Synthetic Methods

Deutsche Ausgabe: DOI: 10.1002/ange.201512015
Internationale Ausgabe: DOI: 10.1002/anie.201512015

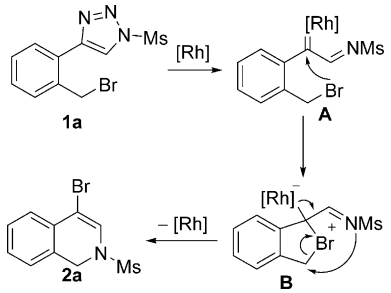
Rhodium-Catalyzed Synthesis of 4-Bromo-1,2-dihydroisoquinolines: Access to Bromonium Ylides by the Intramolecular Reaction of a Benzyl Bromide and an α-Imino Carbene

*Jun He, Yinping Shi, Wanli Cheng, Zengming Man, Dongdong Yang, and Chuan-Ying Li**

Abstract: *Highly functionalized 4-bromo-1,2-dihydroisoquinolines were synthesized from readily available 4-(2-(bromomethyl)phenyl)-1-sulfonyl-1,2,3-triazoles. A bromonium ylide is proposed as the key intermediate, which can be formed by the intramolecular nucleophilic attack of the benzyl bromide on the α-imino rhodium carbene formed in the presence of the rhodium catalyst.*

The N-heterocyclic motif isoquinoline exists in numerous natural products.[1] Isoquinoline alkaloids display diverse biological activity, such as anticancer, antibacterial, anti-HIV, and antiparkinsonian activity. Furthermore, isoquinoline derivatives can be used as chiral ligands in transition-metal catalysis.[2] Many synthetic approaches have been developed to construct this bicyclic skeleton.[3] Traditional methods include Bischler–Napieralski cyclization,[4] Pictet–Spengler synthesis,[5] and Pomeranz–Fritsch synthesis.[6] Other efficient approaches starting from *o*-halobenzaldimines or *o*-alkynyl benzaldimines have been studied extensively.[7] Methods based on C–H activation,[8] the nucleophilic activity of azide group,[9] or the construction of phenyl ring[10] have also been developed. The above methods are widely used and cost-effective. Nevertheless, in view of the importance of the isoquinoline structure, the development of a general and efficient approach to functionalized isoquinoline derivatives is highly desirable.

The transition-metal-catalyzed transformation of diazo compounds or *N*-tosylhydrazones into carbenes has been explored extensively,[11] and non-diazo approaches to metal carbenes have attracted considerable attention recently.[12] In 2008, Fokin, Gevorgyan, and co-workers demonstrated that the ring–chain tautomerization between a 1-sulfonyl-1,2,3-triazole and an α-diazoimine could be utilized to generate an α-imino rhodium carbene.[13] Since then, there has been rapid development in transformations mediated by α-imino carbenes.[14] Notably, an ylide could be formed if the carbene was trapped by a heteroatom, such as sulfur, nitrogen, or oxygen.[15] As part of our research on carbene-mediated chemical transformations,[16] we have synthesized β-amino α,β-unsaturated ketones through the sequential formation and rearrangement of sulfur ylides.[16d] As compared to allyl phenyl sulfides,[15e,f] β-(methylthio)-α,β-unsaturated ketones should be less nucleophilic, yet the reaction could reach completion within several hours. This reaction demonstrates the strong electrophilicity of α-imino rhodium carbenes generated from 1-sulfonyl-1,2,3-triazoles. We envisioned that a benzyl bromide, which is a weak nucleophile, could be used to trap the carbene intramolecularly to give a bromonium ylide (Scheme 1); subsequent rearrangement would lead to the formation of a 4-bromo-1,2-dihydroisoquinoline (DHIQ), such as **2a**, which is a versatile building block.



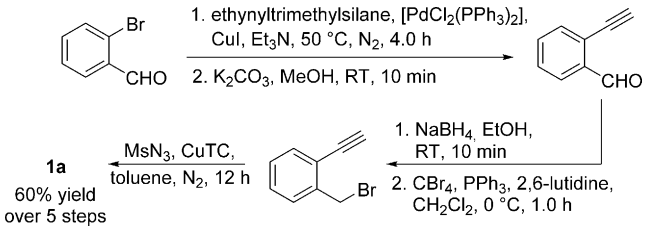
Scheme 1. Initial hypothesis. Ms = methanesulfonyl.

An isoquinoline or 1,2,3,4-tetrahydroisoquinoline (THIQ) could be obtained from **2a**, and the vinyl bromide moiety is a useful handle for the introduction of other functional groups by cross-coupling reactions. Notably, in the limited number of previous reports about halonium ylides derived from carbenes,[17] no intramolecular reaction has been described, and the halogen source was used as a solvent or in at least 10-fold excess. Furthermore, when rhodium carbene intermediates were employed as precursors of halonium ylides, two electron-withdrawing carbonyl groups were necessary to increase the electrophilicity of the carbene center. Herein, we report an intramolecular reaction involving a bromonium ylide which leads to the formation of 4-bromo-1,2-dihydroisoquinolines.

Triazole **1a** could be obtained in 60% overall yield in five steps (Scheme 2). Gratifyingly, when **1a** was treated with $[Rh_2(oct)_4]$ in 1,2-dichloroethane (DCE) at reflux, DHIQ **2a** was obtained in 52% yield (Table 1, entry 1). The use of rhodium(II) catalysts with different ligands resulted in increased yields (Table 1, entries 2–7). The impact of the solvent was also examined (Table 1, entries 8–10), and a high temperature was necessary for this transformation. During the fine-tuning of the reaction parameters, we noticed that **2a** was unstable under the reaction conditions, so we investigated the relationship between the yield and the reaction time (Table 1, entries 11–13). If the reaction was quenched at 0.7 h,

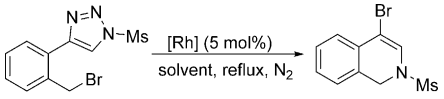
[*] J. He, Y. Shi, W. Cheng, Z. Man, D. Yang, Prof. Dr. C.-Y. Li
Department of Chemistry, Zhejiang Sci-Tech University
Xiasha West Higher Education District, Hangzhou 310018 (China)
E-mail: licy@zstu.edu.cn

Supporting information for this article can be found under http://dx.doi.org/10.1002/anie.201512015.



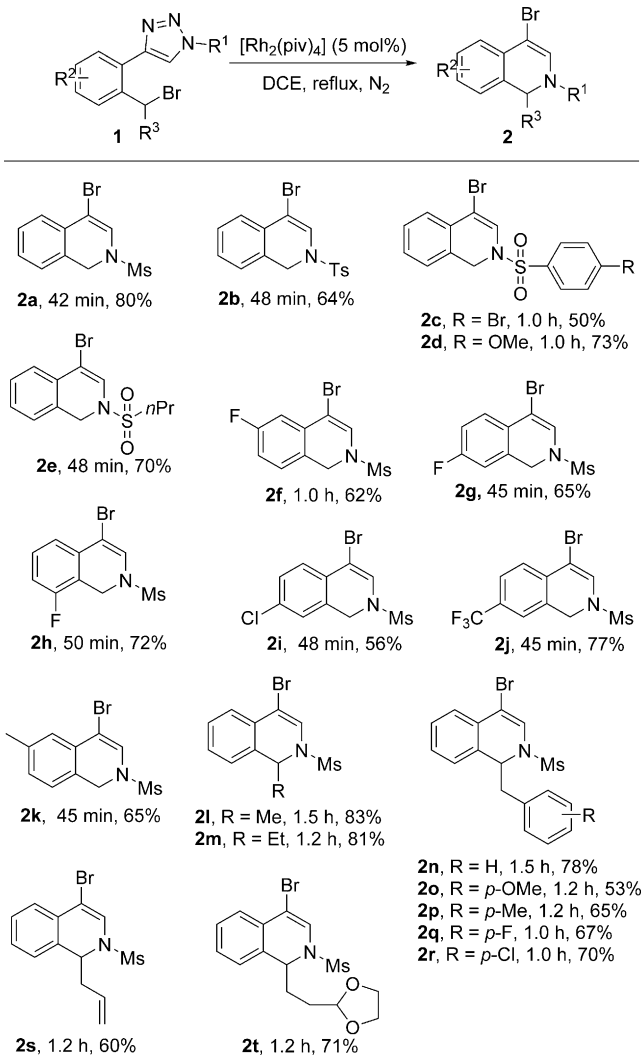
Scheme 2. Synthesis of triazole **1a**. CuTC = copper(I) thiophene-2-carboxylate.

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



Entry	Catalyst	Solvent	*t* [h]	Yield [%][b]
1	$[Rh_2(oct)_4]$	DCE	4.0	52
2	$[Rh_2(OAc)_4]$	DCE	1.5	54
3	$[Rh_2(esp)_2]$	DCE	1.0	60
4	$[Rh_2(piv)_4]$	DCE	1.5	64
5	$[Rh_2\{(S)\text{-ntv}\}_4]$	DCE	1.0	59
6	$[Rh_2\{(S)\text{-nttl}\}_4]$	DCE	1.0	62
7	$[Rh_2(adc)_4]$	DCE	1.0	64
8	$[Rh_2(piv)_4]$	toluene	2.0	59
9	$[Rh_2(piv)_4]$	$CHCl_3$	6.0	31
10	$[Rh_2(piv)_4]$	CH_2Cl_2	6.0	NR[c]
11	$[Rh_2(piv)_4]$	DCE	0.7	69(80)[d]
12	$[Rh_2(piv)_4]$	DCE	1.0	69(89)[d]
13	$[Rh_2(piv)_4]$	DCE	3.0	43
14[e]	$[Rh_2(piv)_4]$	DCE	0.7	80
15[f]	$[Rh_2(piv)_4]$	DCE	0.6	80
16[g]		DCE	24	0

[a] General conditions: **1a** (0.2 mmol), rhodium(II) catalyst (0.01 mmol), solvent (2 mL), reflux, N_2 atmosphere. [b] Yield of the isolated product. [c] No reaction. [d] The conversion of **1a** is given in parentheses. [e] The reaction was carried out with 1 mL of DCE. [f] The reaction was carried out with 0.5 mL of DCE. [g] No rhodium catalyst was added; **1a** decomposed to an unidentified complex mixture. adc = 1-adamantanecarboxylate, esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionate, nttl = *N*-1,8-naphthoyl-*tert*-leucine, ntv = *N*-1,8-naphthoylvaline, oct = octanoate, piv = pivalate.

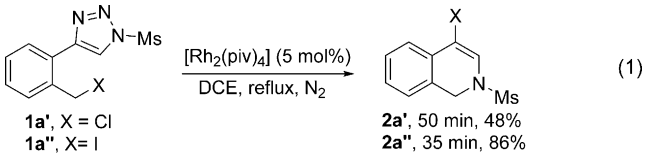


Scheme 3. Scope of the reaction. Reaction conditions: **1** (0.2 mmol), $[Rh_2(piv)_4]$ (0.01 mmol), DCE (1.0 mL), reflux, N_2 atmosphere. Ts = *p*-toluenesulfonyl.

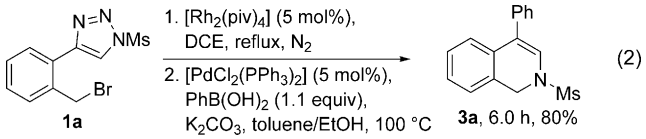
2a could be isolated in 69% yield, and the conversion of **1a** was 80% (Table 1, entry 11). After a reaction time of 1.0 h, **2a** could be isolated in 69% yield, and the conversion in this case was 89% (Table 1, entry 12). Unfortunately, none of the starting material **1a** could be detected after 3 h, and the yield of **2a** decreased to 43% (Table 1, entry 13). When the concentration of **1a** was increased to 0.2 or 0.4 M, **2a** could be obtained in 80% yield (Table 1, entries 14 and 15). In the absence of a rhodium(II) catalyst, **2a** was not produced (Table 1, entry 16).

We were pleased to find that the rhodium(II)-catalyzed reaction enabled the preparation of DHIQs with a variety of substitution patterns (Scheme 3). A range of arylsulfonyl- and alkylsulfonyl-substituted triazoles (substrates **1b–e**) could be synthesized by a similar procedure, and the corresponding DHIQs were obtained conveniently, albeit in lower yield. The reaction proceeded smoothly in moderate to good yield when substrates bearing an electron-withdrawing group on the phenyl ring were used (products **2f–j**). The position of the substituent had little impact on the result (products **2f–h**). DHIQ **2k** with a methyl group on the phenyl ring was also synthesized in 65% yield. The scope of this transformation was further probed by varying the substituent on the benzyl carbon atom (R^3). DHIQs **2l** and **2m** with alkyl substituents were produced in high yield, and a vinyl group and an acetal were tolerated well (products **2s** and **2t**). Since 1-benzylated isoquinolines possess important physiological properties, we attempted to synthesize a series of 1-benzyl-1,2-dihydroisoquinolines. Products **2n–r** were obtained smoothly in 53–78% yield. Additionally, when we synthesized the benzyl chloride **1a′** and benzyl iodide **1a″** and treated them with $[Rh_2(piv)_4]$, **2a′** and **2a″** were produced in 48 and 86% yield, respectively [Eq. (1)].

To simplify the operating procedure, we attempted a one-pot sequential reaction [Eq. (2)]. After a reaction time of 42 min, the reaction mixture was cooled to room temperature,



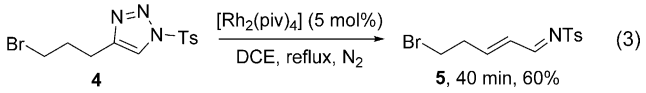
(1)



(2)

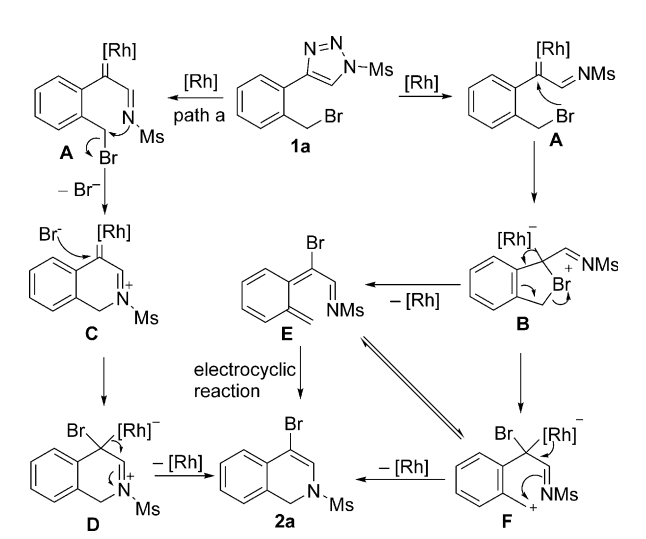
and the solvent 1,2-DCE was evaporated. A palladium catalyst and new reagents were added, and the mixture was reheated to 100 °C until the conversion of **2a** was complete. The cross-coupling product **3a** was obtained in 80% yield. In almost all cases, the yield of the 4-phenyl-1,2-dihydroisoquinoline product **3** of the one-pot cyclization–cross-coupling reaction was comparable to that observed for the synthesis of the corresponding 4-bromo-1,2-dihydroisoquinoline **2** from **1** (see the Supporting Information for more details).

When triazole **4** bearing α-H atoms was synthesized and subjected to the optimized reaction conditions, only the α,β-unsaturated imine **5** was isolated in 60% yield [Eq. (3)]. Thus, the 1,2-H migration reaction predominated in this situation.[14p,q]

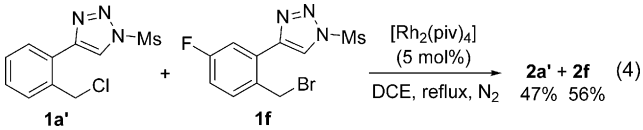


(3)

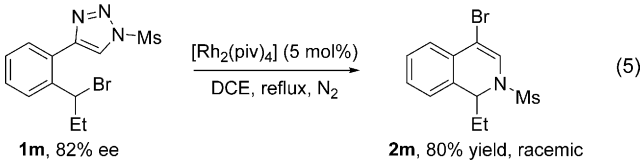
Several mechanistic pathways involving an α-imino rhodium carbene can be conceived at this stage (Scheme 4). Since the bromide at the benzyl position is an excellent leaving group, an intramolecular S_N2 reaction could furnish iminium salt **C** (path a), and subsequent attack of the bromide ion on the carbene carbon atom and electron transfer would result in the formation of **2a**. Alternatively, after the formation of α-imino rhodium carbene **A**, intramolecular nucleophilic attack could lead to the formation of bromonium ylide **B**, and cleavage of one C–Br bond could lead to the formation of benzylic cation **F**. This cation could be in equilibrium with an intermediate **E** by displacement of the rhodium catalyst. A 6 electron electrocyclic ring closure would then yield **2a**. Alternatively, the sulfonamide could simply add to the benzylic cation. When we mixed **1a′** and **1f** together and treated them with the rhodium(II) catalyst, only **2a′** and **2f** could be isolated, in 47 and 56% yield; no cross-reaction product was detected [Eq. (4)]. Additionally, racemic **2m** was obtained when enantiomerically enriched **1m** was used as the substrate [Eq. (5)]. On the basis of the above experiments, path a can be ruled out, and bromonium ylide **B** is proposed to be the key intermediate in this transformation.



Scheme 4. Proposed mechanism.



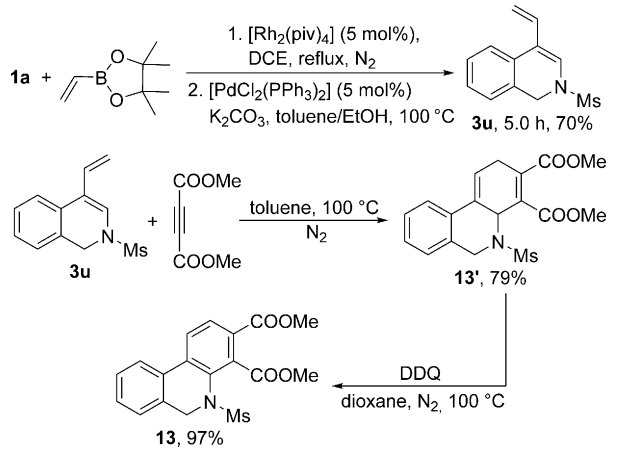
(4)



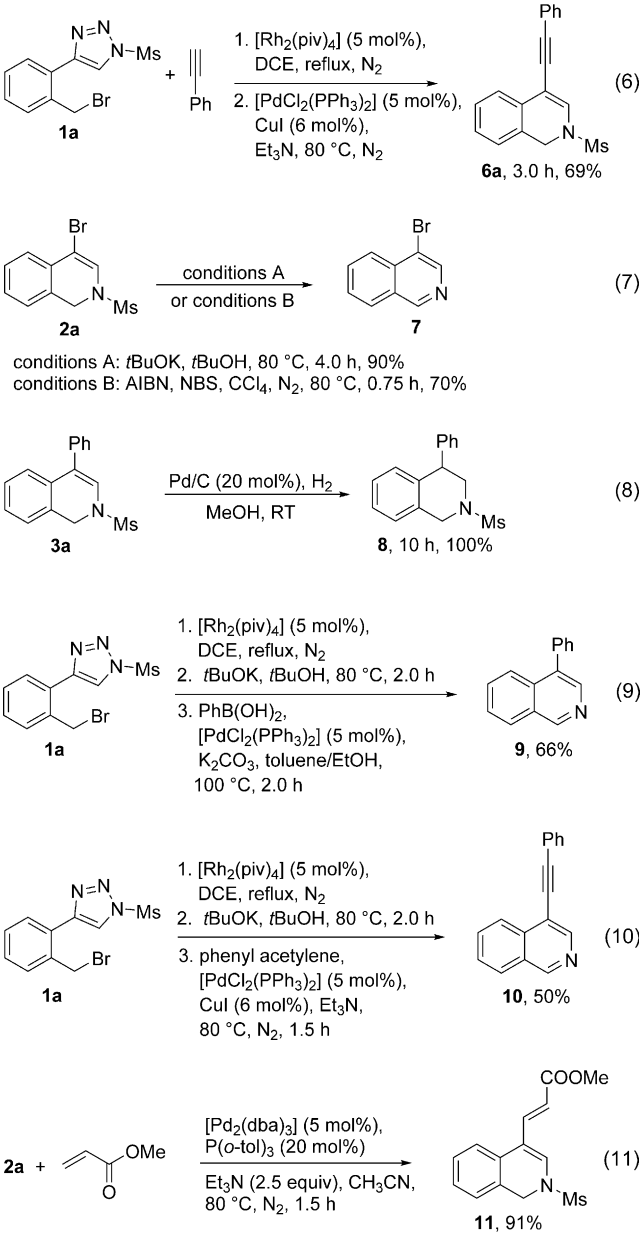
(5)

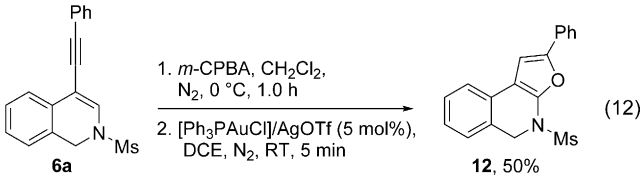
To test the versatility of 4-bromo-1,2-dihydroisoquinolines **2**, we conducted a series of transformations. When we combined the bromonium ylide mediated cyclization with a Sonogashira cross-coupling in a one-pot procedure, 4-alkynyl 1,2-dihydroisoquinoline **6a** was furnished in 69% yield [Eq. (6)]. Compound **2a** could be readily converted into 4-bromoisoquinoline (**7**) by treatment with *t*-BuOK or azobisisobutyronitrile (AIBN)/*N*-bromosuccinimide (NBS) [Eq. (7)]. DHIQ **3a** underwent catalytic hydrogenation smoothly to afford THIQ **8** in quantitative yield [Eq. (8)]. We attempted three-step one-pot procedures involving cyclization, aromatization, and cross-coupling and obtained 4-phenylisoquinoline **9** and 4-(phenylethynyl)isoquinoline **10** from **1a** in 66 and 50% yield, respectively [Eq. (9) and (10)]. DHIQ **2a** also underwent a Heck reaction with methyl acrylate to produce the vinyl-substituted DHIQ **11** in 91% yield [Eq. (11); dba = dibenzylideneacetone, *o*-tol = *o*-tolyl]. When **6a** was oxidized by *m*-chloroperbenzoic acid (*m*-CPBA) and then treated with [Ph_3PAuCl]/AgOTf, the furan-fused DHIQ **12** was isolated in 50% yield [Eq. (12); Tf = trifluoromethanesulfonyl]. Finally, the 5,6-dihydrophenanthridine **13** was obtained from the 4-vinyl-substituted DHIQ **3u** in 77% yield by Diels–Alder cycloaddition and subsequent aromatization (Scheme 5).

In summary, a bromonium ylide was produced intramolecularly from strongly electrophilic α-imino rhodium carbenes with a tethered benzyl bromide. This reaction



Scheme 5. Synthesis of the 5,6-dihydrophenanthridine **13**. DDQ = 2,3-dicyano-5,6-dichlorobenzoquinone.





provides a novel approach to 4-bromo-1,2-dihydroisoquinolines from readily available starting materials. The synthetic potential of the products has been demonstrated by a series of one-pot reactions and the formation of several valuable polycyclic systems.

Experimental Section

Dry DCE (1.0 mL) was added to a reaction flask charged with $[Rh_2(piv)_4]$ (5 mol%) and a 1-sulfonyl-1,2,3-triazole **1** (0.2 mmol) under a nitrogen atmosphere at room temperature, and the reaction mixture was stirred at reflux for the time indicated in Scheme 3. The reaction mixture was then cooled to room temperature and filtered through a short plug of silica gel. The filtrate was concentrated and then purified by flash chromatography with petroleum ether/EtOAc (20:1) as the eluent to give the corresponding product **2**.

Acknowledgements

This research was generously supported by the National Natural Science Foundation of China (21372204), the Program for Innovative Research Team of Zhejiang Sci-Tech University (13060052-Y), and the Young Researchers Foundation of Zhejiang Provincial Top Key Academic Discipline of Chemical Engineering and Technology, Zhejiang Sci-Tech University (ZYG2015004).

Keywords: bromonium ylides · carbenes · isoquinolines · rhodium · triazoles

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4557–4561
Angew. Chem. **2016**, *128*, 4633–4637

[1] a) K. W. Bentley, *The Isoquinoline Alkaloids*, *Vol. 1*, Hardwood Academic, Amsterdam, **1998**; b) J. Keasling, *Nat. Chem. Biol.* **2008**, *4*, 524; c) M. W. Fraaije, A. Mattevi, *Nat. Chem. Biol.* **2008**, *4*, 719; d) P. Cheng, N. Huang, Z.-Y. Jiang, Q. Zhang, Y.-T. Zheng, J.-J. Chen, X.-M. Zhang, Y.-B. Ma, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 2475.

[2] a) F. Durola, J.-P. Sauvage, O. S. Wenger, *Chem. Commun.* **2006**, 171; b) B. A. Sweetman, H. Müller-Bunz, P. J. Guiry, *Tetrahedron Lett.* **2005**, *46*, 4643; c) C. W. Lim, O. Tissot, A. Mattison, M. W. Hooper, J. M. Brown, A. R. Cowley, D. I. Hulmes, A. Blacker, *Org. Process Res. Dev.* **2003**, *7*, 379.

[3] For a review, see: a) M. Chrzanowska, M. D. Rozwadowska, *Chem. Rev.* **2004**, *104*, 3341; for selected reports, see: b) J. Crecente-Campo, M. P. Vázquez-Tato, J. A. Seijas, *Tetrahedron* **2009**, *65*, 2655; c) Y.-Y. Yang, W.-G. Shou, Z.-B. Chen, D. Hong, Y.-G. Wang, *J. Org. Chem.* **2008**, *73*, 3928; d) M. Mori, H. Wakamatsu, K. Tonogaki, R. Fujita, T. Kitamura, Y. Sato, *J. Org. Chem.* **2005**, *70*, 1066.

[4] a) M. Movassaghi, M. D. Hill, *Org. Lett.* **2008**, *10*, 3485; b) T. Ishikawa, K. Shimooka, T. Narioka, S. Noguchi, T. Saito, A.

Ishikawa, E. Yamazaki, T. Harayama, H. Seki, K. Yamaguchi, *J. Org. Chem.* **2000**, *65*, 9143.
[5] a) R. Gitto, S. Agnello, S. Ferro, L. De Luka, D. Vullo, J. Brynda, P. Mader, C. T. Supuran, A. Chimirri, *J. Med. Chem.* **2010**, *53*, 2401; b) S. W. Youn, *J. Org. Chem.* **2006**, *71*, 2521.
[6] a) M. Boudou, D. Enders, *J. Org. Chem.* **2005**, *70*, 9486; b) E. R. Walker, S. Y. Leung, A. G. M. Barrett, *Tetrahedron Lett.* **2005**, *46*, 6537.
[7] a) T.-B. Xiao, P. Peng, Y. Xie, Z.-Y. Wang, L. Zhou, *Org. Lett.* **2015**, *17*, 4332; b) S. Dhara, R. Singha, Y. Nuree, J. K. Ray, *Tetrahedron Lett.* **2014**, *55*, 795; c) R. P. Korivi, C.-H. Cheng, *Chem. Eur. J.* **2010**, *16*, 282; d) R. P. Korivi, Y.-C. Wu, C.-H. Cheng, *Chem. Eur. J.* **2009**, *15*, 10727; e) Y. Ohta, Y. Kubota, T. Watabe, H. Chiba, S. Oishi, N. Fujii, H. Ohno, *J. Org. Chem.* **2009**, *74*, 6299; f) Q.-P. Ding, Z.-Y. Wang, J. Wu, *J. Org. Chem.* **2009**, *74*, 921; g) S. Su, J. A. Porco, *J. Am. Chem. Soc.* **2007**, *129*, 7744; h) S. Su, J. A. Porco, *Org. Lett.* **2007**, *9*, 4983; i) Q.-P. Ding, J. Wu, *Org. Lett.* **2007**, *9*, 4959; j) R. Yanada, S. Obika, H. Kono, Y. Takemoto, *Angew. Chem. Int. Ed.* **2006**, *45*, 3822; *Angew. Chem.* **2006**, *118*, 3906; k) N. Asao, S. S. Yudha, T. Nogami, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2005**, *44*, 5526; *Angew. Chem.* **2005**, *117*, 5662; l) Q.-H. Huang, J. A. Hunter, R. C. Larock, *Org. Lett.* **2001**, *3*, 2973.
[8] a) T.-T. Wang, M. Schrempp, A. Berndhauser, O. Schiemann, D. Menche, *Org. Lett.* **2015**, *17*, 3982; b) B. Sun, T. Yoshino, M. Kanai, S. Matsunaga, *Angew. Chem. Int. Ed.* **2015**, *54*, 12968; *Angew. Chem.* **2015**, *127*, 13160; c) R. Wang, J. R. Falck, *J. Organomet. Chem.* **2014**, *759*, 33; d) S.-G. Lim, J. H. Lee, C. W. Moon, J.-B. Hong, C.-H. Jun, *Org. Lett.* **2003**, *5*, 2759.
[9] a) Y.-N. Niu, Z.-Y. Yan, G.-L. Gao, H.-L. Wang, X.-Z. Shu, K.-G. Ji, Y.-M. Liang, *J. Org. Chem.* **2009**, *74*, 2893; b) D. Fischer, H. Tomeba, N. K. Pahadi, N. T. Patil, Z.-B. Huo, Y. Yamamoto, *J. Am. Chem. Soc.* **2008**, *130*, 15720; c) D. Fischer, H. Tomeba, N. K. Pahadi, N. T. Patil, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2007**, *46*, 4764; *Angew. Chem.* **2007**, *119*, 4848.
[10] a) G. Hirata, N. Yamada, S. Sanada, G. Onodera, M. Kimura, *Org. Lett.* **2015**, *17*, 600; b) T. Iwayama, Y. Sato, *Chem. Commun.* **2009**, 5245; c) Y. Sato, T. Nishimata, M. Mori, *J. Org. Chem.* **1994**, *59*, 6133.
[11] a) T. Ye, M. A. McKervey, *Chem. Rev.* **1994**, *94*, 1091; b) M. P. Doyle, D. C. Forbes, *Chem. Rev.* **1998**, *98*, 911; c) H. Lebel, J. F. Marcoux, C. Molinaro, A. B. Charette, *Chem. Rev.* **2003**, *103*, 977; d) V. K. Aggarwal, C. L. Winn, *Acc. Chem. Res.* **2004**, *37*, 611; e) Q. Xiao, Y. Zhang, J. Wang, *Acc. Chem. Res.* **2013**, *46*, 236; f) X. Guo, W. Hu, *Acc. Chem. Res.* **2013**, *46*, 2427; g) X. Xu, M. P. Doyle, *Acc. Chem. Res.* **2014**, *47*, 1396.
[12] For reviews, see: a) J. Xiao, X. Li, *Angew. Chem. Int. Ed.* **2011**, *50*, 7226; *Angew. Chem.* **2011**, *123*, 7364; b) L. Zhang, *Acc. Chem. Res.* **2014**, *47*, 877; c) H.-S. Yeom, S. Shin, *Acc. Chem. Res.* **2014**, *47*, 966; d) D. Qian, J. Zhang, *Chem. Soc. Rev.* **2015**, *44*, 677; for selected recent reports, see: e) S. N. Karad, R.-S. Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 5444; *Angew. Chem.* **2014**, *126*, 5548; f) D. Qian, H. Hu, F. Liu, B. Tang, W. Ye, Y. Wang, J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 13751; *Angew. Chem.* **2014**, *126*, 13971; g) Y. Wang, Z. Zheng, L. Zhang, *J. Am. Chem. Soc.* **2015**, *137*, 5316; h) C. Shu, Y.-H. Wang, B. Zhou, X.-L. Li, Y.-F. Ping, X. Lu, L.-W. Ye, *J. Am. Chem. Soc.* **2015**, *137*, 9567; i) M. Chen, Y. Chen, N. Sun, J. Zhao, Y. Liu, Y. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 1200; *Angew. Chem.* **2015**, *127*, 1216; j) L. Li, B. Zhou, Y.-H. Wang, C. Shu, Y.-F. Pan, X. Lu, L.-W. Ye, *Angew. Chem. Int. Ed.* **2015**, *54*, 8245; *Angew. Chem.* **2015**, *127*, 8363.
[13] T. Horneff, S. Chuprakov, N. Chernyak, V. Gevorgyan, V. V. Fokin, *J. Am. Chem. Soc.* **2008**, *130*, 14972.
[14] For reviews, see: a) B. Chattopadhyay, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2012**, *51*, 862; *Angew. Chem.* **2012**, *124*, 886; b) A. V. Gulevich, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2013**, *52*, 1371; *Angew. Chem.* **2013**, *125*, 1411; c) H. M. L. Davies, J. S. Alford, *Chem. Soc. Rev.* **2014**, *43*, 5151; d) P. Anbarasan, D. Yadagiri, S. Rajasekar, *Synthesis* **2014**, *46*, 3004; for selected recent reports, see: e) T. Miura, T. Nakamuro, C.-J. Liang, M. Murakami, *J. Am. Chem. Soc.* **2014**, *136*, 15905; f) S. W. Kwok, L. Zhang, N. P. Grimster, V. V. Fokin, *Angew. Chem. Int. Ed.* **2014**, *53*, 3452; *Angew. Chem.* **2014**, *126*, 3520; g) J.-M. Yang, C.-Z. Zhu, X.-Y. Tang, M. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 5142; *Angew. Chem.* **2014**, *126*, 5242; h) H. Shang, Y. Wang, Y. Tian, J. Feng, Y. Tang, *Angew. Chem. Int. Ed.* **2014**, *53*, 5662; *Angew. Chem.* **2014**, *126*, 5768; i) E. E. Schultz, V. N. G. Lindsay, R. Sarpong, *Angew. Chem. Int. Ed.* **2014**, *53*, 9904; *Angew. Chem.* **2014**, *126*, 10062; j) Y. Shi, A. V. Gulevich, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2014**, *53*, 14191; *Angew. Chem.* **2014**, *126*, 14415; k) V. N. G. Lindsay, H. M.-F. Viart, R. Sarpong, *J. Am. Chem. Soc.* **2015**, *137*, 8368; l) T. Miura, Y. Fujimoto, Y. Funakoshi, M. Murakami, *Angew. Chem. Int. Ed.* **2015**, *54*, 9967; *Angew. Chem.* **2015**, *127*, 10105; m) Y. Yang, M.-B. Zhou, X.-H. Ouyang, R. Pi, R.-J. Song, J.-H. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 6595; *Angew. Chem.* **2015**, *127*, 6695; n) D. Yadagiri, P. Anbarasan, *Chem. Sci.* **2015**, *6*, 5847; o) Y. Jiang, R. Sun, Q. Wang, X.-Y. Tang, M. Shi, *Chem. Commun.* **2015**, *51*, 16968; for selected reports about 1,2-H migration reactions of 4-alkyl triazoles, see: p) T. Miura, T. Biyajima, T. Fujii, M. Murakami, *J. Am. Chem. Soc.* **2012**, *134*, 194; q) T. Miura, Y. Funakoshi, M. Morimoto, T. Biyajima, M. Murakami, *J. Am. Chem. Soc.* **2012**, *134*, 17440.
[15] For reviews, see: a) A.-H. Li, L.-X. Dai, V. K. Aggarwal, *Chem. Rev.* **1997**, *97*, 2341; b) L.-X. Dai, X.-L. Hou, Y.-G. Zhou, *Pure Appl. Chem.* **1999**, *71*, 369; c) S. Ye, Y. Tang, X.-L. Sun, *Synlett* **2005**, 2720; d) X.-L. Sun, Y. Tang, *Acc. Chem. Res.* **2008**, *41*, 937; For ylide reaction starting from triazole, see: e) T. Miura, T. Tanaka, A. Yada, M. Murakami, *Chem. Lett.* **2013**, *42*, 1308; f) D. Yadagiri, P. Anbarasan, *Chem. Eur. J.* **2013**, *19*, 15115; g) A. Boyer, *Org. Lett.* **2014**, *16*, 1660; h) F. Medina, C. Besnard, J. Lacour, *Org. Lett.* **2014**, *16*, 3232; i) A. Boyer, *Org. Lett.* **2014**, *16*, 5878; j) D. J. Lee, H. S. Han, J. Shin, E. J. Yoo, *J. Am. Chem. Soc.* **2014**, *136*, 11606; k) H.-D. Xu, Z.-H. Jia, K. Xu, H. Zhou, M.-H. Shen, *Org. Lett.* **2015**, *17*, 66.
[16] a) R.-Q. Ran, J. He, S.-D. Xiu, K.-B. Wang, C.-Y. Li, *Org. Lett.* **2014**, *16*, 3704; b) R.-Q. Ran, S.-D. Xiu, C.-Y. Li, *Org. Lett.* **2014**, *16*, 6394; c) W.-B. Zhang, S.-D. Xiu, C.-Y. Li, *Org. Chem. Front.* **2015**, *2*, 47; d) J. He, Z. Man, Y. Shi, C.-Y. Li, *J. Org. Chem.* **2015**, *80*, 4816; e) Y. Shi, X. Yu, C.-Y. Li, *Eur. J. Org. Chem.* **2015**, 6429.
[17] a) M. C. Pirrung, J. Zhang, K. Lackey, D. D. Sternbach, F. Brown, *J. Org. Chem.* **1995**, *60*, 2112; b) Y. R. Lee, Y. U. Jung, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1309; c) H. V. R. Dias, R. G. Browning, S. A. Polach, H. V. K. Diyabalanage, C. J. Lovely, *J. Am. Chem. Soc.* **2003**, *125*, 9270; d) Y. R. Lee, B. S. Cho, H. J. Kwon, *Tetrahedron* **2003**, *59*, 9333; e) P. Müller, Y. F. Allenbach, G. Bernardinelli, *Helv. Chim. Acta* **2003**, *86*, 3164; f) J. Urbano, A. A. C. Braga, F. Maseras, E. Álvarez, M. M. Díaz-Requejo, P. J. Pérez, *Organometallics* **2009**, *28*, 5968; g) M. R. Smith, A. J. Blake, C. J. Hayes, M. F. G. Stevens, C. J. Moody, *J. Org. Chem.* **2009**, *74*, 9372; h) W. He, L. Xie, Y. Xu, J. Xiang, L. Zhang, *Org. Biomol. Chem.* **2012**, *10*, 3168.

Received: December 29, 2015
Revised: January 30, 2016
Published online: March 2, 2016

