Tetrahedron Letters 57 (2016) 4405-4410

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

A heterogeneous gold(I)-catalyzed ring expansion of unactivated alkynylcyclopropanes with sulfonamides leading to (*E*)-2-alkylidenecyclobutanamines



Feiyan Yi, Bin Huang, Quan Nie, Mingzhong Cai*

Key Laboratory of Functional Small Organic Molecule, Ministry of Education and College of Chemistry & Chemical Engineering, Jiangxi Normal University, Nanchang 330022, PR China

ARTICLE INFO

Article history: Received 22 June 2016 Revised 16 August 2016 Accepted 20 August 2016 Available online 22 August 2016

Keywords: Gold Ring expansion Four-membered carbocycle Magnetic nanoparticle Heterogeneous catalysis

Introduction

Four-membered carbocycles are important structural units frequently present in many natural products of significant biological activities.¹ In addition, substituted cyclobutanes constitute useful building blocks for organic synthesis because of their rich chemistry, they can undergo facile and unique ring-opening and ring-expansion reactions driven by the relief of ring strain.² Despite the high preparative utility of four-membered carbocycles, there are only a limited number of practical and efficient methods for their preparation, which is mainly due to the following reasons. Thermal or catalyzed (2 + 2) cycloaddition reactions of two π components are limited to some special substrates.³ Photochemical (2+2) cycloaddition reaction is another route to substituted cyclobutanes, however, only the intramolecular cycloaddition reaction is efficient and the intermolecular reaction has not been well developed.⁴ Among the various approaches to four-membered carbocycles, ring expansion of cyclopropanes is considered one of the most powerful and versatile methods because the starting materials can be easily prepared by many known methods, such as Simmons–Smith,⁵ Kulinkovich,⁶ de Meijere-Kulinkovich,⁷ and others. Transition metal-promoted ring expansion reactions of cyclopropanes provide a powerful method for construction of a

ABSTRACT

A heterogeneous gold(I)-catalyzed ring expansion of unactivated alkynylcyclopropanes was achieved in 1,2-dichloroethane at 100 °C in the presence of sulfonamides by using a magnetic nanoparticle-supported phosphine gold(I) complex [Fe₃O₄@SiO₂-P-AuOTf] as catalyst, yielding a variety of (*E*)-2-alkylidenecyclobutanamines in moderate to high yields. The new heterogeneous gold catalyst can easily be separated from the reaction mixture by applying an external magnet and recycled at least 10 times without a significant loss of activity.

© 2016 Elsevier Ltd. All rights reserved.

variety of cyclobutanes, a wide range of transition metal catalysts, such as Co,⁸ Ru,⁹ Rh,¹⁰ Fe,¹¹ Pd,¹² and Pt¹³ complexes have been utilized successfully in numerous ring expansion reactions.

Homogeneous gold catalysis has attracted much attention and cationic gold(I) complexes have evolved as mild Lewis acid catalysts for organic transformations requiring the activation of π bonds in the past decade.¹⁴ Since Toste and co-workers reported the first gold(I)-catalyzed ring expansion of alkynylcyclopropanols to alkylidenecyclobutanones,¹⁵ gold(I)-catalyzed ring expansion reactions of cyclopropane derivatives have received great attention in recent years,¹⁶ providing a novel and powerful method to construct synthetically useful four-membered carbocycles. However, industrial applications of these homogeneous gold catalysts remain a challenge because they are quite expensive, cannot be recycled, and difficult to separate from the product mixture, which is a particularly significant drawback for their application in the pharmaceutical industry. In contrast, heterogeneous catalysts have received more and more attention because of the advantages of high catalytic efficiency and easy recycling, which are important for precious metal catalysts and flow chemistry processes.¹⁷ To overcome these limitations, magnetic nanoparticles-supported catalysts are a better choice because their magnetic separation is an alternative to filtration or centrifugation as it prevents loss of catalyst and increases the reusability.¹⁸ In continuing of our efforts to develop economical and eco-friendly synthetic pathways for organic transformations,¹⁹ in this letter, we report the synthesis of a magnetic nanoparticle-supported phosphine gold(I) complex



^{*} Corresponding author. *E-mail address:* caimzhong@163.com (M. Cai).

[Fe₃O₄@SiO₂-P-AuOTf] and its successful application to ring expansion of unactivated alkynylcyclopropanes. To the best of our knowledge, this is the first example of using a heterogeneous gold catalyst for the ring expansion reaction of cyclopropane derivatives with high efficiency. The catalyst could be easily separated from the reaction mixture with the simple application of an external magnet, and its catalytic efficiency remains unaltered even after recycling ten times.

Results and discussion

The magnetic nanoparticle-supported phosphine gold(I) complex was synthesized according to the procedure summarized in Scheme 1. Firstly, Fe₃O₄ nanoparticles were coated with a thin layer of silica through a sol–gel process using Si(OEt)₄ as the silica source and aqueous NH₃ as the hydrolyzing agent to give silica-coated Fe₃O₄ (Fe₃O₄@SiO₂). The latter was treated with commercially available 2-(diphenylphosphino)ethyltriethoxysilane in toluene under reflux for 24 h to afford the phosphino-functionalized magnetic nanoparticles (Fe₃O₄@SiO₂-P), the phosphine content was determined to be 0.44 mmol g⁻¹ by elemental analysis. The supported gold(I) complex (Fe₃O₄@SiO₂-P-AuOTf) was obtained by the reaction of Fe₃O₄@SiO₂-P with AuCl in methanol at 65 °C, followed by the treatment with AgOTf in dichloromethane (DCM), the gold content was determined to be 0.38 mmol g⁻¹ by ICP-AES.

The TEM image revealed that the diameter of the Fe₃O₄@SiO₂-P-AuOTf complex was approximately 30 nm (Fig. 1a). Figure 2 shows the XRD spectra of Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-P-AuOTf, and the recycled Fe₃O₄@SiO₂-P-AuOTf both Fe₃O₄@SiO₂-P-AuOTf and the recycled Fe₃O₄@SiO₂-P-AuOTf obviously show two sets of diffraction peaks, compared with the XRD pattern of Fe₃O₄@SiO₂, the three peaks that appeared at $2\theta = 38.0^{\circ}$, 44.3°,



Scheme 1. Preparation of Fe₃O₄@SiO₂-P-AuOTf complex.

and 64.6° should be attributed to (111), (200) and (220) reflections of the Au species, respectively. EDS analysis of the fresh Fe₃O₄@SiO₂-P-AuOTf complex shows the presence of Si, O, C, P, S, F, Fe, and Au elements (Fig. 3).

The magnetically separable nanocomposite $Fe_3O_4@SiO_2-P-AuOTf$ was then used as catalyst for the ring expansion reaction



Figure 2. XRD patterns of $Fe_3O_4@SiO_2$ (a), $Fe_3O_4@SiO_2\mbox{-}P\mbox{-}AuOTf$ (b), and recycled $Fe_3O_4@SiO_2\mbox{-}P\mbox{-}AuOTf$ (c).



Figure 3. Energy dispersive spectra (EDS) of Fe₃O₄@SiO₂-P-AuOTf.



Figure 1. TEM images of the fresh Fe₃O₄@SiO₂-P-AuOTf (a) and recycled Fe₃O₄@SiO₂-P-AuOTf after 10th run (b).

Table 1

Optimization of the reaction conditions for the ring expansion^a

+ TsNH2 Catalyst Solvent, Temp.					
	la	Za	3a		
Entry	Catalyst (mol %)	Solvent	Temp. (°C)	Time (h)	Yield ^b (%)
1	$Fe_3O_4@SiO_2$ -P-AuOTf (5)	DCE	40	36	0
2	$Fe_3O_4@SiO_2-P-AuOTf(5)$	DCE	60	36	Trace
3	$Fe_3O_4@SiO_2-P-AuOTf(5)$	DCE	80	36	45
4	$Fe_3O_4@SiO_2$ -P-AuOTf (5)	DCE	100	24	66
5	$Fe_3O_4@SiO_2$ -P-AuOTf (5)	DCE	110	24	62
6	$Fe_3O_4@SiO_2$ -P-AuCl (5)	DCE	100	24	Trace
7	$Ph_{3}P$ -AuCl (5)/AgOTf (5)	DCE	100	24	67
8	$Fe_3O_4@SiO_2$ -P-AuOTf (5)	Dioxane	100	24	0
9	$Fe_3O_4@SiO_2$ -P-AuOTf (5)	THF	100	24	0
10	$Fe_3O_4@SiO_2$ -P-AuOTf (5)	Toluene	100	24	23
11	$Fe_3O_4@SiO_2$ -P-AuOTf (5)	TCE	100	24	58
12	$Fe_3O_4@SiO_2$ -P-AuOTf (10)	DCE	100	16	65
13	$Fe_3O_4@SiO_2$ -P-AuOTf (2)	DCE	100	48	49

^a All reactions were performed using phenylethynylcyclopropane (0.5 mmol), TsNH₂ (0.6 mmol) in solvent (5 mL) under Ar.

^b Isolated yield based on phenylethynylcyclopropane.

of alkynylcyclopropanes with sulfonamides. Initial experiments with phenylethynylcyclopropane (1a) and 4-methylbenzenesulfonamide (2a) were performed to optimize the reaction conditions, and the results are summarized in Table 1. At first, the temperature effect was examined by using 5 mol % of Fe₃O₄@SiO₂-P-AuOTf as catalyst in 1,2-dichloroethane (DCE) (entries 1-5). It is evident that the reaction did not occur at 40 °C and the reaction proceeded very slowly even at 60 °C. When the temperature was raised to 80 °C, the desired product 3a was obtained in 45% yield (entry 3). Further raising the temperature to 100 °C gave the highest efficiency with a 66% yield (entry 4). When Fe₃O₄@SiO₂-P-AuCl was employed as the catalyst, only a trace amount of 3a was detected, while a homogeneous Ph₃P-AuOTf complex, generated in situ from Ph₃P-AuCl and AgOTf, also afforded good vield, which indicated that the effective component should be the phosphine-AuOTf complex (entries 6 and 7). Our next studies focused on the effect of solvent on the model reaction and a significant solvent effect was observed. Among the solvents examined, dioxane and THF were inefficient and toluene gave a low yield (entries 8-10). When 1,1,2,2-tetrachloroethane (TCE) was used as solvent, the desired product 3a was obtained in only 58% yield (entry 11), so DCE was the best choice. Increasing the amount of the catalyst could shorten the reaction time, but did not improve the yield (entry 12). Reducing the amount of the catalyst to 2 mol % resulted in a lower yield and a long reaction time was required (entry 13). Thus, the optimized reaction conditions for this transformation are the Fe₃O₄@SiO₂-P-AuOTf (5 mol %) in DCE at 100 °C under Ar for 24 h (entry 4).

With the optimized conditions in hand, we then studied the scope and limitation of this heterogeneous gold-catalyzed ring expansion reaction using a range of alkynylcyclopropanes and various sulfonamides as the substrates²⁰ and the results are listed in Table 2. As shown in Table 2, the reactions of alkynylcyclopropanes **1b–1f** containing electron-deficient aryl groups such as 4-chloro or 3-chlorophenyl, 4-bromophenyl, 4-(trifluoromethyl)phenyl and 4-(methoxycarbonyl)phenyl with TsNH₂ (**2a**) proceeded smoothly under the optimized conditions to afford the desired products **3b–3f** in good yields. We speculated that electron-rich aryl groups in alkynylcyclopropanes would increase the nucleophilicity of the carbon–carbon triple bond toward cationic gold(I) complex due to conjugation with it, making these substrates more reactive. However, it was found that, the more electron-donating the aryl group in the substrate was, the worse the result was. For instance,

p-tolylethynylcyclopropane **1g** afforded a 45% yield and the reaction of (p-methoxyphenyl)ethynylcyclopropane with 2a did not occur at all. Interestingly, the o-chlorophenyl group was also demonstrated as a suitable substituent in the substrate and the desired product 3h was obtained in 77% yield. The bulky and electron-rich 1-naphthyl group turned out to be less suitable, and the reaction gave 3i in only 21% yield. In addition, 3,4-disubstituted phenylethynylcyclopropane 1i could be well transformed into the expected product 3j in 86% yield. Alkyl-substituted alkynylcyclopropanes were also suitable for the ring expansion in addition to aryl-substituted substrates. For example, 1-cyclopropyl-1-octyne **1k** underwent the ring expansion reaction with **2a** smoothly to furnish the desired product **3k** in 54% vield. Furthermore, other sulfonamides such as 4-bromobenzenesulfonamide (2b). 2-nitrobenzenesulfonamide (2c), and methanesulfonamide (2d) also underwent the ring expansion reactions with various alkynylcyclopropanes effectively to afford the corresponding products **31–3u** in good yields. It is noteworthy that, *N*-methyl-*p*tolylsulfonamide (TsNHMe) (2e) was proved to be highly effective trapping reagent and underwent the ring expansion reactions with different alkynylcyclopropanes smoothly to give the desired products **3v-3v** in high yields.

To verify whether the observed catalysis was due to the heterogeneous catalyst $Fe_3O_4@SiO_2$ -P-AuOTf or to a leached gold species in solution, the reaction of phenylethynylcyclopropane (**1a**) with 4-methylbenzenesulfonamide (**2a**) was carried out until an approximately 50% conversion of **1a**. Then the $Fe_3O_4@SiO_2$ -P-AuOTf catalyst was separated magnetically from the solution and the solution was transferred to another sealed tube and stirred again at 100 °C for 12 h. In this case, no significant increase in conversion was observed, indicating that leached gold species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that no gold species could be detected in the solution. These results rule out any contribution to the observed catalysis from a homogeneous gold species, demonstrating that the observed catalysis was intrinsically heterogeneous.

A possible mechanism for this heterogeneous gold(I)-catalyzed ring expansion of unactivated alkynylcyclopropanes is outlined in Scheme 2. Firstly, coordination of the magnetic nanoparticlesimmobilized cationic gold(I) catalyst to alkyne moiety in alkynylcyclopropane (1) and subsequent reaction generates a magnetic nanoparticle-immobilized vinylgold cation intermediate **A**. Then,

Fe₃O₄@SiO₂-P-AuOTf (5 mol%) R٠ R²HN DCE, 100 °C, 24 h 'n1 1 2 3 0 CI R **3a** 66% **3c** 68% **3b** 73% Me Me 0 C 0 .0 CI F₃C MeO₂C **3d** 79% 3e 83% 3f 69% Мe Me .0 Me **3g** 45% **3i** 21% **3h** 77% мे м́е Me CI **3j** 86% **3I** 61% **3k** 54% Мe м́е NO_2 ۷O₂ Me **3m** 71% **3n** 72% 3o 69% Br \cap C NO₂ NOa CI CI Me 3p 79% **3q** 64% **3r** 67% \cap 20 С Me 3s 82% **3t** 69% **3u** 89% Me Me Me CI C **3v** 90% 3w 92% 3x 89% Me

Table 2

Ring expansions of alkynylcyclopropanes with sulfonamides catalyzed by Fe₃O₄@SiO₂-P-AuOTf^{a,b}

^a All reactions were performed using alkynylcyclopropane 1 (0.5 mmol), sulfonamide 2 (0.6 mmol), and Fe₃O₄@SiO₂-P-AuOTf (0.025 mmol) in DCE (5 mL) in a sealed tube at 100 °C under Ar for 24 h. ^b Isolated yield based on alkynylcyclopropane **1** used.

intermediate A undergoes cation-triggered ring expansion by a 1,2-alkyl shift to give a magnetic nanoparticle-immobilized vinylgold cation intermediate **B**. Finally, the cation intermediate **B** is trapped by $TsNH_2$ (2) to afford the desired product (3) and regenerate the gold(I) catalyst.

Me

3y 94%

Мe

For a heterogeneous precious metal catalyst, it is important to examine its ease of separation, good recoverability, and reusability. We next investigated the recyclability of the supported phosphine gold(I) catalyst. More than 99% of the catalyst could simply be recovered by fixing a magnet near to the reaction tube (Fig. 4).

After the completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was easily separated from the product by exposure to an external magnet and decantation of the reaction solution. The remaining magnetic nanoparticles were further washed with DCE to remove residual product, air-dried, and subjected to the next run. As shown in Figure 5, the supported gold catalyst could be reused ten times without a significant loss of activity for the ring expansion reaction of (2-chlorophenyl)ethynylcyclopropane (1h) with TsNHMe (2e). In addition, from the TEM image of the recovered catalyst, much



Scheme 2. A possible mechanism for this Au-catalyzed expansion reaction.



Figure 4. Magneto filtration of finely dispersed magnetic Fe₃O₄@SiO₂-P-AuOTf nanoparticles (*left*: before application of the magnet; *right*: 2 min later).



Figure 5. Recycle of the Fe₃O₄@SiO₂-P-AuOTf catalyst.

change in the morphology and dispersion of nanoparticles was not observed after ten reaction cycles (Fig. 1b), but the partial aggregation of the Fe₃O₄@SiO₂-P-AuOTf nanoparticles was observed due to the repeated heat treatment of the catalyst while carrying out the reactions, which resulted in a slight decrease in yield during the recycle of the catalyst.

Conclusions

In summary, we have developed a novel heterogeneous Au(I)catalyzed ring expansion reaction of unactivated alkynylcyclopropanes, which can be easily prepared from commercially readily available starting materials. Sulfonamides can efficiently trap the *in situ* generated cation from the ring expansion. The reaction tolerates a range of aryl and alkyl substituents with moderate to high yields, providing an efficient and practical method to construct synthetically useful (E)-2-alkylidenecyclobutanamines. More importantly, this new heterogeneous gold(I) catalyst can simply be recovered by applying an external magnet and recycled at least 10 times without a significant loss of catalytic activity, thus making this procedure economically and environmentally more acceptable.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 21462021) and Key Laboratory of Functional Small Organic Molecule, Ministry of Education (No. KLFS-KF-201409) for financial support.

Supplementary data

Supplementary data (experimental procedures for the preparation of Fe₃O₄@ SiO₂-P-AuOTf catalyst and ¹H, ¹³C NMR spectra of the products are described) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet. 2016.08.062.

References and notes

- (a) Bellus, D.; Ernst, B. Angew. Chem. **1988**, 100, 820; (b) Dembitsky, V. M. J. Nat. Med. **2008**, 62, 1; (c) Lee-Ruff, E.; Mladenova, G. Chem. Rev. **2003**, 103, 1449; (d) Hansen, T. V.; Stenstrom, Y. In Organic Synthesis: Theory and Applications; Hudlicky, T., Ed.; Elsevier Science Ltd: New York, NY, 2001; Vol. 5, pp 1–38.
- (a) Namyslo, J. C.; Kaufmann, D. E. Chem. Rev. 2003, 103, 1485; (b) Kabalka, G. W.; Yao, M. L. Tetrahedron Lett. 2003, 44, 7885; (c) Anderson, E. A.; Alexanian, E. J.; Sorensen, E. J. Angew. Chem., Int. Ed. 1998, 2004, 43; (d) Jung, M. E.; Nishimura, N.; Novack, A. R. J. Am. Chem. Soc. 2005, 127, 11206; (e) Liang, Y.; Jiao, L.; Wang, Y.; Chen, Y.; Ma, L.; Xu, J.; Zhang, S.; Yu, Z.-X. Org. Lett. 2006, 8, 5877; (f) Jiang, M.; Shi, M. Org. Lett. 2008, 10, 2239; (g) Jiang, M.; Shi, M. Tetrahedron 2009, 65, 798.
- (a) Kimura, M.; Horino, Y.; Wakamiya, Y.; Okajima, T.; Tamaru, Y. J. Am. Chem. Soc. 1997, 119, 10869; (b) Adam, J.-M.; Ghosez, L.; Houk, K. N. Angew. Chem., Int. Ed. 1999, 38, 2728; (c) Villeneuve, K.; Tam, W. Angew. Chem., Int. Ed. 2004, 43, 610; (d) Inanaga, K.; Takasu, K.; Ihara, M. J. Am. Chem. Soc. 2004, 126, 1352; (e) Inanaga, K.; Takasu, K.; Ihara, M. J. Am. Chem. Soc. 2005, 127, 3668; (f) Canales, E.; Corey, E. J. J. Am. Chem. Soc. 2007, 129, 12686; (g) Ogasawara, M.; Okada, A.; Nakajima, K.; Takahashi, T. Org. Lett. 2009, 11, 177; (h) Feltenberger, J. B.; Hayashi, R.; Tang, Y.; Babiash, E. S. C.; Hsung, R. P. Org. Lett. 2009, 11, 3666.
- (a) Winkler, J. D.; Bowen, C. M.; Liotta, F. Chem. Rev. 1995, 95, 2003; (b) Bach, T. Synthesis 1998, 683; (c) Hoffmann, N. Chem. Rev. 2008, 108, 1052; (d) Du, J.; Yoon, T. P. J. Am. Chem. Soc. 2009, 131, 14604.
- (a) Schuppan, J.; Koert, U. Org. Synth. Highlights IV 2000, 3; (b) Charette, A. B.; Beauchemin, A. Org. React. 2001, 58, 1.
- (a) Kulinkovich, O. G.; de Meijere, A. Chem. Rev. 2000, 100, 2789; (b) Sato, F.; Urabe, H.; Okamoto, S. Chem. Rev. 2000, 100, 2835; (c) Wu, Y.-D.; Yu, Z.-X. J. Am. Chem. Soc. 2001, 123, 5777.
- (a) Chaplinski, V.; de Meijere, A. Angew. Chem., Int. Ed. 1996, 35, 413; (b) de Meijere, A.; Kozhushkov, S. I.; Savchenko, A. I. J. Organomet. Chem. 2004, 689, 2033.
- (a) Iwasawa, N.; Matsuo, T.; Iwamoto, M.; Ikeno, T. J. Am. Chem. Soc. 1998, 120, 3903; (b) Iwasawa, N.; Narasaka, K. Top. Curr. Chem. 2000, 207, 69.
- (a) Trost, B. M.; Yasukata, T. J. Am. Chem. Soc. 2001, 123, 7162; (b) Trost, B. M.; Xie, J.; Maulide, N. J. Am. Chem. Soc. 2008, 130, 17258.
- Xu, H.-D.; Zhang, W.; Shu, D. X.; Werness, J. B.; Tang, W. P. Angew. Chem., Int. Ed. 2008, 47, 8933.
- 11. Chen, A.; Lin, R.; Liu, Q.; Jiao, N. Chem. Commun. 2009, 6842.
- (a) Shi, M.; Liu, L.-P.; Tang, J. J. Am. Chem. Soc. 2006, 128, 7430; (b) Yu, C.-B.; Huang, W.-X.; Shi, L.; Chen, M.-W.; Wu, B.; Zhou, Y.-G. J. Am. Chem. Soc. 2014, 136, 15837.
- 13. Furstner, A.; Aissa, C. J. Am. Chem. Soc. 2006, 128, 6306.
- For selected recent reviews of gold catalysis, see (a) Gorin, D. J.; Toste, F. D. Nature 2007, 446, 395; (b) Hashmi, A. S. K. Chem. Rev. 2007, 107, 3180; (c) Gorin, D. J.; Sherry, B. D.; Toste, F. D. Chem. Rev. 2008, 108, 3351; (d) Li, Z.;

Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239; (e) Wegner, H. A.; Auzias, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 8236; (f) Corma, A.; Leyva-Perez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657; (g) Lu, B.-L; Dai, L.; Shi, M. *Chem. Soc. Rev.* **2012**, *41*, 3318; (h)*Modern Gold Catalyzed Synthesis*; Hashmi, A. S. K., Toste, F. D., Eds.; Wiley-VCH: Weinheim, 2012; (i) Obradors, C.; Echavarren, A. M. *Chem. Commun.* **2014**, 16.

- 15. Markham, J. P.; Staben, S. T.; Toste, F. D. J. Am. Chem. Soc. 2005, 127, 9708.
- 16. (a) Kleinbeck, F.; Toste, F. D. J. Am. Chem. Soc. 2009, 131, 9178; (b) Li, C.-W.; Pati, K.; Lin, G.-Y.; Sohel, S. M. A.; Hung, H.-H.; Liu, R.-S. Angew. Chem., Int. Ed. 2010, 49, 9891; (c) Ye, S.; Yu, Z.-X. Org. Lett. 2010, 12, 804; (d) Zhu, L.-L; Li, X.-X.; Zhou, W.; Li, X.; Chen, Z. J. Org. Chem. 2011, 76, 8814; (e) Pitaval, A.; Leboeuf, D.; Ceccon, J.; Echavarren, A. M. Org. Lett. 2013, 15, 4580; (f) Shu, X.; Zhang, M.; He, Y.; Frei, H.; Toste, F. D. J. Am. Chem. Soc. 2014, 136, 5844; (g) Zheng, H.; Felix, R. J.; Gagne, M. R. Org. Lett. 2014, 16, 2272; (h) Zhang, L.; Wang, Y.; Yao, Z.-J.; Wang, S.; Yu, Z.-X. J. Am. Chem. Soc. 2015, 137, 13290.
- For selected reviews on heterogeneous catalysts, see: (a) Akiyama, R.; Kobayashi, S. Chem. Rev. 2009, 109, 594; (b) Climent, M. J.; Corma, A.; Iborra, S. Chem. Rev. 2011, 111, 1072; (c) Molnar, A. Chem. Rev. 2011, 111, 2251; (d) Yoon, M.; Srirambalaji, R.; Kim, K. Chem. Rev. 2012, 112, 1196.
- For selected reviews, see: (a) Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J.-M. Chem. Rev. 2011, 111, 3036; (b) Nasir Baig, R. B.;

Varma, R. Chem. Commun. 2013, 752; (c) Wang, D.; Astruc, D. Chem. Rev. 2014, 114, 6949.

- (a) Cai, M.; Zheng, G.; Ding, G. Green Chem. 2009, 11, 1687; (b) Cai, M.; Peng, J.; Hao, W.; Ding, G. Green Chem. 2011, 13, 190; (c) Zhao, H.; Cheng, M.; Zhang, J.; Cai, M. Green Chem. 2014, 16, 2515; (d) Zhao, H.; He, W.; Yao, R.; Cai, M. Adv. Synth. Catal. 2014, 356, 3092.
- 20. General procedure for the heterogeneous gold(1)-catalyzed ring expansion reaction of alkynylcyclopropanes with sulfonamides: To a resealable Schlenk tube was added Fe₃O₄@SiO₂-P-AuOTf (66 mg, 0.025 mmol). The reaction tube was evacuated and back-filled with argon and this evacuation/back-fill procedure was repeated one additional time. Alkynylcyclopropane (0.5 mmol), sulfonamide (0.6 mmol) and DCE (5 mL) were then added under a stream of argon. The reaction tube was quickly sealed and the contents were stirred while heating in an oil bath at 100 °C for 24 h. After the reaction mixture was cooled to room temperature, the supported gold catalyst was magnetically separated and the reaction mixture was concentrated under vacuum and then purified by flash chromatography (petroleum ether/ethyl acetate = 7:1) to afford the corresponding product. The recovered gold catalyst was washed with DCE (2×2 mL), air-dried and used directly for the next run.