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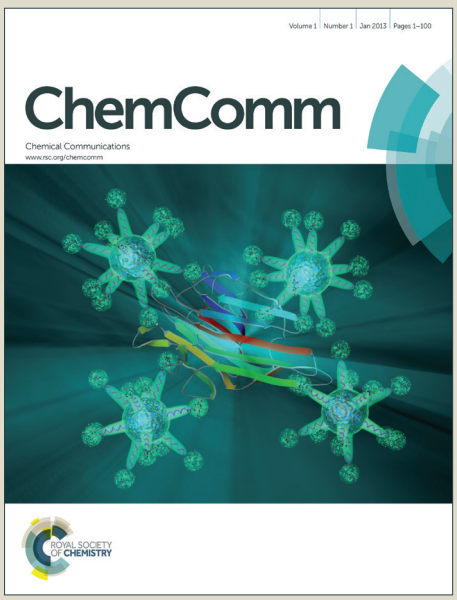

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COMMUNICATION

n-Bu_4NI/TBHP-catalyzed direct amination of allylic and benzylic C(sp^3)−H with anilines under metal-free conditions

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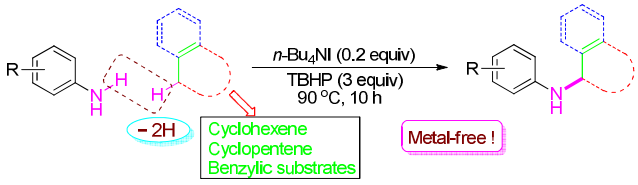
A novel and efficient *n*-Bu_4NI/TBHP-catalyzed direct amination of allylic and benzylic C(sp^3)−H with anilines to *N*-substituted anilines under metal-free conditions has been developed.

The amino moiety, as a key skeletal framework structure in natural products, agrochemicals, polymers, and pharmaceuticals, plays a pivotal role in both chemistry and biology.[1] It has therefore stimulated chemists over several decades to develop the efficient approaches for the C−N bond formation. A general method is employing pre-functionalized starting materials, most representatively (hetero)aryl (pseudo)halides to react with amines or amides.[2] Of particular importance is Buchwald-Hartwig C−N cross-coupling reaction.[3] In recent years, the celebrated strategy involving direct C–H bond activation followed by C−N bond formation of arenes and heteroarenes has received more attention.[4-7] Among these transformations, transition-metal-catalyzed direct oxidative amination by C–H/N–H double activation represents an extremely attractive approach for inducing nitrogen functional groups, which circumvents the need for pre-functionalization of the coupling partners and offers highly efficient to target molecules from the simplest starting materials.[5-8] Compared with the direct C(sp^2)−H bond amination of arenes and heteroarenes, the direct C(sp^3)−H bond amination of saturated hydrocarbons to accomplish the regioselective C(sp^3)−H to C−N transformation is still a challenge and a complementary to the synthesis of valuable nitrogen-containing compounds. Over the last decades, nitrene-induced C(sp^3)−H aminations have been developed form the corresponding secondary amines as typically nitrogen sources bearing electron-withdrawing groups, such as H_2NSO_2R or $H_2NC(O)OR$ and $PhI(OAc)_2$ as an oxidant, providing the corresponding iminoiodinanes intermediates *in situ* in the presence of a transition metal catalyst, Rh,[9] Ru,[10] Cu,[11] Fe,[12] Co,[13] or Mn.[14] On the other hand, alternative nitrene derivatives, chloramines-T,[15] bromamine-T,[16] tosyloxycarbamates,[17] and azides[18] can also be used as the nitrogen sources. In addition, secondary amines, $MeOC(O)NHSO_2R$,[19] $MeNHSO_2Ph$,[20] and *N*-fluorobis(phenylsulfonyl)imide (NFSI)[21] have been used in the C(sp^3)−H amination to afford tertiary sulfonylamines. However, to our knowledge, the most achievements have been made by using nitrogen sources, which have to be attached a very strong electron-withdrawing group on the nitrogen atom with few exception.[22]

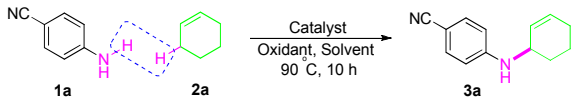
Recently, aromatic amines as the nitrogen sources in the C(sp^3)−H bond amination have been developed,[23] for example, Pd-catalyzed and C−H amination of unactivated C(sp^3)−H bonds[23a] with anilines, and Cu-catalyzed C(sp^3)−H amination of cyclohexene with anilines,[23b] oxidative amination and allylic amination of alkene,[23c] and intermolecular C–H amination of unactivated sp^3 carbons.[23d] However, a transition-metal is essential in the above reactions,[23] and metal-free oxidation is the best choices in the pharmaceutical industry due to the avoidance of metal contamination.[7c] In 2011, Lee described hypoiodite-mediated saturated C−H amination for the synthesis of an oxazaspiroketal-containing cephalostatin analog under metal-free conditions.[24a] In this general direction, an elegant preparation of imidazole and purine nucleoside derivatives was developed recently by Zhu using *n*-Bu_4NI-catalyzed benzylic C−H bond amination.[24b] In our ongoing interest in the construction of nitrogen-containing compounds and metal-free organic reactions,[25] we report herein a novel *n*-Bu_4NI/TBHP-catalyzed oxidative C(sp^3)−H amination of cyclohexene, cyclopentene and benzylic substrates with anilines, which illustrated a practical straightforward route to *N*-substituted anilines from simple and readily available starting materials under metal-free conditions (Scheme 1).



Scheme 1 Direct amination of allylic C(sp^3)−H with anilines

We first chose 4-aminobenzonitrile (**1a**) and cyclohexene (**2a**) as the model substrates to optimize the reaction conditions. The results were summarized in Table 1. When the model reaction was performed in the presence of *n*-Bu_4NI/TBHP (*tert*-butyl hydroperoxide) at 90 °C, 80% yield of product **3a** was obtained under neat conditions (Table 1, entry 1). However, as the analogues of *n*-Bu_4NI, *n*-Bu_4NBr and *n*-Bu_4NCl were ineffective (Table 1, entries 2 and 3). It is reasonable to speculate that iodide anion is an efficient activator for the oxidative amination of cyclohexene (allylic type Csp^3−H) owing to a good candidate as iodide anion of *n*-Bu_4NI. However, KI or I_2 as a direct or indirect iodide anion source could not catalyze the reaction (Table 1, entries 4 and 5). Only TBHP exhibited the excellent activity to the transformation, but, DTBP (di-*tert*-butyl peroxide), TBPB (*tert*-butyl perbenzoate), BQ (1,4-benzoquinone), DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), $K_2S_2O_8$, and $(NH_4)_2S_2O_8$ completely failed (Table 1, entries 1 *vs* 6−11). It did not occur when the reaction was carried out in EtOAc, CH_2Cl_2, 1,2-dichloroethane (DCE), 1,4-dioxane, CH_3CN, DMF, or DMSO (Table 1, entries 12−18). With respect to *n*-Bu_4NI and TBHP

Table 1 Optimization of the reaction conditions [a]



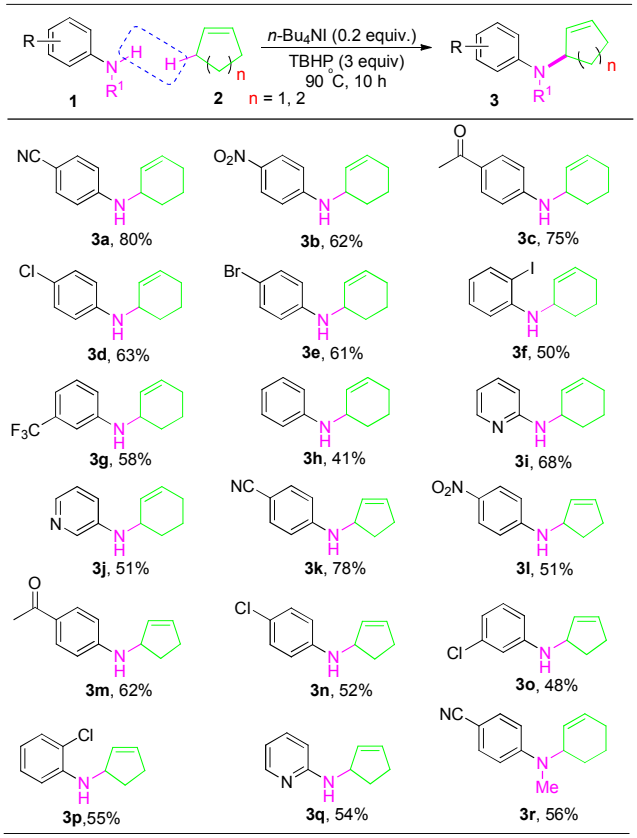
1a 2a 3a

Entry	Catalyst	Oxidant	Solvent	Yield[b] (%)
1	*n*-Bu_4NI	TBHP	neat	80
2	*n*-Bu_4NBr	TBHP	neat	trace
3	*n*-Bu_4NCl	TBHP	neat	trace
4	KI	TBHP	neat	NR
5	I_2	TBHP	neat	trace
6	*n*-Bu_4NI	DTBP	neat	trace
7	*n*-Bu_4NI	TBPB	neat	trace
8	*n*-Bu_4NI	BQ	neat	NR
9	*n*-Bu_4NI	DDQ	neat	NR
10	*n*-Bu_4NI	$K_2S_2O_8$	neat	NR
11	*n*-Bu_4NI	$(NH_4)_2S_2O_8$	neat	NR
12	*n*-Bu_4NI	TBHP	EtOAc	trace [c]
13	*n*-Bu_4NI	TBHP	CH_2Cl_2	trace [c]
14	*n*-Bu_4NI	TBHP	DCE	trace [c]
15	*n*-Bu_4NI	TBHP	Dioxane	trace [c]
16	*n*-Bu_4NI	TBHP	CH_3CN	NR [c]
17	*n*-Bu_4NI	TBHP	DMF	NR [c]
18	*n*-Bu_4NI	TBHP	DMSO	NR [c]

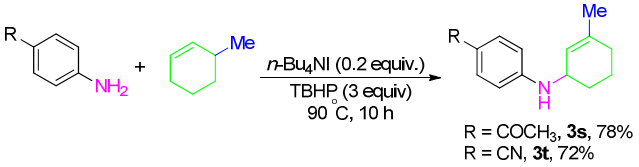
[a] Reaction conditions: 4-aminobenzonitrile (**1a**, 0.50 mmol), cyclohexene (**2a**, 10 mmol, excess, as well as solvent), catalyst (0.20 equiv., 0.10 mmol), oxidant (3.0 equiv., 1.5 mmol), at 90 °C for 10 h. [b] Isolated yields. [c] Additional solvent (2.0 mL) was added and cyclohexene (**2a**) was added in 1.0 mmol.

loading, 0.20 equiv of *n*-Bu_4NI and 3.0 equiv of TBHP were found to be optimal. It should be noted that no **3a** was detected when the model reaction was performed in the absence of *n*-Bu_4NI or TBHP. When the reaction temperature was decreased to 70 °C or increased to 110 °C, the product yield was slightly lower than that obtained at 90 °C.

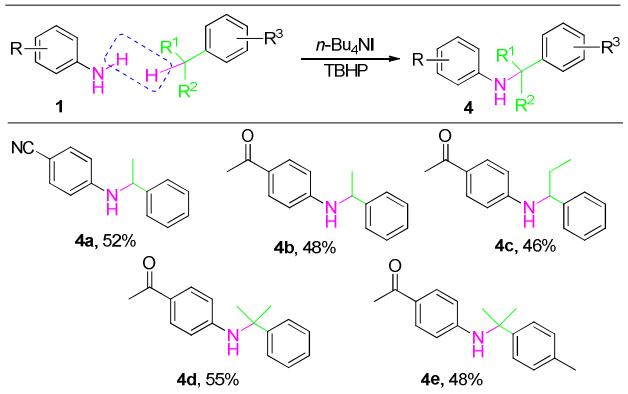
After optimization of the reaction conditions, the reaction scope of C(sp^3)−H amination of cyclohexene (**2a**) with respect to the aryl amine component was evaluated. A variety of anilines with substituents on the benzene rings were examined, and the results were shown in Scheme 2. The direct reactions proceeded well for the reactions of **2a** with anilines with electron-withdrawing groups, such as cyano, nitro, acetyl, halogen, and trifluoromethyl on the benzene rings, and generated the corresponding C−H amination products in 50–80% yields (**3a**–**g**). It is important to note that the reaction of 4-nitroaniline with **2a** afforded the desired product **3b** in 62% yield under the present metal-free conditions, however, the reaction of the same substrates failed under Cu(I)/*t*BuOO*t*Bu system.[23b] The reaction of **2a** with aniline without substituent gave **3h** in 41% yield. However, the present reaction conditions were not suitable for the anilines bearing electron-donating substituents on the benzene rings. It should be noted that 2-aminopyridine and 3-aminopyridine underwent the reaction with **2a** to generate the desired amination products **3i** and **3j** in 68 and 51% yields, respectively. The reactions of cyclopentene (**2b**) with various anilines were also successful under the optimization reaction conditions, but the corresponding product yields are lower than that of cyclohexene (**2a**) with same anilines (**3a** *vs* **3k**, **3b** *vs* **3l**, **3c** *vs* **3m**, **3d** *vs* **3n**, and **3i** *vs* **3q**). An *ortho*-position effect of anilines was not observed in the reactions of 4-, 3- and 2-chloroaniline with cyclopentene (**3n** vs **3o**, vs **3p**). When 4-



Scheme 2 Scope of the substrates [Reaction conditions: aniline (0.50 mmol), cyclohexene or cyclopentene (10 mmol), *n*-Bu_4NI (0.10 mmol), TBHP (1.5 mmol), at 90 °C for 10 h, isolated yields].



Scheme 3 The reactions of 3-methylcyclohex-1-ene with anilines [Reaction conditions: aniline (0.50 mmol), 3-methylcyclohex-1-ene (10 mmol), *n*-Bu_4NI (0.10 mmol), TBHP (1.5 mmol), at 90 °C for 10 h, isolated yields].



Scheme 4 Scope of the substrates [Reaction conditions: aniline (0.50 mmol), benzylic hydrocarbon (10 mmol), *n*-Bu_4NI (0.10 mmol), TBHP (1.5 mmol), at 90 °C for 10 h, isolated yields].

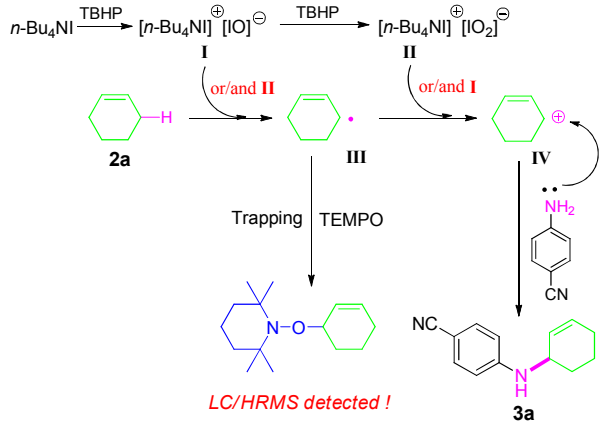
cyano-*N*-methylaniline (a secondary aromatic amine) reacted with **2a** under the optimized reaction conditions, providing the desired product **3r** in 56 % yield. No product was detected for the reaction of *N*-acetylaniline with **2a**, and the complicated oxidation products were observed for the reaction of *N*-methylaniline with **2a** under the present reaction conditions. However, electron-riched aniline, such as 4-methylaniline or 4-methoxyaniline was used in the reaction with cyclohexene under the standard reaction conditions, an oxidative homodimerization of aniline, 4,4'-dimethylazobenzene or 4,4'-dimethoxyazobenzene was isolated in 56% and 51% yield, respectively.

It should be noted that the reactions of 3-methylcyclohex-1-ene with 4-acetylaniline and 4-cyanoaniline under the present reaction conditions afforded the rearrangement amination products[26] **3s** and **3t** with 78% and 72% yield, respectively in good regioselectivity (Scheme 3). In addition, the structure of **3s** was confirmed by single crystal X-ray crystallography.[27]

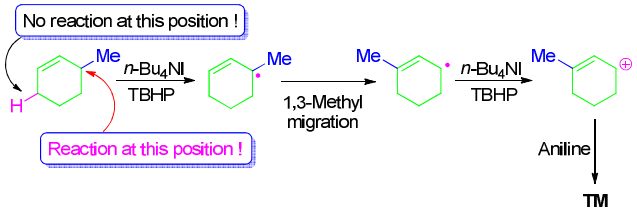
Because of the similar property of benzylic C(sp^3)−H with allylic C(sp^3)−H, one of the substrate was extended to benzylic C(sp^3)−H. The reactions of ethylbenzene and its derivatives with 4-aminobenzonitrile (**1a**) as nitrogen source were examined under the aforementioned conditions. As can be seen from Scheme 4, 52% yield of amination product **4a** was obtained from the reaction of ethylbenzene and **1a**. Similarly, the amination of ethylbenzene with 4-acetylaniline also proceeded to generate the corresponding product **4b** in 48% yield. To our delight, amination of other benzylic compounds, such as propylbenzene, cumene, *p*-cymene with 4-acetylaniline were accomplished to afford the corresponding products, **4c** in 46% yield, **4d** in 55% yield, and **4e** in 48% yield, respectively. Importantly, In the case of *p*-cymene, the amination occurred at 3° benzylic C(sp^3)−H bond compeletely to give the corresponding product **4e**, but not at 1° benzylic C(sp^3)−H bond.

When 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) was added in 0.2 equiv of aniline (equals to *n*-Bu_4NI), **3a** was isolated in 75% yield. While 2.0 equiv. of TEMPO (10 times to *n*-Bu_4NI) was added to the reaction, **3a** was obtained in 43% yield. However, the reaction was completely shut down with the addition of 4.0 equiv. of TEMPO to the system. It is suggested that TEMPO acts as a radical scavenger and the reaction involves a radical process (Electronic Supplementary Information for detail). A possible reaction mechanism was proposed in Scheme 5 based on our results and literature.[22b,24,28] Initially, the active iodine species ammonium hypoiodite **I** or iodite **II** was formed via the oxidation of *n*-Bu_4NI with TBHP. The obtained **I** or/and **II** then reacted with cyclohexene (**2a**) to generate the allylic radical **III**, which was further oxidized by **II** or/and **I** to afford allylic cation **IV**. Finally, the desired product **3a** was formed through a nucleophilic reaction of amine **1a** to **IV**. The proposed mechanism was further investigated through the trapping of free radical intermediate with TEMPO by HPLC-HRMS probe. The coupling product of allylic radical **III** with TEMPO was confirmed by HRMS (ESI for detail). Moreover, the free radical rearrangement of 3-methylcyclohex-1-ene (1,3-methyl migration process) also supported the regioselective formation of **3s** and **3t** (Scheme 6).

In conclusion, we have developed an efficient *n*-Bu_4NI/TBHP-catalyzed direct amination of cyclohexene, cyclopentene, and benzylic compounds with anilines. This new method is complementary to existing C–H amination reactions for expanding scope and practicality. This amination reaction was realized under metal-free conditions and employed aromatic amines as the nitrogen sources which illustrated a practical straightforward route to a variety of *N*-substituted anilines. Further investigations of detail reaction mechanism and the application of this procedure are underway.



Scheme 5 The proposed mechanism



Scheme 6 The free radical rearrangement of 3-methylcyclohex-1-ene

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1 (*a*) *Amino Group Chemistry, From Synthesis to the Life Sciences*; A. Ricci, Ed.; Wiley-VCH: Weinheim, 2008; (*b*) R. Hili and A. K. Yudin, *Nat. Chem. Biol.*, 2006, **2**, 284; (*c*) J. Struff, C. H. Hövelmann, M. Nieger and K. Muñiz, *J. Am. Chem. Soc.*, 2005, **127**, 14586; (*d*) H. M. L. Davies and M. S. Long, *Angew. Chem., Int. Ed.*, 2005, **44**, 3518.

2 (*a*) D. Ma and Q. Cai, *Acc. Chem. Res.*, 2008, **41**, 1450; (*b*) H. Fan, J. Peng, M. T. Hamann and J.-F. Hu, *Chem. Rev.*, 2008, **108**, 264.

3 (*a*) A. R. Muci and S. L. Buchwald, *Top. Curr. Chem.*, 2002, **219**, 131; (*b*) J. F. Hartwig, *Acc. Chem. Res.*, 2008, **41**, 1534; (*c*) D. S. Surry and S. L. Buchwald, *Chem. Sci.*, 2011, **2**, 27; (*d*) J. F. Hartwig, *Nature*, 2008, **455**, 314.

4 (*a*) H. M. L. Davies and J. R. Manning, *Nature,* 2008, **451**, 417; (*b*) Y. Tan and J. F. Hartwig, *J. Am. Chem. Soc.*, 2010, **132**, 3676; (*c*) T. Kawano, K. Hirano, T. Satoh and M. Miura, *J. Am. Chem. Soc.*, 2010, **132**, 6900; (*d*) K.-H. Ng, A. S. C. Chan and W.-Y. Yu, *J. Am. Chem. Soc.*, 2010, **132**, 12862; (*e*) H. Wang, Y. Wang, C. Peng, J.

Zhang and Q. Zhu, *J. Am. Chem. Soc.*, 2010, **132**, 13217; (*f*) K. Sun, Y. Li, T. Xiong, J. Zhang and Q. Zhang, *J. Am. Chem. Soc.*, 2011, **133**, 1694; (*g*) E. J. Yoo, S. Ma, T.-S. Mei, K. S. L. Chan and J.-Q. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 7652.

5 (*a*) W. C. P. Tsang, R. H. Munday, G. Brasche, N. Zheng and S. L. Buchwald, *J. Org. Chem.*, 2008, **73**, 7603; (*b*) G. Brasche and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2008, **47**, 1932.

6 (*a*) M. Wasa and J.-Q. Yu, *J. Am. Chem. Soc.*, 2008, **130**, 14058; (*b*) T.-S. Mei, X. Wang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 10806; (*c*) J.-J. Li, T.-S. Mei and J.-Q. Yu, *Angew. Chem., Int. Ed.* 2008, **47**, 6452.

7 (*a*) E. T. Nadres and O. Daugulis, *J. Am. Chem. Soc.*, 2012, **134**, 7; (*b*) G. He, Y. Zhao, S. Zhang, C. Lu and G. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 3; (*c*) H. J. Kim, J. Kim, S. H. Cho and S. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 16382; (*d*) B. Xiao, T.-J. Gong, J. Xu, Z.-J. Liu and L. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 1466; (*e*) J. A. Jordan-Hore, C. C. C. Johansson, M. Gulias, E. M. Beck and M. J. Gaunt, *J. Am. Chem. Soc.*, 2008, **130**, 16184.

8 (*a*) G.-W. Wang, T.-T. Yuan and D.-D. Li, *Angew. Chem., Int. Ed.*, 2011, **50**, 1380; (*b*) R. I. McDonald and S. S. Stahl, *Angew. Chem., Int. Ed.*, 2010, **49**, 5529.

9 (*a*) K.W. Fiori and J. Du Bois, *J. Am. Chem. Soc.*, 2007, **129**, 562; (*b*) C. Liang, F. Collet, F. Robert-Peillard, P. Muller, R. H. Dodd and P. Dauban, *J. Am. Chem. Soc.*, 2008, **130**, 343.

10 (*a*) E. Milczek, N. Boudet and S. Blakey, *Angew. Chem. Int. Ed.*, 2008, **47**, 6825; (*b*) M. E. Harvey, D. G. Musaev and J. Du Bois, *J. Am. Chem. Soc.*, 2011, **133**, 17207; (*c*) S. K.-Y. Leung,W.-M. Tsui, J.-S. Huang, C.-M. Che, J.-L. Liang and N. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 16629.

11 (*a*) S. Wiese, Y. M. Badiei, R. T. Gephart, S. Mossin, M. S. Varonka, M. M. Melzer, K. Meyer, T. R. Cundari and T. H. Warren, *Angew. Chem., Int. Ed.*, 2010, **49**, 8850; (*b*) D. N. Barman, P. Liu, K. N. Houk and K. M. Nicholas, *Organometallics*, 2010, **29**, 3404.

12 (*a*) E. R. King, E. T. Hennessy and T. A. Betley, *J. Am. Chem. Soc.*, 2011, **133**, 4917; (*b*) Z. Wang, Y. Zhang, H. Fu, Y. Jiang and Y. Zhao, *Org. Lett.*, 2008, **10**, 1863; (*c*) Y. Liu and C.-M. Che, *Chem.-Eur. J.*, 2010, **16**, 10494.

13 V. Lyaskovskyy, A. I. Olivos Suarez, H. Lu, H. Jiang, X. P. Zhang and B. Bruin, *J. Am. Chem. Soc.*, 2011, **133**, 12264.

14 J. Zhang, P.W. H. Chan and C.-M. Che, *Tetrahedron Lett.*, 2005, **46**, 5403.

15 (*a*) M. R. Fructos, S. Trofimenko, M. M. Díaz-Requejo and P. J. Pérez, *J. Am. Chem. Soc.*, 2006, **128**, 11784; (*b*) R. Bhuyan and K. M. Nicholas, *Org. Lett.*, 2007, **9**, 3957.

16 (*a*) J. D. Harden, J. V. Ruppel, G.-Y. Gao and X. P. Zhang, *Chem. Commun.*, 2007, 4644; (*b*) G.-Y. Gao, J. D. Harden and X. P. Zhang, *Org. Lett.*, 2005, **7**, 3191.

17 (*a*) H. Lebel, K. Huard and S. Lectard, *J. Am. Chem. Soc.*, 2005, **127**, 14198; (*b*) H. Lebel and K. Huard, *Org. Lett.*, 2007, **9**, 639.

18 (*a*) B. J. Stokes, H. Dong, B. E. Leslie, A. L. Pumphrey and T. G. Driver, *J. Am. Chem. Soc.*, 2007, **129**, 7500; (*b*) Y. M. Badiei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari and T. H. Warren, *Angew. Chem., Int. Ed.*, 2008, **47**, 9961; (*c*) M. Shen, B. E. Leslie and T. G. Driver, *Angew. Chem., Int. Ed.*, 2008, **47**, 5056.

19 (*a*) G. Liu, G. Yin and L. Wu, *Angew. Chem. Int. Ed.*, 2008, **47**, 4733; (*b*) S. A. Reed, A. R. Mazzotti and M. C. White, *J. Am. Chem. Soc.*, 2009, **131**, 11701; (*c*) G. T. Rice and M. C. White, *J. Am. Chem. Soc.*, 2009, **131**, 11707.

20 (*a*) G. Pelletier and D. A. Powell, *Org. Lett.*, 2006, **8**, 6031; (*b*) D. A. Powell and H. Fan, *J. Org. Chem.*, 2010, **75**, 2726.

21 A. Iglesias, R. Álvarez, Á. R. Lera and K. Muñiz, *Angew. Chem., Int. Ed.*, 2012, **51**, 2225.

22 (*a*) X. Liu, Y. Zhang, L. Wang, H. Fu, Y. Jiang and Y. Zhao, *J. Org. Chem.*, 2008, **73**, 6207; (*b*) Q. Xia, W. Chen and H. Qiu, *J. Org. Chem.*, 2011, **76**, 7577.

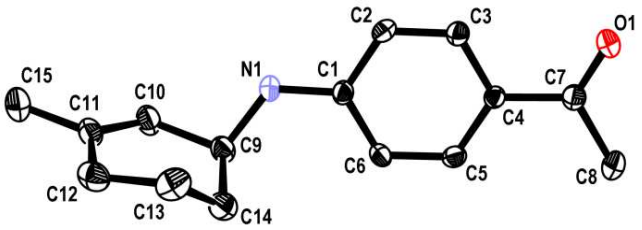
23 (*a*) J. Pan, M. Su and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2011, **50**, 8647; (*b*) R. T. Gephart III, D. L. Huang, M. J. B. Aguila, G. Schmidt, A. Shahu and T. H. Warren, *Angew. Chem., Int. Ed.*, 2012, **51**, 6488; (*c*) T. W. Liwosz and Sherry R. Chemler, *Chem.–Eur. J.*, 2013, **19**, 12771; (*d*) Q. Michaudel, D. Thevenet and P. S. Baran, *J. Am. Chem. Soc.*, 2012, **134**, 2547; (*e*) J. J. Neumann, S. Rakshit, T. Dröge and F. Glorius, *Angew. Chem., Int. Ed.*, 2009, **48**, 6892.

24 (*a*) M. Koag and S. Lee, *Org. Lett.*, 2011, **13**, 4766; (*b*) Q. Xue, J. Xie, H. Li, Y. Cheng and C. Zhu, *Chem. Commun.*, 2013, **49**, 3700.

25 (*a*) W. Chen, Y. Zhang, L. Zhang, M. Wang and L. Wang, *Chem. Commun.*, 2011, **47**, 10476; (*b*) T. He, H. Li, P. Li and L. Wang, *Chem. Commun.*, 2011, **47**, 8946.

26 J. A. Souto, D. Zian and K. Muñiz, *J. Am. Chem. Soc.*, 2012, **134**, 7242.

27 X-ray single crystal structure of **3s**.



28 (*a*) M. Uyanik, H. Okamoto, T. Yasui and K. Ishihara, *Science,* 2010, **328**, 1376; (*b*) J. Feng, S. Liang, S. Chen, J. Zhang, S. Fu and X. Yu, *Adv. Synth. Catal.,* 2012, **354**, 1287; (*c*) Y. Li, B. Li, X. Lu, S. Lin and Z. Shi, *Angew. Chem., Int. Ed.,* 2009, **48**, 3817.