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Synthesis of Diverse Di- to Penta-Substituted 1,2-Dihydropyridine Derivatives from Gold(I)-catalyzed Intramolecular Addition of Tertiary Enamides to Alkynes

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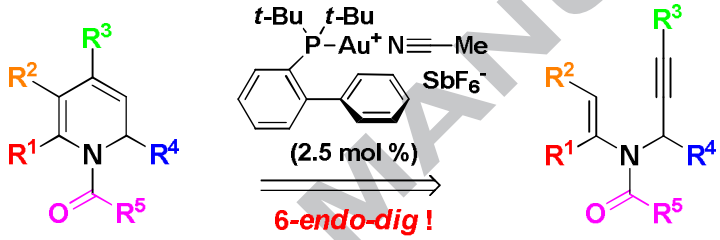


ABSTRACT: As 3-aza-1,5-enynes, internal and terminal alkyne-bearing tertiary enamides underwent an efficient Au(I)-catalyzed 6-*endo-dig* cyclization reaction to afford a variety of di- to penta-substituted 1,2-dihydropyridine derivatives in high yields. The cyclization proceeds through a cascade comprising of intramolecular nucleophilic addition of enaminic carbon to alkyne-gold(I) complex, deprotonation and protodeauration steps. Au(I)-catalyzed tertiary enamide-alkyne cyclization coupled with consecutive oxidative aromatization provided a straightforward route to polysubstituted pyridines.

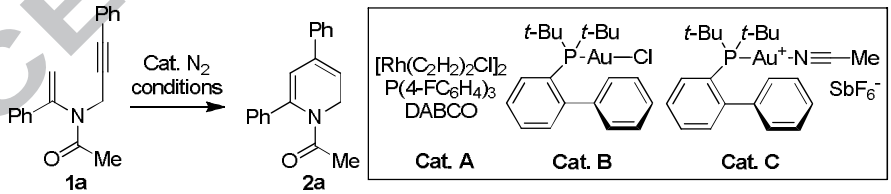
Keywords: tertiary enamide; 1,2-dihydropyridine; gold(I) catalysis; cyclization; pyridine

1,2-Dihydropyridines are versatile intermediates in the synthesis of various alkaloids and important bioactive products such as azasugar derivatives and anti-influenza drug Tamiflu.[1] Major synthetic routes to 1,2-dihydropyridine derivatives include condensation reactions, reduction of and nucleophilic addition to pyridines and pyridinium salts.[2] Pericyclic reactions constitute other methods for the construction of 1,2-dihydropyridine structure.[2] Formation of 1,2-dihydropyridines from Rh(I)-catalyzed cycloisomerization of *N*-propargyl enamines under basic conditions has been report-

ed via a rhodium vinylidene intermediate.[3] Recently, an efficient Au-catalyzed cycloisomerization of *N*-propargyl enamines was also disclosed by Kozmin in the construction of fused *N*-heterocyclic compounds.[4] All methods suffer from at least one of the drawbacks ranging from poor reaction selectivity, limited substrate scope and tedious preparation of reactants and harsh reaction conditions. Development of general, efficient and diversity-orientated synthetic methodologies for 1,2-dihydropyridines is highly desirable.[2]

As enamine variants, enamides have long been recognized as chemically stable species because of the electron-withdrawing effect of *N*-acyl group.[5] It has been shown recently that secondary enamides act as aza-ene components to participate in aza-ene addition reactions with reactive enophiles.[6] However, no reactions occur when tertiary enamides are employed. Considering the cross conjugation system within the molecules, we proposed a few years ago that enabled regulation of delocalization of lone pair electrons on nitrogen into the carbon-carbon double bond would reinvigorate the nucleophilic activity of enamides. Guided by this working hypothesis, enaminic reactions of tertiary enamides have been successfully established towards epoxides,[7] carbonyls,[8] imines[9] and nitriliums,[10] providing unique and powerful methods for the synthesis of diverse heterocyclic compounds.[11] To further explore the reactivity and synthetic utility of tertiary enamides, we studied intramolecular addition reaction of tertiary enamides to alkynes, envisioning the novel strategy to construct *N*-heterocyclic rings. We report herein a highly efficient intramolecular addition of tertiary enamides to various unactivated internal and terminal alkynes. The reaction proceeds through a Au(I)-catalyzed 6-endo-dig cyclization to afford a variety of di- to penta-substituted 1,2-dihydropyridine derivatives.[12] A simple and straightforward method for the preparation of polysubstituted pyridines is also demonstrated.

Table 1. Tertiary enamide-alkyne cyclization of **1a**



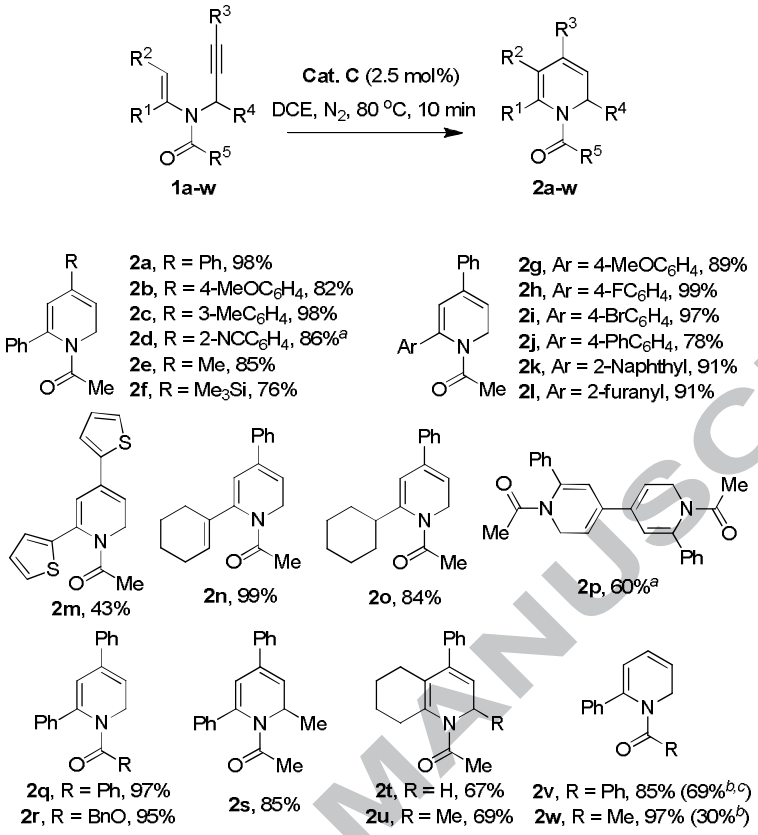
entry	Cat. (mol %)	solvent	temp. (°C)	time	**2a** (%)[a]
1	I_2 (200)	DCM	0 – rt	10 h	-[b]
2	ICl (100)	DCE	rt	8 h	-[b]
3	NBS (100)	DCE	rt	8 h	-[b]

4	Cat. A (5)	DMF	rt	24 h	n.r.[c]
5	$AuCl_3$ (5)	DCM	rt	20 h	29[d]
6	Cat. B (2.5)	DCM	rt	4 h	n.r.[c]
7	Cat. C (2.5)	DCM	rt	10 min	80
8	Cat. C (2.5)	DCM	40	10 min	85
9	Cat. C (2.5)	DCE	rt	4 h	66[e]
10	Cat. C (2.5)	DCE	40	10 min	87
11	Cat. C (2.5)	DCE	80	10 min	98
12	Cat. C (1.0)	DCE	80	2 h	72[f]
13	Cat. C (0.25)	DCE	80	20 h	trace

[a] Isolated yield. [b] An inseparable mixture of compounds was obtained. [c] No reaction was observed, and starting material was recovered in 98%. [d] Starting material was recovered in 43%. [e] Starting material was isolated in 15%. [f] A small amount of starting material was not converted.

We commenced our study by examining the reaction of *N*-(3-phenylprop-2-yn-1-yl)-substituted tertiary enamide **1a** with iodonium and bromonium. Unfortunately, treatment of **1a** with iodine, iodine chloride and NBS did not give any cyclization product. Instead, an inseparable mixture was obtained (entries 1-3, Table 1). A rhodium(I) complex (**Cat. A**), which was reportedly able to catalyze cycloisomerization of *N*-propargyl enamines,[3] was also used. However, no reaction at all was observed with the intact reactant **1a** being recovered almost quantitatively (entry 4, Table 1). We then turned our attention to cationic gold complexes, alkynophilic π-acid species that activate carbon-carbon triple bond.[4,12,13] Although $AuCl_3$ was able to effect the cyclization of **1a**, the catalytic activity was appallingly low. In the presence of $AuCl_3$ (5 mol %), for instance, 1,2-dihydropyridine product **2a** was formed in only 29% yield in 20 h (entry 5, Table 1). While AuCl-phosphine complex (**Cat. B**) exhibited no catalytic activity (entry 6, Table 1), $AuSbF_6$-phosphine complex (**Cat. C**)[14] catalyzed the cyclization efficiently in dichloromethane (DCM) at ambient temperature to afford **2a** in 80% yield in 10 minutes (entry 7, Table 1). The chemical yield was improved to 85% when the reaction was refluxed in DCM (entry 8, Table 1). Reaction proceeded analogously in dichloroethane (DCE) (entries 9 and 10, Table 1). Pleasingly, an almost quantitative yield of **2a** was yielded in 10 minutes when the reaction was conducted at 80 °C in DCE (entry 11, Table 1). Reaction was also effective when catalyst loading was lowered to 1.0 mol % (entry 12, Table). No reaction took place in the absence of a catalyst or the catalyst loading was decreased to 0.25 mol % (entry 13, Table 1).

Table 2. Au(I)-catalyzed cyclization reaction of **1a-u**



[a] **Cat. C** (5 mol %) was used. [b] Yield was obtained from the reaction using **Cat. A** (5 mol %) as a catalyst. [c] Reported chemical yield using **Cat. A** (5 mol %) is 67%.

Under the optimized conditions, the scope of the reaction was scrutinized. Gratifyingly, the cationic Au(I)-catalyzed tertiary enamide-alkyne cyclization appeared very general and highly efficient. As summarized in Table 2, all substrates **1a-w**, which were prepared conveniently following the established procedures (see Supporting Information), were transformed into diverse 1,2-dihydropyridine products in good to excellent yields irrespective of the substitution patterns and of the nature of the substituents. For example, substrates **1a-c** that contain a phenyl or an electron-rich aryl on acetylene underwent cyclization reaction to afford 1-acetyl-4,6-diaryl-1,2-dihydropyridines **2a-c** in high yields. 2-Cyanophenyl-bearing analog **1d** was converted similarly into product **2d** albeit an increased catalyst loading (5 mol %) was required. Enaminic addition of tertiary enamide to methyl (**1e**) and even trimethylsilyl (**1f**) capped acetylenes proceeded equally well to produce 4-alkylated and 4-silylated 1,2-dihydropyridine products **2e** and **2f**, in 85% and 76%, respectively.

In the case of *N*-(3-phenylprop-2-yn-1-yl)-tertiary enamides, substrates bearing a substituted phenyl group (**1g-j**), 2-naphthyl (**1k**) and a hetereoaryl such as 2-furanyl (**1l**) underwent cyclization smoothly to give high yields of the corresponding tri-substituted 1,2-dihydropyridine products **2g-l**. When

2-thienyl-substituted tertiary enamide **1m** was treated with the Au(I) catalyst, 4,6-di(2-thienyl)-1,2-dihydropyridine **2m** was produced in 43% yield. It is worth noting that tertiary enamides containing hexenyl (**1n**) and hexyl (**1o**) underwent the Au(I)-catalyzed cyclization reaction identically, allowing the synthesis of 6-alkenyl and 6-alkyl substituted 1,2-dihydropyridines efficiently. Interestingly, a 1,3-diyne-linked bis-tertiary enamide **1p**, which was readily obtained from homo coupling of **1a** (see Supporting Information), underwent double cyclization reactions to furnish 1,1',2,2'-tetrahydro-4,4'-bipyridine derivative **2p** although a slightly higher catalyst loading (5 mol %) was necessary. Variation of *N*-acetyl moiety to benzoyl (**1q**) and benzyloxycarbonyl (**1r**) group did not impose any unfavorable effect on reaction as respective products **2q** and **2r** were yielded almost quantitatively.

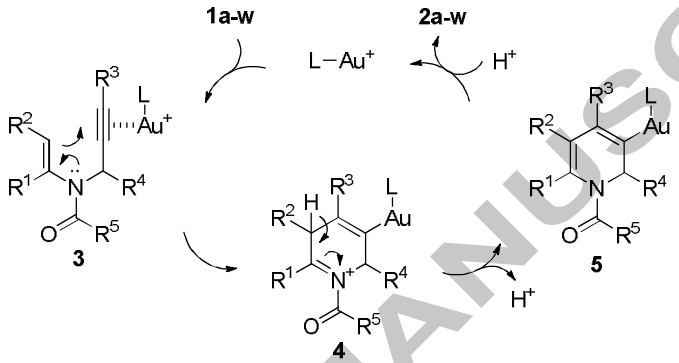
In addition to tri-substituted 1,2-dihydropyridines, tetra- and penta-substituted 1,2-dihydropyridine compounds were also easily synthesized by the Au(I)-catalyzed cyclization reaction. As exemplified in Table 2, reaction employing tertiary enamide **1s** gave rise to the formation of 1,2,4,6-tetra-substututed 1,2-dihydropyridine **2s**, while the use of cyclohexone-derived reactant **1t** led to the generation of 1,4,5,6,-tetrasubstituted 1,2-dihydropyridine compound **2t**. Remarkably, 1-acetyl-2-methyl-4-phenyl-1,2,5,6,7,8-hexahydroqinoline **2u**, a very rare 1,2,4,5,6-penta-substituted 1,2-dihydropyridine species, was obtained nicely in 69%.

It was particularly worth noting that the Au(I) catalyst (**Cat. C**) was also able to catalyze perfectly the intramolecular enaminic addition of tertiary enamides to a terminal alkyne moiety. This has been evidenced convincingly by the high-yielding formation of 1,6-disubstituted 1,2-dihydropyridine products **2v** and **2w** from the reactions of *N*-propargyl-substituted tertiary enamides **1v** and **1w**, respectively. As we mentioned that the rhodium(I) complex (**Cat. A**) was inactive at all to substrates **1a-u** that contain an internal alkyne.[3] For a terminal alkyne substrate, we concurred with Lee's work that *N*-propargyl-*N*-benzoyl enamine **1v** underwent the Rh-catalyzed reaction under basic conditions to give **2v** in 69% yield in 24 h. For a less reactive *N*-propargyl tertiary enamide **1w**, however, the Rh(I)-catalyzed reaction gave 30% of product **2w** in 36 h along with the recovery of starting material **1w** in 27% yield. It is obvious that the Au(I) catalysis is superior to Rh(I) catalysis in terms of substrate scope and catalytic efficiency.

Extensive studies in the field of homogeneous gold catalysis have shown that 1,5-enynes undergo invariably 5-*endo*-*dig* cycloisomerization reactions.[13,15] These reactions have been reported to proceed through the cyclopropyl gold(I) carbene intermediates, which lead to the formation of different five-membered ring products depending on the nature of ligands utilized.[15] In contrast to these reported examples, formation of 1,2-dihydropyridines from Au(I)-catalyzed reaction of 3-aza-1,5-enynes, namely, both internal and terminal alkyne-bearing tertiary enamides **1** indicates undoubtedly the operation of an entirely different reaction mechanism. While further studies are in progress to

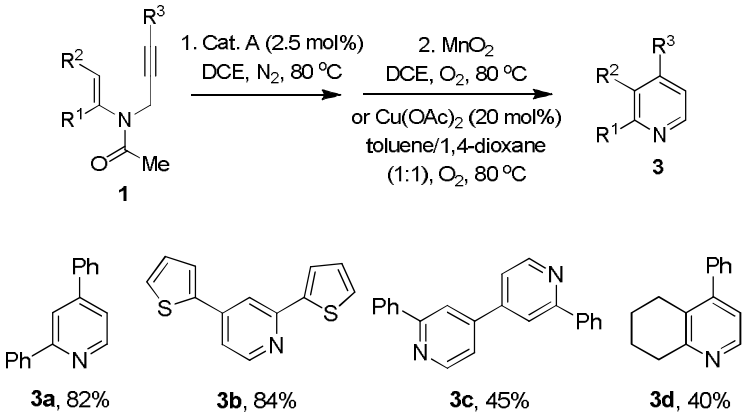
elucidate the details of this cyclization reaction, we propose a most plausible reaction pathway. As depicted in Scheme 1, interaction of Au(I) catalyst with reactants **1** would form a π-complex **3**. Intramolecular nucleophilic addition of the enaminic carbon of tertiary enamides to carbon-carbon triple bond results in the formation of intermediates **4** which undergo deprotonation to give organometallic species **5**. Protodeauration of **5** furnishes the formation of final products **2**. It is the nucleophilic nature of tertiary enamides that lead to 6-*endo-dig* cyclization rather than always encountered 5-*endo-dig* one.

Scheme 1. Proposed mechanism



The resulting 1,2-dihydropyridines of various substituents and substitution patterns would serve as valuable cyclic diene components in synthesis. Additionally, chemical manipulations of unsaturated carbon-carbon bonds would provide diverse piperidine derivatives including alkaloids and their analogs.[1] To demonstrate the synthetic utility of Au(I)-catalyzed tertiary enamide-alkyne cyclization reaction, preparation of substituted pyridine compounds was attempted.[10a,16] As shown in Table 3, without isolation and purification of 1,2-dihydropyridine products, Au(I)-catalyzed tertiary enamide-alkyne cyclization reaction of **1a**, **1o** and **1u**, and consecutive oxidative aromatization using MnO_2 and oxygen as oxidants furnished 2,4-diphenylpyridine **3a**, 2,4-di(2-thienyl)pyridine **3b** and 2,2'-diphenyl-4,4'-dipyridine **3c**, respectively. While compound **3b** has the potential application in advanced optoelectronic material science,[17] 4,4'-dipyridine **3c** is a useful ligand in the construction of coordination complexes.[18] Starting from tertiary enamide **1t**, the same Au(I)-catalyzed cyclization reaction followed by the $Cu(OAc)_2$-catalyzed auto-oxidation reaction[19] produced directly 4-phenyl-5,6,7,8-tetrahydroquinoline **3d**, a privileged heterocyclic scaffold in medicinal chemistry.[20]

Table 3. Preparation of substituted pyridine derivatives



In summary, we have shown that tertiary enamides were able to act as nucleophiles to undergo intramolecular addition to both internal and terminal alkynes under homogeneous gold catalysis. The cationic Au(I)-catalyzed regiospecific 6-*endo-dig* cyclization of 3-aza-1,5-enynes constituted a highly efficient and powerful method for the synthesis of diverse di- to penta-substituted 1,2-dihydropyridine derivatives in high yields. Coupled with the subsequent oxidative aromatization, the method provided a straightforward route to substituted pyridine compounds.

Supporting Information

Experimental procedures, compound characterization data and ^{1}H and ^{13}C NMR spectra.

ACKNOWLEDGMENT

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