Copper-Catalysed Electrophilic Amination of Aryl(alkenyl) Boronic Acids with Nitrogen-Containing Hypervalent Iodine (III) Reagent

Yuanyuan Hu,[a] Songlin Zheng,[a] Wu Fan,[b,]* and Weiming Yuan[a, c,]*

[a] Key Laboratory of Material Chemistry for Energy Conversion and Storage
Ministry of Education
Hubei Key Laboratory of Bioinorganic Chemistry and Materia Medica
School of Chemistry and Chemical Engineering
Huazhong University of Science and Technology (HUST)
1037 Luoyu Road, Wuhan 430074, People's Republic of China
E-mail: yuanwm@hust.edu.cn

[b] Key Laboratory of Tobacco Flavor Basic Research
Zhengzhou Tobacco Research Institute of CNTC
No. 2 Fengyang Street High-Tech Zone, Zhengzhou 450001, People's Republic of China
E-mail: fanwu2015@126.com

[c] Guangdong Provincial Key Laboratory of Catalysis
Southern University of Science and Technology
Shenzhen 518055, People's Republic of China

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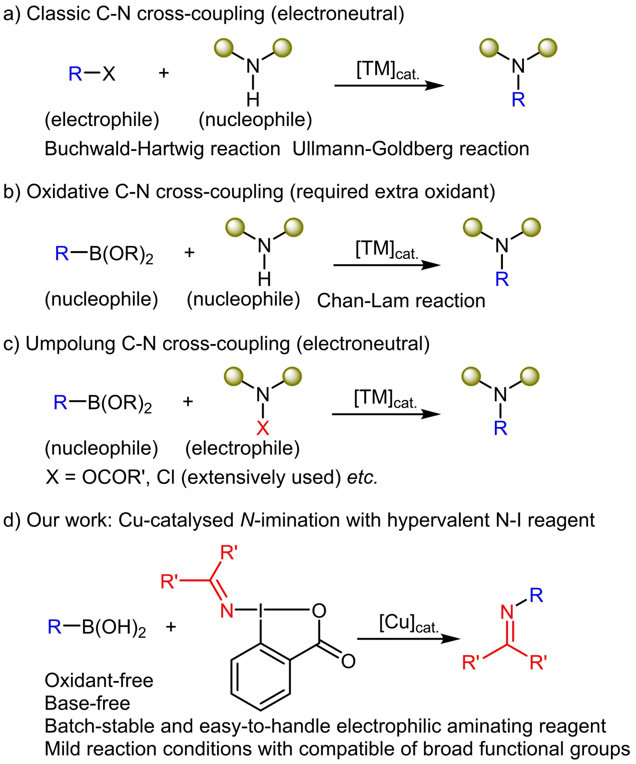
Abstract: A copper-catalysed electrophilic *N*-imination of aryl(alkenyl) boronic acids with a stable hypervalent iodine(III) reagent containing a transferable (diarylmethylene)amino group is developed. The electrophilic C–N cross-coupling reaction proceeds smoothly at room temperature under oxidant-free and base-free conditions, which is further characterized by the broad functional group compatibility, thereof, extending the *N*-electrophile scope of electrophilic C–N cross-coupling outside the limitation of *N*–O and *N*–Cl reagents.

Keywords: C–N bond cross-coupling; Boronic acids; Hypervalent N–I reagent; Copper catalysis; Umpolung amination

The formation of C–N bonds ranks as one of the most important and widely practiced reactions in synthetic chemistry due to the fact that amines and their derivatives are prevalent motifs in numerous natural products and pharmaceutical targets.[1] As a consequence, many efforts have been devoted to the development of highly efficient and synthetically practical methods for the construction of C–N bonds and till now still remains a particularly vibrant topic of research. Among them, transition-metal-catalysed C–N bond cross-couplings predominated owing to the obvious advantages such as high efficiency, good selectivity, mild condition, broad substrate scope and functional group compatibility and so on.[2] Classical C–N bond cross-couplings involving carbon electrophiles and nitrogen nucleophiles, typified by the well-known Ullmann-Goldberg[3] and Buchwald-Hartwig[4] reaction and have been largely extended by many others (Scheme 1a).[5] In contrast, the coupled of carbon nucleophiles and nitrogen nucleophiles to form C–N bonds in the aid of external oxidants and copper catalyst or stoichiometric amount of Cu(II) salts, now termed as Chan-Lam reaction, provides an alternative yet robust approach to metal-catalysed C–N bond cross-coupling (Scheme 1b).[6]

Despite of the significant progress achieved in this excited field, some obstacles still persist. For example, Buchwald-Hartwig reaction typically need expensive transition metal catalysts ligated with structurally complex ligands, elevated temperature and bases and additives to promote. Conversely, Chan-Lam amination could allow C–N bond formation to proceed smoothly under much milder conditions (room temperature, weak base and ambient atmosphere) and obviate to use the expensive catalysts/ligands. However, a stoichio-



Scheme 1. Previous studies and our proposal of electrophilic C–N cross-coupling of boronic acids and hypervalent *N*–I reagent.

metric amount of external oxidant is necessary for this oxidative cross-coupling.

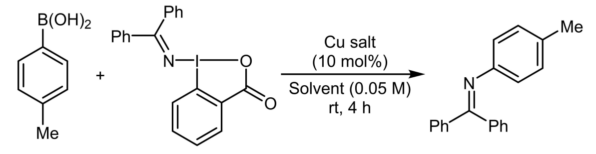
In particular, in both catalytic systems, *N*-nucleophiles are used as nitrogen sources, which commonly possesses a strong nucleophilicity and basicity could potentially undergo unfavourable competitive coordination to transition metals, thereby leading to a decrease of catalyst activity. Besides, the basic condition somewhat restricts the functional group compatibility.

Umpolung strategy represents a powerful and complementary approach for bond forming events, which would not otherwise be possible or difficult-to-access due to the electronic mismatch issues.[7] Umpolung reactions often showcase superior reactivity and selectivity compared to the normal polarity patterns. In this regard, the effective applications of the umpolung strategy in C–N bond cross-couplings are of highly valuable and have received increasing attention during the past decades (Scheme 1c),[8] where the reaction of electrophilic nitrogen sources with nucleophilic carbon sites is thus complementary to Buchwald-Hartwig and Chan-Lam amination for catalytic C–CN bond formation under very mild, non-basic and oxidant-free conditions. Early studies from Erdik[9] and Narasaka[10] et al. reported that the electrophilic *O*-sulfonyl oximes could react with RMgX or RZnX to afford *N*-substituted benzophenone imines in the presence of Cu(I) catalyst. Later on, Johnson[11] and Jarvo[12] and co-workers independently reported Cu or Ni-catalysed electrophilic amination of diorganozinc reagents with *O*-acyl hydroxylamines or *N*-chloroamines, respectively. Compared with Grignard and organozinc reagents, organoborons are a kind of readily available, non-basic, less-toxic and widely compatible organometallic species, which have been widely investigated in copper-mediated/catalysed C–N oxidative cross-couplings (Chan-Lam reaction). In the past decade, aryl boronic acids and their derivatives have also been explored in umpolung aminations with electrophilic R_2N^+ synthons by Liebeskind,[13] Lei,[14] Miura,[15] Kitamura[16] et al. Although a wide range of R_2N^+ synthons have been disclosed for umpolung amination, however, the most reported electrophilic amination reagents are largely limited to the reactive and air- and moisture-sensitive hydroxylamines and *N*-chloroamines. Utilization of those reactive *N*-electrophiles hampered the synthetic practicability and operational convenience, thus, further exploring novel and stable R_2N^+ synthons for catalytic electrophilic amination are of high interesting.

Hypervalent iodine (III) reagents containing a benziodoxolone skeleton have emerged as versatile and environmentally benign reagents for organic chemistry, which are potent atom-transfer reagents and mild oxidants with a good stability to air and moisture.[17] Hypervalent iodine reagents containing a *N*–I bond have been intensively studied in C–H bond oxidative amination,[18] however, they have rarely been used in transition metal-catalysed C–N bond cross-coupling reactions. Due to the importance of C–N bond forming events and the superiority of hypervalent *N*–I reagent over other electrophilic aminating reagents, we envisioned that the hypervalent *N*–I reagent might be used as a mild yet robust electrophilic aminating reagent in copper-catalysed electrophilic C–N cross-couplings (Scheme 1d). Here, we reported our recent discovery.

To test the feasibility, we synthesized (diarylmethylene)amino-substituted cyclic benziodoxolone reagent **2 a**[19] and commenced our reaction with *p*-tolylboronic acid **1 a** in the presence of a catalytic amount of $Cu(OTf)_2$ in MeCN at room temperature (Table 1). To our delight, after 4 hours, the reaction preliminarily delivered the desired product *N*-(*p*-tolyl)benzophenone imine **3 a** in 14% yield (Entry 1). This initial success inspired us to further investigate other reaction parameters. Solvent screening showed that DCM was the best, while polar solvents such as DMF and THF completely retarded the reaction (Entries 2–5). Other copper salts such as $CuBr_2$, CuI or CuCl gave a comparable yield (Entries 6–8). Pleasingly, CuBr and $Cu(CH_3CN)_4PF_6$ could increase the yield up to 60%

Table 1. Optimization of reaction conditions.[a]



1a **2a** **3a**

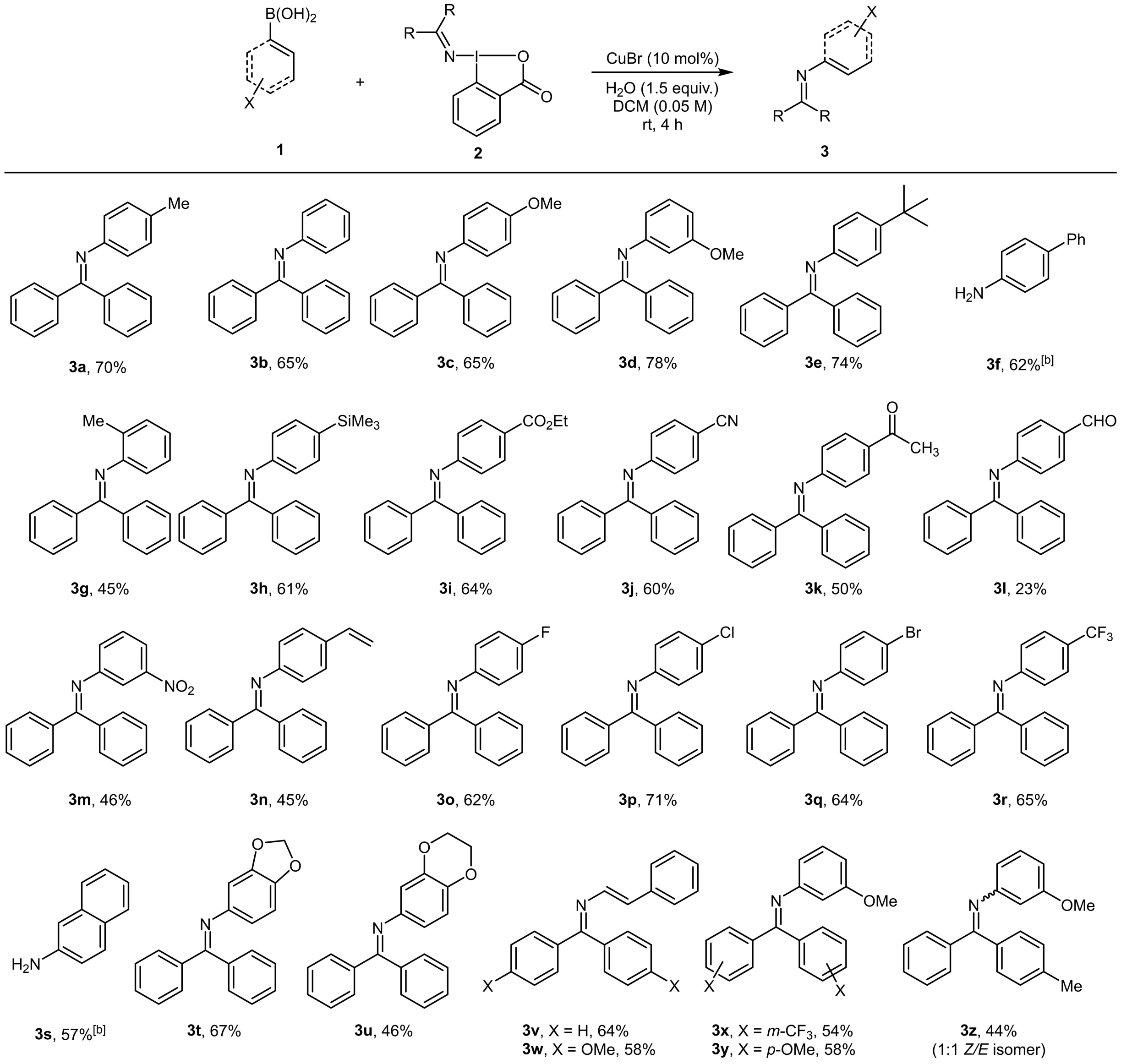
Entry	Catalyst	Solvent	Yield [%][b]
1	$Cu(OTf)_2$	MeCN	14
2	$Cu(OTf)_2$	$PhCH_3$	36
3	$Cu(OTf)_2$	DCM	45
4	$Cu(OTf)_2$	DMF	0
5	$Cu(OTf)_2$	THF	0
6	$CuBr_2$	DCM	43
7	CuI	DCM	53
8	CuCl	DCM	48
9	CuBr	DCM	60
10	$Cu(CH_3CN)_4PF_6$	DCM	58
11[c,d]	CuBr	DCM	76(70)[e]
12	w/o	DCM	0

[a] Reaction conditions: the reaction of **1a** (0.1 mmol), **2a** (0.15 mmol, 1.5 equiv.), Cu-catalyst (10 mol%) in indicated solvent (2 mL, 0.05 M) at room temperature for 4 hours. [b] Corrected GC yield with *n*-tridecane as internal standard. [c] the molar ratio of **1a**:**2a** = 1.5:1. [d] 1.5 equiv. of H_2O was added. [e] Isolated yield.

and 58% (Entries 9–10), respectively. Water had a significant influence on the efficiency, when 1.5 equivalents of H_2O was added to the reaction system and meanwhile adjusted the molar ratio of **1a**:**2a** to 1.5:1, the yield could be further elevated to 76% (Entry 11). We proposed that water facilitated the transmetalation step of arylboronic acid with copper salt. Control experiment indicated that copper catalyst is critical to the reaction (Entry 12), and this was further verified by a series of control experiments: when other transition metal catalysts such as $NiCl_2$, $PdCl_2$, $AgBF_4$ etc. was added, the reaction was completely suppressed (see SI for details).

With the optimized conditions in hand, we studied the scope of the reaction with respect to various arylboronic acids (Scheme 2). A variety of substituted arylboronic acids reacted with **2a** to generate the *N*-imination products in moderate to good yields. The reaction of arylboronic acids containing electron-donating group like methyl, methoxy, *tert*-butyl etc. proceeded efficiently to obtain the corresponding products (**3a**–**3f**). Electron-deficient substrate reacted with a somewhat lower efficiency compared to the electron-rich ones. The steric demanding substrates, for example, *ortho*-methyl substituted arylboronic acid led to a large decrease in yield (**3g**). By taking advantages of the extremely mild reagents and conditions performed, this copper-catalysed electrophilic C–N cross-coupling accommodated a broad scope of functionalities such as silyl, ester, cyano, ketone, aldehyde, nitro, alkene (**3h**–**3n**) as well as halogen groups like F, Cl, Br, and CF_3 (**3o**–**3r**). These highly valued functional groups provided a good platform for further synthetic modifications. 2-Naphthylboronic acid reacted with a moderate yield (**3s**). Heteroarylboronic acids could also react well under the standard conditions (**3t**–**3u**). Apart from arylboronic acid, alkenyl boronic acid could also be able to participate the cross-coupling reaction, and delivered the synthetically useful 2-azadiene in a comparable yield (**3v**–**3w**). Finally, we further investigated the substitution effect on aryl ring of hypervalent *N*–I reagent and the results shown that both electron-rich and electron-poor substituents were well tolerated (**3x**–**3y**). Unsymmetric substrate with 1:1 ratio of *Z*/*E* isomer delivered the product in a mixture form of *Z*/*E* isomer (1:1) in 44% yield (**3z**). Unfortunately, Zhdankin's amidobenziodoxole[20] and phthalimidate-based hypervalent iodine reagent[18d] are not suitable for this transformation (not shown, see SI). It should be noted that in each individual case, *N*-protected imine product can undergo hydrolysis to get benzophenone in a range of 10~20% yield.

To get more insights into the mechanism of this copper-catalysed C–N bond formation reaction, a series of mechanistic experiments were performed: First, MesCu complex was synthesized according to reported procedure[21] and a stoichiometric reaction of MesCu with **2a** gave 40% yield of coupling product **3aa** (Scheme 3, Eq. 1). This result suggested that arylcopper arising from the transmetallation of arylboronic acid with Cu(I) might be an active intermediate for the reaction. The reaction of **1a** and **2a** with a catalytic amount of MesCu also proceeded smoothly, further verified the above conclusion (Eq. 2). Moreover, a stoichiometric reaction of aryl boronic acid with CuBr was conducted, after 4 hours stirring, the mixture was quenched by H_2O and 1,1′-biphenyl was indeed detected in 23% yield. Extended the reaction time to 20 h, the yield increased up to 44% (Eq. 3). These results also provided evidence that transmetallation intermediate ArCu(I) might involved in the system. This preliminary study came to a conclusion diametrically opposed to Lei[14] and Miura's[15] result. After get the answer of transmetallation between arylboronic acid and Cu(I) is the initial step, the next question is how the oxidative addition of arylcopper with hypervalent *N*–I reagent proceeded. To investigate whether the oxidative addition step involved a radical pathway, radical enquiry experiments were performed. The standard reaction with 2.0 equiv. of a radical scavenger like 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) or 1,1-diphenylethylene was not inhibited at all (Eq. 4). However, when butylated hydroxytoluene (BHT) was added, the desired reaction was completely supressed and BHT-trapped species was detected by HRMS analysis (Eq. 5). Moreover, the benzophenoniminyl radical dimerization byproduct was detected by

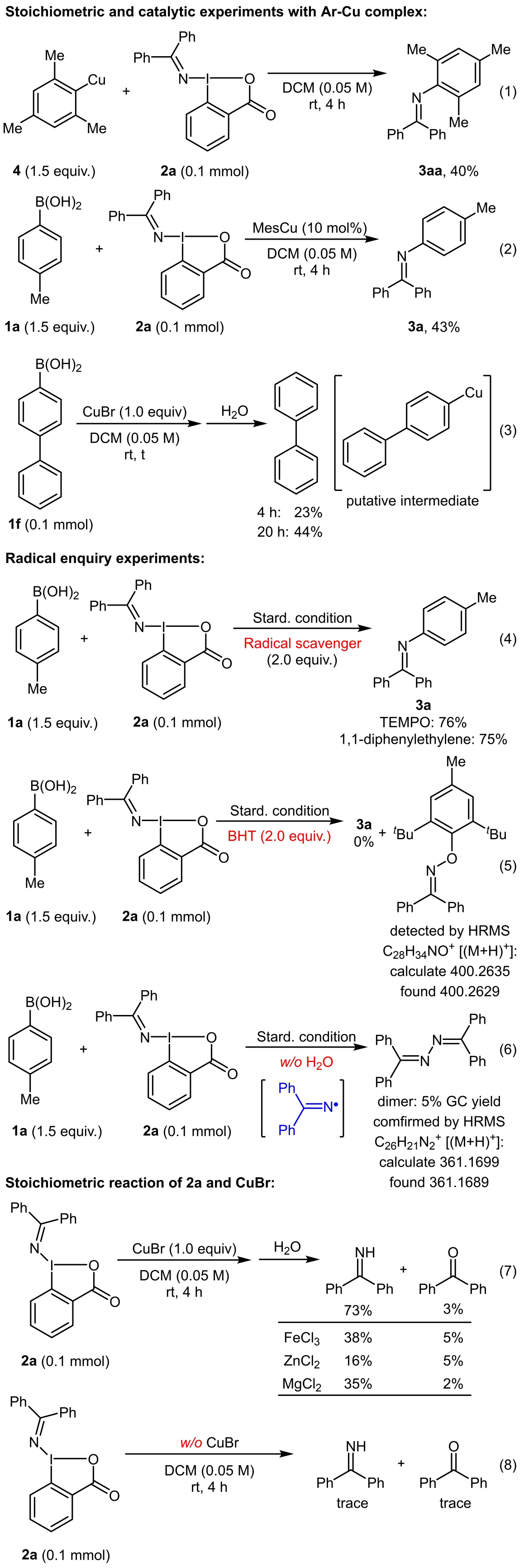


[a] Reaction conditions: The reaction of **1** (0.45 mmol, 1.5 equiv.), **2** (0.3 mmol), CuBr (10 mol%), H_2O (0.45 mmol, 1.5 equiv.) in DCM (0.05 M) at room temperature for 4 hours, the yields are isolated yields by column chromatography on silica gel. [b] In this case, *N*-imination product could not be isolated in its pure form as it was contaminated with the hydrolysis product benzophenone, thus the yield showed here is given for the final hydrolysis product primary amine.

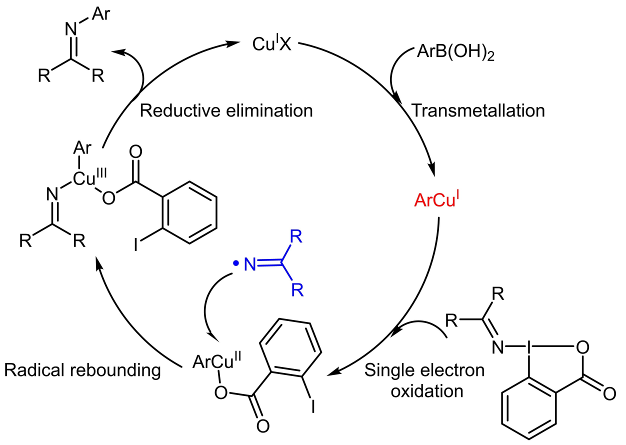
Scheme 2. Substrate scope of CuBr-catalysed electrophilic *N*-imination of aryl(alkenyl)boronic acids.[a]

GC analysis (the standard sample could be obtained by literature's procedure[22]) and further confirmed by HRMS analysis (Eq. 6). Both reactions suggested that the oxidative addition step might involve a radical pathway. Furthermore, a stoichiometric reaction of hypervalent iodine reagent **2a** with CuBr was also conducted: 73% of diphenylmethanimine together with 3% of benzophenone were detected once the resulting mixture was quenched by H_2O (Eq. 7), this result might support the formation of Cu(III) intermediate by the oxidative addition of Cu(I) to **2a**. However, it should be noted that CuBr can also act as Lewis acid to coordinate with carbonyl group of **2a** to decompose the backbone,[17c,f] thus, other metal-based Lewis acids were examined for comparison. Indeed, when added metal salts such as $FeCl_3$, $ZnCl_2$, $MgCl_2$, which are very unlikely to undergo oxidative addition with **2a** to form high valence metal species, various degrees of decomposition of **2a** also happened, despite with a relatively low rate. Besides, **2a** is quite stable in the absence of CuBr (Eq. 8). These experimental results provided the evidence to support the speculation that the oxidative addition of CuBr to **2a** as the initial step in the catalytic cycle is indefinite.

Based on literature' reports[13,14,15] and our mechanistic studies, a rational mechanism was proposed in



Scheme 3. Mechanistic studies.



Scheme 4. Proposed mechanism.

Scheme 4: different from the previous reports on oxidative addition of Cu(I) to electrophilic aminating reagent as the initial step, our experimental results showed that the reaction started from the transmetallation of arylboronic acid with Cu(I), followed by oxidative addition with hypervalent *N*–I reagent to form a putative ArCu(III)N=CR$_2$ intermediate via a single electron oxidation and radical rebounding pathway, which intermediate sequentially underwent reductive elimination to deliver the desired product and simultaneously regenerated Cu(I) catalyst to complete the catalytic cycle. Although several evidences indicated that the reaction was triggered by transmetallation of arylboronic acid with CuBr, an alternative mechanism through the oxidative addition of a hypervalent iodine reagent to Cu(I) followed by a transmetalation cannot be completely ruled out at this stage.

In conclusion, we disclosed here an electrophilic *N*-imination of aryl(alkenyl) boronic acids with a stable hypervalent *N*–I (III) reagent in the presence of catalytic Cu(I) salt. This electrophilic C–N cross-coupling reaction is characterized by its very mild and simple conditions (room temperature, oxidant and base-free) and tolerated a variety of functional groups with moderate to good yields. Of particularly note, mechanistic studies suggested that the reaction might be preferably triggered by the transmetallation of arylboronic acid with Cu(I) followed by oxidative addition with hypervalent *N*–I reagent, which pathway is different from that proposed in previous electrophilic C–N cross-coupling involving *N*–O and *N*–Cl reagents.

Experimental Section

An oven-dried 10 mL Schlenk tube containing a magnetic stir bar was charged with hypervalent *N*–I reagent **2a** (128 mg, 0.30 mmol, 1.0 equiv.), *p*-tolylboronic acid **1a** (61.2 mg, 0.45 mmol, 1.5 equiv.) and CuBr (4.30 mg, 0.030 mmol, 0.10 equiv.). After evacuated and backfilled with nitrogen three times, freshly distilled dichloromethane (6.0 mL) was added to the Schlenk techniques by syringe, then H_2O (8.1 µL, 0.45 mmol, 1.5 equiv.) was added by micro syringe, the resulting mixture was stirred at 25 °C under a static pressure of nitrogen for 4 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on prebasified silica (EA/PE with addition of 0.5% NEt_3) to give the pure product.

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Copper-Catalysed Electrophilic Amination of Aryl(alkenyl) Boronic Acids with Nitrogen-Containing Hypervalent Iodine (III) Reagent

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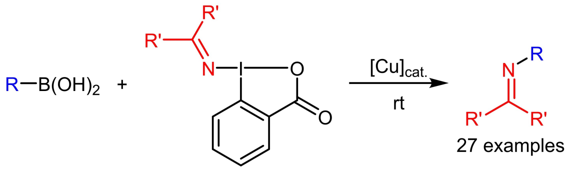
Y. Hu, S. Zheng, W. Fan*, W. Yuan*



√ Oxidant-free √ Base-free √ Batch-stable and easy-to-handle reagents
√ Mild and simple reaction conditions √ Broad functional group tolerance