

Homogeneous Catalysis

Gold-Catalyzed Cycloisomerization Reactions of 2-Tosylamino-phenylprop-1-yn-3-ols as a Versatile Approach for Indole Synthesis**

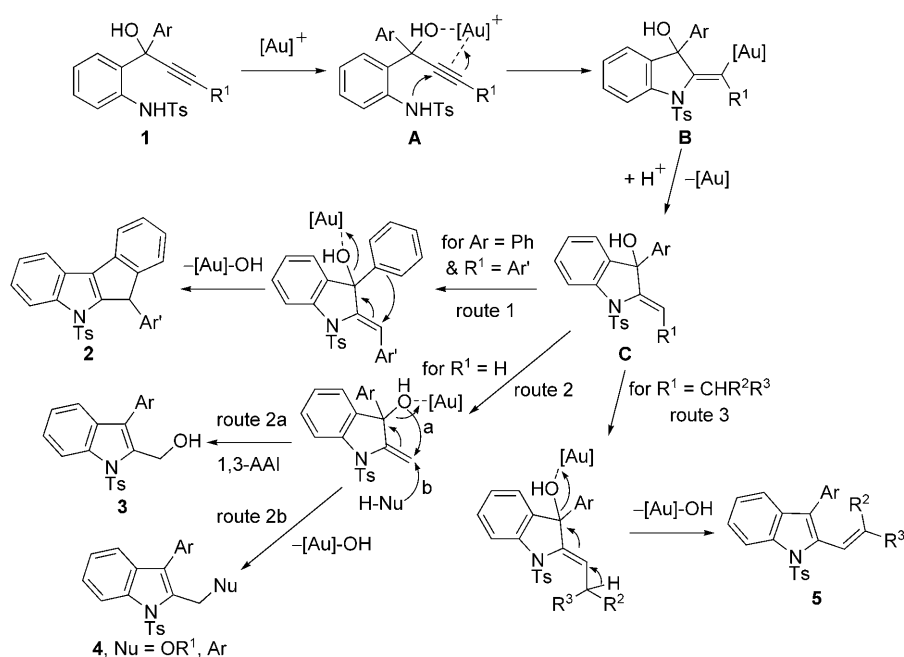
Prasath Kothandaraman, Weidong Rao, Shi Jia Foo, and Philip Wai Hong Chan*

Dedicated to Professor Koichi Narasaka

Indole derivatives are important cyclic structures in organic synthesis because of their ability to serve as building blocks for functional materials and as key components in a myriad of bioactive compounds.^[1] For this reason, the establishment of new efficient synthetic methods to prepare this class of N-heterocycles, with selective control of substitution patterns, from readily available and simple substrates continues to be actively pursued.^[1,2]

Recently, an increasing number of studies have highlighted the utility of unsaturated alcohols as substrates in gold-catalyzed carbon–nitrogen bond-formation strategies.^[3–6] For example, our research group has recently reported an efficient and convenient synthetic route to 1,2-dihydroquinolines involving intramolecular allylic amination of 2-tosylaminophenylprop-1-en-3-ols catalyzed by AuCl₃ with AgSbF₆ as a co-catalyst.^[5a] As part of an ongoing program to develop this type of synthetic approach for carbon–nitrogen bond formation,^[4–6] we reasoned that readily available 2-tosylaminophenylprop-1-yn-3-ol derivatives **1** might also undergo gold-mediated intramolecular cyclization but in a 5-*exo*-dig manner given the exceptional alkynophilicity of the metal catalyst (Scheme 1).^[3,7] The resultant puta-

tive indolyl-substituted vinyl gold species **B**^[8] generated in situ would then be susceptible to protodeauration and intramolecular Friedel–Crafts alkylation^[9] when R¹ = Ar and afford the indenyl-fused indole **2** (route 1 in Scheme 1). On the other hand, we envisaged that a more reactive primary vinyl gold species formed when R¹ = H would be prone to a



Scheme 1. Design of a vinyl gold approach for indole synthesis. Nu = nucleophile, Ts = 4-toluenesulfonyl.

more rapid protodeauration/1,3-allylic alcohol isomerization process (1,3-AAI)^[10] and provide the (1*H*-indol-2-yl)methanol product **3** (route 2a in Scheme 1). In the presence of a strong nucleophile, preferential S_N2' substitution would be expected to give the 2-alkyl-1*H*-indole adduct **4** (route 2b in Scheme 1). Similarly, we reasoned for reactions in which R¹ = CHR²R³, a more facile protodeauration and dehydration step would proceed and deliver 2-vinyl-1*H*-indoles of the type **5** (route 3 in Scheme 1). Herein, we disclose the details of this versatile and efficient gold-catalyzed method for the chemoselective synthesis of indenyl-fused and 2,3-disubstituted indoles that makes use of a putative vinyl gold species formed in situ from cycloisomerization of 2-tosylaminophenylprop-1-yn-3-ols.^[11] Although metal-catalyzed 5-*endo*-dig cycloisomerization of *o*-alkynylanilines have been extensively

[*] P. Kothandaraman, W. Rao, S. J. Foo, Prof. Dr. P. W. H. Chan
Division of Chemistry and Biological Chemistry
School of Physical and Mathematical Sciences
Nanyang Technological University, Singapore 637371 (Singapore)
Fax: (+65) 6791-1961
E-mail: waihong@ntu.edu.sg
Homepage: <http://www3.ntu.edu.sg/home/waihong/>

[**] This work was supported by a University Research Committee Grant (RG55/06) and a Supplementary Equipment Purchase Grant (RG134/06) from Nanyang Technological University, and by Science and Engineering Research Council Grant (092 101 0053) from A*STAR, Singapore. Helpful suggestions made by the referees are also gratefully acknowledged.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201000341>.

explored methods in indole synthesis,^[2f,11] to our knowledge the analogous 5-*exo*-dig process and dehydrative cyclizations of substituted propargylic alcohols of the type **1** have remained sparse.^[2c,f,h]

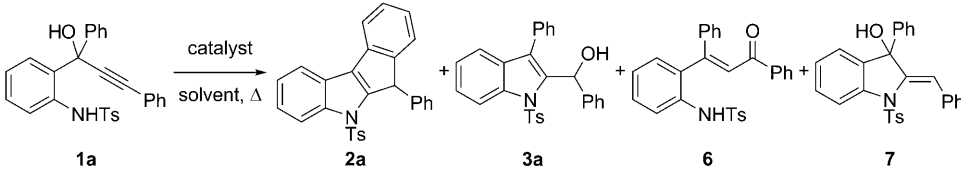
Initially, we chose to focus our attentions on the cycloisomerization/Friedel–Crafts alkylation of **1a** by a variety of Lewis and Brønsted acid catalysts to establish the reaction conditions (Table 1 and Table S1 in the Supporting Information). This initial study revealed that treatment of **1a** with 5 mol % of AuCl and 5 mol % of AgOTf in toluene at reflux gave the indenyl-fused indole **2a** in 74 % yield along with the side product **6**^[12,13] in 25 % yield (Table 1, entry 1). The indole product was confirmed by ¹H NMR analysis (see the Supporting Information for NMR analysis) and X-ray crystal structure analysis of two closely related products.^[14,15] Our studies subsequently showed that the introduction of HMPA resulted in an increase in product yield and formation of **3a** as a side product in 6 % yield (Table 1, entry 2). By using CaSO₄ to remove water from the reaction and in combination with HMPA, formation of this latter byproduct could be suppressed to give **2a** as the sole product in 94 % yield (Table 1, entry 3). In contrast, an inspection of entries 4–10 in Table 1 shows that repeating the reaction with DMI or DMAP in place of HMPA or in other solvents was markedly less effective. Similarly, a survey of other Lewis and Brønsted acid catalysts did not provide improved results (Table 1, entries 11–24 and Table S1 in the Supporting Information). In these latter reactions, a number of the conditions examined also lead to either the recovery of the starting alcohol in yields of up to 64 % or gave the *Z*-indolin-3-ol **7**^[16] as an additional

side product. More importantly, the contrasting catalytic activities observed for the reactions mediated by AgOTf and TfOH, respectively, provided evidence that the cationic Au^I complex is the active species (see Table S1 in the Supporting Information).

To define the scope of the present procedure, we next turned our attention to the reactions of a variety of 1-phenyl-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol derivatives (Table 2). These experiments showed that with AuCl/AgOTf as the catalyst, starting alcohols **1b–k** and **1m** efficiently underwent the tandem cycloisomerization/Friedel–Crafts alkylation process and gave the corresponding products **2b–k** and **2m** in good to excellent yields (Table 2, entries 1–10 and 12). The structure of **2f** was also confirmed by X-ray crystal structure analysis.^[14] Under the standard reaction conditions, *o,p*-dimethylaniline alcohol **1l** was the only example that gave a mixture of decomposition products based on TLC and ¹H NMR analysis of the crude mixture (Table 2, entry 11).

Having established the reaction conditions that gave indenyl-fused indoles, we next examined the scope of this new methodology for the synthesis of 2,3-disubstituted indoles (Table 3). As mentioned earlier, we anticipated such control of product chemoselectivity could be achieved by varying the nature of the R¹ group on the vinyl gold moiety in species **B** shown in Scheme 1. With this in mind, we first tested the reaction of the terminal acetylenic alcohols **1n** and **1o** with 5 mol % of AuCl and AgOTf under the standard conditions and found **3b** and **3c** could be obtained as the sole product in 77 and 86 % yield, respectively (Table 3, entries 1 and 2). Under similar conditions, repeating the reaction of **1n** in the

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



Entry	Catalyst	Solvent	Yield [%] ^[b]				Entry	Catalyst	Solvent	Yield [%] ^[b]			
			2a	3a	6	7				2a	3a	6	7
1	AuCl/AgOTf	toluene	74	–	25	–	13	AuCl ₃ /AgOTf	toluene	61	24	–	–
2 ^[c]	AuCl/AgOTf	toluene	87	6	–	–	14	[Au(PPh ₃) ₃]Cl/AgOTf	toluene	32 ^[g]	11	–	–
3 ^[d]	AuCl/AgOTf	toluene	94	–	–	–	15	[AuL ¹]Cl/AgOTf	toluene	38 ^[g]	26	–	–
4 ^[e]	AuCl/AgOTf	toluene	20	–	67	–	16	[AuL ²]Cl/AgOTf	toluene	5	–	–	52
5 ^[f]	AuCl/AgOTf	toluene	–	–	87	–	17	[AuL ³]Cl/AgOTf	toluene	12	10	76	–
6	AuCl/AgOTf	(CH ₂ Cl) ₂	44	–	40	–	18	[AuL ⁴]Cl/AgOTf	toluene	3	–	72	–
7	AuCl/AgOTf	THF	– ^[g]	–	–	–	19	AuCl	toluene	42	20	–	–
8	AuCl/AgOTf	MeCN	–	–	80	–	20	AuCl ₃	toluene	32	24	–	–
9	AuCl/AgOTf	1,4-dioxane	25	–	55	–	21	[Au(PPh ₃) ₃]Cl	toluene	17 ^[g]	12	–	–
10	AuCl/AgOTf	DMSO	– ^[g]	–	–	–	22	[Au(PPh ₃) ₃]NTf ₂	toluene	14	–	–	47
11	AuCl/AgSbF ₆	toluene	65	32	–	–	23	[AuL ³ MeCN]SbF ₆	toluene	12 ^[g]	7	–	–
12	AuCl/AgPF ₆	toluene	38	–	–	–	24	[AuL ⁴]NTf ₂	toluene	8	57	–	–

[a] All reactions were performed with 0.2 mmol of **1a** in the presence of 5 mol % of catalyst at reflux for 17 hours. [b] Yield of isolated product. [c] Reaction performed with 20 mol % of HMPA for 2 hours. [d] Reaction performed with 20 mol % of HMPA and CaSO₄ (35 mg) for 2 hours. [e] Reaction performed with 20 mol % of DMI and CaSO₄ (35 mg) for 2 hours. [f] Reaction performed with 20 mol % of DMAP and CaSO₄ (35 mg) for 2 hours. [g] Recovery of **1a** in 18–64 % yield. DMAP = 4-dimethylaminopyridine, DMI = 1,3-dimethyl-2-imidazolidinone, DMSO = dimethyl sulfoxide, HMPA = hexamethylphosphoramide, L¹ = tris(4-trifluoromethylphenyl)phosphine; L² = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; L³ = (1,1'-biphenyl-2-yl)-di-*tert*-butylphosphine; L⁴ = 2-dicyclohexyl(2',4',6'-triisopropylbiphenyl)phosphine, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran.

Table 2: Tandem cycloisomerization/Friedel–Crafts alkylation of **1b–m** catalyzed by AuCl/AgOTf.^[a]

Entry	Substrate	Product	Yield [%] ^[b]
1	1b , R = Me	2b	91
2	1c , R = Cl	2c	86
3	1d , R = Br	2d	87
4	1e , R ¹ = H, R ² = Me	2e + 2e' , R ¹ = Me, R ² = H	82 ^[c]
5	1f , R = <i>p</i> -FC ₆ H ₅	2f	94
6	1g , R = <i>p</i> -ClC ₆ H ₅	2g	91
7	1h , R = <i>p</i> -OMeC ₆ H ₅	2h	46
8	1i , R = <i>p</i> -MeC ₆ H ₅	2i	76
9	1j , R ¹ = Br, R ² = H	2j	90
10	1k , R ¹ = Cl, R ² = H	2k	86
11	1l , R ¹ = R ² = Me	2l	— ^[d]
12	1m	2m	82

[a] All reactions were performed with 0.2 mmol of **1** in the presence of 5 mol % of AuCl and AgOTf, 20 mol % of HMPA and CaSO₄ (35 mg) in toluene at reflux for 2 hours. [b] Yield of isolated product. [c] Isolated as an inseparable mixture of regioisomers in a 2:1 ratio. [d] Mixture of unknown side products obtained based on ¹H NMR analysis of the crude mixture.

Table 3: Synthesis of (1*H*-indol-2-yl)methanols **3**, 2-alkyl-1*H*-indoles **4**, and 2-vinyl-1*H*-indoles **5** catalyzed by AuCl/AgOTf.^[a]

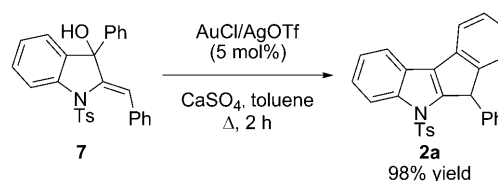
Entry	Substrate	Product	Yield [%] ^[b]
1	1n , R = H	3b	77
2	1o , R = Me	3c	86
3 ^[c]	1n	4a	82
4 ^[d]	1n	4b	76
5	1p , R = H	5a	90
6	1q , R = <i>n</i> Pr	5b	80
7	1r , <i>n</i> = 1	5c	86
8	1s , <i>n</i> = 2	5d	86
9	1t , <i>n</i> = 3	5e	87

[a] All reactions were performed with 0.2 mmol of **1** in the presence of 5 mol % of AuCl and AgOTf, 20 mol % of HMPA and CaSO₄ (35 mg) in toluene at reflux for 2 hours. [b] Yield of isolated product. [c] Reaction conducted in the presence of 8 equivalents of MeOH. [d] Reaction conducted in the presence of 8 equivalents of 2,6-dimethylphenol.

presence of MeOH or 2,6-dimethylphenol gave the corresponding 2-alkyl-1*H*-indoles **4a** and **4b** in 82 and 76 % yield, respectively (Table 3, entries 3 and 4). Likewise, reactions of **1p–t** with a pendant alkyl group on the acetylenic carbon centre proceeded well and furnished the corresponding 2-vinyl-1*H*-indoles **5a–e** in excellent yields (Table 3, entries 5–9). In these latter reactions, the structure of **5e** was also confirmed by X-ray crystal structure analysis^[15] and no other side products were detected by TLC and ¹H NMR analysis of the crude mixtures.

Although the isolation of the *Z*-indolin-3-ol **7** furnished from reactions of **1a** catalyzed by [AuL₂]Cl/AgOTf or [AuPh₃P]NTf₂ outlined in entries 16 and 20 in Table 1 was fortuitous, the result argues in favor of the mechanism put forward in Scheme 1. This argument was further corroborated by the observation that when a solution of **7** in toluene was treated with 5 mol % of AuCl and AgOTf under the conditions shown in Scheme 2, the expected indenyl-fused indole **2a** was obtained as the sole product in

98 % yield. The role of the gold catalyst in facilitating the dehydroxylation step could also be shown by repeating the reaction in the absence of the metal catalyst, which gave **3a** along with recovery of the starting indolin-3-ol in 10 and 90 % yield, respectively.


Scheme 2. Gold-catalyzed intramolecular Friedel–Crafts alkylation of **7**.

Even though the above results provide evidence for the mechanism outlined in Scheme 1, other possible pathways were considered but then discounted based on the following control experiments. As gold carbene species are often proposed in alkyne cycloisomerization reactions mediated by metal catalyst, the reactions of **1n** with Ph₂SO and styrene catalyzed by AuCl/AgOTf under the standard conditions were first examined.^[17] Analysis of the crude mixtures of these reactions by ¹H NMR spectroscopy reveals no adducts resulting from trapping of such a putative species by Ph₂SO or styrene. This test afforded **3b** as the sole product in 72–

75% yield in both experiments, and led us to surmise that an alternative mechanism for the present reaction involving formation of a gold carbene intermediate was unlikely. Our findings that show the near quantitative recovery of starting materials for the reactions of **3a** in the presence or absence of 2,6-dimethylphenol as well as that for **6** exposed to 5 mol % of AuCl/AgOTf under the standard conditions led us to also rule out the possibility of indole formation proceeding via intermediates of the type **3** or **6** (depicted in Table 1).

The beneficial effect of added HMPA led us to initially consider its role as that of a ligand that moderates the reactivity of the Au catalyst through coordination to the metal center in a similar manner to that reported for lanthanide salts.^[18] Indeed, this speculation was supported by ³¹P NMR measurements of an equimolar sample of AuCl/AgOTf + HMPA that shows the phosphorus resonance to shift downfield by $\delta = 3.3$ ppm relative to the respective signal in free HMPA ($\delta = 23.5$ ppm). Further analysis of this mixture by ESI high-resolution mass spectrometry also reveals the presence of a peak at m/z 526 that could be assigned to [AuCl/AgOTf + HMPA + H]⁺. This evidence is comparable to the data reported for lanthanide HMPA complexes.^[18] However, a marked downfield shift from $\delta = 9.41$ to 10.1 and 10.41 ppm of the NH proton signal in the respective ¹H NMR spectra of **1a** and **1a** + AuCl/AgOTf, presumably resulting from hydrogen bonding, upon addition of HMPA implies it could also play a dual role in promoting the cycloisomerization process. Our earlier findings that show a lower product yield obtained for the reaction of **1a** catalyzed AuCl/AgOTf in the absence of HMPA (Table 1, entry 1) would certainly suggest that such interactions are a possibility.

In summary, an efficient gold-catalyzed synthetic route to indenyl-fused and 2,3-disubstituted indoles from a common vinyl gold species generated in situ from easily accessible propargylic alcohol substrates under mild conditions has been reported. Uniquely, the reactions were found to only proceed efficiently and with complete control of product chemoselectivity for a wide variety of starting alcohols in the presence of the combined gold and silver catalyst system. Further exploration of the mechanism, scope, and synthetic applications of the present reaction are currently underway.

Experimental Section

A solution of AuCl (11 μ mol), AgOTf (11 μ mol), and CaSO₄ (35 mg) in toluene (1.5 mL) was stirred under Ar at room temperature for 10 min. Upon completion, HMPA (20 mol %) was added followed by slow dropwise addition of a solution of **1** (0.22 mmol) in toluene (1.5 mL; note: 8 equiv of the nucleophile was also added at this point for reactions of **1n** described in entries 3 and 4 in Table 3). The reaction mixture was then stirred at reflux for 2 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc (20:1)) and gave the indole product.

Received: January 20, 2010

Revised: April 12, 2010

Published online: May 17, 2010

Keywords: gold · homogeneous catalysis · indoles · tandem reactions · unsaturated alcohols

- [1] For recent reviews, see: a) J. Barluenga, F. Rodríguez, F. J. Fañanás, *Chem. Asian J.* **2009**, *4*, 1036–1048; b) O. Miyata, N. Takeda, T. Naito, *Heterocycles* **2009**, *78*, 843–871; c) K. Krüger (née Alex), A. Tillack, M. Beller, *Adv. Synth. Catal.* **2008**, *350*, 2153–2167; d) G. R. Humphrey, J. T. Kuethe, *Chem. Rev.* **2006**, *106*, 2875–2911; e) S. Cacchi, G. Fabrizi, *Chem. Rev.* **2005**, *105*, 2873–2920.
- [2] For selected examples, see: a) Y. Yamane, X. Liu, A. Hamasaki, T. Ishida, M. Haruta, T. Yokoyama, M. Tokunaga, *Org. Lett.* **2009**, *11*, 5162–5165; b) D. Ye, J. Wang, X. Zhang, Y. Zhou, X. Ding, E. Feng, H. Sun, G. Liu, H. Jiang, H. Liu, *Green Chem.* **2009**, *11*, 1201–1208; c) B. Gabriele, R. Mancuso, G. Salerno, E. Lupinacci, G. Ruffolo, M. Costa, *J. Org. Chem.* **2008**, *73*, 4971–4977; d) Y. Miyazaki, S. Kobayashi, *J. Comb. Chem.* **2008**, *10*, 355–357; e) I. Nakamura, U. Yamagishi, D. Song, S. Kōta, Y. Yamamoto, *Angew. Chem.* **2007**, *119*, 2334–2337; *Angew. Chem. Int. Ed.* **2007**, *46*, 2284–2287; f) K. Cariou, B. Ronan, S. Mignani, L. Fensterbank, M. Malacria, *Angew. Chem.* **2007**, *119*, 1913–1916; *Angew. Chem. Int. Ed.* **2007**, *46*, 1881–1884 and references therein; g) Y. Zhang, J. P. Donahue, C.-J. Li, *Org. Lett.* **2007**, *9*, 627–630; h) K. O. Hessian, B. L. Flynn, *Org. Lett.* **2006**, *8*, 243–246; i) M. Alfonsi, A. Arcadi, M. Aschi, G. Bianchi, F. Marinelli, *J. Org. Chem.* **2005**, *70*, 2265–2273.
- [3] For general reviews on gold catalysis, see: a) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221; b) J. Muzart, *Tetrahedron* **2008**, *64*, 5815–5849; c) A. S. K. Hashmi, *Angew. Chem.* **2008**, *120*, 6856–6858; *Angew. Chem. Int. Ed.* **2008**, *47*, 6754–6756; d) H. C. Shen, *Tetrahedron* **2008**, *64*, 3885–3903; e) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766–1775; f) B. H. Lipshutz, Y. Yamamoto, *Chem. Rev.* **2008**, *108*, 2793–3442; g) Y. Yamamoto, *J. Org. Chem.* **2007**, *72*, 7817–7831; h) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403; i) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; j) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Commun.* **2007**, 333–346; k) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; l) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; m) A. Hoffmann-Röder, N. Krause, *Org. Biomol. Chem.* **2005**, *3*, 387–391.
- [4] For recent reviews on the use of alcohols as proelectrophiles, see Ref. [2b] and: a) M. Bandini, N. Tragni, *Org. Biomol. Chem.* **2009**, *7*, 1501–1507; b) N. Ljungdahl, N. Kann, *Angew. Chem.* **2009**, *121*, 652–654; *Angew. Chem. Int. Ed.* **2009**, *48*, 642–644; c) J. Muzart, *Eur. J. Org. Chem.* **2007**, 3077–3089; d) J. Muzart, *Tetrahedron* **2005**, *61*, 4179–4212; e) Y. Tamaru, *Eur. J. Org. Chem.* **2005**, 2647–2656.
- [5] a) P. Kothandaraman, S. J. Foo, P. W. H. Chan, *J. Org. Chem.* **2009**, *74*, 5947–5952; b) W. Rao, P. W. H. Chan, *Chem. Eur. J.* **2008**, *14*, 10486–10495.
- [6] For studies on gold-catalyzed amination of alcohol proelectrophiles, see Refs. [2b,5] and: a) M. Egi, K. Azechi, S. Akai, *Org. Lett.* **2009**, *11*, 5002–5004; b) A. Aponick, C.-Y. Li, J. Malinge, E. F. Marques, *Org. Lett.* **2009**, *11*, 4624–4627; c) M. Georgy, V. Boucard, O. Debleds, C. Dal Zotto, J.-M. Campagne, *Tetrahedron* **2009**, *65*, 1758–1766; d) Y. Lu, X. Fu, H. Chen, X. Du, X. Jia, Y. Liu, *Adv. Synth. Catal.* **2009**, *351*, 129–134; e) X.-Z. Shu, X.-Y. Liu, H.-Q. Xiao, K.-G. Ji, L.-N. Guo, Y.-M. Liang, *Adv. Synth. Catal.* **2008**, *350*, 243–248; f) S. Guo, F. Song, Y. Liu, *Synlett* **2007**, 964–968; g) V. Terrasson, S. Marque, M. Georgy, J.-M. Campagne, D. Prim, *Adv. Synth. Catal.* **2006**, *348*, 2063–2067.
- [7] For recent examples showing competitive coordination of the Au catalyst to the alkyne moiety in propargylic alcohols, see: a) J.-M. Tang, S. Bhunia, S. M. Abu Sohel, M.-Y. Lin, H.-Y. Liao, S.

- Data, A. Das, R.-S. Liu, *J. Am. Chem. Soc.* **2007**, *129*, 15677–15683, and references therein; b) J.-J. Lian, R.-S. Liu, *Chem. Commun.* **2007**, 1337–1339; c) S. Couty, C. Meyer, J. Cossy, *Angew. Chem.* **2006**, *118*, 6878–6882; *Angew. Chem. Int. Ed.* **2006**, *45*, 6726–6730.
- [8] For seminal reports providing X-ray crystal structure analysis and ¹H NMR spectroscopic evidence of a vinyl gold intermediate in related reactions of alkynes with gold salts, see: a) A. S. K. Hashmi, A. M. Schuster, F. Rominger, *Angew. Chem.* **2009**, *121*, 8396–8398; *Angew. Chem. Int. Ed.* **2009**, *48*, 8247–8249; b) G. Seidel, R. Mynott, A. Fürstner, *Angew. Chem.* **2009**, *121*, 2548–2551; *Angew. Chem. Int. Ed.* **2009**, *48*, 2510–2513, and references therein; c) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.* **2008**, *130*, 17642–17643.
- [9] M. Bandini, A. Eichholzer, *Angew. Chem.* **2009**, *121*, 9697–9701; *Angew. Chem. Int. Ed.* **2009**, *48*, 9533–9537, and references therein.
- [10] Please see Ref. [2h] and: C. Morrill, R. H. Grubbs, *J. Am. Chem. Soc.* **2005**, *127*, 2842–2843, and references therein.
- [11] For selected examples of other methods for indole synthesis using gold catalysis, see Refs. [2a,b,d,e,g, and i].
- [12] D. A. Engel, G. B. Dudley, *Org. Biomol. Chem.* **2009**, *7*, 4149–4158, and references therein.
- [13] CCDC 749109 (**6**) 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. Please see the Supporting Information for the ORTEP drawing.
- [14] CCDC 749107 (**2 f**) 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. Please see the Supporting Information for the ORTEP drawing.
- [15] CCDC 749108 (**5 e**) 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. Please see the Supporting Information for the ORTEP drawing.
- [16] CCDC 767163 (**7**) 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. Please see the Supporting Information for the ORTEP drawing.
- [17] a) I. D. G. Watson, S. Ritter, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 2056–2057; b) C. A. Witham, P. Mauleón, N. D. Shapiro, B. D. Sherry, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 5838–5839; c) M. J. Johansson, D. J. Gorin, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 18002–18003.
- [18] a) Y. Kataoka, I. Makihiro, T. Yamagata, K. Tani, *Organometallics* **1997**, *16*, 4788–4795; b) Z. Hou, Y. Zhang, Y. Wakatsuki, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 149–153.