Synthetic Methods

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Iron-Catalyzed C–H and C–C Bond Cleavage: A Direct Approach to Amides from Simple Hydrocarbons**

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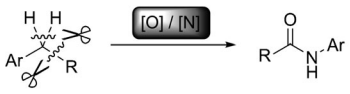
The direct transformation of hydrocarbons by transition-metal-catalyzed selective C–H and C–C bond activation (cleavage) has attracted considerable attention. The attention arises not only from its fundamental scientific interest but also from its potential utility in organic synthesis.[1,2] Recently, the development of more atom-efficient, novel catalytic methods for the preparation of amides under mild reaction conditions has been one of the most exciting topics in organic synthesis. Amides are essential for sustaining life, and they are important moieties in organic chemistry, biological, and pharmaceutical compounds.[3,4] Although the preparation of functionalized compounds by direct C–H or C–C bond activation has been the focus of a significant number of studies, the amide bond formation through C–H or C–C bond cleavage is still an extremely attractive yet challenging goal.[5,6] Herein, we report a novel iron-catalyzed C–H and C–C bond cleavage of benzyl hydrocarbons for the synthesis of amides and enamides under mild reaction conditions [Eq. (1)].



(1)

Azides have been widely used in organic synthesis,[7] including the click reaction.[8] Recently, some novel transformations of an azide species involving C–H bond activation for the synthesis of nitrogen-containing compounds have been developed.[9] By employing azides as the aminating agents, the direct synthesis of nitriles and tetrazoles has also been disclosed.[10] A stabilized azide cation is reported as the key intermediate in these transformations. To additionally validate the utility of azide methodologies for the synthesis nitrogen-containing molecules through C–H or C–C bond cleavage, we investigated the $FeCl_2$-catalyzed oxidative reaction of bis(4-methoxyphenyl)methane (**1a**) in the presence of DDQ and sodium azide in acetic acid (see Table 1 for structures). Interestingly, 4-methoxy-*N*-(4-methoxyphenyl)-benzamide (**2a**) was obtained in 47% yield (GC; see entry 1 of Table S1 in the Supporting Information). Other azide regents such as diphenylphosphoryl azide (DPPA), $(n\text{Bu})_4\text{NN}_3$, and *p*-tosyl azide gave low yields (Table S1, entries 2–4). Intriguingly, the amide product **2a** was directly produced in 90% yield when $TMSN_3$ was employed as the aminating agent (Table S1, entry 5). It is interesting that the reaction of **1a** under the metal-free conditions could also produce **2a** in 73% yield (Table S1, entry 13), probably because the substrates containing electron-donating groups can be easily oxidized by DDQ. The reactions in the presence of other transition metals such as Pd, Cu, Mn, Co, and Ni did not significantly affect the transformation (Table S1, entries 6–12). Hence, it was concluded that the iron salt can efficiently promote the reaction (Table S1, entries 5 and 13). The reactions using BQ, CAN, TBHP, or $Cu(OAc)_2$ as the oxidant did not perform well (Table S1, entries 17–20). The yield decreased to 35% when MeCN was employed as the solvent (Table S1, entry 16). After extensive screening of different parameters (Table S1), the optimal reaction conditions were determined to be those labeled conditions A ($FeCl_2$ (10 mol%), $TMSN_3$ (2.0 equiv), DDQ (2.2 equiv), H_2O (2.0 equiv), HOAc (2 mL), 60°C, under argon). Under these reaction conditions **2a** was obtained in 90% yield (Table S1, entry 5).

The scope of the substrates was investigated under the conditions A (Table 1). Diphenylmethanes bearing electron-donating substituents (OMe, NMe_2 and OEt) afforded the desired products **2a**, **2c**, and **2d** in good to excellent yields (Table 1, entries 1, 3, and 4). However, when diphenylmethane (**1b**) was tested under conditions A, no product was detected (see entry 1 of Table S2 in the Supporting Information). Gratifyingly, when **1b** was treated with DPPA, instead of $TMSN_3$, 41% yield of **2b** was obtained (Table S2, entry 2). Inspired by this, we additionally optimized the reaction conditions by employing **1b** as the model substrate (Table S2, entries 3–20). The reaction did not work in the absence of iron catalysts (Table S2, entries 3). Dramatically, the efficiency is improved by the combination of azides (DPPA/$TMSN_3$ 1:2) in the mixed solvent (HOAc/TFA 1:1). Mn, Co, and Ni can also independently catalyze this transformation but with low yields (Table S2, entries 16–20). Under these alternate reaction conditions (conditions B) **1b** was converted into the desired amide **2b** in 92% yield (Table 1, entry 2). When unsymmetric diphenylmethanes,

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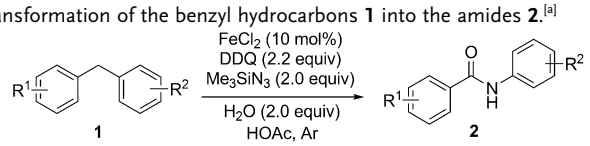
such as 1-benzyl-4-methoxybenzene (**1e**) and 4-benzylbiphenyl (**1f**) were employed, two regioisomers were obtained with the regioselectivities of 1.3:1 and 1.4:1, respectively (Table 1, entries 5 and 6).

Significantly, the present strategy was also applicable to the ring-expansion reactions (Table 1, entries 7–10). Various lactams can be constructed by this direct transformation through C–H and C–C bond cleavage. Six-membered-ring benzyl hydrocarbons 9,10-dihydroanthracene (**1h**) and anthracen-9(10*H*)-one (**1i**) were successfully converted into the same lactam product (**2h**; Table 1, entries 8–9). Eight-membered ring lactam 11,12-dihydrodibenzo[b,f]azocin-6(5*H*)-one (**2j**) was obtained in moderate yield from seven-membered-ring substrate **1j** (Table 1, entry 10). Interestingly, phenanthridine (**2g**) was produced in the reaction of fluorene (**1g**) (Table 1, entry 7), thus suggesting that **2g** is generated by the dehydration of the desired product phenanthridin-6(5*H*)-one. This chemistry provides a novel strategy for ring-expansion reactions through C–H bond functionalization under mild reaction conditions.

In addition, under the originally optimized reaction conditions (conditions A), (*E*)-1,3-diphenypropenes **3** can be converted into the corresponding acrylamides **4** in good to excellent yields (Scheme 1). These results show the high chemoselectivity and indicate that the aryl groups migrate preferentially over the alkenyl groups during the rearrangement process. Substituents at different positions of the arene rings (*para*, *meta*, and *ortho*) did not affect the efficiency of the reaction (**4b**, **4e**, **4i**). Fluoride (**4d**), chloride (**4c**), and bromide (**4f**) substitutents were also compatible with the process, thus producing the corresponding acrylamides in good yields. It is noteworthy that both electron-donating substituents (e.g., OMe, **4j**) and electron-withdrawing substituents (e.g., CF_3, **4g**) are tolerated in the reaction. The reaction of substrates with two different arene rings such as 1-cinnamyl-4-methoxybenzene (**3j**), 1-cinnamyl-4-chlorobenzene (**3k**), and 1-cinnamyl-4-(trifluoromethyl)benzene (**3l**) afforded products consisting of regioisomers in ratios of 1:7.1, 1.4:1, and 5:1, respectively. The regioselectivity may originate from the 3,3-sigmatropic

Table 1: Direct transformation of the benzyl hydrocarbons **1** into the amides **2**.[a]



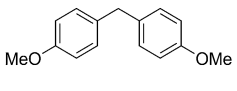
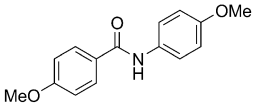
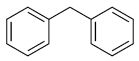
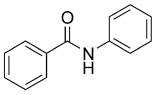
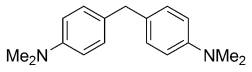
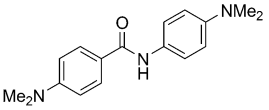
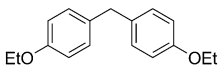
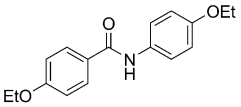
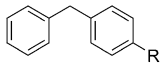
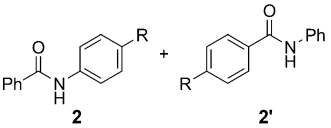
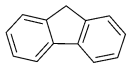
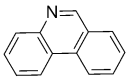
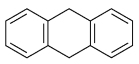
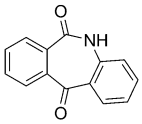
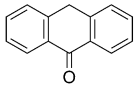
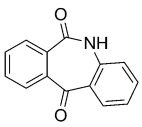
Entry	Substrates	Products	Yield [%][b]
1	 **1a**	 **2a**	90
2[c]	 **1b**	 **2b**	92
3	 **1c**	 **2c**	83
4	 **1d**	 **2d**	92
5	 **1e** R = OMe	 **2e** + **2e′** R = OMe	93 (1.3:1)[d]
6[c]	**1f** R = Ph	**2f** + **2f′** R = Ph	57 (1.4:1)[d]
7[c,e]	 **1g**	 **2g**	57
8[c,f,g]	 **1h**	 **2h**	61
			

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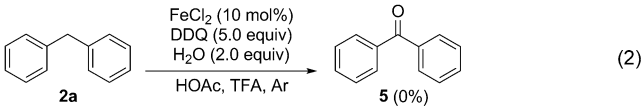
Table 1: (Continued)

Entry	Substrates	Products	Yield [%][b]
9[c,f]	**1i**	**2h**	72
10[c]	**1j**	**2j**	52

[a] Standard conditions: Conditions A: **1** (0.5 mmol) and Me_3SiN_3 (1.0 mmol), $FeCl_2$ (0.05 mmol), H_2O (1.0 mmol), and DDQ (1.1 mmol) in HOAc (2 mL) at 60 °C under Ar for 24 h. [b] Yield of isolated product. [c] Conditions B: **1** (0.5 mmol) and Me_3SiN_3 (2.0 mmol), DPPA (1.0 mmol), $FeCl_2$ (0.05 mmol), H_2O (1.0 mmol), and DDQ (2.5 mmol) in HOAc (1 mL) and TFA (1 mL) at 80 °C under Ar for 48 h. [d] The ratio of isomers was determined by ^{1}H NMR analysis of the purified mixture of products. [e] Solvent: TFA (2 mL). [f] Solvent: TFA (2 mL), stirred at 100 °C for 96 h. [g] 3.5 mmol DDQ was used. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, TFA = trifluoroacetic acid.

rearrangement of the allyl azide intermediate under the reaction conditions, and is obviously affected by the electron density of aromatic rings.[11]

Additional mechanistic studies with possible key intermediates have been investigated. One possible pathway for this transformation is likely to be a tandem oxidative Schmidt reaction process.[12] However, when diphenylmethane (**2a**) was tested in the absence of azides (DPPA and $TMSN_3$), no benzophenone (**5**) was observed [Eq. (2)]. Although **5** can be converted into **2b** under conditions B [Eq. (3)], the yield is much lower than that of **2a** reacting under conditions B. Furthermore, the reaction of **5** did not produce **2b** under Schmidt conditions (in the absence of oxidant) similar to conditions B [Eq. (4)]. All of these results suggest that the reaction does not undergo oxidation of diphenylmethane to benzophenone with a subsequent Schmidt reaction. To further probe the reaction mechanism, (azidomethylene)dibenzene (**6**) was synthesized and subjected to conditions B, **2b** was obtained in 91 % yield [Eq. (5)]. It indicates that the azide species **6** may be involved as the key intermediate in this transformation.



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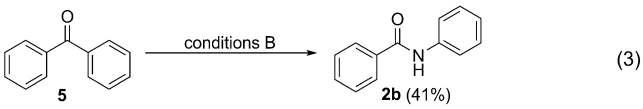

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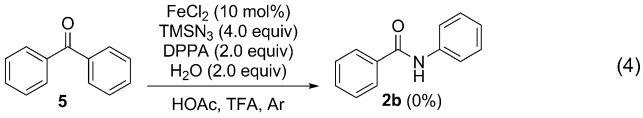

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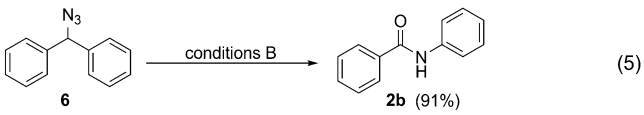

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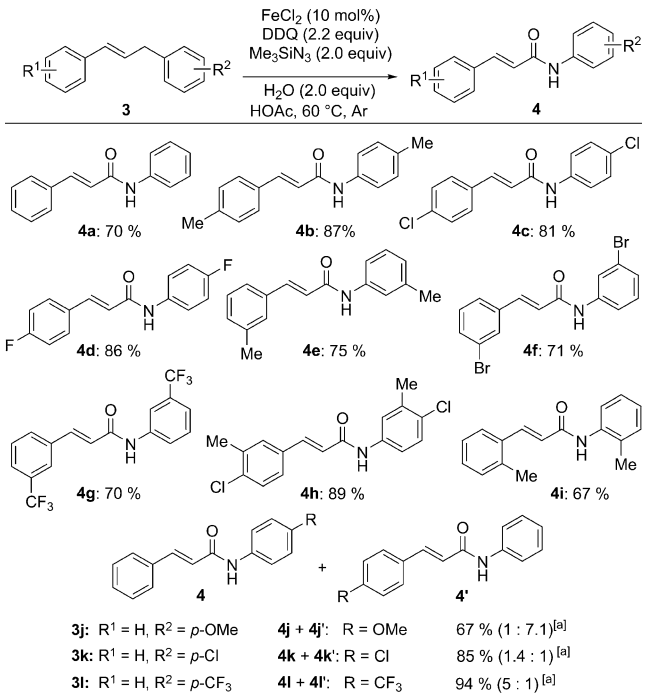

Scheme 1. Transformation of 1,3-diphenylpropenes **3** to acrylamides **4**. Standard conditions: **3** (0.5 mmol), Me_3SiN_3 (1.0 mmol), $FeCl_2$ (0.05 mmol), H_2O (1.0 mmol), and DDQ (1.1 mmol) in HOAc (2 mL) at 60 °C under Ar for 24 h. Yield is that of the isolated product. [a] The ratio of the isomers is determined by ^{1}H NMR analysis of the purified mixture of products.

On the basis the above results, a tentative reaction mechanism is illustrated in Scheme 2. Initially, **1b** undergoes the iron-assisted single-electron-transfer (SET) oxidation with DDQ[13] to produce the corresponding diphenylmethyl radical **A**, which could be additionally oxidized to the diphenylmethyl cation **B**. Then substitution reaction of **B** with an azide anion generates **6**, which would be oxidized to diphenylmethyl azide cation **C** by the iron-assisted DDQ oxidative system. Subsequent isomerization of diphenylmethyl azide cation **C** leads to the intermediate **D**. If the substrate was unsymmetrical, two isomeric iminodiazonium ions (**D** and **D′**) would be produced in this step.[14] As in the Beckmann rearrangement, the *trans* group (Ph^2 in **D** and Ph^1 in **D′**) migrates from the carbon to the nitrogen atom to generate the intermediate **E**. Subsequent nucleophilic attack by H_2O leads to the desired amide product **2b** through the tautomerization of the intermediate **F**. The reaction of **1b** in the presence of $H_2{}^{18}O$ produced the desired isotopically

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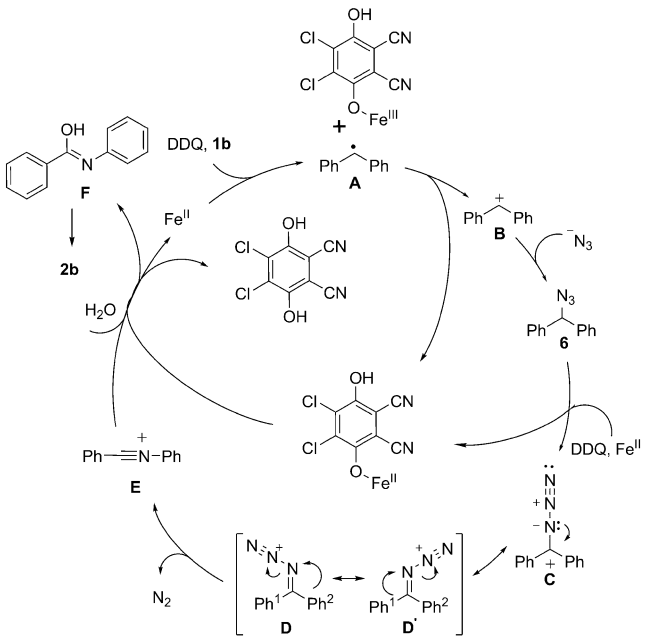
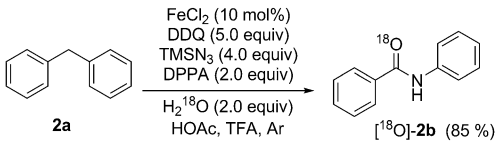


Scheme 2. A plausible mechanism for the amide formation.

labeled product [^{18}O]-**2b** [Eq. (6)], thus supporting this mechanistic hypothesis.

In summary, we have demonstrated a novel iron-catalyzed transformation of benzyl hydrocarbons into corresponding amides through C–H and C–C bond cleavage under mild reaction conditions. Ring expansion can be achieved by this present strategy to generate lactams. The mechanistic study shows that the transformation is a new process involving an



(6)

oxidative rearrangement rather than a tandem oxidative Schmidt reaction. This protocol not only provides a new synthetic tool for constructing synthetically and medicinally important amides, but also offers an opportunity to achieve C–H and C–C bond cleavage under mild reaction conditions. Additional studies on the reaction mechanism and the synthetic applications are ongoing in our group.

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[1] 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. Moura, *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; h) J. Halpern, *Acc. Chem. Res.* **1982**, *15*, 238.

[2] For reviews in recent two years, see: a) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, *46*, 677; b) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681; c) R. Jazzar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654; d) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; e) C. Copéret, *Chem. Rev.* **2010**, *110*, 656; f) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; g) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890; h) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704; i) A. Gunay, K. H. Theopold, *Chem. Rev.* **2010**, *110*, 1060; j) D. Balcells, E. Colt, O. Eisenstein, *Chem. Rev.* **2010**, *110*, 749; k) F. Bellina, R. Rossi, *Chem. Rev.* **2010**, *110*, 1082; l) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293; m) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; n) J. Le Bras, J. Muzart, *Chem. Rev.* **2011**, *111*, 1170; o) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315.

[3] a) K. Ishihara, Y. Furuya, H. Yamamoto, *Angew. Chem.* **2002**, *114*, 3109; *Angew. Chem. Int. Ed.* **2002**, *41*, 2983; b) C.-W. Kuo, J.-L. Zhu, J.-D. Wu, C.-M. Chu, C.-F. Yao, K.-S. Shia, *Chem. Commun.* **2007**, 301; c) E. Choi, C. Lee, Y. Na, S. Chang, *Org. Lett.* **2002**, *4*, 2369; d) K. Yamaguchi, H. Fujiwara, Y. Ogasawara, M. Kotani, N. Mizuno, *Angew. Chem.* **2007**, *119*, 3996; *Angew. Chem. Int. Ed.* **2007**, *46*, 3922; e) T. Oishi, K. Yamaguchi, N. Mizuno, *Angew. Chem.* **2009**, *121*, 6404; *Angew. Chem. Int. Ed.* **2009**, *48*, 6286.

[4] For recent reviews on amide synthesis, see: a) S.-Y. Han, Y.-A. Kim, *Tetrahedron* **2004**, *60*, 2447; b) C. A. G. N. Montalbetti, V. Falque, *Tetrahedron* **2005**, *61*, 10827; c) J. W. Bode, *Curr. Opin. Drug Discovery Dev.* **2006**, *9*, 765; d) E. Valeur, M. Bradley, *Chem. Soc. Rev.* **2009**, *38*, 606; e) C. L. Allen, J. M. J. Williams, *Chem. Soc. Rev.* **2011**, *40*, 3405; f) A. J. A. Watson, J. M. J. Williams, *Science* **2010**, *329*, 635; g) K. Ekoue-Kovi, C. Wolf, *Chem. Eur. J.* **2008**, *14*, 6302.

[5] For some new approaches to amide bond formation, see: a) C. G. Espino, K. W. Fiori, M. Kim, J. Du Bois, *J. Am. Chem. Soc.* **2004**, *126*, 15378; b) K. W. Fiori, J. Du Bois, *J. Am. Chem. Soc.* **2007**, *129*, 562; c) K. Inamoto, T. Saito, M. Katsuno, T. Sakamoto, K. Hiroya, *Org. Lett.* **2007**, *9*, 2931; d) G. Liu, G. Yin, L. Wu, *Angew. Chem.* **2008**, *120*, 4811; *Angew. Chem. Int. Ed.* **2008**, *47*, 4733; e) E. Milczek, N. Boudet, S. Blakey, *Angew. Chem.* **2008**, *120*, 6931; *Angew. Chem. Int. Ed.* **2008**, *47*, 6825; f) S. A. Reed, M. C. White, *J. Am. Chem. Soc.* **2008**, *130*, 3316; g) G. T. Rice, M. C. White, *J. Am. Chem. Soc.* **2009**, *131*, 11707; h) A. Armstrong, J. C. Collins, *Angew. Chem.* **2010**, *122*, 2332; *Angew. Chem. Int. Ed.* **2010**, *49*, 2282; i) J.-S. Tian, T.-P. Loh, *Angew. Chem.* **2010**, *122*, 8595; *Angew. Chem. Int. Ed.* **2010**, *49*, 8417; j) M. Ochiai, K. Miyamoto, T. Kaneaki, S. Hayashi, W. Nakanishi, *Science* **2011**, *332*, 448; k) J.-S. Tian, T.-P. Loh, *Chem. Commun.* **2011**, *47*, 5458; l) C. L. Allen, S. Davulcu, J. M. J. Williams, *Org. Lett.* **2010**, *12*, 5096; m) J. W. Bode, S. S. Sohn, *J. Am. Chem. Soc.* **2007**, *129*, 13798; n) D. Bonne, M. Dekhane, J. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 6926; o) J. Chan, K. D. Baucom, J. A. Murry, *J. Am. Chem. Soc.* **2007**, *129*, 14106; p) K. Ekoue-Kovi, C. Wolf, *Org. Lett.* **2007**, *9*, 3429; q) N. A. Owston, A. J. Parker, J. M. J. Williams, *Org. Lett.* **2007**, *9*, 73; r) S. Seo, T. J. Marks, *Org. Lett.* **2008**, *10*, 317; s) Y. Suto, N. Yamagiwa, Y. Torisawa, *Tetrahedron Lett.* **2008**, *49*, 5732; t) H. U. Vora, T. Rovis, *J. Am. Chem. Soc.* **2007**, *129*, 13796; u) A. J. A. Watson, A. C. Maxwell, J. M. J. Williams, *Org. Lett.* **2009**, *11*, 2667; v) W.-J. Yoo, C.-J. Li, *J. Am. Chem. Soc.* **2006**, *128*, 13064.

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[6] For some recent Schmidt reactions of ketones through C–C bond cleavage, see: a) D. Song, A. Rostami, F. G. West, *J. Am. Chem. Soc.* **2007**, *129*, 12019; b) L. Yao, J. Aubé, *J. Am. Chem. Soc.* **2007**, *129*, 2766; c) J. S. Yadav, B. V. S. Reddy, U. V. S. Reddy, K. Praneeth, *Tetrahedron Lett.* **2008**, *49*, 4742; d) T. Katori, S. Itoh, M. Sato, H. Yamataka, *J. Am. Chem. Soc.* **2010**, *132*, 3413; e) A. P. Mityuk, A. V. Denisenko, O. P. Dacenko, O. O. Grygorenko, P. K. Mykhailiuk, D. M. Volochnyuk, A. A. Tolmachev, *Tetrahedron Lett.* **2010**, *51*, 1790; f) M. Szostak, J. Aubé, *J. Am. Chem. Soc.* **2010**, *132*, 2530.

[7] For some reviews, see: a) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708; *Angew. Chem. Int. Ed.* **2002**, *41*, 2596; b) E. F. V. Scriven, K. Turnbull, *Chem. Rev.* **1988**, *88*, 297; 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. Murphy, *Chem. Soc. Rev.* **2006**, *35*, 146; e) E. Leemans, M. D'Hooghe, N. D. Kimpe, *Chem. Rev.* **2011**, *111*, 3268; f) T. Pasinszki, M. Krebsz, O. Wagner, *Curr. Org. Chem.* **2011**, *15*, 1700.

[8] For some recent reviews on click reactions, see: a) L. Ackermann, H. K. Potukuchi, *Org. Biomol. Chem.* **2010**, *8*, 4503; b) J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1302; c) J. M. Holub, K. Kirshenbaum, *Chem. Soc. Rev.* **2010**, *39*, 1325; d) J. C. Jewett, C. R. Bertozzi, *Chem. Soc. Rev.* **2010**, *39*, 1272.

[9] For some recent examples, see: a) B. J. Stokes, H. Dong, B. E. Leslie, A. L. Pumphrey, T. G. Driver, *J. Am. Chem. Soc.* **2007**, *129*, 7500; b) Y. M. Badiei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari, T. H. Warren, *Angew. Chem.* **2008**, *120*, 10109; *Angew. Chem. Int. Ed.* **2008**, *47*, 9961; c) S. Sengupta, H. Duan, W. Lu, J. L. Petersen, X. Shi, *Org. Lett.* **2008**, *10*, 1493; d) M. Shen, B. E. Leslie, T. G. Driver, *Angew. Chem.* **2008**, *120*, 5134; *Angew. Chem. Int. Ed.* **2008**, *47*, 5056; e) Z. Wang, Y. Zhang, H. Fu, Y. Jiang, Y. Zhao, *Org. Lett.* **2008**, *10*, 1863; f) S. H. Cho, S. Chang, *Angew. Chem.* **2008**, *120*, 2878; *Angew. Chem. Int. Ed.* **2008**, *47*, 2836; g) S. Fantauzzi, E. Gallo, A. Caselli, F. Ragaini, N. Casati, P. Macchi, S. Cenini, *Chem. Commun.* **2009**, 3952; h) S. Chiba, Y.-J. Xu, Y.-F. Wang, *J. Am. Chem. Soc.* **2009**, *131*, 12886; i) H. Lu, V. Subbarayan, J. Tao, X. P. Zhang, *Organometallics* **2010**, *29*, 389; j) W. G. Shou, J. Li, T. Guo, Z. Lin, G. Jia, *Organometallics* **2009**, *28*, 6847; k) K. Sun, R. Sachwani, K. J. Richert, T. G. Driver, *Org. Lett.* **2009**, *11*, 3598; l) Y. Liu, C. M. Che, *Chem. Eur. J.* **2010**, *16*, 10494; m) Y. Liu, J. Wei, C. M. Che, *Chem. Commun.* **2010**, *46*, 6926; n) H. Lu, J. Tao, J. E. Jones, L. Wojtas, X. P. Zhang, *Org. Lett.* **2010**, *12*, 1248; o) Y.-F. Wang, K. K. Toh, J.-Y. Lee, S. Chiba, *Angew. Chem.* **2011**, *123*, 6049; *Angew. Chem. Int. Ed.* **2011**, *50*, 5927; p) B. J. Stokes, S. Liu, T. G. Driver, *J. Am. Chem. Soc.* **2011**, *133*, 4702; q) E. R. King, E. T. Hennessy, T. A. Betley, *J. Am. Chem. Soc.* **2011**, *133*, 4917; r) B. Lu, Y. Luo, L. Liu, L. Ye, Y. Wang, L. Zhang, *Angew. Chem.* **2011**, *123*, 8508; *Angew. Chem. Int. Ed.* **2011**, *50*, 8358; s) P. Magnus, J. M. Bailey, M. J. Porter, *Tetrahedron* **1999**, *55*, 13927.

[10] a) W. Zhou, L. Zhang, N. Jiao, *Angew. Chem.* **2009**, *121*, 7228; *Angew. Chem. Int. Ed.* **2009**, *48*, 7094; b) C. Qin, N. Jiao, *J. Am. Chem. Soc.* **2010**, *132*, 15893; c) W. Zhou, J. Xu, L. Zhang, N. Jiao, *Org. Lett.* **2010**, *12*, 2888; d) F. Chen, C. Qin, Y. Cui, N. Jiao, *Angew. Chem.* **2011**, DOI: 10.1002/anie.201105505; *Angew. Chem. Int. Ed.* **2011**, DOI: 10.1002/anie.201105505; e) W. Zhou, J. Xu, L. Zhang, N. Jiao, *Synlett* **2011**, 887. For some examples from organic azide substrates, see: f) R. Hernández, E. I. León, P. Moreno, E. Suárez, *J. Org. Chem.* **1997**, *62*, 8974; g) S. Sasson, S. Rozen, *Org. Lett.* **2005**, *7*, 2177; h) S. Chiba, L. Zhang, G. Y. Ang, B. W.-Q. Hui, *Org. Lett.* **2010**, *12*, 2052; i) M. Lamani, K. R. Prabhu, *Angew. Chem.* **2010**, *122*, 6772; *Angew. Chem. Int. Ed.* **2010**, *49*, 6622; j) J. He, K. Yamaguchi, N. Mizuno, *J. Org. Chem.* **2011**, *76*, 4606.

[11] 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.

[12] a) K. F. Z. Schmidt, *Angew. Chem.* **1923**, *36*, 511; b) H. Wolff, *Org. React.* **1946**, *3*, 307; c) G. R. Krow, *Tetrahedron* **1981**, *37*, 1283; d) J. Aube, G. L. Milligan, *J. Am. Chem. Soc.* **1991**, *113*, 8965; e) V. Gracias, G. L. Milligan, J. Aube, *J. Am. Chem. Soc.* **1995**, *117*, 8047.

[13] a) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335; b) D. R. Buckle in *Encyclopedia of Reagents for Organic Synthesis*, *Vol. 3* (Ed.: L. A. Paquette), Wiley, Chichester, UK, **1995**, p. 1699; c) D. Walker, J. D. Hiebert, *Chem. Rev.* **1967**, *67*, 153; d) 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; e) Y. Zhang, C.-J. Li, *Angew. Chem.* **2006**, *118*, 1983; *Angew. Chem. Int. Ed.* **2006**, *45*, 1949; f) D. Cheng, W. Bao, *Adv. Synth. Catal.* **2008**, *350*, 1263.

[14] R. D. Bach, G. J. Wolber, *J. Org. Chem.* **1982**, *47*, 239.

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