

Furan-Based *o*-Quinodimethanes by Gold-Catalyzed Dehydrogenative Heterocyclization of 2-(1-Alkynyl)-2-alken-1-ones: A Modular Entry to 2,3-Furan-Fused Carbocycles**

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Abstract: A strategy for *in situ* generation of furan-based *ortho*-quinodimethanes (*o*-QDMs) by the gold(I)-mediated dehydrogenative heterocyclization of 2-(1-alkynyl)-2-alken-1-ones in the presence of pyridine *N*-oxide under mild reaction conditions was developed. These *in situ* furan-based *o*-QDMs were trapped by electron-deficient olefins and alkynes, thus furnishing various 2,3-furan-fused carbocycles in good yields with high diastereo- and regioselectivities.

Furan is a fundamental subunit present in numerous bioactive natural products, as well as in pharmaceuticals, molecular electronics, and functional polymers.^[1] Moreover, furan also functions as a versatile building block for the synthesis of a variety of functional molecules through the oxidation and cycloaddition reactions.^[2] In the past years, much progress has been made on the synthesis of highly substituted furans from acyclic precursors.^[3,4] However, less attention has been paid to the synthesis of 2,3-furan-fused carbocycles,^[4] despite the presence of their ubiquitous structural skeleton in many natural products, such as pinguosone, furodysinins, and furanoeremophilanes (Figure 1).^[5]

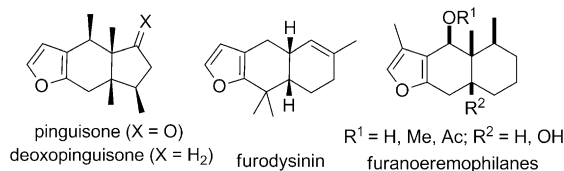
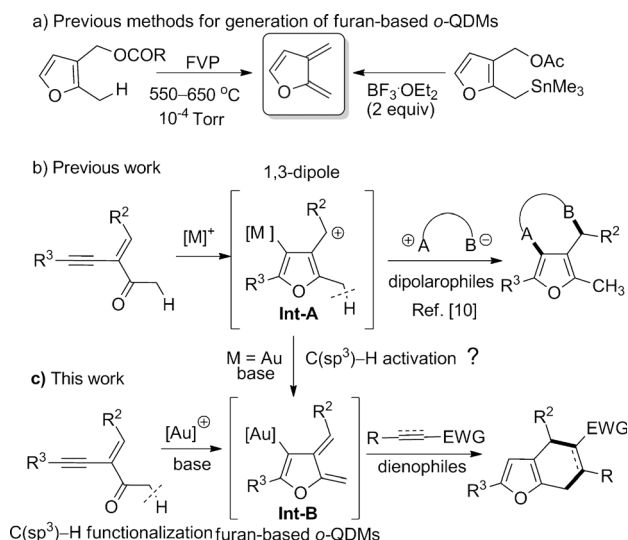


Figure 1. 2,3-Furan-fused carbocycle in natural products.

A Diels–Alder reaction of furan-based *ortho*-quinodimethanes (*o*-QDMs)^[6,7] with dienophiles is the most straightforward approach to 2,3-furan-fused carbocycles. To date, only a few methods for *in situ* generation of furan-based *o*-QDMs have been reported,^[8,9] including flash vacuum

pyrolysis (FVP > 550 °C and 10^{−4} Torr) of 2-methyl-3-furylmethyl ester and 1,4-elimination of 2,3-[2-((tributylstannyl)methyl)furan-3-yl]methylester (Scheme 1a). However, *o*-



Scheme 1. Comparison of previous work and this work. EWG = electron-withdrawing group.

QDMs generated by the FVP method have not yet been used in Diels–Alder reactions because of their rapid [4+4] dimerizations under the reaction conditions.^[9] The latter method is efficient and used in Diels–Alder reactions, but suffers from the use of toxic tin compounds. With respect to atom economy and step economy, *in situ* generation of furan-based *o*-QDMs from readily available acyclic precursors under mild reaction conditions is considered to be the most straightforward and efficient option.

In contrast, since the elegant work by Larock and co-workers,^[10a] 2-(1-alkynyl)-2-alken-1-ones, which could be easily prepared on large scale from simple terminal alkynes and α -bromo- α,β -enones, have emerged as powerful precursors for diversity synthesis.^[10,11] In such transition-metal-catalyzed reactions,^[10] metal all-carbon 1,3-dipole intermediates (**Int-A**) are commonly proposed, and they react with a variety of dipolarophiles, thus leading to 3,4-furan-fused ring systems (Scheme 1b). We envisaged that furan-based *o*-QDMs (**Int-B**) might be generated by the base abstraction of one proton from the 2-methyl group of **Int-A** (M = Au). It is crucial to find an appropriate base that is strong enough to abstract the proton and is also compatible with the Lewis acidic metal catalyst. Herein, we report a mild, efficient, and

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atom-economic strategy for in situ generation of furan-based *o*-QDMs (**Int-B**) from acyclic 2-(1-alkynyl)-2-alken-1-ones through a gold-mediated dehydrogenative heterocyclization in the presence of pyridine *N*-oxide (involving a challenging C(sp³)-H activation of the methyl group). A variety of 2,3-furan-fused carbocycles were obtained in good yields with high regioselectivity and diastereoselectivity, by reacting **Int-B** with a range of electron-deficient olefins and alkynes as dienophiles (Scheme 1c). To the best of our knowledge, our work represents the first approach, since Cava reported the first example of *o*-QDMs 56 years ago,^[6d] toward furan-based *o*-QDMs from acyclic precursors.

To test our hypothesis, the compound **1a** (see Table 1) and dienophile tetracyanoethylene (**2**) were chosen as model substrates. Because the base is crucial to the realization of this reaction, a series of inorganic and organic bases, such as K₂CO₃, 1,4-diazabicyclo[2.2.2]octane (DABCO), Et₃N, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), were examined with the use of [Ph₃PAuCl] as the catalyst. However, to our disappointment, no desired product (**3a**) was observed (for details, see Table S1 in the Supporting Information). Inspired by the delicate findings, by the groups of Zhang^[12] and Liu,^[13] that *N*-oxides of 2,6-lutidine, 2,6-dichloropyridine, and nitrosobenzene could act as weak bases in some gold-catalyzed transformations, pyridine *N*-oxide and nitrosobenzene were tested. Much to our delight, 89% yield of **3a** was isolated when 0.1 equivalents of pyridine *N*-oxide was employed as the weak base.

With the optimized reaction conditions in hand, the reaction scope was first examined by variation of the 2-(1-alkynyl)-2-alken-1-ones (Table 1). Halophenyl groups (**1c** and **1d**) are compatible. To our delight, the [4+2] reactions of the substrates with R² = styryl took place regioselectively, and no product resulting from 6 π -electrocyclization of the furan-based *o*-QDMs was observed, thus indicating that this process is highly chemoselective. The substituent effect of R³ on the alkyne moiety was also studied and showed that

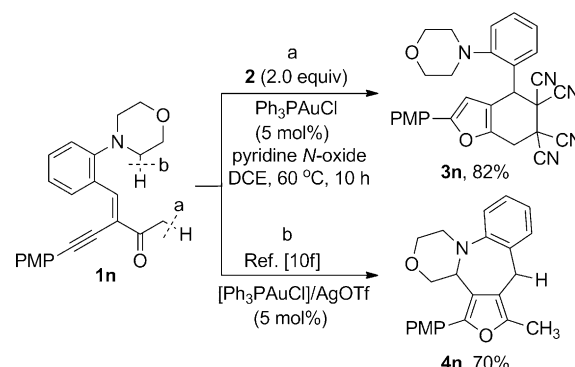
Table 1: The scope of 2-(1-alkynyl)-2-alken-1-one **1** reacting with **2**.

Entry	R ² /R ³ (1)	3	Yield [%] ^[a]
1	Ph/Ph (1a)	3a	89
2	4-MeOC ₆ H ₄ /4-MeOC ₆ H ₄ (1b)	3b	85
3	4-BrC ₆ H ₄ /Ph (1c)	3c	71
4	4-ClC ₆ H ₄ /Ph (1d)	3d	74
5	styryl/Ph (1e)	3e	91
6	styryl/ <i>n</i> Bu (1f)	3f	75
7	Ph/4-MeC ₆ H ₄ (1g)	3g	77
8	Ph/4-MeCOC ₆ H ₄ (1h)	3h	71
9	Ph/4-MeO ₂ CC ₆ H ₄ (1i)	3i	74
10	Ph/4-CF ₃ C ₆ H ₄ (1j)	3j	73
11	Ph/4-O ₂ NC ₆ H ₄ (1k)	3k	78
12	Ph/1-naphthyl (1l)	3l	65
13	Ph/2-thienyl (1m)	3m	85

[a] Yield of the isolated product. DCE = 1,2-dichloroethane.

aromatic (**1g–l**), heteroaromatic (**1m**), and aliphatic (**1f**) groups can be introduced to the products.

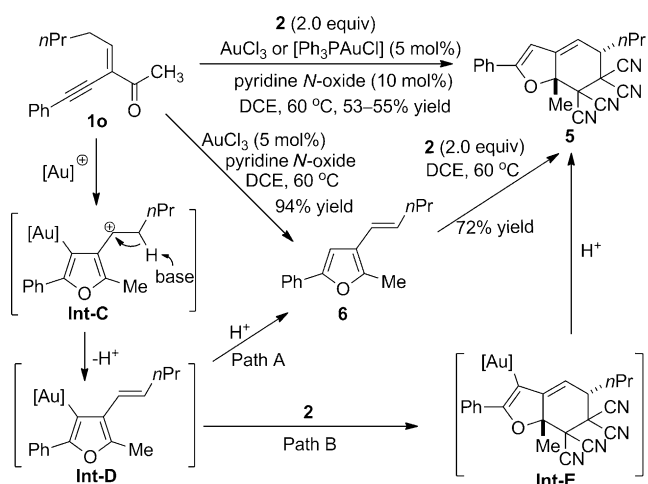
In our previous work,^[10f] the compound **1n** underwent a domino heterocyclization/1,5-H shift/annulation process to give the polyheterocycle **4n** in 70% yield (Scheme 2). With



Scheme 2. Selective transformations of the compound **1n** by two different C(sp³)-H functionalizations. PMP = *para*-methoxyphenyl, Tf = trifluoromethanesulfonyl.

this background, we became curious about whether the tandem furan-based *o*-QDM formation and Diels–Alder reaction could take place, or not, under the present reaction conditions. To our delight, the reaction worked well to produce the desired cycloadduct **3n** in 82% yield, in which the morpholine moiety was untouched. Notably, no **4n** was detectable, thus indicating that the pyridine *N*-oxide can shut down the competing domino reaction by efficient and rapid conversion of the 1,3-dipoles into furan-based *o*-QDMs.

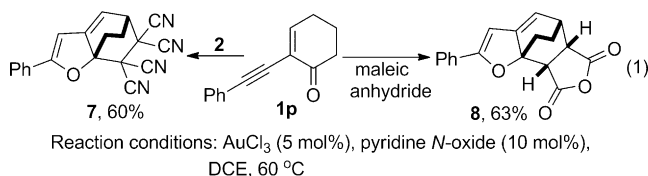
It is interesting to find that a new type of dearomative cycloadduct (**5**) was formed, rather than the expected cycloadduct **3o**, when the compound **1o**, with a butyl group on the olefinic moiety, was used as the substrate (Scheme 3). The compound **5** was obtained in 53 and 55% yields, respectively, under the catalysis of two different gold complexes. Two plausible reaction pathways (Path A and B) might account for



Scheme 3. Transformation of **1o** and mechanistic study.

the formation of **5** from the key vinyl furan intermediate **Int-D**, which is generated from **Int-C** by the deprotonation of the vicinal carbon atom to the carbocation. In Path A, **Int-D** could undergo the protonation to give the trisubstituted furan **6**, with subsequent Diels–Alder reaction with the dienophile **2**. An alternative reaction pathway (Path B) may proceed through the Diels–Alder reaction first with subsequent protonation. To gain insight into the reaction mechanism, some control experiments were carried out. Indeed, the cycloisomerization reaction of **1o** took place in the absence of **2** under the catalysis of AuCl₃, thus affording the trisubstituted furan **6** in 94 % yield. In contrast, no reaction occurred at all with the use of [Ph₃PAuCl] as the catalyst, and only **1o** was recovered. The Diels–Alder reaction of furan **6** with **2** worked well in DCE at 60 °C without the gold catalyst, thus leading to **5** in 72 % yield. All these results strongly support the proposal that the reaction might proceed through Path A under the catalysis of AuCl₃, and Path B under the catalysis of [Ph₃PAuCl].

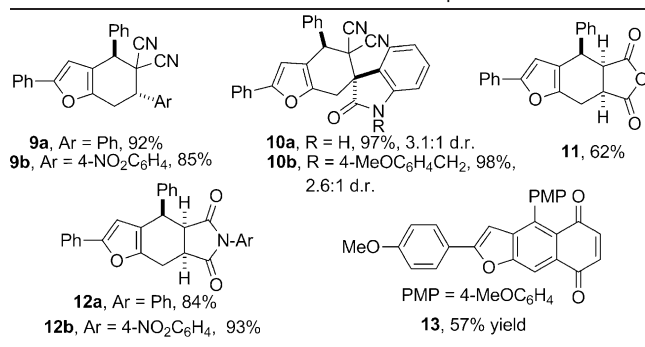
Similarly, the cyclic precursor **1p** [Eq. (1)] could undergo the domino cycloisomerization and Diels–Alder reaction with



2 under the catalysis of AuCl₃ in DCE at 60 °C, thus furnishing 60 % yield of the tricyclic compound **7**,^[14] which has an important and synthetically challenging bridged skeleton. The maleic anhydride was also applicable to this reaction, thus furnishing the tetracycle **8** in 63 % yield. The anhydride moiety of **8** is a useful functional group for synthesis of a variety of compounds.

To our delight, various electron-deficient olefins such as 2-arylidene-malononitrile, maleic anhydride, *N*-aryl maleimide, and benzoquinone could be used as dienophiles (Table 2), thus furnishing the corresponding products **9–13** in good yields under the catalysis of [Ph₃PAuCl]/AgO₂CC₃F₇ (for more results using other silver salts, see Table S2). For example, the reaction of **1a** with *N*-phenyl maleimide afforded 84 % yield of the furan-fused tricycle **12a**.^[14] The

Table 2: Other electron-deficient olefins as dienophiles.



spirocyclic oxindole scaffolds **10a** and **10b**^[14] were also efficiently constructed (97–98 % yields) with moderate diastereoselectivity. To our delight, the naphtho[2,3-*b*]furan-5,8-dione skeleton **13**,^[14] a key subunit in a number of natural products with biological activities, was obtained in 57 % yield with the use of benzoquinone as both dienophile and oxidant.

We then turned our attention to the electron-deficient alkynes such as acetylenedicarboxylates as the dienophiles (Table 3). Halophenyl groups (**14b** and **14c**) could be

Table 3: The reaction of 2-(1-alkynyl)-2-alken-1-ones **1** with DMAD.

Entry	R ² /R ³ /R (14)	<i>t</i> [h]	Yield [%] ^[a]
1	Ph/Ph/Me (14a)	12	70
2	4-ClC ₆ H ₄ /Ph/Me (14b)	8	70
3	4-BrC ₆ H ₄ /Ph/Me (14c)	8	75
4	Ph/4-MeC ₆ H ₄ /Me (14d)	6	64
5	Ph/4-MeOC ₆ H ₄ /Me (14e)	6	79
6	Ph/4-CF ₃ C ₆ H ₄ /Me (14f)	12	50
7	Ph/4-NO ₂ C ₆ H ₄ /Me (14g)	12	52
8	Ph/1-naphthyl/Me (14h)	6	52
9	Ph/2-thienyl/Me (14i)	8	77
10	Ph/1-cyclohexenyl/Me (14j)	10	62
11	Ph/ <i>n</i> -C ₄ H ₉ /Me (14k)	10	59
12	Ph/Ph/Et (14l)	12	76

[a] Yield of the isolated product.

introduced to the products. Variation of the electronic nature of the phenyl ring on the alkyne moiety (R³) showed that electron-rich substrate gave higher yields than those with electron-deficient ones (Table 3, entry 5 versus entries 6 and 7). In addition to the substituted phenyl groups, 1-naphthyl and 2-thienyl were compatible with this reaction, thus furnishing the products **14h** and **14i** in 52 and 77 % yield, respectively (Table 3, entries 8 and 9). Moreover, it should be noted that 1-cyclohexenyl- and *n*-C₄H₉-substituted yne-enones afforded the desired products in moderate yields (Table 3, entries 10 and 11). The diethyl acetylene dicarboxylate produced the corresponding product **14l** in 76 % yield. Moreover, benzofuran could be easily obtained by oxidation of **14** [see Equation (S1) in the Supporting Information].

In summary, we have developed an unprecedented strategy for access to furan-based *o*-QDMs by gold-catalyzed dehydrogenative annulation of 2-(1-alkynyl)-2-alken-1-ones in the presence of pyridine *N*-oxide under mild reaction conditions. These reactive 1,3-dienes can be trapped by various dienophiles, including electron-deficient olefins and alkynes, and thus provides facile access to highly substituted furan-fused carbocycles with high diastereo- and regioselectivities. Furthermore, when aliphatic-substituted 2-(1-alkynyl)-2-alken-1-ones were used, a novel dearomative Diels–Alder reaction was observed, thus efficiently furnishing 2,3-dihydrofuran-fused carbocycles. The salient features of this strategy include mild reaction conditions, readily available starting materials, atom-economy, and general substrate

scope, thus making it a straightforward way to synthesize 2,3-furan-fused carbocycles. Additional studies, including asymmetric catalysis [for a preliminary result, see Equation (S2)] and synthetic applications of this transformation is underway and will be reported in due course.

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- [14] CCDC 984637 (**3b**), 984638 (**7**), 984633 (**10b**), 984634 (**12a**), and 984635 (**13**) contain 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.