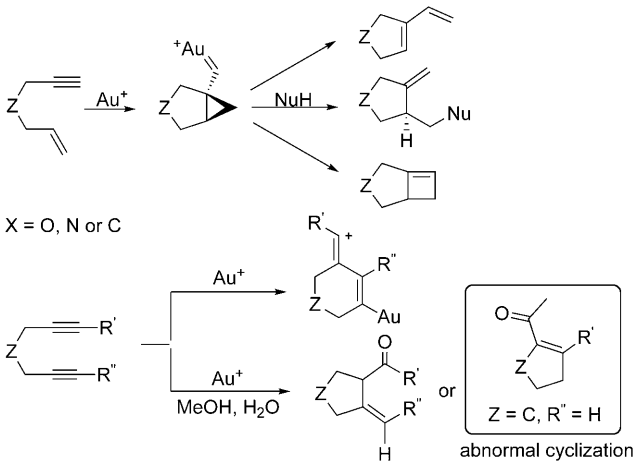
Gold Catalysis

DOI: 10.1002/anie.201006969

Gold(I)-Catalyzed Cycloisomerization of 1,6-Diynes: Synthesis of 2,3-Disubstituted 3-Pyrroline Derivatives**

*Di-Han Zhang, Liang-Feng Yao, Yin Wei, and Min Shi**

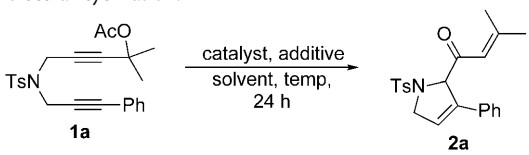
Homogeneous catalysis mediated by gold complexes has received considerable attention in recent years.[1] Among these interesting reactions, gold-catalyzed cycloisomerization of 1,6-enynes and 1,6-diynes[2,3] is one of the most important strategies for the construction of functionalized cyclic structures (Scheme 1). In the context of our ongoing efforts to develop gold-catalyzed tandem reactions, we realized that the gold-catalyzed cascade transformation of 1,6-diynes to abnormal five-membered cycloadducts has been less explored (Scheme 1). Thus far, only one example has been reported, in which a cycloisomerization of terminal 1,6-diynes catalyzed by gold–phosphine gives the cyclopentene products in less than 43% yield (Z = C; Scheme 1).[3f] We therefore anticipated that a new cascade process initiated by gold-induced C–C bond formation along with cycloisomerization might be achieved in a system in which a nitrogen atom connects 1,6-diyne to give heterocyclic products (Z = N). Herein, we report a novel C–C bond formation along with cycloisomerization from 1,6-diyne-containing propargylic ester and arene–yne (arenyne) units toward nitrogen-containing five-membered heterocyclic rings such as 2,3-disubstituted 3-pyrrolines,[4] which have been extensively used as synthetic building blocks in organic synthesis and appear as structural motifs in many natural products, thus exhibiting interesting biological activities.[5]



Scheme 1. Gold-catalyzed cycloisomerization of 1,6-enyne and 1,6-diynes. Nu = nucleophile.

Initial studies using propargylic acetate arenyne **1a** (0.2 mmol) as the substrate were aimed at determining the reaction outcome and subsequently optimizing the reaction conditions. The results are summarized in Table 1. We found that an interesting 3-pyrroline derivative **2a** was formed in 50% yield using [(PPh_3)AuCl]/AgOTf as the catalyst (5 mol%) in toluene at 80°C (Table 1, entry 1). The structure of compound **2a** was confirmed by NMR spectroscopy and X-ray crystal structure analysis (Figure 1).[6] Product **2a** could be

Table 1: Optimization of reaction conditions for gold(I)-catalyzed intramolecular cyclization.[a]



1a **2a**

Entry	Catalyst [5 mol%]	Additive (equiv)	Solvent	*T* [°C]	Yield of **2a** [%][b]
1	[(PPh_3)AuCl]/AgOTf	–	toluene	80	50
2	[(PPh_3)AuCl]/AgOTf	H_2O (1.0)	toluene	80	62
3	[(PPh_3)AuCl]/AgOTf	H_2O (2.0)	toluene	80	–[c]
4	[(PPh_3)AuCl]/AgOTf	MeOH (2.0)	toluene	100	complex
5	[(PPh_3)AuCl]/AgOTf	H_2O (0.5)	toluene	80	52
6	[(PPh_3)AuCl]/AgOTf	H_2O (1.0)	toluene	60	40
7	[(PPh_3)AuCl]/AgOTf	H_2O (1.0)	toluene	100	42
8	[(PPh_3)AuCl]/AgOTf	H_2O (1.0)	CH_3CN	80	NR
9	[(PPh_3)AuCl]/AgOTf	H_2O (1.0)	CH_3NO_2	80	NR
10	[(PPh_3)AuCl]/AgOTf	H_2O (1.0)	DCE	80	65
11	[(tBu$_3$P)AuCl]/AgOTf	H_2O (1.0)	DCE	80	83
12	[(IPr)AuCl]/AgOTf	H_2O (1.0)	DCE	80	26
13	[(PMe_3)AuCl]/AgOTf	H_2O (1.0)	DCE	80	40
14	[(tBu$_3$P)AuCl]/$AgSbF_6$	H_2O (1.0)	DCE	80	NR
15	[(tBu$_3$P)AuCl]/$AgBF_4$	H_2O (1.0)	DCE	80	complex
16	[(tBu$_3$P)AuCl]/$AgNTf_2$	H_2O (1.0)	DCE	80	complex
17	AgOTf	H_2O (1.0)	DCE	80	50
18	[(tBu$_3$P)AuCl]	H_2O (1.0)	DCE	80	NR

[a] All reactions were carried out using **1a** (0.2 mmol), H_2O (X equiv) in the presence of catalyst (5 mol%) in various solvents (2.0 mL) unless otherwise specified. [b] Yield of isolated product. [c] The product is a ketone (see the Supporting Information). IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, NR = no reaction.

[*] D.-H. Zhang, L.-F. Yao, Prof. M. Shi
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
345 Lingling Road, Shanghai 200032 (China)
Fax: (+86) 21-6416-6128
E-mail: mshi@mail.sioc.ac.cn

[**] We thank the Shanghai Municipal Committee of Science and Technology (08dj1400100-2), the National Basic Research Program of China (973)-2009CB825300, and the National Natural Science Foundation of China for financial support (21072206, 20472096, 20872162, 20672127, 20821002, and 20732008).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201006969.

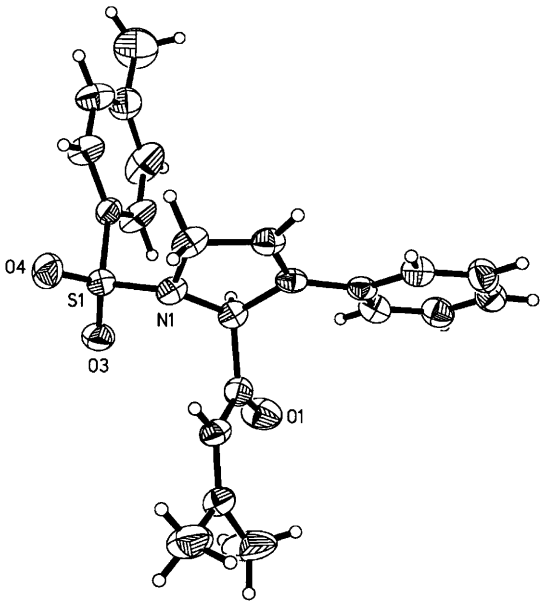
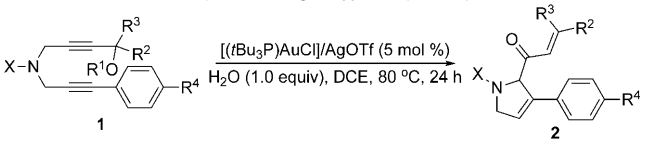


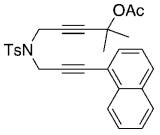
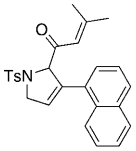
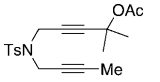
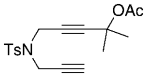
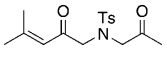
Figure 1. ORTEP Drawing of **2a**. Hydrogen atoms have been omitted for clarity, ellipsoids are drawn at 30 % probability.

obtained in 62 % yield in the presence of H_2O (1.0 equiv; Table 1, entry 2). On the other hand, the addition of H_2O (2.0 equiv) to the reaction system led to the formation of a ketone product rather than **2a** (see product **7a** in the Supporting Information) and replacing H_2O with methanol (2.0 equiv) resulted in a complex mixture at 100 °C (Table 1, entries 3 and 4). Using 0.5 equivalents of water did not increase the yield of **2a** either (Table 1, entry 5). Reducing the reaction temperature to 60 °C or elevating the temperature to 100 °C did not improve the reaction outcome in the presence of H_2O (1.0 equiv; Table 1, entries 6 and 7). Carrying out the reaction in CH_3NO_2 or CH_3CN did not facilitate the formation of **2a** (Table 1, entries 8 and 9). When 1,2-dichloroethane (DCE) was used as a solvent, the yield of **2a** could be improved up to 65 % (Table 1, entry 10). In the presence of [(*t*Bu$_3$P)AuCl], **2a** could be obtained in 83 % yield and [(PMe$_3$)AuCl] as well as [(IPr)AuCl] were not effective gold catalysts in this reaction (Table 1, entries 11–13). Further examination of silver salts revealed that AgOTf was the best choice for the reaction (Table 1, entries 14–16). Control experiments indicated that using AgOTf alone as the catalyst gave **2a** in 50 % yield and using [(*t*Bu$_3$P)AuCl] alone as the catalyst did not promote the reaction (Table 1, entries 17 and 18). Therefore, the optimal reaction conditions were found when the reaction was carried out in DCE at 80 °C using [(*t*Bu$_3$P)AuCl]/AgOTf (5 mol %) as the catalyst in the presence of H_2O (1.0 equiv).

We next examined the substrate generality of the reaction under the optimized conditions and the results are shown in Table 2. When both R^2 and R^3 were ethyl groups, 3-pyrroline derivative **2b** was formed in 50 % yield (Table 2, entry 1). For various propargylic esters in which both R^3 and R^4 were hydrogen atoms, the corresponding cycloadducts **2c**–**2f** could be obtained in 55–84 % yields under the standard conditions (Table 2, entries 2–9). As for substrate **1k** having a methyl

Table 2: Substrate scope of the gold(I)-catalyzed cycloisomerization.[a]

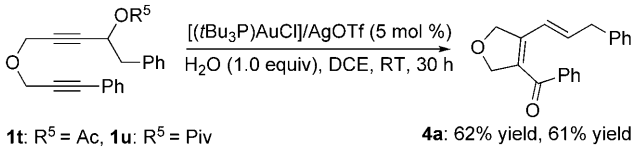


Entry	1	X	R^1	R^2	R^3	R^4	Yield [%][b]
1	**1b**	Ts	Ac	CH_3CH_2	CH_3CH_2	H	**2b**, 50
2	**1c**	Ts	Ac	$CH_3CH_2CH_2$	H	H	**2c**, 84
3	**1d**	Ts	Piv	$CH_3CH_2CH_2$	H	H	**2c**, 80
4	**1e**	Ts	Ac	$PhCH_2CH_2$	H	H	**2d**, 64
5	**1f**	Ts	Piv	$PhCH_2CH_2$	H	H	**2d**, 56
6	**1g**	Ts	Ac	$(CH_3)_2CH$	H	H	**2e**, 60
7	**1h**	Ts	Piv	$(CH_3)_2CH$	H	H	**2e**, 56
8	**1i**	Ts	Ac	$PhCH_2$	H	H	**2f**, 63
9	**1j**	Ts	Piv	$PhCH_2$	H	H	**2f**, 55
10	**1k**	Ts	Ac	CH_3	CH_3	CH_3	**2g**, 88
11	**1l**	Ts	Ac	CH_3	CH_3	Cl	**2h**, 61
12	**1m**	Ns	Ac	CH_3	CH_3	H	**2i**, 66
13	**1n**	Bs	Ac	CH_3	CH_3	H	**2j**, 73
14	**1o**	Ns	Ac	CH_3	CH_3	CH_3	**2k**, 68
15	**1p**	Ts	Ac	$BnOCH_2$	H	H	**2l**, 35
16	**1q**						**2m**, 71
17	**1r**						NR
18	**1s**						**3a**, 71

[a] All reactions were carried out using **1** (0.2 mmol), H_2O (1.0 equiv) in the presence of [(*t*Bu$_3$P)AuCl]/AgOTf (5 mol %) in DCE (2.0 mL) at 80 °C for 24 h. [b] Yield of isolated product. Bn = benzyl, Bs = 4-bromobenzenesulfonyl, Ns = 4-nitrobenzenesulfonyl, Ts = 4-toluenesulfonyl.

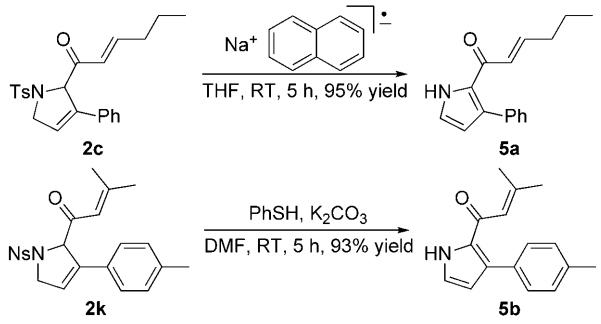
group on the benzene ring ($R^4 = CH_3$) and R^2 and R^3 were methyl groups, the corresponding product **2g** was formed in 88 % yield (Table 2, entry 10). Substrate **1l** having an electron-withdrawing chloro atom on the benzene ring ($R^4 = Cl$) gave the desired product **2h** in 61 % yield (Table 2, entry 11). In the case of other N-sulfonated amines (X = Ns or Bs), the reactions also proceeded smoothly to give the corresponding cycloadducts **2i**–**2k** in 66–73 % yields, thus indicating a broad substrate scope for this reaction (Table 2, entries 12–14). Further examination of substrate **1p** ($R^2 = CH_2OBn$) revealed that the desired product **2l** could be obtained in 35 % yield (Table 2, entry 15). The aromatic group of **1** could also be a naphthyl group (**1q**), thereby giving the corresponding cycloadduct **2m** in 71 % yield (Table 2, entry 16). As for substrate **1r** having a methyl group at the terminal of alkyne moiety, no reaction occurred under the standard conditions (Table 2, entry 17). When the terminal of alkyne moiety is a hydrogen atom (**1s**), the corresponding enone **3a** could be formed in 71 % yield rather than the cyclized product (Table 2, entry 18). The product structures of **2a**–**2m** were determined by NMR spectroscopic analysis, mass spectrometry (MS), and HRMS (see the Supporting Information).

On the other hand, in the case of oxygen-tethered 1,6-diynes containing propargylic ester and arenyne such as substrates **1t** and **1u**, the reactions produced the corresponding 2,5-dihydrofuran derivative **4a** (normal cyclization) in 62% and 61% yield at room temperature (20°C), respectively (Scheme 2).



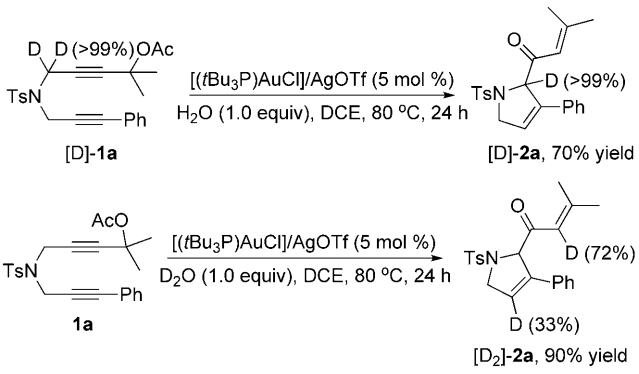
Scheme 2. Gold(I)-catalyzed cycloisomerization of **1t** and **1u**. Piv = pivaloyl, Tf = triflate.

Further transformations of products **2** are shown in Scheme 3. The benzenesulfonyl group and 4-nitrobenzenesulfonyl group could be easily removed by treatment with sodium naphthalene agent[7] or thiophenol in the presence of K_2CO_3,[8] respectively, thus giving the corresponding pyrrole derivatives **5a** and **5b** in good yields.



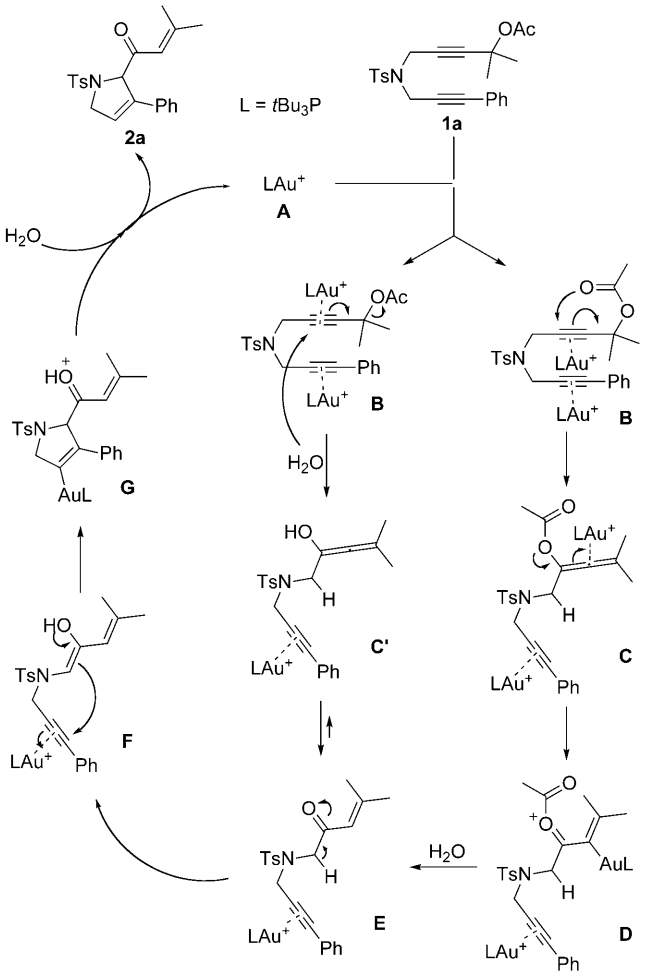
Scheme 3. Further transformations of products **2c** and **2k**.

To elucidate the cycloisomerization mechanism, deuterium labeling experiments were performed as shown in Scheme 4. Propargylic acetate [D]-**1a** containing CD_2 produced cycloadduct [D]-**2a** in 70% yield with > 99% deuterium incorporation at its alkyl carbon center. Carrying out the reaction of propargylic acetate **1a** in the presence of D_2O (1.0 equiv) led to the corresponding product [D_2]-**2a** in 90% yield along with 72% and 33% deuterium incorporation at its olefinic carbon atoms.



Scheme 4. Isotopic labeling experiments.

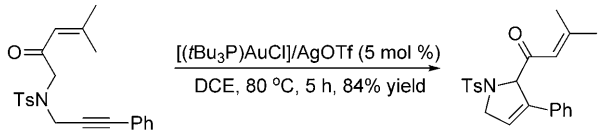
Plausible mechanisms for this reaction are outlined in Scheme 5 on the basis of the above deuterium labeling experiments. Two cationic Au^I complexes **A** first coordinate



Scheme 5. A plausible reaction mechanism. L = ligand.

to the two alkyne moieties of **1a**, respectively, to give intermediate **B**, which undergoes a gold-catalyzed [3,3]-sigmatropic rearrangement[9] to give the corresponding carboxyallene intermediates **C**. The resulting oxonium intermediate **D**[9,10] undergoes hydrolysis to give enone **E**. Alternatively, based on a Meyer–Schuster-like rearrangement,[10b,11] the nucleophilic attack of water on the alkyne moiety of intermediate **B** affords allenol **C′** along with the release of AcO^-, and which can also further tautomerize to the conjugated enone **E**. The enone **E** undergoes a Lewis acid catalyzed enolization to give intermediate **F**. Activation of the remaining alkyne moiety by the gold complex induces a 5-*endo-dig* cycloaddition to give intermediate **G**.[9h] The hydrolysis of intermediate **G** produces cycloadduct **2a** and regenerates the Au^I complex **A** to complete the catalytic cycle. To verify the proposed mechanism, we also synthesized alkynyl

enone **6a**,[12] which is the intermediate **E** in the catalytic cycle. In the control experiment, we found that upon treatment of **6a** with [(tBu$_3$P)AuCl]/AgOTf (5 mol%) in DCE at 80°C for 5 hours, **2a** could be obtained in 84% yield, therefore suggesting that intermediate **E** is the real key species in the catalytic cycle (Scheme 6).



6a **2a**

Scheme 6. Gold(I)-catalyzed cyclization of alkynyl enone **6a**.

As mentioned above, oxygen-tethered 1,6-diynes underwent a different reaction, thereby affording normal cyclization adducts. We hypothesized that the pK_a value of α protons with respect to the carbonyl group in oxygen-tethered 1,6-diynes is larger than that of α protons with respect to the carbonyl group in nitrogen-tethered 1,6-diynes, which may make the proton transfer step (shown in Scheme 5) difficult to occur for the reaction involving oxygen-tethered 1,6-diynes. We chose two simplified model compounds **I** and **II**, and calculated the pK_a value of the α protons with respect to the carbonyl group in aqueous solution at CPCM/UAHF/BHLYP/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ level of theory. Indeed, the calculated pK_a value (pK_a = 32.5) of the α protons with respect to the carbonyl group in compound **II** is larger than that of the α protons with respect to the carbonyl group in compound **I** (pK_a = 18.6) by 13.9 pK_a units (Scheme 7, see the Supporting Information for details). This result supports our assumption, which may explain why oxygen-tethered 1,6-diynes did not undergo the same reaction as nitrogen-tethered 1,6-diynes.

I **II**

pK_a = 18.6 (water) pK_a = 32.5 (water)

Scheme 7. pK_a value of compound **I** and compound **II** on the basis of DFT calculation.

In conclusion, we have developed a novel gold(I)-catalyzed cycloisomerization of 1,6-diynes containing propargylic ester and arenyne to provide an easy access to 3-pyrroline or pyrrole derivatives in good yields upon heating at 80°C. The reaction mechanism has been proposed on the basis of deuterium labeling and control experiments. Further applications of this air- or moisture-tolerant reaction of a gold-catalyzed system and more detailed mechanistic investigation are under way in our laboratory.

Experimental Section

General procedure for gold-catalyzed cyclization of propargylic ester-arenyne: Propargylic ester arenyne **1** (0.2 mmol, 1.0 equiv) was dissolved in 1,2-dichloroethane (2.0 mL, 0.1M) in an Schlenk tube under ambient atmosphere, [(tBu$_3$P)AuCl] (5 mol%) and AgOTf (5 mol%) were added followed by H_2O (3.6 μL, 1.0 equiv). The reaction mixture was stirred at 80°C until the reaction was complete. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **2** in moderate to good yields.

Received: November 6, 2010
Published online: February 15, 2011

Keywords: cycloisomerization · gold · homogeneous catalysis · isotopic labeling · pyrroles

[1] For some selected reviews on gold-catalyzed reactions, see: a) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; b) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; c) N. Bongers, N. Krause, *Angew. Chem.* **2008**, *120*, 2208–2211; *Angew. Chem. Int. Ed.* **2008**, *47*, 2178–2181; d) J. Muzart, *Tetrahedron* **2008**, *64*, 5815–5849; e) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; f) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; g) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; h) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; i) N. T. Patil, Y. Yamamoto, *Chem. Rev.* **2008**, *108*, 3395–3442; j) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221.

[2] For selected examples about gold-catalyzed cycloisomerization reaction of enynes or diynes, see: a) J. Sun, M. P. Conley, L. Zhang, S. A. Kozmin, *J. Am. Chem. Soc.* **2006**, *128*, 9705–9710; b) E. Jiménez-Núñez, C. K. Claverie, C. Nieto-Oberhuber, A. M. Echavarren, *Angew. Chem.* **2006**, *118*, 5578–5581; *Angew. Chem. Int. Ed.* **2006**, *45*, 5452–5455; c) P. Y. Toullec, E. Genin, L. Leseurre, J.-P. Genêt, V. Michelet, *Angew. Chem.* **2006**, *118*, 7587–7590; *Angew. Chem. Int. Ed.* **2006**, *45*, 7427–7430; d) L. Leseurre, P. Y. Toullec, J.-P. Genêt, V. Michelet, *Org. Lett.* **2007**, *9*, 4049–4052; e) C. H. Oh, A. Kim, *New J. Chem.* **2007**, *31*, 1719–1721; f) C. Nieto-Oberhuber, P. Pérez-Galán, E. Herrero-Gómez, T. Lauterbach, C. Rodríguez, S. López, C. Bour, A. Rosellón, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2008**, *130*, 269–279; g) C.-Y. Yang, G.-Y. Lin, H.-Y. Liao, S. Datta, R.-S. Liu, *J. Org. Chem.* **2008**, *73*, 4907–4914; h) H. J. Bae, B. Baskar, S. E. An, J. Y. Cheong, D. T. Thangadurai, I.-C. Hwang, Y. H. Rhee, *Angew. Chem.* **2008**, *120*, 2295–2298; *Angew. Chem. Int. Ed.* **2008**, *47*, 2263–2266; i) V. Michelet, P. Y. Toullec, J.-P. Genêt, *Angew. Chem.* **2008**, *120*, 4338–4386; *Angew. Chem. Int. Ed.* **2008**, *47*, 4268–4315; j) C. A. Sperger, A. Fiksdahl, *J. Org. Chem.* **2010**, *75*, 4542–4553; k) Y. Harrak, A. Simonneau, M. Malacria, V. Gandon, L. Fensterbank, *Chem. Commun.* **2010**, *46*, 865–867. For selected examples about Platinum-catalyzed cycloisomerization reaction of allenynes, see: l) N. Cadran, K. Cariou, G. Hervé, C. Aubert, L. Fensterbank, M. Malacria, J. Marco-Contelles, *J. Am. Chem. Soc.* **2004**, *126*, 3408–3409; m) T. Matsuda, S. Kadowaki, M. Murakami, *Helv. Chim. Acta* **2006**, *89*, 1672–1680; n) R. Zriba, V. Gandon, C. Aubert, L. Fensterbank, M. Malacria, *Chem. Eur. J.* **2008**, *14*, 1482–1491.

[3] a) T. Shibata, R. Fujiwara, D. Takano, *Synlett* **2005**, 2062–2066; b) J.-J. Lian, P.-C. Chen, Y.-P. Lin, H.-C. Ting, R.-S. Liu, *J. Am. Chem. Soc.* **2006**, *128*, 11372–11373; c) J.-J. Lian, R.-S. Liu, *Chem. Commun.* **2007**, 1337–1339; d) C. Zhang, D.-M. Cui, L.-Y. Yao, B.-S. Wang, Y.-Z. Hu, T. Hayashi, *J. Org. Chem.* **2008**, *73*,

7811 – 7813; e) S. M. Abu Sohel, R.-S. Liu, *Chem. Soc. Rev.* **2009**, *38*, 2269 – 2281; f) C. Sperger, A. Fiksdahl, *Org. Lett.* **2009**, *11*, 2449 – 2452; g) J. Meng, Y.-L. Zhao, C.-Q. Ren, Y. Li, Z. Li, Q. Liu, *Chem. Eur. J.* **2009**, *15*, 1830 – 1834; h) D.-M. Cui, Y.-N. Ke, D.-W. Zhuang, Q. Wang, C. Zhang, *Tetrahedron Lett.* **2010**, *51*, 980 – 982.

[4] For synthesis of 3-pyrroline, see: a) L. Vo Quang, H. Gaessler, Y. V. Quang, *Angew. Chem.* **1981**, *93*, 922 – 923; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 880 – 881; b) S. Brandänge, B. Rodriguez, *Synthesis* **1988**, 347 – 348; c) J. S. Warmus, G. J. Dilley, A. I. Meyers, *J. Org. Chem.* **1993**, *58*, 270 – 271; d) K. Ishii, H. Ohno, Y. Takemoto, T. Ibuka, *Synlett* **1999**, 228 – 230; e) H. Kagoshima, T. Akiyama, *J. Am. Chem. Soc.* **2000**, *122*, 11741 – 11742; f) M. P. Green, J. C. Prodger, A. E. Sherlock, C. J. Hayes, *Org. Lett.* **2001**, *3*, 3377 – 3379; g) A. Hercouet, A. Neu, J.-F. Peyronel, B. Carboni, *Synlett* **2002**, 829 – 831; h) N. Morita, N. Krause, *Org. Lett.* **2004**, *6*, 4121 – 4123; i) A. Horváth, J. Benner, J.-E. Bäckvall, *Eur. J. Org. Chem.* **2004**, 3240 – 3243; j) S. Himer, P. Somfai, *Synlett* **2005**, 3099 – 3102; k) F. Bellina, R. Rossi, *Tetrahedron* **2006**, *62*, 7213 – 7256; l) B. Zhang, Z. He, S. Xu, G. Wu, Z. He, *Tetrahedron* **2008**, *64*, 9471 – 9479.

[5] a) J. M. Phang, *Curr. Top. Cell. Regul.* **1985**, *25*, 91 – 132; b) A. B. Mauger, *J. Nat. Prod.* **1996**, *59*, 1205 – 1211; c) K. Ishii, H. Ohno, Y. Takemoto, E. Osawa, Y. Yamaoka, N. Fujii, T. Ibuka, *J. Chem. Soc. Perkin Trans. 1* **1999**, 2155 – 2164; d) D. O'Hagen, *Nat. Prod. Rep.* **2000**, *17*, 435 – 446.

[6] CCDC 748954 (**2a**) contains 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.

[7] a) W. D. Closson, P. Wriede, S. Bank, *J. Am. Chem. Soc.* **1966**, *88*, 1581 – 1583; b) S. Ji, L. B. Gortler, A. Waring, A. J. Battisti, S. Bank, W. D. Closson, P. A. Wriede, *J. Am. Chem. Soc.* **1967**, *89*, 5311 – 5312.

[8] a) T. Fukuyama, C.-K. Jow, M. Cheung, *Tetrahedron Lett.* **1995**, *36*, 6373 – 6374; b) P. G. M. Wuts, J. M. Northuis, *Tetrahedron Lett.* **1998**, *39*, 3889 – 3890.

[9] For [3,3]-sigmatropic rearrangements, see: a) L. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 16804 – 16805; b) L. Zhang, S. Wang, *J. Am. Chem. Soc.* **2006**, *128*, 1442 – 1443; c) A. Buzas, F. Istrate, F. Gagosz, *Org. Lett.* **2006**, *8*, 1957 – 1959; d) S. Wang, L. Zhang, *Org. Lett.* **2006**, *8*, 4585 – 4587; e) S. Wang, L. Zhang, *J. Am. Chem. Soc.* **2006**, *128*, 8414 – 8415; f) A. Buzas, F. Gagosz, *J. Am. Chem. Soc.* **2006**, *128*, 12614 – 12615; g) S. Wang, L. Zhang, *J. Am. Chem. Soc.* **2006**, *128*, 14274 – 14275; h) J. Zhao, C. O. Hughes, F. D. Toste, *J. Am. Chem. Soc.* **2006**, *128*, 7436 – 7437; i) N. Marion, S. Díez-González, P. de Frémont, A. R. Noble, S. P. Nolan, *Angew. Chem.* **2006**, *118*, 3729 – 3732; *Angew. Chem. Int. Ed.* **2006**, *45*, 3647 – 3650; j) T. Schwier, A. W. Sromek, D. M. L. Yap, D. Chernyak, V. Gevorgyan, *J. Am. Chem. Soc.* **2007**, *129*, 9868 – 9878.

[10] a) M. Yu, G. Zhang, L. Zhang, *Org. Lett.* **2007**, *9*, 2147 – 2150; b) M. Yu, G. Li, S. Wang, L. Zhang, *Adv. Synth. Catal.* **2007**, *349*, 871 – 875; c) G. Li, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2008**, *130*, 3740 – 3741; d) Y. Peng, G. Cui, L. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 5062 – 5063.

[11] a) K. H. Meyer, K. Schuster, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 819 – 823; b) M. Georgy, V. Boucard, J.-M. Campagne, *J. Am. Chem. Soc.* **2005**, *127*, 14180 – 14181; c) D. A. Engel, G. B. Dudley, *Org. Lett.* **2006**, *8*, 4027 – 4029; d) N. Marion, P. Carlqvist, R. Gealageas, P. de Frémont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437 – 6451; e) D. A. Engel, G. B. Dudley, *Org. Biomol. Chem.* **2009**, *7*, 4149 – 4158.

[12] a) M. Hanack, C. E. Harding, J.-L. Derocque, *Chem. Ber.* **1972**, *105*, 421 – 433; b) C. E. Harding, S. L. King, *J. Org. Chem.* **1992**, *57*, 883 – 886; c) T. Jin, Y. Yamamoto, *Org. Lett.* **2007**, *9*, 5259 – 5262; d) T. Jin, F. Yang, C. Liu, Y. Yamamoto, *Chem. Commun.* **2009**, 3533 – 3535.

