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An efficient tandem elimination–cyclization–desulfitative arylation of 2-(*gem*-dibromovinyl)phenols(thiophenols) with sodium arylsulfinates†

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An efficient tandem elimination–cyclization–desulfitative arylation of 2-(*gem*-dibromovinyl)phenols(thiophenols) with sodium arylsulfinates has been developed. In the presence of TBAF–$PdCl_2$–$Cu(OAc)_2$–NEt_3, the reactions generated 2-arylbenzofurans(thiophenes) with good yields in one-pot under ligand-free conditions.

Heterocyclic compounds are widely found in nature, such as in biological systems, pharmaceuticals, materials, agriculture and photography.[1] Benzofurans and benzothiophenes are not only important as building blocks, but also as the structural skeleton of natural products and potential drugs.[2] Because of their importance, the development of practical synthetic methods for the synthesis of them is highly desirable. Among the reported synthetic methods, the palladium-catalyzed cross-coupling–cyclization reaction from alkynes and *o*-halophenols (thiophenols) is one of the most efficient protocols.[3] Although it offers functional group tolerance and good yields of the products, the scope of *o*-halophenols(thiophenols) is limited. Recently, the syntheses of benzofurans *via* Pd-catalyzed reaction of phenols with propiolates, and Fe-catalyzed reaction of phenols with β-ketoesters were developed, respectively.[4]

Arenesulfonyl chlorides, as aryl sources for C–C bond formation *via* tandem desulfitative C–C coupling reactions have been explored by Kasahara, Miura, Vogel, and Dong *et al.*[5] After then, Wang developed a desulfitative Heck-type reaction of arylsulfinic acids with alkenes, and the desulfitative addition of arylsulfinic acids to nitriles.[6] Compared with moisture-sensitive arylsulfonyl chlorides and arylsulfinic acids, sodium arylsulfinates are more stable, and may serve as the aryl source *via* the expulsion of SO_2 for C–C bond formation, although they are generally used as sulfonylation reagents[7] and have been less used as an aryl source *via* desulfitative reactions.[8] Most recently, there are several reports on the tandem desulfitative reactions of sodium arylsulfinates, as equivalents of organometallics in the presence of Pd-catalyst, with olefins,[9] nitriles,[10] aldehydes,[11] CuCN,[12] and desulfitative C–H arylation with a variety of heterocyclic compounds.[13] It should be noted that Sato and Okoshi reported a Pd-catalyzed desulfitative biaryl synthesis using sodium sulfinates with aromatic bromides under harsh conditions (at 150 °C) in the presence of an essential *P*-ligand 1,2-bis(diphenylphosphino)-ethane in 1992.[14] However, little progress has been made in this field since then.

gem-Dihaloolefins, as one of the important and valuable synthetic intermediates because of their higher reactivity and easy preparation,[15] have attracted much attention in recent years.[16] Especially, 2-(*gem*-dibromovinyl)phenols, 2-(*gem*-dibromovinyl)thiophenols and 2-(*gem*-dibromovinyl)anilines were used for the synthesis of heterocycles, including indoles,[17] benzothiophenes,[18] and benzofurans[17d,18b] on the basis of transition-metal-catalyzed tandem C–N/C–C coupling with organoborons,[17a,18a] alkenes,[17c] and alkynes.[17d] During the investigation of the mechanistic pathway of Pd-catalyzed C–N/Suzuki reaction, Lautens suggested 2-bromoindole as an intermediate,[17i] and 2-bromobenzofurans(thiophenes) and 2-bromoindoles from 2-(*gem*-dibromovinyl)phenols(thiophenols)[18b] and 2-(*gem*-dibromovinyl)anilines[19] *via* Cu- and Pd-catalyzed intramolecular reactions were obtained. It is essential to expand the application of 2-bromobenzofused heterocycles from *gem*-dibromoolefins and their further transformations.

As part of our ongoing efforts on the organic reactions of *gem*-dihaloolefins,[20] herein, we report a novel tandem elimination–cyclization–desulfitative arylation reaction of 2-(*gem*-dibromovinyl)phenols(thiophenols) with sodium arylsulfinates in the presence of TBAF–$PdCl_2$–$Cu(OAc)_2$–NEt_3. The reactions afforded 2-arylbenzofurans(thiophenes) with good yields in one-pot at 110 °C under mild conditions (Scheme 1).

The initial investigation was focused on the optimization of reaction conditions for a model reaction of 2-(*gem*-

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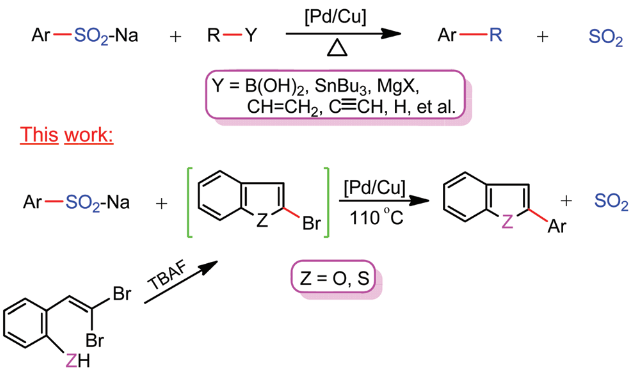
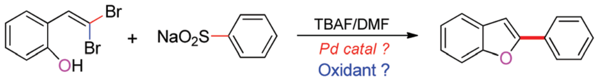


Scheme 1

Table 1 Effect of Pd source and oxidant on the model reaction[a]



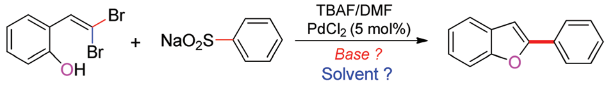
1a **2a** **3a**

Entry	Pd catal.	Oxidant	$3a^b$ [%]
1	$PdCl_2$	$Cu(OAc)_2$	72
2	$PdCl_2$	—	10
3	$Pd(OAc)_2$	$Cu(OAc)_2$	61
4	$Pd(PPh_3)_2Cl_2$	$Cu(OAc)_2$	55
5	$Pd(PPh_3)_4$	$Cu(OAc)_2$	49
6	$Pd(dba)_2$	$Cu(OAc)_2$	45
7	$PdCl_2(CH_3CN)_2$	$Cu(OAc)_2$	38
8	$PdCl_2$	$PhI(OAc)_2$	42
9	$PdCl_2$	$K_2S_2O_8$	35
10	$PdCl_2$	$(NH_4)_2S_2O_8$	32
11	$PdCl_2$	Ag_2O	27
12	$PdCl_2$	DDQ	Trace
13	$PdCl_2$	TBHP	Trace

[a] Reaction conditions: **1a** (0.50 mmol), TBAF (1.0 mmol) in DMF (3.0 mL) at room temperature for 4 h, then **2a** (1.0 mmol), Pd catal. (0.050 mmol), oxidant (1.0 mmol), NEt_3 (1.0 mmol) in DMF at 110 °C for 12 h. [b] Isolated yields.

dibromovinyl)phenol (**1a**) with sodium benzenesulfinate (**2a**). *tetra*-(*n*-Butyl)ammonium fluoride (TBAF), palladium and oxidant are essential in the reaction. As listed in Table 1, $PdCl_2$ exhibited the highest reactivity in the model reaction among the palladium catalysts tested in the presence of TBAF and $Cu(OAc)_2$ in DMF (Table 1, entry 1). In the absence of $Cu(OAc)_2$, the desired product **3a** was isolated only in 10% yield (Table 1, entry 2). Other palladium catalysts, $Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, $Pd(dba)_2$ and $PdCl_2(CH_3CN)_2$ were subsequently inferior (Table 1, entries 3–7). Next, a number of oxidants were examined in the presence of TBAF–$PdCl_2$–NEt_3 in DMF, and Cu-$(OAc)_2$ was found to be the most effective. The use of $PhI(OAc)_2$, $K_2S_2O_8$, $(NH_4)_2S_2O_8$ and Ag_2O showed relatively lower efficiency, and only 27–42% yields of **3a** were obtained (Table 1, entries 8–11). However, DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) and TBHP (*tert*-butyl hydroperoxide) were inactive (Table 1, entries 12 and 13).

Table 2 Effect of base and solvent on the model reaction[a]



1a **2a** **3a**

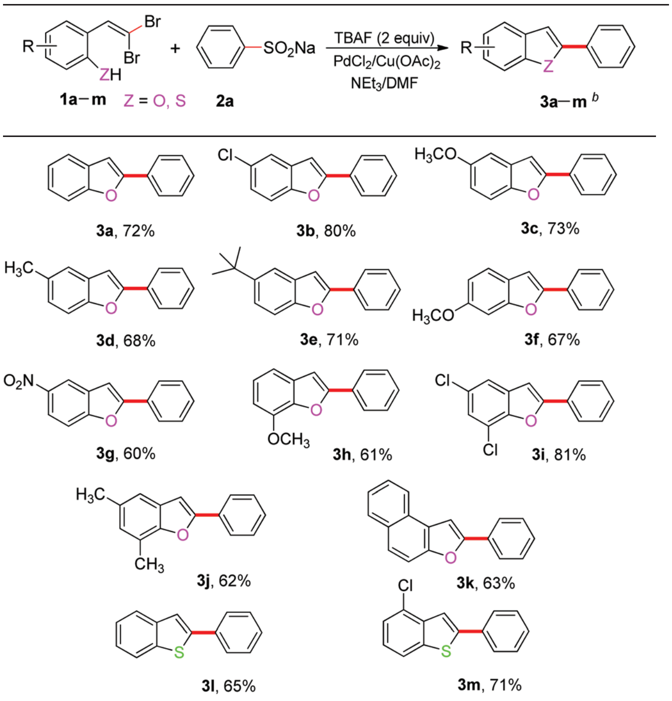
Entry	Base	Solvent	$3a^b$ [%]
1	KF	DMF	17
2	K_2CO_3	DMF	30
3	Cs_2CO_3	DMF	36
4	DBU	DMF	41
5	DABCO	DMF	52
6	N(*n*-Bu)$_3$	DMF	54
7	NEt_3	DMF	72
8	NEt_3	NMP	55
9	NEt_3	THF	44
10	NEt_3	DMSO	41
11	NEt_3	Toluene	35
12	NEt_3	CH_3CN	Trace

[a] Reaction conditions: **1a** (0.50 mmol), TBAF (1.0 mmol) in solvent (3.0 mL) at room temperature for 4 h, then **2a** (1.0 mmol), $PdCl_2$ (0.050 mmol), $Cu(OAc)_2$ (1.0 mmol), base (1.0 mmol) at 110 °C for 12 h. [b] Isolated yields.

On the other hand, the base is also essential in the reaction. A variety of bases were examined and the results indicated that NEt_3 was the most effective one among the examined bases (Table 2, entry 7). Other bases, N(*n*-Bu)$_3$, DABCO (1,4-diazabicyclo[2.2.2]octane), DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene), Cs_2CO_3 K_2CO_3 and KF were inferior and generated **3a** in 17–54% yields (Table 2, entries 1–6). The solvent plays an important role in the model reaction. Among the solvents examined, DMF (*N*,*N*-dimethylformamide) was the most suitable media (Table 2, entry 7). NMP (*N*-methyl-2-pyrrolidone), THF (tetrahydrofuran), DMSO (dimethyl sulfoxide) and toluene were less effective solvents, and 35–55% yields of **3a** were obtained (Table 2, entries 8–11). When the model reaction was performed in CH_3CN, no product was detected and the starting materials were recovered (Table 2, entry 12). The reaction temperature and time also effected the reaction. The model reaction was accomplished in the presence of TBAF–$PdCl_2$–$Cu(OAc)_2$–NEt_3 at 110 °C in 12 h.

The scope of the 2-(*gem*-dibromovinyl)phenols and 2-(*gem*-dibromovinyl)thiophenols was examined in the elimination–cyclization–desulfitative arylation with sodium benzenesulfinate (**2a**) under the optimized reaction conditions. As can be seen from Table 3, the tandem reactions of **2a** with 2-(*gem*-dibromovinyl)phenols (**1a-j**) generated the corresponding products (**3a-j**) in good yields. Electron-donating and electron-withdrawing groups on the benzene rings of 2-(*gem*-dibromovinyl)phenols were tolerated. 2-(*gem*-Dibromovinyl)phenols with an electron-donating group, such as CH_3, CH_3O, and *t*-C_4H_9, and a weak electron-withdrawing group, such as Cl, on the *para*-positions of phenols, gave superior yields of the products (**3b-e**) to that of **3a** and **3g**, without a substituted group and with a strong electron-withdrawing group (NO_2) on the benzene rings. It is obvious that 2-(*gem*-dibromovinyl)phenols

Table 3 The scope of 2-(*gem*-dibromovinyl)phenols(thiophenols) in the reaction[a]



[a] Reaction conditions: **1** (0.50 mmol), TBAF (1.0 mmol) in DMF (3.0 mL) at room temperature for 4 h, then **2a** (1.0 mmol), $PdCl_2$ (0.05 mmol), $Cu(OAc)_2$ (1.0 mmol), NEt_3 (1.0 mmol) in DMF at 110 °C for 12 h. [b] Isolated yields.

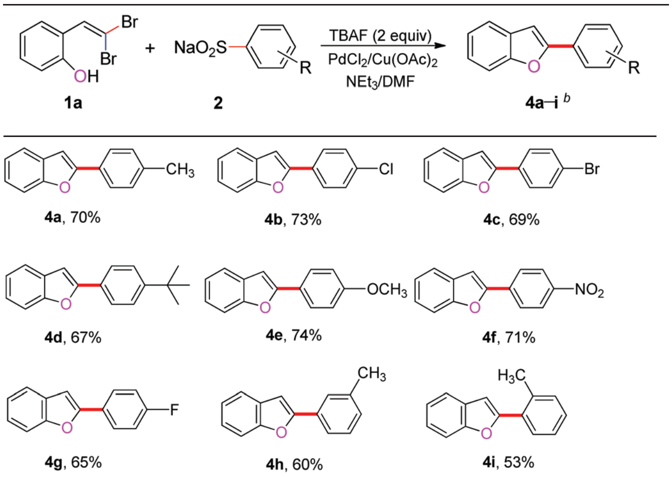
with CH_3O on the *meta*-position of phenol gave an inferior product yield than that on the *para*-position of phenol (**3f** *vs.* **3c**).

Meanwhile, a slight *ortho*-position effect of phenol was observed in the reaction (**3c** and **3f** *vs.* **3h**). 2-(*gem*-Dibromovinyl)(2,4-dichloro)phenol (**1i**) and 2-(*gem*-dibromovinyl)(2,4-dimethyl)phenol (**1j**) underwent the reaction well and afforded the corresponding products **3i** and **3j** in 81% and 62% yields, respectively. Under the present reaction conditions, 1-(*gem*-dibromovinyl)-2-naphthalenol also underwent the tandem reaction to generate **3k** in 63% yield.

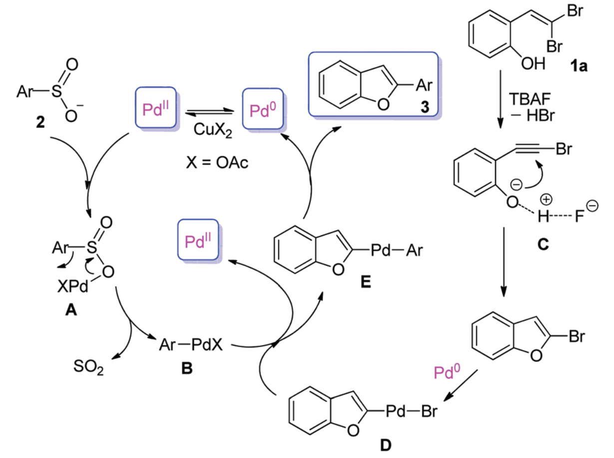
It should be noted that 2-(*gem*-dibromovinyl)thiophenols (**1l** and **1m**) also reacted with **2a** under the present reaction conditions to afford the corresponding products 2-arylbenzothiophenes **3l** and **3m** in 65% and 71% yields, respectively.

On the other hand, the desulfitative arylation reaction between 2-(*gem*-dibromovinyl)phenol (**1a**) with various sodium substituted arylsulfinates was investigated and the results were summarized in Table 4. Sodium arylsulfinates, with different functional groups, including CH_3, Cl, Br, *tert*-C_4H_9, CH_3O, NO_2, F, and CN groups on the *para*- or *meta*-position of benzene rings, reacted with **1a** smoothly to generate the desired products (**4a–h**) in 60–74% yields. It is obvious that an *ortho*-position effect was observed in the reaction and 53% yield of the product (**4i**) was isolated.

Table 4 The scope of sodium arylsulfinates in the tandem reaction[a]

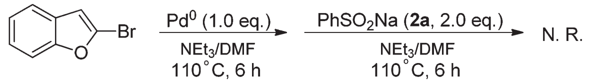


[a] Reaction conditions: **1a** (0.50 mmol), TBAF (1.0 mmol) in DMF (3.0 mL) at room temperature for 4 h, then **2** (1.0 mmol), $PdCl_2$ (0.05 mmol), $Cu(OAc)_2$ (1.0 mmol), NEt_3 (1.0 mmol) in DMF at 110 °C for 12 h. [b] Isolated yields.

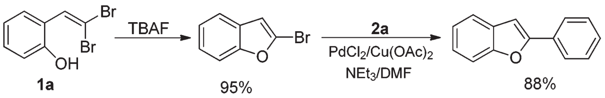


Scheme 2 Possible reaction mechanism.

Although the exact mechanism of this reaction is not clear, a possible pathway is proposed in Scheme 2. The reaction might be through an elimination of 2-(*gem*-dibromovinyl)-phenol and then intramolecular nucleophilic addition (cyclization) affording 2-bromobenzofuran, and Pd-catalyzed desulfitative arylation of sodium arylsulfinate with 2-bromobenzofuran to generate the desired product. Firstly, an elimination of HBr from 2-(*gem*-dibromovinyl)phenol (**1a**) was promoted by TBAF to give an intermediate **C**, followed by an intramolecular nucleophilic addition of **C** assisted by fluoride anion to afford 2-bromobenzofuran. On the other hand, sodium arylsulfinate (**2**) reacted with Pd(II) through a ligand exchange to form a Pd(II)-sulfinate intermediate **A**, which subsequently underwent desulfitation to form an aryl–Pd(II)–X species **B** and release SO_2. The formed **B** reacted with **D**, which was generated from an oxidative addition of the obtained



Scheme 3 The control experiment.



Scheme 4 The formation of 2-bromobenzofuran and its further transformation.

2-bromobenzofuran with Pd(0) to afford **E** *via* transmetalation.[21] After reductive elimination of **E**, the final product **3** was obtained along with the generation of Pd(0). When prepared 2-bromobenzofuran was reacted with Pd(0) black *in situ* from the reduction of PdCl$_2$ in DMF–NEt$_3$ at 110 °C for 6 h, followed by the addition of sodium benzenesulfinate (**2a**, 2.0 equiv.) and then kept at 110 °C for 6 h, no reaction was observed (Scheme 3).

To verify the formation of 2-bromobenzofuran, the reaction of **1a** was carried out in the presence of TBAF and 2-bromobenzofuran was isolated in 95% yield. The obtained 2-bromobenzofuran reacted with **2a** to give **3a** in 88% yield in the presence of the PdCl$_2$–Cu(OAc)$_2$–NEt$_3$ system (Scheme 4).

In conclusion, an efficient tandem elimination–cyclization–desulfitative arylation reaction for the preparation of 2-arylbenzofurans(thiophenes) has been developed. In the presence of TBAF–PdCl$_2$–Cu(OAc)$_2$–NEt$_3$, the reactions of 2-(*gem*-dibromovinyl)phenols(thiophenols) with sodium arylsulfinates proceeded well to afford the desired products with good yields in one-pot under ligand-free conditions. An extended investigation of this kind of reaction and the detailed reaction mechanism are currently under way.

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