

Pd-Catalyzed Synthesis of 9,9'-Bifluorenylidene Derivatives via Dual C–H Activation of Bis-biaryl Alkynes

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S Supporting Information

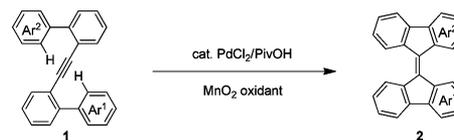
ABSTRACT: We report a novel Pd-catalyzed alkyne-directed dual C–H activation of bis-biaryl alkynes, which produced important and useful products, 9,9'-bifluorenylidene (9,9'BF) derivatives, in high yields with a broad range of functional group compatibility. The combination of the PdCl₂ catalyst with the MnO₂ oxidant and PivOH additive is vital for realization of the present catalytic transformation. Mechanistic evidence suggests that this intramolecular arene/alkyne annulation may take place through unusual dual C–H activation followed by annulation with alkynes.

Transition-metal-catalyzed annulations of alkynes with arenes via direct C–H functionalization without prior functionalization of aromatic C–H bonds have attracted increasing interest as one of the most powerful synthetic methodologies for the construction of π -conjugated polycycles.¹ One of the classical arene/alkyne annulations is intramolecular electrophilic hydroarylation of alkynes catalyzed by palladium and platinum complexes, and Lewis acids, which mainly or exclusively proceeds through 6-*endo-dig* cyclization of electron-rich aromatic rings.^{2–4} In contrast, the research group of Gevorgyan reported an impressive Pd-catalyzed exclusive 5-*exo-dig* cyclization of *o*-alkynylbiaryls having electron-neutral and electron-deficient arenes, affording the fluorene derivatives in high *cis*-stereoselectivity via a C(sp²)–H bond activation.⁵ On the other hand, although only a few examples have been reported, the arene/alkyne annulation via dual C–H bond activation without using arylhalides has become a more challenging methodology for the synthesis of various polycyclic aromatic compounds.^{6,7} For example, Jiao et al. reported a Pd-catalyzed oxidative cycloaromatization of biaryls with alkynes to polycyclic heteroaromatics^{6a} and Itami et al. reported a Pd-catalyzed homoannulation of arylacetylenes toward synthesis of dibenzopentalenes.^{6b}

The twisted π -conjugated molecules of 9,9'-bifluorenylidene (9,9'BF) and its derivatives readily accept one electron to fulfill a 14- π -electron system, which were found to be useful non-fullerene-electron-accepting materials in bulk-heterojunction solar cells.⁸ In general, 9,9'BF derivatives could be synthesized from fluorenones through multiple steps,⁹ and a new Pd-catalyzed double cross-coupling reaction of 9-(dibromomethylene)-9H-fluorene with 9-stannafluorene has been developed by Hiyama et al.¹⁰ Taking those pioneering C–H functionalization methods into consideration and our continuous interest in Pd-

catalyzed C–H activation for the construction of polycyclic fused aromatics,¹¹ we reasoned that the successful implementation of the cyclization of bis-biaryl alkynes (**1**) through a dual C–H activation by seeking appropriate transition-metal-catalyst systems may provide a novel synthetic methodology for the construction of 9,9'BF derivatives. Herein, we report an unprecedented PdCl₂-catalyzed dual C–H activation of bis-biaryl alkynes (**1**) for the construction of 9,9'BF derivatives (**2**) by combining with PivOH and the MnO₂ oxidant (Scheme 1).

Scheme 1. Pd-Catalyzed Arene/Alkyne Annulation via Dual C–H Activation of Bis-biaryl Alkynes

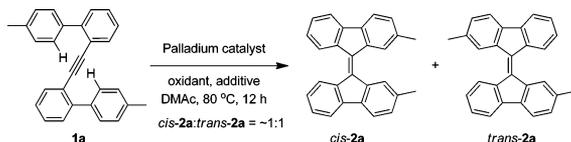


The unexpected mechanistic evidence indicates that the present transformation is in sharp contrast with the previously reported hydroarylation^{2–6} and it seems to proceed through an unusual mechanism involving dual C–H activation followed by carbopalladation with a C–C triple bond.

Our optimization results are summarized in Table 1. The reaction of bis-biphenyl alkyne **1a** with PdCl₂ as a catalyst in *N,N*-dimethylacetamide (DMAc) at 80 °C for 12 h afforded only 3% of the corresponding products *cis*-**2a** and *trans*-**2a** (~1:1) (entry 1). On the basis of the recently reported oxidative dehydrogenation C–H coupling conditions,¹² various oxidants have been examined. The oxidants that were commonly used in Pd-catalyzed transformations, such as K₂S₂O₈, Ag₂O, *o*-chloranil, CuCl₂, and PhI(OAc)₂, were almost totally inactive (entries 2–6). To our delight, the use of activated MnO₂ (2 equiv) as an oxidant drastically increased the reactivity, producing the corresponding products **2a** in 43% yield together with the recovered **1a** in 51% yield (entry 7). Indeed, during the reaction using the PdCl₂ catalyst without using oxidants as shown in entry 1, we observed some amounts of palladium black precipitates and the reaction mixture showed acidity, which indicate the generation of Pd(0) species and hydrochloric acid.¹³ We assumed that MnO₂ could oxidize the Pd(0) species to the active Pd(II) species in the presence of in situ generated HCl, which may accelerate the catalytic cycle. Moreover, we were

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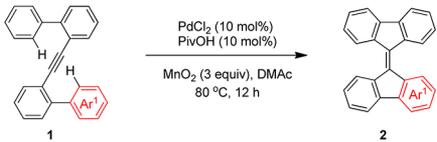
Table 1. Optimization of Reaction Conditions^a


entry	Pd catalyst (10 mol %)	oxidant (2 equiv)	additive (10 mol %)	yield (%) ^b
1	PdCl ₂	none	none	3
2	PdCl ₂	K ₂ S ₂ O ₈	none	5
3	PdCl ₂	Ag ₂ O	none	4
4	PdCl ₂	<i>o</i> -chloranil	none	0
5	PdCl ₂	CuCl ₂	none	0
6	PdCl ₂	PhI(OAc) ₂	none	trace
7	PdCl ₂	MnO ₂	none	43
8	PdCl ₂	MnO ₂	PivOH	82
9	PdBr ₂	MnO ₂	PivOH	69
10	Pd(OAc) ₂	MnO ₂	PivOH	12
11	Pd(OPiv) ₂	MnO ₂	PivOH	4
12	Pd(CH ₃ CN) ₄ (BF ₄) ₂	MnO ₂	PivOH	5
13	Pd ₂ (dba) ₃	MnO ₂	PivOH	3
14	PdCl ₂	MnO ₂ ^c	PivOH	98 (93)
15 ^d	PdCl ₂	MnO ₂ ^c	PivOH	87 ^e

^aReaction conditions: **1a** (0.2 mmol), Pd catalyst (10 mol %), oxidant (2 equiv), DMAc (0.5 M), under a N₂ atmosphere, 80 °C for 12 h. ^b¹H NMR yield determined using CH₂Br₂ as an internal standard. The isolated yields are shown in parentheses. ^cMnO₂ (3 equiv) was used. ^dThe reaction carried out at rt for 24 h. ^eThe ratio of *cis*-**2a** and *trans*-**2a** is 4:1.

pleased to find that the use of pivalic acid (PivOH, 10 mol %) as a cocatalyst further improved the chemical yield of **2a** to 82% (entry 8), which strongly indicates the involvement of a pivalate-assisted C(sp²)-H bond cleavage. It should be mentioned that other oxidants used in entries 2–6 were still inefficient in the presence of PivOH, supporting the important role of the MnO₂ oxidant.¹³ Although other palladium catalysts, such as Pd(OAc)₂, Pd(OPiv)₂, Pd(CH₃CN)₄(BF₄)₂, and Pd₂(dba)₃, were inactive, the PdBr₂ catalyst exhibited good catalytic activity, affording **2a** in 70% yield, indicating an efficient combination of palladium halides with the MnO₂ oxidant (entries 9–13). Other transition metals, such as NiCl₂, PtCl₂, and RhCl(PPh₃)₃, were totally inactive for the present transformation (see Supporting Information (SI)). The use of 3 equiv of MnO₂ further improved the isolated yield of **2a** to 93% (entry 14). It is noted that the product **2a** was obtained as a 1:1 ratio of *cis*- and *trans*-isomers at 80 °C under the above-mentioned conditions (entries 1–14). The reaction also could carry out at rt under the prolonged reaction time (24 h) to give **2a** in 87% yield with a 4:1 mixture of *cis*- and *trans*-isomers (entry 15), in which the predominant isomer *cis*-**2a** was isomerized at rt (3 days) and at 80 °C (12 h) to give a 2:1 and 1:1 mixture of *cis*-**2a** and *trans*-**2a**, respectively (SI, Figure S1). These results suggest that the reaction should proceed in a *cis*-annulation manner followed by a *cis* to *trans* isomerization. Finally, it should be noted that the use of the freshly activated MnO₂ oxidant is important to achieving a high chemical yield of **2a**. Overall, it was concluded that the use of a PdCl₂/PivOH (10 mol %) catalyst system combined with the activated MnO₂ oxidant was optimal for the successful implementation of the present catalytic transformation.

Optimal conditions showed high compatibility and efficiency with various bis-biaryl alkynes for synthesis of a variety of 9,9'BF derivatives (Table 2). Under the standard conditions, 1,2-bis(4'-

Table 2. PdCl₂-Catalyzed Annulation of Various Bis-biphenyl Alkynes^a


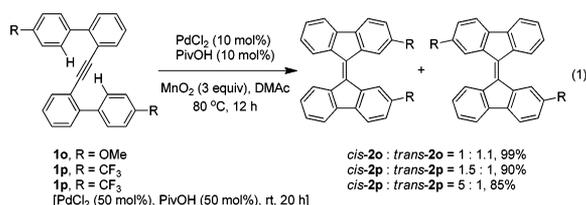
entry	1	2	yield (%) ^b
1	1b , R = H	2b	92
2	1c , R = CHO	2c	65
3	1d , R = CO ₂ Me	2d	91
4	1e , R = F	2e	74 ^c
5	1f , R = OMe	2f	90
6	1g , R = NPh ₂	2g	92
7	1h , R = Me	2h	93
8	1i	2i	82
9	1j	2j	92 ^d
10	1k	2j	88
11	1l	2l	88 ^e
12	1m , X = S	2m , X = S	92
13	1n , X = O	2n , X = O	81

^aReaction conditions: **1** (0.2 mmol), PdCl₂ (10 mol %), PivOH (10 mol %), MnO₂ (3 equiv), under a N₂ atmosphere, 80 °C for 12 h. ^bIsolated yields after silica gel chromatography. ^cThe reaction time is 24 h. ^dA 4:1 mixture of **2j** and **2k** was obtained. ^eA 1.9:1 mixture of **2l** and **2l'** was obtained.

methyl-[1,1'-biphenyl]-2-yl)ethyne (**1b**) without a substituent on the biphenyl rings afforded the corresponding product 9,9'BF (**2b**) in 92% yield (entry 1). The product **2b** was unambiguously confirmed by ¹H and ¹³C NMR comparing with the reported literature.^{8c} Bis-biphenyl alkynes **1c–e** having an electron-withdrawing group, such as aldehyde, ester, and fluorine, were well tolerated, giving the corresponding 9,9'BF derivatives **2c–e** in good to high yields (entries 2–4). The reactions with bis-biphenyl alkynes **1f–k** having an electron-donating group, such as methyl, methoxy, and *N,N*-diphenylamine, produced higher yields of the corresponding products **2f–j** compared with that of

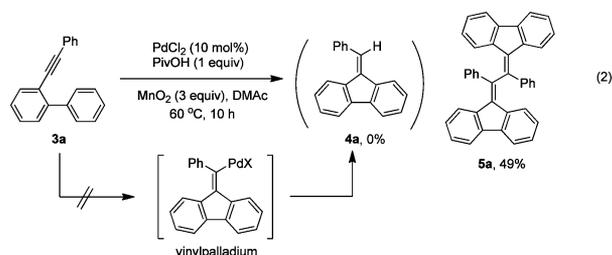
the substrates **1c–e** (entries 5–10), in which **1j** bearing a methyl group at the *meta*-position afforded the corresponding products **2j** and **2k** in 88% yield with a 4:1 ratio (entry 9, SI, Figure S2). Although the 2-naphthyl-substituted biaryl alkyne **1l** showed high reactivity, the product was obtained as a 1.9:1 mixture of regioisomers **2l** and **2l'** (entry 11, SI, Figure S2). The recent interest in heteroaromatic-incorporated 9,9'-BF derivatives as a key unit in low band gap electron donor polymers for organic photovoltaics¹⁴ led us to examine the heteroaromatic-containing bis-biaryl alkynes. Both benzothiophene and benzofuran substituted bis-biaryl alkynes **1m** and **1n** exhibited high stability under our acidic conditions, furnishing the anticipated products **2m** and **2n** in 92% and 81% yields, respectively (entries 12 and 13).

The bis-biphenyl alkynes **1o** and **1p** having two methoxy groups and two trifluoromethyl groups at both 1,2-biphenyl rings, respectively, reacted smoothly to form a mixture of *cis*- and *trans*-products in high yields. (eq 1). Irrespective of the electron-



donating and -withdrawing groups on the biphenyl rings, the substrates **1o** and **1p** produced the *cis*- and *trans*-isomers of **2o** and **2p** in high yields with a ratio of 1:1.1 and 1.5:1 at 80 °C, respectively. Interestingly, the reaction of **1p** took place at rt within 20 h by using a large amount of PdCl₂ and PivOH to give a mixture of *cis*-**2p** and *trans*-**2p** in 85% yield with the former as a predominant product (5:1). The *cis*-**2p** isomer could be isolated by silica gel chromatography, which slowly isomerized to *trans*-**2p** after 24 h in solution to give a mixture of isomers.¹⁵ The remarkable reactivity of the alkyne **1p** having two strong electron-withdrawing groups on the aromatic rings strongly contradicts with the typical electrophilic hydroarylation of alkynes which generally proceeds with the electron-rich aromatic rings.^{2–4} In addition, the selectivity of the *cis*-**2p** isomer at rt implied the involvement of a *cis*-cyclization pathway in this transformation.

We next examined the annulation of *o*-alkynyl biphenyl under our reaction conditions to probe the possible carbopalladation intermediate. However, as shown in eq 2, the reaction of 2-



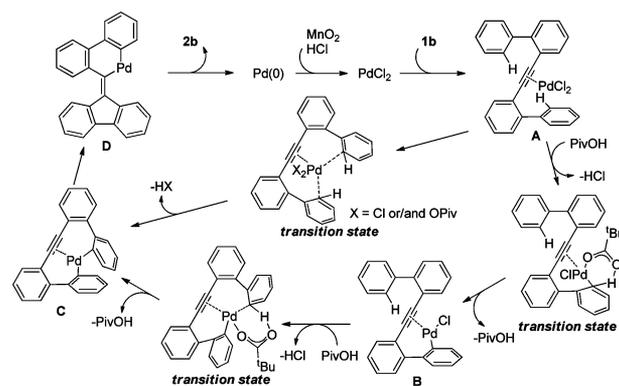
(phenylethynyl)-1,1'-biphenyl (**3a**) afforded an unexpected dimerized fluorenylidene product **5a** in good yield without formation of the desired fluorene product **4a** which was expected to be formed through protonation of a vinylpalladium intermediate as reported by Gevorgyan et al.^{5a} Furthermore, the reaction of **4a** prepared following Gevorgyan's conditions from **3a** under our standard conditions did not proceed at all and

the starting material was recovered, indicating that the potential pathway of the cation radical dimerization¹⁶ of **4a** could be excluded (SI, Scheme S1). It should be emphasized that the reaction of bis-biphenyl alkyne **1b** under the Gevorgyan conditions^{5a} did not afford any of the desired products and the Jiao^{6b} and Itami's conditions^{6b} for the reactions of **1a** were almost inactive (SI, Schemes S2 and S3), indicating that our catalytic system is unique for the formation of 9,9'-BF derivatives from bis-biaryl alkynes.

To further understand the mechanistic insight, the deuterium isotope experiments were performed. Under the standard conditions, the reaction of the deuterated substrate **1k'** produced the corresponding product **2j'** as a mixture of *cis*- and *trans*-isomers in almost quantitative yield without observation of a H–D exchange, indicating the irreversible C–H bond cleavage (SI, Scheme S4). An intermolecular competing reaction of **1k** and **1k'** was also studied (SI, Scheme S5). The product **2j** and the deuterated product **2j'** were obtained with similar kinetic isotope effects (KIEs) of 1.7 and 1.6 at 80 °C (15 min) and rt (2.5 h), respectively. Considering the cleavage of two C–D bonds in the substrate **1k'**, the fact that the C–H bond cleavage occurs during the rate-determining step cannot be fully explained by this KIE value. Instead, this result implies the involvement of alkyne- or pivalate-assisted C–H bond activation.

Overall, the following results have been obtained experimentally: (a) the reaction proceeds in a *cis*-annulation manner; (b) the formation of vinylpalladium intermediate is unlikely; (c) both electron-withdrawing and -donating groups are highly compatible; (d) products **2** and **5a** are unavailable using the reported dual C–H activation conditions, which implied that the current reaction should undergo a different pathway compared with the related reactions.^{2–6} Based on the experimental results and taking into consideration the literature on C–H arylations assisted by σ -chelating directing groups,¹² we propose a mechanism involving biarylpalladium intermediate formation via alkyne-directed dual C–H activation.^{5b} A plausible reaction mechanism is illustrated in Scheme 2. Initially, PdCl₂ coordinates

Scheme 2. Proposed Reaction Mechanism



with the C–C triple bond of **1b** to produce Pd- π -complex **A** which may undergo a direct *ortho*-C–H bond insertion into the adjacent phenyl ring assisted by PivOH to form arylpalladium complex **B**.^{5,6b} Subsequently, the intramolecular PivOH-assisted insertion of the complex **B** into the second *ortho*-C–H bond may take place prior to carbopalladation of the triple bond, affording the cyclized biarylpalladium complex **C**.¹² Alternatively, the simultaneous double *ortho*-C–H activation of the intermediate **A** through a PivOH-assisted transition state to form the complex **C**

also can be considered. Next, the intramolecular alkyne carbopalladation of the biaryl-palladium complex **C** affords the six-membered palladacycle **D**. Subsequent reductive elimination of the intermediate **D** gives the corresponding product **2b** and the Pd(0) species. The MnO₂ oxidant proved to be an efficient oxidant for regeneration of the active PdCl₂ catalyst from the Pd(0) species in the presence of the in situ generated HCl,¹³ which is a key point for the successful implementation of the present catalytic transformation. The PivOH cocatalyst accelerates the *ortho*-C–H bond cleavage through the formation of the pivalate-promoted transition state.^{11,17} Following this proposed mechanism, the unexpected product **5a** in eq 2 should be formed through the intermolecular alkyne directed dual C–H activation to produce the biaryl-palladium analogue,¹² followed by an intramolecular carbopalladation (SI, Scheme S6).¹⁸ This pathway may explain the reason why the expected product **4a** cannot be formed under our reaction conditions.

In summary, we have developed a novel and efficient Pd-catalyzed dual C–H activation/annulation transformation of bi-aryl alkynes under mild reaction conditions. The present reaction provides a new and general synthetic methodology for construction of various new 9,9'BF derivatives with a broad range of functional groups. The use of the PdCl₂ catalyst combined with the MnO₂ oxidant and PivOH additive is vital for the accomplishment of the catalytic cycle sufficiently. The experimental results clearly indicate that a novel dual C–H activation followed by an annulation with alkynes may be operating in the current transformation, which is distinct from the previously reported pathways. Further study of the mechanistic details and application of new 9,9'BF derivatives as n-type materials for optoelectronic devices is in progress.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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