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Palladium-Catalyzed Benzofulvenation of *o*-Arylanilines through C–H Bond Activation by Using Two Diarylacetylenes as an Implicit Benzofulvene

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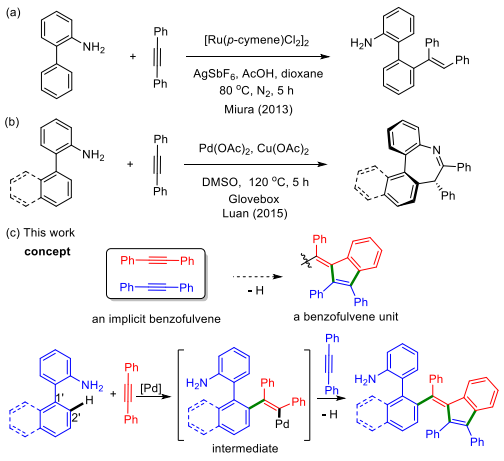
Abstract: We report the first example of Pd(II)-catalyzed highly step- and atom-economical benzofulvenation through free amine–directed *ortho* C−H bond activation of *o*-arylanilines. This paper presents a novel, simple, and efficient approach for the synthesis of benzofulvene derivatives from *o*-arylaniline substrates through C–H bond activation with two diarylacetylenes as an implicit benzofulvene unit. The reactivity of synthesized benzofulvenes toward oxidation was investigated, and they were shown to transform into phenanthridines, oxabenzofulvenes, and fluorescent polycyclics.

Keywords: benzofulvene; C–H bond activation; diphenylacetylene; *o*-arylaniline; palladium

Benzofulvenes are benzo derivatives of fulvenes and aromatic hydrocarbons consisting of an exocyclic double bond.[1] Because of their unique molecular properties, benzofulvenes have extensive applications in the fields of material science[2] and pharmaceutical,[3] polymer,[4] and ligand[5] chemistry. Numerous methodologies have been developed for the synthesis of fulvene skeletons, which are based on the Schmittel cyclization of enyne-allene,[6] Schreiner–Pascal diradical cyclization of enediynes,[7] silver and Brønsted acid-catalyzed Nazarov cyclization of diaryl α-hydroxyallenes,[8] transition-metal-catalyzed cyclization of aromatic ketones with internal alkynes,[9] gold(I)- and dual-gold(I)-catalyzed intramolecular cyclization of arene–diyne,[10] and Pd-catalyzed cycloisomerization of aromatic 1,5-enynes.[11] In addition, Hua et al. reported the Pd(II)-catalyzed cyclodimerization reaction of diarylacetylenes to obtain benzofulvene derivatives through alkyne-directed *ortho* C−H palladation, followed by insertion of another diarylacetylene and cyclization.[12] Furthermore, benzofulvenes can be synthesized using 1,2-bis(arylethynyl)benzenes through the intramolecular coupling of alkynes, followed by palladium-catalyzed arylation.[13]

In another context, since Murai et al. developed the first efficient method of metal-catalyzed alkylation by using ketone as the directing group (DG) through C–H bond activation,[14] transition-metal-catalyzed C–H bond activation has emerged as a powerful tool for selective C–H functionalization.[15] Transition metals, such as rhodium,[16] iridium,[17] cobalt,[18] and palladium,[19] have been used to catalyze cycloaddition of acetylenes with 2-alkenyl anilines, phenols, *N*-substituted anilines, and aryl iodides, respectively, mainly yielding substituted indolines, chromenones, and an extended aromatic π-system. Furthermore, iminoquinone,[20] carbonyl,[21] sulfonyl,[22] alkyl,[23] and aryl-masked[24] amino groups have been identified as favorable groups for directing C–H bond cleavage at the *ortho* or 2′ -position of *o*-phenylanilines and enabling transition-metal-catalyzed insertion of activated olefins, diaryliodonium salts, CO,[60] fullerene, or intramolecular cyclization to yield phenanthridines, substituted triphenylenes, phenanthridinones, fullerobenzoazepines, and carbazoles, respectively.



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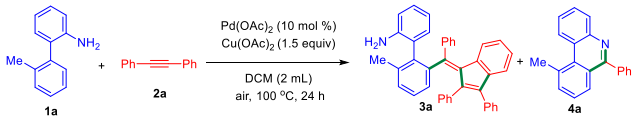
Scheme 1. Transition-metal-catalyzed C2'−H functionalization of *o*-arylanilines.

To our knowledge, using a free amino directing group (DG)[25] is one of the most straightforward approaches of C–H bond activation, especially from an industrial perspective.[26] Moreover, amino groups can be converted for use in other processes by using the Sandmeyer reaction.[27] In this context, Miura reported the Ru-catalyzed amine-directed alkenylation of *o*-arylanilines with internal alkynes (Scheme 1a).[28] Subsequently, Luan demonstrated the palladium-catalyzed [5+2] oxidative annulation of *o*-arylanilines with alkynes to obtain dibenzo[*b*,*d*]azepines (Scheme 1b).[29] We developed an efficient palladium-catalyzed [2+2+2] cycloaddition of *N*-substituted *o*-arylanilines with diarylacetylenes to obtain multisubstituted naphthalenes.[30] Here, we perceive that C2'-benzofulvenation is possible if the alkenyl-palladium intermediate resulting from the first alkynyl insertion can undergo second alkynyl insertion and cyclization. This approach may result in benzofulvenation through C–H bond activation with two diarylacetylenes acting as an implicit benzofulvene unit (Scheme 1c). This method would be synthetically valuable because the benzofulvene moiety has not previously been identified as a transmetallization reagent for functionalization. The benzofulvenated *o*-arylanilines can be transformed into fluorescent diarylazulenes and phenanthridines, with forthcoming applications in the materials science and pharmaceutical fields, respectively.

This work was originally undertaken in our recent study on the palladium(II)-catalyzed [2+2+2] annulation of *N*-([1,1'-biphenyl]-2-yl)acetamides with alkynes through C–H bond activation.[30] After an extensive survey of reaction parameters, we summarized the crucial optimization conditions (Table 1). We first investigated the reaction of 2'-methylbiphenyl-2-amine (**1a**) and diphenylacetylene (**2a**) as model substrates in the presence of $Pd(OAc)_2$ as the catalyst (10 mol%), $Cu(OAc)_2$ as the oxidant (1.5 equiv.), and dichloromethane (DCM, 2 mL) as the solvent in a pressure-affordable sealed tube, which resulted in the unusual *ortho*-benzofulvenation product **3a** in a favorable yield (85%) at 100 °C (Table 1, entry 1). Next, the role of each component was investigated through parameter-tuning experiments. When DCM was replaced with other polar solvents, such as *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc), or chlorinated solvents, such as *ortho*-dichlorobenzene (*o*-DCB) and chlorobenzene (CB), benzofulvene **3a** was obtained in low yields in addition to a side product, phenylphenanthridine **4a**, in various yields (entries 2–5). When 1,2-dichloroethane (DCE) was used as the solvent, the desired product was obtained in a 56% yield and with favorable selectivity (entry 6). This reaction was performed with various fluorinated alcoholic solvents, such as 2,2,2-trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP), and no appreciable amounts of product were produced (entry 7). The solvent DCM outperformed others probably because of its lower boiling point and aprotic property. DCM is capable of making a pseudo gaseous state under high pressure and temperature conditions, which results in faster second alkyne insertion. We noted that phenanthridine **4a** was formed in a favorable yield when DMF, DMAc, *o*-DCB, and CB were used. Replacement of $Cu(OAc)_2$ with another oxidizing agent—such as $CuSO_4{\cdot}5H_2O$, $Cu(BF_4)_2$, AgOAc, $PhI(OAc)_2$, or O_2—resulted in chemical transformations becoming productless (entry 8). However, after the substitution of $Cu(OAc)_2$ by CuOAc as an oxidant, an appreciable amount of the corresponding product **3a** was obtained (entry 9). Use of different palladium catalysts, such as $PdCl_2$, $PdCl_2(PPh_3)_2$, $PdCl_2(CH_3CN)_2$, and $Pd(PPh_3)_4$, did not result in superior product formation to using $Pd(OAc)_2$ for *ortho*-benzofulvenation (entries 10−13).

Table 1. Optimization of the reaction conditions[a]



Entry	Deviations from standard conditions	3a/4a	Yield (%)[b]
1	No deviation	100:0	85
2	DMF instead of DCM	51:49	35
3	DMAc instead of DCM	100:0	18
4	*o*-DCB instead of DCM	47:53	32
5	CB instead of DCM	71:29	45
6	DCE instead of DCM	100:0	56
7	Solvent = TFE or HFIP	-	trace
8	Oxidant = $CuSO_4{\cdot}5H_2O$, $Cu(BF_4)_2$, AgOAc, $PhI(OAc)_2$ or O_2	-	ND[e]
9	CuOAc instead of $Cu(OAc)_2$	100:0	61
10	$PdCl_2$ instead of $Pd(OAc)_2$	100:0	55
11	$PdCl_2(PPh_3)_2$ instead of $Pd(OAc)_2$	100:0	54
12	$PdCl_2(CH_3CN)_2$ instead of $Pd(OAc)_2$	100:0	60
13	$Pd(PPh_3)_4$ instead of $Pd(OAc)_2$	100:0	39
14	$Cu(OAc)_2$ 1.0 equiv. instead of 1.5 equiv	100:0	77
15	O_2 flushed for 5 minutes instead of air	100:0	62
16	N_2 flushed for 5 minutes instead of air	100:0	66
17	condition A[c] or condition B[d]	-	ND[e]

[a]Reaction conditions: **1** (0.30 mmol), **2** (0.72 mmol), $Cu(OAc)_2$ (0.45 mmol), and 10 mol% palladium catalyst under air atmosphere in a sealed tube unless otherwise stated. [b]Yields were measured using ^1H NMR spectroscopy with mesitylene as the internal standard. [c] Condition A:

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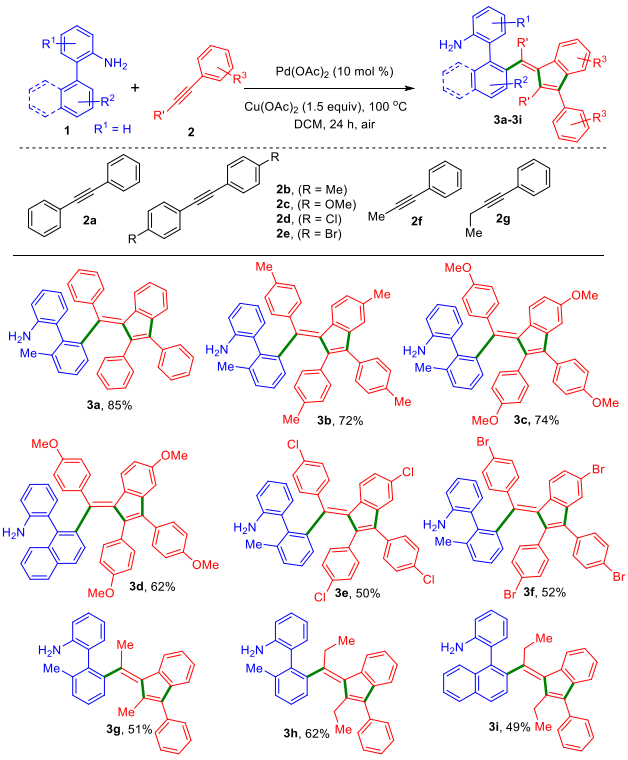
The reaction was completed using $Pd(OAc)_2$ (10 mol%), LiBr (0.4 mmol), pivalic acid (0.6 mmol), and NaOPiv (0.4 mmol) in DMAc (2 mL) at 80 °C for 30 h. [d] Condition B: The reaction was completed using $PdCl_2$ (15 mol%), AgOTf (1.0 equiv.), and *o*-chloranil (1.0 equiv.) in DMAc (2 mL) at 60 °C for 24 h. [e]ND denotes not detected.

Reducing the amount of $Cu(OAc)_2$ (1 equiv.) as an oxidant reduced the formation of the desired product (entry 14). Furthermore, the presence of excessive oxygen and nitrogen appeared detrimental to the chemical process (entries 15 and 16). Excessive oxygen may deactivate palladium catalysts, whereas the absence of sufficient oxygen prevents oxidation of Cu(I) to Cu(II) in the catalytic cycle. Notably, both condition A (that of Hua) for the synthesis of benzofulvene and condition B[31] (that of Itami) for the synthesis of pentalenes from diarylacetylenes were ineffective (entry 17).

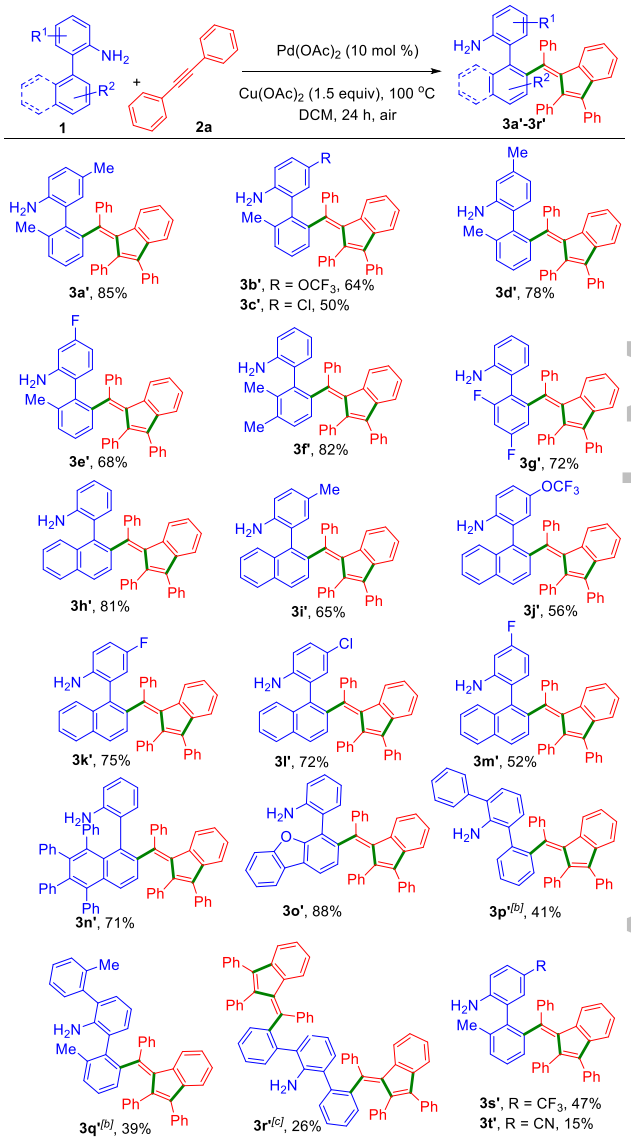
Table 2. Substrate scope of alkynes[a]



[a]All reactions were performed using **1** (0.30 mmol), **2** (0.72 mmol), $Pd(OAc)_2$ (0.03 mmol), $Cu(OAc)_2$ (0.45 mmol), and DCM (2 mL) in a sealed tube at 100 °C under air for 24 h.

The reaction scope of *ortho*-benzofulvenation was examined under optimized conditions with other substituted alkynes (**2b-2g**) containing electron-rich or electron-deficient aromatic groups and alkyl substituents, as shown in Table 2. The symmetrically substituted 1,2-diarylethynes bearing electron-donating groups (EDG) on the *para* position of the aryl rings, such as methyl (**2b**) and methoxy (**2c**) groups, afforded products **3b** and **3c** in favorable yields (72%–74%). When 2-(naphthalen-1-yl)aniline (**1i**) was treated with *para*-methoxy-substituted diphenylacetylene (**2c**), it produced **3d** in a yield of 62%, a slightly lower yield compared with that obtained with **1a**. Furthermore, substrates containing electron-withdrawing groups (EWG), such as *para*-chloro (**2d**) and *para*-bromo (**2e**), substituted diarylethynes and **1a** afforded products **3e** and **3f** in moderate yields (50%–52%). The reactions performed with unsymmetrical alkynes such as 1-phenyl-1-propyne (**2f**) and 1-phenyl-1-butyne (**2g**) formed regioselective products **3g** and **3h**, respectively, in yields of 51%–62%. Similarly, 2-(naphthalen-1-yl)aniline (**1i**) treated with 1-phenyl-1-butyne (**2g**) under standard conditions produced 49% of **3i**. The regiochemistry of the benzofulvenation reaction with asymmetric alkynes was verified through the single-crystal structure of **3h**.[32]

Table 3. Substrate scope of 2-arylanilines[a]



[a]All reactions were performed using **1** (0.30 mmol), **2a** (0.72 mmol), $Pd(OAc)_2$ (0.03 mmol), $Cu(OAc)_2$ (0.45 mmol), and DCM (2 mL) in a sealed tube at 100 °C under air for 24 h. [b]The reaction was performed using **2a** (1.44 mmol), $Pd(OAc)_2$ (0.06 mmol), $Cu(OAc)_2$ (0.9 mmol), and DCM (4 mL) at 100 °C under air for 24 h. [c]The reaction was performed

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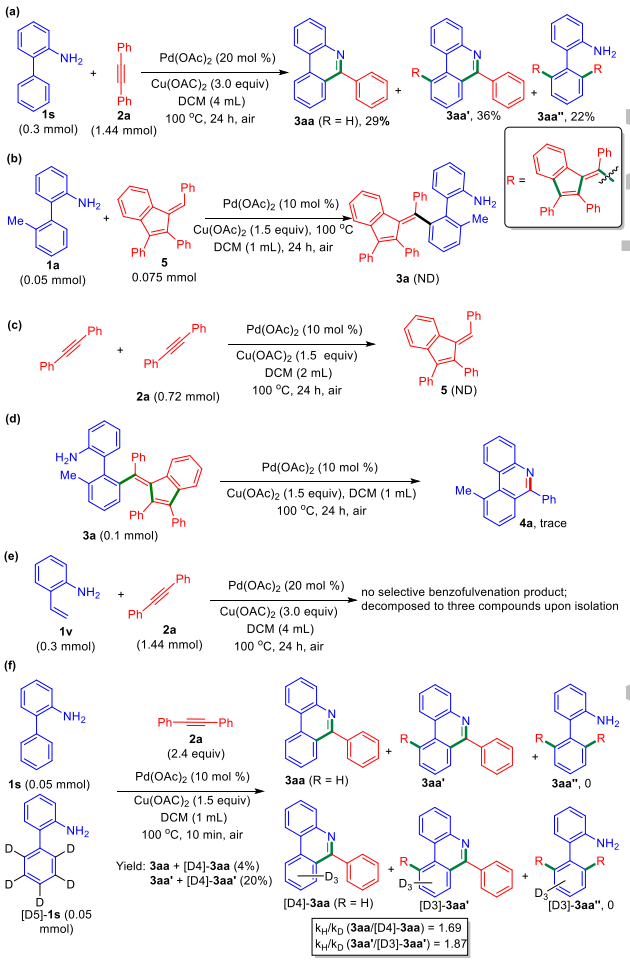
using **3p'** (0.10 mmol), **2a** (0.24 mmol), $Pd(OAc)_2$ (0.01 mmol), $Cu(OAc)_2$ (0.15 mmol), and DCM (2 mL) at 100 °C under air for 24 h.

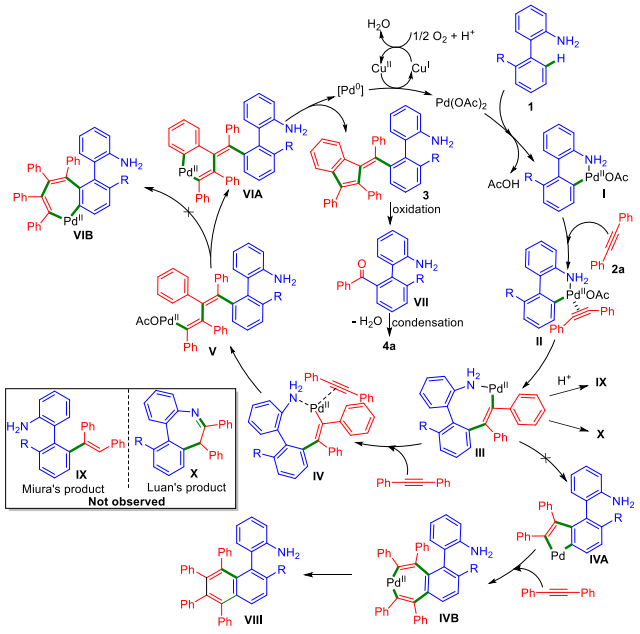
Next, the substrate scope was surveyed using a number of *o*-arylanilines (**1b**−**1r**) for benzofulvenation (Table 3). We discovered that substrate **1**, which bears an EDG (4-methyl) or EWG (4-trifluoromethoxy or 4-chloro) on the upper aryl ring, reacted smoothly with diphenylacetylenes to deliver the corresponding benzofulvenation products (**3a'**-**3c'**, 50%–85%). The substrates with an EDG (5-methyl) or EWG (5-fluoro) substitution in the upper ring of *o*-arylanilines reacted with **2a** to produce the desired products **3d'** and **3e'** in yields of 78% and 68%, respectively. Similarly, substrates bearing EDG and EWG groups such as dimethyl and difluoro moieties on the lower ring resulted in the desired products **3f'** and **3g'** in good yields (72%–82%). The 2-naphthyl anilines reacted with **2a** and produced the benzofulvene product **3h'** in a high yield (81%). However, the reaction involving a substrate bearing an EDG (4-methyl) on the upper aryl ring afforded the corresponding product **3i'** in a 65% yield. Furthermore, the substrates bearing EWGs such as 4-trifluoromethoxy, 4-fluoro, 4-chloro, and 5-fluoro in the upper aryl ring reacted with **2a** to yield the desired products **3j'**–**m'** (52%–75%). The substrate with a 2-naphthyl moiety possessing a tetraphenyl substitution group produced the desired product **3n'** in a 71% yield. This methodology could be extended not only to the benzofulvenation of substrates with a dibenzo[*b*,*d*]furan moiety (**3o'**: 88% yield) but also to substrates with *o*,*o'*-diphenyl and *o*,*o'*-*ortho* tolyl substitutions on the aniline ring, yielding the desired products **3p'** and **3q'** in 41% and 39% yields, respectively. The attempt to perform direct bis-benzofulvenation was not straightforward in this one-pot reaction. However, isolated mono-benzofulvenation compound **3p'** could be treated with **2a** to obtain the bis-benzofulvenation product **3r'** in a yield of 26% under standard conditions. The lower yields obtained in the first and second benzofulvenation were mainly due to the steric effect exerted by the aryl moiety in the 6 position. This steric effect reduced the tendency of second alkyne insertion. Finally, poor yields were also obtained using the substrates with EWGs in the upper aryl ring, such as those with 4-trifluoromethyl and 4-cyano, which reacted with **2a** to yield **3s'** and **3t'** in yields of 47% and 15%, respectively.

We conducted a series of experiments to analyze the reaction mechanism (Scheme 2). Treatment of *o*-phenylaniline (**1s**) with alkyne **2a** (4.8 equiv) afforded the products **3aa**, **3aa'**, and **3aa''** in a 33:42:25 ratio (Scheme 2a). The phenanthridine moiety in **3aa** and **3aa'** was likely formed due to oxidation of the exocyclic double bond in benzofulvene by oxidants and then condensation with amines. Thus, formation of the bis-benzofulvene product **3aa''** resulted in an unsatisfactory yield. Furthermore, 2'-methyl-[1,1'-biphenyl]-2-amine (**1a**) was treated with benzofulvene **5** under optimized standard conditions, but the desired product **3a** was not obtained (Scheme 2b). This indicated that benzofulvene was not formed first in this reaction. Furthermore, benzofulvene **5** was not observed due to the dimerization of diphenylacetylenes under the standard conditions (Scheme 2c). Treatment of **3a** under standard conditions obtained a trace amount of secondary product **4a** with nearly full recovery of **3a** (Scheme 2d). Unfortunately, the reaction involving *ortho*-vinylaniline (**1v**) did not result in a selective benzofulvenation product under the optimized conditions, and the product decomposed quickly upon isolation (Scheme 2e). Free-amine DG-assisted C−H bond activation was investigated using a deuterium-labelling experiment. The intermolecular kinetic isotope effect study revealed k_H/k_D values of 1.69 and 1.87 for formation of **3aa** and **3aa'**, respectively, in a 10 min reaction. This indicated that C−H bond activation was probably the rate-determining step (Scheme 2f). These experimental results indicated that the benzofulvenation proceeded through amine-directed C−H bond activation followed by two respective alkyne insertions to obtain benzofulvenes.



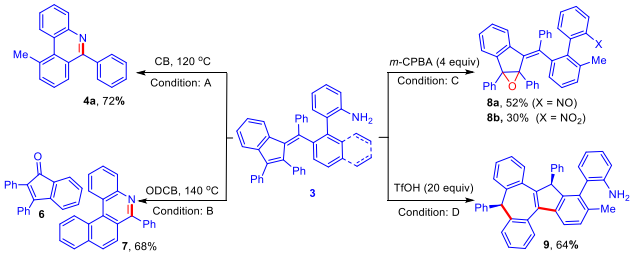
Scheme 2. Control experiments.

A plausible reaction mechanism based on these results and transition-metal-catalyzed C–H bond activation/oxidative cycloaddition reaction is proposed (Scheme 3). Initially, an *ortho* C–H bond is activated on the 2-aryl moiety of **1** by Pd(II) to yield six-membered palladacycle intermediate **I**. Subsequently, alkyne **2a** undergoes coordination and migratory insertion to yield the eight-membered palladacycle intermediate **III** through intermediate **II**. The intermediate **III** propagates the second coordination and insertion of the alkyne through intermediate **IV** to yield **V**. The reaction does not proceed through intermediate **IVB** formed via **IVA** or **VIB** to produce the previously observed multisubstituted naphthalenes **VIII** under developed conditions.[30] Instead, it proceeds via a six-membered palladacycle through C–H bond activation to obtain the *ortho*-benzofulvene product **3** through reductive elimination and generated Pd(0). To continue the catalytic cycle, Pd(0) is reoxidized into Pd(II) by Cu(II). In the presence of oxygen, **3** undergoes oxidation to give **VII**; subsequent condensation yields the phenylphenanthridine product **4a**. In our experiments, we did not observe Miura's alkenylation product **IX** due to absence of a proton source.[28] Luan's dibenzo[*b*,*d*]azepines **X**, which are formed through reductive elimination from **III**, were also not formed under our conditions. Why the reaction proceeded along a different pathway under our conditions remains unclear, but it is likely that under our conditions performed in dichloromethane (b.p. 39.6 °C at 760 mmHg) at 100 °C in a pressure-affordable tube, the second alkyne insertion occurred more quickly to give **V** instead of undergoing reductive elimination to give **X**.



Scheme 3. Proposed catalytic cycle for benzofulvenation.

To demonstrate the synthetic utility of this benzofulvenation methodology (Scheme 4), we treated **3a** with *p*-benzoquinone (*p*-BQ), AcOH, and $Cu(OAc)_2$ in CB. Unexpectedly, the exocyclic double bond of the benzofulvene moiety was oxidized and condensed with amine to afford phenylphenanthridine **4a** in a 72% yield. Furthermore, we attempted to synthesize iptycenes through the treatment of compound **3h'** with *p*-BQ, AcOH, and $Cu(OAc)_2$ in *o*-DCB at 140 °C.[33] However, the exocyclic double bond was oxidized and condensed with amine to give phenanthridine **7** in a 68% yield. Notably, a by-product indenone **6** was isolated in a 57% yield. When **3a** was treated with *m*-CPBA, however, **3a** was converted into the endocyclic epoxidation products **8a** and **8b** in yields of 52% and 30%, respectively.



Conditions: A) **3a** (0.1 mmol), *p*-BQ (1.2 equiv.), AcOH (1.5 equiv.), $Cu(OAc)_2$ (0.2 equiv.), CB (2 mL), 120 °C, 24 h, air. B) **3h'** (0.1 mmol), $Cu(OAc)_2$ (2 equiv.), *p*-BQ (1.2 equiv.), AcOH (1.5 equiv.), *o*-DCB (2 mL), 140 °C, 24 h, air. C) **3a** (0.1 mmol), *m*-CPBA (0.4 mmol), DCM (2 mL), room temperature, 24 h, air. D) **3a** (0.1 mmol), TfOH (20 equiv.), DCM (4 mL), room temperature, 4 h, air.

Scheme 4. Synthetic transformations of benzofulvene **3**.

This indicated that the endocyclic alkene of benzofulvene was more reactive than the exocyclic alkene moiety toward epoxidation. Furthermore, when **3a** was treated with equimolar amount of *m*-CPBA (1.1 equiv), the amine group was first oxidized to a nitroso group (**8c**, see in SI). This result confirmed that the amine moiety was more reactive than the endocyclic double bond. Finally, another synthetic transformation was illustrated by treating **3a** with TfOH in DCM at room temperature. This reaction produced stereoselective polycyclic compound **9** with a 5- and 7-membered fused azulene core structure in a 64% yield (refer to the SI for a proposed mechanism). The unusual structure **9** exhibited fluorescent emission at 396 nm with quantum yields of 39% in a chloroform solution (Figure S1 and S2 in the SI). These *ortho*-benzofulvenation and oxidation products were unambiguously identified using ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction analysis.[32]

In conclusion, we demonstrated unprecedented free amine–directed sequential Pd-catalyzed

benzofulvenation by using two diarylacetylenes as an implicit benzofulvene moiety. The benzofulvenation exhibited robustness because it did not require the exclusion of air and demonstrated a new mode of reactivity between diarylacetylenes and *o*-phenylanilines. The endocyclic alkene moiety of benzofulvenes was more reactive than the exocyclic moiety toward epoxidation. The new benzofulvenes can be further transformed into fluorescent polycyclics, which have applications in material science.

Experimental Section

(*Z*)-2'-((2,3-diphenyl-1*H*-inden-1-ylidene)(phenyl)methyl)-6'-methyl-[1,1'-biphenyl]-2-amine derivatives (3)

An oven-dried 35-mL pressure-affordable tube equipped with a stirring bar was charged with $Pd(OAc)_2$ (10 mol %), $Cu(OAc)_2$ (0.45 mmol), *o*-arylanilines (0.30 mmol), and diarylacetylenes (0.72 mmol) in distilled DCM (2.0 mL) under atmospheric conditions. The pressure tube was then closed using a screw cap, and the reaction mixture was heated for 24 h at 100 °C with constant stirring. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, after which filtration was performed through a thin pad of Celite. The filtrate was concentrated in a vacuum, and the residue was then purified using flash chromatography (hexanes:ethyl acetate = 10:1) to afford product **3**.

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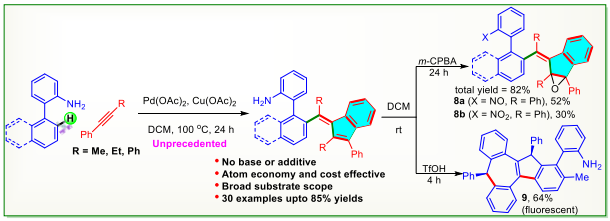
Palladium-Catalyzed Benzofulvenation of *o*-Arylanilines through C–H Bond Activation by Using Two Diarylacetylenes as an Implicit Benzofulvene



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