



Cite this: *Chem. Sci.*, 2018, 9, 2991

# Gold-catalyzed [4+3]- and [4+2]-annulations of 3-en-1-ynamides with isoxazoles *via* novel $6\pi$ -electrocyclizations of 3-azahepta trienyl cations†

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New gold-catalyzed [4+3]-annulations of 3-en-1-ynamides with isoxazoles afford 4*H*-azepines efficiently; this process involves  $6\pi$  electrocyclizations of gold-stabilized 3-azaheptatrienyl cations. In the presence of  $\text{Zn}(\text{OTf})_2$ , the resulting 4*H*-azepines undergo skeletal rearrangement to furnish substituted pyridine derivatives. We subsequently develop new catalytic [4+2]-annulations between the same 3-en-1-ynamides and isoxazoles to deliver substituted pyridine products using  $\text{Au}(\text{I})/\text{Zn}(\text{II})$  catalysts. This work reports the first success of the  $6\pi$  electrocyclizations of heptatrienyl cations that are unprecedented in literature reports.

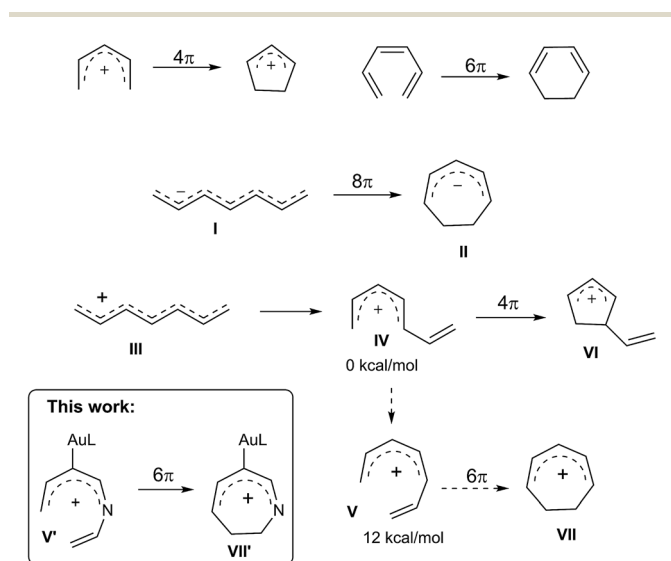
Received 15th January 2018  
Accepted 18th February 2018

DOI: 10.1039/c8sc00232k  
rsc.li/chemical-science

## Introduction

Electrocyclizations of acyclic conjugated  $\pi$ -motifs are powerful tools to access five-, six- and seven-membered carbocycles;<sup>1</sup> prominent examples include Nazarov cyclizations of penta-dienyl cations<sup>2</sup> and  $6\pi$  electrocyclizations of trienes,<sup>3</sup> which have found widespread applications in organic synthesis.

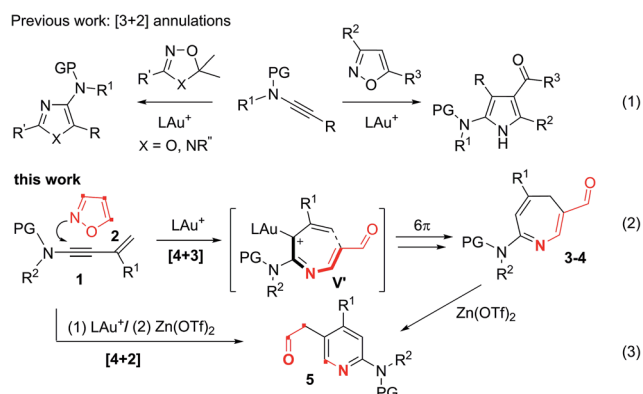
In the context of seven-carbon  $\pi$ -motifs, heptatrienyl anions **I** undergo facile  $8\pi$  electrocyclizations *via* rapid interconversions among various anion configurations (Scheme 1).<sup>4</sup> In contrast, heptatrienyl cations **III**<sup>5</sup> exclusively undergo Nazarov reactions because of the difficulties of forming all  $\sigma$ -*cis* configured cations **V** that have a high energy state.<sup>5b</sup> 1-Aza- and 1-oxaheptatrienyl cations<sup>6</sup> were also reported to follow Nazarov cyclizations. The realization of a  $6\pi$  electrocyclization of conjugated seven-membered cations is formidable but challenging. This work reveals the first success of such seven-membered cyclizations of gold-stabilized 3-azaheptatrienyl cations **V'** to form azacyclic products **3–4** *via* a new C–C bond formation.



Scheme 1 Electrocyclizations of conjugated  $\pi$ -motifs.

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† Electronic supplementary information (ESI) available. CCDC 1589549, 1589562, 1589561, 1589558, 1589559 and 1589560. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc00232k



The advent of gold catalysis has inspired new annulations between alkynes and poor nucleophiles.<sup>7</sup> N–O containing nucleophiles serve as useful building blocks to construct valuable azacyclic frameworks.<sup>7</sup> Ye and Hashmi reported interesting [3+2]-annulations of isoxazoles or benzisoxazoles with electron-

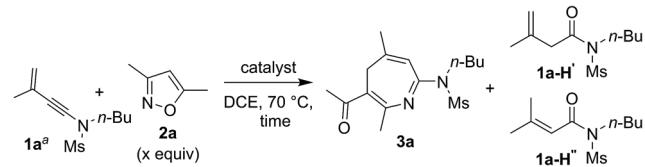


rich ynamides, yielding substituted pyrrole derivatives through aza-Nazarov cyclizations of the key intermediate [eqn (1)].<sup>7,8</sup> These [3+2]-annulations were extensively expanded to other N–O heterocycles including benzisoxazoles, 1,2,4-oxadiazoles, 1,4,2-dioxazoles and 4,5-dihydro-1,2,4-oxadiazoles, yielding additional five-membered azacycles as depicted in [eqn (1)].<sup>9</sup> Here, we report two distinct [4+3]- and [4+2]-annulations between 3-en-1-ynamides and isoxazoles using varied catalysts. An Au(I) catalyst alone delivers 4*H*-azepines **3–4** through 6π electrocyclizations of intermediates **V'** [eqn (2)] whereas a combined action of Au(I)/Zn(II) on the same reactants furnishes highly functionalized pyridines **5** [eqn (3)]. With our convenient synthesis, the synthetic utility of new 4*H*-azepines **3–4** is also reported.<sup>10</sup>

## Results and discussion

We examined the reactions of 3-methyl-3-en-1-ynamide **1a** with 3,5-dimethylisoxazole **2a** using various gold catalysts. Heating this mixture (**1a/2a** = 1 : 2 ratio) in hot DCE with 5 mol% LAuCl/AgNTf<sub>2</sub> [L = *p*-(*t*-Bu)<sub>2</sub>(*o*-biphenyl)] and IPr<sup>a</sup> afforded a [4+3]-annulation product, 4*H*-azepine **3a**, in 64% and 75% yields respectively (Table 1, entries 1–2). Under these conditions, a low loading (1.2 equiv.) of 3,5-dimethylisoxazole **2a** gave **3a** in a decreased yield, *ca.* 62% (entry 3). With a 10 mol% catalyst, IPrAuCl/AgNTf<sub>2</sub> gave a clean reaction, yielding desired **3a** up to 91% (entry 4). We tested other phosphine ligands such as PPh<sub>3</sub> and P(OPh)<sub>3</sub>, yielding desired **3a** in satisfactory yields (78–81%, entries 5–6). Other counter anions such as OTf<sup>−</sup> and SbF<sub>6</sub><sup>−</sup> were also effective in producing **3a** in 85–88% yields (entries 7–8). AgNTf<sub>2</sub> alone was not active at all (entry 9).

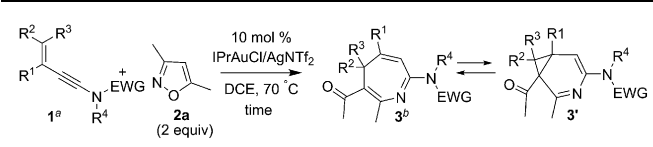
Table 1 [4+3]-Annulations over various gold catalysts



Entry	Catalyst [mol%]	x	Time [h]		Yield <sup>b</sup> [%]		
			1	2	1a	3a	1a-H'/1a-H''
1 <sup>c</sup>	LAuCl/AgNTf <sub>2</sub> [5]	2	3	20	64	—	
2 <sup>d</sup>	IPrAuCl/AgNTf <sub>2</sub> [5]	2	7	12	75	7 [2.5 : 1]	
3	IPrAuCl/AgNTf <sub>2</sub> [5]	1.2	7	23	62	5 [1 : 1]	
4	IPrAuCl/AgNTf <sub>2</sub> [10]	2	3	—	91	Trace	
5	PPh <sub>3</sub> AuCl/AgNTf <sub>2</sub> [10]	2	3.5	—	81	5 [1.25 : 1]	
6	[PhO] <sub>3</sub> PAuCl/AgNTf <sub>2</sub> [10]	2	3.5	—	78	13 [1.1 : 1]	
7	IPrAuCl/AgSbF <sub>6</sub> [10]	2	2.5	—	85	6 [1.4 : 1]	
8	IPrAuCl/AgOTf [10]	2	2	—	88	Trace	
9	AgNTf <sub>2</sub> [10]	2	15	33	—	11	

<sup>a</sup> [1a] = 0.15 M. <sup>b</sup> Product yields are reported after separation from a silica column. <sup>c</sup> L = *p*-(*t*-Bu)<sub>2</sub>(*o*-biphenyl). <sup>d</sup> IPr = 1,3-bis(diisopropylphenyl)-imidazol-2-ylidene. Ms = methanesulfonyl, DCE = 1,2-dichloroethane, and Tf = trifluoromethanesulfonyl.

Table 2 [4+3]-Annulations with various 3-en-1-ynamides



Suitable substituents of 3-en-1-ynamides **1** are crucial to achieve  $6\pi$  cyclizations of 3-azaheptatrienyl cations **V'** [eqn (2)]. We tested the reactions on 3-en-1-yne **1b–1m** bearing a C(3)-substituent to circumvent aza-Nazarov cyclizations as reported in Ye's work.<sup>7</sup> Herein, only entries 9 and 10 showed the presence of 3-azanorcaradienes **3'**. We examined these [4+3]-annulations on 3-methyl-3-en-1-ynamides **1b–1e** bearing various sulfonamides  $\text{NTsR}^4$  ( $\text{R}^4 = \text{Me}$ , cyclopropyl, benzyl and  $\text{N}(n\text{-C}_4\text{H}_9)$  ( $-\text{SO}_2\text{Bu}$ )), affording the desired 4*H*-azepines **3b–3e** in high yields (84–90%, Table 2, entries 1–4). Nevertheless, this new annulation becomes less efficient for 3-en-1-ynamide **1f** bearing an oxazolidin-2-one to yield product **3f** in 64% yield (entry 5).

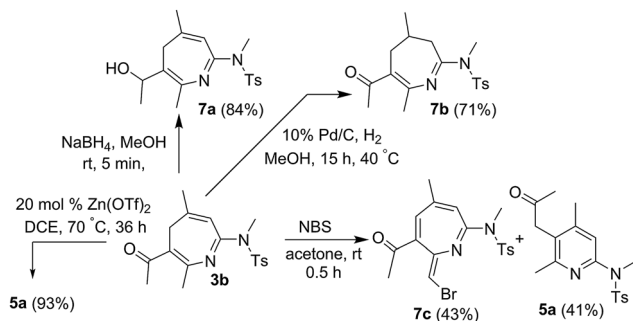
We altered the C(3)-substituents as in substrates **1g–1i**; their resulting products **3g–3h** ( $\text{R}^1 = \text{isopropyl}$  and cyclopropyl) were obtained in 74–79%, and **3i** ( $\text{R}^1 = \text{Ph}$ ) with only 58% yield (entries 6–8). Notably, when a long *n*-butyl group was present as in species **1j** and **1k**, their corresponding reactions afforded compounds **3j/3j'** = 5/1 and **3k/3k'** = 11.1 : 1, respectively, in 55% and 68% yields (entries 9–10). For *E*-configured trisubstituted 3-en-1-yne **1l** ( $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{Ph}$  and  $\text{R}^3 = \text{H}$ ), 4*H*-azepine **3l**

and pyrrole **6l** were obtained in equal proportions (entry 11). When a cyclohexenyl group was present for alkene as in species **1m**, pyrrole product **6m** was dominant over azepine **3m** (entry 12). Accordingly, preferable 3-en-1-yne comprise a small  $\text{R}^2$  or  $\text{R}^3$  substituent whereas  $\text{R}^1$  must be substituted. Herein, the structures of 4*H*-azepines **3b** and **3l**, and pyrrole species **6m** were confirmed with X-ray diffraction.<sup>11</sup>

Isoxazoles of a wide scope are compatible with these [4+3]-annulations, as depicted in Table 3. The reaction of unsubstituted isoxazole **2b** with model 3-en-1-ynamide **1b** afforded the desired 4*H*-azepine **4a** in 84% yield, together with pyrrole **7a'** in only 8% yield (entry 1). Mono-substituted 3-methyl or 5-methyl isoxazoles **2c** and **2d** are also suitable for these annulations to afford compounds **4b** and **4c** in 75% and 87% yields, respectively (entries 2–3). We prepared additional 3,5-disubstituted isoxazoles **2e–2i** with  $\text{R}^1 = \text{alkyl}$  and phenyl, and  $\text{R}^2 = \text{alkyl}$ ; their annulations proceed smoothly to produce desired **4d–4h** in 69–85% yields (entries 4–8). For di-substituted isoxazoles **2j** and **2k** bearing  $\text{R}^2 = \text{Ph}$ , 4*H*-azepines **4i** and **4j** were obtained in 61% and 71% yields respectively, together with their rearrangement products **5i** and **5j** in 15–30% yields (entries 9–10). Compounds **4a** and **5i** were characterized by X-ray diffraction.<sup>11</sup>

Our convenient synthesis of 4*H*-azepines provides new synthetic utilities; several new functionalizations are depicted in Scheme 2.  $\text{NaBH}_4$ -reduction of species **3b** delivered an alcohol derivative **7a** in 84% yield. Selective hydrogenation of the same species afforded 2-aza-1,3-dien-5-one **7b** in 71% yield. A final treatment of 4*H*-azepine **3b** with NBS in acetone afforded compound **7c**, of which the molecular structure was determined by  $^1\text{H}$  NOE spectra.

The Lewis-catalyzed rearrangement of 4*H*-azepines **3–4** to substituted pyridines **5** [eqn (3)] is unprecedented in 4*H*-azepine chemistry.<sup>10</sup> We undertook such novel [4+2]-annulations



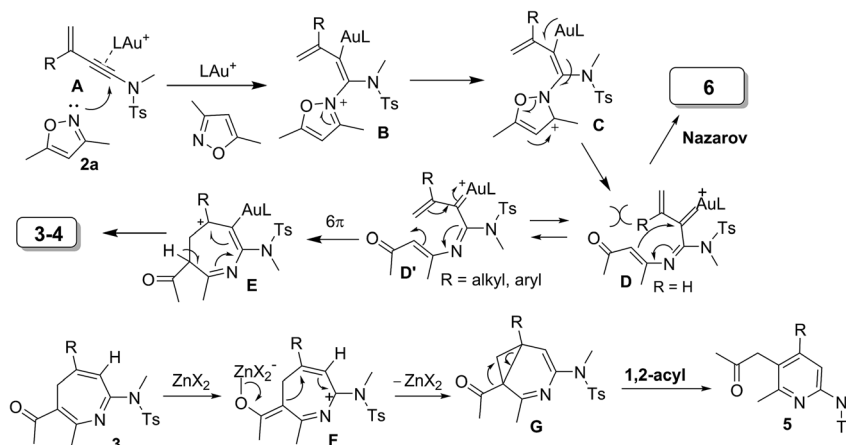
Scheme 2 New functionalization of 4*H*-azepines.

Table 4 [4+2]-Annulations between 3-en-1-ynamides and isoxazoles

Entry	( $\text{R}^1$ , $\text{R}^2$ , EWG)	<b>1</b>	( $\text{R}^3$ , $\text{R}^4$ )	<b>2</b>	Time [h]	Yield [%]	<b>5</b>
(1)	Me, Me, Ts	<b>1b</b>	Me, Me	<b>2a</b>	19	73 (35) <sup>c</sup>	<b>5a</b> (X-ray)
(2)	<i>n</i> -Bu, Me, Ts	<b>1k</b>	Me, Me	<b>2a</b>	33	64	<b>5b</b>
(3)	<i>c</i> -Pr, Me, Ts	<b>1h</b>	Me, Me	<b>2a</b>	20	56	<b>5c</b>
(4)	<i>i</i> -Pr, Me, Ts	<b>1g</b>	Me, Me	<b>2a</b>	15	51	<b>5d</b>
(5)	Me, <i>n</i> -Bu, Ms	<b>1a</b>	Me, Me	<b>2a</b>	28	63	<b>5e</b>
(6)	Me, Me, Ts	<b>1b</b>	<i>n</i> -Bu, <i>n</i> -Bu	<b>2f</b>	19	78	<b>5f</b>
(7)	Me, Me, Ts	<b>1b</b>	Et, Et	<b>2e</b>	16	69	<b>5g</b>
(8)	Me, Me, Ts	<b>1b</b>	<i>n</i> Bu, <i>c</i> -Pr	<b>2h</b>	20	75	<b>5h</b>
(9)	Me, Me, Ts	<b>1b</b>	Ph, Ph	<b>2j</b>	24	80	<b>5i</b> (X-ray)
(10)	Me, Me, Ts	<b>1b</b>	Me, Ph	<b>2k</b>	30	75	<b>5j</b>

<sup>a</sup> [**1**] = 0.15 M. <sup>b</sup> Product yields are reported after separation from a silica column. <sup>c</sup> The value in parentheses is reported using a mixture of  $\text{IPrAuCl/AgNTf}_2$  (10 mol%) and  $\text{Zn}(\text{OTf})_2$  (20 mol%) in hot DCE (70 °C, 48 h); **3b** was also isolated in 28% yield.





Scheme 3 A plausible reaction mechanism.

between 3-en-1-ynamides **1** and isoxazoles **2** using Au(I)/Zn(II) in a relay series, as depicted in Table 4. In the reactions of various 3-substituted 3-en-1-ynamides **1** ( $R^1$  = methyl, *n*-butyl, cyclopropyl and isopropyl) with 3,5-dimethylisoxazole **2a**, substituted pyridines **5a–5d** were obtained in satisfactory yields (51–73%, entries 1–4). In entry 1, if the reaction was performed with combined Au(I)/Zn(II) catalysts in a non-relay operation, compounds **5a** and **3b** were isolated in 35% and 28% yields respectively. For 3-en-1-ynamide **1a** bearing a NMs(*n*-butyl), the corresponding product **5e** was obtained in 63% yield (entry 5). We tested the reactions on 3,5-disubstituted isoxazoles **2e–2f** & **2h** bearing all alkyl substituents, producing desired **5f–5h** in good yields (69–78%, entries 6–8). For such disubstituted isoxazoles bearing  $R^4$  = Ph, the reactions afforded the desired pyridine derivatives **5i** and **5j** in 75–80% yields (entries 9–10). The molecular structures of compounds **5a** and **5i** were characterized by X-ray diffraction.<sup>11</sup>

Scheme 3 rationalizes the crucial roles of substituents of 3-en-1-ynamides in the chemoselectivity that relies on two conformational structures **D** versus **D'**. The N-attack of isoxazole at gold- $\pi$ -ynamide **A** is expected to form a gold-carbene **D'**, which can be visualized as a gold-stabilized cycloheptatrienyl cation. Conformation **D** is favorable with  $R$  = H, which prefers aza-Nazarov reactions.<sup>12</sup> When a C(3)-substituent is present ( $R$  = alkyl and aryl), all  $\sigma$ -*cis* configured species **D'** are the preferable geometry to induce novel  $6\pi$  electrocyclizations. This ring closure is expected to proceed through an attack of enamide at the alkenylgold moiety that is also visualized as a gold-stabilized cation. Additional C(4)-substituents render the formation of cations **D'** difficult, thus yielding pyrrole **6** as byproducts. A loss of an acidic proton from seven-membered cations **E** is expected to yield azepines **3–4**. 4*H*-Azepines **3–4** bear an enone conjugated with a triene; this extensive conjugation is very stable to impede a  $6\pi$  electrocyclization of their triene moieties unless a Lewis acid is present. Zn(OTf)<sub>2</sub> likely coordinates with the carbonyl of 4*H*-azepine **3** to generate a 2-azapentadienyl cation **F** bearing a zinc enolate, further enabling an intramolecular cyclization to generate species **G**. A 1,2-acyl shift<sup>14</sup> of species **G** delivers the observed product **5**.<sup>13</sup>

## Conclusions

In summary, this work describes new gold-catalyzed [4+3] annulations<sup>15</sup> of 3-substituted 3-en-1-ynamides with isoxazoles to form 4*H*-azepines. A relay catalysis is also developed with Au(I)/Zn(II) catalysts to achieve [4+2] annulations from the same reactants. The mechanisms of gold-catalyzed [4+3] annulations involve unprecedented  $6\pi$  electrocyclizations of 3-azacycloheptatrienyl cations to form 4*H*-azepines **3–4** efficiently. Control experiments confirm that 4*H*-azepines **3–4** are catalyzed by Zn(OTf)<sub>2</sub> to undergo new rearrangement reactions to form substituted pyridine derivatives.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

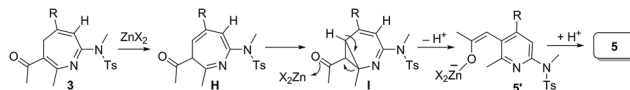
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- 13 As suggested by one reviewer, an alternative mechanism is also possible for the Zn(II)-catalyzed rearrangement; this process involves an isomerization of initial species **3** to an unconjugated iminoyl ketone **H**, followed by a  $6\pi$ -cyclization to generate species **I**. A subsequent Zn(II)-catalyzed aromatization of species **I** is expected to yield the final product **5**. In this process, species **H** is relatively higher than **3** in energy, but its feasibility is not excluded.



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- 15 For reviews of gold-catalyzed cycloaddition or annulation reactions of alkynes, see (a) D. J. Gorin, B. D. Sherry and F. D. Toste, *Chem. Rev.*, 2008, **108**, 3351; (b) A. S. K. Hashmi, *Chem. Rev.*, 2007, **107**, 3180; (c) F. López and J. L. Mascareñas, *Beilstein J. Org. Chem.*, 2011, **7**, 1075; (d) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria and A. Simonneau, *Chem. Rev.*, 2011, **111**, 1954; (e) D. Garayalde and C. Nevado, *ACS Catal.*, 2012, **2**, 1462; (f) M. E. Muratore, A. Homes, C. Obradors and A. M. Echavarren, *Chem.–Asian J.*, 2014, **9**, 3066.

