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COMMUNICATION

Palladium-catalyzed desulfitative C–H arylation of azoles with sodium sulfinates†

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A palladium-catalyzed desulfitative C–H arylation of azoles with sodium sulfinates using $Cu(OAc)_2 \cdot H_2O$ as oxidant has been discovered. The reaction proceeded well for a range of different substrates under oxidative conditions. A series of aryl-substituted azoles have been synthesized in moderate to good yields.

Aryl-substituted azoles are common building blocks for the synthesis of pharmaceuticals, natural products, functional materials, and many other biologically active molecules.[1] The conventional approaches for the preparation of these important compounds mainly rely on either the cross-coupling of 2-aminophenol (or thiophenol) in the presence of Lawesson's reagent[2] or the metal-catalyzed intramolecular cyclization of thioformanilides.[3] Over the past decades, the activation of C–H bonds has received much attention for the straightforward construction of C–C and C–hetero bonds.[4,5] This strategy is even more appealing for the functionalization of heteroaromatic substrates due to problematic homocoupling and poor stability under oxidative conditions.[6] Over the past several years, aryl-substituted azoles have been successfully synthesized by direct C–H activation and subsequent C–C bond formation with aryl halides,[7] arylsilanes,[8] aromatic carboxylic acids,[9] aryl boronic acids,[10] and aryl triflates (or mesylates and sulfamates).[11] Recently, the groups led by Hu and You, Ofial, Yamaguchi and Itami, and Zhang and Li successfully developed various efficient palladium-catalyzed dehydrogenative cross-couplings (CDC)[12] of two heteroarenes which obviate the need for any preactivation of the substrates.[13]

Arenesulfonyl chlorides are active compounds and are used as starting materials for preparing compounds containing sulfonyl groups.[14] They are also used as aryl sources for C–C bond forming reactions *via* desulfitative Heck type reactions under harsh conditions. The first palladium-catalyzed desulfitative C–C bond-forming reactions with arenesulfonyl chlorides were developed by Kasahara *et al.* and Miura and co-workers under high reaction temperature,[15] and Dong and co-workers successfully extended this strategy recently for direct arylation of 2-phenylpyridines.[16]

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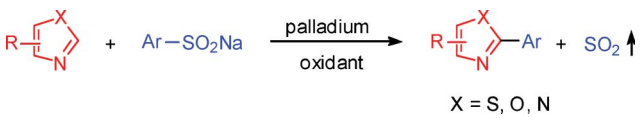
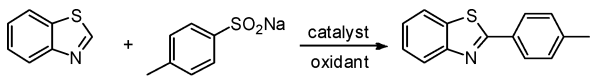
Compared to the active and moisture-sensitive arenesulfonyl chlorides, arenesulfinic acid sodium salts are comparably stable and easy to handle. Thus, arenesulfinic acid sodium salts have the potential to serve as ideal aryl sources for C–C bond forming reactions *via* SO_2 release.[17] In 1992, Sato and Okoshi reported an efficient palladium-catalyzed desulfitative biaryl synthesis between sulfinic acid sodium salts and aromatic bromides under harsh conditions.[18] Since then, however, little progress has been made in this field. Very recently, we and others developed various palladium-catalyzed desulfitative Heck-type coupling and aryl ketone forming reactions between sodium sulfinates and nitriles (or aldehydes) under relatively mild reaction conditions.[19] The desulfitative reactions are not very sensitive to moisture. The extension of this methodology to the direct C–H arylation of azoles would afford a straightforward and alternative synthetic route to aryl-substituted azoles. In continuation of our interest in using aromatic sulfinic acids (salts) as aryl sources under mild reaction conditions, herein we describe the first palladium-catalyzed desulfitative arylation of azoles with aromatic sodium sulfinates *via* C–H activation. (Scheme 1).



Scheme 1 General desulfitative C–H arylation of azoles.

We began our study by examining the reaction of benzothiazole (**1a**) with *p*-toluenesulfinic acid sodium salt (**2a**) in *N*-methyl-2-pyrrolidone (NMP)/diglyme by using $Pd(OAc)_2$ as catalyst and oxygen as oxidant at 120 °C. The desired product was obtained in 42% yield as determined by GC and ^1H NMR methods (Table 1, entry 1). Other oxidants were tested under similar reaction conditions (entries 2–6). The reaction yield could be improved to 51% when TBHP (*tert*-butyl hydroperoxide) was used. $FeCl_3$ and $CuBr_2$ were not efficient oxidants for this kind of transformation (entries 3 and 4). A good yield could be obtained when $CuCl_2 \cdot H_2O$ was used (entry 5). To our delight, the desired product 2-*p*-tolylbenzothiazole (**3a**) was obtained in 91% yield when 2 equivalents of $Cu(OAc)_2 \cdot H_2O$ was used as the oxidant without adding any drying reagent (entry 6). Other palladium salts were also investigated, using $Cu(OAc)_2 \cdot H_2O$ as the oxidant. Among them, $PdCl_2$ and $PdBr_2$ were inefficient catalysts and much lower yields were obtained (entries 7 and 8). Palladium

Table 1 Optimization of the reaction conditions[a]

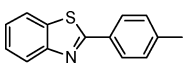
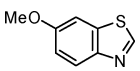
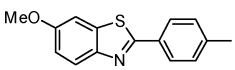
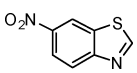
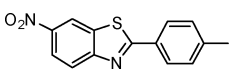
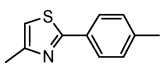
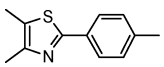
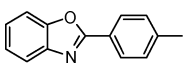
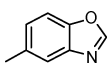
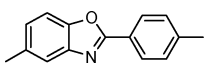
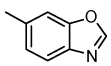
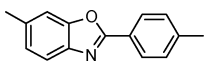
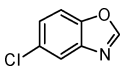
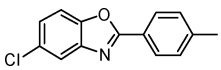
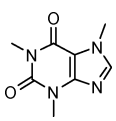
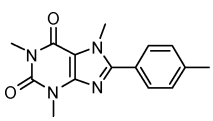


1a 2a 3a

Entry	Catalyst	Oxidant	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	O_2	NMP/diglyme (1 : 3)	42
2	$Pd(OAc)_2$	TBHP	NMP/diglyme (1 : 3)	51
3	$Pd(OAc)_2$	$FeCl_3$	NMP/diglyme (1 : 3)	Trace
4	$Pd(OAc)_2$	$CuBr_2$	NMP/diglyme (1 : 3)	28
5	$Pd(OAc)_2$	$CuCl_2·H_2O$	NMP/diglyme (1 : 3)	74
6	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (1 : 3)	91
7	$PdCl_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (1 : 3)	25
8	$PdBr_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (1 : 3)	18
9	$Pd(CH_3CN)_2Cl_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (1 : 3)	44
10	$Pd(acac)_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (1 : 3)	75
11	$Pd(OH)_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (1 : 3)	74
12	$Pd(NH_3)_4Cl_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (1 : 3)	79
13	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (3 : 1)	58
14	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (1 : 1)	64
15	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	NMP/diglyme (1 : 2)	76
16	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	Dioxane/diglyme (1 : 3)	92
17	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	NMP	56
18	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	Diglyme	49
19	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	Dioxane	52
20	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	DMF	39

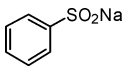
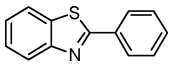
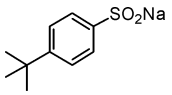
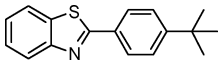
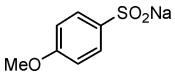
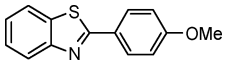
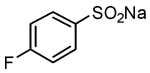
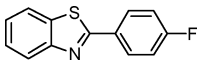
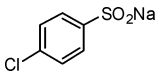
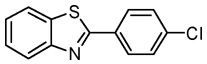
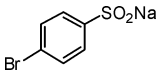
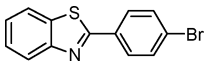
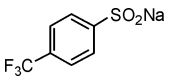
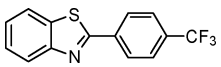
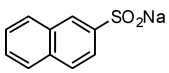
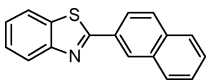
[a] Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (2.5 mol%), oxidant (2 equiv.), 120 °C, 24 h under air unless otherwise noted. [b] GC yield based on **1a**.

Table 2 Desulfitative arylation of **2a** with various heterocyclic compounds[a]

Entry	Azole		Product		Yield (%)[b]
1		**1a**		**3a**	83
2		**1b**		**3b**	76
3[c]		**1c**		**3c**	40
4[c]		**1d**		**3d**	56
5[c]		**1e**		**3e**	45
6		**1f**		**3f**	81
7		**1g**		**3g**	88
8		**1h**		**3h**	78
9		**1i**		**3i**	81
10		**1j**		**3j**	42

[a] Conditions: **1** (0.2 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (2.5 mol%), $Cu(OAc)_2·H_2O$ (2 equiv.), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL), 120 °C, 24 h under air. [b] Isolated yield. [c] Solvent: *N*-methyl-2-pyrrolidone (0.2 mL) and diglyme (0.6 mL).

Table 3 Desulfitative arylation of **1a** with various sodium sulfinates[a]

Entry	Sodium sulfinate		Product		Yield (%)[b]
1		**2b**		**3k**	71
2		**2c**		**3l**	75
3[c]		**2d**		**3m**	70
4[c]		**2e**		**3n**	58
5		**2f**		**3o**	68
6		**2g**		**3p**	50
7[c]		**2h**		**3q**	35
8[c]		**2i**		**3r**	86

[a] Conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $Pd(OAc)_2$ (2.5 mol%), $Cu(OAc)_2 \cdot H_2O$ (2 equiv.), 120 °C, 1,4-dioxane (0.2 mL) and diglyme (0.6 mL), 24 h. [b] Isolated yield. [c] Solvent: *N*-methyl-2-pyrrolidone (0.2 mL) and diglyme (0.6 mL).

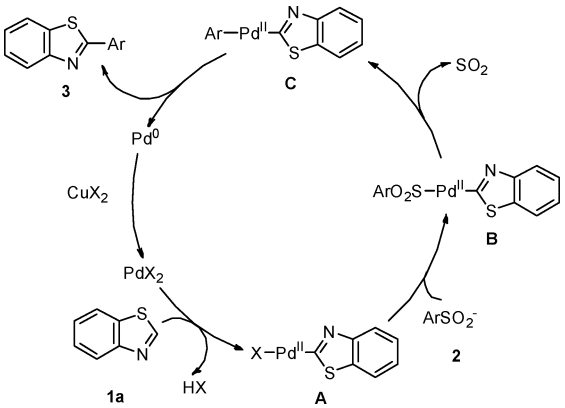
salts such as $Pd(acac)_2$, $Pd(OH)_2$ and $Pd(NH_3)_4Cl_2$ were efficient catalysts and gave the desired product in good yields (entries 10–12). The solvent had a significant impact on the reaction yield. The reaction yield decreased significantly when the ratio of NMP and diglyme changed (entries 13–15). A mixture of 1,4-dioxane and diglyme was also a good solvent system and the desired product was obtained in 92% yield (entry 16). Moderate yields were obtained when the reaction was carried out in pure NMP, diglyme, 1,4-dioxane and DMF (*N*,*N*-dimethylformamide), and the desired product was obtained in 56%, 49%, 52% and 39% yields, respectively (entries 17–20).

With the optimized reaction conditions in hand, we then explored the scope and generality of this transformation. Various azoles bearing electron-withdrawing and donating substituents were investigated (Table 2). 6-Methoxybenzothiazole (**1b**) smoothly coupled with **2a** and gave the desired product in 76% yield (Table 2, entry 2). A nitro group in the C6 position of benzothiazole dramatically decreased the reaction yield (entry 3). 4-Methylthiazole (**1d**) and 4,5-dimethylthiazole (**1e**) both reacted with **2a** and gave the desired products in moderate yields (entries 4 and 5). Benzoxazole and methyl-substituted benzoxazoles were reacted with **2a** and gave the desired products in high yields (entries 6–8). A chloro moiety on benzoxazole was well tolerated under the reaction conditions and afforded the desired product in 81% yield (entry 9). Caffeine is an important biologically active alkaloid with an imidazole motif. Notably, the coupling of caffeine (**1j**) with **2a** afforded the desired product in 42% yield without further optimization of the reaction conditions (about 50% caffeine left, entry 10).

The reaction results of various arylsulfinic acid sodium salts with benzothiazole **1a** are presented in Table 3. A series of functional groups including *tert*-butyl, methoxy, fluoro, chloro, bromo and trifluoromethyl were tolerated under the optimal reaction conditions, and the desired products were obtained in moderate to good yields (entries 2–7). In general, electron-withdrawing substituents on the aromatic sulfinic acids decreased the reaction yields. More bulky substrates such as 2-naphthylsulfinic acid sodium salt (**2i**) also reacted with **1a** efficiently and gave the product in 86% yield (entry 8).

A plausible mechanism to rationalize this transformation is illustrated in Scheme 2. Take arylation of substrate **1a** as an example. First, the Pd(II) catalyst reacts with the benzothiazole **1a** to form an Ar–Pd(II)–X intermediate **A** (X = OAc), which is subsequently displaced by sulfinic acid **2** to form intermediate **B**. This intermediate species undergoes desulfination to generate the aryl-palladium complex **C**. A reductive elimination of **C** affords the desired product **3** and the Pd(0) catalyst is reoxidized to Pd(II) by $Cu(OAc)_2$, thus closing the catalytic cycle.

In summary, we have demonstrated a novel palladium-catalyzed desulfitative direct arylation of azoles in the presence of an oxidant. Various aromatic sulfinic acid sodium salts with or without substituents selectively coupled with azoles and afforded the adducts



Scheme 2 Proposed mechanism.

in moderate to good yields. Unlike decarboxylative coupling reactions, no electron-withdrawing or -donating group *ortho* to the sulfinic acid group was necessary to ensure the desulfitative coupling.[20] Functional groups such as methoxy, bromo, fluoro, and chloro on the aromatic sulfinic acid sodium salts were all well tolerated under these reaction conditions. This method affords an alternative route for the synthesis of heteroaromatic biaryls. The scope, mechanism, and synthetic applications of this reaction are under investigation.

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