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Efficient One-Pot Cross-Coupling of Two Aryl Halides by Stannylation/Stille Reaction in Water under Microwave Irradiation

Xin Tan,[a] Zi Jie Zhou,[a] Jia Xin Zhang,[b] and Xin Hong Duan*[c]

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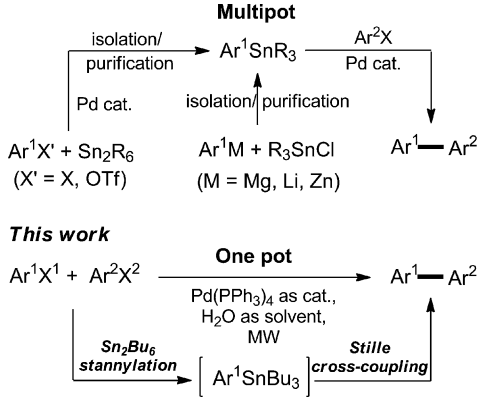
A simple and highly efficient one-pot approach has been developed for the $Pd(PPh_3)_4$-catalyzed cross-coupling of two different aryl or heteroaryl bromides/iodides. This method involves the combined use of microwave irradiation and water as a single solvent to achieve sequential stannylation and Stille cross-coupling reactions, which allows rapid access to a wide variety of biaryls in good to high yields. Furthermore, utilizing this step-economical protocol, 2,5-dibromopyridine was iteratively diarylated and the Boscalid intermediate was also synthesized in a one-pot manner.

Introduction

The Stille reaction has contributed greatly to the straightforward and facile construction of biaryls.[1–4] Owing to its compatibility with a diverse range of functional groups and the stability of aryl stannanes to air and moisture, this cross-coupling reaction has been extensively applied to the synthesis of highly functionalized biaryls.[5–10] Despite these, a major limitation to the Stille reaction is the necessity for the use of preformed (and purified) aryl stannanes. Methods for the preparation of such stannanes typically include transmetalation by an arylmagnesium, lithium, or zinc reagent.[11–14] In 1981, Eaborn et al. reported the Pd-catalyzed stannylation of aryl halides with Sn_2R_6 (R = CH_3, Bu) in refluxing toluene.[15] Since then, this method has been extensively used to stannylate aryl halides or aryl trifluoromethanesulfonates.[16–19] More recently, the sonochemical Barbier reaction of aryl bromides has also been reported to synthesize successfully aryl stannanes.[20] All of these stannane preparations require isolation/purification procedures, which are often troublesome and inevitably lead to toxicity and environmental concerns, and the Stille reaction consists of a tedious multipot synthetic sequence and is, of course, inefficient in terms of step economy (Scheme 1).

We believe that a viable alternative to the Stille cross-coupling reaction can be designed to eliminate the isolation/purification step of the aryl stannanes, and thus the wastes produced and solvents used during the process can be avoided. In this regard, a step-economical strategy that merges stannylation with cross-coupling into one-pot is extremely attractive. We anticipated that the Pd-catalyzed stannylation of aryl halides by using Sn_2Bu_6 could ideally be followed by an in situ Stille reaction (Scheme 1). Clearly, this strategy that employs a single Pd catalyst to couple two different aryl halides in a one-pot manner is remarkably challenging, as it must avoid the generation of unwanted homocoupling resulting from incomplete stannylation. To the best of our knowledge, there have been no reports on such a one-pot Stille coupling reaction.



Scheme 1. Stille methods for cross-coupled biaryls.

However, an ecofriendly solvent can be used to make this one-pot Stille coupling reaction greener. Water is undoubtedly the cheapest and cleanest solvent available, and to date, it has been intensively investigated.[21–28] Apart from its potential economic and environmental gains, water can offer unique reactivity and selectivity.[26–30] Especially if combined with microwave (MW) irradiation, the use of water as a solvent leads to efficient and rapid transition-metal-catalyzed cross-coupling reactions.[31–34] As such, it is highly

[a] College of Materials Science and Technology, Beijing Forestry University,
Beijing 100083, China
[b] College of Chemistry, Beijing Normal University,
Beijing 100875, China
[c] College of Science, Beijing Forestry University,
Beijing 100083, China
E-mail: xinhong116@163.com
http://cos.bjfu.edu.cn

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desired to conduct this one-pot Stille coupling reaction in water by using MW heating.

Herein, we report for the first time a simple and highly efficient method for the synthesis of various biaryls through a $Pd(PPh_3)_4$-catalyzed stannylation/Stille cross-coupling (SSC) reaction. The great advantage of this method lies in the fact that it enables two different aryl or heteroaryl bromides/iodides to be coupled efficiently in a one-pot manner under MW irradiation in combination with water as a single solvent (Scheme 1). Notably, this coupling is also very amenable to N-heterocyclic substrates such as pyridines, of which metallic reagent preparation (i.e., 2-pyridinylboronic acid) and the corresponding cross-couplings (i.e., Suzuki–Miyaura coupling) are usually a very challenging task in organic synthesis.[35]

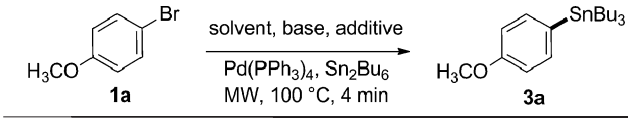
Results and Discussion

Optimization of the Reaction Conditions for the Stannylation Reaction towards the Synthesis of Biaryls

To couple two different aryl bromides/iodides efficiently through the one-pot SSC reaction, complete stannylation of the first halide is required; otherwise, homocoupling can occur. We first examined this key stannylation by using 4-bromoanisole as a model substrate and readily available $Pd(PPh_3)_4$ as the catalyst (Table 1). Under the standard conditions reported (toluene as solvent),[36–38] we found that the stannylation reaction was incomplete and homocoupling evidently occurred (Table 1, entry 1). Moreover, our attempt to perform the reaction in the H_2O/KOH system was unsuccessful if the conventional heating method was used (Table 1, entry 2). Considering the potential of MW-assisted synthesis in water as a solvent,[31–34] we applied this MW-heating approach to the stannylation reaction.

The optimization studies were performed by investigating the efficiency of MW heating with regard to solvent, $Pd(PPh_3)_4$, base, and the additive of tetrabutylammonium bromide (TBAB, summarized in Table 1). Upon using 5 mol-% $Pd(PPh_3)_4$ under MW heating at 100 °C, the reaction in water did not occur, even in the presence of TBAB (Table 1, entries 3 and 4). We screened various bases in TBAB-containing water and found that other bases including KOAc, K_3PO_4, K_2CO_3, and KF were less efficient than KOH (Table 1, entries 5–8). Indeed, the presence of KOH resulted in complete conversion of the bromide to yield the desired stannane in 94% yield after MW heating for 4 min (Table 1, entry 9). Decreasing the loading of $Pd(PPh_3)_4$ to 1 mol-% gave rise to a large decrease in the yield (Table 1, entry 10). Polyethylene glycol 400 (PEG400)/H_2O and DMF/H_2O mixtures were also used as solvents, but the results were unsatisfactory (Table 1, entries 11–15). In contrast, if the same reaction was performed in toluene with MW heating at 100 °C, a poor yield of 59% was obtained, mainly as a result of homocoupling (Table 1, entry 9 vs. 16). The results reveal that the use of a basic aqueous system in combination with MW heating greatly facilitates this stannylation reaction and, moreover, increases the reactivity and selectivity.[39–41] Noteworthy is that under the above-optimized conditions only an almost equimolar amount of Sn_2Bu_6 (1.1 equiv.) was required for complete stannylation and no homocoupled product was observed.

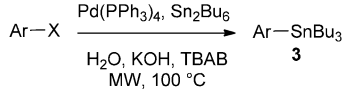
Table 1. Optimization of the reaction conditions for the stannylation reaction.[a]

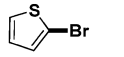
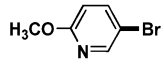
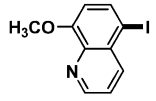
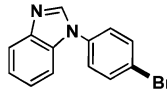


Entry	Solvent	Base	Additive	Yield [%][b]
1[c]	toluene			43 (33)[d]
2[e]	H_2O	KOH		0
3	H_2O			0
4	H_2O		TBAB	7
5	H_2O	KOAc	TBAB	42
6	H_2O	K_3PO_4	TBAB	51
7	H_2O	K_2CO_3	TBAB	49
8	H_2O	KF	TBAB	27
9	H_2O	KOH	TBAB	94
10	H_2O	KOH	TBAB	72[f]
11	PEG400/H_2O (5:1)			10
12	PEG400/H_2O (1:1)			14
13	DMF/H_2O (5:1)			40
14	DMF/H_2O (1:1)			47
15	DMF/H_2O (1:1)	KOH	TBAB	68
16[g]	toluene			59 (26)[d]

[a] Conditions: 4-bromoanisole (**1a**, 1 mmol), Sn_2Bu_6 (1.1 mmol), $Pd(PPh_3)_4$ (5 mol-%), KOH (3 mmol), and TBAB (3 mmol) in H_2O (5 mL). [b] Yield of isolated product. [c] Conditions: **1a** (1 mmol), Sn_2Bu_6 (2 mmol), and $Pd(PPh_3)_4$ (5 mol-%) in toluene (10 mL) under Ar_2 protection at reflux for 4 h with conventional heating. [d] Yield of isolated homocoupled product. [e] Conditions: **1a** (1 mmol), Sn_2Bu_6 (2 mmol), $Pd(PPh_3)_4$ (5 mol-%), and KOH (3 mmol) in H_2O (10 mL) at reflux for 4 h with conventional heating. [f] $Pd(PPh_3)_4$ (1 mol-%). [g] Conditions: **1a** (1 mmol), Sn_2Bu_6 (1.1 mmol), and $Pd(PPh_3)_4$ (5 mol-%) in toluene (5 mL) at 100 °C for 10 min with MW heating.

Table 2. Stannylation reactions.[a]



Entry	ArX	Time [min]	Yield[b] [%]
1		4	**3b**, 91
2		4	**3c**, 92
3		5	**3d**, 74
4		6	**3e**, 87

[a] Reaction was performed on a 1-mmol scale. [b] Yield of isolated product.

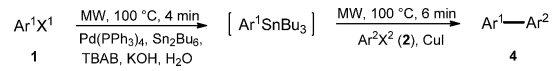
To further illustrate the scope of this method, the stannylation of some other electron-rich and electron-deficient heteroaryl as well as aryl bromides/iodides was examined, and the results are shown in Table 2. Under the above-optimized conditions, the desired stannanes were obtained in 74–92% yield after MW heating for 4–6 min. To the best of our knowledge, this represents the first example of the stannylation of aryl halides in water as a single solvent by using Sn_2Bu_6.

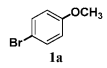
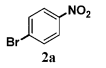
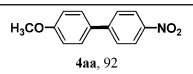
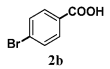
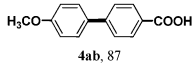
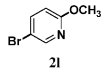
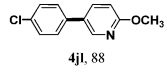
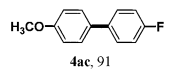
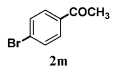
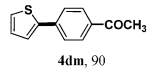
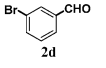
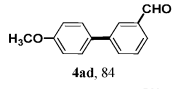
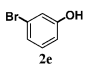
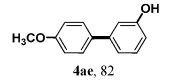
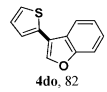
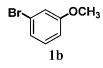
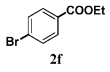
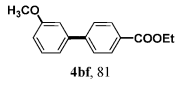
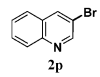
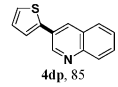
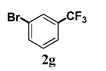
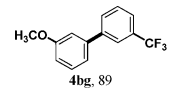
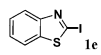
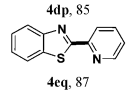
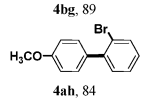
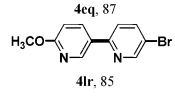
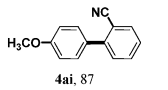
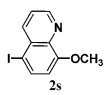
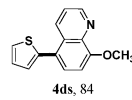
Synthesis of Various Biaryls through the One-Pot, Two-Step SSC Reaction

With the above stannylation method in hand, we next performed a one-pot, two-step SSC reaction to construct biaryls from two aryl halides. To our delight, this was facilely achieved by adding the second aryl bromide or iodide in the same flask[42] upon completion of the stannylation (Table 3). Noteworthy is that the use of only 1.0 equiv. of the second halide led to efficient coupling and no additional $Pd(PPh_3)_4$ catalyst was required.

The scope of this one-pot SSC reaction was investigated by using various aryl and heteroaryl bromides or iodides as coupling partners, and the results are summarized in Table 3. Overall, such a one-pot reaction showed broad substrate scope and remarkable functional group tolerance. Nitrated and fluorinated bromides readily participated in the cross-couplings to furnish the desired biaryls in high yields (Table 3, entries 1, 3 and 7). Free carboxyl and phenolic hydroxy groups were both found to be well tolerated in

Table 3. Scope of the one-pot stannylation/Stille cross-coupling reactions.[a]



Entry	Ar^1X^1	Ar^2X^2	Product, yield[b] [%]	Entry	Ar^1X^1	Ar^2X^2	Product, yield[b] [%]
1	 **1a**	 **2a**	 **4aa**, 92	12	**2k**	**1a**	**4ak**, 41
2	**1a**	 **2b**	 **4ab**, 87	13	**2j**	 **2l**	 **4jl**, 88
3	**1a**	 **2c**	 **4ac**, 91	14	 **1d**	 **2m**	 **4dm**, 90
4	**1a**	 **2d**	 **4ad**, 84	15	**1d**	 **2n**	 **4dn**, 89
5	**1a**	 **2e**	 **4ae**, 82	16	**1d**	 **2o**	 **4do**, 82
6	 **1b**	 **2f**	 **4bf**, 81	17	**1d**	 **2p**	 **4dp**, 85
7	**1b**	 **2g**	 **4bg**, 89	18	 **1e**	 **2q**	 **4eq**, 87
8	**1a**	 **2h**	 **4ah**, 84	19	**2l**	 **2r**	 **4lr**, 85
9	**1a**	 **2i**	 **4ai**, 87	20	**1d**	 **2s**	 **4ds**, 84
10	 **1c**	**2j**	**4cj**, 89	21	**2l**	**2t**	**4lt**, 91
11	**1a**	**2k**	**4ak**, 88	22	**1c**	**2u**	**4cu**, 80 (83)[c]

[a] The stannylation step: the first bromide/iodide (1 mmol), $Pd(PPh_3)_4$ (5 mol-%), Sn_2Bu_6 (1.1 mmol), KOH (3 mmol), and TBAB (3 mmol) in H_2O (5 mL); the Stille step: the second bromide/iodide (1 mmol) and CuI (10 mol-%). [b] Yield of isolated product. [c] Reaction was performed on a 10-mmol scale: bromide **1c** (10 mmol), Sn_2Bu_6 (11 mmol), $Pd(PPh_3)_4$ (5 mol-%), KOH (30 mmol), and TBAB (30 mmol) in H_2O (50 mL) were heated at 100 °C under MW irradiation for 6 min; after cooling, iodide **2u** (10 mmol) and CuI (10 mol-%) were added, and the mixture was heated at 100 °C under MW irradiation for 8 min.

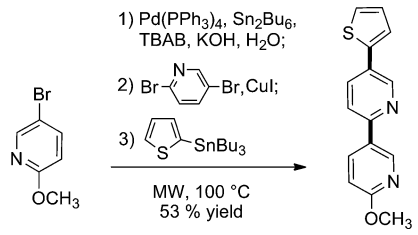
this coupling reaction (Table 3, entries 2 and 5). Notably, an aldehyde and a methyl ketone performed well in the cross-couplings without evident disproportionation and competitive deprotonation (Table 3, entries 4 and 14). Furthermore, ester and cyano groups were also tolerated (and no hydrolysis reactions took place) under the present conditions (Table 3, entries 6 and 9). If both Br and I groups were present on the same substrate, the coupling reaction was selective at the iodo functional group, and the aryl bromide handle was preserved in the biaryl product (Table 3, entries 8 and 11). Moreover, sterically hindered *ortho*-substituted aryl halides could be employed as the substrates in both steps (Table 3, entries 8–10 and 22).

Heterobiaryls have important biological activities, but their synthesis by cross-coupling methods is often challenging. It was demonstrated that such a one-pot method could efficiently cross-couple a large variety of challenging heteroaryl substrates in good to high yields (Table 3, entries 13–19). For example, quinoline iodide and quinoxaline bromide readily underwent the SSC reaction to form new biologically active heterobiaryls[43–45] (Table 3, entries 20 and 21). Furthermore, the SSC reaction of *N*-methyl-protected indolyl iodide proceeded smoothly to furnish a new biologically active analog[46] in a good yield of 80% (Table 3, entry 22). In addition, the present procedure proved to be very easy to scale up. We performed entry 22 on a 10 mmol scale; the yield was almost identical to that obtained on a 1-mmol scale.

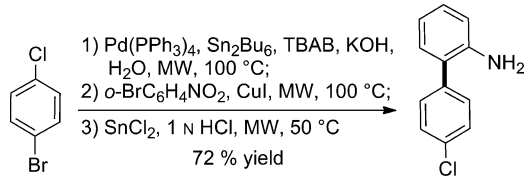
One of the major features of this SSC reaction is the coupling of two different aryl bromides/iodides in one pot. Therefore, the order in which the two aryl halides are added to the reaction can have a significant effect on the yield. In the case of 4-bromo-4′-methoxybiphenyl, for example, if electron-rich 4-bromoanisole was stannylated and electron-deficient 1-bromo-4-iodobenzene was used as the electrophile in the second step, a much higher conversion of 88% was achieved than if they were employed in the reverse order (41% yield; Table 3, entry 11 vs. 12).

Remarkably, this SSC reaction also exhibited high regioselectivity. For example, the arylation of 2,5-dibromopyridine was found to occur selectively at the C2 position (Table 3, entry 19). Given that its diarylation in a one-pot procedure has remained poorly documented to date,[47,48] we preferred to iteratively diarylate this compound in one pot. As seen in Scheme 2, such a regioselective diarylation was achieved by performing the SSC reaction followed directly by the second Stille cross-coupling in a one-pot manner with the use of the $Pd(PPh_3)_4$ catalyst, which led to isolation of the desired double-coupled product in 53% overall yield.

To illustrate the synthetic potential of this one-pot SSC method, 4′-chlorobiphenyl-2-amine,[49,50] known as the key intermediate in the synthesis of the fungicide Boscalid,[51,52] was synthesized by using a one-pot protocol. As illustrated in Scheme 3, the synthesis started from two readily available and cheap bromides, and in situ generated 4′-chloro-2-nitrobiphenyl was then reduced readily to the amine in 72% yield.



Scheme 2. The diarylation of 2,5-dibromopyridine in a one-pot sequence.



Scheme 3. The one-pot synthesis of the Boscalid intermediate.

Conclusions

We developed a highly efficient $Pd(PPh_3)_4$-catalyzed cross-coupling reaction of two aryl halides. The present method merges stannylation with cross-coupling into one pot, which allows the rapid preparation of various biaryls (in 10 min) in good to high yields under microwave heating in water at 100 °C. A number of functional groups were tolerated, and this method could be applied to various substrates such as aryl and heteroaryl bromides or iodides in both coupling partners. Moreover, the reaction showed high regioselectivity in the cross-couplings of 2,5-dibromopyridine, which allowed a one-pot iterative diarylation. The potential application of this method was illustrated in the facile synthesis of the key intermediate of Boscalid.

In summary, the salient advantages of this one-pot method include the elimination of the isolation/purification steps of the aryl stannanes, the use of MW heating, and the use of water as single solvent, which make this protocol not only simple and step economical but also highly efficient for the synthesis of the biaryls.

Experimental Section

General Methods: All reagents required for this study were purchased from commercial sources. ^1H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with a Bruker Avance DPX 400 (400 MHz) spectrometer in $CDCl_3$ by using tetramethylsilane as an internal standard. HRMS were recorded with a micrOTOF-QII mass spectrometer.

General Procedure for the Synthesis of the Aryl Stannanes: A two-neck flask containing a Teflon®-coated magnetic stirrer bar was charged with the bromide/iodide (1 mmol), $Pd(PPh_3)_4$ (58 mg, 50 μmol), Sn_2Bu_6 (638 mg, 1.1 mmol), KOH (180 mg, 3 mmol), TBAB (967 mg, 3 mmol), and H_2O (5 mL). The mixture was heated to 100 °C under MW irradiation (500 W) for the required time until the reaction reached completion. Then, H_2O (10 mL) was added to the cold reaction mixture, which was extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with H_2O

(20 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the stannane product.

General Procedure for the Cross-Coupled Biaryls: A two-neck flask containing a Teflon®-coated magnetic stirrer bar was charged with the first bromide/iodide (1 mmol), $Pd(PPh_3)_4$ (58 mg, 50 μmol), Sn_2Bu_6 (638 mg, 1.1 mmol), KOH (180 mg, 3 mmol), TBAB (967 mg, 3 mmol), and H_2O (5 mL). The mixture was heated to 100 °C under MW irradiation (500 W) for 4 min until the bromide/iodide was consumed. After cooling the mixture to room temperature, the second bromide/iodide (1 mmol) and CuI (19 mg, 100 μmol) were added. Subsequently, the mixture was heated to 100 °C for 6 min until the coupling reaction reached completion. Then, H_2O (15 mL) was added to the cold mixture, which was extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with H_2O (20 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash chromatography or by recrystallization with MeOH to afford the biaryl product.

Supporting Information (see footnote on the first page of this article): Experimental details and copies of the ^1H NMR and ^{13}C NMR spectra.

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