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Gold-Catalyzed 1,2-Oxyalkynylation of *N*-Allenamides with Ethylnylbenziodoxolones

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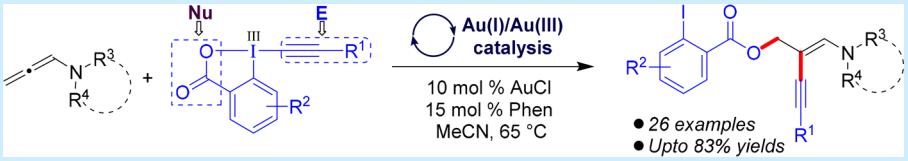
Supporting Information

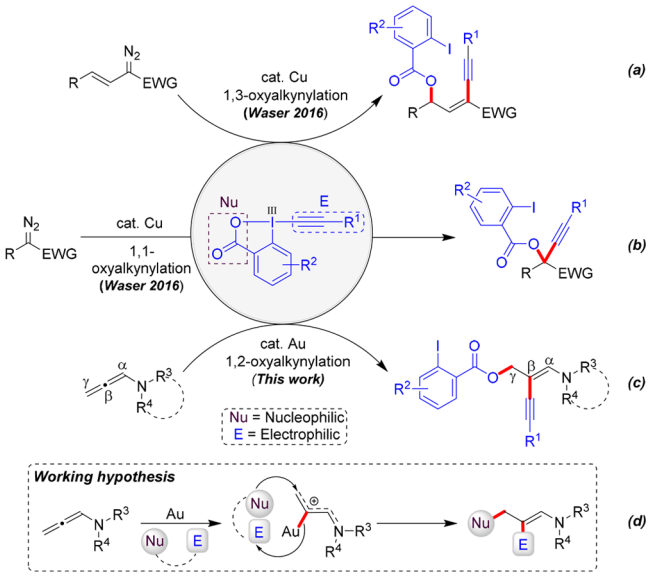


ABSTRACT: A gold-catalyzed 1,2-oxyalkynylation of *N*-allenamides with ethylnylbenziodoxolones (EBXs) has been achieved for the first time. The reaction, which follows a redox-neutral Au(I)/Au(III) catalytic pathway, was enabled in an attempt to exhaust the EBX reagents atom-economically by putting the nucleophilic carboxylate part of EBXs to appropriate use. This constitutes the first example for gold-catalyzed β-alkynylation of *N*-allenamides to construct highly valuable 1,3-enynes. The potential of the sequence is further documented by some follow-up transformations.

Because of the luxury of introducing two distinct functionalities simultaneously, 1,2-difunctionalization across C−C multiple bond continues to fascinate the scientific community.[1] Propelled by transition-metal catalysis, the previous decade have witnessed expeditious growth in this arena.[2] Oxyalkynylation of C−C multiple bonds is one such powerful method and a relatively fresh arrival in the genre.[3] However, because of the unavailability of a sustainable approach, related reports on oxyalkynylation have remained scarce and underdeveloped over the years. Even with groups other than the alkynyl group, such functionalizations (e.g, "oxyarylation") are very rare.[4]

Lately, ethynylbenziodoxolones (EBXs),[5] by merit of their electrophilic alkyne surrogacy, have earned a widespread reputation as excellent reagents for direct C−H alkynylation via π-activation, transition metal-catalyzed chelation assistance, and radical promotion.[6] All of this, coupled with the fact that EBXs are inherent oxidants, has allowed C−H alkynylations through redox-neutral strategies (without external oxidants) especially in gold catalysis.[7] Undoubtedly, the advent of EBXs gave renewed impetus to oxyalkynylation chemistry of C−C multiple bonds by way of direct electrophilic alkynylation strategy, as mentioned previously.[8] Nevertheless, this impressive portfolio of reactivity of EBXs suffers a drawback; 2-iodobenzoic acid is generated as a stoichiometric byproduct, resulting in lower atom economy. More-efficient transformations with EBX reagents have been limited to the report of Yoshikai and co-workers on the palladium-catalyzed condensation of *N*-aryl imines and EBXs to afford multisubstituted furans.[9] In this context, however, using EBXs as potential oxyalkynylating agents by taking advantage of its nucleophilic carboxylate segment have been a missed opportunity so far. Only recently in 2016, the Waser group paved the way for Cu-catalyzed oxyalkynylations of diazo compounds with EBXs.[10] Since metal carbene species display an unmatched reactivity of possessing both nucleophilic and electrophilic centers on a single carbon atom, their endeavor fruitfully led to both the 1,3-oxyalkynylation of vinyl diazo compounds (Scheme 1a) and 1,1-

Scheme 1. Literature Reports, Present Work, and Working Hypothesis of Atom-Economical 1,*n*-Oxyalkynylation



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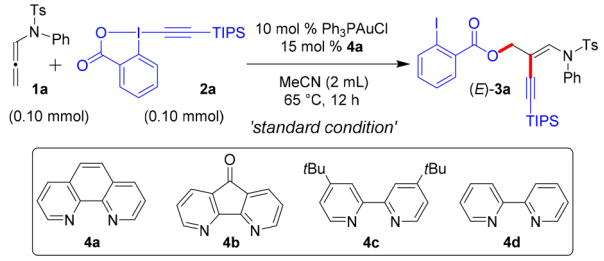
oxyalkynylation of diazo compounds (Scheme 1b). Despite the breakthrough, there has not been any further advancement exploring this channel of atom-economical reactivity for EBXs. In order for this technique to gradually develop to its full capacity as a sustainable oxyalkynylation approach, designing relevant oxyalkynylations is a necessity.

In this regard, we considered the salient features of *N*-allenamide, wherein both nucleophilic and electrophilic characters are embedded.[11] In particular, the electron-rich allenyl units are susceptible to electrophilic activation with π-acids such as Au, promoting the subsequent nucleophile trapping of ensuing allyl cationic gold species.[12] Anticipating the carboxylate of the EBX reagent to serve as a nucleophile here, we further contemplated to trap the resultant cationic allyl gold species with the electophilic alkyne component of EBX (Scheme 1d). Thus, exploiting the classic reactivity of *N*-allenamides under gold catalysis, the possibility of a 1,2-oxyalkynylation[13] with EBXs is envisioned in an atom-economical manner (Scheme 1c). In conjunction with our current research interests focused on the use of gold catalysis for alkynylation with EBXs,[14] we present, in this communication, a successful implementation of this possibility. The obtained 1,3-enynes are versatile building blocks.[15] Moreover, there is hardly any precedence for the straightforward construction of such 1,3-enynes via β-alkynylation[16] of *N*-allenamides. Mechanistically, we discerned a redox-neutral gold catalysis[17] to be in action and is elucidated here.

The reaction between *N*-allenamide (**1a**) and TIPS-EBX (**2a**) unveiled that the conversion to **3a** was possible in a 12-h reaction window at 65 °C in MeCN if 10 mol % of Ph_3PAuCl is used as a catalyst in combination with 15 mol % of **4a** (Table 1, entry 1). Remarkably, the reaction delivered a single isomer (*E*)-**3a**, as confirmed by X-ray diffraction analysis, with a modest 61% yield.

Table 1. Optimization of the Reaction Conditions



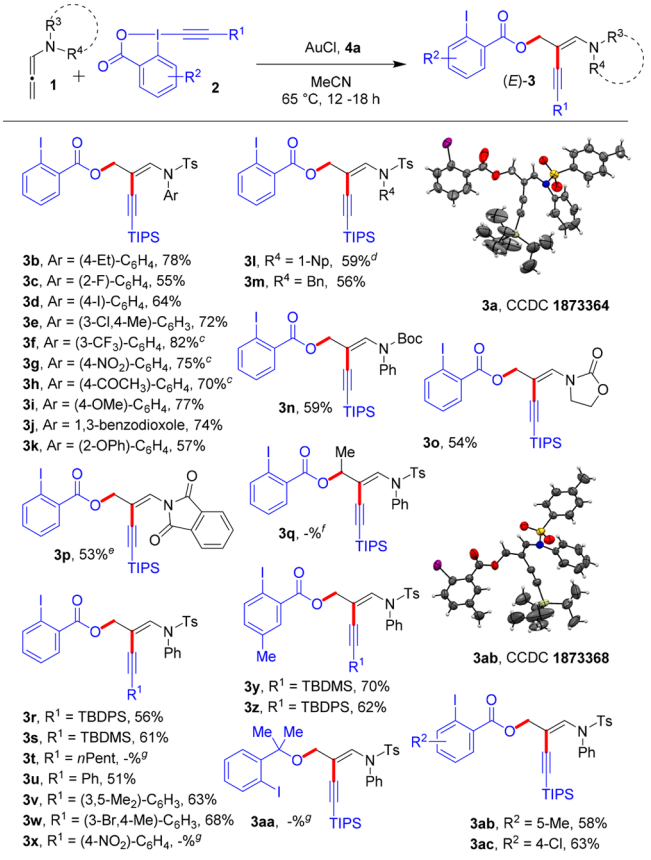
entry	variation of the *"standard condition"*	yield of **3a**[a] (%)
1	none	61
2	without [Au] catalyst	NR[b]
3	without **4a**	29
4	1.3 equiv of **2a**	81
5	**AuCl**	**83**
6	AuCl without **4a**	–[c]
7	AuCl/**4b**	53
8	AuCl/**4c**	64
9	AuCl/**4d**	58
10	$AuCl_3$	–[c]
11	$PicAuCl_2$	–[c]
12	5 mol % of AuCl	70
13	4 Å MS additive	63
14	temperature increased to 80 °C	49
15	DCE instead of MeCN	NR[b]

[a]Isolated yields. [b]NR = no reaction. [c]**1a** decomposed.

In the absence of gold catalysts, no product formation was noticed (Table 1, entry 2); whereas, the absence of ligand **4a** in the reaction mixture brought the yield down to 29% (Table 1, entry 3). With the use of 1.3 equiv of **2a**, we were delighted to see the yield spiking to 81% (Table 1, entry 4). Out of several other gold catalysts screened,[18] AuCl further raised the reaction efficiency, yielding 83% of the oxyalkynylated product (Table 1, entry 5). In addition, the fact that performing the title reaction without **4a** leaves no desirable outcome (Table 1, entry 6) underpinned the choice of ancillary π-acceptor ligands as the key success factor. Opting for alterative π-acceptor ligands such as **4b**, **4c**, or **4d** did little to improve the oxyalkynylation reaction (Table 1, entries 7–9). Not surprisingly, Au(III) catalysts did not promote the reaction (Table 1, entries 10 and 11). On the other hand, tuning parameters such as catalyst loading, additives, temperature, or solvents compromised the yield of the product (Table 1, entries 12–15).

With conditions optimized for most productive conversions (Table 1, entry 5), we set out to explore the reaction horizon, keeping the EBX constant (Scheme 2, **3b**–**3q**). First, several *N*-tosyl, *N*-aryl allenamides **1b**–**1k** were evaluated in combination with TIPS-EBX (**2a**) as a reaction partner. Diverse substitutions on the aromatic ring, irrespective of their electronic nature, were tolerated, as demonstrated by the reactions affording products **3b**–**3k** in good to excellent yields (55%–82%). Strikingly, with

Scheme 2. Scope of 1,2-Oxyalkynylation Reaction[a,b]



[a]Reaction conditions: 0.10 mmol **1**, 0.13 mmol **2**, 10 mol % AuCl, 15 mol % **4a**, MeCN (2 mL), 65 °C, 12–18 h. [b]Isolated yields. [c]Combined yields of (*E*) and (*Z*) isomers. See the Electronic Supporting Information (ESI). [d]2.0 equiv of **2a** was used. [e]Reaction time was 48 h. [f]**1q** remained unreacted. [g]**1a** remained unreacted.

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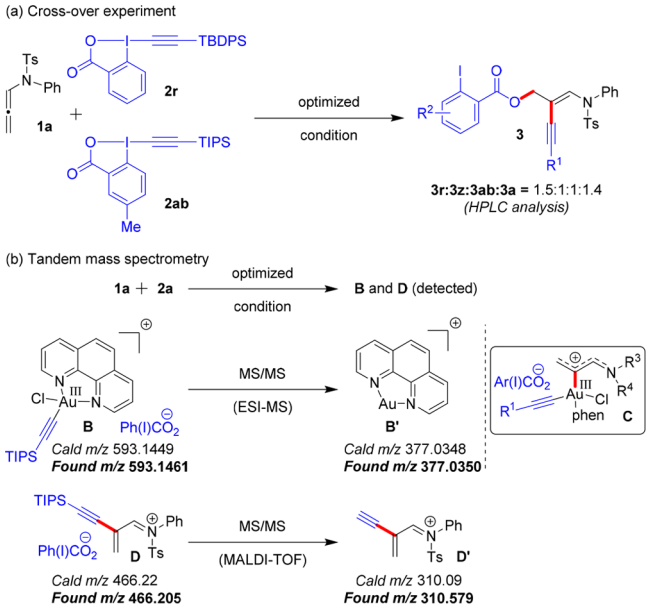
N-allenamides bearing electron-deficient aromatic rings (**1f**–**1h**), the corresponding oxyalkynylated products (**3f**–**3h**) were observed in appreciable *E*:*Z* ratios. However, the yield of the reaction suffered when the aromatic rings in *N*-allenamides such as **1k** or **1l** were sterically encumbered, producing **3k** and **3l** in 57% and 59% yields, respectively. Similarly, the desired product **3m** was obtained in 56% yield, probably because of stability issue of the corresponding *N*-allenamide **1m** under the reaction conditions. After that, we decided to modify the *N*-protecting group in the allenamide system. Under optimal conditions; however, only *N*-Boc protected allenamide **1n** was able to furnish the desired oxyalkynylated product **3n** in a decent 59% yield, reflecting the increased stability provided by *N*-tosyl groups to *N*-allenamides. Furthermore, the 1,3-enynes **3o** and **3p** adjunct with oxazolidin-2-one and isoindoline-1,3-dione motifs could be obtained in 54% and 53% yields, respectively. Unfortunately, γ-substituted allenamide **1q** did not respond to the optimal condition at all and was recovered to the tune of 80% from the reaction mixture.

Next, our efforts to investigate the scope for EBXs (**2**) translated into obtaining a variety of desired oxyalkynylated products with acceptable yields (Scheme 2, **3r**–**3ac**). Initially, when EBXs with varied silyl counterparts (**2r** and **2s**, R^1 = silyl, R^2 = H) at the alkyne terminus were tried, the model *N*-allenamide **1a** comfortably obtained **3r** (56%) and **3s** (61%). Although the oxyalkynylation halted with alkyl-EBXs such as **2t**, a range of aryl-EBXs could be smoothly deployed for the oxyalkynylation of **1a**, resulting in **3u**–**3w** with moderate 51%–68% yields. However, the scope for aryl-EBXs could not be extended to **2x**, bearing electron-deficient aryl substitution at the alkyne terminus because it failed to deliver **3x**. We then moved on to experiment with EBXs possessing simultaneous variations of R^1 and R^2 groups such as **2y**–**2z**. To our gratification, the enynes **3y** and **3z** were synthesized in 70% and 62% yields, respectively. Alkynyl dimethyl benziodoxole **2aa**, which represents an interesting example of a weaker C–I bond, because of a higher *trans* effect,[19] could not afford the desired oxyalkynylated product **3aa**, implying that the carbonyl group is an essential component of EBXs for an efficient oxyalkynylation. Furthermore, when the influence of substituents on the benziodoxolone aromatic ring was investigated, the reaction yields were only minimally influenced, providing **3ab** and **3ac** in 58% and 63% yields, respectively.

The control experiments depicted in Scheme 3 were set up to gain further insights into the mechanism. Significant formation of the crossover products in Scheme 3a is consistent with a pathway in which the carboxylate and alkyne components are added into the *N*-allenamide in stepwise fashion. Taking into consideration the stark contrast between the outcomes of entries 5 and 6 of Table 1, we advocate Au(I)/Au(III) catalysis[7b,20,21] to be operating in the oxyalkynylation reaction, given the fact that the phenanthryl ligand framework (phen, **4a**) is supposed to facilitate oxidative addition.[22] Because of difficulties in the isolation of the reaction intermediates, we sought to investigate the putative Au(III) intermediate(s) through mass spectrometry monitoring of the reaction (Scheme 3b). ESI-HRMS analysis displayed a cation being emerged at *m*/*z* 593.1461, which is quite agreeable with the calculated *m*/*z* 593.1449 for cationic intermediate **B**. Tandem mass spectrometry demonstrated that this ion fragments to a new ion with *m*/*z* 377.0350, which corresponds to the calculated *m*/*z* for the cation **B′** (*m*/*z* 377.0348). Again, the MALDI-TOF analysis of the reaction mixture captured the cation **D** at *m*/*z* 466.205.[23] The MS/MS

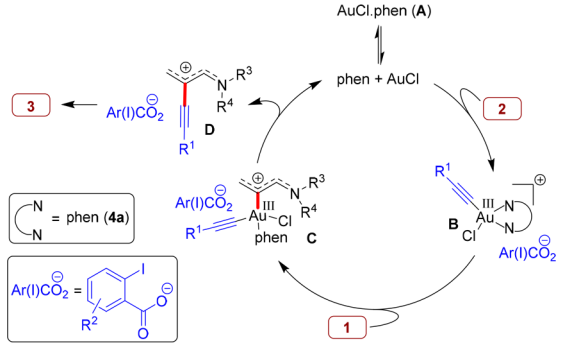
Scheme 3. Control Experiments



pattern for the peak also corroborates with the structure of **D**. In a nutshell, the mass spectrometry analysis suggests the involvement of intermediate **C** as a precursor of intermediate **D**.

On the basis of these evidences, we propose[24] that AuCl[25] undergoes oxidative addition[6c,7a,b] to EBX (**2**) to give the key tetra-coordinated Au(III) species **B**, which is stabilized by **4a** and ion-paired with aryl carboxylate ligand (Scheme 4). Here,

Scheme 4. Proposed Mechanistic Rationale



we surmise that the labile nature of bidentate ligand **4a** is allowing the cationic Au(III) center of **B** to accommodate *N*-allenamide (**1**) in its coordination sphere, leading to **C**. Thereafter, the intermediate **C** upon reductive elimination[26] confers the species **D** and regenerates **A**. The species **D** further undergoes conjugate attack by the laid-over carboxylate ligand to afford the oxyalkynylated product (**3**). The detection of species **D** attests to the fact that reductive elimination precedes the conjugate nucleophilic attack of carboxylate anion to ultimately provide the desired product.

Finally, examination of the synthetic utility of the oxyalkynylation reaction is undertaken (Scheme 5). The dialkyne **5a′** (refer to the Electronic Supporting Information (ESI)), which is the Sonogashira coupling product of **3a**, underwent a transition-metal-catalyzed annulative functional group migration to produce **5a** in 70% yield.[27] Gold-catalyzed C(sp)–C(sp) cross-coupling with TIPS-EBX of terminal alkyne **5b′** (refer to

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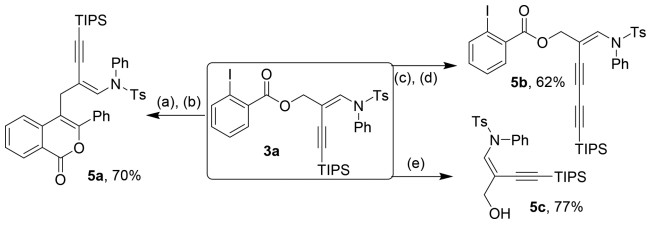
Scheme 5. Product Modifications



[a]Reaction conditions: phenyl acetylene, 2 mol % $Pd(PPh_3)_2Cl_2$, 5 mol % CuI, Et_3N, DCE, 60 °C, 4 h. [b]Reaction conditions: 10 mol % $PtCl_2$, toluene, 70 °C, 4 h. [c]Reaction conditions: TBAF (1 M/THF), THF, rt, 2 h. [d]Reaction conditions: 5 mol % Ph_3PAuCl, 15 mol % phen, TIPS-EBX, MeCN:1,4-dioxane (3:1), 60 °C, 12 h. [e]Reaction conditions: K_2CO_3, EtOH, 75 °C, 12 h.

the ESI) obtained by desilylation of **3a**, derived 1,3-diyne **5b** in 62% yield.[7b] Ester **3a** could be readily hydrolyzed, affording the *β*-alkynylated allylic alcohol **5c** in 77% yield.[10b]

In conclusion, we have discussed the first gold-catalyzed 1,2-oxyalkynylation of *N*-allenamides with proper atom-economical usage of ethylnylbenziodoxolones (EBXs) offering direct access to 1,3-enynes under mild conditions. Such straightforward assembly of 1,3-enynes via *β*-alkynylations of *N*-allenamides have been rarely explored. As evidenced by tandem mass spectrometry analysis, redox-neutral gold catalysis was found to be instrumental in the reaction. Indeed, the usefulness of the method is amplified with further viable manipulations of the resulting scaffold, considering its unique reactive features. More importantly, by offering two concomitant functionalizations from a single EBX reagent, the current methodology creates new opportunities for streamlined reaction design.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03651.

All experimental procedures, analytical data, and copies of ^1H and ^{13}C NMR spectra of all newly synthesized products (PDF)

Accession Codes

CCDC 1873364 and 1873368 contain 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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