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## COMMUNICATION

## Palladium-catalyzed Synthesis of Fluoreones from Bis(2bromophenyl)methanols

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A palladium-catalyzed synthesis of fluorenones has been developed. A variety of bis(2-bromophenyl)methanols could undergo reaction smoothly in the presence of  $Pd(OAc)_2$ , affording a series of fluorenones in moderate to good yield (two steps). Mechanistic studies reveal the reaction might be triggered by oxidation of alcohol followed by intramolecular reductive coupling.

Fluorenone and its derivatives have gained increasing attention due to their importance in biomedical and photoelectric materials.<sup>1</sup> As a result, the construction of this scaffold has received considerable interests. Conventional methods include intramolecular Friedel-Crafts reaction of biaryl carboxylic acids,<sup>2</sup> Pschorr cyclization of 2-amino diaryl ketones,<sup>3</sup> oxidation of fluorenol,<sup>4</sup> and oxidation of fluorene.<sup>5</sup> However, most of the aforementioned methods encounter some limitations such as multi-step procedures and prefunctionalization as well as involvement of hazardous oxidants. On the other hand, transition-metal-catalyzed synthesis of fluorenones has been studied extensively over the past decades. A number of them were accomplished by intramolecular C-C bond forming reactions via C-H functionalization, including palladium catalyzed C-H arylation of o-halo diaryl ketones,<sup>6</sup> cyclocarbonylation of o-halobiaryls, oxidative coupling of diaryl ketones via dual C-H activation,<sup>8</sup> arylation of o-biaryl nitriles,<sup>9</sup> imines,<sup>10</sup> and aldehydes,<sup>11</sup> radical cyclization,<sup>12</sup> rhodium-catalyzed acylation of biarylcarboxylic acids,13 and gold-catalyzed reactions.14 Besides, palladiumcatalyzed tandem oxidative C-H/C-H coupling/Friedel-Crafts acylation<sup>15</sup> and other intermolecular pathways<sup>16</sup> also provide complementary approaches to fluorenone scaffolds. However, some of the above mentioned catalytic methods still suffer from several limitations such as involvement of stoichiometric or excessive amount of oxidants, regioselectivity issue, and requirement of excessive amount of strong acids in some cases. In addition, the formation of a preinstalled carbonyl group from corresponding alcohol requires at least one equivalent of oxidants in some examples.

Palladium-catalyzed reductive coupling of aryl halides has emerged as a useful approach to access biaryls due to the mild reaction conditions and high functionality tolerance.<sup>17</sup> Reducing reagents are usually necessary to regenerate Pd(0) species. Hydroquinone,<sup>18</sup> formate salt,<sup>19</sup> hydrogen gas,<sup>20</sup> amines,<sup>21</sup> and zinc<sup>22</sup> and even alcohols<sup>23</sup> are commonly used for this purpose. Therefore, we hypothesized that formation of a carbonyl group from the secondary alcohol facilitated by an intramolecular reductive coupling of C-X bonds would provide fluorenones by combination of distinctive redox abilities of Pd(II) and Pd(0) species (Scheme 2). We herein disclose the palladium-catalyzed synthesis of fluorenones from bis(2halophenyl)methanols via an oxidation of alcohol/reductive coupling of C-Br bonds sequence for the first time. We demonstrate the current method is also amendable to gramscale synthesis of fluorenone with reduced catalyst loading.



Scheme 1 Our strategy to the synthesis of fluorenones.

The substrates bis(2-halophenyl)methanols of our proposed reaction could be readily synthesized according to literature procedures.<sup>24</sup> To test our hypothesis, we initially examined reaction of bis(2-bromophenyl)methanol **1a** in the presence of 10 mol % of PdCl<sub>2</sub> and 2.5 equivalents of  $Cs_2CO_3$  in toluene at 110 °C for 16 h, affording the desired product **2a** in 20% isolated yield (Table 1, entry 1). In contrast, no product was observed when bis(2-chlorophenyl)methanol was used as the substrate under otherwise identical reaction conditions (Table 1, entry 2). The additive guaternary ammonium salt was

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found to affect the reactivity significantly (Table 1, entries 3-6).<sup>23a</sup> When tetrabutylammonium iodide (TBAI) was used (Table 1, entry 5), fluorenone **2a** was obtained in 45% yield. Other bases such as  $K_2CO_3$  and  $K_3PO_4$  gave inferior results compared to  $Cs_2CO_3$  under otherwise identical reaction conditions (Table 1, entries 7 and 8 vs entry 6). Further scrutiny of catalyst revealed that  $Pd(OAc)_2$  was optimal, which delivered **2a** in 70% yield (Table 1, entry 12). A decreased yield was observed when base and TBAI were reduced to 2 equivalents (Table 1, entry 13). The effect of phosphine ligands were also investigated (Table 1, entries 14-17). However, no further enhancement of yield of **2a** was observed. Therefore, we chose entry 12 in Table 1 as our optimal reaction conditions to determine substrate scope.

**Table 1** Optimization of palladium-catalyzed synthesis of fluorenone 2a from bis(2-bromophenyl)methanol  $1a^{\alpha}$ 

catalyst (10 mol %) Cs<sub>2</sub>CO<sub>3</sub>, *n*Bu<sub>4</sub>NI

	1a	ane, 110°C, 16 n 2a	
Entry	Catalyst	Additive (x equiv)	Yield <sup>b</sup> (%)
1	PdCl <sub>2</sub>	None	20
2 <sup>c</sup>	PdCl <sub>2</sub>	TBAF (2.5)	n.d.
3	PdCl <sub>2</sub>	TBAC (2.5)	36
4	PdCl <sub>2</sub>	TBAB (2.5)	33
5	PdCl <sub>2</sub>	TBAI (2.5)	42
6	PdCl <sub>2</sub>	TBAI (2.5)	45
7 <sup>d</sup>	PdCl <sub>2</sub>	TBAI (2.5)	15
8 <sup>e</sup>	PdCl <sub>2</sub>	TBAI (2.5)	44
9 <sup>f</sup>	PdCl <sub>2</sub>	TBAI (2.5)	trace
$10^{g}$	PdCl <sub>2</sub>	TBAI (2.5)	38
11	PdBr <sub>2</sub>	TBAI (2.5)	55
12	Pd(OAc) <sub>2</sub>	TBAI (2.5)	70
13 <sup><i>h</i></sup>	Pd(OAc) <sub>2</sub>	TBAI (2.0)	65
14	$Pd(PPh_3)_2Cl_2$	TBAI (2.5)	49
15	PdCl <sub>2</sub> /dppf	TBAI (2.5)	69
16	PdCl <sub>2</sub> /xantphos	TBAI (2.5)	67
17	PdCl <sub>2</sub> /X-phos	TBAI (2.5)	52

<sup>*a*</sup>under otherwise noted, all the reactions were carried out with **1a** (0.20 mmol), catalyst (0.02 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.50 mmol) and toluene (2.0 mL) under N<sub>2</sub> atmosphere at 110 °C for 16 h; <sup>*b*</sup>yields of isolated products; <sup>*c*</sup>bis(2chlorophenyl)methanol was used instead of **1a**; <sup>*d*</sup>K<sub>2</sub>CO<sub>3</sub> was used instead of Cs<sub>2</sub>CO<sub>3</sub>; <sup>*e*</sup>K<sub>3</sub>PO<sub>4</sub> was used instead of Cs<sub>2</sub>CO<sub>3</sub>; <sup>*f*</sup>DMSO as solvent; <sup>*a*</sup>1,4-dioxane as the solvent; <sup>*h*</sup>2.0 equivalents of Cs<sub>2</sub>CO<sub>3</sub> was used.

With a set of optimized reaction conditions in hand, the substrate scope was then surveyed as illustrated in Scheme 2. Most of bis(2-bromophenyl)methanols underwent the reaction smoothly to give the corresponding products in reasonable yields. The substrates with electron donating groups gave superior results compared to those with electron withdrawing groups (**2k-m** vs. **2b-h**). It has to be noted that  $PdCl_2$  performed better than  $Pd(OAc)_2$  in some chlorinated

substrates (**2e** and **2f**). Interestingly, substrate **1j** bearing an unprotected OH group did not adversely affect the reaction, producing the corresponding fluorenone **2j** in 42% isolated yield. The current method also tolerates substrates bearing one heteroarene such as thiophene and pyridine, giving the corresponding thiofluorenone and azafluorenones (**2p-2r**) in 42-64% yield.<sup>24</sup>



"Unless otherwise noted, all the reactions were performed with 1 (0.20 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), Cs<sub>2</sub>CO<sub>2</sub> (0.50 mmol), and nBu<sub>4</sub>NI (0.50 mmol) in toluene (2.0 mL) at 110 <sup>°</sup>C for 18 h; <sup>b</sup>Yields in the brackets using PdCl<sub>2</sub> (0.02 mmol) as the catalyst.

Scheme 2 Substrate scope of palladium-catalyzed synthesis of Fluorenones.



#### Scheme 3 Application of current method.

To highlight utility of our method, a gram-scale synthesis was performed. As illustrated in Scheme 3, reaction of **1** (10 mmol scale) in the presence of reduced catalyst loading (2 mol %) could afford corresponding fluorenone **2** in 46% yield (1.1 grams). Reaction of fluorenone **2** with aryImagnesium bromide gave corresponding fluorenols **3a** and **3b** in 80% and 82% yields, respectively.<sup>25</sup> In the presence of AcOH and HCI, **3b** 

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could be further converted to 9,9'-spirobi[fluorene] **4** in 92% yield via a intramolecular Friedel-Crafts alkylation.<sup>25</sup>

We are interested in the mechanism of the reaction. Based on the reaction sequence, there are four plausible scenarios, namely paths A-D as illustrated in Figure 1. In path A, the reaction is initiated by Pd(II) in which the substrate 1a undergoes ligand exchange with PdX<sub>2</sub> to form a Pd(II) alkoxide species I, proceeding  $\beta$ -hydride elimination to generate Pd(0) along with the formation of the diaryl ketone 5. The in-situ generated 5 then could undergo reductive coupling to form fluorenone **1a** with regeneration of PdX<sub>2</sub>.<sup>27</sup> In *path B*, substrate 1a undergoes reductive coupling first to give fluorenol 6 with concurrent formation of  $PdX_2$ . Then intermediate **6** could be oxidized by PdX<sub>2</sub> with assistance of base to form 2a coinciding with regeneration of Pd(0) for the next catalytic cycle. In the alternative scenarios, the reaction could also take place via the intermediate o-bromo biaryl ketone 7 that has been known to form fluorenone by palladium catalysis.<sup>6a</sup> The C-H bond in 7 could be formed either by protonolysis of Ar-Pd bond (path C) or reductive elimination of ArPdH species (path D).



**Figure 1** Plausible reaction pathways: oxidation-reductive coupling sequence (*path A*); reductive coupling-oxidation sequence (*path B*); pro-todebromination-coupling sequence (*path C*); hydro-debromination-coupling sequence (*path D*).

To shed light on which one is most likely pathway, we performed control experiments as illustrated in Scheme 4. Reaction of dibromophenyl ketone **5** under standard reaction conditions (10 mol %  $Pd(OAc)_2$ ) afforded corresponding product **2a** in 10% GC yield, whereas 92% yield of product was observed with 100 mol % of  $Pd(OAc)_2$  (Scheme 4, eq 1). These two control experiments suggest that  $Pd(OAc)_2$  is able to promote intramolecular Ullman coupling of bis(2-bromophenyl)methanone whereas active catalyst could not be regenerated after one catalytic cycle without a reducing reagent such as alcohol. Indeed, 93% GC yield of fluorenone **2a** was observed upon addition of 1.0 equivalent of

diphenylmethanol 8 under otherwise standard reaction conditions (Scheme 4, eq 2). The identical control experiments of biarylmethyl methyl ether 10 did not give any methyl 9fluorenol (Scheme 4, eqs 3 and 4). These results clearly show that direct palladium-catalyzed intramolecular Ullman reaction of bis(2-bromophenyl)methyl methyl ether 10 is not feasible. Therefore, path B should not be possible. Notably, We found the reaction of monobromo alcohol 12 under standard conditions produced only 6% GC yield of fluorenone 2a, whereas the major product was diphenyl ketone 9 (63% GC yield) that was problay formed via reductive debromination (Scheme 4, eq 5). Therefore, two bromos in compounds 1 are essential to prohibit reductive debromination and make this reaction happen. Next, we examined the reaction of monobromo ketone 7 under standard conditions, which gave a 98% GC yield of product 2a (Scheme 4, eg 6). It seems that paths C and D are possible. Further experiments of reaction with deuterium substrates 1-d1 and 1-d1' showed no deuterium incorporated product was observed (Scheme 4, eqs 7 and 8). Additionally, in the presence of 2 equivalents of MeOD, no deuterium incorporated product was observed (Scheme 4, eq 9). Therefore, the pathways C and D could be ruled out. On the basis of these results, our reaction is probably triggered by palladium-catalyzed oxidation of secondary alcohol, which facilitates an intramolecular reductive coupling of C-Br bonds (Figure 1, path A).



Scheme 4 Control experiments.

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### Conclusions

We have developed a simple, novel palladium-catalyzed synthesis of fluorenones by combination of distinctive redox abilities of Pd(0) and Pd(II). A variety of bis(2-bromophenyl)methanols underwent the reaction smoothly, affording the corresponding fluorenones in moderate to good yields via two steps. We demonstrate the present method is also amendable to gram-scale synthesis with reduced catalyst loading. Mechanistic studies revealed the plausible mechanism might undergo oxidation of secondary alcohol first followed by reductive coupling of C-Br bonds.

## **Conflicts of interest**

There are no conflicts to declare.

## **Notes and References**

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