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Lewis Acid Catalyzed Electrophilic Aminomethyloxygenative Cyclization of Alkynols with *N,O*-Aminals

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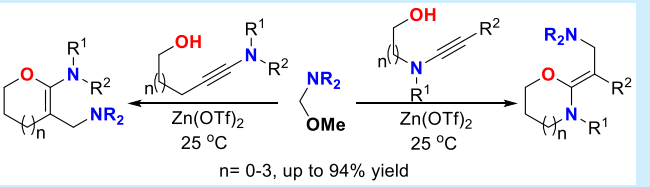
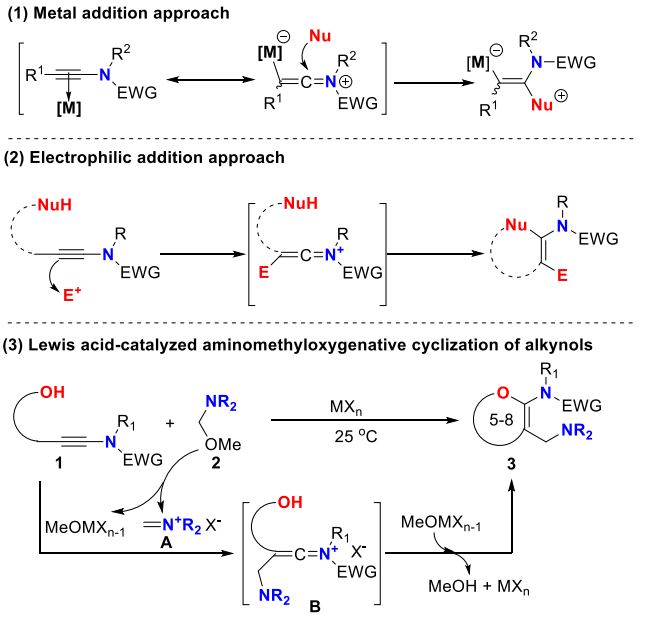
ABSTRACT: Lewis acid enables the electrophilic carbooxygenative cyclization of alkynols with *N,O*-aminals. The new process proceeds efficiently under very mild conditions via a pathway that is opposite to classical carbo-metalation. These reactions exhibit broad substrate generality and functional group compatibility, leading to a wide variety of 5−8-membered oxacycles bearing diverse functional groups. The cyclization products can be elaborated via simple functional group transformations to generate synthetically useful oxacycles.



The ubiquity of oxygen-heterocycles continues to spark the development of a number of cyclization reactions.[1] Among the many ring-forming reactions in oxygen-heterocycle preparation, metal-catalyzed intramolecular addition of an O−H bond across an unsaturated carbon−carbon is particularly attractive.[2] While numerous efforts have been devoted to the development of efficient catalytic systems by turning to the metal catalyst,[2,3] the divergence of products generated from the documented methods is still limited due to the modes of cyclization commonly resulting in protonation.[4] Moreover, the construction of medium-sized rings in an efficient and selective manner is still a challenging task.[5]

Ynamides are special alkynes attached to a nitrogen atom bearing an electron-withdrawing substituent, which holds a unique nature allowing for the regioselective addition of electrophiles or nucleophiles onto the ynamide.[6] These reactions have emerged as versatile tools for the synthesis of a number of important chemical products in both academic and industrial laboratories.[7] Arguably, the most prevalent class of ynamide reactions are π-bond insertion processes in which a metal catalyst binds to π-orbitals of the alkyne and transfers a functional group via an external nucleophilic attack (nucleometalation) (Scheme 1, eq 1).[8] The resulting nucleophilic vinylmetal species can undergo a range of further reaction. However, the formation of vinylmetal species via nucleophilic β-addition is difficult due to the directing effect of the amido group of ynamide[9] and is restricted to specific examples.[10] Compared to the well-established nucleophilic addition pathway, a "polarity-reversed" electrophilic addition pathway that is initiated by electrophilic addition has also been developed (Scheme 1, eq 2) for the addition of acids and halogen-derived reagents to alkynes.[11] However, we are surprised to find that little attention has been payed to carbofunctionalization of alkynes by using such method,[12] although such a catalytic system would preclude the use of reactive organometallics, and more importantly, it can generate a highly reactive keteniminium intermediate. Moreover, the use of such kind of method for the carbooxygenative cyclization of alkynols has remained unexplored, which is presumably due to the lack of suitable carbon electrophiles.

Scheme 1. Proposed Aminomethyloxygenative Cyclization of Alkynols with *N,O*-Aminals



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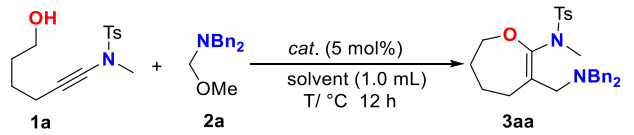
N,O-Aminals are reactive and versatile electrophiles, which could be recognized as latent iminiums.[13] We reasoned that the iminium **A** could be generated from *N,O*-aminal **2** under the assistance of Lewis acid. Upon trapping with the π-rich nucleophile ynamide **1**, the active keteniminium intermediate **B** could be generated from iminium **A**. The resulting keteniminium **B** could undergo oxygenative cyclization to produce the desired β-aminomethyl oxacycles. Herein, we report the development of a Lewis acid−catalyzed electrophilic aminomethyloxygenative cyclization of alkynols with *N,O*-aminals as electrophiles (Scheme 1, eq 3). The reaction proceeds efficiently under very mild conditions and exhibits broad substrate generality and functional group compatibility, leading to a wide variety of 5−8-membered oxacycles bearing diverse functional groups. The oxacycles can be further elaborated through conventional functional group transformations and successfully applied to the formal synthesis of dinotefuran, which is an important insecticide.[14]

To examine the feasibility of the proposed reaction, we initiated the investigations by examining the reaction of *N*-(6-hydroxyhex-1-yn-1-yl)-*N*,4-dimethylbenzenesulfonamide (**1a**) and *N,N*-dibenzyl-1-methoxymethanamine (**2a**). The proposed cyclization reaction was conducted in CH_2Cl_2 at 80 °C under the catalysis of 5 mol % of Lewis acid. After an extensive screening of Lewis acid catalysts, the commonly used Lewis acids, including $Cu(OTf)_2$, $Zn(OTf)_2$, $Yb(OTf)_3$, and $Fe(OTf)_3$, with OTf^- as counteranion stood out as effective catalysts. The target product **3aa** with a seven-membered-ring containing two amine moieties was obtained in 91% yield when $Zn(OTf)_2$ served as catalyst. In contrast, relative lower yields were observed when Cl^- or Br^- served as the counteranion (Table 1, entries 1−7). Inspired by this promising result, we next sought to improve the efficiency of the reaction by screening other reaction conditions. When the temperature dropped to 25 °C, the reaction kept its high activity and selectivity (Table 1, entries 8−10). On the other hand, Brønsted acids, such as TfOH, MsOH, Tf_2NH and 4-$NO_2C_6H_4B(OH)_2$, can also promote this reaction, but only moderate yields were achieved (Table 1, entries 11−14). Screening of the solvent demonstrated that CH_2Cl_2 and toluene both are good choices for achieving high reactivity (Table 1, entries 15−19). Considering the solubility of the catalyst, we chose to use CH_2Cl_2 as the solvent. Finally, no desired product **3aa** was observed in the absence of catalyst (Table 1, entry 20).

Table 1. Optimization of Reaction Conditions[a]



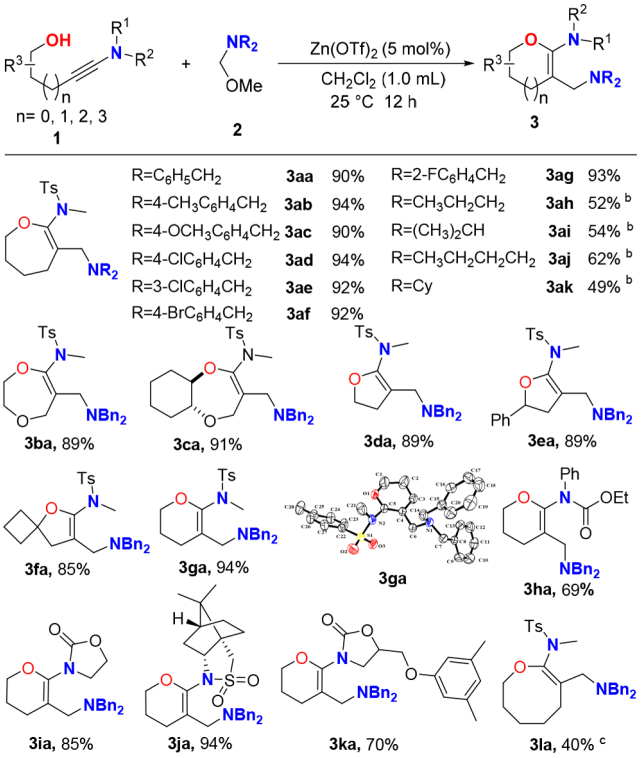
1a 2a 3aa

entry	cat.	solvent	T (°C)	yield[b] (%)
1	$CuCl_2$	CH_2Cl_2	80	10
2	$CuBr_2$	CH_2Cl_2	80	65
3	$Cu(OAc)_2$	CH_2Cl_2	80	81
4	$Cu(OTf)_2$	CH_2Cl_2	80	89
5	$Fe(OTf)_3$	CH_2Cl_2	80	82
6	$Zn(OTf)_2$	CH_2Cl_2	80	91
7	$Yb(OTf)_3$	CH_2Cl_2	80	88
8	$Zn(OTf)_2$	CH_2Cl_2	60	89
9	$Zn(OTf)_2$	CH_2Cl_2	40	87
10	$Zn(OTf)_2$	CH_2Cl_2	25	90
11	TfOH	CH_2Cl_2	25	65
12	MsOH	CH_2Cl_2	25	63
13	Tf_2NH	CH_2Cl_2	25	59
14	4-$NO_2C_6H_4B(OH)_2$	CH_2Cl_2	25	40
15	$Zn(OTf)_2$	MeOH	25	59
16	$Zn(OTf)_2$	Toluene	25	90
17	$Zn(OTf)_2$	CH_3CN	25	89
18	$Zn(OTf)_2$	THF	25	84
19	$Zn(OTf)_2$	DMF	25	46
20		CH_2Cl_2	25	0

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), cat.(5 mol %), solvent (1.0 mL), 12 h. [b]Isolated yield.

With the optimized reaction conditions in hand, we turned our attention to validating the generality of our strategy under the catalysis of $Zn(OTf)_2$, and the results are summarized in Scheme 2. First, the substrate scope of *N,O*-aminal was examined with the reaction of **1a** between various of *N,O*-aminals derived from different amines and methanol. The desired seven-membered cyclic ethers containing a β-aminomethyl functional group (**3aa**−**3ak**) were obtained in good to excellent yields. The reactions of *N,O*-aminals, derived from methanol and benzylamines bearing a variety of electron-withdrawing (−F, −Cl, and −Br) and electron-donating substituents ($-CH_3$ and $-OCH_3$) on the phenyl ring, proceeded well to deliver the desired products in more than 90% yields (**3ab**−**3ag**). However, *N,O*-aminals prepared from methanol and simple aliphatic amines, such as dipropylamine, diisopropylamine, dibutylamine and dicyclohexylamine, could not react with *N*-(6-hydroxyhex-1-yn-1-yl)-*N*,4-dimethylben-

Scheme 2. Substrate Scope of Cyclization[a]



[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.36 mmol), $Zn(OTf)_2$ (5 mol %), CH_2Cl_2 (1.0 mL), 12 h, isolated yield. [b]4-$NO_2C_6H_4B(OH)_2$ (5 mol %). [c]DME (1.0 mL).

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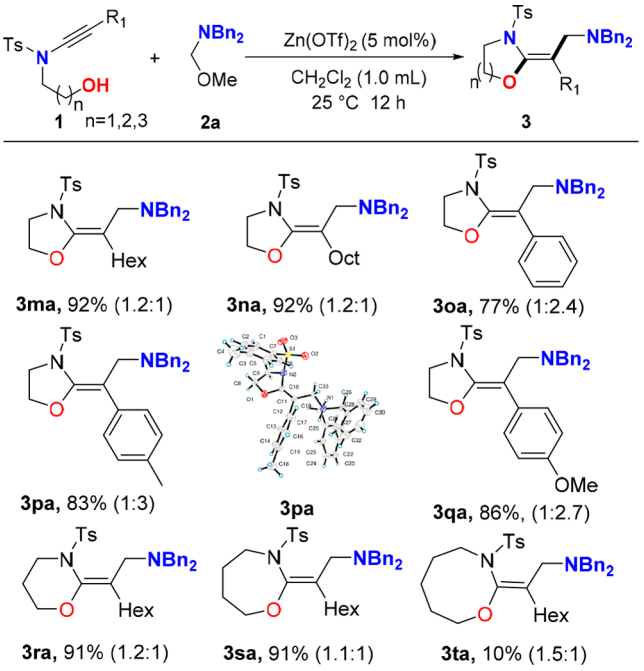
zenesulfonamide (**1a**) under the standard reaction conditions to give the corresponding products. To our delight, when 4-$NO_2C_6H_4B(OH)_2$ was utilized as a catalyst, the desired products could be obtained in moderate yields (Scheme 2, **3ah**−**3ak**). The higher reactivity exhibited here by the boric acid might be attributed to its capability to generate the iminium species via formation of B-OMe complex.

Subsequently, the substrate scope of the alkynol was further explored. As shown in Scheme 2, the 7-*endo* cyclization of *N*-(6-hydroxyhex-1-yn-1-yl)-*N*,4-dimethylbenzenesulfonamide derivatives with *N*,*O*-aminal **2a** performed well to afford the corresponding seven-membered products in excellent yields (Scheme 2, **3aa**−**3ca**). For example, two-oxygen-atom-containing **3ba** and bicyclic heterocycle **3ca** were obtained in excellent yields. Similar to the formation of seven-membered ring products, the five-membered products **3da**−**3fa** were obtained in excellent yields, and the spirocyclic product **3fa** could be efficiently obtained in 85% yield. As expected, the six-membered adducts **3ga**−**3ka** could also be produced in good yields under the standard reaction conditions. The structure of **3ga** was further confirmed by single-crystal X-ray analysis. When the electron-withdrawing group changed from a sulfonamide to a simple amide, the corresponding six-membered products were still obtained in good yields (Scheme 2, **3ha** and **3ia**). The cyclization of **1j** bearing a camphor sultam chiral auxiliary was successful to afford chiral product **3ja** in 94% yield. Moreover, the reaction of metaxalone-derived alkynol **1k** was effectively converted into the corresponding product **3ka** in 70% yield. Further prolonging the tether length, an eight-membered ring product (**3la**) was produced in 40% yield.

Next, the cyclization reactions with *N*-alkynylamino alcohols were examined under the standard reaction conditions. As shown in Scheme 3, the reaction was found to be compatible with a series of aliphatic-substituted *N*-alkynylamino alcohols (R = Hex, Oct) and diverse aromatic *N*-alkynylamino alcohols bearing different substituents on the phenyl ring (R = H, Me, OMe). The five-membered ring products **3ma**−**3qa** were successfully obtained in 77−92% yields. The structure of **3pa** was further confirmed by single-crystal X-ray analysis. In addition, the six- and seven-membered ring products **3ra** and **3sa** were also obtained in excellent yields. However, the analogous eight-membered product **3ta** was obtained in only 10% isolated yield under the standard reaction conditions. The lower activity might be attributed to the unfavorable transannular interactions and entropic factors.

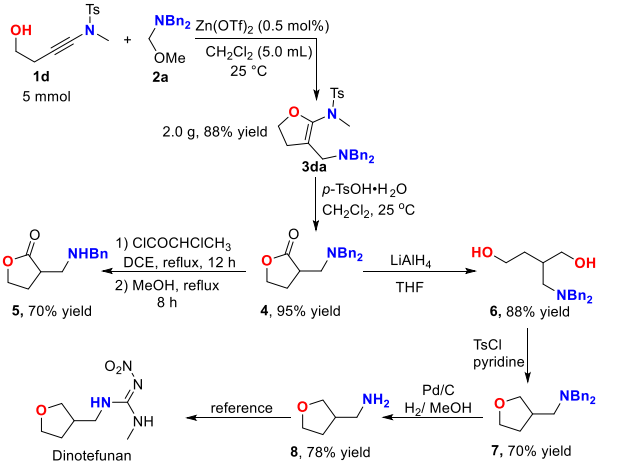
To further demonstrate the utility of this catalytic protocol, transformation of the resulting heterocycles was explored (Scheme 4). The Lewis acid enabled electrophilic amino-methylation/cyclization process proved to be scalable in the presence of 0.5 mol % of $Zn(OTf)_2$ without lowering the yield of this transformation (88% yield). The sulfonamide group could be removed by treatment of **3da** with *p*-TsOH·H_2O in CH_2Cl_2 to afford the corresponding α-aminomethyl butyrolactone **4** in excellent yield.[4c] Meanwhile, one benzyl group contained in product **4** could be removed to give 3-((benzylamino)methyl)dihydrofuran-2(3*H*)-one **5** in 70% yield.[15] In addition, the product **4** could be easily transformed into aminodiol **6** by reduction with $LiAlH_4$.[16] The aminodiol **6** was successfully converted into *N*,*N*-dibenzyl-1-(tetrahydrofuran-3-yl)methanamine **7** via cyclization with TsCl in pyridine.[17] Finally, the benzyl groups contained in product **7** were successfully removed to give (tetrahydrofuran-3-yl)-methanamine **8** in 78% yield through Pd/C-catalyzed hydrogenolysis in the presence of H_2.[18] The (tetrahydrofuran-3-yl)methanamine **8** could be facilely transferred to dinotefuran **9** according to the reported procedure.[19]

Scheme 3. Substrate Scope of Alkynol[a]



[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.36 mmol), $Zn(OTf)_2$ (5 mol %), CH_2Cl_2 (1.0 mL), 12 h. isolated yield. The ratios of *E*/*Z* are given within parentheses and were determined by ^1H NMR.

Scheme 4. Synthetic Transformations



In summary, we have developed a Lewis acid catalyzed synthesis of highly functionalized oxygen-heterocycles from readily accessible alkynols and *N*,*O*-aminals. This method operates through an electrophilic carbofunctionalization pathway that is opposite to the classical carbometalation and could provide a series of strategic bond-forming processes that will have broad appeal in synthetic chemistry. This protocol operates under very mild reaction conditions and exhibits broad substrate generality and functional group compatibility, leading to a wide variety of 5−8-membered ring oxacycles bearing diverse functional groups. The highly functionalized

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oxacycles are versatile synthetic intermediates and can be readily transformed into important heterocyclic motifs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04630.

Experimental details and full spectroscopic data for all new compounds (PDF)

Accession Codes

CCDC 1958217−1958218 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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