Gold-Catalyzed 1,2-Acyloxy Migration/Coupling Cascade of Propargyl Diazoacetates: Synthesis of Isomycin Derivatives

Ming Bao,[†,§,∥] Xin Wang,[†,∥] Lihua Qiu,[§] Wenhao Hu,[†] Philip Wai Hong Chan,*[,‡,¶] and Xinfang Xu*[,†,§]

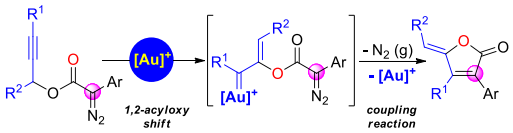
[†]School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou, 510006, China

[§]College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

[‡]School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

[¶]Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom

Supporting Information Placeholder

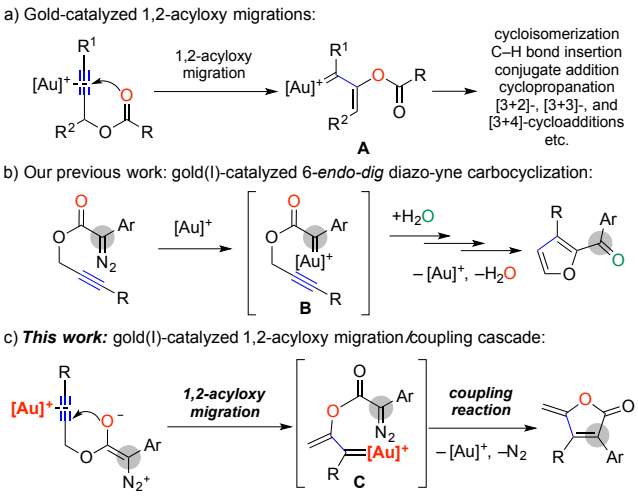


- Preferential 1,2-acyloxy shift of a propargyl ester with a diazo motif
- Novel cascade reaction, mild conditions & broad substrate scope
- Useful isomycin derivatives & amenable to gram-scale synthesis

ABSTRACT: An efficient gold(I)-catalyzed carbocyclization reaction for the synthesis of isomycin derivatives from propargyl diazoacetates has been developed. The suggested cyclization pathway delineated the first example of a vinyl gold carbenoid species generated *in situ* from gold(I)-catalyzed 1,2-acyloxy migration and intercepted by a cross-coupling reaction with the remaining tethered diazo functionality. The use of protic additives was essential to regulating the reaction outcome by fine-tuning the catalytic preference of the gold(I) complex.

Homogeneous gold-catalyzed alkyne transformations have emerged as some of the most powerful tools for the rapid assembly of complex molecules from readily available materials.[1-3] A particularly attractive strategy among the advances made in the field is the [2,3]-sigmatropic rearrangement of propargyl esters (Scheme 1a).[2] This is followed by further functionalization by a remaining pendant moiety of the ensuing vinyl gold carbenoid species **A**.[4-13] In recent years, such subsequent functional group transformations have included intramolecular cyclization/cycloisomerization,[4-6] C–H bond insertion,[7] conjugate addition,[8] cyclopropanation,[9] and [3+*n*]-cycloadditions (n = 2–4)[10-12] amongst others.[13] A cascade process that is initiated by selective 1,2-acyloxy migration of a propargyl ester unit rather than the decomposition of an azide or diazo group in substrates containing both moieties and access to a potentially wider scope of carbocyclic and heterocyclic products, by contrast, has remained unexplored. One possible reason for this could be due to the propensity in such substrates to undergo preferential decomposition of azide or diazo group over alkyne activation.[14,15] Added to this is a recent study by us showing the gold(I)-catalyzed reaction of propargyl diazoacetates favoring the *in situ* formation of the putative organogold intermediate **B** (Scheme 1b).[16] This was followed by a ylide formation, cyclization and cycloisomerization cascade to give a wide variety of 2-furyl-substituted aryl ketone derivatives.

Scheme 1. Catalytic Alkyne Carbocyclizations

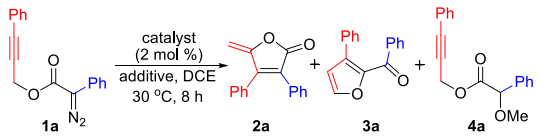


Recently, a number of studies have highlighted carbene/alkyne metathesis (CAM) cascade reactions of alkynyl-tethered diazo compounds to be an efficient and straightforward strategy for the construction of polycyclic frameworks.[17-19] Inspired by these works and as a continuation of our interest in CAM cascade reactions,[19] we were intrigued to the potential reaction chemistry of propargyl diazoacetates **1** initiated by a

gold(I)-catalyzed 1,2-acyloxy migration (Scheme 1c). We envisaged this might be facilitated by exploiting an appropriate gold(I) complex that was more π- than σ-bond acceptor in nature and thus favor alkyne motif activation over direct dinitrogen extrusion.[20] Herein, we report our recent results on this direction involving gold(I)-catalyzed 1,2-acyloxy migration of propargyl diazoacetates with retention of the diazo functionality. This is followed by the cross-coupling reaction of the gold carbenoid motif with the diazo tether in the ensuing organogold species **C** and the delivery of isomycin derivatives in high yields for a wide variety of substrates under mild reaction conditions. It provides a facile and chemoselective route to a core structural motif that is found in many bioactive molecules with anti-inflammatory, antibacterial, and anticancer activities.[21] It also demonstrates the ability to control the chemoselective outcome of such reactions in gold catalysis through the introduction of protic additive(s) that can fine-tune the catalytic preference of the metal complex.[22]

We began our studies by examining the metal-catalyzed cyclizations of propargyl diazoacetate **1a**, readily prepared by esterification of phenylacetic acid with phenylpropiolic alcohol followed by a diazo-transfer reaction, to establish the optimum conditions (Table 1).[16] Initial studies with PPh_3AuNTf_2 as the catalyst in 1,2-dichloroethane (DCE) revealed that the chemoselective outcome of the reaction was dominated by the used additives (entries 1-6). The reaction gave a mixture of the isomycin **2a** and 2-furyl-substituted phenyl ketone **3a** in respective yields of 12 and 57% in the absence of an additive (entry 1). The introduction of 4 Å molecular sieves (MS) to the reaction conditions was found to lead to the dimerization product of the substrate being isolated as a 2:1 mixture of *Z*/*E* isomers in 88% yield (entry 2). In contrast, reactions with either water or methanol or the latter with 4 Å MS were shown to give a mixture of both *O*-heterocycles or the propargyl ester **4a** (entries 3–5). Our investigations subsequently discovered the combination of water and methanol in a 2:1 ratio gave the best result, promoting the desired cyclization to give **2a** in

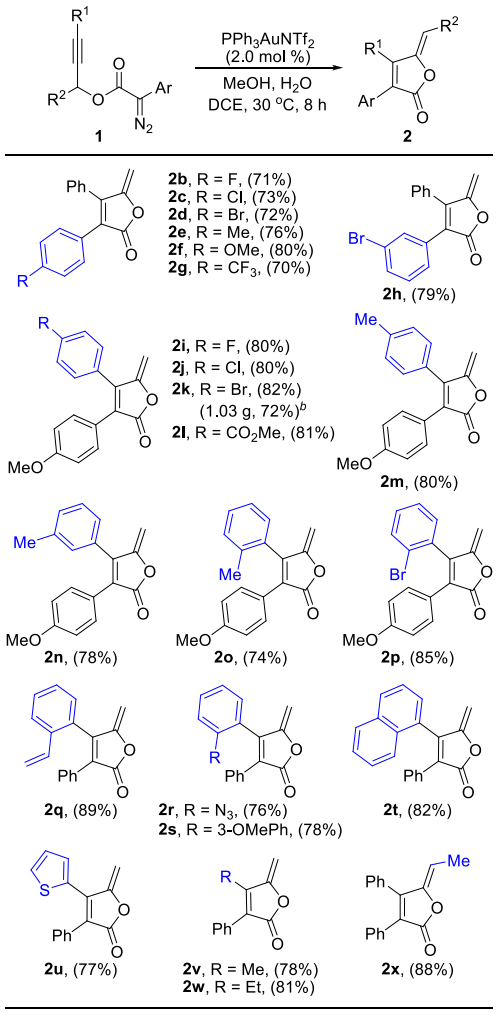
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	additive	yield (%)[b] **2a**/**3a**/**4a**
1	PPh_3AuNTf_2	-	12/57/-
2[c]	PPh_3AuNTf_2	4Å MS	-/-/-
3	PPh_3AuNTf_2	H_2O	11/83/<5
4	PPh_3AuNTf_2	MeOH	43/18/15
5	PPh_3AuNTf_2	MeOH + 4Å MS	-/-/86
6	PPh_3AuNTf_2	MeOH + H_2O	84/<5/<5
7	PPh_3AuCl + $AgSbF_6$	MeOH + H_2O	79/9/<5
8	JohnPhosAu(CH_3CN)SbF_6	MeOH + H_2O	-/23/65
9	$IPrAuNTf_2$	MeOH + H_2O	-/<5/90
10	$AgSbF_6$	MeOH + H_2O	18/<5/70
11	$Rh_2(OAc)_4$	MeOH + H_2O	-/-/74
12	$ZnCl_2$	MeOH + H_2O	-/-/62
13	$Cu(OTf)_2$	MeOH + H_2O	-/-/78[d]
14	PPh_3AuNTf_2	EtOH + H_2O	78/10/-
15	PPh_3AuNTf_2	*i*PrOH + H_2O	83/8/-

[a]Reaction conditions: to a solution of catalyst (2.0 mol %), and additive (10.0 equiv of ROH, 5.0 equiv of H_2O, 100 mg of 4 Å MS) in DCE (1.0 mL), was added **1a** (55.2 mg, 0.2 mmol) in DCE (1.0 mL) *via* a syringe pump in 1 h under an argon atmosphere at 30 °C, and the reaction was running for 8 h under these conditions. [b]Isolated yield. [c]The dimerization product of **1a** was isolated in 88% yield as a 2:1 mixture of *Z*/*E* isomers. [d]Product **4a** was obtained in 78% yield at 60 °C.

Scheme 2. PPh_3AuNTf_2-Catalyzed Cyclizations of 1b–x[a]



[a]Reaction conditions: to a solution of PPh_3AuNTf_2 (3.0 mg, 2.0 mol %), MeOH (10.0 equiv), and H_2O (5.0 equiv) in DCE (1.0 mL), was added **1** (0.2 mmol) in DCE (1.0 mL) *via* a syringe pump in 1 h under an argon atmosphere at 30 °C, and the reaction was running for 8 h under these conditions. Values in parenthesis denote isolated product yields. [b]Isolated yield on a 4.0 mmol scale for 12 h.

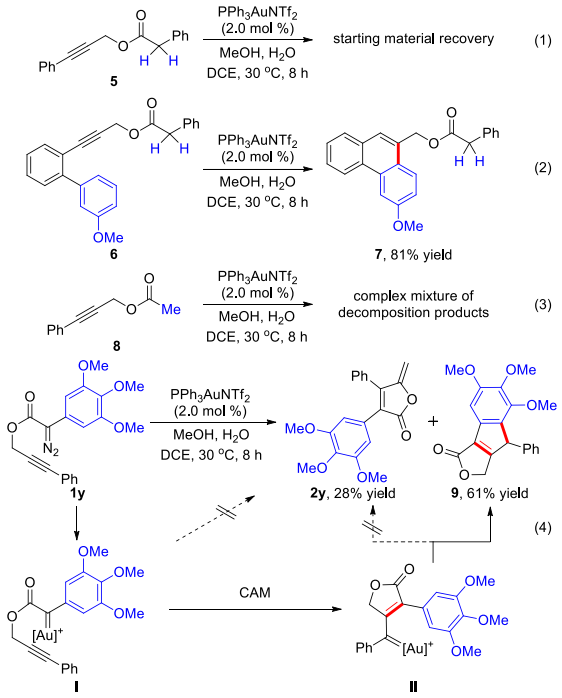
84% yield (entry 6).[22] A comparable product yield of 79% was obtained on switching the counter anion of the gold(I) catalyst from NTf_2^- to SbF_6^- (entry 7).[23] The analogous JohnPhosAu(CH_3CN)SbF_6- and $IPrAuNTf_2$-catalyzed cyclizations were found to influence the outcome of the reaction, giving **3a** and **4a** as the only products in 23 and 65% and <5 and 90% yield (entries 8 and 9). In the case of the control reaction mediated by $AgSbF_6$, a mixture of all three adducts **2a**, **3a** and **4a** in yields of 18, <5 and 70% were found (entry 10). The O–H bond insertion product **4a** was furnished as the only adduct in yields of 62–78% in control experiments with $Rh_2(OAc)_4$, $ZnCl_2$ or $Cu(OTf)_2$ in place of PPh_3AuNTf_2 as the catalyst (entries 11–13). On the other hand, repeating the cyclizations with ethanol or isopropanol instead of methanol was found to afford the isomycin adduct in comparable yields of 78 and 83%, respectively (entries 14 and 15).

With the optimal reaction conditions in hand, the generality of the present procedure was investigated for a series of propargyl diazoacetates (Scheme 2). Overall, the reaction conditions were found to be broad, producing a variety of substitut-

ed isomycins in >70% yields from the corresponding substrates **1b**–**x**. Reactions of starting diazoacetates containging an electron-donating or electron-withdrawing aryl group at the *a*-carbon center to the diazo group were observed to proceed well to afford the corresponding adducts **2b**–**h** in 70–80% yield. Likewise, starting materials in which the distal alkynyl carbon center contained an electron-withdrawing aryl, *p*-tolyl or *m*-tolyl moiety were found to be well tolerated, giving the corresponding products **2i**–**n** in 78–82% yield. This was further exemplified by the reaction of **1k** (4.0 mmol, 1.54 g) at the gram-scale, which furnished **2k** in 72% yield (1.03 g). Substrates with a pendant *o*-tolyl, *o*-bromophenyl, *o*-styrenyl, *o*-azidophenyl or *o*-anisyl group at this position were also shown to have minimal influence on the outcome of the reaction. In these experiments, the corresponding isomycin derivatives **2o**–**s** were obtained in 74–89% yield. Similarly, the 1-naphthyl, 1-thienyl, and alkyl substituted diazo compounds also underwent the reaction smoothly, delivering the corresponding five-membered ring compounds **2t**–**2w** in 77–82% yield. Added to this is one example containing a methyl group at the propargyl carbon center (**1x**), which gave the (*Z*)-alkene adduct **2x** as a single isomer in 88% yield and its structural confirmation by X-ray crystallography.[24] The reactions of substrates containing an acceptor/acceptor or acceptor type diazo functionality or TMS-tethered alkyne group were found to be the only exception (see Figure S10–S12 in the SI for details). In these latter experiments, either the starting material was recovered or a complex mixture of unidentifiable decomposition products was obtained.

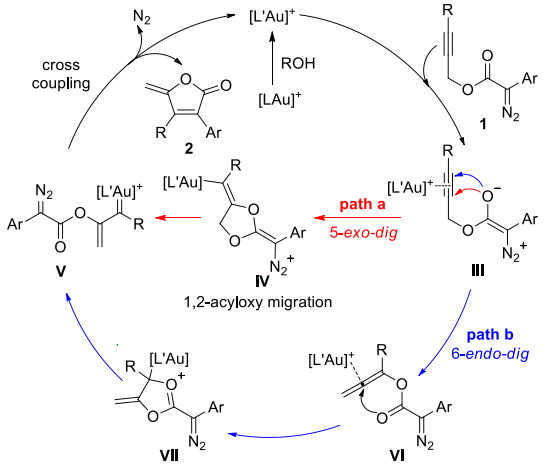
To gain an insight into the reaction mechanism, a series of control experiments were next carried out (Scheme 3). In a first set of control experiments, subjecting the propargyl ester **5** to the gold(I)-mediated standard reaction conditions was found to lead to no reaction (Scheme 3, eq 1). This contrasted to the analogous reaction of propargyl ester **6** containing an electron-rich 1,1'-biaryl motif under gold(I)-mediated standard reaction conditions, which gave the hydroarylation product **7**

Scheme 3. Control Experiments with 1y, 5, 6, and 8



in 81% yield (eq 2). In our hands, treating the propargyl acetate **8** to gold(I)-mediated standard reaction conditions was also found to lead to a mixture of unidentifiable decomposition products (eq 3). Taken together, these findings led us to surmise that delocalization of the diazo group's electron density into the electron-withdrawing carbonyl motif in the substrate to play a key role in promoting the propensity of the latter to undergo the initial 1,2-acyloxy migration step. The observed effect of MeOH and water in deactivating the Au(I) complex toward decomposition of this functional group was also supported by the following control reactions (see Figures S1–S5 in the SI for details).[25] We found subjecting methyl 2-diazo-2-phenylacetate to 2 mol % of PPh_3AuNTf_2 in $CDCl_3$ at 0 °C was found to undergo complete decomposition in 10 mins but required more than 4 h when the reaction was repeated in the presence of MeOH and water (Figures S1 and S2). Likewise, the control experiments with methyl 2-diazo-2-(4-(phenylethynyl)phenyl)acetate was observed to undergo complete decomposition within 10 mins (Figure S3). While no reaction occurred in the presence of methanol and water, complete decomposition of the diazo compound was only found on increasing the reaction temperature to 30 °C after 7 h (Figures S4 and S5). Added to this, the initial premise that product formation did not occur *via* a gold carbenoid species through diazo group decomposition was further supported by our findings for the reaction of **1y** containing a strongly electron-donating trimethoxyphenyl group (Scheme 3, eq 4). Under the standard conditions, the isomycin product **2y** contaminated with tricyclic adduct **9** were obtained in respective yields of 28 and 61%. This would be consistent with the hypothesis that such electronically biased substrates might favor the formation of the gold carbenoid species **I**. Subsequent CAM reaction of this intermediate would then deliver the second gold carbenoid species **II**, which can terminate by an electrophilic aromatic substitution to afford the indenyl-fused γ-lactone.[17,26] It might be anticipated that it would not be possible to form the isomycin **2y** consequently from either generation of the proposed gold carbenoid intermediate species **I** or **II**.

Scheme 4. Proposed Reaction Mechanism



On the basis of above results and previous reports,[2,17] a tentative mechanism for the present Au(I)-catalyzed carbocyclization is presented in Scheme 4. This might initially involve the partial deactivation of the gold(I) complex through its interactions with the alcoholic additive (Figures S7 and S8 in SI for the NMR spectral comparison). As a consequence, this

might sufficiently reduce the propensity of the metal catalyst to preferentially mediate decomposition of the diazo moiety in the substrate. This would then allow the selective activation of the alkyne moiety in **1** to give the organogold complex **III**. Subsequent 1,2-acyloxy migration would give the key vinyl gold carbenoid species **V** *via* **IV** (Scheme 4, path a). A second possibility, that cannot be ruled out, could be the generation of the gold carbenoid species **V** following path b *via* the organogold intermediates **VI** and **VII** in sequence.[27] It might be anticipated that an intramolecular cross-coupling reaction between the tethered diazo group and gold carbenoid motif in **V** would then deliver the product **2**.[28]

In summary, we have disclosed a novel gold(I)-catalyzed 1,2-acyloxy migration/cross-coupling cascade reaction of propargyl diazoacetates, which provides a straightforward method for the synthesis of isomycin derivatives in excellent yields. The salient features of this reaction include readily available starting materials, mild conditions, and broad substrate scope. The mechanistic studies indicate that the synergic effect of an alcoholic additive is essential in this unprecedented cascade carbocyclization transformation, which acts as a regulator of the gold(I) catalyst to preferentially activate the alkyne motif over that of the diazo moiety in the substrate.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental procedure and spectroscopic data for all compounds (PDF), and crystallographic data for **2x** (CIF).

AUTHOR INFORMATION

Corresponding Author

* E-mail: phil.chan@monash.edu
* E-mail: xinfangxu@suda.edu.cn
[I]These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

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crystallographic data centre via www.ccdc.cam.ac.uk/data_request/cif.
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