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C–H Activation

Nickel-Catalyzed Insertion of Alkynes and Electron-Deficient Olefins into Unactivated sp^3 C–H Bonds

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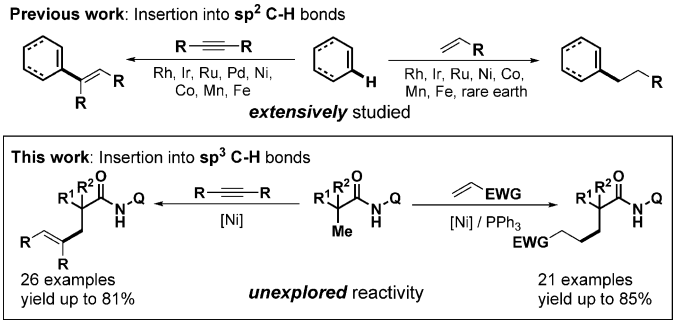
Abstract: Insertion of unsaturated systems such as alkynes and olefins into unactivated sp^3 C–H bonds remains an unexplored problem. We herein address this issue by successfully incorporating a wide variety of functionalized alkynes and electron-deficient olefins into the unactivated sp^3 C–H bond of pivalic acid derivatives with excellent *syn*- and *linear*- selectivity. A strongly chelating 8-aminoquinoline directing group proved beneficial for these insertion reactions, while an air-stable and inexpensive Ni^{II} salt has been employed as the active catalyst.

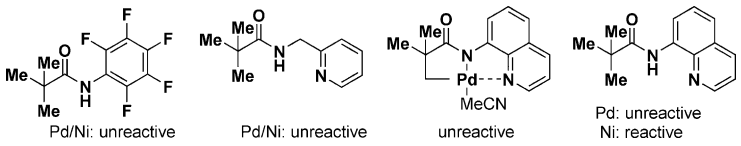


Scheme 1. Alkyne and olefin insertions into C–H bonds: conventional approaches and present work. EWG = electron-withdrawing group.

Alkyne and olefin insertion into C–H bonds are among the most profoundly studied transformations in transition-metal chemistry. To date, a wide variety of Rh,[1] Ir,[2] Pd,[3] Ru,[4] Ni,[5] and Co[6] based catalysts have been developed for these characteristic C–C bond-forming processes. Even relatively less used first-row congeners such as Mn[7] and Fe,[8] and rare-earth metals[9] have been found to deliver promising results. It should be noted that the majority of these insertion reactions were accomplished through the activation of a sp^2 C–H bond irrespective of the transition metal involved (Scheme 1).[4d,6h,10] The related insertion chemistry at sp^3 C–H, however, remains underdeveloped so far.

Previous attempts to incorporate an alkyne/olefin into aliphatic compounds largely focused on those sp^3 C–H bonds that are activated by virtue of their position in the molecule. The scope of the reaction was therefore explored with benzyl,[11] allyl,[12] activated methylene systems[13] and substrates with C–H bonds next to a heteroatom.[14] Accordingly, insertion of alkynes/olefins into unactivated aliphatic sp^3 C–H bonds remains a formidable task.[15]

To address this problem, a suitable substrate–catalyst combination had to be identified. Owing to the absence of a π-electron cloud and a low-lying σ* orbital, metal-mediated cleavage of aliphatic C–H bonds becomes troublesome. Binding with alkyne and olefin might result in undermining the catalyst efficiency[16] and/or [2+2+2] cyclotrimerization reactions.[17] We found that these potential problems can be circumvented in pivalic acid derivatives with the help of Daugulis' chelating 8-aminoquinoline[18] and an appropriate Ni catalyst.[19] Several other directing group/metal catalyst combinations were also tested but promising results could not be obtained in any of the cases. Even stoichiometric reactions with a preformed palladacycle intermediate failed to provide the desired products (Scheme 2). Notably, chelation-assisted insertion into aromatic C–H bonds has been disclosed previously by the independent research groups of Chatani and Daugulis.[20]



Scheme 2. Observations with directing groups and catalyst systems.

The scope of alkyne insertion with various aliphatic substrates is described in Scheme 3. The first alkenylated product was obtained from *N*-(quinolin-8-yl)pivalamide and diphenylacetylene in 81% isolated yield (**3a**, *Z*/*E*, 7:1). The stereoisomeric configuration of the products was determined by 1D NOE and/or 2D NMR (NOESY) experiments. Although an excess of amide was used for alkyne insertion, no side reaction was observed and unreacted starting materials were recovered in considerable amount. It was found that the steric environment of the substrates had a major influence on the reaction outcome. An ethyl group at the α-carbon posed a slight hindrance for the reaction owing to the enhanced steric congestion around the

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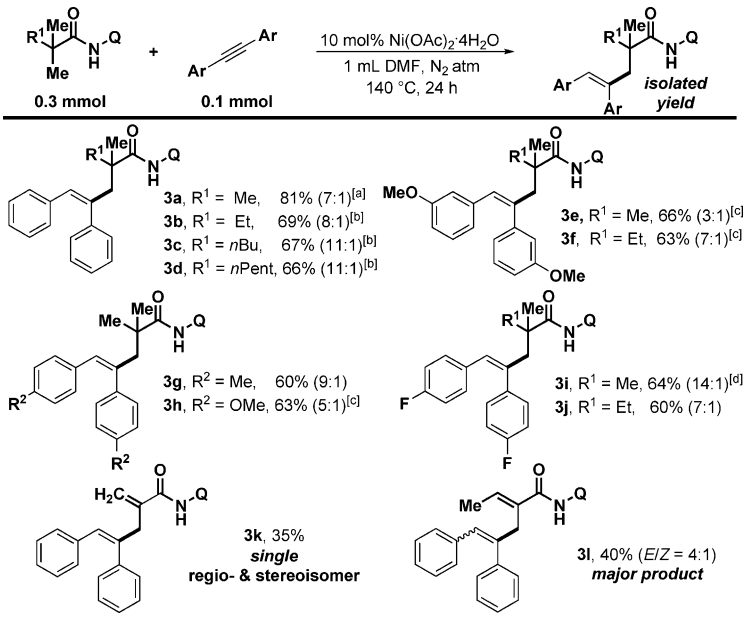


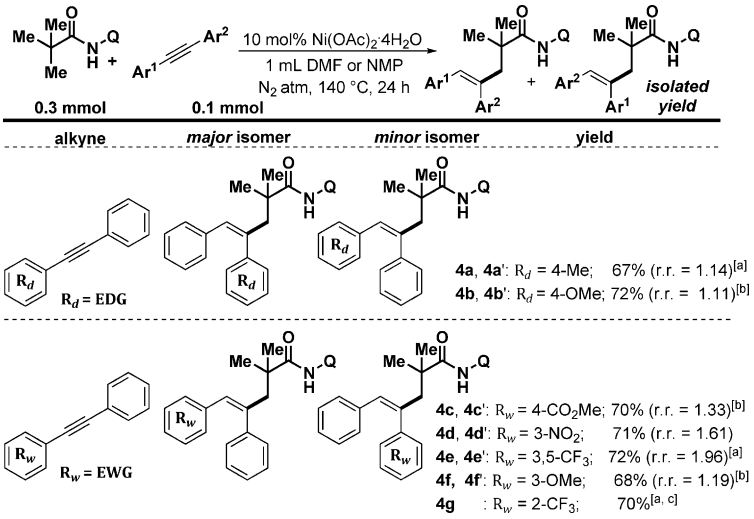
Scheme 3. Scope of aliphatic substrates with symmetrical alkynes. *Z/E* ratios were determined by ^{1}H NMR analysis of the isolated compound and given in parenthesis. [a] 68% yield by GC with 1 equiv of amide. [b] Reaction at 150 °C with 20 mol% PPh_3 ligand. [c] Reaction in NMP solvent. [d] Reaction in DMA solvent with 20 mol% PPh_3 ligand.

quaternary center (**3b**, 69%). Similar results were obtained with successive homologation of alkyl groups in one direction (**3c**, 67% and **3d**, 66%). Other symmetrical diphenylacetylenes with methoxy (**3e**, **3f**, and **3h**) methyl (**3g**), and fluoro (**3i** and **3j**) groups also proved amenable to the current system. Interestingly, diphenylacetylene coupled with an allylic sp^3 C–H bond in preference to an evenly placed vinylic sp^2 C–H bond (**3k**, 35% and **3l**, 40%).[10c]

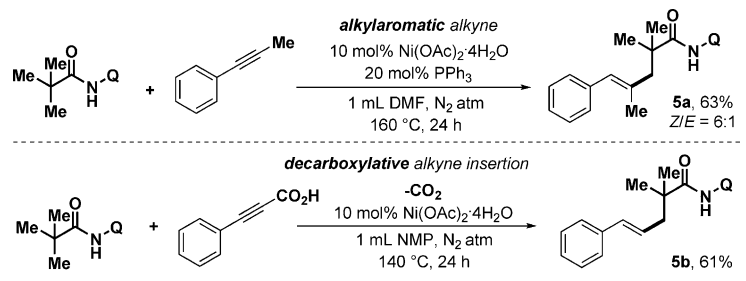
Usually, unsymmetrical alkynes are considered as problematic substrates for insertion reactions as they often generate mixtures of regioisomers, which are difficult to isolate and characterize. Nevertheless, a systematic variation of substituents at *para*-, *meta*- and *ortho*- positions of an alkyne would give the opportunity to look into the underlying mechanism. It was observed that the reaction could distinguish between slight electronic differences imparted by an electron donating 4-methyl group (**4a**/**4a**′, 67%; r.r. = 1.14) or an electron-withdrawing 4-carbomethoxy group (**4c**/**4c**′, 70%; r.r. = 1.33) while retaining the synthetic efficiency (Scheme 4; combined yields: 67–72%). Intriguingly, alkylnickelation preferentially occurred in a way so as to put the metal at the α-styrenyl position of the more electron deficient ring. Similar observations with 4-OMe (**4b**/**4b**′, 72%), 3-NO_2 (**4d**/**4d**′, 71%), 3,5-di-CF_3 (**4e**/**4e**′, 72%) and most prominently with 2-CF_3 (**4g**, 70%) substituted diphenylacetylenes supported electronic dependence of the insertion step.

Alkyl aromatic alkyne, 1-phenyl-1-propyne, gave a single regioisomer in 63% isolated yield (Scheme 5, **5a**). Phenyl propiolic acid underwent decarboxylation prior to insertion into the aliphatic C–H bond, thus providing the styrenyl derivative in useful yield (**5b**, 61%). This observation inspired us to examine terminal alkynes as probable substrates, substrates that are usually incompatible under nickel catalysis. It was found that alkenylation could be performed with terminal alkynes with excellent regio- and stereoselectivity albeit in low yields. Unfortunately, dialkyl alkynes (such as 4-octyne) were found to generate a mixture of regioisomers in less than 30% isolated yield.

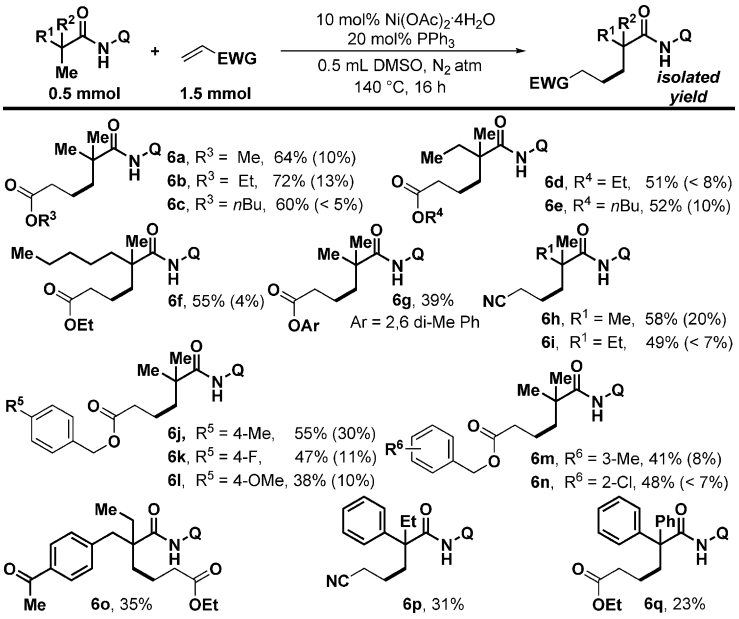
After successful demonstration of the insertion of alkynes into the unactivated sp^3 C–H bond, we tried to incorporate other unsaturated systems with the present method. In fact, a related development with olefins should provide a unique opportunity for (sp^3)C–C(sp^3) bond formation. Surprisingly, despite Murai's seminal discovery back in 2001,[14b] and Sanford[21] and Yu's impressive work on sp^3 C–H olefination,[22] a general olefin insertion into an unactivated aliphatic set-up is yet to be reported. We found that with minor modifications of the reaction conditions, a variety of activated olefins such as functionalized



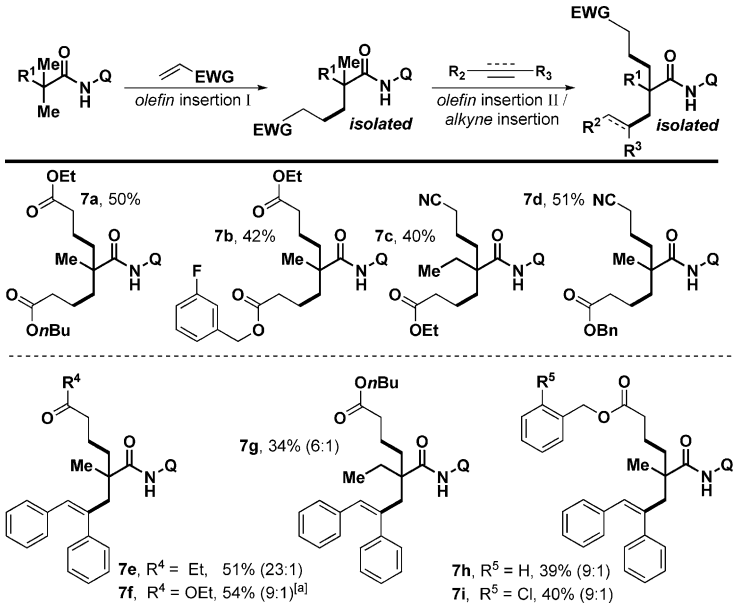
Scheme 4. Scope with unsymmetrical internal alkyne. *Z/E* ratios were determined by ^{1}H NMR analysis of the isolated compound (see the Supporting Information). [a] 20 mol% PPh_3. [b] Reaction in NMP solvent. [c] Another isomer present in 7:1 ratio.



Scheme 5. Regioselective alkyne insertion.



Scheme 6. Insertion of electron-deficient olefins at unactivated sp^3 C–H. Isolated yields of bis-alkylated products are given in parenthesis.



Scheme 7. Sequential insertion of electron-deficient olefins and alkynes. Isolated yields of *second* insertion step given. *Z*/*E* ratios are given in parenthesis. [a] Reaction at 160 °C with PPh_3 as ligand.

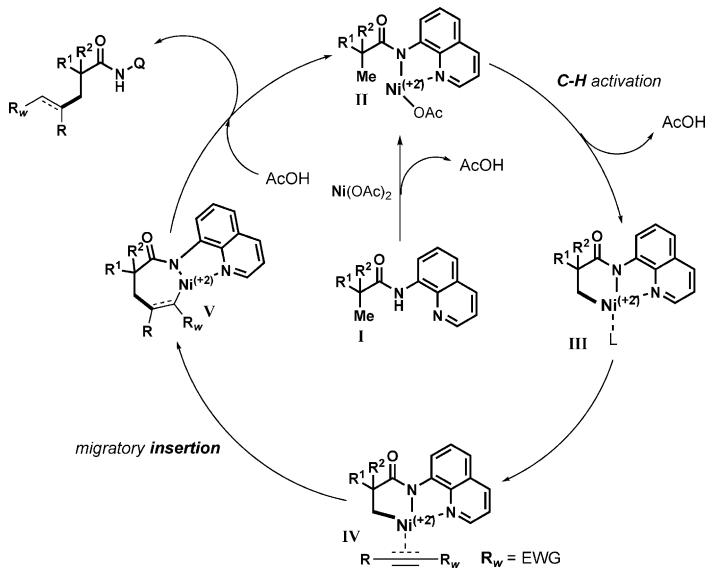
acrylates (with -OMe, -F, -Cl groups), and acrylonitriles could be successfully reacted with useful synthetic yields and exclusive linear selectivity (Scheme 6).

Various alkyl (**6d** and **6f**), benzyl (**6o**) and phenyl (**6p**) groups at the α-carbon can be tolerated as well. Even heavily substituted 2,2-diphenyl-*N*-(quinolin-8-yl)propanamide, which remained completely unreacted with diphenylacetylene, was found to undergo the desired reaction with acrylates albeit in low yield (**6q**). These results indicate the potential intermediacy of a seven-membered nickellacycle, the formation and stability of which can be influenced by the steric environment of the adjacent quaternary center (see below, migratory insertion from **IV** to **V** in Scheme 8). The absence of a bis-alkenylated product with alkynes in Schemes 3 and 4 further supports the steric dependence of the present reaction. In sharp contrast, minor amounts bis-alkylation were observed in case of the sterically less demanding acrylates/acrylonitriles on several occasions. We thought to take advantage of this observation and planned for successive insertion of activated olefins into the aliphatic amides (Scheme 7).

Similar to the hetero-bis-alkylation, iterative olefin and alkyne insertion was also envisaged. It should be noted that tethered functional groups with ligating atoms might inhibit the progress of the reaction by competitive coordination of the vacant site on the nickellacycle intermediate **IV** (Scheme 8). In reality, substrates with a nitrile group at δ-positions (Scheme 6, **6h** and **6i**) were found to be completely unreactive in the sequential alkyne insertion step. Nonetheless, ester functional groups containing alkylated products were further alkenylated with a slight excess of nickel catalyst.

The modest stereoselectivity observed in several cases might be attributed to a long-lived Ni–H species, although any experimental evidence for such species could not be obtained at this point. In terms of the crucial C–H activation step, a direct oxidative addition of Ni^{II} to the sp^3 C–H bond seems less likely. A concerted metalation–deprotonation (CMD) pathway can be proposed, despite the fact that addition of bases did not help in the progress of the reaction.[19b,h,23] In our best assumption, an acetate counter anion is aiding the C–H activation step and acting as a proton shuttle to close the catalytic cycle (Scheme 8). A detail investigation is planned for mechanistic understanding of these insertion reactions.

In summary, we have developed the first insertion of alkynes and electron-deficient olefins into unactivated sp^3 C–H bonds. A broad range of symmetrical and unsymmetrical alkynes and activated olefins with different functional groups such as -OMe, -F, -Cl, -Br, $-CO_2Me$, $-NO_2$, $-CF_3$ have been included in this study. Rational design of the substrates shed light on the electronic dependence of the insertion step. In addition, inexpensive and a shelf-stable Ni^{II} salt has been successfully employed for the synthesis of more than 50 new chemical entities. This work is expected to inspire related developments in the near future.



Scheme 8. Plausible mechanism for alkyne and olefin insertion.

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Keywords: alkynes · insertion · nickel · olefins · unactivated sp^3

[1] a) D. J. Schipper, M. Hutchinson, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6910; b) N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449; c) J. Kwak, Y. Ohk, Y. Jung, S. Chang, *J. Am. Chem. Soc.* **2012**, *134*, 17778 – 17788; d) B. Ye, N. Cramer, *Science* **2012**, *338*, 504; e) D. Zhao, Z. Shi, F. Glorius, *Angew. Chem. Int. Ed.* **2013**, *52*, 12426; *Angew. Chem.* **2013**, *125*, 12652; f) C. M. Filloux, T. Rovis, *J. Am. Chem. Soc.* **2014**, *136*, 508; g) B. Ye, P. A. Donets, N. Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 507; *Angew. Chem.* **2014**, *126*, 517.

[2] a) C. S. Sevov, J. F. Hartwig, *J. Am. Chem. Soc.* **2013**, *135*, 2116; b) T. Shibata, T. Shizuno, *Angew. Chem. Int. Ed.* **2014**, *53*, 5410; *Angew. Chem.* **2014**, *126*, 5514; c) G. E. M. Crisenza, N. G. McCreanor, J. F. Bower, *J. Am. Chem. Soc.* **2014**, *136*, 10258.

[3] a) C. G. Jia, W. J. Lu, J. Oyamada, T. Kitamura, K. Matsuda, M. Irie, Y. Fujiwara, *J. Am. Chem. Soc.* **2000**, *122*, 7252; b) C. G. Jia, D. G. Piao, J. Z. Oyamada, W. J. Lu, T. Kitamura, Y. Fujiwara, *Science* **2000**, *287*, 1992; c) N. Tsukada, T. Mitsuboshi, H. Setoguchi, Y. Inoue, *J. Am. Chem. Soc.* **2003**, *125*, 12102; d) M. Ahlquist, G. Fabrizi, S. Cacchi, P.-O. Norrby, *J. Am. Chem. Soc.* **2006**, *128*, 12785; e) N. Chernyak, V. Gevorgyan, *J. Am. Chem. Soc.* **2008**, *130*, 5636; f) Y. Minami, Y. Shiraishi, K. Yamada, T. Hiyama, *J. Am. Chem. Soc.* **2012**, *134*, 6124; g) M. R. Kuram, M. Bhanuchandra, A. K. Sahoo, *Angew. Chem. Int. Ed.* **2013**, *52*, 4607; *Angew. Chem.* **2013**, *125*, 4705.

[4] a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993**, *366*, 529 – 531; b) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826 – 834; c) M. Schinkel, I. Marek, L. Ackermann, *Angew. Chem. Int. Ed.* **2013**, *52*, 3977; *Angew. Chem.* **2013**, *125*, 4069; d) L. Ackermann, *Acc. Chem. Res.* **2014**, *47*, 281.

[5] a) Y. Nakao, K. S. Kanyiva, S. Oda, T. Hiyama, *J. Am. Chem. Soc.* **2006**, *128*, 8146; b) K. S. Kanyiva, Y. Nakao, T. Hiyama, *Angew. Chem. Int. Ed.* **2007**, *46*, 8872; *Angew. Chem.* **2007**, *119*, 9028; c) Y. Nakao, K. S. Kanyiva, T. Hiyama, *J. Am. Chem. Soc.* **2008**, *130*, 2448; d) Y. Nakao, N. Kashihara, K. S. Kanyiva, T. Hiyama, *J. Am. Chem. Soc.* **2008**, *130*, 16170; e) Y. Nakao, H. Idei, K. S. Kanyiva, T. Hiyama, *J. Am. Chem. Soc.* **2009**, *131*, 15996; f) Y. Nakao, N. Kashihara, K. S. Kanyiva, T. Hiyama, *Angew. Chem. Int. Ed.* **2010**, *49*, 4451; *Angew. Chem.* **2010**, *122*, 4553; g) R. Tamura, Y. Yamada, Y. Nakao, T. Hiyama, *Angew. Chem. Int. Ed.* **2012**, *51*, 5679; *Angew. Chem.* **2012**, *124*, 5777; h) J. S. Bair, Y. Schramm, A. G. Sergeev, E. Clot, O. Eisenstein, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 13098; i) P. A. Donets, N. Cramer, *Angew. Chem. Int. Ed.* **2015**, *54*, 633; *Angew. Chem.* **2015**, *127*, 643.

[6] a) K. Gao, P.-S. Lee, T. Fujita, N. Yoshikai, *J. Am. Chem. Soc.* **2010**, *132*, 12249; b) K. Gao, N. Yoshikai, *J. Am. Chem. Soc.* **2011**, *133*, 400; c) K. Gao, N. Yoshikai, *Angew. Chem. Int. Ed.* **2011**, *50*, 6888; *Angew. Chem.* **2011**, *123*, 7020; d) P.-S. Lee, T. Fujita, N. Yoshikai, *J. Am. Chem. Soc.* **2011**, *133*, 17283; e) L. Ilies, Q. Chen, X. Zeng, E. Nakamura, *J. Am. Chem. Soc.* **2011**, *133*, 5221; f) Z. Ding, N. Yoshikai, *Angew. Chem. Int. Ed.* **2013**, *52*, 8574; *Angew. Chem.* **2013**, *125*, 8736; g) P.-S. Lee, N. Yoshikai, *Angew. Chem. Int. Ed.* **2013**, *52*, 1240; *Angew. Chem.* **2013**, *125*, 1278; h) T. Andou, Y. Saga, H. Komai, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.* **2013**, *52*, 3213; *Angew. Chem.* **2013**, *125*, 3295.

[7] a) B. Zhou, H. Chen, C. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 1264; b) R. He, Z.-T. Huang, Q.-Y. Zheng, C. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4950; *Angew. Chem.* **2014**, *126*, 5050; c) B. Zhou, P. Ma, H. Chen, C. Wang, *Chem. Commun.* **2014**, *50*, 14558.

[8] a) J. Kischel, I. Jovel, K. Mertins, A. Zapf, M. Beller, *Org. Lett.* **2006**, *8*, 19; b) M. Y. Wong, T. Yamakawa, N. Yoshikai, *Org. Lett.* **2015**, *17*, 442.

[9] a) B.-T. Guan, Z. Hou, *J. Am. Chem. Soc.* **2011**, *133*, 18086; b) G. Luo, Y. Luo, J. Qu, Z. Hou, *Organometallics* **2012**, *31*, 3930; c) J. Oyamada, Z. Hou, *Angew. Chem. Int. Ed.* **2012**, *51*, 12828; *Angew. Chem.* **2012**, *124*, 13000; d) G. Song, W. N. O. Wylie, Z. Hou, *J. Am. Chem. Soc.* **2014**, *136*, 12209.

[10] a) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208; b) D.-G. Yu, F. de Azambuja, T. Gensch, C. G. Daniliuc, F. Glorius, *Angew. Chem. Int. Ed.* **2014**, *53*, 9650; *Angew. Chem.* **2014**, *126*, 9804; c) D. Zhao, F. Lied, F. Glorius, *Chem. Sci.* **2014**, *5*, 2869; d) W. Xu, N. Yoshikai, *Angew. Chem. Int. Ed.* **2014**, *53*, 14166; *Angew. Chem.* **2014**, *126*, 14390; e) X. Hu, D. Martin, M. Melaimi, G. Bertrand, *J. Am. Chem. Soc.* **2014**, *136*, 13594; f) M. C. Reddy, M. Jeganmohan, *Chem. Commun.* **2013**, *49*, 481; g) Q. Tang, D. Xia, X. Jin, Q. Zhang, X.-Q. Sun, C. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 4628; h) T. A. Davis, T. K. Hyster, T. Rovis, *Angew. Chem. Int. Ed.* **2013**, *52*, 14181; *Angew. Chem.* **2013**, *125*, 14431; i) P. A. Donets, N. Cramer, *J. Am. Chem. Soc.* **2013**, *135*, 11772; j) S. Pan, N. Ryu, T. Shibata, *J. Am. Chem. Soc.* **2012**, *134*, 17474; k) J. Ryu, S. H. Cho, S. Chang, *Angew. Chem. Int. Ed.* **2012**, *51*, 3677; *Angew. Chem.* **2012**, *124*, 3737.

[11] a) Y. Minami, K. Yamada, T. Hiyama, *Angew. Chem. Int. Ed.* **2013**, *52*, 10611; *Angew. Chem.* **2013**, *125*, 10805; b) B. Liu, T. Zhou, B. Li, S. Xu, H. Song, B. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4191; *Angew. Chem.* **2014**, *126*, 4275.

[12] S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585.

[13] N. Chernyak, S. I. Gorelsky, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2011**, *50*, 2342; *Angew. Chem.* **2011**, *123*, 2390.

[14] a) C.-H. Jun, *Chem. Commun.* **1998**, 1405; b) N. Chatani, T. Asaumi, S. Yorimitsu, T. Ikeda, F. Kakiuchi, S. Murai, *J. Am. Chem. Soc.* **2001**, *123*, 10935; c) S. Pan, K. Endo, T. Shibata, *Org. Lett.* **2011**, *13*, 4692; d) G. Lahm, T. Opatz, *Org. Lett.* **2014**, *16*, 4201; e) M. Schinkel, L. Wang, K. Bielefeld, L. Ackermann, *Org. Lett.* **2014**, *16*, 1876; f) E. Chong, J. W. Brandt, L. L. Schafer, *J. Am. Chem. Soc.* **2014**, *136*, 10898; g) B. DeBoef, S. J. Pastine, D. Sames, *J. Am. Chem. Soc.* **2004**, *126*, 6556; h) L. Shi, Y.-Q. Tu, M. Wang, F.-M. Zhang, C.-A. Fan, Y.-M. Zhao, W.-J. Xia, *J. Am. Chem. Soc.* **2005**, *127*, 10836; i) Y.-J. Jiang, Y.-Q. Tu, E. Zhang, S.-Y. Zhang, K. Cao, L. Shi, *Adv. Synth. Catal.* **2008**, *350*, 552; j) A. A. Kulago, B. F. Van Steijvoort, E. A. Mitchell, L. Meerpoel, B. U. W. Maes, *Adv. Synth. Catal.* **2014**, *356*, 1610; k) S. D. Bergman, T. E. Storr, H. Prokopcova, K. Aelvoet, G. Diels, L. Meerpoel, B. U. W. Maes, *Chem. Eur. J.* **2012**, *18*, 10393; l) S. Pan, Y. Matsuo, K. Endo, T. Shibata, *Tetrahedron* **2012**, *68*, 9009; m) L. Huang, K. Cheng, B. Yao, J. Zhao, Y. Zhang, *Synthesis* **2009**, 3504.

[15] Y. Nakao, E. Morita, H. Idei, T. Hiyama, *J. Am. Chem. Soc.* **2011**, *133*, 3264.

[16] R. Jazzar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654.
[17] N. Mori, S. Ikeda, K. Odashima, *Chem. Commun.* **2001**, 181.
[18] a) V. G. Zaitsev, D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2005**, *127*, 13154; b) G. Qiu, J. Wu, *Org. Chem. Front.* **2015**, *2*, 169; c) Z. Huang, G. Dong, *Tetrahedron Lett.* **2014**, *55*, 5869.
[19] a) G. Rouquet, N. Chatani, *Angew. Chem. Int. Ed.* **2013**, *52*, 11726; *Angew. Chem.* **2013**, *125*, 11942; b) Y. Aihara, N. Chatani, *J. Am. Chem. Soc.* **2014**, *136*, 898; c) Y. Aihara, N. Chatani, *J. Am. Chem. Soc.* **2013**, *135*, 5308; d) Y. Aihara, M. Tobisu, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2014**, *136*, 15509; e) R. Shang, L. Ilies, A. Matsumoto, E. Nakamura, *J. Am. Chem. Soc.* **2013**, *135*, 6030; f) M. Iyanaga, Y. Aihara, N. Chatani, *J. Org. Chem.* **2014**, *79*, 11933; g) A. Yokota, Y. Aihara, N. Chatani, *J. Org. Chem.* **2014**, *79*, 11922; h) X. Wu, Y. Zhao, H. Ge, *J. Am. Chem. Soc.* **2014**, *136*, 1789; i) X. Wu, Y. Zhao, H. Ge, *Chem. Eur. J.* **2014**, *20*, 9530.
[20] a) H. Shiota, Y. Ano, Y. Aihara, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2011**, *133*, 14952; b) G. Rouquet, N. Chatani, *Chem. Sci.* **2013**, *4*, 2201; c) K. Shibata, N. Chatani, *Org. Lett.* **2014**, *16*, 5148; d) L. Grigorjeva, O. Daugulis, *Angew. Chem. Int. Ed.* **2014**, *53*, 10209; *Angew. Chem.* **2014**, *126*, 10373; e) L. Grigorjeva, O. Daugulis, *Org. Lett.* **2014**, *16*, 4684.
[21] K. J. Stowers, K. C. Fortner, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 6541.
[22] a) M. Wasa, K. M. Engle, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 3680; b) S. Li, G. Chen, C.-G. Feng, W. Gong, J.-Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 5267; c) R.-Y. Zhu, J. He, X.-C. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 13194.
[23] Y. Dang, S. Qu, J. W. Nelson, H. D. Pham, Z.-X. Wang, X. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 2006.

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