

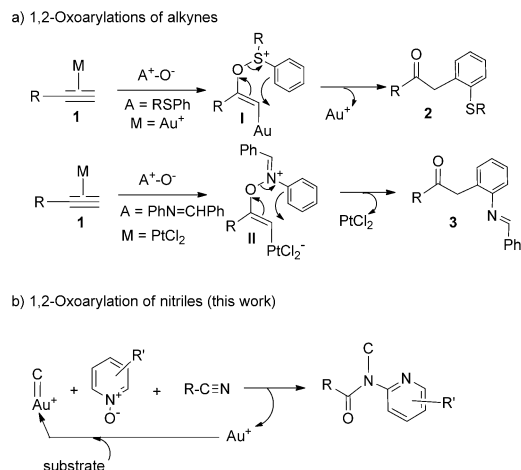
Gold-Catalyzed 1,2-Oxoarylations of Nitriles with Pyridine-Derived Oxides**

Somnath Narayan Karad and Rai-Shung Liu*

Abstract: We report the first success in the gold-catalyzed oxoarylations of nitriles with pyridine-derived *N*-oxides using gold carbenes as initiators. These oxoarylations were also achieved satisfactorily in intermolecular three-component oxidations, including diverse alkenyldiazo esters, nitriles, and pyridine-based oxides.

Catalytic oxidations of alkynes with organic oxides emerge as thriving topics in current gold and platinum catalysis.^[1–5] These oxidations lead to 1,2-oxofunctionalization products by two paths. With pyridine-derived *N*-oxides, the oxidations typically generate α -oxo carbenes which can be functionalized with a tethered or external nucleophile.^[2,3] For sulfoxides and some nitrones, the initial intermediates (**I** and **II**, respectively) undergo 3,3-sigmatropic shifts to afford the 1,2-oxoarylation products **2** and **3**, respectively (Scheme 1a).^[4,5] Although nitriles and alkynes are two common triple-bond motifs, catalytic oxidations of nitriles with organic or inorganic oxides still remain a formidable task.^[6,7] Commonly used nitrile oxides are not prepared from direct oxidations of nitriles.^[8] In the presence of an oxidant, nitriles typically undergo either a hydration reaction^[6] or a C–H oxidation with an elimination of the nitrile.^[7] The development of a new strategy to achieve a nitrile oxidation is significant and highly desired in catalysis. Herein, we report the catalytic 1,2-oxoarylations^[9] of nitriles through a three-component coupling reaction (Scheme 1b). Our approach involves the initial generation of gold carbenes to trap the nitrile and generate a gold-containing nitrilium species, which is subsequently oxidized by pyridine-based *N*-oxides to afford *N*-(pyridin-2-yl)amide derivatives in an atom-economic fashion. Related to this work are the stoichiometric reactions between stable nitrilium salts and quinoline *N*-oxides, which produced distinctly different products resulting from a 1,5-shift.^[10] Although similar *N*-(pyridin-2-yl)amides were yielded from the reactions between imidoyl chlorides and pyridine *N*-oxides, these noncatalytic reactions also produced the undesired 3-chloropyridine in an appreciable amount.^[11]

The utility of this synthesis allows a rapid entry to the *N*-(pyridin-2-yl)amide framework, which is found as the core structure in several bioactive molecules, including piroxiocam,



Scheme 1. 1,2-Oxoarylation reactions.

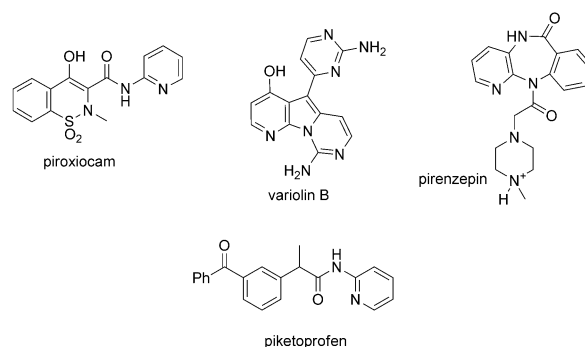


Figure 1. Representative bioactive molecules.

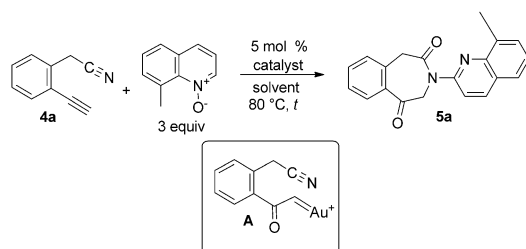
cam,^[12] variolin B,^[13] pirenzepin,^[14] and piketoprofen (Figure 1).^[15]

Table 1 shows the realization of an unprecedented 1,2-oxoarylation of 2-cyanomethyl-1-ethynylbenzene (**4a**) with 8-methyl quinoline *N*-oxide (3 equiv) using various gold catalysts. Our initial trial with AuCl₃ (5 mol %) in hot 1,2-dichloroethane (80 °C, 12 h) resulted in an incomplete conversion, from which the double oxidation product **5a** was isolated in 22 % yield, together with unreacted **4a** (55 %; entry 1). We switched to cationic gold catalysts such as PPh₃AuCl/AgSbF₆, P(*t*Bu)₂(*o*-biphenyl)AuCl/AgSbF₆, and IPrAuCl/AgSbF₆ (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene), which provided **5a** in 48, 75, and 82 % yield, respectively (entries 2–4). Different counter anions to IPrAuCl/AgX (X = OTf and NTf₂) maintained satisfactory product yields (entries 5 and 6). AgSbF₆ and HNTf₂ were catalytically inactive (entries 7 and 8). We tested the reactions

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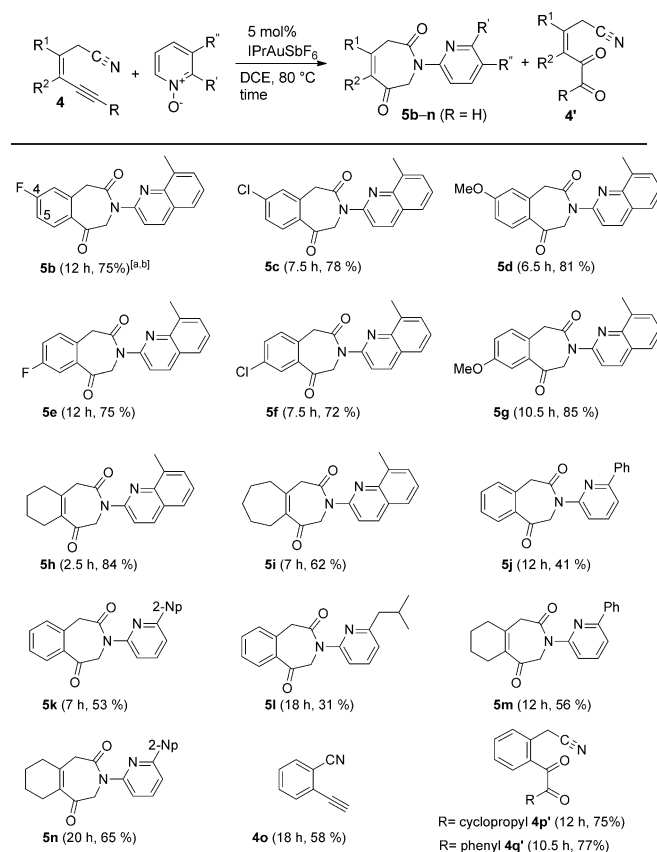
Table 1: Catalyst screening for 1,2-oxoarylations of nitriles.


Entry	Catalyst	Solvent ^[b]	t [h]	Yield [%] ^[c]	
				4a	5a
1	AuCl ₃	DCE	12	55	22
2	PPh ₃ AuCl/AgSbF ₆	DCE	12	15	48
3	LAuCl/AgSbF ₆ ^[a]	DCE	10	–	75
4	IPrAuCl/AgSbF ₆	DCE	7.5	–	82
5	IPrAuCl/AgOTf	DCE	9	–	80
6	IPrAuCl/AgNTf ₂	DCE	9.5	–	79
7	AgSbF ₆	DCE	9.5	85	–
8	HNTf ₂	DCE	24	80	–
9	IPrAuCl/AgSbF ₆	C ₆ H ₅ Cl	10.5	–	72
10	IPrAuCl/AgSbF ₆	1,4-dioxane	12.5	–	54

[a] L = P(*t*Bu)₂(*o*-biphenyl). [b] [4a] = 0.20 m. [c] Product yields are reported for product isolated after purification using a silica gel column. DCE = 1,2-dichloroethane, IPr = 1,3-bis(diisopropyl phenyl)imidazol-2-ylidene, Tf = trifluoromethanesulfonyl.

in other solvents, such as chlorobenzene and 1,4-dioxane, thus affording **5a** in 72 and 54 % yields, respectively (entries 9 and 10). The molecular structure of **5a** was verified by an X-ray diffraction study,^[16] thus confirming the working mechanism (Scheme 1 b), which involves the initial formation of the α -oxo gold carbene **A**.

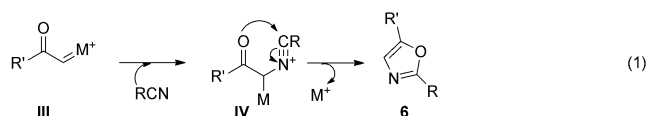
Table 2 shows the substrate scope of such 1,2-oxoarylations using various 5-cyano-3-en-1-ynes and pyridine-derived *N*-oxides. The results show the reactions for the benzenoid substrates **4b–d** bearing various 4-phenyl substituents (R¹ = F, Cl and OMe), thus yielding the desired oxoarylation products **5b–d** in 75–81 % with 8-methylquinoline *N*-oxide as an oxidant. The same reactions were extended to the analogous benzenoid substrates **4e–g**, and yielded the desired **5e–g** in 72–85 % yields. For the nonbenzenoid substrates **4h** and **4i**, the corresponding products **5h** and **5i** were obtained in 84 and 62 % yield, respectively. Such oxoarylations were compatible with 2-substituted pyridine *N*-oxides (R' = phenyl, 2-naphthyl, isobutyl; R'' = H), thus affording the oxoarylation products **5j–l** in 31–53 % yields. The presence of the 2-pyridinyl substituents impede its coordination with gold(I) to maintain the acidity of the gold species. Gold-catalyzed reactions between **4h** and 2-substituted pyridine *N*-oxides (R' = phenyl and 2-naphthyl) proceeded smoothly to afford the desired products **5m** and **5n** in 56 and 65 % yield, respectively. We also prepared 2-cyano-1-ethynylbenzene (**4o**) which was recovered in 58 % yield after a longer reaction time (18 h). For the internal alkyne substrates **4p** (R = cyclopropyl) and **4q** (R = phenyl) we obtained the 1,2-diketone species **4p'** (75 %) and **4q'** (77 %), respectively. The reactions were inapplicable to 2-chloro- or bromo-substituted pyridine *N*-oxides, which worked well in the intermolecular three-

Table 2: Gold-catalyzed oxoarylations of 5-cyano-3-en-1-ynes.


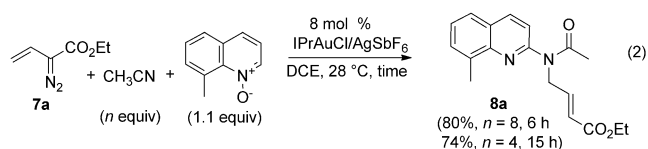
[a] *N*-Oxide (3.0 equiv). [4] = 0.20 m. [b] Product yields are reported for product isolated after purification using a silica gel column.

component system (see Table 3) and they failed to oxidize 5-cyano-3-en-1-yne (**4a**).

Although a catalytic 1,2-oxoarylation of nitriles was proven to be feasible, it is imperative to achieve an intermolecular reaction among gold carbenes, nitriles, and organic oxides to access acyclic molecules. The α -oxo metal carbenes **III** were reported to undergo facile [3+2] cycloadditions to form the oxazole products **6** [Eq. (1)].^[17] We thus



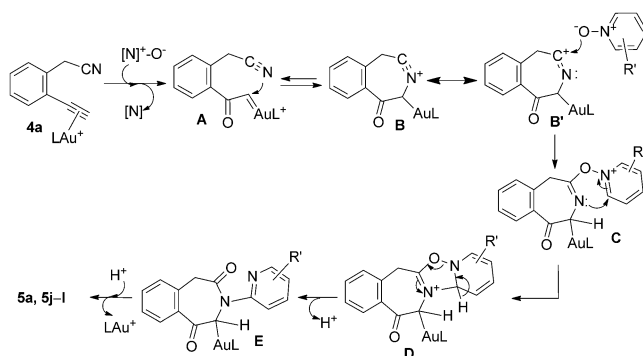
sought to use the alkenyldiazo ester **7a** to form a gold alkenyl carbene species to induce a nucleophilic attack of the nitrile at the alkenyl C3. Such regioselectivity avoids the formation of undesired oxazole products.^[18b, 19] The reaction between **7a**, IPrAuSbF₆ (8 mol %), 8-methylquinoline *N*-oxide (1.1 equiv), and CH₃CN (8 equiv) in DCE (28 °C, 6 h, 0.2 m) gave the oxoarylation product **8a** in 80 % yield [Eq. (2)]. Notably, we found no pyrrole derivatives resulting from a [3+2] cycloaddition of the alkenylgold carbene with nitriles.^[18b] The yield was slightly decreased to 74 % when using a smaller amount of acetonitrile (4 equiv).



The scope of this intermolecular process was assessed with various diazo species (**7**), IPrAuSbF₆ (8 mol %), nitriles (4 equiv), and *N*-oxides (1.1 equiv), as shown in Table 3. Notably, the resulting 1,2-oxoarylation products **8c** and **8d** resulted from the addition of benzonitrile and styrylnitrile, respectively, which reacted with the vinyl diazo ester **7a** ($R^1 = R^2 = H$) at C3 of the alkenylgold carbene intermediates, and is consistent with the reported regiochemistry in the literature.^[18b,19,20] The results also show the applicability of this oxoarylation to *n*-butynitrile to afford the desired product **8b** in satisfactory yield. These gold-catalyzed reactions were amenable to halo-containing pyridine *N*-oxides, including 2-bromo, 2-chloro, and 2,4-dichloro substrates, thus yielding desired products **8e–g** in 42–71% yields. The less basic pyridines tended to bind to gold(I) weakly to maintain the acidity of the gold complex. For 2-phenyl- and 2-(2-naphthyl)pyridine *N*-oxides, the corresponding products **8h,i** were obtained in reasonable yields (62–68%). We prepared the 2-substituted alkenyldiazo esters **7b** ($R^1 = Me$, $R^2 = H$) and **7c** ($R^1 = Ph$, $R^2 = H$), both of which provided desired the 1,2-

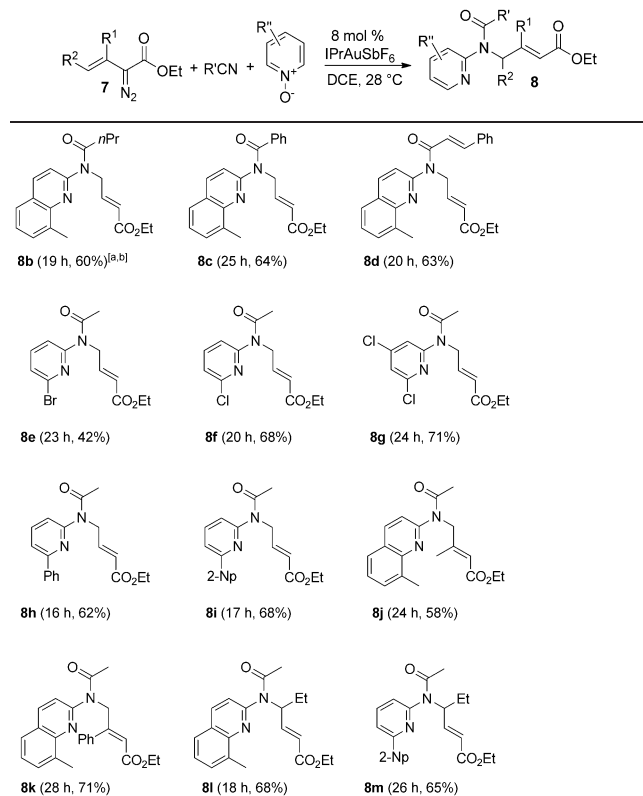
oxoarylation products **8j** and **8k**, respectively, in 58–71% yield. The reactions were also suitable for the 3-substituted alkenyldiazo ester **7d** ($R^1 = H$, $R^2 = Et$), which reacted with 8-methylquinoline *N*-oxide and 2-naphthylpyridine *N*-oxide to afford desired compounds **8l** (68%) and **8m** (65%), respectively.

We postulate a mechanism to rationalize the 1,2-oxoarylations of 2-cyanomethyl-1-ethynylbenzene (**4a**) with pyridine-based *N*-oxides, as depicted in Scheme 2. In the presence



Scheme 2. Proposed mechanism for 1,2-oxoarylations of nitriles.

Table 3: Gold-catalyzed intermolecular 1,2-oxoarylations of nitriles.



[a] [**7**] = 0.20 M, nitrile (4 equiv), *N*-oxide (1.1 equiv). [b] Product yields are reported for product isolated after purification using a neutral alumina column.

of IPrAuSbF₆, this mixture is expected to generate the α -oxo gold carbene **A** which is attacked by a tethered nitrile to form the seven-membered nitrilium species **B**. The species **B** might possess a vinyl cation resonance form (**B'**) to reduce the ring strain. A subsequent attack of the pyridine-based oxide on **B'** (or **B**) is expected to form the adduct **C**, and the pyridinium ring then undergoes attack by the iminyl nitrogen atom to produce the azacyclic species **D**. A ring cleavage of this azacyclic species forms the gold-containing *N*-(pyridin-2-yl)amide **E**, together with a loss of proton. Notably, a 2,3-sigmatropic shift in the transformation **C**→**E** is distinct from the reported 1,5-shift for the reactions of quinoline *N*-oxide with imidoyl chlorides or nitrilium species, and thus yields a pyridine derivative.^[10,21–22] The proton ultimately implements the protodeauration of **E** to afford the observed *N*-(pyridin-2-yl)amides **5a** and **5j–l**. This nitrile oxoarylation failed to work with **4o** (Table 2) because the corresponding six-membered nitrilium intermediate is too strained. This proposed mechanism also rationalizes the 1,2-oxoarylation products **8** resulting from the three-component couplings involving nitriles, alkenyldiazo esters, and pyridine-based oxides as depicted in Table 3 (see details in the Supporting Information).

Although alkynes and nitriles are two common triple-bond species, catalytic oxidations of nitriles with oxidants have no precedent. We report herein the first successful gold-catalyzed oxoarylation of nitriles with pyridine-derived *N*-oxides using gold carbenes as initiators. Initial investigations indicate that a variety of oxoarylation products can be accessed from a number of 5-cyano-3-en-1-yne and pyridine-based *N*-oxides.^[23] Seven-membered cyclic nitriliums were involved as key intermediates. These gold-catalyzed nitrile oxoarylations were also achieved satisfactorily for

intermolecular three-component oxidations, including various alkenyldiazo esters, nitriles, and pyridine-based *N*-oxides. This work reports the first examples of the oxidations of nitriles with organic *N*-oxides. Expansion of this nitrile oxoarylation, which involves distinct nitrilium species,^[21,22] to generate organic and inorganic oxides is under current investigation.

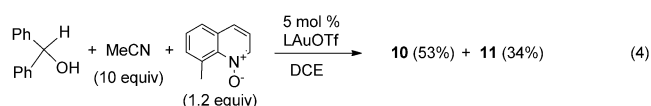
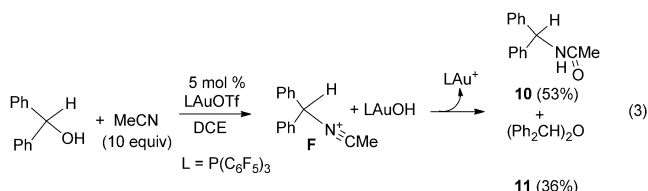
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[21] We attempted to realize an oxoarylation reaction with the nitrilium intermediates **F** generated from diphenylmethanol and acetonitrile (10 equiv) according to Hashmi's report^[22] [Eq. (3)]. We obtained the amide **10** and ether **11** in 53 and 36% yield, respectively, without any oxidant. In the presence of 8-methylquinoline *N*-oxide (1.2 equiv), we obtained no oxoarylation product in tractable amount [Eq. (4)] whereas species **10** and **11** were still formed. Accordingly, not every nitrilium species can be used in the oxoarylation reaction.



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[23] Unsubstituted pyridine and quinoline *N*-oxides were inapplicable substrates for the reaction in Tables 2–3 because the released pyridine and quinoline were expected to poison gold catalyst.