Angewandte
Chemie

DOI: 10.1002/ange.201109027

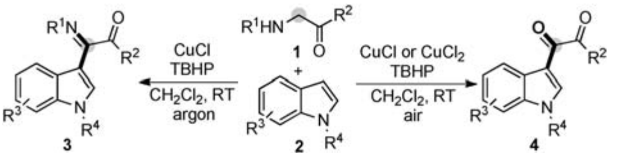
Synthetic Methods

Copper-Catalyzed C–H Oxidation/Cross-Coupling of α-Amino Carbonyl Compounds**

*Ji-Cheng Wu, Ren-Jie Song, Zhi-Qiang Wang, Xiao-Cheng Huang, Ye-Xiang Xie, and Jin-Heng Li**

Functionalization of α-C–H bonds to the carbonyl group in α-amino carbonyl compounds is a hot topic in organic synthesis because many natural products or biomolecules contain these modified α-amino carbonyl units in their structures.[1–4] Among the efficient reactions for the functionalization of C–H bonds α to a carbonyl group,[1–4] transition-metal-catalyzed α-arylation reactions have attracted significant interest because of their synthetic utility.[3,4] Despite considerable progress in the field, examples of transition-metal-catalyzed α arylation of α-amino carbonyl compunds are much less abundant and are more limited: the α-arylation reaction is realized through deprotonation (in situ generation of carbonyl enolate) with the aid of a base and requires the use of both expensive aryl sources (often aryl halides or pseudohalides) and transition-metal catalysts (often Pd). Recently, transition-metal-catalyzed oxidative deprotonation emerged as a powerful tool in numerous C–H functionalization reactions, wherein bases are not necessary.[2i,5,6] However, to our knowledge, transition-metal-catalyzed α arylation of α-amino carbonyls leading to α-aryl α-iminocarbonyls using a C–H oxidation strategy has not been established.

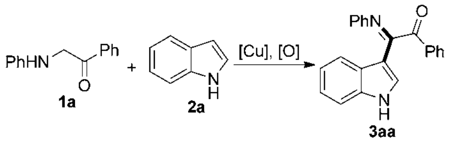
Herein we report a novel and mild route to the selective synthesis of 2-(1*H*-indol-3-yl)-2-imino-carbonyls (**3**) and 2-(1*H*-indol-3-yl)-2-oxo-carbonyls (**4**) by copper-catalyzed C–H oxidation/cross-coupling of α-amino carbonyl compounds (**1**) with indoles (**2**) in the presence of *tert*-butyl hydroperoxide (TBHP; Scheme 1). Interestingly, the selectivity for either **3** or **2** can be tuned by a slight modification of the reaction conditions. It is noteworthy that the products, 3-substituted indoles, are valuable synthetic intermediates and important structural units found in numerous natural products, pharmaceuticals, and functional materials.[7]



Scheme 1. Copper-catalyzed C–H oxidation.

Our investigation began with the reaction of 1-phenyl-2-(phenylamino)ethanone (**1a**) with 1*H*-indole (**2a**) and 10 mol% CuCl in CH_2Cl_2 at room temperature under an argon atmosphere (entry 1; Table 1): a trace of the desired 2-(1*H*-indol-3-yl)-1-phenyl-2-(phenylimino)ethanone (**3aa**) was observed. These results encouraged us to optimize the other reaction parameters. After a series of trials, we were pleased to find that the yield of **3aa** could be enhanced in the

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



Entry	[Cu] (mol%)	[O] (equiv)	Solvent	Yield [%][b]
1	CuCl (10)	–	CH_2Cl_2	trace
2	CuCl (10)	oxone (2)	CH_2Cl_2	32
3	CuCl (10)	mCPBA (2)	CH_2Cl_2	34
4	CuCl (10)	TBHP (2)	CH_2Cl_2	83
5[c]	CuCl (10)	TBHP (3)	CH_2Cl_2	28
6	CuCl (10)	TBHP (1.3)	CH_2Cl_2	15
7	CuBr (10)	TBHP (2)	CH_2Cl_2	73
8	CuI (10)	TBHP (2)	CH_2Cl_2	71
9[d]	$CuCl_2$ (10)	TBHP (2)	CH_2Cl_2	65
10	$Cu(OTf)_2$ (10)	TBHP (2)	CH_2Cl_2	58
11	–	TBHP (2)	CH_2Cl_2	0
12	CuCl (20)	TBHP (2)	CH_2Cl_2	79
13[e]	CuCl (5)	TBHP (2)	CH_2Cl_2	80
14	CuCl (10)	TBHP (2)	–	60
15	CuCl (10)	TBHP (2)	CH_2ClCH_2Cl	10
16	CuCl (10)	TBHP (2)	DMSO	5
17	CuCl (10)	TBHP (2)	MeCN	38
18	CuCl (10)	TBHP (2)	toluene	36
19[f]	CuCl (10)	TBHP (2)	CH_2Cl_2	33

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), [Cu] and solvent (2 mL) under argon atmosphere for 12 h. TBHP (2 equiv, 70% in water). [b] Yield of isolated product. [c] Some unidentified products were observed by GC/MS analysis in addition to the 10% yield of **4aa**. [d] Product **4aa** was isolated in 20% yield. [e] For 20 h. [f] Anhydrous TBHP (5 M in decane). Product **4aa** was isolated in 28% yield. DMSO = dimethylsulfoxide, Tf = trifluoromethanesulfonyl.

---

[*] J.-C. Wu,[+] R.-J. Song,[+] Z.-Q. Wang, X.-C. Huang, Y.-X. 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
J.-C. Wu,[+] Z.-Q. Wang, X.-C. Huang
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.

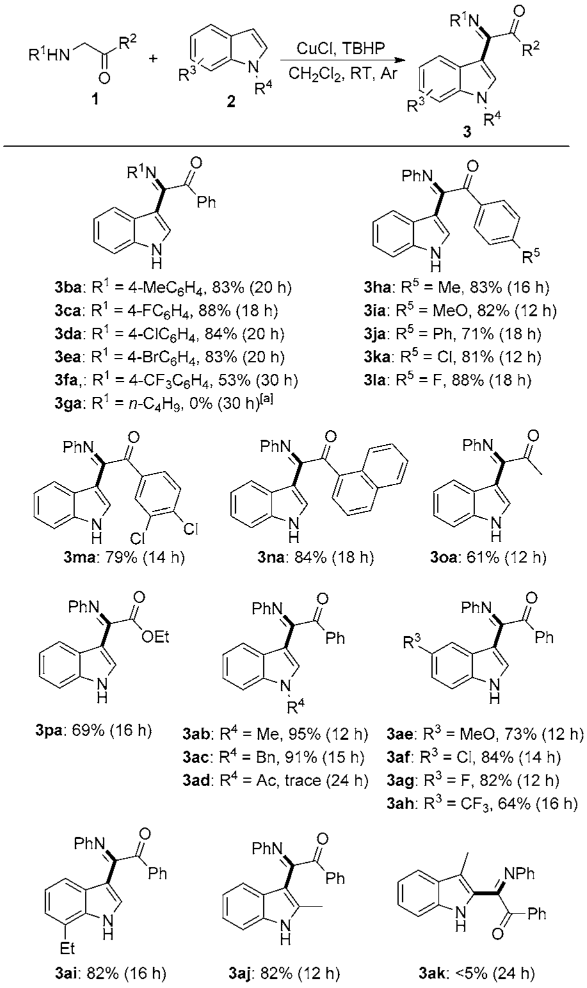
[**] We thank the Natural Science Foundation of China (No. 21172060) and Fundamental Research Funds for the Central Universities (Hunan University) for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201109027.

presence of oxidants, including oxone (entry 2), *m*CPBA (entry 3), and TBHP (entry 4). Screening revealed that the amount of TBHP affected the reaction (entries 5 and 6). Both 3 equivalents and 1.3 equivalents of TBHP offered the desired product **3aa** in a low yield. Another product, 1-(1*H*-indol-3-yl)-2-phenylethane-1,2-dione (**4aa**), was isolated in 10% yield when 3 equivalents of TBHP was used (entry 5). Subsequently, a series of other copper catalysts, including CuBr, CuI, $CuCl_2$, and $Cu(OTf)_2$, were tested (entries 7–10), and they displayed high catalytic efficiency for the reaction in the presence of TBHP, but were inferior to CuCl. Notably, product **4aa** was obtained when $CuCl_2$ was used as the catalyst (entry 9). Notably, the reaction cannot take place without a copper catalyst (entry 11). Gratifyingly, good yields were still achieved when using either 20 mol% or 5 mol% CuCl, but the latter required a prolonged reaction time (entries 12 and 13). It was interesting to discover that the reaction could be carried out under neat reaction conditions, thus furnishing **3aa** in moderate yield (entry 14). Among the solvents examined, CH_2Cl_2 was the most effective (entries 15–18). When using anhydrous TBHP, however, the reaction afforded a mixture of the products **3aa** and **4aa** in 33% and 28% yields, respectively (entry 19).

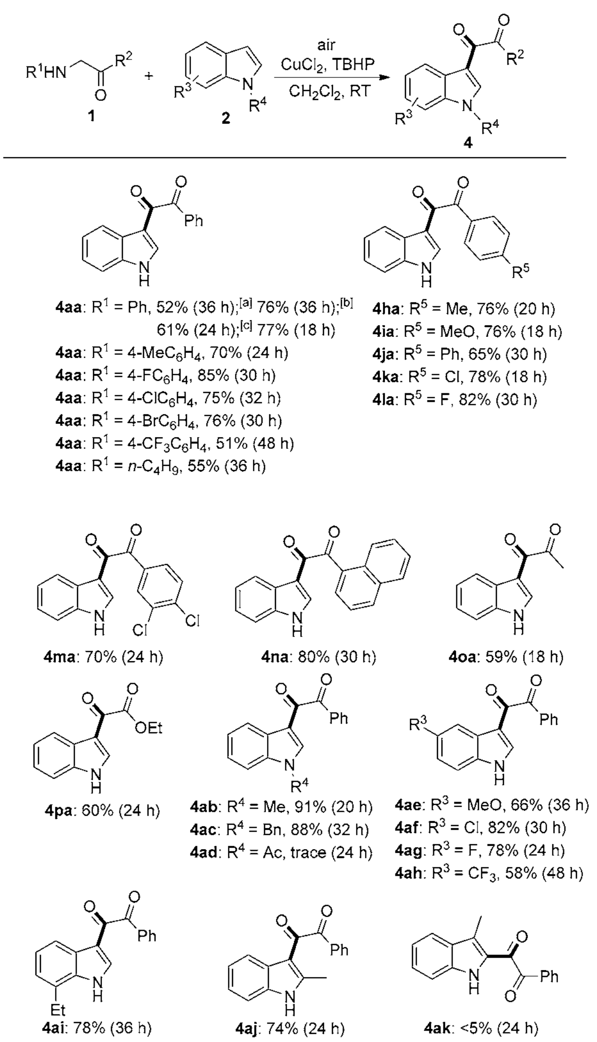
With the optimal reaction conditions in hand, the scope of both the α-amino carbonyls **1** and indoles **2** was explored (Scheme 2). Initially, several N-aryl groups on **1** were investigated in the presence of 1*H*-indole (**2a**), CuCl, TBHP, and argon. The reactivity of the electron-rich N-aryl group was superior to that of the electron-withdrawing N-aryl groups, and some halo substituents (F, Cl, or Br) were tolerated (**3ba**–**3fa**). However, substrates with an N-*n*Bu group, an aliphatic group, did not lead to the desired product **3ga**, but **4aa** was isolated in 50% yield. Gratifyingly, substituents, including aryl and alkyl groups, at the 1-position of **1** were consistent with the optimal reaction conditions (**3ha**–**3oa**). For examples, substrates with a *para*-substituted aryl group, such as *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-PhC_6H_4, *p*-ClC_6H_4, or *p*-FC_6H_4, smoothly underwent the reaction with **2a**, CuCl, and TBHP under argon, thus affording the corresponding products **3ha**–**3la** in good yields. Good yield was still achieved when using the dichloro-substituted substrate (**3ma**). Substrate 1-(phenylamino)propan-2-one, lead to the desired product **3oa** in 61% yield. Notably, ethyl 2-oxo-3-(phenylamino)propanoate, an amino ester, was also a suitable substrate, thus leading to the target product **3pa** in 69% yield.

Subsequently, the scope of the indoles **2** was examined in the presence of **1a**, CuCl, TBHP and argon (**3ab**–**3ak**). Screening revealed that 1-alkyl indoles (1-Me or 1-Bn) were suitable for the reaction (**3ab** and **3ac**), but 1-acetyl-substitued indole has no reactivity (**3ad**). Interestingly, the reaction had high functional group compatibility as several functional groups, including MeO, Cl, F, CF_3, Et, and Me, on the aromatic ring of **2** were well tolerated. 5-Methoxy-1*H*-indole, for instance, underwent the reaction with substrate **1a**, CuCl, and TBHP, thus providing **3ae** in 73% yield. Importantly, substituents, Cl and F, were compatible with the optimal reaction conditions, thereby providing a means for additional modifications at the halogenated positions (**3af** and **3ag**). Indole having the electron-withdrawing CF_3 group delivered a moderate product yield (**3ah**). It is noteworthy that 2-methyl indole furnishes the desired product **3aj** in 82% yield, but 3-methyl indole is an unsuitable substrate (**3ak**).



Scheme 2. CuCl-catalyzed synthesis of 2-(1*H*-indol-3-yl)-2-iminocarbonyls (**3**) under an atmosphere of argon. Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), CuCl (10 mol%), TBHP (2 equiv, 70% in water) and CH_2Cl_2 (2 mL) at room temperature under argon atmosphere. [a] Product **4aa** was isolated in 50% yield.

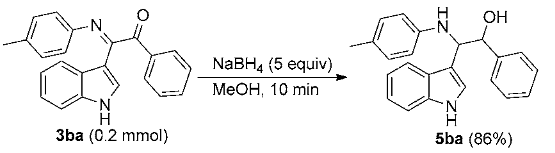
As shown in Scheme 3, the selectivity of the reaction shifted towards 1,2-diones or 2-keto esters when the reaction was carried out under an atmosphere of air. For example, treatment of **1a** with **2a**, CuCl, TBHP, and air for 36 hours afforded **4aa** exclusively in 52% yield. The results demonstrated that the amount of TBHP affects the reaction, and that 3 equivalents of TBHP gives then best results. Notably, the reaction time was shortened to 18 hours when $CuCl_2$ was employed as the catalyst instead of CuCl. In light of these results, the $CuCl_2$/TBHP/air catalytic system was used in the preparation of various 1,2-diones and 2-keto esters. Gratifyingly, the $CuCl_2$/TBHP/air catalytic system is consistent with a wide range of substituents, including MeO, Br, Cl, F, CF_3, Ph, Et, and Me, on the aromatic rings of **1** or **2**. Screening disclosed that in the presence of $CuCl_2$, TBHP, and air a variety of α-amino carbonyls were oxidatively cross-coupled with **2a**, thus leading the corresponding products **4aa** and



Scheme 3. $CuCl_2$-catalyzed synthesis of 2-(1*H*-indol-3-yl)-2-oxo-carbonyls (**4**) under an atmosphere of air. Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), $CuCl_2$ (10 mol%), TBHP (3 equiv, 70% in water) and CH_2Cl_2 (2 mL) at room temperature under air (1 atm) conditions. [a] CuCl (10 mol%) and TBHP (2 equiv). [b] CuCl (10 mol%) and TBHP (3 equiv) in either air or O_2 (1 atm). [c] CuCl (10 mol%) and TBHP (4 equiv).

4ha–**4pa** in moderate to good yields. Moreover, a number of indoles were also successfully reacted with **1a** under the same reaction conditions. However, attempts at reacting 3-methyl-1*H*-indole failed.

The hydrogenation of **3ba** is summarized in Equation (1). In the presence of $NaBH_4$ and MeOH, **3ba** was converted into



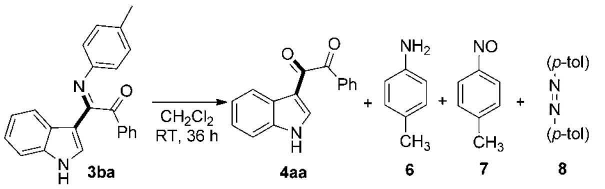
(1)

2-(1*H*-indol-3-yl)-1-phenyl-2-(*p*-tolylamino)ethanol (**5ba**), an amino alcohol, in 86% yield.

To elucidate the mechanism, some control experiments were carried out.[8] The results shwon in Equation (2) showed that $CuCl_2$, TBHP, and air are important factors in the conversion of **3ba** into **4aa**. The product **3ba** was converted into **4aa** in 76% yield using the $CuCl_2$/TBHP/air system [Eq. (2)], however, the conversion decreased sharply in the absence air, TBHP, and $CuCl_2$. Additinally, **3ba** could not be transformed in the presence of either air [Eq. (2)] or THBP alone (entry 10, Table 1). However, the conversion of **3ba** could take place using air combined with either hydrous or anhydrous TBHP. It was found that the $CuCl_2$/H_2O/air system only gave 22% yield of **4aa** without the aid of TBHP. The results in Equation (2) suggest that TBHP plays an important role in the conversion of **3ba** into **4aa**. Notably, among these reactions some other products, including *p*-toluidine (**6**), 1-methyl-4-nitrobenzene (**7**), and 1,2-dip-tolyldiazene (**8**), were observed by GC/MS analysis Equation (2). Interestingly, 1-phenyl-2-(phenylimino)ethanone [**9**; see structure in Eq. (3)] is observed by in situ GC/MS analysis, and disappears when the reaction is completed. This process was illustrated distinctly in the reaction profile.[10] Thus, the reaction between **2a** and **9** was investigated [Eq. (3)], and in the presence of CuCl and argon and absence of TBHP only a trace amount of **3aa** was observed; however with 2 equivalents of TBHP **3aa** was exclusively isolated in 72% yield. Gratifyingly, the $CuCl_2$/TBHP/air system furnished product **4aa** alone in 55% yield. Notably, 1-phenyl-2-(phenylamino)propan-1-one (**1q**) was not a suitable substrate for the reaction [Eq. (4)]. The ^{18}O-labeling experiments disclosed that the oxygen atom in the newly formed carbonyl group of product **4aa** is derived from water [Eq. (5)],[8] and implies that **4aa** is formed from the hydrolysis of an imino compound.[9] Notably, a stoichiometric amount of two radical inhibitors, 2,2,6,6-tetramethylpiperidine oxide (TEMPO) and 2,6-di-*tert*-butylphenol, were also used in the reaction of **1a** with **2a** using either the CuCl/TBHP/Ar catalytic system or $CuCl_2$/TBHP/O_2 catalytic system. A significant drop in yield was observed in the presence of these radical inhibitors, thus suggesting that the present reaction includes a radical process.[8]

To our surprise, **4aa** could not be obtained in the presence of CuCl, 70% TBHP in water, and argon. However **4aa** was isolated in 28% yield when using 5 M TBHP in decane instead of 70% TBHP in water (entries 4 and 19; Table 1). Moreover, **4aa** was observed when using either $CuCl_2$ or as much as 3 equivalents of TBHP (entries 5 and 9; Table 1). These results simply show that the stronger oxidizing conditions favor the hydrolysis reaction. On the basis of the above results and the results in Eqs. (2)–(5), the Cu^{II} species is the real catalyst for hydrolyzing imine **3**, and two roles of TBHP are proposed: 1) as an oxidizing agent to regenerate the active Cu^{II} species, and 2) as an oxygen atom (H_2O) source through decomposition with O_2.

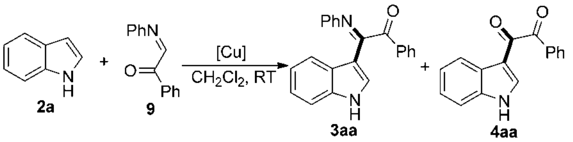
Consequently, a possible mechanism is proposed (Scheme 4).[5,6,10,11] Initially oxidative deprotonation of substrate **1a** by TBHP takes place to yield intermediate **9**,[10,11] which is supported by the reaction profile.[10] Consequently, the in situ Friedel–Crafts alkylation of **2a** with intermediate **9** affords product **3aa**.[5,6] Product **3aa** is hydrolyzed by H_2O to



(2)

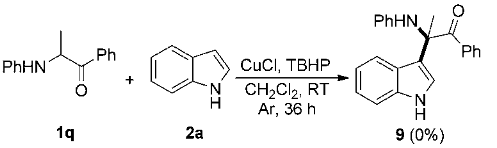
CuCl$_2$/TBHP/air: 76%
CuCl$_2$/TBHP/Ar: 30%
CuCl$_2$/air: 16%
TBHP/air: 21%
TBHP (in decane)/air: 30%
air: trace
CuCl$_2$/H$_2$O/air: 22%

35% (GC) 8% (GC) <5% (GC)

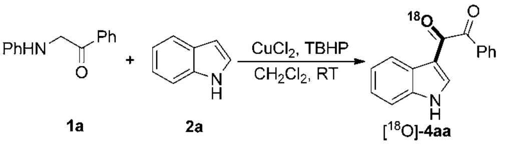


(3)

	3aa	4aa
CuCl (10 mol%) Ar:	trace	0%
CuCl (10 mol%), TBHP (2 equiv), Ar:	72%	0%
CuCl$_2$ (10 mol%), TBHP (3 equiv), air:	0%	55%



(4)

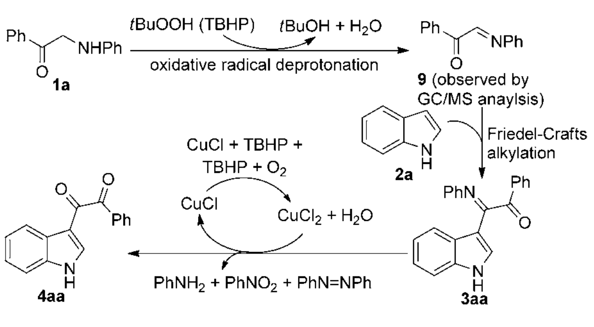


(5)

$^{18}O_2$: 55% (15% ^{18}O)
$^{16}O_2$, $H_2{}^{18}O$ (15 mol%): 62% (5% ^{18}O)
$^{16}O_2$, $H_2{}^{18}O$ (10 equiv): 65% (51% ^{18}O)

produce **4aa**, PhNH$_2$, and CuCl with the aid of CuCl$_2$, TBHP, and O$_2$.

In summary, we have described that inexpensive copper salts could catalyze the C–H oxidative/cross-coupling of α-amino carbonyls with indoles to selectively furnish 2-(1*H*-indol-3-yl)-2-imino-carbonyls and 2-(1*H*-indol-3-yl)-2-oxo-carbonyls with the aid of TBHP. Notably, a mechanism was proposed given the results of the ^{18}O-labeling experiments and the control experiments. Applications of this copper-catalyzed oxidative transformation in organic synthesis are currently underway in our laboratory.



Scheme 4. Possible mechanism.

Experimental Section

Typical experimental procedure for the copper-catalyzed synthesis of 2-(1*H*-Indol-3-yl)-2-imino-carbonyls (**3**): α-Amino carbonyl **1** (0.3 mmol), indole **2** (0.36 mmol), CuCl (10 mol%), TBHP (2 equiv), and CH$_2$Cl$_2$ (2 mL) were added to a Schlenk tube. Then the tube was charged with argon, and the reaction mixture stirred at room temperature for the indicated time until complete consumption of starting material as determined by TLC and GC/MS analyses. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na$_2$SO$_4$, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 5:1) to afford the desired product **3**.

Typical experimental procedure for the copper-catalyzed synthesis of 2-(1*H*-indol-3-yl)-2-oxo-carbonyls (**4**): α-Amino carbonyl **1** (0.3 mmol), indole **2** (0.36 mmol), CuCl$_2$ (10 mol%), TBHP (3 equiv), and CH$_2$Cl$_2$ (2 mL) were added to a Schlenk tube. Then the tube was charged with air, and the reaction mixture was stirred at room temperature for the indicated time until complete consumption of starting material as determined by TLC and GC/MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na$_2$SO$_4$, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 3:1) to afford the desired product **4**.

Received: December 21, 2011
Revised: January 15, 2012

Keywords: amines · copper · heterocycles · oxidation · synthetic methods

---

[1] For selected reviews, see: a) S. Hunt, *Chemistry and Biochemistry of the Amino Acids* (Ed.: G. C. Barrett), Chapman and Hall, London, **1985**, p. 55; b) Y. Ohfune, *Acc. Chem. Res.* **1992**, *25*, 360; c) S. H. Gellman, *Acc. Chem. Res.* **1998**, *31*, 173.

[2] a) D. Obrecht, M. Altorfer, C. Lehmann, P. Schönholzer, K. Müller, *J. Org. Chem.* **1996**, *61*, 4080; b) D. Obrecht, U. Bohdal, C. Broger, D. Bur, C. Lehmann, R. Ruffieux, P. Schönholzer, C. Spiegler, K. Müller, *Helv. Chim. Acta* **1995**, *78*, 563; c) D. D. Schoepp, D. E. Jane, J. A. Monn, *Neuropharmacology* **1999**, *38*, 1431; d) A. Takahashi, H. Naganawa, D. Ikeda, Y. Okami, *Tetrahedron* **1991**, *47*, 3621; e) D. Schirlin, F. Gerhart, J. M. Hornsperger, M. Hamon, J. Wagner, M. J. Jung, *J. Med. Chem.* **1988**, *31*, 30; f) J. J. Walsh, D. E. Metzler, D. Powell, R. A. Jacobson, *J. Am. Chem. Soc.* **1980**, *102*, 7136; g) V. Lupi, M. Penso, F. Foschi, F. Gassa, V. Mihali, A. Tagliabue, *Chem. Commun.* **2009**, 5012; h) M. A. Beenen, D. J. Weix, J. A. Ellman, *J. Am. Chem. Soc.* **2006**, *128*, 6304; i) L. Zhao, C.-J. Li, *Angew. Chem.* **2008**, *120*, 7183; *Angew. Chem. Int. Ed.* **2008**, *47*, 7075.

[3] For reviews, see: a) R. M. Williams, J. A. Hendrix, *Chem. Rev.* **1992**, *92*, 889; b) D. Culkin, J. F. Hartwig, *Acc. Chem. Res.* **2003**, *36*, 234; c) M. Miura, M. Nomura, *Top. Curr. Chem.* **2002**, *219*, 211; d) F. Bellina, R. Rossi, *Chem. Rev.* **2010**, *110*, 1082.

[4] a) O. Gaertzen, S. L. Buchwald, *J. Org. Chem.* **2002**, *67*, 465; b) X. Liu, J. F. Hartwig, *Org. Lett.* **2003**, *5*, 1915; c) S. Lee, N. A. Beare, J. F. Hartwig, *J. Am. Chem. Soc.* **2001**, *123*, 8410; d) M. S. Sigman, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, *120*, 5315; e) M. S. Sigman, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, *120*, 4901; f) K. L. Reddy, K. B. Sharpless, *J. Am. Chem. Soc.* **1998**, *120*, 1207; g) M. Chaari, A. Jenhi, J.-P. Lavergne, P. Viallefont, *Tetrahedron* **1991**, *47*, 4619; h) M. J. O'Donnell, W. D. Bennett,

W. N. Jacobsen, Y. Ma, J. C. Huffman, *Tetrahedron Lett.* **1989**, *30*, 3909; i) B. M. Trost, X. Aeiza, *J. Am. Chem. Soc.* **1999**, *121*, 10727; j) M. Hocek, *Heterocycles* **2004**, *63*, 1673; k) S. P. Marsden, E. L. Watson, S. A. Raw, *Org. Lett.* **2008**, *10*, 2905.

[5] For reviews, see: a) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J. Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242; b) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335; c) C. J. Scheuermann, *Chem. Asian J.* **2010**, *5*, 436; d) W.-J. Yoo, C.-J. Li, *Top. Curr. Chem.* **2010**, *292*, 281; e) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; f) T. Newhouse, P. S. Baran, *Angew. Chem.* **2011**, *123*, 3422; *Angew. Chem. Int. Ed.* **2011**, *50*, 3362; g) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem.* **2011**, *123*, 11256; *Angew. Chem. Int. Ed.* **2011**, *50*, 11062.

[6] a) S. Velusamy, T. Punniyamurthy, *Tetrahedron Lett.* **2003**, *44*, 8955; b) S.-I. Murahashi, N. Komiya, H. Terai, T. Nakae, *J. Am. Chem. Soc.* **2003**, *125*, 15312; c) Z. Li, C.-J. Li, *Org. Lett.* **2004**, *6*, 4997; d) Z. Li, C.-J. Li, *J. Am. Chem. Soc.* **2005**, *127*, 3672; e) Z. Li, D. S. Bohle, C.-J. Li, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 8928; f) Z. Li, C.-J. Li, *J. Am. Chem. Soc.* **2005**, *127*, 6968; g) O. Baslé, C.-J. Li, *Green Chem.* **2007**, *9*, 1047; h) O. Baslé, C.-J. Li, *Org. Lett.* **2008**, *10*, 3661; i) O. Baslé, N. Borduas, P. Dubois, J. M. Chapuzet, T.-H. Chan, J. Lessard, C.-J. Li, *Chem. Eur. J.* **2010**, *16*, 8162; j) E. Boess, D. Sureshkumar, A. Sud, C. Wirtz, C. Farès, M. Klussmann, *J. Am. Chem. Soc.* **2011**, *133*, 8106; k) D. Huang, H. Wang, F. Xue, Y. Shi, *J. Org. Chem.* **2011**, *76*, 7269; l) D. Huang, H. Wang, H. Guan, H. Huang, Y. Shi, *Org. Lett.* **2011**, *13*, 1548; m) W. Wu, W. Su, *J. Am. Chem. Soc.* **2011**, *133*, 11924; n) B.-X. Tang, R.-J. Song, C.-Y. Wu, Y. Liu, M.-B. Zhou, W.-T. Wei, G.-B. Deng, D.-L. Yin, J.-H. Li, *J. Am. Chem. Soc.* **2010**, *132*, 8900; o) B.-X. Tang, R.-J. Song, C.-Y. Wu, Z.-Q. Wang, Y. Liu, X.-C. Huang, Y.-X. Xie, J.-H. Li, *Chem. Sci.* **2011**, *2*, 2131; p) Z.-Q. Wang, W.-W. Zhang, L.-B. Gong, R.-Y. Tang, X.-H. Yang, Y. Liu, J.-H. Li, *Angew. Chem.* **2011**, *123*, 9130; *Angew. Chem. Int. Ed.* **2011**, *50*, 8968; q) A. J. Young, M. C. White, *Angew. Chem.* **2011**, *123*, 6956; *Angew. Chem. Int. Ed.* **2011**, *50*, 6824; r) M. Ohta, M. P. Quick, J. Yamaguchi, B. Wünsch, K. Itami, *Chem. Asian J.* **2009**, *4*, 1416; s) K. Schröder, B. Join, A. J. Amali, K. Junge, X. Ribas, M. Costas, M. Beller, *Angew. Chem.* **2011**, *123*, 1461; *Angew. Chem. Int. Ed.* **2011**, *50*, 1425; t) C. Zhang, N. Jiao, *J. Am. Chem. Soc.* **2010**, *132*, 28; u) C. Zhang, Z. Xu, L. Zhang, N. Jiao, *Angew. Chem.* **2011**, *123*, 11284; *Angew. Chem. Int. Ed.* **2011**, *50*, 11088; v) S. Chiba, L. Zhang, J.-Y. Lee, *J. Am. Chem. Soc.* **2010**, *132*, 7266; w) T. Hamada, X. Ye, S. S. Stahl, *J. Am. Chem. Soc.* **2008**, *130*, 833; x) A. E. King, T. C. Brunold, S. S. Stahl, *J. Am. Chem. Soc.* **2009**, *131*, 5044; y) A. E. King, L. M. Huffman, A. Casitas, M. Costas, X. Ribas, S. S. Stahl, *J. Am. Chem. Soc.* **2010**, *132*, 12068; z) J. M. Hoover, S. S. Stahl, *J. Am. Chem. Soc.* **2011**, *133*, 16901; aa) H. Wang, Y. Wang, D. Liang, L. Liu, J. Zhang, Q. Zhu, *Angew. Chem.* **2011**, *123*, 5796; *Angew. Chem. Int. Ed.* **2011**, *50*, 5678.

[7] a) R. J. Sundberg, *The Chemistry of Indoles*; Academic Press, New York, **1970**; b) R. J. Sundberg, *Indoles*, Academic Press, London, **1996**; c) T. L. Gilchrist, *Heterocyclic Chemistry*, 3rd ed., Addison Wesley, Essex England, **1998**.

[8] See Figure S1 and Scheme S1 in the Supporting Information.

[9] a) R. C. Shah, J. S. Chaubal, *J. Chem. Soc.* **1932**, 650; b) T. Sasaki, S. Eguchi, N. Toi, *J. Org. Chem.* **1979**, *44*, 3711; c) Y. Suzuki, A. Bakar Md., T. Tanoi, N. Nomura, M. Sato, *Tetrahedron* **2011**, *67*, 4710.

[10] See Figure S2 in the Supporting Information, and N. J. Leonard, G. W. Leubner, *J. Am. Chem. Soc.* **1949**, *71*, 3408.

[11] a) N. Gommermann, C. Koradin, K. Polborn, P. Knochel, *Angew. Chem.* **2003**, *115*, 5941; *Angew. Chem. Int. Ed.* **2003**, *42*, 5763; b) C. Koradin, N. Gommermann, K. Polborn, P. Knochel, *Chem. Eur. J.* **2003**, *9*, 2797; c) C. Wei, C. J. Li, *J. Am. Chem. Soc.* **2002**, *124*, 5638; d) R. D. Patila, S. Adimurthy, *Adv. Synth. Catal.* **2011**, *353*, 1695.