

N-Oxide as a Traceless Oxidizing Directing Group: Mild Rhodium(III)-Catalyzed C–H Olefination for the Synthesis of *ortho*-Alkenylated Tertiary Anilines**

Xiaolei Huang, Jingsheng Huang, Chenglong Du, Xingyi Zhang, Feijie Song, and Jingsong You*

Tertiary anilines are important structural motifs frequently found in pharmaceuticals, dyes, natural products, biologically active molecules, and organic functional materials,^[1] and their functionalization has been attracting great interest in the synthetic organic chemistry community. It is well known that the electron-donor characteristics and the steric hindrance of tertiary amino groups commonly lead to the preferential *para*-functionalization of anilines through the Friedel–Crafts pathway and renders the *ortho*-selective C–H functionalization of tertiary anilines difficult. Therefore, the transition-metal-catalyzed chelation-assisted aromatic C–H functionalization through a cyclometalation should be an ideal strategy to meet these substantial challenges.^[2]

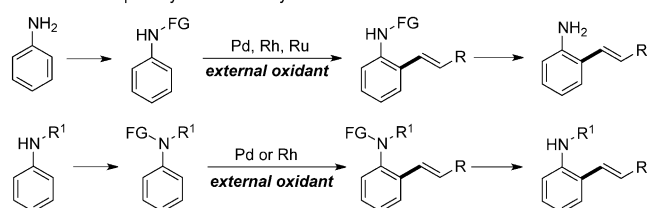
Generally, primary and secondary anilines can be conveniently substituted to install various directing groups (e.g., the NH- or N-substituted urea and amide, phosphoramidate, 2-pyridylsulfonyl, 2-pyridyl, *N*-nitroso, and methanesulfonamide groups) for aromatic C–H functionalization at the proximal site.^[3] Very recently, Miura et al. and Jiao et al. have reported that primary anilines can serve as a directing group for *ortho* C–H olefination and azidation, respectively.^[4,5] In addition, the *N,N*-dimethylaminomethyl group has been disclosed as a directing group for both oxidative Heck and arylation reactions.^[6] However, the transition-metal-catalyzed C–H activation of tertiary anilines remains less developed except for few examples on *para*-selective transformations^[7] and the recently reported oxidative *ortho* C–H alkenylation/*N*-dealkylative carbonylation of tertiary anilines (tertiary amines probably act as a directing group).^[8] Therefore, it is highly valuable to develop C–H activation for the synthesis of *ortho*-functionalized tertiary anilines.

While the amino group of tertiary anilines is directly used as the directing group, the four-membered cyclometalated intermediate will be formed. This type of cyclometalated species is usually not easily available. Recently, the use of oxidizing directing groups as both internal oxidants and

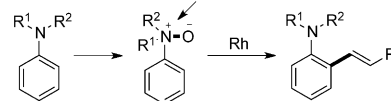
directing groups is starting to attract interest in C–H activation,^[9] which has the clear advantages of high levels of selectivity for *ortho* and monocoupling as well as improved levels of reactivity. The elegant contributions from the research groups of Cui and Wu, Fagnou, Glorius, Ackermann, Hartwig, Li, Jeganmohan, Chiba, and Lu have disclosed that quinoline *N*-oxides, hydroxamic acids and their derivatives, oximines, vinyl azides, and *N*-phenoxyacetamides can undergo an external-oxidant-free C–H activation reactions.^[10] It is known that easily available tertiary aniline *N*-oxides are not only prototypical oxidants,^[11] but also coordinate readily to metal centers.^[12] In addition, several reports have shown that the functionalization at *ortho* position to the nitrogen atom of pyridine and other heterocycles can be achieved by using the *N*-oxide group as a key platform.^[10a,13] Therefore, we envisioned that these properties could be combined to develop a strategy based on a traceless oxidizing directing group to achieve the *ortho*-selective aromatic C–H functionalization of tertiary anilines, in which the five-membered cyclometalated intermediate could be formed easily.

The metal-catalyzed oxidative olefination of aryl C–H bonds has emerged as one of the most important methods for creating functionally diverse and structurally complex aromatic compounds.^[14,15] In recent reports, acetanilide and its derivatives, *N*-(2-pyridyl)sulfonyl anilines, and *N*-nitrosamines have proven to be very effective in directing transition-metal-catalyzed C–H olefination (Scheme 1).^[3g,i,16] Herein, we report on the Rh-catalyzed *ortho* C–H olefination of tertiary aniline *N*-oxides to illustrate our strategy based on a directing group that is also an internal oxidant for the *ortho* functionalization of tertiary anilines (Scheme 1).

Previous work: primary and secondary anilines



This work: tertiary anilines
traceless DG and internal oxidant



Scheme 1. Evolution of the transition-metal-catalyzed *ortho*-selective C–H olefination of diverse anilines. FG = functional group, DG = directing group.

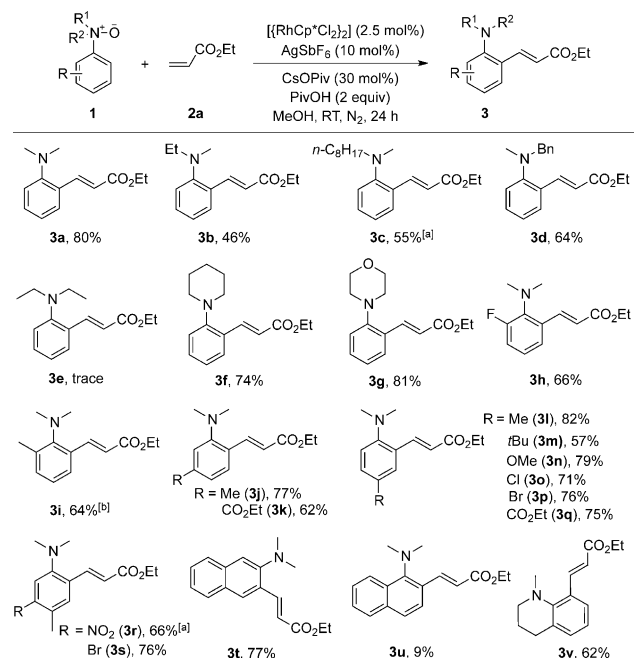
[*] X. Huang, J. Huang, C. Du, X. Zhang, Dr. F. Song, Prof. Dr. J. You
Key Laboratory of Green Chemistry and Technology of Ministry of
Education, College of Chemistry
and State Key Laboratory of Biotherapy
West China Medical School, Sichuan University
29 Wangjiang Road, Chengdu 610064 (PR China)
E-mail: jsyou@scu.edu.cn

[**] This work was supported by grants from the National Basic
Research Program of China (973 Program, 2011CB808600), and the
National NSF of China (nos. 21025205, 21272160, 21021001, and
J1103315J0104).

Supporting information for this article is available on the WWW
under <http://dx.doi.org/10.1002/anie.201307174>.

We started our exploration with attempts to perform the olefination of *N,N*-dimethylaniline *N*-oxide (**1a**) with ethyl acrylate (**2a**) to afford the *ortho*-alkenylated *N,N*-dimethylaniline **3a** (for details, see Table S1 in the Supporting Information). After we had screened several parameters (e.g., metal source, additive, and solvent), the catalytic system comprising $[(\text{Cp}^*\text{RhCl}_2)_2]$ (2.5 mol %), $(\text{Cp}^* = \text{C}_5\text{Me}_5)$, AgSbF_6 (10 mol %), CsOPiv (30 mol %), and PivOH (2.0 equiv) in MeOH proved to be efficient. Under these conditions, **3a** was obtained in 75 % yield along with a trace amount of *N,N*-dimethylaniline (less than 5 %), which ruled out the action of tertiary aniline *N*-oxides as external oxidants (Table S1, entry 15). Further experiments indicated that an excess of *N*-oxide **1a** turned out to benefit the coupling reaction, and **3a** was obtained in 89 % yield at 90 °C (Table S1, entry 16). We were pleased to find that the reaction could give the coupled product **3a** in 80 % yield along with the recovery of 0.8 equiv of *N*-oxide **1a** at room temperature (Table S1, entries 17 and 18). It is worth noting that no product was observed when *N,N*-dimethylaniline was used instead of **1a** (Table S1, entry 19).

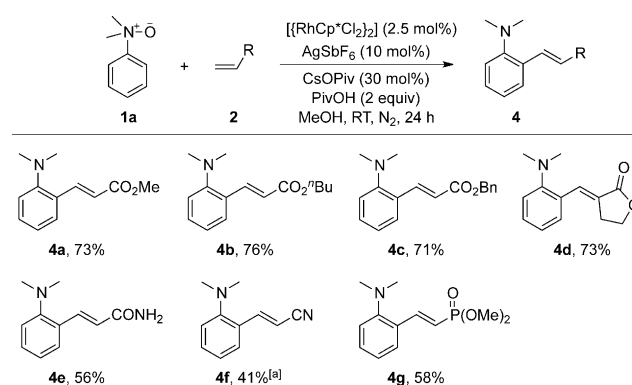
With the optimized conditions in hand, we next examined the scope of this methodology. As summarized in Scheme 2, various *N*-methyl-*N*-alkylaniline *N*-oxides smoothly reacted with acrylate **2a** to afford the corresponding mono-alkenylated products in moderate to high yields. For example, *N*-benzyl-*N*-methylaniline *N*-oxide coupled with **2a** to afford **3d** in 64 % yield. The reactive site is located in the C2 position of the aniline rather than the aromatic ring of the benzyl group. Moreover, cyclic amine *N*-oxides could be transformed to the desired products in satisfactory yields (**3f** and **3g**). Aniline *N*-



Scheme 2. The scope of the tertiary aniline *N*-oxides. Unless otherwise noted, the reactions were performed using **1** (1.0 mmol), **2a** (0.5 mmol), and MeOH (1 mL) at room temperature for 24 h. Yields refer to the yield of isolated product based on **2a**. [a] Reaction temperature: 90 °C. [b] Reaction time: 48 h.

oxides possessing either electron-donating or electron-withdrawing groups on the phenyl ring could undergo the olefination (**3h–3q**). 3,4-Disubstituted *N,N*-dimethylaniline *N*-oxides smoothly afforded the products in good yields (**3r** and **3s**). The completely regioselective coupling occurred at the sterically less hindered position. Surprisingly, the 2-naphthylamine-derived *N*-oxide gave the C3-alkenylated product in 77 % yield, whereas *N,N*-dimethyl-1-naphthylamine *N*-oxide produced the C2-alkenylated target in only 9 % yield (**3t** and **3u**). *N*-Methyl-1,2,3,4-tetrahydroquinoline *N*-oxide underwent this transformation in 62 % yield (**3v**). It is notable that *N,N*-diethylaniline *N*-oxide had limited reactivity under the optimized conditions probably due to the steric hindrance of diethyl group (**3e**).

Subsequently, we investigated the scope of olefins and found that other acrylates had similar reactivity (Scheme 3, **4a–4d**). Acrylamide and vinyl phosphonate also served in the olefination to give products in acceptable yields (Scheme 3, **4e** and **4g**). The rhodium-catalyzed coupling of acrylonitrile with **1a** required an elevated temperature (90 °C).



Scheme 3. The scope of the olefins. Unless otherwise noted, the reactions were performed using **1** (1.0 mmol), **2a** (0.5 mmol), and MeOH (1 mL) at room temperature. Yields refer to the yield of isolated product based on **2**. [a] Reaction temperature: 90 °C.

Alkenylated tertiary anilines frequently appear in organic functional materials such as OLEDs and photoluminescent materials.^[1a,b,d,17] In this context, we examined the synthetic usefulness of our protocol for the rapid elongation of π -conjugated skeletons of existing tertiary dianilines for the screening of fluorescent molecules. (*E,E*)-2,5-Bis[2-(ethoxycarbonyl)ethenyl]-1,4-dipiperidinobenzene (**6a**), a minimal fluorophore reported by the Shimizu group,^[17a] could be obtained in a very simple manner through the coupling of 1,4-bis(*N*-piperidinyl)benzene *N,N'*-dioxide (**5a**) with ethyl acrylate (**2a**). Nonfluorescent *N,N,N,N*-tetramethyl-(1,1'-biphenyl)-4,4'-diamine and *N,N,N,N*-tetramethyl-(1,1'-biphenyl)-3,3'-diamine could be conveniently transformed to the luminescent dialkenylated tertiary dianilines **6b** and **6c**, respectively. These novel π -conjugated molecules with a “push–pull” π -electron system exhibited significant fluorescence emission in both the solid state and in solution (Figure 1; for details, see Figures S1–S3 and Tables S2–S4 in the Supporting Information).

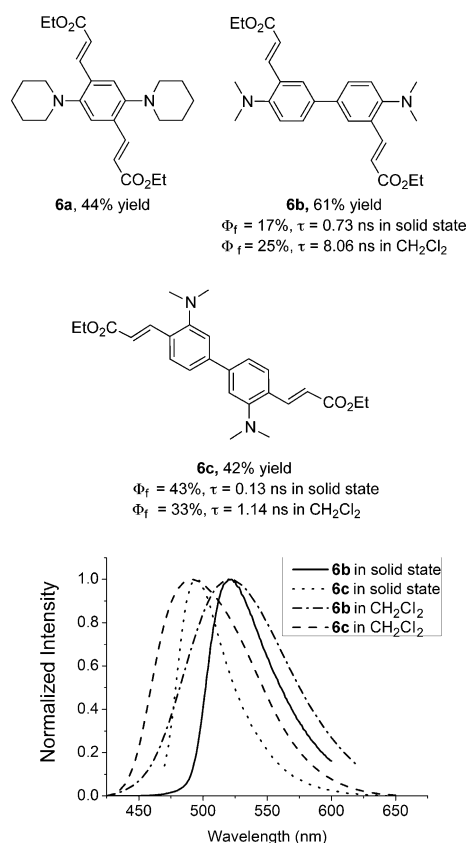
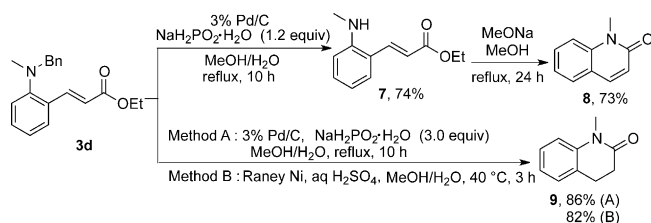


Figure 1. Top: Structures of **6a–c**. Bottom: Normalized emission spectra of **6b** and **6c**.

Subsequently, we tried to perform debenzylation of **3d** (Scheme 4). Using 3% Pd/C and 1.2 equiv of NaH₂PO₂·H₂O in MeOH/H₂O,^[18a] we obtained the secondary aniline **7** in

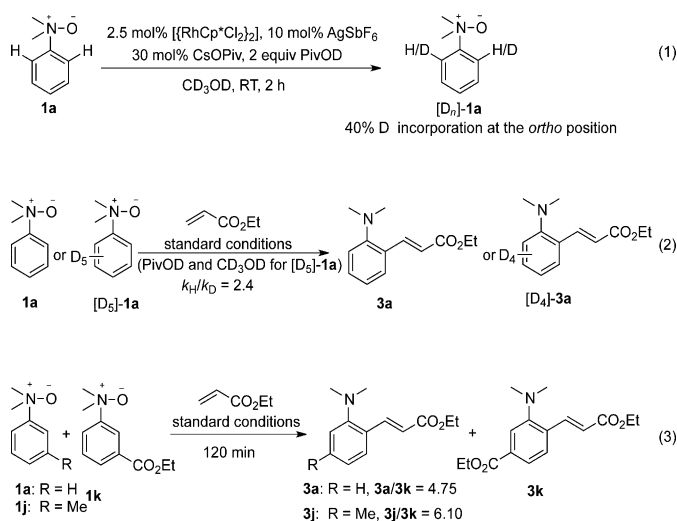


Scheme 4. Debenzylation of **3d**.

74% yield, which could further be transformed into 1-methylquinolin-2(1*H*)-one (**8**) in 73% yield.^[18b] Interestingly, when we increased the amount of NaH₂PO₂·H₂O to 3.0 equiv, debenzylation and reduction of alkene occurred synchronously to produce 1-methyl-3,4-dihydroquinolin-2(1*H*)-one (**9**) in 86% yield. The system of Raney Ni in MeOH/H₂O/H₂SO₄ could also realize this transformation in 82% yield.^[18c] It is worth noting that both quinolin-2(1*H*)-one and 3,4-dihydroquinolin-2(1*H*)-one derivatives are structural units found in many pharmacologically important natural and synthetic compounds, and also are versatile building blocks for the synthesis of structurally complex compounds.^[3i,19]

To gain insight into the mechanism of the olefination, the following experiments were conducted. A hydrogen/deuterium exchange experiment showed that cleavage of the *ortho* C–H bond was a reversible process [Eq. (1)]. A primary kinetic isotopic effect (KIE) of 2.4 was observed for two parallel competition reactions between **1a** and [D₅]-**1a** with ethyl acrylate (**2a**) [Eq. (2)],^[10i,20,21] which revealed that the C–H bond cleavage might be involved in the rate-determining step.^[22] In addition, the competition reactions between electronically differentiated **1a** and **1k**, and **1j** and **1k** with **2a** afforded **3a/3k** and **3j/3k** in ratios of 4.75 and 6.10, respectively [Eq. (3)]. The higher reactivity of the electron-rich arenes suggests that an electrophilic-type rhodation might be involved in the catalytic cycle.^[23]

Fortunately, the five-membered cyclometalated Rh^{III} complex **10** was obtained and its structure was established by X-ray crystallographic analysis (Figure 2).^[24] The complex **10** could not only react stoichiometrically with ethyl acrylate (**2a**), but also catalyze the olefination of **1p** to afford the



desired product **3p** in 42% and 63% yield, respectively (for details, see the Supporting Information, Part IX), which implies the possible intermediacy of a five-membered complex in the catalytic cycle.

Based on the above observations, a plausible mechanistic pathway is proposed (Scheme 5). First, the cyclorhodium intermediate **A** was formed through the reaction of *N*-oxide with the [Rh^{III}Cp*] species generated from [(RhCp*Cl₂)₂] and AgSbF₆, and a subsequent reversible carboxylate-assisted

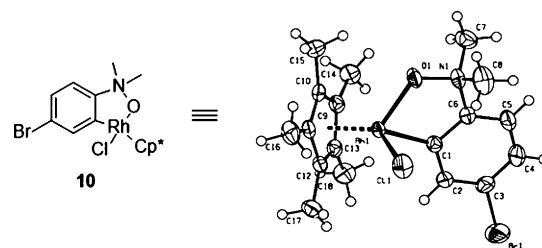
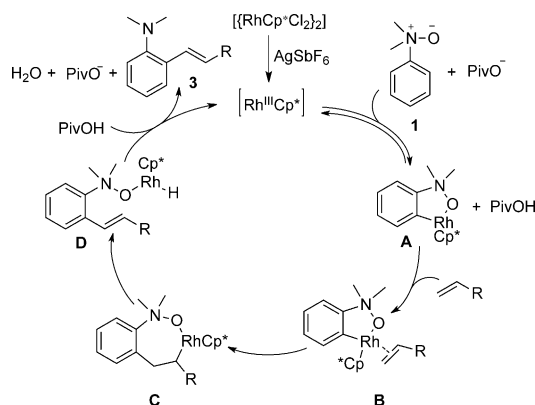


Figure 2. ORTEP diagram of complex **10**. Thermal ellipsoids are shown at the 50% probability level.



Scheme 5. Plausible mechanistic pathway.

electrophilic C–H activation process.^[2b,23] The resulting intermediate **A** coordinated with an olefin to give the complex **B**, which was transformed into **C** by migratory insertion of alkene. After β -hydride elimination along with the N–O bond cleavage, the desired product was released, and $[\text{Rh}^{\text{III}}\text{Cp}^*]$ species was regenerated to complete the catalytic cycle.

In summary, we have addressed a novel strategy based on a traceless directing group that is also an internal oxidant to achieve the *ortho* C–H functionalization of tertiary anilines. This tactic was used for the highly selective *ortho* C–H olefination of easily available tertiary aniline *N*-oxides to prepare 2-alkenylated tertiary anilines. The rhodium-catalyzed external-oxidant-free synthesis presents a series of advantages, such as very mild conditions (room temperature), avoidance of bisolefinated anilines, complete *ortho* selectivity, and relatively broad functional group tolerance. We believe that this protocol represents a practical route to alkenylated tertiary anilines.

Received: August 15, 2013

Published online: November 12, 2013

Keywords: anilines · C–H activation · olefination · directing groups

- [1] For selected reviews, see: a) C.-T. Chen, *Chem. Mater.* **2004**, *16*, 4389; b) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595; c) P. Ruiz-Sanchis, S. A. Savina, F. Albericio, M. Álvarez, *Chem. Eur. J.* **2011**, *17*, 1388; d) M. Liang, J. Chen, *Chem. Soc. Rev.* **2013**, *42*, 3453; For selected books, see: e) C.-G. Wermuth, *The Practice of Medicinal Chemistry*, 3rd ed., Academic Press, London, **2008**; f) M. Waser in *Progress in the Chemistry of Organic Natural Products*, Vol. 96 (Eds.: A. D. Kinghorn, H. Falk, J. Kobayashi), Springer, New York, **2012**.
- [2] For selected reviews, see: a) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; b) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315; c) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; d) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788.
- [3] For selected examples, see: a) X. Wan, Z. Ma, B. Li, K. Zhang, S. Cao, S. Zhang, Z. Shi, *J. Am. Chem. Soc.* **2006**, *128*, 7416; b) A. Jean, J. Cantat, D. Bérard, D. Bouchu, S. Canesi, *Org. Lett.* **2007**, *9*, 2553; c) C. E. Houlden, C. D. Bailey, J. G. Ford, M. R. Gagné, G. C. Lloyd-Jones, K. I. Booker-Milburn, *J. Am. Chem. Soc.* **2008**, *130*, 10066; d) B.-J. Li, S.-L. Tian, Z. Fang, Z.-J. Shi, *Angew. Chem.* **2008**, *120*, 1131; *Angew. Chem. Int. Ed.* **2008**, *47*, 1115; e) M. Tobisu, Y. Ano, N. Chatani, *Org. Lett.* **2009**, *11*, 3250; f) J. Chen, G. Song, C.-L. Pan, X. Li, *Org. Lett.* **2010**, *12*, 5426; g) A. García-Rubia, B. Urones, R. G. Arrayás, J. C. Carretero, *Angew. Chem.* **2011**, *123*, 11119; *Angew. Chem. Int. Ed.* **2011**, *50*, 10927; h) B. C. Chary, S. Kim, Y. Park, J. Kim, P. H. Lee, *Org. Lett.* **2013**, *15*, 2692; i) B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, *J. Am. Chem. Soc.* **2013**, *135*, 468.
- [4] C. Suzuki, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2013**, *15*, 3990.
- [5] C. Tang, N. Jiao, *J. Am. Chem. Soc.* **2012**, *134*, 18924.
- [6] a) G. Cai, Y. Fu, Y. Li, X. Wan, Z. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 7666; b) R. Feng, J. Yao, Z. Liang, Z. Liu, Y. Zhang, *J. Org. Chem.* **2013**, *78*, 3688.
- [7] a) C.-L. Ciana, R. J. Phipps, J. R. Brandt, F.-M. Meyer, M. J. Gaunt, *Angew. Chem.* **2011**, *123*, 478; *Angew. Chem. Int. Ed.* **2011**, *50*, 458; b) Y. Mizuta, Y. Obora, Y. Shimizu, Y. Ishii, *ChemCatChem* **2012**, *4*, 187.
- [8] At the time we submitted our manuscript, Lei et al. reported an efficient strategy to prepare 3-methyleneindolin-2-one derivatives by palladium/copper-catalyzed selective C–H alkenylation and the subsequent N-dealkylative carbonylation of tertiary anilines. See: R. Shi, L. Lu, H. Zhang, B. Chen, Y. Sha, C. Liu, A. Lei, *Angew. Chem.* **2013**, *125*, 10776; *Angew. Chem. Int. Ed.* **2013**, *52*, 10582.
- [9] For a Highlight article, see: F. W. Patureau, F. Glorius, *Angew. Chem.* **2011**, *123*, 2021; *Angew. Chem. Int. Ed.* **2011**, *50*, 1977.
- [10] For selected examples, see: a) J. Wu, X. Cui, L. Chen, G. Jiang, Y. Wu, *J. Am. Chem. Soc.* **2009**, *131*, 13888; b) N. Guimond, C. Gouliaras, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6908; c) Y. Tan, J. F. Hartwig, *J. Am. Chem. Soc.* **2010**, *132*, 3676; d) N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449; e) Y.-F. Wang, K. K. Toh, J.-Y. Lee, S. Chiba, *Angew. Chem.* **2011**, *123*, 6049; *Angew. Chem. Int. Ed.* **2011**, *50*, 5927; f) S. Rakshit, C. Grohmann, T. Besset, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2350; g) L. Ackermann, S. Fenner, *Org. Lett.* **2011**, *13*, 6548; h) X. Zhang, D. Chen, M. Zhao, J. Zhao, A. Jia, X. Li, *Adv. Synth. Catal.* **2011**, *353*, 719; i) R. K. Chinnagolla, S. Pimparkar, M. Jeganmohan, *Org. Lett.* **2012**, *14*, 3032; j) H. Wang, F. Glorius, *Angew. Chem.* **2012**, *124*, 7430; *Angew. Chem. Int. Ed.* **2012**, *51*, 7318; k) G. Liu, Y. Shen, Z. Zhou, X. Lu, *Angew. Chem.* **2013**, *125*, 6149; *Angew. Chem. Int. Ed.* **2013**, *52*, 6033; l) Y. Shen, G. Liu, Z. Zhou, X. Lu, *Org. Lett.* **2013**, *15*, 3366.
- [11] a) D. H. R. Barton, A. Fekih, X. Lusinch, *Tetrahedron Lett.* **1985**, *26*, 4603; b) B. Jousseau, E. Chanson, *Synthesis* **1987**, 55; c) P. Ilankumaran, S. Chandrasekaran, *Tetrahedron Lett.* **1995**, *36*, 4881.
- [12] a) X. Liu, L. Lin, X. Feng, *Acc. Chem. Res.* **2011**, *44*, 574; b) K. Shen, X. Liu, L. Lin, X. Feng, *Chem. Sci.* **2012**, *3*, 327.
- [13] a) S. H. Cho, S. J. Hwang, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 9254; b) Y. Tan, F. Barrios-Landeros, J. F. Hartwig, *J. Am. Chem. Soc.* **2012**, *134*, 3683; c) W. Liu, Y. Li, B. Xu, C. Kuang, *Org. Lett.* **2013**, *15*, 2342.
- [14] a) J. Le Bras, J. Muzart, *Chem. Rev.* **2011**, *111*, 1170; b) S. I. Kozhushkov, L. Ackermann, *Chem. Sci.* **2013**, *4*, 886.
- [15] For selected examples, see: a) D.-H. Wang, K. M. Engle, B.-F. Shi, J.-Q. Yu, *Science* **2010**, *327*, 315; b) C. Wang, H. Chen, Z. Wang, J. Chen, Y. Huang, *Angew. Chem.* **2012**, *124*, 7354; *Angew. Chem. Int. Ed.* **2012**, *51*, 7242; c) X. Cong, J. You, G. Gao, J. Lan, *Chem. Commun.* **2013**, *49*, 662; d) G. Li, D. Leow, L. Wan, J.-Q. Yu, *Angew. Chem.* **2013**, *125*, 1283; *Angew. Chem. Int. Ed.* **2013**, *52*, 1245.

- [16] a) M. D. K. Boele, G. P. F. van Strijdonck, A. H. M. de Vries, P. C. J. Kamer, J. G. de Vries, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2002**, *124*, 1586; b) T. Nishikata, B. H. Lipshutz, *Org. Lett.* **2010**, *12*, 1972; c) F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9982; d) L. Ackermann, L. Wang, R. Wolfram, A. V. Lygin, *Org. Lett.* **2012**, *14*, 728.
- [17] For selected examples, see: a) M. Shimizu, Y. Takeda, M. Higashi, T. Hiyama, *Angew. Chem.* **2009**, *121*, 3707; *Angew. Chem. Int. Ed.* **2009**, *48*, 3653; b) M. Shimizu, R. Kaki, Y. Takeda, T. Hiyama, N. Nagai, H. Yamagishi, H. Furutani, *Angew. Chem.* **2012**, *124*, 4171; *Angew. Chem. Int. Ed.* **2012**, *51*, 4095; c) W. Qin, D. Ding, J. Liu, W. Z. Yuan, Y. Hu, B. Liu, B. Z. Tang, *Adv. Funct. Mater.* **2012**, *22*, 771.
- [18] a) B. M. Adger, C. O. Farrell, N. J. Lewis, M. B. Mitchell, *Synthesis* **1987**, 53; b) P. G. Gassman, R. L. Parton, *J. Chem. Soc. Chem. Commun.* **1977**, 694; c) M. Okimoto, Y. Takahashi, Y. Nagata, M. Satoh, S. Sueda, T. Yamashina, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1405.
- [19] a) H. Hayashi, Y. Miwa, I. Miki, S. Ichikawa, N. Yoda, A. Ishii, M. Kono, F. Suzuki, *J. Med. Chem.* **1992**, *35*, 4893; b) R. Uchida, R. Imasato, K. Shiomi, H. Tomoda, S. Omura, *Org. Lett.* **2005**, *7*, 5701; c) J. He, U. Lion, I. Sattler, F. A. Gollmick, S. Grabley, J. Cai, M. Meiners, H. Schünke, K. Schaumann, U. Dechert, M. Krohn, *J. Nat. Prod.* **2005**, *68*, 1397; d) S. Vangveravong, Z. Zhang, M. Taylor, M. Bearden, J. Xu, J. Cui, W. Wang, R. R. Luedtke, R. H. Mach, *Bioorg. Med. Chem.* **2011**, *19*, 3502; e) L. Zhang, L. Sonaglia, J. Stacey, M. Lautens, *Org. Lett.* **2013**, *15*, 2128.
- [20] For [D₅]-**1a**, PivOD and CD₃OD instead of PivOH and CH₃OH were used to exclude any influence on the kinetic isotope effect. See: J. Willwacher, S. Rakshit, F. Glorius, *Org. Biomol. Chem.* **2011**, *9*, 4736. Also see Ref. [10].
- [21] For [D₅]-**1a**, when PivOH and CH₃OH were used, a KIE value of 1.7 was obtained.
- [22] E. M. Simmons, J. F. Hartwig, *Angew. Chem.* **2012**, *124*, 3120; *Angew. Chem. Int. Ed.* **2012**, *51*, 3066.
- [23] a) L. Li, W. W. Brennessel, W. D. Jones, *Organometallics* **2009**, *28*, 3492; b) V. S. Thirunavukkarasu, K. Raghuvanshi, L. Ackermann, *Org. Lett.* **2013**, *15*, 3286.
- [24] CCDC 953990 (**10**) contains 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.