Organic LETTERS

Letter

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Autotandem Catalysis: Synthesis of Pyrroles by Gold-Catalyzed Cascade Reaction

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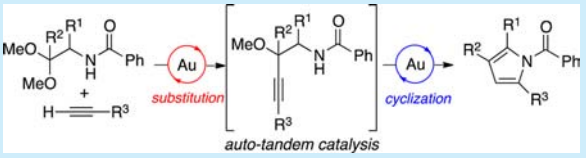
Supporting Information

ABSTRACT: A novel synthesis of substituted pyrroles by a gold(I)-catalyzed cascade reaction has been developed. The reaction proceeded with an autotandem catalysis consisting of an initial addition of gold−acetylide to an acetal moiety and was followed by gold-catalyzed 5-*endo-dig* cyclization and aromatization. Gold catalysts play a dual role in activating nucleophilicity or electrophilicity of terminal acetylenes by forming gold−acetylides or by π-coordination. The formal (3 + 2) annulation of two components provided a variety of substituted pyrroles in a modular fashion.



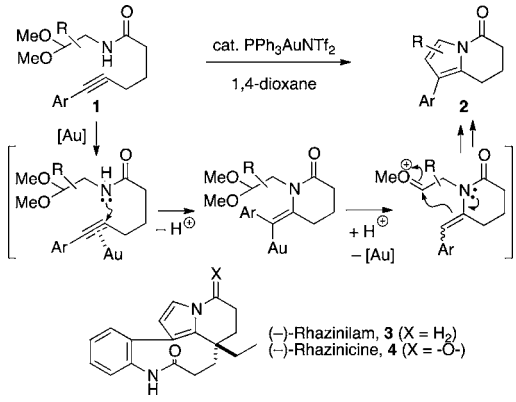
Pyrroles are an important nitrogen-containing heterocycle often observed in biologically significant natural products,[1] pharmaceutical substances,[2] and functional materials.[3] Therefore, the development of a novel construction of pyrrole has inspired synthetic chemists, and numerous methods have been reported to date. However, most of the well-known classical methods, such as the Paal−Knorr[4] and Hantzsh[5] pyrrole syntheses, have limited utility concerning functional group compatibility because these methods usually require relatively harsh conditions such as heating in the presence of a strong acid. However, many transition metal-catalyzed formations of substituted pyrroles have also been developed in the past decade.[6] Because of mild reaction conditions, these reactions enable a wide substrate scope and have enjoyed high synthetic utility for the construction of substituted pyrroles. In particular, gold catalysts have recently received considerable attention for their low catalyst loading and excellent functional group tolerance owing to mild reaction conditions.[7,8]

Against this background, we recently reported a highly efficient construction of indolizinones **2** by a gold-catalyzed cascade double cyclization of linear yneamide **1** (Scheme 1). The utility of this reaction was fully demonstrated by our total syntheses of (−)-rhazinilam **3** and (−)-rhazinicine **4**.[9] The proposed mechanism is initiated by intramolecular nucleophilic addition of nitrogen to the activated alkyne by π-coordination of cationic gold catalyst, affording an enamide intermediate. Then, after protonolysis of the gold−carbon bond, the resultant enamide should undergo cyclization; the subsequent elimination of methanol and aromatization should lead to indolizinone **2**. We demonstrated the intermediacy of the enamide species by isolating the enamide as a mixture of *E*/*Z* isomers.[9] We observed that a gold catalyst was indispensable to promote not only enamide formation but also pyrrole ring formation from the enamide intermediate.[9]

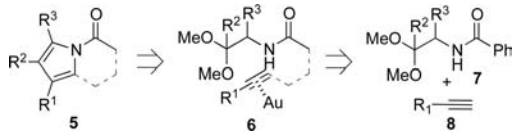
Because the indolizinone skeleton is regarded as a substituted pyrrole, we envisioned that the application of the intramolecular process using the linear substrates **1** to an intermolecular reaction using acetals **7** and terminal acetylenes **8** would lead to a new pyrrole synthesis (Scheme 2). Herein, we report a new synthesis of substituted pyrroles via a gold-catalyzed cascade reaction. The reaction was found to proceed by autotandem catalysis,[10] in which one gold catalyst catalyzed two consecutive processes by two different modes of activation of terminal alkynes: σ-activation by forming gold−acetylides to activate its nucleophilicity and activation of its electrophilicity by π-coordination.

At the outset, we examined the reaction of *N*-(2,2-dimethoxyethyl)benzamide **7a** and phenylacetylene **8a** under the standard conditions established for the intramolecular

Scheme 1. Formation of Indolizinones by Gold-Catalyzed Cascade Double Cyclization Developed in Our Group



Scheme 2. Working Hypothesis of Intermolecular Reaction



Received: August 20, 2014
Published: September 9, 2014

   dx.doi.org/10.1021/ol5024695 | *Org. Lett.* 2014, 16, 4948−4951

Scheme 3. Unexpected Regiochemistry in the First Trial of Intermolecular Reaction

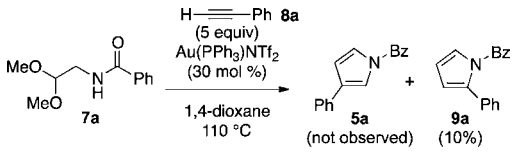
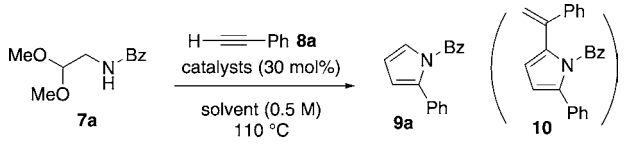
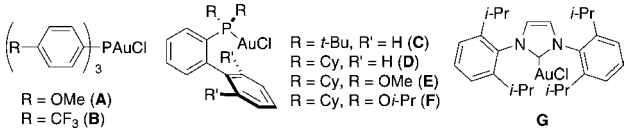


Table 1. Optimization of Gold-Catalyzed Pyrrole Formation



entry	catalysts	solvent	time (h)	yield (%)
1[a]	$Au(PPh_3)NTf_2$	1,4-dioxane	3	10
2[a]	$Au(PPh_3)NTf_2$	toluene	5	13
3	PPh_3AuCl, $AgNTf_2$	toluene	3.5	15
4	PPh_3AuCl, $AgPF_6$	toluene	5	19
5	PPh_3AuCl, $AgBF_4$	toluene	1.5	23
6	PPh_3AuCl, AgOTf	toluene	1	37
7	**A**, AgOTf	toluene	1	29
8	**B**, AgOTf	toluene	1	40
9	**C**, AgOTf	toluene	2	53
10	**D**, AgOTf	toluene	45 min	48
11	**E**, AgOTf	toluene	1	41
12	**F**, AgOTf	toluene	1	53
13	**G**, AgOTf	toluene	1	46
14[b]	**F**, AgOTf	toluene	2	77
15[b,c]	**F**, AgOTf	toluene	1	78
16[d]	**G**, AgOTf	xylene	10 min	77

[a] $Au(PPh_3)NTf_2$ was prepared by premixing PPh_3AuCl with $AgNTf_2$. [b] Conditions: **F** (10 mol %), AgOTf (10 mol %) in toluene (0.25 M). [c] The corresponding diisopropylacetal **7b** was used as the substrate. [d] Conditions: **G** (3 mol %), AgOTf (3 mol %) in xylene (0.5 M) at 140 °C.

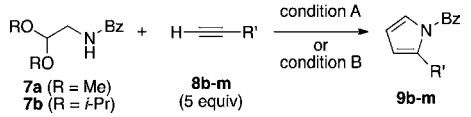


reaction (Scheme 3).[9] Heating of a 1,4-dioxane solution of **7a** (0.5 M) and five equivalents of **8a** in the presence of Gagosz's catalyst, $Au(PPh_3)NTf_2$,[11] at 110 °C gave a pyrrole as a single isolable product in low yield. Surprisingly, the structure of the product was not that of 3-phenylpyrrole derivative **5a**, which we expected on the basis of the intramolecular reaction; the product was instead 2-phenylpyrrole derivative **9a**. The structure of **9a** was unambiguously determined on the basis of its ^1H NMR spectrum.[12]

Although we obtained unexpected results, we optimized the reaction to maximize the yield of the pyrrole product (Table 1). The yield of **9a** was slightly improved when toluene was used as a solvent (Table 1, entry 2). Reactions using combinations of PPh_3AuCl and various silver salts (Table 1, entries 3–6) revealed that AgOTf gave the best result to provide **9a** in 37% yield (Table 1, entry 6). We then surveyed a series of catalysts bearing a variety of ligands (Table 1, entries 7–13). A comparison of catalysts bearing triarylphosphine ligands (Table 1, entries 6–8) revealed that catalyst **B**, which bore a *para*-trifluoromethyl group, improved the yield (Table 1, entry 8). Among a series of catalysts **C**–**F** with bulky biphenyl moieties[13] (Table 1, entries 9–12), **C** and **F** proved to be superior to the others and to **B**. In addition, catalyst **G**,[14] which bore a *N*-heterocyclic carbene ligand, gave **9a** in a yield similar to those obtained with **C**–**F** (Table 1, entry 13). At this point, we carefully analyzed the side products of the reaction of entry 12 in Table 1 and isolated pyrrole derivative **10** in 13% yield; this compound should be generated by a gold-catalyzed overreaction of **9a** with **8a**. The generation of **10** was substantially suppressed under diluted conditions (0.25 M); more importantly, the yield of **9a** was increased up to 77% (Table 1, entry 14). Finally, the reaction time could be shortened when diisopropyl acetal **8b** was used instead of **8a** (Table 1, entry 15). In addition, the reaction could be conducted with reduced catalyst loading (3 mol %) at higher temperature (140 °C) when catalyst **G** was used (Table 1, entry 16). Ultimately, we selected two sets of conditions, entries 15 and 16 (Table 1), as optimal conditions.

Encouraged by these results, we then directed our attention toward the substrate scope. Subjection of various terminal arylalkynes **8b**–**m** to condition set A (acetal **7b**, catalyst **F**, and AgOTf in toluene at 110 °C) and to condition set B (acetal **7a**, catalyst **G**, and AgOTf in xylene at 140 °C) revealed that a broad range of functional groups is compatible with these reaction conditions (Table 2). Arylalkynes **8b**–**e**, bearing electron-donating substituents, such as methoxy, methyl, and protected

Table 2. Substrate Scope of Acetylenes

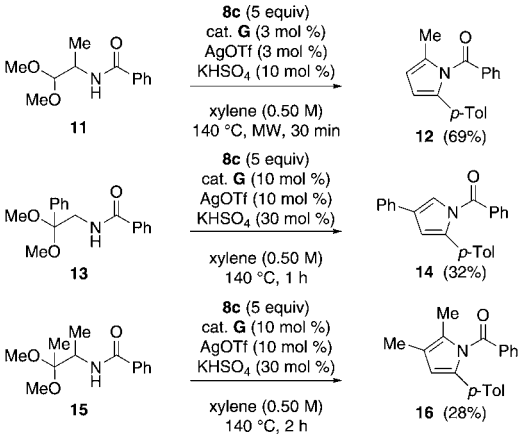


entry	substrate	R'	condition[a]	time (min)	product	yield(%)
1	**8b**		A	15	**9b**	89
			B[b]	120		52
2	**8c**		A	30	**9c**	73
			B	30		85
3	**8d**		A	30	**9d**	49
4	**8e**		A	15	**9e**	73
			B	30		79
5	**8f**		A	30	**9f**	63
			B	60		64
6	**8g**		A	30	**9g**	46
			B	60		35
7	**8h**		A	30	**9h**	69
			B	30		71
8	**8i**		A	30	**9i**	71
			B	10		74
9	**8j**		A	10	**9j**	77
			B	45		52
10	**8k**		A	10	**9k**	81
			B	60		58
11	**8l**		A	30	**9l**	77
			B	10		80
12	**8m**	*n*-Bu	B[c]	60	**9m**	51[d]

[a] Conditions **A**: Substrate **7b**, **F**/AgOTf (10 mol %) in toluene (0.25 M) at 110 °C. Conditions **B**: Substrate **7a**, **G**/AgOTf (3 mol %) in xylene (0.5 M) at 140 °C. [b] Conditions: **G**/AgOTf (5 mol %) at 140 °C. [c] Conditions: Substrate **7b**, **G**/AgOTf (5 mol %) in xylene (0.25 M) at 120 °C. [d] A 3-substituted pyrrole was obtained in 7% yield.

dx.doi.org/10.1021/ol5024695 | *Org. Lett.* 2014, 16, 4948–4951

Scheme 4. Syntheses of Tri- and Tetrasubstituted Pyrroles



amino groups, and a halogen, such as a bromo group at the para position of the benzene ring, gave the corresponding pyrroles **9b–e** in good to high yields (Table 2, entries 1–4).

However, alkynes **8f** and **8g**, which bear electron-withdrawing groups, exhibited lower reactivity and afforded pyrroles **9f** and **9g** in modest yields (Table 2, entries 5 and 6). Substrates **8h–l**, which bear ortho- and meta-disubstituted phenyl and naphthyl groups, also gave the desired products **9h–l** in good to high yields (Table 2, entries 7–11). Finally, an alkyl-substituted alkyne, such as 1-hexyne **8m**, was observed to be feasible in the reaction and under condition set B; the corresponding pyrrole **9m**, which is associated with a small amount of the 3-substituted regioisomers, was obtained in moderate yield (Table 2, entry 12).

Significantly, further functionalized acetal fragments were found to be applicable to the reaction for providing multisubstituted pyrroles via a slight optimization of the reaction conditions (Scheme 4).[9] Thus, reaction of acetal **11**, which was readily prepared from (−)-alanine,[15] proceeded smoothly under a modified version of condition set B (i.e., microwave irradiation in the presence of catalytic $KHSO_4$) to give 1,2,5-trisubstituted pyrrole derivative **12** in good yield. In addition, acetal **13**, which was synthesized from glycine in a few steps, gave the corresponding 1,2,4-trisubstituted pyrrole derivative **14** in modest yield under a modified version of condition set B. Furthermore, reaction of acetal **15** with **8c** afforded 1,2,3,5-tetrasubstituted pyrrole derivative **16**.

To gain mechanistic insights, we conducted several model reactions. First, two modified substrates were subjected to condition set A to identify the initial reaction site. The reaction of amide **17** with no acetal moiety gave only a trace amount of enamide **18**, with recovery of the starting material **17** in 93% yield (Scheme 5). This result indicated that the initial process was not a C–N bond-forming reaction by nucleophilic addition of a nitrogen atom to the activated alkyne, as that which occurs in the intramolecular reaction (Scheme 1). However, the reaction of amide **19**, whose nitrogen was protected by a methyl group,

Scheme 5. Control Reaction Using Benzamide Lacking Acetal Moiety

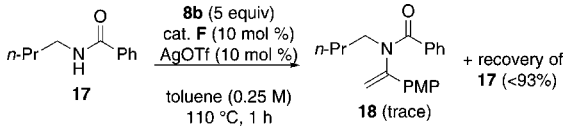
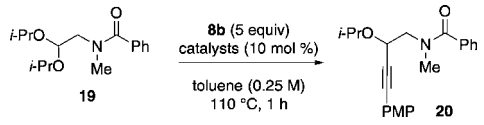
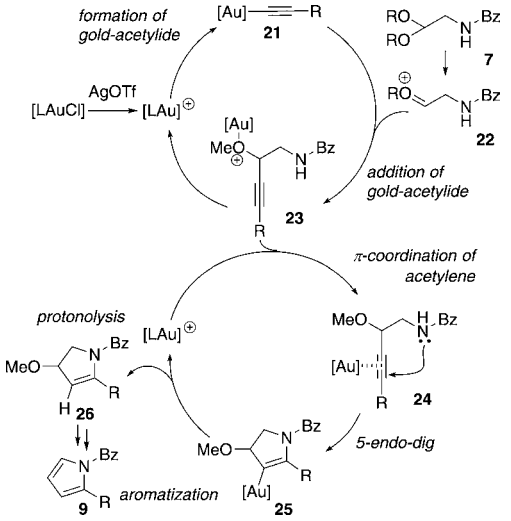


Table 3. Control Reactions Using *N*-Methyl Amide



		yield (%)	
entry	catalysts	**19**	**20**
1	**F**/AgOTf	0	63
2	AgOTf	37	0
3	**F**	89	0
4	none	90	0

Scheme 6. Plausible Mechanism of Autotandem Gold Catalysis in the Cascade Reaction



resulted in clean formation of acetylene adduct **20**, strongly suggesting that a gold–acetylide[16] should be generated from the cationic gold catalyst and terminal alkyne, which would add to an oxonium ion formed from the acetal (Table 3, entry 1). The generation of a gold–acetylide is supported by recent literature[16] and by the results of control experiments reported in Table 3. Thus, reactions using AgOTf or catalyst **F** did not provide **20** (Table 3, entries 2 and 3).

A plausible mechanism based on the control reactions is shown in Scheme 6.[17] The reaction should be initiated by formation of gold–acetylide **21** to activate the nucleophilicity of the terminal acetylene, which undergoes addition to oxonium ion **22**[10h] to give the alkyne adduct **23**. Then, 5-*endo*-*dig* cyclization[8c,d,g] should occur via activation of the electrophilicity of alkyne moieties by π-coordination of the gold catalyst. Finally, protonolysis of the carbon–gold bond **25**, followed by aromatization, furnishes the corresponding pyrroles **9**, with regeneration of the cationic gold catalyst. As a whole, our proposed mechanism involves autotandem catalysis,[10] in which the same catalyst catalyzes in two different modes of activation of acetylene; this mechanism thus clearly explains the different regiochemical outcomes between the intramolecular reactions that we previously reported[9] and the intermolecular reaction developed in this study.

In summary, we have developed a new addition–cyclization sequence for the synthesis of multisubstituted pyrroles; this sequence is promoted by autotandem gold catalysis. The advantage of this reaction is its versatility and convergency to

dx.doi.org/10.1021/ol5024695 | *Org. Lett.* 2014, 16, 4948–4951

synthesis of a variety of substituted pyrroles in a modular fashion by combination of two acyclic substrates with substituents installed beforehand. In addition, we have also shown that the cationic gold catalyst serves a dual role in the activation of both nucleophilicity and electrophilicity of an alkyne by forming gold–acetylide and by π-coordination, respectively.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and procedures, compound characterization data, and copies of ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Cabinet Office, Government of Japan through its Funding Program for Next Generation World-Leading Researchers (LS008), a Grant-in-aid for Scientific Research (A) (26253001) and Young Scientists (B) (21790004 and 26860004), JSPS, and the Sumitomo Foundation.

■ DEDICATION

Professor Amos B. Smith, III on the occasion of his 70th birthday.

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