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An Efficient Domino Approach for the Synthesis of Multisubstituted Pyrroles *via* Gold/Silver-Catalyzed Amination/Cycloisomerization of (*Z*)-2-En-4-yn-1-ols

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Abstract: An efficient and one-pot synthesis of multisubstituted pyrroles with high diversity and in a regioselective manner from the reactions of suitably substituted (*Z*)-enynols with amines or sulfonamides under mild reaction conditions has been developed. This synthesis was realized *via* a cascade process in the presence of gold/silver (Au/Ag) or boron trifluoride·etherate/gold/silver ($BF_3 \cdot Et_2O$/Au/Ag) catalysts, which could catalyze amination and cycloisomerization reactions in the same vessel.

Keywords: amination; cycloisomerization; (*Z*)-enynols; gold catalysis; pyrroles

Pyrroles are one of the most important classes of heterocyclic compounds as they widely occur as key structural subunits in numerous natural products which exhibit interesting biological activities,[1] and can find a variety of applications in pharmaceutical use[2] and materials science.[3] Furthermore, substituted pyrroles are of significant interest since they are useful and versatile synthetic intermediates for further structural elaboration.[4] As a consequence, much attention has been paid to the synthesis of pyrrole derivatives either by classic methods such as the Paal–Knorr[5] and Hantzsch syntheses[6] or by transition metal-catalyzed reactions.[7] Nevertheless, enhancing the efficiency of the synthesis that allows the facile assembly of substituted pyrroles, especially, in a regioselective manner, from readily available precursors under mild reaction conditions is highly attractive. Recently, we have reported a general synthetic approach to furans and stereodefined dihydrofurans *via* gold-catalyzed cyclization[8] of (*Z*)-2-en-4-yn-1-ols.[9] Enynes bearing nitrogen nucleophiles such as (*Z*)-(2-en-4-ynyl)amines would represent an important class of suitable substrates in a metal-catalyzed strategy for pyrroles due to the structural analogy with (*Z*)-enynols. However, there are only limited reports about the cyclization of (*Z*)-enynamines to pyrroles. Gabriele et al. have reported that $CuCl_2$ or PdX_2/KX could catalyze cycloisomerizations of these substrates to a variety of pyrroles under neutral conditions.[7b] They also disclosed that a spontaneous cyclization occurred without the use of a metal when specific substrates (i.e., terminal alkynes) were employed. However, the reactions were usually carried out in a dipolar aprotic solvent such as DMA, and, especially with enynamines bearing a substituent at C-3, a high temperature of 100 °C was required. Recently, Gagosz et al. have shown that a gold(I) complex of $Ph_3PAuNTf_2$ could act as an efficient catalyst in the cyclization of enynamines (only enynamines unsubstituted at C-1 have been tested in this work).[7c] In these methods, the substrate enynamines were generally prepared from (*Z*)-enynols through tedious multistep transformations involving bromination/amination (for enynamines unsubstituted at C-1) or through oxidation/condensation with amine/addition of organolithiums to the performed imines (for enynamines substituted at C-1) that are usually synthesized prior to such usage. An ideal strategy for such cyclizations is through a domino process directly from (*Z*)-enynols and amines catalyzed by a single-pot catalyst to improve the efficiency. On the other hand, we recently developed a straightforward synthesis of allylic amines from allylic alcohols[10] through direct amination[11] by utilization of gold as catalyst under mild reaction conditions. Based on this work, we envisioned

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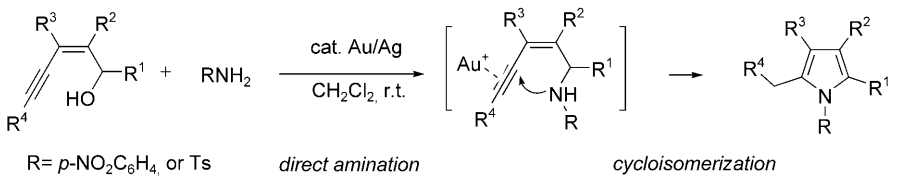


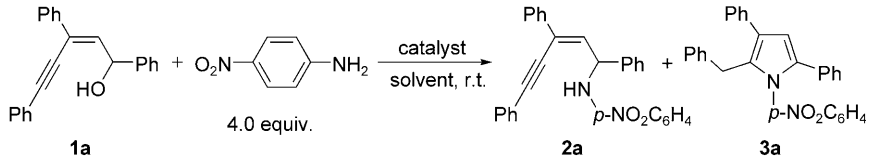
Scheme 1.

that pyrroles might be constructed directly from (*Z*)-enynols. Herein, we describe our study of this new approach which combines an initial Au/Ag-catalyzed amination of (*Z*)-enynols followed by an intramolecular hydroamination[12] (or cycloisomerization) of the alkyne moiety in a one-pot procedure,[13] and there is no need to isolate the intermediate enynamines (Scheme 1).

In the proposed process, two independent reactions should occur sequentially by a single-set catalyst. Our initial efforts were made on the optimization of an efficient one-pot catalyst system for pyrrole formation from the readily available 3-phenyl-substituted (*Z*)-enynol. On the basis of our previous observations, we first examined the reaction of **1a** with 4-nitroaniline in the presence of $AuCl_3$ (Table 1, entry 1). However, only amination product **2a** was obtained in 65% yield. After much effort, we were delighted to find that the reaction proceeded smoothly and provided an 84% yield of the pyrrole **3a** at room temperature in 1 h with 5 mol% (p-MeOC$_6$H$_4$)$_3$P-AuCl and 10 mol% $AgBF_4$ as catalysts (Table 1, entry 2). Using TsNH$_2$ instead of 4-nitroaniline afforded a low yield of the desired pyrrole (some other by-products were formed). Decreasing the amount of amine or the catalyst loading of $AgBF_4$ resulted in a decreased yield of **3a** (66% and 54%, respectively, Table 1, entries 3 and 4). Ph$_3$P-AuCl could also be used but resulted in a lower yield of 62% (Table 1, entry 5). A control experiment showed that the silver salt alone could only afford the substitution product **2a** in a high yield of 90% (Table 1, entry 6). When addition of 5 mol% gold catalyst to the reaction mixture after formation of **2a** catalyzed by $AgBF_4$, the cyclization product **3a** was obtained in 83% yield (Table 1, entry 7). The results indicated that the pyrrole derivative **3a** might be formed through a cationic Au(I)-catalyzed intramolecular cycloisomerization of the enynamine intermediate **2a**. The structure of the pyrroles was further confirmed by X-ray crystallographic analysis of **3a**.[14]

The present method could be applied successfully to various enynols **1** and **4**, both acyclic and/or bearing a cyclic ring, to provide the corresponding pyrroles in generally good to high yields (Table 2 and Table 3). The domino-type cyclizations of enynols **1a**–**1k** bearing a substituent at the C-3 position were investigated firstly. It was found that the aromatic ring of R^1 at C-1 bearing an electron-withdrawing group

Table 1. Optimization studies for the formation of pyrroles.



Entry	Catalyst	Solvent	Time	Yield [%] of **2a**[a]	Yield [%] of **3a**[a]
1	5% $AuCl_3$	CH_3CN	4 h	65	trace
2	5% (p-MeOC$_6$H$_4$)$_3$P-AuCl, 10% $AgBF_4$	CH_2Cl_2	1 h		84
3	5% (p-MeOC$_6$H$_4$)$_3$P-AuCl, 10% $AgBF_4$[b]	CH_2Cl_2	1 h		66
4	5% (p-MeOC$_6$H$_4$)$_3$P-AuCl, 5% $AgBF_4$	CH_2Cl_2	20 h	trace	54
5	5% Ph$_3$P-AuCl, 10% $AgBF_4$	CH_2Cl_2	1 h	trace	62
6	10% $AgBF_4$	CH_2Cl_2	4 h	90	—[c]
7	i) 10% $AgBF_4$, 3 h, ii) 5% (p-MeOC$_6$H$_4$)$_3$P-AuCl, 3 h	CH_2Cl_2			83

[a] Isolated yields.
[b] 2 equiv. of 4-nitroaniline were used.
[c] Not observed.

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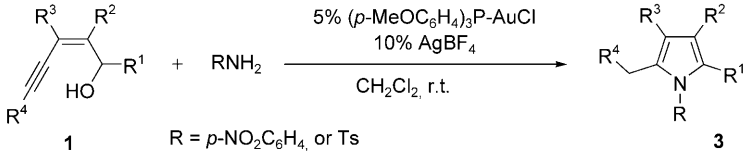
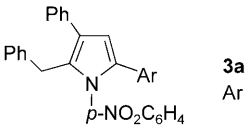
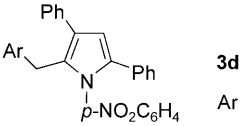
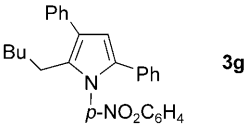
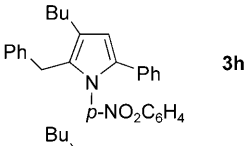
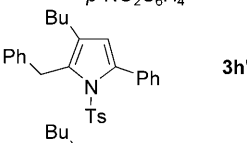
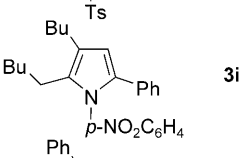
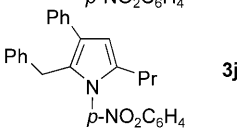
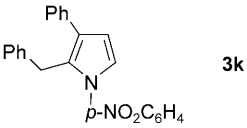
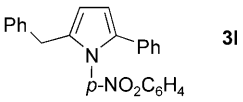
Table 2. One-pot synthesis of pyrroles through the reactions of (*Z*)-enynols with amines.



Entry	Enynol	R^1	R^2	R^3	R^4	Time	Product	Yield [%][a]
1	**1a**	Ph	H	Ph	Ph	4 h		**3a** Ar = Ph 84
2	**1b**	*p*-ClC_6H_4	H	Ph	Ph	4 h	Ar = *p*-ClC_6H_4	**3b** 72
3	**1c**	*p*-$MeOC_6H_4$	H	Ph	Ph	4 h	Ar = *p*-$MeOC_6H_4$	**3c** 59
4	**1d**	Ph	H	Ph	*p*-ClC_6H_4	4 h		**3d** Ar = *p*-ClC_6H_4 77
5	**1e**	Ph	H	Ph	3,5-di$MeOC_6H_3$	1 h	Ar=3,5-di$MeOC_6H_3$	**3e** 75
6	**1f**	Ph	H	Ph	*p*-$MeOC_6H_4$	12 h	Ar=*p*-$MeOC_6H_4$	**2f** 40[b]
7	**1g**	Ph	H	Ph	Bu	5 h		**3g** 88
8	**1h**	Ph	H	Bu	Ph	1 h		**3h** 77
9	**1h**	Ph	H	Bu	Ph	4 h		**3h'** 62
10	**1i**	Ph	H	Bu	Bu	1 h		**3i** 68
11	**1j**	Pr	H	Ph	Ph	7 h		**3j** 82[c]
12	**1k**	H	H	Ph	Ph	8h		**3k** 46[d]
13	**1l**	Ph	H	H	Ph	10 h		**3l** 51[c]

[a] Isolated yields.
[b] In this case, only amination product of **2f** was obtained, which was concomitant with small amount of by-product.
[c] 5% $BF_3{\cdot}Et_2O$, room temperature, 2–4 h, then 5% $(p\text{-}MeOC_6H_4)_3P\text{-}AuCl$/10% $AgBF_4$, room temperature, *ca.* 5 h.
[d] 2 equiv of $BF_3{\cdot}Et_2O$, 50 °C, 4.5 h, then 5% $(p\text{-}MeOC_6H_4)_3P\text{-}AuCl$/10% $AgBF_4$, room temperature, 2 h, in DCE.

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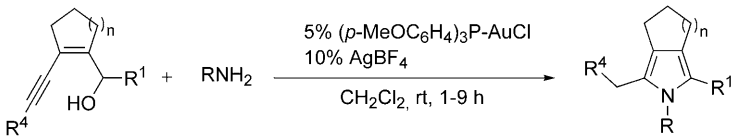
Table 3. Formation of pyrroles fused with carbocycles.



Entry	Enynol	n	R^1	R^4	R	Product	Yield [%][a]
1	**4a**	1	Ph	Ph	p-$NO_2C_6H_4$	**5a**	80
2	**4a**	1	Ph	Ph	Ts	**5a'**	76
3	**4b**	1	p-MeC_6H_4	Ph	Ts	**5b**	70
4	**4c**	1	1-biphenyl-4-yl	Ph	Ts	**5c**	57
5	**4d**	1	p-BrC_6H_4	Ph	Ts	**5d**	76
6	**4e**	1	2-naphthyl	Ph	Ts	**5e**	54
7	**4f**	2	Ph	Bu	Ts	**5f**	72[b]

[a] Isolated yields.
[b] 5% $BF_3{\cdot}Et_2O$, room temperature, 1 h, then 5% $(p\text{-}MeOC_6H_4)_3P\text{-}AuCl$/10% $AgBF_4$, room temperature, 2 h.

(Cl) or an electron-donating group (OMe) were all compatible under the reaction conditions, furnishing the corresponding pyrroles **3b** and **3c** in 72% and 59% yields, respectively (Table 2, entries 2 and 3). The aryl substituents on the alkyne moiety had a big influence on the reaction process, whereas a p-Cl (**1d**) or 3,5-dimethoxy-substituted **1e** afforded the corresponding products **3d** and **3e** in good yields, the p-MeO-substituted **1f** only led to amination product **2f** in 40% yield, along with several by-products (Table 2, entries 4 and 6). The reaction also proceeded smoothly with C-5 or C-3-alkyl-substituted enynols **1g–i** to produce the products **3g–i** in 62–88% yields (Table 2, entries 7–10). A tosylated pyrrole **3h′** could also be obtained in 62% yield in the case of enynol **1h** (Table 2, entry 9). Notably, the enynol **1j**, bearing an alkyl-substitutent at C-1, afforded **3j** in a low yield of 17%, moreover, the furan derivative was isolated as the major product.[15] The results, by comparison with the yields obtained from C-1 aryl-substituted enynols, indicated that the reaction rate of amination in this case is much slower than the cycloisomerization through an oxygen nucleophile due to the lower stability of the allylic cation intermediate formed *in situ*. It also showed that the substituent effect on C-1 played an important role in the amination. We then tried the reaction of **1j** by first addition of 10% $AgBF_4$ to the reaction mixture, to our surprise, no reaction took place under these conditions. Next, we were pleased to find that $BF_3{\cdot}Et_2O$ can remarkably promote the amination. Thus, by first stirring the reaction mixture in the presence of 5 mol% $BF_3{\cdot}Et_2O$ for 2 h, and then subsequent addition of Au/Ag catalysts, the desired pyrrole **3j** could be obtained in a high yield of 82% (Table 2, entry 11). Analogously, enynol **1k** unsubstituted at C-1 or **1l** unsubstituted both at C-2 and C-3 afforded the corresponding products **3k** and **3l** in 46% and 51% yields, respectively (Table 2, entries 12 and 13).

The cyclization has also been successfully extended to various enynols **4a–f** fused with 5- or 6-membered carbocycles, and moderate to good yields were realized for all cases. It should be noted that for enynol **4f** fused with a six-membered ring, the use of $BF_3{\cdot}Et_2O$ was required to first achieve the amination (Table 3, entry 7).

To further understand the reaction mechanism, the cycloisomerization of isolated enynamine **2a** was carried out (Scheme 2). Interestingly, it was found that only a 38% yield of **3a** was formed along with several by-products in the absence of any additives. To our surprise, when 3 equiv. of 4-nitrophenylamine was used as an additive, the desired **3a** was isolated in 90% yield. The results showed that the excess amine played an important role in the cycloisomerization of **2a**, and also in the one-pot process. It may facilitate a clean cyclization by serving as a co-ligand to stabilize the cationic gold(I) intermediates.

In summary, we have developed an Au/Ag-catalyzed amination/cycloisomerization of (Z)-enynols with amines or sulfonamides under mild reaction conditions, which provided an efficient one-pot route to multisubstituted pyrroles with high diversity and in a regioselective manner. The Lewis acid $BF_3{\cdot}Et_2O$ was required in some cases to realize a successful domino process, depending on the substitution pattern on the

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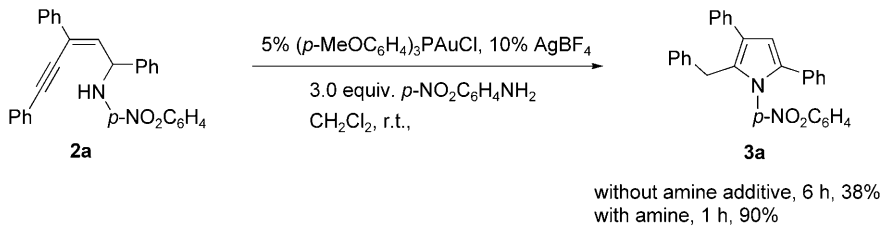

Scheme 2.

enynols. These compounds are potentially useful in pharmaceutical and materials science. Further studies to extend the scope of synthetic utility for this Au/Ag-catalyzed cascade reaction are in progress in our laboratory.

Experimental Section

General Procedure for the Au/Ag-Catalyzed One-Pot Synthesis of Pyrroles from (*Z*)-2-En-4-yn-1-ols

To a solution of (*Z*)-enynols **1** or **4** (0.3 mmol) in 10 mL CH_2Cl_2 was added 4-nitroaniline (1.2 mmol). After the 4-nitroaniline had dissolved, $(p\text{-}MeOC_6H_4)_3P\text{-}AuCl$ (5 mol%) and $AgBF_4$ (10 mol%, used as a 0.05 M solution in toluene) were added successively. The resulting solution was stirred at room temperature until the reaction was complete as monitored by thin-layer chromatography. The solvent was removed under vacuum and the residue was purified by chromatography on silica gel to afford the pyrrole derivatives.

Supporting Information

Experimental details and spectroscopic characterization of all new compounds are given in the Supporting Information file.

Acknowledgements

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[15] See Supporting information.

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