Homogeneous Catalysis

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Palladium-Catalyzed Decarboxylative C−H Bond Arylation of Thiophenes**

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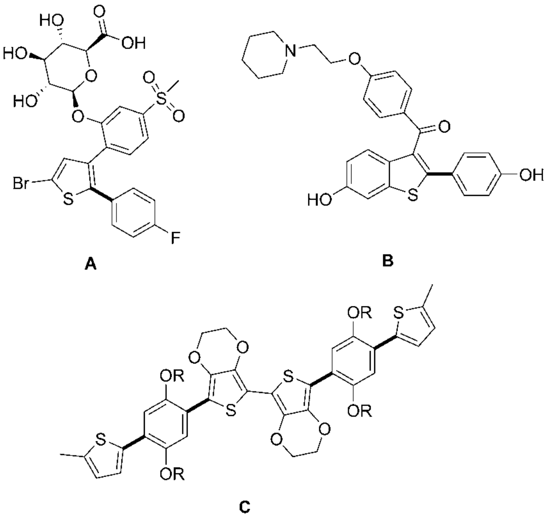
2-Arylthiophene is an ubiquitous structural motif in natural products,[1] pharmaceuticals,[2] and functional organic materials,[3] as exemplified by the three 2-arylthiophene-containing molecules depicted in Scheme 1.



Scheme 1. Three examples illustrating the importance of compounds containing a 2-arylthiophene moiety: A natural product (**A**);[1a] Evista (**B**), a medicine used to prevent and treat osteoporosis;[2b] ITPEEPT (**C**), an electrochromic device.[3b]

Conventionally, 2-arylthiophenes are synthesized by cross-coupling reactions of (hetero)aryl halides with (hetero)aryl organometallic reagents.[4] Owing to the wide applications of this family of compounds, the development of new methods for the synthesis of valuable 2-arylthiophenes from simple and readily available starting materials by concise steps continues to be a target of intense interest.[4–6] In this context, the direct C−H arylation of thiophenes with aryl iodides and bromides has been achieved by using Pd,[5a–f] Ir,[5g] Rh,[5h] and Cu[5i] catalysts; thus thiophenes were directly used to replace expensive thienyl organometallic reagents in traditional cross-coupling reactions. As a highly efficient approach to 2-arylthiophenes, the oxidative cross-coupling of two unfunctionalized arenes has been realized in the palladium-catalyzed reactions of thiophenes with C−H acidic polyfluoroarenes[6a] and nitrogen-containing heteroarenes.[6b] Moreover, metal-free oxidative cross-couplings of thiophenes with electron-rich arenes has also been reported.[6c] Although these transformations represent substantial progress toward the syntheses of 2-arylthiophenes in an atom-economical and environmentally benign way, there is significant room for improvement with respect to the generality and functional-group tolerance of these state-of-the-art methods.

On the other hand, the use of carboxylic acids as cross-coupling components by a metal-promoted decarboxylation process is a rapidly growing area of research because of their low cost, diversity, and ready availability.[7–12] Recently, decarboxylative cross-coupling reactions have been expanded to decarboxylative C−H bond functionalization,[11] including intramolecular reactions for the syntheses of dibenzofurans,[11b] intermolecular reactions for the selective arylation of indoles,[11c,d] *ortho* acylation of acetanilides,[11g,h] the construction of azole–azole linkages,[11i] and the direct arylation of C−H acidic polyfluorobenzenes.[11f,j] A decarboxylative C−H bond functionalization that combines two newly emerging approaches, that is, decarboxylation and direct C−H bond functionalization, offers a new synthetic strategy in synthesis. However, the challenges posed by this promising process remain. For example, many of the decarboxylative C−H bond functionalization reactions were restricted to a narrow range of arene carboxylic acids because the reactivity of the arene carboxylic acids toward decarboxylation is very sensitive to the substitutents on benzene rings. Herein, we report the decarboxylative C−H bond arylation of thiophenes catalyzed by a $Pd(OAc)_2/Ag_2CO_3$ system; electron-rich, electron-deficient, and heterocyclic benzoic acids can all be used as aryl sources in this reaction and a broad spectrum of functional groups can be tolerated.

As generally proposed for similar processes, the Pd/Ag-catalyzed decarboxylative C−H arylation of thiophenes may involve a Pd-promoted C−H cleavage to form a palladium intermediate, a Ag-promoted decarboxylation to generate an aryl silver species, a subsequent aryl transfer from Ag to Pd, and reductive elimination (Scheme 2). In light of this proposal, we envisioned that the major problems impeding the execution of the target process would result from the following side reactions: 1) the unstable aryl silver intermediate is liable to protodecarboxylation[12] and decarboxylative homocoupling[10j] if the desired cross-coupling reaction

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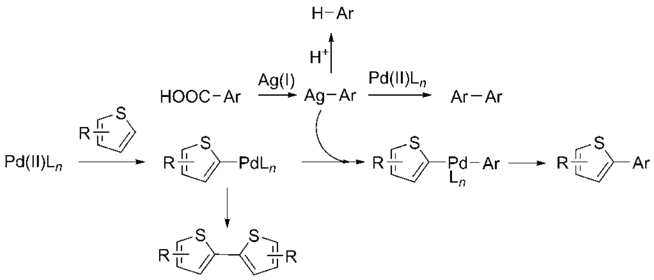
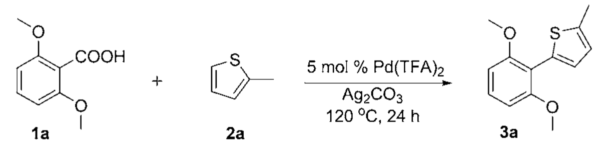


Scheme 2. Proposed mechanism for decarboxylative C−H bond arylation of thiophenes.

is not sufficiently fast; 2) the homocoupling of thiophenes occurs in the presence of a Pd catalyst under the oxidative conditions.[13] To avoid these unwanted side reactions, the reaction system must achieve a balance between the rate of the Ag-promoted decarboxylation and the rate of the steps that involve Pd. Our strategy was to identify the factors controlling the Ag-mediated decarboxylation step, the inhibitors of the homocoupling of the thiophenes, and the promoter for the steps involving the Pd-catalyzed cross-coupling reaction. Previous studies performed by our group[8c–e,11d,j] and others[8a,9b,o,12b,c] have shown that variation of the solvent, temperature, and silver source exerts a significant effect on the Ag-mediated decarboxylation. Moreover, sterically bulky ancillary ligands such as phosphines are well known to accelerate the reductive elimination step, and may also favor the transmetalation step since in many cases transmetalation has been proposed to occur via a three-coordinate palladium intermediate, which is generated by the dissociation of ligands.[14] Meanwhile, by reducing the electrophilicity of the thienyl palladium intermediate, which was generated from the palladation of the thiophene, electron-donating ligands can inhibit further electrophilic attack of this palladium intermediate on thiophene and therefore suppress the homocoupling reaction of thiophenes.

The reaction of 2,6-dimethoxybenzoic acid (**1a**) with 2-methylthiophene (**2a**) was chosen as a model reaction for the optimization studies. Table 1 presents some selected results from these optimization studies that show the effects of the solvent, phosphine ligand, and other factors on the reaction outcome. Initially, we examined the feasibility of this model reaction using the reaction conditions we previously established for the decarboxylative C−H bond arylation of polyfluorobenezenes.[11j] Gratifyingly, the reaction of **1a** with 1.5 equivalent of **2a** conducted in a DMSO/dioxane (1:20) solvent system at 120 °C in the presence of 5 mol% of Pd(TFA)$_2$, 10 mol% of PCy$_3$, and 2 equivalents of Ag$_2$CO$_3$ gave the desired product **3a** in 65% yield (entry 1). Varying the ratio of DMSO to dioxane in the mixed solvent system led to changes in both the yield of **3a**, and the amount of unwanted protodecarboxylation product (entries 1–3). When the ratio of DMSO to dioxane was changed to 2:18 the best yield was obtained, under otherwise identical reaction conditions (entry 2). The use of more-polar solvents, such as DMSO/DMF (1:20) and NMP, resulted in only a trace of **3a** with a lot of the protodecarboxylation by-product formed because the Ag-promoted decarboxylation was too fast (entries 4 and 5). The other phosphine ligands that were tested proved to be inferior to PCy$_3$, except for *tert*-butyl Xphos (entries 6–12 and 14), which was as efficient as PCy$_3$ (entry 13). Compared with PCy$_3$, the less-effective phosphine ligands probably retarded the Pd-promoted steps since more

Table 1: Selected results from the optimization studies for the decarboxylative C−H arylation of 2-methylthiophenes with 2,6-dimethoxybenzoic acid.[a]

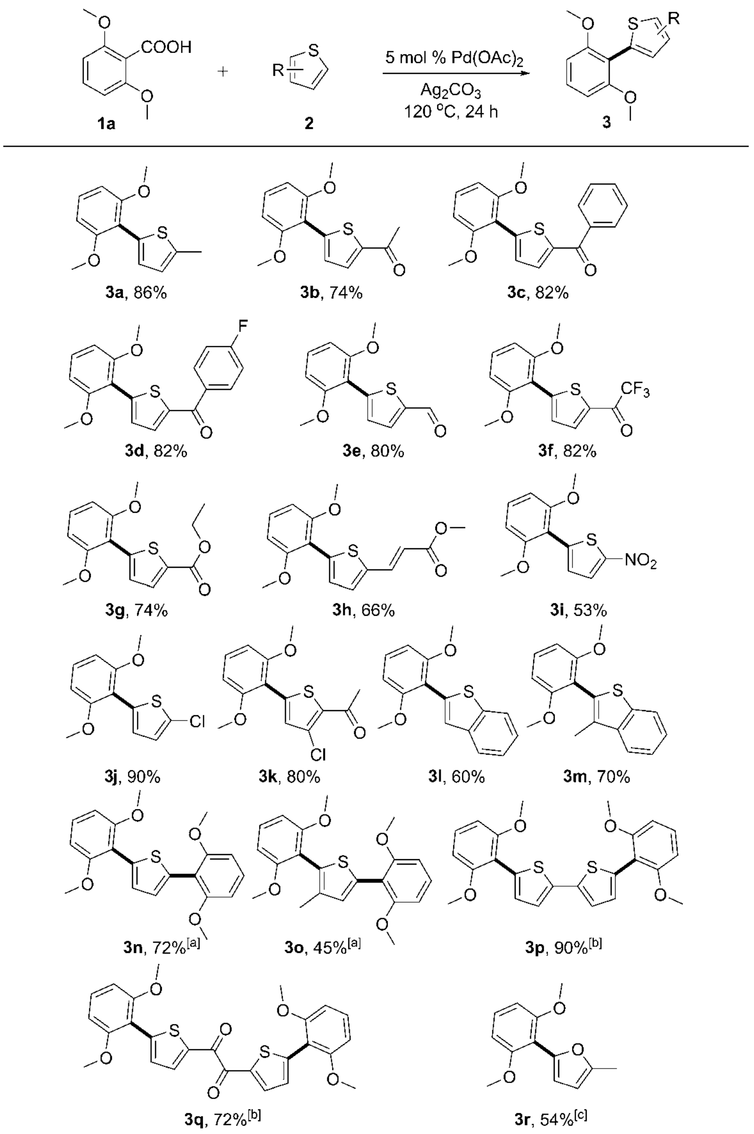


Entry	**1a/2a** (mol:mol)	Ligand	Solvent (v:v)	Yield [%][b]
1	1:1.5	PCy$_3$	DMSO/dioxane (1:20)	65
2	1:1.5	PCy$_3$	DMSO/dioxane (2:18)	72
3	1:1.5	PCy$_3$	DMSO/dioxane (4:16)	67
4	1:1.5	PCy$_3$	DMSO/DMF (1:20)	trace
5	1:1.5	PCy$_3$	NMP	trace
6	1:1.5	PPh$_3$	DMSO/dioxane (2:18)	48
7	1:1.5	tBu$_3$P·HBF$_4$	DMSO/dioxane (2:18)	68
8	1:1.5	PCp$_3$·HBF$_4$	DMSO/dioxane (2:18)	64
9	1:1.5	iPr$_3$P·HBF$_4$	DMSO/dioxane (2:18)	66
10	1:1.5	tBu$_2$MeP·HBF$_4$	DMSO/dioxane (2:18)	66
11	1:1.5	S-Phos	DMSO/dioxane (2:18)	67
12	1:1.5	Davephos	DMSO/dioxane (2:18)	61
13	1:1.5	*t*-butyl XPhos	DMSO/dioxane (2:18)	73
14	1:1.5	XPhos	DMSO/dioxane (2:18)	63
15[c]	1:1.5	PCy$_3$	DMSO/dioxane (2:18)	75
16[c]	1:1.5	PCy$_3$	DMSO/DME (2:18)	72
17[c]	1:1.5	PCy$_3$	DMSO/DME (3:17)	83
18[c]	1:1.5	PCy$_3$	DMSO/DME (4:16)	68
19[c]	1:1.5	–	DMSO/DME (3:17)	70
20[c]	**1.2:1**	**PCy$_3$**	**DMSO/DME (3:17)**	**86**
21[d]	1.2:1	PCy$_3$	DMSO/DME (3:17)	0

[a] Reaction conditions: 5 mol% of Pd(TFA)$_2$, 10 mol% of phosphine ligand, 2 equiv of Ag$_2$CO$_3$, 2 mL of solvent, 120 °C, 24 h. [b] Yields of the isolated products. [c] Pd(OAc)$_2$ was used in place of Pd(TFA)$_2$.
[d] Reaction was run in the absence of Pd(OAc)$_2$. Cy = cyclohexyl, DME = 1,2-dimethoxylethane, DMSO = dimethylsulfoxide, NMP = *N*-methylpyrrolidone, Pd(TFA)$_2$ = palladium(II) trifluoroacetate.

protodecarboxylation by-product was obtained with these ligands, thus indicating that the Ag-mediated decarboxylation was unaffected and went to completion. $Pd(OAc)_2$ was observed to perform slightly better than $Pd(TFA)_2$ (entry 15 versus entry 2). With 5 mol % of $Pd(OAc)_2$ as the catalyst, further investigations of the solvent effect revealed that a DMSO/DME (3:17) solvent system afforded the product in 83 % yield. Interestingly, the best yield (86 %) was obtained from the reaction of **2a** with nearly an equimolar amount of **1a** (**2a**/**1a** = 1:1.2), when 2-methylthiophene was the limiting reagent. It is worthy of note that even though 70 % yield was achieved in the absence of PCy_3 (entry 19), PCy_3 played a key role in overcoming side reactions and enhancing the efficiency of the desired reaction when the substrate scope was expanded beyond the scope of the model reaction. A control experiment showed that a Pd source was required for this reaction (entry 21).

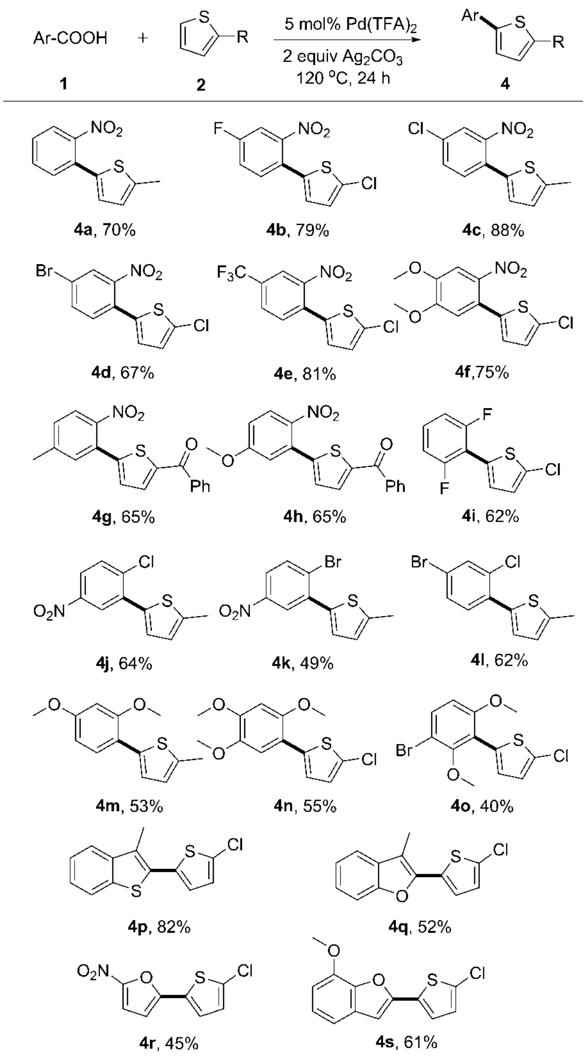
With the optimized reaction conditions established, the substrate scope with respect to the thiophenes was examined (Scheme 3). This reaction was compatible with keto, aldehyde, ester, trifluoromethyl, alkenyl, nitro, fluoro, and chloro substituents, and furnished the desired products in generally good to excellent yields. In addition to thiophenes, benzothiophenes also smoothly underwent this reaction to generate the corresponding products in good yields (**3l** and **3m**). In reactions with thiophenes having two nucleophilic positions available for reaction, diarylation took place with moderate to excellent yields (**3n**–**3q**). Notably, thiophene-based π-conjugated systems (**3n**–**3q**), which are widely studied in material science,[3] can be easily constructed by means of this reaction. Furthermore, 2-methylfuran, a different heterocycle, was also an appropriate reactant for the reaction (**3r**).



Scheme 3. Scope of thiophenes. Reactions were run under the reaction conditions in Table 1, entry 20. Yields are of the isolated products (average of two runs). [a] 2.4 equiv of **1a** and 4 equiv of Ag_2CO_3 were used. [b] 10 mol % of $Pd(OAc)_2$, 20 mol % of PCy_3, 2.4 equiv of **1a**, and 4 equiv of Ag_2CO_3 were used. [c] 5 mol % of $Pd(TFA)_2$ was used as the catalyst.

Considering that the acidity and decarboxylation rate of benzoic acids depend to a high degree on the electronic nature of the substitutents on the benzene rings, we reasoned that the reaction conditions would need to be adjusted for different benzoic acids to achieve efficient transformations. Gratifyingly, slight modifications to the optimal reaction conditions established above allowed the use of a variety of benzoic acids (Scheme 4). Generally, tuning the concentration of DMSO and/or the loading of PCy_3 was effective to inhibit the unwanted side reactions and enhance the desired reaction. Consequently, electron-rich, electron-deficient, and heterocyclic benzoic acids were all suitable substrates. A variety of substituents on both coupling partners were tolerated. Particularly noteworthy was the tolerance, in most cases, to halogen groups, which provide a versatile synthetic handle for further functionalization of the products. The ease with which aryl units bearing electron-withdrawing groups could be installed onto thiophenes constitutes another advantage of this reaction since the electron-deficient aryl organometallic reagents that are used in traditional cross-coupling reactions are either difficult to synthesize or have a low reactivity. In addition, the nitro-substituted products from this reaction could be easily converted by selective reduction into amino-substituted 2-arylthiophenes, which are widely found in bioactive compounds.[1,2]

In conclusion, the $PCy_3/Pd(OAc)_2$ or $Pd(TFA)_2$ systems, in combination with Ag_2CO_3, proved to be a versatile catalysts that efficiently promoted the decarboxylative C–H bond arylation of thiophenes with inexpensive and readily available benzoic acids as arylating reagents. This protocol exhibited broad substrate scope with respect to both the thiophenes and the benzoic acids, thus providing an attractive alternative to the existing methods for the syntheses of 2-arylthiophenes.



Scheme 4. Scope of aryl carboxylic acids. Reaction conditions: 5 mol% of Pd(TFA)$_2$, 10–15 mol% of PCy$_3$, 2 equiv of Ag$_2$CO$_3$, 120 °C, 24 h, and 2 mL of solvent. Yields are of the isolated products (average of two runs).

The establishment of a balance between the Ag-mediated decarboxylation and the Pd-promoted process was the key to expanding this reaction to a wide range of benzoic acids. This approach is a useful strategy to develop new decarboxylative C–H bond functionalization methods.

Experimental Section

In a glove box, a 25 mL tube equipped with a stir bar was charged with Pd(OAc)$_2$ (0.01 mmol), PCy$_3$ (0.02 mmol), 2,6-dimethoxybenzoic acid (0.24 mmol), 2-methylthiophene (0.2 mmol), Ag$_2$CO$_3$ (0.4 mmol), DMSO (0.3 mL), and DME (1.7 mL). The tube was fitted with a Teflon screwcap and removed from the glove box. The reaction mixture was stirred at 120 °C for 24 h. After cooling to RT, the reaction mixture was diluted with diethyl ether (10 mL) and filtered through a pad of silica gel; the pad of silica gel was then washed with the same solvent (20–50 mL). The filtrate was washed with a saturated aqueous solution of NaCl (30 mL). The organic phase was dried over Na$_2$SO$_4$, filtered, and then concentrated under reduced pressure. The residue was then purified by flash column chromatography on silica gel (1% diethyl ether/*n*-hexane as eluent) to provide the corresponding product **3a** in 86% yield.

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Keywords: carboxylic acids · C–H arylation · decarboxylation · palladium · sulfur heterocycles

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