ChemPubSoc Europe

DOI: 10.1002/open.201500181

Open Access ChemistryOPEN Communications

Gold-Catalyzed Intramolecular Cyclizations of Cyclopropenes with Propargylic Esters

Peng-Long Zhu,[a] Xiang-Ying Tang,*[b] and Min Shi*[a, b]

Homogeneous gold catalysts are interesting as they can act as potent carbophilic Lewis acids to activate the π bonds of alkynes, allenes, and alkenes. Many impressive applications for the formation of C–C or C–heteroatom bonds have been found due to the excellent functional group compatibility of these catalysts and the air and moisture tolerance of their reactions. Here, we have developed gold-catalyzed novel intramolecular cycloisomerizations of nitrogen or oxygen-tethered cyclopropenes with propargylic esters. The reaction proceeded through different pathways according to different substituent styles, affording 5-azaspiro[2.5]oct-7-enes and bicyclo[4.1.0]-heptanes.

Homogeneous gold catalysis has been a hot topic over the last decade. Such catalysts act as potent carbophilic Lewis acids to activate the π bonds of alkynes, allenes, and alkenes. Many impressive applications for the formation of C–C or C–heteroatom bonds have been found due to the excellent functional group compatibility of these catalysts and the air and moisture tolerance of their reactions.[1] In the presence of gold catalysts, propargylic esters readily undergo 1,2- or 1,3-acyloxy migration, resulting in different cascade reactions.[2] Indeed, many groups including ours have made numerous contributions in this research area.[3]

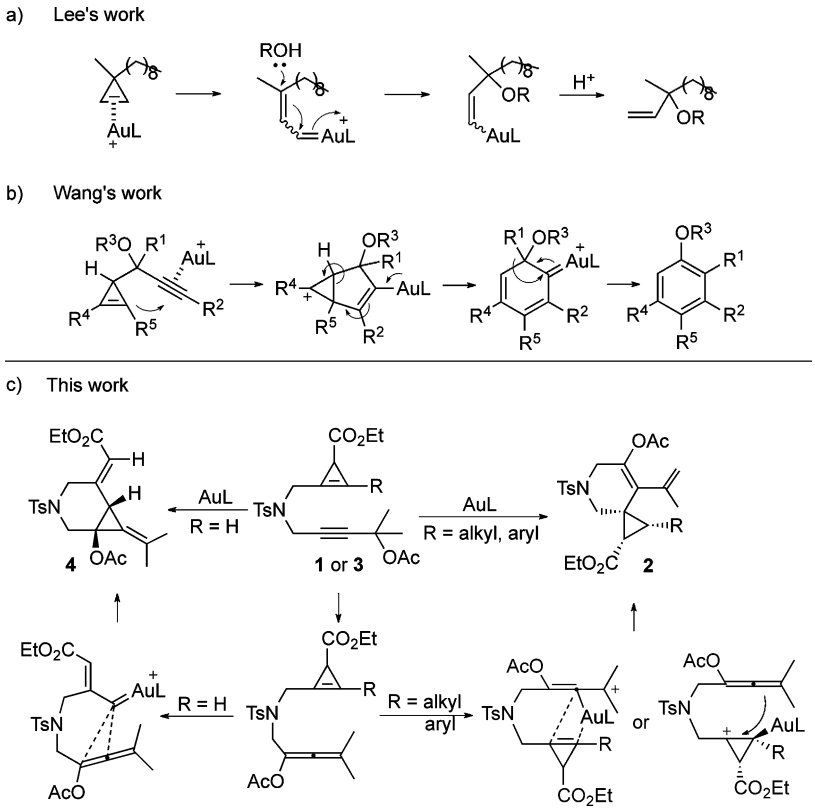
On the other hand, cyclopropenes are highly strained but readily prepared compounds that can serve as useful building blocks in organic synthesis.[4] In the presence of a gold(I) catalyst, activated cyclopropene undergoes a ring-opening process to give a vinyl gold carbene or gold-stabilized allylic carbocation which can be regarded as a pair of resonant structures.[1e,5] Such a carbenoid can readily accept a nucleophilic attack from many kinds of nucleophiles, such as alcohols, arenes, and carbonyl groups. For instance, Lee and colleagues reported the addition of alcohols to cyclopropenes in the presence of a gold catalyst (Scheme 1 a). Besides being the precursor of vinyl carbene, cyclopropenes can also serve as nucleophiles to attack other functional groups which have been activated by a gold(I) catalyst. In 2010, Wang's group reported the intramolecular cycloisomerization of cyclopropene-ynes catalyzed by a gold complex, in which cyclopropene served as a nucleophile to attack the gold-activated alkynes (Scheme 1 b).[6] Considering that both propargylic ester and cyclopropene can serve as good π donors, we envisaged that a substrate which combined these two components could exhibit versatile reactivities under gold catalysis. Herein, we wish to report a novel cycloisomerization of cyclopropenyl propargylic esters, which afford an efficient access to multifunctionalized 5-azaspiro-[2.5]oct-7-enes **2** and bicyclo[4.1.0]heptanes **4**. The reaction outcomes are controlled by the substituent on cyclopropene. When the substituent R is not a hydrogen atom, there are two possible reaction pathways yielding products. The *syn*-addition of the C–Au bond with cyclopropene takes place, or the cyclopropane cation derived from the activation by gold(I) catalyst is attacked by the in-situ-generated allene moiety, giving the corresponding *cis*-substituted cyclopropanes **2**. If R = H, the cyclopropanation of allene by the in-situ-generated carbene species delivers the corresponding products **4**.

Initially, we commenced our studies using propargylic acetate cyclopropene **1a** as model substrate to optimize the reaction conditions. The results are summarized in Table 1. We found an interesting six-membered spiro-heterocyclic product **2a**, which was formed in 55% yield upon treating **1a** with *t*BuXPhosAu(NCMe)SbF_6 in toluene at 100 °C (Table 1, entry 1). Various gold(I) catalysts were first examined, such as PPh_3AuNTf_2, JackiePhosAuNTf_2, Me_4*t*BuXPhosAuOTf, CyJohnPhosAu(NCMe)SbF_6, and SPhosAuNTf_2, giving inferior results (Table 1, entries 2–6). IPrAuNTf_2 was also used as the catalyst to carry out the reaction under the standard conditions, giving the desired product **2a** in 51% yield (Table 1, entry 7). The combination of *t*BuXPhosAuCl (5 mol%) with different silver(I) salts (5 mol%), for instance, AgOTf, $AgSbF_6$, or $AgNTf_2$, did not give better results either (Table 1, entries 8–10). Increasing catalyst loading to 10 mol% delivered **2a** in a decreased yield of only 49% (Table 1, entry 11). Fine-tuning catalyst loading to 2.5 mol% gave **2a** in a moderate yield of 53%, indicating that

[a] P.-L. Zhu, Prof. M. Shi
Key Laboratory for Advanced Materials and Institute of Fine Chemicals
East China University of Science and Technology
130 Mei Long Road, Shanghai 200237 (P. R. China)

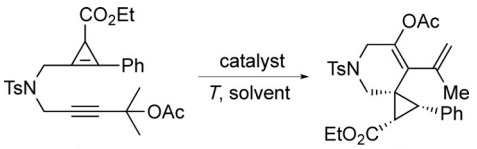
[b] Dr. X.-Y. Tang, Prof. M. Shi
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences, 345 Linglin Lu, Shanghai 200032 (P. R. China)
E-mail: mshi@mail.sioc.ac.cn
siocxiangying@mail.sioc.ac.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/open.201500181. The Supporting Information contains spectroscopic data of the compounds shown in Tables 1–2 and Schemes 3,4,5,7, the detailed descriptions of experimental procedures, and the crystal structures of **2o** (CCDC 988350), **2q** (CCDC 1041452), **4c** (CCDC 1038182), and **5a** (CCDC 807812). CCDC 988350, 1041452, 1038182 and 807812 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



Scheme 1. General reactivity of cyclopropenes in the presence of gold catalysts.

Table 1. Optimal reaction conditions for the intramolecular cycloisomerizations.



1a **2a**

Entry	Catalyst [mol%]	T [°C]	Solvent	Yield [%][a]
1	*t*BuXPhosAu(NCMe)SbF_6 [5]	100	toluene	55
2	PPh^3 $AuNTf_2$ [5]	100	toluene	27
3	JackiePhosAuNTf_2 [5]	100	toluene	45
4	Me_4*t*BuXPhosAuOTf [5]	100	toluene	39
5	CyJohnPhosAu(NCMe)SbF_6 [5]	100	toluene	43
6	SPhosAuNTf_2 [5]	100	toluene	43
7	IPrAuNTf_2 [5]	100	toluene	51
8	*t*BuXPhosAuCl/AgOTf [5]	100	toluene	41
9	*t*BuXPhosAuCl/AgSbF_6 [5]	100	toluene	35
10	*t*BuXPhosAuCl/AgNTf_2 [5]	100	toluene	43
11	*t*BuXphosAu(NCMe)SbF_6 [10]	100	toluene	49
12	*t*BuXphosAu(NCMe)SbF_6 [2.5]	100	toluene	53
13	*t*BuXphosAu(NCMe)SbF_6 [5]	100	THF	ND
14	*t*BuXphosAu(NCMe)SbF_6 [5]	100	MeCN	53
15	*t*BuXphosAu(NCMe)SbF_6 [5]	100	DCE	59
16	*t*BuXphosAu(NCMe)SbF_6 (5]	80	DCE	49
17	*t*BuXphosAu(NCMe)SbF_6 [5]	120	DCE	56
18	*t*BuXPhosAuOTf [5]	100	DCE	69 (73[b])

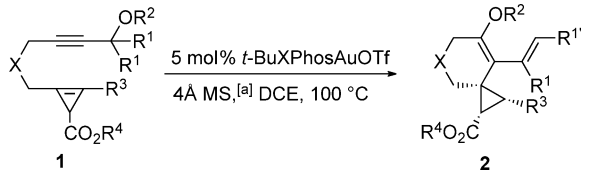
All reactions were carried out using **1a** (0.1 mmol) in the presence of catalyst (x mol%) in various solvents (1.0 mL); [a] Yield of isolated product; [b] 4 Å MS (100 mg) were added to the reaction mixtures.

only a small amount of the catalyst can maintain the catalytic cycle (Table 1, entry 12).

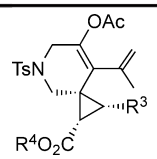
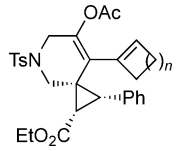
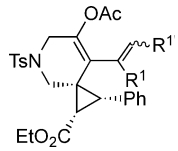
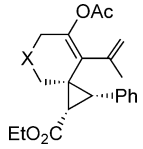
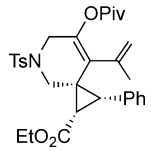
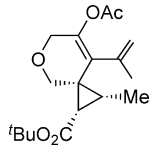
The solvent effect was also evaluated. No product was formed in tetrahydrofuran (THF) (Table 1, entry 13). Changing the solvent to acetonitrile gave the desired product **2a** in 53% yield (Table 1, entry 14). Finally we found that 1,2-dichloroethane (DCE) was the best solvent in this transformation, giving **2a** in 59% yield (Table 1, entry 15). Decreasing the reaction temperature to 80 °C or elevating the temperature to 120 °C did not improve the reaction outcome either, giving the corresponding product **2a** in 49% and 56% yields, respectively (Table 1, entries 16 and 17). Different coordination anions of the gold(I) catalyst were also tested. The use of *t*BuXPhosAuOTf turned out to be very effective in the reaction, giving the desired product **2a** in 69% yield in DCE and in 73% yield with 4 Å molecular sieves (MS) in the reaction mixture (Table 1, entry 18) (for more detailed information, see Table S1 in the Supporting Information).

With the optimized reaction conditions in hand, we set out to explore the substrate scope (Table 2). Aromatic rings (R^3) bearing electron-withdrawing groups (fluorine and bromine) or electron-donating groups (3,5-di-methyl) were all tolerated in this reaction, giving the spirocyclic products **2b–d** in moderate to good yields, and electron-donating groups were proved to improve the efficiency of the reaction. With a change of R^3 to an alkyl substituent such as methyl, cyclopropyl, and isopropyl groups, the reactions delivered the corresponding products **2e–g** in good yields. Various propargylic esters were then examined. For cycloalkyl-group-substituted propargylic esters, the reactions proceeded smoothly to give the desired products **2h–j** in 56–81% yields. Interestingly, larger ring sizes resulted in better yields. When R^1 was replaced by linear alkyl substituents such as ethyl, *n*-propyl, and *n*-butyl groups, the reactions delivered the corresponding products **2k–m** as *Z*/*E* isomeric mixtures. Next, several sulfonyl amides such as *p*-bromobenzenesulfonyl (Bs) and *p*-nitrobenzenesulfonyl (Ns) were tested, and products **2n–o** were obtained in excellent yields. The structure of **2o** was confirmed by X-ray diffraction.[7] A substrate with a pivaloyl (Piv) group in place of an acyl (Ac) group produced the diene product **2p** in 86% yield. When a substrate with an oxygen linker was employed, the corresponding product **2q** was afforded in 47% yield in the presence of AgOTf. In general, AgOTf could catalyze this reaction as well, but only

Table 2. Substrate scope of the intramolecular cycloisomerization.



1 2

Entry	Substrate	Product and yield
1		**2b**, R^3 = 4-FC_6H_4, 54% yield **2c**, R^3 = 4-BrC_6H_4, 71% yield **2d**, R^3 = 3, 5-*di*-Me-C_6H_3, 90% yield **2e**, R^3 = Me, R^4 = Et, 72% yield **2f**, R^3 = cyclopropyl, R^4 = Me, 67% yield **2g**, R^3 = *i*Pr, R^4 = Me, 84% yield
2		**2h**, *n* = 1, 56% yield **2i**, *n* = 2, 68% yield **2j**, *n* = 3, 81% yield
3		**2k**, R^1 = Et, $R^{1\prime}$ = Me, 53% yield, *E*/*Z* = 1:1 **2l**, R^1 = *n*-Pr, $R^{1\prime}$ = Et, 81% yield, *E*/*Z* = 1:1 **2m**, R^1 = *n*Bu, $R^{1\prime}$ = *n*-Pr, 97% yield, *E*/*Z* = 1:1
4		**2n**, X = BsN, 99% yield **2o**, X = NsN, 84% yield (X-ray)
5		**2p**, 86% yield
6		**2q**, 47% yield[b] (X-ray)

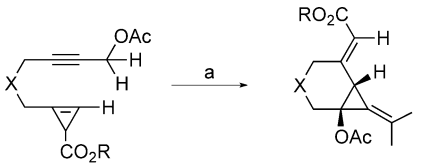
[a] 100 mg of 4 Å molecular sieves (MS) were added to the reaction mixtures. [b] Catalyzed by AgOTf at 120 °C in a sealed tube.

afforded the corresponding product in low yield. The structure of **2q** was also determined by X-ray diffraction studies.[7]

Surprisingly, when substituent R^3 was a proton instead of an aromatic or alkyl substituent, bicyclo[4.1.0]heptane products **4a–c** were obtained in moderate yields (Scheme 2). The structure of **4c** was determined by X-ray diffraction.[7]

To elucidate the mechanism, deuterium labeling experiments were performed as shown in Scheme 3. Carrying out the reaction of [D]-**1a** in the presence of gold catalyst, product [D]-**2a** was produced in 52% yield with 99% D content at the phenyl-substituted carbon, indicating that a *syn*-addition might occur instead of the nucleophilic attack from the back side of the gold-activated alkene.

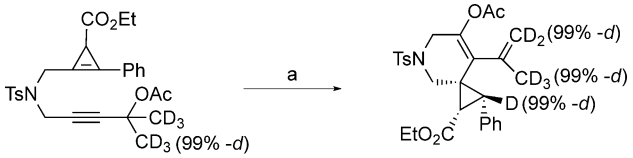
Plausible mechanisms[8] for the formation of **2** and **4** are outlined in Scheme 4. The cationic gold(I) complex first coordi-



3

4a, X = TsN, R = Et
4b, X = BsN, R = Et
4c, X = BsN, R = Me

Scheme 2. Intramolecular cycloisomerization of proton-substituted cyclopropenes **3**. *Reagents and conditions*: a) *t*-BuXPhosAuOTf (5 mol%), 4 Å MS, DCE, 100 °C, 2 h, **4a**: 59%, **4b**: 43%, **4c**: 41% (X-ray).

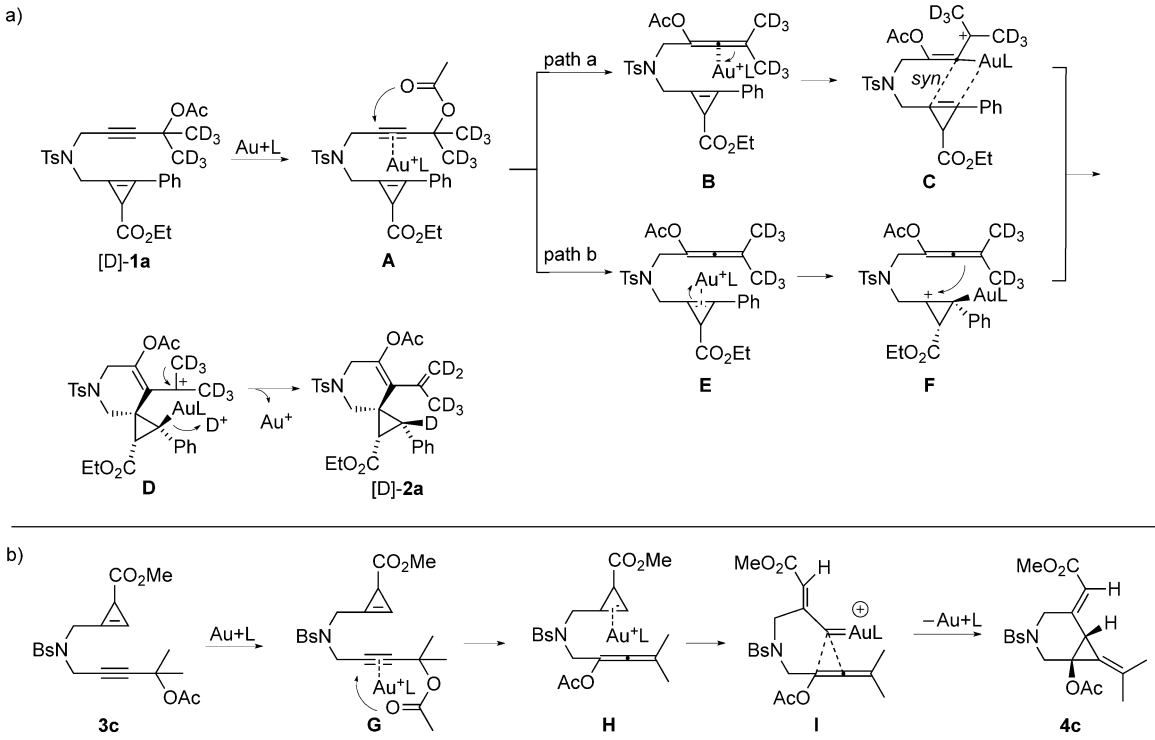


[D]-**1a** [D]-**2a**

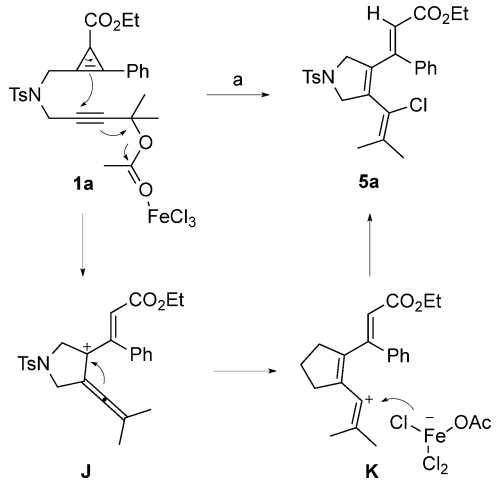
Scheme 3. Deuterium labeling experiment. *Reagents and conditions*: a) *t*-BuXPhosAuOTf (5 mol%), 4 Å MS, DCE, 100 °C, 2 h, 52%.

nates with the alkyne moiety of [D]-**1a** to give intermediate **A**. Then gold-catalyzed [3,3]-sigmatropic rearrangement takes place to deliver the corresponding carboxyallene intermediate **B**. The following activation of allene by gold affords vinyl gold intermediate **C**, which then results in the cyclopropyl gold intermediate **D** after *syn*-addition of C–Au bond to cyclopropane (path a). Alternatively, the gold(I) catalyst can activate the cyclopropene moiety (intermediate **E**) to form the corresponding cyclopropane cationic intermediate **F**. Due to the steric hindrance between the phosphine ligand and the ester group, the coordination of the gold(I) catalyst with the cyclopropene should be on the opposite face from where the ester group is placed. This would force the phenyl group to go to the same face with the ester group. Then cationic intermediate **F** underwent nucleophilic attack by the allene to give the intermediate **D** (path b). Finally, the desired product [D]-**2a** is formed after protodeauration. Due to the bukyl phosphine ligand of gold catalyst, the *cis*-addition to cyclopropene from the back side of the ester group is favored (Scheme 4a). On the other hand, for the synthesis of **4**, substrate **3c** is first transformed to intermediate **G** upon coordination. The [3,3]-sigmatropic rearrangement delivers the allenic intermediate **H**, which is activated by the gold catalyst. The following ring opening of cyclopropene furnishes gold carbene **I**, which is trapped by the double bond of carboxyallene, furnishing the final product **4c** (Scheme 4b).

To further demonstrate the versatile reactivity of cyclopropene, we also examined the performance of **1a** in the presence of $FeCl_3$ (1.2 equiv), but the reaction of **1a** gave a new triene derivative **5a** in 40% yield. Upon coordination of the ester group with $FeCl_3$, the nucleophilic addition of the cyclopropene to the alkyne along with acyloxy group departure affords carbocation **J**, which gives rise to intermediate **K** after isomerization. Subsequent chlorination delivers the final product **5a** (Scheme 5). The structure of **5a** was determined by X-ray diffraction.[7]



Scheme 4. Plausible mechanisms for the formation of **2** and **4**.



Scheme 5. $FeCl_3$-mediated intramolecular cycloisomerization. *Reagents and conditions*: a) $FeCl_3$ (1.2 eq), DCE, rt, 3 d, 40%.

In conclusion, we have developed a highly efficient gold-catalyzed intramolecular cycloisomerization of propargylic esters with cyclopropenes. By varying the substituents on the cyclopropenes (R^3 as a proton or not), two types of products could be obtained. The reaction mechanism is proposed on the basis of deuterium labeling experiments and previous literature. Substrate **1a** can also undergo cycloisomerization in the presence of $FeCl_3$, affording a new triene product **5a** after a tandem ring-opening process. Further applications of cyclopropene chemistry are underway in our laboratory.

Acknowledgements

The authors are grateful for financial support from the National Basic Research Program of China ((973)-2015CB856603) and the National Natural Science Foundation of China (21102166, 21361140350, 20472096, 21372241, 21302203, 20672127, 21121062, 20732008, and 21572052).

Keywords: cationic intermediates · cyclopropenes · gold carbenes · gold catalysis · propargylic esters

[1] a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; *Angew. Chem.* **2006**, *118*, 8064–8105; b) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; c) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Commun.* **2007**, 333–346; d) A. Fürstner, P. W. Davies, *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; *Angew. Chem.* **2007**, *119*, 3478–3519; e) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2008**, *47*, 6754–6756; *Angew. Chem.* **2008**, *120*, 6856–6858; f) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; g) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; h) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; i) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; j) S. M. Abu Sohel, R.-S. Liu, *Chem. Soc. Rev.* **2009**, *38*, 2269–2281; k) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221; l) S. Sengupta, X. Shi, *ChemCatChem* **2010**, *2*, 609–619; m) A. Corma, A. Leyva-Pérez, M. J. Sabater, *Chem. Rev.* **2011**, *111*, 1657–1712; n) N. Krause, C. Winter, *Chem. Rev.* **2011**, *111*, 1994–2009; o) M. Bandini, *Chem. Soc. Rev.* **2011**, *40*, 1358–1367; p) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.* **2012**, *41*, 2448–2462; q) B.-L. Lu, L. Dai, M. Shi, *Chem. Soc. Rev.* **2012**, *41*, 3318–3339; r) D.-H. Zhang, X.-Y. Tang, M. Shi, *Acc. Chem. Res.* **2014**, *47*, 913–924; s) A. S. K. Hashmi, *Acc. Chem. Res.* **2014**, *47*, 864–876; t) M. E. Muratore, A. Homs, C. Obradors, A. M. Echavarren, *Chem. Asian J.* **2014**, *9*, 3066–3082; u) W. Yang, A. S. K. Hashmi, *Chem. Soc. Rev.* **2014**, *43*, 2941–2955; v) Y.-M. Wang, A. D. Lackner, F. D. Toste, *Acc. Chem. Res.* **2014**, *47*, 889–901; w) L. Zhang, *Acc. Chem. Res.* **2014**, *47*, 877–888; x) C. Obradors, A. M. Echavarren, *Acc. Chem. Res.* **2014**, *47*, 902–912; y) L. Fensterbank, M. Malacria, *Acc. Chem.*

Res. **2014**, *47*, 953 – 965; z) H.-S. Yeom, S. Shin, *Acc. Chem. Res.* **2014**, *47*, 966 – 977.

[2] For selected examples of recent Au-catalyzed reactions of propargylic esters, see: a) Y.-M. Wang, C. N. Kuzniewski, V. Rauniyar, C. Hoong, F. D. Toste, *J. Am. Chem. Soc.* **2011**, *133*, 12972 – 12975; b) W. Rao, D. Susanti, P. W. H. Chan, *J. Am. Chem. Soc.* **2011**, *133*, 15248 – 15251; c) W. Rao, M. J. Koh, P. Kothandaraman, P. W. H. Chan, *J. Am. Chem. Soc.* **2012**, *134*, 10811 – 10814; d) W. Rao, M. J. Koh, D. Li, H. Hirao, P. W. H. Chan, *J. Am. Chem. Soc.* **2013**, *135*, 7926 – 7932; e) W. Rao, Sally, M. J. Koh, P. W. H. Chan, *J. Org. Chem.* **2013**, *78*, 3183 – 3195; f) W. Rao, P. W. H. Chan, *Chem. Eur. J.* **2014**, *20*, 713 – 718; g) W. Rao, Sally, S. N. Berry, P. W. H. Chan, *Chem. Eur. J.* **2014**, *20*, 13174 – 13180; h) D. Li, W. Rao, G. L. Tay, B. J. Ayers, P. W. H. Chan, *J. Org. Chem.* **2014**, *79*, 11301 – 11315; i) D. Lebœuf, A. Simonneau, C. Aubert, M. Malacria, V. Gandon, L. Fensterbank, *Angew. Chem. Int. Ed.* **2011**, *50*, 6868 – 6871; *Angew. Chem.* **2011**, *123*, 7000 – 7003; j) D. Garayalde, E. Gómez-Bengoa, X. Huang, A. Goeke, C. Nevado, *J. Am. Chem. Soc.* **2010**, *132*, 4720 – 4730; k) D. Garayalde, K. Krűger, C. Nevado, *Angew. Chem. Int. Ed.* **2011**, *50*, 911 – 915; *Angew. Chem.* **2011**, *123*, 941 – 945; l) D. Wang, X. Ye, X. Shi, *Org. Lett.* **2010**, *12*, 2088 – 2091; m) D. Wang, Y. Zhang, A. Harris, L. N. S. Gautam, Y. Chen, X. Shi, *Adv. Synth. Catal.* **2011**, *353*, 2584 – 2588; n) Y. Su, Y. Zhang, N. G. Akhmedov, J. L. Petersen, X. Shi, *Org. Lett.* **2014**, *16*, 2478 – 2481; o) T.-M. Teng, R.-S. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 9298 – 9300; p) S. Cai, Z. Liu, W. Zhang, X. Zhao, D. Z. Wang, *Angew. Chem. Int. Ed.* **2011**, *50*, 11133 – 11137; *Angew. Chem.* **2011**, *123*, 11329 – 11333; q) A. S. K. Hashmi, W. Yang, Y. Yu, M. M. Hansmann, M. Rudolph, F. Rominger, *Angew. Chem. Int. Ed.* **2013**, *52*, 1329 – 1332; *Angew. Chem.* **2013**, *125*, 1368 – 1371; r) Y. Yu, W. Yang, F. Rominger, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2013**, *52*, 7586 – 7589; *Angew. Chem.* **2013**, *125*, 7735 – 7738; s) T. Lauterbach, S. Gatzweiler, P. Nösel, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Adv. Synth. Catal.* **2013**, *355*, 2481 – 2487; t) C. H. Oh, J. H. Kim, L. Piao, J. Yu, S. Y. Kim, *Chem. Eur. J.* **2013**, *19*, 10501 – 10505; u) C. Zhao, X. Xie, S. Duan, H. Li, R. Fang, X. She, *Angew. Chem. Int. Ed.* **2014**, *53*, 10789 – 10793; *Angew. Chem.* **2014**, *126*, 10965 – 10969.

[3] For recent reviews on propargylic esters, see: a) C. Bruneau, *Angew. Chem. Int. Ed.* **2005**, *44*, 2328 – 2334; *Angew. Chem.* **2005**, *117*, 2380 – 2386; b) J. Marco-Contelles, E. Soriano, *Chem. Eur. J.* **2007**, *13*, 1350 – 1357; c) N. Marion, S. P. Nolan, *Angew. Chem. Int. Ed.* **2007**, *46*, 2750 – 2752; *Angew. Chem.* **2007**, *119*, 2806 – 2809; d) S. Wang, G. Zhang, L. Zhang, *Synlett* **2010**, 692 – 706; e) X.-Z. Shu, D. Shu, C. M. Schienebeck, W. Tang, *Chem. Soc. Rev.* **2012**, *41*, 7698 – 7711; f) R. Kazem Shiroodi, V. Gevorgyan, *Chem. Soc. Rev.* **2013**, *42*, 4991 – 5001. For our work on propargylic esters, see: g) Z. Zhang, M. Shi, *Eur. J. Org. Chem.* **2011**, 2610 – 2614; h) Z. Zhang, M. Shi, *Tetrahedron Lett.* **2011**, *52*, 6541 – 6544; i) D.-H. Zhang, L.-F. Yao, Y. Wei, M. Shi, *Angew. Chem. Int. Ed.* **2011**, *50*, 2583 – 2587; *Angew. Chem.* **2011**, *123*, 2631 – 2635; j) J.-M. Yang, Z. Zhang, Y. Wei, M. Shi, *Tetrahedron Lett.* **2012**, *53*, 6173 – 6176; k) Z. Zhang, M. Shi, *Chem. Eur. J.* **2012**, *18*, 3654 – 3658.

[4] a) A. S. K. Hashmi, A. R. Nass, J. W. Bats, M. Bolte, *Angew. Chem. Int. Ed.* **1999**, *38*, 3370 – 3373; *Angew. Chem.* **1999**, *111*, 3565 – 3567; b) A. S. K. Hashmi, F. Naumann, R. Probst, J. W. Bats, *Angew. Chem. Int. Ed. Engl.Angew. Chem. Int. Ed.* **1997**, *36*, 104 – 106; *Angew. Chem.* **1997**, *109*, 127 – 130; c) A. S. K. Hashmi, *Trends Organomet. Chem.* **2003**, 33 – 45; for recent reviews of cyclopropenes, see: d) M. S. Baird, *Chem. Rev.* **2003**, *103*, 1271 – 1294; e) J. M. Fox, N. Yan, *Curr. Org. Chem.* **2005**, *9*, 719 – 732; f) I. Marek, S. Simaan, A. Masarwa, *Angew. Chem. Int. Ed.* **2007**, *46*, 7364 – 7376; *Angew. Chem.* **2007**, *119*, 7508 – 7520; g) Z.-B. Zhu, Y. Wei, M. Shi, *Chem. Soc. Rev.* **2011**, *40*, 5534 – 5563; h) M. Rubin, M. Rubina, V. Gevorgyan, *Chem. Rev.* **2007**, *107*, 3117 – 3179; i) F. Miege, C. Meyer, J. Cossy, *Beilstein J. Org. Chem.* **2011**, *7*, 717 – 734.

[5] a) G. Seidel, R. Mynott, A. Fürstner, *Angew. Chem. Int. Ed.* **2009**, *48*, 2510 – 2513; *Angew. Chem.* **2009**, *121*, 2548 – 2551; b) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482 – 486; c) J. T. Bauer, M. S. Hadfield, A.-L. Lee, *Chem. Commun.* **2008**, 6405 – 6407; d) M. S. Hadfield, J. T. Bauer, P. E. Glena, A.-L. Lee, *Org. Biomol. Chem.* **2010**, *8*, 4090 – 4095; e) Z.-B. Zhu, M. Shi, *Chem. Eur. J.* **2008**, *14*, 10219 – 10222; f) C. Li, Y. Zeng, J. Wang, *Tetrahedron Lett.* **2009**, *50*, 2956 – 2959; g) E. Seraya, E. Slack, A. Ariafard, B. F. Yates, C. J. T. Hyland, *Org. Lett.* **2010**, *12*, 4768 – 4771; h) Y. Zhou, B. G. Trewyn, R. J. Angelici, L. K. Woo, *J. Am. Chem. Soc.* **2009**, *131*, 11734 – 11743; i) M. S. Hadfield, A.-L. Lee, *Chem. Commun.* **2011**, *47*, 1333 – 1335; j) F. Miege, C. Meyer, J. Cossy, *Org. Lett.* **2010**, *12*, 4144 – 4147; k) L. Nunes dos Santos Comprido, J. E. M. N. Klein, G. Knizia, J. Kästner, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2015**, *54*, 10336 – 10340; *Angew. Chem.* **2015**, *127*, 10477 – 10481.

[6] C. Li, Y. Zeng, H. Zhang, J. Feng, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2010**, *49*, 6413 – 6417; *Angew. Chem.* **2010**, *122*, 6557 – 6561.

[7] The molecular structures of products **2o**, **2q**, **4c** and **5a** have been determined by means of X-ray diffraction. Their ORTEP drawings and the corresponding CIF data have been presented in the Supporting Information.

[8] A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2010**, *49*, 5232 – 5241; *Angew. Chem.* **2010**, *122*, 5360 – 5369.

Received: August 25, 2015
Published online on October 12, 2015

