SCIENCE CHINA
Chemistry

• ARTICLES • doi: 10.1007/s11426-014-5140-9
• SPECIAL ISSUE • In Honor of the 80th Birthday of Professor QIAN Changtao

Copper-catalyzed direct oxidation and *N*-arylation of benzylamines with diaryliodonium salts

LIU Xin, MAO Dan, WU ShengYing, YU JianJun, HONG Gang,
ZHAO Qiao & WANG LiMin*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology,
Shanghai 200237, China

Received March 3, 2014; accepted March 21, 2014

An efficient approach for the synthesis of *N*-arylated amides was developed via copper(II) triflate-catalyzed direct oxidation of (aryl)methylamines to primary arylamides by air and subsequent *N*-arylation by diaryliodonium salts. Various substituted benzylamines could be applied in the reaction, providing a series of *N*-arylated amides in moderate to good yields. This method showed convenient, practical, and environment friendly advantages.

copper(II) triflate, diaryliodonium salts, *N*-arylated amides, oxidation

1 Introduction

N-arylamides are important compounds, which are widely employed in the fields of pharmaceutical chemistry and materials science [1]. Therefore, the synthesis of *N*-arylamides is one of the most exciting topics in practical organic synthesis, and several strategies for their synthesis have been developed [1–4]. Traditionally, one of the most common methods for the synthesis of *N*-arylamides is Goldberg reaction (copper-catalyzed *N*-arylation of amides) [2]. However, it is usually carried out under harsh conditions, which limits its broad application in organic synthesis. In recent decades, the ligand assisted metal-catalyzed amidation of aryl halides has aroused great interest among organic chemists as a practical and efficient method for the construction of C–N bonds [3, 4]. The use of this strategy in Goldberg reaction greatly simplifies the synthesis of *N*-arylamides [5]. For example, the Cu- or Pd-catalyzed *N*-arylations of amides have been demonstrated by Buchwald *et al.* [6], Hartwig *et al.* [7] and Ma *et al.* [8], respectively. Tang *et al.* [9a], Mizuno *et al.* [9b, 9c] and Kaneda *et al.* [9d] reported the successful Ru oxidants-catalyzed oxygenation of primary amines to primary amides, respectively. Fu *et al.* [10] demonstrated the copper-catalyzed aerobic oxidative synthesis of primary amides from (aryl)methylamines. Zhong *et al.* [11] reported the successful Cu-catalyzed oxygenation of primary amines to *N*-arylated amides with the aid of O_2. Xiang *et al.* [12] developed a copper-catalyzed amination of aryl halides with nitriles.

Recently, diaryliodonium salts have been widely used as a supplement for aryl halides, especially used as electrophilic arylating agents in various reactions, such as nucleophilic substitution reactions with nitrogen nucleophiles, carbon nucleophiles, and others, as well as Cu- and Pd-catalyzed coupling reactions, and trapping reactions (in which they are used as benzyne precursors) [13–16]. Our group [17] have also been interested in the use of diaryliodonium salts in organic synthesis. However, the application of diaryliodonium salts for the synthesis of *N*-arylated amides has not been reported yet. Herein, we report the synthesis of *N*-arylated amides through the $Cu(OTf)_2$-catalyzed oxidation and arylation reaction of benzylamines with diaryliodonium salts, which is efficient, convenient, practical, and environmentally friendly.

---

*Corresponding author (email: wanglimin@ecust.edu.cn)

2 Experimental

2.1 Materials and methods

All reagents were used as received from commercial sources, unless otherwise specified, or prepared as described in the literature. All reagents were weighed and handled in air. DMF and DMSO were distilled under reduced pressure from CaH_2. Toluene and 1,4-dioxane were distilled from sodium and benzophenone immediately before use.

^1H NMR and ^{13}C NMR spectra were respectively recorded at 400 and 100 MHz, using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively.

2.2 General procedure for the $Cu(OTf)_2$-catalyzed direct oxidation and *N*-arylation of benzylamines with diaryliodonium salts

Diaryliodonium salt (0.20 mmol), $Cu(OTf)_2$ (10 mol%), K_2CO_3 (2.5 equiv.), 1,10-phenanthroline (20 mol%), benzylamine (0.60 mmol) and DMSO (2 mL) were added to a Schlenck tube with a magnetic stir bar in the air atmosphere. Then the Schlenck tube was sealed and stirred in an oil bath (150 °C) for 24 h. After the reaction was complete, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2, and washed with brine. The combined organic extracts were dried over Na_2SO_4, concentrated under vacuum, and the resulting residue was purified by silica gel column chromatography to afford the desired product. The characterizations of compounds **3a**–**o** were listed in the Supporting Information online.

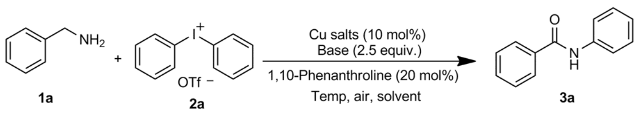
3 Results and discussion

Initially, benzylamine (**1a**) and diphenyliodonium triflate (**2a**) were chosen as the model substrates to optimize the reaction conditions in terms of catalysts, bases, solvents, and reaction temperatures under air (Table 1). To our delight, while using 10 mol% CuI as the catalyst, 2.5 equiv. K_2CO_3 as base and DMSO as solvent at 120 °C for 24 h, *N*-phenylbenzamide (**3a**) was obtained in 20% yield (Table 1, entry 1). When the temperature was increased to 140 or 150 °C, the desired arylated product **3a** was observed in 43% and 73% yields (Table 1, entries 1–3). Other copper catalysts were tried (Table 1, entries 4–9), and $Cu(OTf)_2$ showed the best activity (Table 1, entry 9). The by-product *N*-benzylidene-1-phenyl-methylamine was mainly generated when DMF or 1,4-dioxane was used as solvent (Table 1, entries 10–12). When the reaction was carried in excessive neat **1a**, the desired arylated product **3a** was isolated in 61% yield (Table 1, entry 13).

Next, diphenyliodonium salts (**2a**), bearing different counter anions (Table 2, entries 1, 2) were studied. Among all the tested reagents, diphenyliodonium triflate furnished the desired product **3a** in best yield (91%, Table 2, entry 4), whereas tetrafluoroborate, bromide only gave the by-product *N*-benzylidene-1-phenylmethylamine (Table 2, entries 1, 2). Then, a series of ligands, including 1,10-phenanthroline (**L1**), L-proline (**L2**), ethylenediamine (**L3**), 2,2′-dipyridyl (**L4**) and *N*,*N*′-dimethylethylenediamine (DMEDA, **L5**) were evaluated for the reaction (Table 2, entries 4–8). It was observed that the ligands significantly affected the yields and 1,10-phenanthroline (**L1**) gave the best result. Then, K_2CO_3 was replaced by different bases, such as Cs_2CO_3, K_3PO_4, KOH, Et_3N and so on. The results indicated that K_2CO_3 was the best base for this reaction (Table 2, entries 9–16). Without K_2CO_3, *N*-phenylbenz- amide (**3a**) was not detected (Table 2, entry 17). Finally, we investigated the influence of catalyst-ligand ratio and two substrates' ratio. We find that the reaction gave best results when $Cu(OTf)_2$/1,10-phenanthroline = 10%:20% and benzylamine/diphenyliodonium salts = 0.6:0.2 (mmol/mmol). The details are shown in the Supporting Information online.

With the optimal reaction conditions in hand, the electronic and steric effects of substituted benzylamines and diaryliodonium salts were investigated (Table 3). Initially, a set of benzylamine derivatives (**1a**–**i**) were examined by reacting with diphenyliodonium triflate (**2a**) (Table 3, entries 1–9). The result showed that the reaction was sensitive to the electronic effects on the aromatic ring of the benzylamines. For example, benzylamines bearing electron-withdrawing groups, such as Cl, F, 3,4-F,F and CF_3 (Table 3, entries 2–4, 9) showed slightly higher reactivity than those with electron-donating groups, like methyl and methoxy moieties (Table 3, entries 7, 8). When the substrate scope was

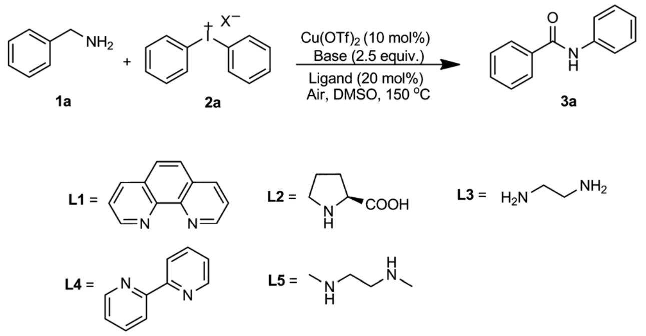
Table 1 Optimization of the reaction conditions [a)]



Entry	[Cu] (mol%)	Solvent	*T* (°C)	Yield [b)] (%)
1	CuI (10)	DMSO	120	20
2	CuI (10)	DMSO	140	43
3	CuI (10)	DMSO	150	73
4	CuBr (10)	DMSO	150	44
5	CuCl (10)	DMSO	150	40
6	$Cu(OAc)_2 \cdot H_2O$(10)	DMSO	150	29
7	$CuCl_2 \cdot 2H_2O$ (10)	DMSO	150	25
8	$CuSO_4$ (10)	DMSO	150	65
9	$Cu(OTf)_2$ (10)	DMSO	150	91
10	$Cu(OTf)_2$ (10)	DMF	150	trace
11	$Cu(OTf)_2$ (10)	toluene	150	32
12	$Cu(OTf)_2$ (10)	1,4-dioxane	150	n.d.[c)]
13	$Cu(OTf)_2$ (10)	benzylamine	150	61
14	–	DMSO	150	0

a) Reaction conditions: **1a** (0.60 mmol), **2a** (0.20 mmol), Cu salts (10 mol%), K_2CO_3 (2.5 equiv.), 1,10-phenanthroline (20 mol%), DMSO (2 mL), 24 h; b) isolated yields; c) no detection.

Table 2 Optimization of Cu-catalyzed *N*-arylation of benzylamine (**1a**) and diphenyliodonium triflate (**2a**) a)



Entry	X^-	Ligand	Base	Yield b) (%)
1	BF_4	**L1**	K_2CO_3	trace
2	Br	**L1**	K_2CO_3	n.d.
3	OTf	–	K_2CO_3	40
4	OTf	**L1**	K_2CO_3	91
5	OTf	**L2**	K_2CO_3	55
6	OTf	**L3**	K_2CO_3	12
7	OTf	**L4**	K_2CO_3	75
8	OTf	**L5**	K_2CO_3	83
9	OTf	**L1**	Cs_2CO_3	48
10	OTf	**L1**	K_3PO_4	78
11	OTf	**L1**	KOH	15
12	OTf	**L1**	Ag_2CO_3	n.d.
13	OTf	**L1**	Et_3N	10
14	OTf	**L1**	*t*-BuOK	45
15	OTf	**L1**	Na_2CO_3	25
16	OTf	**L1**	$NaHCO_3$	10
17	OTf	**L1**	–	n.d.

a) Reaction conditions: **1a** (0.60 mmol), **2a** (0.20 mmol), $Cu(OTf)_2$ (10 mol%), base (2.5 equiv.), ligand (20 mol%) , DMSO (2 mL), 150 °C, 24 h; b) isolated yields.

extended to 3- or 2-fluorobenzylamine, the corresponding products were obtained in lower yields (Table 3, entries 5, 6).

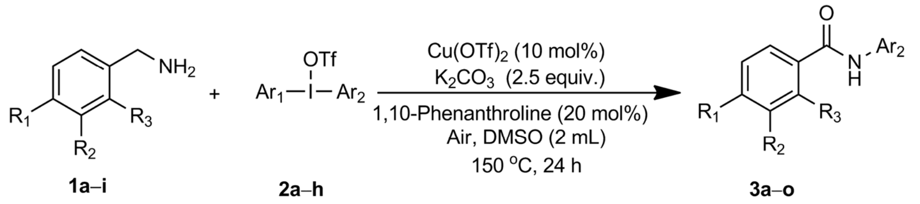
Subsequently, various substituted diaryliodonium salts were employed in this reaction. As shown in Table 3, diaryliodonium salts with halogen substituents gave higher yields than their mesityl equivalents (Table 3, entries 10–16). However, it is worth mentioning that the unsymmetrical salt **2h** selectively transferred the phenyl group to the benzylamine in moderate yield (Table 3, entry 16).

A possible catalytic mechanism for this transformation is illustrated in Scheme 1. Initially, copper-catalyzed aerobic oxidation of benzylamine (**1**) provides the corresponding imine (**I**), which reacts with H_2O to give **II**. Further oxidation of **II** affords primary arylamide **B** [18], which is exposed to the copper catalyst **A** to generate the metallic intermediate **C**. Diaryliodonium salt **2** undergoes an oxidative addition to intermediate **C** to form the metallic intermediate **D**, which then produces the final product **3** through a reductive elimination reaction and releases the catalyst **A** to complete the catalytic cycle.

4 Conclusions

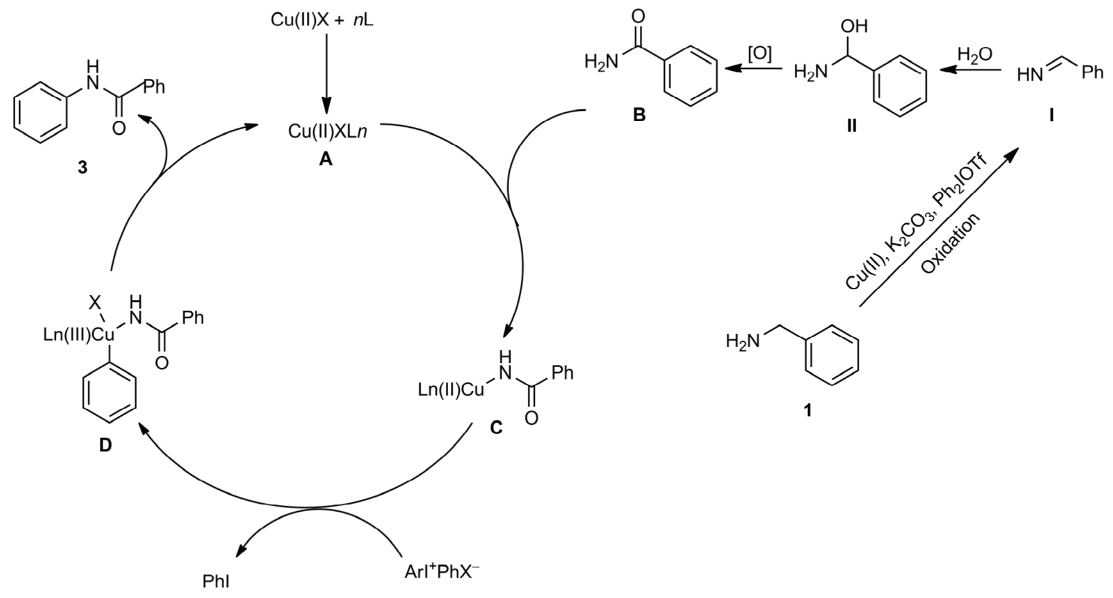
In summary, we have developed a new, simple and practical copper-catalyzed domino method for the synthesis of *N*-arylamides using diaryliodonium salts as the electrophilic coupling partners. The protocol uses cheap and readily available $Cu(OTf)_2$ as the catalyst, (aryl)methylamines as

Table 3 Copper-catalyzed amination of different benzylamine with diaryliodonium salts a)



Entry	R_1	R_2	R_3	Ar_1	Ar_2	Product	Yield b) (%)
1	H	H	H	Ph	Ph	**3a**	91
2	Cl	H	H	Ph	Ph	**3b**	80
3	F	H	H	Ph	Ph	**3c**	85
4	F	F	H	Ph	Ph	**3d**	93
5	H	H	F	Ph	Ph	**3e**	60
6	H	F	H	Ph	Ph	**3f**	75
7	CH_3	H	H	Ph	Ph	**3g**	70
8	OCH_3	H	H	Ph	Ph	**3h**	72
9	CF_3	H	H	Ph	Ph	**3i**	89
10	H	H	H	4-BrC_6H_4	4-BrC_6H_4	**3j**	84
11	H	H	H	4-ClC_6H_4	4-ClC_6H_4	**3k**	81
12	H	H	H	4-FC_6H_4	4-FC_6H_4	**3l**	86
13	H	H	H	4-$OCH_3C_6H_4$	4-$OCH_3C_6H_4$	**3m**	70
14	H	H	H	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	**3n**	67
15	H	H	H	mesityl	mesityl	**3o**	45
16	H	H	H	phenylethynyl	Ph	**3a**	70

a) Reaction conditions: **1** (0.60 mmol), **2** (0.20 mmol), $Cu(OTf)_2$ (10 mol%), K_2CO_3 (2.5 equiv.), 1,10-phenanthroline (20 mol%), DMSO (2 mL), air, 150 °C , 24 h; b) isolated yields.



Scheme 1 Proposed catalytic mechanism for this transformation.

the starting materials, and economical and environmentally friendly air as the oxidant. The corresponding *N*-arylamides were afforded in moderate to good yields. The overall process is easy to handle without the need of an inert atmosphere. Efforts to explore the detailed mechanism are underway in our laboratory.

This work was financially supported by the National Nature Science Foundation of China (21272069, 20672035) and the Fundamental Research Funds for the Central Universities and Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

1 a) Valeur E, Bradley M. Amide bond formation: beyond the myth of coupling reagents. *Chem Soc Rev*, 2009, 38: 606–631; b) Allen CL, Williams JMJ. Amide bond formation: beyond the myth of coupling reagents. Metal-catalysed approaches to amide bond formation. *Chem Soc Rev*, 2011, 40: 3405–3415; c) Zhang DW, Zhao X, Hou JL, Li ZT. Aromatic amide foldamers: structures, properties, and functions. *Chem Rev*, 2012, 112: 5271–5316; d) Garcia-Alvarez R, Crochet P, Cadierno V. Metal-catalyzed amide bond forming reactions in an environmentally friendly aqueous medium: nitrile hydrations and beyond. *Green Chem*, 2013, 15: 46–66; e) Alécio AC, Bolzani VS, Young MCM, Kato MJ, Furlan M. Antifungal amide from leaves of piper hispidum. *J Nat Prod*, 1998, 61: 637–639; f) Onnis V, Cocco MT, Fadda R, Congiu C. Synthesis and evaluation of anticancer activity of 2-arylamino-6-trifluoromethyl-3-(hydrazonoca-rbonyl) pyridines. *Bioorgan Med Chem*, 2009, 17: 6158–6165

2 a) Goldberg I. Ueber phenylirungen bei gegenwart von kupfer als katalysator. *Ber Dtsch Chem Ges*, 1906, 39: 1691–1692; b) Freeman HS, Butler JR, Freedman LD. Acetyldiarylamines by arylation of acetanilides. Some applications and limitations. *J Org Chem*, 1978, 43: 4975–4977; c) Ito A, Saito T, Tanaka K, Yamabe T. Synthesis of oligo (*m*-aniline). *Tetrahedron Lett*, 1995, 36: 8809–8812; d) Sugahara M, Ukita T. A facile copper-catalyzed Ullmann condensation: *N*-arylation of heterocyclic compounds containing an –NHCO– moiety. *Chem Pharm Bull*, 1997, 45: 719–721; e) Lange JHM, Hofmeyer LJF, Hout FAS, Osnabrug SJM, Verveer PC, Kruse CG, Feenstra RW. Monopositive chlorocarbonium ions. *Tetrahedron Lett*, 2002, 43: 1101–1104

3 a) Jiang YW, Ma DW. Copper-catalyzed ligand promoted Ullmann-type coupling reactions. In: Bullock RM, Ed. *Catalysis without Precious Metals*. Weinheim: Wiley Blackwell, 2010; b) Wang Y, Zeng J, Cui X. Recent progress in copper-catalyzed C–N coupling reactions. *Chin J Org Chem*, 2010, 30: 181–199 (in Chinese)

4 a) Guram AS, Buchwald SL. Palladium-catalyzed aromatic aminations with *in situ* generated aminostannanes. *J. Am Chem Soc*, 1994, 116: 7901–7902; b) Paul F, Patt J, Hartwig JF. Palladium-catalyzed formation of carbon-nitrogen bonds. Reaction intermediates and catalyst improvements in the hetero cross-coupling of aryl halides and tin amides. *J Am Chem Soc*, 1994, 116: 5969–5970; c) Lindley J. Copper assisted nucleophilic substitution of aryl halogen. *Tetrahedron*, 1984, 40: 1433–1456; d) Yin J, Buchwald SL. Palladium-catalyzed intermolecular coupling of aryl halides and amides. *Org Lett*, 2000, 2: 1101–1104; e) Yin J, Buchwald SL. Pd-catalyzed intermolecular amidation of aryl halides: the discovery that xantphos can be *trans*-chelating in a palladium complex. *J Am Chem Soc*, 2002, 124: 6043–6048

5 a) Klapars A, Antilla JC, Huang X, Buchwald SL. A general and efficient copper catalyst for the amidation of aryl halides and the *N*-arylation of nitrogen heterocycles. *J Am Chem Soc*, 2001, 123: 7727–7729; b) Klapars A, Huang X, Buchwald SL. A general and efficient copper catalyst for the amidation of aryl halides. *J Am Chem Soc*, 2002, 124: 7421–7428; c) Crawford KR, Padwa A. Copper-catalyzed amidations of bromo substituted furans and thiophenes. *Tetrahedron Lett*, 2002, 43: 7365–7368; d) Mallesham B, Rajesh BM, Reddy PR, Srinivas D, Trehan S. Highly efficient CuI-catalyzed coupling of aryl bromides with oxazolidinones using buchwald's protocol: a short route to linezolid and toloxatone. *Org Lett*, 2003, 5: 963–965; e) Deng W, Wang YF, Zou Y, Liu L, Guo QX. Amino acid-mediated Goldberg reactions between amides and iodides. *Tetrahedron Lett*, 2004, 45: 2311–2315; f) Hosseinzadeh R, Tajbakhsh M, Mohadjerani M, Mehdinejad H. Copper-catalyzed amidation of aryl iodides using KF/Al_2O_3: an improved protocol. *Synlett*, 2004: 1517–1520; g) Strieter ER, Blackmond DG, Buchwald SL. The role of chelating diamine ligands in the Goldberg reaction: a kinetic study on the copper-catalyzed amidation of aryl iodides. *J Am Chem Soc*, 2005, 127: 4120–4121; h) Zheng N, Buchwald SL. Copper-catalyzed regiospecific synthesis of *N*-alkylbenzimidazoles. *Org Lett*, 2007, 9: 4749–4751; i) Altman RA, Hyde AM, Huang X,

Buchwald SL. Orthogonal Pd- and Cu-based catalyst systems for the *C*- and *N*-arylation of oxindoles. *J Am Chem Soc*, 2008, 130: 9613–9620; j) Monnier F, Taillefer M. Catalytic C–C, C–N, and C–O ullmann-type coupling reactions: copper makes a difference. *Angew Chem Int Ed*, 2008, 47: 3096–3099; k) Strieter ER, Bhayana B, Buchwald SL. Mechanistic studies on the copper-catalyzed *N*-arylation of amides. *J Am Chem Soc*, 2009, 131: 78–88; l) Wang C, Liu L, Wang W, Ma DS, Zhang H. Copper-catalyzed *N*-arylation of amides using (*S*)-*N*-methylpyrrolidine-2-carboxylate as the ligand. *Molecules*, 2010, 15: 1154–1160; m) Wang M, Yu H, You X, Wu J, Shang Z. A general and efficient CuBr$_2$-catalyzed *N*-arylation of secondary acyclic amides. *Chin J Chem*, 2012, 30: 2356–2362

6 a) Fors BP, Dooleweerdt K, Zeng Q, Buchwald SL. An efficient system for the Pd-catalyzed cross-coupling of amides and aryl chlorides. *Tetrahedron*, 2009, 65: 6576–6583; b) Su MJ, Buchwald SL. A bulky biaryl phosphine ligand allows for palladium-catalyzed amidation of five-membered heterocycles as electrophiles. *Angew Chem Int Ed*, 2012, 51: 4710–4713; c) Ikawa T, Barder TE, Biscoe MR, Buchwald SL. Pd-catalyzed amidations of aryl chlorides using monodentate biaryl phosphine ligands: a kinetic, computational, and synthetic investigation. *J Am Chem Soc*, 2007, 129: 13001–13007; d) Dooleweerdt K, Fors BP, Buchwald SL. Pd-catalyzed cross-coupling reactions of amides and aryl mesylates. *Org Lett*, 2010, 12: 2350–2353

7 Shen QL, Hartwig JF. Lewis acid acceleration of C–N bond-forming reductive elimination from heteroarylpalladium complexes and catalytic amidation of heteroaryl bromides. *J Am Chem Soc*, 2007, 129: 7734–7735

8 Xu LT, Jiang YW, Ma DW. Synthesis of 3-substituted and 2,3-disubstituted quinazolinones via Cu-catalyzed aryl amidation. *Org Lett*, 2012, 14: 1150–1153

9 a) Tang R, Diamond SE, Neary N, Mares F. Homogeneous catalytic oxidation of amines and secondary alcohols by molecular oxygen. *J Chem Soc*, *Chem Commun*, 1978: 562–562; b) Kim JW, Yamaguchi K, Mizuno N. Heterogeneously catalyzed efficient oxygenation of primary amines to amides by a supported ruthenium hydroxide catalyst. *Angew Chem Int Ed*, 2008, 47: 9249–9251; c) Wang Y, Kobayashi H, Yamaguchi K, Mizuno N. Manganese oxide-catalyzed transformation of primary amines to primary amides through the sequence of oxidative dehydrogenation and successive hydration. *Chem Commun*, 2012, 48: 2642–2644; d) Mori K, Yamaguchi K, Mizugaki T, Ebitani K, Kaneda K. Catalysis of a hydroxyapatite-bound Ru complex: efficient heterogeneous oxidation of primary amines to nitriles in thepresence of molecular oxygen. *Chem Commun*, 2001: 461–462

10 Xu W, Jiang YY, Fu H. Copper-catalyzed aerobic oxidative synthesis of primary amides from (aryl)methanamines. *Synlett*, 2012, 23: 801–804

11 Xu M, Zhang XH, Shao YL, Han JS, Zhong P. The synthesis of *N*-arylated amides via copper(II) triflate-catalyzed direct oxygenation and *N*-arylation of benzylamines with aryl iodides. *Adv Synth Catal*, 2012, 354: 2665–2670

12 Xiang SK, Zhang DX, Hu H, Shi JL, Liao LG, Feng C, Wang BQ, Zhao KQ, Hu P, Yang H, Yu WH. Synthesis of *N*-arylamides by copper-catalyzed amination of aryl halides with nitriles. *Adv Synth Catal*, 2013, 355: 1495–1499

13 a) Zhdankin VV, Stang PJ. Recent developments in the chemistry of polyvalent iodine compounds. *Chem Rev*, 2002, 102: 2523–2584; b) Zhdankin VV, Stang PJ. Chemistry of polyvalent iodine. *Chem Rev*, 2008, 108: 5299–5358; c) Merritt EA, Olofsson B. Diaryliodonium salts: a journey from obscurity to fame. *Angew Chem Int Ed*, 2009, 48: 9052–9070

14 a) Kalyani D, Deprez NR, Desai LV, Sanford MS. Oxidative C–H activation/C–C bond forming reactions: synthetic scope and mechanistic insights. *J Am Chem Soc*, 2005, 127: 7330–7331; b) Deprez NR, Kalyani D, Krause A, Sanford MS. Room temperature palladium-catalyzed 2-arylation of indoles. *J Am Chem Soc*, 2006, 128: 4972–4973; c) Phipps RJ, Grimster NP, Gaunt MJ. Cu(II)-catalyzed direct and site-selective arylation of indoles under mild conditions. *J Am Chem Soc*, 2008, 130: 8172–8174; d) Deprez NR, Sanford MS. Synthetic and mechanistic studies of Pd-catalyzed C–H arylation with diaryliodonium salts: evidence for a bimetallic high oxidation state Pd intermediate. *J Am Chem Soc*, 2009, 131: 11234–11241; e) Phipps RJ, Gaunt MJ. A meta-selective copper-catalyzed C–H bond arylation. *Science*, 2009, 323: 1593–1597; f) Xiao B, Fu Y, Xu J, Gong JJ, Dai JY, Liu L. Pd(II)-catalyzed C–H activation/aryl-aryl coupling of phenol esters. *J Am Chem Soc*, 2010, 132: 468–469; g) Ciana CL, Phipps RJ, Brandt JR, Meyer FM, Gaunt MJ. A highly *para*-selective copper(II)-catalyzed direct arylation of aniline and phenol derivatives. *Angew Chem Int Ed*, 2011, 50: 458–462; h) Duong HA, Gilligan RE, Cooke ML, Phipps RJ, Gaunt MJ. Copper(II)-catalyzed *meta*-selective direct arylation of α-aryl carbonyl compounds. *Angew Chem Int Ed*, 2011, 50: 463–466; i) Vaddula B, Leazer J, Varma RS. Copper-catalyzed ultrasound-expedited *N*-arylation of sulfoximines using diaryliodonium salts. *Adv Synth Catal*, 2012, 354: 986–990; j) Xu J, Zhang PB, Gao YZ, Chen YY, Tang G. Zhao YF. Copper-catalyzed *P*-arylation via direct coupling of diaryliodonium salts with phosphorus nucleophiles at room temperature. *J Org Chem*, 2013, 78: 8176–8183; k) Lv TY, Wang Z, You JS, Lan JB, Gao G. Copper-catalyzed direct aryl quaternization of *N*-substituted imidazoles to form imidazolium salts. *J Org Chem*, 2013, 78: 5723–5730; l) Sinai Á, Mészáros Á, Gáti T, Kudar V, Palló A, Novák Z. Copper-catalyzed oxidative ring closure and carboarylation of 2-ethynylanilides. *Org Lett*, 2013, 15: 5654–5657; m) Cullen SC, Shekhar S, Nere NK. Cu-catalyzed couplings of aryl iodonium salts with sodium trifluoromethanesulfinate. *J Org Chem*, 2013, 78: 12194–12201; n) Wang Y, Chen C, Peng J, Li M. Copper(II)-catalyzed three-component cascade annulation of diaryliodoniums, nitriles, and alkynes: a regioselective synthesis of multiply substituted quinolines. *Angew Chem Int Ed*, 2013, 52: 5323–5327; o) Su X, Chen C, Wang Y, Chen JJ, Lou ZB, Li M. One-pot synthesis of quinazoline derivatives via [2+2+2] cascade annulation of diaryliodonium salts and two nitriles. *Chem Commun*, 2013, 49: 6752–6754

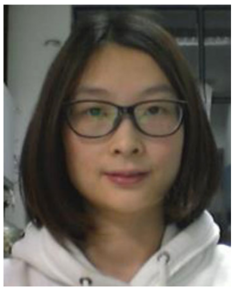
15 Kang SK, Lee HW, Choi WK, Choi WK, Hong RK, Kim JS. Palladium-catalyzed synthesis of arylamines from diphenyliodonium tetrafluoroborate and secondary amine. *Synth Commun*, 1996, 26: 4219–4224

16 Kang SK, Lee SH, Lee D. Copper-catalyzed *N*-arylation of amines with hypervalent iodonium salts. *Synlett*, 2000, 2000: 1022–1024

17 a) Guo FL; Wang LM, Wang PQ, Yu JJ, Han JW. transition-metal-free *N*-arylation of carbazoles and *C*-arylation of tetrahydrocarbazoles by using diaryliodonium salts. *Asian J Org Chem*, 2012, 1: 218–221; b) Guo FL, Han JW, Mao S, Li J, Geng X, Yu JJ, Wang LM. Direct *C*-arylation of polyfluoroarenes with diaryliodonium salts via Pd(OAc)$_2$-catalysis. *RSC Adv*, 2013, 3: 6267–6270; c) Mao S, Guo F, Li J, Geng X, Yu JJ, Han JW, Wang LM. Copper-catalyzed direct *N*-arylation of naphthalimides using diaryliodonium salts. *Synlett*, 2013, 24: 1959–1962

18 a) Xu W, Jiang YY, Fu H. Copper-catalyzed aerobic oxidative synthesis of primary amides from (aryl)methanamines. *Synlett*, 2012, 23: 801–804; b) Wang Y, Kobayashi H, Yamaguchi K, Mizuno N. Manganese oxide-catalyzed transformation of primary amines to primary amides through the sequence of oxidative dehydrogenation and successive hydration. *Chem Commun*, 2012, 48: 2642–2644

LIU Xin received his BSc degree from East China University of Science and Technology in 2011. Subsequently, he joined Professor Limin Wang's group in the same university. His research focuses on the transition metal catalyzed cascade reaction.



MAO Dan received her BSc degree from East China University of Science and Technology in 2010. She is currently pursuing her PhD in Fine Chemicals in the same university under the supervision of Professor Limin Wang. Her research interests focus on organic reactions catalyzed by rare earth metals.

WANG LiMin is Professor at East China University of Science and Technology. He received his PhD in Applied Chemistry from Dalian University of Technology in 1998 under the supervision of Professor Zuwang Wu, and carried out a postdoctoral research at SIOC under the supervision of Professor Changtao Qian. He was a visiting scientist under Professor David B. Collum at Cornell University, NY, from 2009 to 2010. His main scientific interests include chemistry of rare earth metals, synthetic methodology and fine chemicals.