Heterocycle Synthesis

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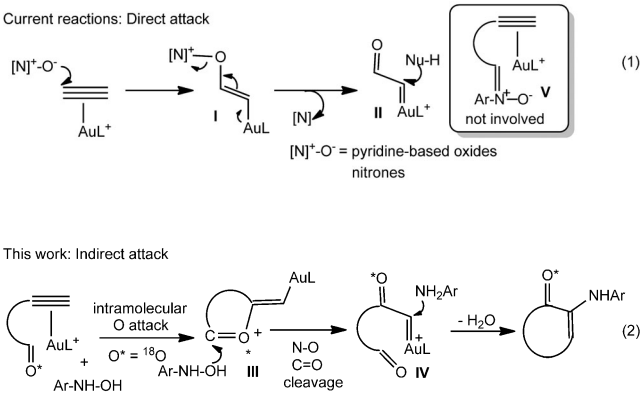
Gold-catalyzed Intermolecular Oxidations of 2-Ketonyl-1-ethynyl Benzenes with N-Hydoxyanilines to Yield 2-Aminoindenones via Gold Carbene Intermediates

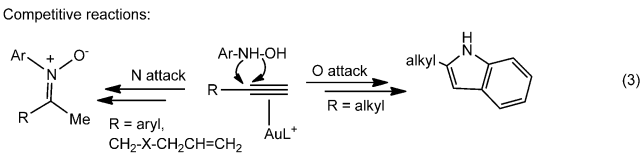
*Bhanudas Dattatray Mokar, Deepak B. Huple, and Rai-Shung Liu**

Abstract: *Gold-catalyzed oxidations of 2-ketonyl-1-ethynyl benzenes with N-hydroxyanilines yield 2-aminoindenone derivatives efficiently. Experimental data suggests that this process involves an α-oxo gold carbene intermediate, generated from the attack of N-hydroxyaniline on furylgold carbene intermediate, rather than the typical attack of oxidants on π-alkynes.*

The gold-catalyzed intermolecular oxidations of alkynes with either pyridine-based oxides or nitrones, have been intensively investigated.[1] The resulting α-oxo gold carbenes are versatile in various reactions, including X–H additions (X = O, NR),[2] C–H functionalizations,[3] cyclopropanations,[4] and annulation reactions.[5] These alkyne oxidations are synthetically appealing as readily available alkynes replace α-oxo diazo species as the initial reagents. The reported oxidations proceed exclusively by an attack of highly basic N–O oxides at gold–π-alkynes, as depicted in Equation (1). Catalytic oxidations from alkynes, through a distinct and novel mechanism, are highly significant and challenging. In seeking a breakthrough, we report the gold-catalyzed oxidations of 2-ketonyl-1-ethynylbenzenes with N-hydroxyanilines to yield 2-aminoindenones efficiently [Eq. (2)]. Herein, N-hydroxyaniline serves as one oxygen donor to oxidize terminal alkynes into ketones before becoming aniline. This reaction sequence produces water as a byproduct, thus fulfilling atom economy.



Notably, these new alkyne oxidations do not involve attack of the N-hydroxyanilines on the gold–π-alkynes.[6–8] Gold-catalyzed intermolecular reactions of terminal alkylalkynes with N-hydroxyanilines generally follow proceed by O attack [Eq. (3)], thus yielding indoles preferably.[7] The preference for N attack is noted for terminal arylalkynes and 1,6-enynes to afford easily hydrolyzed nitrones [Eq. (3)].[8] The strategy of this work involves an initial formation of the oxonium intermediate **III** which is attacked subsequently by the N-hydroxyaniline to generate the α-oxo gold carbene **IV** [Eq. (2)] by cleavage of the C=O and N–O bonds. Experimental data to support this atypical mechanism and to exclude nitrone intermediates (**V**)[9] are described in detail.



Fused five-membered azacyclic ketones are present in bioactive molecules, and two selected examples, **VI** and **VII**, are provided in Figure 1. The compound **VI** (MR16924) represents one prominent example of the tripentone family and shows remarkable antitubulin effects over tested lines

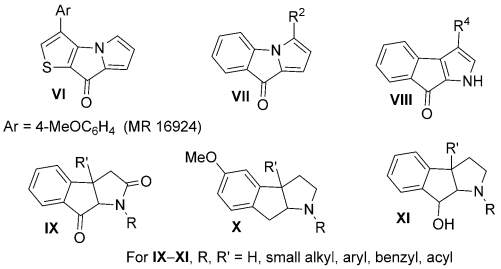


Figure 1. Bioactive indene molecules containing nitrogen.

including leukemia, central nervous system, ovarian and breast cancers,[10] whereas the fluorazone derivatives **VII** are nontoxic, anti-proliferative agents in melanoma cells.[11] Our new syntheses lead to the 2-aminoindanonyl derivatives **VIII**–**XI**. The synthesis of indeno-[2,1-*b*]-pyrroles **VIII** has attracted considerable attention because of their structural similarity to fluorazones (**VII**). Notably, **VIII** can be converted into other bioactive molecules (**IX–XI**), which have

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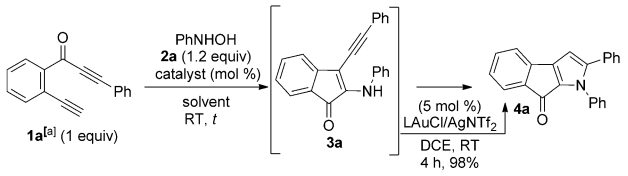
been claimed in a US patent to possess analgesic or anti-inflammatory activities.[12a] Our target **VIII** serves an intermediate for useful S–N-containing heterocycles.[12b,c]

Table 1 presents optimized reactions conditions for 1-alkynoyl-2-ethynylbenzene (**1a**) with N-hydroxyaniline (**2a**; 1.2 equiv) in the presence of various gold catalysts (5–8 mol%). We tested the reactions with LAuCl/$AgNTf_2$ [L = $P(tBu)_2$(*o*-biphenyl), 5 mol%] in 1,2-dichloroethane (DCE;

Table 1: Catalyst screening over various gold catalysts.



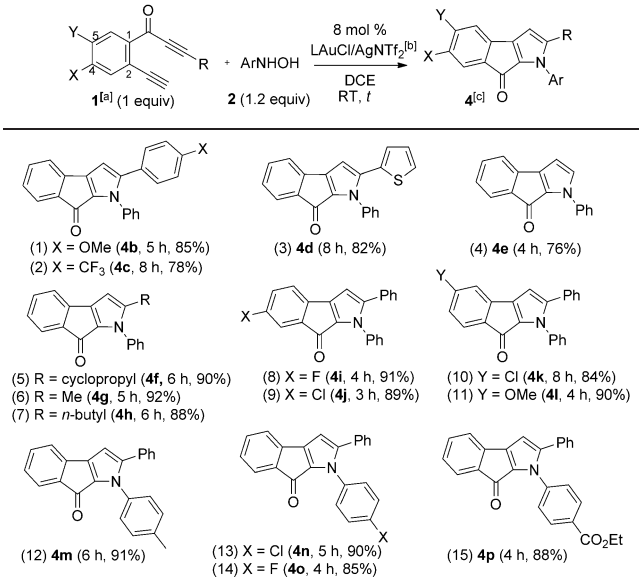
Entry	Catalyst[b] (mol%)	*t* [h]	Solvent	Yields [%][c]		
				1a	**3a**	**4a**
1	LAuCl/$AgNTf_2$ (5)	18	DCE	–	12	82
2	LAuCl/$AgNTf_2$ (8)	8	DCE	–	–	94
3	LAuCl/AgOTf (8)	16	DCE	–	10	68
4	LAuCl/$AgSbF_6$ (8)	8	DCE	–	–	85
5	PPh_3AuCl/$AgNTf_2$ (8)	16	DCE	–	–	80
6	IPrAuCl/$AgNTf_2$ (8)	12	DCE	–	–	90
7	$AgNTf_2$ (8)	24	DCE	82	–	–
8	LAuCl/$AgNTf_2$ (8)	10	DCM	–	–	88
9	LAuCl/$AgNTf_2$ (8)	12	toluene	–	–	80
10	LAuCl/$AgNTf_2$ (8)	36	1,4-dioxane	–	8	44

[a] **1a** (0.05 M). [b] L = (1,1′-biphenyl-2-yl)di-*tert*-butylphosphine. [c] Yield is that of the isolated product after silica chromatography. DCE = 1,2-dichloroethane, DCM = dichloromethane, Tf = trifluoromethanesulfonyl.

25 °C, 18 h), thus yielding the indenone **3a** and indeno[2,1-*b*]pyrrol-8(1*H*)-one **4a** in 12 and 82% yield, respectively (entry 1). A large loading (8 mol%) of this catalyst enabled complete transformation of **1a** into **4a** in 94% yield (entry 2). In a separate experiment, LAuCl/$AgNTf_2$ (5 mol%) allowed complete conversion of **3a** into **4a** in 98% yield. A change of silver salts as in LAuCl/AgOTf and LAuCl/$AgSbF_6$, each at 8 mol%, afforded **4a** in 68 and 85% yield, respectively (entries 3 and 4). PPh_3AuCl/$AgNTf_2$ and IPrAuCl/$AgNTf_2$ [IPr = 1,3-bis(2,6-diisopropylphenyl) imidazole-2-ylidene] were also effective to give **4a** in 80 and 90% yield, respectively (entries 5 and 6). Notably, $AgNTf_2$ alone was not catalytically active at all (entry 7). Other solvents like toluene and 1,4-dioxane were less efficient for the LAuCl/$AgNTf_2$ catalyst (entries 9 and 10). The molecular structures of **3a** and **4a** were confirmed by X-ray diffraction studies.[13]

We assessed the scope of reaction of such indeno[2,1-*b*]pyrrol-8(1*H*)-one syntheses with various 2-alkynoyl-1-ethynylbenzenes (**1b–l**) and the N-hydroxyanilines **2b–e** using the LAuCl/$AgNTf_2$ catalyst [L = $P(tBu)_2$(*o*-biphenyl), 8 mol%; Table 2]. The results in entries 1–2 show the compatibility of this reaction with **1b** and **1c**, bearing R = 4-XC_6H_4 (X = OMe and CF_3), thus giving the desired products **4b** and **4c**, respectively, in satisfactory yields (78–85%). The reactions were extended to the substrates **1d** and **1e** (R = 2-thienyl, H),

Table 2: Catalytic synthesis of indeno[2,1-*b*]pyrrol-8(1*H*)-ones.



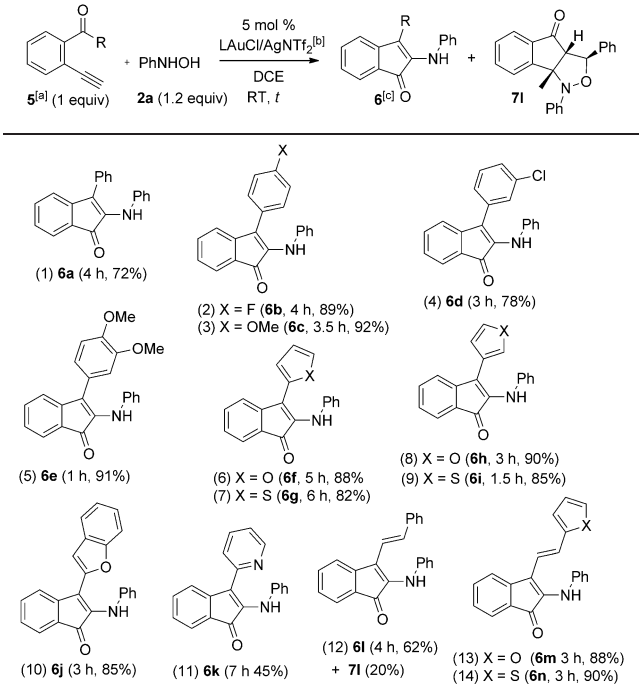
[a] [substrate] = (0.05 M). [b] L = $P(tBu)_2$(*o*-biphenyl), [c] Yields are those for product isolated after silica chromatography.

thus yielding the desired **4d** and **4e**, respectively, in satisfactory yields (entries 3 and 4). For the alkyl-substituted analogues **1f–h** (R = cyclopropyl, methyl, and *n*-butyl), the corresponding products **4f–h** were produced in excellent yields (entries 5–7). These catalytic reactions worked well with various 4- or 5-phenyl-substituted substrates **1i–l** (X = F, Cl or Y = Cl, OMe), thus giving the compounds **4i–l** with yields exceeding 84% (entries 8–11). Entries 12–15 show the compatibility of these reactions with various 4-substituted N-hydroxyanilines (**2b–e**; X = Me, Cl, F and CO_2Et), thus delivering the compounds **4m–p** in 85–91% yields.

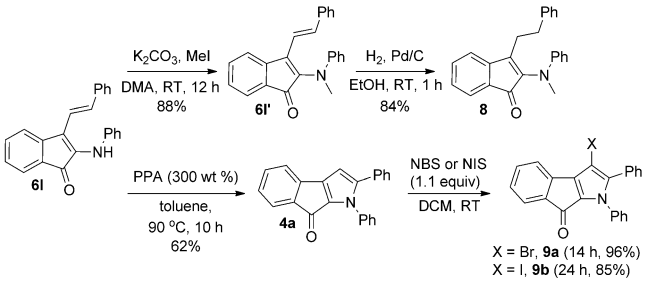
To our pleasure, the scope of these reactions became considerably expanded by using various aryl- or heteroaryl ketones (**5a–k**) to yield the desired 2-aminoindenones **6** efficiently (Table 3). Gold-catalyzed reactions of the phenylketone-derived substrates **5a–e** with **2a** afforded **6a–e** in 72–92% yields (entries 1–5). The 3,4-dimethoxyphenylketone derivative **5e** showed the best efficiency at a brief period (1 h). We tested the reactions of 2- and 3- substituted thienyl and furylketones (**5f**,**g** and **5h**,**i**) and they delivered the desired 2-aminoindenones **6f–i** in satisfactory yields (entries 6–9). For 2-benzofuryl- and 2-pyridinylketone derivatives, **5j** and **5k**, respectively, led to the corresponding products **6j** (85%) and **6k** (45%; entries 10 and 11). We prepared the alkenylketone substrates **5l–n**, which afforded the desired products **6l–n** in 62–90% yields (entries 12–14). Herein the byproduct **7l** was obtained in a minor proportion (20%) because of a N-attack of the hydroxyaniline on **5l** (entry 12).[8] An electron-rich heteroaryl group avoids this byproduct because the oxomium intermediate **III** forms rapidly [Eq. (2)].

Alkyl-substituted phenylketones are not suitable substrates because they form nitrone species,[14] thus giving distinct isoindole products.[9b] Such 3-alkyl indenones were

Table 3: Various arylketone- and alkenylketone-derived substrates.



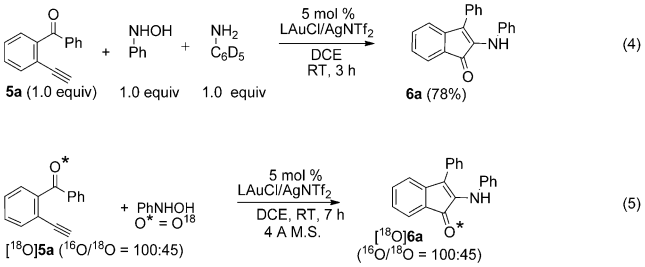
[a] [substrate] = (0.05 M). [b] L = P(*t*Bu)$_2$(*o*-biphenyl), [c] Yields are those for products isolated after silica chromatography.

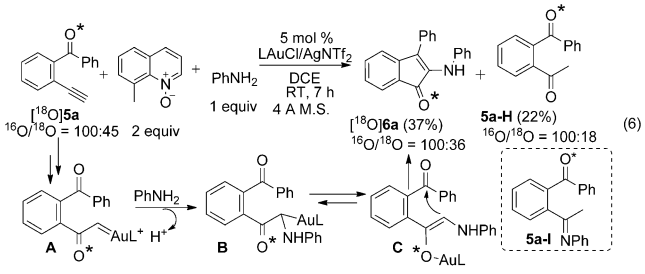


Scheme 1. Chemical transformations. DMS = dimethylsulfoxide, NBS = *N*-bromosuccinimide, NIS = *N*-iodosuccinimide, PPA = polyphosphoric acid.

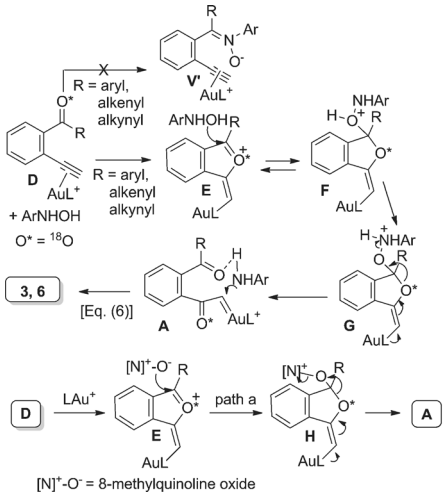
alternatively prepared from **6l** through selective hydrogenation of its N-methyl derivative (Scheme 1). The compound **6l** was converted into the indeno[2,1-*b*]pyrrol-8(1*H*)-one **4a**, by using a Brønsted acid, efficiently and then into the bromo and iodo derivatives **9a** and **9b**, respectively, in good yields.

We performed isotope-labeling experiments to elucidate the mechanism. As depicted in Equation (4), the treatment of 2-phenylketonyl-1-ethynylbenzene (**5a**) with N-hydroxyaniline and $C_6D_5NH_2$, in a molar ratio 1:1, yielded **6a** bearing no deuterium. This information indicates that N-hydroxyaniline is the only source of the amino moiety of **6a**. Our ^{18}O-labeling experiment [Eq. (5)] was informative because [^{18}O]**5a** was transformed into the product [^{18}O]**6a** without loss of ^{18}O content upon comparison of their mass spectra (see Figure S1 in the Supporting Information). Additional mechanistic insight is inferred from the oxidation of species [^{18}O]**5a** with 8-methylquinoline oxide and aniline in dry DCE, yielding the desired [^{18}O]**6a** in 37% yield, with a small loss of the ^{18}O content [Eq. (6)]. This observation indicates the intermediacy of the α-oxo gold carbene **A**, which is subsequently attacked by aniline to form the C- and O-bound α-amino enolates **B** and **C**, respectively, to enable an aldol reaction. Herein, the oxo group of **A** arises partly from the ketone group of [^{18}O]**5a**, and is indicative of an indirect attack as the major route. Although **6a** can be produced alternatively from this three-component coupling, as depicted in [Eq. (6)], the efficiency is poor because of the hydroamination product **5a–I** as well as an imination of **5a** at its phenyl ketone. These imination products are easily hydrolyzed into the ketone **5a–H** during the workup.





A plausible mechanism is depicted in Scheme 2. Our ^{18}O-labeling experiment in Equation (5) indicates that the carbonyl oxygen atom of the resulting indenone **6a** arises completely from the ketones of **5a**, thus excluding the intermediacy of the nitrone **V′**. The nitrone **V′** is known to be too unstable to exist for aryl-, alkenyl-, and alkynyl-substituted arylketones.[15] Herein, we propose prior attack of the tethered ketones on the gold–π-alkynes **D** to form the oxonium species **E**.[16] This intramolecular *5-exo*-dig cyclization is much more rapid than that for an intermolecular attack of N-hydroxyaniline at gold π-alkynes, thus avoiding either indole or nitrone byproducts [Eq. (3)]. An attack of the N-hydroxyaniline on **E** yields the O-bound product **F**, which might undergo a 1,2-proton transfer to form the ammonium species **G** because the nitrogen center is more basic than the oxygen center. The ammonium centers in **G** induce an N–O bond cleavage, thus generating **A**, which is a viable intermediate for the final products **3** or **6** [Eq. (6)]. We envisage that the released aniline captures **A** rapidly as this acid–base pair is in close proximity through a NH···O=C hydrogen bonding. This hypothesis rationalizes the observation in



Scheme 2. Proposed reaction mechanism.

Equation (4). The feasibility of the **E**→**F**→**G** path is supported by the oxoamination of [^{18}O]**5a** with 8-methylquinoline oxide and aniline [Eq. (6)]. This mechanism is depicted in the **D**→**E**→**H** transformation.

Before this work, a gold-catalyzed attack of N–O-containing oxides on alkynes was the only path to initiate alkyne oxidations.[17] We report an atypical route in the gold-catalyzed intermolecular oxidations of ketonylalkynes with N-hydroxyanilines. These oxidations involve initial formation of oxonium species which are subsequently attacked by N-hydroxyaniline, and lead to oxoamination products. This path is strongly supported by ^{18}O-labeling experiments. In one control experiment, our resulting 2-aminoindenones were alternatively produced from the same ketonylalkynes, 8-methylquiniline oxide, and aniline, but the efficiency was low. Gold carbenes generated from oxonium, and possibly other stable carbocations, may inspire future work on this area.

Acknowledgments

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Keywords: alkynes · carbenes · gold · heterocycles · oxidations

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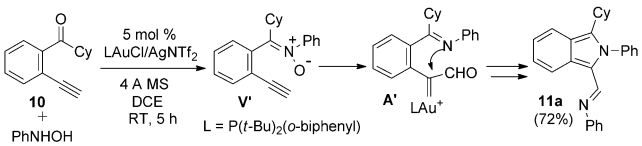
[13] Crystallographic data of compounds **3a**, **4a** and **11a** were deposited at Cambridge Crystallographic Center: **3a**, CCDC 1480847; **4a**, CCDC 11480848; **11a**, CCDC 1481886.

[14] We prepared a cyclohexyl phenylketone **10**, which can form nitrones species.[15] In the presence of gold catalyst, this alkyl derivative afforded the isoindole product **11a** in 72% yield. Its molecular structure was confirmed by X-ray diffraction.



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Communications

Heterocycle Synthesis

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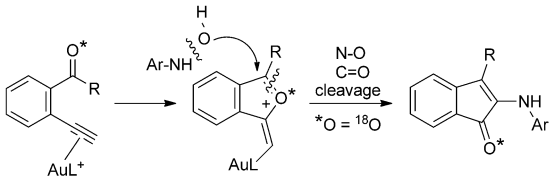
Gold-catalyzed Intermolecular Oxidations of 2-Ketonyl-1-ethynyl Benzenes with N-Hydoxyanilines to Yield 2-Aminoindenones via Gold Carbene Intermediates



Under attack: The title reaction efficiently yields 2-aminoindenone derivatives. Experimental data suggests that this process involves an α-oxo gold carbene intermediate, generated from the attack of N-hydroxyaniline on a furylgold carbene intermediate, rather than the typical attack of oxidants on π-alkynes.