Synthetic Methods

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Synthesis of Oxindoles by Iron-Catalyzed Oxidative 1,2-Alkylarylation of Activated Alkenes with an Aryl C(sp^2)–H Bond and a C(sp^3)–H Bond Adjacent to a Heteroatom**

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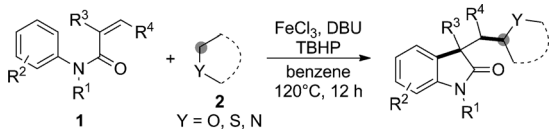
Oxindoles are important heterocycles found in a wide range of bioactive natural products and pharmaceutical molecules.[1,2] In addition, functionalized oxindoles are versatile synthetic blocks for the preparation of natural products and in asymmetric synthesis. As a result, considerable efforts were directed toward the development of efficient methods for their synthesis,[1–7] with metal-catalyzed cyclization/functionalization 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(sp^2)-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 Et_3N (base).[5a] Subsequently, Jia and Kündig developed a direct intramolecular oxidative coupling of an aryl C(sp^2)-H bond and a C(sp^3)-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(sp^2)–H bond and a C(sp^3)–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(sp^2)–H bond and a C(sp^3)–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 Et_2O (**2a**; 20 equiv), $FeCl_3$ (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 Et_2O (**2a**; entries 4–7): several Fe salts, such as $FeCl_2$, $FeBr_3$, or [Fe(acac)$_2$], and $CuCl_2$ showed high catalytic activity, but were inferior to $FeCl_3$. 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 $FeCl_3$ 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

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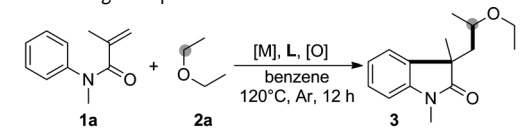
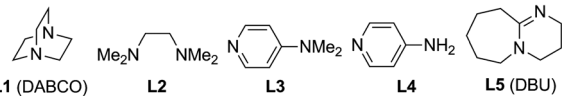
Table 1: Screening for optimal reaction conditions.[a]

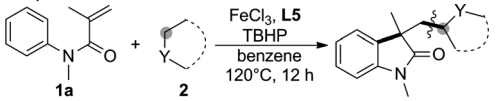


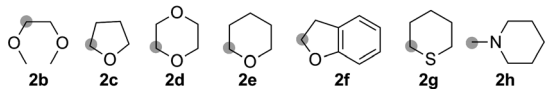


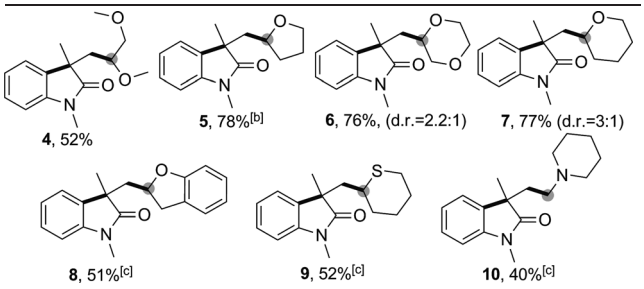
Entry	[M] [mol%]	L [mol%]	Yield [%][b]
1[c]	$FeCl_3$ (5)	–	15
2	$FeCl_3$ (5)	–	23
3	$FeCl_3$ (5)	**L1** (10)	70
4	$FeCl_2$ (5)	**L1** (10)	57
5	$FeBr_3$ (5)	**L1** (10)	48
6	$[Fe(acac)_2]$ (5)	**L1** (10)	23
7	$CuCl_2$ (5)	**L1** (10)	32
8	–	**L1** (10)	0
9	$FeCl_3$ (10)	**L1** (20)	69
10	$FeCl_3$ (2)	**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.

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







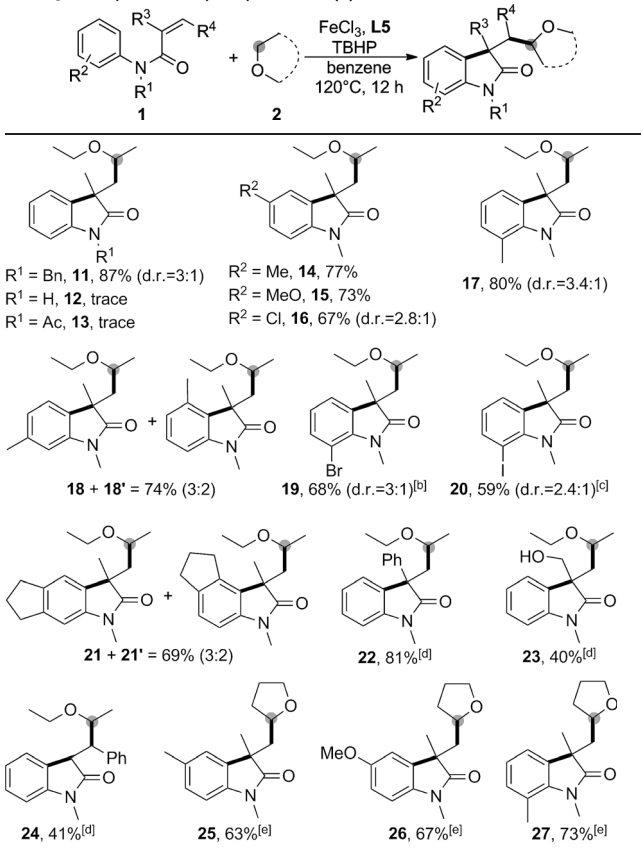
[a] Reaction conditions: **1** (0.3 mmol), **2** (20 equiv), $FeCl_3$ (5 mol%), **L5** (10 mol%), TBHP (2 equiv), and benzene (anhydrous, 0.5 mL) at 120°C under argon atmosphere for 12 h. [b] $CuCl_2$ (5 mol%) was added. [c] At 140°C for 48 h.

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).

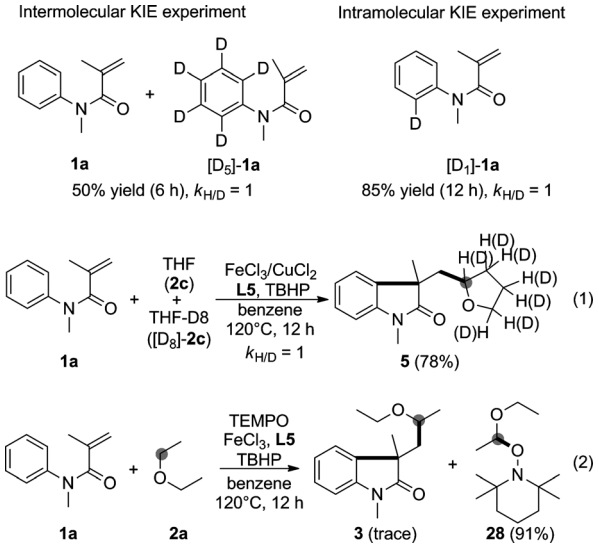
The scope of the reaction with respect to *N*-arylacrylamides **1** and substrates **2** with a $C(sp^3)$–H bond adjacent to a heteroatom is summarized in Tables 2 and 3. We first investigated the scope of substrates **2** with a $C(sp^3)$–H bond adjacent to a heteroatom (Table 2). In the presence of $FeCl_3$, 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 $C(sp^3)$–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 yield, thereby making this methodology more useful in organic synthesis. A screening disclosed that a $C(sp^3)$–H bond adjacent to a sulfur atom was also suitable for the reaction: treatment of tetrahydro-2*H*-thiopyran (**2g**) with amide **1a**, $FeCl_3$, TBHP, and **L5** afforded the corresponding product **9** in moderate yield. Gratifyingly, amine **2h** could selectively react with amide **1a**, $FeCl_3$, TBHP, and **L5** to furnish the desired oxindole **10** in moderate yield.

We next exploited the scope of *N*-arylacrylamides **1** in reactions with Et_2O (**2a**) or THF (**2c**) in the presence of $FeCl_3$, 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 Et_2O (**2a**), $FeCl_3$, 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 CH_2OH 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 $FeCl_3/CuCl_2$ co-catalysts into the corresponding oxindoles **25**–**27** in good yields.

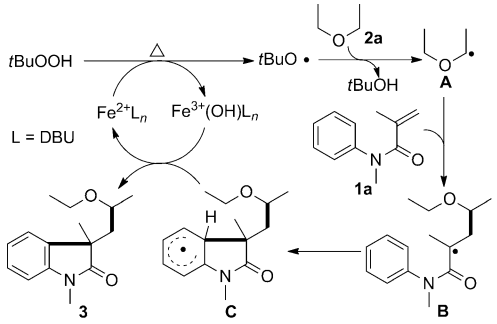
Table 3: Scope of *N*-arylacrylamides (**1**).[a]



[a] Reaction conditions: **1** (0.3 mmol), **2** (20 equiv), $FeCl_3$ (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] $CuCl_2$ (5 mol%) was added.



Scheme 2. Control experiments.



Scheme 3. Possible mechanism.

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 ($k_H/k_D = 1.0$) 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 [D_8]THF ($k_H/k_D = 1.0$) 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, Et_2O 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 Fe^{2+} into a *tert*-butoxy radical and Fe^{3+}(OH). In the presence of a *tert*-butoxy radical, substrate **2a** with C(sp^3)–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 an aryl ring gives radical intermediate **C**. Finally, hydrogen abstraction of radical intermediate **C** by Fe^{3+}(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(sp^2)–H bond and a C(sp^3)–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.-l. 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.

