



Gold-Catalyzed Intermolecular C–S Bond Formation: Efficient Synthesis of α -Substituted Vinyl Sulfones**

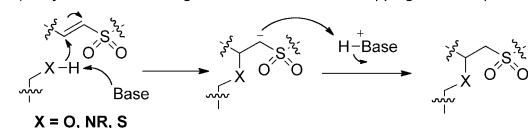
Yumeng Xi, Boliang Dong, Edward J. McClain, Qiaoyi Wang, Tesia L. Gregg, Novruz G. Akhmedov, Jeffrey L. Petersen, and Xiaodong Shi*

Abstract: A general method for the synthesis of α -substituted vinyl sulfones makes use of a combination of a triazole gold complex and gallium triflate. This efficient C–S bond formation between simple terminal alkynes and sulfinic acids provides access to various α -substituted vinyl sulfones.

The formation of C–S bonds is one of the fundamental transformations in organic synthesis.^[1] Organosulfur compounds do not only contain fundamental functional groups, such as thiol, sulfide, or disulfide units, which render them useful synthetic intermediates, but they also exist abundantly in biological systems ranging from small natural metabolites to proteins. Vinyl sulfones represent one particularly interesting sulfur-containing functional group. Vinyl sulfones have found widespread applications in biological research as covalent protease inhibitors^[2] or as substrates for bioconjugation^[3] owing to their good ability to act as a Michael acceptor to trap nucleophiles through the formation of stable covalent adducts (Scheme 1a). In principle, α -substituted vinyl sulfones, with a much less hindered β -carbon atom, should react faster in these transformations and should therefore be more suitable substrates for Michael addition reactions. However, in most cases, only *trans*- β -substituted vinyl sulfones are used. This is mainly due to the limited availability of methods for vinyl sulfone synthesis.

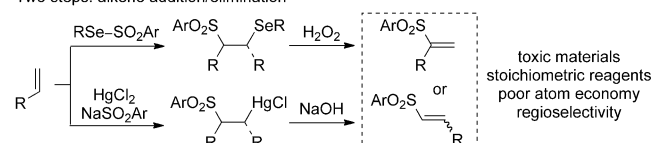
Previously described methods for the synthesis of vinyl sulfones generally involve 1) the elimination from α - or β -substituted sulfones, 2) the oxidation of vinyl sulfides, or 3) olefination reactions (e.g., Wittig, Horner–Wadsworth–Emmons, Julia reaction), which often take several steps from either toxic or unstable starting materials.^[4] For example, the two-step addition/elimination strategy usually requires toxic mercury- or selenium-containing starting materials, and the reactions suffer from poor regioselectivity (Scheme 1b). In contrast, transition-metal-catalyzed alkyne or alkene addition reactions allow the rapid formation of C–S and C–C bonds and have been applied to the synthesis of vinyl sulfones.

a) Vinyl sulfones in biological research: covalent trapping of nucleophiles

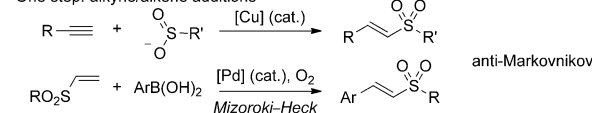


b) Current strategies for vinyl sulfone synthesis

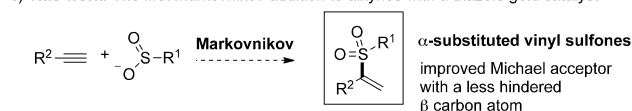
Two steps: alkene addition/elimination



One step: alkyne/alkene additions



c) This work: The first Markovnikov addition to alkynes with a triazole gold catalyst



Scheme 1. Vinyl sulfones: synthesis and biological applications.

However, both the copper-catalyzed sulfonyl radical addition to alkynes and the palladium-catalyzed Mizoroki–Heck reaction of vinyl sulfones gave exclusively the *trans*-configured β -substituted products, as anti-Markovnikov addition is preferred.^[5,6] To the best of our knowledge, procedures for the efficient synthesis of α -substituted vinyl sulfones have rarely been described.^[7] Most of the reported reactions suffer from limited substrate scope and poor α/β regioselectivity. Herein, we report a general synthesis of α -substituted vinyl sulfones that is enabled by the gold-catalyzed Markovnikov addition of sulfinic acids to alkynes with exclusive α regioselectivity.

Our general rationale entails that unlike for the radical reaction and the metal-catalyzed (Mizoroki–Heck) coupling reaction, the sulfinic acid addition to the π -acid activated alkyne should favor the formation of Markovnikov product with high efficiency. The challenge is to identify proper π -acid catalysts that can tolerate sulfinic acid while remaining active. Cationic gold species have been identified as one of the most effective catalysts for alkyne activation.^[8] However, gold(I)-catalyzed C–S bond formations have rarely been described in the literature, with most cases being intramolecular reactions.^[9] This could be attributed to the fact that S nucleophiles could form stable complexes with cationic gold(I) species, which dampens the reactivity and accelerates the rate of

[*] Y. Xi, B. Dong, E. J. McClain, Q. Wang, T. L. Gregg, Dr. N. G. Akhmedov, Prof. J. L. Petersen, Prof. X. Shi
C. Eugene Bennett Department of Chemistry
West Virginia University
Morgantown, WV 26506 (USA)
E-mail: Xiaodong.Shi@mail.wvu.edu
Homepage: <http://community.wvu.edu/~xs007/>

[**] We are grateful to the NSF (CAREER-CHE-0844602 and CHE-1228336) and the NSFC (21228204) for financial support.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201310142>.

decomposition.^[10] Furthermore, sulfoxides have been used as the O nucleophile in promoting similar alkyne addition reactions that involve gold carbenoid intermediates.^[11] We envisioned that the sulfinic acid might be a suitable nucleophile for gold(I)-catalyzed reactions, because 1) the sulfur atom of sulfinic acid is less basic, so that the sulfinic acid should not form a stable complex with the cationic gold(I) species, 2) the pK_a (ca. 3)^[12] of sulfinic acid is similar to that of carboxylic acids and phosphoric acids, which are suitable substrates for such addition processes,^[13] and 3) the gold(I)-alkyne complex will likely prefer S addition over O addition because of its soft nature. We commenced our investigations with the evaluation of various π -philic Lewis acids using *p*-toluenesulfinic acid (**1a**) and phenylacetylene (**2a**) as the starting materials.

As shown in Table 1, [Ph₃PAuCl]/AgX gave the best result (11%; entry 1); after six hours at room temperature, no further reaction was observed. Other π acids, such as PtCl₂, AuCl₃, Ga(OTf)₃, and In(OTf)₃, did not promote this reaction

Table 1: Optimization of the reaction conditions.^[a]

Entry	Catalyst (mol %)	Additive (mol %)	Time [h]	Yield ^[c] [%]
1	[Ph ₃ PAuCl]/AgOTf (5)	–	6	11
2	PtCl ₂ (10)	–	18	0
3	AuCl ₃ (10)	–	18	0
4	Ga(OTf) ₃ (10)	–	18	0
5	In(OTf) ₃ (10)	–	18	0
6	AgSbF ₆ (10)	–	18	6
7	[Ph ₃ PAuCl]/AgBF ₄ (5)	–	6	14
8	[Ph ₃ PAuCl]/AgSbF ₆ (5)	–	6	18
9	[Ph ₃ PAuNTf ₂] (5)	–	6	13
10 ^[b]	[IPrAuCl]/AgX (5)	–	6	≤ 25
11 ^[b]	[XPhosAuCl]/AgX (5)	–	6	≤ 60
12 ^[b]	[BrettPhosAuCl]/AgX (5)	–	6	≤ 76
13	[BrettPhosAu(TA)]OTf (5)	–	6	32
14	[BrettPhosAu(TA)]OTf (5)	Ga(OTf) ₃ (5)	6	80
15	[BrettPhosAu(TA)]OTf (5)	Ga(OTf) ₃ (10)	6	91

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.4 equiv), gold catalyst (5 mol %), and additive (if applicable) in dry DCE (0.8 mL) under argon atmosphere. [b] X[–] = TfO[–], Tf₂N[–], SbF₆[–]. [c] The yield was determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. DCE = 1,2-dichloroethane, TA = 1*H*-benzotriazole, Tf = tri-fluoromethanesulfonyl.

at all (entries 2–5). A small amount of product was formed in the presence of AgSbF₆ (10 mol %) after a prolonged reaction time (18 h). Encouraged by these results, we then tried to optimize the reaction by screening silver salts with different counteranions (entry 7–9). Unfortunately, no significant changes were observed. When a more strongly electron-donating N-heterocyclic carbene was employed as the ligand, the yields improved slightly, but were still unsatisfactory (up to 25%; entry 10). The bulky and electron-rich ligand 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos)

promoted the desired transformation much more efficiently (60%; entry 11). This strongly implies that the yield is directly related to the ligand used. We then turned our attention to an even bulkier and more electron-rich ligand, namely 2-(dicyclohexylphosphino)-3,6-dimethoxy-2',4',6'-triisopropyl-1,1'-biphenyl (BrettPhos), which was introduced to homogeneous gold catalysis by Zhang and co-workers.^[14] An even higher yield (76%; entry 12) was obtained with [BrettPhosAuCl]/AgSbF₆. This is presumably due to the fact that steric congestion, which is imposed by the bulky substituents, stabilizes the cationic gold center, thus preventing decomposition. Encouraged by our recent finding that the 1,2,3-triazole gold complex is thermally stable, yet less reactive, we synthesized [BrettPhosAu(TA)]OTf (TA = 1*H*-benzotriazole).^[15] As expected, it gave a much slower reaction rate (entry 13). However, the addition of Ga(OTf)₃ as an external additive substantially accelerated the rate of the reaction,^[16] giving the desired product in 80% yield. Increasing the gold/gallium ratio from 1:1 to 1:2 led to 91% yield. Control experiments showed that Ga(OTf)₃ alone could not catalyze this reaction, which rules out the possibility that the alkyne was activated by the Ga^{III} center.

With the optimized conditions in hand, we embarked on the evaluation of the substrate scope (Table 2). Distinct reactivities were observed with different alkynes. First, various aromatic alkynes were tested and gave the corresponding products in modest to good yields. The electronic effect of substituents at the *para* position of the aryl acetylene was evaluated (entries 1–5). The reaction tolerated both electron-withdrawing (**3bc**, **3be**) and electron-donating groups (**3bb**, **3bd**). Aromatic alkynes with substituents at the *meta* and *ortho* positions (**3bf–3bh**) also gave the vinyl sulfones in good yields. Heteroaromatic alkynes could also be used as coupling partners in this transformation (**3bi**, **3bj**). Impressively, an enyne underwent this transformation to give the desired diene sulfone **3bk**, demonstrating the mildness of the reaction conditions. Aliphatic alkynes generally led to the corresponding vinyl sulfones in modest yield (35–45%) at room temperature. Better yields were obtained by employing harsher conditions (**3al–3ap**; see the Supporting Information). Unfortunately, internal alkynes were not suitable substrates for this transformation.^[17] Notably, 1-trimethylsilyl-1-propyne afforded the corresponding α -methyl vinyl sulfone **3an**, which must otherwise be synthesized from propyne gas. Moreover, amino acid derivative **3bq**, estrone derivative **3br**, and cholesterol derivative **3as** were also successfully prepared, which highlights the good functional group tolerance and potential applications of this method. The regioselectivity of the nucleophilic addition was first confirmed by ¹H NMR analysis and later unequivocally established by X-ray crystallography (**3bh**).^[18] It should be noted that some products have small amounts of impurities in the NMR spectra because of their relatively poor stability. In these cases, NMR yields are given.

To fully evaluate this method, different sulfinic acids were tested. In practice, however, the unstable sulfinic acids rapidly decompose through an undesired oxidation, which largely limits their synthetic utility. To develop a robust synthetic method, bench-stable sodium benzenesulfinate was employed

Table 2: Alkyne scope.^[a]

$\text{R}-\text{C}_6\text{H}_4-\text{SO}_2\text{Na} + \text{R}'\text{C}\equiv\text{C} \xrightarrow[\text{dry DCE (0.25 M), RT-45 }^\circ\text{C, Ar}]{[\text{BrettPhosAu(TA)}]\text{OTf (5 mol\%)} \text{ Ga(OTf)}_3 \text{ (10 mol\%)}} \text{R}-\text{C}_6\text{H}_4-\text{SO}_2\text{C(R')=CH}_2$	
1a (R = Me) 1b (R = H)	2
3	
3ba , 91% ^[b] 3bb , 69% ^[c,d] 3bc , 50% 3bd , 80% 3be , 76% 3bf , 84% 3bg , 62% ^[b] 3bh , 85% 3bi , 59% ^[b] 3bj , 74% ^[b] 3bk , 78% ^[c] 3al , 71% ^[c,e] 3bm , 70% ^[e] 3an , 85% ^[e] 3ao , 87% ^[c,e] 3ap , 82% ^[e] 3bq , 54% ^[d] 3br , 86% ^[e] 3as , 62% ^[b,f]	
Crystal structure of 3bh	

[a] General reaction conditions: **1b** (0.2 mmol), **2** (0.4 mmol), [BrettPhosAu(TA)]OTf (5 mol%), and Ga(OTf)₃ (10 mol%) in DCE (0.8 mL) under argon atmosphere. Yields of isolated products are given. See the Supporting Information for detailed conditions. [b] Yields determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as the internal standard. [c] Contains < 5% of an impurity. [d] [BrettPhosAuNTf₂] was used. [e] Ga(OTf)₃ (20 mol%) and [BrettPhosAu(TA)]OTf (10 mol%). [f] Ga(OTf)₃ (30 mol%) and [BrettPhosAu(TA)]OTf (15 mol%).

as a suitable precursor to generate the corresponding sulfinic acid in situ in the presence of a stoichiometric amount of acid. Bearing this idea in mind, different acids were screened in the presence of the gold and gallium catalysts (Scheme 2). Trifluoroacetic acid (TFA) was found to be the best choice of acid, giving the desired product in 91% yield (determined by NMR spectroscopy) through this one-pot procedure. The addition of methanesulfonic acid (MsOH) gave the product in only modest yield, whereas acetic acid did not promote this reaction at all.

Therefore, a practical one-pot synthesis of vinyl sulfones has been developed. We then evaluated the scope of sulfinic acids. Several commercially available sodium sulfonates were examined (Table 3). In general, substituted benzenesulfonates gave promising yields (**3aa–3ea**). The halogen substituent on

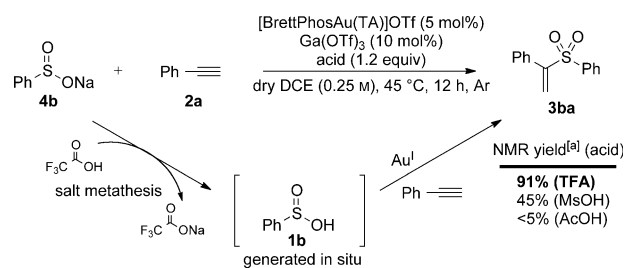

Scheme 2. One-pot synthesis of vinyl sulfone **3ba** from bench-stable sodium benzenesulfonate (**4b**). [a] Yield determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as the internal standard.

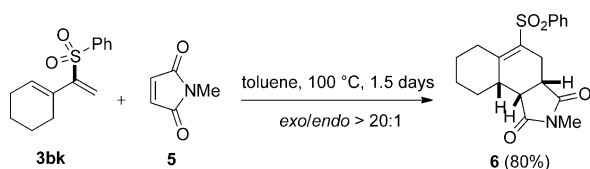
Table 3: Sulfinic acid scope.^[a]

$\text{R}-\text{SO}_2\text{Na} + \text{Ph}-\text{C}\equiv\text{C} \xrightarrow[\text{dry DCE (0.25 M), 45 }^\circ\text{C, 12 h, Ar}]{[\text{BrettPhosAu(TA)}]\text{OTf (5 mol\%)} \text{ Ga(OTf)}_3 \text{ (10 mol\%)} \text{ TFA (1.2 equiv)}} \text{R}-\text{SO}_2\text{C(Ph)=CH}_2$	
4	2a
3	
3ba , 91% ^[b] 3aa , 86% ^[c] 3ca , 79% 3da , 83% 3ea , 68% 3fa , 82% 3ga , 70% 3ha , 73% 3ia , 81% ^[b]	

[a] General reaction conditions: **4** (0.2 mmol), TFA (0.24 mmol), **2a** (0.3 mmol), [BrettPhosAu(TA)]OTf (5 mol%) and Ga(OTf)₃ (10 mol%) in DCE (0.8 mL), argon atmosphere, 45 °C. Yields of isolated products are given. [b] Yields determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as the internal standard. [c] **1a** was used instead of sodium sulfinate and TFA; reaction run at RT.

the benzene ring allows for further derivatization through transition-metal-catalyzed cross-coupling reactions. A heterocyclic sulfinic acid was also a successful substrate for this transformation (**3fa**). Aliphatic sulfinic acids gave the corresponding vinyl sulfones in slightly lower yields (**3ga–3ia**).

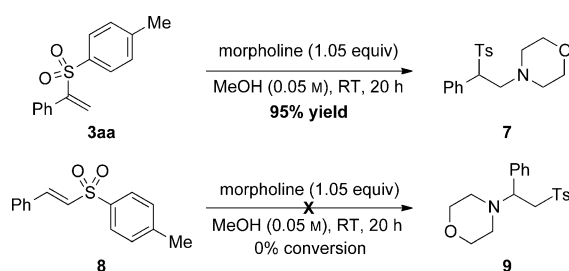
The synthetic utility of α -substituted vinyl sulfones still remains underexplored because of the paucity of these compounds. However, their close resemblance to β -substituted vinyl sulfones and disubstituted vinyl sulfones suggests potential applications of these compounds in cycloaddition reactions, Michael addition, and desulfonylation with different regioselectivity. Furthermore, this method provides a concise and regioselective synthesis of 2-sulfonyl dienes, a valuable synthon in organic synthesis.^[19] The Diels–Alder reaction^[20] of **3bk** and *N*-methyl maleimide afforded the tricyclic ring system with excellent *endo* selectivity (Scheme 3). The product stereochemistry was confirmed by



Scheme 3. Diels-Alder reaction between 2-sulfonyl diene **3bk** and N-methyl maleimide (**5**).

comprehensive 1D and 2D NMR analysis (see the Supporting Information for details).

As mentioned earlier, our initial impetus to develop this method was to provide a general method for the synthesis of Michael receptors with properties that are superior to those of the corresponding β -substituted vinyl sulfones. To this end, α -substituted vinyl sulfone **3aa** and β -substituted vinyl sulfone **8** were subjected to the secondary amine morpholine as the nucleophile.^[21] Gratifyingly, the α -substituted vinyl sulfone gave the Michael adduct in almost quantitative yield at room temperature. In sharp contrast, the β -substituted vinyl sulfone gave no conversion at all under the same set of conditions. This result suggests that the α -substituted vinyl sulfone may find applications in biological science as a valuable counterpart to the widely used β -substituted vinyl sulfones (Scheme 4).



Scheme 4. Comparison of the aza-Michael addition of morpholine to α - or β -substituted vinyl sulfones. Ts = 4-toluenesulfonyl.

In summary, we have developed a general method for the synthesis of α -substituted vinyl sulfones from simple terminal alkynes and sulfinic acids. Efficient C–S bond formation was enabled by homogenous gold catalysis and by overcoming the inherent reactivity of cationic gold(I) species through the rational selection of a nucleophile, which sheds light on other challenging carbon–heteroatom bond formations in gold catalysis. Furthermore, a comparison of α - and β -substituted vinyl sulfones towards Michael addition highlights the potential application of the former compounds in the biological and pharmaceutical sciences. Such investigations, along with a study of the detailed reaction mechanism, are currently underway in our laboratory.

Received: November 21, 2013
Revised: February 5, 2014
Published online: April 1, 2014

Keywords: C–S bond formation · gold · Lewis acids · Markovnikov addition · vinyl sulfones

- [1] a) A. Vigalok, *C–X Bond Formation*, Springer, Heidelberg, **2010**; b) A. K. Yudin, *Catalyzed Carbon-Heteroatom Bond Formation*, Wiley-VCH, Weinheim, **2012**; c) H. Liu, X. Jiang, *Chem. Asian J.* **2013**, *8*, 2546.
- [2] a) J. T. Palmer, D. Rasnick, J. L. Klaus, D. Bromme, *J. Med. Chem.* **1995**, *38*, 3193; b) M. M. M. Santos, R. Moreira, *Mini-Rev. Med. Chem.* **2007**, *7*, 1040; c) I. D. Kerr, J. H. Lee, C. J. Farady, R. Marion, M. Rickert, M. S. Kailash, C. Pandey, C. R. Caffrey, J. Legac, E. Hansell, J. H. McKerrow, C. S. Craik, P. J. Rosenthal, L. S. Brinen, *J. Biol. Chem.* **2009**, *284*, 25697; d) A. F. Kisselev, W. A. van der Linden, H. S. Overkleeft, *Chem. Biol.* **2012**, *19*, 99; e) L. Ni, X. S. Zheng, P. K. Somers, L. K. Hoong, R. R. Hill, E. M. Marino, K.-L. Suen, U. Saxena, C. Q. Meng, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 745.
- [3] a) J. Morales-Sanfrutos, J. Lopez-Jaramillo, M. Ortega-Munoz, A. Megia-Fernandez, F. Perez-Balderas, F. Hernandez-Mateo, F. Santoyo-Gonzalez, *Org. Biomol. Chem.* **2010**, *8*, 667; b) F. J. Lopez-Jaramillo, F. Hernandez-Mateo, F. Santoyo-Gonzalez, *Integrative Proteomics* (Ed.: H.-C. E. Leung), InTech, Rijeka, **2012**, pp. 301–327.
- [4] a) V. Nair, A. Augustine, T. D. Suja, *Synthesis* **2002**, 2259; b) D. C. Meadows, J. Gervay-Hague, *Med. Res. Rev.* **2006**, *26*, 793; c) H. Qian, X. Huang, *Synlett* **2001**, 1913; d) X. Huang, D. Duan, W. Zheng, *J. Org. Chem.* **2003**, *68*, 1958; e) W. M. Xu, E. Tang, X. Huang, *Synthesis* **2004**, 2094; f) D. Díez, P. García, I. S. Marcos, N. M. Garrido, P. Basabe, H. B. Broughton, J. G. Urones, *Tetrahedron* **2005**, *61*, 699; g) Z.-H. Guan, W. Zuo, L.-B. Zhao, Z.-H. Ren, Y.-M. Liang, *Synthesis* **2007**, 1465; h) G. Signore, C. Malanga, R. Menicagli, *Tetrahedron* **2008**, *64*, 11218; i) B. Das, M. Lingaiah, K. Damodar, N. Bhunia, *Synthesis* **2011**, 2941; j) S. Liang, R.-Y. Zhang, G. Wang, S.-Y. Chen, X.-Q. Yu, *Eur. J. Org. Chem.* **2013**, 7050.
- [5] a) J. M. Baskin, Z. Wang, *Org. Lett.* **2002**, *4*, 4423; b) V. Nair, A. Augustine, T. G. George, L. G. Nair, *Tetrahedron Lett.* **2001**, 42, 6763; c) S. Cacchi, G. Fabrizi, A. Goggiani, L. M. Parisi, R. Bernini, *J. Org. Chem.* **2004**, *69*, 5608; d) A. Battace, T. Zair, H. Doucet, M. Santelli, *Synthesis* **2006**, 3495; e) F. Huang, R. A. Batey, *Tetrahedron* **2007**, *63*, 7667; f) M. Bian, F. Xu, C. Ma, *Synthesis* **2007**, 2951; g) D. C. Reeves, S. Rodriguez, H. Lee, N. Haddad, D. Krishnamurthy, C. H. Senanayake, *Tetrahedron Lett.* **2009**, *50*, 2870; h) Q.-L. Xu, L.-X. Dai, S.-L. You, *Org. Lett.* **2010**, *12*, 800; i) N. Taniguchi, *Synlett* **2011**, 1308; j) N. Taniguchi, *Synlett* **2012**, 1245.
- [6] Radical intermediates favor anti-Markovnikov addition; see Ref. [5] and: Q. Lu, J. Zhang, G. Zhao, Y. Qi, H. Wang, A. Lei, *J. Am. Chem. Soc.* **2013**, *135*, 11481.
- [7] a) R. Chawla, R. Kapoor, A. K. Singh, L. D. S. Yadav, *Green Chem.* **2012**, *14*, 1308; b) J. W. Lee, C.-W. Lee, J. H. Jung, D. Y. Oh, *Synth. Commun.* **2000**, *30*, 2897; c) K. Inomata, S.-i. Sasaoka, T. Kobayashi, Y. Tanaka, S. Igarashi, T. Ohtani, H. Kinoshita, H. Kotake, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1767; d) K. Inomata, T. Kobayashi, S.-i. Sasaoka, H. Kinoshita, H. Kotake, *Chem. Lett.* **1986**, *15*, 289; e) J. B. Hendrickson, P. S. Palumbo, *Tetrahedron Lett.* **1985**, *26*, 2849; f) C.-N. Hsiao, H. Shechter, *Tetrahedron Lett.* **1982**, *23*, 3455; g) T. G. Back, S. Collins, *J. Org. Chem.* **1981**, *46*, 3249; h) H. Kotake, K. Inomata, M. Sumita, *Chem. Lett.* **1978**, *7*, 717; i) S. Chodroff, W. Whitmore, *J. Am. Chem. Soc.* **1950**, *72*, 1073.
- [8] a) A. S. K. Hashmi, F. D. Toste, *Modern Gold Catalyzed Synthesis*, Wiley-VCH, Weinheim, **2012**; b) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2012**, *41*, 2448; c) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351; d) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266; e) E. Jiménez-Núñez, A. M.

- Echavarren, *Chem. Rev.* **2008**, *108*, 3326; f) R. A. Widenhoefer, *Chem. Eur. J.* **2008**, *14*, 5382; g) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; h) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410; i) L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271; j) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896.
- [9] a) N. Morita, N. Krause, *Angew. Chem.* **2006**, *118*, 1930; *Angew. Chem. Int. Ed.* **2006**, *45*, 1897; b) I. Nakamura, T. Sato, Y. Yamamoto, *Angew. Chem.* **2006**, *118*, 4585–4587; *Angew. Chem. Int. Ed.* **2006**, *45*, 4473–4475; c) P. W. Davies, S. J. C. Albrecht, *Chem. Commun.* **2008**, 238; d) I. Nakamura, T. Sato, M. Terada, Y. Yamamoto, *Org. Lett.* **2008**, *10*, 2649; e) L. L. Santos, V. R. Ruiz, M. J. Sabater, A. Corma, *Tetrahedron* **2008**, *64*, 7902; f) A. Aponick, C.-Y. Li, J. Malinge, E. F. Marques, *Org. Lett.* **2009**, *11*, 4624; g) X. Zhao, Z. Zhong, L. Peng, W. Zhang, J. Wang, *Chem. Commun.* **2009**, 2535; h) P. W. Davies, S. J. C. Albrecht, *Angew. Chem.* **2009**, *121*, 8522; *Angew. Chem. Int. Ed.* **2009**, *48*, 8372; i) M. Jean, J. Renault, P. van de Weghe, N. Asao, *Tetrahedron Lett.* **2010**, *51*, 378; j) R. J. Mudd, P. C. Young, J. A. Jordan-Hore, G. M. Rosair, A.-L. Lee, *J. Org. Chem.* **2012**, *77*, 7633; k) A. Corma, A. Leyva-Pérez, M. J. Sabater, *Chem. Rev.* **2011**, *111*, 1657.
- [10] P. C. Young, S. L. J. Green, G. M. Rosair, A.-L. Lee, *Dalton Trans.* **2013**, 42, 9645.
- [11] For representative examples, see: a) N. D. Shapiro, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 4160; b) G. Li, L. Zhang, *Angew. Chem.* **2007**, *119*, 5248; *Angew. Chem. Int. Ed.* **2007**, *46*, 5156; c) C.-W. Li, K. Pati, G.-Y. Lin, H.-H. Hung, R.-S. Liu, *Angew. Chem.* **2010**, *122*, 10087; *Angew. Chem. Int. Ed.* **2010**, *49*, 9891; d) B. Lu, Y. Li, Y. Wang, D. H. Aue, Y. Luo, L. Zhang, *J. Am. Chem. Soc.* **2013**, *135*, 8512.
- [12] D. De Filippo, F. Momicchioli, *Tetrahedron* **1969**, *25*, 5733.
- [13] a) B. C. Chary, S. Kim, *J. Org. Chem.* **2010**, *75*, 7928; b) T. Luo, M. Dai, S. L. Zheng, S. L. Schreiber, *Org. Lett.* **2011**, *13*, 2834; c) M. R. Kuram, M. Bhanuchandra, A. K. Sahoo, *J. Org. Chem.* **2010**, *75*, 2247; d) P. H. Lee, S. Kim, A. Park, B. C. Chary, S. Kim, *Angew. Chem.* **2010**, *122*, 6958; *Angew. Chem. Int. Ed.* **2010**, *49*, 6806. Sulfonic acids are also suitable substrates for such addition reactions; see: e) D.-M. Cui, Q. Meng, J.-Z. Zheng, C. Zhang, *Chem. Commun.* **2009**, 1577.
- [14] L. Ye, W. He, L. Zhang, *Angew. Chem.* **2011**, *123*, 3294; *Angew. Chem. Int. Ed.* **2011**, *50*, 3236.
- [15] a) H. Duan, S. Sengupta, J. L. Petersen, N. G. Akhmedov, X. Shi, *J. Am. Chem. Soc.* **2009**, *131*, 12100; b) Y. Chen, W. Yan, N. G. Akhmedov, X. Shi, *Org. Lett.* **2010**, *12*, 344; c) D. Wang, X. Ye, X. Shi, *Org. Lett.* **2010**, *12*, 2088; d) D. Wang, L. N. S. Gautam, C. Bollinger, A. Harris, M. Li, X. Shi, *Org. Lett.* **2011**, *13*, 2618; e) Q. Wang, S. Aparaj, N. G. Akhmedov, J. L. Petersen, X. Shi, *Org. Lett.* **2012**, *14*, 1334; f) D. Wang, R. Cai, S. Sharma, J. Jirak, S. K. Thummanapelli, N. G. Akhmedov, H. Zhang, X. Liu, J. L. Petersen, X. Shi, *J. Am. Chem. Soc.* **2012**, *134*, 9012; g) Y. Xi, B. Dong, X. Shi, *Beilstein J. Org. Chem.* **2013**, *9*, 2537; h) Y. Yu, W. Yang, F. Rominger, A. S. K. Hashmi, *Angew. Chem.* **2013**, *125*, 7735; *Angew. Chem. Int. Ed.* **2013**, *52*, 7586; i) Y. Xi, D. Wang, X. Ye, N. G. Akhmedov, J. L. Petersen, X. Shi, *Org. Lett.* **2014**, *16*, 306; j) Y. Xi, Q. Wang, Y. Su, M. Li, X. Shi, *Chem. Commun.* **2014**, 50, 2158; k) Q. Wang, S. E. Motika, N. G. Akhmedov, J. L. Petersen, X. Shi, *Angew. Chem.* **2014**, DOI: 10.1002/ange.201402614; *Angew. Chem. Int. Ed.* **2014**, DOI: 10.1002/anie.201402614.
- [16] See Ref. [15i]. According to our previous observations, the role of gallium triflate involves coordination to the triazole ligand, which frees the cationic gold complex.
- [17] The α,β -diaryl and α -aryl- β -alkyl alkynes gave complex reaction mixtures, which is presumably due to the decomposition of sulfinic acid at higher temperatures. The α,β -dialkyl alkynes gave some products, the structures of which could not be identified yet (but they are not the desired vinyl sulfones).
- [18] CCDC 966046 (**3bh**) 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.
- [19] a) J.-E. Bäckvall, R. Chinchilla, C. Najera, M. Yus, *Chem. Rev.* **1998**, *98*, 2291; b) T. G. Back, K. N. Clary, D. Gao, *Chem. Rev.* **2010**, *110*, 4498.
- [20] a) J.-E. Bäckvall, S. K. Juntunen, *J. Am. Chem. Soc.* **1987**, *109*, 6396; b) T.-S. Chou, S.-C. Hung, *J. Org. Chem.* **1988**, *53*, 3020; c) R. F. de la Pradilla, C. Montero, M. Tortosa, A. Viso, *Chem. Eur. J.* **2005**, *11*, 5136.
- [21] T. G. Back, M. Parvez, H. Zhai, *J. Org. Chem.* **2003**, *68*, 9389.