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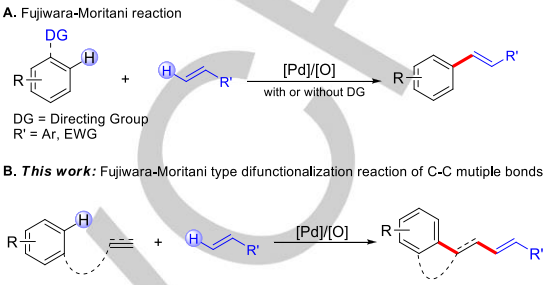
Palladium-Catalyzed Tandem Oxidative Arylation/Olefination of Aromatic Tethered Alkenes/Alkynes

Yang Gao,[a, b] Yinglan Gao,[b] Wanqing Wu,[b] Huanfeng Jiang*,[b] Xiaobo Yang,[a] Wenbo Liu,[a] Chao-Jun Li*[a]

Abstract: We herein described a palladium-catalyzed tandem oxidative arylation/olefination reaction of aromatic tethered alkenes/alkynes for the synthesis of dihydrobenzofurans and 2*H*-chromene derivatives. This reaction features a 1,2-difunctionalization of C-C π bond with two C–H bonds using O_2 as terminal oxidant at room temperature. The products obtained are valuable synthons and important scaffolds in biological agents and natural products.

Carbon−carbon bond formation is a central theme of chemical syntheses.[1] The cross-dehydrogenative coupling (CDC) reactions are among the most straightforward strategies to construct C-C bonds by joining two C−H bonds directly.[2] Among CDC reactions, the palladium-catalyzed coupling between arenes and olefins, commonly known as the Fujiwara−Moritani reaction,[3] has proven to be a highly useful process for constructing C(sp^2)-C(sp^2) bonds (scheme 1A). In the last decades, through the introduction of directing groups or external ligands,[4] tremendous progress has been made to achieve such oxidative C-H/C-H couplings regioselectively. Meanwhile, the intramolecular aromatic C–H alkenylation reactions have also been developed.[5] Despite the efficiency in forming a single C-C bond, it would be highly desirable to further impove the synthetic efficiency, with respect to “step and atom economy”, by forming multiple C-C bonds related to such C-H/C-H couplings. As our ongoing interest in CDC reactions, we envisaged a tandem oxidative arylation/alkenylation of aromatic tethered C-C bond with two C–H bonds, a Fujiwara−Moritani-type difunctionalization reaction of C-C mutiple bond with aromatic C–H bond and vinylic C–H bond (Scheme 1B). Such a reaction will lead to the simultaneous formation of two new vicinal C-C bonds, and thus could rapidly increase molecular complexity. [6]

On the other hand, benzo-fused heterocycles such as dihydrobenzofurans and 2*H*-chromene are prominent in a variety of natural products and biologically active compounds [*e.g.* Parviflorene J (**I**), Morphine (**II** and **III**) and Tephrowatsin B (**IV**), Figure 1], which exhibit a wide range of important biological activities.[7] Consequently, tremendous effort has been made in developing new synthetic methods towards these scaffolds. Previously, the intramolecular Heck-type reactions, initiated



Scheme 1. The concept of Fujiwara-Moritani type difunctionalization reaction.

either by oxidative addition of C(sp^2)-X bonds or transmetalation, have been reported to produce benzoheterocycles.[8] In addition, intramolecular hydroarylation of alkenes/alkynes,[9] radical addition/cyclization reactions[10] and electrophilic cyclization reactions[11] have been employed as well. Recently, Liu, Zhu and co-workers reported the Pd^{II}/Pd^{IV} oxidative arylacetoxylation, arylalkylation and aryltrifluoromethylation methods for the synthesis of oxindoles.[12] While these reactions are only limited to the *N*-arylacrylamides substrates and stoichiometric stronger oxidants such as $PhI(OAc)_2$ are needed. None of these precedents allows the tandem arylation/olefination of C-C multiple bonds via the functionalization of two C–H bonds, with green oxdiant such as O_2 under mild conditions. Herein, we presented such a strategy.

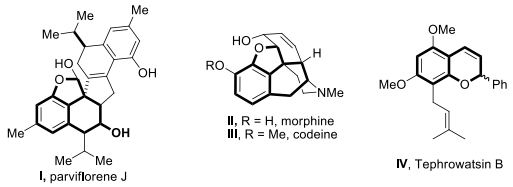


Figure 1. Representative bioactive compounds with dihydrobenzofurans and 2*H*-chromene structural motifs.

Our investigation began with the coupling of 1-methoxy-4-(2-methylallyloxy)benzene (**1a**) and methyl acrylate (**2a**) using $Pd(OAc)_2$ (10 mol %) as catalyst in HOAc (0.5 mL) under 1 atm O_2, and the desired product **3a** was detected in 10% NMR yield (Table 1, entry 1). The addition of trifluoroacetic acid (TFA) was found to be critical to improve the yields and **3a** was obtained as a mixture of isomers (**3a**:**3a'** = 7:1) in 41% NMR yield with TFA (3.0 equiv) as additive (Table 1, entry 2). During the reaction, some decomposition of the catalyst, as palladium black or mirror, was observed. Adding ligands such as pyridine and DMSO which have been proven to be useful in oxidative palladium processes,[13] only afforded **3a** in 12% and 40% NMR yields, respectively (Table 1, entries 3 and 4). No improvement in yield was observed by addding some common bases such as

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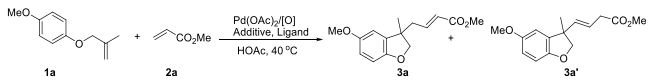
NaOAc and CsOPiv, which are known to assist the C–H activation via the CMD process[14] (Table 1, entries 5 and 6). Various oxidants such as 1,4-benzoquinone (BQ), TBHP and AgOAc were then examined, which could only increase the yields slightly (Table 1, entries 7-9). Next, inspired by the co-oxidant system,[15] i.e. the BQ(0.1eq)/FePC/O_2 system (Table 1, entriy 10) and the classical Cu^{2+}/O_2 system (Table 1, entry 11), we were pleased to find the yield could be increased significantly to 76% when 0.2 equiv $Cu(OAc)_2$ was added as co-oxidant. Since BQ could stabilize the Pd(0) species by in situ generating the Pd(0)-BQ complexes,[16] the yield was further improved in presence of BQ (10 mol%) and no palladium black was observed (Table 1, entry 12). Finally, the selectivity of **3a** to **3a'** was improved to 15:1 when the reaction temperature was decreased to room temperature (Table 1, entry 13).

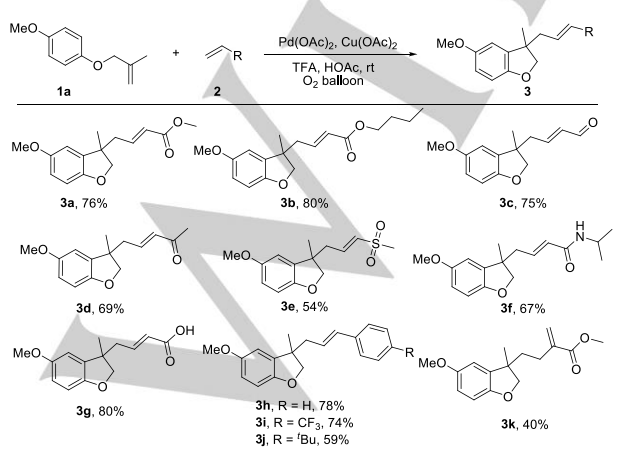
Table 1. Optimization studies for the formation of **3a**.[a]



Entry	Oxidant	Ligand	Additive	**3a**:**3a'**	Yield%[b]
1[c]	O_2	-	-	-	10
2	O_2	-	-	7:1	41
3[d]	O_2	Py	-	-	12
4[d]	O_2	DMSO	-	9:1	40
5[e]	O_2	-	NaOAc	6:1	36
6[f]	O_2	-	CsOPiv	7:1	30
7	BQ (2.0 equiv)	-	-	5:1	43
8	TBHP (2.0 equiv)	-	-	6:1	55
9	AgOAc (2.0 equiv)	-	-	10:1	46
10[g]	BQ/FePC/O_2	-	-	5:1	40
11[h]	$Cu(OAc)_2/O_2$	-	-	8:1	76
12	$Cu(OAc)_2$/BQ/O_2	-	-	9:1	85
13[i]	**$Cu(OAc)_2$/BQ/O_2**	-	-	**15:1**	**83 (76)**

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (10 mol%), TFA (3.0 equiv) in HOAc (0.5 mL) under 1 atm O_2 at 60 °C for 10 h. [b] The yield was determined by NMR analysis with mesitylene as the internal standard (isolated yield is in parentheses). [c] Without TFA. [d] Ligand (20 mol%). [e] NaOAc (1.0 equiv). [f] CsOPiv (1.0 equiv). [g] BQ (0.1 equiv)/FePC (0.05 equiv)/O_2. [h] $Cu(OAc)_2$ (0.2 mmol)/BQ (0.1 mmol)/O_2. [i] $Cu(OAc)_2$ (0.2 mmol)/BQ (0.1 mmol)/O_2 at room temperature.

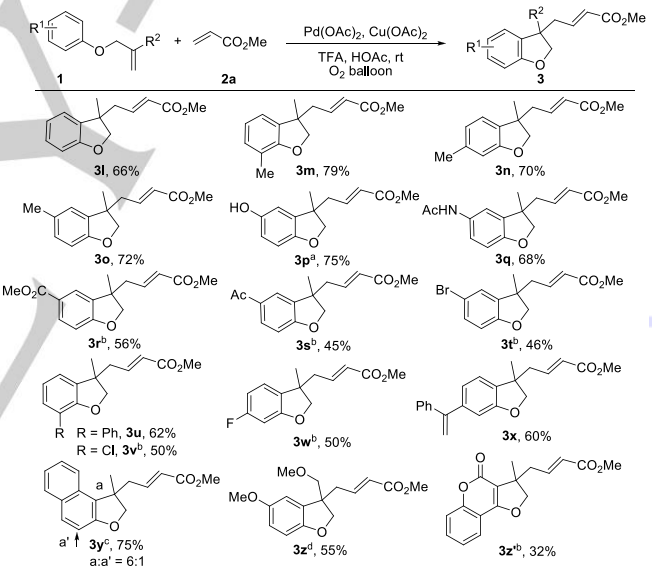
Table 2. Substrate scope of olefins **2**



Reaction conditions A: all reactions were performed with **1** (0.1 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (20 mol%), BQ (10 mol%), TFA (3.0 equiv) in HOAc (0.5 mL) under 1 atm O_2 at room temperature for 10 h. Isolated yields are given in all cases.

With the optimized reaction conditions in hand, we next investigated the substrate scope of this transformation. As summarized in Table 2, apart from acrylates, other electron deficient olefins, such as acrylaldehyde (**3c**), but-3-en-2-one (**3d**), methylsulfonylethene (**3e**), *N*-isopropylacrylamide (**3f**) and even acrylic acid (**3g**) all showed effectiveness in this tandem CDC reaction to give the desired dihydrobenzofurans in moderate to good yields (54%-80%). Gratifyingly, styrenes also delivered comparable yields under the optimized conditions and various styrenyl derivatives (**3h**−**3j**) were obtained in 59%-74% isolated yields. Notably, this reaction showed an excellent stereoselectivity, with *E*-configuration product obtained exclusively in most cases. Interestingly, the reaction of **1a** with *α*-methyl substituted acrylates proceeded to form the terminal alkene **3k** rather than the more stable internal isomer.

Table 3. Substrate scope of allyl ethers **1**



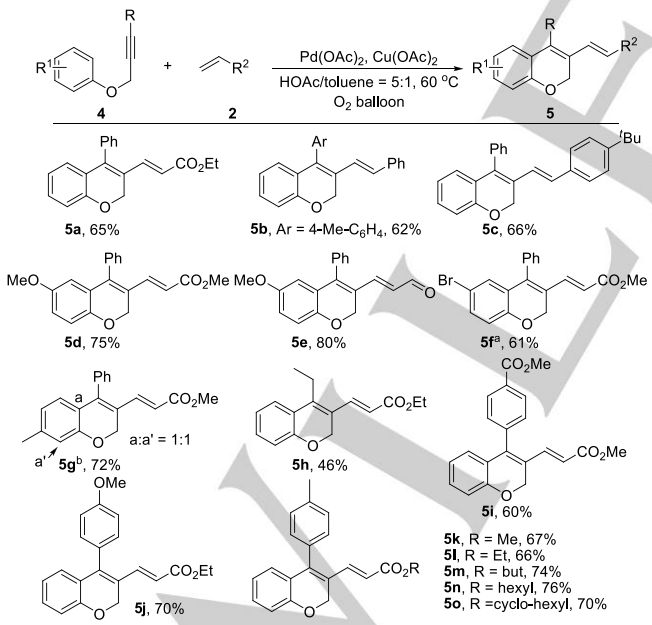
All reactions performed under condition A. Isolated yields are given in all cases. [a] In toluene 0.5 mL. [b] TFA 0.1 mL was used as co-solvent, at 40 °C for 12h. [c] Ratio determined by crude ^{1}H NMR. [d] TFA (5.0 equiv), **2a** (2.0 equiv) at 80 °C for 12h.

Next, a range of allyl ethers **1** derived from commercially available phenols were investigated, leading to highly substituted dihydrobenzofurans products. As illustrated in Table 3, various functional groups such as methyl, methoxyl, fluoro, chloro, bromo, ester, alkenyl, free hydroxyl and amide, were all well tolerated; and the desired products were isolated in moderate to good yields (45%-79%). The halogenated substrates (**3t**, **3v**) highlight the potential for further product elaboration. The substituent position has little influence on the product yields (*e.g.*, **3m**, **3n** and **3o**). Notably, with *meta*-substituted substrates, the reaction occurred selectively with the

less-hindered C−H bond, as was confirmed by NOE (**3n**, **3w** and **3x**). Electronic effect also played an important role in this reaction, since electron-rich substrates (**3m**-**3q**) performed much better than those bearing electron-withdrawing groups such as CO_2Me (**3r**), Ac (**3s**) and F (**3w**). 2-(Allyloxy)naphthalene also proceeded well under the optimized conditions and the more electron-rich C1 position was favoured to form the product **3y** with good selectivity (a:a' = 20:3). Moreover, substrate with *β*-OMe could also be converted to the corresponding product **3z** in 55% yield. Notably, as important pharmaceutically relevant compound, the 4-(2-methylallyloxy)-2*H*-chromen-2-one could also afford the corresponding product **3z'**.

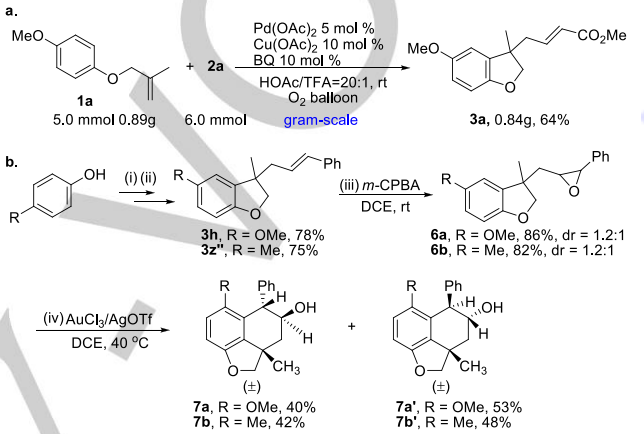
Subsequently, such a tandem oxidative arylation/vinylation was also found to be effective for difunctionalization of aromatic tethered alkynes, by slightly modifying the reaction conditions. Various 2*H*-chromenes derivatives, which are important structural motifs in pharmaceuticals and functional materials,[17] were obtained readily. Acrylate, styrene, and acrylaldehyde were all good reaction partners in this reaction (**5a**-**5e**). Different aryl propargyl ethers **4** were smoothly converted into the corresponding 2*H*-chromene products in moderate to good yields (46%-80%). Functional groups such as OMe (**5d**), Br (**5f**) and CO_2Me (**5i**) were all tolerated, with the electron-rich substrates produced higher yields. With *meta*-methyl substituted, a mixture of isomers (**5g**, *a:a'* = 1:1) was obtained. It should be noted that some of the products are fluorescent, which may find applications in optoelectronic materials and the fluorescence properties of **5d** and **5e** were preliminary tested (see SI for detail).

Table 4. Substrate scope of 2*H*-chromene products

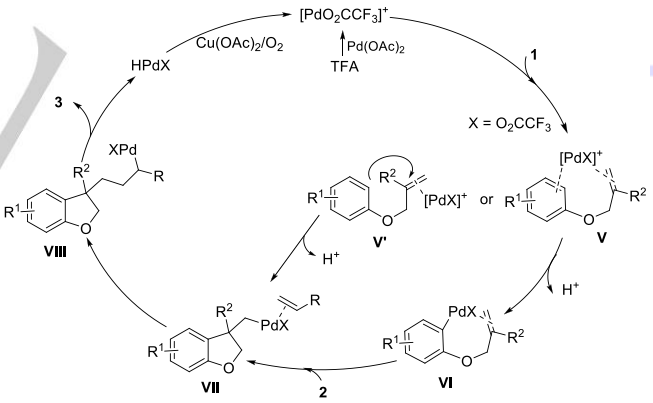


All reactions were performed with **4** (0.1 mmol), **2** (0.15 mmol), $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (10 mol%), BQ (10 mol%) in HOAc/toluene = 5:1 (0.6 mL) under 1 atm O_2 at 60 °C for 8 h. Isolated yields are given in all cases. [a] TFA (1.0 equiv) was added. [b] Ratio determined by crude ^1H NMR.

To further demonstrate the synthetic utility of this transformation, a gram-scale synthesis of product **3a** was carried out (0.84 g, 64% yield). Moreover, given the importance of 2*a*,3,4,5-*tetra*hydro-2*H*-naphtho[1,8-*bc*]furan in natural products as illustrated in Figure 1, the present method provides an efficient and practical synthesis of this motif by the following sequence: the corresponding dihydrobenzofuran derivatives were obtained by the present method in two steps from the commercially available phenols; then, treatment of the derivatives by *m*-CPBA afforded the epoxide **6**; finally, Au^{3+} catalyzed epoxide-ring-opening delivered the desired **7** in good yields.[18]



Scheme 2. Gram-scale synthesis of **3aa** and synthetic utilities. (i) 3-bromo-2-methylprop-1-ene (1.2 equiv), K_2CO_3 (2.0 equiv), DMF, rt. (ii) Condition A. (iii) *m*-CPBA = *meta*-chloroperbenzoic acid. (iv) $AuCl_3$ 2.5 mol %, AgOTf 7.5 mol %.



Scheme 3. A tentative mechanism for this Fujiwara−Moritani-type C-C π bond difunctionalization reaction.

On the basis of the above results, a tentative mechanism for this Fujiwara−Moritani-type C-C π bond difunctionalization reaction is proposed (Scheme 3). The reaction could be initiated by the electrophilic metalation of the cationic species $[Pd(TFA)]^+$ to the substrate **1** to produce the aryl-Pd species **VI.** In this process, the selective *ortho* C-H bond functionalization could be controlled by the coordination of cationic species $[Pd(TFA)]^+$ to the C=C bond.[19] Then, intramolecular insertion of olefin into the C−Pd bond formed the alkyl-Pd intermediate **VII**, which was followed by insertion of activated olefin and *β*-hydride elimination, afforded the corresponding product **3** and regenerated the active

Pd(II) species by the oxidation of Cu^{2+}/O_2. Alternatively, the alkyl-Pd intermediate **VII** could be formed via the intramolecular *trans*-nucleopalladation of aryl to C=C bond.[20] A kinetic isotope effect experiment (K_H/K_D = 1.9, see SI for detail) did not provide concluding evidence for either mechanism.

In summary, a tandem oxidative Fujiwara−Moritani-type 1,2-difunctionalization of C-C multiple bonds with two C–H bonds has been developed. A wide range of important dihydrobenzofurans and 2*H*-chromene derivatives bearing various function groups can be synthesized readily via this process. As an application, an efficient route from the commercially available phenols to the important 2*a*,3,4,5-*tetra*hydro-2*H*-naphtho[1,8-*bc*]furans was accomplished. This reaction extends the concept and applicability of the present CDC reaction. Ongoing studies in our laboratory are dedicated to the asymmetric catalysis and synthetic applications of this transformation.

Experimental Section

To a 10 mL U-shape tube were added into allyl ethers **1** (0.1 mmol), acrylates **2** (0.15 mmol), $Pd(OAc)_2$ (2.24 mg, 10 mol%), $Cu(OAc)_2$ (3.60 mg, 20 mol%), BQ (1.08 mg, 10 mol%), TFA (24 uL, 3.0 equiv) in 0.5 mL HOAc. Then the tube was sealed and the mixture was stirred at room temperature under 1 atm O_2 (oxygen balloon) for 10 hours. After completion, the reaction was quenched with aqueous $NaHCO_3$ and the crude product was extracted with ethyl acetate. The organic extracts were concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography using light petroleum ether/ethyl acetate as eluent to afford the desired products **3**.

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Keywords: Pd-catalyzed • CDC • Fujiwara−Moritani reaction • dihydrobenzofurans • 2*H*-chromene

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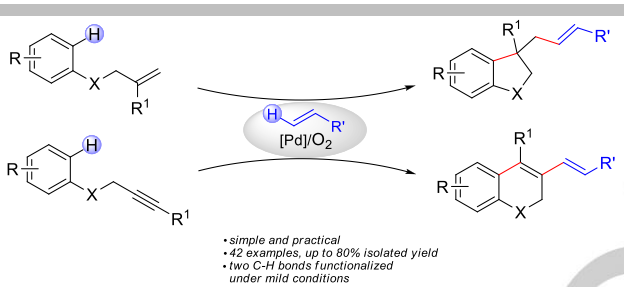
A Fujiwara−Moritani-type 1,2-difunctionalization of C-C multiple bonds with two C–H bonds has been developed. This protocol provides an efficient and economic rout for the synthesis of dihydrobenzofurans and 2*H*-chromene derivatives with broad functional group compatibility.



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