Facile and Selective Synthesis of Propargylic Amines and 1,6-Diynes: One-Pot Three-Component Coupling Reactions of Alkynylsilanes, Aldehydes and Amines by a Cooperative Catalytic System Comprised of CuCl and $Cu(OTf)_2$

Norio Sakai,* Naoki Uchida, Takeo Konakahara

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science (RIKADAI), Noda, Chiba 278-8510, Japan
E-mail: sakachem@rs.noda.tus.ac.jp

Received 10 March 2008

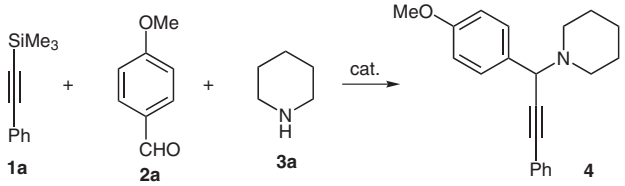
Abstract: Described herein is a three-component coupling reaction of alkynylsilanes, aldehydes and amines by a cooperative catalytic system comprised of CuCl and $Cu(OTf)_2$, leading to the production of a variety of propargyl amine derivatives. This catalytic system was successfully applied to the practical preparation of 1,6-diyne derivatives via twice-performed, domino-type coupling reactions.

Keyword: multicomponent coupling reaction, copper catalyst, alkynylsilane, propargylic amine, 1,6-diyne

The facile and practical preparation of multifunctionalized propargyl amines is attractive and important, since a number of their derivatives constitute basic units in naturally occurring products and related biologically active substances.[1] Until now, the major approach to the preparation of these compounds has been the nucleophilic addition of a variety of alkynyl metals to carbon electrophiles, such as imines,[2] enamines,[3] nitrones,[4] acetals[5] and aminals.[6] Quite recently, a metal-promoted three-component coupling reaction of alkynes, aldehydes, and amines, leading to propargylic amines in an organic–aqueous medium, has been favored by organic and pharmaceutical chemists, because of the achievement of a multibond formation in a single step and its facile operation in the experiment.[7] On the other hand, alkynylsilanes have been widely employed as a convenient partner in common organic reactions, due to ready availability and a high tolerance to functional groups.[8] However, reactions using convenient silane compounds as substrates in multicomponent coupling reactions, as described above, have rarely been reported. In addition, development of a new method for direct activation of an alkynylsilane without an additive, such as a fluoride ion and a base, would enable us to clear a new aspect of organosilicon chemistry. We therefore planned the development of a novel multicomponent coupling reaction using an alkynylsilane. Taking into account the harmful influence of a chemical process apparatus and environmental impact, we intended to avoid the use of the catalyst, which produces a fluoride ion, to activate the carbon–silicon bond in an alkynylsilane. Thus, we focused our attention on the interesting results reported by Ito and Hosomi, in which the silyl group of alkynylsilanes was cleaved by CuCl in a unique polar solvent to generate a copper acetylide, followed by a coupling reaction of the acetylide with acyl chlorides, which produced α-alkynones.[8g] Based on this result, we examined a novel three-component coupling reaction of alkynylsilanes, aldehydes, and amines utilizing the activation of the C–Si bond principally using a copper catalyst. In this letter, we report the preliminary results wherein a cooperative catalytic system consisting of CuCl and $Cu(OTf)_2$ promoted a three-component coupling reaction of alkynylsilanes, aldehydes, and amines, producing polyfunctionalized propargylic amine derivatives. Herein, we also disclose that the use of formaldehyde as the reaction substrate selectively produced 1,6-diyne derivatives in good yields via twice-performed, domino-type three-component coupling reactions.

As a model reaction, we initially examined the three-component coupling of 1-phenyl-2-(trimethylsilyl)acetylene

Table 1 Examination of Reaction Conditions[a]



Entry	Catalyst (mol%)	Solvent	Time (h)	Yield (%)[b]
1	CuCl (10)	1,4-dioxane	24	87
2	$Cu(OTf)_2$ (10)	1,4-dioxane	24	83
3	AgOTf (10)	1,4-dioxane	24	78
4	$AlCl_3$ (10)	1,4-dioxane	24	ND[c]
5	$Zn(OTf)_2$ (10)	1,4-dioxane	24	ND[c]
6	$Hf(OTf)_4$ (10)	1,4-dioxane	24	ND[c]
7	CuCl (5) + $Cu(OTf)_2$ (5)	1,4-dioxane	6	96
8	CuCl (5) + $Cu(OTf)_2$ (5)	MeCN	2	99
9	none	meCN	24	48

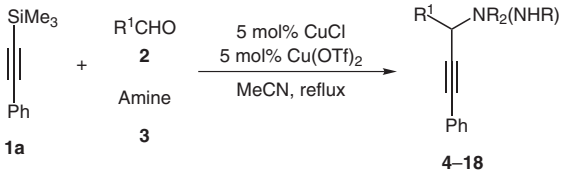
[a] Molar ratio: alkyne **1a**/aldehyde **2a**/amine **3a** = 1.2:1:1.2.
[b] Isolated yield.
[c] ND: not determined.

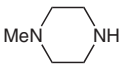
SYNLETT 2008, No. 10, pp 1515–1519
Advanced online publication: 16.05.2008
DOI: 10.1055/s-2008-1077790; Art ID: U01608ST

(**1a**), *p*-methoxybenzaldehyde (**2a**), and piperidine (**3a**) in the presence of CuCl in 1,4-dioxane under reflux conditions. As a result, the expected reaction proceeded cleanly to produce the desired propargylic amine **4** in 87% yield (Table 1, entry 1).[9] Similarly, when the reaction was run with $Cu(OTf)_2$, the same propargylic amine was obtained in 83% yield (entry 2). AgOTf also showed a similar effect for the reaction (entry 3). However, a typical Lewis acid, such as $AlCl_3$, $Zn(OTf)_2$ and $Hf(OTf)_4$ was ineffective in the coupling reaction and resulted in the recovery of the starting materials (entries 4–6). It is noteworthy that when the reaction was performed using a catalytic system comprised of both $Cu(OTf)_2$ and CuCl, the reaction time was shortened to within six hours, and the yield was enhanced to a nearly quantitative yield (entry 7). Moreover, it was found that the use of MeCN instead of 1,4-dioxane further reduced the reaction time. These reaction conditions were the best for the coupling reaction (entry 8).[10]

To generalize the reaction, the coupling reaction of alkynylsilane **1a** with various aldehydes and amines, was carried out under optimal conditions. The results are summarized in Table 2. Based on the results in Table 1, for example, when the reaction was run using benzaldehydes **2b** and **2c** having a hydroxyl group and a chloro substituent, and piperidine (**3a**), the desired reaction was completed in a short time (<3 h) to produce the corresponding propargyl amine derivatives **5** and **6** in good to excellent yields (entries 2 and 3). Additionally, this copper catalytic system accommodated various heterocyclic aldehydes, aliphatic aldehydes and paraformaldehyde (entries 4–8). Alternatively, use of 2-formylpyridine (**2f**) led to a coupling reaction to produce the corresponding propargylic amine **9** in only 13% yield, but the indolizine derivative **9′**, which was formed through intramolecular cycloisomerization of the amine **9**, was isolated as the major product (56%; entry 6). The detailed results will be discussed below. When the reaction was run using other cyclic amines and aliphatic amines, such as morpholine, *N*-methylpiperazine, diethylamine or diallylamine, the corresponding products were also obtained in good to excellent yields (entries 9–12). On the other hand, when a primary amine, such as butylamine or benzylamine was

Table 2 Synthesis of a Variety of Propargylic Amines[a]

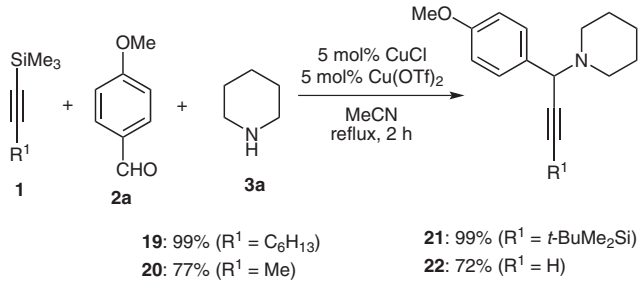


Entry	Aldehyde R^1		Amine		Time (h)	Yield (%)[b]
1	*p*-$MeOC_6H_4$	**2a**	piperidine	**3a**	2	99 (**4**)
2	*o*-HOC_6H_4	**2b**	piperidine	**3a**	3	75 (**5**)
3	*p*-ClC_6H_4	**2c**	piperidine	**3a**	2	99 (**6**)
4	2-furyl	**2d**	piperidine	**3a**	6	45 (**7**)
5	2-thienyl	**2e**	piperidine	**3a**	6	57 (**8**)
6	2-pyridyl	**2f**	piperidine	**3a**	2	13 (**9**)[c]
7	*n*-Pr	**2g**	piperidine	**3a**	12	75 (**10**)
8	H[d]	**2h**	piperidine	**3a**	12	72 (**11**)
9	*p*-$MeOC_6H_4$	**2a**	morpholine	**3b**	2	98 (**12**)
10	*p*-$MeOC_6H_4$	**2a**		**3c**	2	92 (**13**)
11	*p*-$MeOC_6H_4$	**2a**	Et_2NH	**3d**	4	95 (**14**)
12	*p*-$MeOC_6H_4$	**2a**	$(allyl)_2NH$	**3e**	6	80 (**15**)
13	*p*-$MeOC_6H_4$	**2a**	*n*-$BuNH_2$	**3f**	24	30 (**16**)
14	*p*-$MeOC_6H_4$	**2a**	*t*-$BuNH_2$	**3g**	24	16 (**17**)
15	*p*-$MeOC_6H_4$	**2a**	$BnNH_2$	**3h**	24	21 (**18**)

[a] Molar ratio: alkyne **1**/aldehyde **2**/amine **3** = 1.5:1:1.2.
[b] Isolated yield.
[c] Indolizine **9′** was formed in 56% yield.
[d] Paraformaldehyde was used.

used, the reaction required a longer reaction time, and the yield was drastically reduced to less than 30% (entries 13–15).

The reaction of several alkynylsilanes **1** with *p*-methoxybenzaldehyde (**2a**) and piperidine (**3a**) was then conducted under optimal conditions (Scheme 1). For example, when the reactions were run with the alkyne involving an aliphatic group, such as a hexyl and a methyl group, the reactions proceeded cleanly producing the corresponding propargylic amines **19** and **20** in good to excellent yields. Interestingly, the use of an internal alkyne having both a TBS (*t*-butyldimethylsilyl) group and a TMS group produced the propargylic amine **21** quantitatively, in which the more bulky TBS group remained on the terminal carbon. This result indicates that the copper catalytic system, due to the steric effect for substituents on the silicon atom, selectively cleaved the smaller substituent, the TMS group. Similarly, when the reaction was conducted with trimethylsilylacetylene, the desired propargylic amine **22** with no substituent group on the carbon–carbon triple bond was obtained in good yield.

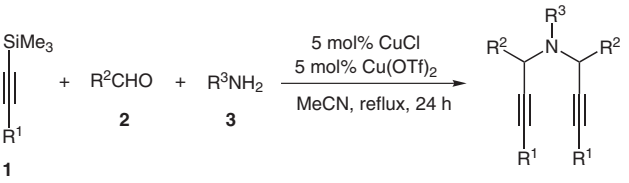


Scheme 1

Then, we anticipated that a reaction using a primary amine and an excess amount of alkynylsilane and paraformaldehyde, would form a symmetrical 1,6-diyne derivative through consecutive three-component coupling reactions.[11] After many examinations it was found that, unlike the result shown in Table 2, when the coupling reaction of alkynylsilane **1a** (3 equiv) and formaldehyde (**2h**; 3 equiv) with benzylamine (**3h**) was conducted with our copper catalytic system, the reaction completed cleanly within 24 hours to produce the expected 1,6-diyne **23** in 80% yield (Table 3, entry 1).[12] In addition, this catalytic system accommodated the coupling reaction using *n*-butylamine and other types of alkynylsilanes having an aliphatic group and a TBS group in good yields (entries 2–5). When the reaction with an aromatic aldehyde, such as *p*-methoxybenzaldehyde, was carried out, the corresponding propargylic amine **18** was obtained in a low yield (entry 6). Unfortunately, an aliphatic aldehyde led to the production of a complex mixture (entries 7 and 8).

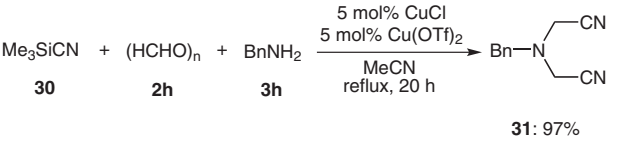
On the other hand, when the reaction was run using trimethylsilyl cyanide (**30**) instead of a silylacetylene, the expected double Strecker-type reactions cleanly proceeded to produce the corresponding tertiary amine **31** in a nearly quantitative yield (Scheme 2).

Table 3 Synthesis of Symmetrical 1,6-Diynes[a]



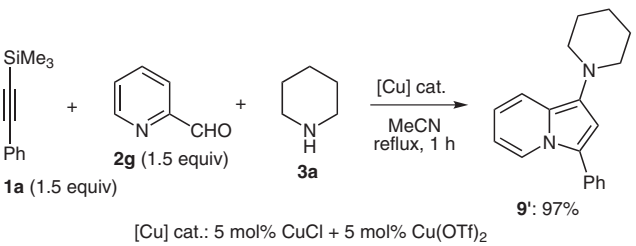
Entry	R^1	R^2	R^3	Yield (%)[b]	Diyne
1	Ph	H[c]	Bn	80	**23**
2	Ph	H[c]	*n*-Bu	60	**24**
3	C_6H_{13}	H[c]	Bn	71	**25**
4	Me	H[c]	Bn	70	**26**
5	TBS	H[c]	Bn	67	**27**
6	Ph	*p*-$MeOC_6H_4$	Bn	16	**18**
7	Ph	*n*-Pr	Bn	ND	**28**
8	Ph	CF_3	Bn	ND	**29**

[a] Molar ratio: alkyne **1**/aldehyde **2**/amine **3** = 3:3:1.
[b] Isolated yield.
[c] Paraformaldehyde was used.



Scheme 2

Recently, several groups have reported the metal-catalyzed cycloisomerization of propargylic pyridine and its derivatives leading to the preparation of indolizine derivatives.[13] These reports strongly motivated us to develop a more general method for the synthesis of a nitrogen-containing heterocycle from an alkynylsilane, an aldehyde and an amine in the presence of these copper catalysts. Thus, when the similar reaction with alkynylsilane **1a**, 2-formylpyridine (**2a**) and piperidine (**3a**) was conducted under conditions shown in Scheme 3, the desired cycloisomerization proceeded quantitatively to produce the corresponding indolizine **9′** (vide entry 6 in Table 2).[14] It was found that our copper catalytic system could be successfully applied to the synthesis of nitrogen-containing heterocycles via intramolecular cycloisomerization.



Scheme 3

There is no clear explanation for the role of each of these copper catalysts. We assumed that CuCl activates the C–Si bond of an alkynylsilane to generate a copper acetylide,[8g,i,15] and that $Cu(OTf)_2$ has a role, in which it behaves as a Lewis acid for in situ generation of the iminium intermediate, which forms from the starting materials, an aldehyde and an amine.

Thus far, we have demonstrated that a cooperative catalytic system comprised of CuCl and $Cu(OTf)_2$ effectively catalyzes a three-component coupling reaction of alkynylsilanes, aldehydes, and primary/secondary amines to produce a variety of propargylic amine derivatives in moderate to excellent yields. We have also found that use of an excess amount of paraformaldehyde and alkynylsilanes selectively produced 1,6-diyne derivatives in good yields through twice-performed, domino-type three-component coupling reactions.

Acknowledgment

This work was partially supported by a grant for a 'High-Tech Research Center' project awarded to private universities and a matching fund subsidy from MEXT, 2000-2004, and 2005-2007.

References and Notes

(1) In *Encyclopedia of the Alkaloids*; Glasby, J. S., Ed.; Plenum Press: New York, **1975**.

(2) (a) Jiang, B.; Si, Y.-G. *Tetrahedron Lett.* **2003**, *44*, 6767. (b) Wei, C.; Li, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 5638. (c) Fischer, C.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 4319. (d) Saidi, M. R.; Javanshir, S.; Mojtahedi, M. M. *J. Chem. Res., Synop.* **1999**, 330.

(3) Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem. Int. Ed.* **2002**, *41*, 2535.

(4) Frantz, D. E.; Fässler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **1999**, *121*, 11245.

(5) (a) Sakai, N.; Kanada, R.; Hirasawa, M.; Konakahara, T. *Tetrahedron* **2005**, *61*, 9298. (b) Sakai, N.; Hirasawa, M.; Konakahara, T. *Tetrahedron Lett.* **2003**, *44*, 4171. (c) Fleming, J. J.; Fiori, K. W.; Du Bois, J. *J. Am. Chem. Soc.* **2003**, *125*, 2028. (d) Barluenga, J.; Campos, P. J.; Canal, G. *Synthesis* **1989**, 33.

(6) (a) Gommermann, N.; Koradin, C.; Knochel, P. *Synthesis* **2002**, 2143. (b) Ahn, J. H.; Joung, M. J.; Yoon, N. M.; Oniciu, D. C.; Katritzky, A. R. *J. Org. Chem.* **1999**, *64*, 488.

(7) (a) Kantam, M. L.; Balasubrahmanyam, V.; Kumar, K. B. S.; Venkanna, G. T. *Tetrahedron Lett.* **2007**, *48*, 7332. (b) Kidwai, M.; Bansal, V.; Mishra, N. K.; Kumar, A.; Mozumdar, S. *Synlett* **2007**, 1581. (c) Lo, V. K. Y.; Liu, Y.; Wong, M. K.; Che, C. M. *Org. Lett.* **2006**, *8*, 1529. (d) Wei, C.; Li, Z.; Li, C.-J. *Synlett* **2004**, 1472. (e) Black, D. A.; Arndtsen, B. A. *Org. Lett.* **2004**, *6*, 1107. (f) Li, C.-J.; Wei, C. *Chem. Commun.* **2002**, 268. (g) McNally, J. J.; Youngman, M. A.; Dax, S. L. *Tetrahedron Lett.* **1998**, *39*, 967.

(8) For selected papers for the reactions using an alkynylsilane, see: (a) Yadav, J. S.; Raju, A. K.; Sunitha, V. *Tetrahedron Lett.* **2006**, *47*, 5269. (b) Montel, F.; Beaudegnies, R.; Kessabi, J.; Martin, B.; Muller, E.; Wendeborn, S.; Jung, P. M. J. *Org. Lett.* **2006**, *8*, 1905. (c) Kitazawa, T.; Minowa, T.; Mukaiyama, T. *Chem. Lett.* **2006**, *35*, 1002. (d) Lettan, R. B.; Scheidt, K. A. *Org. Lett.* **2005**, *7*, 3227. (e) Nishihara, Y.; Ikegashira, K.; Hirabayashi, K.; Ando, J.-I.; Mori, A.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 1780. (f) Abele, E.; Rubina, K.; Abele, R.; Popelis, J.; Mazeika, I.; Lukevics, E. *J. Organomet. Chem.* **1999**, *586*, 184. (g) Ito, H.; Arimoto, K.; Sensui, H.; Hosomi, A. *Tetrahedron Lett.* **1997**, *38*, 3977. (h) Hayashi, M.; Inubushi, A.; Mukaiyama, T. *Chem. Lett.* **1987**, *16*, 1975. (i) Ikegashira, K.; Nishihara, Y.; Hirabayashi, K.; Mori, A.; Hiyama, T. *Chem. Commun.* **1997**, 1039.

(9) **General Procedure for the Synthesis of a Propargyl Amine**: To a MeCN solution (300 μL) in a screw-capped vial under an N_2 atmosphere, alkynylsilane **1** (0.45 mmol), aldehyde **2** (0.30 mmol), amine **3** (0.36 mmol), $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) and CuCl (1.5 mg, 0.015 mmol) were successively added, and the vial was sealed with a cap containing a PTFE septum. The reaction mixture was heated at 100 °C until the reaction was completed as monitored by TLC. After the reaction, the mixture was directly subjected to SiO_2 gel without the usual extraction, and was purified by flash column chromatography (hexane–EtOAc) to give the corresponding propargyl amines in the yields shown in Table 2.
1-[1-(4-Methoxyphenyl)-3-phenylpropyn-2-yl]-4-methylpiperazine (**13**): pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.21 (s, 3 H), 2.40 (m, 4 H), 2.59 (m, 4 H), 3.74 (s, 3 H), 4.69 (s, 1 H), 6.82 (d, *J* = 7.5 Hz, 2 H), 7.23 (m, 3 H), 7.42 (m, 2 H), 7.46 (d, *J* = 7.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 46.0, 48.8, 55.3, 55.3, 61.0, 85.7, 88.1, 113.4, 113.5, 123.2, 128.0, 128.2, 129.6, 130.4, 131.8, 159.1. MS (EI): *m*/*z* = 320. HRMS (FAB): *m*/*z* calcd for $C_{21}H_{24}N_2O$: 320.1889; found: 320.1876.
N-(*tert*-Butyl)-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-amine (**17**): colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (s, 9 H), 3.80 (s, 3 H), 4.80 (s, 1 H), 6.89 (d, *J* = 7.5 Hz, 2 H), 7.29 (m, 3 H), 7.42 (m, 2 H), 7.51 (d, *J* = 7.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.9, 48.2, 51.2, 55.3, 84.1, 92.8, 113.9, 123.6, 127.9, 128.2, 128.5, 131.4, 135.0, 158.9. MS (EI): *m*/*z* = 293. HRMS (FAB): *m*/*z* calcd for $C_{20}H_{23}NO$: 293.1780; found: 293.1785.

(10) When a similar coupling reaction was carried out with phenylacetylene, propargylic amine **4** was obtained in a 61% yield (7 h).

(11) (a) Bonfield, E. R.; Li, C.-J. *Org. Biomol. Chem.* **2007**, *5*, 435. (b) Sakaguchi, S.; Mizuta, T.; Furuwan, M.; Kubo, T.; Ishii, Y. *Chem. Commun.* **2004**, 1638.

(12) **General Procedure for the Synthesis of a Symmetrical 1,6-Diyne**: To a MeCN solution (300 μL) in a screw-capped vial under a N_2 atmosphere, alkynylsilane **1** (0.90 mmol), paraformaldehyde **2h** (0.90 mmol), primary amine **3** (0.30 mmol), $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) and CuCl (1.5 mg, 0.015 mmol) were successively added, and the vial was sealed with a cap containing a PTFE septum. The reaction mixture was heated at 100 °C for 24 h. After the reaction, the mixture was directly subjected to SiO_2 gel without the usual extraction, and was purified by flash column chromatography (hexane–EtOAc) to give the corresponding 1,6-diynes in the yields shown in Table 3.
N-Benzyl-*N*,*N*-bis[3-(*tert*-butyldimethylsilyl)propyn-2-yl]amine (**27**): colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.12 (s, 12 H), 0.96 (s, 18 H), 3.40 (s, 4 H), 3.69 (s, 2 H), 7.32 (m, 5 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.5, 16.5, 26.1, 43.1, 56.9, 88.2, 101.7, 127.3, 128.3, 129.4, 138.0. MS (EI): *m*/*z* = 411. HRMS (FAB): *m*/*z* calcd for $C_{25}H_{42}NSi_2$: 412.2856; found: 412.2866.

(13) (a) Kim, I.; Choi, J.; Won, H. K.; Lee, G. H. *Tetrahedron Lett.* **2007**, *48*, 6863. (b) Yan, B.; Zhou, Y.; Zhang, H.; Chen, J.; Liu, Y. *J. Org. Chem.* **2007**, *72*, 7783. (c) Yan, B.; Liu, Y. *Org. Lett.* **2007**, *9*, 4323. (d) Seregin, I. V.; Schammel, A. W.; Gevorgyan, V. *Org. Lett.* **2007**, *9*, 3433. (e) Schwier, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 9868. (f) Seregin, I. V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2006**, *128*, 12050.

(14) **Procedure for the Synthesis of 1-Aminoindolizine 9′**: To a MeCN solution (300 μL) in a screw-capped vial under a N_2 atmosphere, alkynylsilane **1a** (78 mg, 0.45 mmol), aldehyde **2g** (48 mg, 0.45 mmol), amine **3a** (26 mg, 0.30 mmol) and $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) were successively added, and the vial was sealed with a cap containing a PTFE septum. The reaction mixture was heated at 100 °C for 1 h. After the reaction, the mixture was directly subjected to Al_2O_3 gel without the usual extraction, and was purified by flash column chromatography (hexane–EtOAc) to give 1-aminoindolizine **9′** in 97% yield (80 mg).
3-Phenyl-1-piperidin-1-ylindolizine (**9′**): yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.50 (quint, *J* = 6.0 Hz, 2 H), 1.71 (quint, *J* = 6.0 Hz, 4 H), 2.94 (t, *J* = 6.0 Hz, 4 H), 6.30 (t, *J* = 7.5 Hz, 1 H), 6.44 (t, *J* = 7.5 Hz, 1 H), 6.60 (s, 1 H), 7.22 (t, *J* = 7.5 Hz, 1 H), 7.36 (m, 3 H), 7.47 (d, *J* = 7.0 Hz, 2 H), 8.11 (d, *J* = 7.5 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.4, 26.5, 55.2, 105.7, 110.7, 114.3, 118.1, 121.6, 126.7, 127.5, 127.7, 128.6, 128.9, 131.1, 132.6. MS (EI): *m*/*z* = 276.

(15) Nishihara, Y.; Takemura, M.; Mori, A.; Osakada, K. *J. Organomet. Chem.* **2001**, *620*, 282.