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VIP

Aryl Triolborates: Novel Reagent for Copper-Catalyzed N Arylation of Amines, Anilines, and Imidazoles

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: The N arylation of primary and secondary aliphatic amines, anilines, and imidazoles with novel potassium aryl triolborates was carried out in the presence of a reoxidant and a catalytic amount of $Cu(OAc)_2$ (10 mol%). Aryl triolborates were found to be better reagents than aryl boronic acids or potassium aryl trifluoroborates as the former achieved high yields under mild conditions. Coupling of primary and secondary aliphatic amines to give *N*-aryl amines in excellent yields was performed under oxygen atmosphere. The reactions of anilines and imidazoles to provide *N*-aryl anilines and *N*-aryl imidazoles in good yields proceeded smoothly when trimethylamine *N*-oxide was used as an oxidant.

Keywords: amines · boron · copper · cross-coupling · synthetic methods

Introduction

The synthesis of *N*-aryl amines, *N*-aryl anilines, and *N*-aryl imidazoles has attracted significant interest owing to the frequent occurrence of these fragments in pharmaceutically and agriculturally interesting compounds. The palladium-catalyzed amination of haloarenes developed by Buchwald and Hartwig[1] and copper-mediated N arylation with aryl boron, lead, bismuth, stannane, or silicon compounds[2] are two practical and straightforward methods that have been employed for various syntheses of these *N*-aryl compounds. Among these extensive works in N arylation, the coupling between an N–H, O–H, or S–H bond and aryl boronic acids, discovered independently by Chan et al.,[3a] Evans et al.,[3b] and Lam et al.[3c] in 1998, attracted much attention because of the very mild conditions: the reactions smoothly take place typically in air at room temperature. Although a stoichiometric amount of copper(II) salt and several equivalents of an external base/ligand were used in the original discovery,[3a,4] the synthetic value of this protocol was greatly improved when a reoxidant was employed for a catalytic amount of copper complex.[5] On the basis of these pioneering studies, the catalytic protocol has been further improved by many groups.[6–8] Air oxidation was used for the N arylation of aromatic and aliphatic amines as well as imidazoles.[5a,b,d] Pyridine *N*-oxide or 2,2,6,6-tetramethylpipedinyloxy (TEMPO) was effective for the N arylation of amines, NH heterocycles, and phenols.[5c] A ligand- and base-free Cu-catalyzed C–N bond coupling of potassium aryl trifluoroborate was reported by Quach and Batey.[7] We recently invented novel cyclic triolborates with high reactivity toward metal-catalyzed reactions, including copper-catalyzed N arylation with aryl boronic acids.[9] Herein, we report a new set of reaction conditions optimized for the copper(II)-catalyzed N arylation of primary and secondary amines, anilines, and imidazoles with potassium aryl triolborates (Scheme 1).

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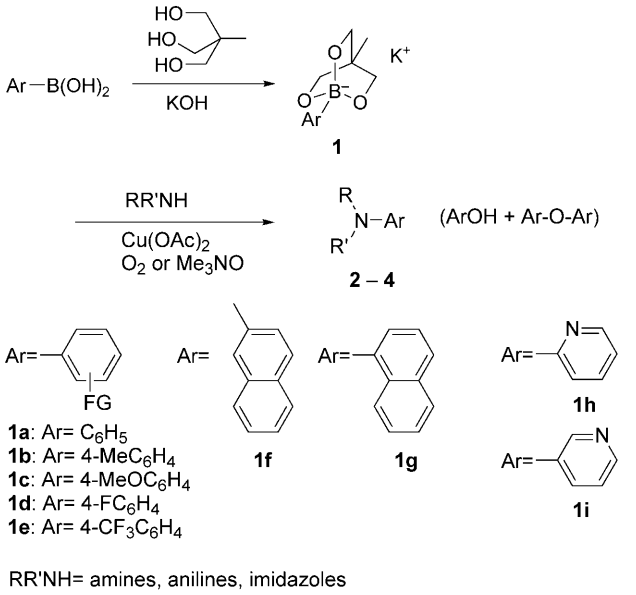
Results and Discussion

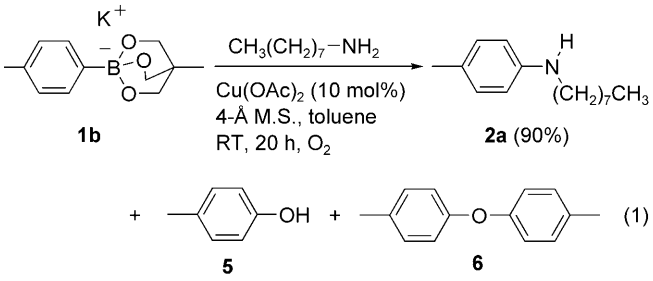
Reaction Conditions

Initially, we chose potassium tolyl triolborate **1b**[9] to examine its efficiency toward copper(II)-catalyzed reaction with octylamine [Eq. (1)]. Thus, the N arylation of octylamine (1.0 equiv) with **1b** (1.5 equiv), 10 mol% $Cu(OAc)_2$, and powdered 4-Å molecular sieves (M.S.) in CH_2Cl_2 under molecular oxygen charged in a teflon bag at room temperature for 20 h gave an excellent yield of N-arylation product (**2a**,

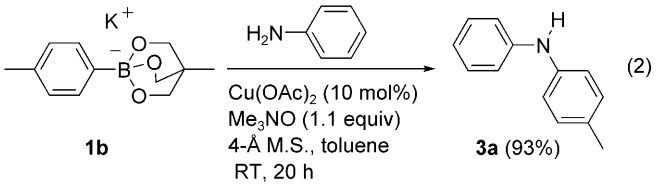


Scheme 1. Cu^{II}-catalyzed arylation of N–H bonds.

90%) with cresol **5** and ditolyl ether (**6**) as by-products.[3b,5b,10] Other solvents such as diethyl ether, THF, EtOAc, *N*,*N*-dimethylformamide (DMF), and MeOH also afford **2a** in good yields, but these solvents increased the formation of cresol and ditolyl ether. Finally, the desired amine was selectively afforded in 90% yield when the reaction was carried out in toluene for 20 h [Eq. (1)]. No trace of cresol or ditolyl ether was observed.



Arylation of anilines and imidazoles resulted in low yields when molecular oxygen was used as the reoxidant. The role of oxygen has been hypothesized as facilitating the oxidation of the low-valent copper species to higher oxidation states to recycle the catalyst. Another role of molecular oxygen is oxidation of the $Cu^{II}(NR_2)(Ar)$ intermediate to Cu^{III} species. The Cu^{III} complex, being in a higher oxidation state, can undergo more facile reductive elimination than the corresponding Cu^{II} complex to form the C–N cross-coupled product.[5b,9] Recently, Lam et al. reported that pyridine *N*-oxide is more efficient than molecular oxygen for the conversion of the Cu^{II} complex into the Cu^{III} complex.[5c] Among various oxidizing reagents, including pyridine *N*-oxide (23%), trimethylamine *N*-oxide (96%), *t*BuOOH (14%), *m*-chloroperbenzoic acid (MCPBA; 5%), $K_3[Fe(CN)_6]$ (0%), $AgSbF_6$ (9%), and $AgBF_4$ (9%), trimethylamine *N*-oxide was found to be the best oxidant: it gave **3a** in 93% yield at room temperature [Eq. (2)]. Trimethylamine *N*-oxide was also recognized to be the best reagent for the arylation of imidazoles in DMF.



The results of reaction velocity in the coupling of representative boron compounds such as $PhB(OH)_2$, $(PhBF_3)K$, and potassium phenyl triolborate **1a** with piperidine are shown in Figure 1. The reaction of potassium phenyl triolborate was three times faster than that of $PhB(OH)_2$ because of the easier transmetalation of the negatively charged complex **1** relative to the neutral latter compound.[11] On the other hand, the analogous complex $(PhBF_3)K$ resulted in very slow reaction owing to its low nucleophilicity and poor solubility in toluene.

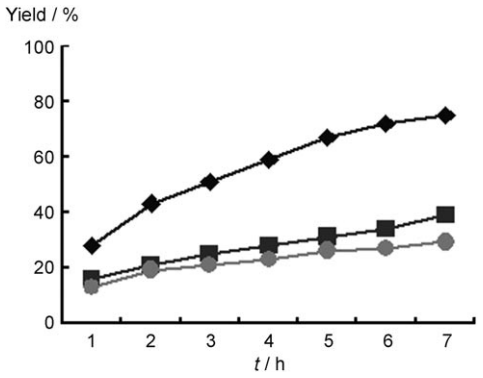


Figure 1. N arylation of piperidine with phenyl triolborate **1a** (♦), phenylboronic acid (■), and $(PhBF_3)K$ (●) at room temperature under oxygen atmosphere (1 atm) in the presence of $Cu(OAc)_2$ (10 mol%) and molecular sieves in toluene.

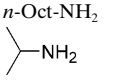
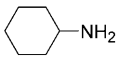
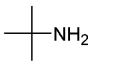
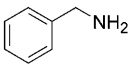
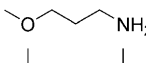
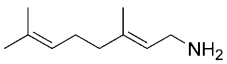
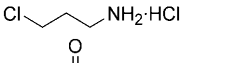
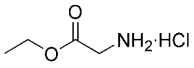
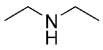
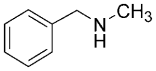
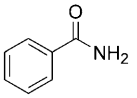
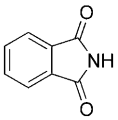
Abstract in Japanese:

新規に開発したアリールトリオールボレートカリウム塩を用いて、１級と２級脂肪族アミン、アニリンおよびイミダゾールのNーアリール化反応を触媒量の酢酸第二銅および再酸化剤存在下で行った。トリオールボレート塩は従来から用いられてきたボロン酸やトリフルオロボレート塩より穏和な条件で高い収率を達成した。また、脂肪族アミンのカップリングには酸素が再酸化剤として優れており、またアニリンとイミダゾールの反応にはトリメチルアミンNーオキシドが良い結果を与える。

N Arylation of Aliphatic Amines

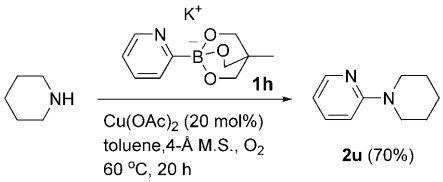
The scope and limitation of the method for various aliphatic amines and potassium aryl triolborates were studied under conditions thus optimized (Table 1). The N arylation of a variety of primary amines (Table 1, entries 1–9) and secondary amines (Table 1, entries 10–13) with **1a** produced **2a–c** in high yields. Functional groups such as ether, ester, alkene, and halide were tolerated (Table 1, entries 6–9). The reaction was carried out at 40–60 °C for bulky *tert*-butylamine (Table 1, entry 4) and secondary amines (Table 1, entries 10, 11, 14, and 15) as well as for an amide and imide whose N–H bonds have low nucleophilicity (Table 1, entries 12 and 13). Representative potassium aryl triolborates with an electron-withdrawing or -donating substituent group afforded aryl amines in good yields (Table 1, entries 16–20).

Table 1. N arylation of aliphatic amines.[a]

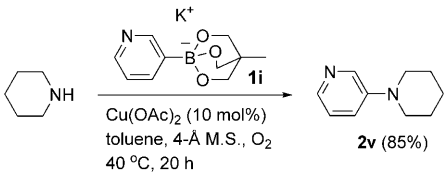
Entry	Borate	R^1R^2NH	T [°C]	Prod.	Yield [%][b]
1	**1b**	*n*-Oct-NH_2	RT	**2a**	90
2	**1b**		RT	**2b**	94
3	**1b**		RT	**2c**	93
4	**1b**		60	**2d**	60
5	**1b**		RT	**2e**	88
6	**1b**		RT	**2f**	92
7	**1b**		RT	**2g**	93
8	**1b**[c]		RT	**2h**	88
9	**1b**[c]		RT	**2i**	89
10	**1b**		60	**2j**	55
11	**1b**		60	**2k**	64
12	**1b**		60	**2l**	90
13	**1b**		40	**2m**	86
14	**1b**		40	**2n**	96
15	**1b**		RT	**2o**	95
16	**1c**		RT	**2p**	98
17	**1d**		RT	**2q**	94
18	**1e**		RT	**2r**	92
19	**1f**		RT	**2s**	81
20	**1g**		RT	**2t**	67

[a] A mixture of amine (1.0 equiv), borate **1** (1.5 equiv), $Cu(OAc)_2$ (10 mol%), and 4-Å M.S. in toluene was stirred at room temperature to 60 °C for 20 h under O_2 (1 atm). [b] Yield of isolated product. [c] 2 equivalents of borate were used.

The cross-coupling reaction of pyridine-derived boronic acids has proven to be greatly challenging: only a few relevant studies can be found in the literature.[12,13] The primary problem associated with these boronic acids is sensitivity to hydrolytic C–B bond cleavage with water and their slow rate of transmetalation, which can be attributed to the electron deficiency of the heteroaromatic ring.[13] Notably, copper(II)-catalyzed coupling of potassium 2-pyridine triolborate **1h** with piperidine gave the desired product **2u** in 70% yield [Eq. (3)]. Similarly, potassium 3-pyridine triolborate **1i** was also suitable and formed **2v** in 85% yield [Eq. (4)].



(3)

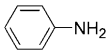
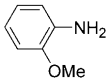
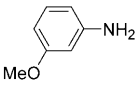
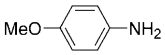
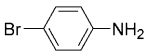
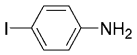
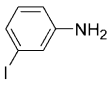
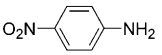
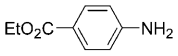
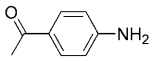
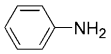
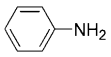
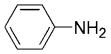
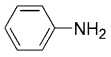
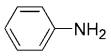


(4)

N Arylation of Aromatic Amines

The successful outcome led us to investigate the scope and limitations for various aryl triolborates and anilines. Anilines with an electron-donating methoxy group or a weakly electron-withdrawing halogen atom were smoothly coupled with **1b** at room temperature (Table 2, entries 2–7), but more-electron-deficient anilines with a nitro, ester, or keto group resulted in moderate yields even at 40 °C (Table 2, entries 8–10). Among them, the reaction selectively provided a single monoarylation product for *o*- and *m*-anisidine in the presence of 1.5 equivalents of **1b** (Table 2, entries 2 and 3), but *p*-anisidine gave a mixture of mono- and diarylation products. To avoid this bisarylation, a slightly excess of *p*-anisidine (1.1 equiv) was used with **1b** to form **3d** selectively in 85% yield (Table 2, entry 4). The reaction tolerates various functional groups on the aromatic rings in anilines (Table 2, entries 2–10) and aryl triolborates (Table 2, entries 11–15).

Table 2. N Arylation of aromatic amines.[a]

Entry	Borate	Aniline	*T* [°C]	Prod.	Yield [%][b]
1	**1b**		RT	**3a**	93 (96)
2	**1b**		40	**3b**	71
3	**1b**		RT	**3c**	91
4	**1b**[c]		RT	**3d**	85
5	**1b**		RT	**3e**	85
6	**1b**		RT	**3f**	87
7	**1b**		RT	**3g**	93
8	**1b**		40	**3h**	66
9	**1b**		40	**3i**	73
10	**1b**		40	**3j**	73
11	**1c**		RT	**3k**	94
12	**1d**		RT	**3l**	85
13	**1e**		40	**3m**	89
14	**1f**		40	**3n**	81
15	**1g**		40	**3o**	53

[a] A mixture of aniline (1.0 equiv), borate **1** (1.5 equiv), $Cu(OAc)_2$ (10 mol%), trimethylamine *N*-oxide (1.1 equiv), and 4-Å M.S. in toluene was stirred at room temperature to 40 °C for 20 h under O_2 (1 atm). [b] Yield of isolated product; yield determined by NMR spectroscopy in parentheses. [c] 1.3 equivalents of borate were used.

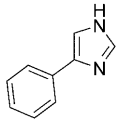
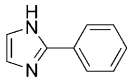
N Arylation of Imidazoles

The application of this methodology to the arylation of imidazoles with potassium aryl triolborates was also explored by using trimethylamine *N*-oxide as reoxidant and DMF as solvent (Table 3). Such coupling of **1b** with various imidazoles formed aryl imidazoles **4a–e** in yields no less than 83% (Table 3, entries 1–5), except for 2-phenylimidazole, which resulted in 43% yield due to steric hindrance of the phenyl group (Table 3, entry 6). The representative aryl borates were suitable for the arylation of imidazoles and gave the products in 70–90% yield (Table 3, entries 7–10).

Conclusions

Potassium aryl triolborates were found to be better aryl donors than traditional boronic acids and trifluoroborates for copper(II)-catalyzed N arylation. Because of the high nucleophilicity and high stability to air and water of triolborates, extension to other metal-catalyzed reactions will be the topic of further accounts from this laboratory.

Table 3. N arylation of imidazoles.[a]

Entry	Borate	Imidazole	*T* [°C]	Prod.	Yield [%][b]
1	**1b**		60	**4a**	93
2	**1b**		60	**4b**	95
3	**1b**		60	**4c**	92
4	**1b**		60	**4d**	84
5	**1b**		60	**4e**	83
6	**1b**		60	**4f**	43
7	**1c**		80	**4g**	70
8	**1d**		60	**4h**	90
9	**1e**		60	**4i**	83
10	**1f**		80	**4j**	71

[a] A mixture of imidazole (1.0 equiv), borate **1** (2.0 equiv), $Cu(OAc)_2$ (10 mol%), trimethylamine *N*-oxide (1.1 equiv), and 4-Å M.S. in DMF was stirred at 60–80 °C for 20 h under O_2 (1 atm). [b] Yield of isolated product.

Experimental Section

General

Infrared (IR) spectra were recorded on a Thermo Nicolet AVATAR 320 FTIR spectrometer. Frequencies of maximum absorbance are quoted in cm^{-1}. ^1H NMR spectra were recorded on a JEOL JNM-400II spectrometer (400 MHz) in $CDCl_3$ ($\delta_H = 7.25$ ppm) with tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million (ppm), and signals are expressed as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). ^{13}C NMR spectra were recorded on a JEOL JNM-400II spectrometer (100 MHz) in $CDCl_3$ ($\delta_C = 77.0$ ppm) with tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million (ppm). High-resolution mass spectrometry (HRMS) was performed on a JEOL JMS AX-500 or a JEOL JMS-SX102A mass spectrometer at the Center for Instrumental Analysis, Hokkaido University. GC analysis was performed with a Hitachi G-3500 chromatograph equipped with a glass column (OV-101 or OV-17 on Uni-

port B, 2 m). Kanto Chemical silica gel 60(particle size 0.063–0.210 mm) was used for flash column chromatography.

Toluene was distilled from sodium benzophenone ketyl under argon. 4-Å molecular sieves were purchased from Aldrich Chemical Company in powdered form. All glassware were oven-dried at 130 °C and allowed to cool under a stream of dry oxygen. All other chemicals were purchased from Aldrich, Wako Chemicals, TCI, or Kanto Chemicals and used as received.

The spectra of compounds **2a**,[14] **2b**,[15] **2c**,[16] **2d**,[15] **2e**,[5a] **2i**,[17] **2j**,[18] **2k**,[19] **2l**,[20] **2m**,[21] **2n**,[5a] **2o**,[18] **2p**,[5a] **2q**,[22] **2r**,[23] **2s**,[24] **2t**,[25] **2u**,[26] **2v**,[27] **3a**,[5d] **3b**,[5d] **3c**,[5a] **3d**,[5d] **3e**,[28] **3g**,[29] **3h**,[30] **3i**,[5d] **3j**,[31] **3k**,[5d] **3l**,[32] **3m**,[33] **3n**,[24] **3o**,[34] **4a**,[5a] **4b**,[5a] **4d**,[35] **4e**,[5a] **4g**,[5a] **4h**,[5a] **4i**,[3c] and **4j**[36] are identical to those reported in the literature.

Syntheses

Typical procedure for Cu^{II}-catalyzed N arylation of aliphatic amines and ammonium salts with potassium aryl triolborates (Table 1): A mixture of potassium aryl triolborate **1** (1.5 mmol), $Cu(OAc)_2$ (0.10 mmol), and powdered 4-Å molecular sieves (300 mg) in dry toluene (6.0 mL) was stirred for 5 min at room temperature. Amine (1.0 mmol) was added, and the flask was then charged with molecular oxygen in a teflon bag. The mixture was stirred for 20 h at the temperature shown in Table 1. The crude mixture was filtered through a plug of celite to remove the molecular sieves and any insoluble by-products. The filtrate was then concentrated in vacuo to afford the crude product, which was then subjected to chromatography on silica gel with hexanes/EtOAc (99:1–9:1) to give the analytically pure product.

2f: 3-Methoxypropyl-4-tolylamine: IR (neat): $\tilde{\nu}$ = 3391, 2921, 2867, 1617, 1519, 1256, 1183, 1115, 807 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.92 (tt, J = 5.9, 6.3 Hz, 2H), 2.30 (s, 3H), 3.24 (t, J = 6.3 Hz, 2H), 3.40 (s, 3H), 3.55 (t, J = 5.9 Hz, 2H), 3.83 (br s, 1H), 6.59 (d, J = 8.3 Hz, 1H), 7.04 ppm (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 29.3, 41.9, 58.5, 71.0, 112.8, 126.1, 129.6, 146.1 ppm; HRMS (EI): m/z calcd for $C_{11}H_{17}NO$: 179.1306 $[M]^+$; found: 179.1310.

2g: 3,7-Dimethylocta-2,6-dienyl-4-tolylamine: IR (neat): $\tilde{\nu}$ = 3408, 2916, 2857, 1617, 1518, 1248, 805 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.60 (s, 3H), 1.69 (s, 3H), 2.01–2.05 (m, 2H), 2.09 (t, J = 6.3 Hz, 2H), 2.24 (s, 3H), 3.44 (br s, 1H), 3.68 (d, J = 6.8 Hz, 2H), 5.09 (t, J = 6.4 Hz, 1H), 5.33 (t, J = 6.4 Hz, 1H), 6.54 (d, J = 8.3 Hz, 2H), 6.98 ppm (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2, 17.6, 20.3, 25.6, 26.4, 39.4, 42.2, 112.9, 123.9, 126.2, 129.5, 131.4, 138.5, 146.1 ppm; HRMS (EI): m/z calcd for $C_{17}H_{25}N$: 243.1995 $[M]^+$; found: 243.1987.

2h: 3-Chloropropyl-4-tolylamine: IR (neat): $\tilde{\nu}$ = 2918, 1616, 1516, 1253, 806 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.03 (t, J = 6.5 Hz, 2H), 2.08 (t, J = 6.2 Hz, 2H), 2.23 (s, 3H), 3.31 (t, J = 6.5 Hz, 2H), 3.56 (br s, 1H), 3.65 (t, J = 6.2 Hz, 2H), 6.56 (d, J = 8.6 Hz, 1H), 7.00 ppm (d, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 38.7, 41.0, 42.5, 112.8, 126.5, 129.6, 145.5 ppm; HRMS (EI): m/z calcd for $C_{10}H_{14}NCl$: 183.0805 $[M]^+$; found: 183.0815.

Typical procedure for Cu^{II}-catalyzed N arylation of anilines with potassium aryl triolborates (Table 2): A mixture of potassium aryl triolborate (1.5 mmol), $Cu(OAc)_2$ (0.10 mmol), trimethylamine *N*-oxide (1.1 mmol), and powdered 4-Å molecular sieves (300 mg) in toluene (6.0 mL) was stirred for 5 min at room temperature. Aniline (1.0 mmol) was then added. The mixture was stirred for 20 h at the temperature shown in Table 2. The product was isolated by chromatography on silica gel with hexane/EtOAc/MeOH (90:10:1).

3f: 4-Iodo-*N*-*p*-tolylbenzenamine: IR (neat): $\tilde{\nu}$ = 3416, 1611, 1587, 1512, 1309, 1176, 998, 807 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 5.61 (br s, 1H), 6.78 (d, J = 6.8 Hz, 1H), 6.80 (d, J = 6.8 Hz, 1H), 7.01 (d, J = 6.4 Hz, 1H), 7.03 (d, J = 6.4 Hz, 1H), 7.13 (d, J = 6.4 Hz, 1H), 7.16 (d, J = 6.4 Hz, 1H), 7.51 (d, J = 6.8 Hz, 1H), 7.53 ppm (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 81.1, 118.3, 119.5, 129.9, 131.6, 137.8, 139.2, 143.8 ppm; HRMS (EI): m/z calcd for $C_{13}H_{12}NI$: 308.9998 $[M]^+$; found: 309.0015.

Typical procedure for Cu^{II}-catalyzed N arylation of imidazoles with potassium aryl triolborates (Table 3): A mixture of potassium aryl triolborate (2.0 mmol), imidazole (1.0 mmol), $Cu(OAc)_2$ (0.10 mmol), trimethylamine *N*-oxide(1.1 mmol), and powdered 4-Å molecular sieves (300 mg) in DMF (6.0 mL) was stirred for 20 h at the temperature shown in Table 3. The product was isolated by chromatography on silica gel with hexane/EtOAc/MeOH (90:10:1).

4c: 1-(*p*-Tolyl)-4-methylimidazole: IR (neat): $\tilde{\nu}$ = 1516, 1469, 1413, 1307, 822, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 2.39 (s, 3H), 6.97 (s, 1H), 7.25 (s, 4H), 7.75 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 20.9, 114.8, 121.1, 130.3, 134.6, 135.0, 137.1, 139.0 ppm; HRMS (EI): m/z calcd for $C_{11}H_{12}N_2$: 172.0994 $[M]^+$; found: 234.1000.

4f: 1-(*p*-Tolyl)-4-phenylimidazole: IR (neat): $\tilde{\nu}$ = 1514, 1464, 1413, 1306, 821, 693, 562 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 7.08–7.12 (m, 3H), 7.17–7.19 (m, 2H), 7.24–7.27 (m, 4H), 7.38–7.41 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 122.9, 125.6, 128.1, 128.3, 128.5, 130.0, 130.1, 135.8, 138.1, 146.5 ppm; HRMS (EI): m/z calcd for $C_{16}H_{14}N_2$: 234.1149 $[M]^+$; found: 234.1157.

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