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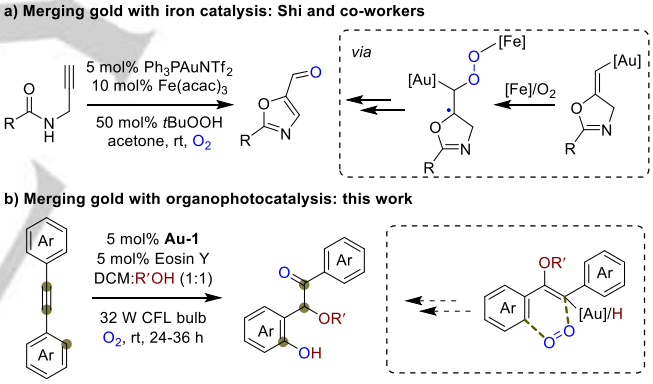
ortho-Oxygenative 1,2-Difunctionalization of Diarylalkynes under Merged Gold/Organophotoredox Relay Catalysis

Shashank P. Sancheti,[a] Manjur O. Akram,[b],[c] Rupam Roy,[a] Vaibhav Bedi,[a] Shubhankar Kundu,[a] and Nitin T. Patil*[a]

Abstract: Reported herein, is an *ortho*-oxygenative 1,2-difunctionalization of diarylalkynes under merged gold/organophotoredox catalysis to access highly functionalized 2-(2-hydroxyaryl)-2-alkoxy-1-arylethan-1-ones. Detailed mechanistic studies suggested a relay process, initiating with gold-catalyzed hydroalkoxylation of alkynes to generate enol-ether followed by a key formal [4+2]-cycloaddition reaction. The successful application of the present methodology was also shown for the synthesis of benzofurans.

Owing to the inherent carbophilic nature, gold complexes have emerged significantly as the best activators of C–C multiple bonds over the past few decades.[1] In the majority of cases, gold catalyst selectively activates alkynes, allenes and alkenes towards an intra- or inter-molecular nucleophilic addition forming an organo-gold species, which typically undergoes fast protodeauration to afford hydrofunctionalized products.[2] Expanding the horizons of gold catalysis beyond the traditional carbophilic activation chemistry, it has been coupled with various other modes of activation. In this regard, binary catalysis[3] has emerged as a pivotal tool allowing the merger of gold with other catalytic systems including secondary amines,[4] Brönsted acids,[5] and other metals.[6] In particular, reports on merging gold with photoredox catalysis, have increased drastically in the past decade.[7] However, merged gold/photoredox catalysis remains confined to the use of Au/Ru binary catalytic system.[7] Additionally, as far as the utility of an organophotoredox catalyst with gold complexes is concerned, there exists only report by Glorius and co-workers wherein a three component oxyarylation reaction of olefin was reported.[8] To further expand the repertoire of gold/organophotoredox catalysis, research in this direction is highly necessary.

The selective oxidation of organic molecules is a formidable challenge in synthetic organic chemistry. Molecular oxygen, also referred as triplet oxygen ($^3O_2$), is the most abundant and least expensive oxidant available, and thus used extensively in organic transformations.[9] The redox stability of gold-complexes towards oxygen makes it unique and allows the development of new modes of reactivities.[10] Several reports have emphasized on the use of molecular oxygen in gold catalysis to effect oxygenation of multiple bonds, including oxidative cleavage.[11] As far as binary catalysis is concerned, Jiao and Shi employed a Au/Fe catalyst system for the synthesis of heterocyclic aldehydes using molecular oxygen as an oxygenating agent (Scheme 1a).[12] Mechanistically, an intriguing pathway involving a Fe-assisted oxygen radical addition to in situ generated vinyl-gold intermediates was found to be operating. In addition to molecular oxygen, oxygenation reactions utilizing photochemically generated singlet oxygen ($^1O_2$) has also evolved as an alternative method.[13] Banking on these reports along with our ongoing interest in the field of merged gold/photoredox catalysis;[14] we questioned the possibility of a [4+2] cycloaddition reaction of photocatalytically generated $^1O_2$ with the vinyl-gold species or enol-ethers generated *in situ via* hydroalkoxylation of diarylalkynes with alcohols (Scheme 1b).[15] A detailed investigation of the above-mentioned hypothesis resulted into novel reaction involving *ortho*-oxygenative 1,2-difunctionalization of diarylalkynes under merged gold/organophotoredox catalysis to access functionalized 2-(2-hydroxyaryl)-2-alkoxy-1-arylethan-1-ones. The detailed development and implementation of this strategy is disclosed herein.



Scheme 1: Merging gold with other catalysts for oxygenation reactions using molecular oxygen: known and present work.

To test our hypothesis, diphenylacetylene (**1a**) was used as a model substrate (Table 1). In light of the well-established reactivity of Eosin Y as a organophotocatalyst,[16] especially in combination with molecular oxygen; we decided to use Eosin Y in combination with gold catalysts. To our delight, when **1a** was treated with 5 mol% $Ph_3PAuNTf_2$, 5 mol% Eosin Y as photocatalyst in O_2 purged DCM/MeOH (1:1) under the irradiation of a 32 W CFL bulb for 24 h; product **3a** was obtained in 21% yields (entry 1). The structure of the compound **3a** was confirmed by X-ray crystallography. Encouraged by the results, we then began the optimization process to achieve the most productive outcome. Considering the initial gold-catalyzed hydroalkoxylation as the limiting factor for the subsequent cycloaddition, we began screening of various gold catalysts. Accordingly, when gold catalysts such as $Ph_3PAuOTf$, $Ph_3PAuSbF_6$, and $Ph_3PAu(NCMe)SbF_6$ were examined (entries 2-4), the latter was found to be better giving **3a** in 33% yield. Excited by this lead, we turned our attention to investigate

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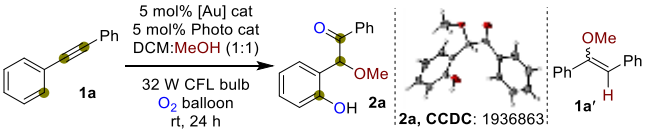
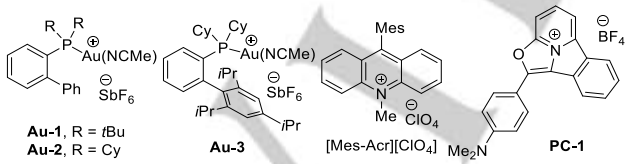
various ligands associated with the gold(I) (entries 5-7). To our delight an improved yield was observed when **Au-1** was used as catalyst; giving the product **3a** in 62% yield. Further variation of photocatalysts like rose bengal, methylene blue, etc. had detrimental effect and resulted in either no reaction or afforded desired product in traces (entries 8-12). Interestingly, when one of our previously reported pyridinium-oxazole dyad[17] was used as a photocatalyst, we obtained the desired product, albeit in 30% yield (entry 13). Unfortunately, any change from the formerly employed solvent system exhibited detrimental effect,[18] which led us to the final optimized conditions as: 1 equiv. of **1a** to be stirred with 5 mol% of **Au-1** and Eosin Y in O_2 purged DCM/MeOH (1:1) solution under 32 W CFL bulb for 24 h. Next the necessity of both **Au-1** and Eosin Y was confirmed as the reaction did not proceed in absence of either of the catalyst (entries 14 and 15). Further, performing the reaction in a one-pot sequential fashion did not improve the outcome.[18]

Table 1: Optimization of the reaction conditions.[a]



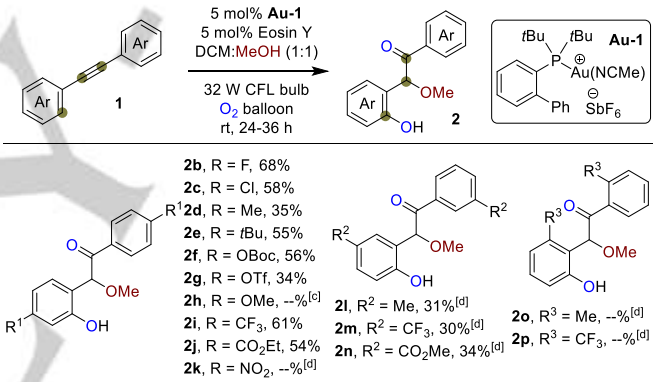
Entry	[Au] cat	Photo cat	Yield %[b]
1	$Ph_3PAuNTf_2$	Eosin Y	21
2	$Ph_3PAuOTf$[c]	Eosin Y	NR[d]
3	$Ph_3PAuSbF_6$[c]	Eosin Y	29
4	$Ph_3PAu(NCMe)SbF_6$	Eosin Y	33
5	**Au-1**	**Eosin Y**	**62**
6	**Au-2**	Eosin Y	50
7	**Au-3**	Eosin Y	41
8	**Au-1**	Rose bengal	traces[d]
9	**Au-1**	Methylene blue	traces[d]
10	**Au-1**	[Mes-Acr][ClO_4]	NR[d]
11	**Au-1**	$[Ru(bpy)_3](PF_6)_3$	traces[d]
12	**Au-1**	$[Ru(phen)_3]Cl_2$	traces[d]
13	**Au-1**	**PC-1**	30
14	**Au-1**	--	NR[e]
15	--	Eosin Y	NR[d]



[a] Reaction conditions: 0.10 mmol **1a**, 5 mol% [Au] cat, 5 mol% photocat, 0.05 M DCM/MeOH (1:1), O_2 balloon, 32 W CFL bulb, rt, 24 h. [b] Isolated yields. [c] Generated in situ by mixing 5 mol% Ph_3PAuCl and 5 mol% AgX (X = OTf, SbF_6). [d] Unreacted **1a** was recovered in quantitative yields. [e] Compound **1a** was fully consumed and **1a'** was isolated in 52% yield.

With the optimum reaction conditions (Table 1, entry 5), several symmetrical diarylalkynes were evaluated to find the scope of the reaction (Table 2). To our delight, the reaction was found to work satisfactorily when we varied the substituents at the *para*-position of the diarylalkynes. For instance, symmetrical diarylalkynes having −F and −Cl at the *para*-position gave the corresponding products **2b** and **2c** in 68 and 58% yields, respectively. Further, diarylalkynes containing electron-donating –Me, −*t*Bu, –OBoc and –OTf also gave the corresponding products **2d-g** in 34-56% yields. Unfortunately, stronger electron-donating diarylalkynes bearing –OMe gave a complex mixture of products (*cf*. **2h**). On the other hand, symmetrical diarylalkynes bearing electron-withdrawing $–CF_3$ and $–CO_2Et$ at *para*-position gave the corresponing products **2i** and **2j** in 61 and 54% yields, respectively. Unfortunately, highly electron-withdrawing $–NO_2$ group was found to be unreactive (**2k**); as the hydroalkoxylation step did not work under the standard reaction conditions. Next, when we varied the substituents at the *meta*-position of the symmetrical diarylalkynes, compound **2l**, **2m** and **2n** were obtained in 31, 30 and 34% yields, respectively. The drop in the yield was possibly due to the high dependancy of the hydroalkoxylation reaction on steric encumbrance around the ethylene-moiety. For the same reason, we did not observe any product formation for the symmetrical diarylalkynes bearing the substituents at the *ortho*-position (**2o** and **2p**).

Table 2: Scope of symmetrical diarylalkynes.[a],[b]

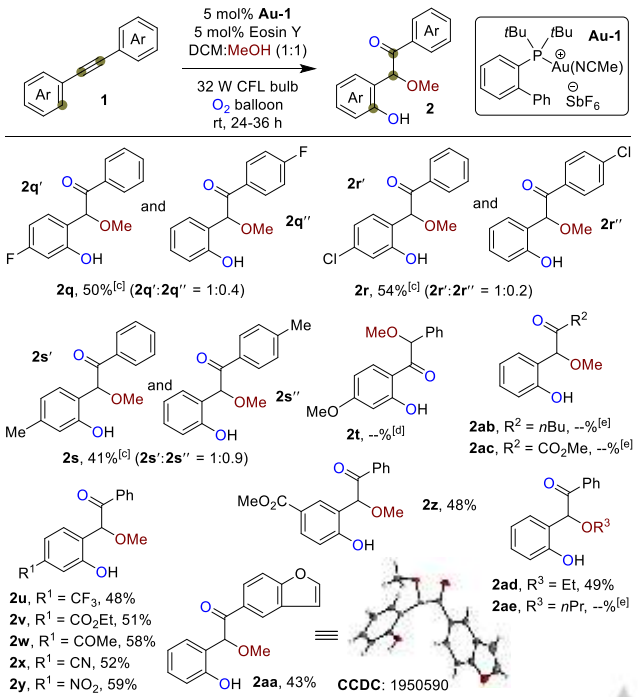


[a] Reaction conditions: 0.20 mmol **1a**, 5 mol% **Au-1**, 5 mol% Eosin Y, 0.05 M DCM/MeOH (1:1), O_2 balloon, 32 W CFL bulb, rt, 24 h. [b] Isolated yields. [c] Complex reaction mixture. [d] Starting material was recovered in quantitative yields.

Moving on to unsymmetrical diarylalkynes (Table 3), we tested several substituents on one of the aryl ring keeping the other aryl ring as phenyl. Diarylalkynes having –F and –Cl at *para*-position afforded desired products **2q** and **2r** in 50 and 54% yields, respectively, as a mixture of two inseparable isomers. Further, we tested the effect of various electron donating groups at *para*-position. In this regard, diarylalkynes bearing –Me group also worked to afford **2s** in 41% yields. Unfortunately, highly electron donating –OMe only provided a complex mixture of products (*cf*. **2t**) under the standard reaction conditions. Moving on to electron withdrawing substituents, $–CF_3$, $–CO_2Et$, –COMe, –CN and $–NO_2$ were well-tolerated and produced the desired products **2u-y** in 48-59% yields. Further, diarylalkynes bearing $–CO_2Me$ at *meta*-position afforded **2z** in 48% yield. Next, the applicability of the methodology was extended to heteroaryl consisting unsymmetrical diarylalkynes. To our delight, compound **2aa** was obtained in 43% yield. Be noted that, alkyl or $–CO_2Me$ substituted arylacetylenes were not tolerated under the present reaction conditions (*cf.* **2ab** and **2ac**). Next, when ethanol was used as the solvent, **2ad** was

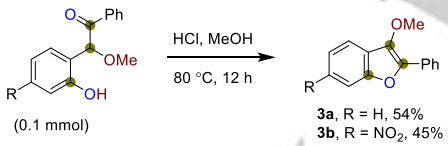
obtained in 49% yield. Unfortunately, *n*-propanol did not afford any product **2ae**, supposedly due to the slow hydroalkoxylation.

Table 3: Scope with unsymmetrical diarylalkynes.[a],[b]



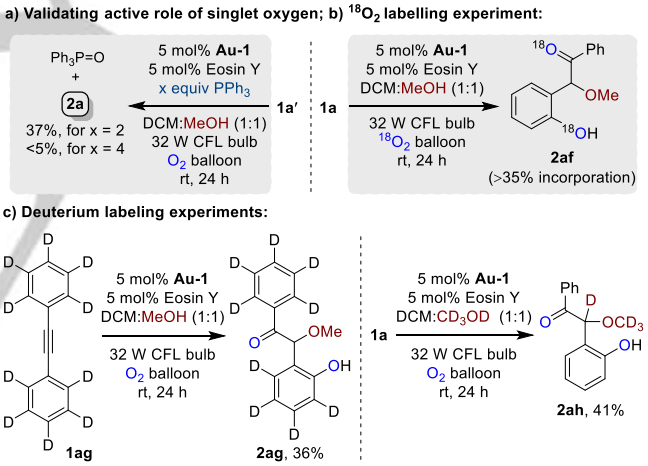
[a] Reaction conditions: 0.20 mmol **1a**, 5 mol% **Au-1**, 5 mol% Eosin Y, 0.05 M DCM/MeOH (1:1), O_2 balloon, 32 W CFL bulb, rt, 24 h. [b] Isolated yields. [c] Combined yield. [d] Complex reaction mixture. [e] Starting material was recovered in quantitative yields.

Demonstrating the synthetic potential of the reaction, we successfully transformed our product into benzofurans **3a** and **3b** in 54 and 45% yields, respectively (Scheme 2).



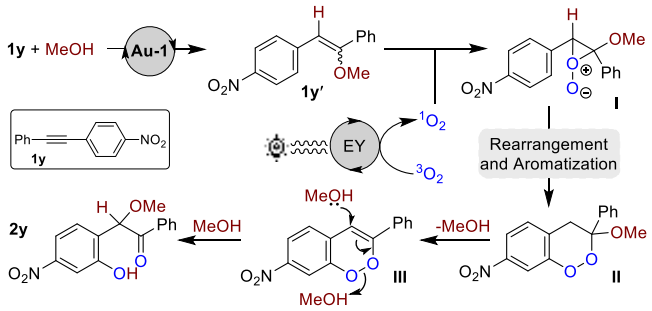
Scheme 2: Utility of the products.

The control experiments outlined in Scheme 3 were set up to gain further insights into the mechanism. As control experiments supported that the reaction follows a relay path via the intermediacy of enol-ether **1a'**; and gold(I)-catalyst has essentially no role in the photocatalytic process,[18] we sought to understand the energy transfer process between intermediate **1a'**, Eosin Y and O_2. The absorption maxima of **1a'** and Eosin Y are 294 and 521 nm, respectively, suggesting that the radiated visible light was exclusively absorbed by the Eosin Y.[18] To explore the elementary step following the excitation of the Eosin Y, a photoluminescence quenching experiment was performed. However, we did not observe any fluorescence quenching of Eosin Y with **1a'**, indicating a possible energy transfer from photoexcited Eosin Y to oxygen.[18]] To confirm this, we performed another fluorescence quenching experiment using traditionally used singlet oxygen quenching probes 9,10-diphenylanthracene (9,10-DPA) and 1,3-diphenylisobenzofuran (DPBF). A drastic photochemical degradation of both 9,10-DPA and DPBF was observed when Eosin Y was added in presence of dissolved molecular oxygen in 1:1 DCM/MeOH solution.[18] These experiments suggest that 9,10-DPA and DPBF react with in situ generated singlet oxygen ($^1O_2$), as a result of energy transfer process between Eosin Y and $^3O_2$.[18] To further vindicate the generation of singlet oxygen by chemical methods; **1a** was reacted with oxygen in the presence of Eosin Y and triphenylphosphine (Scheme 3a).[19] As anticipated, a drastic drop in the yield was observed with increase in equivalence of triphenylphosphine along with the formation of triphenylphosphine oxide as the major product. The results clearly validate the generation of singlet oxygen and its crucial role in driving the reaction forward. Next, when an ^{18}O-labelling experiment was performed under the standard conditions using $^{18}O_2$, **2af** was observed with >35% ^{18}O-incorporation; validating molecular oxygen to be the source of oxygen in the product (Scheme 4b). To gain insights into the subsequent ring-opening pathway being followed after a formal [4 + 2] cycloaddition, deuterium labeling experiments were performed (Scheme 3c). First, **1ag** was subjected to standard reaction conditions, product **2ag** was obtained in 36% yield without any deuterium migration at α-position of carbonyl. Next, when **1a** was subjected to standard reaction conditions in presence of deuterated methanol, product **2ah** was obtained in 41% yield. The presence of –D (–H) and $–OCD_3$ ($–OCH_3$) on the same carbon suggested a possible methanol elimination-addition pathway operating.



Scheme 3: Mechanistic studies.

Based on the fluorescence quenching studies and control experiments, a plausible mechanism is outlined in Scheme 4. At first, a gold-catalyzed hydroalkoxylation reaction[20] of **1y** generates an enol-ether **1y'**. In the meantime, photoexcited Eosin Y undergoes an energy transfer event with triplet oxygen to sponsor the necessary singlet oxygen. The enol-ether reacts with singlet oxygen to furnish perepoxide intermediate **I**[21] which eventually undergoes intramolecular rearrangement[16] followed by rearomatization (cf. **II**) to form intermediate **III.** The whole process from the conversion of **1y'** to **II** could be considered as a formal [4+2] cycloaddition reaction. Further, addition of methanol to **III** would result in the formation of product after O-O bond cleavage.



Scheme 4: A plausible mechanism.

In conclusion, an *ortho*-oxygenative 1,2-difunctionalization of diarylalkynes under merged gold/organophotoredox catalysis has been reported. The method provided substituted 2-(2-hydroxyaryl)-2-alkoxy-1-arylethan-1-ones in moderate yields. Mechanistic investigations revealed a relay process initiating with the in situ formation of enol-ether followed by formal [4+2]-cycloaddition reaction with singlet oxygen. The mechanism of the reaction was investigated through meticulously designed experiments and fluorescence quenching studies. The successful application of the present methodology was also shown for the synthesis of benzofurans.

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Keywords: gold catalysis • organocatalyst • photoredox • binary catalyst system • synthetic methodology

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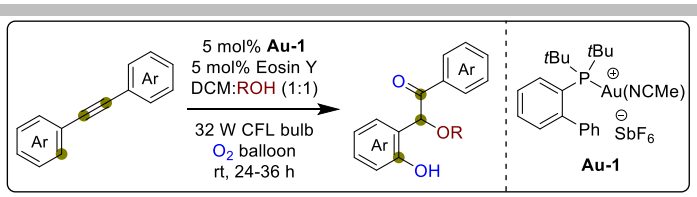

An *ortho*-oxygenative 1,2-difunctionalization of diarylalkynes under merged gold/organophotoredox catalysis to access highly functionalized 2-(2-hydroxyaryl)-2-alkoxy-1-arylethan-1-ones has been reported. The key features of the mechanism includes the formal [4+2]-cycloaddition reaction between in situ generated enol-ether with singlet oxygen. The mechanism of the reaction was investigated through meticulously designed experiments and fluorescene quenching studies.

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ortho-Oxygenative 1,2-Difunctionalization of Diarylalkynes under Merged Gold/Organophotoredox Relay Catalysis