Gold(I)-Catalyzed Bis-Alkynylation Reaction of Aromatic Aldehydes with Alkynylsilanes

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Abstract: The first successful gold(I)-catalyzed reaction of aryl aldehydes with trimethyl(arylethynyl)silanes to furnish bis-alkynylated derivatives is reported. Key C–C bond-forming events involved in the catalytic cycle are analyzed.

Keywords: aldehydes; alkynes; coupling; gold; silicon

Nowadays gold catalysis offers a valuable tool in searching for new chemical transformations^[1] and approaching a swift increase of molecular complexity from carbon-carbon unsaturations.^[2] The selective activation of an alkyne by a proper carbophilic gold centre is often at the onset of these reactions.^[3,4]

A significant bis-alkynylation reaction of aromatic aldehydes and alkynylsilanes was recently disclosed. Cooperation of two metals, a rhenium(I) complex and gold(I) chloride, is required to provide catalytic access to the depicted 1,4-diyne scaffolds (Scheme 1).^[5] The synergic action of the two catalysts to accomplish the overall bis-alkynylation process is required. This claim is solidly supported by pertinent experimental work. Also, concerning the second C–C bond-forming event, which eventually furnishes the products through an intermediate propargyl cation, the central role that the rhenium catalyst plays was proven,^[5,6] and gold chloride was shown to be inefficient to assist this task.

On the basis of our ongoing research program in gold catalysis^[7] and the acquired experience in iodonium-mediated activation of C–C unsaturations for reaction discovery,^[8] we were intrigued about the possibility of timely developing an entirely gold-based approach to achieve this demanding aldehyde bi-functionalization process, which ultimately relies on the catalytic and consecutive creation of two C–C bonds in one synthetic operation.^[9] Considering the conceptual frame graphically outlined in Scheme 2, we reasoned that tuning the nature of the electrophilic metal would allow execution of this tandem process on the exclusive basis of gold catalysis.^[10]

First, as a consequence of the activation of the alkyne by the carbophilic gold catalyst, and likely assisted by the presence of the added carbonyl group, the reaction could give rise to the formation of the corresponding gold acetylide. In turn, this would pro-



(Kuninobu, Takai et al. ref.^[5])

Scheme 1. Seminal work on the synthesis of diethynylmethane frames by the rhenium/gold-catalyzed direct coupling between aldehydes and alkynylsilanes.

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Scheme 2. Working hypothesis to obtain 1,4-diynes from aldehydes and alkynylsilanes under sole gold(I)-catalysis.

vide an activated form of the carbonyl group as the result of its interaction with the *in situ* generated source of an oxophilic silicon reagent.^[11] This set-up would favour the formation of the first C–C bond, which affords an O-silylated propargyl alcohol. Next, the inherent basic character of the ether would facilitate its activation, again as a consequence of its competent role to capture an additionally released silicon-based electrophile. In the end, the eventually resulting propargyl cation would trap another molecule of the gold acetylide and deliver the noticed 1,4-diyne scaffold.^[12]

We decided to explore the validation of this hypothesis making use of the already well recognized alteration in the reactivity trend for gold(I) catalysts as function of the nature of the ancillary ligand. This notion provides a key designing feature in attempting to meet the goal of accessing the target catalytic bisalkynylation reaction on the ground of a single gold catalyst.^[13] In the screening of gold catalysts, the room temperature reaction of benzaldehyde **1a** with trime-thyl(phenylethynyl)silane **2a** for a period of 90 min was investigated as model (Scheme 3).



Scheme 3. Gold catalysts for aldehyde bis-alkynylation.

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Several ligands were found to be useful to produce gold(I) complexes that behave as active catalysts for the target transformation. The best result in the direct assembly of 3a was accomplished using di-tert-butyl-(o-biphenyl)-phosphine (JohnPhos) as the ancillary ligand. Besides, bis(trifluoromethanesulfonyl)imidate (NTf_2) was selected as counteranion, on a routine basis. Compared with halides, its use avoids the need for adding silver salts to generate gold catalysts endowed of high electrophilicity, as early documented by Gagosz.^[14] For the reaction of **1a** with **2a**, heating allows us to shorten the reaction time. Furthermore, more demanding substrates required this option to react efficiently. In this scenario, the gold(I) complex with JohnPhos (Scheme 3, ligand L3) was found to be superior to the other ligands tested.^[15]

The scope of the reaction was further investigated using thermal conditions, in search for both a fast reaction and wide aldehyde compatibility. After some initial exploratory studies, it was found that simply conducting the reaction at 70 °C, in 1,2-dichloroethane as solvent, provides convenient experimental conditions for various aldehydes. The results for the John-PhosAuNTf₂-catalyzed reaction of the trimethylsilyl derivative of phenylacetylene towards a variety of carbonyl derivatives are now summarized and depicted in Table 1.

The reaction allows us to prepare a representative set of 3-aryl-substituted 1,4-diynes in fair to good yield. Interestingly and for the first time, this transformation is shown to take place under the sole influence of gold(I) catalysis. Aryl- and naphthyl-substituted aldehydes (entries 4 and 5) react satisfactorily under these conditions. For the former the substituent at the 4-position was modified and the process was found to be compatible with both electron-donating groups (see, for instance, entries 7 and 9) and electron-withdrawing groups (entries 1, 6 and 8). The reaction outcome is also of practical utility for substrates in which the substituent switches from the para- to the ortho-position (entries 2 and 3). Even a more densely functionalized molecule was efficiently transformed (see entry 10).

Hexanal, a simple aliphatic aldehyde, failed to react using the same experimental protocol. Nevertheless, simply changing the solvent, using acetonitrile rather than 1,2-dicholoroethane, allows the first addition step to take place (Scheme 4); thus, matching the early noticed scope for the reaction of aliphatic aldehydes catalyzed by the bimetallic system, but relying only on a proper gold catalyst.^[5]

Next, a microwave-assisted heating protocol was developed and found to be useful for reducing the reaction time and the catalyst loading at once. For instance, diyne **3h** was prepared from 4-methoxybenzaldehyde and phenylacetylene in parallel yield to the one accomplished under the standard thermal condi-





Table 1. Gold-catalyzed bis-alkynylation of aryl aldehydes.





[a] Isolated yield after chromatography.

[b] Yield measured from the crude reaction by NMR, using acetanilide as internal standard. Mono-alkynylated 4g also present in 12% yield.



Scheme 4. Catalytic mono alkynylation of hexanal.



Scheme 5. 1,4-Diynes: microwave-assisted gold catalysis.

tions developed earlier (Table 1, entry 7), but now using only 1 mol% of JohnPhosAuNTf₂, 3 min reaction time and lower excess of alkyne (Scheme 5).

This protocol was further tested over additional model compounds. The results are reported in Table 2.

The catalyst loading was diminished in all cases. For most of alkynylsilanes the reaction time was reduced without much affecting the yield, which even was slightly improved for some specific products, such as for 3c. Besides, under these alternative experimental conditions, silyl-substituted aliphatic terminal alkynes (entries 9-11) were found to be useful partners in processes taking place at 120°C, under microwave irradiation. Although still in modest yield, and requir-

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Table 2. Microwave-assisted aldehyde bis-alkynylation.



^[a] Isolated yield after chromatography.

^[b] 57% yield for **3m** using the conditions depicted in Table 1 (70°C, 4 h, 5 mol% of catalyst).

^[c] 65% yield for **3n** under the conditions depicted in Table 1 (4 h at 70°C, 5 mol% of added catalyst).

^[d] At 120 °C (MW), 5 mol% catalyst loading.

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ing further optimization, this finding expands the scope for the known metal-catalyzed direct bis-alkynylation reaction of aldehydes and alkynylsilanes.^[5,16] Moreover, the reactivity of a two-ends silicon-caped and chemically differentiated surrogate for acetylene is challenging. Thus, starting from readily available TMS-C=C-TBDMS, the attractive diyne **3s** (Table 2, entry 12) was directly assembled from benzaldehyde.

This experimental protocol is robust. Typically, reactions were conducted on a 0.4-mmol scale of aldehyde **1**. Remarkably, using the protocol defined in Scheme 5, **3c** was prepared after chromatography (silica gel, hexane-CH₂Cl₂, 20:1) on a gram scale (1.2 g, 65%) from the reaction of **1c** (6 mmol) and **2a** (2.5 equiv.) catalyzed by JohnPhosAuNTf₂ (1 mol%), in 1,2dichloroetane (12 mL) heating under microwave irradiation at 150°C for 15 min.

The content reported in Table 1 and Table 2 agrees with the assumption outlined in Scheme 1 and reveals that gold, in its own right, is a proper metal to catalyze the desired bis-alkynylation process, simply on adjusting the electrophilic nature and stability of the intended catalyst. Further experimental work was conducted to scrutinize this claim and to offer a rationale for some of the noticed findings. Relevant data are given in the following paragraphs.

At the onset, the possibility of aldehydes directly reacting with gold acetylides was ruled out on an experimental basis. A mixture of **1a** and the gold acetylide **6a** (1:2.5 molar ratio) was stirred at room temperature, in 1,2-dichloroethane, for one hour and a half without noticeable change. Subsequently, the mixture was heated at 70 °C for an identical period of time. NMR inspection of the crude reaction shows a lack of C–C bond-forming processes taking place.

The proposal formulated in Scheme 1 invokes the addition of gold(I) acetylide^[17] to the aldehyde activated by the *in situ* generated active silicon.^[18] Additional support to validate this arrangement comes from the experiment depicted in Scheme 6.



Scheme 6. Activating aldehydes towards gold acetylides.

The examples in Scheme 6 endorse the intended active involvement of a gold acetylide as a reactive intermediate. Interestingly, this experimental protocol stands for the labile heterocyclic indole scaffold.^[19]

The activation of alkynylsilanes 2 by gold(I) was also tested. Exposing 2a to JohnPhosAuNTf₂ in the absence of 1 proves that alkyne desilylation smoothly occurs. In this regard, addition of 2a to a solution of the above mentioned gold source $(2.5 \times 10^{-3} \text{ M in dry CDCl}_3$, at room temperature, 1.0:1.5 molar ratio for gold and the alkyne, respectively) furnishes the σ,π -digold phenylacetylene adduct 7a.^[20,21]



Alternatively, a fast formation of **7a** was also evident upon NMR monitoring of the evolution of the



Scheme 7. Gold(I) catalysis: alkynylation of propargyl silyl ether.

reaction of JohnPhosAuNTf₂ (0.05 mmol) with excess (1 mmol) of **2a**, in dry CDCl₃. Almost instantaneously, a representative peak is evident from the ³¹P NMR spectrum. This new signal at δ =62.7 ppm is indicative of the desilylation^[21c] and accounts well for the formation of **7a** under the reaction conditions.

The capability of JohnPhosAuNTf₂ to catalytically promote the second alkynylation step was also documented (Scheme 7).

This time, **2a** was allowed to react with pure **4a** in the presence of the catalyst, at room temperature, to afford the target bis-alkynylated derivative **3a** in 60% isolated yield. The observed outcome for this reaction offers clear proof of the competence of the title modification of gold(I) to effect catalytic access to the second key C–C bond-forming event.^[22]

Besides, ongoing activity on dinuclear gold σ,π alkyne complexes and their impact on various processes involving dual catalysis^[23] prompted us to broach the reactivity of **7a** in this new synthetic scenario.^[24] In this regard, reaction of **1h** with **2a** under the catalytic influence of the σ,π -digold catalyst **7a** (2.5 mol%) was totally inefficient to produce the desired **3h**, either at room temperature or heating in 1,2-dichloroetane at 70 °C. Remarkably, carrying out the reaction at 150 °C, under microwave irradiation, affords **3h** in 72% isolated yield, in 30 min (Scheme 8).

Eventually, altogether those experiments nicely provide compelling evidence that firmly support the invoked hypothesis behind the aim for this study.^[25] Overall, and for the first time, gold(I) catalysis has been found to be efficient to accomplish a direct aldehyde bis-alkynylation synthetic operation. The outcome of the herein reported protocol, based on the sole use of JohnPhosAuNTf₂ as catalyst parallels, and slightly enlarges, the scope noticed for the bimetallic catalytic systems based on Re(I) and Au(I) used in the pioneering work by Kuninobu and Takai. Reasearch is in progress in our laboratory to further investigate the impact of this transformation. Main efforts will be devoted to unveil new catalytic processes where the unique combination of gold and silicon might acts as a trigger as the result of the in situ switching from carbophilic to oxophilic control.



Scheme 8. σ,π -Digold species in the catalytic aldehyde bis-alkynylation reaction.

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Experimental Section

General Procedure

A mixture of aldehyde **1** (1 equiv.), alkynylsilane **2** (3.75 equiv.) and JohnPhosAuNTf₂ (5 mol%) was dissolved in 1,2-dichloroethane (0.5 M) and heated at 70 °C to afford bis-alkynylation product **3**, which was purified by flash chromatography (silica gel, hexane).

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References

- For an overall view, see: a) Modern Gold Catalyzed Synthesis, (Eds.: A. S. K. Hashmi, F. D. Toste), Wiley-VCH, Weinheim, 2012. For selected recent reviews, see: b) A. S. K. Hashmi, M. Bührle, Aldrichimica Acta 2010, 43, 27–33; c) N. D. Shapiro, F. D. Toste, Synlett 2010, 675–691; d) S. Wang, G. Zhang, L. Zhang, Synlett 2010, 692–706; e) A. Corma, A. Leyva-Pérez, M. J. Sabater, Chem. Rev. 2011, 111, 1657–1712; f) N. Krause, C. Winter, Chem. Rev. 2011, 111, 1994–2009; g) H. Huang, Y. Zhou, H. Liu, Beilstein J. Org. Chem. 2011, 7, 897–936.
- [2] For selected recent reviews: a) A. Fürstner, *Chem. Soc. Rev.* 2009, 38, 3208–3221; b) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.* 2012, 41, 2448–2462; c) F. Gagosz, in: *Modern Tools for the Synthesis of Complex Bioactive Molecules*, (Eds.: J. Cossy, S. Arseniyadis), J. Wiley & Sons, Chichester, 2012, pp 111–154.
- [3] For reviews covering early basics for gold-catalyzed alkyne activation, see: a) A. S. K. Hashmi, G. J. Hutchings, Angew. Chem. 2006, 118, 8064–8105; Angew. Chem. Int. Ed. 2006, 45, 7896–7936; b) A. Fürstner, P. W. Davies, Angew. Chem. 2007, 119, 3478–3519; Angew. Chem. Int. Ed. 2007, 46, 3410–3449.
- [4] For recent selected examples, see: a) A. S. K. Hashmi, I. Braun, P. Nösel, J. Schädlich, M. Wieteck, M. Rudolph, F. Rominger, Angew. Chem. 2012, 124, 4532-4536; Angew. Chem. Int. Ed. 2012, 51, 4456-4460; b) G. Ung, M. Soleilhavoup, G. Bertrand, Angew. Chem. 2013, 125, 787-790; Angew. Chem. Int. Ed. 2013, 52, 758–761; c) A. Gómez-Suárez, S. Dupuy, A. M. Z. Slawin, S. P. Nolan, Angew. Chem. 2013, 125, 972-976; Angew. Chem. Int. Ed. 2013, 52, 938–942; d) M. S. Hansmann, M. Rudolph, F. Rominger, A.S.K. Hashmi, Angew. Chem. 2013, 125, 2653-2659; Angew. Chem. Int. Ed. 2013, 52, 2593-2598; e) C. Obradors, A. M. Echavarren, Chem. Eur. J. 2013, 19, 3547-3355; f) A. Zhdanko, M. E. Maier, Chem. Eur. J. 2013, 19, 3932-3942; g) E. Gross, J. H. Liu, S. Alayoglu, M. A. Marcus, S. C. Fakra, F. D. Toste, G. A. Somorjai, J. Am. Chem. Soc. 2013, 135, 3881-3886; h) V. Lavallo, J. H.

Wright II, F. S. Tham, S. Quinlivan, Angew. Chem.
2013, 125, 3255–3258; Angew. Chem. Int. Ed. 2013, 52, 3172–3176; i) H. Ito, A. Harada, H. Ohmiya, M. Sawamura, Adv. Synth. Catal. 2013, 355, 647–652; j) Y. Wang, L. Liu, L. Zhang, Chem. Sci. 2013, 4, 739–746; k) S. Ghorpade, M.-D. Su, R.-S. Liu, Angew. Chem.
2013, 125, 4323–4328; Angew. Chem. Int. Ed. 2013, 52, 4229–4234; l) T. Iwai, H. Okochi, H. Ito, M. Sawamura, Angew. Chem. 2013, 125, 4333–4336; Angew. Chem. Int. Ed. 2013, 52, 4239–4242.

- [5] Y. Kuninobu, E. Ishii, K. Takai, Angew. Chem. 2007, 119, 3360–3363; Angew. Chem. Int. Ed. 2007, 46, 3296– 3299.
- [6] For rhenium-catalyzed coupling reactions of propargyl alcohols with allyl silanes, see: M. R. Luzung, F. D. Toste, J. Am. Chem. Soc. 2003, 125, 15760–15761.
- [7] a) S. Suárez-Pantiga, C. Hernández-Díaz, E. Rubio, J. M. González, Angew. Chem. 2012, 124, 11720–11723; Angew. Chem. Int. Ed. 2012, 51, 11552–11555; b) S. Suárez-Pantiga, C. Hernández-Díaz, M. Piedrafita, E. Rubio, J. M. González, Adv. Synth. Catal. 2012, 354, 1651–1657; c) S. Suárez-Pantiga, E. Rubio, C. Álvarez-Rúa, J. M. González, Org. Lett. 2009, 11, 13–16.
- [8] a) S. Suárez-Pantiga, J. M. González, Pure Appl. Chem. 2013, 85, 721–739; for iodonium-mediated C–C bondforming reactions from alkynylsilanes, see: b) J. Barluenga, I. Llorente, L. J. Álvarez-García, J. M. González, P. J. Campos, M. R. Díaz, S. García-Granda, J. Am. Chem. Soc. 1997, 119, 6933–6934.
- [9] a) A. S. K. Hashmi, L. Schwarz, P. Rubenbauer, M. C. Blanco, Adv. Synth. Catal. 2006, 348, 705–708; b) V. Nair, N. Vidya, K. G. Abhilash, Tetrahedron Lett. 2006, 47, 2871–2873. For related bisindolylation reactions of alkynes and allenes, see: c) C. Ferrer, C. H. M. Amijs, A. M. Echavarren, Chem. Eur. J. 2007, 13, 1358–1373; d) J. Barluenga, A. Fernández, F. Rodríguez, F. J. Fañanás, J. Organomet. Chem. 2009, 694, 546–550; e) M. P. Muñoz, M. C. de La Torre, M. A. Sierra, Chem. Eur. J. 2012, 18, 4499–4504.
- [10] For a review on tandem catalysis, see: D. E. Fogg, E. N. dos Santos, *Coord. Chem. Rev.* 2004, 248, 2365–2379.
- [11] For the addition of catalytically generated alkynyl copper(I) acetylides to aldehydes promoted by trimethylsilyl triflate: Y. Asano, H. Ito, K. Hara, M. Sawamura, *Organometallics* **2008**, *27*, 5984–5996.
- [12] For catalytic approaches to the synthesis of 1,4-diynes, see: titanocene-catalyzed bis-alkynylation reaction of aldehydes with iodoalkynes, see: a) C. A. Campos, J. B. Gianino, D. M. Pinkerton, B. L. Ashfeld, Org. Lett. 2011, 13, 5680–5683; reaction of propargyl alcohols and terminal alkynes: b) T. Wang, X.-l. Chen, L. Chen, Z.-p. Zhan, Org. Lett. 2011, 13, 3324–3327; c) T. Wang, R.-d. Ma, L. Liu, Z.-p. Zhan, Green Chem. 2010, 12, 1576–1579; d) J. S. Yadav, B. V. Subba Reddy, N. Thrimurtulu, N. Mallikarjuna Reddy, A. R. Prasad, Tetrahedron Lett. 2008, 49, 2031–2033.
- [13] For a review on ligand effects in gold catalysis, see:
 D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* 2008, 108, 3351–3378.
- [14] a) N. Mézailles, L. Ricard, F. Gagosz, Org. Lett. 2005,
 7, 4133–4136; b) A. Buzas, F. Gagosz, J. Am. Chem. Soc. 2006, 128, 1264–1265.

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- [15] For instance, the reaction of 4-bromobenzaldehyde **1b** with **2a** requires additional heating to take place satisfactorily. When the mixture was heated at 80°C, for 105 min, in 1,2-dichloroethane, **1b** was fully consumed and the bis-alkynylated derivative **3b** was obtained. The yield was dependent on the ligand on gold, with the JohnPhos (L3) catalyst giving rise to best isolated yield for **3b** (75%). Under these conditions, the gold catalyst with the phosphite ligand (L1) affords a less clean reaction and furnishes **3b** in the range of 60%, whereas the IPr-containing catalyst gives 65% yield.
- [16] Under the heating process conditions reported in Table 1, these aldehydes fail to produce the corresponding compounds 3. Only mono-addition products were detected, except for the case of 2p that gave rise to trace amounts of 3p.
- [17] For recent reports involving gold(I) acetylides, see:
 a) A. S. K. Hashmi, I. Braun, M. Rudolph, F. Rominger, *Organometallics* 2012, *31*, 644–661; b) D. M. Schultz, N. R. Babij, J. P. Wolfe, *Adv. Synth. Catal.* 2012, *354*, 3451–3455; c) P. Starkov, F. Rota, J. M. D'Oyley, T. D. Sheppard, *Adv. Synth. Catal.* 2012, *354*, 3217–33224; d) A. Leyva-Pérez, A. Doménech, S. I. Al-Resayes, A. Corma, *ACS Catal.* 2012, *2*, 121–126; e) A. Simonneau, F. Jaroschik, D. Lesage, M. Karanik, R. Guillot, M. Malacria, J.-C. Tabet, J.-P. Goddard, L. Fensterbank, V. Gandon, Y. Gimbert, *Chem. Sci.* 2011, *2*, 2417–2422; f) M. J. Campbell, F. D. Toste, *Chem. Sci.* 2011, *2*, 1369–1378; g) T. J. Brown, R. A. Widenhoefer, *Organometallics* 2011, *30*, 6003–6009.
- [18] a) A. Schulz, A. Villinger, Angew. Chem. 2012, 124, 4602–4604; Angew. Chem. Int. Ed. 2012, 51, 4526–4528;
 b) H. Čičak, H. Vančik, Z. Mihalić, J. Org. Chem. 2010, 75, 6969–6972; c) C. Li, F. Mo, W. Li, J. Wang, Tetrahedron Lett. 2009, 50, 6053–6056.
- [19] Previously, 3t was prepared in 45% from the catalytic reaction of 1t and 2a using the conditions outlined in Scheme 2 and Table 1, except for running the reaction at room temperature for 2 h.
- [20] For experimental details and characterization data, see the Supporting Information.
- [21] For recent work on digold-acetylide complexes, see: a) A. S. K. Hashmi, T. Lauterbach, P. Nösel, M. H. Vil-

helmsen, M. Rudolph, F. Rominger, *Chem. Eur. J.* **2013**, *19*, 1058–1065; b) A. Grirrane, H. Garcia, A. Corma, E. Álvarez, *ACS Catal.* **2011**, *1*, 1647–1653. For relevant structural work on the interaction of gold(I) with silyl-substituted alkynes, see: c) T. N. Hooper, M. Green, C. A. Rusell, *Chem. Commun.* **2010**, *46*, 2313– 2315; d) N. D. Shapiro, F. D. Toste, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 2779–2782. For additional recent relevant structures from the interaction of alkynes and gold(I), see: e) T. J. Brown, R. A. Widenhoefer, *J. Organomet. Chem.* **2011**, *696*, 1216–1220; f) H. V. Rasika Dias, J. A. Flores, J. Wu, P. Kroll, *J. Am. Chem. Soc.* **2009**, *131*, 11249–11255; g) S. Flügge, A. Anoop, R. Goddard, W. Thiel, A. Fürstner, *Chem. Eur. J.* **2009**, *15*, 8558–8565.

- [22] For gold-catalyzed C-C bond forming reactions from arenes and activated alcohols, see: a) K. Mertins, I. Iovel, J. Kischel, A. Zapf, M. Beller, Adv. Synth. Catal. 2006, 348, 691-695. Recent reviews on metal-catalyzed functionalization of propargylic alcohols and their derivatives: b) E. Bauer, Synthesis 2012, 44, 1131-1151; c) B. Biannic, A. Aponick, Eur. J. Org. Chem. 2011, 6605-6617; d) O. Debleds, E. Gayon, E. Vrancken, J.-M. Campagne, Beilstein J. Org. Chem. 2011, 7, 866-877.
- [23] For a highlight on this topic, see: a) A. Gómez-Suárez, S. P. Nolan, Angew. Chem. 2012, 124, 8278–8281; Angew. Chem. Int. Ed. 2012, 51, 8156–8159. For an early report, see: b) P. H.-Y. Cheong, P. Morganelli, M. R. Luzung, K. N. Houk, F. D. Toste, J. Am. Chem. Soc. 2008, 130, 4517–4526. For recent leading work, see: c) P. Nösel, T. Lauterbach, M. Rudolph, F. Rominger, A. S. K. Hashmi, Chem. Eur. J. 2013, 19, 8634–8641; d) I. Braun, A. M. Asiri, A. S. K. Hashmi, ACS Catal. 2013, 3, 1902–1907.
- [24] **7a** is easily prepared from **6a** and JohnPhosAuNTf₂, see the Supporting Information. Alternatively, the desired transformation can be accomplished in comparable yield from a reaction relying on *in situ* performing the catalyst, just mixing JohnPhosAuNTf₂ and **6a** in 1:1 molar ratio.
- [25] A. S. K. Hashmi, Angew. Chem. 2010, 122, 5360–5369; Angew. Chem. Int. Ed. 2010, 49, 5232–5241.

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