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Gold-Catalyzed Cascade Cyclization of (Azido)ynamides: An Efficient Strategy for the Construction of Indoloquinolines

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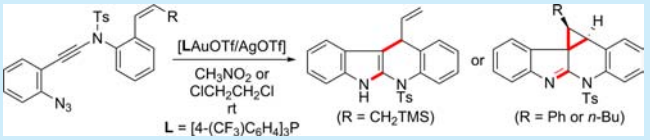
Supporting Information

ABSTRACT: (Azido)ynamides were efficiently converted into indoloquinolines by the use of a gold catalyst. While ynamides bearing an allylsilane gave terminal alkenes, ynamides bearing a simple alkene gave cyclopropanes. This reaction proceeds through the formation of an α-amidino gold carbenoid.



During the past decade, gold has attracted considerable attention as an effective π-acid for the activation of alkynes and allenes,[1] and the gold-catalyzed reactions of alkynes and alkenes have been used extensively to synthesize a broad range of natural products and complex molecules in an efficient and chemoselective manner.[2] In addition to its ability to activate π-bonds, gold ions bearing alkenyl or alkynyl ligands are electron-donating and have the ability to form gold-carbenoid species, which have been reported as intermediates in the reactions of enynes,[3] diynes,[4] and alkynes with *N*-oxides,[5] as well as the rearrangement reactions of 1,2-propargylic esters.[5a,6] In 2005, Toste et al.[7a] reported the use of azide as an effective nitrene equivalent for the generation of a gold-carbenoid species in their synthesis of pyrroles. Following on from this pioneering work, Gagosz[7b] and Zhang[7c] independently reported the development of a novel method for the synthesis of indoles from alkynyl azides by the nucleophilic addition of alcohols or arenes to gold carbenoids. In contrast to these studies, there have been no reports in the literature to date pertaining to the reactivity of ynamides with azides, despite the potential utility of this reaction in the synthesis of α-carboline-type fused indoles.

As a part of our ongoing research toward the development of gold-catalyzed reactions for the construction of the core structures of pharmaceutically important compounds,[8] we became interested in the direct synthesis of the α-carbolines and indoloquinolines. These heterocyclic frameworks can be found in numerous bioactive natural products (Figure 1),[9] as well as a wide range of synthetic derivatives exhibiting antimalarial and antitumor activities.[10] It was envisaged that the gold-catalyzed reaction of (azido)ynamide **A** would lead to the formation of an α-amidino gold-carbenoid **B**, which could be used to produce various indoloquinolines **C**–**E** through an intramolecular trapping reaction with an alkene or arene (Scheme 1). For example, the reaction of the carbenoid **B** with an allylsilane or simple alkene moiety would give terminal alkene **C** or cyclopropane **D**, respectively. It was also envisaged that the reaction of carbenoid **B** with an arene would be effective for the formation of fused indole **E**. Herein, we report the development of a novel method for the construction of indoloquinoline compounds by the gold-catalyzed cascade cyclization of (azido)ynamides.

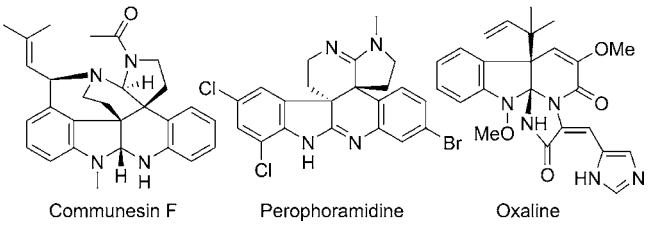
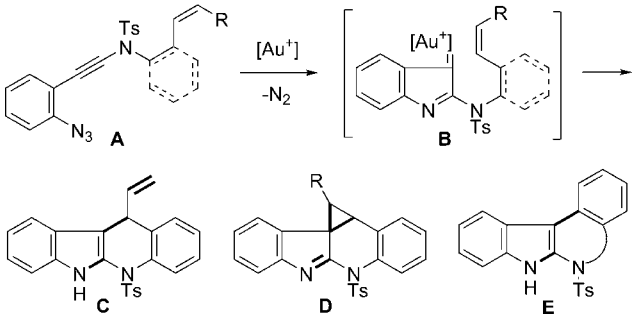


Figure 1. Natural products containing an α-carboline/indoloquinoline framework.

Scheme 1. Concept of This Work



The (azido)ynamide **1a** was prepared by the reaction of tosylamides with a Waser-type alkynylating reagent (Scheme 2).[11] It is noteworthy that bromoalkyne, which has been widely used as an alkynylating reagent for the preparation of ynamides,[12] was ineffective in our hands for the preparation of (azido)-ynamides. Ynamides **1b**–**g** were also prepared in a similar manner (see Supporting Information).

For our initial experiments, we investigated the optimization of the reaction conditions for the synthesis of indoloquinoline **2a**

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Scheme 2. Preparation of (Azido)ynamide 1a

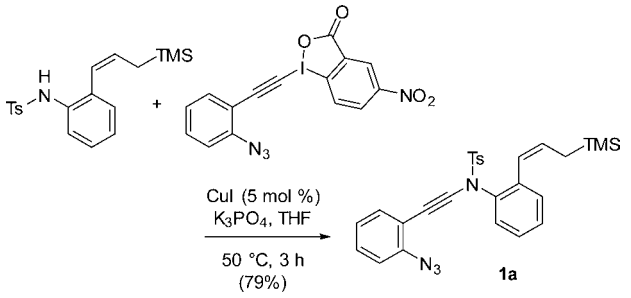
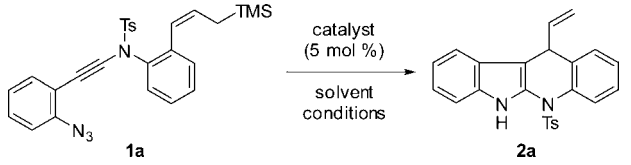
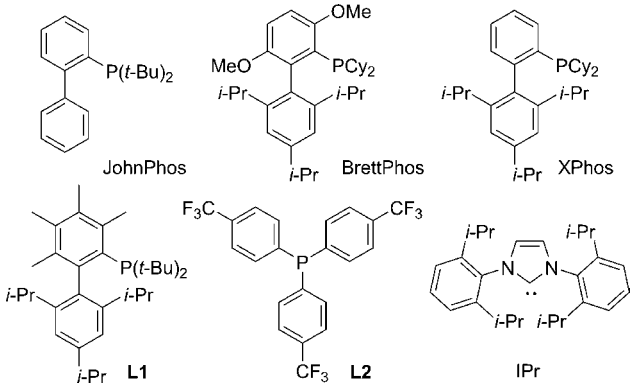


Table 1. Optimization of Reaction Conditions



entry	catalyst	solvent	conditions	yield (%)[a]
1	IPrAuCl/AgNTf$_2$	ClCH$_2$CH$_2$Cl	50 °C, 15 h	11
2	PPh$_3$AuCl/AgNTf$_2$	ClCH$_2$CH$_2$Cl	rt, 10 min	64
3	JohnPhosAuCl/AgNTf$_2$	ClCH$_2$CH$_2$Cl	50 °C, 1.5 h	74
4	BrettPhosAuCl/AgNTf$_2$	ClCH$_2$CH$_2$Cl	50 °C, 10 h	43
5	XPhosAuCl/AgNTf$_2$	ClCH$_2$CH$_2$Cl	50 °C, 10 h	47
6	**L1**AuCl/AgNTf$_2$	ClCH$_2$CH$_2$Cl	50 °C, 4 h	37
7	**L2**AuCl/AgNTf$_2$	ClCH$_2$CH$_2$Cl	rt, 10 min	78
8	PtCl$_4$	ClCH$_2$CH$_2$Cl	40 °C, 12 h	63
9	PtCl$_2$	ClCH$_2$CH$_2$Cl	70 °C, 2 h	trace
10	[**L2**AuCl/AgOTf][b]	ClCH$_2$CH$_2$Cl	rt, 10 min	90
11	[**L2**AuCl/AgOTf][b]	CH$_3$NO$_2$	rt, 10 min	94
12	[**L2**AuCl/AgOTf][b,c]	CH$_3$NO$_2$	rt, 30 min	94

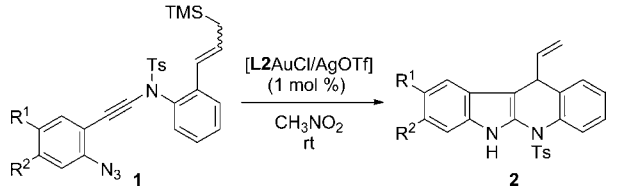
[a]Isolated yield. [b]The catalyst was used following filtration through a pad of Celite. [c]1 mol % of the catalyst was used.



using ynamide **1a** as a model substrate (Table 1). The reaction of **1a** with 5 mol % of IPrAuCl/AgNTf$_2$ in 1,2-dichloroethane at 50 °C gave the desired product **2a**, albeit in a low yield of 11% (entry 1). The use of PPh$_3$AuCl/AgNTf$_2$ as the catalyst led to a significant improvement in the yield, with **2a** being isolated in 64% yield within 10 min at rt (entry 2). Several other phosphine ligands were also screened in the reaction (entries 3−7) with the use of the triarylphosphine **L2** providing **2a** in 78% yield after 10 min at rt (entry 7). PtCl$_4$ was also found to catalyze the reaction, whereas PtCl$_2$ showed barely any activity (entries 8 and 9). Following an extensive period of screening, we found that a combination of **L2**AuCl/AgOTf in nitromethane provided the highest level of activity with **2a** being formed in 94% yield with a decreased loading of the catalyst (1 mol %) (entries 10−12). To the best of our knowledge, this reaction represents the first example of the use of allylsilane as a nucleophilic trapping agent for the capture of a gold-carbenoid species.[13]

With the optimal reaction conditions in hand (Table 1, entry 12), we proceeded to evaluate the substituent effect of the (azido)ynamide **1** (Table 2). Ynamide **1b** bearing an electron-donating methoxy group as the R^1 substituent reacted smoothly under the optimized conditions to give the desired product in 91% yield (entry 1). In contrast, ynamide **1c** bearing an electron-withdrawing trifluoromethyl group at the same position reacted much less efficiently and gave the corresponding product in only 60% yield (entry 2). Electron-donating and -withdrawing groups (i.e., methyl, and methoxycarbonyl and chloro groups, respectively) positioned *para* (R^2) to the alkyne were well tolerated (entries 3−5), although the electron-deficient ynamides **1e** and **1f** required an increase in the loading of the catalyst to 2 mol % (entries 4 and 5). The application of the optimized reaction conditions to (*E*)-allylsilane **1g** resulted in the formation of **2a** in 95% yield (entry 6), which was the same product as that obtained from the corresponding (*Z*)-isomer **1a** (Table 1). These reaction conditions were also successfully applied to the allylamine-type ynamide **3**, where they gave exomethylene derivative **4** in 66% yield (Scheme 3).[14]

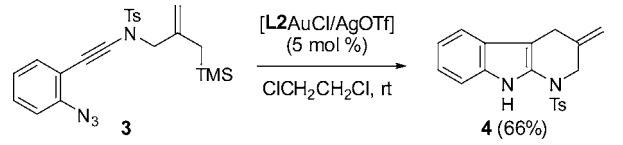
Table 2. Evaluation of the Substituent Effect



entry	substrate (*E*/*Z*)	R^1	R^2	product (%)[a]
1	**1b** (*Z*)	OMe	H	**2b** (91)
2	**1c** (*Z*)	CF$_3$	H	**2c** (60)
3	**1d** (*Z*)	H	Me	**2d** (97)
4	**1e** (*Z*)	H	CO$_2$Me	**2e** (90)[b]
5	**1f** (*Z*)	H	Cl	**2f** (86)[b]
6	**1g** (*E*)	H	H	**2a** (95)

[a]Isolated yield. [b]2 mol % of the catalyst was used.

Scheme 3. Reaction of Allylamine-Type Ynamides 3



We then moved on to investigate the reaction of (azido)-ynamides with simple alkenes with the aim of synthesizing cyclopropane-fused indoloquinolines (Table 3). As expected, ynamides **5a−d**, which had a phenyl or *n*-butyl group as one of their alkene substituents, provided the corresponding cyclopropane compounds **6a−d** in good to excellent yields (entries 1−4).[15] PPh$_3$AuCl/AgNTf$_2$ was used as the catalyst for the reaction of ynamide **5b** because the reaction did not proceed to completion with **L2**AuCl/AgOTf (entry 2). These reactions were found to be stereospecific and provided different products depending on the geometry of the alkene (compare entry 1 vs 3 or entry 2 vs 4). In contrast, the reaction of ynamide **5e** bearing a

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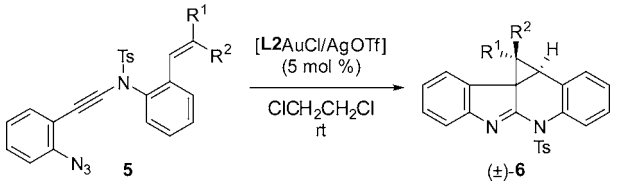
Table 3. Reaction Scope for the Synthesis of Cyclopropanes[a]



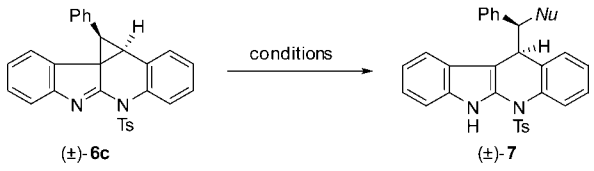
entry	substrate	R^1	R^2	product (%)[b]
1	**5a**	Ph	H	**6a** (94)
2	**5b**	*n*-Bu	H	**6b** (74)[c]
3	**5c**	H	Ph	**6c** (75)
4	**5d**	H	*n*-Bu	**6d** (93)
5	**5e**	H	H	**6e**[d]

[a]Reactions were conducted with 5 mol % of [**L2**AuCl/AgOTf] in 1,2-dichloroethane. [b]Isolated yield. [c]5 mol % of $PPh_3AuCl/AgNTf_2$ was used as the catalyst. [d]Produced as an inseparable mixture.

terminal alkene moiety afforded cyclopropane **6e** as an inseparable mixture of products, presumably because of its instability (entry 5).

We also investigated the ring-opening reactions of cyclopropane **6c** to evaluate the synthetic utility of these cyclopropane-fused indoloquinolines **6** (Scheme 4). The use of

Scheme 4. Ring-Opening Reaction of Cyclopropane

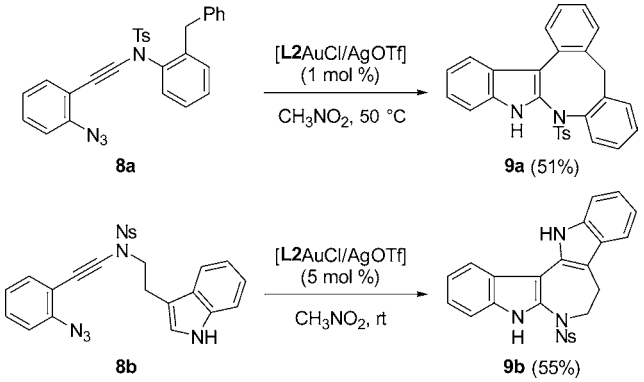


ethanol, NaN_3, and TMSCl as nucleophiles for the ring-opening reaction of **6c** led to the efficient diastereoselective cleavage of the cyclopropane ring to give the corresponding indoloquinoline derivatives **7a**–**c** in excellent yields.[15] These results demonstrated that oxygen, nitrogen, and halogen functional groups could be introduced stereoselectively to the α-position of the side chain.

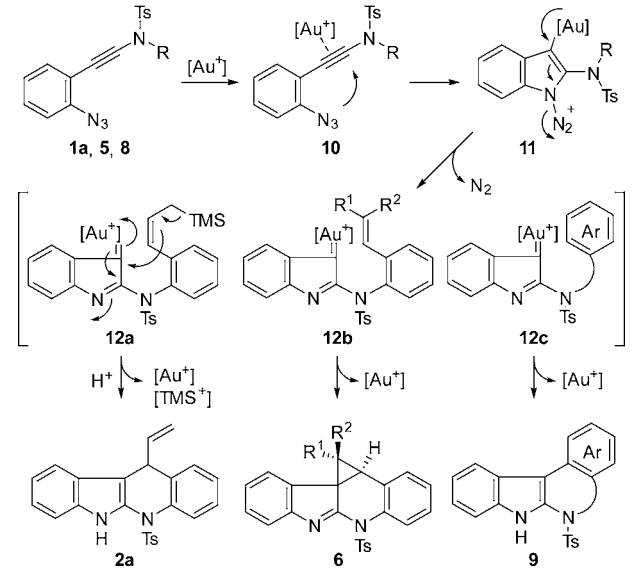
To complete this research, we examined the reaction of (azido)ynamides **8** bearing an aryl group as the trapping functional group (Scheme 5). As expected, the (azido)ynamides **8** underwent a cascade cyclization reaction via the arylation of the corresponding gold carbenoids with a benzene or indole ring to give the azocine- or azepine-fused pentacyclic indoles **9a** and **9b**, respectively, in moderate yields.

Plausible reaction mechanisms for the formation of **2a**, **6**, and **9** by the intramolecular reactions of (azido)ynamides are shown in Scheme 6. Coordination of the gold catalyst to the alkyne as shown in **10** would induce the nucleophilic attack of the azide nitrogen to form **11**. The gold-carbenoids **12a**–**c** would then be formed by the release of molecular nitrogen. Ynamide **1a** bearing an allylsilane moiety would undergo an electrophilic cyclization reaction through the gold carbenoid **12a** to give a carbocation, and subsequent elimination of the TMS group followed by deauration with concomitant aromatization would give indoloquinoline **2a**. The carbenoid **12b** without a silyl group would undergo cyclopropanation of the corresponding gold carbenoid to give **6**.[16] Compound **2a** could also be formed from the

Scheme 5. Construction of Medium-Sized Rings through Arylation



Scheme 6. Plausible Mechanisms for the Reactions of (Azido)ynamides



cyclopropane intermediate **6** (R^1 = H, R^2 = CH_2TMS) by the desilylative cleavage of the cyclopropane ring. In the case of ynamides bearing an aryl group, arylation of the carbenoid moiety would take place from **12c** to give **9** via a nucleophilic addition or C–H insertion pathway.[17]

In summary, we have developed a novel method for the synthesis of indoloquinoline compounds via the gold-catalyzed cascade cyclization of (azido)ynamides. We have shown that a variety of trapping functional groups can be used for this reaction, including allylsilane, simple alkenes, and arenes. This reaction provides a new approach for the synthesis of biologically interesting α-carboline and indoloquinoline-type compounds. Further studies focused on the application of this reaction to the total synthesis of indoloquinoline alkaloids are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data for all new compounds. This material is available freely via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Table 3 and Scheme 5 contained errors in the version published ASAP May 29, 2014; the correct version reposted June 6, 2014.