

Synthetic Methods

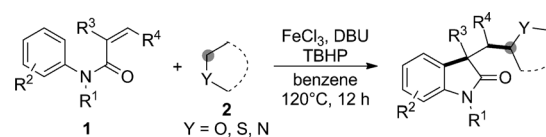
Synthesis of Oxindoles by Iron-Catalyzed Oxidative 1,2-Alkylarylation of Activated Alkenes with an Aryl C(sp²)–H Bond and a C(sp³)–H Bond Adjacent to a Heteroatom**

Wen-Ting Wei, Ming-Bo Zhou, Jian-Hong Fan, Wei Liu, Ren-Jie Song, Yu Liu, Ming Hu, Peng Xie, and Jin-Heng Li*

Oxindoles are important heterocycles found in a wide range of bioactive natural products and pharmaceutical molecules.^[1,2] In addition, functionalized oxindoles are versatile synthetic blocks for the preparation of natural products and in asymmetric synthesis. As a result, considerable efforts were directed toward the development of efficient methods for their synthesis,^[1–7] with metal-catalyzed cyclization/function-alization approaches becoming increasingly popular because of their particular efficiency.^[2–6] However, these approaches suffer from use of both expensive and commercially not available *ortho*-functionalized anilines and noble-metal catalysts, thereby limiting their wide application in organic chemistry research and industry.^[2–4]

Recently, *ortho*-nonfunctionalized anilines were found to be viable substrates for metal-mediated direct aryl C(sp²)-H functionalization/cyclization reactions, however, these transformations are quite rare.^[5,6] In 2003, Hennessey and Buchwald first used *ortho*-nonfunctionalized anilines (α -chloroacetanilides) in the formation of oxindole by a variant of the Friedel–Crafts procedure through palladium-catalyzed C–H functionalization in the presence of 2-(di-*tert*-butylphosphino)-biphenyl (ligand) and Et₃N (base).^[5a] Subsequently, Jia and Kündig developed a direct intramolecular oxidative coupling of an aryl C(sp²)-H bond and a C(sp³)-H center for the preparation of 3,3-disubstituted oxindoles, even though these reactions needed a stoichiometric amount of Cu catalyst combined with a base.^[5b,c] Very recently, the groups of Neuville and Zhu^[6a] and Liu and co-workers^[6b–d] independently established a very useful access to oxindoles by Pd-catalyzed oxidative difunctionalization of alkenes in *N*-arylacrylamides under acidic or neutral conditions. These

Pd-catalyzed oxidative transformations are more fascinating than the methods reported earlier,^[5] because additional functional groups can be introduced into the oxindole framework; however, use of highly expensive Pd/hypervalent iodine reagent systems make their application less desirable.^[6] Herein, we report a new oxidative 1,2-alkylarylation of activated alkenes with an aryl C(sp²)-H bond and a C(sp³)-H bond adjacent to a heteroatom for selective synthesis of functionalized 3-(2-oxoethyl)indolin-2-ones. This oxidative 1,2-alkylarylation is catalyzed by economical and environmentally benign iron^[8] and involves the use of *tert*-butyl hydrogenperoxide (TBHP) as oxidant and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU, **L5**) as ligand (Scheme 1). To the best of our knowledge, this work represents the first example of metal-catalyzed difunctionalization of an alkene with an aryl C(sp²)-H bond and a C(sp³)-H bond adjacent to a heteroatom.^[6b–d,9]



Scheme 1. Fe-catalyzed oxidative 1,2-alkylarylation.

We initially studied the reaction of *N*-methyl-*N*-phenylmethacrylamide (**1a**; 0.3 mmol) with Et₂O (**2a**; 20 equiv), FeCl₃ (5 mol %) in benzene at 120 °C under argon atmosphere (entry 1 in Table 1), and were able to isolate the desired oxindole **3** in 15 % yield. The presence of TBHP as oxidant enhanced the yield to 23 % (entry 2). Gratifyingly, the yield increased significantly to 70 % when the ligand DABCO (**L1**) was used (entry 3). Encouraged by these results, different metal catalysts were evaluated for the reaction between amide **1a** and Et₂O (**2a**; entries 4–7): several Fe salts, such as FeCl₂, FeBr₃, or [Fe(acac)₃], and CuCl₂ showed high catalytic activity, but were inferior to FeCl₃. We noted that the absence of metal catalysts resulted in no detectable amounts of product **3** (entry 8). With regard to the optimal amount of the catalyst, the reaction with 5 mol % of FeCl₃ provided the best results (entry 3 vs. entries 9 and 10). Interestingly, screening showed that DBU (**L5**) was the most efficient ligand among nitrogen-containing ligands **L1–L5** (entries 3 and 11–13 vs. entry 14), furnishing indolin-2-one **3** in 85 % yield. The results indicated that using 200 mol % of DBU (**L5**) afforded the product in the same yield as using 10 mol % of DBU, but use

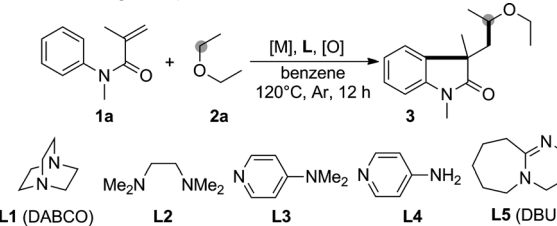
[*] Dr. W.-T. Wei,^[†] Dr. M.-B. Zhou,^[†] J.-H. Fan, W. Liu, R.-J. Song, Y. Liu, M. Hu, P. Xie, Prof. Dr. J.-H. Li
State Key Laboratory of Chemo/Biosensing and Chemometrics,
College of Chemistry and Chemical Engineering, Hunan University
Changsha 410082 (China)
E-mail: jhli@hnu.edu.cn

M. Hu, P. Xie
Key Laboratory of Chemical Biology & Traditional Chinese Medicine
Research (Ministry of Education), Hunan Normal University
Changsha 410081 (China)

[†] These authors contributed equally to this work.

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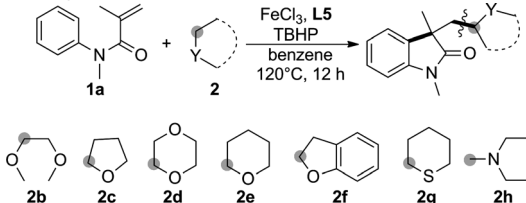
Table 1: Screening for optimal reaction conditions.^[a]


Entry	[M] [mol %]	L [mol %]	Yield [%] ^[b]
1 ^[c]	FeCl ₃ (5)	—	15
2	FeCl ₃ (5)	—	23
3	FeCl ₃ (5)	L1 (10)	70
4	FeCl ₂ (5)	L1 (10)	57
5	FeBr ₃ (5)	L1 (10)	48
6	[Fe(acac) ₃] (5)	L1 (10)	23
7	CuCl ₂ (5)	L1 (10)	32
8	—	L1 (10)	0
9	FeCl ₃ (10)	L1 (20)	69
10	FeCl ₃ (2)	L1 (4)	36
11	FeCl ₃ (5)	L2 (10)	59
12	FeCl ₃ (5)	L3 (10)	32
13	FeCl ₃ (5)	L4 (10)	36
14	FeCl ₃ (5)	L5 (10)	85
15	FeCl ₃ (5)	L5 (200)	81
16	FeCl ₃ (5)	L5 (5)	58
17 ^[d]	FeCl ₃ (5)	L5 (10)	80

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (20 equiv), catalyst [M], ligand L, TBHP (anhydrous, 5 m in decane, 2 equiv), and benzene (anhydrous, 0.5 mL) at 120°C under argon atmosphere for 12 h. Some side products, such as arylamines and amides from decomposition of amide **1a**, 3-ethyl-1,3-dimethylindolin-2-one (TBHP acts as a methylating reagent), 2-(1-ethoxyethoxy)-2-methylpropane, and ethyl acetate, were observed by GC-MS analysis. [b] Yield of product **3** (d.r. was about 3:1). [c] Without TBHP. [d] Substrate **1a** (50 mmol) for 48 h. TBHP = *tert*-butyl hydrogenperoxide, DTBP = di-*tert*-butyl peroxide.

of 5 mol % of DBU lowered the yield to 58 % (entries 15 and 16), thus implying that DBU acts as a ligand, not as a base. This observation is also supported by results of UV/Vis titration (Figure S1 in the Supporting Information). However, we cannot rule out that the alkalinity of DBU promotes the reaction. It is noteworthy that a good yield is still achieved by using 50 mmol of **1a** (entry 17).

The scope of the reaction with respect to *N*-arylacrylamides **1** and substrates **2** with a C(sp³)–H bond adjacent to a heteroatom is summarized in Tables 2 and 3. We first investigated the scope of substrates **2** with a C(sp³)–H bond adjacent to a heteroatom (Table 2). In the presence of FeCl₃, TBHP, and DBU (**L5**), a variety of ethers, including 1,2-dimethoxyethane (**2b**), THF (**2c**), 1,4-dioxane (**2d**), tetrahydro-2*H*-pyran (**2e**), and 2,3-dihydrobenzofuran (**2f**), were successfully reacted with *N*-methyl-*N*-phenylmethacrylamide (**1a**) in moderate to good yields (products **4–8**). For example, 1,2-dimethoxyethane (**2b**) was a viable substrate, and the reaction exclusively occurred at the C(sp³)–H bond of the ethane moiety to afford product **4** in 51 % yield. Using THF (**2c**), 1,4-dioxane (**2d**) or tetrahydro-2*H*-pyran (**2e**), good yields were still achieved under the optimal conditions (products **5–7**). Interestingly, 2,3-dihydrobenzofuran (**2f**) could also undergo the reaction, giving product **8** in moderate

Table 2: Scope of substrates **2**.^[a]


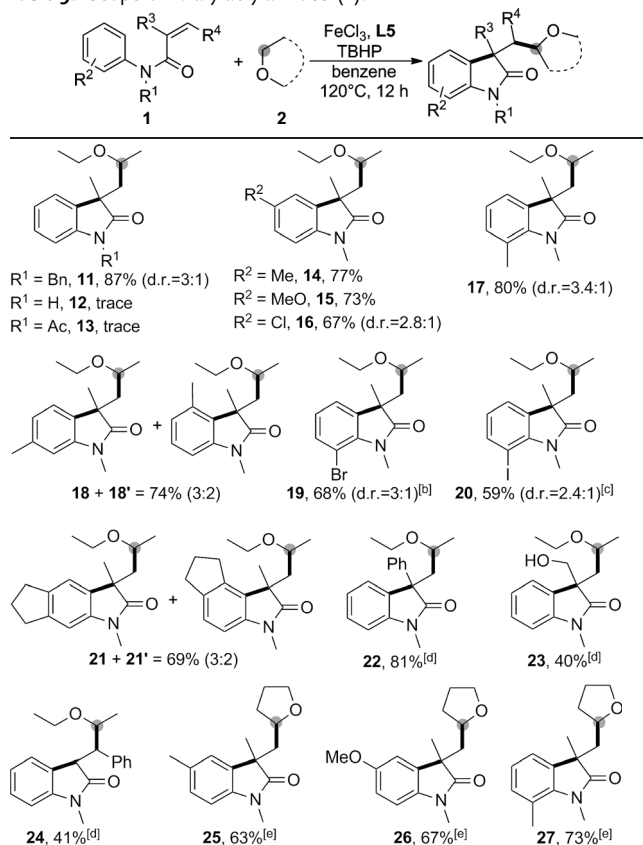
Product	Yield [%]	d.r.
4	52%	—
5	78% ^[b]	—
6	76%	(d.r.=2.2:1)
7	77%	(d.r.=3:1)
8	51% ^[c]	—
9	52% ^[c]	—
10	40% ^[c]	—

[a] Reaction conditions: **1** (0.3 mmol), **2** (20 equiv), FeCl₃ (5 mol %), **L5** (10 mol %), TBHP (2 equiv), and benzene (anhydrous, 0.5 mL) at 120°C under argon atmosphere for 12 h. [b] CuCl₂ (5 mol %) was added. [c] At 140°C for 48 h.

yield, thereby making this methodology more useful in organic synthesis. A screening disclosed that a C(sp³)–H bond adjacent to a sulfur atom was also suitable for the reaction: treatment of tetrahydro-2*H*-thiopyran (**2g**) with amide **1a**, FeCl₃, TBHP, and **L5** afforded the corresponding product **9** in moderate yield. Gratifyingly, amine **2h** could selectively react with amide **1a**, FeCl₃, TBHP, and **L5** to furnish the desired oxindole **10** in moderate yield.

We next exploited the scope of *N*-arylacrylamides **1** in reactions with Et₂O (**2a**) or THF (**2c**) in the presence of FeCl₃, TBHP, and **L5** (Table 3). The amide in which the *N*-methyl substituent in **1a** is replaced by a benzyl group is a viable substrate for the reaction (product **11**), however replacement of the methyl substituent by a hydrogen atom or an acetyl group did not result in the corresponding products **12** and **13**. The effect of substituents at the *N*-aryl moiety was subsequently examined (products **14–21**). Screening showed that several substituents, such as alkyl, MeO, Cl, Br, and I groups, were well tolerated under the optimal conditions. For example, amides with a methyl group at the *para*, *ortho*, or *meta* position of the aromatic ring displayed high reactivity in the reaction with Et₂O (**2a**), FeCl₃, TBHP, and **L5**, providing the corresponding oxindoles **14**, **17**, and **18** in good yields. Gratifyingly, Cl, Br, and I groups were also well tolerated, thereby facilitating possible additional modifications at the halogenated positions (products **16**, **19**, and **20**). Notably, *meta*-substituted substrates gave a mixture of two regioselective products (products **18/18'** and **21/21'**). We were pleased to discover that Ph and CH₂OH substituents at the 2 position of the acrylamide moiety were also compatible with the optimal conditions (products **22** and **23**). Interestingly, *N*-methyl-*N*-phenylcinnamamide, which contains an internal alkene, was also a viable substrate for the reaction (product **24**). Using THF (**2c**), amides with substituents on the *N*-aryl moiety were successfully converted by FeCl₃/CuCl₂ co-catalysts into the corresponding oxindoles **25–27** in good yields.

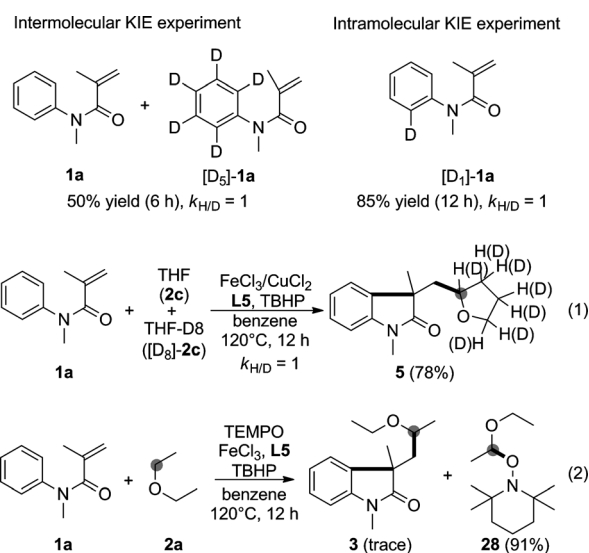
Table 3: Scope of *N*-arylacrylamides (**1**).^[a]



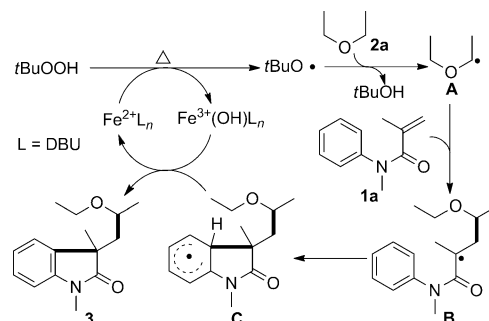
[a] Reaction conditions: **1** (0.3 mmol), **2** (20 equiv), FeCl₃ (5 mol %), L5 (10 mol %), TBHP (2 equiv), and benzene (anhydrous, 0.5 mL) at 120°C under argon atmosphere for 12 h. [b] Product **3** was isolated in 8% yield. [c] Product **3** was isolated in 12% yield. [d] For 48 h. [e] CuCl₂ (5 mol %) was added.

Some control experiments were carried out to understand the mechanism of the reaction (Scheme 2). The results demonstrated that there is no kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.0$) in either intramolecular or intermolecular experiments. These observations imply that the iron-catalyzed oxidative difunctionalization proceeds through either the SEAr mechanism or the free-radical mechanism.^[10] The result of the experiment between THF and [D₈]THF ($k_{\text{H}}/k_{\text{D}} = 1.0$) supports the free-radical mechanism [Eq. (1)].^[9a] To verify this mechanism, two radical inhibitors, TEMPO [Eq. (2)] and 2,6-di-*tert*-butylphenol, were added to the difunctionalization reaction: a stoichiometric amount of radical inhibitor (2.5 equiv) resulted in no conversion of amide **1a**, however, Et₂O was transformed by TEMPO into 1-(1-ethoxyethoxy)-2,2,6,6-tetramethylpiperidine (**28**) in 91% yield. The results suggest that a diethyl ether radical is involved.

A possible mechanism (Scheme 3) is proposed on the basis of the results described above.^[5b,6-9] Initially, TBHP is split by Fe²⁺ into a *tert*-butoxy radical and Fe³⁺(OH). In the presence of a *tert*-butoxy radical, substrate **2a** with C(sp³)–H bonds adjacent to an oxygen atom is readily transformed into radical intermediate **A**. Addition of radical intermediate **A** to the C=C bond of amide **1a** results in the formation of radical intermediate **B**, which upon intramolecular cyclization with



Scheme 2. Control experiments.



Scheme 3. Possible mechanism.

an aryl ring gives radical intermediate **C**. Finally, hydrogen abstraction of radical intermediate **C** by Fe³⁺(OH) takes place to afford oxindoles **3**.

In summary, we have developed a novel Fe-catalyzed oxidative 1,2-alkylarylation of activated alkenes with an aryl C(sp²)–H bond and a C(sp³)–H bond adjacent to a heteroatom. It provides efficient and selective access to a variety of functionalized oxindoles through difunctionalization of the C=C bond in *N*-arylacrylamide. Studies are currently underway in our laboratory to apply this radical 1,2-alkylarylation to the synthesis of other bioactive molecules.

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- [1] For reviews, see: a) B. S. Jensen, *CNS Drug Rev.* **2002**, 8, 353; b) C. Marti, E. M. Carreira, *Eur. J. Org. Chem.* **2003**, 2209; c) H. Lin, S. J. Danishefsky, *Angew. Chem.* **2003**, 115, 38; *Angew. Chem. Int. Ed.* **2003**, 42, 36; d) C. V. Galliford, K. A. Scheidt, *Angew. Chem.* **2007**, 119, 8902; *Angew. Chem. Int. Ed.* **2007**, 46,

- 8748; e) A. Millemaggi, R. J. K. Taylor, *Eur. J. Org. Chem.* **2010**, 4527; f) F. Zhou, Y.-L. Liu, J. Zhou, *Adv. Synth. Catal.* **2010**, 352, 1381; g) S. R. S. Rudrangi, V. K. Bontha, V. R. Manda, S. Bethi, *Asian J. Res. Chem.* **2011**, *4*, 335; for selected papers, see: h) G. Deak, M. Doda, L. Gyorgy, L. Hazai, L. Sterk, *J. Med. Chem.* **1977**, *20*, 1384; i) A. Numata, P. Yang, C. Takahashi, R. Fujiki, M. Nabae, E. Fujita, *Chem. Pharm. Bull.* **1989**, *37*, 648; j) S. Hibino, T. Choshi, *Nat. Prod. Rep.* **2001**, *18*, 66; k) A. S. Ratnayake, W. Y. Yoshida, S. L. Mooberry, T. K. Hemscheidt, *J. Org. Chem.* **2001**, *66*, 8717; l) M. Kuriyama, S. Tanigawa, Y. Kubo, Y. Demizu, O. Onomura, *Tetrahedron: Asymmetry* **2010**, *21*, 1370; m) B. M. Trost, J. Xie, J. D. Sieber, *J. Am. Chem. Soc.* **2011**, *133*, 20611.
- [2] For special reviews on transition-metal-mediated routes, see: a) R. Grigg, V. Sridharan, *J. Organomet. Chem.* **1999**, *576*, 65; b) B. M. Trost, M. K. Brennan, *Synthesis* **2009**, 3003; c) J. E. M. N. Klein, R. J. K. Taylor, *Eur. J. Org. Chem.* **2011**, 6821.
- [3] For selected papers on the use of *N*-(*o*-haloaryl)acrylamides for metal-catalyzed Heck-cyclization reactions, see: a) M. Mori, Y. Ban, *Tetrahedron Lett.* **1976**, *17*, 1807; b) V. Arumugam, A. Routledge, C. Abell, S. Balasubramanian, *Tetrahedron Lett.* **1997**, *38*, 6473; c) A. Ashimori, T. Matsuura, L. E. Overman, D. J. Poon, *J. Org. Chem.* **1993**, *58*, 6949; d) T. Matsuura, L. E. Overman, D. J. Poon, *J. Am. Chem. Soc.* **1998**, *120*, 6500; e) A. B. Dounay, K. Hatanaka, J. J. Kodanko, M. Oestreich, L. E. Overman, L. A. Pfeifer, M. M. Weiss, *J. Am. Chem. Soc.* **2003**, *125*, 6261; f) C. A. Busacca, D. Grossbach, R. C. So, E. M. O'Brien, E. M. Spinelli, *Org. Lett.* **2003**, *5*, 595; g) A. Pinto, Y.-X. Jia, L. Neuville, J. Zhu, *Chem. Eur. J.* **2007**, *13*, 961; h) A. Salcedo, L. Neuville, J. Zhu, *J. Org. Chem.* **2008**, *73*, 3600; i) S. Jaegli, W. Erb, P. Retailleau, J.-P. Vors, L. Neuville, J. Zhu, *Chem. Eur. J.* **2010**, *16*, 5863; j) S. Jaegli, J.-P. Vors, L. Neuville, J. Zhu, *Tetrahedron* **2010**, *66*, 8911; k) T. Piou, L. Neuville, J. Zhu, *Angew. Chem.* **2012**, *124*, 11729; *Angew. Chem. Int. Ed.* **2012**, *51*, 11561.
- [4] For pioneering papers on other transition-metal-mediated routes, see: Pd: a) S. Lee, J. F. Hartwig, *J. Org. Chem.* **2001**, *66*, 3402; b) F. Glorius, G. Altenhoff, R. Goddard, C. Lehmann, *Chem. Commun.* **2002**, 2704; c) T. Arao, K. Kondo, T. Aoyama, *Tetrahedron Lett.* **2006**, *47*, 1417; d) F. Bonnaterre, M. B. Choussy, J. Zhu, *Org. Lett.* **2006**, *8*, 4351; e) E. P. Kündig, T. M. Seidel, Y.-X. Jia, G. Bernardinelli, *Angew. Chem.* **2007**, *119*, 8636; *Angew. Chem. Int. Ed.* **2007**, *46*, 8484; f) L. Ackermann, R. Vicente, N. Hofmann, *Org. Lett.* **2009**, *11*, 4274; g) L.-L. Wu, L. Falivene, E. Drinkel, S. Grant, A. Linden, L. Cavallo, R. Dorta, *Angew. Chem.* **2012**, *124*, 2924; *Angew. Chem. Int. Ed.* **2012**, *51*, 2870; h) L. Yin, M. Kanai, M. Shibasaki, *Angew. Chem.* **2011**, *123*, 7762; *Angew. Chem. Int. Ed.* **2011**, *50*, 7620; i) P. Tolstoy, S. X. Y. Lee, C. Sparr, S. V. Ley, *Org. Lett.* **2012**, *14*, 4810; j) B. El Ali, K. Okuro, G. Vasapollo, H. Alper, *J. Am. Chem. Soc.* **1996**, *118*, 4264; k) T.-S. Jiang, R.-Y. Tang, X.-G. Zhang, X.-H. Li, J.-H. Li, *J. Org. Chem.* **2009**, *74*, 8834; l) A. Pinto, L. Neuville, J. Zhu, *Angew. Chem.* **2007**, *119*, 3355; *Angew. Chem. Int. Ed.* **2007**, *46*, 3291; Rh: m) M. P. Doyle, M. S. Shanklin, H. Q. Pho, S. N. Mahapatro, *J. Org. Chem.* **1988**, *53*, 1017; n) D. S. Brown, M. C. Elliott, C. J. Moody, T. J. Mowlem, J. P. Marino, Jr., A. Padwa, *J. Org. Chem.* **1994**, *59*, 2447; Cu: o) J. E. M. N. Klein, A. Perry, D. S. Pugh, R. J. K. Taylor, *Org. Lett.* **2010**, *12*, 3446; p) V. A. Lgnatenko, N. Deligonul, R. Viswanathan, *Org. Lett.* **2010**, *12*, 3594; Ni: q) Y. Nakao, S. Ebata, A. Yada, T. Hiyama, M. Ikawa, S. Ogoshi, *J. Am. Chem. Soc.* **2008**, *130*, 12874.
- [5] a) E. J. Hennessy, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 12084; b) Y.-K. Jia, E. P. Kündig, *Angew. Chem.* **2009**, *121*, 1664; *Angew. Chem. Int. Ed.* **2009**, *48*, 1636; c) A. Perry, J. K. Taylor, *Chem. Commun.* **2009**, 3249.
- [6] a) S. Jaegli, J. Dufour, H.-I. Wei, T. Piou, X.-H. Duan, J.-P. Vors, L. Neuville, J. Zhu, *Org. Lett.* **2010**, *12*, 4498; b) T. Wu, X. Mu, G.-S. Liu, *Angew. Chem.* **2011**, *123*, 12786; *Angew. Chem. Int. Ed.* **2011**, *50*, 12578; c) X. Mu, T. Wu, H.-Y. Wang, Y.-L. Guo, G.-S. Liu, *J. Am. Chem. Soc.* **2012**, *134*, 878; d) H. Zhang, P. Chen, G. Liu, *Synlett* **2012**, 2749.
- [7] For selected papers on radical reactions using *ortho*-functionalized anilines, see: a) K. Jones, M. Thompson, C. Wright, *J. Chem. Soc. Chem. Commun.* **1986**, 115; b) W. R. Bowman, H. Heaney, B. M. Jordan, *Tetrahedron Lett.* **1988**, *29*, 6657; c) K. Jones, C. McCarthy, *Tetrahedron Lett.* **1989**, *30*, 2657; d) K. Jones, J. Wilkinson, R. Ewin, *Tetrahedron Lett.* **1994**, *35*, 7673; e) W. Cabri, I. Candiani, M. Colombo, L. Franzoi, A. Bedeschi, *Tetrahedron Lett.* **1995**, *36*, 949; f) T. A. Khan, R. Tripoli, J. J. Crawford, C. G. Martin, J. A. Murphy, *Org. Lett.* **2003**, *5*, 2971; g) L.-D. Cao, C.-Z. Li, *Chin. J. Chem.* **2010**, *28*, 1640; h) A. Beyer, J. Buendia, C. Bolm, *Org. Lett.* **2012**, *14*, 3948; for organocatalytic reactions using *ortho*-unfunctionalized anilines, see: i) T. Wu, H. Zhang, G.-S. Liu, *Tetrahedron* **2012**, *68*, 5229.
- [8] a) C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217; b) *Iron Catalysis in Organic Chemistry: Reactions and Applications* (Ed.: B. Plietker), Wiley-VCH, Weinheim, **2008**; c) A. Correa, O. G. Mancheño, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108; d) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500; e) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293.
- [9] For reviews, see: a) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335; b) M. Tobisu, N. Chatani, *Angew. Chem.* **2006**, *118*, 1713; *Angew. Chem. Int. Ed.* **2006**, *45*, 1683; for papers on difunctionalization of alkenes with ethers, see: haloalkylation: c) K. Cao, Y.-J. Jiang, S.-Y. Zhang, C.-A. Fan, Y.-Q. Tu, Y.-J. Pan, *Tetrahedron Lett.* **2008**, *49*, 4652; oxyalkylation: d) K. Cheng, L.-H. Huang, Y.-H. Zhang, *Org. Lett.* **2009**, *11*, 2908; e) J. Y. Kim, J. C. Park, H. Song, K. H. Park, *Bull. Korean Chem. Soc.* **2010**, *31*, 3509; f) H. Sun, Y. Zhang, F. Guo, Z. Zha, Z. Wang, *J. Org. Chem.* **2012**, *77*, 3563; hydroalkylation: g) R. L. Jacobs, G. G. Ecke, *J. Org. Chem.* **1963**, *28*, 3036; h) S. J. Pastine, K. M. McQuaid, D. Sames, *J. Am. Chem. Soc.* **2005**, *127*, 12180; i) K. M. McQuaid, D. Sames, *J. Am. Chem. Soc.* **2009**, *131*, 402; j) K. M. McQuaid, J. Z. Long, D. Sames, *Org. Lett.* **2009**, *11*, 2972.
- [10] a) W. D. Jones, *Acc. Chem. Res.* **2003**, *36*, 140; b) A. Pinto, L. Neuville, P. Retailleau, J. Zhu, *Org. Lett.* **2006**, *8*, 4927; c) W. D. Jones, F. J. Feher, *J. Am. Chem. Soc.* **1986**, *108*, 4814; d) X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790.