Carbenes

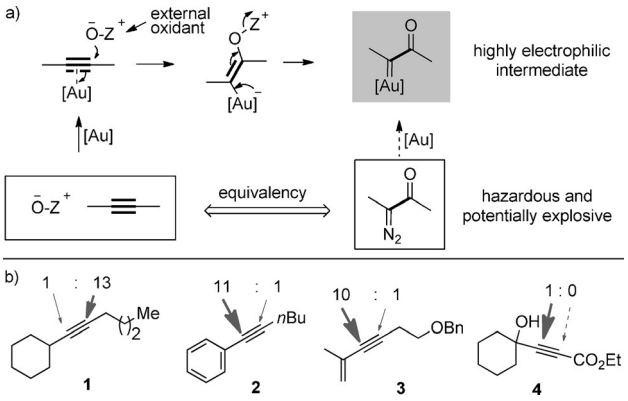
International Edition: DOI: 10.1002/anie.201504511
German Edition: DOI: 10.1002/ange.201504511

A Desulfonylative Approach in Oxidative Gold Catalysis: Regiospecific Access to Donor-Substituted Acyl Gold Carbenes

*Hongyi Chen and Liming Zhang**

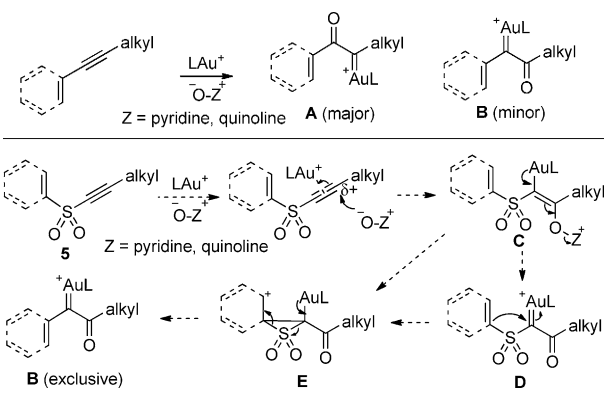
Abstract: *Donor-substituted acyl gold carbenes are challenging to access selectively by gold-promoted intermolecular oxidation of internal alkynes as the opposite regioisomers frequently predominate. By using alkynyl sulfones or sulfonates as substrates, the oxidative gold catalysis in the presence of substituted pyridine N-oxides offers regiospecific access to acyl/aryl, acyl/alkenyl, and acyl/alkoxy gold carbenes by in situ expulsion of sulfur dioxide. The intermediacies of these reactive species are established by their reactivities, including undergoing further oxidation by the same oxidant, cyclopropanation of styrenes, engaging in a [3+2] cycloaddition with α-methylstyrene, and conversion into dienones.*

Gold-catalyzed intermolecular oxidation of alkynes[1] has become an increasingly popular approach to accessing highly electrophilic α-oxo gold carbene intermediates since the first report in 2010[2] (Scheme 1a). This strategy permits ready explorations of these reactive intermediates without resorting to hazardous and potentially explosive diazo ketone precursors,[3] and thereby facilitates the development of versatile synthetic methods.[2,4,5] While terminal alkynes are most frequently oxidized to terminal gold carbene intermediates, regioselective oxidations of internal alkynes can be challenging, and often only one of the two regioisomers can be accessed selectively based on structural biases and on optimizations of catalyst, oxidant, and other reaction conditions. For example, in our previous work,[6] under optimal reaction conditions, differences in steric bulk at the two ends of the alkyne were used to achieve selective oxygen delivery to the less hindered C(sp) (e.g., **1**; Scheme 1b), and with electronically biased internal alkynes oxidation occurs selectively at the end which best accommodates the developing positive charge upon gold coordination, that is, proximal to aryl, alkenyl, and *N*-amido groups (e.g., **2** and **3**;[7] Scheme 1b)[5l-o,6] and distal to electron-withdrawing groups (e.g., **4**; Scheme 1b).[4f,5e,f] There is, however, no viable approach to generating α-oxo gold carbenes selectively with regiochemistries opposite to the structurally preferred ones, let alone regiospecifically. Hence, the potentially rich reactivities of the minor regioisomeric gold carbenes could not be readily explored. Herein, we disclose a solution to this challenge with regard to arylalkyne, enyne, and alkoxyalkyne by using a desulfonylative strategy, and explore the reactivities of these regiospecifically generated donor-substituted acyl carbenes, including acyl/aryl, acyl/alkenyl, and acyl/alkoxy gold carbenes. Notably, most of these types of carbenes[5a] studied so far are generated either from the corresponding diazo precursors[,3j] or by oxidation of activated aryl/alkenyl-terminated ynamides, instead of typical internal alkynes.[5b,o]



Scheme 1. A) Oxidative gold catalysis: a facile, non-diazo access to α-oxo gold carbenes. B) Examples of regioselective oxidative gold catalysis with the optimized ratios shown.

Our approach is shown in Scheme 2. While arylalkynes and enynes would often lead to selective generation of the α-oxo gold carbene **A** over its regioisomer **B**, which is an acceptor- and donor-substituted gold carbene, it is envisioned that **B** could be generated exclusively from a different class of substrates, namely, alkynyl sulfones (**5**). Hence, upon its coordination to a cationic gold(I) catalyst, the C≡C bond, polarized by the electron-withdrawing sulfonyl group, should



Scheme 2. A desulfonylative approach toward exclusive generation of the typically minor α-oxo gold carbene intermediates.

[*] H. Chen, Prof. Dr. L. Zhang
Department of Chemistry and Biochemistry, University of California Santa Barbara, CA (USA)
E-mail: zhang@chem.ucsb.edu
Homepage: http://www.chem.ucsb.edu/~zhang/index.html

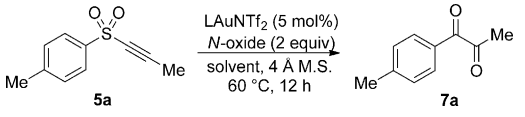
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201504511.

be attacked by a *N*-oxide regiospecifically at the β-C(sp). Such a process, followed by redox rearrangement, would lead to the dual acceptor-substituted gold carbene intermediate **D**. The carbene moiety is likely to be highly electrophilic, and could react intramolecularly with the aryl/alkenyl group on the other side of the sulfonyl group, thus leading to the formation of the episulfone intermediate **E**. Alternatively, this intermediate could be formed directly from the initial adduct **C**, that is, the precursor to the carbene **D**, by a 3-*exo*-*trig* cyclization.[5p] The desulfonylative fragmentation of **E**[8] would then afford only the α-oxo gold carbene **B**. It is noteworthy that **B** is a donor-substituted acyl gold carbene and should display a reactivity which is characteristically different from those without donor substitution.

As shown in Table 1, we set out to validate the above design and discover optimal reaction conditions by using the readily prepared[9] alkynyl sulfone **5a** as the substrate. It is anticipated that the gold carbene of type **B** could be further oxidized by the same *N*-oxide to deliver the corresponding 1,2-diketone **7a**. When the Gagosz catalyst $Ph_3PAuNTf_2$[10] was employed with DCE as the solvent and 2,6-dichloropyridine *N*-oxide (**6a**) as the oxidant, the desired product **7a** was indeed formed, albeit in a low 15% yield (entry 1). Subsequent catalyst screenings revealed that the N-heterocyclic-carbene-based catalyst $IPrAuNTf_2$ performed noticeably better (entries 2–5). Given our concern over potential chloride abstraction[11] of the solvent DCE by highly electrophilic gold carbene intermediates of type **C**, we used $PhCF_3$ instead. Much to our delight, the reaction yield was improved to a decent 72% (entry 6). Our ensuing screenings of the *N*-oxides revealed large variations of reaction efficiencies (entries 7–10). Among them, 2-*tert*-butyl-4-chloropyridine *N*-oxide (**6c**), first reported by Gagosz,[5i] proved to be the most effective (entry 8), and **7a** was isolated in 80% yield. It is notable that **7a** could not be generated cleanly by gold-catalyzed double oxidation[5k,12] of the corresponding 1-methyl-4-(prop-1-yn-1-yl)benzene, as facile 1,2-C–H insertions by the isomeric gold carbenes of type **A** would lead to the formation of enone side products.[6,13]

We explored the scope of this desulfonylative double oxidation chemistry. As shown in Table 2, the *p*-tolyl group of **5a** could be replaced with either an electron-rich 4-methoxyphenyl (entry 1) or a slightly electron-deficient 4-bromophenyl (entry 2). The reaction yields correlated well with the trend of the benzene ring reacting with electrophiles and are consistent with the envisioned reaction mechanism. When the alkynyl terminal methyl group was replaced with a *n*-butyl group in **5d** (entry 3), the desired 1,2-diketone **7d** was formed in only 19% yield. Instead, the sulfonylcyclopentanone **7d′** was isolated in 54% yield. This side product must be the result of C–H insertion[4h] by an acyl/sulfonyl-substituted gold carbene of type **D**. It was envisioned that a more-electron-rich phenyl ring in **D** could accelerate its desulfonylative rearrangement, thereby minimizing side reactions. Indeed,

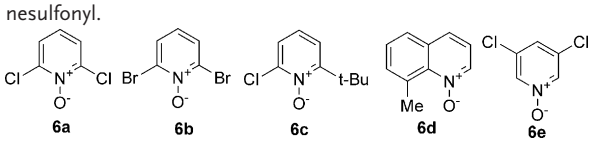
Table 1: Optimization of reaction conditions for double oxidation.[a]



5a **7a**

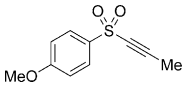
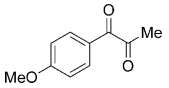
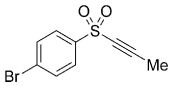
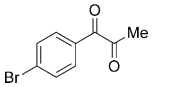
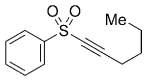
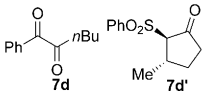
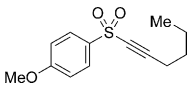
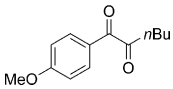
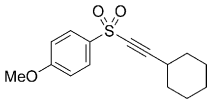
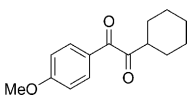
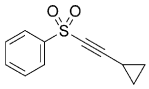
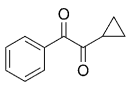
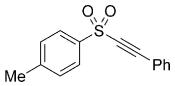
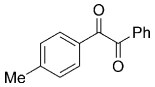
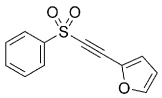
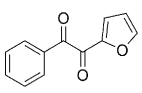
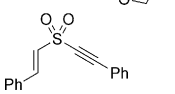
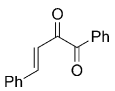
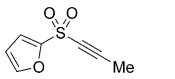
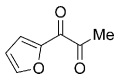
Entry	L	Solvent	*N*-Oxide	Yield [%][b]	Conv. [%]
1	PPh_3	DCE	**6a**	15	57
2	$(2,4\text{-}tBu_2PhO)_3P$	DCE	**6a**	8	40
3	Mor-DalPhos	DCE	**6a**	10	100
4	$tBuMe_4XPhos$	DCE	**6a**	17	93
5	IPr	DCE	**6a**	22	45
6	IPr	$PhCF_3$	**6a**	72	100
7	IPr	$PhCF_3$	**6b**	32	61
8	IPr	$PhCF_3$	**6c**	80[c]	100
9	IPr	$PhCF_3$	**6d**	8	91
10	IPr	$PhCF_3$	**6e**	20	96

[a] All reactions were run in sealed vials. [b] Determined by ^1H NMR analysis using diethyl phthalate as an internal reference. [c] Yield of isolated product. DCE = 1,2-dichloroethane, IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene, M.S. = molecular sieves, Tf = trifluoromethanesulfonyl.



6a **6b** **6c** **6d** **6e**

Table 2: Scope of desulfonylative double oxidation.[a]

Entry	5	7	Yield [%]
1		**5b** 	**7b** 96
2		**5c** 	**7c** 59
3		**5d**  **7d** **7d′**	19 (54)[b]
4		**5e** 	**7e** 69[c]
5[d]		**5f** 	**7f** 65[c]
6[d]		**5g** 	**7g** 67
7		**5h** 	**7h** 78
8[d]		**5i** 	**7i** 60
9[d]		**5j** 	**7j** 75
10[d]		**5k** 	**7k** 87

[a] The reactions were run using the optimized reaction conditions (i.e., Table 1, entry 8), and the yield of isolated product is reported. [b] Yield of the C–H insertion product **7d′**. [c] C–H insertion product < 5%. [d] **6a** used as oxidant.

with the anisyl sulfone substrate **5e**, the double oxidation displayed a much improved yield, while the C–H insertion product was formed in less than 5% yield (entry 4). Similarly, a cyclohexyl group at the alkyne terminus was allowed (entry 5). In addition, the alkyne terminus could accommodate a cyclopropyl (entry 6), a phenyl (entry 7), and a furan-2-yl (entry 8) group, the last two of which allowed regiospecific generation of diaryl-substituted α-oxo gold carbenes by simply using appropriate aryl alkynyl sulfone substrates. Besides phenyl-based sulfones, a *trans*-β-styryl sulfone (**5j**; entry 9) and a furan-2-yl sulfone (**5k**; entry 10) underwent the reaction without incident, thus affording the diketone products **7j** (75%) and **7k** (87%), respectively. Of note, in some cases (entries 5,6, and 8–10), 2,6-dichloropyridine *N*-oxide (**6a**) was more efficient than **6c**.

While these results are consistent with acyl gold carbene intermediates of type **B**, the fact that the C≡C bond is oxidized into a symmetric 1,2-dicarbonyl moiety prevented us from unequivocally establishing the regiochemistry of these carbenes, despite the difficulty in formulating an alternative mechanism for the formation of its isomer **A**. Liu and coworkers[14] previously demonstrated that that carbenes related to **B**, which are generated by intramolecular alkyne oxidation, can undergo cyclopropanation reactions with styrenes. When the oxidation of the alkynyl sulfone **5a** was performed in the presence of styrene, the intended cyclopropanation reaction indeed occurred, and the cyclopropyl ketone **8a** was formed selectively in 80% yield upon isolation (Table 3). This result offers strong support for the regiospecific generation of gold carbenes of the type **B**, and reveals that the pyridine byproduct does not interfere the intermolecular cyclopropanation. The reaction scope was then examined. As shown (**8b–e**), the aryl sulfones **5** with different aryl groups, including furan-2-yl (**8d**), underwent the reaction smoothly. The terminal substituents of the alkyne could be either a phenyl (**8e**) or a cyclopropyl (**8f**). Our attempt to vary the styrene led to successful reaction with 4-bromostyrene (**8g**) and 4-*tert*-butylstyrene (**8h**), but in the case of 4-methoxystyrene, polymerization occurred during the reaction. Other electron-rich alkenes, such as ethyl vinyl ether, were also not suitable.

With α-methylstyrene as a solvent, a stepwise, formal [3+2] cycloaddition occurred, thus affording the dihydrofuran **9** in a serviceable yield (Table 3).[5a] This divergent reactivity can be understood by considering that the benzylic position of the styrene can better accommodate positive charge and has increased steric hindrance, both of which disfavor the expected concerted cyclopropanation reaction.

The success with the β-styryl sulfone **5j** (Table 2, entry 9) encouraged us to examine other alkenyl sulfones. As shown in Equation (1), the 2-methylprop-1-en-1-yl sulfone **5l** underwent the gold-catalyzed oxidative desulfonylation, but the isolated product was the *trans*-dienone **10**, instead of the corresponding diketone. Our attempt to trap the alkenyl acyl gold carbene intermediate with styrene was futile. This result highlights the facile nature of the carbene to undergo E1-type elimination under the reaction conditions, as outlined in the equation. With the cyclohexen-1-yl sulfone **5m** as the substrate, the expected dienone product **11** was isolated, along with the bicyclic furan **12** [Eq. (2)]. The formation of the latter product should involve a 4π electrocyclic ring closure, which is in line with the related work reported by the group of Liu[5b] and ourselves.[15]

To further investigate the desulfonylative carbene rearrangement, we surmised that instead of an aryl or alkenyl group an alkoxy might behave in a similar manner, thereby leading to the generation of a new type of donor/acceptor-

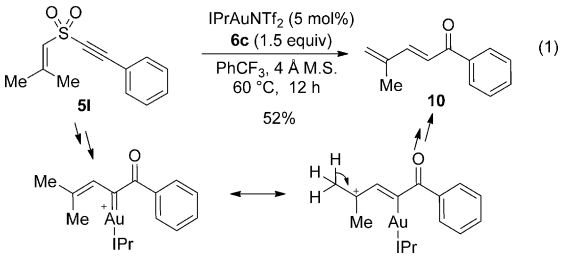
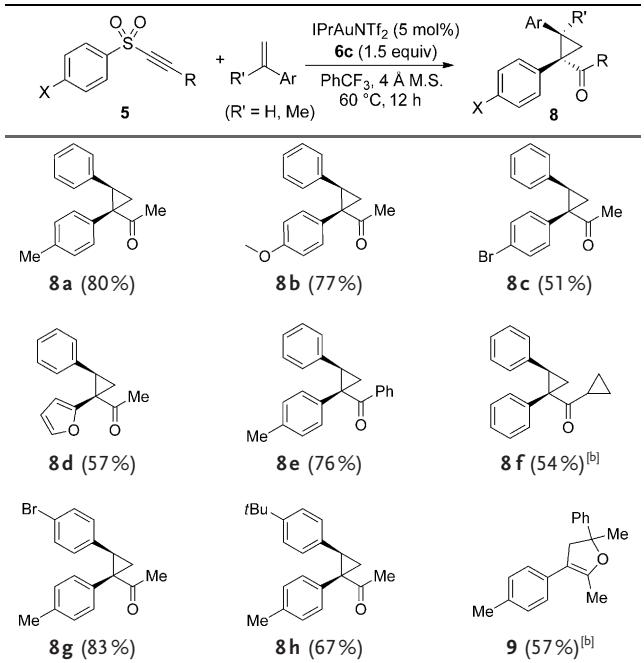
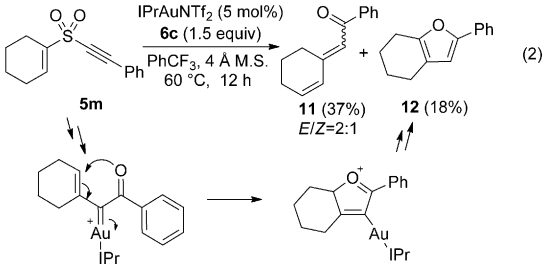
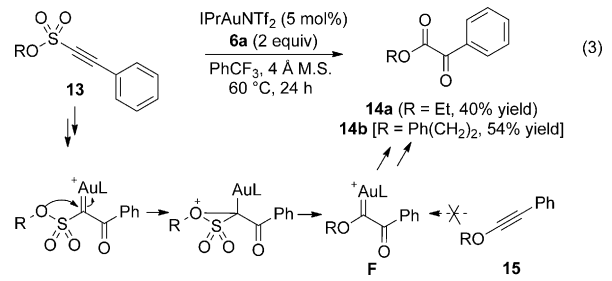


Table 3: Cyclopropanation with styrenes: Scope.[a]



[a] All reactions run in vials. The oxidant was introduced by syringe pump over a 12 h period, and the product d.r. > 95:5. [b] **6b** was used as the oxidant, and α-methylstyrene as solvent.

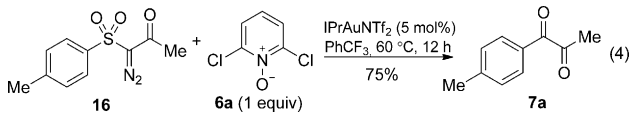




(3)

substituted gold carbenes, that is, the acyl/alkoxy gold carbenes **F** [Eq. (3)]. When the alkynesulfonates **13** were subjected to the reaction, the α-ketoesters **14**, apparently resulting from further oxidation of the gold carbene intermediates, were indeed formed, albeit with moderate yields in both cases. In these cases, **6a** was a better oxidant than **6c** as slower reactions and lower yields were observed with the latter (e.g., 2 days, ca. 14% yield). Notably, **F** could not be possibly derived from the alkynyl ethers **15** by direct oxidative gold catalysis because of their opposite polarized nature, even though the same diketone products might be formed from these electron-rich alkynes under the same gold catalysis via isomeric gold carbene intermediates.

To further corroborate the initial oxidative generation of the gold carbene **D** and its subsequent desulfonylative rearrangement into **B** (Scheme 2), we prepared the α-sulfonyl-α-diazoacetone **16** and subjected it to the optimal reaction conditions, with the only exception being the use of 1 equivalent of **6a** [Eq. (4)]. Indeed, the diketone **7a** was



(4)

formed smoothly in 75% yield, which was slightly higher than that of our oxidative gold catalysis (Table 1, entry 6). However, the desulfonylative cyclopropanation reaction with **16** was not successful.

In summary, we have implemented a novel approach to achieving regiospecific generation of donor-substituted acyl gold carbenes. These intermediates are either often formed as minor isomers, or cannot not be generated at all from the corresponding donor-substituted alkynes because the polarization of the π bonds upon coordination to gold leads selectively to the opposite regioisomer. With alkynyl sulfones or alkynesulfonates as substrates, the oxidative gold catalysis using substituted pyridine *N*-oxides as oxidants provide regiospecific access to acyl/aryl, acyl/alkenyl, and acyl/alkoxy gold carbenes by expulsion of sulfur dioxide. These underexplored carbenes can readily undergo further oxidation by the same oxidant, cyclopropanate styrenes, undergo [3+2] cycloaddition with α-methylstyrene, and be converted into dienones. Having established access to the carbenes and their basic reactivities, the synthetic utilities of these intermediates will soon be explored in ring-forming intramolecular processes.

Acknowledgements

We acknowledge support from the NSF (CHE-1301343), the NIH shared instrument grant (S10OD012077) for a 400 MHz NMR instrument, and the NSF MRSEC (DMR-1121053) and the NSF (CNS-0960316) for the Center for Scientific Computing from the CNSI and MRL.

Keywords: carbenes · gold · oxidation · sulfur · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 11775–11779
Angew. Chem. **2015**, *127*, 11941–11945

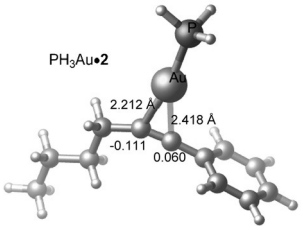
[1] L. Zhang, *Acc. Chem. Res.* **2014**, *47*, 877–888.
[2] L. Ye, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 3258–3259.
[3] a) M. P. Doyle, M. A. McKervey, T. Ye, *Modern catalytic methods for organic synthesis with diazo compounds: from cyclopropanes to ylides*, Wiley, New York, **1998**; b) M. R. Fructos, T. R. Belderrain, P. de Fremont, N. M. Scott, S. P. Nolan, M. M. Diaz-Requejo, P. J. Perez, *Angew. Chem. Int. Ed.* **2005**, *44*, 5284–5288; *Angew. Chem.* **2005**, *117*, 5418–5422; c) A. Prieto, M. R. Fructos, M. Mar Díaz-Requejo, P. J. Pérez, P. Pérez-Galán, N. Delpont, A. M. Echavarren, *Tetrahedron* **2009**, *65*, 1790–1793; d) S. K. Pawar, C.-D. Wang, S. Bhunia, A. M. Jadhav, R.-S. Liu, *Angew. Chem. Int. Ed.* **2013**, *52*, 7559–7563; *Angew. Chem.* **2013**, *125*, 7707–7711; e) V. V. Pagar, A. M. Jadhav, R.-S. Liu, *J. Org. Chem.* **2013**, *78*, 5711–5716; f) A. M. Jadhav, V. V. Pagar, R.-S. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 11809–11813; *Angew. Chem.* **2012**, *124*, 11979–11983; g) Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu, J. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 6904–6907; h) J. F. Briones, H. M. L. Davies, *J. Am. Chem. Soc.* **2012**, *134*, 11916–11919; i) Z.-Y. Cao, X. Wang, C. Tan, X.-L. Zhao, J. Zhou, K. Ding, *J. Am. Chem. Soc.* **2013**, *135*, 8197–8200; j) Y. Xi, Y. Su, Z. Yu, B. Dong, E. J. McClain, Y. Lan, X. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 9817–9821; *Angew. Chem.* **2014**, *126*, 9975–9979.
[4] a) K. Ji, Y. Zhao, L. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 6508–6512; *Angew. Chem.* **2013**, *125*, 6636–6640; b) Y. Wang, K. Ji, S. Lan, L. Zhang, *Angew. Chem. Int. Ed.* **2012**, *51*, 1915–1918; *Angew. Chem.* **2012**, *124*, 1951–1954; c) Y. Luo, K. Ji, Y. Li, L. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 17412–17415; d) L. Ye, W. He, L. Zhang, *Angew. Chem. Int. Ed.* **2011**, *50*, 3236–3239; *Angew. Chem.* **2011**, *123*, 3294–3297; e) W. He, C. Li, L. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 8482–8485; f) L. Ye, W. He, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8550–8551; g) B. Lu, C. Li, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 14070–14072; h) Y. Wang, Z. Zheng, L. Zhang, *J. Am. Chem. Soc.* **2015**, *137*, 5316–5319; i) K. Ji, Z. Zheng, Z. Wang, L. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 1245–1249; *Angew. Chem.* **2015**, *127*, 1261–1265.
[5] a) C.-W. Li, G.-Y. Lin, R.-S. Liu, *Chem. Eur. J.* **2010**, *16*, 5803–5811; b) R. B. Dateer, K. Pati, R.-S. Liu, *Chem. Commun.* **2012**, *48*, 7200–7202; c) S. Ghorpade, M.-D. Su, R.-S. Liu, *Angew. Chem. Int. Ed.* **2013**, *52*, 4229–4234; *Angew. Chem.* **2013**, *125*, 4323–4328; d) S. Bhunia, S. Ghorpade, D. B. Huple, R.-S. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 2939–2942; *Angew. Chem.* **2012**, *124*, 2993–2996; e) D. Qian, J. Zhang, *Chem. Commun.* **2012**, *48*, 7082–7084; f) D. Qian, J. Zhang, *Chem. Commun.* **2011**, *47*, 11152–11154; g) P. W. Davies, *Pure Appl. Chem.* **2010**, *82*, 1537–1544; h) P. W. Davies, A. Cremonesi, N. Martin, *Chem. Commun.* **2011**, *47*, 379–381; i) G. Henrion, T. E. J. Chavas, X. Le Goff, F. Gagosz, *Angew. Chem. Int. Ed.* **2013**, *52*, 6277–6282; *Angew. Chem.* **2013**, *125*, 6397–6402; j) M. Xu, T.-T. Ren, C.-Y. Li, *Org. Lett.* **2012**, *14*, 4902–4905; k) S. Shi, T. Wang, W. Yang, M. Rudolph, A. S. K. Hashmi, *Chem. Eur. J.* **2013**, *19*, 6576–

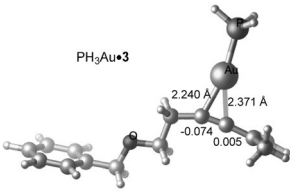
6580; l) T. Wang, S. Shi, M. M. Hansmann, E. Rettenmeier, M. Rudolph, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2014**, *53*, 3715 – 3719; *Angew. Chem.* **2014**, *126*, 3789 – 3793; m) F. Pan, S. Liu, C. Shu, R.-K. Lin, Y.-F. Yu, J.-M. Zhou, L.-W. Ye, *Chem. Commun.* **2014**, *50*, 10726 – 10729; n) L. Wang, X. Xie, Y. H. Liu, *Angew. Chem. Int. Ed.* **2013**, *52*, 13302 – 13306; *Angew. Chem.* **2013**, *125*, 13544 – 13548; o) L. Li, C. Shu, B. Zhou, Y.-F. Yu, X.-Y. Xiao, L.-W. Ye, *Chem. Sci.* **2014**, *5*, 4057 – 4064; p) M. Chen, Y. Chen, N. Sun, J. Zhao, Y. Liu, Y. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 1200 – 1204; *Angew. Chem.* **2015**, *127*, 1216 – 1220.

[6] B. Lu, Y. Li, Y. Wang, D. H. Aue, Y. Luo, L. Zhang, *J. Am. Chem. Soc.* **2013**, *135*, 8512 – 8524.

[7] DFT calculations were performed with the alkynes **2** and **3** coordinated to PH_3Au^+ at the B3LYP/6-311G(d,p)/SDD(Au) level of theory. The optimized structures are shown below. The gold atom moves slightly away from the phenyl or 2-isopropenyl group, and the NBO analysis of the alkyne carbon atoms promixal to these groups show that they are more electron-deficient than their distal counterparts. These results are consistent with the experimental outcomes.

[8] C. Nájera, M. Yus, *Tetrahedron* **1999**, *55*, 10547 – 10658.





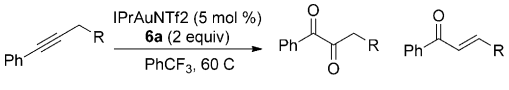
[9] J. J. Eisch, M. Behrooz, S. K. Dua, *J. Organomet. Chem.* **1985**, *285*, 121 – 136.

[10] N. Mézailles, L. Ricard, F. Gagosz, *Org. Lett.* **2005**, *7*, 4133 – 4136.

[11] W. He, L. Xie, Y. Xu, J. Xiang, L. Zhang, *Org. Biomol. Chem.* **2012**, *10*, 3168 – 3171.

[12] C.-F. Xu, M. Xu, Y.-X. Jia, C.-Y. Li, *Org. Lett.* **2011**, *13*, 1556 – 1559.

[13] Indeed when the related 1-phenyl-1-alkynes were subjected to the reaction, the enones were formed as side products. With R = H, the diketone was the major product because in this case, the steric bias that is due to the rather small Me group predominates the regioselectivity



R	Reaction time	Conversion	Yield	
H	overnight	86%	60%	20%
Bu	8 h	50%	16%	24%

[14] G.-Y. Lin, C.-W. Li, S.-H. Hung, R.-S. Liu, *Org. Lett.* **2008**, *10*, 5059 – 5062.

[15] Z.-Y. Yan, Y. Xiao, L. Zhang, *Angew. Chem. Int. Ed.* **2012**, *51*, 8624 – 8627; *Angew. Chem.* **2012**, *124*, 8752 – 8755.

Received: May 19, 2015
Revised: July 4, 2015
Published online: August 12, 2015

