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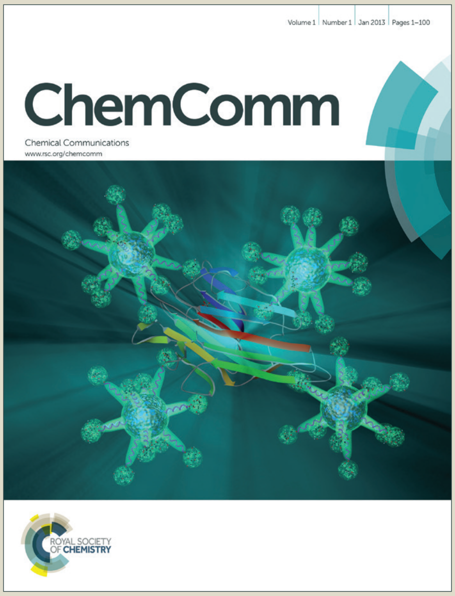

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Metal-Free Carbonyl $C(sp^2)$-H Oxidative Alkynylation of Aldehydes With Hypervalent Iodine Reagents Leading to Ynones

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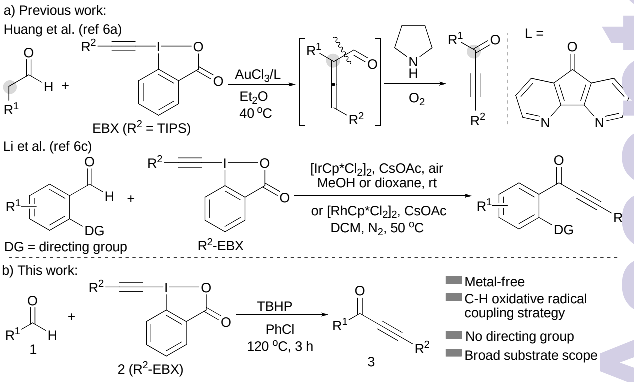
A new metal-free *tert*-butyl hydroperoxide (TBHP)-mediated carbonyl $C(sp^2)$-H oxidative alkynylation of aldehydes with ethynyl benziodoxolones (EBX) for the synthesis of ynones is described. This method is based on a carbonyl $C(sp^2)$-H oxidative radical coupling process according to mechanistic studies, and provides a general route to the assembly of diverse ynones with broad substrate scope and excellent functional-group compatibility.

Alkynes, including ynones, are arguably important construct motifs in bioactive molecules and materials, as well as are versatile intermediates for the assembly of structurally diverse molecules in synthesis.[1,2] Consequently, considerable efforts have been dedicated to the development of efficient methods for such compound synthesis.[2-5] Despite impressive progress in the field, efficiently practical synthesis of ynones still presents a more stringent challenge. The most frequent classic method for ynone synthesis is the oxidation of the corresponding propargyl alcohols.[3] However, many propargyl alcohols are unavailable, and among the oxidant processes the competing side reactions (e.g. site- or over-oxidation) restrict the substrate scopes and the selectivity control. The Sonogashira cross-couplings[2] of terminal alkynes with acyl chlorides[4] or aryl halides/CO[5] represent a general and convenient alternative to achieve this goal, but such successful C-alkynylation approaches face limitations associated with the use of pre-functionalized organic electrophiles (e.g., organic halides) and the requirement of the expensive transition-metal/ligand catalytic system (e.g., palladium/phosphine). Recent successes in the C-alkynylation of aldehydes with alkynes provided an appealing route to these ynone molecules.[6] Huang and co-workers[6a] have reported a new gold/amine synergistic catalysis for the synthesis of 1-(triisopropylsilyl)-3-alkyl-1-yn-3-ones from aliphatic aldehydes and (triisopropylsilyl)ethynyl benziodoxolones (TIPS-EBX) by a sequence of α-vinylidenation[6b] and in situ aerobic cleavage of the C-C bond. Very recently, Li and co-workers[6c] illuatrated an ortho-chelation-assistant strategy to access 1-aryl-2-yn-1-ones by iridum- and rhodium-catalyzed C-H activation and formyl alkynylation of benzaldehydes with enynyl benziodoxolones. However, these approaches also suffer from the requirement of noble transition metals (Au, Ir or Rh) and the narrow substrate scope (aliphatic aldehydes in the Huang method[6a] and ortho-substituted benzaldehydes in the Li method[6b]).

The C-H oxidative coupling reactions have emerged as one of the most powerful methods for the C-C bond formation.[7] In this content, the oxidative couplings of the aldehyde $C(sp^2)$-H bonds offer a particularly effective and highly atom economical tool to incorporate an acyl group into the product through the construction of the C-C bonds.[8] Herein, we report the first example of a TBHP-mediated carbonyl $C(sp^2)$-H oxidative radical alkynylation of aldehydes with enynyl benziodoxolones[9] for ynone synthesis under metal-free conditions that exhibits broad substrate scope and excellent functional group tolerance (Scheme 1b); this method proceeds through a carbonyl $C(sp^2)$-H oxidative radical coupling, and provides a highly efficient practical route to constructing the $C(sp^2)$-C(sp) bonds.



Scheme 1. Reactions of Aldehydes with Ethynyl Benziodoxolones.

Our initial investigation focused on the alkynylation between 1*H*-indole-3-carbaldehyde (**1a**) and TIPS-EBX **2a** (Table 1). The results demonstrated that treatment of aldehyde **1a** with 1.5 equiv TIPS-EBX **2a** and 2 equiv TBHP (5M in decane) in PhCl at 120 °C for 3 h afforded the desired ynone **3aa** in 81% yield (entry 1). The reaction temperatures were found to affect the alkynylation, as a higher or lower reaction temperature had a negative effect on the reaction (entries 1-3). Notably, increasing amount of TBHP to 3 equiv gave the identical results to those of 2 equiv TBHP (entries 1 and 4). However, no expected alkynylation reaction occurred without TBHP oxidant (entry 5). Three other peroxide oxidants, namely, 70% aqueous TBHP, di-tert-butyl peroxide (DTBP) and dicumylperoxide (DCP), showed activity for the alkynylation, but less effective than TBHP in decane (entry 1 versus entries 6-8). DMF as medium proved ineffective for the alkynylation (entry 9), and other solvents, including CH_2ClCH_2Cl, *n*-BuOAc and MeCN, were found to be less effective than PhCl (entry 1 versus entries 10-12).

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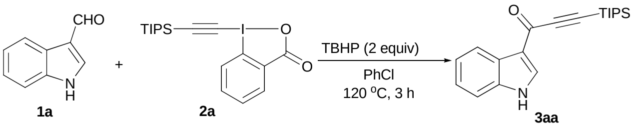
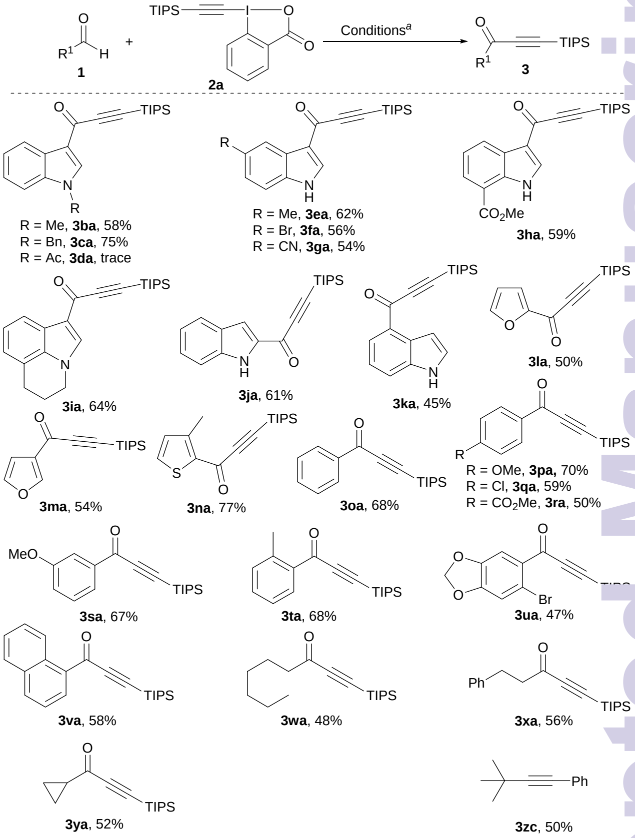
Table 1 Screening of the optimal reaction conditions[a]



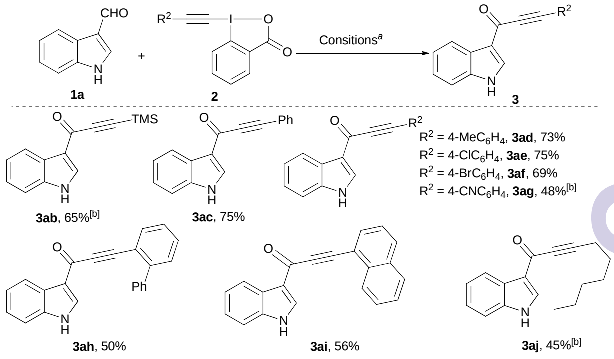
Entry	Variation from the Standard Conditions	[O] (equiv)
1	none	81
2	at 80 °C	56
3[b]	at 140 °C	61
4	TBHP (3 equiv)	78
5	without TBHP	0
6	70% aqueous TBHP	40
7	DTBP instead of TBHP	29
8	DCP instead of TBHP	15
9	DMF instead of PhCl	trace
10	CH_2ClCH_2Cl instead of PhCl	30
11	*n*-BuOAc instead of PhCl for 12 h	18
12	MeCN instead of PhCl for 12 h	68

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), TBHP (5 M in decane; 2 equiv) and PhCl (3 mL) at 120 °C under argon atmosphere for 3 h. [b] Some substrate **2a** was decomposed.

The scope of this metal-free C-H oxidative radical alkynylation protocol with respect to aldehydes **1** (Scheme 2) and ethynyl benziodoxolones **2** (Scheme 3) was probed under the optimal reaction conditions. The optimal conditions were found applicable to a wide range of aldehydes, including aryl (**1b-v**) and alkyl aldehydes (**1w-x**) (Scheme 2). In the presence of TIPS-EBX **2a** and TBHP, 1*H*-indole-3-carbaldehydes **1b** or **1c**, having a methyl group or a benzyl group on the nitrogen atom, gave the expected ynones **3ba** and **3ca** in good yields. However, 1*H*-indole-3-carbaldehyde **1d** with a *N*-Ac group was inert and led to no formation of **3da**. Moderate yields were obtained with 1*H*-indole-3-carbaldehydes **1e-i** possessing varying electronic properties (**3ea-ia**). It was noted that indoles **1j-k** containing a carbaldehyde group at the **2** or **5** position were also viable to furnish ynone **3ja** and **3ka**. Gratifyingly, other types of heteroaromatic ynone **3la-na** were obtained through the C-H oxidative alkynylation of aldehydes bearing furan (**1l−m**) and thiophene (**1n**) rings. The optimal conditions were also compatible with various benzaldehydes with electron-donating or electron-withdrawing substituents on the aromatic ring (**3oa-3va**). Importantly, halogen groups, Cl and Br, were perfectly tolerated, thus providing opportunities for further additional modifications of the product (**3qa** and **3ua**). Efficient reactivity was still observed with aliphatic aldehydes **1w-z** (**3wa-ya and 3zc**). For example, treatment of 3-phenylpropanal (**1x**) with TIPS-EBX **2a** and TBHP afforded ynone **3xa** in 56% yield. We were pleased to find that tertiary aliphatic aldehyde **1z** was also viable to furnish alkyne **3zc** in moderate yield *via* decarbonylation.We next set out to investigate the feasibility of ethynyl benziodoxolones (R^2-EBX) **2** for the alkynylation with 1H-indole-3-carbaldehyde (**1a**) and TBHP (Scheme 3). Gratifyingly, TMS-EBX **2b** was a suitable coupling partner and delivered **3ab** in 65% yield. The optimal conditions were found to be consistent with an array of Ar-EBX **2c-i** with several aryl groups, such as Ph, 4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-CNC$_6$H$_4$, 2-PhC$_6$H$_4$ and naphthalen-1-yl, at the terminal alkyne (**3ac-ai**). High yield of **3ac** was observed in the alkynylation of Ph-EBX **2c** with aldehyde **1a** and TBHP. Ar-EBX **2d-h** having aryl groups of varying electronic and steric properties could be converted to **3ad-ah** with 48-75% yields. Using naphthalen-1-yl-EBX **2i** to couple with aldehyde **1a** and TBHP led to **3ai** in moderate yield. We were pleased to find that aliphatic EBX **2j** was also viable to furnish ynone **3aj** in moderate yield.



Scheme 2. Variation of the Aldehydes (1). [a] Reaction conditions: **1** (0. mmol), **2a** (1.5 equiv), TBHP (5 M in decane; 2 equiv) and PhCl (3 mL) at 120 °C under argon atmosphere for 3 h.



Scheme 3 Variation of the Ethynyl Benziodoxolones (**2**). [a] For reaction conditions, see Table 1 and Scheme 2. [b] In MeCN (3 mL) for 12 h.

Control experiments in Scheme 4 disclosed that th

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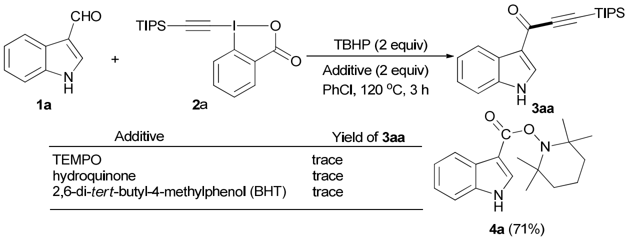
reaction of aldehyde **1a** with TIPS-EBX **2a** and TBHP was completely suppressed when a stoichiometric amount of radical inhibitors, including TEMPO, hydroquinone and BHT, were added. In addition, product **4a** was formed from aldehyde **1a** reacted with TEMPO. These results suggest that the C-H oxidative alkynylation proceeds via a radical process.

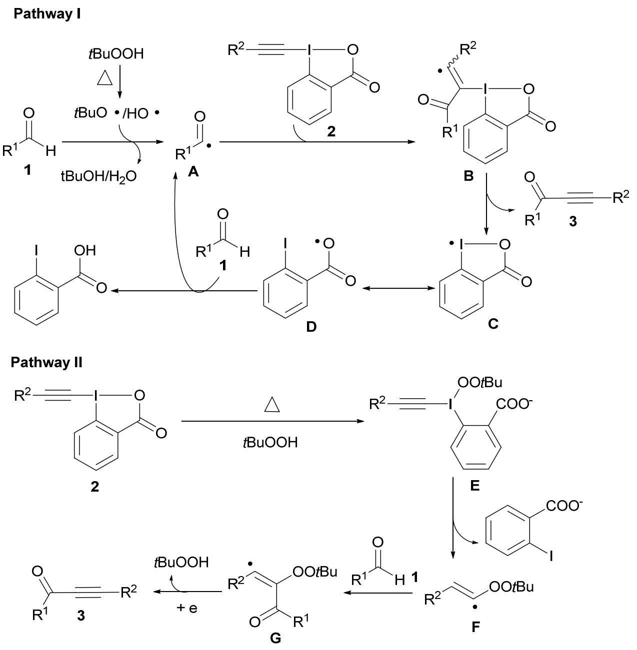


Additive	Yield of 3aa
TEMPO	trace
hydroquinone	trace
2,6-di-*tert*-butyl-4-methylphenol (BHT)	trace

Scheme 4 Control Experiments.

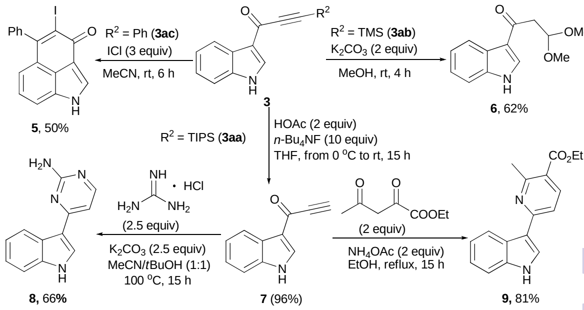
The mechanisms for the C-H oxiative alkynylation reaction was proposed on the basis of the present results and previous reports (Scheme 5).[6-10] Initially, carbonyl radical **A** is formed from aldehyde **1** by reacting with TBHP under heating conditions.[6,7] Addition of the carbonyl radical **A** to a C-C triple bond in EBX **2** affords intermediate **B**,[9s-v] followed by *β*-elimination of intermediate **B** leads to the desired ynone **3** and benziodoxolonyl radical **C**.[10] Finally, benziodoxolonyl radical **C** is transformed into 2-iodobenzoic acid (**10**) via H-abstraction of aldehyde **1 (Pathway I)**.

Pathway II was also proposed. Initially, the ligand exchange on hypervalent iodine center to yield alkynyl(*tert*-butylperoxy)iodoarene **E**, which is followed by the homolytic cleavage of I-O bond affording *tert*-butylperoxy radical **F**.[9w] Addition of aldehyde **1** to the carbon-carbon double bond of radical **F** affording radical intermediate **G**. Finally, *beta*-hydrogen elimination and reductive elimination of intermediate **G** generates the desired alkyne **3**.



Scheme 5 Possible Reaction Mechanisms.

The utilizations of ynones are summarized in Scheme 6. Ynone **3ac** underwent the electrophilic cyclization smoothly, providing benzo[cd]indol-3(1*H*)-one **5** in 50% yield.[11a] TMS containing ynone **3ab** readily converted into acetal **6** in the presence of MeOH and K_2CO_3.[4b] Terminal alkyne **7** was synthesized from ynone **3aa** reacted with TBAF and acetic acid in excellent yield.[6a] Having terminal alkyne **7** in hand, 4-(1*H*-indol-3-yl)pyrimidin-2-amine **8**[5d] and ethyl 6-(1*H*-indol-3-yl)-2-methylnicotinate **9**[11b] were prepared in high yields.



Scheme 6 Utilizations of **3**.

In summary, we have developed a novel carbonyl C(sp^2)-H oxidative alkynylation of aldehydes with ethynyl benziodoxolones using TBHP oxidant under metal-free conditions, which provides a simple and efficient tool to access a variety of highly functionalized ynones. This method features an incorporation of an acyl group into the product via the C-H oxidative radical coupling. Moreover, the unitizations of ynones were performed that show the ynone chemistry with widely potential applications in synthesis.

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Notes and references

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