

Cyclization

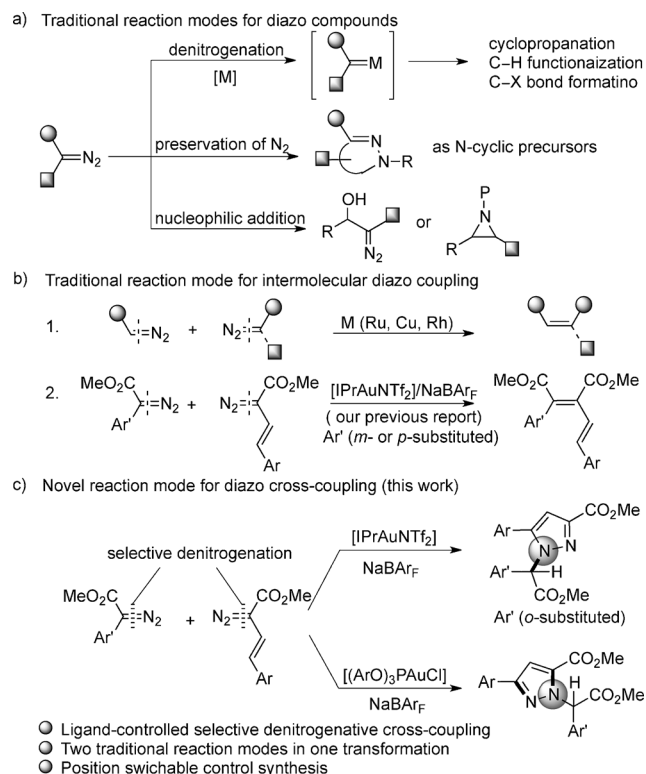
Gold(I)-Catalyzed Diazo Cross-Coupling: A Selective and Ligand-Controlled Denitrogenation/Cyclization Cascade**

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Abstract: An unprecedented gold-catalyzed ligand-controlled cross-coupling of diazo compounds by sequential selective denitrogenation and cyclization affords *N*-substituted pyrazoles in a position-switchable mode. This novel transformation features selective decomposition of one diazo moiety and simultaneous preservation of the other one from two substrates. Notably, the choice of the ancillary ligand to the gold complex plays a pivotal role on the chemo- and regioselectivity of the reactions.

The past decade has witnessed the rapid progress of gold catalysis and many novel and efficient methodologies have been developed.^[1] In 2005, Nolan et al. reported the first gold-catalyzed carbene transfer from diazoacetates.^[2] However, only few related studies were reported after that.^[3] Nevertheless, the continuous development of gold catalysis, especially the introduction of various ancillary ligands to cationic gold(I),^[1d,4] enabled investigation of gold-mediated formal carbene transfer from diazo compounds and led to the discovery of novel transformations which proceeded well for gold but were less effective for other metals.^[5]

Generally, there are three traditional reaction modes for diazo compounds. Namely, the formation of metal carbene^[6] with the extrusion of nitrogen, use as *N*-heterocyclic precursors in cycloadditions,^[7] and use as substrates in nucleophilic additions (Scheme 1a).^[8] Moreover, the coupling of diazo compounds to generate alkenes by complete decomposition of two diazo moieties was usually considered to be an undesired side reaction. However, this process can also be utilized to construct C=C bonds in synthetically useful applications (Scheme 1b).^[9] In contrast, the selective decomposition of one of two diazo moieties, to our knowledge, has not been reported previously. Continuing with our interests in diazo chemistry,^[10] we describe here an unprecedented catalyst-controlled cross-coupling reaction by selective denitrogenation to produce *N*-substituted pyrazoles in a position-



Scheme 1. Metal-catalyzed cross-coupling of diazo compounds. BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, Tf = trifluoromethanesulfonyl.

switchable way (Scheme 1c). Notably, the two traditional reaction modes for diazo compounds could be observed in a single transformation.

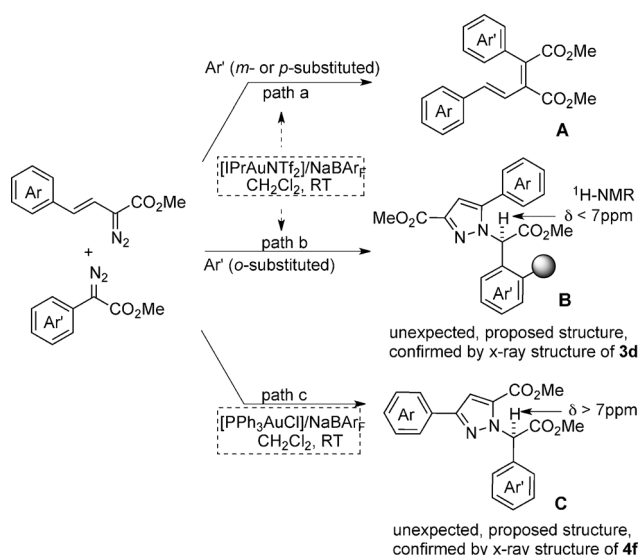
Recently, we reported the first gold-catalyzed selective cross-coupling of aryl- and vinyl diazoacetates to access *Z*-selective tetrasubstituted alkenes catalyzed by [IPrAuNTf₂]-NaBARF (Scheme 1b1).^[10e] We found that the cross-coupling was favored over the self-dimerization through trapping of the initial carbenoid with the other diazo substrate, thus making full use of the decomposition rate difference between the two diazo compounds, and was consistent with the previous observations made by the groups of Barluenga^[9h] and Davies.^[9k] As this reaction was further explored, two unexpected phenomena were observed. First, the diene formation was only applicable to *meta*- or *para*-substituted aryl diazoacetates (Scheme 2, path a). The expected dienes (**A**) were not obtained but the compounds (**B**) were isolated from the *ortho*-substituted aryl diazoacetates and resulted from the selective decomposition of one diazo moiety (Scheme 2, path b). This phenomenon indicated that steric hindrance of aryl diazoacetates significantly affected the reaction pathway.

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Scheme 2. Gold-catalyzed cross-coupling of diazo compounds.

Secondly, the use of $[\text{Ph}_3\text{PAuCl}]$ afforded another type of N-substituted pyrazole (**C**) rather than the dienes (Scheme 2, path c). The structures of **B** and **C** were proposed from spectra analyses and further confirmed by X-ray crystallography of **3d** and **4f** (see Table 2).^[11] It is worth noting that for all of the type **B** compounds, the chemical shift of the hydrogen atom on the saturated carbon atom was less than $\delta = 7$ ppm in the ^1H NMR spectrum. In contrast, the shift was greater than $\delta = 7$ ppm for all of the type **C** compounds. The above-mentioned phenomena intrigued us and we were further motivated to investigate the reaction process.

We then set out to optimize the reaction conditions for the selective denitrogenation reaction using the vinyl diazoacetate **1a** and aryl diazoacetate **2a** as model substrates in dichloromethane at room temperature in the presence of various gold catalysts (Table 1). Initially, the use of $[\text{IPrAuCl}]/\text{NaBAR}_\text{F}$ afforded **3a** as the single regioisomer in 41% yield (entry 1). The yield was improved to 67% by $[\text{IPrAuNTf}_2]/\text{NaBAR}_\text{F}$ (entry 2), while $[\text{IMesAuNTf}_2]/\text{NaBAR}_\text{F}$ provided lower reactivity (entry 3). Next, we investigated the influence of phosphine- or phosphite-derived gold complexes in this reaction. The initial use of $[\text{Ph}_3\text{PAuCl}]/\text{NaBAR}_\text{F}$ delivered **4a** as the single isomer in only 23% yield (entry 6). We envisioned that the reaction could be improved by tuning the electronic effect of the ancillary ligands of gold complexes. Indeed, the gold catalysts bearing electron-deficient ligands gave better results (entries 8–10). In contrast, poor reactivity was observed for more electron-rich phosphine ligands (entry 7). Gratifyingly, the highest yield of the isolated **4a** (79%) was obtained when $[(\text{ArO})_3\text{PAuCl}]/\text{NaBAR}_\text{F}$ ($\text{Ar} = 2,4\text{-tBu}_2\text{C}_6\text{H}_3$) was employed (entry 10). In addition, either without NaBAR_F or by replacing it with AgSbF_6 , low yields were observed (entries 4, 5, 12, and 13). It is of note that the diene **A** (Scheme 2) was not detected through the optimization process.

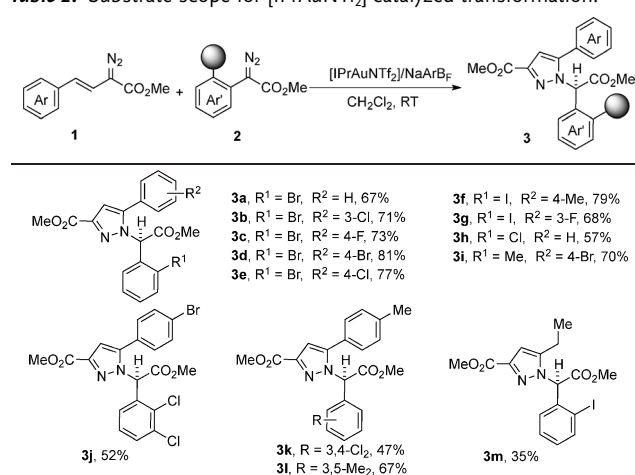
Inspired by the above results, we further investigated the substrate scope for the $[\text{IPrAuNTf}_2]/\text{NaBAR}_\text{F}$ -catalyzed process (Table 2). As the *ortho* substituent on the aromatic ring

Table 1: Optimization for the selective denitrogenative cross-coupling of diazo compounds.^[a]

Entry	Catalyst	Conv. [%] ^[b]	Yield [%] ^[c] 3a	4a
1	$[\text{IPrAuCl}]/\text{NaBAR}_\text{F}$	100	41	0
2	$[\text{IPrAuNTf}_2]/\text{NaBAR}_\text{F}$	100	67	0
3	$[\text{IMesAuNTf}_2]/\text{NaBAR}_\text{F}$	86	32	0
4	$[\text{IPrAuNTf}_2]/\text{AgSbF}_6$	60	28	0
5	$[\text{IPrAuNTf}_2]$	31	12	0
6	$[\text{Ph}_3\text{PAuCl}]/\text{NaBAR}_\text{F}$	62	0	23
7 ^[d]	$[\text{R}_3\text{PAuCl}]/\text{NaBAR}_\text{F}$	< 20	0	< 5
8	$[(\text{C}_6\text{F}_5)_3\text{PAuCl}]/\text{NaBAR}_\text{F}$	85	0	46
9	$[(\text{PhO})_3\text{PAuCl}]/\text{NaBAR}_\text{F}$	100	0	72
10	$[(\text{ArO})_3\text{PAuCl}]/\text{NaBAR}_\text{F}$	100	0	79
11	$[(2,4\text{-tBu}_2\text{C}_6\text{H}_3\text{O})_3\text{PAuNTf}_2]/\text{NaBAR}_\text{F}$	100	0	45
12	$[(2,4\text{-tBu}_2\text{C}_6\text{H}_3\text{O})_3\text{PAuCl}]/\text{AgSbF}_6$	52	0	30
13	$[(2,4\text{-tBu}_2\text{C}_6\text{H}_3\text{O})_3\text{PAuCl}]$	39	0	16

[a] Reactions were carried out with **1a** and **2a** (1 mmol each) and catalyst (5 mol%) in CH_2Cl_2 (10 mL) at RT for 10 h. [b] Determined by NMR analysis of the crude reaction mixture. [c] Yield of isolated product. [d] R = Cy, Et or *n*Bu.

Table 2: Substrate scope for $[\text{IPrAuNTf}_2]$ -catalyzed transformation.^[a,b]



[a] Reactions were conducted with **1** and **2** (1 mmol each), $[\text{IPrAuNTf}_2]/\text{NaBAR}_\text{F}$ (5 mol%) in CH_2Cl_2 (10 mL) at RT for 10 h. [b] Yield of isolated product.

of aryl diazoacetates was essential for this transformation, a series of substituents such as iodo, bromo, chloro and methyl groups were examined. As observed, all of the reactions proceeded to afford **3** in moderate to high yields. Next, the scope of vinyl diazoacetates was also investigated and we found the *ortho*-, *meta*-, or *para*-substituted styryl diazoacetates on the phenyl ring were all tolerated, and thus indicated that the position of substitution on the aryl ring of the vinyl diazoacetates did not affect the reaction mode. The highest yield was obtained for **3d** (81% yield). Meanwhile, 2,3- and 2,4-

dichloro-substituted phenyldiazoacetates gave the corresponding products in moderate yields (**3j** and **3k**), and 2,5-dimethylphenyldiazoacetate afforded **3l** in 67% yield. However, the use of alkyl vinyl diazoacetate afforded the product **3m** in low yield.

Next, to demonstrate the generality of denitrogenation coupling reaction catalyzed by $[(\text{ArO})_3\text{PAuCl}]/\text{NaBAR}_\text{F}$, the scope of substrates was examined under the optimal reaction conditions. As presented in Table 3, various

Table 3: Substrate scope for $[(\text{ArO})_3\text{PAuCl}]$ -catalyzed transformation.^[a,b]

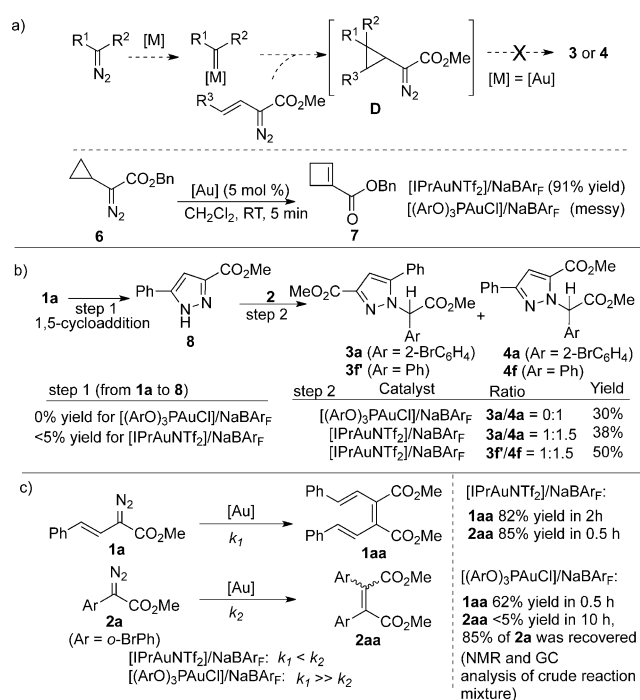
1 	2
4 	
4a , R = 2-Br, 79% 4b , R = 4-Cl, 76% 4c , R = 3-Me, 60% 4d , R = 4-OMe, 64% 4e , R = 4-F, 71% 4f , R = H, 72% 4g , R = 2-OMe, 47% 4h , R = 1-Naph, 63% 4i , R = 4-Cl, 85% 4j , R = 4-Br, 84% 4k , R = 3-F, 74% 4l , R ¹ = 4-Me, R ² = 4-Me, 60% 4m , R ¹ = 3-Cl, R ² = 2-Me, 72% 4n , R ¹ = 3-Cl, R ² = 2-Cl, 76% 4o , R ¹ = 3-F, R ² = 2-I, 41% 4p , R ¹ = 1-Naph, R ² = 2-Br, 70% 4q , 67% 4r , 65% 4s , 72%	

[a] Reactions were conducted on 1 mmol scale, $[(\text{ArO})_3\text{PAuCl}]/\text{NaBAR}_\text{F}$ (5 mol %) in CH_2Cl_2 (10 mL) at RT for 10 h. [b] Yield for isolated product.

aryldiazoacetates and styryldiazoacetates with *ortho*, *para*, and *meta* substituents on the aromatic ring were all tolerated. The reactions proceeded smoothly to produce the corresponding products in moderate to good yields (41–85%). Generally, aryldiazoacetates and vinyl diazoacetates bearing electron-withdrawing groups on the aromatic ring gave higher yields than those bearing electron-donating groups, except **4o**. The highest yield was obtained for **4i** (85%). Moreover, similar activity was observed for different carboxylates of aryldiazoacetates (**4q–s**) and benzyl ester gave slight higher yield (**4s**).

To better understand the reaction process, control experiments were conducted. As reported by Barluenga et al.,^[9b] the cross-coupling of simple and vinyl diazoacetates generated cyclobutenes by a tandem cyclopropanation/ring enlargement catalyzed by copper(I)-complexes. We wondered whether our approaches would undergo a similar pathway to give **D** first with subsequent ring enlargement to give **3** or **4** as the target product (Scheme 3a). However, treatment of the α -diazoacetate **6**^[12] with gold catalysts indicated that this reaction pattern should be excluded. The use of $[\text{IPrAuNTf}_2]/\text{NaBAR}_\text{F}$ afforded the cyclobutene **7** in 91% yield whereas $[(\text{ArO})_3\text{PAuCl}]/\text{NaBAR}_\text{F}$ gave a complex mixture.

To test another possibility, namely the preferential formation of **8** from vinyl diazoacetate by 1,5-cycloaddition with subsequent gold-catalyzed N–H insertion (Scheme 3b),



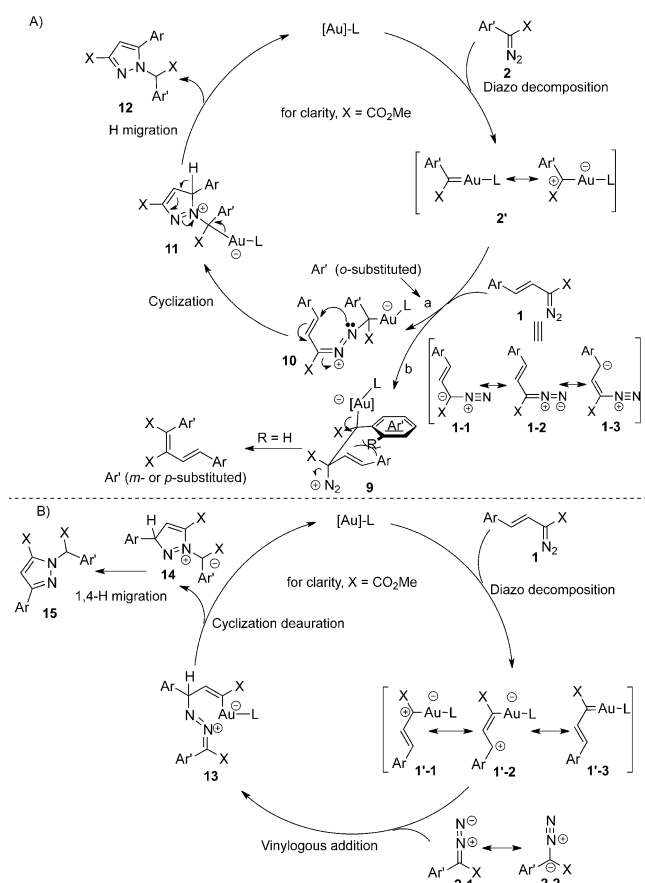
Scheme 3. Control experiments.

the reactions between **8** and **2** were performed. We observed that **4a** was obtained as single isomer in 30% yield when $[(\text{ArO})_3\text{PAuCl}]$ was used and 38% overall yield for **3a** and **4a** in 1:1.5 ratio with $[\text{IPrAuNTf}_2]/\text{NaBAR}_\text{F}$. The reaction of **8** and **2h** gave **3f** and **4f** in 50% yield in 1:1.5 ratio too (Scheme 3b, step 2). More importantly, the experiments indicated that **8** cannot be prepared directly from **1a** in the presence of gold catalysts (Scheme 3b, step 1). Therefore, the hypothesis for the preferential formation of pyrazole also was excluded.

Next, the dimerizations of **1a** and **2a** were conducted respectively to compare their relative reactivities toward different gold catalysts (Scheme 3c). In the presence of $[\text{IPrAuNTf}_2]$, **1aa** was obtained for 82% yield in 2 hours and **2aa** was isolated in 85% yield in 30 minutes. Clearly, the comparison of rate constant ($k_1 < k_2$) was obtained. On the contrary, $k_1 \gg k_2$ was observed for the $[(\text{ArO})_3\text{PAuCl}]$ -catalyzed transformation. These experiments indicated that aryldiazoacetates exhibited higher reactivity than vinyl diazoacetates during the $[\text{IPrAuNTf}_2]$ -catalyzed cross-coupling reactions while the result reversed when $[(\text{ArO})_3\text{PAuCl}]$ was employed.

The nature of gold-carbenoids remains elusive and recent reports partly provided some insights.^[5d,13] The exact reaction mechanism for the selective decomposition of diazo compounds/cyclization cascade is unknown currently, and based on the above experiments, two possible reaction pathways were proposed (Scheme 4). Clearly, the preferential formation of gold-carbenoid from either aryldiazoacetates or styryldiazoacetates would serve as electrophile and the other one would behave as nucleophile.

As depicted in Scheme 4A, the preferential formation of the gold carbenoid **2'** from the aryldiazoacetate **2** would serve as the electrophile and undergo nucleophilic addition by the



Scheme 4. Proposed reaction mechanism.

vinylidiazooacetate **1** to yield the active intermediate (**9** or **10**). We speculated that the steric effect of aryldiazooacetates should be crucial to the reaction mode. The reaction between **2'** and **1** would produce dienes as single isomer for the less steric aryldiazooacetates through carbanion nucleophilic attack (via **1-1**; Scheme 4A, step b), while the *ortho*-substituted aryldiazooacetates cannot deliver dienes because of the steric effect, but can afford **10** through nitrogen attack (via **1-2**; Scheme 4A, step a), which then would undergo sequential cyclization and hydrogen migration to give **12** as the final product. However, if the preferential formation of the vinylcarbenoid was preferred, then aryldiazooacetate would serve as nucleophile (Scheme 4B). Thus, the vinylogous addition^[14] and cyclization deauration cascade generates the zwitterionic intermediate **14**, which then undergoes 1,4-hydrogen migration to afford the target product **15**. According to the structure analysis of **3** and **4** as well as the results of the control experiments, we reason that the catalytic cycle in Scheme 4A is reasonable for the [IPrAuNTf₂]-catalyzed process and vice versa, while the catalytic cycle in Scheme 4B is responsible for [(ArO)₃PAuCl]-catalyzed transformation.

In summary, we have demonstrated here an unprecedented and selective ligand-controlled denitrogenation/cyclization cascade of diazo compounds to afford *N*-substituted pyrazoles in a position-switchable mode. The coupling reactions feature the preferential formation of a gold-carbenoid either from an aryldiazooacetate or styryldiazooacetate,

which serves as an electrophile and undergoes nucleophilic attack by the other one, thus leading to the formation of regioisomers. Moreover, we proposed two possible mechanisms to explain the different reaction modes in the presence of different gold complexes.

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- [1] For selected reviews, see: a) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; b) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266; c) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326; d) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351.
- [2] M. R. Frutos, T. R. Belderrain, P. de Frémont, N. M. Scott, S. P. Nolan, M. M. Díaz-Requejo, P. J. Pérez, *Angew. Chem. Int. Ed.* **2005**, *44*, 5284; *Angew. Chem.* **2005**, *117*, 5418.
- [3] a) M. R. Frutos, P. de Frémont, S. P. Nolan, M. M. Díaz-Requejo, P. J. Pérez, *Organometallics* **2006**, *25*, 2237; b) A. Prieto, M. R. Frutos, M. M. Díaz-Requejo, P. J. Pérez, P. Pérez-Galán, N. Delpont, A. M. Echavarren, *Tetrahedron* **2009**, *65*, 1790; c) I. Rivilla, B. P. Gómez-Emeterio, M. R. Frutos, M. M. Díaz-Requejo, P. J. Pérez, *Organometallics* **2011**, *30*, 2855; d) V. V. Pagar, A. P. Jadhav, R.-S. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 20728; e) Z.-Y. Cao, X. Wang, C. Tan, X.-L. Zhao, J. Zhou, K. Ding, *J. Am. Chem. Soc.* **2013**, *135*, 8197; f) J. Barluenga, G. Lonzi, M. Tomás, L. A. López, *Chem. Eur. J.* **2013**, *19*, 1573; g) A. M. Jadhav, V. V. Pagar, R.-S. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 11809; *Angew. Chem.* **2012**, *124*, 11979; h) S. K. Pawar, C.-D. Wang, S. Bhunia, A. M. Jadhav, R.-S. Liu, *Angew. Chem. Int. Ed.* **2013**, *52*, 7559; *Angew. Chem.* **2013**, *125*, 7707; i) G. Lonzi, L. A. López, *Adv. Synth. Catal.* **2013**, *355*, 1948; j) E. López, G. Lonzi, L. A. López, *Organometallics* **2014**, DOI: 10.1021/om500638t.
- [4] For selected example, see: a) P. Mauleón, R. M. Zeldin, A. Z. González, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 6348; b) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482.
- [5] a) J. F. Briones, H. M. L. Davies, *J. Am. Chem. Soc.* **2012**, *134*, 11916; b) J. F. Briones, H. M. L. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 13314; c) Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu, J. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 6904; d) Y. Xi, Y. Su, Z. Yu, B. Dong, E. J. McClain, Y. Lan, X. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 9817; *Angew. Chem.* **2014**, *126*, 9975.
- [6] For reviews, see: a) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861; b) H. M. L. Davies, J. R. Denton, *Chem. Soc. Rev.* **2009**, *38*, 3061; c) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704; d) H. M. L. Davies, J. R. Denton, *Chem. Soc. Rev.* **2011**, *40*, 1857; e) D. Gillingham, N. Fei, *Chem. Soc. Rev.* **2013**, *42*, 4918; f) Y. Xia, Y. Zhang, J. Wang, *ACS Catal.* **2013**, *3*, 2586.
- [7] For selected examples, see: a) H. Mao, A. Lin, Y. Shi, Z. Mao, X. Zhu, W. Li, H. Hu, Y. Cheng, C. Zhu, *Angew. Chem. Int. Ed.* **2013**, *52*, 6288; *Angew. Chem.* **2013**, *125*, 6408; b) C. Sun, M. J. O'Connor, D. Lee, D. J. Wink, R. D. Milligan, *Angew. Chem. Int. Ed.* **2014**, *53*, 3197; *Angew. Chem.* **2014**, *126*, 3261; c) A. Kuznetsov, A. V. Gulevich, D. J. Wink, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2014**, *53*, 9021; *Angew. Chem.* **2014**, *126*, 9167, and references therein.
- [8] For selected examples, see: a) W. Baratta, A. Del Zotto, P. Rigo, *Chem. Commun.* **1997**, 2163; b) A. Del Zotto, W. Baratta, G. Verardo, P. Rigo, *Eur. J. Org. Chem.* **2000**, 2795; c) M. P. Doyle,

- W. Hu, I. M. Phillips, *Org. Lett.* **2000**, 2, 1777; d) J. Barluenga, L. A. López, O. Lober, M. Tomas, S. Garcia-Granda, C. Alvarez-Rua, J. Borge, *Angew. Chem. Int. Ed.* **2001**, 40, 3392; *Angew. Chem.* **2001**, 113, 3495; e) G.-Y. Li, C.-M. Che, *Org. Lett.* **2004**, 6, 1621; f) D. M. Hodgson, D. Angrish, *Chem. Commun.* **2005**, 4902; g) D. M. Hodgson, D. Angrish, *Chem. Eur. J.* **2007**, 13, 3470; h) J. Barluenga, L. Riesgo, L. A. López, E. Rubio, M. Tomás, *Angew. Chem. Int. Ed.* **2009**, 48, 7569; *Angew. Chem. Int. Ed.* **2009**, 48, 1439; *Angew. Chem.* **2009**, 121, 1467; j) Y. Zhou, B. G. Trewyn, R. Angelici, L. K. Woo, *J. Am. Chem. Soc.* **2009**, 131, 11734; k) J. H. Hansen, B. T. Parr, P. Pelphrey, Q. Jin, J. Autschbach, H. M. L. Davies, *Angew. Chem. Int. Ed.* **2011**, 50, 2544; *Angew. Chem.* **2011**, 123, 2592; l) Y. Xia, Z. Liu, Q. Xiao, P. Qu, R. Ge, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2012**, 51, 5714; *Angew. Chem.* **2012**, 124, 5812.
- [9] For selected examples, see: a) L. Huang, W. D. Wulff, *J. Am. Chem. Soc.* **2011**, 133, 8892; b) B. M. Trost, S. Malhotra, P. Koschker, P. Ellerbrock, *J. Am. Chem. Soc.* **2012**, 134, 2075.
- [10] a) G. Liu, J. Li, L. Qiu, L. Liu, G. Xu, B. Ma, J. Sun, *Org. Biomol. Chem.* **2013**, 11, 5998; b) D. Ding, G. Liu, G. Xu, J. Li, G. Wang, J. Sun, *Org. Biomol. Chem.* **2014**, 12, 2533; c) D. Ding, X. Lv, J. Li, G. Xu, B. Ma, J. Sun, *Chem. Asian J.* **2014**, 9, 1539; d) H. Guo, D. Zhang, C. Zhu, J. Li, G. Xu, J. Sun, *Org. Lett.* **2014**, 16, 3110; e) D. Zhang, G. Xu, D. Ding, C. Zhu, J. Li, J. Sun, *Angew. Chem. Int. Ed.* **2014**, 53, 11070; *Angew. Chem.* **2014**, 126, 11250.
- [11] CCDC 1026497 (**3d**) and CCDC 1026498 (**4f**) 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.
- [12] H. Xu, W. Zhang, D. Shu, J. B. Werness, W. Tang, *Angew. Chem. Int. Ed.* **2008**, 47, 8933; *Angew. Chem.* **2008**, 120, 9065.
- [13] a) R. E. M. Brooner, T. J. Brown, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2013**, 52, 6259; *Angew. Chem.* **2013**, 125, 6379; b) G. Seidel, A. Fürstner, *Angew. Chem. Int. Ed.* **2014**, 53, 4807; *Angew. Chem.* **2014**, 126, 4907.
- [14] For selected examples on the gold-mediated vinylogous addition, see Ref. [3i] and [5b].