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Highly Chemo-, Regio- and *E*/*Z*-Selective Intermolecular Heck-Type Dearomative [2 + 2 + 1] Spiroannulation of Alkyl Bromoarenes with Internal Alkynes

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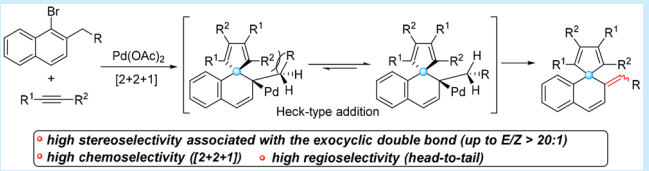
Supporting Information

ABSTRACT: Described herein is a palladium-catalyzed dearomative annulation of alkyl bromoarenes with internal alkynes. Challenges in this spiroannulation include the chemoselectivity among [2 + 2 + 1], [2 + 2 + 2], and [3 + 2] annulations and the *E*/*Z*-selectivity associated with the generated exocyclic double bond. In the presence of $Pd(OAc)_2$ and a phosphine ligand, a variety of highly functionalized spirocyclopentadienes with an exocyclic carbon−carbon double bond are provided in good to excellent yields with high chemo-, regio-, and *E*/*Z*-selectivity via a Heck-type pathway.



The development of highly efficient methods for the rapid assembly of complex molecules with a high level of chemo-, regio-, and stereoselectivity from easily available precursors is a long-standing objective in organic synthetic chemistry.[1,2] In particular, the achievement of chemo- and regioselectivity switch by alternation of the reaction pathway to afford distinctly different architectures would be highly attractive.[3] Transition-metal-catalyzed annulation reactions of haloarenes with diarylacetylenes are considered as one of the most straightforward and efficient approaches for the construction of highly functionalized polycyclic hydrocarbons,[4] which widely exist in organic optical and electronic materials. Typically, the in situ generated arylmetallic species would attack the internal alkyne(s) to form an alkenylmetallic intermediate, which then approach the *peri*-sites of the aromatic ring to give a formal [2 + 2 + 2] or [3 + 2] annulated product.[5] In contrast, the attack of the alkenylmetallic species at the *ipso*-position to deliver a spirocyclic skeleton is rather difficult owing to the challenge in breaking the aromaticity (resonance stabilization energy for phenyl ring, ca. 30 kcal/mol).[6] Moreover, the highly congested structures of the target products (at least five carbon cycles around the pentadiene motif) further hamper the [2 + 2 + 1] annulation of haloarenes with diarylacetylene.

Spirocycles are prevalent core structures in natural products, bioactive molecules, organic functional materials, and chiral ligands.[7,8] Among the known synthetic methods, transition-metal-catalyzed dearomatization of aromatic compounds, which is pioneered by Hamada,[9] Buchwald,[10] You,[11] Feringa,[12] and Luan,[13] is regarded as one of the most efficient and reliable approaches to construct three-dimensional spirocycles from planar arenes. Despite significant progresses, the reported methods typically focus on using electronically activated aromatics, such as phenols and naphthols, and heteroarenes, such as indoles, pyrroles, and pyridines, as substrates owing to their favorable keto−enol tautomerism and/or lower resonance stabilization energy (22 kcal/mol for pyrrole and 27 kcal/mol for pyridine).[5,9−14] Furthermore, as compared with the extensively investigated enantioselective dearomatization reactions,[11,12,13c] the transition-metal-catalyzed dearomative spiroannulations involving an *E*/*Z* selectivity is seldom disclosed. Thus, the development of novel dearomative spirocyclizations that enable researchers to overcome the above substrate restriction is still in high demand. Herein, we disclose a palladium-catalyzed intermolecular dearomative annulation of readily available alkyl bromoarenes with internal alkynes for the one-step synthesis of spiro[4,5]-cyclopentadienes with an exocyclic double bond (Scheme 1). The introduction of an alkyl group onto the aromatic ring allows the reaction to undergo a [2 + 2 + 1] annulation, in which a Heck-type pathway is involved, rather than a common [2 + 2 + 2] or [3 + 2] annulation.

Our investigation began with the reaction of 1-bromo-2-methylnaphthalene (**1a**) and diphenylacetylene (**2a**) as the model substrates (Table 1). To our delight, the desired dearomatizative product **3a** was obtained in 70% yield in the presence of $Pd(OAc)_2$ (5 mol %), PPh_3 (12 mol %), and Cs_2CO_3 (1.0 equiv) in 1,4-dioxane (Table 1, entry 1). Other common phosphine ligands, including PCy_3, P(*p*-tol)$_3$, P(*p*-anisyl)$_3$, JohnPhos ((2-biphenyl)di-*tert*-butylphosphine), and Cy-JohnPhos ((2-biphenyl)dicyclohexylphosphine), were also effective for this transformation (Table 1, entries 2−6). P(*p*-anisyl)$_3$ proved to be the most suitable ligand, giving **3a** in 94% yield (Table 1, entry 4). However, the trial with X-Phos led to a rather poor yield (Table 1, entry 7). The reaction could also

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Org. Lett. XXXX, XXX, XXX−XXX

Scheme 1. Transition-Metal-Catalyzed Dearomative Spiroannulation of Aromatics with Internal Alkynes

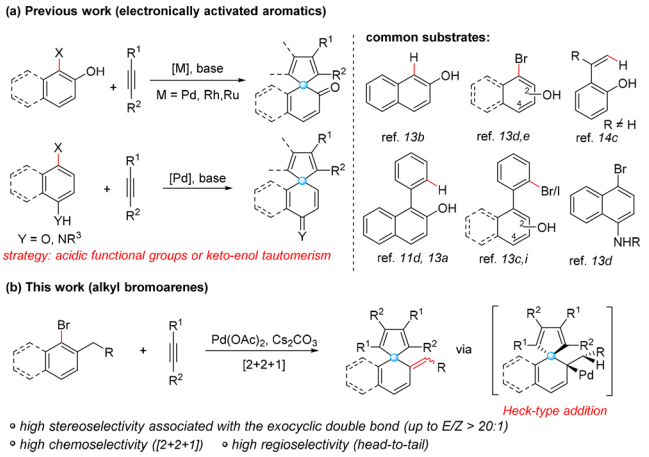
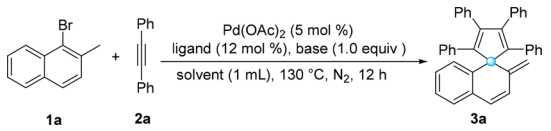


Table 1. Optimization of the Reaction Conditions[a]



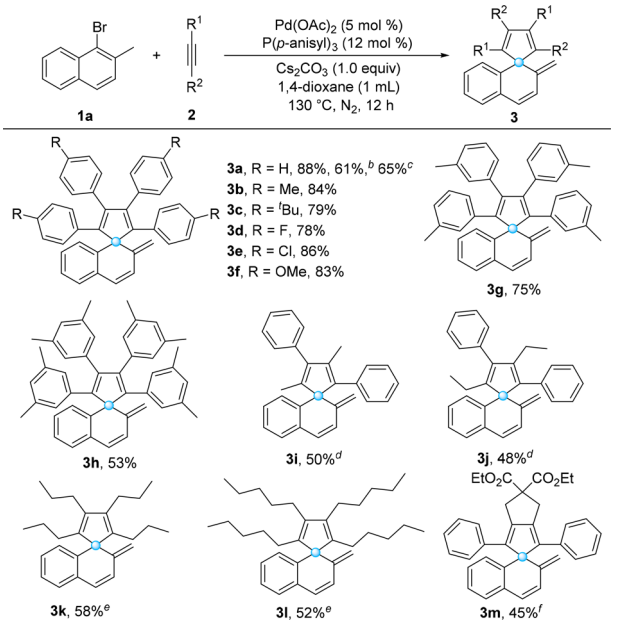
entry	ligand	base	solvent	yield (%)[b]
1	PPh_3	Cs_2CO_3	dioxane	70
2	PCy_3	Cs_2CO_3	dioxane	65
3	P(*p*-tol)$_3$	Cs_2CO_3	dioxane	76
4	P(*p*-anisyl)$_3$	Cs_2CO_3	dioxane	94 (88)[c]
5	JohnPhos	Cs_2CO_3	dioxane	72
6	Cy-JohnPhos	Cs_2CO_3	dioxane	92
7	X-Phos	Cs_2CO_3	dioxane	<10
8	–	Cs_2CO_3	dioxane	42
9	P(*p*-anisyl)$_3$	K_2CO_3	dioxane	62
10	P(*p*-anisyl)$_3$	Na_2CO_3	dioxane	43
11	P(*p*-anisyl)$_3$	K_3PO_4	dioxane	<10
12	P(*p*-anisyl)$_3$	KO^{t}Bu	dioxane	<10
13	P(*p*-anisyl)$_3$	Cs_2CO_3	toluene	80
14	P(*p*-anisyl)$_3$	Cs_2CO_3	DMF	34
15	P(*p*-anisyl)$_3$	Cs_2CO_3	THF	30
16	P(*p*-anisyl)$_3$	Cs_2CO_3	DCE	n.d.
17	P(*p*-anisyl)$_3$	Cs_2CO_3	dioxane	78[d]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (5 mol %), ligand (12 mol %), and base (1.0 equiv) in solvent (1 mL) at 130 °C for 12 h under an N_2 atmosphere. [b]NMR yield using dibromethane as an internal standard. [c]Isolated yield in parentheses. [d]Under an air atmosphere. JohnPhos = (2-biphenyl)di-*tert*-butylphosphine; Cy-JohnPhos = (2-biphenyl)dicyclohexylphosphine.

take place even in the absence of a phosphine ligand (Table 1, entry 8). The attempts with several common bases instead of Cs_2CO_3 all led to inferior results (Table 1, entries 9–12). Subsequently, the solvents were screened. Toluene exhibited a slightly inferior efficiency for this reaction (Table 1, entry 13). Polar solvent DMF and ether solvent THF afford **3a** in only 34% and 30% yields, respectively (Table 1, entries 14 and 15). No desired reaction was detected when DCE was used (Table 1, entry 16). Finally, an attempt under air was conducted, giving the target product **3a** in 78% yield (Table 1, entry 17).

With the optimized condition in hand, we next explored the substrate scope of alkynes (Scheme 2). A diverse set of symmetrical and unsymmetrical internal alkynes could react

Scheme 2. Scope of Internal Alkynes[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (5 mol %), P(*p*-anisyl)$_3$ (12 mol %), and Cs_2CO_3 (1.0 equiv) in 1,4-dioxane (1 mL) at 130 °C for 12 h under an N_2 atmosphere. [b]Using 1-iodo-2-methylnaphthalene instead of **1a**. [c]Three millimole scale at 18 h. [d]Using Cy-JohnPhos instead of P(*p*-anisyl)$_3$. [e]Without ligand. [f]1,6-Diyne (0.3 mmol) as the substrate and toluene as the solvent.

with **1a** to afford the corresponding dearomatizative products in moderate to good yields. Diaryl alkynes containing electron-donating, -neutral, and -withdrawing groups at different positions smoothly underwent the expected transformation under the standard conditions (Scheme 2, **3b–h**). Good functional group tolerance was observed, and even chloro could survive in the present palladium catalytic conditions. In general, the spiroannulation reaction using unsymmetrical alkynes may lead to three regioisomers. Interestingly, the attempts with unsymmetrical phenyl alkyl alkynes exclusively delivered the head-to-tail regioisomers in moderate yields (Scheme 2, **3i** and **3j**). The resulting unsymmetrical cyclopentadiene moieties were identified by the signals for alkyl groups in ^1H and ^{13}C NMR spectra. Surprisingly, when dialkyl alkynes were subjected to the standard conditions, [3 + 2] annulation rather than [2 + 2 + 1] annulation took place predominately, leading to a large amount of methyl-1,2-dialkylacenaphthalenes. However, the desired spiroannulation reactions could proceed smoothly in the absence of a phosphine ligand, giving **3k** and **3l** in moderate yields. In addition, 1,6-diyne (**2m**) also worked under the palladium catalytic conditions, furnishing a tetracyclic architecture in 45% yield. The attempts using terminal alkynes such as phenylacetylene and 1-hexyne gave rise to the alkynylation products.

It would be highly challenging to achieve the *E*/*Z*-selectivity in the [2 + 2 + 1] annulation of alkynes and bromoarenes bearing other alkyl groups rather than the methyl group owing to the geometric isomerism of the generated exocyclic double bond. Indeed, when 1-bromo-2-ethylnaphthalene was subjected to the standard conditions, a mixture of *E*/*Z*-isomers (*E*/*Z* = 3/1) were obtained in an 85% total yield (see SI). To improve the stereoselectivity (*E*/*Z*-selectivity), the phosphine ligands were further optimized. Cy-JohnPhos was found to be

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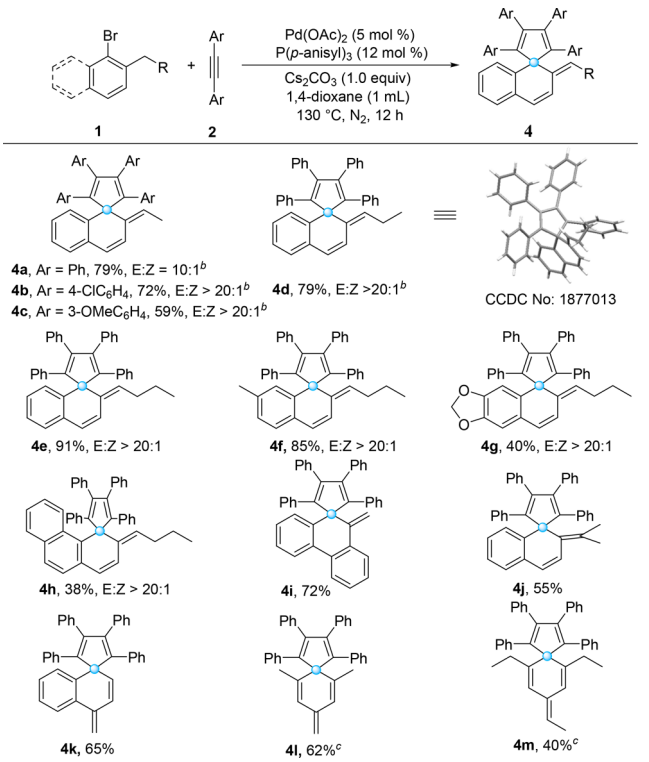
Org. Lett. XXXX, XXX, XXX–XXX

the most effective, providing **4a** in 79% yield with a high *E*/*Z* value (*E*/*Z* = 10/1). Other alkyl bromoarenes also successfully delivered the desired products in moderate to excellent yields with a high *E*/*Z* value (*E*/*Z* > 20/1) (Scheme 3, **4b**–**h**). The

Scheme 3. Scope of Alkyl Bromoarenes[a]



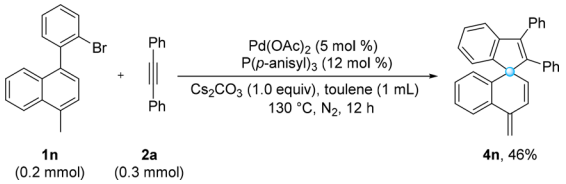
[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (5 mol %), $P(p\text{-anisyl})_3$ (12 mol %), and Cs_2CO_3 (1.0 equiv) in 1,4-dioxane (1 mL) at 130 °C for 12 h under an N_2 atmosphere. [b]Using Cy-JohnPhos instead of $P(p\text{-anisyl})_3$. [c]Using $Pd(dppf)Cl_2$ instead of $Pd(OAc)_2$ and $P(p\text{-anisyl})_3$. $Pd(dppf)Cl_2$ = [1,1′-bis-(diphenylphosphino)ferrocene]dichloropalladium(II).

configuration of **4d** was confirmed unambiguously by X-ray crystallographic analysis. When the chain length of the *ortho*-substituted alkyl groups are longer than that of the propyl group, the employment of Cy-JohnPhos instead of $P(p\text{-anisyl})_3$ was not necessary (Scheme 3, **4e**–**h**). In addition to alkyl bromonaphthalenes, alkyl-substituted bromophenanthrenes and bromobenzenes could also participate in this reaction. However, the reaction with 3-butyl-4-bromophenanthrene gave only the spirocyclic product **4h** in 38% yield, probably owing to large steric hindrance. It is worth noting that the bromoarenes with alkyl substituents at the *para* site were also effective substrates (Scheme 3, **4k**). When bromobenzenes bear aliphatic chains at both *ortho* and *para* positions, the *β*–H elimination selectively took place at the *para* substituent (Scheme 3, **4l** and **4m**).

Additionally, the biaryl-based substrates, which bear the bromo and alkyl groups at different aromatic rings, could also work under the standard conditions, as exemplified by the reaction of 1-(2-bromophenyl)-4-methylnaphthalene (**1n**) with diphenylacetylene (Scheme 4).

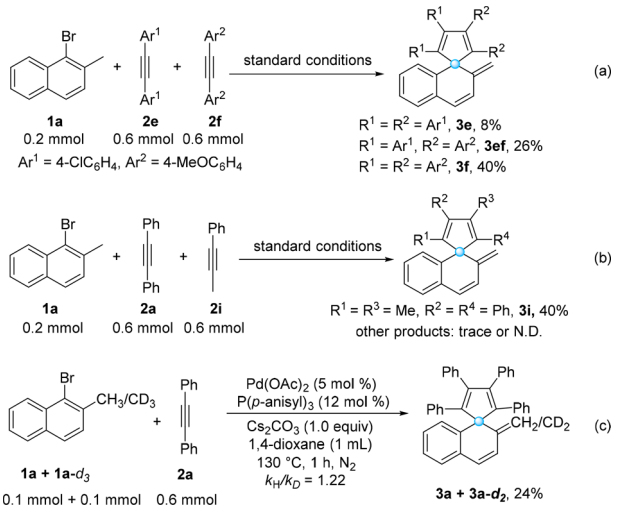
Next, two intermolecular competition experiments were conducted to clarify the reactivity of alkynes. The competition reaction between two diaryl alkynes with different electronic

Scheme 4. Pd-Catalyzed Dearomative [3 + 2] Spiroannulation Reaction



properties indicated that the electron-donating substituents were more favorable to this transformation (Scheme 5a).

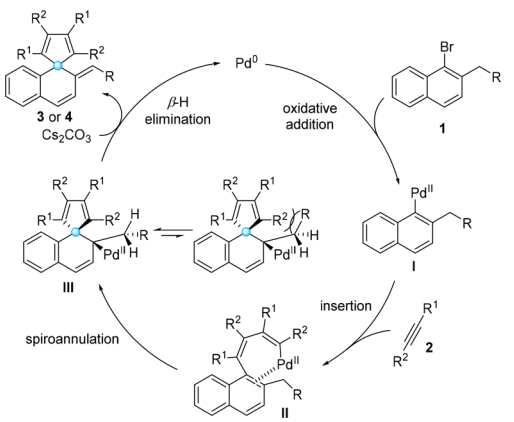
Scheme 5. Competition Experiments and Kinetic Isotope Effect Experiments



Surprisingly, when the reaction with an equimolar mixture of diphenyl acetylene and methyl phenyl acethylene was conducted, only one reigoisomer **3i** was observed, which resulted from the annulation of **1a** with **2i** (Scheme 5b). Finally, a kinetic isotopic effect (KIE) value of 1.22 was observed in the competition reaction between **1a** and **1a**-d_3 with **2a** (Scheme 5c). This result suggested that *β*–H elimination might not be in the rate-determining step.

On the basis of the above results and previous reports,[5a,c,13d,15] a tentative mechanism is proposed in Scheme 6. Initially, migratory insertion of internal alkyne **2** into the in-situ-formed arylpalladium intermediate **I** delivers an alkenyl-

Scheme 6. Plausible Mechanistic Pathway



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palladium(II) species **II**. The following Heck-type cyclization produces spiro[4,5]cyclopentadiene **III**, which then undergoes β−H elimination to give the final product **3** or **4**.

In summary, we have disclosed a palladium-catalyzed dearomative [2 + 2 + 1] annulation reaction of simple alkyl bromoarenes with internal alkynes to afford a variety of highly functionalized spirocyclopentadienes in good to excellent yields with high chemo-, regio-, and *E*/*Z*-selectivity. The alkyl group on the aromatic ring of bromoarenes proved to be critical for the *5-exo-trig* cyclization via a Heck-type pathway. Further extension of the substrate scope and investigation on the applications of the spirocyclopentadienes are ongoing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00099.

Detailed experimental procedures, characterization data, and ^{1}H and ^{13}C NMR spectra of final products (PDF)

Accession Codes

CCDC 1877013 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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