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Palladium-Catalyzed Cascade Arene/Alkyne Annulation: Synthesis of Fluorene-Benzoxazine Derivatives

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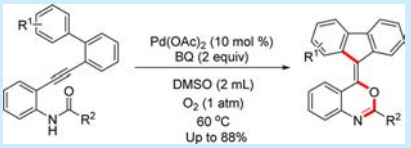
Supporting Information

ABSTRACT: A palladium-catalyzed cascade arene/alkyne annulation reaction for the synthesis of fluorene-benzoxazine derivatives is developed. This transformation involves a 6-*exo*-*dig* cyclization, a 1,3-oxazine vinylpalladium intermediate, and a C−H bond activation.



The design and characterization of polycyclic aromatic hydrocarbons (PAHs) has been studied intensively in the fields of electrochemistry, photochemistry, and functional materials science since the PAHs exhibit excellent stability, enhanced ability to transport charge, and superior fluorescent properties in the solid state.[1] Fluorene is one of most important PAHs since it could be extensively applied to the manufacture of advanced materials[2] and used as effective ligands[3] and unique protecting groups.[4] Fluorene also could be employed in the pharmaceutical industry.[5−7] For example, it could be used as an anti-inflammatory agent,[5] a cyclophilin A inhibitor,[6] and a cholesterol acyltransferase (ACAT) inhibitor (Figure 1).[7]

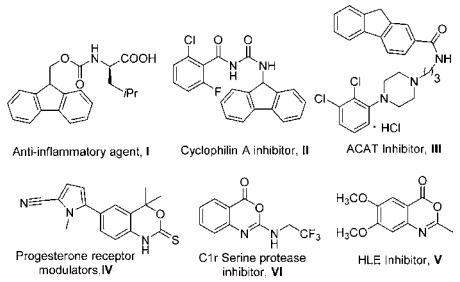


Figure 1. Fluorene and benzoxazine derivatives.

Hence, efficient synthetic methods leading to functionalized fluorenes are expected to assist the rapid developments of fluorene-based functional molecules.[8] Generally, the fluorene derivatives could be obtained via Brønsted or Lewis acid promoted Friedel−Crafts-type reactions.[9] Recently, transition-metal-catalyzed direct C−H bond activation,[10] diazo insertion,[11] cation rearrangement reaction,[12] and radical reaction[13] have emerged as efficient tools for the construction of fluorene derivatives. Benzoxazine derivatives are an important branch of *N*-heterocycles and play increasingly crucial roles in the area of medicinal science over the past decades because of their distinct biological and pharmaceutical activities such as fungicidal, anti-inflammatory, and anticonvulsant activities.[14] They are also confirmed as the progesterone receptor modulators,[15] DNA-binding antitumor agents,[16] human leukocyte elastase (HLE) inhibitors, and C1r serine protease inhibitors (Figure 1).[17] Several synthetic procedures to build benzoxazine derivatives, which suffer from limitations, such as low yield, bad regioselectivity, and/or harsh reaction conditions, were reported.[18] Recently, Saito, Novák, Zeni, and Wang et al. reported several efficient strategies to synthesize substituted benzoxazines through palladium-, iron-, copper-, or iodine-catalyzed/mediated regioselective 6-*exo*-*dig* cyclization of *o*-ethynylanilides.[19] Moreover, the tandem radical reaction strategy was employed in the manufacturing of CF_3-containing and SCN-containing benzoxazines, respectively.[20] To the best of our knowledge, the direct and efficient methodology for the construction of fluorene-benzoxazines has not been developed.

Devising novel transition-metal-catalyzed hydroarylation of alkynes via direct C−H bond functionalization that achieves the construction of multiple bonds in one step is a significant challenge in modern organic synthesis.[21] Such domino processes avoid prefunctionalization, as well as protection−deprotection steps, which represent a more environmentally friendly and economic strategy for construction of polycyclic aromatic hydrocarbons (PAHs).[22] In 2000, a palladium-catalyzed intramolecular hydroarylation of alkynes through 6-*endo*-*dig* cyclization of electron-rich aromatic rings was first reported by Fujiwara's group.[23] Afterward, it was found that some other transition metals[24] and Lewis acids[25] can promote this transformation successfully (Scheme 1, eq 1). A Friedel−Crafts-type electrophilic aromatic substitution mechanism is generally accepted for this transformation. In contrast, Gevorgyan and co-workers report the first example of C−H bond activation/annulations of electron-neutral and -deficient *ortho*-alkynyl biaryls via a 5-*exo*-*dig* cyclization (Scheme 1, eq 2).[26] Shortly afterward, the arene/alkyne annulation via C−H bond activation has been exploited to construct various privileged polycyclic aromatic hydrocarbons (PAHs) effectively.[27] Recently, Jin and co-workers reported a novel and efficient palladium-catalyzed dual C−H bond activation/

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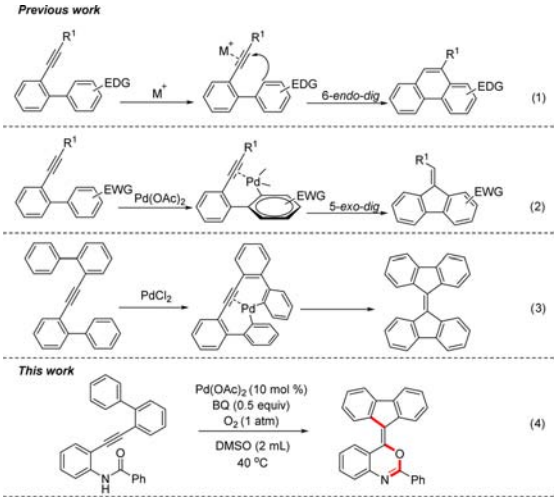
Scheme 1. Hydroarylation of Alkynes

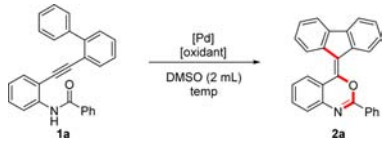


annulation of bisbiaryl alkynes for construction of important and useful 9,9′-bifluorenylidene (9, 9′BF) and its derivatives (Scheme 1, eq 3). The unexpected mechanistic evidence indicates an unusual mechanism that the reaction proceeds through dual C−H bond activation followed by an annulation with a C−C triple bond; it is distinct from the previously reported hydroarylation.[28] As a continuation of our ongoing effort toward development of fluorene derivatives and benzoxazine derivatives, as well as direct C−H functionalization,[29] we report herein a novel palladium-catalyzed hydroarylation of alkynes via direct C−H bond functionalization for the first synthesis of fluorene-benzoxazine derivatives (Scheme 1, eq 4).

At the outset of this study, the cascade coupling reaction of *ortho*-alkynyl biaryl **1a** was carried out in DMSO (2 mL), at 40 °C, using a catalytic amount of $Pd(OAc)_2$ as the promoter and 0.5 equiv of BQ (benzoquinone) with oxygen as a combined oxidant system. To our delight, the desired fluorene-benzoxazine **2a** was formed in 44% LC-yield. To improve the yield, various Pd catalysts, solvents, and oxidants were screened (for details, see Supporting Information). The desired fluorene-benzoxazine **2a** was formed in a lower yield when the reaction was carried out in the presence of O_2 without BQ (Table 1, entry 2). Similar low yields were obtained when the reaction was operated under an Ar or air atmosphere (Table 1, entries 3−4). Not surprisingly, no desired fluorene-benzoxazine **2a** was detected when the reaction was carried out without BQ and O_2 (Table 1, entry 5). An improvement in reaction yield was obtained when the amount of BQ was increased to 1.0, 2.0, and 3.0 equiv, thus giving the desired fluorene-benzoxazine **2a** in 46%, 67%, and 63% yield, respectively (Table 1, entries 6−8). Gratifyingly, the desired fluorene-benzoxazine **2a** was obtained in 90% LC-yield (86% isolated yield) when the reaction temprature was increased to 60 °C and the 10 mol % $Pd(OAc)_2$ was added twice (Table 1, entry 9).

Having established the optimized reaction conditions, the scope of this domino reaction was explored by varying the substituents (R^1) on the biphenyl ring (Table 2). Replacing the substituent of the biphenyl ring with halogen groups, such as fluorine and chlorine, resulted in a good yield of **2b**, **2c**, and **2d**, respectively. Luckily, a single crystal of **2b** was cultivated, and the structure of **2b** was further confirmed by single-crystal X-ray analysis. As expected, the presence of an electron-rich substituent

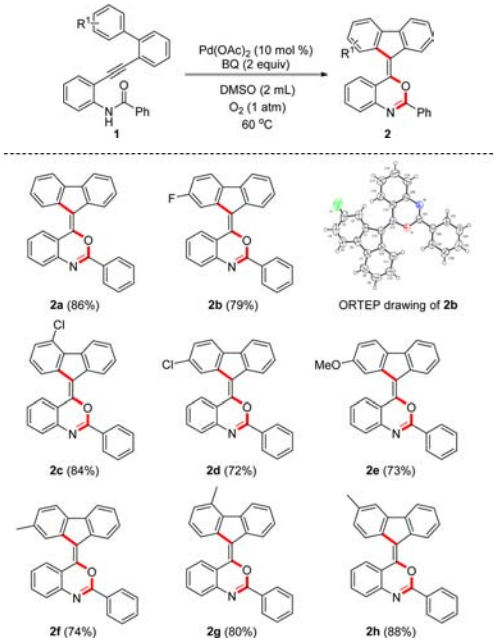
Table 1. Optimization of the Reaction Conditions[a]



entry	cat. (equiv)	oxidant	yield[b]
1	$Pd(OAc)_2$ (0.1)	BQ (0.5 equiv) + O_2	44
2	$Pd(OAc)_2$ (0.1)	O_2	23
3	$Pd(OAc)_2$ (0.1)	BQ (0.5 equiv) + Ar	28
4	$Pd(OAc)_2$ (0.1)	BQ (0.5 equiv) + air	36
5	$Pd(OAc)_2$ (0.1)	Ar	NR
6	$Pd(OAc)_2$ (0.1)	BQ (1.0 equiv) + O_2	46
7	$Pd(OAc)_2$ (0.1)	BQ (2.0 equiv) + O_2	67
8	$Pd(OAc)_2$ (0.1)	BQ (3.0 equiv) + O_2	63
9	$Pd(OAc)_2$ (0.1)	BQ (2.0 equiv) + O_2	90 (86)[c]

[a]Reaction conditions: **1a** (0.5 mmol), cat. (0.05 mmol), and oxidant as indicated; solvent (2.0 mL) was stirred at 40 °C for 12 h. [b]The yields were determined by LC analysis using biphenyl as the internal standard. [c]The reaction was stirred at 60 °C with $Pd(OAc)_2$ (0.025 mmol) for 6 h, followed by addition of $Pd(OAc)_2$ (0.025 mmol) and stirring at 60 °C for another 6 h.

Table 2. Substrate Scope for Palladium-Catalyzed Cascade Arene/Alkyne Annulation[a]



[a]Reaction conditions: **1** (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), BQ (1.0 mmol), and DMSO (2 mL), O_2 (1 atm). The reaction was stirred at 60 °C with $Pd(OAc)_2$ (0.025 mmol) for 6 h, followed by addition of $Pd(OAc)_2$ (0.025 mmol) and stirring at 60 °C for another 6 h.

biaryl led to an efficient reaction which generated **2e** in 73% isolated yield. Moreover, methyl substituents at the *para*, *meta*, and *ortho* position of the biphenyl ring afford the desired fluorene-benzoxazines **2f−h** in good yields.

Next, we set out to explore the scope of this tandem reaction by employing differently substituted *ortho*-ethynylanilides as shown in Table 3. It is found that the desired fluorene-benzoxazines could be obtained in good yields when the methyl, ethyl, methoxy, and chlorine substituted benzamides were applied to this reaction (**2i−n**, 71−88%). Meanwhile, the *N*,

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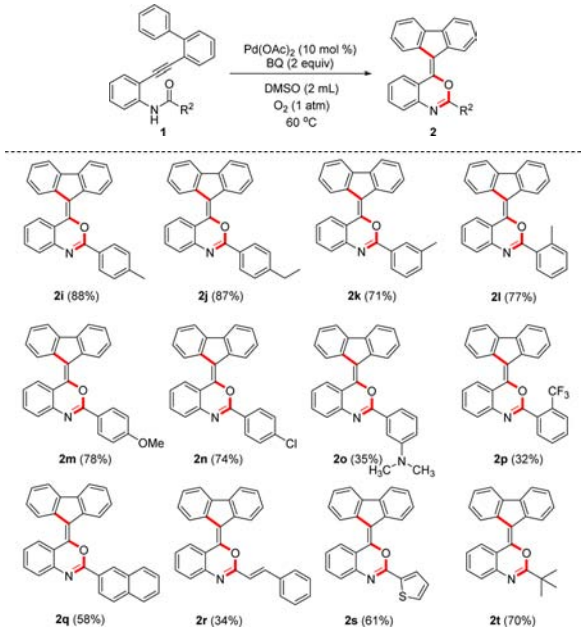
Table 3. Substrate Scope for Palladium-Catalyzed Cascade Arene/Alkyne Annulation[a]

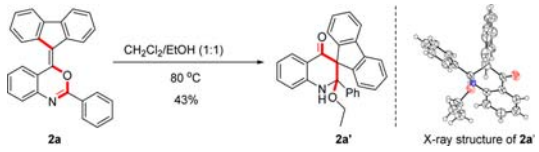


[a]Reaction conditions: **1** (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), BQ (1.0 mmol), DMSO (2 mL), O_2 (1 atm). The reaction was stirred at 60 °C with $Pd(OAc)_2$ (0.025 mmol) for 6 h, followed by addition of $Pd(OAc)_2$ (0.025 mmol) and stirring at 60 °C for another 6 h.

N-dimethylamino and trifluoromethyl-substituted *ortho*-ethynylanilide could proceed smoothly and generate the desired products **2o** and **2p** in 35% and 32% yield, respectively. Notably, the reaction could smoothly convert into the fluorene-benzoxazine derivatives in moderate yields when 2-naphthamide, cinnamamide, and thiophene-2-carboxamide were used (**2q**–**s**, 34–61%). Furthermore, an acceptable yield (70%) was obtained when pivaloyl-substituted *ortho*-ethynylanilide was subjected to the reaction (**2t**).

Interestingly, an unexpected product spiro[fluorene-quinolin]-4′-one **2a′** was obtained when fluorene-benzoxazine **2a** was treated with EtOH under reflux conditions, and the structure of **2a′** was unambiguously confirmed based on single-crystal X-ray analysis (Scheme 2). The fluorene-benzoxazine **2a** may undergo

Scheme 2. Construction of Spiro[fluorene-quinolin]-4′-one

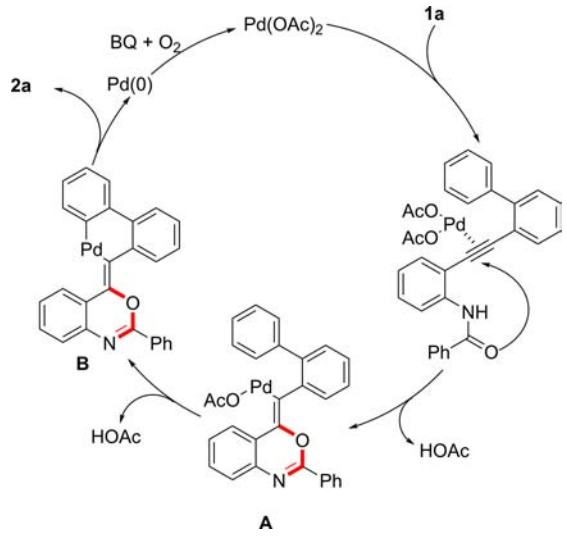


an addition of imine with EtOH, a ring-opening-closing reaction. Further investigations to understand the mechanism of this reaction are ongoing in our laboratory.

To gather further insight into the palladium-catalyzed arene/alkyne annulation, kinetic isotope effect studies were performed under the standard conditions (for more details, see the Supporting Information). An intramolecular isotope effect of K_H/K_D = 1.94 was obtained for the hydroarylation of alkyne. This, together with the significant intermolecular KIE (K_H/K_D = 2.57), implies the C–H bond cleavage occurs during the rate-determining step.

On the basis of these observations, a plausible mechanism for the palladium-catalyzed cascade arene/alkyne annulation is illustrated in Scheme 3. The $Pd(OAc)_2$ activated alkyne π-

Scheme 3. A Plausible Mechanism



bond is attacked by the carbonyl oxygen to afford 1,3-oxazine vinylpalladium species **A** via a 6-*exo*-*dig* cyclization. The C–H bond activation occurred to provide a six-membered palladacycle **B**. The desired fluorene-benzoxazine **2a** was formed through a reductive elimination of **B**. Meanwhile, the Pd(II) species are regenerated from oxidation of the Pd(0) species by BQ and O_2 to start a new catalytic cycle.

In summary, we have developed a novel and straightforward method for the first synthesis of fluorene-benzoxazine derivatives through the palladium-catalyzed cascade arene/alkyne annulation. Kinetic isotope effect studies and control experiments seem to converge on a description that this transformation involves a 6-*exo*-*dig* cyclization, a 1,3-oxazine vinylpalladium intermediate, and a C–H bond activation. The domino reaction is operationally simple, is compatible with a broad substrate scopes, and represents an efficient, step- and atom-economic way for the construction of scarcely known fluorene-benzoxazine derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02224.

Crystal structure data for **2b** (CIF)
Crystal structure data for **2a′** (CIF)
Detailed experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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