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Gold-Catalyzed 1,4-Carbooxygenation of 3-En-1-ynamides with Allylic and Propargylic Alcohols *via* Non-Claisen Pathways

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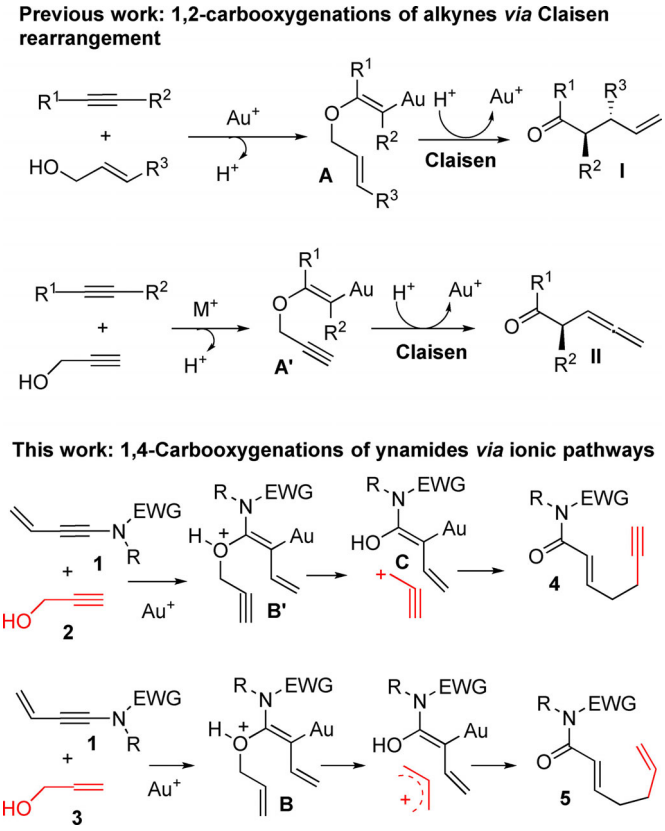
Abstract: Gold-catalyzed 1,4-carbooxygenations of 3-en-1-ynamides with allylic alcohols and propargylic alcohols yield α,β-unsaturated amides through non-Claisen pathways; the mechanisms involve ionization of the initial gold enol ethers to form C-bound gold dienolates that capture allylic or propargylic cations to yield the observed products. Our ^{18}O-labeling experiments exclude a direct gold-catalyzed allylation or propargylation on these 3-en-1-ynamides.

Keywords: allylic and propargylic alcohols; 1,4-carbooxygenation; 3-en-1-ynamides; gold catalysis; non-Claisen pathways

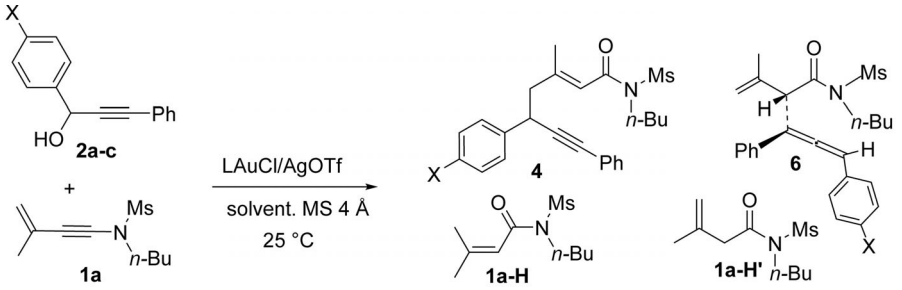
The advent of gold catalysis has inspired new functionalizations of alkynes with a broad range of nucleophiles to afford valuable molecules.[1] Gold-catalyzed reactions of alkynes with allylic or propargylic alcohols are powerful tools to access 1,5-enones **I** and 1,5-allenyl ketones **II**,[2,3] which serve as versatile building blocks in organic synthesis.[4,5] Such one-pot reactions have been thoroughly examined by Aponick,[2a] Nolan,[2b] Hsung,[2c,3a,b] and others[2,3] using gold or acid catalysts; the mechanisms typically involve initial hydroalkoxylations,[6] followed by Claisen rearrangements[7] (Scheme 1). In the reaction mechanism, there is no support for the participation of vinylgold ethers **A** or **A′** in the [3,3]-sigmatropic rearrangement before protodeaurations, although this gold-containing rearrangement is calculated to possess only a small barrier.[2b] Here, we report gold-catalyzed 1,4-carbooxygenations of 3-en-1-ynamides with allylic and propargylic alcohols, yielding α,β-unsaturated amides **4** and **5** efficiently. These atypical products imply an ionization of the initial vinylgold intermediates **B** and **B′** to form C-bound gold dienolates **C** that capture allylic or propagylic cations to yield 1,4-carbooxygenation products **4** and **5** through non-Claisen pathways. Our ^{18}O-labeling experiments exclude a direct allylation or propargylation of 3-en-1-ynamides catalyzed by gold complexes.[8]

Ynamides are common substrates for gold-catalyzed reactions because of their high electrophilicity.[9,10] Ynamides were selected as target substrates because their Lewis acid-catalyzed reactions with propargylic alcohols can proceed at room temperature,[3c,d] yielding Claisen-type products **6**.[3a,b,11] We examined the chemoselectivity of the reaction between 3-en-1-



Scheme 1. A summary of the catalytic reactions.

Table 1. Non-Claisen *versus* Claisen products.



Entry	Alcohol[a]	LAuX(10 mol%)	Solvent/Time [h]	Products (Yields)[b,c]
1	X = H (**2a**)	L = PPh_3	toluene/1.5	**6a** (77%), **1a-H/1a-H'** (5%, 1:1)
2	X = Me (**2b**)	L = PPh_3	toluene/4	**6b** (40%), **1a-H/1a-H'** (35%, 1.2:1)
3	X = Me (**2b**)	L = IPr	toluene/4	**4b** (25%), **6b** (12%), **1a-H/1a-H'** (25%, 1:1)
4	X = OMe (**2c**)	L = PPh_3	toluene/1.5	**4c** (91%)
5	X = OMe (**2c**)	L = IPr	toluene/0.3	**4c** (26%), **1a-H** (62%)
6	X = OMe (**2c**)	$Zn(OTf)_2$	toluene/5	**4c** (33%), **6c** (42%)
7	X = OMe (**2c**)	$Sc(OTf)_3$	toluene/5	**4c** (45%),**1a-H/1a-H'** (51%, 1:1)
8	X = OMe (**2c**)	AgOTf	toluene/1.5	**4c** (71%), **1a-H/1a-H'** (21%, 1:1)
9	X = OMe (**2c**)	HOTf	toluene/0.5	**4c** (25%)[d]
10	X = OMe (**2c**)	L = PPh_3	DCM/0.5	**4c** (76%), **1a-H** (18%)
11	X = OMe (**2c**)	L = PPh_3	MeCN/1	**4c** (77%), **1a-H** (8%)
12	X = OMe (**2c**)	L = PPh_3[e]	toluene/1	**4c** (91%), **1a-H** (3%)

[a] [**1a**] = 0.15 M.
[b] Product yields are reported after separation on a silica column.
[c] *dr* > 20:1 for species **6a–6c**.
[d] HNMs(*n*-Bu) was isolated in 61% due to a hydration of amides **1a-H** or **1a-H′**.
[e] This complex is free of silver salts.

ynamides **1a** with propargylic alcohols using Lewis acid catalysts. Table 1 shows the effects of aryl substituents of propargylic alcohol **2a–c** on the chemoselectivitiy. Our initial tests on propargylic alcohols **2a** and **2b** (1.1 equiv.) with Ph_3PAuCl/AgOTf (10 mol%) in dry toluene at 25 °C yielded 1,2-oxoallenylation products **6a** and **6b** in 77% and 40% yields, respectively, corresponding to Claisen-type products (entries 1 and 2). Allenyl compounds **6a** and **6b** were formed with high diastereoselectivity (*dr* > 20:1); the molecular structure of species **6a** was inferred from that of its tosylamide analogue **6a′**.[12] The reactions of alcohols **2b** with IPrAuOTf (10 mol%)[13a] afforded additional non-Claisen compound **4b** in 25% yield (entry 3). With a switch to electron-rich propargylic alcohol **2c**, $Ph_3PAuOTf$ afforded a distinct 1,4-oxopropargylation product **4c** in 91% (entry 4), whereas IPrAuOTf yielded the desired **4c** and hydration product **1a-H** in 26% and 62% yields, respectively (entry 5). $Zn(OTf)_2$ gave two carbooxygenation compounds **4c** and **6c**, in 33% and 42% yields, respectively (entry 6) whereas highly acidic $Sc(OTf)_3$ yielded compound **4c** in 45% yield because of a competitive hydration reaction (entry 7). Less acidic AgOTf gave non-Claisen product **4c** in a satisfactory yield (71%, entry 8). Notably, HOTf was an ineffective catalyst to yield 1,4-addition product **4c** in 25% yield because this acid gave HNMs(*n*-Bu) in 61% yield (entry 9). MeCN and DCM were also efficient solvents with Ph_3PAuCl/AgOTf to afford compound **4c** in 77% and 76% yields respectively (entries 10 and 11). To ensure the catalytic role of Ph_3PAu^+, silver-free $Ph_3PAuOTf$[13b] was tested in this reaction and yielded compound **4c** in 91% (entry 12). The non-Claisen re-

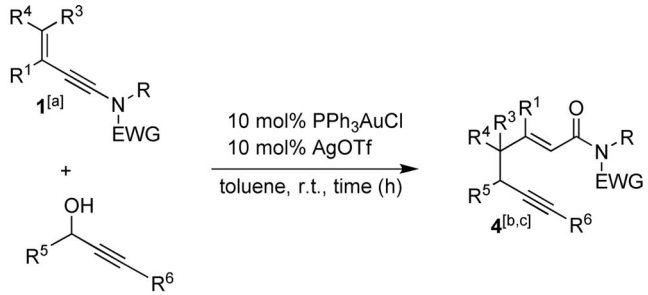
actions occur preferably with electron-rich propargylic alcohol **2c** using less acidic catalysts AgOTf or LAuOTf (L = Ph_3P or IPr), but AgOTf and IPrAuOTf were also troubled with hydration products **1a-H**/**1a-H′** (entries 5 and 8).

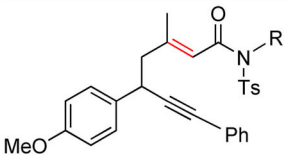
We assessed the scope of 1,4-oxopropargylations with various 3-en-1-ynamides **1** and electron-rich propargylic alcohols **2**. The reactions were performed with Ph_3PAuCl/AgOTf in toluene; the resulting 1,4-oxopropargylation products **4d–4n** were present mainly in *E*-configurations (*E*/*Z* > 20:1, Table 2, entries 1–11). For species **1b** and **1c** bearing alterable sulfonamides [NR⁴EWG = NTsMe, NTs(*n*-Bu)], their corresponding 1,4-oxopropargylation products **4d** and **4e** were produced with good yields (74–76%) and high *E*-selectivity (*E*/*Z* > 20:1) over 4 h. In a brief period (0.8 h), 3-en-1-ynamide **4d** gave two isomers with *E*/*Z* = 2.7:1. These different *E*/*Z* ratios at two time periods indicate that $Ph_3PAuOTf$ catalyzed the *Z*→*E* isomerization of species **4d** (entries 1 and 2). For propargylic alcohols **2d** and **2e** bearing varied alkynyl substituents (R^6 = *n*-butyl and isopropyl), their propargyl derivatives **4f** and **4g** were obtained in 58–61% yields (entries 3 and 4). 2-Thienyl-containing propargylic alcohols **2f–2h** (R^5 = 2-thienyl, R^6 = Ph, isopropyl and *n*-butyl) were also applicable substrates to yield propargyl species **4h–4j** in moderate yields (47–61%, entries 5–7). For ynamide **1d** bearing a *trans*-styryl group (R^4 = Ph, R^1 = R^3 = H), the reactions with two propargylic alcohols **2c** and **2f** (R^5 = 4-$MeOC_6H_4$ and 2-thienyl) afforded similar products **4k** and **4l** in satisfactory yields (65–68%), albeit in two diastereomers (*dr* = 4.1:1 and 2.2:1, entries 8 and 9). For 3-en-1-ynamide **1e** bearing a *gem*-dimethylvinyl substituent (R^1 = H, R^4 = R^3 = Me), its reactions with two alcohol substrates **2c** and **2f** afforded compounds **4m** and **4n** in 72% and 78% yields respectively (entries 10 and 11).

Our next aim was to realize novel 1,4-oxoallylations of 3-en-1-ynamide **1a** with electron-rich allylic alcohols **3**; the results are summarized in Table 3. All resulting 1,4-oxoallylation products **5** were present as *E*-isomers (*E*/*Z* > 20:1) except **5f** with *E*/*Z* = 5:1. Besides 1,4- and 1,2-oxoallylation products **5** and **7**, hydration compounds **1a-H** and **1a-H′** were present but are not reported here. Gold-catalyzed reactions of 3-en-1-ynamide **1a** with 1-phenylprop-2-en-1-ol **3a** or 1,1-dimethylprop-2-en-1-ol **3b** followed the Claisen reaction, yielding 1,2-oxoallylation products **7a** and **7b** in 89% and 63% yields, respectively (entries 1 and 2). The use of easily ionizable 1,3-diphenylprop-2-en-1-ol **3c** enabled the desired 1,4-oxoallylation product **5c** with a yield of up to 95% (entry 3). Notably, such gold-catalyzed reactions of 3-en-1-ynamide **1a** with two allylic alcohols **3d** and **3e** afforded the same compound **5d** in satisfactory yields (63–67%, entries 4 and 5). A 1,4-oxoallylation of 3-en-1-ynamide **1a** with tertiary allylic alcohol **3f** occurred at the less hindered allylic carbon, yielding compound **5f** in 35% yield with two isomers (*E*/*Z* = 5:1, entry 6). The reactions of this enynamide with 1,1-dimethyl-3-phenylpropr-2-en-1-ol **3g** and 3,3-dimethyl-1-phenylpropr-2-en-1-ol **3h** gave compounds **5g** and **5g′** in comparable proportions. In the course of these reactions, Ph_3PAuCl/AgOTf catalyzed the isomerizations between the allylic alcohols **3g** and **3h**.

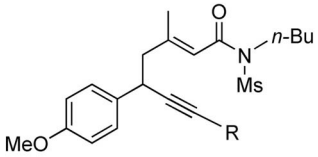
We also tested other 3-en-1-ynamides **1** to expand the reaction scope; the results are summarized in Table 4. For initial species **1b** and **1c** bearing alterable sulfonamides [NR′EWG = NTsMe, NTs(*n*-Bu)], their resulting 1,4-oxoallylation products **5h** and **5i** were obtained with high *E*-selectivity (*E*/*Z* > 20:1) over a 2 h period. The reaction worked well with other 3-

Table 2. Scope for Non-Claisen reactions.[a–c]

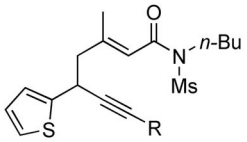




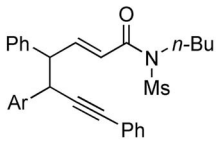
(1) **4d** (R = Me, 0.8 h, 78%, *E*/*Z* = 2.7:1; 4 h, 76%, *E*/*Z* > 20:1)
(2) **4e** (R = ^{n}Bu, 4 h, 74%)



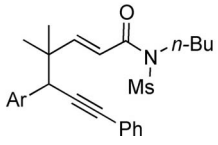
(3) **4f** (R = *n*-Bu, 3 h, 58%)
(4) **4g** (R = *i*-Pr, 3 h, 61%)



(5) **4h** (R = Ph, 3 h, 47%)
(6) **4i** (R = *i*-Pr, 3 h, 55%)
(7) **4j** (R = *n*-Bu, 4 h, 61%)



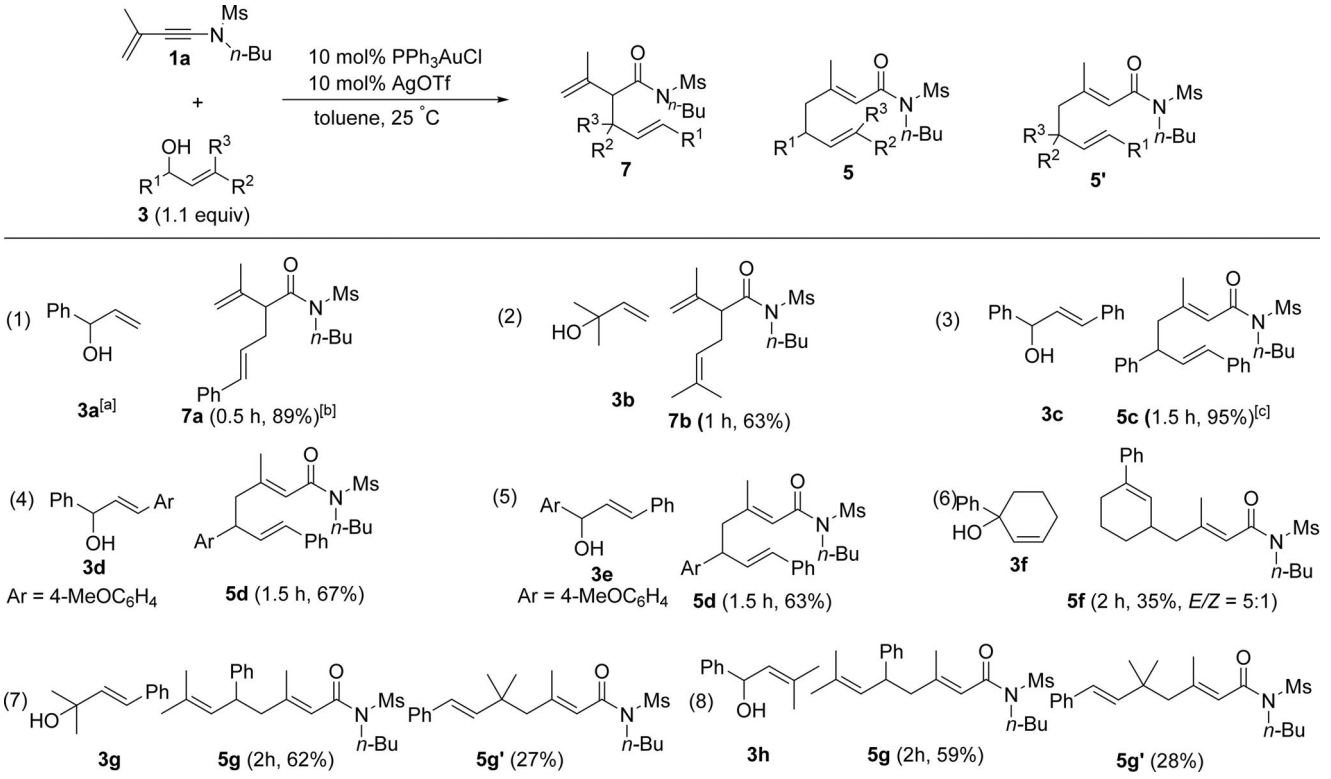
(8) **4k** (Ar = 4-$MeOC_6H_4$, 3 h, 65%, *dr* = 4.1:1)
(9) **4l** (Ar = 2-thienyl, 4 h, 65%, *dr* = 2.2:1)



(10) **4m** (Ar = 4-$MeOC_6H_4$, 2 h, 72%)
(11) **4n** (Ar = 2-thienyl, 2 h, 78%)

[a] [**1a**] = 0.15 M.
[b] *E*/*Z* > 20:1 for entries 2–11.
[c] Product yields are reported after separation from a silica column.

Table 3. Effects of allylic alcohols on 1,2- or 1,4-addition reactions.[a–c]

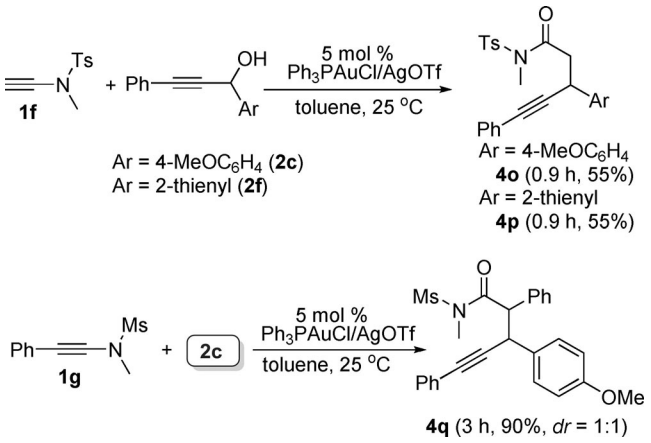


[a] [**1a**] = 0.15 M.
[b] Product yields are reported after separation on a silica column.
[c] *E*/*Z* > 20:1 for products **5c**, **5d**, **5g** and **5g′**.

substituted 3-en-1-ynamides **1h** and **1i** (R^1 = Ph and *n*-Bu, $R^2 = R^3 = H$), yielding the desired products **5j** and **5k** in 70% and 92% yields, respectively; but for 4,4-dimethylvinyl derivative **1e**, we obtained only its Claisen-reaction product **8c** in 70% yield with *dr* = 10:1 (entry 5).

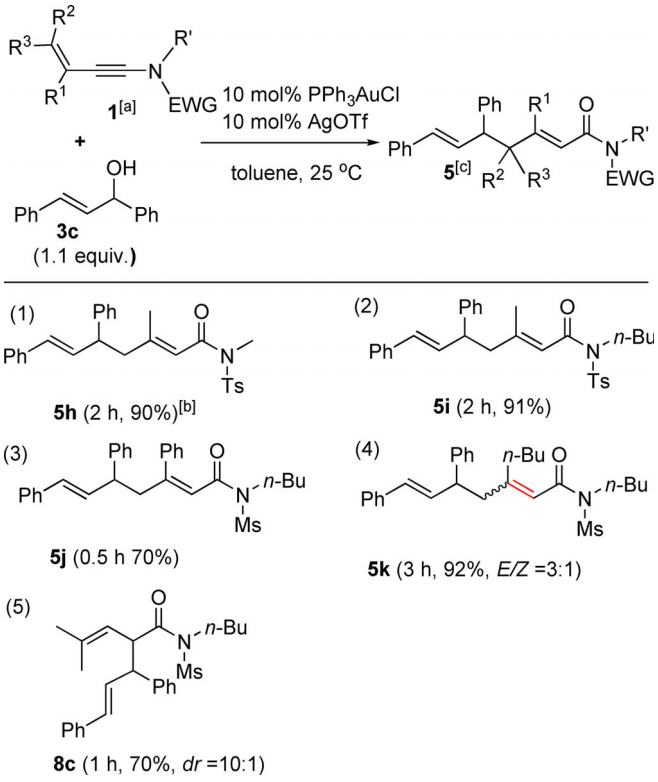
Common ynamides **1f** and **1g** were also applicable to these non-Claisen reactions to expand the reaction scope; we employed highly ionizable propargylic alcohols **2c** and **2f** to confirm this pathway (Scheme 2). The reactions of these two ynamides with alcohols afforded 1,2-progarylation products **4o**, **4p** and **4q** in reasonable yields. Herein, we isolated no 1,2-oxoallenation product from the Claisen reactions. Unactivated alkynes such as phenylacetylene failed to react with propargylic alcohol under similar catalytic conditions.

To gain mechanistic insights, we prepared ^{18}O-containing allylic alcohol **^{18}O-3c** with the content, $^{16}O/^{18}O = 1.00:1.03$. At 50% conversion in wet toluene, the resulting 1,4-oxoallylation product **^{18}O-5c** bore the ratio $^{16}O/^{18}O = 1.00:0.76$, indicating a small loss of ^{18}O content (Scheme 3). At the end of reaction, the ^{18}O–H group of unreacted alcohol **^{18}O-3c** bore the ratio, $^{16}O/^{18}O = 1.00:0.56$, due to a slow exchange with H_2O. These results indicate that the hydroxy oxygen of the initial allylic alcohol **3c** is the main source of the amide oxygen of compound **^{18}O-5c**. Accordingly, we exclude a mechanism involving an initial formation of allylic cation **D**, followed by an attack of 3-en-1-ynmide **1a** because this route is expected to yield **^{16}O-5c** as the major species. Similarly, an S_N2' reaction between species **1a** and **^{18}O-3c** is also excluded. Hydration products **1a-H** and **1a-H′** were inactive toward allylic alcohol **3c** in the presence of

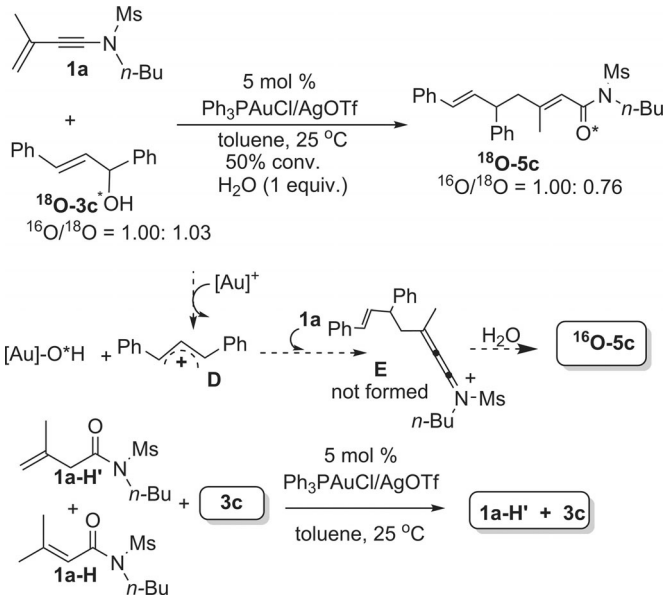


Scheme 2. The reaction with common ynamides.

Table 4. 1,4-Oxoallylations for various 3-en-1-ynamides.[a–c]



[a] [**1**] = 0.15 M.
[b] *E*/*Z* > 20:1 for entries 1–3.
[c] Product yields are reported after separation from a silica column.

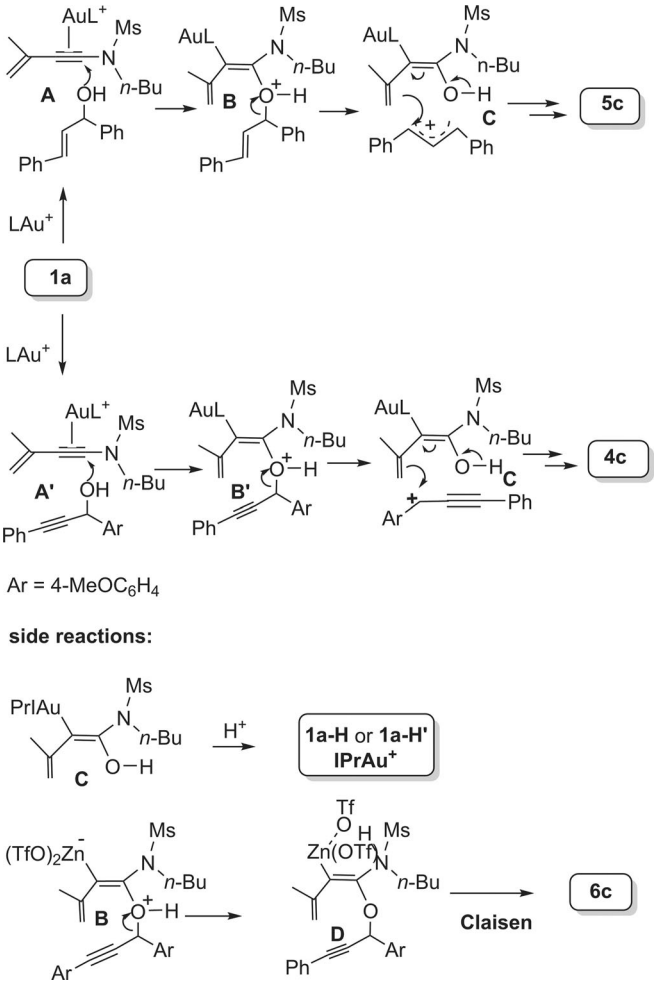


Scheme 3. Experiments to elucidate the mechanism.

$Ph_3PAuCl/AgOTf$ under similar conditions. According to a recent report,[14] a mixture of trimethoxymethane and AgOTf catalyst enabled the conversion of unactivated ketones to enol ethers that undergo subsequent α-alkylations with propargylic alcohols to give propylation products.[14] That no reaction occurred for these reactants is not surprising.

Scheme 4 shows a postulated mechanism to rationalize the 1,4-carbooxygenations of initial 3-en-1-ynamide **1a**. According to the ^{18}O experiments, the addition of allylic alcohols and propargylic alcohols to π-alkynes **A** is the initial step to yield species **B** or **B′** respectively. With electron-rich allylic or propargylic alcohols, species **B** or **B′** undergoes self-ionization to form gold enols **C** together with allylic or propargylic cations. Intramolecular reactions of these pairs are expected to yield 1,4-carbooxygenation products **5c** and **4c**, respectively.

This model rationalizes well the side products of some catalysts in Table 1; enolate **C** bearing electron-rich IPrAu tends to undergo protonation to form hydration products **1a-H** or **1a-H′** (entry 5). For $Zn(OTf)_2$, its vinyl propargyl ether **B** is expected to release HOTf to form a dual acid species **D**,[15b] thus giving additional Clasien product **6c** (entry 6).



Scheme 4. A postulated mechanism.

Previously, gold-catalyzed reactions of alkynes with allylic and propargylic alcohols exclusively afforded 1,5-enones and 1,5-allenyl ketones though initial hydroalkoxylations, followed by the Claisen rearrangements.[15] Here, we report gold-catalyzed 1,4-carbooxygenations of 3-en-1-ynamides[16] with allylic alcohols and propargylic alcohols, yielding α,β-unsaturated amides through non-Claisen pathways. The mechanism involves self-ionizations of initial gold enol ethers to form C-bound gold dienolates **C** that capture allylic or propargylic cations to yield the observed products. These reactions work with a wide scope of 3-en-1-ynamides and electron-rich propargylic or allylic alcohols; common ynamides are also applicable substrates. The new finding of this work increases the utility of gold-catalyzed hydroalkoxylations of alkynes.

Experimental Section

Synthesis of (*E*)-*N*-Butyl-5-(4-methoxyphenyl)-3-ethyl-*N*-(methylsulfonyl)-7-phenylhept-2-en-6-ynamide (4c)

To a dry toluene solution (2 mL) of Ph_3PAuCl (0.023 g, 0.046 mmol) and AgOTf (0.012 g, 0.046 mmol) was added a toluene (1 mL) solution of *N*-butyl-*N*-(3-methylbut-3-en-1-yn-1-yl)methanesulfonamide **1a** (0.10 g, 0.46 mmol) and 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol **2c** (0.11 g, 0.46 mmol) at room temperature; the resulting mixture was stirred for 1.5 h. The resulting solution was filtered over a short celite bed and evaporated under reduced pressure. The residues were purified on a silica gel column using ethyl acetate/hexane (1:9) as eluent to give compound **4c** as a yellow oil; yield: 0.191 g (0.42 mmol, 91%).

Typical Procedure for the Synthesis of (2*E*,6*E*)-*N*-Butyl-3-methyl-*N*-(methylsulfonyl)-5,7-diphenylhepta-2,6-dienamide (5c)

To a dry toluene solution (2 mL) of Ph_3PAuCl (0.021 g, 0.042 mmol) and AgOTf (0.011 g, 0.042 mmol) was added a toluene (1 mL) solution of *N*-butyl-*N*-(3-methylbut-3-en-1-yn-1-yl)methanesulfonamide **1a** (0.09 g, 0.42 mmol) and (*E*)-1,3-diphenylprop-2-en-1-ol, **3c** (0.088 g, 0.42 mmol) at room temperature; the resulting mixture was stirred for 2.5 h. The resulting solution was filtered over a short celite bed, and evaporated under reduced pressure. The residues were purified on a silica gel column using ethyl acetate/hexane (1:9) as eluent to give compound **5c** as a yellow oil; yield: 0.168 g (0.39 mmol, 95%).

Acknowledgements

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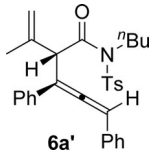

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