AuPPh₃Cl/AgOTf-catalyzed reaction of terminal alkynes: nucleophilic addition to activated C=O bond

Changkun Li, Fanyang Mo, Weibin Li, Jianbo Wang *

Beijing National Laboratory of Molecular Sciences (BNLMS), and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China
The State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

ARTICLE INFO

ABSTRACT

Terminal alkynes, under Au-catalyzed conditions, react with aromatic aldehyde diethyl acetals, affording propargylation products through C=O bond addition. Furthermore, AuPPh₃Cl/AgOTf-catalyzed three-component reaction of aldehydes, alkynes, and triethyl orthoformate is developed. Gold alkynilides are supposed to be reactive intermediates in these reactions.

© 2009 Elsevier Ltd. All rights reserved.

Development of catalytic reactions that lead to C–C bond formation is of fundamental importance in modern synthetic organic chemistry. In this regard, metalated terminal alkynes are versatile nucleophiles that can react with a wide variety of electrophiles.[1] Traditionally, metalated terminal alkynes are generated by the reaction with organolithium or organomagnesium reagents through deprotonation. In these cases, the metalated terminal alkynes must be generated in a separate step due to the strong nucleophilicity of organolithium or organomagnesium reagents. Obviously, catalytic processes that can lead to the generation of metal alkynilides under mild conditions are highly desirable. Carreira and co-workers have reported an efficient catalytic in situ generation of Zn(II)-alkynilides that add to C=N bond efficiently. The catalytic asymmetric version has also been subsequently developed by the same group.[1c,2] Terminal alkyne additions that are catalyzed by In,[3] Ru,[4] Rh,[5] Ir,[6] Cu,[7] Fe,[8] Ag,[9] Hg,[10] and Au[11] complexes have appeared subsequently. In most of these reactions, metal alkynilides are suggested as reactive intermediates (Scheme 1).

Among these reactions, Au-catalyzed nucleophilic additions have attracted attentions. Recently, Au complexes have emerged as efficient catalysts for a wide variety of transformations involving alkynes, allenes, and alkenes.[12] The research activities in this field so far have been mostly concentrated on the reaction of gold-activated alkynes functioning as electron-deficient species to accept nucleophilic attack. The process that gold-alkyne species function

as nucleophile has been much less developed except simple protonation or elimination. Wei and Li have reported a gold-catalyzed three-component coupling reaction of aldehydes, alkynes, and amines. A gold acetylide species, which adds to C=N bond of iminium ion, is proposed as the reactive intermediate.[11a] Wang and Zhang have reported a Au(III)-catalyzed acyl migration of propargylic esters in which the intramolecular attack of nucleophilic Au(III)–C(sp²) to C=O bond is supposed as the key step in the reaction mechanism.[11d,13] These results indicate that the nucleophilicity of Au–C bond can be exploited in the formation of C–C bond.

In this context, we have reported a AuCl₃/CuBr-catalyzed three-component reaction of aldehydes, amines, and alkynes. The reaction gives quinoline derivatives through a sequential catalytic process, involving initial formation of propargyl amine via nucleophilic addition of gold alkynilide intermediate to C=N bond (Eq. 1).[11f] Furthermore, we have recently reported Au-catalyzed reaction of terminal alkynes and benzyl trichloroacetimidates, which leads to benzylacetylene products through nucleophilic substitution by gold acetylide (Eq. 2).[14] As a continuation of our re-
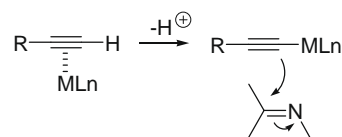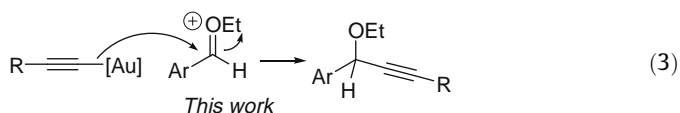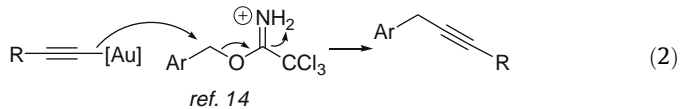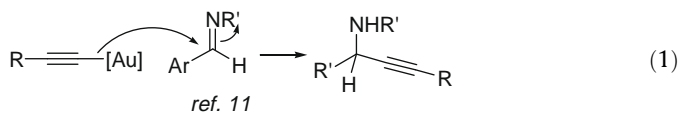

M = In, Ru, Rh, Ir, Cu, Fe, Ag, Hg, Au

Scheme 1. Metal-catalyzed reaction of terminal alkyne.

* Corresponding author.
E-mail address: wangjb@pku.edu.cn (J. Wang).

search program aiming at C–H activation of terminal alkynes with transition metal catalysis, we proceeded to study the nucleophilic addition of gold acetylide to C=O bond in similar catalytic system (Eq. 3). Herein we report a Au-catalyzed three-component reaction of aldehyde, alkyne, and triethyl orthoformate, which affords propargylation products in good yields.

$$R\text{---}\!\!\equiv\!\!\text{---}[Au] \quad \overset{NR'}{\underset{Ar}{\diagdown}}\!\!\diagup\!H \longrightarrow \overset{NHR'}{\underset{R'}{\underset{H}{\diagup}}}\!\!R \quad (1)$$

ref. 11

$$R\text{---}\!\!\equiv\!\!\text{---}[Au] \quad \overset{\oplus NH_2}{\underset{Ar}{\diagdown}O}\!\!\diagup CCl_3 \longrightarrow Ar\text{---}\!\!\equiv\!\!\text{---}R \quad (2)$$

ref. 14

$$R\text{---}\!\!\equiv\!\!\text{---}[Au] \quad \overset{\oplus OEt}{\underset{Ar}{\diagdown}}\!\!\diagup H \longrightarrow \overset{OEt}{\underset{Ar}{\underset{H}{\diagup}}}\!\!R \quad (3)$$

This work

On the outset of this investigation, we have attempted the nucleophilic addition of terminal alkyne to aldehyde by gold catalyst. The reaction failed to give any C=O bond addition products. The failure might be attributed to the low reactivity of aldehyde carbonyl group toward nucleophiles. We then examined the oxocarbenium ion, which can be generated from benzaldehyde diethyl acetal.[15] We were delighted to find that addition of terminal alkyne occurs with AuPPh$_3$Cl/AgOTf catalyst (Scheme 2).

Several other metal complexes have also been examined and the results are summarized in Table 1. AuCl$_3$/AgOTf was less effective to afford **3a** in 66% yield (entry 1). Without AgOTf as co-catalyst, AuPPh$_3$Cl or AuCl$_3$ gave very low yields of **3a** (entries 2 and 3). However, AgOTf alone afforded the product in the yield similar to the reaction with AuCl$_3$/AgOTf (entry 4). It was also noted that base additive completely shut down the reaction (entry 5). Other metal catalysts, such as PtCl$_2$, CuI, Cu(CH$_3$CN)$_4$PF$_6$, and Zn(OTf)$_2$, all failed to catalyze this reaction.

During the course of this investigation, we observed that AuPPh$_3$Cl/AgOTf could efficiently catalyze the formation of benzaldehyde diethyl acetal from benzaldehyde and triethyl orthoformate. This observation led us to conceive that a three-component reaction of aldehydes, alkynes, and triethyl orthoformate might be catalyzed by the same catalytic system. To test this hypothesis, benzaldehyde, phenylacetylene, and triethyl orthoformate were subjected to the reaction with catalytic AuPPh$_3$Cl/AgOTf. Upon refluxing in 1,2-dichloroethane (DCE) for 1 h, product **3a** could be isolated in 87% yield (Table 2, entry 1). Other catalytic systems were also examined. For the gold catalyst, co-catalyst AgOTf was found necessary (entries 2 and 5). AuCl$_3$ and AuCl were also found to catalyze the formation of **3a** when AgOTf was used as co-catalyst, albeit in much lower yields (entries 3 and 4). Control experiment showed that AgOTf alone failed to catalyze the reaction (entry 6). Solvent has marginal effect, as seen by the similar result obtained with benzene (entry 7). However, water can completely shut down the reaction (entry 8).

Other metal complexes, such as PtCl$_2$, CuI, Cu(CH$_3$CN)$_4$PF$_6$, ZnI$_2$, and Zn(OTf)$_2$, all failed to catalyze the reaction (entries 9–13). Interestingly, strong protic acid TfOH could catalyze the reaction,
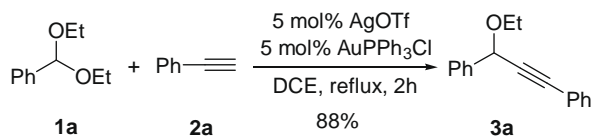
Table 1
Reactions of **1a** and **2a** under various catalytic conditions[a]

Entry	Cat. (5 mol %)	t (h)	Yield[b] (%)
1	AuCl$_3$/AgOTf	6	66
2	AuPPh$_3$Cl	12	Trace
3	AuCl$_3$	48	9
4	AgOTf	24	59
5	AuCl$_3$/AgOTf/DIPEA[c]	24	0
6	PtCl$_2$	24	Trace
7	CuI	18	Trace
8	Cu(CH$_3$CN)$_4$PF$_6$	24	Trace
9	Zn(OTf)$_2$	24	Trace

[a] Reaction was carried out in refluxing DCE.
[b] Isolated yield.
[c] DIPEA: Diisopropylethylamine.

Table 2
Three-component reactions under various catalytic conditions

$$\underset{4a}{\overset{O}{\underset{Ph}{\diagdown}}\!\!\diagup H} + HC(OEt)_3 + \underset{2a}{\equiv\!\!\text{---}Ph} \xrightarrow[DCE,\ 83\ ^\circ C]{cat.(5\ mol\%)} \underset{3a}{\overset{OEt}{\underset{Ph}{\diagdown}}\!\!\equiv\!\!\text{---}Ph}$$
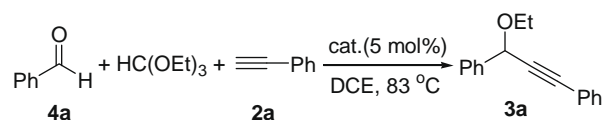
Entry	Cat. (5 mol %)	t (h)	Yield[a] (%)
1	AuPPh$_3$Cl/AgOTf	1	87
2	AuPPh$_3$Cl	24	0
3	AuCl/AgOTf	24	31
4	AuCl$_3$/AgOTf[b]	1	32
5	AuCl$_3$	24	0
6	AgOTf	24	Trace
7[c]	AuPPh$_3$Cl/AgOTf	2	84
8[d]	AuPPh$_3$Cl/AgOTf	2	0
9	PtCl$_2$	12	0
10	CuI	12	0
11	Cu(CH$_3$CN)$_4$PF$_6$	12	Trace
12	ZnI$_2$	12	Trace
13	Zn(OTf)$_2$	12	0
14	TfOH	3	24

[a] Isolated yield.
[b] 15 mol % AgOTf.
[c] Benzene as solvent.
[d] Water as solvent.

albeit in low yield (entry 14). Very recently, highly efficient TfOH-catalyzed reaction of alkenes and alkynes has been documented.[16] Thus, for the current Au-catalyzed reaction the possibility existed that small amount of TfOH could be generated in situ, which catalyzed the three-component reaction. However, this should not be the major reaction pathway in view of the fact that TfOH-catalyzed reaction gave much lower yield of the product as compared with AuPPh$_3$Cl/AgOTf-catalyzed reaction.

With AuPPh$_3$Cl/AgOTf catalytic system, the scope of the three-component reaction was examined by a series of aldehydes and alkynes, and triethyl orthoformate. The results are summarized in Table 3. For a wide range of aromatic aldehydes and alkynes, the reaction afforded the addition products in moderate to good yields. 1-Naphthaldehyde and 2-naphthaldehyde gave similar results (entries 10 and 11). Secondary cyclohexanecarbaldehyde could react with aromatic alkyne smoothly and give moderate yield (entry 16). The electron-donating group makes the reaction faster than the electron-withdrawing groups. p-Nitrobenzaldehyde and basic pyridinecarbaldehyde failed to react.

To account for the three-component reaction, two possible reaction mechanisms are considered (Scheme 3). The first mechanism (path a) involves the generation of gold alkynilide **B**, which adds to the C=O bond of oxocarbenium ion **D**, as proposed previ-

$$\underset{1a}{\overset{OEt}{\underset{Ph}{\diagdown}}\!\!\diagup OEt} + \underset{2a}{Ph\text{---}\!\!\equiv} \xrightarrow[\substack{5\ mol\%\ AgOTf \\ 5\ mol\%\ AuPPh_3Cl \\ DCE,\ reflux,\ 2h \\ 88\%}]{} \underset{3a}{\overset{OEt}{\underset{Ph}{\diagdown}}\!\!\equiv\!\!\text{---}Ph}$$

Scheme 2. Au-catalyzed reaction of **1a** and **2a**.

Table 3
The scope of the three-component reaction[17]

Entry	**4**, R^1	**2**, R^2	t (h)	Yield^a (%)
1	**a**, C$_6$H$_5$	**a**, C$_6$H$_5$	1	**3a**, 87
2	**b**, o-CH$_3$C$_6$H$_4$	**a**, C$_6$H$_5$	2	**3b**, 82
3	**c**, o-AllylOC$_6$H$_4$	**a**, C$_6$H$_5$	2	**3c**, 55
4	**d**, m-BrC$_6$H$_4$	**a**, C$_6$H$_5$	4	**3d**, 80
5	**e**, m-CH$_3$OC$_6$H$_4$	**a**, C$_6$H$_5$	3	**3e**, 81
6	**f**, m-CF$_3$C$_6$H$_4$	**a**, C$_6$H$_5$	6	**3f**, 76
7	**g**, p-BrC$_6$H$_4$	**a**, C$_6$H$_5$	2	**3g**, 87
8	**h**, p-ClC$_6$H$_4$	**a**, C$_6$H$_5$	2	**3h**, 82
9	**i**, p-C$_6$H$_5$C$_6$H$_4$	**a**, C$_6$H$_5$	15	**3i**, 87
10	**j**, 1-Naphthyl	**a**, C$_6$H$_5$	3	**3j**, 88
11	**k**, 2-Naphthyl	**a**, C$_6$H$_5$	15	**3k**, 80
12	**a**, C$_6$H$_5$	**b**, p-BrC$_6$H$_4$	2	**3l**, 66
13	**a**, C$_6$H$_5$	**c**, p-PhC$_6$H$_4$	2	**3m**, 71
14	**a**, C$_6$H$_5$	**e**, p-NO$_2$C$_6$H$_4$	4	**3n**, 38
15	**a**, C$_6$H$_5$	**f**, 2-Naphthyl	1	**3o**, 76
16	**l**, C$_6$H$_{11}$	**b**, p-BrC$_6$H$_4$	12	**3p**, 51
17	**m**, p-CH$_3$OC$_6$H$_4$	**a**, C$_6$H$_5$	4	**3q**, 30^b
18	**n**, $trans$-C$_6$H$_5$CH=CHC$_6$H$_4$	**a**, C$_6$H$_5$	2	**3r**, 32^c

^{a} Isolated yield.
^{b} 1,5-Diphenyl-3-(p-methoxyphenyl) pent-1,4-diyne was isolated in 52%.
^{c} The product was 1:1 mixture of **3r** and $trans$-1-Methoxy-3,5-diphenyl-1- penten-4-yne.

Scheme 3. Mechanistic rationale.
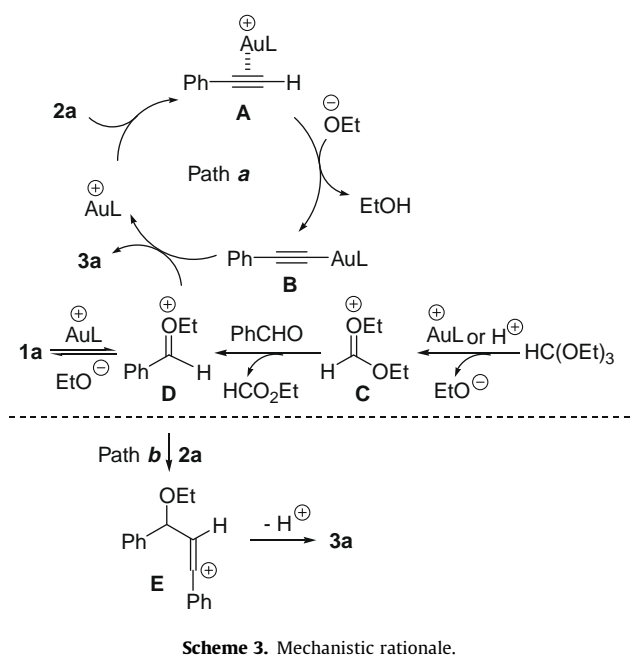
ously. In view of the fact that TfOH could also catalyze the reaction, the second possible mechanism (path b), which involves a Prinstype reaction,[18] is suggested. In this case, the oxocarbenium ion **D** is added to the alkyne directly to give vinyl cation **E**. The Au catalyst may function as Lewis acid to promote the generation of **D**.

Several experiments were carried out in order to differentiate the two reaction pathways. First, Prins-type reaction might occur when phenyl acetylene is replaced by styrene. However, no reaction occurred under the same conditions with styrene. Second, it was observed that when the reaction was carried out in benzene,

possible Friedel–Crafts reaction with benzene was not detected, and the reaction gave three-component reaction product in similar yield. All these observations were not in favor of the Prins-type reaction mechanism (path b).

Gold alkynilide species has been previously synthesized and characterized in stoichiometric reaction.[17] These species have also been suggested in the reaction mechanism of Au-catalyzed reactions of terminal alkynes.[11,14] Based on these reports and our own observation in this study, we consider that the mechanism path a, which involves nucleophilic addition of gold alkynilide **B**, is most plausible.

In summary, we have developed an AuPPh$_3$Cl/AgOTf-catalyzed three-component reaction of terminal alkyne, aldehyde, and amine. The three-component reaction is highly efficient, providing propargyl ether in good yields.[19] The reaction may involve gold alkynilide intermediates, which add to the activated C=O bond. The catalytic processes are carried out under mild conditions to provide propargyl ethers in good yields.

Acknowledgments

Supplementary data

Supplementary data (characterization data, ^{1}H and ^{13}C NMR spectra for all new compounds, these materials are available free of charge via the Internet) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.08.049.

References and notes

1. For selected reviews, see: (a) Brandsma, L. *Preparative Acetylene Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; (b)*Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; (c) Frantz, D. E.; Fässler, R.; Tomooka, C. S.; Carreira, E. M. *Acc. Chem. Res.* **2000**, *33*, 373–381; (d) Negishi, E.-i.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979–2017; (e)*Handbook of C–H Transformations*; Dyker, G., Ed.; Wiley-VCH: Weinheim, 2005; Vol. 1, pp 31–78.
2. (a) Frantz, D. E.; Fässler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **1999**, *121*, 11245–11246; (b) Anand, N. K.; Carreira, E. M. *J. Am. Chem. Soc.* **2001**, *123*, 9687–9688.
3. (a) Takita, R.; Fukuta, Y.; Tsuji, R.; Ohshima, T.; Shibasaki, M. *Org. Lett.* **2005**, *7*, 1363–1366; (b) Takita, R.; Yakura, K.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2005**, *127*, 13760–13761; (c) Zhang, Y.; Li, P.; Wang, M.; Wang, L. *J. Org. Chem.* **2009**, *74*, 4364–4367.
4. (a) Wei, C.; Li, C.-J. *Green Chem.* **2002**, *4*, 39–41; (b) Li, C.-J.; Wei, C. *Chem. Commun.* **2002**, 268–269.
5. Dhondi, P. K.; Chisholm, J. D. *Org. Lett.* **2006**, *8*, 67–69.
6. Fischer, C.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 4319–4321.
7. (a) Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2535–2538; (b) Gommermann, N.; Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 5763–5766; (c) Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2002**, *124*, 5638–5639; (d) Asano, Y.; Hara, K.; Ito, H.; Sawamura, M. *Org. Lett.* **2007**, *9*, 3901–3904; (e) Motoki, R.; Kanai, M.; Shibasaki, M. *Org. Lett.* **2007**, *9*, 2997–3000; (f) Shi, L.; Tu, Y.-Q.; Wang, M.; Zhang, F.-M.; Fan, C.-A. *Org. Lett.* **2004**, *6*, 1001–1003; (g) Choudary, B. M.; Sridhar, C.; Kantam, M. L.; Sreedhar, B. *Tetrahedron Lett.* **2004**, *45*, 7319–7321; (h) Wang, M.; Li, P.; Wang, L. *Eur. J. Org. Chem.* **2008**, 2255–2261; (i) Kantam, M. L.; Yadav, J.; Laha, S.; Jha, S. *Synlett* **2009**, 1791–1794.
8. Li, P.; Zhang, Y.; Wang, L. *Chem. Eur. J.* **2009**, *15*, 2045–2049.
9. (a) Yao, X.; Li, C.-J. *Org. Lett.* **2005**, *7*, 4395–4398; (b) Dodda, R.; Zhao, C.-G. *Org. Lett.* **2007**, *9*, 165–167; (c) Wei, C.; Li, Z.; Li, C.-J. *Org. Lett.* **2003**, *5*, 4473–4475; (d) Li, P.; Wang, L.; Zhang, Y.; Wang, M. *Tetrahedron Lett.* **2008**, *49*, 6650–6654.
10. Li, P.; Wang, L. *Chin. J. Chem.* **2005**, *23*, 1076–1080.
11. (a) Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2003**, *125*, 9584–9585; (b) Lo, V. K.-Y.; Liu, Y.; Wong, M.-K.; Che, C.-M. *Org. Lett.* **2006**, *8*, 1529–1532; (c) Huang, B.; Yao, X.; Li, C.-J. *Adv. Synth. Catal.* **2006**, *348*, 1528–1532; (d) Yao, X.; Li, C.-J. *Org. Lett.* **2006**, *8*, 1953–1955; (e) Skouta, R.; Li, C.-J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1117–1119; (f) Xiao, F.; Chen, Y.; Liu, Y.; Wang, J. *Tetrahedron* **2008**, *64*, 2755–2761; (g) Zhang, X.; Corma, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4358–4361.
12. For selected recent reviews on Au-catalyzed reactions, see: (a) Dyker, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 4237–4239; (b) Hashmi, A. S. K. *Gold Bull.* **2004**, *37*, 51–65; (c) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2005**, *44*,

6990–6993; (d) Hoffmann-Röder, A.; Krause, N. *Org. Biomol. Chem.* **2005**, *3*, 387–391; (e) Bruneau, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 2328–2334; (f) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410–3449; (g) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180–3211; (h) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239–3265; (i) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266–3325; (j) Jiménez-Núñnez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326–3350; (k) Gorin, D. J.; Sherry, B. B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351–3378.

13. (a) Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006**, *128*, 8414–8415; (b) Dubé, P.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 12062–12063; (c) Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006**, *128*, 14274–14275.

14. Li, C.; Li, W.; Wang, J. *Tetrahedron Lett.* **2009**, *50*, 2536–2539.

15. (a) Howk, B. W.; Sauer, J. C. *J. Am. Chem. Soc.* **1958**, *80*, 4607–4609; (b) Sakurai, H.; Sasaki, K.; Hosomi, A. *Tetrahedron Lett.* **1981**, *22*, 745–748.

16. (a) Anderson, L. L.; Arnold, J.; Bergman, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 14542–14543; (b) Sun, J.; Kozmin, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 13512–13513; (c) Li, Z.; Zhang, J.; Brouwer, C.; Yang, C.-G.; Reich, N. W.; He, C. *Org. Lett.* **2006**, *19*, 4175–4178; (d) Rosenfeld, D. C.; Shekhar, S.; Takemiya, A.; Utsunomiya, M.; Hartwig, J. F. *Org. Lett.* **2006**, *19*, 4179–

4182; (e) Rozenman, M. M.; Kanan, M. W.; Liu, D. R. *J. Am. Chem. Soc.* **2007**, *129*, 14933–14938.

17. *General procedure for the gold-catalyzed three-component reaction of aldehydes, alkynes, and triethyl orthoformate*: To a 25 mL round-bottomed flask was added AuClPPh$_3$ (12.4 mg, 0.05 equiv), AgOTf (6.4 mg, 0.05 equiv), and 3 mL 1,2-dichloroethane. The solution was stirred at room temperature for 5 min. Phenylacetylene **2a** (61 mg, 1.2 equiv), benzaldehyde **4a** (53 mg, 1.0 equiv), and HC(OEt)$_3$ (88 mg, 1.2 equiv) were added to the solution. The resulting mixture was heated to reflux and monitored by TLC and GC–MS. When the reaction was complete, the solvent was removed in vacuo and the crude product was purified by column chromatography on silica gel with petroleum and ethyl acetate (100:1) to give 3-ethoxy-1,3-diphenylprop-1-yne (103 mg, 87% yield) as a yellow oil.

18. Vicente, J.; Chicote, M.-T.; Abrisqueta, M.-D. *J. Chem. Soc., Dalton Trans.* **1995**, 497–498.

19. Selected reviews on multicomponent reactions, see: (a) For multicomponent reactions, see: *Multicomponent Reactions*; Zhu, J., Bienayme, H., Eds.; Wiley: Weinheim, 2005. (b) Armstrong, R. W.; Combs, A. P.; Tempest, P. A.; Brown, S. D.; Keating, T. A. *Acc. Chem. Res.* **1996**, *29*, 123–131.