ChemComm

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c4cc09245g

Received 19th November 2014,
Accepted 13th December 2014

DOI: 10.1039/c4cc09245g

www.rsc.org/chemcomm

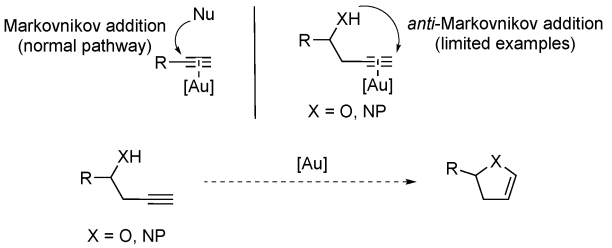
Efficient and practical synthesis of enantioenriched 2,3-dihydropyrroles through gold-catalyzed anti-Markovnikov hydroamination of chiral homopropargyl sulfonamides†

Yong-Fei Yu,[a] Chao Shu,[a] Bo Zhou,[a] Jian-Qiao Li,[a] Jin-Mei Zhou[a] and Long-Wu Ye*[ab]

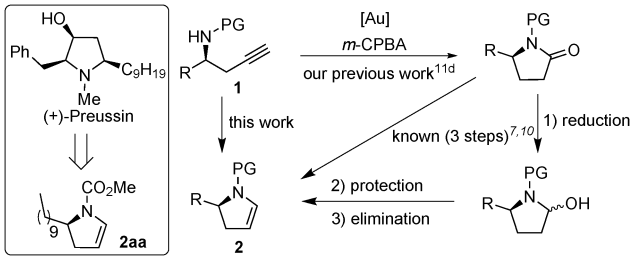
A direct gold-catalyzed 5-*endo-dig* cycloisomerization of chiral homopropargyl sulfonamides has been developed. A range of enantioenriched 2,3-dihydropyrroles are readily accessed by utilizing this approach. Importantly, this gold-catalyzed cycloisomerization reaction proceeds through an anti-Markovnikov addition by using a catalytic base as the additive, which completely suppresses the undesired dimerization.

During the past decade, gold-catalyzed addition of a heteroatom nucleophile to a C–C multiple bond, in most cases an alkyne, has proven to be an extremely powerful approach in organic synthesis,[1] and an incredible variety of efficient synthetic methods have been developed for the construction of intricate scaffolds based on this study.[2] It is surprising, however, that only a few examples have been reported about gold-catalyzed 5-*endo-dig* cyclization of terminal alkynes except for indole formation.[3] In particular, to the best of our knowledge, the gold-catalyzed 5-*endo-dig* cyclization of chiral homopropargyl alcohols or amides towards the synthesis of 2,3-dihydrofurans or 2,3-dihydropyrroles has not been reported (Scheme 1). This could be explained by the point that the gold-catalyzed cycloisomerization reaction[4] involves an anti-Markovnikov addition, while a Markovnikov regioselectivity was normally observed for the gold-catalyzed nucleophilic addition to a terminal alkyne (Scheme 1).

2,3-Dihydropyrroles constitute an important category of heterocyclic ring systems which exist in a large number of bioactive natural and synthetic molecules.[5] In addition, they are also widely employed as valuable building blocks for the construction of complex molecules due to their latent reactivity and the large panel of h ighly selective transformations they can undergo.[6] For example, 2,3-dihydropyrrole **2aa** is the key intermediate for the synthesis of the antifungal pyrrolidinol alkaloid (+)-preussin (Scheme 2).[7] However, despite the fact that numerous preparative methods have been developed in the past decade,[8] there are only limited examples of enantioselective synthesis of 2,3-dihydropyrroles,[9] including those based on other metal-catalyzed cycloisomerization towards chiral 2,3-dihydropyrroles.[9c,g,h] In particular, these chiral compounds are generally prepared through multistep routes. For example, a typical route starts from reduction of chiral γ-lactams with superhydride to form the lactamols, which then undergo the subsequent protection and elimination to deliver the final 2,3-dihydropyrrole compounds (Scheme 2).[7,10] Therefore, the development of novel methods for the synthesis of chiral 2,3-dihydropyrroles is highly desirable, especially those with high enantioselectivity, flexibility and good modularity. As part of our continuous efforts to study gold-catalyzed cycloisomerization reactions,[11] we reported gold-catalyzed tandem cycloisomerization–oxidation[11d] (Scheme 2) and tandem



Scheme 1 Gold-catalyzed nucleophilic addition to terminal alkynes.



Scheme 2 Synthesis design for the formation of 2,3-dihydropyrroles through gold-catalyzed cycloisomerization of homopropargyl sulfonamides.

[a] State Key Laboratory for Physical Chemistry of Solid Surfaces & The Key Laboratory for Chemical Biology of Fujian Province, Department of Chemistry, Xiamen University, Xiamen, 361005, Fujian, P. R. China. E-mail: longwuye@xmu.edu.cn; Fax: +86-592-218-5833

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

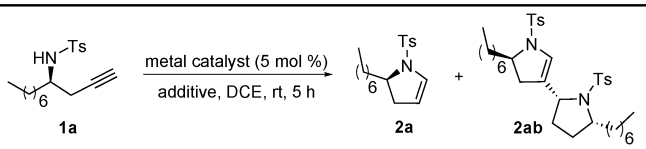
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4cc09245g

cycloisomerization–dimerization[11c] from readily available chiral homopropargyl sulfonamides, leading to the efficient formation of enantioenriched γ-lactams and pyrrolidines, respectively. Inspired by these results, we envisioned that by fine tuning the basicity of the reaction, the preparation of 2,3-dihydropyrroles **2** might be achieved directly through the gold-catalyzed cycloisomerization of chiral homopropargyl sulfonamides **1** (Scheme 2). Herein, we report the first gold-catalyzed synthesis of 2,3-dihydropyrroles directly from homopropargyl sulfonamides by combining Ellman's *tert*-butylsulfinimine chemistry and gold catalysis. Importantly, this gold-catalyzed hydroamination reaction proceeds through an anti-Markovnikov addition by using a catalytic base as the additive, which completely suppresses the undesired dimerization.

At the outset, homopropargyl sulfonamide **1a** was chosen as a model substrate and a series of experiments were performed in order to validate our approach (Table 1). As expected, only dimer **2ab** was obtained by employing 5 mol% $IPrAuNTf_2$ as the catalyst (entry 1). We then sought to use additives to suppress the unwanted dimer byproduct (entries 2–8). As seen from Table 1, the screening of different inorganic or organic bases revealed that the use of 0.5 equiv. of 2,6-dibromopyridine or 2 mol% Et_3N could give the desired 2,3-dihydropyrrole **2a** in 40% and 41% yields, respectively (entries 5 and 7). Notably, the use of 0.5 equiv. of 2.6-lutidine or 5 mol% Et_3N failed to give any product (entries 4 and 8). To our delight, by combining the Et_3N (2 mol%) and 2,6-dibromopyridine (0.5 equiv.) as the additives, the yield of product **2a** could be increased to 65% (entry 9). In addition, various typical gold catalysts with a range of electronic and steric characteristics were screened (entries 10–14) and the desired product **2a** was formed in quantitative yield by using $BrettPhosAuNTf_2$ as the catalyst (entry 14). Finally, it should be mentioned that the reaction failed to give even a trace of **2a** by employing $AgNTf_2$ as the catalyst (entry 15) and AgOAc was also not effective in promoting this reaction even at 40 °C for 10 h with or without base as the additive (entries 16 and 17).[12]

The chiral homopropargyl sulfonamide substrates were readily prepared with excellent enantiomeric excesses by using Ellman's *tert*-butylsulfinimine chemistry.[13] With these substrates in hand, we then turned our attention to survey the generality of the current reaction under the optimized reaction conditions. As summarized in Table 2, all of the homopropargyl sulfonamides **1** underwent smooth cycloisomerization to produce the corresponding 2,3-dihydropyrroles **2** in excellent yields (91–99%). Moreover, excellent enantioselectivities could be achieved in all cases and essentially no epimerization was detected, therefore constituting a good combination of chiral *tert*-butylsulfinimine chemistry with gold catalysis. In addition, the use of (*S*)-(+)-*tert*-butylsulfinamide-derived homopropargyl sulfonamide **1a′** also delivered the anticipated 2,3-dihydropyrrole **2a′** with the opposite enantioselectivity (entry 16). Thus, this approach provides a highly efficient and practical route for the preparation of both enantiomers of 2,3-dihydropyrrole **2** just by a simple choice of the starting chiral source. The product configuration was assumed based on the reaction mechanism involving the gold-catalyzed cycloisomerization reaction

Table 1 Optimization of reaction conditions[a]



Entry	Metal catalyst	Additive	Yield[b] (%) 2a	2b	1a
1	$IPrAuNTf_2$	—	<1	65	<1
2	$IPrAuNTf_2$	NaOAc (0.5 equiv.)	14	15	43
3	$IPrAuNTf_2$	Na_2CO_3 (0.5 equiv.)	27	13	35
4	$IPrAuNTf_2$	2,6-Lutidine (0.5 equiv.)	<1	<1	42
5	$IPrAuNTf_2$	2,6-Dibromopyridine (0.5 equiv.)	40	<1	42
6	$IPrAuNTf_2$	1 mol% Et_3N	20	28	20
7	$IPrAuNTf_2$	2 mol% Et_3N	41	6	40
8	$IPrAuNTf_2$	5 mol% Et_3N	<1	<1	>95
9[c]	$IPrAuNTf_2$	2 mol% Et_3N	65	<1	<1
10[c]	PPh_3AuNTf_2	2 mol% Et_3N	<1	36	45
11[c]	$Et_3PAuNTf_2$	2 mol% Et_3N	<1	27	50
12[c]	$(4\text{-}CF_3C_6H_4)_3PAuNTf_2$	2 mol% Et_3N	<1	32	48
13[c]	$XPhosAuNTf_2$	2 mol% Et_3N	<1	40	43
14[c,d]	$BrettPhosAuNTf_2$	2 mol% Et_3N	99	<1	<1
15[c]	$AgNTf_2$ (5 mol%)	2 mol% Et_3N	<1	<1	>95
16[c,e]	AgOAc (20 mol%)	2 mol% Et_3N	23	<1	65
17[e]	AgOAc (20 mol%)	—	20	<1	66

[a] Reaction conditions: [**1a**] = 0.05 M; DCE: 1, 2-dichloroethane. [b] Estimated by ^1H NMR using diethyl phthalate as the internal reference. [c] 0.5 equiv. of 2,6-dibromopyridine was added. [d] 1 h. [e] 40 °C, 10 h.

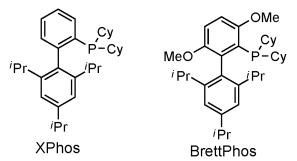
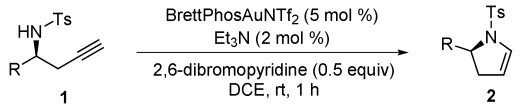


Table 2 Reaction scope for the formation of enantioenriched 2,3-dihydropyrroles[a]



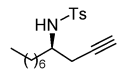
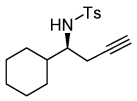
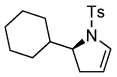
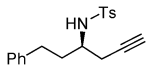
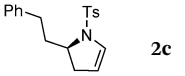
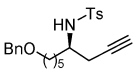
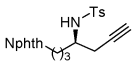
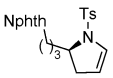
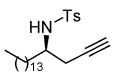
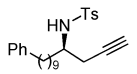
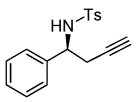
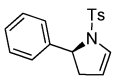
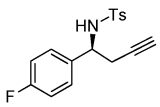
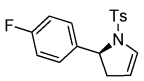
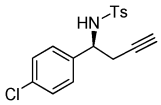
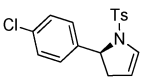
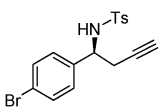
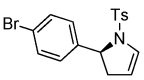
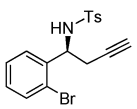
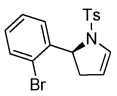
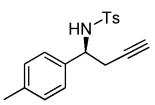
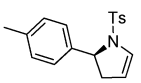
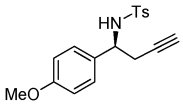
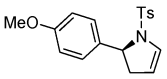
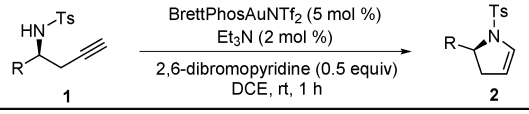
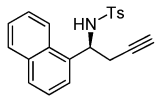
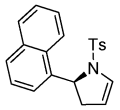
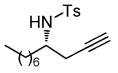
Entry	Substrate	1	ee (%)	Product	2	Yield (%)	ee (%)
1		**1a**	99		**2a**	99	99
2		**1b**	99		**2b**	92	99
3		**1c**	99		**2c**	99	98
4		**1d**	98		**2d**	99	98
5		**1e**	97		**2e**	99	98
6		**1f**	97		**2f**	94	98
7		**1g**	99		**2g**	91	99
8		**1h**	99		**2h**	99	99
9		**1i**	99		**2i**	95	99
10		**1j**	98		**2j**	99	97
11		**1k**	99		**2k**	99	98
12		**1l**	97		**2l**	98	96
13		**1m**	99		**2m**	99	97
14		**1n**	99		**2n**	98	98

Table 2 (*continued*)

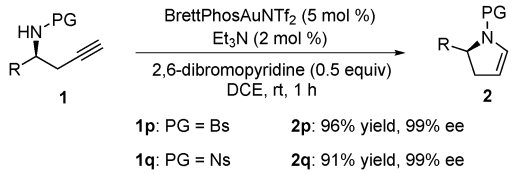


Entry	Substrate	1	ee (%)	Product	2	Yield (%)	ee (%)
15		**1o**	98		**2o**	95	98
16[b]		**1a′**	99		**2a′**	99	99

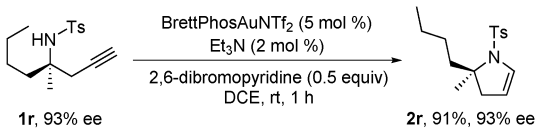
[a] Reactions run in vials; [**1**] = 0.05 M; isolated yields are reported; ees are determined using HPLC on a chiral stationary phase. [b] Using (*S*)-(+)-*tert*-butylsulfinamide-derived homopropargyl amide **1a′** as the substrate.

and further confirmed by comparing the specific rotation and the HPLC profile of compound **2h** with those of the reported compound in the literature.[12a]

Besides the tosyl group, it was found that the reaction could work well for Bs (*p*-bromobenzenesulfonyl) and Ns (*o*-nitrobenzenesulfonyl) protected substrates **1p–1q**, leading to the efficient formation of the corresponding **2p** and **2q** in excellent yields and excellent ees (eqn (1)), thus providing an easier way for its later removal. In addition, this chemistry can also be extended to the preparation of 2,2-disubstituted 2,3-dihydropyrrole **2r** in 91% yield with well-maintained enantioselectivity (eqn (2)).

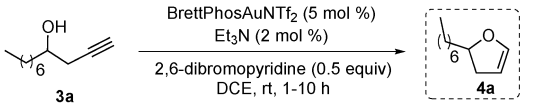


(1)



(2)

However, attempts to expand this chemistry to homopropargyl alcohols were not successful. As shown in eqn (3), the reaction only gave a complicated mixture of products and no desired **4a** was obtained under the relevant reaction conditions.[14]

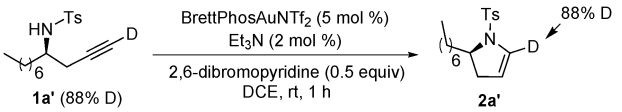


(3)

(a) messy; (b) without Et_3N, messy; (c) without 2,6-dibromopyridine, messy; (d) without 2,6-dibromopyridine and Et_3N, messy.

Finally, we performed deuterium labeling studies. It was found that when substrate **1a′** (88% D) was treated under the optimal reaction conditions, no deuterium loss was detected (eqn (4)), indicating that the reaction presumably proceeds through a gold-catalyzed direct 5-*endo-dig* cyclization of homopropargyl amides

and the gold vinylidene intermediate pathway is less likely,[15] which is substantially different from the other relevant transition metal (Ru, Rh, Mo, *etc.*) catalyzed cycloisomerization reactions.[14a,f,i]



(4)

In summary, we have developed a flexible and general solution for the enantioselective synthesis of various 2,3-dihydropyrroles *via* a gold-catalyzed cycloisomerization of chiral homopropargyl sulfonamides. Most importantly, this gold-catalyzed hydroamination reaction proceeds through an anti-Markovnikov addition by using a catalytic base as the additive, which completely inhibits the formation of unwanted dimers. The use of readily available substrates, a simple procedure, and mild reaction conditions and, in particular, no need to exclude moisture or air ("open flask") render this method potentially useful in organic synthesis.

We are grateful for the financial support from the National Natural Science Foundation of China (No. 21102119 and 21272191), the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT) and NFFTBS (No. J1310024).

Notes and references

1 For recent selected reviews for gold catalysis, see: (*a*) H.-S. Yeom and S. Shin, *Acc. Chem. Res.*, 2014, **47**, 966; (*b*) L. Zhang, *Acc. Chem. Res.*, 2014, **47**, 877; (*c*) A. V. Gulevich, A. S. Dudnik, N. Chernyak and V. Gevorgyan, *Chem. Rev.*, 2013, **113**, 3084; (*d*) N. Krause and C. Winter, *Chem. Rev.*, 2011, **111**, 1994; (*e*) A. Corma, A. Leyva-Pérez and M. J. Sabater, *Chem. Rev.*, 2011, **111**, 1657; (*f*) J. J. Hirner, Y. Shi and S. A. Blum, *Acc. Chem. Res.*, 2011, **44**, 603; (*g*) J. Xiao and X. Li, *Angew. Chem., Int. Ed.*, 2011, **50**, 7226; (*h*) S. Sengupta and X. Shi, *ChemCatChem*, 2010, **2**, 609; (*i*) A. Fürstner, *Chem. Soc. Rev.*, 2009, **38**, 3208; (*j*) S. M. A. Sohel and R.-S. Liu, *Chem. Soc. Rev.*, 2009, **38**, 2269.

2 For reviews on gold catalysis in total synthesis, see: (*a*) M. Rudolph and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2012, **41**, 2448; (*b*) M. Rudolph and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2008, **37**, 1766.

3 (*a*) S. Fustero, P. Bello, J. Miró, M. Sánchez-Roselló, M. A. Maestro, J. González and C. del Pozo, *Chem. Commun.*, 2013, 1336; (*b*) H. Shi, L. Fang, C. Tan, L. Shi, W. Zhang, C.-c. Li, T. Luo and Z. Yang, *J. Am. Chem. Soc.*, 2011, **133**, 14944; (*c*) V. Belting and N. Krause, *Org. Lett.*, 2006, **8**, 4489; (*d*) A. S. K. Hashmi, L. Schwarz, J.-H. Choi and T. M. Frost, *Angew. Chem., Int. Ed.*, 2000, **39**, 2285.

4 For selected reviews on gold-catalyzed cycloisomerization reactions, see: (*a*) P. Belmont and E. Parker, *Eur. J. Org. Chem.*, 2009, 6075; (*b*) E. Jiménez-Núñez and A. M. Echavarren, *Chem. Rev.*, 2008, **108**, 3326; (*c*) L. Zhang, J. Sun and S. A. Kozmin, *Adv. Synth. Catal.*, 2006, **348**, 2271.

5 For representative examples, see: (*a*) D. Antonow and D. E. Thurston, *Chem. Rev.*, 2011, **111**, 2815; (*b*) A. B. Smith III, A. K. Charnley and R. Hirschmann, *Acc. Chem. Res.*, 2011, **44**, 180; (*c*) K. M. Rahman, C. H. James, T. T. T. Bui, A. F. Drake and D. E. Thurston, *J. Am. Chem. Soc.*, 2011, **133**, 19376; (*d*) D. Antonow, M. Kaliszczak, G. D. Kang, M. Coffils, A. C. Tiberghien, N. Cooper, T. Barata, S. Heidelberger, C. H. James, M. Zloh, T. C. Jenkins, A. P. Reszka, S. Neidle, S. M. Guichard, D. I. Jodrell, J. A. Hartley, P. W. Howard and D. E. Thurston, *J. Med. Chem.*, 2010, **53**, 2927; (*e*) K. M. Rahman, H. Vassoler, C. H. James and D. E. Thurston, *ACS Med. Chem. Lett.*, 2010, **1**, 427; (*f*) W. Li, A. Khullar, S. Chou, A. Sacramo and B. Gerratana, *Appl. Environ. Microbiol.*, 2009, **75**, 2869; (*g*) I. V. Magedov, G. Luchetti, N. M. Evdokimov, M. Manpadi, W. F. A. Steelant, S. Van Slambrouck, P. Tongwa, M. Y. Antipin and A. Kornienko, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 1392; (*h*) D. O'Hagan, *Nat. Prod. Rep.*, 2000, **17**, 435; (*i*) D. E. Thurston and D. S. Bose, *Chem. Rev.*, 1994, **94**, 433.

6 For recent selected examples, see: (*a*) C. Wu and J. Zhou, *J. Am. Chem. Soc.*, 2014, **136**, 650; (*b*) H. Zhang, K. O. Jeon, E. B. Hay, S. J. Geib, D. P. Curran and M. G. LaPorte, *Org. Lett.*, 2014, **16**, 94; (*c*) H. Zhang, E. B. Hay, S. J. Geib and D. P. Curran, *J. Am. Chem. Soc.*, 2013, **135**, 16610; (*d*) T. Miura, T. Tanaka, K. Hiraga, S. G. Stewart and M. Murakami, *J. Am. Chem. Soc.*, 2013, **135**, 13652; (*e*) N. Gigant and I. Gillaizeau, *Org. Lett.*, 2012, **14**, 4622; (*f*) B. Cheng, F. Wu, X. Yang, Y. Zhou, X. Wan and H. Zhai, *Chem. – Eur. J.*, 2011, **17**, 12569; (*g*) H. Xu, S. J. Zuend, M. G. Woll, Y. Tao and E. N. Jacobsen, *Science*, 2010, **327**, 986; (*h*) Y.-L. Liu, B.-L. Wang, J.-J. Cao, L. Chen, Y.-X. Zhang, C. Wang and J. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 15176; (*i*) G.-H. Hou, J.-H. Xie, P.-C. Yan and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 1366; (*j*) U. Gross, M. Nieger and S. Bräse, *Org. Lett.*, 2009, **11**, 4740; (*k*) J. B. Feltenberger, R. Hayashi, Y. Tang, E. S. C. Babiash and R. P. Hsung, *Org. Lett.*, 2009, **11**, 3666; (*l*) J. Zhou and B. L. Xu, *Chin. Chem. Lett.*, 2008, **19**, 921.

7 (*a*) T. Bach, H. Brummerhop and K. Harms, *Chem. – Eur. J.*, 2000, **6**, 3838; (*b*) T. Bach and H. Brummerhop, *Angew. Chem., Int. Ed.*, 1998, **37**, 3400.

8 For recent selected examples, see: (*a*) S. W. Kwok, L. Zhang, N. P. Grimster and V. V. Fokin, *Angew. Chem., Int. Ed.*, 2014, **53**, 3452; (*b*) M. C. Martin, D. V. Patil and S. France, *J. Org. Chem.*, 2014, **79**, 3030; (*c*) W. V. Rossom, Y. Matsushita, K. Ariga and J. P. Hill, *RSC Adv.*, 2014, **4**, 4897; (*d*) M. Yoshida, K. Kinoshita and K. Namba, *Org. Biomol. Chem.*, 2014, **12**, 2394; (*e*) M. K. Ghorai and D. P. Tiwari, *J. Org. Chem.*, 2013, **78**, 2617; (*f*) L. Zhang, H. Yu, Z. Yang, H. Liu, Z. Li, J. Guo, Y. Xiao and H. Guo, *Org. Biomol. Chem.*, 2013, **11**, 8235; (*g*) L. A. Polindara-García and L. D. Miranda, *Org. Lett.*, 2012, **14**, 5408; (*h*) J. Cheng, X. Jiang, C. Zhu and S. Ma, *Adv. Synth. Catal.*, 2011, **353**, 1676; (*i*) P. A. Wender and D. Strand, *J. Am. Chem. Soc.*, 2009, **131**, 7528; (*j*) Y. Zhu, C. Zhai, Y. Yue, L. Yang and W. Hu, *Chem. Commun.*, 2009, 1362.

9 For recent examples, see: (*a*) Y. Xia, X. Liu, H. Zheng, L. Lin and X. Feng, *Angew. Chem., Int. Ed.*, 2014, **53**, DOI: 10.1002/anie.201407880; (*b*) K. Oe, Y. Ohfune and T. Shinada, *Org. Lett.*, 2014, **16**, 2550; (*c*) D. Chen and M.-H. Xu, *Chem. Commun.*, 2013, 1327; (*d*) G. Zhang, Y. H. Zhang, X. X. Jiang, W. J. Yan and R. Wang, *Org. Lett.*, 2011, **13**, 3806; (*e*) R. A. Brawn and J. S. Panek, *Org. Lett.*, 2009, **11**, 473; (*f*) C. Guo, M.-X. Xue, M.-K. Zhu and L.-Z. Gong, *Angew. Chem., Int. Ed.*, 2008, **47**, 3414; for a palladium-catalyzed cycloisomerization towards chiral 2,3-dihydropyrroles, see: (*g*) J. Yu, V. Truc, P. Riebel, E. Hierl and B. Mudryk, *Tetrahedron Lett.*, 1998, **39**, 5081; (*h*) L. B. Wolf, K. C. M. F. Tjen, H. T. ten Brink, R. H. Blaauw, H. Hiemstra, H. E. Schoemaker and F. P. J. T. Rutjes, *Adv. Synth. Catal.*, 2002, **344**, 70.

10 (*a*) J. Yu, V. Truc, P. Riebel, E. Hierl and B. Mudryk, *Tetrahedron Lett.*, 2005, **46**, 4011; (*b*) T. Bach and H. Brummerhop, *J. Prakt. Chem.*, 1999, **341**, 312; (*c*) D. F. Oliveira, P. C. M. L. Miranda and C. R. D. Correia, *J. Org. Chem.*, 1999, **64**, 6646; (*d*) R. K. Dieter and R. R. Sharma, *J. Org. Chem.*, 1996, **61**, 4180.

11 (*a*) C. Shu, L. Li, C.-B. Chen, H.-C. Shen and L.-W. Ye, *Chem. – Asian J.*, 2014, **9**, 1525; (*b*) C. Shu, C.-B. Chen, W.-X. Chen and L.-W. Ye, *Org. Lett.*, 2013, **15**, 5542; (*c*) Y.-F. Yu, C. Shu, C.-H. Shen, T.-Y. Li and L.-W. Ye, *Chem. – Asian J.*, 2013, **8**, 2920; (*d*) C. Shu, M.-Q. Liu, S.-S. Wang, L. Li and L.-W. Ye, *J. Org. Chem.*, 2013, **78**, 3292; (*e*) C. Shu, M.-Q. Liu, Y.-Z. Sun and L.-W. Ye, *Org. Lett.*, 2012, **14**, 4958.

12 For silver-mediated cycloisomerization of 1-aryl substituted homopropargyl sulfonamides, see: (*a*) H. M. Wisniewska and E. R. Jarvo, *Chem. Sci.*, 2011, **2**, 807; (*b*) R. Martin, A. Jäger, M. Böhl, S. Richter, R. Fedorov, D. J. Manstein, H. O. Gutzeit and H.-J. Knölker, *Angew. Chem., Int. Ed.*, 2009, **48**, 8042.

13 (*a*) M. T. Robak, M. A. Herbage and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 3600; (*b*) J. A. Ellman, *Pure Appl. Chem.*, 2003, **75**, 39; (*c*) J. A. Ellman, T. D. Owens and T. P. Tang, *Acc. Chem. Res.*, 2002, **35**, 984.

14 For selected examples on the other transition metal-catalyzed cycloisomerization of homopropargyl alcohols, see: (*a*) P. N. Liu, F. H. Su, T. B. Wen, H. H.-Y. Sung, I. D. Williams and G. Jia, *Chem. – Eur. J.*, 2010, **16**, 7889; (*b*) B. Alcaide, P. Almendros, T. M. del Campo and R. Carrascosa, *Eur. J. Org. Chem.*, 2010, 4912; (*c*) J. C. Jury, N. K. Swamy, A. Yazici, A. C. Willis and S. G. Pyne, *J. Org. Chem.*, 2009, **74**, 5523; (*d*) S. Arimitsu and G. B. Hammond, *J. Org. Chem.*, 2007, **72**, 8559; (*e*) B. Koo and F. E. McDonald, *Org. Lett.*, 2007, **9**, 1737; (*f*) B. M. Trost and Y. H. Rhee, *J. Am. Chem. Soc.*, 2003, **125**, 7482; (*g*) F. E. McDonald and B. H. White, *Org. Synth.*, 2002, **79**, 27; (*h*) F. E. McDonald and M. M. Gleason, *J. Am. Chem. Soc.*, 1996, **118**, 6648; (*i*) F. E. McDonald, C. B. Connolly, M. M. Gleason, T. B. Towne and K. D. Treiber, *J. Org. Chem.*, 1993, **58**, 6952.

15 For a review on gold vinylidenes, see: A. S. K. Hashmi, *Acc. Chem. Res.*, 2014, **47**, 864.

