). The higher frequency region peak (Figure 2B-1) at 1734 cm^{-1} is similar to that of the >C=O stretching frequency of neat IPM. Whereas the new peak at 1725 cm^{-1} (Figure 2B-2) is corresponds to the H-bonded >C=O of IPM with phenylboronic acid. Nevertheless, high population (86%) of H-bonded >C=O stretching band has been observed from the variation of Gaussian profiles (area fraction) of the normalized spectra. Hence, it may be concluded that most of the IPM molecules are forming H-bond with the complementary modules of phenylboronic acid and providing unique platform for the homocoupling reaction of arylboronic acid.

Experimental

General Comments

Unless stated otherwise, all reagents such as Palladium acetate, arylboronic acids and solvents were used as received from commercial suppliers. NMR spectra were recorded on 300 MHz spectrometer at 298 K with calibration done on the basis of solvent residual peak. FTIR spectra in the 400−4000 cm^{-1} window were recorded on a Perkin Elmer Spectrum RXI spectrometer (USA) (Absorbance mode) with 100 number scans and spectral resolution of 4 cm^{-1} at 303K. Deconvolution of spectra has been made with the help of Gaussian curve fitting program (Origin software). Products were purified using column chromatography on silica gel (60-120 mesh). Ethyl acetate and petroleum ether (60-80^{o}C) were used as eluents. Progress of reaction was monitored using silica gel TLC.

General procedure for the synthesis of biphenyls

In a 25 mL round bottom flask 1mmol of aryl boronic acid was taken. 1 mmol of K$_2$CO$_3$, 0.25 mmol IPM and 3 mL water were added to it. The reaction mixture was stirred at 15 minutes at room temperature. Then it was poured into water and the organic layer was extracted with DCM. The organic layer was dried by passing over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude material was further purified by column chromatography using petroleum ether as eluent.

Recycling of reaction medium

To the water portion left after the solvent extraction, phenylboronic acid (1 equiv) was added and the reactions were carried for 15 minutes at room temperature. No added base or catalyst was required for the four subsequent runs.

Analytical data for biaryl products

(1) Biphenyl[19]
White solid; mp 68-71 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.30–7.35 (m, 2 H), 7.39–7.45 (m, 4 H), 7.56–7.59 (m, 4 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 127.26, 127.34, 128.85, 141.31.

(2) 3,3'-dimethylbiphenyl[19]

Colourless liquid; bp 286 °C; ^{1} H NMR (300 MHz, $CDCl_3$): δ 2.406 (s, 6H), 7.14 (d, *J*=7.5 Hz, 2H), 7.28-7.33 (m, 2H), 7.37-7.37 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.61, 124.34, 127.97, 128.03, 128.66, 138.30, 141.40.

(3) 4,4’-dimethoxybiphenyl[19]
White solid; mp 177-179 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.537 (s, 6H), 6.93-6.98 (m, 4H), 7.45-7.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.36, 114.18, 127.76, 133.48, 158.70.

(4) 4,4’-dicyanobiphenyl[8]
White solid; mp 233-234 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68-7.72 (m, 4H), 7.77-7.81 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 112.44, 118.44, 127.95, 132.91, 143.53.

(5) 4,4’-difluorobiphenyl[8]
Pale yellow solid; mp 88-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08-7.15 (m, 4 H), 7.45-7.52 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.70 (d, *J*= 21 Hz), 128.58 (d, *J*= 8 Hz), 136.39 (d, *J*= 3 Hz), 162.42 (d, *J*= 245 Hz).

(6) 1,1’-binapthyl[20]
Colourless solid; mp 141-143 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.23 (2H, m), 7.30-7.37 (2H, m), 7.39-7.43 (4H, m), 7.46-7.53 (2H, m), 7.85-7.88 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): 124.34, 124.76, 124.93, 125.51, 126.78, 126.84, 127.10, 131.79, 132.46, 137.40.

(7) 2,2’-dichlorobiphenyl[20]
White solid; mp 59-62 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.29 (m, 2H), 7.32-7.35 (m, 4H), 7.47-7.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.50, 129.23, 129.44, 131.18, 133.52, 138.36.

(8) 3,3’- dinitrobiphenyl[21]
Yellow solid; mp 201-202 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (t, *J*=8.0 MHz, 2H), 7.96-8.0 (m, 2H), 8.29-8.33 (m, 2H), 8.51 (t, *J*= 2.1, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 122.13, 123.32, 130.32, 133.09, 140.34, 148.88.

(9) 1,1´-biphenyl-4,4´-dicarbaldehyde[20]
White solid; mp 146-148 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79-7.82 (m, 4H), 7.98-8.02 (m, 4H), 10.09 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.03, 130.36, 136.00, 145.56, 191.73.

(10) 2,2’-dithiophene[19]
White solid; mp 33-34 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00-7.03 (m, 2 H), 7.18 (dd, *J*=3.6 Hz, *J*=1.2 Hz, 2 H), 7.22 (dd, *J*= 5.1 Hz, *J*=0.9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 123.77, 124.36, 127.78, 137.40.

(11) 5,5’-dimethyl-2,2’-dithiophene[22]
Yellow solid; mp 65-68 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.46 (m, 6H), 6.62-6.63 (m, 2 H), 6.86-6.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.31, 122.87, 125.74, 135.51, 138.48.

Conclusions

In summary, we have reported an efficient reaction environment in combination of $Pd(OAc)_2$ and green additives that can effectively support smooth homocoupling of a range of arylboronic acids in water and aerobic condition at room temperature. The reaction uses low catalyst loading and completes within a short span of 15 minutes. Substrates bearing electron rich and electron withdrawing substituents are all well tolerated in the reaction. Heteroarylboronic acids also performed well in the reaction condition. Interestingly, a class of new green additives stand as a relevant parameter for the design and development of catalysts for homocoupling reactions in water. We are presently investigating the possibilities to broaden this concept to advance catalytic process as future outlook.

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