

Implanting Nitrogen into Hydrocarbon Molecules through C–H and C–C Bond Cleavages: A Direct Approach to Tetrazoles**

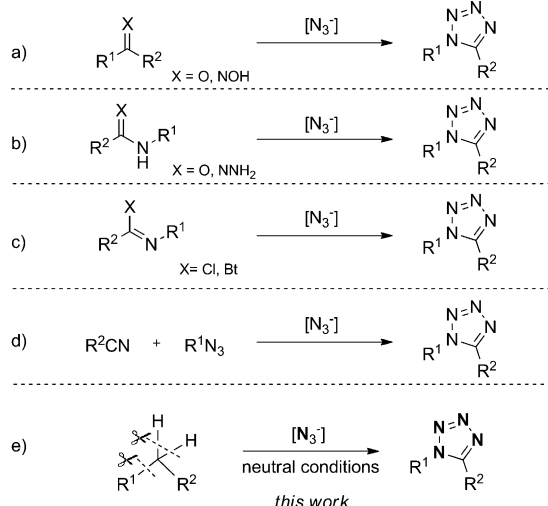
Feng Chen, Chong Qin, Yuxin Cui, and Ning Jiao*

The development of novel methods for the preparation of tetrazoles is of long-standing interest and a challenge for organic chemists because of the importance of these compounds in chemistry and biology. In particular, 1,5-disubstituted tetrazoles are very useful compounds in medicinal chemistry and important synthetic intermediates.^[1,2] In the past several decades, some general strategies for the synthesis of 1,5-disubstituted tetrazoles from functionalized starting materials have been developed (Scheme 1). These methods include: a) the reactions of ketones^[3] or oximes^[4] with sodium azide and hydrogen azides, b) the reactions of amides with sodium azides in the presence of phosphorus(V) chloride or triflic anhydride and^[5] the reactions of amidrazones with

dinitrogen tetroxide or nitrous acid,^[6] c) the reactions of imidoyl chlorides^[7a] or imidoylbenzotriazoles^[7b] with sodium azides and, d) the reactions of nitriles with alkyl azides.^[8] These developed methods significantly improved the synthesis of tetrazoles, but these approaches have some limitations, such as the use of protic acid catalysts, tedious workups, and the use of functionalized starting materials, hence encouraging scientists to discover new strategies.

The direct transformation of hydrocarbon molecules by transition-metal-catalyzed selective C–H and C–C bond activation (cleavage) has attracted considerable attention, owing not only to its fundamental scientific appeal but also to its potential utility in organic synthesis.^[9,10] A direct approach to tetrazoles through C–H and C–C bond cleavages of simple hydrocarbon molecules is still an extremely attractive yet challenging goal. Herein, we demonstrate a novel and efficient Cu-promoted implanting of nitrogen into simple hydrocarbon molecules to construct 1, 5-disubstituted tetrazoles through C–H and C–C bond cleavages, and C–N bond formation under mild and neutral reaction conditions (Scheme 1 e).

Azide has been widely used as a useful aminating reagent in organic synthesis.^[11,12] The application of azides for the direct synthesis of aryl nitriles^[13] and alkenyl nitriles^[13c–d] through C–H bond cleavage has been recently reported. Recent achievements on the functionalization of C–H and C–C bonds^[9–10] encouraged us to try the direct synthesis of



Scheme 1. Strategies for the preparation of 1,5-disubstituted tetrazoles. Bt = benzotriazole.

Table 1: The direct transformation of (*E*)-1,3-diphenylprop-1-ene (**1a**) into (*E*)-1-phenyl-5-styryl-1*H*-tetrazole (**2a**).^[a]

Entry	Catalyst (mol %)	TMSN ₃ (equiv)	Oxidant (equiv)	Yield [%] ^[b]
1 ^[c]	CuI (20)	2.0	DDQ (2.0)	27
2 ^[c]	CuI (20)	4.0	DDQ (2.0)	63
3	CuI (20)	4.0	DDQ (2.0)	73
4	CuI (20)	5.5	DDQ (2.0)	80
5	CuI (15)	5.5	DDQ (2.0)	80
6	CuI (10)	5.5	DDQ (2.0)	88
7	CuI (5)	5.5	DDQ (2.0)	80
8	none	5.5	DDQ (2.0)	76
9	CuI (10)	5.5	DDQ (3.0)	24
10	CuI (10)	5.5	DDQ (1.5)	52

[a] Reaction conditions: **1a** (0.3 mmol), TMSN₃, catalyst, oxidant, molecular sieves (4 Å; 30 mg), MeCN (2 mL), stirred at 80 °C under Ar. [b] Yield of the isolated product. [c] The reaction was carried out in the absence of molecular sieves (4 Å). DDQ = 2, 3-dichloro-5,6-dicyano-1,4-benzoquinone, M.S. = molecular sieves, TMS = trimethylsilyl.

[*] F. Chen, C. Qin, Dr. Y. Cui, Dr. N. Jiao
 State Key Laboratory of Natural and Biomimetic Drugs
 School of Pharmaceutical Sciences, Peking University
 Xue Yuan Road 38, Beijing 100191 (China)
 E-mail: jiaoning@bjmu.edu.cn
 Homepage: http://sklnbd.bjmu.edu.cn/nj

Dr. N. Jiao
 State Key Laboratory of Organometallic Chemistry
 Chinese Academy of Sciences, Shanghai 200032 (China)

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nitrogen-containing compounds by the functionalization of simple hydrocarbon molecules using azide. The preliminary investigation employed (*E*)-1,3-diphenylprop-1-ene (**1a**) as the substrate. When the reaction was performed in the presence of azidotrimethylsilane (TMSN₃) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) using CuI as the catalyst at 80 °C in MeCN, (*E*)-1-phenyl-5-styryl-1*H*-tetrazole (**2a**) was obtained in 27% yield (Table 1, entry 1). The structure of **2a** was further confirmed by single-crystal X-ray analysis (Figure S1 in the Supporting Information). The high chemoselectivity of this result indicates that the aryl groups have a greater migratory aptitude to the nitrogen atom than alkenyl groups in the rearrangement process. Taking into consideration that at least 2.0 equivalents of TMSN₃ is required to realize this transformation, the amount of TMSN₃ was increased from 2 equivalents to 4 equivalents. Under these reaction conditions, **2a** was obtained in 63% yield (Table 1, entry 2). A 73% yield of **2a** was achieved in the presence of molecular sieves (4 Å; Table 1, entry 3). Furthermore, the yield rose to 88% using 10 mol % of CuI, as the catalyst, in the presence of 5.5 equivalents of TMSN₃ (Table 1, entry 6). When the amount of CuI was reduced to 5% a lower yield was obtained (Table 1, entry 7). Although the addition of copper salt did not significantly improve the yield in this case (Table 1, entry 8), it significantly affected the efficiencies in other reactions (Table S1 in the Supporting Information). The reaction also could be conducted at room temperature and under air to give the products in moderate yields (Table S1 in the Supporting Information). Importantly, when the amount of DDQ was increased **2a** was produced in lower yield because of decomposition of the substrate; a decrease in the amount of DDQ also gave a lower yield, owing to the lack of oxidant in this catalytic system (Table 1, entries 9–10).

Under the optimized reaction conditions, the scope of this copper-facilitated tetrazole formation was investigated (Table 2). Notably a variety of substituted 1,3-diphenylprop-1-enes could easily be converted into the corresponding tetrazoles in moderate to excellent yields (up to 94%). Various electron-donating (Me, OMe, OCF₃, *t*Bu; Table 2, entries 5–9) and electron-withdrawing substituents (F, Cl, Br, CF₃; Table 2, entries 3, 4, 10 and 11) on the aryl group were tolerated in this transformation. Furthermore, the position of the substituents on the aryl group (*para*-, *meta*-, and *ortho*-position) did not affect the efficiency of the reaction (Table 2, entries 5, 9, and 12). It is noteworthy that halo-substituted 1,3-diarylprop-1-ene reacted well, thus leading to halo-substituted products, which could be used for further transformations (Table 2, entries 3, 11, 13, and 15). In addition, the heteroaryl-substituted substrate (*E*)-2-(3-(thiophen-2-yl)allyl)thiophene (**1n**) could be converted into the target product **2n** in 58% yield (Table 2, entry 14). Regioisomers were

Table 2: Direct conversion of 1,3-diarylprop-1-enes into tetrazoles.^[a]

Entry	Substrate 1	R	Product 2	Yield [%] ^[b]
1		H	2a	88
2		OMe	2b	81
3		Cl	2c	80
4		F	2d	77
5		Me	2e	90
6		OCF ₃	2f	61
7		<i>t</i> Bu	2g	76
8		OMe	2h	90
9		Me	2i	83
10		CF ₃	2j	27
11		Br	2k	49
12		Me	2l	90
13		Br	2m	30
14		–	2n	58
15		–	2o	76
16		OMe	2p:2p' (13:1)	94
17		Me	2q:2q' (6.2:1)	88
18		F	2r:2r' (1:1.0)	83
19		Cl	2s:2s' (1.1:3)	66
20		–	2t:2t' (1.2:1)	80
21		–	2u:2u' (1:2.3)	62

[a] Reaction conditions: **1a** (0.3 mmol), TMSN₃ (1.65 mmol), CuI (0.03 mmol), DDQ (0.6 mmol), molecular sieves (4 Å; 30 mg), MeCN (2 mL), stirred at 80 °C under Ar atmosphere. [b] Yield of the isolated product.

obtained when unsymmetric 1,3-diphenylprop-1-enes were employed as the substrates under the standard reaction conditions (Table 2, entries 16–21). The structures of the isomers were determined by HMBC spectroscopy or single-crystal X-ray analysis (see the Supporting Information). It is noteworthy that the regioselectivity can be significantly influenced by the electronic nature of the substituents

(Table 2, entries 16–19). Substrates with electron-rich aryl groups, such as 1-cinnamyl-4-methoxybenzene (**1p**), could be highly regioselectively converted into the corresponding tetrazole (94% yield, 13:1 ratio; Table 2, entry 16). In addition, the sterics of the substrate also has a big influence on the regioselectivity. For example, **2t** and **2t'** were obtained in the ratio of 1.2:1 (determined by HMBC spectroscopy, see the Supporting Information) in the reaction of 1-cinnamyl-2-methylbenzene (**1t**, 80%; Table 2, entry 20).

Notably, bisaryl methanes could also be successfully converted into the corresponding 1,5-diaryl tetrazoles in moderate yields under these reaction conditions (Table 3). Moreover, the bisheteroaryl methane compound bis(1-Boc-1*H*-indol-3-yl)methane (**3d**) was also tolerated in this transformation giving the desired tetrazole **4d** in 32% yield (Table 3, entry 4).

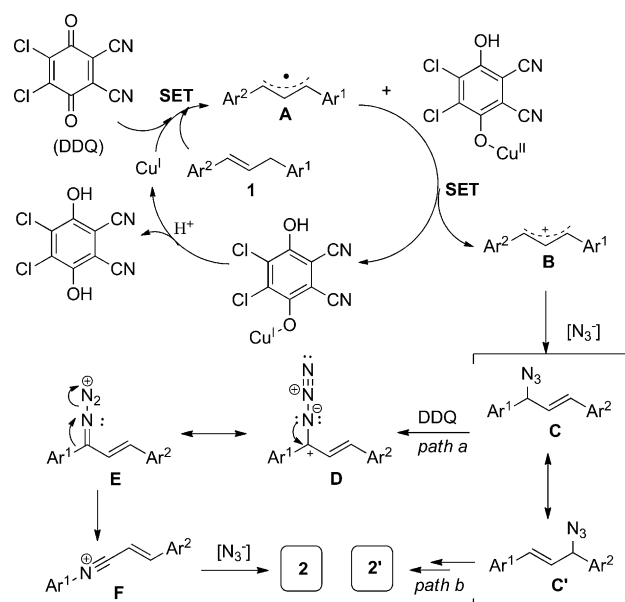
Table 3: Direct Transformation of diarylmethane **3** into tetrazoles.^[a]

$\text{R}^1\text{---CH}_2\text{---R}^1 + \text{TMSN}_3 \xrightarrow[\text{M.S. (4\AA), MeCN, 80 }^\circ\text{C, 12 h}]{\text{CuI (10 mol\%), DDQ (2 equiv)}} \text{R}^1\text{---N}=\text{N}=\text{C}(\text{R}^1)\text{---N}=\text{N}$			
No.	Substrate 3	Product 4	Yield [%] ^b
1		OMe (3a)	4a 65
2		OEt (3b)	4b 57
3		NMe ₂ (3c)	4c 54
4	 3d	 4d	32

[a] Reaction conditions: **1a** (0.3 mmol), TMSN₃ (1.65 mmol), CuI (0.03 mmol), DDQ (0.6 mmol), molecular sieves (4 Å; 30 mg), MeCN (2 mL), stirred at 80°C under argon. [b] Yield of the isolated product. Boc = *tert*-butoxycarbonyl.

To probe the mechanism of this novel transformation, control experiments were conducted under the optimized reaction conditions. When chalcone (**5**) and *N*-phenylcinnamamide (**6**) were employed as the substrate, no desired product **2a** was obtained and 60% of the starting material (**5** and **6**) was recovered respectively [Eq. S1–2 in the Supporting Information]. The results suggest that the traditional Schmidt reaction^[14] via a ketone intermediate is not involved in this novel process.

On the basis of the above experimental observations, a plausible mechanism for this transformation is proposed (Scheme 2). Initially, substrates **1** undergo a copper-assisted single-electron-transfer (SET) oxidation with DDQ^[15] to produce the corresponding allyl radical **A**, which could be further oxidized to the allyl cation **B**. Subsequently, the substitution reaction of allyl cation **B** would generate allyl azides **C** and **C'**, which would exist as an equilibrating mixture by [3,3] sigmatropic rearrangement.^[16] The allyl azide **C** could



Scheme 2. A proposed pathway for tetrazole formation.

then be oxidized to allyl azide cation **D** by the copper-assisted DDQ oxidative system. Subsequent isomerization of **D** would lead to intermediate **E**. Then the highly chemoselective aryl migration from the carbon atom to the nitrogen atom could occur to generate intermediate **F**.^[14] Subsequent nucleophilic addition and cyclization with another azide would lead to the desired tetrazole product **2**.^[17] For unsymmetrical substrates, the regioisomer **2'** could be generated by the same procedure via the allyl azide **C'** (Scheme 2).

In summary, we have demonstrated a novel Cu-promoted direct implanting of nitrogen into simple hydrocarbon molecules. 1,5-Disubstituted tetrazoles were efficiently constructed by two C_{sp}³–H and one C–C bond cleavages under mild and neutral reaction conditions. This protocol not only extends the application of azides in organic transformations, but also offers an alternative method to prepare 1,5-disubstituted tetrazoles, which are ubiquitous structural units in a number of biologically active compounds. This method provides a new and unique strategy to functionalize simple and readily available hydrocarbon molecules by C–H and C–C bond cleavages. Further investigation of the scope and synthetic application of these reactions are ongoing in our group.

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- [1] a) L. V. Myznikov, A. Hrabalek, G. I. Koldobskii, *Chem. Heterocycl. Compd.* **2007**, *43*, 1; b) D. R. Armour, K. M. L. Chung, M. Congreve, B. Evans, S. Guntrip, T. Hubbard, C. Kay, D. Middlemiss, J. E. Mordaunt, N. A. Pegg, M. V. Vinader, P. Ward, S. P. Watson, *Bioorg. Med. Chem. Lett.* **1996**, *6*, 1015; c) B. J. Al-Hourani, S. K. Sharma, J. Y. Mane, J. Tuszynski, V.

- Baracos, T. Kniess, M. Suresh, J. Pietzsch, F. Wuest, *Bioorg. Med. Chem. Lett.* **2011**, 21, 1823.
- [2] a) D. Moderhack, *J. Prakt. Chem.* **1998**, 340, 687; b) L. M. T. Frija, I. V. Khmelinskii, M. L. S. Cristiano, *Tetrahedron Lett.* **2005**, 46, 6757; c) M. J. Schnermann, D. L. Boger, *J. Am. Chem. Soc.* **2005**, 127, 15704; d) D. Potts, P. J. Stevenson, N. Thompson, *Tetrahedron Lett.* **2000**, 41, 275; e) J. Quintin, G. Lewin, *J. Nat. Prod.* **2004**, 67, 1624; f) D. Enders, A. Lenzen, M. Muller, *Synthesis* **2004**, 1486; g) P. Jankowski, K. Plesniak, J. Wicha, *Org. Lett.* **2003**, 5, 2789; h) A. Fettes, E. M. Carreira, *Angew. Chem.* **2002**, 114, 4272; *Angew. Chem. Int. Ed.* **2002**, 41, 4098.
- [3] a) A. L. Tokes, G. Litkei, *Synth. Commun.* **1993**, 23, 895; b) H. Suzuki, Y. S. Hwang, C. Nakaya, Y. Matano, *Synthesis* **1993**, 1218; c) A. S. El-Ahl, S. S. Elmorsy, H. Soliman, F. A. Amer, *Tetrahedron Lett.* **1995**, 36, 7337; d) A. G. Schultz, A. Wang, C. Alva, A. Sebastian, S. D. Glick, D. C. Deecher, J. M. Bidlack, *J. Med. Chem.* **1996**, 39, 1956.
- [4] R. N. Butler, D. A. O'Donoghue, *J. Chem. Res. Synop.* **1983**, 18.
- [5] a) J. Zabrocki, J. B. Dunbar, Jr., K. W. Marshall, M. V. Toth, G. R. Marshall, *J. Org. Chem.* **1992**, 57, 202; b) E. W. Thomas, *Synthesis* **1993**, 767; c) A. LeTiran, J. P. Stables, H. Kohn, *Bioorg. Med. Chem.* **2001**, 9, 2693; d) J. Xiao, X. Zhang, D. Wang, C. Yuan, *J. Fluorine Chem.* **1999**, 99, 83; e) A. F. Hegarty, N. M. Tynan, S. Fergus, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1328.
- [6] a) J. V. Duncia, M. E. Pierce, J. B. Santella III, *J. Org. Chem.* **1991**, 56, 2395; b) L. W. Deady, S. M. Devine, *J. Heterocycl. Chem.* **2004**, 41, 549.
- [7] a) T. V. Artamonova, A. B. Zhivich, M. Yu. Dubinskii, G. I. Koldobskii, *Synthesis* **1996**, 1428; b) A. R. Katritzky, C. Cai, N. K. Meher, *Synthesis* **2007**, 1204.
- [8] a) D. Cantillo, B. Gutmann, C. O. Kappe, *J. Am. Chem. Soc.* **2011**, 133, 4465; b) P. B. Palde, T. F. Jamison, *Angew. Chem.* **2011**, 123, 3587; *Angew. Chem. Int. Ed.* **2011**, 50, 3525; c) F. Couty, F. Durrat, D. Prim, *Tetrahedron Lett.* **2004**, 45, 3725; d) F. Himo, Z. P. Demko, L. Noodleman, K. B. Sharpless, *J. Am. Chem. Soc.* **2003**, 125, 9983; e) Z. P. Demko, K. B. Sharpless, *Angew. Chem.* **2002**, 114, 2217; *Angew. Chem. Int. Ed.* **2002**, 41, 2113; f) Z. P. Demko, K. B. Sharpless, *Angew. Chem.* **2002**, 114, 2214; *Angew. Chem. Int. Ed.* **2002**, 41, 2110; g) N. Ueyama, T. Yanagisawa, T. Kawai, M. Sonogawa, H. Baba, S. Mochizuki, K. Kosakai, T. Tomiyama, *Chem. Pharm. Bull.* **1994**, 42, 1841.
- [9] For some reviews, see: a) R. H. Crabtree, *Chem. Rev.* **1985**, 85, 245; b) M. Murakami, Y. Ito in *Activation of Unreactive Bonds and Organic Synthesis* (Ed.: S. Murai), Springer, New York, **1999**, p. 97; c) B. Rybtchinski, D. Milstein, *Angew. Chem.* **1999**, 111, 918; *Angew. Chem. Int. Ed.* **1999**, 38, 870; d) C.-H. Jun, *Chem. Soc. Rev.* **2004**, 33, 610; e) T. Satoh, M. Mouri, *Top. Organomet. Chem.* **2005**, 14, 1; f) C.-H. Jun, J. W. Park, *Top. Organomet. Chem.* **2007**, 24, 117; g) Z. Xi, *Acc. Chem. Res.* **2010**, 43, 1342.
- [10] For some recent reviews on C-H activation, see: a) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, 121, 5196; *Angew. Chem. Int. Ed.* **2009**, 48, 5094; b) C.-J. Li, *Acc. Chem. Res.* **2009**, 42, 335; c) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, 42, 1074; d) M. T. Whited, R. H. Grubbs, *Acc. Chem. Res.* **2009**, 42, 1607; e) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, 121, 9976; *Angew. Chem. Int. Ed.* **2009**, 48, 9792; f) A. A. Kulkarni, O. Daugulis, *Synthesis* **2009**, 4087; g) P. Thansandote, M. Lautens, *Chem. Eur. J.* **2009**, 15, 5874; h) F. Collet, R. H. Dodd, P. Dauban, *Chem. Commun.* **2009**, 5061; i) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, 46, 677; j) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, 110, 681; k) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, 110, 624; l) C. Copéret, *Chem. Rev.* **2010**, 110, 656; m) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, 110, 1147; n) I. A. I. Mkhali, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, 110, 890; o) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, 110, 704; p) A. Gunay, K. H. Theopold, *Chem. Rev.* **2010**, 110, 1060; q) D. Balcells, E. Colt, O. Eisenstein, *Chem. Rev.* **2010**, 110, 749; r) F. Bellina, R. Rossi, *Chem. Rev.* **2010**, 110, 1082; s) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, 111, 1293; t) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, 111, 1215; u) J. Le Bras, J. Muzart, *Chem. Rev.* **2011**, 111, 1170; v) L. Ackermann, *Chem. Rev.* **2011**, 111, 1315.
- [11] For some reviews, see: a) E. F. V. Scriven, K. Turnbull, *Chem. Rev.* **1988**, 88, 297; b) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, 114, 2708; *Angew. Chem. Int. Ed.* **2002**, 41, 2596; c) S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem.* **2005**, 117, 5320; *Angew. Chem. Int. Ed.* **2005**, 44, 5188; d) S. Lang, J. A. Murphy, *Chem. Soc. Rev.* **2006**, 35, 146; e) S. Cenini, E. Gallo, A. Caselli, F. Ragaini, S. Fantauzzi, C. Piangiolino, *Coord. Chem. Rev.* **2006**, 250, 1234; f) T. G. Driver, *Org. Biomol. Chem.* **2010**, 8, 3831; g) E. Leemans, M. D'hooghe, N. De Kimpe, *Chem. Rev.* **2011**, 111, 3268; h) T. Pasinski, M. Krebs, O. Wagner, *Curr. Org. Chem.* **2011**, 15, 1700; for some recent reviews on click reactions, see: i) J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, 39, 1302; j) J. M. Holub, K. Kirshenbaum, *Chem. Soc. Rev.* **2010**, 39, 1325; k) J. C. Jewett, C. R. Bertozzi, *Chem. Soc. Rev.* **2010**, 39, 1272, and references therein.
- [12] For some recent examples, see: a) H. Lu, H. Jiang, L. Wojtas, X. P. Zhang, *Angew. Chem.* **2010**, 122, 10390; *Angew. Chem. Int. Ed.* **2010**, 49, 10192; b) W. Yao, L. Pan, Y. Zhang, G. Wang, X. Wang, C. Ma, *Angew. Chem.* **2010**, 122, 9396; *Angew. Chem. Int. Ed.* **2010**, 49, 9210; c) S. Chiba, L. Zhang, J.-Y. Lee, *J. Am. Chem. Soc.* **2010**, 132, 7266; d) B. J. Stokes, C. V. Vogel, L. K. Urnezis, M. Pan, T. G. Driver, *Org. Lett.* **2010**, 12, 2884; e) R. Hushman, Y. S. Na, C. Bolm, S. Chang, *Chem. Commun.* **2010**, 46, 5494; f) K. Weidner, A. Giroult, P. Panchaud, P. Renaud, *J. Am. Chem. Soc.* **2010**, 132, 17511; g) W. Chen, M. Hu, J. Wu, H. Zou, Y. Yu, *Org. Lett.* **2010**, 12, 3863; h) D. Hong, Z. Chen, X. Lin, Y. Wang, *Org. Lett.* **2010**, 12, 4608; i) Y.-F. Wang, K. K. Toh, J.-Y. Lee, S. Chiba, *Angew. Chem.* **2011**, 123, 6049; *Angew. Chem. Int. Ed.* **2011**, 50, 5927; j) K. Sun, S. Liu, P. M. Bec, T. G. Driver, *Angew. Chem.* **2011**, 123, 1740; *Angew. Chem. Int. Ed.* **2011**, 50, 1702; k) Y.-F. Wang, K. K. Toh, E. P. J. Ng, S. Chiba, *J. Am. Chem. Soc.* **2011**, 133, 6411; l) I. Cano, E. Álvarez, M. C. Nicasio, P. J. Peréz, *J. Am. Chem. Soc.* **2011**, 133, 191; m) B. J. Stokes, S. Liu, T. G. Driver, *J. Am. Chem. Soc.* **2011**, 133, 4702; n) H. Dong, R. T. Latka, T. G. Driver, *Org. Lett.* **2011**, 13, 2726; o) J. Bonnamour, C. Bolm, *Org. Lett.* **2011**, 13, 2012; p) S. Zhang, J. Zhao, W.-X. Zhang, Z. Xi, *Org. Lett.* **2011**, 13, 1626; q) J. Wang, J. Wang, Y. Zhu, P. Lu, Y. Wang, *Chem. Commun.* **2011**, 47, 3275; r) Z. Chen, C. Ye, L. Gao, J. Wu, *Chem. Commun.* **2011**, 47, 5623; s) B. Lu, Y. Luo, L. Liu, L. Ye, Y. Wang, L. Zhang, *Angew. Chem.* **2011**, 123, 8508; *Angew. Chem. Int. Ed.* **2011**, 50, 8358; t) A. Wetzl, F. Gagosz, *Angew. Chem.* **2011**, 123, 7492; *Angew. Chem. Int. Ed.* **2011**, 50, 7354.
- [13] a) W. Zhou, L. Zhang, N. Jiao, *Angew. Chem.* **2009**, 121, 7228; *Angew. Chem. Int. Ed.* **2009**, 48, 7094; b) W. Zhou, J. Xu, L. Zhang, N. Jiao, *Org. Lett.* **2010**, 12, 2888; c) C. Qin, N. Jiao, *J. Am. Chem. Soc.* **2010**, 132, 15893; d) W. Zhou, J. Xu, L. Zhang, N. Jiao, *Synlett* **2011**, 887; for some examples of organic azide substrates, see: e) R. Hernández, E. I. León, P. Moreno, E. Suárez, *J. Org. Chem.* **1997**, 62, 8974; f) S. Sasson, S. Rozen, *Org. Lett.* **2005**, 7, 2177; g) S. Chiba, L. Zhang, G. Y. Ang, B. W.-Q. Hui, *Org. Lett.* **2010**, 12, 2052; h) M. Lamani, K. R. Prabhu, *Angew. Chem.* **2010**, 122, 6772; *Angew. Chem. Int. Ed.* **2010**, 49, 6622; i) J. He, K. Yamaguchi, N. Mizuno, *J. Org. Chem.* **2011**, 76, 4606.
- [14] a) K. F. Schmidt, *Angew. Chem.* **1923**, 36, 511; b) H. Wolff, *Org. React.* **1946**, 307; c) G. R. Krow, *Tetrahedron* **1981**, 37, 1283; d) J. Aube, G. L. Milligan, *J. Am. Chem. Soc.* **1991**, 113, 8965.

- [15] a) D. Walker, J. D. Hiebert, *Chem. Rev.* **1967**, 67, 153; b) Y.-Z. Li, B.-J. Li, X.-Y. Lu, S. Lin, Z.-J. Shi, *Angew. Chem.* **2009**, 121, 3875; *Angew. Chem. Int. Ed.* **2009**, 48, 3817; c) Y. Zhang, C.-J. Li, *Angew. Chem.* **2006**, 118, 1983; *Angew. Chem. Int. Ed.* **2006**, 45, 1949; d) Y. Li, W. Bao, *Adv. Synth. Catal.* **2009**, 351, 865.
- [16] a) A. Gagneux, S. Winstein, W. G. Young, *J. Am. Chem. Soc.* **1960**, 82, 5956; b) A. Padwa, M. M. Sá, *Tetrahedron Lett.* **1997**, 38, 5087.
- [17] a) M. I. K. Amer, B. L. Booth, *J. Chem. Res. Synop.* **1993**, 4; b) E. Cubero, M. Orozco, F. J. Luque, *J. Am. Chem. Soc.* **1998**, 120, 4723; c) T. Lioux, G. Gosselin, C. Mathé, *Eur. J. Org. Chem.* **2003**, 3997.
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