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

Sovan Sundar Giri and Rai-Shung Liu *

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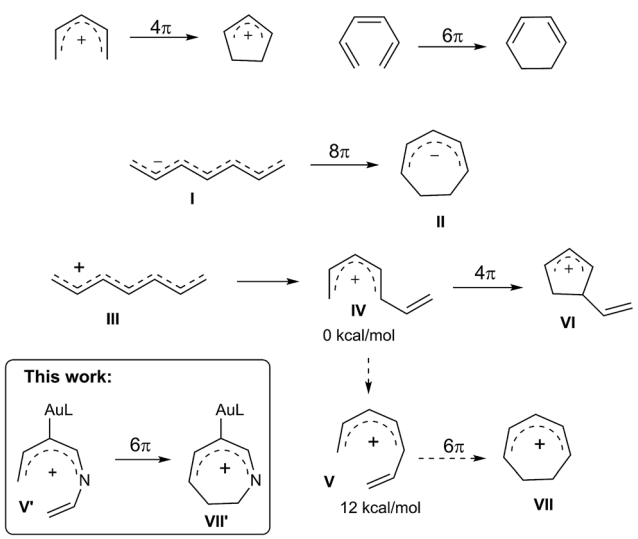
New gold-catalyzed [4+3]-annulations of 3-en-1-ynamides with isoxazoles afford 4*H*-azepines efficiently; this process involves 6π electrocyclizations of gold-stabilized 3-azaheptatrienyl cations. In the presence of $Zn(OTf)_2$, the resulting 4*H*-azepines undergo skeletal rearrangement to furnish substituted 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 Au(I)/Zn(II) catalysts. This work reports the first success of the 6π electrocyclizations of heptatrienyl cations that are unprecedented in literature reports.

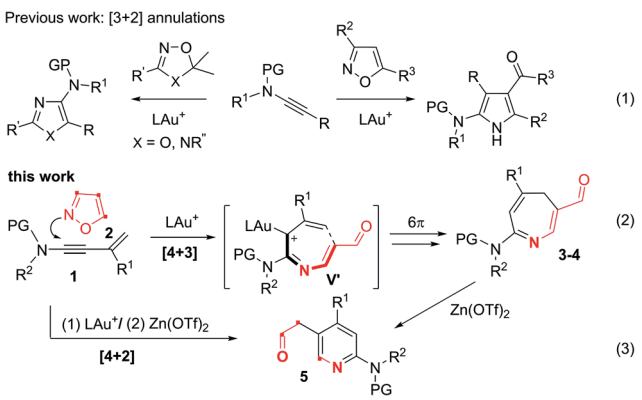
Introduction

Electrocyclizations of acyclic conjugated π-motifs are powerful tools to access five-, six- and seven-membered carbocycles;[1] prominent examples include Nazarov cyclizations of pentadienyl cations[2] and 6π electrocyclizations of trienes,[3] which have found widespread applications in organic synthesis.



Scheme 1 Electrocyclizations of conjugated π-motifs.

In the context of seven-carbon π-motifs, heptatrienyl anions **I** undergo facile 8π electrocyclizations *via* rapid interconversions among various anion configurations (Scheme 1).[4] In contrast, heptatrienyl cations **III**[5] exclusively undergo Nazarov reactions because of the difficulties of forming all σ-*cis* configured cations **V** that have a high energy state.[5b] 1-Aza- and 1-oxaheptatrienyl cations[6] were also reported to follow Nazarov cyclizations. The realization of a 6π 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.



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

Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan, Republic of China. E-mail: rsliu@mx.nthu.edu.tw

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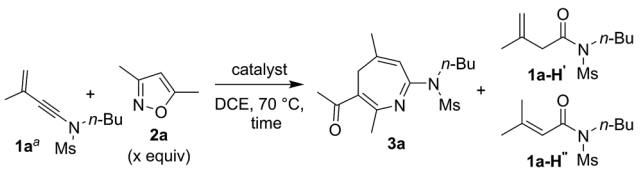
rich ynamides, yielding substituted pyrrole derivatives through aza-Nazarov cyclizations of the key intermediate [eqn (1)].[7,8] These [3+2]-annulations were extensively expanded to other N–O heterocycles including benzisoxazoles, 1,2,4-oxadiazoles, 1,4,2-dioxazoles and 4,5-dihydro-1,2,4-oxadiazoles, yielding additional five-membered azacycles as depicted in [eqn (1)].[9] 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.[10]

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/$AgNTf_2$ [L = $p(t\text{-Bu})_2(o\text{-biphenyl})$ and IPr] 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/$AgNTf_2$ gave a clean reaction, yielding desired **3a** up to 91% (entry 4). We tested other phosphine ligands such as PPh_3 and $P(OPh)_3$, yielding desired **3a** in satisfactory yields (78–81%, entries 5–6). Other counter anions such as OTf^- and SbF_6^- were also effective in producing **3a** in 85–88% yields (entries 7–8). $AgNTf_2$ alone was not active at all (entry 9).

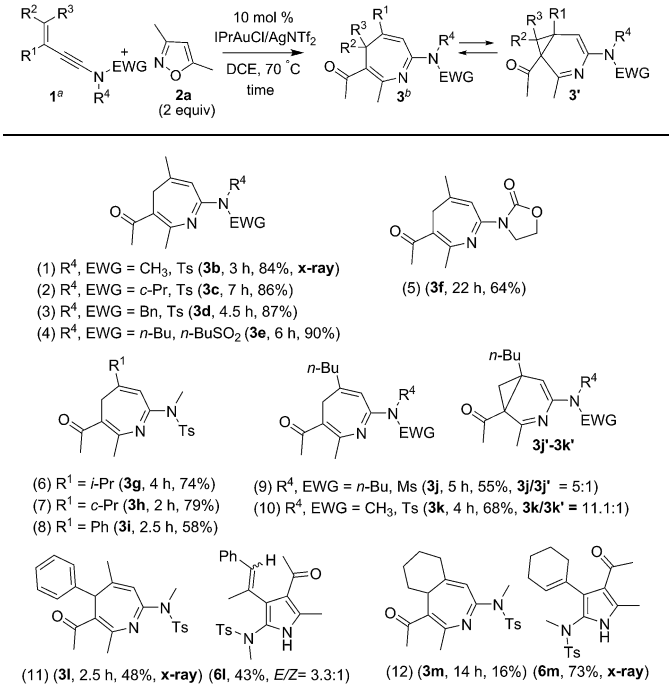
Table 1 [4+3]-Annulations over various gold catalysts



Entry	Catalyst [mol%]	x	Time [h]	Yield[b] [%] 1a	3a	1a–H′/1a–H″
1[c]	LAuCl/$AgNTf_2$ [5]	2	3	20	64	—
2[d]	IPrAuCl/$AgNTf_2$ [5]	2	7	12	75	7 [2.5 : 1]
3	IPrAuCl/$AgNTf_2$ [5]	1.2	7	23	62	5 [1 : 1]
4	**IPrAuCl/$AgNTf_2$ [10]**	**2**	**3**	**—**	**91**	**Trace**
5	PPh_3AuCl/$AgNTf_2$ [10]	2	3.5	—	81	5 [1.25 : 1]
6	$[PhO]_3$PAuCl/$AgNTf_2$ [10]	2	3.5	—	78	13 [1.1 : 1]
7	IPrAuCl/$AgSbF_6$ [10]	2	2.5	—	85	6 [1.4 : 1]
8	IPrAuCl/AgOTf [10]	2	2	—	88	Trace
9	$AgNTf_2$ [10]	2	15	33	—	11

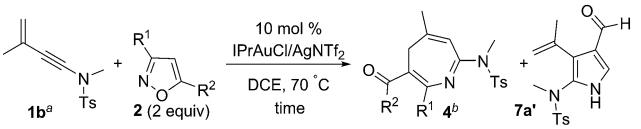
[a] [**1a**] = 0.15 M. [b] Product yields are reported after separation from a silica column. [c] L = $p(t\text{-Bu})_2(o\text{-biphenyl})$. [d] IPr = 1,3-bis(diisopropylphenyl)-imidazol-2-ylidene. Ms = methanesulfonyl, DCE = 1,2-dichloroethane, and Tf = trifluoromethanesulfonyl.

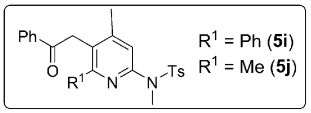
Table 2 [4+3]-Annulations with various 3-en-1-ynamides



[a] [**1**] = 0.15 M. [b] Product yields are reported after separation from a silica column. EWG = electron withdrawing group.

Table 3 [4+3]-Annulations with various isoxazoles

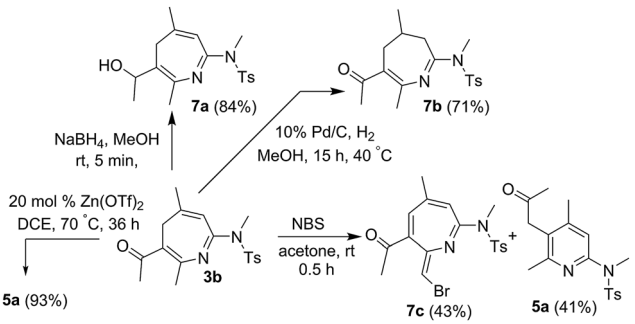


Entry	(R^1, R^2)	2	Time [h]	Yield [%]	4
(1)	H, H	**2b**	4	84	**4a** (X-ray)
				8	**7a′**
(2)	H, Me	**2d**	3	75	**4b**
(3)	Me, H	**2c**	3	87	**4c**
(4)	Et, Et	**2e**	6	85	**4d**
(5)	*n*-Bu, *n*-Bu	**2f**	7	81	**4e**
(6)	Me, *n*-Bu	**2g**	3	82	**4f**
(7)	*n*-Bu, *c*-Pr	**2h**	2	77	**4g**
(8)	Ph, *n*-Bu	**2i**	4	69	**4h**
(9)	Ph, Ph	**2j**	6.5	61	**4i**
				30	**5i** (X-ray)
(10)	Me, Ph	**2k**	4	71	**4j**
				15	**5j**

[a] [**1b**] = 0.15 M. [b] Product yields are reported after separation from a silica column.

Suitable substituents of 3-en-1-ynamides **1** are crucial to achieve 6π cyclizations of 3-azaheptatrienyl cations **V′** [eqn (2)]. We tested the reactions on 3-en-1-ynes **1b–1m** bearing a C(3)-substituent to circumvent aza-Nazarov cyclizations as reported in Ye's work.[7] 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 NTsR^4 (R^4 = Me, cyclopropyl, benzyl and N(n-C_4H_9) (−SO_2Bu)), 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** (R^1 = isopropyl and cyclopropyl) were obtained in 74–79%, and **3i** (R^1 = 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** (R^1 = Me, R^2 = Ph and R^3 = 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-ynes comprise a small R^2 or R^3 substituent whereas 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.[11]



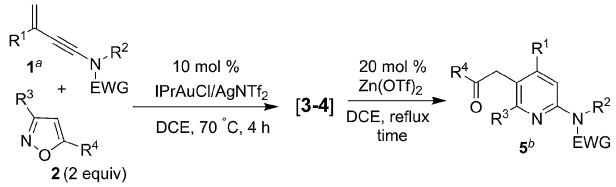
Scheme 2 New functionalization of 4*H*-azepines.

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 R^1 = alkyl and phenyl, and R^2 = 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 R^2 = 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.[11]

Our convenient synthesis of 4*H*-azepines provides new synthetic utilities; several new functionalizations are depicted in Scheme 2. $NaBH_4$-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}H NOE spectra.

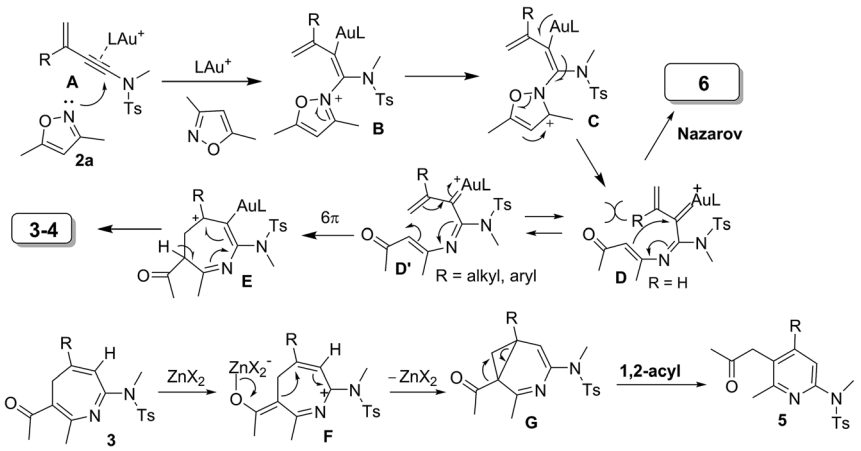
The Lewis-catalyzed rearrangement of 4*H*-azepines **3–4** to substituted pyridines **5** [eqn (3)] is unprecedented in 4*H*-azepine chemistry.[10] We undertook such novel [4+2]-annulations

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



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

^{a} [**1**] = 0.15 M. ^{b} Product yields are reported after separation from a silica column. ^{c} The value in parentheses is reported using a mixture of IPrAuCl/$AgNTf_2$ (10 mol%) and $Zn(OTf)_2$ (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.[11]

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-π-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.[12] When a C(3)-substituent is present (R = alkyl and aryl), all σ-*cis* configured species **D′** are the preferable geometry to induce novel 6π 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 6π electrocyclization of their triene moieties unless a Lewis acid is present. $Zn(OTf)_2$ 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[14] of species **G** delivers the observed product **5**.[13]

Conclusions

In summary, this work describes new gold-catalyzed [4+3] annulations[15] 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 6π 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 $Zn(OTf)_2$ 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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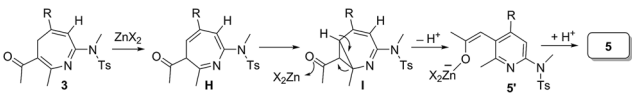
11 Crystallographic data of compounds **3b**, **3l**, **4a**, **5a**, **5i**, and **6m** were deposited in Cambridge Crystallographic Data Center: **3b**: CCDC 1589549, **3l**: CCDC 1589562, **4a**: CCDC 1589561, **5a**: CCDC 1589558, **5i**: CCDC 1589559 and **6m** CCDC 1589560.†

12 For the aza-Nazarov cyclizations, see: (*a*) D. A. Klumpp, Y. Zhang, M. J. O'Connor, P. M. Esteves and L. S. de Almeida, *Org. Lett.*, 2007, **9**, 3085; (*b*) Z. X. Ma, S. He, W. Song and R. P. Hsung, *Org. Lett.*, 2012, **14**, 5736; (*c*) R. L. Sahani and R. S. Liu, *Angew. Chem., Int. Ed.*, 2017, **56**, 12736; (*d*) S. K. Pawar, R. L. Sahani and R. S. Liu, *Chem.–Eur. J.*, 2015, **21**, 10843; (*e*) C. Shu, Y. H. Wang, C. H. Shen, P. P. Ruan, X. Lu and L. W. Ye, *Org. Lett.*, 2016, **18**, 3254.

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 6π-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.



14 (*a*) S. M. Wang and L. Zhang, *Org. Lett.*, 2006, **8**, 4585; (*b*) G. Li, G. Zhang and L. Zhang, *J. Am. Chem. Soc.*, 2008, **130**, 3704; (*c*) S. B. Wagh and R. S. Liu, *Chem. Commun.*, 2015, **51**, 15462; (*d*) R. Chaudhuri, A. Das, H. Y. Liao and R. S. Liu, *Chem. Commun.*, 2010, **46**, 4601.

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.