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Gold-Catalyzed Synthesis of Tropone and Its Analogues via Oxidative Ring Expansion of Alkynyl Quinols

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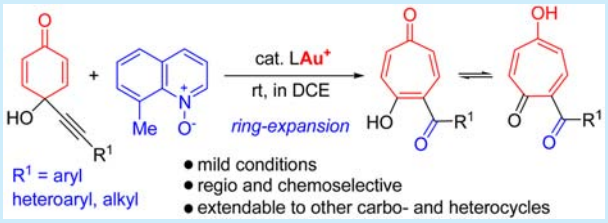
Supporting Information

ABSTRACT: A new and convenient strategy for the synthesis of functionalized tropone derivatives based on the gold-catalyzed oxidative ring expansion of alkynyl quinols has been developed. The reaction proceeds via gold-catalyzed highly regioselective oxidation followed by 1,2-migration of a vinyl or phenyl group. Extension of this chemistry allows ready access to various seven- or six-membered ring systems such as benzotropones, benzooxepines, phenanthrenes, and quinolin-2(1*H*)-ones.



Tropones and their 2-hydroxylated derivative tropolones constitute one of the most important nonbenzenoid seven-membered aromatic compounds, and they have attracted considerable interest due to their novel structures and their presence in various natural products with biological interest.[1] For example, colchicine (Figure 1) is one of the most studied

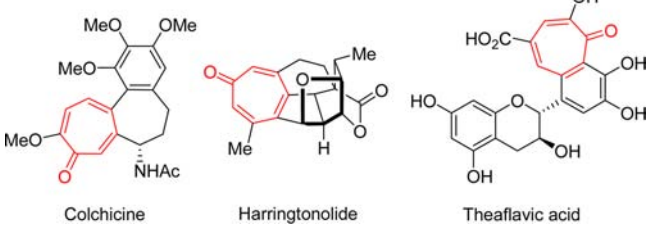
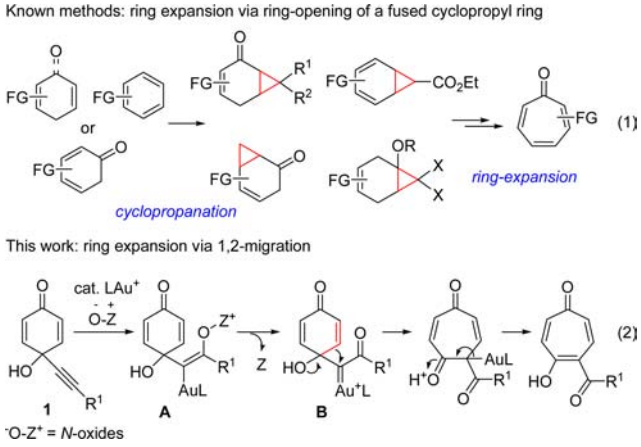


Figure 1. Representative naturally occurring bioactive tropone derivatives.

tropolones, which was commonly used to treat acute gout,[2] familial Mediterranean fever,[3] and prophylaxis of gout flares. The cage-like harringtonolide was found to possess antineoplastic and antiviral activities.[4] Theaflavic acid was found to display a variety of important biological activities such as anti-inflammatory and cytotoxic activities.[5] Tropones have also been used as efficient building blocks in a diverse array of higher order cycloaddition reactions such as [4 + 2],[6a] [6 + 3],[6b] [6 + 4],[6c] [8 + 2],[6d] or [8 + 3][6e] cyclizations leading to fused ring systems.[6] Therefore, the development of efficient methodologies for the synthesis of tropone and its derivatives is highly attractive.[1c,7−9]

Among many approaches, ring expansion of six-membered ring compounds via cyclopropanation/ring-expansion reactions was the most often used protocol[1c,8] (typical examples are shown in Scheme 1, eq 1), which has been applied successfully to the synthesis of tropone and tropolone-containing natural products.[9] However, these reactions usually require multistep synthesis for either the cyclopropanation precursors or the desired tropone

Scheme 1. Synthesis of Tropones via Ring Expansion Reactions



products, and in some cases, highly unstable reagents such as diazo-compounds or dihalocarbenes need to be employed to ensure efficient cyclopropanation. Recently, we have reported a gold-catalyzed highly regio- and chemoselective oxidative ring expansion[10] of 2-alkynyl-1,2-dihydropyridines to azepines[10a] using pyridine-*N*-oxide as the oxidant,[11] which proceeds via exclusive 1,2-migration of a vinyl or phenyl group. Inspired by this result, we envisioned that an α-carbonyl gold carbenoid intermediate **B** might be generated through the gold-catalyzed oxidation of alkynyl quinols **1** bearing a tertiary propargyl alcohol moiety, which may undergo ring expansion via 1,2-migration of the vinyl group (pinacol type) to furnish the tropone derivatives. It was noted that most of the gold-catalyzed reactions involving a ring-enlargement process focused on the reactions of small-sized ring compounds such as alkynyl-cyclopropanol or -cyclobutanols

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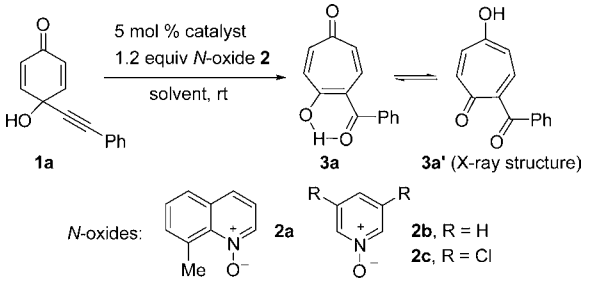
or were restricted to cycloalkanes,[12] while the reactions of larger-sized ring compounds, especially via the migration of a vinyl or phenyl group from a carbocycle, were quite rare.[13] Developing such methodologies would allow the efficient synthesis of medium- to large-sized carbo- and heterocycles, which is often a challenge in organic synthesis. Herein, we report a new and convenient strategy for the ring expansion of six-membered ring compounds to functionalized tropones via the gold-catalyzed oxidative rearrangement of alkynyl quinols (Scheme 1, eq 2), which can be easily prepared with a one-step reaction from readily accessible quinones via acetylide addition. In addition, the method was also extended to the synthesis of various fused-ring systems such as benzotropones, benzooxepines, phenanthrenes, and quinolin-2(1*H*)-ones.

To study the feasibility of the hypothesis, we initially investigated the gold-catalyzed oxidative reaction of alkynyl quinol **1a** with a phenyl substituent at the alkyne terminus (Table 1). To our delight, the desired tropone product **3a** was formed

Table 1. Optimization Studies for the Formation of 3a

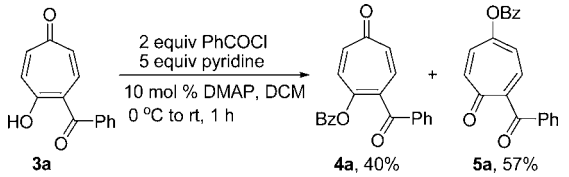


entry	*N*-oxide	catalyst	solvent	time (h)	yield (%)[a]
1	**2a**	**PPh_3AuNTf_2**	**DCE**	**2**	**91**
2	**2a**	$PPh_3AuCl/AgOTf$	DCE	4	83
3	**2a**	$PPh_3AuCl/AgSbF_6$	DCE	4	91
4	**2a**	$PPh_3AuCl/AgBF_4$	DCE	4	84
5	**2a**	$PPh_3AuCl/AgPF_6$	DCE	4	85
6	**2a**	$PicAuCl_2$	DCE	12	58
7	**2b**	PPh_3AuNTf_2	DCE	24	70
8	**2c**	PPh_3AuNTf_2	DCE	6	40
9	**2a**	PPh_3AuNTf_2	toluene	4	88
10	**2a**	PPh_3AuNTf_2	THF	4	78
11	**2a**	PPh_3AuCl	DCE	6	0 (98)
12	**2a**	$AgNTf_2$	DCE	12	0 (89)

[a]Isolated yields. The yields of the recovered **1a** are shown in parentheses.

quantitatively at room temperature within hours upon treatment of **1a** with 5 mol % of PPh_3AuNTf_2 and 1.2 equiv of 8-methylquinoline *N*-oxide in DCE. However, the NMR analysis of **3a** indicated that it contained a trace amount of impurity, which was difficult to remove by column chromatography. In view of the acidic property of tropone **3a** due to the presence of an enolic hydroxyl group,[14] we found that **3a** could be obtained in high purity and also with a high yield of 91% by treatment of the reaction mixture with 0.5 M NaOH aqueous solution followed by acidification and subsequent column chromatography (Table 1, entry 1). Further screening of the catalysts and reaction conditions revealed that changing the counterions on the gold catalysts to OTf^-, SbF_6^-, BF_4^-, or PF_6^- only have a slight influence on the reaction course, as **3a** was obtained in 83−91% yields in these cases (Table 1, entries 2−5). In the presence of gold(III) complex $PicAuCl_2$ (dichloro(2-pyridinecarboxylato)-gold),[15] however, the desired **3a** was formed in a lower yield of 58% (Table 1, entry 6). The use of toluene or THF as the solvent also afforded **3a** in good yields of 78−88% (Table 1, entries 9−10). Control experiments with PPh_3AuCl or $AgNTf_2$ alone did not give the desired product (Table 1, entries 11−12). It should be noted that the X-ray crystallographic analysis of **3a**[16] showed a structure of 2-benzoyl-5-hydroxy tropone (**3a′**). However, HMBC experiments of **3a** and other related products in $CDCl_3$ indicated that the hydroxyl group is close to the phenylcarbonyl group (structure of **3a**). Moreover, protection of **3a** afforded a mixture of **4a**[16] and **5a** (Scheme 2). Thus, it is

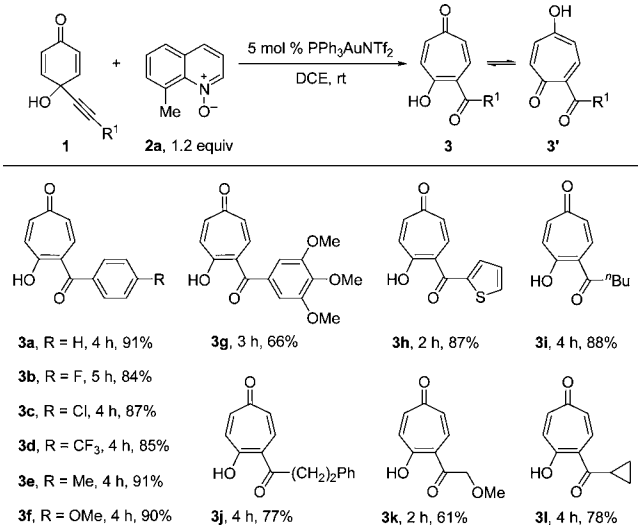
Scheme 2. Protection of 3a



likely that, in solution, tropone **3a** equilibrates with **3a′**, in which **3a** is the dominant species due to exhibiting intramolecular H-bonding. However, the equilibrium can shift to **3a′** in different solvents or under certain conditions. **3a′** predominates in its solid form, possibly caused by the intermolecular H-bonding.

Next, the substrate scope of this ring-expansion reaction was evaluated under the reaction conditions shown in Table 1, entry 1. As shown in Scheme 3, a wide range of diversely substituted

Scheme 3. Gold-Catalyzed Ring Expansion of Alkynyl Quinols to Tropones[a]



[a]Isolated yields. All reactions were carried out on 0.3 mmol scale.

aryl and alkyl alkynes were suitable for this reaction, and the desired tropones **3a−3l** were obtained in good to excellent yields within a short reaction time.[17] Both of the electron-deficient (*p*-F, *p*-Cl, *p*-CF_3) and electron-rich substituents (*p*-Me, *p*-OMe, 3,4,5-$(MeO)_3$) on the aryl rings were tolerated well during the reaction, leading to **3b−3g** in 66−91% yields. The results indicated that, in general, the electronic nature of the aryl substituents had some influence on the product yields. A heteroaryl-substituted alkyne such as thienyl-substituted one was also compatible in this reaction, furnishing **3h** in 87% yield. The

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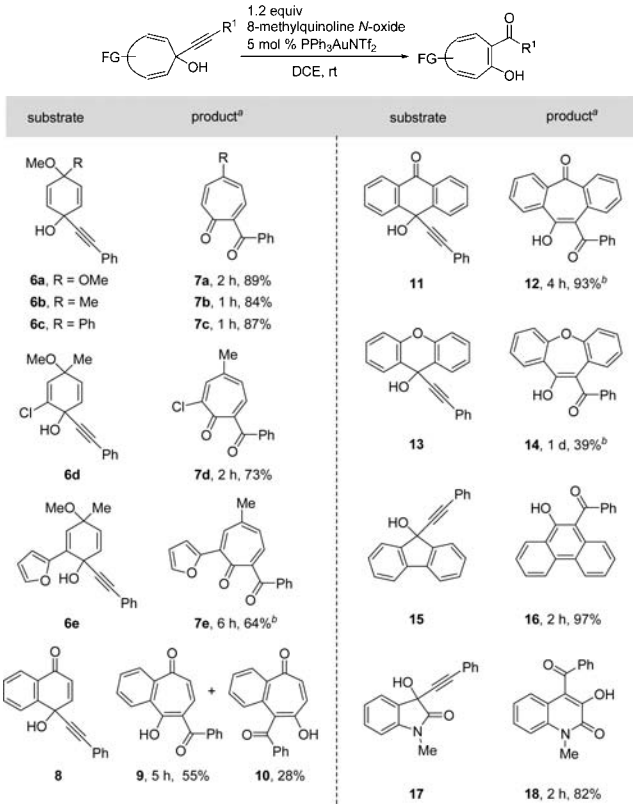
reactions also proceeded smoothly with the alkyl-substituted alkynes. For example, a linear alkyl group such as *n*-butyl- or phenylethyl-substituted alkynes provided **3i** and **3j** in 88% and 77% yields, respectively. An alkyne with a methyl-protected alcohol moiety was transformed into **3k** in a satisfactory yield of 61%. A cyclopropyl substituted alkyne was also well tolerated, furnishing **3l** in 78% yield, while the cyclopropane ring remained intact.

Encouraged by these results, we next anticipated that a broad range of substrates with different structural features could undergo ring expansion with comparable efficiency. In principle, any appropriate cyclic compounds bearing a propargyl alcohol moiety could be suitable substrates for the construction of new carbo- or heterocycles with one-carbon ring expansion by this chemistry. The representative results are shown in Table 2. Our

Table 2. Gold-Catalyzed Ring Expansion of Various Carbo- or Heterocycles

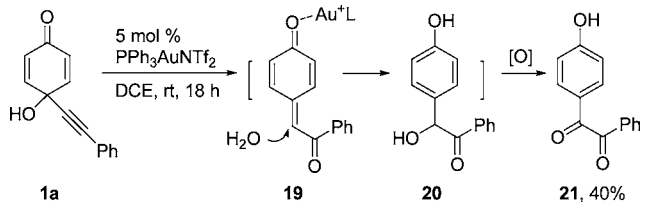


[a]Isolated yields. [b]Pyridine *N*-oxide was used.

initial results of gold-catalyzed ring expansion of alkynyl quinol derivatives with a MeO− substituent at the C-4 position were very promising, leading to tropones **7a**−**7c** in 84−89% yields. Alkoxy, alkyl, and aryl groups as R substituents were all compatible in these reactions. The results also revealed that further elimination of a methoxy group occurred during the process, possibly, assisted by a gold catalyst. In the case of **6d** functionalized with a chlorine substituent, selective migration of the alkenyl moiety bearing no substituent occurred to give **7d** exclusively in 73% yield, indicating a more nucleophilic alkene side migrated preferentially. The steric effect of the chlorine group may also account for the selectivity. Regioselective migration of the nonsubstituted vinyl group was also observed in furanyl-substituted **6e**, possibly due to steric hinderance. Alkyne **8** derived from 1,4-naphthoquinone afforded benzotropone as a mixture of two regioisomers. The predominant product in this reaction was ketone **9** via 1,2-vinyl migration, indicating that the migratory aptitude of a vinyl group is more favorable than a phenyl group. Major isomer **9** possibly also forms an equilibrium with its tautomer similar to that of **3** and **3′**, although the 2D NMR spectra (HMBC) indicated that the OH group is close to the phenylcarbonyl group. Ring expansion of **11** derived from anthracene-9,10-dione proceeded quite efficiently in the presence of simple pyridine *N*-oxide as the oxidant, furnishing dibenzotropone **12** in 93% yield. Similar ring expansion was also observed in the reaction of **13**, in which the carbonyl group had been replaced by an oxygen atom. The corresponding benzooxepine **14** was formed with a lower yield of 39%. Substrate **15** derived from 9-fluorenone underwent the ring-expansion reaction efficiently to produce 9-hydroxyphenanthrene **16** in a high yield of 97%. Alkyne **17** derived from isatin was also a perfect substrate for this ring-expansion reaction, leading to 3-hydroxy-quinolin-2(1*H*)-one derivative **18** via a selective 1,2-phenyl migration in 82% yield, while a product derived from a 1,2-carbonyl migration was not detected. 3-Hydroxy-quinolinones are present in a variety of biologically active substances or natural products,[18] which are usually prepared by ring expansion of diazo adducts of isatins.[19] Our method could avoid the use of the hazardous diazo compounds. The results in Table 2 indicate that the current method can be a general and attractive approach for the synthesis of a diverse type of carbo- or heterocycles, especially for medium-sized ring compounds which are difficult to access. The structures of the obtained products were further confirmed by X-ray crystallographic analyses of **7c**, **7e**, **10**, **12**, and **18**.[16] It was noted that most of the products listed in Table 2 can be purified directly by column chromatography on silica gel.

In the absence of *N*-oxide, a diketone product **21** was obtained in 40% yield, along with 17% of 4-(phenylethynyl)phenol **22** (Scheme 4). The results were in complete contrast with Pt-

Scheme 4. Formation of Diketone 21



catalyzed reactions of alkynyl quinols, in which a 1,2-alkynyl migration followed by cyclization occurs to afford 5-hydroxybenzofurans.[20] The formation of **21** might be rationalized by first generating enone **19** via gold-catalyzed Meyer−Schuster rearrangement[21] of **1a** with water contaminated in the reaction mixture followed by conjugate addition and oxidation. Addition of 1 equiv of water could accelerate the reaction (3 h), however, producing the same yield of **21** (40%). ^{18}O-isotope labeling experiments with $H_2{}^{18}O$ indicated that both of the carbonyl oxygens were labeled, which supported the proposed mechanism.

In summary, we have developed a new and convenient strategy for the synthesis of functionalized tropones based on the gold-catalyzed oxidative ring expansion of alkynyl quinols. The reaction proceeds via a gold-catalyzed highly regioselective oxidation followed by the 1,2-migration of a vinyl or phenyl group. Extension of this chemistry allows ready access to various

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seven- or six-membered ring systems such as benzotropones, benzooxepines, phenanthrenes, and quinolin-2(1*H*)-ones. These results demonstrate the great synthetic utility of this methodology. Further applications of this chemistry toward highly valuable carbo- or heterocycles are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03160.

Experimental details, spectroscopic characterization of all new compounds (PDF)
X-ray crystallography of **3a′** (CIF)
X-ray crystallography of **3e′** (CIF)
X-ray crystallography of **4a** (CIF)
X-ray crystallography of **7c** (CIF)
X-ray crystallography of **7e** (CIF)
X-ray crystallography of **10** (CIF)
X-ray crystallography of **12** (CIF)
X-ray crystallography of **18** (CIF)

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Notes

The authors declare no competing financial interest.

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(14) The ^{1}H NMR analysis of the reaction mixture indicated that the hydroxyl proton of **3a** was absent, possibly due to the existence of basic species such as 8-methylquinoline in the reaction mixture, which captured this acidic proton.

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(16) The X-ray crystallography of **3a′**, **3e′**, **4a**, **7c**, **7e**, **10**, **12**, and **18** are shown in the Supporting Information.

(17) TsOH·H_2O was required as an additive to complete the reaction when the reaction was scaled up; for details, see the Supporting Information.

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