Advanced Synthesis & Catalysis

Accepted Article

Title: Gold(III)-Catalyzed Intermolecular Oxidation-Cyclization of Ynones: Access to 4-Substituted Chroman-3-ones

Authors: Jian Li, Fang Yang, Yang-Ting Ma, and Kegong Ji

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201900260

Link to VoR: http://dx.doi.org/10.1002/adsc.201900260

10.1002/adsc.201900260

UPDATE

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Gold(III)-Catalyzed Intermolecular Oxidation-Cyclization of Ynones: Access to 4-Substituted Chroman-3-ones

Jian Li, [a] Fang Yang, [a]* Yang-Ting Ma, [a] and Kegong Ji [a]*

[a] College of Chemistry and Pharmacy, Northwest A&F University; Shaanxi Key Laboratory of Natural Products & Chemical Biology, 3 Taicheng Road, Yangling, 712100, Shaanxi (P.R. China).
[E-mail addresses: yf10@nwsuaf.edu.cn; jikegong@nwsuaf.edu.cn]

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. A synthesis of 4-substituted chroman-3-one derivatives has been developed through a gold(III) catalyzed oxidation-cyclization of ynones in good to excellent yield using easily prepared substrates. A broad range of synthetically useful functional groups (halide, alkene, alkyne, phenolic hydroxyl) were tolerated. Further application of this method paves a new way to prepare the skeleton of oblarotenoids. A cascade oxidative cyclization for construction of pyrano[2,3-c]chromen-1(5H)-one derivatives is also presented.

Keywords: Gold(III) catalyzed; Oxidation; 4-substituted chroman-3-ones; Pyrano[2,3-c]chromen-1(5H)-ones

The chroman-one motif is a common structure pattern found at the skeleton of numerous natural products of varying complexity.[1] Furthermore, 4-acyl-3-hydroxychromans as well as its tautomers are also important structural units that occur in many natural products such as oblarotenoids A and C, hydroxymunduserone and munduserone.[2a] These compounds possess diverse biological activities including insecticidal, piscicidal, icthyocidal and anti-cancer activities (Figure 1). [2b] The most frequent methods to synthesize the 4-acyl-chroman-3-one units rely on the reported procedures through multistep routes from basic chemicals. In brief, the typical process was started from 2-benzyloxybenzaldehyde, with 6 steps, to afford 4-acyl-chroman-3-one motifs in less than 20% yield (Scheme 1A),[3] which is very inefficient. Recently, a transition-metal-catalyzed aromatic C-H insertion of α-diazo β-ketoesters was reported providing an alternative route to 4-carbonyl chroman ester derivatives (Scheme 1B). Although the route is accessible, the α-diazo compounds are toxic, explosive and difficult to obtain.[4] Considering the multistep process as well as limited scope and the drawbacks associated with applying diazo-compounds of the reported approaches, it is still highly desirable to pave a novel and efficient route to access the highly substituted and functionalized 4-acyl-chroman-3-one derivatives.

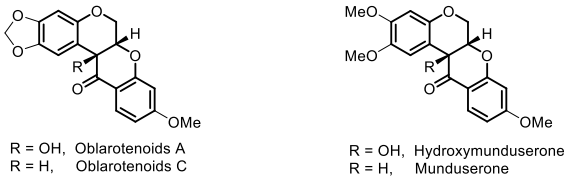


Figure 1. Natural products containing chromanones.

In recent years, homogeneous gold catalyzed reactions have been recognized as one of the most useful and powerful tools in organic synthesis.[5] Due to the propensity of gold to act as a soft and carbophilic Lewis acid in the activation of carbon-carbon π-bonds,[5l, 6] it has been used to catalyze various carbene transfer reactions such as X-H (X = C, N, O) insertion,[7] cyclopropanation,[8] and cycloaddition[9] reactions. On the other hand, gold(I)-catalyzed oxidation reactions of ynones *via* the α-oxo gold carbene intermediates also gained much attention due to their flexible ability to participate in a wide range of transformations.[10] However, in the oxidation of alkynes using *N*-oxide as oxidant, gold(III) is a less efficient catalyst, because of its strong oxophilic nature. For a more useful approach to oxidation of alkynes and the development of a gold catalyst, as shown in Scheme 1C, our design anticipated that with phenoxyl-ynone substrates **1** and π-philicity/oxophilicity nature of gold(III) as catalyst, a novel non-carbene model of allenyloxygold(III)-species was proposed and subsequently the allenyloxygold(III)-species would be attacked by an appropriately tethered internal phenoxyl group via concerted S_N2' type addition to affords 4-substituted

10.1002/adsc.201900260

chroman-3-one **3,** which is an important motif in natural products. Herein, we report an efficient access to obtian 4-substituted chroman-3-ones through gold(III)-catalyzed oxidation of readily available phenoxyl-ynones.

Scheme 1. Accesses to chroman-3-one motifs

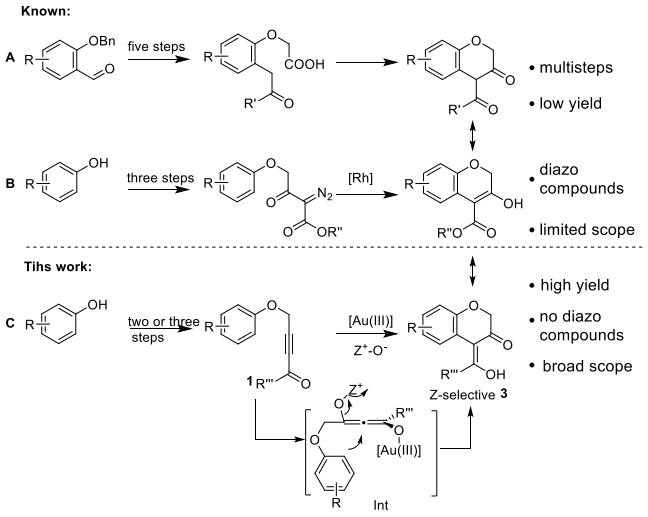
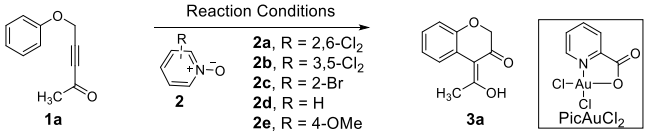


Table 1 Optimization of Reaction Conditions[a]



Entry	Catalyst (5 mol %)	Conditions	Yield (%)[b]
1	$Ph_3PAuCl/AgNTf_2$	PhF, rt, 24 h	0(95)[h]
2	$IPrAuCl/AgNTf_2$	PhF, rt, 24 h	0(93)[h]
3	$Me_4{}^tBuXPhosAuCl/AgNTf_2$	PhF, rt, 24 h	11(80)[h]
4	$PicAuCl_2$	PhF, rt, 24 h	47
5	$PicAuCl_2$	PhF, 40 °C, 16 h	60
6	$PicAuCl_2$	PhF, 50 °C , 8 h	66
7	$PicAuCl_2$	PhF, 60 °C , 5 h	72
8	$PicAuCl_2$	PhF, 70 °C, 2 h	70
9	$PicAuCl_2$	PhF, 80 °C, 2 h	68
10	$PicAuCl_2$	DCE, 60 °C, 5 h	55
11	$PicAuCl_2$	$CHCl_3$, 60 °C, 5 h	49
12	$PicAuCl_2$	$PhCH_3$, 60 °C, 5 h	76
13	$PicAuCl_2$	PhCl, 60 °C, 1.5 h	82
14 [c]	$PicAuCl_2$	PhCl, 60 °C, 4 h	61
15 [d]	$PicAuCl_2$	PhCl, 60 °C, 6 h	55
16 [e]	$PicAuCl_2$	PhCl, 60 °C, 6 h	52
17 [f]	$PicAuCl_2$	PhCl, 60 °C, 6 h	44
18 [g]	$PicAuCl_2$	PhCl, 60 °C, 6 h	20

[a]Reaction conditions: All reactions were run in vials in the presence of **1a** (0.2 mmol), **2** (0.3 mmol); [**1a**] = 0.5 M.
[b]Isolated yields.
[c]3 mol % catalyst was used.
[d]**2b** as oxidant.
[e]**2c** as oxidant.
[f]**2d** as oxidant.
[g]**2e** as oxidant.
[h]Recovery of **1a**.

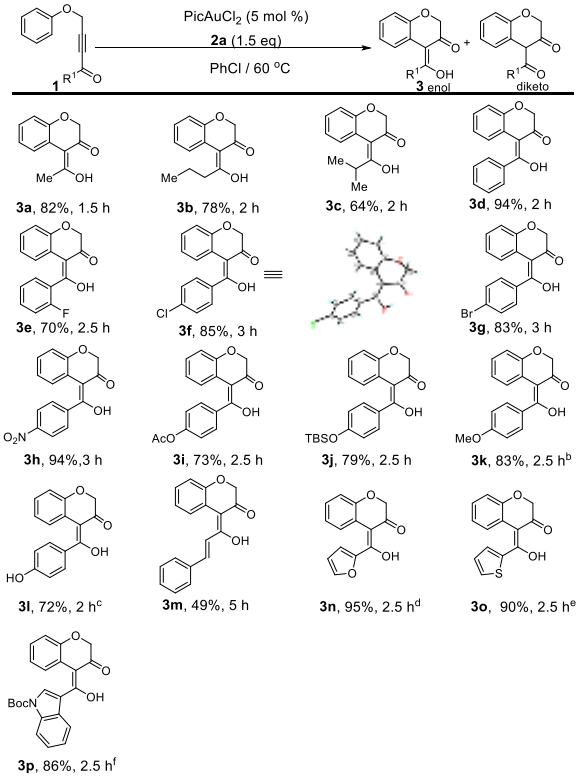
Initially, reactions of 5-phenoxypent-3-yn-2-one **1a** with pyridine *N*-oxide **2** in the presence of various gold catalysts were investigated to achieve the optimal reaction conditions. Interestingly, when the reaction was conducted in fluorobenzene (PhF) for 24 h, in the presence of gold(I) catalysts derived from typical ligands such as Ph_3P, Phosphite, IPr, and $Me_4{}^tBuXPhos$, no desired product was achieved, only leading to an 82-95% recovery of starting material **1a** (Table 1, entries 1 - 3). On the other hand, the use of 5 mol % $PicAuCl_2$ as the catalyst and the 2,6-dichloropyridine *N*-oxide **2a** as the oxidant in PhF resulted in the formation of 4-(1-hydroxyethylidene)chroman-3-one **3a** in 47% yield after 24 h at room temperature (Table 1, entry 4). That revealed that the gold(III) catalyst was more efficient than the gold(I) catalyst, this mainly due to the carbophilicity and oxophilicity of gold(III) catalyst. In addition to the alkynyl activation, the gold(III) catalyst shows stronger Lewis acidity to activate the carbonyl group of the ynone to trigger this cyclization. When increasing the temperature to 40, 50 or 60 °C, a slight improvement in the yield was observed (Table 1, entries 5-7). When the reaction temperature was further increased to 70 or 80 °C, a slight decrease in the yield was observed (Table 1, entries 8-9). These results indicated that the optimal reaction temperature was 60 °C. A solvent study showed that changing the solvents to DCE or $CHCl_3$, resulted in lower yields (Table 1, entries 10 and 11). When toluene and chlorobenzene (PhCl) were used as the solvents, the yields of **3a** were obtained in 74% and 82%, respectively (Table 1, entries 12 and 13), with PhCl turning out to be superior to other solvents. Subsequent lowering of catalyst loading to 3 mol % afforded **3a** in 61% yield, even after a longer time. (Table 1, entry 14). Moreover, Pyridine *N*-oxides, **2b-2e**, were less efficient than oxidant **2a** (Table 1, entries 15 - 18). Finally, Lewis acids such as $Cu(OTf)_2$, $Zn(OTf)_2$ and $AgNTf_2$, which showed strong activation toward carbonyl group, but did not catalyze this reaction (for details, see Supporting Information (SI), table 1).

With the optimal conditions established (Table 1, entry 10), a variety of functionalized ynones were first examined in the oxidation-cyclization (Scheme 2). As expected, the reaction was proved to be compatible with various R^1 groups on the ynone moieties. When R^1 groups were aliphatic groups (propyl and *i*-propyl) the desired chroman-ones **3b** and **3c** were obtained in moderate to good yields. Varying the R^1 group to a phenyl group, **3d** was obtained in an excellent yield. Switching substituents installed on the aromatic groups of the ynones resulted a considerable change in the yields of desired

10.1002/adsc.201900260

products. Both electron-deficient (*o*-F, *p*-Cl, *p*-Br and *p*-NO_2) and rich (*p*-OAc, *p*-OTBS and *p*-OMe) ynones underwent the reaction smoothly providing the corresponding products **3e** - **3k** in excellent yields of 70 - 94%, irrespective of electronic effects. Notably, the substrate **1l** bearing a free phenolic hydroxyl group also smoothly participated in this reaction and the expected product **3l** was delivered in a 72% yield. In addition, the heteroaryl substituents such as 2-furyl, 2-thienyl and N-Boc protected 3-indolyl groups were well tolerated under the reaction conditions, thus giving **3n** - **3p** in excellent yields ranging from 86% to 95%. Interestingly, the styryl derived substrate **1m** yielded **3m** in a moderate yield indicating that the conjugated-ene was also suitable for this annulation reaction. The stereochemistry of **3f** was established by X-ray crystallographic analysis (CCDC 1816739)[12] and other 4-substituted chroman-3-one derivatives were assigned by analogy.

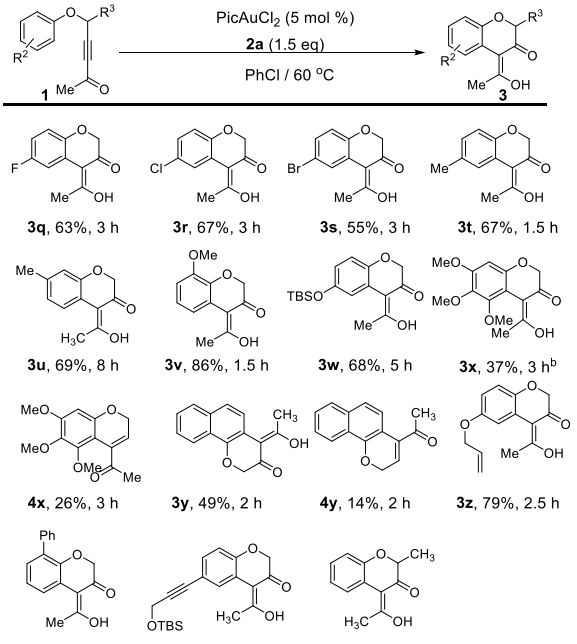
Scheme 2. Substrate Scope of Substituted Ynones[a]



[a]All reactions were carried out in 4 mL PhCl in the presence of **1** (0.2 mmol), **2a** (0.3 mmol); isolated yields are reported.
[b]enol : diketo = 25 : 1.
[c]enol : diketo = 33 : 1.
[d]enol : diketo = 6.3 : 1.
[e]enol : diketo = 7.1 : 1.
[f]enol : diketo = 9 : 1.

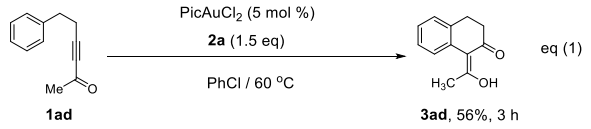
Next, we anticipated that the use of substrates derived from the functional phenoxyl ethers would enable the incorporation of substituents R^2 on the various positions of the phenyl rings (Scheme 3). Generally, substrates bearing both electron-withdrawing (*p*-F, *p*-Cl, *p*-Br) and electron-donating (*p*-Me, *m*-Me, *o*-OMe, and *p*-OTBS) substituents on the phenyl rings were well compatible for this reaction, furnishing **3q** - **3w** in good to high yields. The substrates with electron-rich substituent 3,4,5-trimethoxyphneyl and naphthyl groups proceeded smoothly under the standard conditions, and the corresponding products **3x** and **3y** were obtained in 37% and 49% yields separately, along with 26% and 14% yields of 1-(2*H*-chromen-4-yl)ethanones **4x** and **4y**, which were formed directly through a competitive gold catalyzed 6-*endo-dig* cyclization. Ynone **1z** equipped with O-allyl substituent on the phenyl ring could also undergo the desired cyclization giving **3z** in a 79% yield without interfering the π bond. A sterically demanding *o*-phenyl group on the aryl ring was well suited, affording **3aa** in a 75% yield. In the case of **1ab**, the gold catalyst activated the ynone selectively rather than the TBS protected propargyl-ol motif, providing the target molecule **3ab** in a moderate yield, which could offer opportunities for further structural diversification via various reported methods. Specially, the substrate, 5-phenoxyhex-3-yn-2-one, gave a high yield of the desired product **3ac**.

Scheme 3. Substrate Scope of Aromatic Ethers[a]



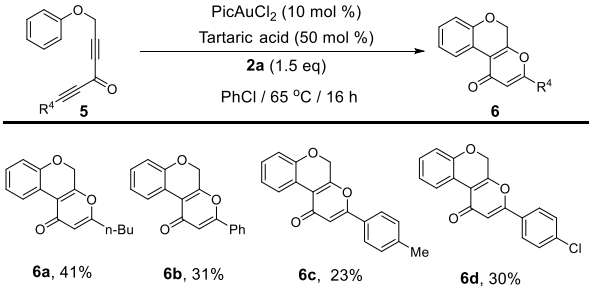
[a]All reactions were carried out in 4 mL PhCl in the presence of **1** (0.2 mmol), **2a** (0.3 mmol); isolated yields are reported.
[b]enol : diketo = 2.3 : 1.

Moreover, we attempted to expand the chemistry to the all-carbon counterpart of **1a**, i.e., 6-phenylhex-3-yn-2-one **1ad**. As illustrated in eq (1), the desired (Z)-1-(1-hydroxyethylidene)-3,4-dihydronaphthalen-2(1H)-one **3ad** was also obtained in a 56% yield, which is a useful motif in natural products.



Inspired by the scaffolds of natural products[2], and the reported literature, which indicates that diynones could participate in diversified cascade cyclization and rearrangement reactions,[11] we explored the reactions of diynones (Scheme 4). Under the standard conditions, the diynones did not convert into the corresponding products efficiently. Various reactions were tested to screen out optimal reaction conditions (for details, see SI, Table 2). In brief, employing Brønsted acids as additives gave better results than other additives such as bases, Lewis acids and some other coordinating reagents; in particular, tartaric acid turned out to be the best additive, which could activate the carbonyl group of the ynone moiety to help to trigger the 6-endo-dig cyclization. Treating the substrate **5a** in the presence of $PicAuCl_2$ (10 mol %) and tartaric acid (0.5 equiv), the oxidation proceeded selectively at the C-5 atom of the tethered diynones resulting **6a** in a 41% yield. Moreover, switching substituents of the diynones resulted a slight change in the yields of desired products. The phenyl, 4-tolyl and 4-chlorophenyl substituted diynones were also tolerated.

Scheme 4. Substrate Scope of Diynones[a]

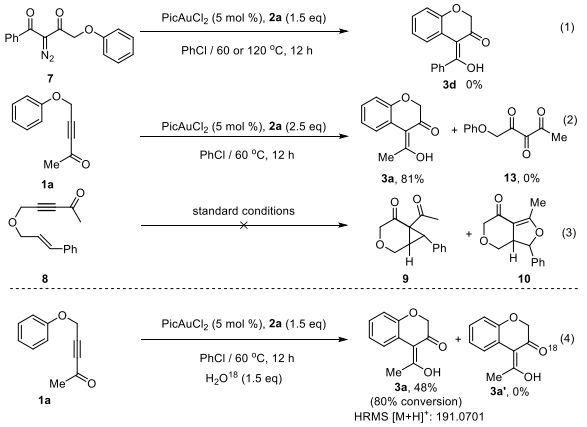


[a]All reactions were carried out in 4 mL PhCl in the presence of **5** (0.2 mmol), **2a** (0.3 mmol); isolated yields.

In order to gather additional experimental evidence for the mechanism, we investigated the gold(III)-catalyzed the authentic diazo carbonyl species **7** in PhCl at 60 or 120 °C for 12 h as shown in Scheme 5, where the desired product **3d** was not observed.[13] We also carried out **1a** with an excess of *N*-oxide **2a** (2.5 equiv), where the double oxidation by-product **13** was not observed and the desired product **3a** was isolated in 81% yield. 5-(Cinnamyloxy)pent-3-yn-2-one **8**[10g] was also tested under standard conditions, but no desired gold carbene cyclopropanation product **9** and cycloisomerization product **10** were observed. These control experiments implied that the pure α-oxo gold carbene might not be the true reactive intermediate in this reaction (for details, see SI).

Additionally, in order to seek out the source of the new oxygen atom of the 4-substituted chroman-3-ones, several experiments were investigated. We carried out the reaction in the presence of H_2O (1.5 eq.) without adding *N*-oxide **2a**; however, no reaction was observed. The reaction was also attempted in the

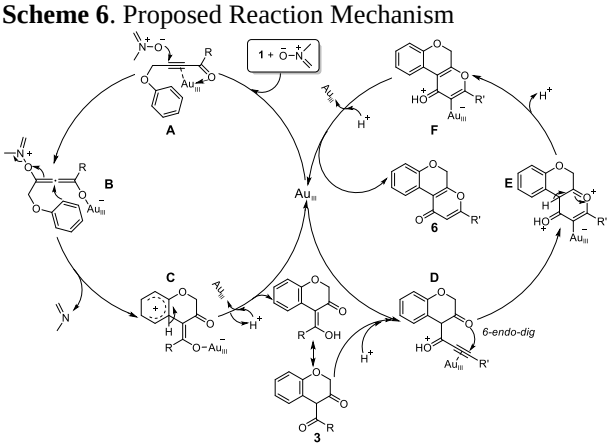
Scheme 5. Mechanistic Studies



presence of H_2O^{18}, and no O^{18} labeled product **3a′** was detected from HRMS, indicating that the new oxygen of **3a** was from the *N*-oxidant **2a** (Scheme 5, Eq(4)), (for control experiment details, see SI).

Based on these observations, a postulated mechanism of these reactions is depicted in scheme 6. Gold(III) first coordinates with C-C triple bonds and carbonyl group, where the N-oxide subsequently attacks the distal end of ynone to give allenyloxy-gold(III)-species **B**. Then, the aryl group as a nucleophile attacks at the C-2 position of the allenyloxy-gold(III) intermediate **B** to drive the 2,6-dichloropyridine away *via* S_N2'-type addition, resulting in the formation of intermediate **C**, which aromatizes to give chromanone scaffold **3** and releases the gold complex. When an alkynyl R′ group is installed on an ynone moiety, the acid activates the carbonyl group, and the gold(III) coordinates with the alkynyl in the ynone system, which is attacked by the internal ketone group *via* a *6-endo-dig* cyclization to give the oxonium species E. Finally, the oxonium species **E** is rapidly isomerized to give product **6** and release the gold complex.

Scheme 6. Proposed Reaction Mechanism



During the derivatization of 4-substituted chroman-3-ones, the esterification of **3l** with 4-bromobenzoyl chloride afforded the corresponding diester derivative **11** in a good yield (Scheme 7). Interestingly, the structure of the diester derivative was not in accordance with its precursor, but was similar to the tautomer

Scheme 7. Esterification of **3l**

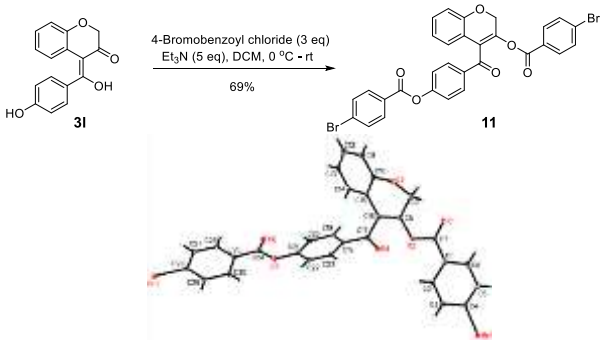
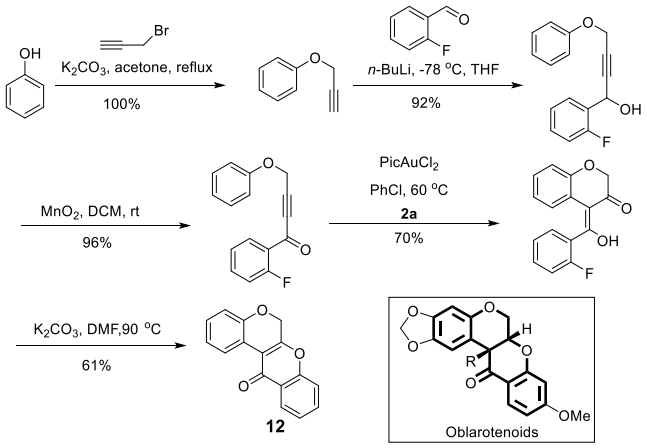


Figure 2. Solid-state molecular structure of **11**

(3-hydroxyl-2H-chromene-4-carbalone), and the relative stereochemistry of **11** was determined by X-ray crystallographic analysis (CCDC 1860836)[12] (Figure 2). Additionally, chroman-one **3e**, which could be prepared easily from phenol, was subjected to further transformations to access more complex scaffolds. The main skeleton of oblarotenoids **12** were obtained by heating **3e** and K_2CO_3 in DMF at 90 °C in an acceptable yield (Scheme 8).

Scheme 8. Synthesis of the Butacyclic Skeleton of oblarotenoids



In conclusion, we have demonstrated an unprecedented gold(III)-catalyzed oxidation/ cycloaddition of phenoxyl ynones to yield biologically important and highly impactful 4-substituted chroman-3-one derivatives. Easily prepared starting material, good to excellent yield and broad functional group compatibility make this new protocol attractive and practical. The synthetic utility of this chemistry is also indicated by the synthesis of the skeleton of some bioactive compounds. Additionally, the diynone substrates could also be screened for the construction of pyrano[2,3-c]chromen-1(5H)-one derivatives. These methods provide concise and efficient access to synthesize the main skeleton of some natural products.

Experimental Section

A 2, 6-dichloropyridine *N*-oxide (1.5 eq, 0.3 mmol, 48.9 mg), $PicAuCl_2$ (5 mol %, 0.01 mmol, 3.9 mg), PhCl (3 mL) were added successively to a flame-dried vial at room temperature and then a ynone **1a** (0.2 mmol) dissolved in PhCl (1 mL) was added to the above mixture. Then the vial was capped with a Teflon-coated cap, and the resulting solution was stirred at room temperature for 5 min, and then was heated at 60 °C until the reaction was complete, as monitored by thin layer chromatography. Upon completion, the solvent was removed under vacuo, the residue was purified by chromatography to get the desired compound **3a** as a colorless oil.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSF-21702170, 21502150), Natural Science Foundation of Shaanxi (2018JQ2072) and the Youth Training Programme of Northwest A&F University (Nos. 2452016006, 2452017034).

References

[1] S. T. Saengchantara, T. W. Wallace, *Nat. Prod. Rep.*, **1986**, *3*, 465-475.

[2] a) T. Deyou, M. Marco, M. Heydenreich, F. Pan, A. Gruhonjic, P. A. Fitzpatrick, A. Koch, S. Derese, J. Pelletier, K. Rissanen, A. Yenesew, M. Erdélyi, *J. Nat. Prod.*, **2017**, *80*, 2060-2066. b) N. Ling, *Science for Conservation*, **2003**, *211*, 1-40.

[3] a) S.A.N.N. Bokhari, W.B. Whalley, *J. Chem. Soc.*, **1963**, 5322-5327. b) L. Farkas, Á. Gottsegen, M. Nógrádi, S. Antus, *J. Chem. Soc., C*, **1971**, 1994-2000. c) S. Antus, L. Farkas, M. Nógrádi, F. Boross, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 948-953. d) S. Jammi, J. Maury, J.-S. Suppo, M. P. Bertrand, L. Feray, *J. Org. Chem.*, **2013**, *78*, 12566-12576.

[4] X. Zhang, M. Lei, Y.-N. Zhang, L.-H. Hu, *Tetrahedron*, **2014**, *70*, 3400-3406.

[5] a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.*, **2006**, *45*, 7896-7936. b) D.J. Gorin, F. D. Toste, *Nature*, **2007**, *446*, 395-403. c) A. S. K. Hashmi, *Chem. Rev.*, **2007**, *107*, 3180-3211. d) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.*, **2008**, *37*, 1766-1775. e) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.*, **2008**, *108*, 3326-3350. f) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.*, **2008**, *108*, 3351-3378. g) S. M. A. Sohel, R.-S. Liu, *Chem. Soc. Rev.*, **2009**, *38*, 2269-2281. h) P. Garcia, M. Malacria, C. Aubert, V. Gandon, L. Fensterbank, *ChemCatChem*, **2010**, *2*, 493-497. i) K. M. Engle, T.-S. Mei, X. Wang, J.-Q. Yu, *Angew. Chem.*

Int. Ed., **2011**, *50*, 1478-1491. j) H. A. Wegner, M. Auzias, *Angew. Chem. Int. Ed.*, **2011**, *50*, 8236-8247. k) M. N. Hopkinson, A. D. Gee, V. Gouverneur, *Chem. Eur. J.*, **2011**, *17*, 8248-8262. l) A. Corma, A. Leyva-Pérez, M. Sabater, *J. Chem. Rev.*, **2011**, *111*, 1657-1712. m) N. Krause, C. Winter, *Chem. Rev.*, **2011**, *111*, 1994-2009. n) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.*, **2012**, *41*, 2448-2462. o) H. Ohno, *Isr. J. Chem.*, **2013**, *53*, 869-882. p) M. E. Muratore, A. Homs, C. Obradors, A. M. Echavarren, *Chem. - Asian J.*, **2014**, *9*, 3066-3082. q) R. Dorel, A. M. Echavarren, *Chem. Rev.*, **2015**, *115*, 9028-9072. r) D. Qian, J. Zhang, *Chem. Soc. Rev.*, **2015**, *44*, 677-698. s) J. Miró, C. del Pozo, *Chem. Rev.*, **2016**, *116*, 11924-11966. t) Z. Zheng, Z. Wang, Y. Wang, L. Zhang, *Chem. Soc. Rev.*, **2016**, *45*, 4448-4458. u) F. Pan, C. Shu, L.-W. Ye, *Org. Biomol. Chem.*, **2016**, *14*, 9456-9465. v) K. Chen, S. Zhu, *Synlett*, **2017**, *28*, 640-653. w) M. O. Akram, S. Banerjee, S. S. Saswade, V. Bedi, N. T. Patil, *Chem. Commun.*, **2018**, *54*, 11069-11083.

[6] A. Fürstner, P.W. Davies, *Angew. Chem. Int. Ed*., **2007**, *46*, 3410-3449.

[7] a) Y. Luo, K. Ji, Y. Li, L. Zhang, *J. Am. Chem. Soc.*, **2012**, *134*, 17412-17415. b) K. Ji, Y. Zhao, L. Zhang, *Angew. Chem. Int. Ed.*, **2013**, *52*, 6508-6512. c) Y. Wang, Z. Zheng, L. Zhang, *J. Am. Chem. Soc.*, **2015**, *137*, 5316-5319. d) J. F. Briones, H. M. L. Davies, *J. Am. Chem. Soc.*, **2012**, *134*, 11916-11919. e) Y. Wang, K. Ji, S. Lan, L. Zhang, *Angew. Chem. Int. Ed.*, **2012**, *51*, 1915-1918.

[8] K. Ji, L. Zhang, *Org. Chem. Front.*, **2014**, *1*, 34-38.

[9] A. D. Melhado, G. W. Amarante, Z. J. Wang, M. Luparia, F. D. Toste, *J. Am. Chem. Soc.*, **2011**, *133*, 3517-3527.

[10] a) L. Zhang, *Acc. Chem. Res.*, **2014**, *47*, 877-888. b) C. Shu, L. Li, X.-Y. Xiao, Y.-F. Yu, Y.-F. Ping, J.-M. Zhou, L.-W. Ye, *Chem. Commun.*, **2014**, *50*, 8689-8692. c) F. Pan, S. Liu, C. Shu, R.-K. Lin, Y.-F. Yu, J.-M. Zhou, L.-W. Ye, *Chem. Commun.*, **2014**, *50*, 10726-10729. d) Z. Xu, R. Zhai, T. Liang, L. Zhang, *Chem. Eur. J.*, **2017**, *23*, 14133-14137. e) K. Ji, L. Zhang, *Adv. Synth. Catal.*, **2018**, *360*, 647-651. f) D. Qian, H. Hu, F. Liu, B. Tang, W. Ye, Y. Wang, J. Zhang, *Angew. Chem. Int. Ed.*, **2014**, *53*, 13751-13755. g) D. Qian, J. Zhang, *Chem. Commun.*, **2011**, *47*, 11152-11154. h) D. Qian, J. Zhang, *Chem. Commun.*, **2012**, *48*, 7082-7084. i) J. Fu, H. Shang, Z. Wang, L. Chang, W. Shao, Z. Yang, Y. Tang, *Angew. Chem. Int. Ed.*, **2013**, *52*, 4198-4202. j) G. Henrion, T. E. J. Chavas, X. L. Goff, F. Gagosz, *Angew. Chem. Int. Ed.*, **2013**, *52*, 6277-6282. k) N. Hamada, A. Yamaguchi, S. Inuki, S. Oishi, H. Ohno, *Org. Lett.*, **2018**, *20*, 4401-4405. l) K. Ji, F. Yang, S. Gao, J. Tang, J. Gao, *Chem. Eur. J.*, **2016**, *22*, 10225-10229. m) J. Li, H.-W. Xing, F. Yang, Z.-S. Chen, K. Ji, *Org. Lett.*, **2018**, *20*, 4622-4626.

[11] R. K. Shiroodi, M. Soltani, V. Gevorgyan, *J. Am. Chem. Soc.*, **2014**, *136*, 9882-9885.

[12] CCDC - 1860836, 1816739 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] A. V. Zhukhovitskiy, I. J. Kobylianskii, C.-Y. Wu, F. D. Toste, *J. Am. Chem. Soc*. **2018**, *140*, 466−474.

10.1002/adsc.201900260

COMMUNICATION

Gold(III)-Catalyzed Intermolecular Oxidation-Cyclization of Ynones: Access to 4-Substituted Chroman-3-ones

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Jian Li, Fang Yang, Yang-Ting Ma, and Kegong Ji