CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Gold(I)-catalyzed cycloisomerization of ortho-(propargyloxy)arenemethylenecyclopropanes controlled by adjacent substituent at aromatic rings

Authors: Min Shi, Wei Fang, Yin Wei, and Xiang-Ying Tang

To be cited as: *Chem. Eur. J.* 10.1002/chem.201700600

Link to VoR: http://dx.doi.org/10.1002/chem.201700600

Supported by
ACES

WILEY-VCH

10.1002/chem.201700600

Gold Catalysis

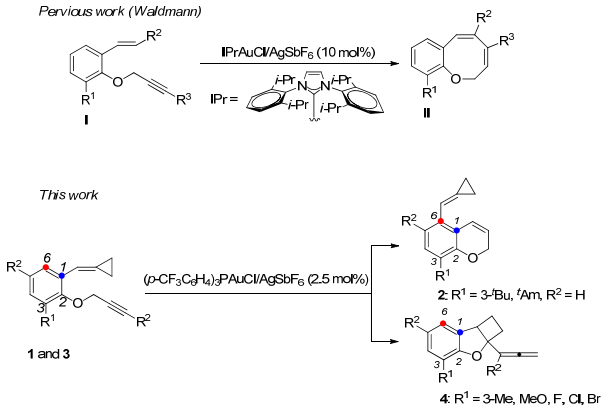
Gold(I)-catalyzed cycloisomerization of *ortho*-(propargyloxy)arenemethylenecyclopropanes controlled by adjacent substituent at aromatic rings

*Wei Fang, Yin Wei, Xiang-Ying Tang, and Min Shi**

Abstract: *Gold(I)-catalyzed cycloisomerization of ortho-(propargyloxy)arenemethylenecyclopropanes afforded two different types of products, including methylenecyclopropane migration products and cycloisomerization products from methylenecyclopropane moiety, controlled jointly by electronic effect and steric effect of the adjacent substituents. Furthermore, the corresponding cycloisomerization products could be also produced in an enantiomerically enriched manner.*

Gold catalysis as a convenient and powerful tool for synthetic organic chemistry[1] now has witnessed a rushing development in the past decades due to its potential for the rapid and available construction of the constitutional units,[2] which was widely employed in organic transformations, medicinal chemistry and total synthesis.[2f, 3] Metal-catalyzed cycloisomerization along with carbon skeleton migration is a very important strategy for the construction of complex molecules in organic synthesis. During the past decades, gold(I)-catalyzed such cycloisomerizations[4] and carbon skeleton migration reactions have made significant progress including H-migration,[5] halogen migration,[6] N-migration,[7] O-migration,[8] and C-migration.[3r, 9]

Recently, Waldmann's group reported that *ortho*-(propargyloxy) styrenes **I** could be converted to 2*H*-1-benzoxocines **II** based on an 8-*endo*-dig cyclization under gold catalysis (Scheme 1).[10] Methylenecyclopropanes as useful building blocks due to their highly strained ring energy[2l, 11] have been extensively investigated under transition metal catalysis or Lewis acid catalysis.[12] Therefore, we envisaged that methylenecyclopropane moiety replacing alkene moiety would be able to initiate a new cycloisomerization process to give novel cyclization product upon gold catalysis. Consequently, we designed and prepared *ortho*-(propargyloxy)arenemethylenecyclopropanes as substrates t examine the reaction outcome. Herein, we wish to report that tw different types of cycloisomerization products can be afforded in th presence of gold catalyst. When the adjacent substituents were ^{t}B or ^{t}Am group, methylenecyclopropane migration product 2*H* chromenes **2** were formed efficiently. When aromatic core wa substituted by Me, MeO or halogen atom, the corresponding 2,3 dihydrobenzofuran fused allene derivatives **4** derived from rin enlargement of methylenecyclopropane moiety along with migratio of propargyl group could be produced (Scheme 1). To the best c our knowledge, this is the first report with regard to the migration c entire methylenecyclopropane unit upon gold catalysis. Furthermor the corresponding allenic products could be also produced in a enantiomerically enriched manner in the presence of chiral gol catalyst.



Scheme 1. Previous work and this work.

We initially optimized the reaction conditions for the formatio of **2d** using **1d** as a model substrate and the screening results ar shown in Table 1. Using JohnPhosAuCl/AgSbF$_6$, Me$_4$ ^{t}BuXPhosAuCl/AgSbF$_6$, ^{t}BuXPhosAuCl/AgSbF$_6$, an Ph$_3$PAuCl/AgSbF$_6$ as catalyst and carrying out the reaction in 1,2 dichloroethane (DCE) at room temperature, the reactions did nc take place along with the recovery of **1d** (Table 1, entries 1-4) However, in the presence of (p-FC$_6$H$_4$)$_3$PAuCl/AgSbF$_6$ (2.5 mol%), **2d** was given in 70% yield within 6 hours (Table 1, entry 5). Using (p-CF$_3$C$_6$H$_4$)$_3$PAuCl/AgSbF$_6$ (2.5 mol%) as the catalyst afforded **2d** in a yield up to 75% in DCE at room temperature within 6 hours (Table 1, entry 6). Replacing AgSbF$_6$, the counter anion of gold complex, with AgNTf$_2$ and AgOTf, we found that the yields of **2d** decreased significantly (Table 1, entries 7 and 8). Carrying out the reaction in DCE at 90 ^{o}C did not give **2d** in the presence of JohnPhosAuCl/AgSbF$_6$ (2.5 mol%) (Table 1, entry 9), and complex product mixture was formed in the presence of Me$_4$-^{t}BuXPhosAuCl/AgSbF$_6$ (2.5 mol%) (Table 1, entry 10). The yield

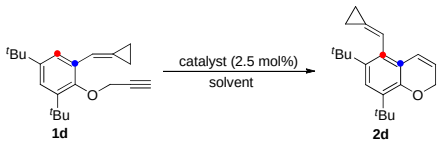
[*] W. Fang, Prof. Dr. M. Shi
Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Meilong Road No. 130, Shanghai, 200237 (China)
Y. Wei, X. Y. Tang, Prof. Dr. M. Shi
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
345 Lingling Road, Shanghai, 200032 (China)
E-mail: mshi@mail.sioc.ac.cn.
Prof. Dr. M. Shi
State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, P. R. China.

[**] We are grateful for the financial support from the National Basic Research Program of China (973)-2015CB856603, the Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. XDB20000000, the National Natural Science Foundation of China (20472096, 21372241, 21572052, 20672127, 21421091, 21372250, 21121062, 21302203, and 20732008), and the Fundamental Research Funds for the Central Universities 222201717003. We are grateful for the facility support from Shanghai Supercomputer Center.
Supporting information for this article is available on the WWW under http://www.chem.org or from the author.

10.1002/chem.201700600

of **2d** was 62% in DCE at 90 °C within 6 hours using (p-$CF_3C_6H_4)_3PAuCl/AgSbF_6$ (2.5 mol%) as the catalyst (Table 1, entry 11). Finally, the examination of solvent effects revealed that no reaction occurred in THF and 65% and 72% yields of **1d** were obtained in dichloromethane (DCM) and toluene, respectively (Table 1, entries 12-14).

Table 1. Optimization of the reaction conditions for the synthesis of **2d**.

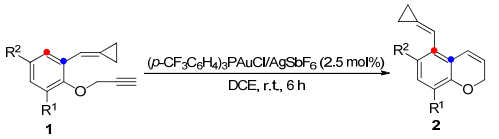


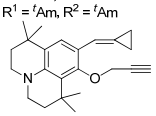
entry[a]	catalyst	solvent	temp (°C)	time (h)	yield (%)
1	JohnPhosAuCl/$AgSbF_6$	DCE	r.t.	6	NR
2	Me_4-*t*-BuXPhosAuCl/$AgSbF_6$	DCE	r.t.	4	NR
3	*t*-BuXPhosAuCl/$AgSbF_6$	DCE	r.t.	4	NR
4	$Ph_3PAuCl/AgSbF_6$	DCE	r.t.	4	NR
5	$(p\text{-}FC_6H_4)_3PAuCl/AgSbF_6$	DCE	r.t.	6	70
6	$(p\text{-}CF_3C_6H_4)_3PAuCl/AgSbF_6$	DCE	r.t.	6	75
7	$(p\text{-}CF_3C_6H_4)_3PAuCl/AgNTf_2$	DCE	r.t.	6	37[b]
8	$(p\text{-}CF_3C_6H_4)_3PAuCl/AgOTf$	DCE	r.t.	6	24[b]
9	JohnPhosAuCl/$AgSbF_6$	DCE	90	6	NR
10	Me_4-*t*-BuXPhosAuCl/$AgSbF_6$	DCE	90	1	complex
11	$(p\text{-}CF_3C_6H_4)_3PAuCl/AgSbF_6$	DCE	90	6	62[b]
12	$(p\text{-}CF_3C_6H_4)_3PAuCl/AgSbF_6$	DCM	r.t.	6	65[b]
13	$(p\text{-}CF_3C_6H_4)_3PAuCl/AgSbF_6$	THF	r.t.	6	NR
14	$(p\text{-}CF_3C_6H_4)_3PAuCl/AgSbF_6$	toluene	r.t.	6	72[b]

[a] Reaction conditions: **1d** (0.2 mmol), catalyst (2.5 mol %), solvent (2.0 mL), isolated yields. [b] Yields were determined by ^1H NMR spectroscopy. NR is no reaction.

With these reaction conditions established, we next investigated the scope of the reaction with respect to various substituted *ortho*-(propargyloxy)arenemethylenecyclopropanes **1**. As shown in Table 2, when the substituent R^1 was ^{t}Bu and substituent R^2 was H, Me, Et, and ^{t}Bu group, the desired 2*H*-chromenes **2a**, **2b**, **2c**, and **2d** were afforded in 94%, 80%, 78%, and 75% yields, respectively; and the structure of **2d** was assigned by X-ray diffraction (see Supporting Information for the details). With the increase of steric hindrance of the substituent R^2, the yields of **2** decreased (Table 2, entries 1-4), presumably due to that the steric hindrance of R^2 impaired the migration of methylenecyclopropane moiety, thereby resulting in the formation of **2** in lower yields. When the substituent R^1 was a ^{t}Bu group and substituent R^2 was a MeO, the reaction gave a product mixture (Table 2, entry 5). Consistent with the above results, when the substituent R^1 was ^{t}Am and R^2 was H or ^{t}Am, the target products **2f** and **2g** were afforded in 84% and 75% yields, respectively (Table 2, entries 6 and 7). Meanwhile, we also synthesized substrate **1h** bearing a nitrogen atom at the aromatic ring, but found that none of the corresponding product could be yielded under the optimal reaction conditions (Table 2, entry 8).

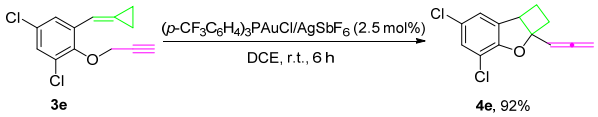
Table 2. Substrate scope of *ortho*-(propargyloxy)arenemethylenecyclopropanes **1** to 2*H*-chromenes **2**.



entry	R^1, R^2	yield (%)
1	**1a**, R^1 = ^{t}Bu, R^2 = H	**2a**, 94
2	**1b**, R^1 = ^{t}Bu, R^2 = Me	**2b**, 80
3	**1c**, R^1 = ^{t}Bu, R^2 = Et	**2c**, 78
4	**1d**, R^1 = ^{t}Bu, R^2 = ^{t}Bu	**2d**, 75
5	**1e**, R^1 = ^{t}Bu, R^2 = MeO	**2e**, complex
6	**1f**, R^1 = ^{t}Am, R^2 = H	**2f**, 84
7	**1g**, R^1 = ^{t}Am, R^2 = ^{t}Am	**2g**, 75
8	**1h**, 	**2h**, NR

Reactions were carried out by use of **1** (0.2 mmol) in 1,2-dichloroethane (DCE) (2.0 mL) with (p-$CF_3C_6H_4)_3PAuCl/AgSbF_6$ (3.5 mg, 2.5 mol%/1.7 mg, 2.5 mol%), isolated yields. NR is no reaction.

In the proceeding on the examination of substrate scope, w found that the corresponding 2,3-dihydrobenzofurans **4** wer obtained when the substituent R^1 is not a sterically bulky one. In thi reaction, methylenecyclopropane underwent ring-expanding an nucelophilic attack by oxygen atom along with the rearrangement c propargyl group to give the 2,3-dihydrobenzofurans **4**. Utilizing th above optimal reaction condition, substrate **3e** was converted to 2,3 dihydrobenzofuran **4e** in a satisfied 92% yield (Scheme 2). Thus, w did not further screen the reaction conditions and utilized it as th optimal reaction conditions for this transformation.

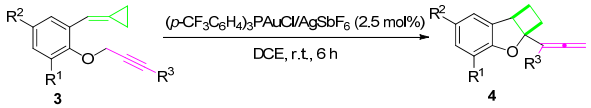


Scheme 2. Optimal reaction conditions for the synthesis of **4e**.

We next examined the generality of this reaction under th optimal conditions shown in Scheme 2, and the results are shown i Table 3. When R^3 was a H atom; R^1 was a Me, halogen atom, c MeO; and R^2 was a H atom or a halogen atom, these reaction proceeded smoothly under the optimal condition, giving the desire products in good to excellent yields; although in the cases of **3a** an **3c**, the reaction temperature was raised to 60 °C (Table 3, entries 1 8). When R^3 was an alkyl or aryl group, the reactions also proceede efficiently to afford the desired products in moderate to good yields As for substrates **3i-3l**, in which both of R^1 and R^2 were Br atom an R^3 was a Me, Et, ^{n}Am or cyclopropyl group, the desired products **4i** **4l** were obtained in 72%, 69%, 58%, 62%, and 56% yields respectively (Table 3, entries 9-12). The decrease of yields may b due to that the terminal alkynyl substituent sterically does nc facilitate the intramolecular cyclization. Introducing heterocycle a terminal alkyne, the corresponding substrate **3m** was als transformed to the desired product **4m** in 56% yield (Table 3, entr 13). When R^3 was a phenyl group; R^1 was a halogen atom or methoxy group; R^2 was a H atom or a halogen atom, the desire products **4n-4r** were also produced in good yields ranging from 65% to 82% yields, respectively (Table 3, entries 14-18). Interestingly, i the case of substrate **3s**, in which R^3 was a phenyl group; both of R and R^2 were ^{t}Bu group, the corresponding product **4s** was formed in 63% yield under the optimal conditions rather than the methylenecyclopropane migration, suggesting that the terminal alkynyl substituent would block out the intramolecular hydroarylation (Table 3, entry 19). Moreover, introducing CO_2Et and TIPS at terminal alkyne (substrates **3t** and **3u**) did not produce the desired products under the standard conditions (Table 3, entries 20 and 21).

Table 3. Substrate scope of *ortho*-(propargyloxy)arenemethylenecyclopropanes **3** to 2,3-dihydrobenzofurans **4**.

10.1002/chem.201700600

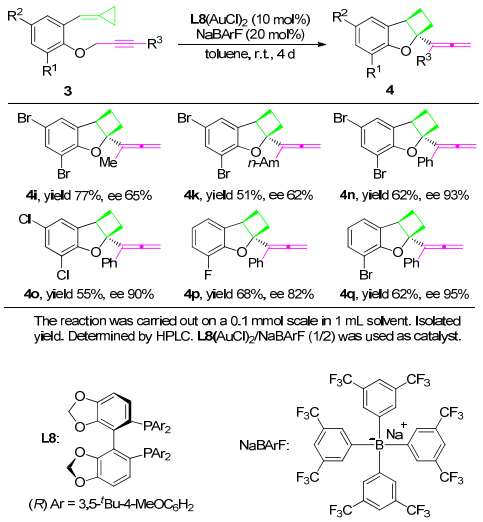


3 4

entry	R^1, R^2, R^3	yield (%)
1	**3a**, R^1 = Me, R^2 = H, R^3 = H	**4a**, 65[a]
2	**3b**, R^1 = F, R^2 = H, R^3 = H	**4b**, 93
3	**3c**, R^1 = Cl, R^2 = H, R^3 = H	**4c**, 73[a]
4	**3d**, R^1 = Br, R^2 = H, R^3 = H	**4d**, 94
5	**3e**, R^1 = Cl, R^2 = Cl, R^3 = H	**4e**, 92
6	**3f**, R^1 = Br, R^2 = Br, R^3 = H	**4f**, 95
7	**3g**, R^1 = Br, R^2 = Cl, R^3 = H	**4g**, 90
8	**3h**, R^1 = OMe, R^2 = Br, R^3 = H	**4h**, 91
9	**3i**, R^1 = Br, R^2 = Br, R^3 = Me	**4i**, 72
10	**3j**, R^1 = Br, R^2 = Br, R^3 = Et	**4j**, 69
11	**3k**, R^1 = Br, R^2 = Br, R^3 = ^{n}Am	**4k**, 58
12	**3l**, R^1 = Br, R^2 = Br, R^3 = cyclopropyl	**4l**, 62
13	**3m**, R^1 = Cl, R^2 = Cl, R^3 = 	**4m**, 56
14	**3n**, R^1 = Br, R^2 = Br, R^3 = Ph	**4n**, 65
15	**3o**, R^1 = Cl, R^2 = Cl, R^3 = Ph	**4o**, 76
16	**3p**, R^1 = F, R^2 = H, R^3 = Ph	**4p**, 80
17	**3q**, R^1 = Br, R^2 = H, R^3 = Ph	**4q**, 66
18	**3r**, R^1 = OMe, R^2 = Br, R^3 = Ph	**4r**, 82[a]
19	**3s**, R^1 = ^{t}Bu, R^2 = ^{t}Bu, R^3 = Ph	**4s**, 63
20	**3t**, R^1 = Cl, R^2 = Cl, R^3 = CO_2Et	**4t**, NR
21	**3u**, R^1 = Cl, R^2 = Cl, R^3 = TIPS	**4u**, NR

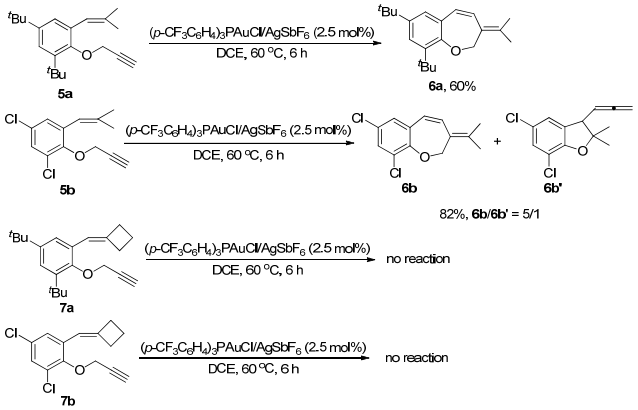
Reactions were carried out by use of **1** (0.2 mmol) in 1,2-dichloroethane (DCE) (2.0 mL) with $(p\text{-}CF_3C_6H_4)_3PAuCl/AgSbF_6$ (3.5 mg, 2.5 mol%/1.7 mg, 2.5 mol%), isolated yields. [a] Reaction temperature was 60 °C. NR is no reaction.

On the basis of the above outcomes, we attempted to develop an asymmetric variant for the synthesis of 2,3-dihydrobenzofurans **4**. The optimization of these chiral gold catalysts revealed that DTBM-SegPhos ligand coordinated gold complex with NaBArF[13] gave the highest ee value in toluene (see Table S1 in the Supporting Information for the details). As shown in Scheme 3, the corresponding products **4** could be obtained in moderate to good yields along with 62-95% ee values. The substituent R^3 has a vital effect on ee value in the asymmetric production of 2,3-dihydrobenzofurans **4**. When the substituent R^3 was alkyl group, the corresponding product was formed in a lower enantioselectivity. If the substituent R^3 was a phenyl group, the ee value of **4q** could reach to 95% perhaps due to that phenyl ring could improve enantioselectivity during the migration of propargyl group. The absolute configuration of **4n** has been assigned by X-ray diffraction (see Supporting Information for the details).



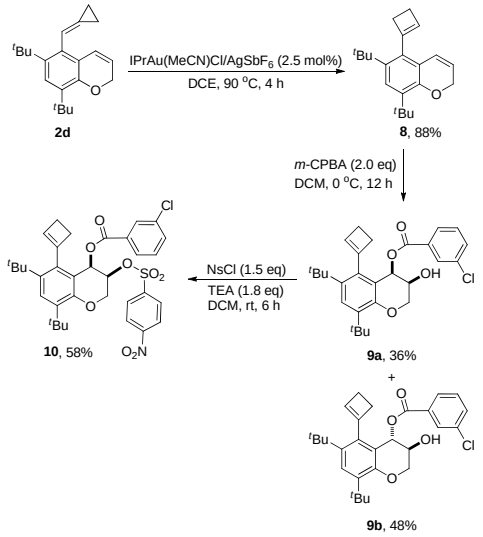
Scheme 3. Asymmetric version for the production of **4**.

In addition, we also prepared substrates **5a** and **5b** bearing an isoproylidene moiety as well as substrates **7a** and **7b** bearing a cyclobutylidene moiety and examined their reaction outcomes under the standard conditions. The results are shown in Scheme 4. As for substrate **5a**, a ring-closure process along with 1,3-cationic skeletal rearrangement[14] took place to afford a seven-membered ring product **6a** in 60% yield rather than the expected migration product (see Scheme S1 in the Supporting Information). The structure of **6a** has been assigned by X-ray diffraction (see Supporting Information for the details). In the case of substrate **5b**, seven-membered ring product **6b** and allenic product **6b'** were both formed in 82% total yield at the same time. These reactions are able to access seven-membered ether fused with a benzene. This type of product can be accessed by other gold reactions.[15] However, as for substrates **7a** and **7b**, no reactions occurred along with the recovery of substrates **7a** and **7b**.



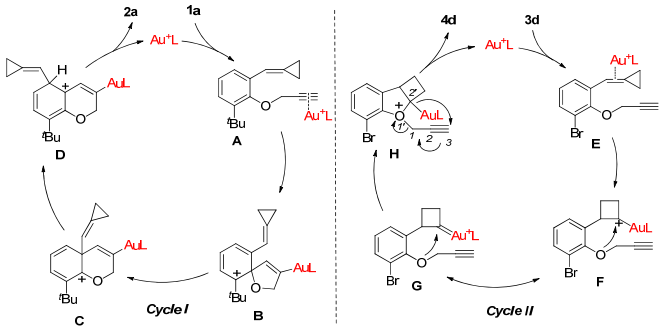
Scheme 4. Reactions of substrates **5a** and **5b** and **7a** and **7b** upon gold(I) catalysis .

On the basis of our previous investigation,[16] we carried out further transformation of **2d** as shown in Scheme 5. Compound **2** could be converted into the corresponding cyclobutene **8** in a 88% yield at 90 °C in DCE via a ring enlargement in the presence o IPrAuCl/$AgSbF_6$ (2.5 mol%) within 4 hours. Next, we also explore the regioselective epoxidation of **8** with *meta*-chloroperbenzoic aci (*m*-CPBA) in DCM at 0 °C. In consequence, the correspondin products *cis*-**9a** and *trans*-**9b**, derived from the ring-opening of th *in situ* generated epoxide at six-membered olefin and furthe esterification with *meta*-chlorobenzoic acid, were yielded in 36% and 48% yields, respectively (Scheme 5). Upon treatment of **8** wit *para*-nitrobenzenesulfonyl chloride (NsCl) and triethylamine (TEA) compound *cis*-**9a** could be transformed into compound *cis*-**10** i 58% yield in DCM at room temperature within 6 hours along wit 36% recovery of *cis*-**9a**. The relative configuration of *cis*-**10** ha been unambiguously assigned by X-ray diffraction (see Supportin Information for the details).



Scheme 5. Further transformation of **2d**.

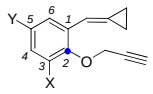
On the basis of the above results and previously reported literature, the plausible mechanisms for these reactions are described in Scheme 6. In Cycle I, the gold complex initially coordinated with the triple bond of substrate **1a** to give intermediate **A**, which afforded the vinyl-gold[17] intermediate **B** containing a five-membered ring through cyclization. Next, the ring enlargement of intermediate **B** took place to afford intermediate **C**. Then, intermediate **C** underwent three-membered ring transition state **TS3** (Shown in Scheme 7) to form intermediate **D** via intramolecular cyclopropanation[18] and methylenecyclopropane migration. Finally, intermediate **D** underwent dehydro-aromatization and reprotonation to afford **2a** along with the regeneration of gold(I) catalyst. In Cycle II, the gold complex initially activated the double bond of methylenecyclopropane to produce intermediate **E**, which rearranged to the corresponding cyclobutenyl cationic intermediate **F** through ring enlargement.[12e, 19] Intermediate **G**, likely bearing some gold carbenoid character,[20] was a resonance structure of intermediate **F**. Then O atom attacked the cyclobutenyl cation to give the corresponding propargylic ether oxonium ylide[21] intermediate **H**, which underwent the corresponding [2,3]-sigmatropic rearrangement[22] by C-O bond cleavage (O1'-C1) and C-C bond formation (C2'-C3) and simultaneously dissociation of gold catalyst to give the final product **4d**.



Scheme 6. Proposed reaction mechanism.

We believe that the electronic effects of *ortho*-substituents in substrates influence the electron densities of carbon atom (C2 position) at the aromatic ring substituted by the methylenecyclopropanes, which is the root for the different reaction pathways of substrates **1** and **3**. The calculation of Natural Population Analysis (NPA) charge on the C2 atom influenced by *ortho*-substituents was carried out on the basis of the B3LYP/6-31G(d, p) level, revealing that the electron densities on C2 atom follow the order of ^{t}Bu > Me > Br > Cl > MeO > F (Table 4). This result suggests that the *ortho*-substituents can influence the formation of five-membered ring intermediate (**Int-B** in Scheme 7) through changing the electron densities on C2 atom. When *ortho*-substituent is a ^{t}Bu group, the cyclization can efficiently take place due to higher electron density on C2 atom, thereby affording the corresponding methylenecyclopropane migration product exclusively.

Table 4. *Ortho*-substituent effects.

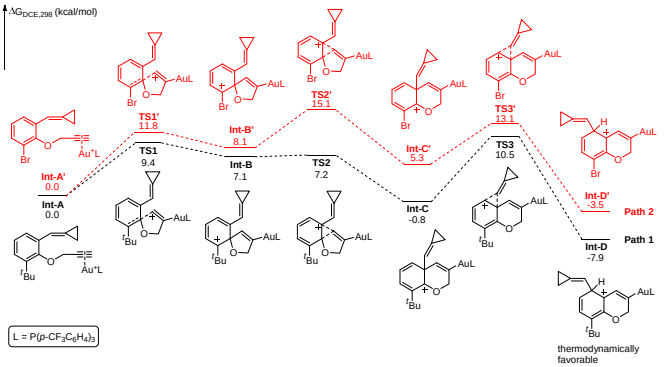


X	Y	NPA charge of C2 atom[a]
F	H	0.258
MeO	Br	0.278
Cl	H	0.297
Br	H	0.298
Me	H	0.307
^{t}Bu	H	0.322

[a] Calculated at B3LYP/6-31G(d, p) level.

Furthermore, we performed DFT calculations on the reactio pathway about the unknown migration of methylenecyclopropan moiety in Cycle I using substrates **1a** and **3d** and the reaction energ profile was described in Scheme 7 (for computational details, se Supporting Information). Initially, coordination of gold(I) catalyst t the alkyne moiety of substrates **1a** and **3d** give gold complex **Int-** and **Int-A'**, respectively. Undergoing a ring-closure process, a intermediate **Int-B** containing five-membered ring is formed vi transition state **TS1** with an energy barrier of 9.4 kcal/mol along th Path **1**. Similarly, an intermediate **Int-B'** is formed via transitio state **TS1'** with an energy barrier of 11.8 kcal/mol along the Path 2 correspondingly. Transition state **TS1'** is higher than transition stat **TS1** in energy by 2.4 kcal/mol, indicating that the substrate **1** having ^{t}Bu substituent is more kinetically favored to undergo th ring-closure step, presumably due to the more positive charge on C atom as shown in Table 4. Subsequently, **Int-B** undergoes rin enlargement via transition state **TS2** with an energy barrier of 0. kcal/mol along the Path **1**, producing another intermediate **Int-C Int-C'** is formed via transition state **TS2'** with an energy barrier c 7.0 kcal/mol along the Path **2**. The energy of transition state **TS2'** i still higher than that of transition state **TS2** by 7.9 kcal/mol. Ther intramolecular cyclopropanation takes place to give intermediat **Int-D** via transition state **TS3** with an energy barrier of 11. kcal/mol along the Path **1**. Intermediate **Int-D'** is formed vi transition state **TS3'** with an energy barrier of 7.8 kcal/mol along th Path **2**. Transition state **TS3'** is higher than transition state **TS3** i energy by 2.6 kcal/mol. These calculation results also show that a intermediates along the Path **1** are more stable than thos corresponding intermediates along path **2**, thus the Path **1** is also thermodynamically favorable. Therefore, we conclude that the reaction of substrate **1a** along the Path **1** takes place more easily, affording the corresponding product **2a**. However, utilizing **3d** as substrate, the reaction is more difficult to occur along the Path **2**; presumably, it proceeded via the reaction process shown in Cycle II more easily involving the ring enlargement of methylenecyclopropane and [2,3]-sigmatropic rearrangement which are already well-known and have been reported by Fürstner,[12e] Echavarren,[19] Tang[22d] et al. Herein, we have no further study about the reaction pathway in Cycle II.

10.1002/chem.201700600



Scheme 7. DFT studies on reaction pathway in cycle I.

In summary, we have developed a new strategy for the cycloisomerization along with carbon skeleton migration of *ortho*-(propargyloxy)arenemethylenecyclopropanes to afford two different types of products in the presence of $(p\text{-}CF_3C_6H_4)_3PAuCl/AgSbF_6$ catalyst. The product distributions were jointly controlled by electronic effect and steric effect of the adjacent substituents at the phenyl ring. When substituent was a sterically bulky one, this transformation yielded methylenecyclopropane migration products **2** in good yields. When substituent was Me, MeO or halogen atom, ring enlargement of methylenecyclopropane along with rearrangement of propargyl group takes place to give products **4**. The corresponding products could be also produced in an enantiomerically enriched manner through an asymmetric version. Further investigations on the mechanistic details and exploration of new methodology based on gold catalyzed transformations of methylenecyclopropanes as well as their asymmetric variants are currently underway in our laboratory.

Experimental Section

General procedure for the synthesis of compound 2a. To a flame-dried flask were added the methylenecyclopropane (0.20 mmol, 1.0 equiv) and the $(p\text{-}CF_3C_6H_4)_3PAuCl/AgSbF_6$ (0.005 mmol, 0.025 equiv), and the flask was evacuated and backfilled with Ar for 3 times. DCE (2.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred for 6 hours at room temperature. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum pump at low temperature. Then, the crude product was purified by a silica gel chromatography (PE) to get the desired product **2a** (45 mg, 94%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.16-1.19 (m, 2H, CH_2), 1.35-1.40 (m, 11H, CH_2, $3CH_3$), 4.65 (dd, J_1 = 4.0 Hz, J_2 = 1.6 Hz, 2H, CH_2), 5.75 (dt, J_1 = 10.0 Hz, J_2 = 4.0 Hz, 1H, =CH), 6.84 (d, J = 10.0 Hz, 1H, =CH), 6.95 (s, 1H, =CH), 7.13 (d, J = 8.0 Hz, 1H, Ar), 7.25 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.2, 4.2, 29.7, 34.3, 63.4, 114.2, 118.9, 120.8, 121.6, 122.4, 126.0, 126.1, 132.5, 136.0, 152.8. IR (neat) ν 3080, 2956, 2869, 1780, 1637, 1588, 1485, 1392, 1272, 1191, 1093, 967, 828 cm^{-1}. MS (%) m/e 240 (M^+, 1.55), 225 (16.49), 201 (100.00), 183 (34.02), 155 (16.75), 128 (30.27), 115 (33.49), 91 (24.92), 77 (17.52). HRMS (EI) calcd. for $C_{17}H_{20}O$: 240.1514, found: 240.1512.

General procedure for the synthesis of compound 4a. To a flame-dried flask were added the methylenecyclopropane (0.20 mmol, 1.0 equiv) and the $(p\text{-}CF_3C_6H_4)_3PAuCl/AgSbF_6$ (0.005 mmol, 0.025 equiv), and the flask was evacuated and backfilled with Ar for 3 times. DCE (2.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred for 6 hours at room temperature. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum pump at low temperature. Then, the crude product was purified by silica gel chromatography (PE) to get the desired product **4a** (26 mg, 65%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.89-1.97 (m, 1H, CH_2), 2.23 (s, 3H, CH_3), 2.29-2.39 (m, 1H, CH_2), 2.51-2.55 (m, 2H, CH_2), 3.79 (d, J = 7.6 Hz, 1H, CH), 5.00 (dd, J_1 = 6.4 Hz, J_2 = 1.6 Hz, 2H, =CH_2), 5.54 (t, J = 6.4 Hz, 1H, =CH), 6.80 (dd, J_1 = J_2 = 7.6 Hz, 1H, Ar), 6.98 (d, J = 7.6 Hz, 1H, Ar), 7.01 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 15.5, 23.8, 32.8, 47.9, 78.3, 87.6, 92.8, 120.4, 120.6, 122.3, 129.5, 131.3, 158.7, 207.8. IR (neat) ν 3055, 2987, 2942, 2857, 1955, 1712, 1595, 1461, 1379, 1288, 1132, 1097, 922, 848 cm^{-1}. MS (%) m/e 198 (M^+, 15.37), 183 (8.72), 170 (100.00), 155 (8.45), 141 (30.69), 128 (8.23), 11 (30.87), 91 (12.41), 77 (12.79). HRMS (EI) calcd. for $C_{14}H_{14}C$ 198.1045, found: 198.1046.

Computational methods. All DFT calculations were performe with Gaussian 09 program.[23] The geometries of all minima an transition states have been optimized using PBE1PBE functional.[2 The SDD basis set and pseudopotential were used for the gold aton and the 6-31G(d) basis set was used for other atoms. The subsequer frequency calculations on the stationary points were carried out a the same level of theory to ascertain the nature of the stationar points as minima or first-order saddle points on the respectiv potential energy surfaces. All transition states were characterized b one and only one imaginary frequency pertaining to the desire reaction coordinate. The intrinsic reaction coordinate (IRC calculations were carried out at the same level of theory to furthe authenticate the transition states. The conformational space c flexible systems has first been searched manually. Thermochemica corrections to 298.15 K have been calculated for all minima fror unscaled vibrational frequencies obtained at this same level. Th solvent effect was estimated by the IEFPCM method[25] with rad and nonelectrostatic terms for SMD salvation model[26] i dichloroethane (ε = 10.37). Solution-phase single point energ calculations (SDD basis set and pseudopotential used for the gol atom, and the 6-31+G(d,p) basis set used for other atoms) wer performed based on the gas phase optimized structures.

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

Keywords: gold-catalyzed, metheneylcyclopropane, migration, [2,3 sigmatropic rearrangement, cycloisomerization.

[1] a) B. W. Gung, L. N. Bailey, D. T. Craft, C. L. Barnes, K. Kirschbaun *Organometallics* **2010**, *29*, 3450; b) M. Bandini, A. Bottoni, M Chiarucci, G. Cera, G. P. Miscione, *J. Am. Chem. Soc.* **2012**, *134*, 20690; c) G. Cera, M. Chiarucci, M. Bandini, *Pure Appl. Chem.* **2012**, *84*, 1673; d) N. T. Patil, *Chem. - Asian J.* **2012**, *7*, 2186; e) V. Michelet, *Top Curr Chem* **2015**, *357*, 95; f) A. La-Venia, N. S. Medran, V. Krchnak, S. A. Testero, *ACS Comb. Sci.* **2016**, *18*, 482.

[2] For recent reviews on homogeneous gold catalysis, see: a) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395; b) A. Fürstner, P. W. Davies, *Angew. Chem. Int. Ed.* **2007**, *46*, 3410; *Angew. Chem.* **2007**, *119*, 3478; c) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326; d) M. M. Díaz-Requejo, P. J. Pérez, *Chem. Rev.* **2008**, *108*, 3379; e) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208; f) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.* **2012**, *41*, 2448; g) C. Obradors, A. M. Echavarren, *Chem. Commun.* **2014**, *50*, 16; h) A. S. K. Hashmi, *Acc.*

Chem. Res. **2014**, *47*, 864; i) L. Zhang, *Acc. Chem. Res*. **2014**, *47*, 877; j) Y.-M. Wang, A. D. Lackner, F. D. Toste, *Acc. Chem. Res.* **2014**, *47*, 889; k) C. Obradors, A. M. Echavarren, *Acc. Chem. Res*. **2014**, *47*, 902; l) D.-H. Zhang, X.-Y. Tang, M. Shi, *Acc. Chem. Res.* **2014**, *47*, 913; m) A. Fürstner, *Acc. Chem. Res*. **2014**, *47*, 925; n) B. Alcaide, P. Almendros, *Acc. Chem. Res*. **2014**, *47*, 939; o) L. Fensterbank, M. Malacria, *Acc. Chem. Res.* **2014**, *47*, 953; p) H.-S. Yeom, S. Shin, *Acc. Chem. Res*. **2014**, *47*, 966; q) Y. Wang, M. E. Muratore, A. M. Echavarren, *Chem. - Eur. J.* **2015**, *21*, 7332; u) B. J. Ayers, P. W. H. Chan, *Synlett*. **2015**, *26*, 1305; v) D. P. Day, P. W. H. Chan, *Adv. Synth. Catal.* **2016**, *358*, 1368.

[3] a) C. Ecob, *Tecnol. Chim.* **2000**, *20*, 84; b) A. Fürstner, P. Hannen, *Chem. - Eur. J.* **2006**, *12*, 3006; c) L. Xin, K. -S. J. Joshua, F. D. Toste, *Angew. Chem. Int. Ed.* **2007**, *46*, 7671; *Angew. Chem.* **2007**, *119*, 7815; d) A. Fürstner, A. Schlecker, *Chem. - Eur. J.* **2008**, *14*, 9181; e) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766; f) L. Cui, L. M. Zhang, *Sci. China: Chem.* **2010**, *53*, 113; g) R. M. Zeldin, F. D. Toste, *Chem. Sci.* **2011**, *2*, 1706; h) C. M. Lemon, P. J. Brothers, B. Boitrel, *Dalton Trans.* **2011**, *40*, 6591; i) W. Chaladaj, M. Corbet, A. Fürstner, *Angew. Chem. Int. Ed.* **2012**, *51*, 6929; *Angew. Chem.* **2012**, *124*, 7035; j) H. C. Shen, T. H. Graham, *Drug Discov Today Technol* **2013**, *10*, 3; k) L. Hoffmeister, P. Persich, A. Fürstner, *Chem. - Eur. J.* **2014**, *20*, 4396; l) H. G. Raubenheimer, H. Schmidbaur, *J. Chem. Educ.* **2014**, *91*, 2024; m) D. Shukla, S. Krishnamurthy, S. V. Sahi, *Front Plant Sci* **2014**, *5*, 652; n) L. Hoffmeister, T. Fukuda, G. Pototschnig, A. Fürstner, *Chem. - Eur. J.* **2015**, *21*, 4529; o) A. Homs, M. E. Muratore, A. M. Echavarren, *Org. Lett.* **2015**, *17*, 461; p) J. Carreras, M. S. Kirillova, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2016**, *55*, 7121; *Angew. Chem.* **2016**, *128*, 7237; q) A. M. Echavarren, A. S. K. Hashmi, F. D. Toste, *Adv. Synth. Catal.* **2016**, *358*, 1347; r) M. S. Kirillova, M. E. Muratore, R. Dorel, A. M. Echavarren, *J. Am. Chem. Soc.* **2016**, *138*, 3671; s) D. Nishiyama, A. Ohara, H. Chiba, H. Kumagai, S. Oishi, N. Fujii, H. Ohno, *Org. Lett.* **2016**, *18*, 1670; t) S. Naoe, Y. Yoshida, S. Oishi, N. Fujii, H. Ohno, *J. Org. Chem.* **2016**, *81*, 5690; u) D. Pflaesterer, A. S. K. Hashmi, *Chem. Soc. Rev.* **2016**, *45*, 1331; v) B. Ranieri, C. Obradors, M. Mato, A. M. Echavarren, *Org. Lett.* **2016**, *18*, 1614.

[4] a) W. Rao, Sally, S. N. Berry and P. W. H. Chan, *Chem. - Eur. J.* **2014**, *20*, 13174; b) D. Susanti, L.-J. Liu, W. Rao, S. Lin, D.-L. Ma, C.-H. Leung, P. W. H. Chan, *Chem. - Eur. J.* **2015**, *21*, 9111; c) D. B. Huple, B. D. Mokar, R.-S. Liu, *Angew. Chem. Int. Ed.* **2015**, *54*, 14924; *Angew. Chem.* **2016**, *55*, 3253; d) W. Rao, D. Susanti, B. J. Ayers, P. W. H. Chan, *J. Am. Chem. Soc.* **2015**, *137*, 6350; e) D. B. Huple, S. Ghorpade, R.-S. Liu, *Adv. Synth. Catal.* **2016**, *358*, 1348; f) W. Rao, J. W. Boyle, P. W. H. Chan, *Chem. - Eur. J.* **2016**, *22*, 6532; g) S. B. Wagh, Y.-C. Hsu, R.-S. Liu, *ACS Catal.* **2016**, *6*, 7160.

[5] a) A. S. Dudnik, Y. Xia, Y. Li, V. Gevorgyan, *J. Am. Chem. Soc.* **2010**, *132*, 7645; b) G. Mazzone, N. Russo, E. Sicilia, *J. Chem. Theory Comput.* **2010**, *6*, 2782; c) R. E. M. Brooner, B. D. Robertson, R. A. Widenhoefer, *Organometallics* **2014**, *33*, 6466; d) T. J. Brown, B. D. Robertson, R. A. Widenhoefer, *J. Organomet. Chem.* **2014**, *758*, 25; e) R. K. Shiroodi, O. Koleda, V. Gevorgyan, *J. Am. Chem. Soc.* **2014**, *136*, 13146.

[6] a) A. W. Sromek, M. Rubina, V. Gevorgyan, *J. Am. Chem. Soc.* **2005**, *127*, 10500; b) R. Kazem Shiroodi, A. S. Dudnik, V. Gevorgyan, *J. Am. Chem. Soc.* **2012**, *134*, 6928; c) J. Jiang, C. Hou, S. Zhang, Z. Luan, C. Zhao, Z. Ke, *J. Org. Chem.* **2015**, *80*, 1661; d) P. Noesel, V. Mueller, S. Mader, S. Moghimi, M. Rudolph, I. Braun, F. Rominger, A. S. K. Hashmi, *Adv. Synth. Catal.* **2015**, *357*, 500.

[7] a) S. Boussert, I. Diez-Perez, M. J. Kogan, E. de Oliveira, E. Giralt, *ACS Nano* **2009**, *3*, 3091; b) H. V. Adcock, T. Langer, P. W. Davies, *Chem. - Eur. J.* **2014**, *20*, 7262; c) Y. Tokimizu, S. Oishi, N. Fujii, H. Ohno, *Angew. Chem. Int. Ed.* **2015**, *54*, 7862; *Angew. Chem.* **2015**, *127*, 7973.

[8] a) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *Org. Lett.* **2001**, *3*, 3769; b) X. Moreau, J.-P. Goddard, M. Bernard, G. Lemiere, J. M. Lopez-Romero, E. Mainetti, N. Marion, V. Mouries, S. Thorimbert, L. Fensterbank, M. Malacria, *Adv. Synth. Catal.* **2008**, *350*, 43; c) J. A. Rodriguez, L. Feria, T. Jirsak, Y. Takahashi, K. Nakamura, F. Illas, *J. Am. Chem. Soc.* **2010**, *132*, 3177; d) Y. Harrak, M. Makhlouf, S. Azzaro, E. Mainetti, J. M. L. Romero, K. Cariou, V. Gandon, J.-P. Goddard, M. Malacria, L. Fensterbank, *J. Organomet. Chem.* **2010**, *696*, 388; e) T. de Haro, E. Gomez-Bengoa, R. Cribiu, X. Huang, C. Nevado, *Chem. - Eur. J.* **2012**, *18*, 6811; f) Y.-W. Sun, X.-Y. Tang, M. Shi, *Chem. Commun.* **2015**, *51*, 13937; g) B. Vulovic, D. Kolarski, F. Bihelovic, R. Matovic, M. Gruden, R. N. Saicic, *Org. Lett.* **2016**, *18*, 3886.

[9] a) B. Crone, S. F. Kirsch, *Chem. - Eur. J.* **2008**, *14*, 3514; b) R. Sanz, D. Miguel, F. Rodriguez, *Angew. Chem. Int. Ed.* **2008**, *47*, 7354; *Angew. Chem.* **2008**, *120*, 7464; c) X.-Z. Shu, X.-Y. Liu, K.-G. Ji, H.-Q. Xiao, Y.-M. Liang, *Chem. - Eur. J.* **2008**, *14*, 5282; d) H. Gao, X. Zhao, Y. Yu, J. Zhang, *Chem. - Eur. J.* **2010**, *16*, 456; e) G. Li, Y. Liu, *J. Org. Chem.* **2010**, *75*, 3526; f) R. Sanz, D. Miguel, M. Gohain, P. Garcia-Garcia, M. A. Fernandez-Rodriguez, A. Gonzalez-Perez, O. Nieto-Faza, A. R. de Lera, F. Rodriguez, *Chem. - Eur. J.* **2010**, *16*, 9818; g) W. Li, Y. Li, J. Zhang, *Chem. - Eur. J.* **2010**, *16*, 6447; h) N. Ibrahim, A. S. K. Hashmi, F. Rominger, *Adv. Synth. Catal.* **2011**, *353*, 461; i) W. Li, Y. Li, G. Zhou, X. Wu, J. Zhang, *Chem. - Eur. J.* **2012**, *18*, 15113; j) Y. Yu, W. Yang, F. Rominger, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2013**, *52*, 7586; *Angew. Chem.* **2013**, *125*, 7735; k) M. Zhang, J. Zhang, *Isr. J. Chem.* **2013**, *53*, 911; l) Y. Qiu, C. Fu, X. Zhang, S. Ma, *Chem. - Eur. J.* **201** *20*, 10314; m) Q. Zhou, Y. Li, *J. Am. Chem. Soc.* **2014**, *136*, 1505; n) I Jin, Y. Wu, X. Zhao, *J. Org. Chem.* **2015**, *80*, 3547; o) F. Rekhroukh, F Brousses, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2015**, *5* 1266; *Angew. Chem.* **2015**, *127*, 1282; p) X. Zhang, Z. Geng, *RSC Ad* **2016**, *6*, 62099; q) Y.-Q. Gu, P.-P. Zhang, J.-K. Fu, S. Liu, Y. Lan, J.-X Gong, Z. Yang, *Adv. Synth. Catal.* **2016**, *358*, 1392.

[10] K. Wittstein, K. Kumar, H. Waldmann, *Angew. Chem. Int. Ed.* **2011**, *5* 9076; *Angew. Chem.* **2011**, *123*, 9242.

[11] For selected reviews, see: a) L. Yu, R. Guo, *Org. Prep. Proced. In* **2011**, *43*, 209; b) A. Brandi, S. Cicchi, F. M. Cordero, A. Goti, *Chem Rev.* **2014**, *114*, 7317; c) L. Yu, M. Liu, F. Chen, Q. Xu, *Org. Biomo Chem.* **2015**, *13*, 8379.

[12] For recent contributions from our group and others, see: a) M. Shi, F Xu, J.-W. Huang, *Org. Lett.* **2004**, *6*, 1175; b) J. Brabec, J. Pittner, *Phys. Chem. A* **2006**, *110*, 11765; c) L.-X. Shao, B. Xu, J.-W. Huang, M Shi, *Chem. - Eur. J.* **2006**, *12*, 510; d) M. Shi, L.-P. Liu, J. Tang, *J. Am Chem. Soc.* **2006**, *128*, 7430; e) A. Fürstner, C. Aiessa, *J. Am. Chem Soc.* **2006**, *128*, 6306; f) M. Shi, M. Jiang, L.-P. Liu, *Org. Biomol. Chem* **2007**, *5*, 438; g) B. Hu, S. Xing, Z. Wang, *Org. Lett.* **2008**, *10*, 5481; H B. Hu, J. Zhu, S. Zing, J. Fang, D. Du, Z. Wang, *Chem. - Eur. J.* **2009** *15*, 324; i) H. Taniguchi, T. Ohmura, M. Suginome, *J. Am. Chem. Soc* **2009**, *131*, 11298; j) M. Jiang, M. Shi, *Org. Lett.* **2010**, *12*, 2606; k) K Chen, Z. Zhang, Y. Wei, M. Shi, *Chem. Commun.* **2012**, *48*, 7696; l) M Shi, J.-M. Lu, Y. Wei, L.-X. Shao, *Acc. Chem. Res.* **2012**, *45*, 641; m) T Kippo, K. Hamaoka, I. Ryu, *J. Am. Chem. Soc.* **2013**, *135*, 632; n) K Chen, Z.-Z. Zhu, Y.-S. Zhang, X.-Y. Tang, M. Shi, *Angew. Chem. Int Ed.* **2014**, *53*, 6645; *Angew. Chem.* **2014**, *126*, 6763; o) Z.-Z. Zhu, K Chen, L.-Z. Yu, X.-Y. Tang, M. Shi, *Org. Lett.* **2015**, *17*, 5994; p) T Ohmura, H. Taniguchi, M. Suginome, *ACS Catal.* **2015**, *5*, 3074; q) Z Zhu, K. Chen, Q. Xu, M. Shi, *Adv. Synth. Catal.* **2015**, *357*, 3081; r) K Chen, X.-Y. Tang, M. Shi, *Chem. Commun.* **2016**, *52*, 1967; s) K. Chen Z.-Z. Zhu, J.-X. Liu, X.-Y. Tang, Y. Wei, M. Shi, *Chem. Commun.* **201** *52*, 350.

[13] F. Kleinbeck, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 9178.

[14] a) C. Nieto-Oberhuber, P. M. Munoz, E. Bunuel, C. Nevado, D. Cardenas, A. M. Echavarren, *Angew. Chem., Int. Ed*. **2004**, *43*, 240 *Angew. Chem.* **2004**, *116*, 2456; b) M.-Y. Lin, A. Das, R.-S. Liu, *J. Am Chem. Soc.* **2006**, *128*, 9340; c) Q. Zhou, Y. Li, *J. Am. Chem. Soc.* **201** *136*, 1505.

[15] a) S. A. Gawade, S. Bhunia, R.-S. Liu, *Angew. Chem., Int. Ed*. **2012**, *5* 7835; *Angew. Chem.* **2012**, *124*, 7955; b) S. N. Karad, S. Bhunia, R.-S Liu, *Angew. Chem., Int. Ed*. **2012**, *57*, 8122; *Angew. Chem.* **2012**, *12* 8852; c) R. L. Sahani, R.-S. Liu, *Chem. Commun.* **2016**, *52*, 7482.

[16] W. Fang, X.-Y. Tang, M. Shi, *RSC Adv.* **2016**, *6*, 40474.

[17] a) R. L. LaLonde, B. D. Sherry, E. J. Kang, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 2452; b) I. Nakamura, T. Sato, M. Terada, Y. Yamamoto, *Org. Lett.* **2007**, *9*, 4081; c) L.-P. Liu, G. B. Hammond, *Chem Asian J* **2009**, *4*, 1230; d) G. Cera, S. Piscitelli, M. Chiarucci, G. Fabrizi, A. Goggiamani, R. S. Ramon, S. P. Nolan, M. Bandini, *Angew. Chem. Int. Ed.* **2012**, *51*, 9891; *Angew. Chem.* **2012**, *124*, 10029; e) W. Wang, G. B. Hammond, B. Xu, *J. Am. Chem. Soc.* **2012**, *134*, 5697; f) Y. Tang, J. Li, Y. Zhu, Y. Li, B. Yu, *J. Am. Chem. Soc.* **2013**, *135*, 18396; g) A. Zhdanko, M. E. Maier, *Organometallics* **2013**, *32*, 2000; h) A. Zhdanko, M. E. Maier, *Angew. Chem. Int. Ed.* **2014**, *53*, 7760; *Angew. Chem. Int. Ed.* **2014**, *126*, 7894; i) D. V. Patil, H. Yun, S. Shin, *Adv. Synth. Catal.* **2015**, *357*, 2622; j) H. Peng, N. G. Akhmedov, Y.-F. Liang,

N. Jiao, X. Shi, *J. Am. Chem. Soc.* **2015**, *137*, 8912; k) A. Zhdanko, M. E. Maier, *ACS Catal.* **2015**, *5*, 5994; l) R. E. M. Brooner, T. J. Brown, M. A. Chee, R. A. Widenhoefer, *Organometallics* **2016**, *35*, 2014; m) L. Huang, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2016**, *55*, 4808; *Angew. Chem.* **2016**, *128*, 4888.

[18] W. v. E. Doering, W. R. Roth, *Tetrahedron* **1963**, *19*, 715.

[19] Y. Wang, M. E. Muratore, Z. Rong, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2014**, *53*, 14022; *Angew. Chem.* **2014**, *126*, 14246.

[20] D.-Y. Li, Y. Wei, I. Marek, X.-Y. Tang, M. Shi, *Chem. Sci.* **2015**, *6*, 5519.

[21] a) J. Li, X. Liu, D. Lee, *Org. Lett.* **2012**, *14*, 410; b) S. Mukherjee, P. N. Tripathi, S. B. Mandal, *Org. Lett.* **2012**, *14*, 4186; c) D. Malhotra, G. B. Hammond, B. Xu, *Top. Curr. Chem.* **2015**, *357*, 1.

[22] For selected reports on the [2,3]-sigmatropic rearrangement with regard to allylic or propargylic ether oxonium ylide under Rh(II) or Au(I) catalysis: a) D. M. Hodgson, M. Petroliagi, *Tetrahedron: Asymmetry* **2001**, *12*, 877; b) S. Kitagaki, Y. Yanamoto, H. Tsutsui, M. Anada, *Tetrahedron Lett.* **2001**, *42*, 6361; c) N. Shimada, S. Nakamura, M. Anada, M. Shiro, S. Hashimoto, *Chem. Lett.* **2009**, *38*, 488; Z. d) Li, V. Boyarskikh, J. H. Hansen, J. Autschbach, D. G. Musaev, H. M. L. Davies, *J. Am. Chem. Soc.* **2012**, *134*, 15497; e) J. Fu, H. Shang, Z. Wang, L. Chang, W. Shao, Z. Yang, Y. Tang, *Angew. Chem. Int. Ed.* **2013**, *52*, 4198; *Angew. Chem.* **2013**, *125*, 4292; f) H. Zhang, B. Wang, H. Yi, Y. Zhang, J. Wang, *Org. Lett.* **2015**, *17*, 3322.

Recently, a similar gold-catalyzed [2,3]-sigmatropic rearrangement has been reported by Prabhu's group, see: g) S. Rao, K. R. Prabhu, *Org. Lett.* **2017**, *19*, 846.

[23] *Gaussian 09*, revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. . Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc.: Wallingford, CT, **2009**.

[24] (a) E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 303 (b) B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151.

[25] (a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *7* 3865; (b) J. P. Perdew, K. Burke M., Ernzerhof, *Phys. Rev. Lett.* **199** *78*, 1396; (c) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158.

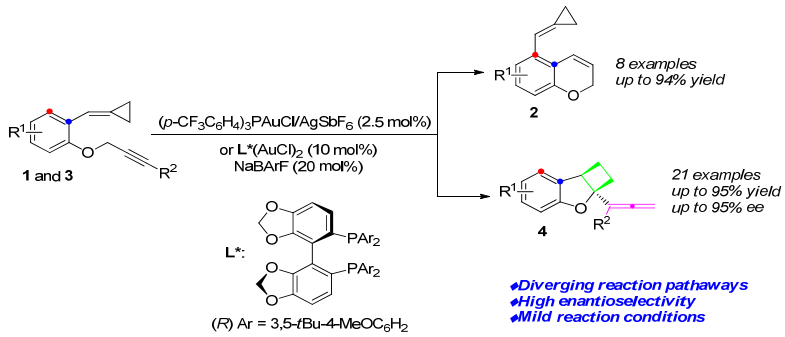
[26] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Chem. Phys. B* **200** *113*, 6378.

10.1002/chem.201700600

Gold Catalysis

Wei Fang, Yin Wei, Xiang-Ying Tang, and Min Shi* _____ **Page – Page**

Gold(I)-catalyzed cycloisomerization of *ortho*-(propargyloxy)arenemethylenecyclopropanes controlled by adjacent substituent at aromatic rings



We have developed a new strategy for the cycloisomerization along with carbon skeleton migration of ortho-(propargyloxy)arenemethylenecyclopropanes to attain migration products of methylenecyclopropane and intramolecular cycloisomerization products in good to excellent yields upon gold catalysis along with an asymmetric variant to give the product in an enantiomerically enriched manner.