

Tandem Gold(III)-Catalyzed Amination-Intramolecular Hydroamination Reactions of 1-En-4-yn-3-ols with Sulfonamides: Efficient Approach to Highly Substituted Pyrroles

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Abstract: A simple, convenient and efficient synthetic approach to highly substituted pyrroles has been developed by utilizing a gold(III)-catalyzed tandem amination-intramolecular hydroamination reaction. The first examples of gold-catalyzed, selective amination of 1-en-4-yn-3-ols have also been disclosed.

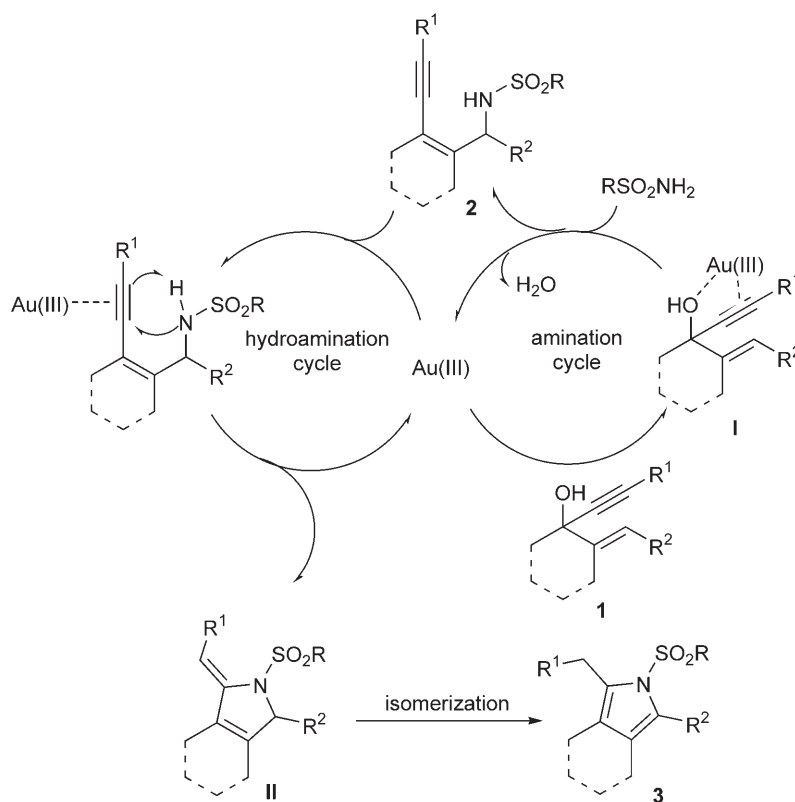
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The pyrrole core is an important heteroaromatic system found in a diverse array of structures, including those of many natural products,^[1] biologically active agents,^[2] and components in polymers.^[3] The construction of this important class of heterocycle typically relies on reactions which date from the 19th century, such as the Paal–Knorr cyclization^[4] and the Hantzsch synthesis.^[5] These classic condensation reactions can be limited in their efficiency, functional group compatibility, regioselectivity, and substituent diversity. Although more recent progress in pyrrole syntheses including catalytic multicomponent coupling approaches^[6] and transition metal-based strategies^[7] looks attractive, a general approach by converting commercially available or readily accessible materials in one step to highly substituted pyrroles is still lacking.

Gold catalysts have recently been shown to be superior reagents in activating alkynes and alkenes towards nucleophilic attack,^[8] especially in the field of hydroamination^[9] which offers an attractive alternative means for C–N bond formation. However, only few examples of the gold-catalyzed synthesis of highly

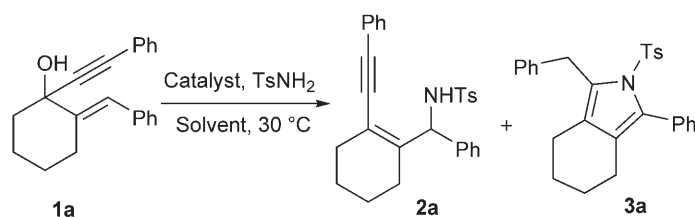
substituted pyrroles have been reported.^[10] This strongly motivated us to extend our research into this area. In our ongoing efforts to develop new methodologies for the synthesis of heterocycles promoted by transition metal catalysts,^[11] we envisioned that 1-en-4-yn-3-ols **1**, readily available from alkynes and α,β -unsaturated ketones, might undergo the following process (Scheme 1), leading to highly substituted pyrroles. First, being activated by gold catalysts,^[12] propargylic alcohols **1** should undergo an amination process with excellent regiochemical selectivity to afford enynamines **2**.^[13] Then compounds **2** could undergo intramolecular hydroamination to afford products **II** followed by facile isomerization resulting in the pyrroles **3**. Herein, we report a convenient synthetic approach to highly substituted pyrroles by utilizing a gold(III)-catalyzed tandem amination-hydroamination process. In this simple two-step, one-pot reaction, readily available propargylic alcohols **1** and sulfonamides are used as starting materials to produce pyrrole products **3** with high diversity.

We started by treating propargylic alcohol **1a** (0.3 mmol) and TsNH₂ (15 equivs.) with 5 mol % of H₂AuCl₄·4H₂O in CH₃CN (2 mL) and, gratifyingly, the desired product **3a** was formed in 21 % yield after 8 h, along with uncyclized enynamine **2a** (37 % yield; Table 1, entry 1). To our delight, on increasing the amount of catalyst to 20 %, an excellent yield (81 %) of **3a** was obtained and no intermediate **2a** could be isolated (Table 1, entry 3). With other gold catalysts, such as NaAuCl₄·2H₂O, AuCl₃, AuCl and Au(I) systems generated from silver salts, no superior results were obtained (Table 1, entries 4–8). PtCl₂ and protic acid such as chloroacetic acid have also been applied to the reaction under identical conditions, but no reaction occurred (Table 1, entries 9 and 10). Other solvents like CH₂Cl₂, toluene and THF produced lower



Scheme 1. Proposed gold(III)-catalyzed synthesis of substituted pyrroles.

Table 1. Optimization of reaction conditions.^[a]



Entry	Catalyst (mol %)	Solvent	Yield [%] ^[b]	
			2a	3a
1	HAuCl ₄ ·4H ₂ O (5)	CH ₃ CN	37	21
2	HAuCl ₄ ·4H ₂ O (10)	CH ₃ CN	15	46
3	HAuCl ₄ ·4H ₂ O (20)	CH ₃ CN	0	81
4	NaAuCl ₄ ·2H ₂ O (20)	CH ₃ CN	23	42
5	AuCl ₃ (20)	CH ₃ CN	0	51
6	AuCl (20)	CH ₃ CN	37	trace
7	Au(PPh ₃)Cl (20)/AgBF ₄ (20)	CH ₃ CN	0	42
8	Au(PPh ₃)Cl (20)/AgSbF ₆ (20)	CH ₃ CN	0	37
9 ^[c]	PtCl ₂ (20)	CH ₃ CN	0	0
10 ^[d]	ClCH ₂ CO ₂ H (20)	CH ₃ CN	0	0
11	HAuCl ₄ ·4H ₂ O (20)	THF	0	0
12	HAuCl ₄ ·4H ₂ O (20)	CH ₂ Cl ₂	0	24
13	HAuCl ₄ ·4H ₂ O (20)	toluene	0	8

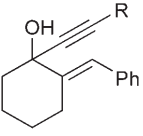
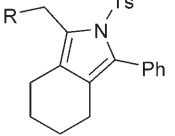
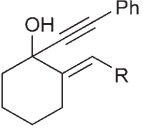
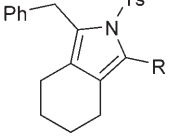
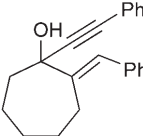
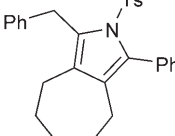
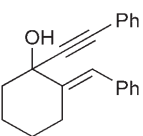
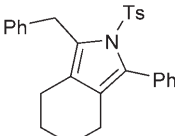
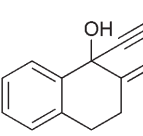
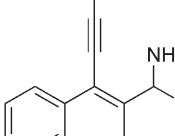
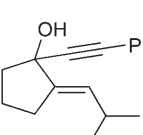
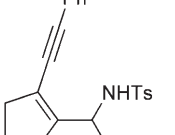
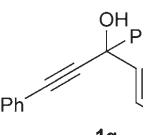
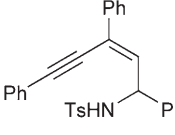
^[a] Reactions were conducted with 0.3 mmol of **1a**, 15 equivs. of TsNH₂ (13–14 equivs. of TsNH₂ could be recovered after the reaction in most cases) in 2 mL of solvent at 30 °C for 8 h.

^[b] Isolated yield.

^[c] 93 % of **1a** was recovered.

^[d] 90 % of **1a** was recovered.

Table 2. Gold(III)-catalyzed reaction of propargylic alcohols **1** with TsNH₂.^[a]

Entry	Substrate	Product	Time [h]	Yield [%] ^[b]
1	 1a – 1h	 3a – 3h	8	81
2			48	40
3			8	64
4			7	75
5			9	70
6			2	75
7			1	74
8			5	54
9	 1i – 1l	 1i – 1l	7	83
10			8	25
11			7	46
12			4.5	64
13	 1m	 3m	10	78
14	 1n	 3n	8	74
15	 1o	 2b	1	96
16	 1p	 2c	1	76
17 ^[c]	 1q	 2d	0.5	89

^[a] Reactions were conducted with 0.3 mmol of **1**, 15 equivs. of TsNH₂ (13–14 equivs. of TsNH₂ could be recovered after the reaction in most cases), 20 mol % of H₂AuCl₄·4H₂O in 2 mL of CH₃CN at 30 °C.

^[b] Isolated yield.

^[c] The *Z* isomer was always the most stable product.^[14]

yields of the desired products (Table 1, entries 11–13). Thus, the use of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (20 mol %) in CH_3CN at 30°C was found to be the most efficient and used as the standard conditions.

With these optimal conditions in hand, we examined the scope of this reaction, as shown in Table 2. Compared with previous conclusion^[15] that arylacetylenes were not effective for the gold(III)-catalyzed intramolecular hydroamination, various aryl substituents on the alkyne, including phenyl, electron-rich, and electron-poor ones, were compatible with this reaction, and generally good yields of the corresponding pyrroles were obtained (entries 1–5). When aliphatic and terminal alkynes were used, the reaction proceeded faster, furnishing the corresponding products in high yields within 2 h (entries 6 and 7). Alkynes with heteroaromatic groups such as 2-thienyl also proceeded smoothly (entry 8). Substitution on the allyl moiety was tolerated. With an electron-withdrawing aryl group, propargylic alcohol **1i** afforded the desired product **3i** in 83% yield (entry 9). However, when electron-rich ones were used, the yields of corre-

sponding products were decreased (entries 10–12).^[16] Propargylic alcohols with larger ring size, such as a seven-membered substrate, reacted smoothly to yield **3m** in 78% yield (entry 13). Substitution on the ring was also tolerated (entry 14) (Figure 1).^[17] Although, **1o–1q** could efficiently undergo the formal amination in excellent yields (up to 96%), the following intramolecular hydroamination could not proceed even after 24 h under reflux (entries 15–17).

Interestingly, with the use of **1r** as the substrate, bis(pyrrol-2-yl)arylene **3o** was obtained in 61% yield after 8 h (Scheme 2). Such bis(pyrrol-2-yl)arylenes could be used to provide electroactive poly[bis(pyrrol-2-yl)arylene] polymers^[18] with polypyrrole-like electrochromic properties that are useful for biomedical applications.^[19]

Then we investigated various sulfonamides, amides, and amines under these optimized conditions. Besides *p*-methylphenylsulfonamide, phenylsulfonamide could also be employed as an efficient nucleophile (Table 3, entry 1). However, with the use of *p*-bromophenylsulfonamide or alkylsulfonamides, such as methylsul-

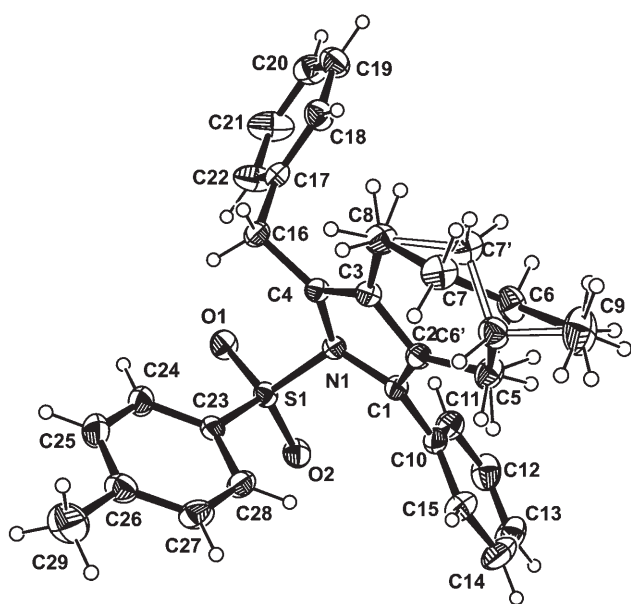


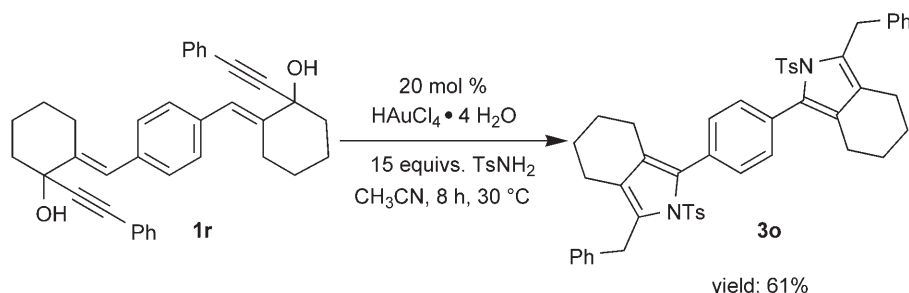
Figure 1. X-ray structure of **3n**.

Table 3. Gold(III)-catalyzed synthesis of substituted pyrroles **3** by cyclization of **1a** with sulfonamides.^[a]

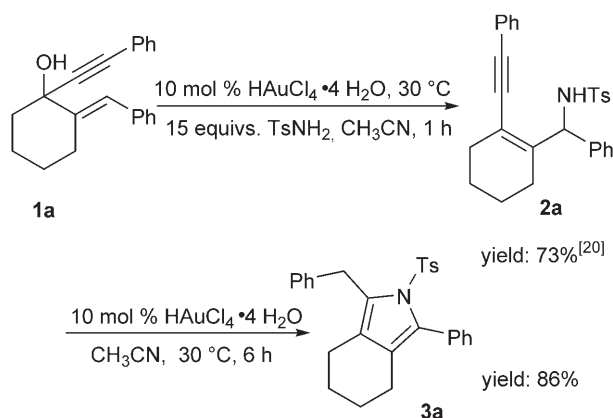
Entry	R	3 (Yield [%]) ^[b]
1	C_6H_5	3p (62)
2	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	3a (81)
3	<i>p</i> - BrC_6H_4	0
4	CH_3	3q (34)

^[a] Reactions were conducted with 0.3 mmol of **1a**, 15 equivs. of RSO_2NH_2 (13–14 equivs. of RSO_2NH_2 could be recovered after the reaction in most cases), 20 mol % of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in 2 mL of CH_3CN at 30°C .

^[b] Isolated yield.



Scheme 2. One pot synthesis of bis(pyrrol-2-yl)arylene **3o**.



Scheme 3. Two-step synthesis of pyrrole **3a**.

fonamide, the reactions gave no or low yields of the desired products (Table 3, entries 3 and 4). Amides and amines did not work as nucleophiles for this reaction.

In order to confirm the mechanism shown in Scheme 1 for the one-pot reaction, we next conducted the reactions, as shown in Scheme 3. After the reaction was run with 10 mol % of $\text{H[AuCl}_4\text{]} \cdot 4 \text{H}_2\text{O}$ for 1 h, an intermediate **2a** was isolated in 73 % yield along with 18 % of pyrrole **3a**. Compound **2a** could subsequently be converted to **3a** in high yield (up to 86 %) under the same conditions. These results strongly support our proposed two-step mechanism. Compared with two-step reactions, one-pot procedure with low amounts of gold catalysts are usually problematic. This may be due to the noble character of gold, which is easily deactivated by reduction.^[21] The choice of N-nucleophiles might be crucial, they must exert enough nucleophilicity in each step of the reaction but should not deactivate the gold catalysts.^[22] Thus sulfonamides with low Lewis basicity should be the appropriate choice as a dual nucleophile for this process. Furthermore, to compete with the rapid decomposition of the substrate, the use of an excess amount of sulfonamides was also needed.

In summary, we have developed a simple, convenient and efficient synthetic approach to highly substituted pyrroles utilizing a gold(III)-catalyzed tandem amination-intramolecular hydroamination reaction followed by facile isomerization. Various substituents of propargylic alcohols **1**, such as alkyl, aryl, proton and heteroaromatic groups are tolerated. The reaction proceeds efficiently under mild conditions with commercially available catalysts without any additive.

Experimental Section

General Procedure for the Preparation of Enamines **2** and Substituted Pyrroles **3**

To a stirred solution of propargylic alcohol **1** (0.30 mmol) and TsNH_2 (774 mg, 4.5 mmol) in CH_3CN (2.0 mL) was

added 24.7 mg (20 mol %) of $\text{H[AuCl}_4\text{]} \cdot 4 \text{H}_2\text{O}$ under air at 30 °C. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was diluted with diethyl ether (20 mL) and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford the corresponding products.

2a: Compound **2a** was prepared according to the above method, but employing 10 mol % of $\text{H[AuCl}_4\text{]} \cdot 4 \text{H}_2\text{O}$ to afford **2a** as a solid; yield: 73 %; mp: 184–186 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.84–7.81 (d, J = 8.1 Hz, 2H), 7.44–7.17 (m, 12H), 5.93–5.91 (d, J = 8.1 Hz, 1H), 5.64–5.61 (d, J = 8.1 Hz, 1H), 2.34 (s, 3H), 2.19–2.13 (m, 1H), 2.04–1.87 (m, 2H), 1.73–1.62 (m, 1H), 1.46–1.29 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ = 143.2, 142.2, 139.2, 137.2, 131.5, 129.2, 128.5, 128.3, 128.1, 127.5, 127.4, 126.2, 123.3, 118.8, 93.3, 89.0, 60.0, 30.0, 23.9, 21.8, 21.6, 21.4; IR (KBr): ν = 3268, 2928, 2858, 1597, 1492, 1449, 1328, 1159 cm^{-1} ; anal. calcd. for $\text{C}_{28}\text{H}_{27}\text{NO}_2\text{S}$: C 76.16, H 6.16, N 3.17; found: C 76.23, H 6.19, N, 3.01.

3a: The reaction mixture was chromatographed using 40:1 hexanes/EtOAc to afford the indicated compound as a solid; yield: 107.2 mg (81 %); mp: 118.5–119.5 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.33–7.17 (m, 10H), 7.04–6.97 (m, 4H), 4.30 (s, 2H), 2.47–2.42 (m, 2H), 2.31 (s, 3H), 2.27–2.23 (m, 2H), 1.67–1.63 (m, 2H), 1.60–1.55 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 143.7, 139.9, 136.3, 132.4, 131.2, 131.1, 130.0, 129.0, 128.4, 128.2, 127.3, 127.1, 126.7, 125.8, 125.5, 125.0, 32.1, 23.3, 23.2, 22.4, 22.1, 21.5; IR (KBr): ν = 3028, 2930, 2858, 1712, 1598, 1492, 1446, 1367, 1171 cm^{-1} ; anal. calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_2\text{S}$: C 76.16, H 6.16, N, 3.17; found: C 76.21, H 6.11, N 3.12.

Acknowledgements

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