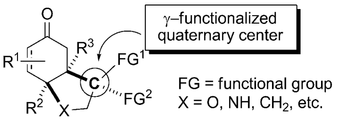
DOI: 10.1002/ange.201104028

Homogeneous Catalysis

Gold-Catalyzed [3+2] Cycloaddition/Hydrolytic Michael Addition/Retro-Aldol Reactions of Propargylic Esters Tethered to Cyclohexadienones[**]

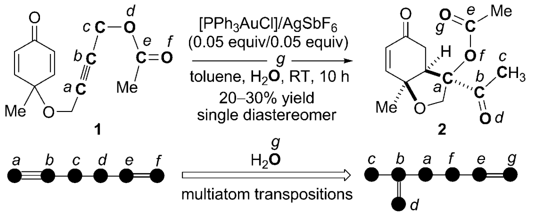
Shunyou Cai, Zheng Liu, Weibin Zhang, Xinyang Zhao, and David Zhigang Wang[*]

Functionalized cyclohexenones and cyclohexanones represent two recurring structural motifs found in many bioactive natural products.[1] Synthetically, a very important approach for accessing these compounds is to take advantage of the oxidative de-aromatization/conjugate addition sequence using the corresponding phenolic precursors.[2] In this context, a number of highly efficient catalysis methods have been established and can deliver the desired conjugate addition event with excellent reactivity and selectivity.[3] However, these methods usually fail when a putative nucleophile contains a hard and sterically demanding quaternary carbon center. Up to the present, there appears to be no generally useful method reported to adequately address this difficult problem.[4] A possible approach for the facile preparation of such cyclohexenones or cyclohexanones bearing a γ-quaternary stereogenic carbon center (Scheme 1) would therefore invite consideration of new catalysis scenarios. Ideally, such an approach, once defined, would not only yield cyclohexenone or cyclohexanone rings with γ-quaternary moieties in high regio- and stereocontrol, but also enable the operation to be applied to related quaternary carbon residues (FG^1 and FG^2) for additional structural and functional editing.



Scheme 1. Cyclohexenones or cyclohexanones bearing stereogenic γ-functionalized quaternary centers.

We report herein our recent discovery of a formal gold-catalyzed tandem [3+2] cycloaddition/hydrolytic Michael addition/retro-aldol sequence that offers a surprisingly simple and efficient solution to the above challenge under very mild reaction conditions. Upon treating the prochiral propargylic-acetate-tethered cyclohexadienones **1** at room temperature with equal amounts (5% mol each) of $[PPh_3AuCl]$ and $AgSbF_6$ in toluene under an atmosphere of air (i.e., not predried), it was found that the cyclohexenone products **2**, functionalized with a γ-quaternary ketoester, were formed in 20–30% yield upon isolation and with complete diastereomeric control (Scheme 2). As suggested by a mechanistic analysis (see below), it was remarkable that in this desymmetrization transformation up to four carbon atoms and three oxygen atoms appeared to have been formally transpositioned in a highly orchestrated multiple-bond rearrangement sequence.[5]



Scheme 2. Gold-catalyzed multiatom transposition reaction sequence leading to cyclohexenones functionalized with γ-quaternary center.

In an attempt to improve the catalysis efficiency under similar reaction conditions, we screened other potential catalyst systems for carbon–carbon triple bond π activation, including AgOTf (Tf = trifluorosulfonyl),[6] $PtCl_2$,[7] and $PtCl_2$/CO (1 atm)[7], but all resulted in failures. Fortunately, an interesting and useful "aryl effect" next emerged from the observation that the simple replacement of the acetate with benzoate (see structure **3** in Table 1) resulted in much cleaner reaction. By using this aryl propargylic ester as a new substrate, subsequent optimizations on the reaction revealed $[PPh_3AuCl]$/AgOTf to be the optimal catalyst combination, and that there was an important solvent effect. When the solvent was THF, MeCN, or 1,4-dioxane, the process was completely inhibited under otherwise identical reaction conditions; when the solvent was Et_2O or CH_2Cl_2, the product yield was improved to 62% and 78%, respectively; and when the solvent was 1,2-dichloroethane (DCE), the yield was markedly increased to greater than 90%. The catalyst loading could be reduced to 2% mol without affecting the reaction, but we decided to employ 4 mol% so as to achieve a practical reaction time and product yield. Interestingly, the reproduciblity of the reaction necessitated water as the reaction yielded no product when run under a nitrogen atmosphere or

---

[*] S. Y. Cai, Z. Liu, W. B. Zhang, X. Y. Zhao, Prof. D. Z. Wang
Key Laboratory of Chemical Genomics, School of Chemical Biology and Biotechnology, Shenzhen Graduate School of Peking University
Shenzhen University Town, Shenzhen 518055 (China)
E-mail: dzw@szpku.edu.cn

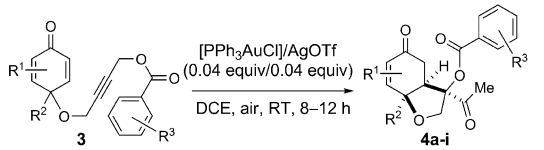
[**] We thank the National Natural Science Foundation of China (Grants 20872004 and 20972008), the national "973 Project" of the State Ministry of Science and Technology, the Shenzhen Bureau of Science and Technology, and the Shenzhen "Shuang Bai Project" for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104028.

strictly in dry air. However, when water was purposefully introduced into the solvent, the reaction gave rise to complex reaction mixtures. Thus, moist air was elected as a practically simple source of water. Under these conditions, the product could be obtained in 92 % yield in 8 hours.[8]

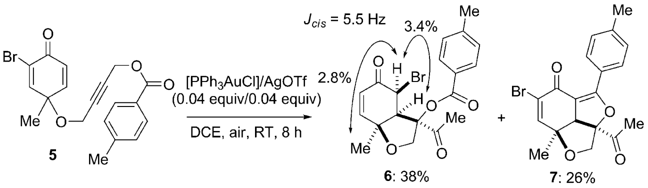
This technology could be readily extended to a series of other aryl propargylic-ester-tethered cyclohexadienones **3**, and the results are compiled in Table 1. The reactions generally finished in 8–12 hours and yielded the desired products containing two well-differentiated γ-quaternary carbon residues (acyl and ester) in good to excellent yields upon isolation(70–92 %). The reactions appeared to be stereospecific because in each of the cases examined, the corresponding product was as a single diastereomer. The R^2 substituent on the substrate's prochiral allylic carbon center had an influence on the catalysis efficiency; from **4a** to **4b** and **4c**, a decrease of product yield was observed with the increase in the steric bulk of R^2 (Table 1, entries 1–3). When unsymmetrical R^1-substituted cyclohexadienones were used, such as those in the cases of **4d** and **4e** (Table 1, entries 4 and 5), reaction was regiospecific and took place at the less-substituted enone double bonds. The electronic characteristics of the substituents (R^3) on the aromatic ring on the benzoates also played a significant role in affecting the reaction: when R^3 is electron releasing in nature (R^3 = Me, OMe, F, Cl, or Ph), the corresponding products (**4a** and **4f**–**4i**) were all obtained in high yields (Table 1, entries 1, and 6–9); when R^3 is a strong electron-withdrawing group, such as NO_2 or CF_3, the reactions gave complicated mixtures. Analogous aliphatic esters (such as *i*Pr, *t*Bu, and cyclohexyl esters) also gave relatively low product yields (< 30 %).

Table 1: Survey of the reaction scope.



Entry	4	R^1	R^2	R^3	Yield [%][a]
1	**4a**	H	Me	*p*-Me	92
2	**4b**	H	Et	*p*-Me	89
3	**4c**	H	*i*Pr	*p*-Me	70
4	**4d**	α Me	Me	*p*-Me	90
5	**4e**	β Me	Me	*p*-Me	91
6	**4f**	H	Me	*p*-OMe	88
7	**4g**	H	Me	*p*-F	87
8	**4h**	H	Me	*p*-Cl	89
9	**4i**	H	Me	1-naphthalenyl	85

[a] Yield of isolated product.

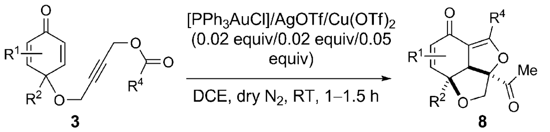


Scheme 3. Reactivity of the bromo-substituted cyclohexadienone **5**.

When the bromo-substituted cyclohexadienone **5** was examined, the reaction was found to proceed cleanly but in addition to the expected product **6** (isolated in 38 % yield), a new species, which we spectroscopically assigned to be the dihydrofuran-fused cyclohexenone **7**, was also obtained in 26 % yield (Scheme 3). The result not only implied that **7** might serve as an intermediate under catalysis conditions leading to the final ring-opened product, but also suggested the possibility of intercepting the reaction course for the purposeful preparation of such synthetically interesting and useful tricyclic ring skeletons.[9] A comparison on the structures of **6** and **7** showed the incorporation of an oxygen atom from an apparently external source, which in this system is the moist water. Accordingly, the dihydrofuran ring-opening seemed to have involved a gold-promoted hydrolytic conjugate addition and subsequent retro-Aldol event.[10]

Indeed, when the reactions were run under a strictly dry nitrogen atmosphere, the corresponding dihydrofuran-fused cyclohexenone products **8** were consistently isolated in good to excellent yields, and again with virtually complete diastereomeric control. Moreover, it was discovered that the reactions were significantly accelerated with $Cu(OTf)_2$ as a cocatalyst. Thus, with this new $[PPh_3AuCl]/Ag(OTf)/Cu(OTf)_2$ three-component catalyst system, the reactions were typically complete within just 1–1.5 hours. The results are summarized in Table 2. The steric influence of the R^1/R^2 substituents of **3** upon the reactivity was found to parallel those observed previously for the substrates in Table 1, but the formation of **8** was evidently more tolerant of variations on the ester substituent R^4. A variety of substrates carrying

Table 2: Preparation of dihydrofuran-fused cyclohexenones.

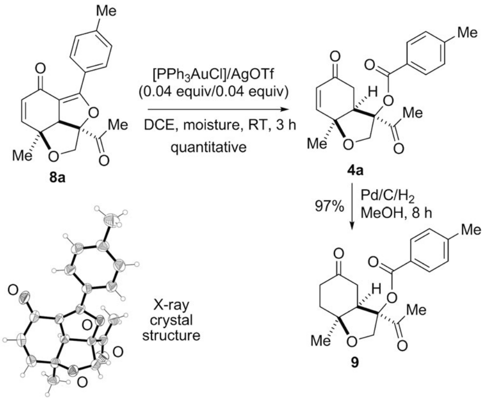


Entry	8	R^1	R^2	R^4	Yield [%][a]
1	**8a**	H	Me	*p*-MeC_6H_4	91
2	**8b**	H	Me	Ph	90
3	**8c**	H	Me	*p*-ClC_6H_4	89
4	**8d**	H	Me	*p*-FC_6H_4	92
5	**8e**	H	Me	*p*-$OMeC_6H_4$	83
6	**8f**	H	Me	*p*-$NO_2C_6H_4$	65
7	**8g**	H	Me	1-naphthalenyl	85
8	**8h**	H	Me	*o*-MeC_6H_4	91
9	**8i**	H	Me	furanyl	75
10	**8j**	H	Me	thiophenyl	82
11	**8k**	H	Et	*i*Pr	52
12	**8l**	H	*i*Pr	cyclohexyl	72
13	**8m**	H	Me	*t*Bu	85
14	**8n**	H	Me	*trans*-CH=CHPh	90
15	**8o**	H	Me	*p*-MeC_6H_4	86
16	**8p**	H	Me	*p*-MeC_6H_4	65
17	**8q**	α Me	*i*Pr	*p*-MeC_6H_4	83
18	**8r**	β Me	Me	*p*-MeC_6H_4	68

[a] Yield of isolated product.

electron-releasing (**8a**–**8e** and **8o**–**8r**) and electron-withdrawing (**8f**) aryl substituents worked smoothly (Table 2, entries 1–6, and 15–18). Furthermore, naphthalenyl (**8g**), *ortho*-substituted phenyl (**8h**), heterocyclic (**8i**–**8j**), aliphatic (**8k**–**8m**), as well as olefinic esters (**8n**) were all comparably efficient (Table 2, entries 8–14). Interestingly, it merits a note here that, in terms of steric effects, a larger R^4 group seemed to be beneficial, but not detrimental, to the observed reactivity. For example, for electronically similar systems, such as aromatic esters **8a** and **8h**, or aliphatic ones **8k**, **8l**, and **8m**, the reactions are comparable and even favorable with the increasing steric bulk of R^4. This trend is rather unexpected since, regardless of the detailed mechanistic pathways, the 1,2-acyloxy migration of $R^4C(O)$ towards an intramolecular nucleophilic attack on the gold-activated triple bond seems to be an inevitable step. These results, in conjunction with the aforementioned moist air versus water effect, implied a delicate operation of the interplay between kinetic and thermodynamic control in these systems.

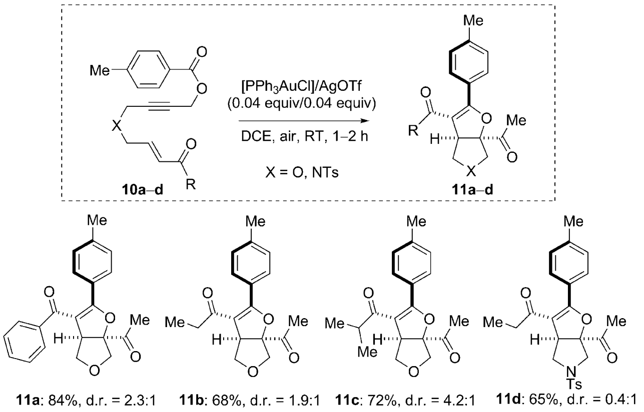
A single crystal of **8a** was successfully obtained and subjected to X-ray diffraction analysis, thus confirming unambiguously its stereochemical assignment (Scheme 4).



Scheme 4. X-ray crystal structure[18] and synthetic elaborations of **8a**. The thermal ellipsoids are shown at 30% probablilty.

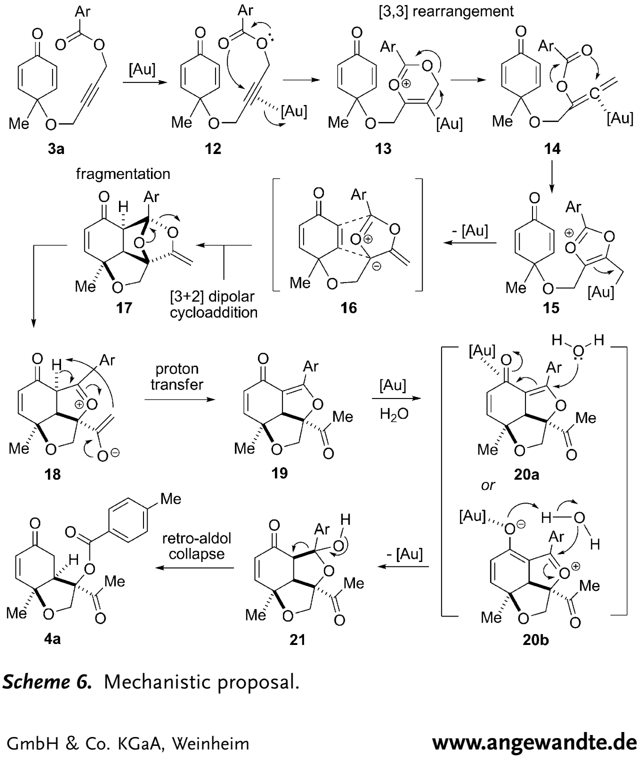
Notably, **8a** was found to be stable for days upon exposure to water with or without AgOTf, but was quickly converted into **4a** in quantitative yield when treated again with the standard catalysis conditions (i.e., 4% mol of $[PPh_3Au]/AgOTf$ and moist air), thus suggesting the critical role of the gold catalyst during the ring-opening event. Additionally, the enone double bond in **4a** was readily hydrogenated by Pd/C reagent, thus leading to the functionalized cyclohexanone **9** in 97% yield upon isolation.

It should be noted that although the cyclohexadienone-containing substrates **3** are highly attractive for additional structural manipulations, neither the cyclic enone moiety nor the oxygen atom linker is a structural requisite for the cascade reactivity outlined above. Simpler propargylic-ester-linked acyclic enones work with comparable efficiencies, thus significantly expanding the synthetic utility of the method. As shown in Scheme 5, the linear substrates **10a**–**d** readily cyclize to give **11a**–**d**, which feature not only the *cis*-fused tetrahydrofuran (or pyrrolidine) dihydrofuran motifs frequently found in many bioactive natural products,[11] but also stereochemically fascinating "inherently chiral" alkenes (helical chirality) that are generated by the steric overcrowding of the double bond substituents (with helical diastereomeric ratios ranging from 4.2:1 to 0.4:1).[12] These products do not undergo further ring-opening because of the apparent loss of planar geometry on their corresponding enone units (for example, the enone carbonyl in **11c** was found to have a significantly downfield-shifted resonance at $\delta = 201.0$ ppm).



Scheme 5. Reactivity of propargylic-ester-linked acyclic enones.

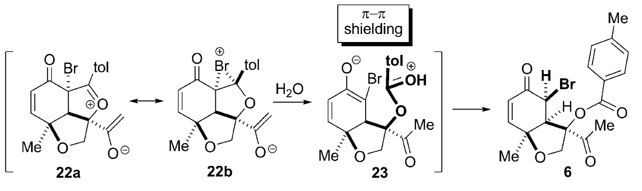
Mechanistically, we believe that these experimental findings collectively point to a cascade catalysis network that might involve a rare gold-promoted [3+2] cycloaddition/ hydrolytic Michael addition/retro-aldol reaction sequence. Such a proposal is illustrated in Scheme 6. With the substrate **3a** as a model system that is electronically and sterically unbiased in its local propargylic positions,[13a–b] the cascade is triggered by electrophilic activation of the alkyne triple bond



Scheme 6. Mechanistic proposal.

in the Au^{I}-complexed intermediate **12**, upon which a subsequent attack by the ester carbonyl group and [3,3] rearrangement/[2,3]-shift[13] generates the gold-coordinated allene species **14**. Carbonyl addition to this allene and concomitant allylic elimination of the gold catalyst yields a 1,3-dipole which then undergoes [3+2] cycloaddition[14] with the enone double bond via the transition-state **16** to give the vinyl ketal **17**.[15] The significant rate acceleration effect brought about by the Lewis acidic cocatalyst Cu(OTf)$_2$ in reactions of Table 2 may thus be rationalized by its activation to the enone system. Next, strain release drives a vinyl ketal fragmentation in **17** to generate the putative zwitterionic intermediate **18**, in which a rapid intramolecular proton-transfer event produces the dihydrofuran-fused cyclohexenone **19**. Therefore in the absence of any moisture, **19** was the experimentally observed product. The conversion of **19** into the final product **4a** requires the participation of both water and Au^{I} catalysis. The activation of **19** by the soft gold metallic center likely proceeded through the complexation of its enone π system with the catalyst (**20a**), and nucleophilic attack to the enone by water would yield the labile hemiketal species **21**, which upon a retro-aldol collapse produces **4a**. It should be emphasized here that the above-mentioned aryl effect upon promoting this catalysis is seen in the transformation of **19** into **4a**, a transformation that was found to depend on the presence of a phenyl group. We have found that when R^4 is a heterocyclic (furanyl or thiophenyl) or an aliphatic group (Table 2, entries 9 and 10), the resultant products **8** could not be converted cleanly into their final ring-opened γ-functionalized compounds **4**. These results may imply that an electronically highly polarized (therefore considerably soft) enone–phenyl extended π system is critical for its complexation with the gold center and subsequent electrophilic activation. This electronic polarization effect, in conjunction with the unique bowl-shaped tricyclic skeletal twisting in **19**, may in turn suggest an alternative possibility that the initial enone–gold π activation could stimulate charge separation to give a new zwitterionic intermediate, that is, the gold–enolate/oxonium **20b**.[16] The compound **20b** then reacts with water to yield **4a** following the same retro-aldol pathway.

Within the above mechanistic framework, the reaction in Scheme 4 involving the bromo-substituted substrate **5** clearly requires a refined pathway as an intramolecular proton-transfer event in **18**→**19** would become impossible. A plausible proposal (Scheme 7) may leverage on the stabilization of the initially formed cation **22a** by the bromonium ion resonance structure **22b**. The subsequent water trapping followed by charge separation would yield the new bromo-enolate species **23**, in which a protonation event occurrs exclusively from the back face of the enolate (unshielded by the π–π stacking effect) to give **6** with the indicated relative stereochemistry.[17]



Scheme 7. Refined reaction pathway leading to **6**.

In summary, by subjecting a series of propargylic-ester-tethered cyclohexadienones and acyclic enones to gold catalysis under mild reaction conditions, we discovered a unique cascade process that leads to simultaneous multiatom transpositions in an essentially stereospecific manner. The mechanistic course is believed to follow a highly orchestrated sequence: enone [3+2] cycloaddition/hydrolytic Michael addition/retro-aldol collapse. Other π-activating transition-metal catalysts were found inactive under otherwise similar reaction conditions, thus suggesting that the judicious combination of highly polarized enone–aryl π systems with Au^{I} catalysts are important for synergistic electrophilic activation. By modulating the participation of water, the methodology can be diverted to purposeful construction of either dihydrofuran-fused cyclohexenones, or cyclohexenones and cyclohexanones bearing a γ-quaternary stereogenic carbon center amenable to additional structural editing. Given the importance of these common structural skeletons that are present in bioactive natural products, and the simplicity in implementing such cascade catalysis methodologies, it can be anticipated that these technologies will find their synthetic utility in the stereoselective preparations of pharmaceutically meaningful compounds and libraries of their structural mimics. Ongoing efforts along these lines will be reported in due course.

Received: June 12, 2011
Revised: July 30, 2011

Keywords: cycloaddition · gold · heterocycles · homogeneous catalysis · synthetic methods

---

[1] For bioactive natural products having cyclohexenone or cyclohexanone substructures, see: a) J.-T. Zhang, X.-P. Cao, *J. Org. Chem.* **2011**, *76*, 3946–3959; b) J. C. Kwan, H. Luesch, *J. Nat. Prod.* **2010**, *73*, 463–466; c) Y. Kan, Y. Hokama, *J. Nat. Prod.* **1998**, *61*, 152–155; d) K. L. Malloy, W. H. Gerwick, *J. Nat. Prod.* **2011**, *74*, 95–98; e) F. A. Marques, M. N. Eberlin, *J. Nat. Prod.* **2004**, *67*, 1939–1941; f) J. M. David, G. A. Cordell, *J. Nat. Prod.* **1998**, *61*, 287–289; g) N. D. Tommasi, A. Braca, *J. Nat. Prod.* **2001**, *64*, 892–895.

[2] For some applications of phenol oxidative dearomatization/conjugate addition methods, see: a) G. Lemière, J. Clayden, *Chem. Commun.* **2011**, *47*, 3745–3747; b) Q.-F. Wu, S.-L. You, *Angew. Chem.* **2011**, *123*, 4547–4550; *Angew. Chem. Int. Ed.* **2011**, *50*, 4455–4458; c) J. Cornelisse, *Chem. Rev.* **1993**, *93*, 615–669.

[3] For a recent review on asymmetric conjugate additions, see: R. H. Syuzanna, D. H. Tim, G. Koen, J. M. Adriaan, L. F. Ben, *Chem. Rev.* **2008**, *108*, 2824–2852.

[4] Examples of natural products containing γ-functionalized quaternary centers of cyclohexenones or cyclohexanones: a) B. Victoria, B. Gonzalo, C. Luz, G. Begoña, R. P. José, *J. Nat. Prod.* **2002**, *65*, 1703–1706; b) H. Lee, S. H. Shim, *Helv. Chim. Acta* **2011**, *94*, 643–649; c) G. Li, F. Liu, L. Shen, H. Zhu, K. Zhang, *J. Nat. Prod.* **2011**, *74*, 296–299.

[5] For recent reviews on gold catalysis, see: a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; b) A. S. K. Hashmi, *Chem.*

Rev. **2007**, *107*, 3180–3211; c) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403; d) L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271–2296; e) S. Ma, S. Yu, Z. Gu, *Angew. Chem.* **2006**, *118*, 206–209; *Angew. Chem. Int. Ed.* **2006**, *45*, 200–203; f) A. Corma, A. Leyva-Perez, M. J. Sabater, *Chem. Rev.* **2011**, *111*, 1657–1712; g) M. Bandini, *Chem. Soc. Rev.* **2011**, *40*, 1358–1367; h) N. Krause, C. Winter, *Chem. Rev.* **2011**, *111*, 1994–2009; For recent closely relevant applications: i) T. Luo, S. L. Schreiber, *Angew. Chem.* **2007**, *119*, 8398–8401; *Angew. Chem. Int. Ed.* **2007**, *46*, 8250–8253; j) T. Luo, S. L. Schreiber, *J. Am. Chem. Soc.* **2009**, *131*, 5667–5674; k) J. Zhao, C. O. Hughes, F. D. Toste, *J. Am. Chem. Soc.* **2006**, *128*, 7436–7437; l) A. S. Dudnik, T. Schwier, V. Gevorgyan, *Org. Lett.* **2008**, *10*, 1465–1468.

[6] For recent work on catalytic activations of alkynes by AgOTf, see: a) C. H. Oh, S. Karmakar, H. Park, Y. Ahn, J. W. Kim, *J. Am. Chem. Soc.* **2010**, *132*, 1792–1793; b) R. F. Sweis, M. P. Schramm, S. A. Kozmin, *J. Am. Chem. Soc.* **2004**, *126*, 7442–7443.

[7] For recent reviews on PtCl$_2$ catalysis, see: a) R. A. Widenhoefer, X. Han, *Eur. J. Org. Chem.* **2006**, 4555–4563; b) A. Fürstner, P. W. Davis, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; for initial observation of CO acceleration of PtCl$_2$ catalysis, see: c) A. Fürstner, P. W. Davies, T. Gress, *J. Am. Chem. Soc.* **2005**, *127*, 8244–8245; for a recent application of PtCl$_2$/CO system, see: d) H. Zheng, J. Zheng, B. Yu, Q. Chen, X. Wang, Y, He, Z. Yang, X. She, *J. Am. Chem. Soc.* **2010**, *132*, 1788–1789.

[8] For recent work on desymmetrization of cyclohexadienones, see: a) Q. Gu, Z.-Q. Rong, C. Zheng, S.-L. You, *J. Am. Chem. Soc.* **2010**, *132*, 4056–4057; b) R. Tello-Aburto, A. M. Harned, *Org. Lett.* **2009**, *11*, 3998–4000.

[9] For reports on dihydrofuran-fused cyclohexenones, see: a) P. Albin, J. Blum, E. Dunkelblum, Y. Sasson, *J. Org. Chem.* **1975**, *40*, 2402–2403; b) R. D. Shailesh, K. G. Vinayak, V. B. Sujata, *J. Org. Chem.* **1992**, *57*, 2467–2468; c) R. Chuard, A. Giraud, P. Renaud, *Angew. Chem.* **2002**, *114*, 4497–4499; *Angew. Chem. Int. Ed.* **2002**, *41*, 4321–4323.

[10] The resistance of **7** towards hydrolytic dihydrofuran ring opening should originate from the bromo substitution that likely retards activation of the enone carbonyl group by gold (analogous to structures **20a–b**) through competitive steric and/or electronic Br–Au interactions.

[11] For some illustrative examples, see: a) B. Zhao, J. Chang, Q. Wang, Y. Du, K. Zhao, *Synlett* **2008**, 2993–2996; b) R. W. Fitch, T. F. Spande, H. M. Garraffo, J. C. H. Yeh, J. W. Daly, *J. Nat. Prod.* **2010**, *73*, 331–337; c) T. Fukuda, Y. Sakabe, H. Tomoda, S. Omura, *Chem. Pharm. Bull.* **2006**, *54*, 1659–1661.

[12] Helically inherent chiral alkenes can be important building blocks for so-called chiroptical molecular switches. See: B. L. Feringa, *Acc. Chem. Res.* **2001**, *34*, 504–513.

[13] a) P. Mauleón, J. L. Krinsky, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 4513–4520; for reviews, see: b) S.-Z. Wang, G.-Z. Zhang, L. Zhang, *Synlett* **2010**, 692–706; c) J. Marco-Contelles, E. Soriano, *Chem. Eur. J.* **2007**, *13*, 1350–1357; d) References [5b and d].

[14] For recent work on gold-catalyzed [3+2] cycloadditions, see: a) A. D. Melhado, M. Luparia, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 12638–12639; b) A. D. Melhado, G. W. Amarante, Z. J. Wang, M. Luparia, F. D. Toste, *J. Am. Chem. Soc.* **2011**, *133*, 3517–3527; c) G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2008**, *130*, 12598–12599; d) X. Huang, L. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 6398–6399; e) C.-Y. Yang, C.-D. Wang, S.-F. Tian, R.-S. Liu, *Adv. Synth. Catal.* **2010**, *352*, 1605–1609; f) C.-W. Li, G.-Y. Lin, R.-S. Liu, *Chem. Eur. J.* **2010**, *16*, 5803–5811; g) N. Kim, Y. Kim, W. Park, D. Sung, A. K. Gupta, C. H. Oh, *Org. Lett.* **2005**, *7*, 5289–5291; h) H. Kusama, Y. Miyashita, J. Takaya, N. Iwasawa, *Org. Lett.* **2006**, *8*, 289–292; i) D. V. Partyka, J. B. Updegraff III, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2007**, *26*, 183–186; j) A. Adé, E. Cerrada, M. Contel, M. Laguna, P. Merino, T. Tejero, *J. Organomet. Chem.* **2004**, *689*, 1788–1795.

[15] Alternatively, a stepwise mechanism might be proposed and involve the addition of allyl Au to the enone followed by intramolecular enolate trapping. However, such a pathway would likely be retarded by the significant steric volume residing on this tertiary Au nucleophile. For a relevant study, see: M. Uemura, I. D. G. Watson, M. Katsukawa, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 3464–3465.

[16] For the first report on the X-ray structure of a gold enolate, see: a) Y. Ito, M. Inouye, M. Suginome, M. Murakami, *J. Organomet. Chem.* **1988**, *342*, C41–C44; for catalysis involving an oxonium/Au/enolate species, see: b) J.-M. Tang, T.-A. Liu, R.-S. Liu, *J. Org. Chem.* **2008**, *73*, 8479–8483.

[17] For an example of enolate chemistry involving π–π stacking, see: M. Stefano, G. N. Ana, F. M. Carlos, *J. Org. Chem.* **2009**, *74*, 6888–6890.

[18] CCDC 845089 (**8a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif