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Graphical Abstract

Efficient synthesis of 2-arylquinazolines *via* copper-catalyzed dual oxidative benzylic C-H aminations of methylarenes

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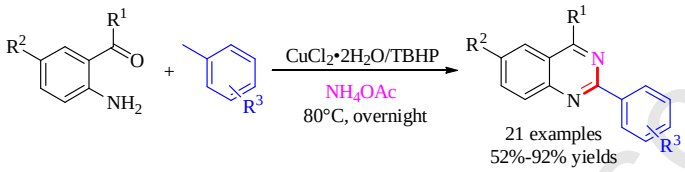

A novel copper-catalyzed dual oxidative benzylic C-H aminations of methylarenes with 2-aminobenzoketones in the presence of ammonium acetate was developed. This reaction represents a new avenue for 2-arylquinazolines with good yields.

Original article

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ABSTRACT

A novel copper-catalyzed dual oxidative benzylic C-H aminations of methylarenes with 2-aminobenzoketones in the presence of ammonium acetate was developed. This reaction represents a new avenue for 2-arylquinazolines with good yields. A key intermediate was detected and the kinetics isotope effect (KIE) indicated that C-H bond cleavage was the rate-determining step.

1. Introduction

In recent years, the synthesis of quinazolines and its derivatives has become a hot spot in organic synthetic chemistry due to their broad biological and medicinal activities, such as antibacterial, anticarcinogenic and antihypertensive properties [1-5]. Usually, the traditional synthesis of quinazolines involves reactions of Bischler cyclization, dicarbonyl compounds with diamines and reactions from 2-aminobenzonitriles or anthranilic acids as well as N-arylbenzamides [6-9]. Our group have been focusing in the synthesis of quinazolines and a variety of excellent approaches to the quinazolines were developed [10-13]. At the same time, other groups also developed some novel methods to prepare these quinazoline derivatives [14-20]. For example, Li [20] developed a KI-catalyzed synthesis of quinazolines from 2-aminobenzoketones, toluene and ammonium salt. In these syntheses, the key step is to construct C-N bonds of the cyclization. Recently, transition-metal-catalyzed oxidative aminations of sp^3 C-H bond have emerged as important methods for C-N bond formations because of short steps and atom-economical advantages [21-38]. In particular, copper as an inexpensive and lowly toxic metal catalyst, has been employed to catalyze the formation of C-N bond *via* a sp^3 C-H amination [39-49]. For instance, copper-catalyzed cascade coupling of 2-halobenzaldehyde with acetamidine hydrochloride (or benzaldehyde) to construct C-N bond was reported [53-54]. Nevertheless, these methods generally suffered from limitations of substrate generality and availability of starting material. Especially, for those substrates bearing electro-withdrawing group, there reaction hardly occurs. Therefore, to develop some novel and efficient method for the synthesis of quinazolines still remains highly desirable.

Herein, we report a novel copper-catalyzed double oxidative C-H aminations of methylarenes with 2-aminobenzoketones and ammonium acetate, constructing one C=N bond and one C-N bond in one step.

2. Experimental

Unless otherwise indicated, all commercial reagents and solvent were used without additional purification.^{1}H-NMR spectra were recorded with a Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ =0) in $CDCl_3$ as internal standard. ^{13}C spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.00). HRMS (ESI) were recorded on a Waters^{TM} Q-TOF Premier Mass Spectrometer.

2.1. Preparation of substrates

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Substrates **1a**, **1f**, **1m** and **1n** are commercially available. Other substrates (**1b-1e**, **1g-1l** and **1o**) were prepared using our previous literature procedure [10].

*2.2. Experimental Procedure for preparation of **3***

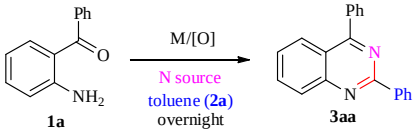
Substrate **1** (0.2 mmol), NH_4OAc (31.2 mg, 0.4 mmol), $CuCl_2·2H_2O$ (6.8 mg, 20 mol%), TBHP (90 μL, 70% aq, 0.6 mmol), were added to a tube, followed by addition of solvent **2** (2 mL). The mixture was stirred at assigned temperature and monitored by TLC. The solution was cooled to r.t., diluted with ethyl acetate (5 mL), washed with saturated aqueous sodium hydrogen sulfite. The aqueous layers was extracted with EtOAc (3×10 mL), the combined organic layers were dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 20:1) to afford the desired product **3**.

Characterization data of compounds **3** were given in Supporting information.

3. Results and discussion

We began our studies with the reaction of (2-amino-phenyl)-phenyl-methanone (**1a**, 1 equiv.), NH_4OAc (2 equiv.), *tert*-butyl hydroperoxide (TBHP, 70% in water, 2 equiv.) as an oxidant, 20 mol% $Cu(OAc)_2$ as catalyst and 2 mL toluene (**2a**) as the solvent and reagent. When heated under air at 80 °C overnight, 2,4-diphenyl quinazoline (**3aa**) was obtained in 43% yield (Table 1, entry 1). When we replaced $Cu(OAc)_2$ with other transition metal acetates, the reaction yield was reduced (Table 1, entries 2-4). Among various copper salts examined (Table 1, entries 5-9), copper chloride dehydrate gave the best yield of 86% (Table 1, entry 6). Next, we optimized the oxidant such as di-*tert*-butyl peroxide (DTBP), cumene hydroperoxide (CHP), H_2O_2 (30% in water) and O_2 (Table 1, entries 10-13). Also, the nitrogen sources (Table 1, entries 14-16) and the reaction temperature (Table 1, entries 17-19) were optimized, but no better yield was obtained. In addition, we increased the loading of TBHP to 3 equiv. since **1a** was not used out, giving **3aa** in 88% yield (Table 1, entry 20). Finally, the optimal conditions were described in entry 20.

Table 1.
Optimization of reaction conditions. [a]



1a **3aa**

Entry	Catalyst	Oxidant	N sources	Temp (°C)	Yield (%)[b]
1	$Cu(OAc)_2$	TBHP	NH_4OAc	80	43
2	$Co(OAc)_2·4H_2O$	TBHP	NH_4OAc	80	42
3	$Ni(OAc)_2·4H_2O$	TBHP	NH_4OAc	80	38
4	$Pd(OAc)_2$	TBHP	NH_4OAc	80	24
5	$CuBr_2$	TBHP	NH_4OAc	80	46
6	$CuCl_2·2H_2O$	TBHP	NH_4OAc	80	86
7	$Cu(OH)_2$	TBHP	NH_4OAc	80	62
8	$CuSO_4·5H_2O$	TBHP	NH_4OAc	80	67
9	$CuCO_3$	TBHP	NH_4OAc	80	51
10	$CuCl_2·2H_2O$	DTBP	NH_4OAc	80	<10
11	$CuCl_2·2H_2O$	CHP	NH_4OAc	80	43
12	$CuCl_2·2H_2O$	H_2O_2	NH_4OAc	80	n.d.
13	$CuCl_2·2H_2O$	O_2	NH_4OAc	80	n.d.
14	$CuCl_2·2H_2O$	TBHP	NH4Cl	80	50
15	$CuCl_2·2H_2O$	TBHP	$(NH_4)_2SO_4$	80	45
16	$CuCl_2·2H_2O$	TBHP	$NH_3·H_2O$[c]	80	65
17	$CuCl_2·2H_2O$	TBHP	NH_4OAc	90	78
18	$CuCl_2·2H_2O$	TBHP	NH_4OAc	100	70
19	$CuCl_2·2H_2O$	TBHP	NH_4OAc	110	65
20	$CuCl_2·2H_2O$	TBHP	NH_4OAc	80	88[d]

[a] Reaction conditions: **1a** (0.2 mmol), N source (0.4 mmol), catalyst (0.04 mmol), oxidant (0.4 mmol), **2a** (2 mL), overnight.
[b] Isolated yield, n.d.=not detected.
[c] 25% in water.
[d] 0.6 mmol TBHP was used.

Subsequently, we investigated the substrate scope of this reaction under the optimized reaction conditions and obtained the product (**3aa-3oa**, Fig.1). Firstly, when R^1 is an aromatic substituent, the reaction of substrates **1a-1d** can be carried out to give the corresponding products **3aa-3da** with good yields. Substrates with electro-withdrawing group (4-F and 4-Br) gave higher yields than substrates with electro-donating group (4-Me) on the phenyl ring. When R^1 is a 2-naphthyl substituent, the corresponding product **3ea** was generated with an 88% yield. To our delight, substrate **1f-1l** with aliphatic substituents also gave the corresponding products **3fa-3la** in good yields. When R^1 is an aliphatic alkyl group, the alkyl with the tertiary carbon favoured the reaction, as shown in **3la**.

Notably, it was found that R^1 benzylic C-H can be oxidized into C=O bond to give **3ga'**. On the other hand, R^2 substituent had a little influence on the reaction. When R^2 alternated from electron-donation group (5-Me) to electro-withdrawing group (5-Cl and 5-NO_2), the yields was reduced to some extent, as shown in **3ma**, **3na** and **3oa**.

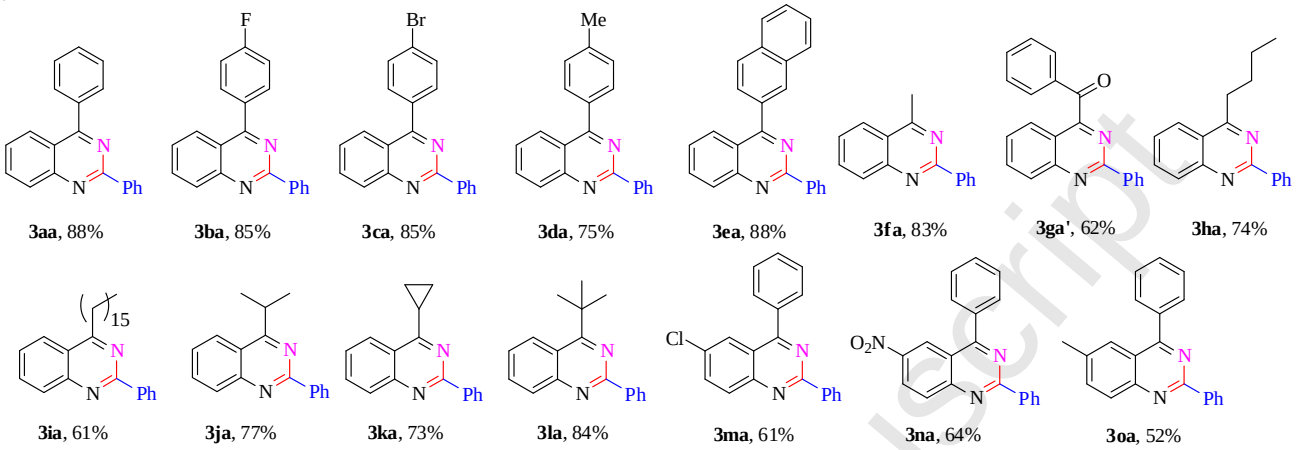
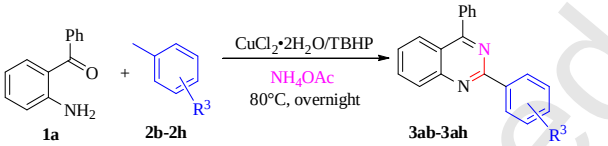


Fig.1. Structures and yields of compounds **3aa-3oa**.

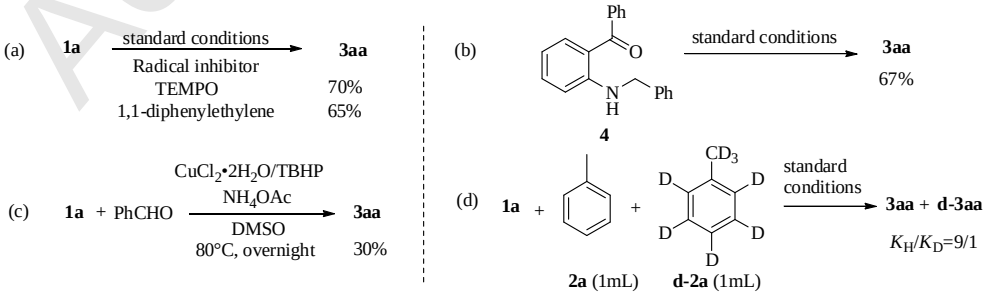
Then we tried to use different methylarenes **2** as the solvent and regent to extend generality of this reaction (Table 2). Both methylarenes bearing electro-donating group (**2b-2e**) and weaker electro-withdrawing group (**2f** and **2g**) could generate the desired products **3ab-3ag** with good to excellent yields. The position of the methyl group on the phenyl ring of **2** affected the reaction yields slightly (Table 2, entries 1-3). However, when a strong electro-withdrawing-group was induced into *ortho*-position (**2h**), no product was detected (Table 2, entry 7), perhaps due to the strong electronic effect of the nitro group.

Table 2. Substrate scope of methylarenes. [a]



Entry	R^3	Product	Yield (%)[b]
1	*o*-Me (**2b**)	**3ab**	92
2	*m*-Me (**2c**)	**3ac**	90
3	*p*-Me (**2d**)	**3ad**	90
4	3,5-di-Me (**2e**)	**3ae**	86
5	*p*-Cl (**2f**)	**3af**	87
6	*p*-Br (**2g**)	**3ag**	87
7	*o*-NO_2 (**2h**)	**3ah**	n.d.

[a] Reaction conditions: **1a** (0.2 mmol), NH_4OAc (0.4 mmol), TBHP (70% in water, 0.6 mmol), $CuCl_2 \cdot 2H_2O$ (0.04 mmol), **2** (2 mL), 80 °C, overnight.
[b] Isolated yield.
n.d. = not detected.

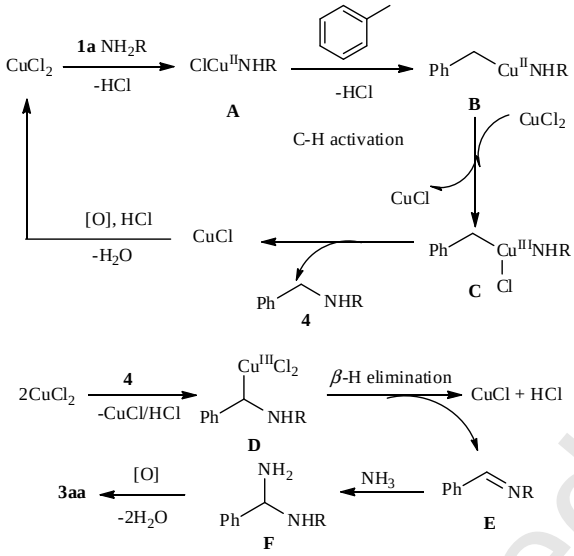


Scheme 1. Control experiment and KIE experiment

To gain an insight into the mechanism, several control experiments were carried out. Firstly, it was observed that the reaction was not obviously inhibited in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 1,1-diphenylethlene. No benzyl radical was obtained by EPR experiment [55, 56]. Two results suggested that the reaction did not undergo a radical pathway (Scheme 1a).

When (2-benzylamino-phenyl)-(phenyl)-methanone **4** was employed as a substrate to carry out the reaction under standard conditions, 67% of **3aa** was obtained. This indicated that **4** may be the intermediate of the reaction (Scheme 1b). Moreover, trace amount of benzaldehyde could be detected in the model reaction. However, when 1 equiv. of benzaldehyde was used as substrate, only 30% yield of **3aa** was obtained (Scheme 1c). This indicated that benzaldehyde may be not the intermediate of the reaction. Finally, a large intermolecular kinetics isotope effect ($k_H/k_D = 9$) was observed by ^{1}H NMR and HRMS from toluene and d_8-toluene, which indicated that the C-H cleavage was a rate-determining step (Scheme 1d).

On the basis of the above results and the previous reports [39-50], a plausible catalytic cycle of this transformation is proposed (Scheme 2). Initially, the coordination of **1a** to one Cu^{II} species and subsequent ligand exchange generates the copper complex **A**, which forms the benzyl/Cu^{II} species **B** by benzylic C-H activation. Then the oxidation of **B** with another Cu^{II} species gives the benzyl/Cu^{III} complex **C** and one Cu^{I} species. Reductive elimination of **C** gives the intermediate **4** and another Cu^{I} species. And **4** were converted into **E** with β-H elimination. Finally, **E** with NH_3 were converted into **F** *via* a similar catalytic cycle, which forms **3aa** through a condensation and oxidation. The generated Cu^{I} species is then oxidized to the Cu^{II} species by TBHP.



Scheme 2. A plausible catalytic cycle.

4. Conclusion

In summary, we developed a copper-catalyzed oxidative amination of benzylic C-H Bonds of methylarenes with ammonia and 2-aminobenzoketones under mild conditions. By virtue of this method, a series of 2-arylquinazolines was efficiently synthesized in good yields. Copper-catalyzed oxidative C-H amination of methylarenes for the synthesis of other heterocycles is ongoing in our laboratory.

Acknowledgments

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References

[1] P.A. Plé, T.P. Green, L.F. Hennequin, et al., Discovery of a new class of anilinoquinazoline inhibitors with high affinity and specificity for the tyrosine kinase domain of c-Src, J. Med. Chem. 47 (2004) 871-887.
[2] L.A. Doyle, D.D. Ross, Multidrug resistance mediated by the breast cancer resistance protein BCRP (ABCG2), Oncogene 22 (2003) 7340-7358.
[3] K. Waisser, J. Gregor, H. Dostál, et al., Influence of the replacement of the oxo function with the thioxo group on the antimycobacterial activity of 3-aryl-6, 8-dichloro-2H-1, 3-benzoxazine-2, 4 (3H)-diones and 3-arylquinazoline-2, 4 (1H, 3H)-diones, Farmaco 56 (2001) 803-807.
[4] J.P. Michael, Quinoline, quinazoline and acridone alkaloids, Nat. Prod. Rep. 25 (2008) 166-187.
[5] V. Colotta, D. Catarzi, F. Varano, et al., Structural investigation of the 7-chloro-3-hydroxy-1H-quinazoline-2, 4-dione scaffold to obtain AMPA and kainate receptor selective antagonists. Synthesis, pharmacological, and molecular modeling studies, J. Med. Chem. 49 (2006) 6015-6026.
[6] A. Witt, J. Bergman, Recent developments in the field of quinazoline chemistry, Curr. Org. Chem. 7 (2003) 659-677.
[7] D.J. Connolly, D. Cusack, T.P. O'Sullivan, et al., Synthesis of quinazolinones and quinazolines, Tetrahedron, 61 (2005) 10153-10202.
[8] L. Jiarong, C. Xian, S. Daxin, et al., A new and facile synthesis of quinazoline-2, 4 (1 H, 3 H)-diones, Org. Lett. 11 (2009) 1193-1196.
[9] P.R. Marsham, A.L. Jackman, A.J. Barker, et al., Quinazoline antifolate thymidylate synthase inhibitors: replacement of glutamic acid in the C2-methyl series, J. Med. Chem. 38 (1995) 994-1004.
[10] J. Zhang, D. Zhu, C. Yu, et al., A simple and efficient approach to the synthesis of 2-phenylquinazolines via sp3 C− H functionalization, Org. Lett. 12 (2010) 2841-2843.

[11] J. Zhang, C. Yu, S. Wang, et al., A novel and efficient methodology for the construction of quinazolines based on supported copper oxide nanoparticles, Chem. Commun. 46 (2010) 5244-5246.
[12] Y. Yan, Z. Wang, Metal-free intramolecular oxidative decarboxylative amination of primary α-amino acids with product selectivity, Chem. Commun. 47 (2011) 9513-9515.
[13] Y. Yan, Y. Zhang, C Feng, et al., Selective iodine-catalyzed intermolecular oxidative amination of C (sp3)-H bonds with ortho-carbonyl-substituted anilines to give quinazolines, Angew. Chem. Int. Ed. 51 (2012) 8077-8081.
[14] R. Sarma, D. Prajapati, Microwave-promoted efficient synthesis of dihydroquinazolines, Green Chem. 13 (2011) 718-722.
[15] Z.H. Zhang, X.N. Zhang, L.P. Mo, et al., Catalyst-free synthesis of quinazoline derivatives using low melting sugar–urea–salt mixture as a solvent, Green Chem. 14 (2012) 1502-1506.
[16] Z. Chen, J. Chen, M. Liu, et al., Unexpected copper-catalyzed cascade synthesis of quinazoline derivatives, J. Org. Chem. 78 (2013) 11342-11348.
[17] B. Han, C. Wang, R.F. Han, et al., Efficient aerobic oxidative synthesis of 2-aryl quinazolines via benzyl C–H bond amination catalyzed by 4-hydroxy-TEMPO, Chem. Commun. 47 (2011) 7818-7820.
[18] X. Su, C. Chen, Y. Wang, et al. One-pot synthesis of quinazoline derivatives via [2+ 2+ 2] cascade annulation of diaryliodonium salts and two nitriles. Chem. Commun. 49 (2013) 6752-6754.
[19] Y. Wang, X. Su, C. Chen, One-Pot synthesis of multiply substituted quinoline and quinazoline derivatives via [2+ 2+ 2] cascade annulation with diaryliodonium salts, Synlett, 24 (2013) 2619-2623.
[20] D. Zhao, Q. Shen, J.-X. Li, Potassium iodide-catalyzed three-component synthesis of 2-arylquinazolines via amination of benzylic C- H bonds of methylarenes, Adv. Synth. Catal. 357 (2015) 339-344.
[21] W.W. Sun, P. Cao, R.Q. Mei, et al., Palladium-catalyzed unactivated C (sp3)–H bond activation and intramolecular amination of carboxamides: a new approach to β-lactams, Org. Lett. 16 (2013) 480-483.
[22] R. Xia, H.Y. Niu, G.R. Qu, et al., CuI controlled C–C and C–N bond formation of heteroaromatics through C (sp3)–H activation, Org. Lett. 14 (2012) 5546-5549.
[23] H. Lu, Y. Hu, H. Jiang, et al., Stereoselective radical amination of electron-deficient C (sp3)–H bonds by Co (II)-based metalloradical catalysis: direct synthesis of α-amino acid derivatives via α-C–H amination, Org. Lett. 14 (2012) 5158-5161.
[24] H.J. Kim, J. Kim, S.H. Cho, et al., Intermolecular oxidative C–N bond formation under metal-free conditions: control of chemoselectivity between aryl sp2 and benzylic sp3 C–H bond imidation, J. Am. Chem. Soc. 133 (2011) 16382-16385.
[25] W.C. Gao, S. Jiang, R.L. Wang, et al., Iodine-mediated intramolecular amination of ketones: the synthesis of 2-acylindoles and 2-acylindolines by tuning N-protecting groups, Chem. Commun. 49 (2013) 4890-4892.
[26] H.Y. Thu, W.Y. Yu, C.M. Che, Intermolecular amidation of unactivated sp2 and sp3 CH bonds via palladium-catalyzed cascade CH activation/nitrene insertion, J. Am. Chem. Soc. 128 (2006) 9048-9049.
[27] E. T. Nadres, O. Daugulis, Heterocycle synthesis via direct C–H/N–H coupling, J. Am. Chem. Soc. 134 (2012) 7-10.
[28] T. Kang, Y. Kim, D. Lee, et al., Iridium-catalyzed intermolecular amidation of sp3 C–H bonds: late-stage functionalization of an unactivated methyl group, J. Am. Chem. Soc. 136 (2014) 4141-4144.
[29] G. He, Y. Zhao, S. Zhang, et al., Highly efficient syntheses of azetidines, pyrrolidines, and indolines via palladium catalyzed intramolecular amination of C (sp3)–H and C (sp2)–H bonds at γ and δ positions, J. Am. Chem. Soc. 134 (2012) 3-6.
[30] J.J Neumann, S. Rakshit, T. Dröge, et al. Palladium-katalysierte amidierung nichtaktivierter C (sp3)-H-bindungen: von anilinen zu indolinen, Angewandte Chemie, Angew. Chem. Int. Ed. 121 (2009) 7024-7027.
[31] J. Pan, M. Suand, S.L. Buchwald, Palladium (0)-catalyzed intermolecular amination of unactivated C sp3-H bonds, Angew. Chem. Int. Ed. 50 (2011) 8647-8651.
[32] K.W. Fiori, J. Du Bois, Catalytic intermolecular amination of C-H bonds: method development and mechanistic insights, J. Am. Chem. Soc. 129 (2007) 562-568.
[33] C.G. Espino, J. Du Bois, A Rh-catalyzed C-H insertion reaction for the oxidative conversion of carbamates to oxazolidinones, Angew. Chem. Int. Ed. 113 (2001) 618-620.
[34] X. Ye, Z. He, T. Ahmed, et al., 1, 2, 3-Triazoles as versatile directing group for selective sp2 and sp3 C–H activation: cyclization vs substitution. Chem. Sci. 4 (2013) 3712-3716.
[35] Q. Zhang, K. Chen, W. Rao, et al., Stereoselective synthesis of chiral α-amino-β-lactams through palladium (II)-catalyzed sequential monoarylation/amidation of C (sp3)-H bonds, Angew. Chem. Int. Ed. 52 (2013) 13588-13592.
[36] G. He, S.Y. Zhang, W.A. Nack, et al., Use of a readily removable auxiliary group for the synthesis of pyrrolidones by the palladium-catalyzed intramolecular amination of unactivated γ C (sp3)-H bonds, Angew. Chem. Int. Ed. 52 (2013) 11124-11128.
[37] A. McNally, B. Haffemayer, B.S.L. Collins, et al., Palladium-catalysed CH activation of aliphatic amines to give strained nitrogen heterocycles, Nature 510 (2014) 129-133.
[38] M. Yang, B. Su, Y. Wang, et al., Silver-catalysed direct amination of unactivated C–H bonds of functionalized molecules, Nat. Commun. 5 (2014) 4707-4712.
[39] C.P. Allen, T. Benkovics, A.K. Turek, et al., Oxaziridine-mediated intramolecular amination of sp3-hybridized C−H bonds, J. Am. Chem. Soc. 131 (2009) 12560-12561.
[40] Q. Michaudel, D. Thevenet, P.S. Baran, Intermolecular Ritter-type C–H amination of unactivated sp3 carbons, J. Am. Chem. Soc. 134 (2012) 2547-2550.
[41] Q. Li, Y. Huang, T. Chen, et al., Copper-catalyzed aerobic oxidative amination of sp3 C–H bonds: efficient synthesis of 2-hetarylquinazolin-4 (3 H)-ones, Org. Lett. 16 (2014) 3672-3675.
[42] B.L. Tran, B. Li, M. Driess, et al., Copper-catalyzed intermolecular amidation and imidation of unactivated alkanes, J. Am. Chem. Soc. 136 (2014) 2555-2563.
[43] X. Wu, Y. Zhao, G. Zhang, et al., Copper-catalyzed site-selective intramolecular amidation of unactivated C (sp3)-H bonds, Angew. Chem. Int. Ed. 53 (2014) 3706-3710.
[44] R. Xia, H.Y. Niu, G.R. Qu, et al., CuI controlled C–C and C–N bond formation of heteroaromatics through C (sp3)–H activation, Org. Lett. 14 (2012) 5546-5549.

[45] Q. Michaudel, D. Thevenet, P.S. Baran, Intermolecular Ritter-type C–H amination of unactivated sp3 carbons, J. Am. Chem. Soc. 134 (2012) 2547-2550.
[46] R.T. Gephart, D.L. Huang, M.J.B. Aguila, et al., Catalytic C-H amination with aromatic amines, Angew. Chem. Int. Ed. 51 (2012) 6488-6492.
[47] Z. Wang, J. Ni, Y. Kuninobu, et al., Copper-catalyzed intramolecular C. H and C (sp2)-H amidation by oxidative cyclization, Angew. Chem. Int. Ed. 53 (2014) 3496-3499.
[48] S.N. Gavade, R.S. Balaskar, M.S. Mane, et al., An efficient method for the N-arylation of phenylurea via copper catalyzed amidation, Chin. Chem. Lett. 22 (2011) 675-678.
[49] W. Liu, L.Y. Hai, R.L. Liu, et al., Copper-catalyzed N-arylation of 2-arylindoles with aryl halides, Chin. Chem. Lett. 25 (2014) 1240-1243.
[50] C. Huang, Y. Fu, H. Fu, et al., Highly efficient copper-catalyzed cascade synthesis of quinazoline and quinazolinone derivatives, Chem. Commun. 47 (2008) 6333-6335.
[51] X. Liu, H. Fu, Y. Jiang and Y. Zhao, A simple and efficient approach to quinazolinones under mild copper-catalyzed conditions, Angew. Chem. Int. Ed. 48 (2009) 348-351.
[52] X. Yang, H. Liu, H. Fu, et al., Efficient copper-catalyzed synthesis of 4-aminoquinazoline and 2, 4-diaminoquinazoline derivatives, Synlett 1 (2010) 101-106.
[53] V.L. Truong, M. Morrow, Mild and efficient ligand-free copper-catalyzed condensation for the synthesis of quinazolines, Tetrahedron Lett. 51 (2010) 758-760.
[54] J. Ju, R. Hua, J. Su, Copper-catalyzed three-component one-pot synthesis of quinazolines, Tetrahedron 68 (2012) 9364-9370.
[55] L. Zhang, J.H. Su, S. Wang, et al., Direct electrochemical imidation of aliphatic aminesvia anodic oxidation, Chem. Commun. 47 (2011) 5488-5490.
[56] Z. Zhang, J. Su, Z. Zha, et al., Electrochemical synthesis of the aryl α-ketoesters from acetophenones mediated by KI, Chem. Eur. J. 19 (2013) 17711-17714.