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Gold Catalysis

Gold-Catalyzed Intramolecular Tandem Cyclization of Indole-Ynamides: Diastereoselective Synthesis of Spirocyclic Pyrrolidinoindolines

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Abstract: A gold-catalyzed intramolecular tandem cyclization of indole-ynamide affords tetracyclic spirocyclic pyrrolidinoindoline bearing an all-carbon quaternary stereocentre in a single step; however, when the reaction was carried out in the presence of $BF_3{\cdot}Et_2O$, the corresponding tricyclic spirocyclic pyrrolidinoindoline-based enones are produced through a key 1,5-hydride shift. The developed chemistry provides a diastereoselective and straightforward entry to structurally diverse polycyclic pyrrolidinoindolines from indole-ynamides in one-pot reactions under mild conditions.

Spirocyclic pyrrolidinoindolines are privileged scaffolds present in a growing number of alkaloids, such as echitamidine **1**,[1] elacomine **2**,[2] kopsifoline D **3**,[3] aspidophytine **4**,[4] and aspidospermine **5**[5] (Figure 1). The biological importance and intriguing molecular architectures of these alkaloids render them highly attractive targets in the synthetic community, and intensive efforts have been concentrated on the development of synthetic methods and strategies for their total synthesis.[6]

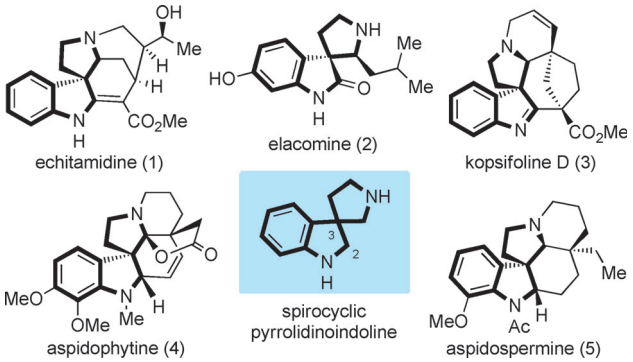

Figure 1. Spirocyclic pyrrolidinoindoline-based alkaloids.

During the past decade, ynamides have emerged as versatile heterocyclic building blocks that have been widely used in the synthesis of structurally diverse heterocycles.[7] Brønsted acid-catalyzed intermolecular vinylation of indoles with ynamides (Scheme 1 a),[8] and gold-catalyzed intermolecular alkylation of indoles with ynamides (Scheme 1 b)[9] have been successfully applied to the synthesis of structurally diverse 3-substituted indole derivatives.

Inspired by the above-mentioned chemistry, we intended to explore the intramolecular consecutive annulation of indole-ynamide **A** to generate pyrrolidinoindoline **D**, and keteniminium ion **B** and iminium ion[10] were proposed as key intermediates in this transformation (Scheme 1 c). However, the step from **A** to **C** could alternatively go through a Au-catalyzed direct auration step from the starting material **A**.[11]

Herein we report an unprecedented keteniminium ion-initiated and iminium ion-mediated cascade annulation based on Au-catalyzed reaction from functionalized indole-ynamides. The chemistry developed allows the diastereoselective synthesis of two types of spirocyclic pyrrolidinoindolines **D** and **F** from common starting material **A**.

Ynamide **6** was prepared from the Cu^{II}-catalyzed cross-coupling of the corresponding indole-sulfonamide and protected alkynyl alcohol.[12] Initial reaction conditions tested for the target reaction made use of the most commonly used Brønsted acids (TsOH,[13] TfOH,[7] and Tf_2NH[7,14]) and Lewis acids (AgOTf[15] and $AuCl_3$[16]) as catalysts, DCM and 1,2-dichloroethane (DCE) > were chosen as solvents as they are commonly used in this type of reaction. Only a small amount of desired annulated product **7** was obtained when trifluoroacetic acid

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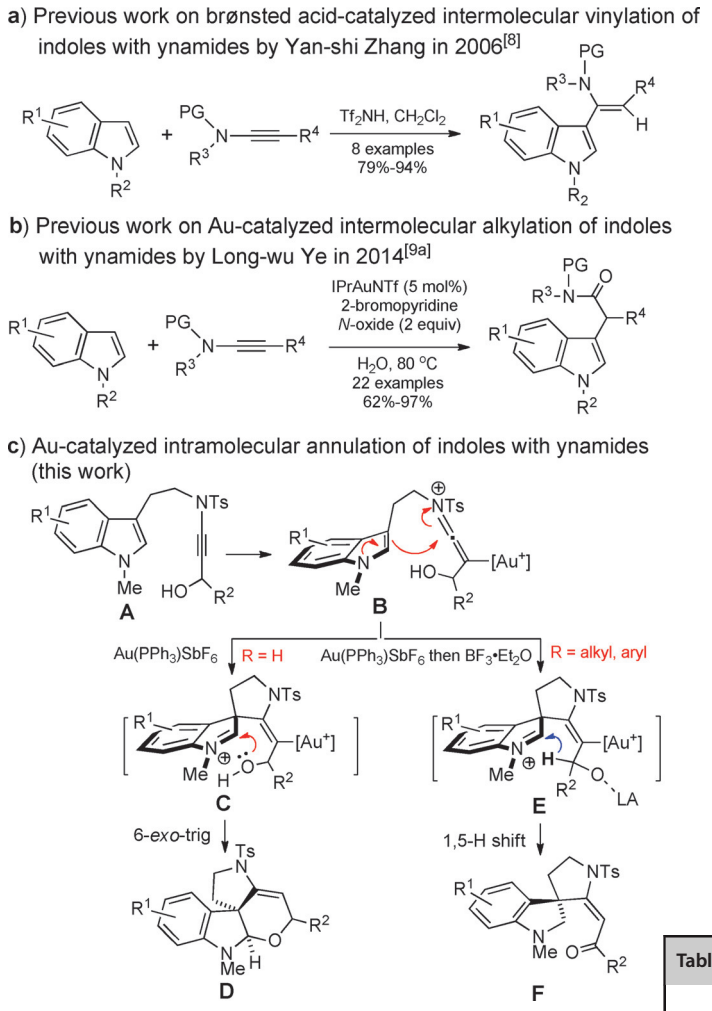


Scheme 1. Previous work and our synthetic analysis.

(TfOH) and triflimide (Tf_2NH) were used (Table 1, entries 2 and 3), and extensive decomposition of ynamide **6** was observed under the other reaction conditions tested (Table 1, entries 1–5).

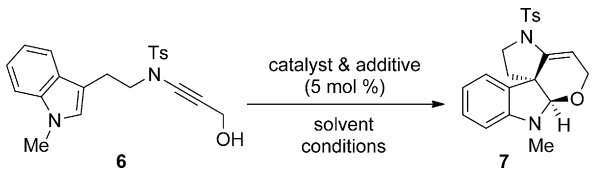
Recently, gold-catalyzed reactions of ynamides have emerged as powerful methods for syntheses of structurally diverse scaffolds.[17] We therefore started to explore Au-catalyzed annulation for the synthesis of product **7** from ynamide **6**. We first tested [(IPr)AuCl]/$AgNTf_2$ (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) as a catalyst,[7q] and to our delight, the desired product **7** was obtained in 60% yield when the reaction was carried out in DCM at 25 °C for 30 min. The structure of **7** was confirmed by 2D-NMR spectroscopy, and later supported by an X-ray crystal structure of its derivative **9q** (Table 2, see the Experimental Section).

To find the optimal reaction conditions, we studied the effect of various reaction parameters (catalyst, solvent, temperature, etc.) on the outcome of the reaction. We found that among the catalysts tested such as [(IPr)AuCl]/$AgNTf_2$, [(IPr)AuCl]/$AgSbF_6$,[12] [PPh_3AuCl]/$AgNTf_2$,[12] [PPh_3AuCl]/$AgSbF_6$,[7q,17c] $PtCl_2$,[17d] [PPh_3AuCl]/$AgSbF_6$ was the most efficient combination. Among the solvents used, DCE was the better choice, and the reaction at 25 °C gave a better and faster result than at 0 °C. Product **7** was obtained in 94% when 5 mol% of [PPh_3AuCl]/$AgSbF_6$ was used at 25 °C in DCE.

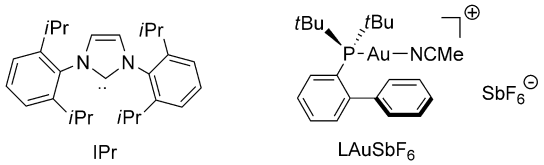
To delineate the scope of this annulation, other ynamides such as **8a**–**8q** were synthesized as their racemic forms, and **8s** was prepared as an enantiomeric pure substrate (see the Supporting Information for details), and annulated under the optimized reaction conditions, and the results are listed in Table 2. All the tested substrates gave satisfactory yields and the reaction went to completion at 25 °C in less than 30 min using the conditions described.

From the results in Table 2, the following observations were made: (1) the use of a benzyl *N*-protecting group (R^1) on the indole ring gave better results than *p*ara-methoxybenzyl (PMB) or allyl groups; (2) varying the ynamide *N*-protecting groups (R^2) from 4-toluenesulfonyl (Ts) to 4-nitrobenzenesulfonyl (Ns) or methanesulfonyl (Ms) (**8d** and **8e**) did not significantly influence the product yields; (3) the presence of electron-donating groups on the indole ring led to higher yields of annulation product than electron-withdrawing groups (**9j**–**9p**), presumably because electron-rich indoles favor the formation of the keteniminium ion-induced spirocyclic pyrrolidinoindolines; (4) 2-methyl indole-based ynamides an-

Table 1. Screening of the reaction conditions.[a]

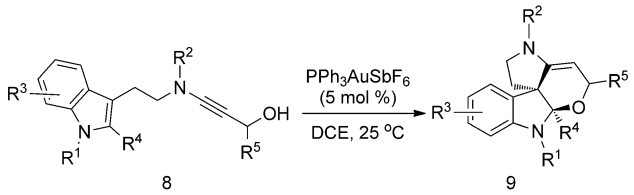


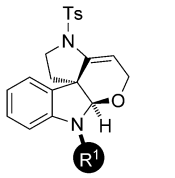
Entry	Catalyst	Additive	T [°C]	Solvent	t	Yield [%][b]
1[c]	TsOH	–	25	DCE	6 h	0
2	TfOH	–	25	DCE	5 min	13
3	Tf_2NH	–	25	DCE	1 h	14
4	AgOTf	-	25	DCE	1 h	0
5	$AuCl_3$	–	25	DCE	5 min	0
6	$PtCl_2$	–	60	DCE	2 h	0
7	(IPr)AuCl	$AgNTf_2$	25	DCM	30 min	60
8	(IPr)AuCl	$AgNTf_2$	0	DCM	30 min	55
9	(IPr)AuCl	$AgSbF_6$	25	DCM	15 min	76
10	PPh_3AuCl	$AgSbF_6$	25	DCM	5 min	89
11	PPh_3AuCl	$AgSbF_6$	25	DCE	5 min	94
12	PPh_3AuCl	$AgNTf_2$	25	DCE	15 min	77
13	$LAuSbF_6$	–	25	DCE	15 min	71
14	–	$AgNTf_2$	25	DCE	1 h	0



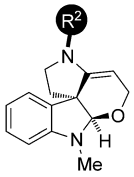
[a] Reaction conditions: **6** = 0.02 M (0.2 mmol). [b] Isolated yield. [c] The TsOH loading is 20 mol%.

Table 2. Substrate scope for tetracyclic pyrrolidinoindolines **9**.[a]

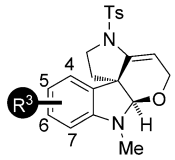




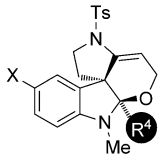
9a: R^1 = Bn, 89%
9b: R^1 = PMB, 86%
9c: R^1 = Allyl, 74%



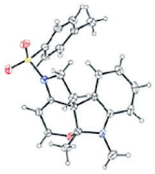
9d: R^2 = Ns, 88%
9e: R^2 = Ms, 90%



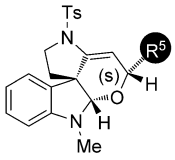
9f: R^3 = 5-OMe, 85%
9g: R^3 = 5-Me, 82%
9h: R^3 = 6-Me, 77%
9i: R^3 = 7-OMe, 76%
9j: R^3 = 5-F, 72%
9k: R^3 = 5-Cl, 75%
9l: R^3 = 5-Br, 70%
9m: R^3 = 5-CN, 52%
9n: R^3 = 5-CO_2Me, 63%
9o: R^3 = 4-CO_2Me, 56%
9p: R^3 = 5-CF_3, 68%

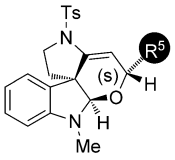


9q: R^4 = Me, X = H, 89%
9r: R^4 = Me, X = F, 78%



X-ray structure of **9q**





9s and **9s'**:[b] R^5 = Me, 69%, d.r. = 1:1

[a] The yields of the products **9a**–**9q**, which are isolated as pairs of enantiomers. For products **9m**, **9n**, **9o** and **9s**, the reaction time was 30 min and for other substrates, the reaction was completed within 5 min. [b] Substrate **8s** was used as its optical pure form.

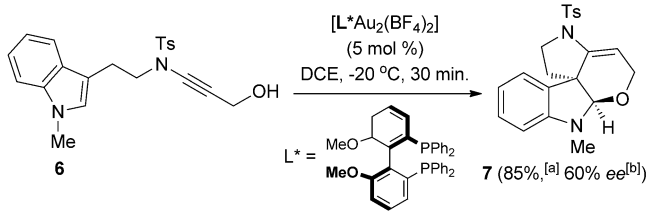
nulated smoothly to afford the expected products **9q** and **9r** in good yields, and again the electron-rich substrate **8q** gave better results than the electron-deficient substrate **8r**; (5) in contrast to a previous report,[18] when enantiomerically pure substrate **8s** underwent annulation under the typical reaction conditions, products **9s** and **9s'** were obtained as a pair of diastereomers in a 1:1 ratio, indicating that the stereogenic center of R^5 does not have any diastereoselective effect on the spirocyclization of ynamides.

To achieve an asymmetric synthesis, we then tested the gold-catalyzed annulation in the presence of chiral ligands.[19] We expected that when an Au-catalyst bearing chiral ligands approached the ynamide, the Au-associated keteniminium species formed could induce the asymmetric nucleophilic addition of indole,[20] thus affording chiral spirocyclic pyrrolidinoindoline. To explore this possibility, several commercially available ligands were tested (see the Supporting Information), and we found that when ynamide **6** was annulated under the optimized conditions in the presence of chiral ligand (*S*)-L*, product **7** was obtained in 85% yield with 60% *ee* (Scheme 2).

To demonstrate the potential of our pyrrolidinoindolines in the synthesis of complex molecules, we then selected compound **9b** as a model, and transformed it into the useful synthetic intermediate **11**,[21] which could potentially be applied to the total synthesis of spirocyclic pyrrolidinoindoline-based natural products, such as those shown in Figure 1. In the event, compound **9b** was easily reduced with $Na(BH_3)CN$, and the resultant allylic alcohol **10** was then oxidized to aldehyde **11** through a Dess–Martin periodinane (DMP)-oxidation in 71% overall yield over two steps (Scheme 3).

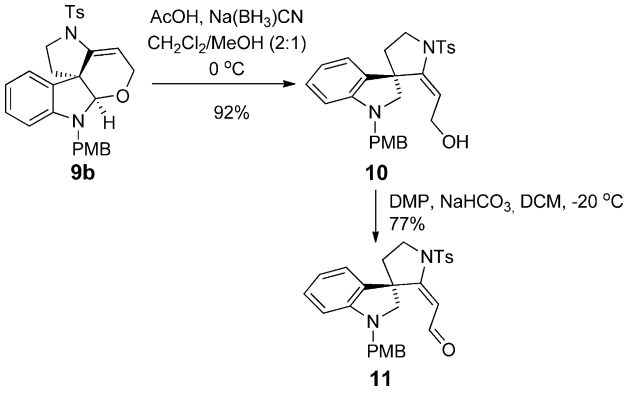
To study the substrate scope of the ynamide annulation, we also interestingly found that the ynamides **12** bearing secondary alcohols could be directly converted into their corresponding tricyclic products **13** in moderate-to-good yields when the reactions were carried out in the presence of additional $BF_3{\cdot}Et_2O$ (Table 3). It is worthwhile to mention that when ynamide **12f** with a substituent at the C2 position of the indole was used, product **13f** was obtained as a single diastereomer.

Scheme 4 highlights our proposed reaction mechanism to account for the observed Au-catalyzed intramolecular tandem cyclization of indole-ynamides and 1,5-hydride shift for the formation of the α,β-unsaturated carbonyl compounds. Accordingly, after coordination of gold catalyst to ynamide **A**, the resultant keteniminium **B** might undergo *5-endo-trig* cyclization[22] to form intermediate **C** (through an *anti*-addition format). Thus, if the reaction proceeded without an additional Lewis acid, the intermediate **C** would undergo a direct *6-exo-trig* nucleophilic addition to afford a tetracyclic product **D**, and the regenerated Au-catalyst could enter into another catalytic cycle. On the other hand, if the reaction proceeded with an additional Lewis acid, such as $BF_3{\cdot}Et_2O$, product **D** would coordinate with the Lewis acid to form intermediate **E** through a hemi-aminol ring opening reaction, which in turn could undergo a 1,5-hydride shift to afford product **F** in a diastereoselective manner.[23] It is noteworthy to mention that other potentially competing reactions, such as the Wagner–Meerwein rearrangement, was not observed in this reaction.[9b,c]



Scheme 2. Application of the chiral dinuclear gold catalyst.
[a] Isolated yield. [b] Determined by HPLC analysis with a chiral column.

To further support our proposed reaction mechanism, two additional experiments were conducted. Our first experiment

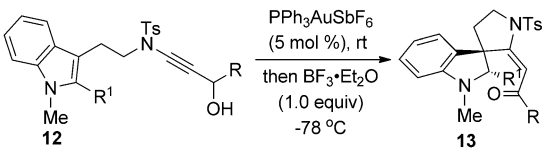


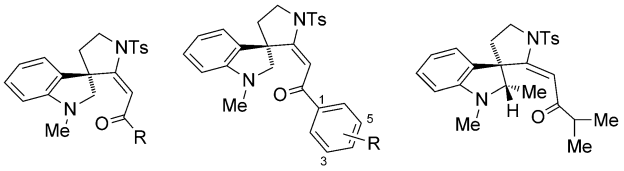
Scheme 3. Synthesis of aldehyde **11**.

was carried out by treating substrate **9b** with $BF_3{\cdot}Et_2O$ (1.0 equiv) in CH_2Cl_2 at −78 °C, as expected, product **11** was obtained in 55% yield, indicating that intermediate **D** (Scheme 4) could be converted into **F** in the presence of Lewis acid. Our second experiment deals with the proposed 1,5-hydride shift in the catalytic cycle. To this end, we have synthesized the deuterated ynamide **12g** in a racemic form, and annulated it under the optimized reaction conditions (Table 2). As expected, the desired product **13g** was obtained in 77% yield as a pair of enantiomers. As the deuterium in **12g** was completely transferred to the C2 position of the indole ring in a diastereoselective manner (see the Supporting Information for 2D-NMR analysis), indicating that the proposed 1,5-hydride shift proceeded through a tight six-membered ring transition state (Scheme 5).

In summary, we have developed a one-pot intramolecular gold-catalyzed tandem cyclization reaction of indole-ynamides for the stereoselective synthesis of structurally complex tetracyclic and tricyclic spiropyrrolidinoindolines with an all-carbon quaternary center. A unique 1,5-hydride shift was observed during the synthesis of the tricyclic pyrrolidinoindoline-based enones. Further investigations on the application of this method in total synthesis of natural products and additional mechanistic studies focused on the 1,5-hydride shift are in progress.

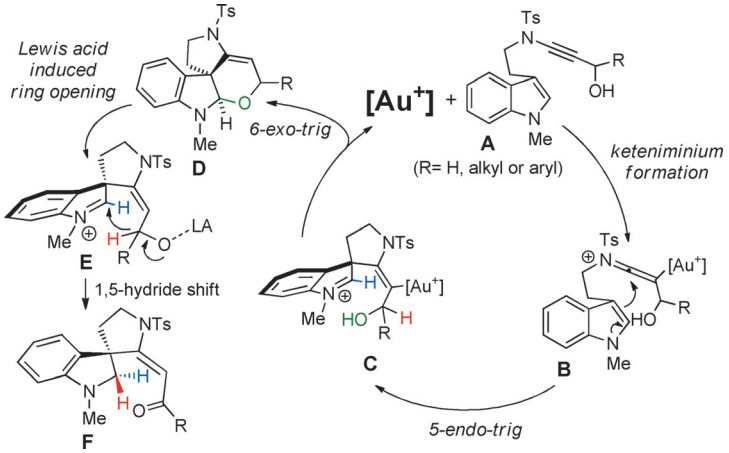
Table 3. One-pot synthesis of tricyclic pyrolidinoindolines **13**.[a]





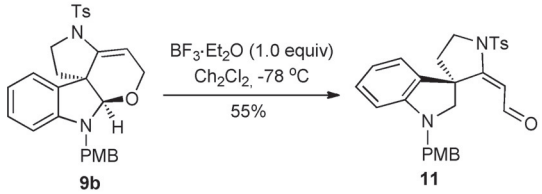
13a:[b] (R = Me, 62%)
13b:[b] (R = Et, 70%)
13c:[b] (R = *i*Pr, 75%)
13d:[b] (R = *i*Bu, 68%)
13ea:[b] (R = H, 54%)
13eb:[b] (R = 4-Me, 60%)
13ec:[b] (R = 3,5-2OMe, 66%)
13f:[b] (81%)

[a] Isolated yield. [b] all the products exist as a pair of enantiomers.

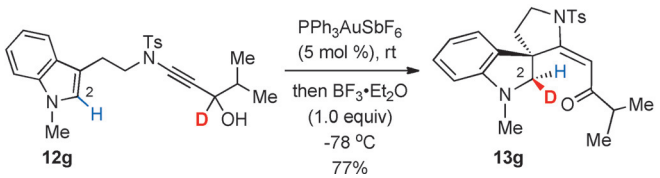


Scheme 4. Proposed reaction mechanism.

■ Lewis acid mediated ring-opening reaction and 1,5-hydride shift for the formation of **11**.



■ Deuterated experiment for the synthesis of **13g** from **12g**.



Scheme 5. Synthesis of compounds **11** and deuterated **13g**.

Experimental Section

The synthetic procedures and characterization of the compounds studied herein can be found in the Supporting Information. CCDC 1401360 (**9q**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Acknowledgements

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Keywords: 1,5-hydride shif · cyclizationt · diastereoselectivity · gold · spirocyclic pyrrolidinoindoline

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