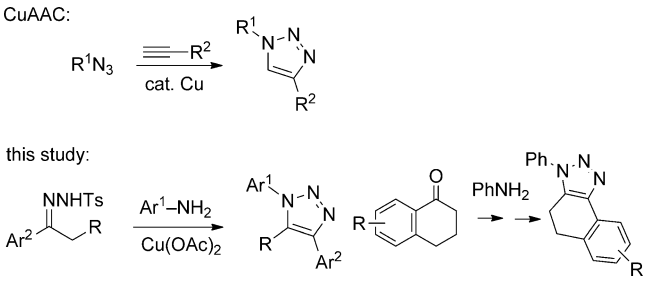
Nitrogen Heterocycles

DOI: 10.1002/anie.201306416

Copper-Mediated Synthesis of 1,2,3-Triazoles from *N*-Tosylhydrazones and Anilines**

*Zhengkai Chen, Qiangqiang Yan, Zhanxiang Liu, Yiming Xu, and Yuhong Zhang**

1,2,3-Triazoles have found wide application in chemistry, biology, and materials science.[1] Therefore, general methods for their synthesis are of considerable importance.[2] Conventionally, triazoles are prepared by the uncatalyzed thermally induced dipolar cycloaddition of alkynes with organic azides, as explored by Huisgen and co-workers.[3] A significantly improved version of the Huisgen-type reaction is the copper-catalyzed azide–alkyne cycloaddition (CuAAC) discovered by the research groups of Sharpless[4] and Meldal[2a] (Scheme 1). Copper catalysis leads to a remarkable increase



Scheme 1. Two distinct approaches to 1,2,3-triazoles. Ts = *p*-toluenesulfonyl.

in the reaction rate and the regioselectivity for the 1,4-disubstituted triazole isomer. The CuAAC reaction has had a huge impact on organic synthesis as the premier example of a "click reaction".[5] Other routes to 1,2,3-triazoles include the regioselective 1,3-dipolar cycloaddition of an azide with an enamine or ketone by organocatalysis,[6] the palladium-catalyzed reaction of alkenyl halides with sodium azide,[7] the copper-catalyzed cycloaddition of organic azides with 1-iodoalkynes or 1-bromoalkynes,[8] and the ruthenium-catalyzed azide–alkyne cycloaddition reaction.[9] However, all of these transformations involve the use of sodium azides or organic azides, which are toxic and potentially shock-sensitive (explosive). Furthermore, the preparation of 1,4,5-trisubstituted 1,2,3-triazoles by the CuAAC reaction is very limited owing to the reduced reactivity of internal alkynes and uncontrolled regioselectivity.[10]

The transition-metal-promoted formation of C–N bonds has become one of the most important strategies for the synthesis of heterocycles.[11] In particular, synthesis through C–H cleavage has attracted much attention owing to its high atom- and step-economical characteristics.[12] As stable and reactive reagents, hydrazones have been widely studied in both coupling reactions[13] and C–H activation reactions[14] as good precursors. Herein, we report a synthesis of 1,4-disubstituted and 1,4,5-trisubstituted 1,2,3-triazoles (Scheme 1) from readily available *N*-tosylhydrazones and anilines. The corresponding triazoles were obtained with unprecedented regioselectivity under mild reaction conditions. The reaction involves the spontaneous formation of a C–N bond through C–H cleavage and N–N bond formation.

The *N*-tosylhydrazone substrates were obtained quite conveniently by the simple stirring of *N*-tosylhydrazines with aryl ethanone derivatives in methanol. We initially examined the reaction between *p*-toluidine (**1b**) and *N*-tosylhydrazone **2a** in the presence of $Cu(OAc)_2$ (1 equiv) and Li*O*t*Bu* (2 equiv) in toluene at 100 °C. The reaction proceeded in a regioselective manner to give exclusively the 1,4-disubstituted isomer 4-phenyl-1-*p*-tolyl-1*H*-1,2,3-triazole (**3b**) in 55 % yield (Table 1, entry 1). Further studies revealed that the addition of PivOH (2 equiv) significantly improved the reaction to give the triazole **3b** in 70 % yield (Table 1, entry 2). Surprisingly to us, the use of PivOH (2 equiv) in the absence of Li*O*t*Bu* resulted in the formation of triazole **3b** in 88 % yield (Table 1, entry 3). The yield decreased to 36 % when the reaction was carried out without Li*O*t*Bu* and PivOH (Table 1, entry 4). Other copper salts tested, including $CuCl_2$, $Cu(OTf)_2$, $Cu(OTFA)_2$, CuI, and CuBr, showed poor reactivity (see the Supporting Information). In the absence of a copper salt, no triazole product was observed. The reaction could also be performed in 1,4-dioxane, *N*,*N*-dimethylformamide (DMF), and CH_3CN (see the Supporting Information). When the reaction was performed under a N_2 atmosphere, the yield decreased to 42 % (Table 1, entries 7). However, the reaction was almost halted by the side reaction of the dimerization of *N*-tosylhydrazone when the reaction was performed under an atmosphere of pure oxygen (Table 1, entry 8).

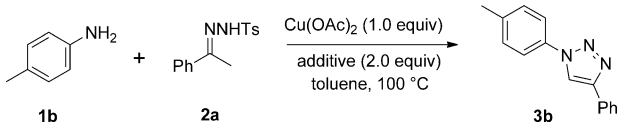
Various anilines could be used in this reaction (representative results are summarized in Scheme 2). Generally, the

[*] Z. Chen, Q. Yan, Z. Liu, Y. Xu, Prof. Dr. Y. Zhang
ZJU-NHU United R&D Center
Department of Chemistry, Zhejiang University
Hangzhou 310027 (China)
E-mail: yhzhang@zju.edu.cn
Prof. Dr. Y. Zhang
State Key Laboratory of Applied Organic Chemistry
Lanzhou University
Lanzhou 730000 (China)

[**] We gratefully acknowledge the National Basic Research Program of China (no. 2011CB936003), the Natural Science Foundation of China (no. 2107216 and no. 21272205), and the Program for the Zhejiang Leading Team of Science and Technology Innovation for their financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306416.

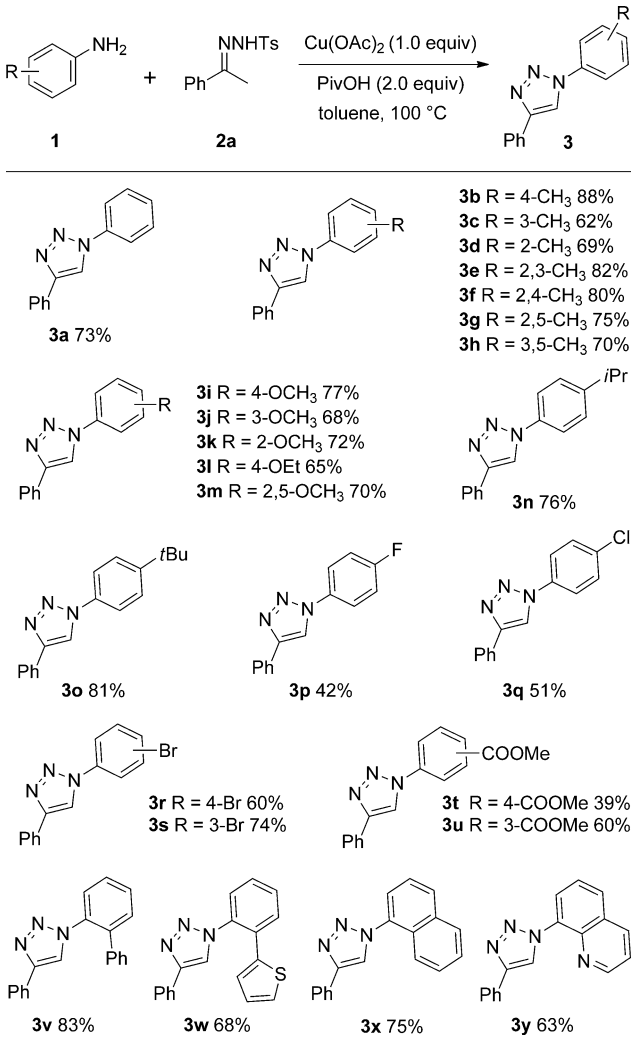
Table 1: Optimization of the reaction conditions.[a]



1b 2a 3b

Entry	Additive	Atmosphere	Yield [%][b]
1	LiO*t*Bu	air	55
2	PivOH/LiO*t*Bu	air	70
3	**PivOH**	**air**	**88**
4	–	air	36
5	PivOH	air	85[c]
6	PivOH	air	86[d]
7	PivOH	N_2	42
8	PivOH	O_2	17[e]

[a] Reaction conditions: *p*-toluidine (0.4 mmol), **2a** (0.2 mmol), $Cu(OAc)_2$ (1.0 equiv), additive (2.0 equiv), toluene (2 mL), 100 °C, 12 h. [b] Yield of the isolated product. [c] The reaction was carried out with 1.5 equivalents of $Cu(OAc)_2$. [d] The reaction was carried out with 2.0 equivalents of $Cu(OAc)_2$. [e] The reaction was carried out with a catalytic amount of $Cu(OAc)_2$ (20 mol%). Piv = pivaloyl.

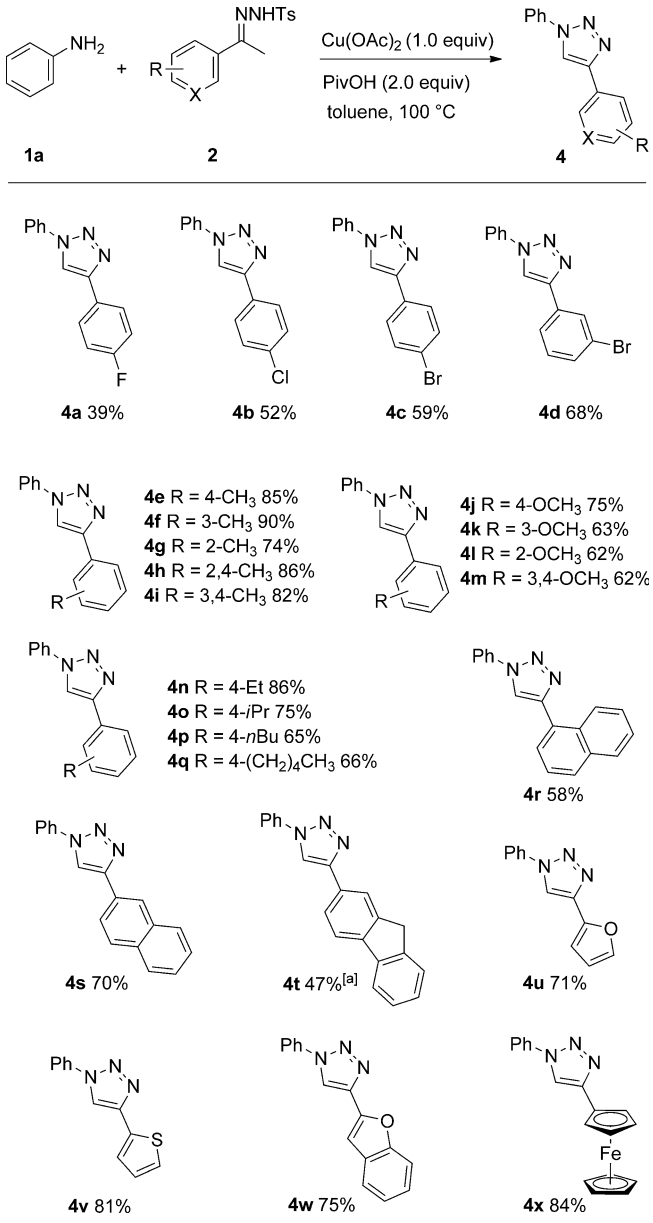


Scheme 2. Synthesis of 1,2,3-triazoles from a variety of aniline derivatives. Reaction conditions: **1** (0.6 mmol), **2a** (0.3 mmol), $Cu(OAc)_2$ (0.3 mmol), PivOH (0.6 mmol), toluene (3 mL), 100 °C, 12 h. The yields given are for the isolated product.

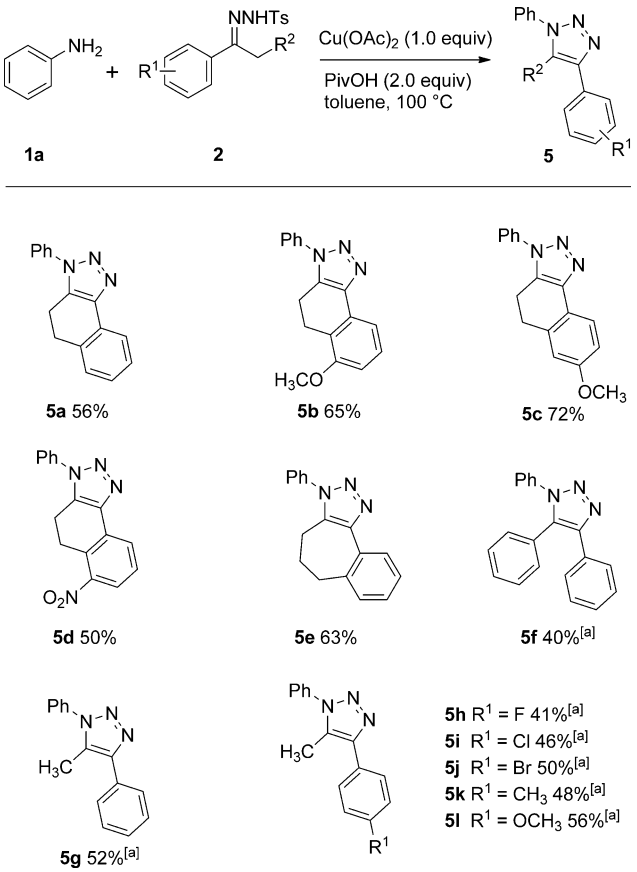
reaction proceeded smoothly with a variety of anilines to afford a wide range of 1,4-diaryl-substituted 1,2,3-triazoles. Electron-rich anilines showed high reactivity to afford the corresponding triazoles **3b–o** in good yields. However, aniline substrates with electron-withdrawing substituents at the *para* position, including F, Cl, Br, and COOMe groups, showed lower reactivity, and the corresponding triazoles **3p–r** and **3t** were obtained in lower yields. When the electron-withdrawing group was at the *meta* position (products **3s** and **3u**), higher reactivity was observed owing to a decreased conjugation effect. Significantly, both *ortho*- and *meta*-substituted anilines were converted into the triazole products in good yields (products **3c**,**d** and **3j**,**k**). These results suggest that the steric bulk of the anilines had little effect on the reaction. Disubstituted anilines underwent the cyclization quite well (products **3e–h**, **3m**). 2-Phenylaniline and 2-(thiophen-2-yl)aniline were successfully converted into the corresponding products **3v**,**w** under the standard reaction conditions. Notably, 1-naphthylamine and quinolin-8-amine participated in the reaction efficiently to give the corresponding triazoles **3x**,**y**. The reaction was highly regioselective, with the exclusive formation of 1,4-disubstituted 1,2,3-triazoles. The treatment of aliphatic amines under these reaction conditions gave a complex mixture, and the desired product was not isolated. The structure of the 1,4-disubstituted triazole **3v** was further confirmed by single-crystal X-ray diffraction analysis (see the Supporting Information).

To further evaluate the scope of the reaction, we next investigated the transformation of a range of *N*-tosylhydrazones with different substitution patterns (Scheme 3). The reaction system displayed good tolerance toward a range of functional groups. Aromatic groups bearing electron-donating (products **4e–q**) or electron-withdrawing substituents (products **4a–d**) were all tolerated, but the higher reactivity of electron-rich substrates led to the formation of the products in higher yields. Steric hindrance had little effect on this transformation, and both *ortho*- and *meta*-substituted *N*-tosylhydrazones presented good reactivity (products **4f**,**g** and **4k**,**l**). Disubstituted *N*-tosylhydrazones participated in the reaction smoothly to afford the desired products **4h**,**i** and **4m** in good yields. 1-Naphthyl, 2-naphthyl, and 2-fluorenyl *N*-tosylhydrazones were good substrates for this transformation, which gave the desired products **4r–t** smoothly. Interestingly, the corresponding ferrocenyl *N*-tosylhydrazone was compatible with the reaction conditions and was converted into the ferrocenyl-substituted triazole **4x** in 84% yield. Furthermore, triazoles with heterocyclic substituents, such as furyl, thiophenyl, and benzofuryl groups, were obtained in high yields from the corresponding *N*-tosylhydrazones (products **4u–w**).

It is not easy to prepare the 1,4,5-trisubstituted triazoles by the CuAAC reaction owing to the reduced reactivity of internal alkynes and regioselectivity issues. We therefore turned our attention to the possibility of extending the scope of the reaction to the use of hydrazone substrates derived from α-substituted aryl ketones to enable the formation of 1,4,5-trisubstituted 1,2,3-triazoles. To our delight, hydrazones derived from various 3,4-dihydronaphthalen-1(2*H*)-ones reacted with aniline to give the corresponding 1,4,5-trisubstituted triazoles under the reaction conditions (Scheme 4,



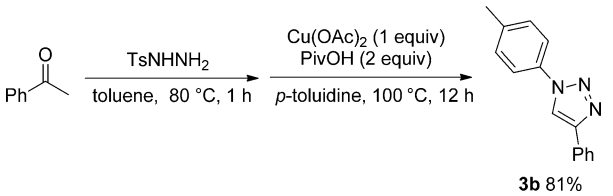
Scheme 3. Synthesis of 1,2,3-triazoles from a variety of *N*-tosylhydrazones. Reaction conditions: aniline (0.6 mmol), **2** (0.3 mmol), $Cu(OAc)_2$ (0.3 mmol), PivOH (0.6 mmol), toluene (3 mL), 100 °C, 12 h. The yields given are for the isolated product. [a] The reaction was carried out under a N_2 atmosphere.



Scheme 4. Formation of 1,4,5-trisubstituted triazoles. Reaction conditions: aniline (0.6 mmol), **2** (0.3 mmol), $Cu(OAc)_2$ (0.3 mmol), PivOH (0.6 mmol), toluene (3 mL), 100 °C, 12 h. The yields given are for the isolated product. [a] The reaction was carried out at 115 °C.

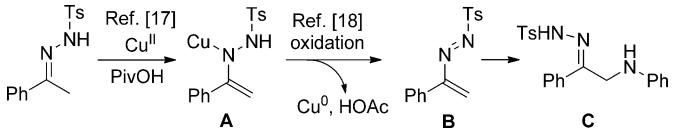
5a–d). More importantly, the hydrazone formed from 1-benzosuberone also reacted well to afford the corresponding triazole **5e** in 63% yield. A higher reaction temperature was required when the α substituent was a methyl or a phenyl group (Scheme 4, **5f–l**). Thus, this new transformation provides an efficient approach to 1,4,5-trisubstituted 1,2,3-triazoles.

Following the success of the formation of triazoles from aniline and *N*-tosylhydrazones, we explored the possibility of performing a one-pot transformation of the aniline, the aryl ethanone, and *N*-tosylhydrazine. Significantly, the triazole could be obtained in almost the same yield from the one-pot tandem reaction, in which a mixture of the aryl ethanone and *N*-tosylhydrazine in toluene was stirred for 1 h and then treated with aniline, PivOH, and $Cu(OAc)_2$ under the standard reaction conditions (Scheme 5).



Scheme 5. One-pot synthesis of triazole **3b**.

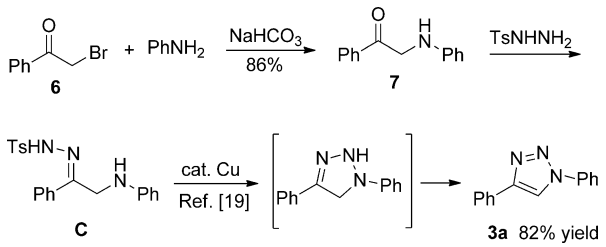
Preliminary mechanistic investigations excluded the possibility that the reaction occurs by a radical process.[15] The reaction mechanism of this new transformation for the synthesis of 1,2,3-triazoles is not clear at the moment. On the basis of the imine–enamine shift observed in the presence of transition metals,[16] we speculate that the *N*-tosylhydrazone may isomerize to **A** as shown in Scheme 6 in the presence of $Cu(OAc)_2$ and PivOH. Subsequent oxidation gives a 1-tosyl-2-vinyldiazene **B**,[17] which undergoes an aza-Michael addition with aniline to generate the intermediate **C**.



Scheme 6. Plausible intermediates in the transformation.

The copper-catalyzed cyclization of intermediate **C** with the formation of a N–N bond[18] and subsequent aromatization produce the triazole.

We prepared compound **C**, treated it with $Cu(OAc)_2$ (20 mol%) and PivOH (2.0 equiv), and indeed obtained the 1,4-disubstituted 1,2,3-triazole **3a** in 82% yield (Scheme 7). Powder X-ray diffraction analysis of the residue formed under



Scheme 7. Preparation of **3a** from compound **C**.

the standard reaction conditions revealed the formation of copper metal (see the Supporting Information). The use of more than 1 equivalent of $Cu(OAc)_2$ was shown to be unnecessary (Table 1, entries 5 and 6). In fact, the formation of a red precipitate forebodes the success of the reaction. More elaborate research is required for the elucidation of the reaction mechanism.

In conclusion, we have developed a new general method for the synthesis of 1,4-disubstituted and 1,4,5-trisubstituted triazoles from anilines and *N*-tosylhydrazones through a copper-mediated reaction. Notable features of this transformation include the exclusive formation of 1,4- or 1,4,5-substituted regioisomers, its broad scope with respect to both the *N*-tosylhydrazone and the aniline substrate, the low cost of reagents, and the convenient operating conditions. This discovery could have important consequences for the synthesis of triazole structures. Further investigations to extend the reaction scope and elucidate the reaction mechanism are in progress.

Experimental Section

Typical procedure: *p*-Toluidine (**1b**; 0.6 mmol) was added to a mixture of $Cu(OAc)_2$ (0.3 mmol), PivOH (0.6 mmol), and the *N*-tosylhydrazone **2a** (0.3 mmol) in toluene (3 mL), and the resulting mixture was stirred at 100 °C in air for 12 h. The reaction mixture was then cooled to ambient temperature, and the solvent was removed in vacuo. Purification of the crude product by column chromatography on silica gel with petroleum ether/EtOAc (10:1) afforded **3b** (62 mg, 88%) as a white solid.

Received: July 23, 2013
Revised: September 24, 2013
Published online: October 15, 2013

Keywords: aniline derivatives · copper · hydrazones · synthetic methods · triazoles

[1] a) H. Wamhoff in *Comprehensive Heterocyclic Chemistry*, *Vol. 5* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon, Oxford, **1984**, pp. 669; b) S. T. Abu-Orabi, M. A. Atfah, I. Jibril, F. M. Mari'i, A. A. Ali, *J. Heterocycl. Chem.* **1989**, *26*, 1461–1468.

[2] a) C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057–3064; b) A. K. Feldman, B. Colasson, V. V. Fokin, *Org. Lett.* **2004**, *6*, 3897–3899; c) F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless, V. V. Fokin, *J. Am. Chem. Soc.* **2005**, *127*, 210–216; d) B. Chattopadhyay, C. I. R. Vera, S. Chuprakov, V. Gevorgyan, *Org. Lett.* **2010**, *12*, 2166–2169; e) S. W. Kwok, J. R. Fotsing, R. J. Fraser, V. O. Rodionov, V. V. Fokin, *Org. Lett.* **2010**, *12*, 4217–4219.

[3] a) R. Huisgen, *Angew. Chem.* **1963**, *75*, 604–637; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 565–598; b) R. Huisgen, *Angew. Chem.* **1963**, *75*, 742–754; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 633–645; c) R. Huisgen, R. Knorr, L. Möbius, G. Szeimies, *Chem. Ber.* **1965**, *98*, 4014–4021.

[4] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708–2711; *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599.

[5] a) *Click Chemistry for Biotechnology and Materials Science* (Ed.: J. Lahann), Wiley, Weinheim, **2009**; b) A. E. Speers, G. C. Adam, B. F. Cravatt, *J. Am. Chem. Soc.* **2003**, *125*, 4686–4687; c) L. V. Lee, M. L. Mitchell, S.-J. Huang, V. V. Fokin, K. B. Sharpless, C.-H. Wong, *J. Am. Chem. Soc.* **2003**, *125*, 9588–9589; d) J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev.* **2007**, *36*, 1249–1262; e) M. Meldal, C. W. Tornøe, *Chem. Rev.* **2008**, *108*, 2952–3015; f) P. Thirumurugan, D. Matosiuk, K. Jozwiak, *Chem. Rev.* **2013**, *113*, 4905–4979.

[6] a) D. B. Ramachary, K. Ramakumar, V. V. Narayana, *Chem. Eur. J.* **2008**, *14*, 9143–9147; b) L. J. T. Danence, Y. Gao, M. Li, Y. Huang, J. Wang, *Chem. Eur. J.* **2011**, *17*, 3584–3587; c) M. Belkheira, D. E. Abed, J.-M. Pons, C. Bressy, *Chem. Eur. J.* **2011**, *17*, 12917–12921.

[7] J. Barluenga, C. Valdés, G. Beltrán, M. Escribano, F. Aznar, *Angew. Chem.* **2006**, *118*, 7047–7050; *Angew. Chem. Int. Ed.* **2006**, *45*, 6893–6896.

[8] a) B. H. M. Kuijpers, G. C. T. Dijkmans, S. Groothuys, P. J. L. M. Quaedflieg, R. H. Blaauw, F. L. van Delft, F. P. J. T. Rutjes, *Synlett* **2005**, 3059–3062; b) J. E. Hein, J. C. Tripp, L. B. Krasnova, K. B. Sharpless, V. V. Fokin, *Angew. Chem.* **2009**, *121*, 8162–8165; *Angew. Chem. Int. Ed.* **2009**, *48*, 8018–8021; c) C. Spiteri, J. E. Moses, *Angew. Chem.* **2010**, *122*, 33–36; *Angew. Chem. Int. Ed.* **2010**, *49*, 31–33.

[9] a) L. Zhang, X. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 15998–15999; b) B. C. Boren, S. Narayan, L. K. Rasmussen, L. Zhang, H. Zhao, Z. Lin, G. Jia, V. V. Fokin, *J. Am. Chem. Soc.* **2008**, *130*, 8923–8930.

[10] a) J. Wei, J. Chen, J. Xu, L. Cao, H. Deng, W. Sheng, H. Zhang, W. Cao, *J. Fluorine Chem.* **2012**, *133*, 146–154; b) J. Li, Y. Zhang, D. Wang, W. Wang, T. Gao, L. Wang, J. Li, G. Huang, B. Chen, *Synlett* **2010**, 1617–1622.

[11] a) A. V. Gulevich, A. S. Dudnik, N. Chernyak, V. Gevorgyan, *Chem. Rev.* **2013**, *113*, 3084–3213; b) T. R. M. Rauws, B. U. W. Maes, *Chem. Soc. Rev.* **2012**, *41*, 2463–2497; c) R. Martín, M. R. Rivero, S. L. Buchwald, *Angew. Chem.* **2006**, *118*, 7237–7240; *Angew. Chem. Int. Ed.* **2006**, *45*, 7079–7082; d) B. Zou, Q. Yuan, D. Ma, *Angew. Chem.* **2007**, *119*, 2652–2655; *Angew. Chem. Int. Ed.* **2007**, *46*, 2598–2601; e) M. Nagamochi, Y.-Q. Fang, M. Lautens, *Org. Lett.* **2007**, *9*, 2955–2958; f) P. Sang, M. Yu, H. Tu, J. Zou, Y. Zhang, *Chem. Commun.* **2013**, *49*, 701–703.

[12] a) P. Thansandote, M. Lautens, *Chem. Eur. J.* **2009**, *15*, 5874 – 5883; b) G. Brasche, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 1958 – 1960; *Angew. Chem. Int. Ed.* **2008**, *47*, 1932 – 1934; c) D. A. Colby, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 3645 – 3651; d) Q. Xiao, W.-H. Wang, G. Liu, F.-K. Meng, J.-H. Chen, Z. Yang, Z.-J. Shi, *Chem. Eur. J.* **2009**, *15*, 7292 – 7296; e) A. Armstrong, J. C. Collins, *Angew. Chem.* **2010**, *122*, 2332 – 2335; *Angew. Chem. Int. Ed.* **2010**, *49*, 2282 – 2285; f) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem.* **2011**, *123*, 11256 – 11283; *Angew. Chem. Int. Ed.* **2011**, *50*, 11062 – 11087; g) Y. Yang, C. Xie, Y. Xie, Y. Zhang, *Org. Lett.* **2012**, *14*, 957 – 959.

[13] a) J. Barluenga, C. Valdés, *Angew. Chem.* **2011**, *123*, 7626 – 7640; *Angew. Chem. Int. Ed.* **2011**, *50*, 7486 – 7500; b) Z. Shao, H. Zhang, *Chem. Soc. Rev.* **2012**, *41*, 560 – 572; c) Q. Xiao, Y. Zhang, J. Wang, *Acc. Chem. Res.* **2013**, *46*, 236 – 247; d) J. Barluenga, N. Quiñones, M.-P. Cabal, F. Aznar, C. Valdés, *Angew. Chem.* **2011**, *123*, 2398 – 2401; *Angew. Chem. Int. Ed.* **2011**, *50*, 2350 – 2353; e) E. Brachet, A. Hamze, J.-F. Peyrat, J.-D. Brion, M. Alami, *Org. Lett.* **2010**, *12*, 4042 – 4045; f) L. Zhou, F. Ye, J. Ma, Y. Zhang, J. Wang, *Angew. Chem.* **2011**, *123*, 3572 – 3576; *Angew. Chem. Int. Ed.* **2011**, *50*, 3510 – 3514; g) J. Barluenga, M. Tomás-Gamasa, F. Aznar, C. Valdés, *Nat. Chem.* **2009**, *1*, 494 – 499; h) J. Barluenga, M. Tomás-Gamasa, C. Valdés, *Angew. Chem.* **2012**, *124*, 6052 – 6054; *Angew. Chem. Int. Ed.* **2012**, *51*, 5950 – 5952.

[14] a) X. Zhao, G. Wu, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 3296 – 3299; b) T. Yao, K. Hirano, T. Satoh, M. Miura, *Angew. Chem.* **2012**, *124*, 799 – 803; *Angew. Chem. Int. Ed.* **2012**, *51*, 775 – 779; c) Q. Xiao, L. Ling, F. Ye, R. Tan, L. Tian, Y. Zhang, J. Wang, *J. Org. Chem.* **2013**, *78*, 3879 – 3885.

[15] The addition of radical-scavenging reagents, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT), did not influence the reaction (see the Supporting Information).

[16] a) B. Qian, S. Guo, J. Shao, Q. Zhu, L. Yang, C. Xia, H. Huang, *J. Am. Chem. Soc.* **2010**, *132*, 3650 – 3651; b) M. Rueping, N. Tolstoluzhsky, *Org. Lett.* **2011**, *13*, 1095 – 1097; c) B. Qian, P. Xie, Y. Xie, H. Huang, *Org. Lett.* **2011**, *13*, 2580 – 2583; d) H. Komai, T. Yoshino, S. Matsunaga, M. Kanai, *Org. Lett.* **2011**, *13*, 1706 – 1709.

[17] a) J. M. Hatcher, D. M. Coltart, *J. Am. Chem. Soc.* **2010**, *132*, 4546 – 4547; b) C. E. Sacks, P. L. Fuchs, *J. Am. Chem. Soc.* **1975**, *97*, 7372 – 7374.

[18] a) J. J. Neumann, M. Suri, F. Glorius, *Angew. Chem.* **2010**, *122*, 7957 – 7961; *Angew. Chem. Int. Ed.* **2010**, *49*, 7790 – 7794; b) S. Ueda, H. Nagasawa, *J. Am. Chem. Soc.* **2009**, *131*, 15080 – 15081; c) D.-G. Yu, M. Suri, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 8802 – 8805; d) M. Suri, T. Jousseaume, J. J. Neumann, F. Glorius, *Green Chem.* **2012**, *14*, 2193 – 2196; e) H. Mori, K. Sakamoto, S. Mashito, Y. Matsuoka, M. Matsubayashi, K. Sakai, *Chem. Pharm. Bull.* **1993**, *41*, 1944 – 1947.

