JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Iridium-Catalyzed C–H Amination with Anilines at Room Temperature: Compatibility of Iridacycles with External Oxidants

Hyunwoo Kim,[‡,†] Kwangmin Shin,[‡,†] and Sukbok Chang*[,†,‡]

[†]Center for Catalytic Hydrocarbon Functionalization, Institute of Basic Science (IBS), Daejeon 305-701, Korea
[‡]Department of Chemistry, Korea Advanced Institute of Science & Technology (KAIST), Daejeon 305-701, Korea

Supporting Information

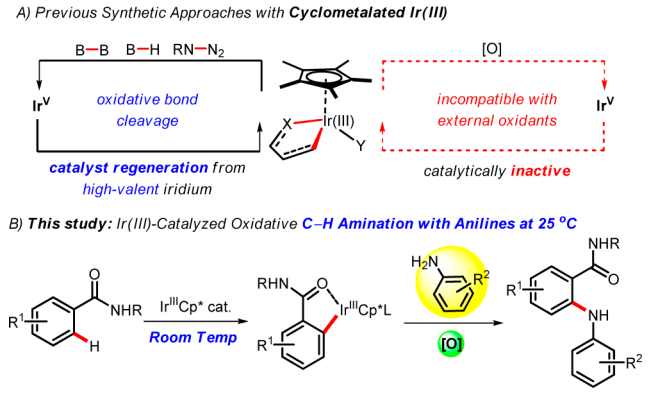
ABSTRACT: Described herein is the development of an iridium-catalyzed direct C–H amination of benzamides with anilines at room temperature, representing a unique example of an Ir catalyst system that is compatible with external oxidants. Mechanistic details, such as the isolation and characterization of key iridacycle intermediates, are also discussed.

Cyclometalated iridium(III) half-sandwich complexes have received intensive research interest because of their catalytic activity toward various chemical transformations.[1] In particular, these isolable Ir complexes are known to mediate a range of C–H functionalizations in *a stoichiometric manner*.[2] However, Cp*Ir(III) metallacycles have been observed to be catalytically inactive under oxidative conditions, mainly due to structural robustness and *incompatibility with external oxidants*. Notable advances, however, have been made in the ligand-assisted Ir-catalyzed C–H borylation,[3] in which the desired oxidative C–H functionalization is facilitated by utilizing B–B or B–H bonds as an internal oxidant.[3,4] In addition, we developed an Ir-catalyzed direct C–H amidation by employing organic azides as a nitrogen source as well as an internal oxidant via N–N_2 bond cleavage.[5] Despite this progress, it remains to be determined whether cyclometalated Ir(III) complexes are compatible with external oxidants, thus eventually enabling a catalytic cycle in oxidative C–H functionalization (Scheme 1A).

As a straightforward and economical approach, catalytic transformation of unreactive C–H bonds to C–heteroatom bonds has been extensively investigated.[1a,6] In particular, inspired by great advances in the Cu- and Pd-catalyzed cross-coupling of (hetero)aryl halides with amines leading to C–N bond formation,[7] metal-mediated direct C–H amination received intensive research focus in recent years.[8] While important issues remain to be addressed in this area in terms of substrate scope, reaction conditions, and functional group tolerance, most previous intermolecular C–H aminations employ either (sulfon)amide-based coupling partners[9a,b] or preactivated amine precursors.[5,9c−n]

In this regard, there remains a major challenge: direct utilization of non-preactivated amines as a reactant.[10] In particular, the use of anilines as a nitrogen source without preactivation is highly desirable considering the fact that a wide range of anilines are accessible, and the resulting arylamine products are useful in organic synthesis, medicinal chemistry, and materials science.[11] However, the direct use of anilines usually

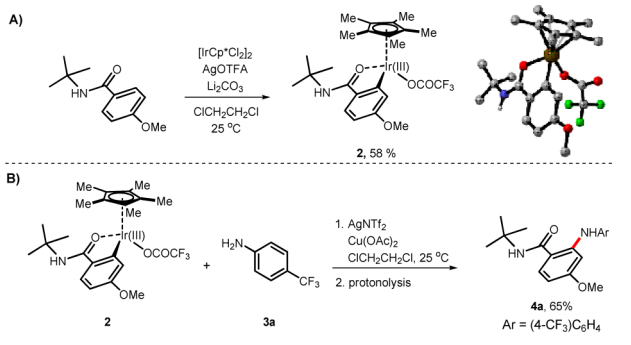
Scheme 1. [Cp*Ir(III)]-Catalyzed C–H Functionalization



results in significantly decreased activity of employed catalyst systems, mainly because of the highly nucleophilic nature of anilines.[12] As a result, the development of mild catalytic C–H amination procedures allowing the use of anilines is an important research goal. These considerations led us to investigate Ir-catalyzed C–H amination of arenes with anilines, giving rise to the development of *a room-temperature amination of benzamides with anilines* (Scheme 1B).

After a number of trials (see the Supporting Information (SI) for details), we were able to synthesize an iridacyclic species (**2**) by treating benzamide **1a** with $[IrCp^*Cl_2]_2$ in the presence of AgOTFA and Li_2CO_3 (Scheme 2A). The structure of the iridacycle **2** was unambiguously characterized by X-ray crystallographic analysis. It shows a three-legged piano stool geometry,

Scheme 2. Preliminary Stoichiometric Reactions



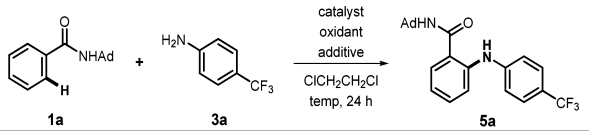
Received: March 5, 2014
Published: April 6, 2014

dx.doi.org/10.1021/ja502270y | J. Am. Chem. Soc. 2014, 136, 5904–5907

with two slightly longer Ir−C bonds (2.24 and 2.23 Å) to the Cp* ring than the remaining three (2.12, 2.14, and 2.14 Å). The distance between the Ir and the carbonyl O atom is 2.12 Å, the same as that between Ir and the trifluoroacetato O atom. It revealed that *the Ir metal is coordinated to the carbonyl O atom rather than the amide nitrogen atom*, in contrast to the previously reported palladacycle complexes in which the metal bonds to an amide nitrogen atom.[13] It should be empathized that, to the best of our knowledge, this species **2** represents *the first example of a crystal structure of an iridacycle generated from a benzamide*. We were pleased to see that the new iridacycle **2** underwent amination upon treatment with (4-trifluoromethyl)aniline (**3a**) at 25°C in the presence of a Ag(I) species and copper acetate to afford **4a** in 65% yield after protonolysis (Scheme 2B).

Encouraged by the above results of the *stoichiometric* amination, we were strongly driven to search for optimal conditions that would allow the reaction to be *catalytic* (Table 1). *N*-Adamantylbenzamide (**1a**) was chosen as a model substrate since we initially envisaged that the steric bulky of the *N*-alkyl group could help the facile formation of an iridacyclic intermediate.[14]

Table 1. Optimization of Reaction Parameters[a]

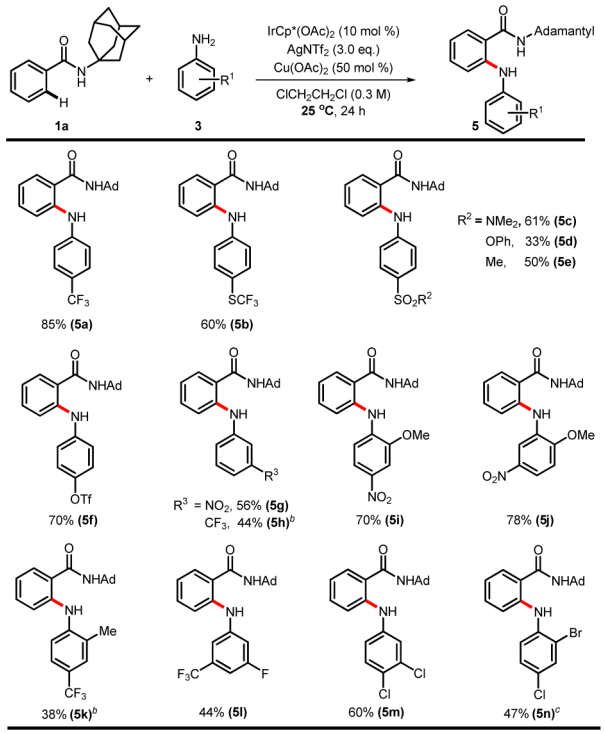


entry	catalyst (mol %)	additive (equiv)	oxidant (equiv)	temp (°C)	yield (%)[b]
1	$[IrCp^*Cl_2]_2$ (5)	$Cu(OAc)_2$ (0.5)	$AgNTf_2$ (3.0)	80	70
2	$[IrCp^*Cl_2]_2$ (5)	$Cu(OAc)_2$ (0.5)	–	80	n.r.
3	$[IrCp^*Cl_2]_2$ (5)	–	–	80	n.r.
4	$[IrCp^*Cl_2]_2$ (5)	$Cu(OAc)_2$ (0.5)	$AgNTf_2$ (3.0)	25	71
5	$[IrCp^*Cl_2]_2$ (5)	–	$AgNTf_2$ (3.0)	25	20
6	–	$Cu(OAc)_2$ (0.5)	$AgNTf_2$ (3.0)	25	n.r.
7	$[IrCp^*Cl_2]_2$ (5)	NH_4OAc (1.0)	$AgNTf_2$ (3.0)	25	60
8	$[IrCp^*Cl_2]_2$ (5)	Na_2CO_3 (1.0)	$AgNTf_2$ (3.0)	25	15
9	$[IrCp^*Cl_2]_2$ (5)	$Cu(OAc)_2$ (0.5)	NFSI[c] (2.0)	25	n.r.
10	$[IrCp^*Cl_2]_2$ (5)	$Cu(OAc)_2$ (0.5)	$Na_2S_2O_8$ (4.0)	25	n.r.
11	**$IrCp^*(OAc)_2$ (10)**	**$Cu(OAc)_2$ (0.5)**	**$AgNTf_2$ (3.0)**	**25**	**91 (85)**
12	$Pd(OTf)_2$ (5)	–	$Na_2S_2O_8$ (4.0)	80	n.r.
13[d]	$Cu(OAc)_2$ (100)	Na_2CO_3 (1.0)	air (1 atm)	80	n.r.

[a] **1a** (0.2 mmol), **3a** (0.21 mmol), catalyst, oxidant, and additive in 1,2-dichloroethane (DCE, 0.66 mL) for 24h. [b] Yield based on ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 as the internal oxidant (isolated yield in parentheses). n.r. = no reaction. [c] *N*-Fluorobenzenesulfonimide. [d] DMSO (2.0 mL) solvent.

We were delighted to observe that a catalytic reaction indeed did proceed in the presence of $Cu(OAc)_2$ and $AgNTf_2$ co-additives (entry 1). However, the amination did not occur in the absence of Ag additives (entries 2, 3). Surprisingly, this catalytic amination was found to be high-yielding even at room temperature (entry 4). The efficiency was decreased significantly in the absence of $Cu(OAc)_2$ (entry 5). The Ir catalyst was essential for the amination (entry 6). The type of acetate additives turned out to be important, and among various acetates screened (e.g., entries 7 and 8; see SI for full data), $Cu(OAc)_2$ (0.5 equiv to **1a**) was most effective. Likewise, the choice of oxidants was another key to success. For instance, when frequently employed oxidants such as NFSI or $Na_2S_2O_8$ were

Table 2. Substrate Scope of Anilines[a]



[a] **1a** (0.2 mmol) and **3** (0.21 mmol) in DCE (0.66 mL) at 25°C for 24h (isolated yields). [b] Conducted at 80°C, 3h. [c] For 48h.

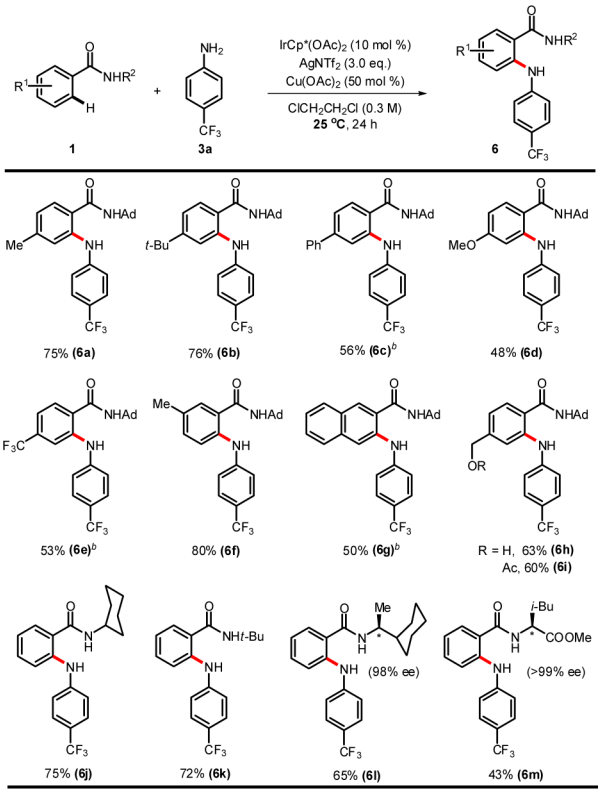
examined,[9a,k,15] the amination did not proceed at all (entries 9 and 10). When a separately prepared iridium acetate complex, $[IrCp^*(OAc)_2]$,[16] was used as a catalyst, the desired product was obtained in excellent yield (entry 11). It was noteworthy that $Pd(OTf)_2$ or $Cu(OAc)_2$ (1.0 equiv) metal systems, which were previously employed in the C−H amidation/amination reactions,[10f,15] were ineffective for the present amination with aniline **3a** (entries 12, 13).

With the optimized conditions for the Ir-catalyzed direct C−H amination in hand, we next investigated the scope of the current procedure by testing various aniline derivatives in the reaction with *N*-adamantylbenzamide **1a** (Table 2). Anilines bearing electron-withdrawing substituents, such as trifluoromethyl (**3a**), trifluoromethylthio (**3b**), sulfonyl (**3c−e**), and triflic (**3f**) groups, smoothly participated in the amination in moderate to high yields. Anilines having a *meta*-substituent (**3g,h**) afforded the desired products in moderate yields. In addition, we found that a series of disubstituted anilines also reacted to furnish the corresponding amination products (**5i−n**). Interestingly, anilines possessing both electron-donating and -withdrawing groups underwent the amination with high efficiency (**5i−k**). Anilines bearing mono- or dihalogens showed reasonable reactivity (**5l−n**). Functional group tolerance was excellent in the current amination procedure as demonstrated by the successful reactions with anilines bearing sensitive groups such as thioether, sulfonyl, triflate, and halides. Meanwhile, reactivity of aniline or its derivatives bearing electron-donating substituents was observed to be low, and no desired products were obtained under present conditions. In addition, *N*-substituted anilines were not reacted even at higher temperature (100°C), providing a clue about the reaction mechanism (*vide infra*).

The present amination method was successfully applied to a wide range of benzamides with **3a** as the coupling partner (Table

dx.doi.org/10.1021/ja502270y | J. Am. Chem. Soc. 2014, 136, 5904−5907

Table 3. Substrate Scope of Benzamides[a]



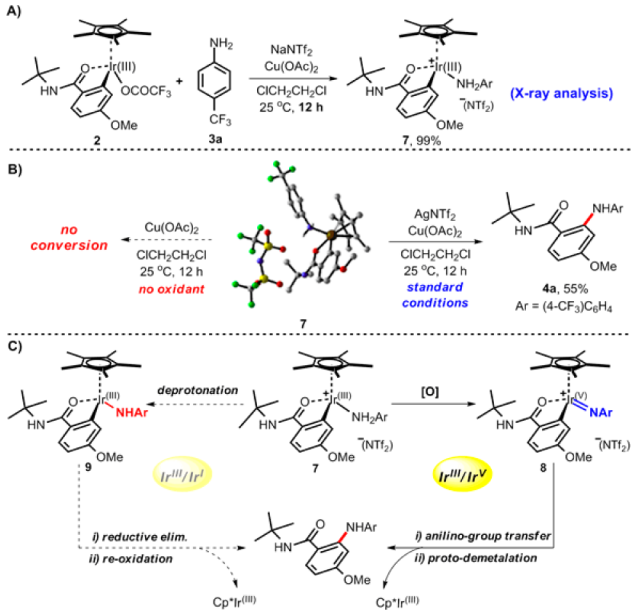
[a]**1** (0.2 mmol) and **2a** (0.21 mmol) in DCE (0.66 mL) at 25°C for 24h (isolated yields). [b]At 80°C in *α,α,α*-trifluorotoluene (0.66 mL) for 3h.

3). It was revealed that the reaction efficiency was maintained irrespective of the electronic properties of the substrate (**6a**−**e**). As anticipated, the amination took place at the sterically more accessible C−H bonds (**6f**,**g**). Again, functional group tolerance was excellent, as seen in the successful amination of benzamides having free or acetate-masked hydroxyl groups (**6h**,**i**). Moreover, the reaction was not greatly affected by varying the *N*-alkyl group on the benzamide substrate (**6j**−**m**).[17] In fact, not only benzamides bearing simple *N*-alkyl moieties (**6j**,**k**), but also derivatives bearing a stereogenic center were readily aminated with retention of stereochemical purity (**6l**,**m**). *N*-Alkyl-substituted amide products obtained in this study can readily be converted to the corresponding *N*-arylanthranilic acids or 2-(arylamino)benzamides according to the reported procedures.[9m]

To investigate the mechanistic details of the present Ir-catalyzed C−H amination reaction, a series of stoichiometric reactions using isolated iridacycles was initially planned. When an iridacycle species **2** was treated with aniline **3a**, the desired amination did not occur in the absence of Ag(I) oxidant. Instead, an aniline-coordinated iridacycle complex (**7**) was obtained quantitatively (Scheme 3A). The structure of **7** was unambiguously characterized by NMR and X-ray analyses. The bond length between the Ir metal center and nitrogen atom of aniline in **7** was 2.16 Å, in the range of several aniline complexes previously known.[12,18]

Stoichiometric reactions of **7** provided interesting results: whereas treatment of **7** with $Cu(OAc)_2$ alone failed to induce any conversion; the desired aminated product (**4a**) was obtained by adding Ag oxidant in the presence of $Cu(OAc)_2$ (Scheme 3B). Other oxidants were also examined for this reaction, revealing

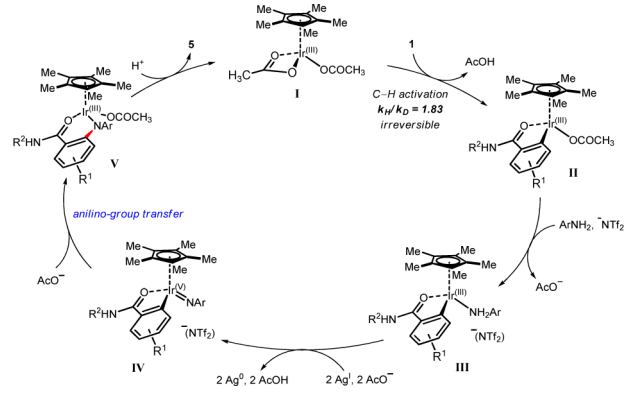
Scheme 3. Mechanistic Studies



that only Ag(I) salt was effective.[19] Although more comprehensive studies are required to elucidate details of an amino-transfer pathway, this result suggests that the amination may proceed via formation of a high-valent Ir(V) nitrenoid species (**8**), potentially consistent with enhanced reactivity with electron-poor anilines. It is proposed that **8** will subsequently undergo a nitrenoid insertion and then proto-demetalation to deliver an aminated product with concurrent regeneration of Cp*Ir(III) species. An alternative pathway involving an Ir(III)/Ir(I) cycle, in which Ir(III) amido species (**9**) undergoes reductive elimination and the resulting Ir(I) is reoxidized, is reasoned to be less likely (Scheme 3C).

Based on the above mechanistic studies and relevant literature,[1a−c,2e,20] we depict a plausible catalytic cycle in Scheme 4. First, an Ir species induces an irreversible C−H cleavage of

Scheme 4. Proposed Mechanistic Pathway



benzamides to generate a cyclometalated Ir(III) complex **II**, believed to be a rate-limiting step on the basis of kinetic isotope effect studies (see SI for details). A ligand exchange of acetate with aniline delivers an isolable cationic aniline complex **III**. Oxidation of a metallacycle **III** is proposed to occur forming an Ir(V)-nitrenoid species **IV** that then undergoes an anilino-group transfer leading to an Ir complex **V**. Finally, proto-demetalation

dx.doi.org/10.1021/ja502270y | J. Am. Chem. Soc. 2014, 136, 5904−5907

from **V** will occur to deliver desired *N*,*N*-diarylamine products with regeneration of the catalyst.

In conclusion, we report an Ir-catalyzed direct C−H amination of benzamides using simple aniline coupling partners without preactivations. This advance is a significant example of an iridium catalyst system being compatible with external oxidants to allow an anilino-group transfer even at room temperature for the first time. A catalytic cycle involving high-valent Ir species is proposed, and further methodologies of C−H functionalization are anticipated to be developed based on this mechanistic understanding.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

sbchang@kaist.ac.kr

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Institute of Basic Science (IBS). We thank Mr. Jaeyune Ryu (KIST) for helpful discussions, and Mr. Jin Kim and Jinseong Gwak for X-ray analysis.

■ REFERENCES

(1) (a) Albrecht, M. *Chem. Rev.* **2010**, *110*, 576. (b) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Pölleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210. (c) Li, L.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 12414. (d) Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 8730. (e) Kashiwame, Y.; Kuwata, S.; Ikariya, T. *Chem.—Eur. J.* **2010**, *16*, 766. (f) Wang, C.; Pettman, A.; Bacsa, J.; Xiao, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 7548. (g) Wang, C.; Villa-Marcos, B.; Xiao, J. *Chem. Commun.* **2011**, *47*, 9773.

(2) (a) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (b) Lohrenz, J. C. W.; Jacobsen, H. *Angew. Chem., Int. Ed.* **1996**, *35*, 1305. (c) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (d) Young, K. J. H.; Mironov, O. A.; Periana, R. A. *Organometallics* **2007**, *26*, 2137. (e) Turlington, C. R.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2014**, *136*, 3981.

(3) (a) Liskey, C. W.; Wei, C. S.; Pahls, D. R.; Hartwig, J. F. *Chem. Commun.* **2009**, 5603. (b) Chotana, G. A.; Vanchura, B. A., II; Tse, M. L.; Staples, R. J.; Maleczka, R. E. J.; Smith, M. R., III *Chem. Commun.* **2009**, 5731.

(4) (a) Cho, J. Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E.; Smith, M. R., III *Science* **2002**, *295*, 305. (b) Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. *J. Am. Chem. Soc.* **2003**, *125*, 16114. (c) Hartwig, J. F. *Acc. Chem. Res.* **2012**, *45*, 864.

(5) (a) Ryu, J.; Kwak, J.; Shin, K.; Lee, D.; Chang, S. *J. Am. Chem. Soc.* **2013**, *135*, 12861. (b) Lee, D.; Kim, Y.; Chang, S. *J. Org. Chem.* **2013**, *78*, 11102. (c) Kim, J.; Chang, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 2203.

(6) (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (b) Bergman, R. G. *Nature* **2007**, *446*, 391. (c) Wencel-Delord, J.; Droge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740. (d) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (e) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (f) Li, C.-J. *Acc. Chem. Res.* **2009**, *42*, 335. (g) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (h) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (i) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (j) Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222. (k) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (l) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (m) Seregin, I. V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173. (n) Hirano, L.; Miura, M. *Synlett* **2011**, 294. (o) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Commun.* **2010**, *46*, 677.

(7) (a) Ullmann, F. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2382. (b) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054. (c) Rao, H.; Fu, H. *Synlett* **2011**, *6*, 745. (d) Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 5969. (e) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901.

(8) (a) Armstrong, A.; Collins, J. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 2282. (b) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (c) Lu, H.; Zhang, X. P. *Chem. Soc. Rev.* **2011**, *40*, 1899. (d) Collet, F.; Lescot, C.; Dauban, P. *Chem. Soc. Rev.* **2011**, *40*, 1926. (e) Roizen, J. L.; Harvey, M. E.; Du Bois, J. *Acc. Chem. Res.* **2012**, *45*, 911.

(9) (a) Thu, H.-Y.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2006**, *128*, 9048. (b) Zhao, H.; Shang, Y.; Su, W. *Org. Lett.* **2013**, *15*, 5106. (c) Kawano, T.; Hirano, K.; Satoh, T.; Miura, M. *J. Am. Chem. Soc.* **2010**, *132*, 6900. (d) Sun, K.; Li, Y.; Xiong, T.; Zhang, J.; Zhang, Q. *J. Am. Chem. Soc.* **2011**, *133*, 1694. (e) Yoo, E. J.; Ma, S.; Mei, T.-S.; Chan, K. S. L.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 7652. (f) Grohmann, C.; Wang, H.; Glorius, F. *Org. Lett.* **2012**, *14*, 656. (g) Ng, K.-H.; Zhou, Z.; Yu, W.-Y. *Org. Lett.* **2012**, *14*, 272. (h) Grohmann, C.; Wang, H.; Glorius, F. *Org. Lett.* **2013**, *15*, 3014. (i) Shang, M.; Zeng, S.-H.; Sun, S.-Z.; Dai, H.-X.; Yu, J.-Q. *Org. Lett.* **2013**, *15*, 5286. (j) Ng, K.-H.; Chan, A. S. C.; Yu, W.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 12862. (k) Tang, R.-J.; Luo, C.-P.; Yang, L.; Li, C.-J. *Adv. Synth. Catal.* **2013**, *355*, 869. (l) Kim, J. Y.; Park, S. H.; Ryu, J.; Cho, S. H.; Kim, S. H.; Chang, S. *J. Am. Chem. Soc.* **2012**, *134*, 9110. (m) Ryu, J.; Shin, K.; Park, S.; Kim, J.; Chang, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 9904. (n) Shin, K.; Baek, Y.; Chang, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 8031.

(10) (a) Uemura, T.; Imoto, S.; Chatani, N. *Chem. Lett.* **2006**, *35*, 842. (b) John, A.; Nicholas, K. M. *J. Org. Chem.* **2011**, *76*, 4158. (c) Zhao, H.; Wang, M.; Su, W.; Hong, M. *Adv. Synth. Catal.* **2010**, *352*, 1301. (d) Tran, L. D.; Roane, J.; Daugulis, O. *Angew. Chem., Int. Ed.* **2013**, *52*, 6043. (e) Louillat, M.-L.; Patureau, F. W. *Chem. Soc. Rev.* **2014**, *43*, 901. (f) Shang, M.; Sun, S.-Z.; Dai, H.-X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 3354.

(11) Lawrence, S. A. *Amines: Synthesis Properties and Applications*; Cambridge University Press: Cambridge, UK, 2004.

(12) Davies, D. L.; Al-Duaij, O.; Giardiello, M.; Hilton, S. T.; Russel, D. R. *Dalton. Trans.* **2003**, 4132.

(13) Zhang, X.-G.; Dai, H.-X.; Wasa, M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2012**, *134*, 11948.

(14) Wehman-Ooyevaar, I. C. M.; Luitwieler, I. F.; Vatter, K.; Grove, D. M.; Smeets, W. J. J.; Horn, E.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1996**, *252*, 55.

(15) Xiao, B.; Gong, T.-J.; Xu, J.; Liu, Z.-J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 1466.

(16) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *30*, 127.

(17) However, amination of amide substrates derived from primary amines was not effective under the current conditions.

(18) Chen, J.-T.; Chen, Y.-K.; Chu, J.-B.; Lee, G.-H.; Wang, Y. *Organometallics* **1997**, *16*, 1476.

(19) For selected reports on the use of Ag as an oxidant in C−H functionalization, see: (a) Stuart, D. R.; Villemure, E.; Fagnou, K. *J. Am. Chem. Soc.* **2007**, *129*, 12072. (b) Feng, C.-G.; Ye, M.; Xiao, K.-J.; Li, S.; Yu, J.-Q. *J. Am. Chem. Soc.* **2013**, *135*, 9322.

(20) (a) Sau, Y.-K.; Yi, X.-Y.; Chan, K.-W.; Lai, C.-S.; Williams, I. D.; Leung, W.-H. *J. Organomet. Chem.* **2010**, *695*, 1399. (b) Dick, A. R.; emy, M. S.; Kampf, J. W.; Sanford, M. S. *Organometallics* **2007**, *26*, 1365. (c) Ke, Z.; Cundari, T. R. *Organometallics* **2007**, *29*, 821. (d) Park, S. H.; Kwak, J.; Shin, K.; Ryu, J.; Park, Y.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 2492.