

# Silver(I)-Catalyzed Hydroazidation of Ethynyl Carbinols: Synthesis of 2-Azidoallyl Alcohols<sup>\*\*</sup>

Zhenhua Liu, Jianquan Liu, Lin Zhang, Peiqiu Liao, Jinna Song, and Xihe Bi\*

**Abstract:** The hydroazidation of alkynes is the most straightforward pathway to synthetically useful vinyl azides. However, a general hydroazidation of alkynes remains elusive. Herein, a chemo- and regioselective transformation of ethynyl carbinols into vinyl azides is described. This reaction produces a wide variety of 2-azidoallyl alcohols with high efficiency and in good to excellent yields. These compounds constitute a new class of densely functionalized synthetic intermediates. Their synthetic potential has been demonstrated by further transformations into NH aziridines. The mechanistic aspects of the reaction will attract the attention of chemists working on alkyne chemistry and silver catalysis. The findings that are described in this paper represent significant advances in the regioselective hydroelementation of alkynes and open a new reaction manifold for exploitation.

Hydroelementation of alkynes is a powerful means of accessing functionalized alkenes.<sup>[1]</sup> For unsymmetric alkynes, the control of the chemo- and regioselectivity of such reactions is a challenging issue. Vinyl azides are a class of unique functionalized alkenes.<sup>[2]</sup> They have attracted considerable attention because of their high intrinsic reactivity.<sup>[3]</sup> However, the limited access to this kind of compounds has seriously hampered the wider exploitation of their synthetic potential. The hydroazidation of alkynes is an ideal route to vinyl azides.<sup>[4]</sup> However, known variants of this transformation are nearly all limited to the addition of an azide species to electron-deficient alkynes. With regard to unactivated alkynes, only two isolated examples have been mentioned in previous reports.<sup>[4d, 5a]</sup> Very recently, Jiao and co-workers described novel chemoselective transformations of alkynes into nitriles<sup>[5a]</sup> and amides<sup>[5b]</sup> (Figure 1a). Complete chemoselectivity was achieved by using suitable catalysts. During our preparation of this manuscript, Echavarren and Gaydou reported another chemoselective reaction of terminal alkynes

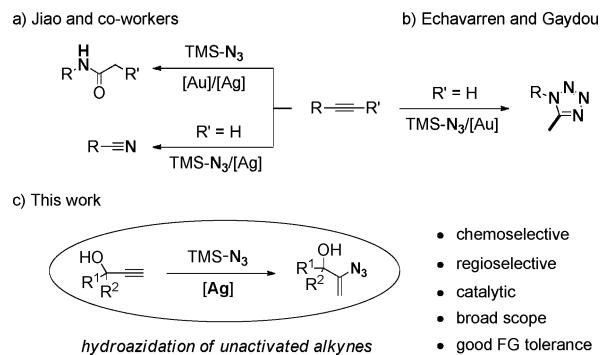


Figure 1. Chemoselective reactions of alkynes with TMS-N<sub>3</sub>.

with trimethylsilyl azide (TMS-N<sub>3</sub>) using gold catalysis, affording tetrazoles (Figure 1b).<sup>[6]</sup> Inspired by Jiao's pioneering work and by our long-standing interest in developing transition-metal-catalyzed organic reactions,<sup>[7]</sup> we herein wish to report an unprecedented chemo- and regioselective hydroazidation of ethynyl carbinols. A general and efficient method to access 2-azidoallyl alcohols has thus been developed (Figure 1c). The hydroxy group that is close to the alkyne unit plays a critical role in directing the chemoselectivity.

Ethynyl carbinols are easily available bifunctional building blocks. The potential of such compounds to undergo reactions that are different from those of isolated alkynes results from the close proximity of the hydroxy group to the C≡C bond.<sup>[8]</sup> Herein, we focus on the reaction of ethynyl carbinols with trimethylsilyl azide (TMS-N<sub>3</sub>) under silver-catalyzed conditions,<sup>[9]</sup> and a hydroxy-directed regioselective hydroazidation of terminal alkynes was discovered. Among the tested silver salts, silver carbonate (Ag<sub>2</sub>CO<sub>3</sub>) gave the best yield (85 %) of vinyl azide **2a** (Table 1, entries 1–3). Notably, unlike in Jiao's work,<sup>[5a]</sup> 2-hydroxy-2-phenylacetonitrile, a product generated from **2a**, was not detected by <sup>1</sup>H NMR spectroscopy of the reaction mixture. This clearly demonstrates the unusual ability of the hydroxy group to stabilize vinyl azides. In contrast to the silver catalysts, other metal salts, such as Pd(OAc)<sub>2</sub> and CuI, were not effective (entries 4 and 5). The solvent also exerted a significant influence on the reaction. For example, in dimethylformamide (DMF), **2a** was obtained in 69 % yield (entry 6). Toluene and methanol turned out to be ineffective (entries 7 and 8). Sources of azides other than TMS-N<sub>3</sub>, including sodium and tosyl azide, were also tested, but only the former afforded a reasonable yield of **2a**. Consequently, TMS-N<sub>3</sub> was used as the azide source in the studies described below.

After determining the optimized reaction conditions, we investigated the scope of the reaction for many different

[\*] Z. Liu, J. Liu, L. Zhang, Dr. P. Liao, Prof. J. Song, Prof. X. Bi

Department of Chemistry  
Northeast Normal University  
Changchun 130024 (China)  
E-mail: bixh507@nenu.edu.cn

Prof. X. Bi  
State Key Laboratory of Elemento-Organic Chemistry  
Nankai University  
Tianjin 300071 (China)

[\*\*] This work was supported by the NNSFC (21172029, 21202016, 21372038, 31101010), the Ministry of Education of the People's Republic of China (NCET-13-0714), and the Jilin Provincial Research Foundation for Basic Research (20140519008JH).

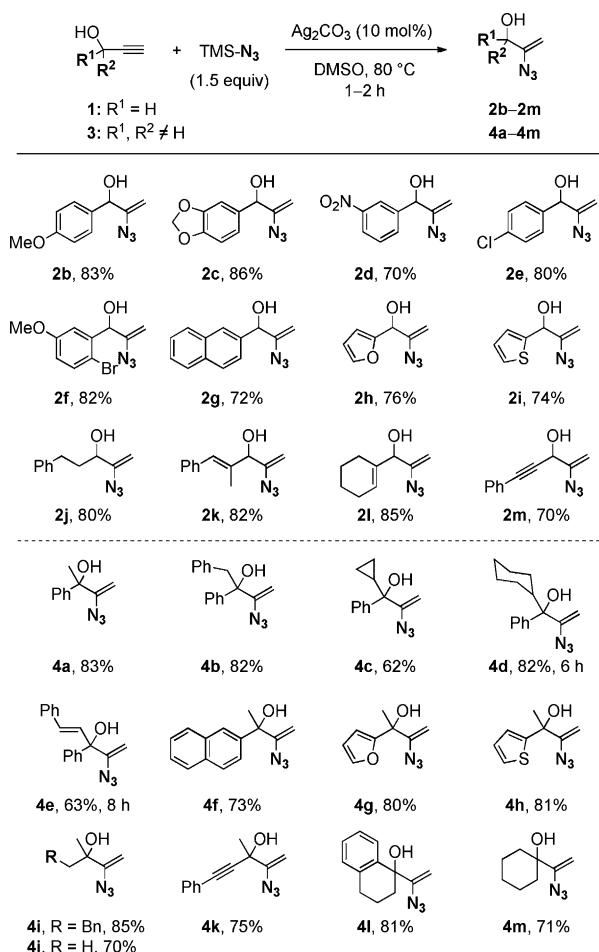
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201310264>.

**Table 1:** Screening of the reaction conditions.<sup>[a]</sup>

Entry	Catalyst	Solvent	Yield <sup>[b]</sup> [%]
1	AgNO <sub>3</sub>	DMSO	75
2	AgF	DMSO	62
3	Ag <sub>2</sub> CO <sub>3</sub>	DMSO	85
4	Pd(OAc) <sub>2</sub>	DMSO	0
5	CuI	DMSO	0
6	Ag <sub>2</sub> CO <sub>3</sub>	DMF	69
7	Ag <sub>2</sub> CO <sub>3</sub>	toluene	trace
8	Ag <sub>2</sub> CO <sub>3</sub>	MeOH	0

[a] Reactions were carried out with **1a** (0.5 mmol) and TMS-N<sub>3</sub> (0.75 mmol) in the presence of a catalyst (10 mol %) in 2 mL of solvent at 80 °C under ambient atmosphere for 2 h. [b] Yields of isolated products.

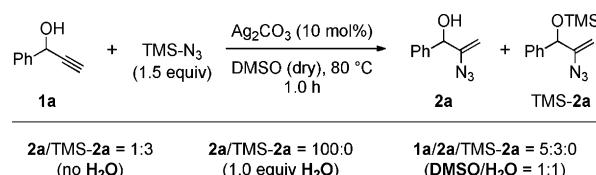
ethynyl carbinols (Scheme 1). In general, the substrate scope is quite broad, and a wide variety of secondary and tertiary ethynyl carbinols with various substituents can be subjected to this new silver-catalyzed reaction, giving the corresponding products (**2** and **4**) in good to excellent yields. All of the reactions proceeded smoothly and were completed within 0.5–2 hours; only for **4d** (6 h) and **4e** (8 h), slightly extended



**Scheme 1.** Scope of the reaction. Bn = benzyl.

reaction times were required, which might be due to steric effects. Aside from these common electron-rich and -deficient (hetero)aryl and alkyl groups, several highly reactive functional groups, including alkenyl (**2k**, **2l**, **4e**), alkynyl (**2m**, **4k**), and cyclopropyl (**4c**) moieties, were found to be well tolerated. The dense arrangement of several functional groups in one molecular scaffold renders 2-azidoallyl alcohols highly attractive synthetic intermediates; however, only one report on their synthesis by Trofimov and co-workers could be found in the literature; they described a method that proceeds by the addition of hydrazoic acid to acetylenic hydroxy acid nitriles.<sup>[10]</sup> Therefore, we have developed an efficient route to this kind of compounds with great synthetic potential.

To determine the source of hydrogen in the above hydroazidation, the effect of residual water (H<sub>2</sub>O) in the DMSO solvent was investigated (Scheme 2). In dry DMSO,

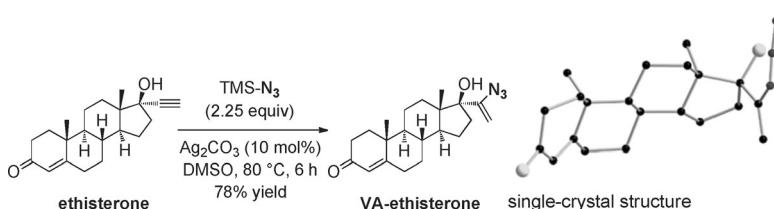


**Scheme 2.** The effect of water on the reaction outcome.

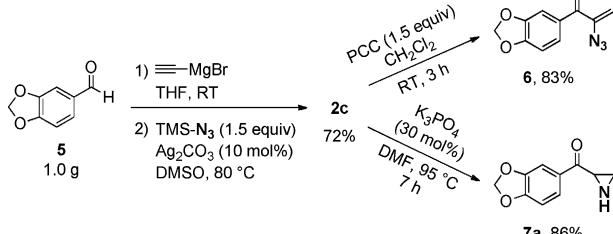
a mixture of **2a** and O-trimethylsilylated **TMS-2a** was obtained in a 1:3 ratio, which was determined by <sup>1</sup>H NMR analysis of the crude product. Once H<sub>2</sub>O (1.0 equiv) had been added to the reaction, only **2a** was produced, without **TMS-2a**. Notably, **TMS-2a** remained intact in the presence of H<sub>2</sub>O (1.0 equiv) and Ag<sub>2</sub>CO<sub>3</sub> (10 mol %) in DMSO at 80 °C, thus excluding the possibility that **TMS-2a** was first formed and then converted into **2a** by hydrolysis. Increasing the amount of H<sub>2</sub>O up to 1 mL (for 0.5 mmol of **1a**) resulted in a large amount of unreacted substrate **1a** in the reaction mixture.

Ethisterone is the first orally active progestin.<sup>[11]</sup> The structural modification of ethisterone is highly interesting because of its significance for structure–activity relationship (SAR) studies.<sup>[12]</sup> However, the site-specific manipulation of the alkynyl group is challenging because of its close proximity to the reactive hydroxy group. The present method was applied to derivatize ethisterone, resulting in a single functional group transformation from alkyne to vinyl azide that did not change the chiral center (Scheme 3). The structure of vinyl azide modified ethisterone (VA-ethisterone) was unambiguously confirmed by X-ray diffraction.<sup>[13]</sup> This compound may be interesting to medicinal chemists.

Furthermore, the practicality of this silver-catalyzed hydroazidation of ethynyl carbinols was demonstrated by a gram-scale synthesis (Scheme 4). For example, vinyl azide **2c** was directly prepared from piperonyl aldehyde (**5**) in 72 % yield in a one-pot reaction. The stability of vinyl azide **2c** was confirmed by standard <sup>1</sup>H NMR spectroscopy, and compound **2c** was found to remain intact in CDCl<sub>3</sub> under ambient conditions for at least one month without any obvious changes. Their stability and easy availability persuaded us to



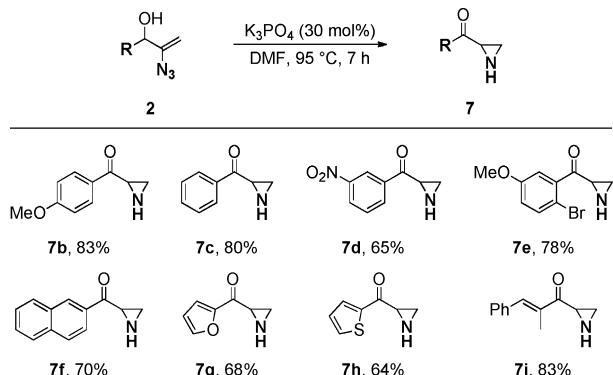
Scheme 3. Modification of ethisterone.



Scheme 4. Gram-scale synthesis and further transformations.

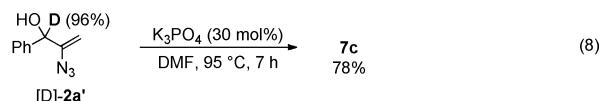
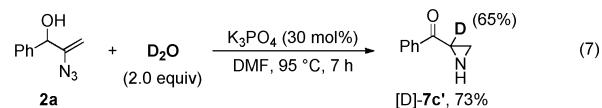
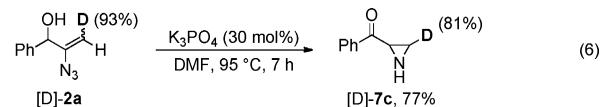
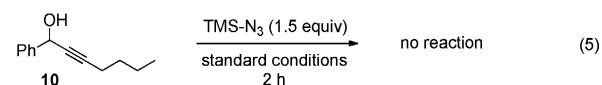
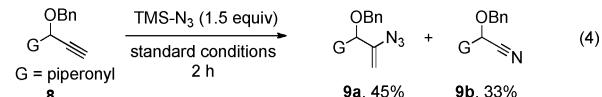
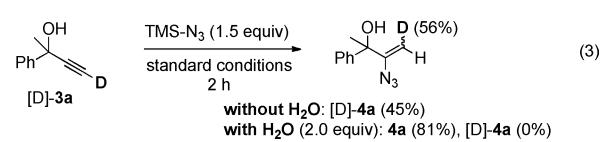
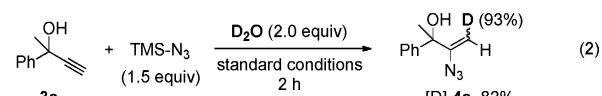
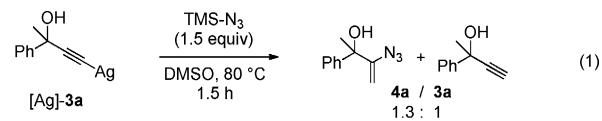
exploit synthetic transformations of 2-azidoallyl alcohols. First, the oxidation of **2c** to  $\alpha$ -carbonyl vinyl azide **6** in 83 % yield was achieved using pyridinium chlorochromate (PCC) as the oxidant. More importantly, an unprecedented conversion of **2c** into NH aziridine **7a**, which is catalyzed by potassium phosphate ( $K_3PO_4$ ), was discovered.<sup>[14]</sup> These results demonstrate the usefulness of 2-azidoallyl alcohols as synthetic intermediates.

Aziridines are important synthetic building blocks for the construction of complex nitrogen-containing compounds.<sup>[15]</sup> Many methods for constructing aziridine ring systems have been identified over the past decades.<sup>[16]</sup> However, most approaches require a protecting group at the nitrogen atom, such as a tosyl group. Thus far, approaches to NH aziridines are much less common.<sup>[17]</sup> The synthesis of NH aziridine **7a** from 2-azidoallyl alcohols is attractive because of the clean conversion and the mild reaction conditions. Therefore, the scope of the reaction was expanded by varying the 2-azidoallyl alcohol. A variety of NH aziridines (**7b–7i**) were prepared in good yields by choosing the appropriate 2-azidoallyl alcohol (Scheme 5).



Scheme 5. Transformations of 2-azidoallyl alcohols into NH aziridines.

Furthermore, control experiments were performed to gain insights into the reaction pathway (Scheme 6). In the absence of  $Ag_2CO_3$ , silver acetylidyne [Ag]-**3a** reacted with TMS-N<sub>3</sub> and afforded a mixture of vinyl azide **4a** and ethynyl carbinol **3a** in a 1.3:1 ratio [Eq. (1)]. When two equivalents of deuterium oxide ( $D_2O$ ) were added to the reaction of **3a** with TMS-N<sub>3</sub>,



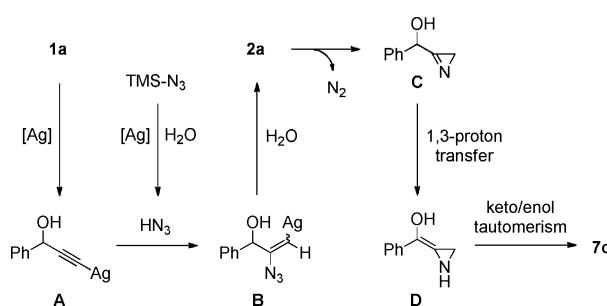
Scheme 6. Mechanistic investigations.

a mono-deuterated product **[D]-4a** was generated with a deuterium content of 93 % under the standard reaction conditions [ $Ag_2CO_3$  (10 mol %), DMSO, 80 °C; Eq. (2)]. This result implies that a silver intermediate might be generated during the reaction. The deuterated substrate **[D]-3a** afforded **[D]-4a** in 45 % yield with a deuterium content of 56 % in dry DMSO, whereas adding  $H_2O$  (2.0 equiv) to the reaction only afforded **4a**, without **[D]-4a** [Eq. (3)]. The reaction of benzyl-protected **8** with TMS-N<sub>3</sub> generated a mixture of vinyl azide **9a** (45 %) and cyanide **9b** (33 %), which implies that the free hydroxy group plays a role in stabilizing the vinyl azide products [Eq. (4)]. A terminal alkyne was necessary

for the alkyne hydroazidation because the internal alkynyl carbinol **10** was not converted into the desired product [Eq. (5)]. The reaction of **1c** proceeded well in the presence of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and afforded the vinyl azide product **2c** in 77% yield, so that a radical process can be excluded for this reaction.

The possible mechanism for the transformation of 2-azidoallyl alcohols into NH aziridines was also studied. First, the deuterated product [ $D$ ]-**7c** was obtained with 81% deuterium content using [ $D$ ]-**2a** as the starting material, suggesting that the alkenyl hydrogen atom of [ $D$ ]-**2a** is not removed during ring closure [Eq. (6)]. The addition of  $D_2O$  (2.0 equiv) to the reaction of **2a** produced a deuterated product [ $D$ ]-**7c'** with a deuterium content of 65% at the  $\alpha$ -carbonyl position [Eq. (7)]. Interestingly, deuterated substrate [ $D$ ]-**2a'** only gave undeuterated product **7c** [Eq. (8)]. When we directly analyzed the reaction mixture of [ $D$ ]-**2a'** by high-resolution mass spectrometry (HRMS), a peak that corresponds to monodeuterated aziridine was found, implying that the deuterium atom of [ $D$ ]-**2a'** might migrate to the N–H position of **7c** and then be removed by proton exchange after work-up.

Following these preliminary mechanistic studies, a plausible reaction mechanism is tentatively proposed. The initial step involves the formation of silver acetylide intermediate **A** from the interaction of reactant **1a** with the silver catalyst (Scheme 7).<sup>[18]</sup> The subsequent addition reaction takes place



Scheme 7. Proposed mechanism.

with hydrazoic acid ( $HN_3$ ) that was generated in situ by silver-catalyzed hydrolysis of  $TMS-N_3$ , to give vinyl silver intermediate **B**.<sup>[4]</sup> Product **2a** was then produced through the protonation of **B** with a trace amount of  $H_2O$  in the  $DMSO$  solvent. For the conversion of vinyl azide **2a** into aziridine **7c**, 2H-azirine **C** may first be generated from **2a** under thermal conditions. Following sequential 1,3-proton transfer and keto/enol tautomerism, the NH aziridine **7c** is formed.

In conclusion, a chemo- and regioselective transformation of ethynyl carbinols into vinyl azides has been described. This reaction produces a wide variety of 2-azidoallyl alcohols with high efficiency and in good to excellent yields. These compounds represent a class of densely functionalized synthetic intermediates. Their synthetic potential has been demonstrated by further transformations into NH aziridines. The mechanistic aspects of this reaction are also interesting and will attract the attention of chemists working on alkyne

chemistry and silver catalysis. The findings that are described in this paper represent significant advances in the regioselective hydrofunctionalization of alkynes and open a new reaction manifold for exploitation.

Received: November 26, 2013

Revised: January 18, 2014

Published online: ■■■■■, ■■■■■

**Keywords:** aziridines · ethynyl carbinols · hydroazidation · silver catalysis · vinyl azides

- [1] For general reviews on the hydroelementation of alkynes, see: a) F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2004**, *104*, 3079–3159; b) X. Zeng, *Chem. Rev.* **2013**, *113*, 6864–6900.
- [2] For a comprehensive review on the synthesis and reactions of vinyl azides, see: K. Banert in *Organic Azides: Syntheses and Applications* (Eds.: S. Bräse, K. Banert), Wiley, Chichester, **2010**.
- [3] For examples, see: a) F. Chen, T. Shen, Y. Cui, N. Jiao, *Org. Lett.* **2012**, *14*, 4926–4929; b) Y.-F. Wang, K. K. Toh, J.-Y. Lee, S. Chiba, *Angew. Chem.* **2011**, *123*, 6049–6053; *Angew. Chem. Int. Ed.* **2011**, *50*, 5927–5931; c) Y.-F. Wang, K. K. Toh, E. P. J. Ng, S. Chiba, *J. Am. Chem. Soc.* **2011**, *133*, 6411–6421; d) Y.-F. Wang, S. Chiba, *J. Am. Chem. Soc.* **2009**, *131*, 12570–12572; e) B. J. Stokes, H. Dong, B. E. Leslie, A. L. Pumphrey, T. G. Driver, *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501; f) B. Hu, Z. Wang, N. Ai, J. Zheng, X.-H. Liu, S. Shan, Z. Wang, *Org. Lett.* **2011**, *13*, 6362–6365; g) W. Chen, M. Hu, J. Wu, H. Zou, Y. Yu, *Org. Lett.* **2010**, *12*, 3863–3865; h) B. J. Stokes, C. V. Vogel, L. K. Urnezis, M. Pan, T. G. Driver, *Org. Lett.* **2010**, *12*, 2884–2887; i) S. Chiba, L. Zhang, G. Y. B. Ang, W.-Q. Hui, *Org. Lett.* **2010**, *12*, 2052–2055; j) Y.-F. Wang, K. K. Toh, S. Chiba, K. Narasaka, *Org. Lett.* **2008**, *10*, 5019–5022; k) S. Chiba, Y.-F. Wang, G. Lapointe, K. Narasaka, *Org. Lett.* **2008**, *10*, 313–316; l) H. Dong, M. Shen, J. E. Redford, B. J. Stokes, A. L. Pumphrey, T. G. Driver, *Org. Lett.* **2007**, *9*, 5191–5194.
- [4] a) I. F. D. Hyatt, M. P. Croatt, *Angew. Chem.* **2012**, *124*, 7629–7632; *Angew. Chem. Int. Ed.* **2012**, *51*, 7511–7514; b) F. Palacios, D. Aparicio, J. M. de Los Santos, I. Perez de Heredia, G. Rubiales, *Org. Prep. Proced. Int.* **1995**, *27*, 171–178; c) M. Haddach, R. Pastor, J. G. Riess, *Tetrahedron* **1993**, *49*, 4627–4638; d) K. Banert, *Chem. Ber.* **1989**, *122*, 1175–1178; e) T. Kitamura, P. J. Stang, *Tetrahedron Lett.* **1988**, *29*, 1887–1889; f) M. Ochiai, M. Kunishima, K. Fuji, Y. Nagao, *J. Org. Chem.* **1988**, *53*, 6144–6145; g) V. G. Ostroverkhov, E. A. Shilov, *Ukr. Khim. Zh.* **1957**, *23*, 615–622.
- [5] a) T. Shen, T. Wang, C. Qin, N. Jiao, *Angew. Chem.* **2013**, *125*, 6809–6812; *Angew. Chem. Int. Ed.* **2013**, *52*, 6677–6680; b) C. Qin, P. Feng, Y. Ou, T. Shen, T. Wang, N. Jiao, *Angew. Chem.* **2013**, *125*, 8004–8008; *Angew. Chem. Int. Ed.* **2013**, *52*, 7850–7854.
- [6] M. Gaydou, A. M. Echavarren, *Angew. Chem.* **2013**, *125*, 13710–13713; *Angew. Chem. Int. Ed.* **2013**, *52*, 13468–13471.
- [7] a) J. Liu, Z. Fang, Q. Zhang, Q. Liu, X. Bi, *Angew. Chem.* **2013**, *125*, 7091–7095; *Angew. Chem. Int. Ed.* **2013**, *52*, 6953–6957; b) L. Zhang, X. Bi, X. Guan, X. Li, Q. Liu, B.-D. Barry, P. Liao, *Angew. Chem.* **2013**, *125*, 11513–11517; *Angew. Chem. Int. Ed.* **2013**, *52*, 11303–11307; c) Z. Wang, X. Bi, P. Liao, X. Liu, D. Dong, *Chem. Commun.* **2013**, *49*, 1309–1311; d) T. Xiong, Y. Li, X. Bi, Y. Lv, Q. Zhang, *Angew. Chem.* **2011**, *123*, 7278–7281; *Angew. Chem. Int. Ed.* **2011**, *50*, 7140–7143; e) Z. Wang, X. Bi, P. Liao, R. Zhang, Y. Liang, D. Dong, *Chem. Commun.* **2012**, *48*, 7076–7078; f) K. Wang, X. Bi, S. Xing, P. Liao, Z. Fang, X. Meng, Q. Zhang, Q. Liu, Y. Ji, *Green Chem.* **2011**, *13*, 562–565; g) L.

- Zhang, Z. Liu, H. Li, G. Fang, B.-D. Barry, T. A. Belay, X. Bi, Q. Liu, *Org. Lett.* **2011**, *13*, 6536–6539.
- [8] For selected examples of transition-metal-catalyzed reactions of alkynyl carbinols, see: a) Z. Li, V. Boyarskikh, J. H. Hansen, J. Autschbach, D. G. Musaev, H. M. L. Davies, *J. Am. Chem. Soc.* **2012**, *134*, 15497–15504; b) B. S. L. Collins, M. G. Suero, M. J. Gaunt, *Angew. Chem.* **2013**, *125*, 5911–5914; *Angew. Chem. Int. Ed.* **2013**, *52*, 5799–5802; c) G. Cera, S. Piscitelli, M. Chiarucci, G. Fabrizi, A. Goggiamani, R. S. Ramón, S. P. Nolan, M. Bandini, *Angew. Chem.* **2012**, *124*, 10029–10033; *Angew. Chem. Int. Ed.* **2012**, *51*, 9891–9895; d) T. Kimura, K. Kamata, N. Mizuno, *Angew. Chem.* **2012**, *124*, 6804–6807; *Angew. Chem. Int. Ed.* **2012**, *51*, 6700–6703; e) P. Lenden, D. A. Entwistle, M. C. Willis, *Angew. Chem.* **2011**, *123*, 10845–10848; *Angew. Chem. Int. Ed.* **2011**, *50*, 10657–10660; f) N. Chinkov, A. Warm, E. M. Carreira, *Angew. Chem.* **2011**, *123*, 3014–3018; *Angew. Chem. Int. Ed.* **2011**, *50*, 2957–2961; g) M. Ikeda, Y. Miyake, Y. Nishibayashi, *Angew. Chem.* **2010**, *122*, 7447–7451; *Angew. Chem. Int. Ed.* **2010**, *49*, 7289–7293; h) S. Minakata, I. Sasaki, T. Ide, *Angew. Chem.* **2010**, *122*, 1331–1333; *Angew. Chem. Int. Ed.* **2010**, *49*, 1309–1311; i) R. Shintani, K. Takatsu, T. Katoh, T. Nishimura, T. Hayashi, *Angew. Chem.* **2008**, *120*, 1469–1471; *Angew. Chem. Int. Ed.* **2008**, *47*, 1447–1449; j) H. Jiang, C. Qiao, W. Liu, *Chem. Eur. J.* **2010**, *16*, 10968–10970; k) T. Miura, Y. Funakoshi, M. Morimoto, T. Biyajima, M. Murakami, *J. Am. Chem. Soc.* **2012**, *134*, 17440–17443; l) L. Ye, W. He, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8550–8551; m) S. Yoshida, K. Fukui, S. Kikuchi, T. Yamada, *J. Am. Chem. Soc.* **2010**, *132*, 4072–4073; n) B. M. Trost, R. C. Livingston, *J. Am. Chem. Soc.* **2008**, *130*, 11970–11978; o) X. Pu, J. M. Ready, *J. Am. Chem. Soc.* **2008**, *130*, 10874–10875; p) D. K. Friel, M. L. Snapper, A. H. Hoveyda, *J. Am. Chem. Soc.* **2008**, *130*, 9942–9951; q) Y. Sugawara, W. Yamada, S. Yoshida, T. Ikeno, T. Yamada, *J. Am. Chem. Soc.* **2007**, *129*, 12902–12903; r) D. Zhang, J. M. Ready, *J. Am. Chem. Soc.* **2007**, *129*, 12088–12089; s) Y. Yamauchi, G. Onodera, K. Sakata, M. Yuki, Y. Miyake, S. Uemura, Y. Nishibayashi, *J. Am. Chem. Soc.* **2007**, *129*, 5175–5179; t) Y. Yamamoto, J.-i. Ishii, H. Nishiyama, K. Itoh, *J. Am. Chem. Soc.* **2005**, *127*, 9625–9631.
- [9] *Silver in Organic Chemistry* (Ed.: M. Harmata), Wiley, Hoboken, **2010**.
- [10] B. A. Trofimov, A. G. Mal'kina, R. N. Kudyakova, *Zh. Org. Khim.* **1993**, *29*, 1942–1946.
- [11] For a review, see: A. B. Forinash, S. L. Evans, *Pharmacotherapy* **2003**, *23*, 1573–1591.
- [12] P. M. Levine, K. Imberg, M. J. Garabedian, K. Kirshenbaum, *J. Am. Chem. Soc.* **2012**, *134*, 6912–6915.
- [13] For details, see the Supporting Information.
- [14] Thermolysis of vinyl azides generally produces unsaturated 2H-azirines; for examples, see: a) A. Padwa, A. Ku, H. Ku, A. Mazzu, *J. Org. Chem.* **1978**, *43*, 66–72; b) M. Komatsu, S. Ichijima, Y. Ohshiro, T. Agawa, *J. Org. Chem.* **1973**, *38*, 4341–4342; c) A. Hassner, E. S. Ferdinand, R. J. Isbister, *J. Am. Chem. Soc.* **1970**, *92*, 1672–1675; d) K. Isomura, M. Okada, H. Taniguchi, *Tetrahedron Lett.* **1969**, *10*, 4073–4076; e) G. L'Abbé, A. Hassner, *Angew. Chem.* **1971**, *83*, 103–109; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 98–104.
- [15] For selected reviews, see: a) S. Florio, R. Luisi, *Chem. Rev.* **2010**, *110*, 5128–5157; b) S. Stanković, M. D'hooghe, S. Catak, H. Eum, M. Waroquier, V. Van Speybroeck, N. De Kimpe, H.-J. Ha, *Chem. Soc. Rev.* **2012**, *41*, 643–665; c) A. L. Cardoso, T. M. V. D. Pinho e Melo, *Eur. J. Org. Chem.* **2012**, 6479–6501.
- [16] a) I. D. G. Watson, L. Yu, A. K. Yudin, *Acc. Chem. Res.* **2006**, *39*, 194–206; b) T. Ibuka, *Chem. Soc. Rev.* **1998**, *27*, 145–154.
- [17] For examples of the synthesis and reactions of NH aziridines, see: a) B. R. Buckley, A. P. Patel, K. G. U. Wijayantha, *J. Org. Chem.* **2013**, *78*, 1289–1292; b) F. von Kieseritzky, J. Lindströma, *Tetrahedron Lett.* **2011**, *52*, 4558–4561; c) S. Baktharaman, N. Afagh, A. Vandersteen, A. K. Yudin, *Org. Lett.* **2010**, *12*, 240–243; d) A. B. Pulipaka, S. C. Bergmeier, *J. Org. Chem.* **2008**, *73*, 1462–1467; e) D. M. Hodgson, P. G. Humphreys, S. M. Miles, C. A. J. Brierley, J. W. Ward, *J. Org. Chem.* **2007**, *72*, 10009–10021; f) D. L. Warner, A. M. Hibberd, M. Kalman, A. Klapars, E. Vedejs, *J. Org. Chem.* **2007**, *72*, 8519–8522; g) Z. Lu, Y. Zhang, W. D. Wulff, *J. Am. Chem. Soc.* **2007**, *129*, 7185–7194; h) M. Sasaki, S. Dalili, A. K. Yudin, *J. Org. Chem.* **2003**, *68*, 2045–2047; i) B. Olofsson, R. Wijtmans, P. Somfai, *Tetrahedron* **2002**, *58*, 5979–5982; j) S. C. Bergmeier, P. P. Seth, *Tetrahedron Lett.* **1999**, *40*, 6181–6184; k) A. Koohang, C. L. Stanchina, R. M. Coates, *Tetrahedron* **1999**, *55*, 9669–9686.
- [18] U. Létinois-Halbes, P. Pale, S. Berger, *J. Org. Chem.* **2005**, *70*, 9185–9190.

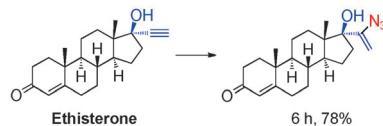
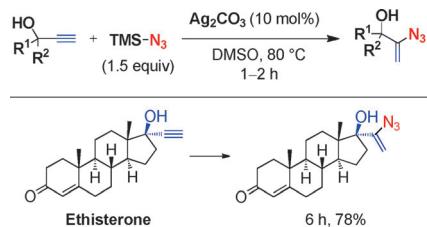
**Communications**



**Hydroazidation**

Z. Liu, J. Liu, L. Zhang, P. Liao, J. Song,  
X. Bi\* ————— ■■■—■■■

Silver(I)-Catalyzed Hydroazidation of  
Ethynyl Carbinols: Synthesis of 2-  
Azidoallyl Alcohols



**Azides and aziridines:** The hydroazidation of unactivated alkynes by means of silver catalysis is described. A variety of ethynyl carbinols are capable of reacting with trimethylsilyl azide to produce 2-azidoallyl alcohols in good to excellent yields. The synthetic utility of 2-azidoallyl alcohols was demonstrated by further conversion into NH aziridines.