Highly Substituted Pyrroles by a Gold(I)-Catalyzed Tandem Reaction of 1-(1-Alkynyl)cyclopropyl Oxime Ethers with Nucleophiles

Yanqing Zhang,[a] Junliang Zhang*[a,b]

[a] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 North, Zhongshan Road, Shanghai 200062, P. R. of China

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. of China
Fax +86(21)62235039; E-mail: jlzhang@chem.ecnu.edu.cn

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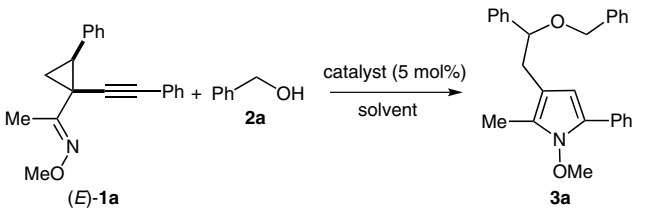
Abstract: A gold(I)-catalyzed tandem reaction of 1-(1-alkynyl) cyclopropyl oxime ethers with nucleophiles under mild conditions has been developed, which provides a facile access to highly substituted pyrroles in moderate to excellent yields.

Key words: pyrroles, gold, nucleophiles, cyclization, cyclopropane

Pyrroles are one of the most popular core units in various natural products,[1] materials science,[2] and medicinal agents.[3] For example, Lipitor, as an (HMG-CoA) reductase inhibitor used to lower LDL cholesterol levels, is the best-selling drug in past several years, which contains the pyrrole as the core structural unit. Meanwhile, *N*-alkoxypyrroles could be used as insecticides in crop protecting.[4] As a consequence, these properties continue to stimulate interest in the development of new synthetic methods for pyrroles.[5] The Hantzsch procedure,[6,7] Paal–Knorr synthesis,[6,8] and Knorr synthesis[6,9] have been widely used as classic approaches but with drawbacks such as multistep synthesis, limited scope, and inaccessible starting materials. Recently, more and more attention has been paid on metal-catalyzed reactions,[10] because of their high efficiency and mild conditions. For example, palladium,[11] copper,[12] gold,[13] silver,[14] ruthenium,[15] and iron[16] were shown to be active catalysts in the pyrrole ring formation reactions.

On the other hand, gold-catalyzed transformations of strained small rings such as cyclopropanes and expoxides have been nicely summarized by Hashmi[17,18] and Shi,[19] respectively. Recently, 1-(1-alkynyl)cyclopropyl ketones have been developed as readily available precursors for the synthesis of highly substituted furans under the catalysis of transition metals.[20] During the course of studying the chemistry of 1-(1-alkynyl)cyclopropyl ketones, we envisaged that 1-(1-alkynyl)cyclopropyl oxime ethers, easily prepared from the corresponding ketones, might react with nucleophiles, furnishing highly substituted pyrroles by a metal-catalyzed tandem addition–heterocyclization.

Table 1 Optimization Studies on Cycloaddition of **1a** and **2a**[a]



Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	$PPh_3AuCl/AgOTf$	toluene	25	3	49 (78)
2[c]	$PPh_3AuCl/AgOMs$	toluene	80	20	63 (74)
3	$PPh_3AuCl/AgSbF_6$	toluene	25	16	22 (26)
4	$AuCl_3/AgOTf$	toluene	25	11	38
5	AgOTf	toluene	40	14	33
6	$Yb(OTf)_3$	toluene	80	10.5	trace
7	$Sc(OTf)_3$	toluene	80	29	trace
8	(L1)AuCl/AgOTf	toluene	25	9	52
9	(L2)AuCl/AgOTf	toluene	40	7.5	70
10	(L3)AuCl/AgOTf	toluene	25	10.5	82
11	(L4)AuCl/AgOTf	toluene	25	27	50
12	$PCy_3AuCl/AgOTf$	toluene	25	4.5	87
13	$PCy_3AuCl/AgOTf$	DCE	50	14	42
14	$PCy_3AuCl/AgOTf$	$CHCl_3$	25	10	44
15	$PCy_3AuCl/AgOTf$	DMF	25	10	n.r.
16	$PCy_3AuCl/AgOTf$	THF	25	10	n.r.

[a] All reactions were carried out using **1a** (0.3 mmol), **2a** (0.6 mmol), and catalyst (5 mol%) in toluene (3 mL).
[b] Yields in parentheses are determined by ^1H NMR spectroscopy, which based on CH_2Br_2 as the internal standard.
[c] The reactions in parentheses were carried out at r.t. for 23 h.

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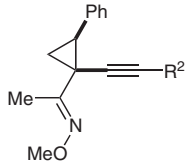
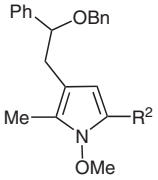
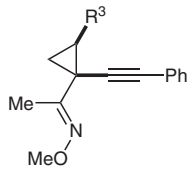
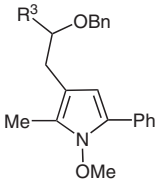
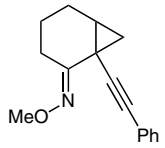
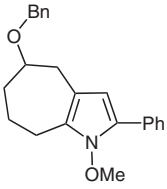
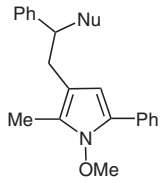
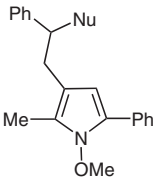
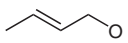
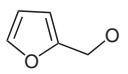
This hypothesis was initially tested by reacting (*E*)-1-[2-phenyl-1-(phenylethynyl)cyclopropyl]ethanone *O*-methyl oxime [(*E*)-**1a**] with benzyl alcohol (**2a**) in the presence of $PPh_3AuCl/AgOTf$. The reaction afforded an air-sensitive product **3a** in 49% isolated yield, which inspired us to explore better conditions to improve the yield. We tested other silver salts such as $AgSbF_6$, and AgOMs. The latter led to 63% isolated yield but a higher temperature was required (Table 1, entries 1–3). Only 38% yield of **3a**[21] could be isolated when the reaction was carried out under the catalysis of $AuCl_3/AgOTf$ (Table 1, entry 4). AgOTf, $Yb(OTf)_3$, and $Sc(OTf)_3$ are not effective even at higher temperature (Table 1, entries 5–7). Several phosphine- and phosphite-derived cationic gold complexes were then investigated (Table 1, entries 8–12, Figure 1). Gratifyingly, 87% yield was obtained when the reaction was carried out in toluene in the presence of 5 mmol% of $PCy_3AuCl/AgOTf$ at room temperature (Table 1, entry 12). The attempt to improve the yield was failed by

Table 2 Reaction Scope of (*E*)-**1** with NuH **2**[a]

Entry	**1**		**2**	Time (h)	**3**		Isolated yield (%)
1		**1b** R^2 = 1-naphthyl	BnOH (**2a**)	10		**3b** R^2 = 1-naphthyl	93
2		**1c** R^2 = 4-$MeOC_6H_4$	**2a**	4.5		**3c** R^2 = 4-$MeOC_6H_4$	72
3		**1d** R^2 = 4-MeC_6H_4	**2a**	9.5		**3d** R^2 = 4-MeC_6H_4	74
4		**1e** R^2 = 1-cyclohexenyl	**2a**	12		**3e** R^2 = 1-cyclohexenyl	72
5		**1f** R^2 = *n*-Bu	**2a**	11		**3f** R^2 = *n*-Bu	72
6		**1g** R^2 = C_2H_4OAc	**2a**	22.5		**3g** R^2 = C_2H_4OAc	63
7		**1h** R^2 = *c*-Pr	**2a**	13.5		**3h** R^2 = *c*-Pr	49
8		**1i** R^3 = 4-$MeOC_6H_4$	**2a**	11		**3i** R^3 = 4-$MeOC_6H_4$	56
9		**1j** R^3 = 4-MeC_6H_4	**2a**	9.5		**3j** R^3 = 4-MeC_6H_4	74
10[b]		**1k** R^3 = *n*-Bu	**2a**	12		**3k** R^3 = *n*-Bu	82
11		**1l** R^3 = H	**2a**	7		**3l** R^3 = H	78
12[b]		**1m**	**2a**	13		**3m**	68
13		**1a**	MeOH (**2b**)	12.5		**3n** Nu = MeO	67
14		**1a**	*i*-PrOH (**2c**)	29.5		**3o** Nu = *i*-PrO	88
15		**1a**	*t*-BuOH (**2d**)	7		**3p** Nu = *t*-BuO	71
16		**1a**	(*E*)-but-2-en-1-ol (**2e**)	13.5		**3q** Nu = 	76
17		**1a**	furfuryl alcohol (**2f**)	12.5		**3r** Nu = 	62
18		**1a**	PhOH (**2g**)	7.5		**3s** Nu = PhO	70
19		**1a**	AcOH (**2h**)	7.5		**3t** Nu = AcO	80
20		**1a**	$PhNH_2$ (**2i**)	28		**3u** Nu = PhNH	99

[a] All reactions were carried out using **1** (0.3 mmol), **2a** (0.6 mmol), and $PCy_3AuCl/AgOTf$ (5 mol%) in toluene (3 mL) at r.t. unless otherwise specified.
[b] 80 °C.
[c] 60 °C.

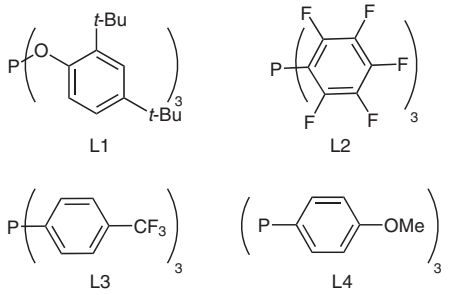
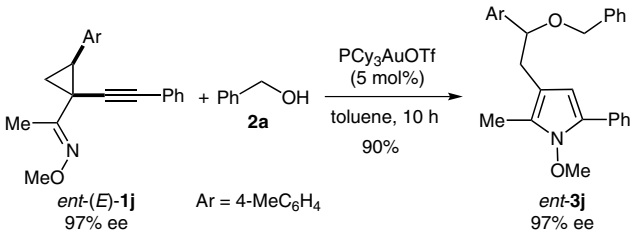


Figure 1

screening various solvents such as DCE, chloroform, polar DMF, and THF (Table 1, entries 13–16).

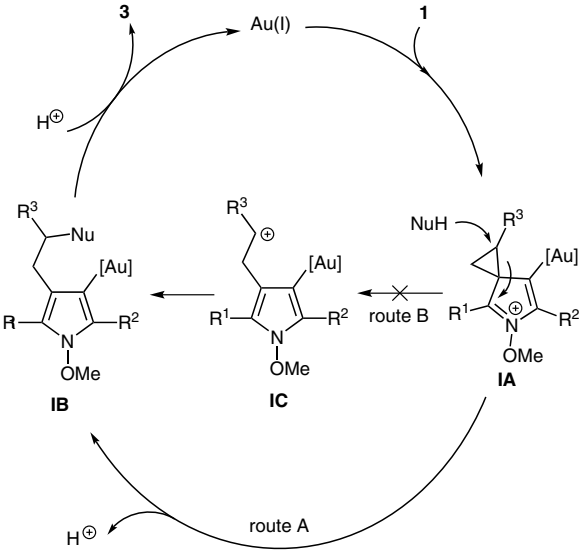
With the optimal conditions in hand, the scope and limitation of this transformation were next explored by variation of the 1-(1-alkynyl)cyclopropyl oxime ether component. Firstly, the substituent effect of R^2 was studied by introduction of different alkynyl groups. For example, when the R^2 substituent was a naphthyl group, the pyrrole **3b** was obtained in 93% yield (Table 2, entry 1), whereas, only modest yield was obtained when R^2 was a cyclopropyl group (Table 1, entry 7). Variously substituted aryl and functionalized alkyl groups can be well introduced to the pyrroles (Table 2, entries 2–6). The substituent effect of R^3 was next investigated, and it was found that both aromatic and aliphatic R^3 was compatible, affording the desired products in 56–82% yields (Table 2, entries 8–10). The reaction of **1l** with R^3 = H also proceeded smoothly to give the **3l** in 78% yield (Table 2, entry 11). Finally, a fused bicyclic pyrrole **3m** could also be easily synthesized from the corresponding substrate **1m** and benzyl alcohol (**2a**) at 80 °C in 68% yield (Table 2, entry 12). After studying the scope of oxime ethers (*E*)-**1**, we then turned our attention on examination of the reaction scope by variation of nucleophile component **2**. Not only methanol (**2b**), secondary isopropanol (**2c**), but also bulky *tert*-butyl alcohol (**2d**) were applicable to this transformation, yielding pyrroles **3n**–**p** in 67–88% yields, but the last reaction required higher temperature (Table 2, entries 13–15). (*E*)-But-2-en-1-ol (**2e**) and furfuryl alcohol (**2f**) were also compatible, affording **3q** and **3r** in 76% and 62% yields, respectively (Table 2, entries 16 and 17). The reaction of **1a** with phenol (**2g**) also proceeded smoothly to afford the desired product **3s** in 70% yield (Table 2, entry 18). Finally, it is noteworthy that both acetic acid (**2h**) and aniline (**2i**) are good nucleophiles in this transformation, furnishing the corresponding ester **3t** and amine **3u** in high yields (Table 2, entries 19 and 20), indicating there is a general substrate scope.

After that, the asymmetric version of this gold(I)-catalyzed tandem reaction was carried out. A 97% ee of *ent*-(*E*)-**1j** reacting with benzyl alcohol (**2a**) under the optimized reaction conditions afforded the desired cycloadduct *ent*-**3j** in 90% yield with 97% ee. The optical activity was maintained, and this result indicated that the reaction underwent via a S_N2 reaction pathway (Equation 1).



Equation 1

The mechanism that accounts for this transformation is depicted in Scheme 1. Under the optimized conditions, the gold complex coordinates with the substrates **1**, leading to heterocyclization and thus giving the oxocarbenium intermediate **IA**.[20] This would make the cyclopropane reactive enough to be attacked by the nucleophiles via an S_N2 pathway and substituted gold–pyrrole species **IB** would be formed via route A. Subsequent protonation of **IB** would lead to the final product **3** and regenerate the gold(I) species. An alternative reaction pathway via the carbocation intermediate **IC** (route B) can be excluded by the result of Equation 1.



Scheme 1 Plausible mechanism for the tandem reaction

In summary, we have developed a novel, efficient, and general method to synthesize highly substituted pyrroles from readily 1-(1-alkynyl)cyclopropyl oxime ethers with nucleophiles by a gold-catalyzed tandem regioselective addition and heterocyclization under mild conditions. We also found that there was no loss of the chirality information during the reaction. A plausible mechanism was also brought forward. Further studies including the mechanism and synthetic application of this methodology in our laboratory are under way and will be reported in due course.

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(21) **General Procedure for the Gold(I)-Catalyzed Tandem Reaction of 1-(1-Alkynyl)cyclopropyl Oxime Ethers with Nucleophiles**

A solution of PCy_3AuOTf (generated from 1:1 mol ratio of PCy_3AuCl/AgOTf, 3 mL, 0.005 M in toluene, 5 mol%) was added to a dry Schlenk tube under Ar. Oxime ether **1a** (0.20 mmol, 57.8 mg) and nucleophile **2a** (0.4 mmol, 43.3 mg) were added to the mixture. The resulting mixture was stirred at r.t. unless otherwise specified until the reactions were complete, as determined by TLC analysis. The residue was purified by flash column chromatography on silica gel (hexanes–EtOAc = 30:1) to afford the pure product **3a** (0.17 mmol, 68.8 mg) in 87% yield; oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.48 (m, 2 H), 7.30–7.04 (m, 13 H), 5.96 (s, 1 H), 4.42–4.34 (m, 2 H), 4.20 (d, *J* = 12.4 Hz, 1 H), 3.51 (s, 3 H), 2.92–2.86 (m, 1 H), 2.66–2.60 (m, 1 H), 1.80 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.22, 138.69, 131.57, 128.44, 128.20, 128.13, 127.54, 127.40, 127.28, 126.88, 125.77, 125.68, 125.60, 124.06, 112.25, 104.78, 82.63, 70.43, 65.07, 35.59, 8.08 ppm. IR (neat): ν = 1602, 1517, 1493, 1452, 1351, 1263, 1238, 1218, 1068, 1026, 971, 910 cm^{-1}. MS (EI): *m/z* (%): 397 (15.33) $[M]^+$, 91 (100). HRMS: *m/z* calcd for $C_{27}H_{27}NO_2$: 397.2042; found: 397.2045.