ACES Asian Chemical Editorial Society

DOI: 10.1002/asia.201501095

CHEMISTRY AN ASIAN JOURNAL Communication

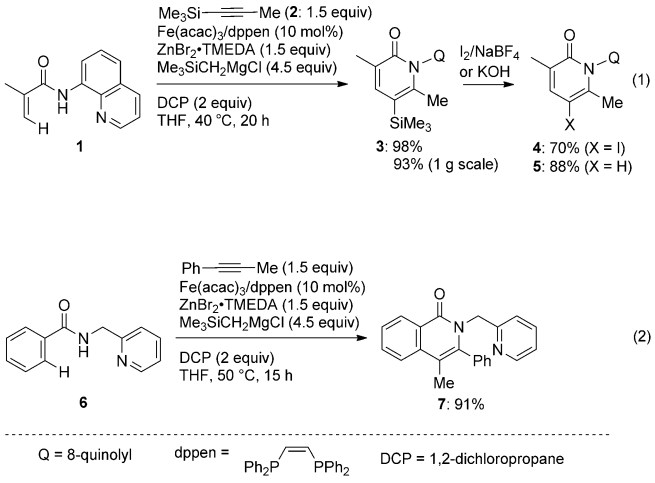
C–H Activation

Oxidative C–H Activation Approach to Pyridone and Isoquinolone through an Iron-Catalyzed Coupling of Amides with Alkynes

Tatsuaki Matsubara, Laurean Ilies,* and Eiichi Nakamura*[a]

Abstract: An iron catalyst combined with a mild organic oxidant promotes both C–H bond cleavage and C–N bond formation, and forms 2-pyridones and isoquinolones from an alkene- or arylamide and an internal alkyne, respectively. An unsymmetrical alkyne gives the pyridone derivative with high regioselectivity, this could be due to the sensitivity of the reaction to steric effects because of the compact size of iron.

2-Pyridones and isoquinolones are ubiquitous structural moieties in a variety of biologically active compounds[1] of medicinal interest.[2] A straightforward synthetic route towards this class of compounds[3] includes coupling of an alkyne with an α,β-unsaturated amide through activation of the C–H bond in the β-position *cis* to a *N*-quinolylamide group (cf. **1**), which directly produces 2-pyridone [Eq. (1)]. Similarly, coupling with a benzamide produces an isoquinolone,[4] where a picolinyl amide can be used as a removable directing group [Eq. (2)]. While similar C–H activation[5] approaches to isoquinolones have recently seen considerable success,[4] the synthesis of 2-pyridones has met with limited success. Only a few examples involving Rh, Ru, or Co catalysis have been reported,[6,7] because of problems with either loss of *cis*/*trans* stereospecificity of the C–H activation step or with the regioselectivity of the insertion step when an unsymmetrical alkyne is used as a substrate.[6d,8] The literature examples of 2-pyridone syntheses have either used symmetrical alkynes[6a–c] or produced a mixture of regioisomers when unsymmetrical alkynes were used.[6d] We report here an oxidative iron-catalyzed[9,10] regioselective annulation reaction of an α,β-unsaturated amide with alkynes that produces a 2-pyridone with a synthetically useful level of regioselectivity for unsymmetrical alkynes.[11] The reaction is also applicable to isoquinolone synthesis by C–H activation at an *ortho* position of a benzamide. The regioselectivity might be ascribed to the compact size of iron, which results in sensitivity of the iron species to steric bias; the *cis*-stereospecificity of the C–H activation step may be caused by the high-valent iron species, as the possibility of olefin isomerization through donative metal/olefin interaction is minimized.[12,13]



A typical procedure is shown for the reaction of a 2-methacrylamide bearing an *N*-8-quinoline group[14] (**1**) with an internal alkyne such as 1-trimethylsilyl-1-propyne (**2**): A solution of **1** (1 g, 4.71 mmol) and **2** (1.5 equiv) is mixed in the presence of $Fe(acac)_3$, *cis*-1,2-bis(diphenylphosphino)ethylene (dppen) as a ligand, in situ-generated bis(trimethylsilylmethyl)zinc as a base, and 1,2-dichloropropane as an oxidant in tetrahydrofuran (THF) at 40 °C, to produce 2-pyridone **3** in 93% yield as a single regioisomer. The reaction was very clean and no by-products were observed caused by direct coupling of **1** with the silylmethyl anion[12] nor homocoupling of the silylmethyl reagent,[15] the latter suggests that iron(III) did not oxidize this organometallic reagent.[16] The silylpyridone **3** can be converted into the iodopyridone **4** with iodine/sodium tetrafluoroborate in anhydrous methanol at 0 °C [Eq. (1)]. The silyl group in **3** can also be removed by treatment with a dimethyl sulfoxide (DMSO)/H_2O solution of KOH to obtain **5** in 88% yield.[17] As shown in [Eq. (2)], a similar reaction of *N*-picolinylbenzamide **6** with 1-phenyl-1-propyne gave isoquinolone **7** in 91% yield with complete regioselectivity.

[a] *T. Matsubara, Dr. L. Ilies, Prof. Dr. E. Nakamura*
Department of Chemistry
School of Science
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5800-6889
E-mail: laur@chem.s.u-tokyo.ac.jp
nakamura@chem.s.u-tokyo.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201501095.

This manuscript is part of a special issue on catalysis and transformation of complex molecules. Click here to see the Table of Contents of the special issue.

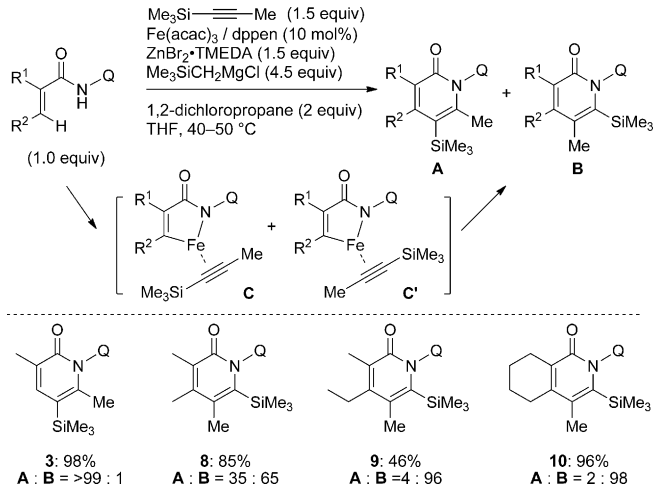


Figure 1. Dependence of regioselectivity on the β-substituent (R^2).

The regioselectivity shown in Figure 1 suggests that the C–C bond-formation process is highly sensitive to the β-substituent of the acrylamide, possibly owing to steric hindrance, as shown by the transition in the product distribution from **3**, **8**, **9**, to **10**. For **3**, where there is no substituent at the β-position, the regioisomer **A** was favored over **B**, whereas, for β-methylated **8**, the **A**/**B** ratio eroded to 35:65. Interestingly, a slight change in the β-methyl group in **8** to an ethyl group (**9**) favors **B** over **A** (4:96). Similarly, cyclohexenecarboxamide **10** was obtained in a 2:98 (**A**/**B**) ratio. Assuming that the activation of the C–H bond by an iron catalytic intermediate is the first step of the reaction, we can consider that the regioselectivity reflects the steric effects in intermediate **C** or **C′**, and that the small atomic radius enhances the selectivity.

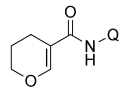
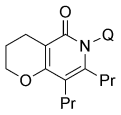
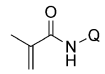
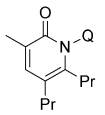
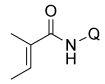
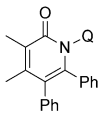
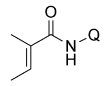
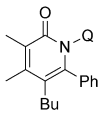
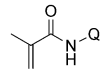
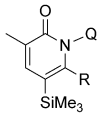
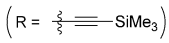
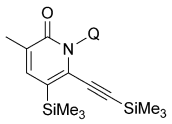
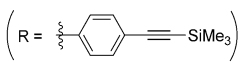
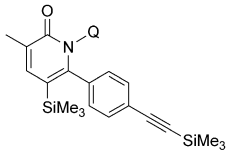
The study on the key parameters of this reaction (Equation (1)) is summarized below and described in the Supporting Information. As previously observed,[12b,c,13] a bidentate directing group is essential, probably because of its ability to stabilize the iron intermediate. Substrates such as *N*-methylbenzamide were unreactive. The nature of the organometallic base is also important: a Grignard reagent or a monoorganozinc halide instead of the diorganozinc afforded the desired product **3** in low yield (33% and 40%, respectively). Out of the 4.5 equivalents of trimethylsilylmethylmagnesium chloride used (98% yield, [Eq. (1)]), 1 equivalent deprotonates the amide proton, and the remaining 3.5 equivalents contributes to formation of a diorganozinc or a zincate intermediate by reaction with zinc halide (1.5 equiv). A small amount of starting material (2-methacrylamide) was recovered when 4.0 equivalents of Grignard reagent was used (**3** in 91% yield). This might suggest participation of an ferrate species in the catalytic cycle of this reaction.[18] A diphosphine bearing a conjugated backbone such as *cis*-1,2-bis(diphenylphosphino)ethylene (dppen) is necessary to achieve high yields, the saturated analogue, 1,2-bis(diphenyphosphino)ethane (dppe), gave **3** in only 43% yield. As previously suggested,[12b,c,13] dppen might stabilize by single-electron transfer an intrinsically unstable iron(I) intermediate formed after C–C bond formation through reductive elimination of an iron(III) species.[19] A 2,2′-bipyridine-type ligand[12a] was ineffective. Without the oxidant (DCP), only one catalytic turnover occurred, suggesting that DCP brings the catalytic cycle back to the initial step by oxidizing the iron(I) intermediate to regenerate an iron(III) reactive species. 1,2-Dichloroethane and 1,2-dibromopropane behaved similarly, albeit less efficiently (47% and 48% yield, respectively). Terminal alkynes did not give the desired annulation product.

This reaction has a considerable synthetic scope, as exemplified by the data in Table 1, Equations (1) and (2), and Figure 1. Both cyclic and acyclic alkenes reacted well, and isomerization of the starting acyclic substrates was not observed. The reaction proceeded well with β-oxo- (Table 1, entry 1), β-alkyl (Table 1, entry 3), and β-unsubstituted alkeneamides (Table 1, entry 2), but α-unsubstituted substrates such as acrylamide gave low yields (ca. 20%) with poor mass balance, possibly because of decomposition of the substrate. Internal alkynes possessing alkyl, alkenyl, aryl, heteroaryl, allyl, alkynyl, and silyl groups could be successfully employed in the reaction. For an unsymmetrical acetylene substituted by an aryl and an alkyl group (Table 1, entry 4), 5-alkyl-6-aryl pyridone was obtained as the major isomer in 96:4 ratio, as confirmed by ^{1}H NMR spectroscopy and single-crystal X-ray crystallographic analysis. As also shown in Equation (1), trimethylsilyl alkynes having alkyl, aryl (Table 1, entries 5–8), alkenyl (Table 1, entry 9), thienyl (Table 1, entry 10), allyl (Table 1, entry 11), and alkynyl (Table 1, entries 12 and 13) groups reacted with methacrylamide **1** in high yield and good regioselectivity (Table 1, entries 5–13). Chloride (Table 1, entry 6) and bromide (Table 1, entry 8) groups were well tolerated. An enyne compound (Table 1, entry 9) reacted in high yield and without isomerization on the double bond. A 1,3-diyne (Table 1, entry 12) reacted cleanly to give 6-alkynylpyridone quantitatively—a rare example of functionalization of a C–H bond with a 1,3-diyne.[20] 1,4-Bis(alkynyl)-benzene reacted selectively at only one alkyne site, thus leaving one alkyne group intact (Table 1, entry 13).

The reaction was found to be useful also for isoquinolone synthesis (Table 2). Thus, the reaction of *N*-quinolin-8-yl-3-tolylamide (Table 2, entry 1) or *N*-picolinylbenzamide (Table 2, entry 2) with 4-octyne under identical reaction conditions gave the corresponding isoquinolones in high yield. The reaction of the *N*-picolinylbenzamide with an unsymmetrical alkyne such as 1-phenyl-1-propyne proceeded with high regioselectivity [Eq. (2)], while the same reaction with a quinolylamide substrate was very slow (Table 2, entries 3 and 4). The picolinyl group in the product can be removed using the procedure reported by Chatani and co-workers.[4e]

The reaction of benzamide **11** with 4-octyne gave either an alkenylated product **12**,[21] or the annulated product **13**, depending on the organometallic base used (Figure 2). When a monoorganozinc halide was used as the base, the alkenylated product **12** was obtained as the major product regardless of the presence or absence of the oxidant DCP. However, when a diorganozinc was used in the presence of DCP, the cyclized product **13** was formed exclusively. The results suggest a common intermediate **D** for both paths and also that the diorganozinc is a strong enough silylmethyl donor to iron and

Table 1. Iron-catalyzed annulation of alkene carboxamides with various internal alkynes.[a]

Entry	Amide	Alkyne	Product	Yield [%][b]
1				87
2				99
3				99
4				98 (96:4)
5				77 (R = Ph)
6				90 (R = 4-ClC$_6$H$_4$)
7				93 (R = 4-CF$_3$C$_6$H$_4$)
8				68[d] (R = 4-BrC$_6$H$_4$)
9				97 (R = *E*-styryl)
10				49 (R = 2-thienyl)
11				40 (R = allyl)
12				98
13				58

[a] The reaction was carried out using amide (0.4 mmol), alkyne (0.6 mmol), Fe(acac)$_3$/dppen (0.04 mmol), ZnBr$_2$·TMEDA (0.6 mmol), Me$_3$SiCH$_2$MgCl (1.8 mmol), and 1,2-dichloropropane (0.8 mmol), as described in the text. [b] The yield is based on the pure isolated product obtained by silica gel chromatography. See the Supporting Information for details. [c] Ratio of regioisomers was determined using ^{1}H NMR spectroscopy. [d] Debrominated compound was obtained in 9% yield.

generates a ferrate species, which is then oxidized by DCP to form the C–N bond.[18]

In conclusion, we have developed the annulation of alkene- and areneamides with internal alkynes that produces 2-pyridone and isoquinolone derivatives. An iron catalyst effects stereospecific C–H activation of alkene substrates, and steric factors are crucial for the control of regioselectivity in the reaction of unsymmetrical alkynes. When benzamide was used as the substrate, the nature of the base strongly affected product selectivity. Thus, the present study demonstrates that the sensitivity of organoiron species to steric bias can be exploited as a tool for the design of regioselective synthesis.

Experimental Section

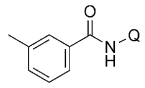
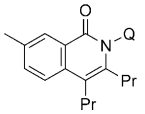
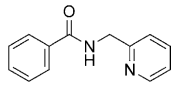
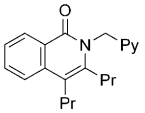
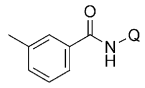
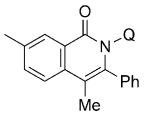
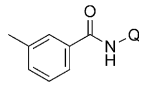
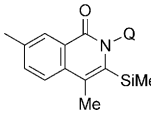
To an oven-dried Schlenk tube was added *N*-(quinolin-8-yl)methacrylamide (**1**, 1.00 g, 4.71 mmol), ZnBr$_2$·TMEDA (2.42 g, 7.1 mmol, TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), dppen (186 mg, 0.47 mmol), and 1-trimethylsilyl-1-propyne (797 mg, 7.1 mmol, 1.5 equiv), and the mixture was dissolved in THF (5 mL). A solution of trimethylsilylmethylmagnesium chloride in THF (21.2 mL, 1.0 mol L^{-1}, 21.2 mmol, 4.5 equiv) was added dropwise, and then 1,2-dichloropropane (917 μL, 9.4 mmol, 2.0 equiv) was added. After stirring the solution at room temperature for several minutes, Fe(acac)$_3$ (166 mg, 0.47 mmol, acac = acetylacetonato) was added, and the reaction mixture was heated to 40 °C. After stirring for 20 h, the reaction mixture was quenched by the addition of a saturated aqueous solution of potassium sodium tartrate and saturated aqueous solution of ammonium chloride. After aqueous workup, the organic layer was extracted with EtOAc (20 mL × 3). The combined organic layer was passed through a pad of Florisil, concentrated in vacuo, and purified by column chromatography on silica gel (gradient hexane/EtOAc from 4:1 to 1:1, then EtOAc) to afford 3,6-dimethyl-5-trimethylsilyl-1-(quinolin-8-yl)pyridin-2(1*H*)-one (**3**) as a pale yellow solid (1.27 g, 93% yield). M.p. 143–145 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.89 (d, J = 3.7 Hz, 1H), 8.21 (d, J = 9.7 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.67–7.61 (m, 2H), 7.42 (dd, J = 10.3, 5.2 Hz, 1H), 7.38 (s, 1H), 2.16 (s, 3H), 1.93 (s, 3H), 0.31 ppm (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 164.0, 151.3, 149.1, 143.8, 142.1, 137.4, 136.0, 129.2, 129.1, 128.8, 126.2, 125.5, 121.6, 110.9, 21.2, 16.8, 0.0 ppm. GC-MS (EI) *m*/*z* (relative intensity): 322 (M^+, 60), 321 (100), 307 (37), 305 (14), 249 (55), 170 (6), 128 (5), 101 (4), 73 (15). HRMS (APCI+): *m*/*z* calcd for C$_{19}$H$_{22}$N$_2$OSi [M+H$^+$] 323.1574; found: 323.1580.

CCDC-1420101 (**3**) and CCDC-1420102 (Table 1, entry 4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank MEXT for financial support (Grant-in-Aid for Young Scientists (A) No. 26708011 to L.I.). This work was supported by CREST, JST. T.M. thanks the Japan Society for the Promotion of Science for Young Scientists for a Research Fellowship (No. 26-11422), and for support through the Program for Leading Graduate Schools (MERIT). We thank Kazutaka Shoyama and Yuki Itabashi for assistance with the single-crystal X-ray crystallographic analysis.

Table 2. Iron-catalyzed annulation of arenecarboxamides with internal alkynes to produce isoquinolones.[a]

Entry	Amide	Alkyne	Product	Yield [%][b]
1				98
2				88
3				22[c,d,e]
4				< 1[c,d,e]

[a] The reaction was carried out using amide (0.4 mmol), alkyne (0.6 mmol), $Fe(acac)_3$/dppen (0.04 mmol), $ZnBr_2$·TMEDA (0.6 mmol), Me_3SiCH_2MgCl (1.8 mmol), and 1,2-dichloropropane (0.8 mmol), as described in the text. [b] The yield is based on the pure isolated product obtained by silica gel chromatography. See the Supporting Information for details. [c] The reaction was performed at 50 °C. [d] The yield was determined by GC analysis, using hexadecane as an internal standard. [e] Regioselectivity was not determined.

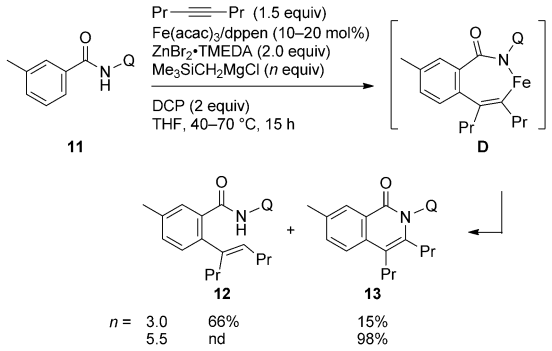


Figure 2. Bifurcation of reaction pathways depending on the nature of the silylmethylzinc reagent.

Keywords: alkynes · amides · C–H activation · iron · 2-pyridones

[1] a) A. P. Kozikowski, W. Tückmantel, *Acc. Chem. Res.* **1999**, *32*, 641–650; b) M. E. Wall, M. C. Wani, C. E. Cook, K. H. Palmer, A. I. McPhail, G. A. Sim, *J. Am. Chem. Soc.* **1966**, *88*, 3888–3890.

[2] a) L. A. Mitscher, *Chem. Rev.* **2005**, *105*, 559–592; b) I. M. Lagoja, *Chem. Biodiversity* **2005**, *2*, 1–50; c) S. Hibi, K. Ueno, S. Nagato, K. Kawano, K. Ito, Y. Norimine, O. Takenaka, T. Hanada, M. Yonaga, *J. Med. Chem.* **2012**, *55*, 10584–10600.

[3] M. Torres, S. Gil, M. Parra, *Curr. Org. Chem.* **2005**, *9*, 1757—1779.

[4] (Rh) a) N. Guimond, C. Gouliaras, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6908–6909; b) T. Hyster, T. Rovis, *J. Am. Chem. Soc.* **2010**, *132*, 10565–10569; c) H. Wang, C. Grohmann, C. Nimphius, F. Glorius, *J. Am. Chem. Soc.* **2012**, *134*, 19592–19595. (Ru) d) L. Ackermann, A. V. Lygin, N. Hofmann, *Angew. Chem. Int. Ed.* **2011**, *50*, 6379–6382; *Angew. Chem.* **2011**, *123*, 6503–6506. (Ni) e) H. Shiota, Y. Ano, Y. Aihara, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2011**, *133*, 14952–14955.

[5] a) *Handbook of C–H Transformations* (Ed.: G. Dyker), Wiley-VCH, Weinheim, **2005**; b) K. Godula, D. Sames, *Science* **2006**, *312*, 67–72; c) W. R. Gutekunst, P. S. Baran, *Chem. Soc. Rev.* **2011**, *40*, 1976–1991; d) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369–375; e) Y. Segawa, T. Maekawa, K. Itami, *Angew. Chem. Int. Ed.* **2015**, *54*, 66–81; *Angew. Chem.* **2015**, *127*, 68–83.

[6] a) L. Grigorjeva, O. Daugulis, *Angew. Chem. Int. Ed.* **2014**, *53*, 10209–10212; *Angew. Chem.* **2014**, *126*, 10373–10376; b) L. Ackermann, A. V. Lygin, N. Hofmann, *Org. Lett.* **2011**, *13*, 3278–3281; c) Y. Su, K. Han, G. Song, X. Li, *Org. Lett.* **2010**, *12*, 5462–5465; d) T. K. Hyster, T. Rovis, *Chem. Sci.* **2011**, *2*, 1606–1610.

[7] Intramolecular reaction: X. Xu, Y. Liu, C.-M. Park, *Angew. Chem. Int. Ed.* **2012**, *51*, 9372–9376; *Angew. Chem.* **2012**, *124*, 9506–9510.

[8] For the annulation of alkene substrates and alkynes to give heterocycles, see: a) P. C. Too, T. Noji, Y. J. Lim, X. Li, S. Chiba, *Synlett* **2011**, 2789—2794; b) T. K. Hyster, T. Rovis, *Chem. Commun.* **2011**, *47*, 11846–11848; c) D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326–18339; d) S. Yotphan, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 2452–2453; e) K. Parthasarathy, M. Jeganmohan, C.-H. Cheng, *Org. Lett.* **2008**, *10*, 325–328; f) S. Duttwyler, C. Lu, A. L. Rheingold, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2012**, *134*, 4064–4067; g) D. A. Colby, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 3645–3651; h) L. Wang, L. Ackermann, *Org. Lett.* **2013**, *15*, 176–179; i) T. Yamakawa, N. Yoshikai, *Org. Lett.* **2013**, *15*, 196–199; j) L. Adak, W.-C. Chan, N. Yoshikai, *Chem. Asian J.* **2011**, *6*, 359–362; k) S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585–9587.

[9] Selected reviews: a) C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254; b) *Iron Catalysis in Organic Chemistry* (Ed.: B. Plietker); Wiley-VCH, Weinheim, **2008**; c) S. Enthaler, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321; *Angew. Chem.* **2008**, *120*, 3363–3367; d) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500–1511; e) W. M. Czaplik, M. Mayer, J. Cvengros, A. Jacobi von Wangelin, *ChemSusChem* **2009**, *2*, 396–417; f) E. Nakamura, N. Yoshikai, *J. Org. Chem.* **2010**, *75*, 6061–6067; g) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293–1314; h) L. Ilies, E. Nakamura, Iron-Catalyzed Cross-Coupling Reactions in *The Chemistry of Organoiron Compounds* (Eds.: I. Marek, Z. Rappoport), Wiley, Chichester, **2014**; i) E. Nakamura, T. Hatakeyama, S. Ito, K. Ishizuka, L. Ilies, M. Nakamura, *Org. React.* **2014**, *83*, 1–209; j) I. Bauer, H.-J. Knölker, *Chem. Rev.* **2015**, *115*, 3170–3387.

[10] a) C. Bolm, *Nat. Chem.* **2009**, *1*, 420; b) E. Nakamura, K. Sato, *Nat. Mater.* **2011**, *10*, 158–161.

[11] Iron-catalyzed carbometalation of alkynes: a) T. Yamagami, R. Shintani, E. Shirakawa, T. Hayashi, *Org. Lett.* **2007**, *9*, 1045–1048; b) E. Shirakawa, S. Masui, R. Narui, R. Watabe, D. Ikeda, T. Hayashi, *Chem. Commun.* **2011**, *47*, 9714–9716; c) L. Ilies, T. Yoshida, E. Nakamura, *Synlett* **2014**, *25*, 527–530. Iron/copper cooperative carbometalation: d) E. Shirakawa, D. Ikeda, S. Masui, M. Yoshida, T. Hayashi, *J. Am. Chem. Soc.* **2012**, *134*, 272–279.

[12] a) L. Ilies, S. Asako, E. Nakamura, *J. Am. Chem. Soc.* **2011**, *133*, 7672–7675; b) R. Shang, L. Ilies, S. Asako, E. Nakamura, *J. Am. Chem. Soc.* **2014**, *136*, 14349–14352; c) L. Ilies, S. Ichikawa, S. Asako, T. Matsubara, E. Nakamura, *Adv. Synth. Catal.* **2015**, *357*, 2175–2179; d) B. M. Monks, R. E. Fruchey, S. P. Cook, *Angew. Chem. Int. Ed.* **2014**, *53*, 11065–11069; *Angew. Chem.* **2014**, *126*, 11245–11249; e) R. E. Fruchey, B. M. Monks, S. P. Cook, *J. Am. Chem. Soc.* **2014**, *136*, 13130–13133.

[13] L. Ilies, T. Matsubara, S. Ichikawa, S. Asako, E. Nakamura, *J. Am. Chem. Soc.* **2014**, *136*, 13126–13129.

[14] a) V. G. Zaitsev, D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2005**, *127*, 13154–13155; b) G. Rouquet, N. Chatani, *Angew. Chem. Int. Ed.* **2013**, *52*, 11726–11743; *Angew. Chem.* **2013**, *125*, 11942–11959; c) O. Daugulis, J. Roane, L. D. Tran, *Acc. Chem. Res.* **2015**, *48*, 1053–1064.

[15] a) G. Cahiez, C. Chaboche, F. Mahuteau-Betzer, M. Ahr, *Org. Lett.* **2005**, *7*, 1943–1946; b) T. Nagano, T. Hayashi, *Org. Lett.* **2005**, *7*, 491–493.

[16] R. B. Bedford, *Acc. Chem. Res.* **2015**, *48*, 1485–1493.

[17] S. R. Wilson, L. A. Jacob, *J. Org. Chem.* **1986**, *51*, 4833–4836.

[18] Y. Nakamura, L. Ilies, E. Nakamura, *Org. Lett.* **2011**, *13*, 5998 – 6001.
[19] S. Blanchard, E. Derat, M. Murr, L. Fensterbank, M. Malacria, V. Mouries-Mansuy, *Eur. J. Inorg. Chem.* **2012**, 376 – 389.
[20] D.-G. Yu, F. de Azambuja, T. Gensch, C. G. Daniliuc, F. Glorius, *Angew. Chem. Int. Ed.* **2014**, *53*, 9650 – 9654; *Angew. Chem.* **2014**, *126*, 9804 – 9809.
[21] M. Y. Wong, T. Yamakawa, N. Yoshikai, *Org. Lett.* **2015**, *17*, 442 – 445.

Manuscript received: October 9, 2015
Accepted Article published: October 16, 2015
Final Article published: November 4, 2015