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Palladium-catalyzed regioselective C–H alkynylation of indoles with haloalkynes: access to functionalized 7-alkynylindoles†

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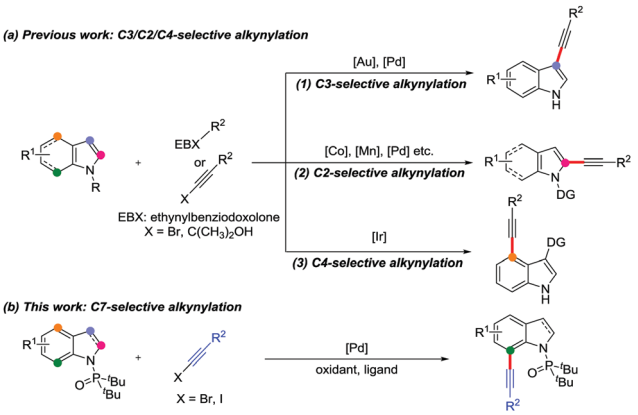
A palladium-catalyzed uniquely regioselective C–H alkynylation of indoles has been described. In this protocol, simple and readily available haloalkynes are employed as efficient alkynylating reagents, affording a series of functionalized 7-alkynylindoles in moderate to good yields. Moreover, further transformations of 7-alkynylated products were performed, which demonstrated the potential application of this method in organic synthesis.

Indole skeletons are core motifs in medicinal chemistry, organic synthesis and materials science due to their individual biological activity.[1] Consequently, the development of synthetic methods for functionalized indole derivatives has become one of the research hotspots.[2,3] Among which, most of the studies focus on the synthesis of high-value alkynylated indoles due to the significant chemical properties of the alkyne moiety.[3] In recent years, regioselective direct C–H alkynylation has been regarded as an efficient and powerful approach to construct alkynylindoles.[4–6] Generally, for indole skeletons, there are multiple C–H bonds including pyrrole rings (C2–C3 positions) and benzenoid rings (C4–C7 positions) that can be alkynylated. However, the direct C–H alkynylation of indoles is mainly at the C3 position[5] owing to the abundant electron effects and C2 position[6] near the nitrogen atom due to the intrinsic reactivity[7] of the indole ring (Scheme 1a, eqn (1) and (2)). Moreover, utilizing a carbonyl directing group (DG) at the C3 position results in the C4-selective alkynylation (Scheme 1a, eqn (3)).[8] Despite considerable progress made with indole alkynylation, the selective C7 alkynylation of indoles is rarely reported owing to the following issues: (i) the C–H bond at this electron-deficient position is difficult to activate due to the inherently poor reactivity; (ii) the high selectivity is interfered by the reactivity of C2 and C3 postions.[9] Recently, Miura *et al.* developed an iridium-catalyzed and sulfur-directed C4/C7–H alkynylation between indoles and ethynylbenziodoxole.[10] In view of the importance of alkynes, novel and convenient methods for the selective installation of alkynyl groups at the C7 position of indoles is still desirable and challenging.



Scheme 1 Regioselective C–H alkynylations of indoles.

Over the past few years, haloalkynes as valuable building blocks, featuring synthetic convenience and high practicability, have exhibited versatile reactivities in organic chemistry.[11] In particular, in cross-coupling reactions, haloalkynes can be used as simple and effective alkynylating reagents to obtain the desired alkynyl products.[12] In recent years, we have investigated a series of cross-coupling reactions involving haloalkynes, including palladium-catalyzed bromoalkynylation of norbornenes,[13] directed alkynylation of biaryl compounds[14] and C2-selective alkynylation of indoles.[15] Based on our continuous interest in haloalkyne chemistry, herein, we disclose a novel palladium-catalyzed C7-selective alkynylation of indoles with di-*tert*-butylphosphinoyl as an effective directing group[16] and simple haloalkynes as alkynylating reagents (Scheme 1b). It is noteworthy that this protocol shows specific regioselectivity to form 7-alkynylated indoles. In addition,

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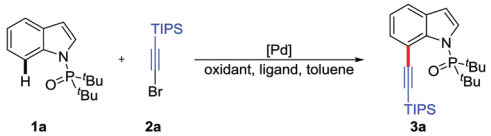
the availability of starting materials and the derivatization of alkynylated products show the practicability of this method.

Initially, the directed C7-alkynylation of indoles was tested using di-*tert*-butyl(1*H*-indol-1-yl)phosphine oxide (**1a**) and (bromoethynyl)triisopropylsilane (**2a**) as the coupling models (Table 1). Delightfully, in the presence of $Pd(OAc)_2$ (10 mol%) as the catalyst, Ag_2CO_3 (2 equiv.) and $Cu(OTf)_2$ (1 equiv.) as additives, the desired product **3a** was obtained in 43% yield at 120 °C (Table 1, entry 1). However, employing AgF instead of Ag_2CO_3 reduced the yield of **3a** to 15% and changing $Cu(OTf)_2$ to CuO inhibited the formation of **3a** (Table 1, entries 2 and 3). Next, the exploration of different catalysts showed that Pd(0) catalysts suppressed the formation of C3-alkynylated product and $Pd_2(dba)_3$ could maintain the yield of **3a** at 43% (Table 1, entries 4 and 5). To promote this reaction, a series of N-ligands were studied and **L5** was proved to be the most suitable ligand for the alkynylation, which might be caused by the optimum balance between the electronic and steric properties (Table 1, entries 6–10). The transformation was further improved by the screening of other reaction parameters, such as the ratio of additives, substrate amounts and dosage of toluene, giving the desired product **3a** in 81% isolated yield (Table 1, entry 11). Besides, control experiments showed that the co-existence of Ag_2CO_3 and $Cu(OTf)_2$ was critical for this alkynylation (Table 1, entries 12 and 13) and no reaction occurred without palladium catalyst (Table 1, entry 14) (see the ESI† for details).

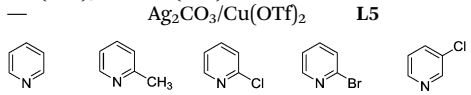
With the optimized reaction conditions in hand, a systemic investigation of the substrate scope was implemented (Table 2).

Table 1 Optimization of the reaction conditions[a]



1a 2a 3a

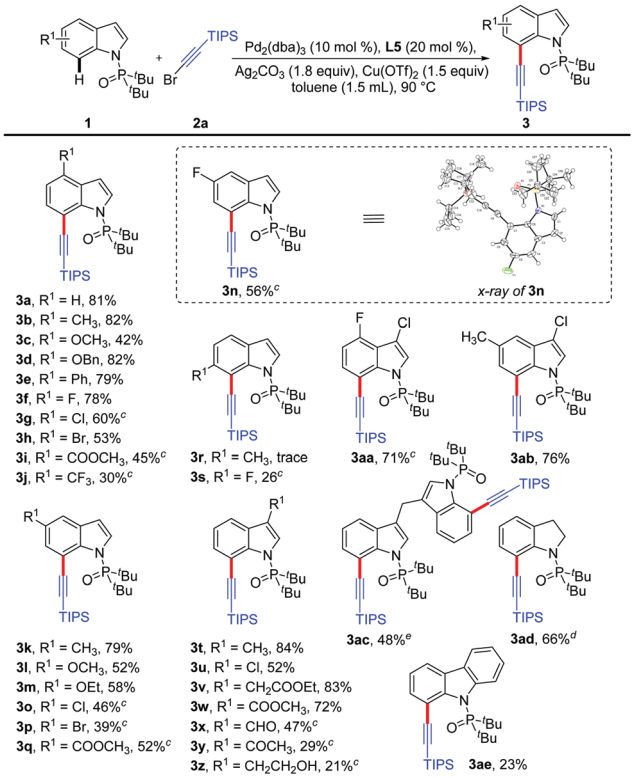
Entry	Catalyst	Additives	Ligand	Yield[b] (%)
1	$Pd(OAc)_2$	$Ag_2CO_3/Cu(OTf)_2$	—	43
2	$Pd(OAc)_2$	$AgF/Cu(OTf)_2$	—	15
3	$Pd(OAc)_2$	Ag_2CO_3/CuO	—	n.d.
4	$Pd_2(dba)_3$	$Ag_2CO_3/Cu(OTf)_2$	—	43
5	$Pd(PPh_3)_4$	$Ag_2CO_3/Cu(OTf)_2$	—	34
6	$Pd_2(dba)_3$	$Ag_2CO_3/Cu(OTf)_2$	**L1**	38
7	$Pd_2(dba)_3$	$Ag_2CO_3/Cu(OTf)_2$	**L2**	Trace
8	$Pd_2(dba)_3$	$Ag_2CO_3/Cu(OTf)_2$	**L3**	50
9	$Pd_2(dba)_3$	$Ag_2CO_3/Cu(OTf)_2$	**L4**	49
10	$Pd_2(dba)_3$	$Ag_2CO_3/Cu(OTf)_2$	**L5**	51
11[c,d,e]	**$Pd_2(dba)_3$**	**$Ag_2CO_3/Cu(OTf)_2$**	**L5**	**83 (81[f])**
12[c,d]	$Pd_2(dba)_3$	Ag_2CO_3	**L5**	n.d.
13[c,e]	$Pd_2(dba)_3$	$Cu(OTf)_2$	**L5**	n.d.
14[c]	—	$Ag_2CO_3/Cu(OTf)_2$	**L5**	n.d.



L1 L2 L3 L4 L5

[a] Conditions: unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (2 equiv.), catalyst (10 mol%), ligand (20 mol%), Ag salt (2 equiv.), and Cu salt (1 equiv.) in toluene (1.0 mL), under air at 90 °C for 12 h. [b] Monitored by NMR using CH_2Br_2 as the internal standard. [c] **2a** (1.8 equiv.), toluene (1.5 mL). [d] Ag_2CO_3 (1.8 equiv.). [e] $Cu(OTf)_2$ (1.5 equiv.). [f] Isolated yield.

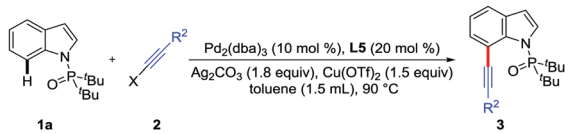
Table 2 Substrate scope of indoles[a,b]



[a] Conditions: unless otherwise noted, all reactions were performed with **1** (0.1 mmol), **2a** (0.18 mmol), $Pd_2(dba)_3$ (10 mol%), Ag_2CO_3 (1.8 equiv.), $Cu(OTf)_2$ (1.5 equiv.), and **L5** (20 mol%) in toluene (1.5 mL) under air at 90 °C for 12 h. [b] Isolated yield. [c] **L4** (20 mol%). [d] 2 h. [e] **2a** (0.36 mmol), $Pd_2(dba)_3$ (15 mol%), **L5** (30 mol%), Ag_2CO_3 (3.6 equiv.), $Cu(OTf)_2$ (3.0 equiv.), and toluene (2.0 mL).

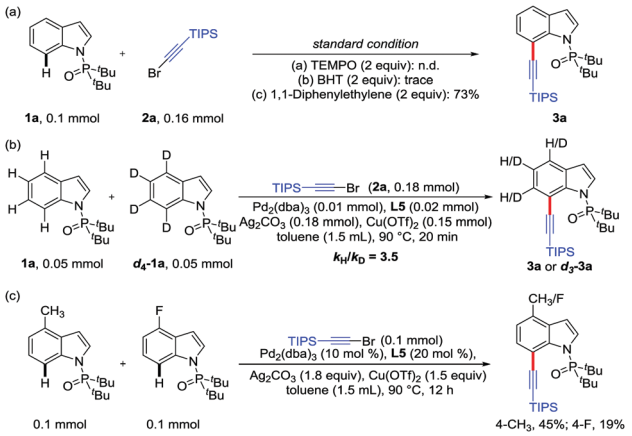
Gratifyingly, various substitution patterns of the indole backbone were applicable in this reaction and the desired C7 alkynylated products could be obtained in moderate to excellent yields. It was found that the indole derivatives **1** with either electron-donating (–CH_3, –OCH_3, –OBn and –OCH_2CH_3) or electron-withdrawing (–Ph, –F, –Cl, –Br, –$COOCH_3$ and –CF_3) substituents at the C4 and C5 positions were successfully transformed to the corresponding C7-alkynylated products **3b–3q** in 30–82% yields. The molecular structure could be verified by X-ray crystallography of **3n** (CCDC 1915232†). However, the substitution at the C6 position did not show good tolerance (**3r–3s**). Moreover, the substrates **1** bearing various substituents (–CH_3, –Cl, –CH_2COOEt, –$COOCH_3$, and –CHO) at the C3 position were smoothly alkynylated to provide the products **3t–3x**. The desired products **3y** and **3z** were obtained in low yields without C2-alkynylated products detected. Additionally, the 3-Cl-4-F and 3-Cl-5-CH_3 disubstituted indole substrates also showed favorable reactivity and the corresponding products **3aa** and **3ab** could be obtained in 71% and 76% yields, respectively. Then, the alkynylation between the 3,3′-diindolylmethane derivative and two molecules of bromoalkyne afforded **3ac** in 48% yield. When the indoline substrate was subjected to this alkynylation protocol, **3ad** was formed quickly in 66% yield within 2 h. It should be noted that a sterically demanding carbazole substrate

Table 3 Examination of haloalkynes[a]



Entry	Haloalkyne 2	Product 3	Yield of 3[b] (%)
1	X = I, R^2 = TIPS	**3a**	44
2	X = Cl, R^2 = TIPS	**3a**	n.d.
3	X = Br, R^2 = TBDMS	**3af**	67
4	X = Br, R^2 = TES	**3ag**	Trace
5	X = Br, R^2 = TMS	**3ah**	n.d.

[a] Conditions: unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2** (0.18 mmol), $Pd_2(dba)_3$ (10 mol %), Ag_2CO_3 (1.8 equiv.), $Cu(OTf)_2$ (1.5 equiv.), and **L5** (20 mol %) in toluene (1.5 mL), under air at 90 °C for 12 h. [b] Isolated yield.

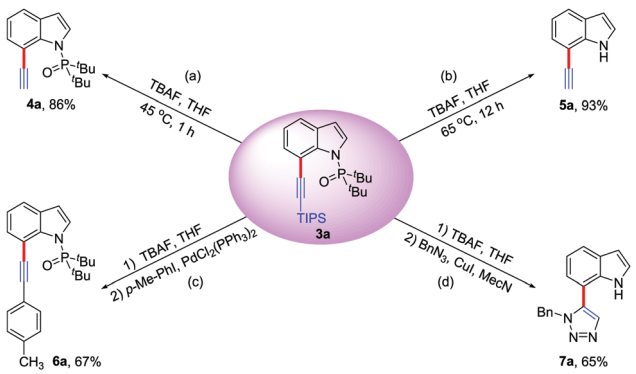


Scheme 3 Mechanistic studies.

could also be transformed to the monoalkynylation product **3ae**, albeit in a low yield.

After evaluating the scope of indole derivatives **1**, we further investigated the effects of various haloalkynes **2** (Table 3). Ethynyltriisopropylsilanes with different halogen atoms were first examined. Pleasingly, the desired product **3a** could be obtained in 44% yield when using (iodoethynyl)triisopropylsilane as the alkynylating reagent (Table 3, entry 1). However, no reaction occurred with (chloroethynyl)triisopropylsilane as the substrate (Table 3, entry 2). Moreover, the effects of substituents at silane were also examined. (Bromoethynyl)(*tert*-butyl)dimethylsilane was compatible with this catalytic system and the corresponding product **3af** could be obtained in 67% yield, while replacing the isopropyl group to triethyl or trimethyl just showed poor reactivity (**3ag–3ah**), which might be caused by the coordination between low sterically hindered bromoalkynes and palladium catalyst *via* π bonding.[17] Unfortunately, ethyl 3-bromopropiolate and (bromoethynyl)benzene were found to be not suitable for the C7 alkynylation.

Furthermore, the potential applications of C7-alkynlated products as useful synthetic blocks are illustrated (Scheme 2). With appropriate reaction temperature and time, both the triisopropylsilyl group and the directing group could be easily removed upon treatment with TBAF to deliver the desilylation



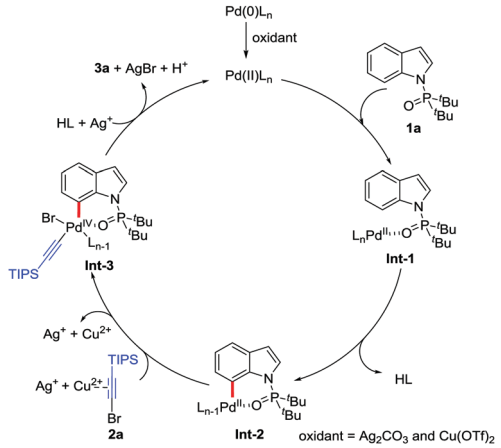
Scheme 2 Derivatizations of alkynylation product **3a** (conditions: see the ESI† for details).

product **4a** or 7-ethynyl-1*H*-indole **5a**. The Sonogashira coupling reaction of **4a** offered the phenylacetylene product **6a** in 67% yield. Additionally, in the presence of CuI, **5a** could react with BnN_3 to give triazole indole **7a** in 65% yield *via* a Click reaction, which might be used for medicinal chemistry and materials science.[18]

Several control experiments were then carried out to shed light on the reaction mechanism (Scheme 3). When this C7 alkynylation was respectively carried out in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) or BHT (2,6-di-*tert*-butyl-*p*-cresol), the yields of alkynylation product **3a** dramatically dropped. However, **3a** could be obtained in 73% yield when 1,1-diphenylethylene was added in this reaction under the optimized conditions (Scheme 3a), indicating that the oxidation system was important and specific for this transformation, and the radical pathway should not be involved in this process. Then, an intermolecular KIE of k_H/k_D = 3.5 suggested that the rate-determining step plausibly was the cleavage of the C7–H bond of substrate **1a** in this alkynylation reaction (Scheme 3b). In addition, the competition experiment indicated that electron-rich indole substrates reacted preferentially (Scheme 3c).

On the basis of the experimental results and related studies,[14,19] a plausible catalytic cycle is proposed for this C7-selective alkynylation (Scheme 4). First, the Pd(II) species is formed by the oxidation of $Pd_2(dba)_3$ in the presence of Ag_2CO_3 and $Cu(OTf)_2$. Then the intermediate **Int-1** is generated by complexation between the Pd(II) species and **1a**. Subsequently, as the rate-determining step, the palladacycle **Int-2** is obtained by the intramolecular selective C–H activation of **Int-1**. After **2a** is activated by Ag(I) and Cu(II), the **Int-2** can further undergo oxidative addition to form the Pd(IV) complex **Int-3**. Finally, the AgBr precipitate will promote the reductive elimination of **Int-3**, which leads to the formation of the alkynylation product, along with the regeneration of the Pd(II) catalyst to complete this catalytic cycle.

In conclusion, we have developed a Pd-catalyzed di-*tert*-butylphosphinoyl directed C7-selective activation/alkynylation between indoles and haloalkynes, affording a series of highly functionalized 7-alkynylindole derivatives in good yields. The remarkable regioselectivity and good substrate compatibility



Scheme 4 Proposed mechanism.

have been highlighted in this reaction. In addition, the easy availability of starting materials and the functionalization of the newly formed alkynylated products show the synthetic practicality of this protocol. Further investigations of this method in pharmacochemistry are currently underway in our laboratory.

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Conflicts of interest

We have a patent (CN Pat., 109867694A, 2019) relevant to this work.

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