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Copper-Catalyzed Direct Amination of 1,2,3-Triazole *N*-Oxides by C–H Activation and C–N Coupling

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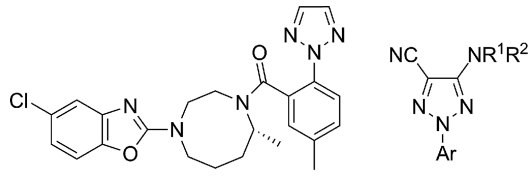
An efficient approach for the synthesis of 4-amino-2-aryl-1,2,3-triazole derivatives has been developed through the copper-catalyzed direct C–H amination of 2-aryl-1,2,3-triazole *N*-oxides under mild reaction conditions. Various amines, including primary and secondary aliphatic and aromatic amines, can be employed as effective coupling partners. The general performance of our method was also demonstrated by the oxidative amination of thiazole and imidazole *N*-oxides.

Introduction

Five-membered heterocycles with amine substituents are an important class of molecules and have been widely used as synthetic building blocks, bioactive molecules, pharmaceuticals, and organic materials.[1] Over recent decades, remarkable progress has been made in transition-metal-catalyzed C–N bond-forming reactions such as palladium-catalyzed Buchwald–Hartwig-type cross-couplings,[2] Chan–Lam coupling reactions,[3] and copper-catalyzed Ullmann and Goldberg couplings.[4] Although significant advances have been achieved, the direct installation of amino groups or their surrogates on unfunctionalized arenes or heterocyclic compounds is still challenging.[5] To meet this demand, a huge surge of interest has recently been directed towards transition-metal-catalyzed C–H amination reactions to obviate the preparation of preactivated substrates.

A pioneering study on the copper-mediated directed amination of arene C–H bonds was reported by Yu et al. in 2006.[6] Subsequently, several other groups have shown that unfunctionalized arenes or heterocyclic compounds can be aminated by employing copper salts.[7] Recently, palladium-catalyzed intermolecular aromatic C–H aminations,[8] cobalt- or manganese-catalyzed direct aminations of azoles,[9] and iodide-catalyzed oxidative aminations of heteroarenes have been developed.[10] Since 2005, pyridine, diazine, azine, azole, and heterocyclic *N*-oxides have been introduced as readily available and stable substrates in direct cross-coupling reactions by Fagnou[11] and others.[12] Inspired by their studies, we envisaged that 2-aryl-1,2,3-triazole *N*-oxides could be employed as more-reactive, halogen-free electrophilic coupling partners in catalytic amination reactions. We describe herein our successful copper catalyst systems for the direct synthesis of 4-amino-2-aryl-1,2,3-triazoles by a direct C–H amination protocol with primary and secondary amines under mild reaction conditions. We were very pleased to find that the targeted N^+–O^- bond cleavage can be observed during the reaction; thus the use of an additional deoxygenation step is obviated. More recently, Cui and co-workers developed a simple and highly efficient protocol for the direct amination of quinoline *N*-oxide and its analogues with secondary aliphatic amines based on a one-pot copper-catalyzed C–H bond activation.[13] However, the deoxygenation of the obtained 2-aminoquinoline *N*-oxides requires an additional step.

The 1,2,3-triazole heterocyclic system has been known for more than one hundred years. In the last two decades, the development of the chemistry of 1,2,3-triazoles has gained a new impetus owing to the discovery of the diverse biological activities of many triazole derivatives (Figure 1).[14] 1,2,3-Triazoles have found applications as agrochemicals, dyes, anticorrosive agents, and photographic materials. For example, 2-aryl-1,2,3-triazoles have been used as



1a (Suvorexant) **1b** (antibacterial activity)

Figure 1. Medicinally important molecules containing 1,2,3-triazole.

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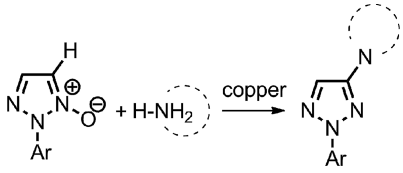
optical brighteners.[15] The number of patents dealing with the use of these derivatives as drugs and agrochemicals has grown rapidly.[16] Several synthetic methods have been developed for the preparation of these heterocycles. For example, "click" chemistry has been applied to the synthesis of N-1-substituted triazoles from sodium azide and alkynes with a Cu^{I} catalyst.[17] However, the synthesis of N-2-substituted triazoles remains a challenge,[18] especially for 2,4-disubstituted substrates.

Results and Discussion

On the basis of these advances, we hypothesized that a copper-catalyzed cross-deprotonative coupling (CDC) process for the amination of 1,2,3-triazole *N*-oxides with amines should be possible (Scheme 1). Bearing in mind the aforementioned background, we commenced our studies by evaluating the CDC reaction between 2-phenyl-1,2,3-triazole *N*-oxide (**2a**) and pyrrolidine (**3a**) with $Pd(OAc)_2$/$AgBF_4$/1,10-phenanthroline monohydrate as the catalyst system; the aminated product **4a** was not obtained, but the homocoupling product **5** was obtained in 25% yield (Table 1, Entry 1).

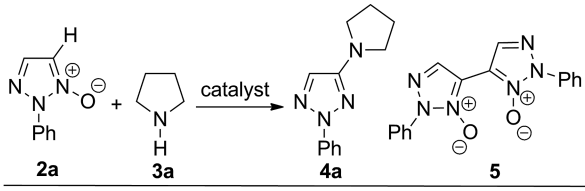


Scheme 1. Copper-catalyzed amination of 1,2,3-triazole *N*-oxides.

Subsequently, various catalyst systems, including $Pd(OAc)_2$/Ag_2CO_3/1,10-phenanthroline monohydrate, Ag_2CO_3/$PhCO_2H$, Ag_2CO_3/Na_2CO_3, and $NiCl_2$/bipyridine, were screened, and in all cases only a trace amount of **4a** was detected (Table 1, Entries 2–5). When 20 mol-% of $Cu(OAc)_2$ and 2.0 equiv. of NaOAc were used as the catalyst and base, the desired aminated product **4a** was obtained in a yield of 36% (Table 1, Entry 6). Interestingly, no homocoupling product **5** was observed under these reaction conditions. Encouraged by this preliminary result, various copper salts were screened under similar conditions; $Cu(OAc)_2$ showed the highest activity and efficacy, and the other tested salts, namely, $CuCl_2$, $CuSO_4$, CuI, Cu_2O, and CuCN, were less effective (Table 1, Entries 7–11). Furthermore, the solvent had a significant effect on the product yield, and dimethoxyethane (DME) showed the best performance (Table 1, Entry 13). However, *N*,*N*-dimethylformamide (DMF) completely suppressed the reaction (Table 1, Entry 15). Finally, we examined the effect of the base on the reaction and found that K_3PO_4 performed better than the other bases (Table 1, Entries 16–19). Through the optimization of the reaction conditions, the best conditions were found to be 20 mol-% of $Cu(OAc)_2$ with 2 equiv. of K_3PO_4 in DME at 80 °C for 12 h.

Having determined the optimal conditions, we explored the substrate scope of this method. We first investigated the reaction between various 2-aryl-1,2,3-triazole *N*-oxides **2** and pyrrolidine (Scheme 2). Alkyl- or halogen-substituted 2-aryl-1,2,3-triazole *N*-oxides could be aminated with perfect regioselectivity to yield the desired 2-aryl-4-(pyrrolidin-1-yl)-2*H*-1,2,3-triazoles **4a**–**4h** in up to 82% yield. Notably,

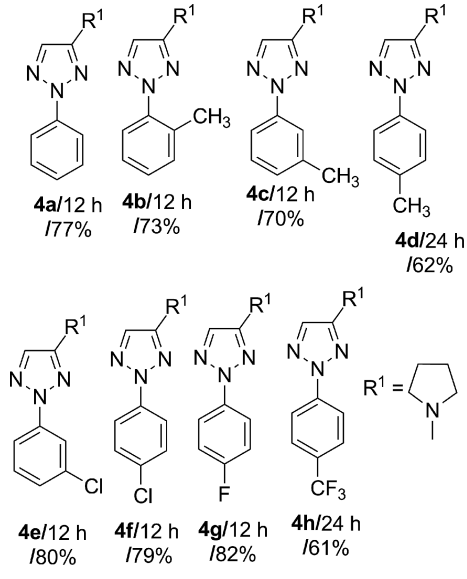
Table 1. Optimization of reaction conditions.[a]



2a 3a 4a 5

Entry	Catalyst	Additive	Solvent/Temp. [°C]	Yield (%)[b]
1[c]	$Pd(OAc)_2$/$AgBF_4$	1,10-phen	xylene/120	25[e]
2[c]	$Pd(OAc)_2$/Ag_2CO_3	1,10-phen	xylene/120	21[e]
3[d]	Ag_2CO_3	$PhCO_2H$	xylene/120	trace
4[d]	Ag_2CO_3	Na_2CO_3	xylene/120	trace
5	$NiCl_2$	bipyridine	xylene/120	trace
6	$Cu(OAc)_2$	NaOAc	xylene/120	36
7	$CuCl_2$	NaOAc	xylene/120	22
8	$CuSO_4$	NaOAc	xylene/120	20
9	CuI	NaOAc	xylene/120	25
10	Cu_2O	NaOAc	xylene/120	30
11	CuCN	NaOAc	xylene/120	trace
12	$Cu(OAc)_2$	NaOAc	toluene/110	16
13	$Cu(OAc)_2$	NaOAc	DME/80	67
14	$Cu(OAc)_2$	NaOAc	CH_3CN/80	43
15	$Cu(OAc)_2$	NaOAc	DMF/120	trace
16	$Cu(OAc)_2$	Na_2CO_3	DME/80	65
17	$Cu(OAc)_2$	LiOH	DME/80	63
18	$Cu(OAc)_2$	*t*BuOK	DME/80	55
19	$Cu(OAc)_2$	K_3PO_4	DME/80	77

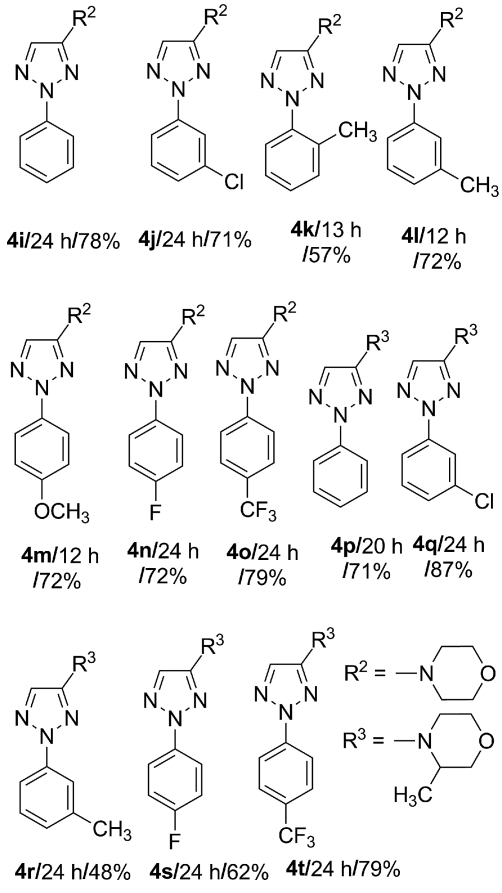
[a] Conditions: **2a** (0.2 mmol), **3a** (0.6 mmol), catalyst (0.04 mmol), additive (0.4 mmol), and solvent (1 mL), 12 h. [b] Isolated yield. [c] $Pd(OAc)_2$ (0.01 mmol), silver salt (0.03 mmol), 24 h. [d] Catalyst (0.3 mmol), 24 h. [e] Yield of **5**.



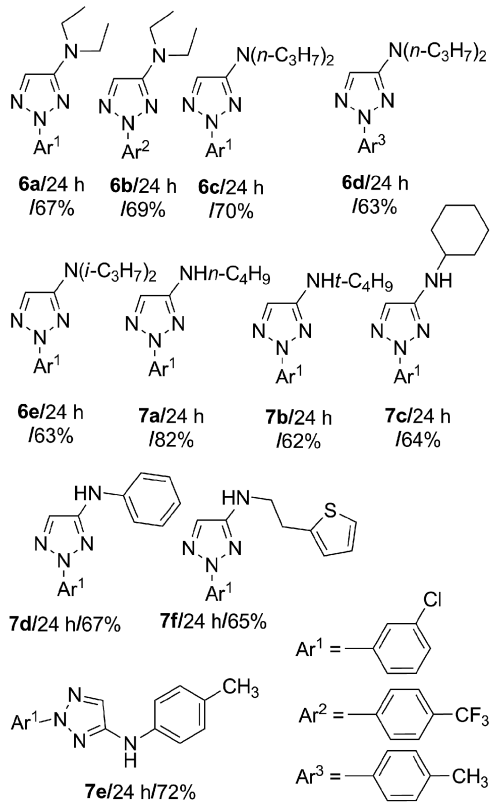
Scheme 2. Amination of 2-aryl-1,2,3-triazole *N*-oxides **2** with pyrrolidine (**3a**). Reaction conditions: **2** (0.2 mmol), **3a** (0.6 mmol), $Cu(OAc)_2$ (20 mol-%), K_3PO_4 (2 equiv.), and DME (1 mL), 80 °C. Isolated yields reported.

triazoles bearing *o*-tolyl (**4b**), *m*-tolyl (**4c**), *p*-tolyl (**4d**), 3-chlorophenyl (**4e**), 4-chlorophenyl (**4f**), 4-fluorophenyl (**4g**), and 4-(trifluoromethyl)phenyl (**4h**) moieties at the N-2 position of the triazole ring can also be used for this cross-coupling reaction. It was clear that 2-aryl-1,2,3-triazole *N*-oxides bearing electron-withdrawing groups, such as fluoro and chloro groups, are more reactive than those bearing electron-donating groups, such as methyl groups. However, a decrease in yield was observed when 4-(trifluoromethyl)-phenyl-1,2,3-triazole *N*-oxide was engaged (**4h**). Importantly, the Cl atoms of products **4e** and **4f** were retained under the amination reaction conditions. In general, the amination of aryl halides with amines has been achieved by palladium- and copper-catalyzed routes.[19]

Next, we performed the reactions between various 2-aryl-1,2,3-triazole *N*-oxides **2** and morpholine (**3b**) as well as 2-methylpiperidine (**3c**, Scheme 3). We found that 2-substituted 1,2,3-triazole *N*-oxides bearing electron-donating and -withdrawing substituents gave the expected products in moderate-to-excellent yields. The good functional-group tolerance of the reaction suggests that the substituted groups do not have a significant influence on the reaction. Furthermore, we were pleased to find that steric bulk posed no problem in this reaction, as exemplified by the high yield of the 2-methylpiperidine product **4q**. The structure of product **4o** was unambiguously determined by single-crystal X-ray diffraction (see Supporting Information). In addition, acyclic secondary amines such as diethylamine, dipropylamine, and diisopropylamine reacted smoothly with **2** to give the corresponding products **6a**–**6e** in good yields (Scheme 4).



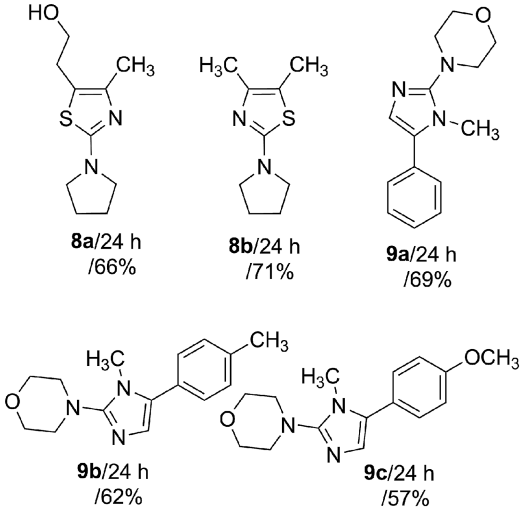
Scheme 3. Amination of 2-aryl-1,2,3-triazole *N*-oxides **2** with morpholine (**3b**) as well as 2-methylpiperidine (**3c**). Reaction conditions: **2** (0.2 mmol), **3b** or **3c** (0.6 mmol), $Cu(OAc)_2$ (20 mol-%), K_3PO_4 (2 equiv.), and DME (1 mL), 80 °C. Isolated yields reported.



Scheme 4. Amination of 2-aryl-1,2,3-triazole *N*-oxides **2** with various amines. Reaction conditions: **2** (0.2 mmol), amine (0.8 mmol), $Cu(OAc)_2$ (20 mol-%), K_3PO_4 (1.8 equiv.), *t*BuOK (20 mol-%), and DME (1 mL), 80 °C. Isolated yields reported.

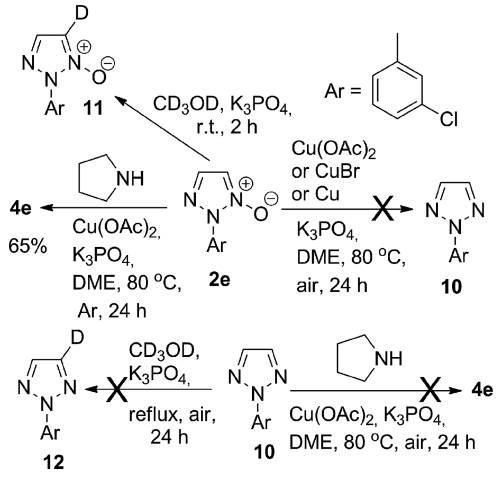
Owing to the promising results for secondary amine formation, we further explored the possibility of extending the reaction to primary amines. Notably, the oxidative amination of benzoxazoles with primary amines in Co-[9] and Cu-catalyzed[7c] coupling failed to furnish the coupled products. In light of this observation, we continued our exploration on the amination of 2-aryl-1,2,3-triazole *N*-oxides **2** with primary amines. Under the optimal reaction conditions, aniline coupled with 2-(3-chlorophenyl)-2*H*-1,2,3-triazole *N*-oxide, but the yield was only 8%; the yield improved dramatically to 67% with K_3PO_4 (1.8 equiv.) and *t*BuOK (20 mol-%) as bases (**7d**). As depicted in Scheme 4, both aliphatic and aromatic primary amines reacted with 3-chlorophenyl-1,2,3-triazole *N*-oxide to afford the corresponding aminated products **7** in good yields. Unexpectedly, the sterically hindered 2-methylpropan-2-amine coupled efficiently with 2-(3-chlorophenyl)-2*H*-1,2,3-triazole *N*-oxide in up to 62% isolated yield (**7b**).

To further expand the scope of our methodology, the oxidative aminations of other *N*-oxides, such as thiazole *N*-oxides, and imidazole *N*-oxides, were then tested. As shown in Scheme 5, the tested thiazole *N*-oxides acted as good substrates for the reaction with pyrrolidine and furnished the corresponding products **8** in good yields. For instance, 4,5-dimethylthiazole 3-oxide successfully underwent the oxidative amination with pyrrolidine in 71% yield under our reaction conditions. The deacetylated product **8a** was obtained in 66% yield when 5-(2-acetoxyethyl)-4-methylthiazole 3-oxide was used as the substrate. However, only a trace amount of the desired product **9a** was observed when 1-methyl-5-phenyl-1*H*-imidazole 3-oxide was subjected to the optimized conditions. To our delight, after further optimization of the reaction parameters, we found that the oxidative amination of imidazole *N*-oxides with morpholine proceeded well in the presence of $Cu(OAc)_2$, Na_2CO_3, and pyridine under 1 atm of O_2 at 120 °C, and the desired products **9** were produced in moderate yields.



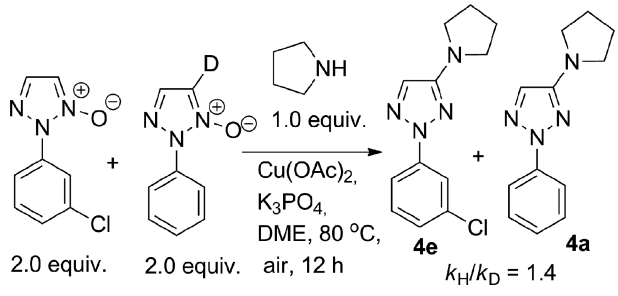
Scheme 5. Amination of substituted thiazole *N*-oxides and imidazole *N*-oxides with amines. For thiazole *N*-oxides, the reactions were performed with *N*-oxide (0.2 mmol), pyrrolidine (0.6 mmol), $Cu(OAc)_2$ (20 mol-%), K_3PO_4 (2 equiv.), and DME (1 mL) at 80 °C, yields reported after isolation. For imidazole *N*-oxides, the reactions were performed with *N*-oxide (0.2 mmol), morpholine (0.4 mL), $Cu(OAc)_2$ (20 mol-%), Na_2CO_3 (2 equiv.), and pyridine (0.2 mmol) at 120 °C under 1 atm of O_2.

To better understand the reaction mechanism, some control experiments were performed. Firstly, we tested the reaction in the absence of the amine partner (Scheme 6). No deoxygenation product **10** was observed at all. Secondly, 1,2,3-triazole **10** was subjected to the standard procedure, and no aminated product was detected. These results indicate that the deoxygenation of 1,2,3-triazole *N*-oxides occurs after the C–N bond formation step. Thirdly, the amination of **2e** with **3a** under an argon atmosphere (in the absence of molecular oxygen) furnished **4e** in 65% yield; therefore, molecular oxygen is not crucial for the reaction. Some groups reported that *N*-oxides are prototypical oxidants and have been routinely used in some reactions.[11b,20,21] Fourthly, we performed the experiment with fully deuterated methanol (CD_3OD) and analyzed the distribution of the deuterium incorporation. As shown in Scheme 6, the degree of deuterium incorporation at C-5 of the triazole *N*-oxide ring is 100%; therefore, the deuterium exchange between **2e** and CD_3OD proceeds very quickly in the presence of K_3PO_4 to give the deuterated product **11**. In contrast, the H/D exchange at C-4 of **10** with CD_3OD under basic reaction conditions (K_3PO_4, CD_3OD, reflux) afforded only the starting materials. This result indicates that the *N*-oxide group imparts a dramatic increase in the reactivity for the direct C-5 amination of **2e**. Fifthly, when **10** was subjected to the reaction conditions, no product was observed. This result indicates that H/D exchange at C-4 of **10** did not occur under our reaction conditions.



Scheme 6. Control experiments.

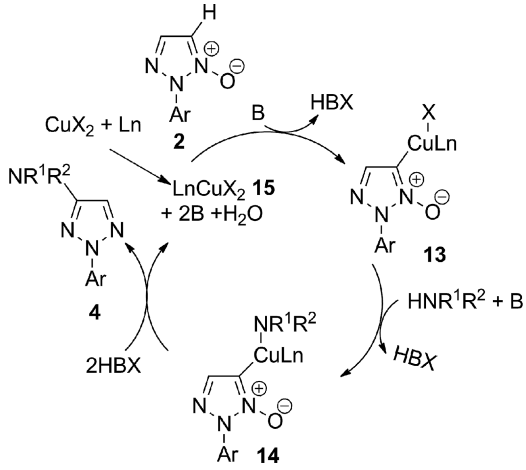
Intermolecular competition experiments between *N*-oxide **2e** and 5-deuterio *N*-oxide **13** were performed in the reaction with pyrrolidine under the reaction conditions. The observed kinetic isotope effect (KIE) of 1.4 (Scheme 7) indicates that cleavage of the *N*-oxide C–H bond is not involved in the rate-determining step.



Scheme 7. KIE experiments.

Although mechanisms for copper-catalyzed oxidative C–N couplings have been proposed,[5d,7] the details remain uncertain. A plausible mechanism for the direct coupling of 1,2,3-triazole *N*-oxides with amines is outlined in Scheme 8.[20] The H atom of the triazole would be replaced with the Cu^{II} center to form organocopper **13**, which reacts

further with the amine to furnish intermediate **14**. A subsequent reductive elimination produces the coupling product **4** along with a copper species of the lower oxidation state, which would be oxidized to give Cu^{II} species **15** to complete the catalytic cycle.



Scheme 8. Plausible mechanism for copper-catalyzed amination of **2**.

Conclusions

An efficient copper-catalyzed direct C–H amination of 2-aryl-1,2,3-triazole *N*-oxides with various amines has been developed and produces the desired products in moderate-to-excellent yields with high regioselectivity. The general performance of our method was also demonstrated by the oxidative amination of thiazole and imidazole *N*-oxides. We were very pleased to find that the targeted N^+–O^- bond cleavage can be observed during the reaction; thus, the use of an additional deoxygenation step is obviated. The advantages of this new method are operational simplicity, high atom-economy, and the use of inexpensive and environmentally friendly $Cu(OAc)_2$ as the catalyst. In addition, this method avoids the use of air-sensitive reagents; therefore, the reaction can be performed under relatively mild conditions and provides a powerful tool for the synthesis of 4-amino-2-aryl-1,2,3-triazole derivatives. Moreover, the high halogen compatibility of the process enables facile access to chloride-substituted 2-aryl-4-amino triazoles.

Experimental Section

General Procedure for the Preparation of 4: To a solution of 2-aryl-1,2,3-triazole *N*-oxide (0.2 mmol), $Cu(OAc)_2$ (0.04 mmol), and K_3PO_4 (0.4 mmol) in DME (1 mL) was added a secondary amine (0.6 mmol) under an air atmosphere, and the mixture was stirred at 80 °C for 12–24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography [eluent: EtOAc/petroleum ether (EtOAc/PE) 1:4] to yield the corresponding product **4**.

General Procedure for the Preparation of 6–8: To a solution of *N*-oxide (0.2 mmol), $Cu(OAc)_2$ (0.04 mmol), *t*BuOK (0.04 mmol), and K_3PO_4 (0.36 mmol) in DME (1 mL) was added amine (0.8 mmol) under an air atmosphere, and the mixture was stirred at 80 °C for 24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (eluent: EtOAc/PE 1:2) to yield the corresponding product **6**, **7**, or **8**.

General Procedure for the Preparation of 9: A sealed tube containing the imidazole *N*-oxide (0.2 mmol), $Cu(OAc)_2$ (0.04 mmol), and Na_2CO_3 (0.4 mmol) was evacuated and filled with dioxygen gas from an oxygen-containing balloon. Then, pyridine (0.2 mmol) and morpholine (0.4 mL) were sequentially added to the system under an oxygen atmosphere with a syringe. The mixture was stirred at 120 °C for 24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (eluent: EtOAc/PE 1:1) to yield the corresponding product **9**.

2-Phenyl-4-(pyrrolidin-1-yl)-2*H*-1,2,3-triazole (4a): Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.01 (dt, J = 3.2, 6.7 Hz, 4 H, 2 × CH_2), 3.39 (dt, J = 3.2, 6.7 Hz, 4 H, 2 × CH_2), 7.13 (s, 1 H, Ar-H), 7.23 (m, 1 H, Ar-H), 7.43 (m, 2 H, Ar-H), 7.96 (d, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 48.6, 117.5, 121.3, 125.6, 129.1, 140.2, 155.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1566, 1498, 944 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{15}N_4$ $[M + H]^+$ 215.1296; found 215.12917 (100%).[11c]

4-(Pyrrolidin-1-yl)-2-(*o*-tolyl)-2*H*-1,2,3-triazole (4b): Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.01 (dt, J = 3.3, 6.7 Hz, 4 H, 2 × CH_2), 2.43 (s, 3 H, CH_3), 3.38 (dt, J = 3.3, 6.7 Hz, 4 H, 2 × CH_2), 7.15 (s, 1 H, Ar-H), 7.25–7.31 (m, 3 H, Ar-H), 7.54 (d, J = 9.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 25.3, 48.7, 120.4, 124.7, 126.4, 127.6, 131.6, 132.4, 139.9, 155.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1566, 1495, 950, 760 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{17}N_4$ $[M + H]^+$ 229.14532; found 229.14471 (100%).

4-(Pyrrolidin-1-yl)-2-(*m*-tolyl)-2*H*-1,2,3-triazole (4c): Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.00 (dt, J = 3.3, 6.7 Hz, 4 H, 2 × CH_2), 2.42 (s, 3 H, CH_3), 3.39 (dt, J = 3.3, 6.7 Hz, 4 H, 2 × CH_2), 7.04 (d, J = 7.5 Hz, 1 H, Ar-H), 7.12 (s, 1 H, Ar-H), 7.30 (t, J = 7.5 Hz, 1 H, Ar-H), 7.76 (t, J = 8.1 Hz, 1 H, Ar-H), 7.79 (d, J = 8.1 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 25.4, 48.6, 114.8, 118.1, 121.1, 126.5, 128.9, 139.1, 140.1, 155.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1567, 1491, 952, 785 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{17}N_4$ $[M + H]^+$ 229.14532; found 229.14469 (100%).

4-(Pyrrolidin-1-yl)-2-(*p*-tolyl)-2*H*-1,2,3-triazole (4d): Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.01 (dt, J = 3.2, 6.7 Hz, 4 H, 2 × CH_2), 2.38 (s, 3 H, CH_3), 3.39 (dt, J = 3.2, 6.7 Hz, 4 H, 2 × CH_2), 7.10 (s, 1 H, Ar-H), 7.22 (d, J = 8.2 Hz, 2 H, Ar-H), 7.83 (d, J = 8.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 25.4, 48.6, 117.5, 120.8, 129.6, 135.4, 138.0, 155.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1549, 1511, 1446, 1353, 627, 942, 819 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{17}N_4$ $[M + H]^+$ 229.14532; found 229.14531 (100%).

2-(3-Chlorophenyl)-4-(pyrrolidin-1-yl)-2*H*-1,2,3-triazole (4e): Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.02 (dt, J = 3.2, 6.7 Hz, 4 H, 2 × CH_2), 3.39 (dt, J = 3.2, 6.7 Hz, 4 H, 2 × CH_2), 7.14 (s, 1 H, Ar-H), 7.18 (ddd, J = 8.2, 2.0, 1.0 Hz, 1 H, Ar-H), 7.34 (t, J = 8.2 Hz, 1 H, Ar-H), 7.83 (ddd, J = 8.2, 2.0, 1.0 Hz, 1 H, Ar-H), 7.97 (t, J = 2.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 48.5, 115.5, 117.7, 122.0, 125.4, 130.1, 134.9, 155.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1569, 1485, 1111, 946, 782 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}ClN_4$ $[M + H]^+$

249.09070 (100%), 251.08775 (32%); found 249.09010 (100%), 251.08696 (32%).

2-(4-Chlorophenyl)-4-(pyrrolidin-1-yl)-2*H*-1,2,3-triazole (4f): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (dt, J = 3.3, 6.6 Hz, 4 H, 2×CH_2), 3.39 (dt, J = 3.3, 6.6 Hz, 4 H, 2×CH_2), 7.13 (s, 1 H, Ar-H), 7.38 (dt, J = 2.9, 8.9 Hz, 2 H, Ar-H), 7.89 (dt, J = 2.9, 8.9 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 48.5, 118.6, 121.7, 129.1, 130.9, 138.7, 155.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1539, 1493, 1088, 941, 824 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}ClN_4$ [M + H]$^+$ 249.09070 (100%), 251.08775 (32%); found 249.09000 (100%), 251.08696 (32%).

2-(4-Fluorophenyl)-4-(pyrrolidin-1-yl)-2*H*-1,2,3-triazole (4g): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (dt, J = 3.3, 6.6 Hz, 4 H, 2×CH_2), 3.38 (dt, J = 3.3, 6.6 Hz, 4 H, 2×CH_2), 7.10 (s, 1 H, Ar-H), 7.12 (dt, J = 2.2, 9.2 Hz, 2 H, Ar-H), 7.92 (dt, J = 2.2, 9.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 48.5, 115.7 (d, J = 23.0 Hz), 119.1 (d, J = 8.1 Hz), 136.6, 155.5, 160.7 (d, J = 244.5 Hz) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1595, 1508, 1210, 943, 831, 628 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}FN_4$ [M + H]$^+$ 233.12025; found 233.11968 (100%).

4-(Pyrrolidin-1-yl)-2-[4-(trifluoromethyl)phenyl]-2*H*-1,2,3-triazole (4h): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03 (dt, J = 3.3, 6.7 Hz, 4 H, 2×CH_2), 3.41 (dt, J = 3.3, 6.7 Hz, 4 H, 2×CH_2), 7.18 (s, 1 H, Ar-H), 7.67 (d, J = 8.5 Hz, 2 H, Ar-H), 8.05 (d, J = 8.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 48.4, 117.2, 122.7, 124.4 (d, J = 271.7 Hz), 126.3 (q, J = 3.7 Hz), 127.2 (d, J = 32.8 Hz), 142.3, 115.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1584, 1325, 1162, 1114, 1065, 932, 839 cm^{-1}. MS-EI: *m*/*z* (%) = 70 (12), 145 (28), 213 (5), 226 (15), 254 (12), 263 (13), 282 (100). $C_{13}H_{13}F_3N_4$ (282.2693): calcd. C 55.32, H 4.64, N 19.85; found C 55.17, H 4.93, N 19.62.

4-(2-Phenyl-2*H*-1,2,3-triazol-4-yl)morpholine (4i): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.31 (t, J = 4.8 Hz, 4 H, 2×CH_2), 3.87 (t, J = 4.8 Hz, 4 H, 2×CH_2), 7.24–7.29 (m, 2 H, Ar-H), 7.44 (dt, J = 2.0, 8.8 Hz, 2 H, Ar-H), 7.95 (dt, J = 2.0, 8.8 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.4, 66.3, 117.8, 121.9, 126.2, 129.1, 140.0, 157.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1595, 1560, 1497, 1264, 1177, 913, 756 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{15}N_4O$ [M + H]$^+$ 231.12459; found 231.12380 (100%).

4-[2-(3-Chlorophenyl)-2*H*-1,2,3-triazol-4-yl]morpholine (4j): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.31 (t, J = 4.8 Hz, 4 H, 2×CH_2), 3.87 (t, J = 4.8 Hz, 4 H, 2×CH_2), 7.22 (dt, J = 2.0, 8.0 Hz, 1 H, Ar-H), 7.28 (s, 1 H, Ar-H), 7.36 (t, J = 8.0 Hz, 1 H, Ar-H),7.84 (dt, J = 2.0, 8.0 Hz, 1 H, Ar-H), 7.97 (t, J = 2.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.2, 66.2, 115.7, 118.0, 122.6, 126.1, 130.2, 135.0, 140.7, 157.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1592, 1542, 1484, 1446, 1117, 779 cm^{-1}. MS-EI: *m*/*z* (%) = 111 (22), 171 (2), 206 (80), 220 (4), 264 (100). $C_{12}H_{13}ClN_4O$ (264.71): calcd. C 54.45, H 4.95, N 21.17; found C 54.18, H 5.09, N 20.89.

4-[2-(*o*-Tolyl)-2*H*-1,2,3-triazol-4-yl]morpholine (4k): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 3.29 (t, J = 4.8 Hz, 4 H, 2×CH_2), 3.88 (t, J = 4.8 Hz, 4 H, 2×CH_2), 7.26–7.32 (m, 4 H, Ar-H), 7.52–7.56 (m, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 48.5, 66.3, 121.2, 124.7, 126.5, 128.0, 131.7, 132.3, 139.7, 157.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1549, 1497, 1455, 1268, 1119, 762 cm^{-1}. HRMS (ESI) calcd. for $C_{13}H_{17}N_4O$ [M+ H]$^+$ 245.14024; found 245.13967 (100%).

4-[2-(*m*-Tolyl)-2*H*-1,2,3-triazol-4-yl]morpholine (4l): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 3.31 (dt, J = 3.4, 4.8 Hz, 4 H, 2×CH_2), 3.87 (dt, J = 3.4, 4.8 Hz, 4 H, 2×CH_2), 7.08 (d, J = 7.8 Hz, 1 H, Ar-H), 7.26 (s, 1 H, Ar-H), 7.32 (t, J = 7.8 Hz, 1 H, Ar-H), 7.76 (d, J = 7.8 Hz, 1 H, Ar-H), 7.79 (s, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 48.4, 66.3, 115.0, 118.4, 121.7, 127.1, 129.0, 139.2, 139.9, 157.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1578, 1556, 1452, 1267, 1133, 918, 787 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{17}N_4O$ [M + H]$^+$ 245.14024; found 245.13957 (100%).

4-[2-(4-Methoxyphenyl)-2*H*-1,2,3-triazol-4-yl]morpholine (4m): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.29 (t, J = 4.8 Hz, 4 H, 2×CH_2), 3.85 (s, 3 H, OCH_3), 3.88 (t, J = 4.8 Hz, 4 H, 2×CH_2), 6.96 (dt, J = 2.2, 7.0 Hz, 2 H, Ar-H), 7.22 (s, 1 H, Ar-H), 7.86 (dt, J = 2.2, 7.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.5, 55.6, 66.3, 114.2, 119.3, 121.2, 133.9, 157.3, 158.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1550, 1510, 1251, 1113, 834 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{17}N_4O$ [M + H]$^+$ 261.13515; found 261.13465 (100%).

4-[2-(4-Fluorophenyl)-2*H*-1,2,3-triazol-4-yl]morpholine (4n): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30 (t, J = 4.8 Hz, 4 H, 2×CH_2), 3.87 (t, J = 4.8 Hz, 4 H, 2×CH_2), 7.13 (dt, J = 2.2, 9.1 Hz, 2 H, Ar-H), 7.25 (s, 1 H, Ar-H), 7.92 (dt, J = 2.2, 9.1 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.3, 66.3, 115.9 (d, J = 23.2 Hz), 116.2 (d, J = 8.1 Hz), 121.9, 136.3 (d, J = 2.6 Hz), 157.5, 161.0 (d, J = 245.5 Hz) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1548, 1508, 1444, 1213, 1112, 835 cm^{-1}. MS-EI: *m*/*z* (%) = 95 (25), 109 (17), 190 (84), 217 (6), 233 (8), 248 (100). $C_{12}H_{13}FN_4O$ (248.26): calcd. C 58.06, H 5.28, N 22.57; found C 57.78, H 5.51, N 22.29.

4-{2-[4-(Trifluoromethyl)phenyl]-2*H*-1,2,3-triazol-4-yl}morpholine (4o): Waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.33 (t, J = 4.8 Hz, 4 H, 2×CH_2), 3.88 (t, J = 4.8 Hz, 4 H, 2×CH_2), 7.32 (s, 1 H, Ar-H), 7.69 (d, J = 8.6 Hz, 2 H, Ar-H), 8.06 (d, J = 8.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.1, 66.2, 117.5, 123.1, 124.0 (d, J = 271.7 Hz), 126.4 (q, J = 3.6 Hz), 127.8 (d, J = 33.0 Hz), 142.1, 157.8 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1616, 1550, 1359, 1171, 1110, 1062, 842 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{14}F_3N_4O$ [M + H]$^+$ 299.11197; found 299.11123 (100%).

2-Methyl-1-(2-phenyl-2*H*-1,2,3-triazol-4-yl)piperidine (4p): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, J = 6.7 Hz, 3 H, CH_3), 1.62–1.78 (m, 5 H), 1.84–1.93 (m, 1 H), 3.08 (dt, J = 13.3, 3.7 Hz, 1 H), 3.55 (dt, J = 13.4, 3.7 Hz, 1 H), 4.02–4.09 (m, 1 H), 7.21–7.25 (m, 2 H, Ar-H), 7.43 (dt, J = 2.0, 8.8 Hz, 2 H, Ar-H), 7.95 (dt, J = 2.0, 8.8 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 19.0, 25.2, 30.3, 42.8, 50.0, 117.6, 122.4, 125.7, 129.0, 140.2, 157.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1556, 1500, 1129, 952 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{19}N_4$ [M + H]$^+$ 243.16097; found 243.16052 (100%).

1-[2-(3-Chlorophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylpiperidine (4q): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, J = 5.8 Hz, 3 H, CH_3), 1.57–1.69 (m, 4 H), 1.72–1.79 (m, 1 H), 1.82–1.92 (m, 1 H), 3.05 (dt, J = 13.2, 4.1 Hz, 1 H), 3.55 (dt, J = 13.2, 4.1 Hz, 1 H), 4.01–4.10 (m, 1 H), 7.18 (ddd, J = 8.1, 2.0, 1.0 Hz, 1 H, Ar-H), 7.22 (s, 1 H, Ar-H), 7.33 (t, J = 8.1 Hz, 1 H, Ar-H), 7.83 (ddd, J = 8.1, 2.0, 1.0 Hz, 1 H, Ar-H), 7.97 (t, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.2, 18.8, 25.2, 30.2, 42.6, 49.9, 115.5, 117.7, 123.0, 125.5, 130.1, 134.9, 141.0, 157.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1592, 1550, 1485, 1449, 951, 777 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{18}ClN_4$ [M + H]$^+$ 277.12200 (100%), 279.11905 (32%); found 277.12135 (100%), 279.11843 (32%).

2-Methyl-1-[2-(*m*-tolyl)-2*H*-1,2,3-triazol-4-yl]piperidine (4r): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, J = 6.7 Hz, 3 H, CH_3), 1.58–1.69 (m, 4 H), 1.72–1.78 (m, 1 H), 1.85–1.93 (m, 1 H), 2.42 (s, 3 H, CH_3), 3.08 (dt, J = 13.3, 4.0 Hz, 1 H), 3.57 (dt, J = 13.3, 4.0 Hz, 1 H), 4.01–4.08 (m, 1 H), 7.06 (d, J = 7.8 Hz, 1

H, Ar-H), 7.21 (s, 1 H, Ar-H), 7.31 (t, J = 7.8 Hz, 1 H, Ar-H), 7.75 (t, J = 7.8 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 18.9, 21.5, 25.3, 30.3, 42.8, 50.0, 114.8, 118.1, 122.2, 126.6, 128.9, 139.1, 140.1, 157.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1577, 1538, 1494, 1462, 958, 785 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{21}N_4$ [M + H]$^+$ 257.17662; found 257.17609 (100%).

1-[2-(4-Fluorophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylpiperidine (4s): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, J = 6.7 Hz, 3 H, CH_3), 1.57–1.68 (m, 4 H), 1.72–1.79 (m, 1 H), 1.83–1.92 (m, 1 H), 3.07 (dt, J = 13.4, 3.7 Hz, 1 H), 3.22 (dt, J = 13.4, 3.7 Hz, 1 H), 3.98–4.08 (m, 1 H), 7.10 (dt, J = 3.4, 8.4 Hz, 2 H, Ar-H), 7.20 (s, 1 H, Ar-H), 7.91 (dt, J = 2.2, 9.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 18.9, 25.2, 30.3, 42.8, 50.0, 115.7 (d, J = 23.1 Hz), 119.1 (d, J = 8.1 Hz), 122.3, 136.5 (d, J = 2.6 Hz), 157.1, 160.8 (d, J = 244.4 Hz) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1549, 1510, 1224, 1143, 952, 835 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{18}FN_4$ [M + H]$^+$ 261.15155; found 261.15115 (100%).

2-Methyl-1-{2-[4-(trifluoromethyl)phenyl]-2*H*-1,2,3-triazol-4-yl}piperidine (4t): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, J = 6.7 Hz, 3 H, CH_3), 1.60–1.70 (m, 4 H), 1.72–1.80 (m, 1 H), 1.83–1.92 (m, 1 H), 3.08 (dt, J = 13.2, 4.2 Hz, 1 H), 3.58 (dt, J = 13.2, 4.2 Hz, 1 H), 4.03–4.12 (m, 1 H), 7.27 (s, 1 H, Ar-H), 7.67 (d, J = 8.6 Hz, 2 H, Ar-H), 8.04 (d, J = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.2, 18.8, 25.2, 30.2, 42.5, 49.9, 117.3, 120.1, 123.5, 124.2 (q, J = 271.7 Hz), 126.3 (d, J = 3.7 Hz), 142.3, 157.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1614, 1545, 1437, 1322, 1161, 1121, 949, 842 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{18}F_3N_4$ [M + H]$^+$ 311.14836; found 311.14781 (100%).

2-(3-Chlorophenyl)-*N*,*N*-diethyl-2*H*-1,2,3-triazol-4-amine (6a): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.1 Hz, 6 H, 2×CH_3), 3.39 (q, J = 7.1 Hz, 4 H, 2×CH_2), 7.17 (s, 1 H, Ar-H), 7.18 (dd, J = 8.1, 1.2 Hz, 1 H, Ar-H), 7.34 (t, J = 8.1 Hz, 1 H, Ar-H), 7.83 (dd, J = 8.1, 1.2 Hz, 1 H, Ar-H), 7.96 (t, J = 1.2 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 43.9, 115.4, 117.6, 122.0, 125.3, 130.0, 134.8, 141.0, 156.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1573, 1485, 1449, 1130 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{15}ClN_4$ [M + H]$^+$ 251.10635 (100%), 253.10340 (32%); found 251.10571 (100%), 253.10272 (32%).

***N*,*N*-Diethyl-2-[4-(trifluoromethyl)phenyl]-2*H*-1,2,3-triazol-4-amine (6b):** Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, J = 7.1 Hz, 6 H, 2×CH_3), 3.40 (q, J = 7.1 Hz, 4 H, 2×CH_2), 7.21 (s, 1 H, Ar-H), 7.67 (d, J = 8.6 Hz, 2 H, Ar-H), 8.04 (d, J = 8.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 43.8, 117.1, 119.1 (d, J = 125.5 Hz), 122.6, 126.3 (d, J = 3.9 Hz), 142.3, 147.3, 156.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1575, 1325, 1161, 1124 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{16}F_3N_4$ [M + H]$^+$ 285.13271; found 285.13179 (100%).

2-(3-Chlorophenyl)-*N*,*N*-dipropyl-2*H*-1,2,3-triazol-4-amine (6c): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.4 Hz, 6 H, 2×CH_3), 1.64 (m, 4 H, 2×CH_2), 3.28 (t, J = 7.4 Hz, 4 H, 2×CH_2), 7.13 (s, 1 H, Ar-H), 7.17 (dq, J = 2.0, 8.0 Hz, 1 H, Ar-H), 7.33 (t, J = 8.0 Hz, 1 H, Ar-H), 7.82 (dq, J = 2.0, 8.0 Hz, 1 H, Ar-H), 7.94 (t, J = 2.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 20.8, 52.1, 115.3, 117.5, 121.7, 125.2, 130.0, 134.8, 141.0, 156.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1573, 1485, 1451, 1147, 783 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{20}ClN_4$ [M + H]$^+$ 279.13765 (100%), 281.13470 (32%); found 279.13690 (100%), 281.13391 (32%).

***N*,*N*-Dipropyl-2-*p*-tolyl-2*H*-1,2,3-triazol-4-amine (6d):** Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.5 Hz, 6 H, 2×CH_3), 1.65 (m, 4 H, 2×CH_2), 2.37 (s, 3 H, CH_3), 3.27 (t, J = 7.5 Hz, 4 H, 2×CH_2), 7.09 (s, 1 H, Ar-H), 7.21 (d, J = 8.4 Hz, 2 H, Ar-H), 7.81 (d, J = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 20.8, 52.2, 117.4, 120.5, 129.5, 135.1, 138.1, 156.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1569, 1514, 1447, 1130 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{23}N_4$ [M + H]$^+$ 259.19227; found 259.19122 (100%).

2-(3-Chlorophenyl)-*N*,*N*-diisopropyl-2*H*-1,2,3-triazol-4-amine (6e): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (d, J = 6.8 Hz, 12 H, 4×CH_3), 3.89 (septet, J = 6.8 Hz, 2 H, 2×CH), 7.17 (d, J = 8.0 Hz, 1 H, Ar-H), 7.22 (s, 1 H, Ar-H), 7.33 (t, J = 8.0 Hz, 1 H, Ar-H), 7.83 (dd, J = 8.0, 1.9 Hz, 1 H, Ar-H), 7.95 (t, J = 1.9 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.5, 47.8, 115.3, 117.5, 123.3, 125.2, 130.0, 134.8, 141.0, 153.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1557, 1486, 1450, 1136 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{20}ClN_4$ [M + H]$^+$ 279.13765 (100%), 281.13470 (32%); found 279.13691 (100%), 281.13392 (32%).

***N*-Butyl-2-(3-chlorophenyl)-2*H*-1,2,3-triazol-4-amine (7a):** Brown yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.3 Hz, 3 H, CH_3), 1.39–1.50 (m, 2 H, CH_2), 1.59–1.68 (m, 2 H, CH_2), 3.27 (t, J = 7.0 Hz, 2 H, CH_2), 3.84 (s, 1 H, NH), 7.18 (s, 1 H, Ar-H), 7.20 (dq, J = 8.1, 1.9 Hz, 1 H, Ar-H), 7.35 (t, J = 8.1 Hz, 1 H, Ar-H), 7.82 (dq, J = 8.1, 1.9 Hz, 1 H, Ar-H), 7.95 (t, J = 1.9 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 20.1, 31.9, 44.6, 115.5, 117.7, 122.6, 125.7, 130.1, 134.9, 140.8, 155.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3417, 1574, 1484, 1448, 1130 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{16}ClN_4$ [M + H]$^+$ 251.10635 (100%), 253.10340 (32%); found 251.10572 (100%), 253.10275 (32%).

***N*-*tert*-Butyl-2-(3-chlorophenyl)-2*H*-1,2,3-triazol-4-amine (7b):** Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (s, 9 H, 3×CH_3), 3.83 (s, 1 H, NH), 7.20 (dd, J = 8.1, 1.9 Hz, 1 H, Ar-H), 7.23 (s, 1 H, Ar-H), 7.35 (t, J = 8.1 Hz, 1 H, Ar-H), 7.83 (dd, J = 8.1, 1.9 Hz, 1 H, Ar-H), 7.96 (t, J = 1.9 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.5, 51.8, 115.5, 117.7, 125.1, 125.7, 130.1, 134.9, 140.8, 153.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3410, 1559, 1484, 1449, 1361, 1223, 773 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{16}ClN_4$ [M + H]$^+$ 251.10635 (100%), 253.10340 (32%); found 251.10579 (100%), 253.10267 (32%).

2-(3-Chlorophenyl)-*N*-cyclohexyl-2*H*-1,2,3-triazol-4-amine (7c): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18–1.30 (m, 3 H), 1.35–1.47 (m, 2 H), 1.63–1.71 (m, 1 H), 1.74–1.83 (m, 2 H), 2.06–2.15 (m, 2 H), 3.30–3.40 (m, 1 H), 3.79 (s, 1 H, NH), 7.17 (s, 1 H, Ar-H), 7.19 (dd, J = 8.1, 1.9 Hz, 1 H, Ar-H), 7.34 (t, J = 8.1 Hz, 1 H, Ar-H), 7.81 (dd, J = 8.1, 1.9 Hz, 1 H, Ar-H), 7.95 (t, J = 1.9 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 25.8, 33.5, 53.2, 115.5, 117.7, 123.0, 125.6, 130.1, 134.9, 140.9, 154.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3405, 1566, 1484, 1106, 950, 782 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{18}ClN_4$ [M + H]$^+$ 277.12200 (100%), 279.11905 (32%); found 277.12141 (100%), 279.11834 (32%).

2-(3-Chlorophenyl)-*N*-phenyl-2*H*-1,2,3-triazol-4-amine (7d): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.20 (s, 1 H, NH), 7.01 (t, J = 7.1 Hz, 1 H, Ar-H), 7.24–7.31 (m, 3 H, Ar-H), 7.33–7.43 (m, 3 H, Ar-H), 7.55 (s, 1 H, Ar-H), 7.91 (d, J = 8.0 Hz, 1 H, Ar-H), 8.04 (s, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.9, 116.3, 118.1, 121.3, 124.7, 126.4, 129.5, 130.3, 135.1, 140.6, 141.3, 150.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3355, 1595, 1558, 1484, 1448, 1132, 739 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{12}ClN_4$ [M + H]$^+$ 271.07505 (100%), 273.07210 (32%); found 271.07438 (100%), 273.07138 (32%).

2-(3-Chlorophenyl)-*N*-*p*-tolyl-2*H*-1,2,3-triazol-4-amine (7e): Waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.19 (s, 3 H, CH_3), 6.16 (s, 1 H, NH), 7.16 (t, J = 8.7 Hz, 2 H, Ar-H), 7.19 (t, J = 8.7 Hz, 2 H, Ar-H), 7.25 (dq, J = 8.1, 1.9 Hz, 1 H, Ar-H), 7.39 (t, J =

8.1 Hz, 1 H, Ar-H), 7.51 (s, 1 H, Ar-H), 7.88 (dq, J = 8.1, 1.9 Hz, 1 H, Ar-H), 7.89 (t, J = 1.9 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6, 115.8, 116.7, 118.0, 124.5, 126.2, 129.9, 130.2, 130.9, 135.0, 138.8, 140.6, 150.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3357, 1594, 1561, 1485, 1116, 787 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{14}ClN_4$ [M + H]$^+$ 285.09070 (100%), 287.08775 (32%); found 285.09012 (100%), 287.08704 (32%).

2-[(3-Chlorophenyl)-*N*-(2-thiophen-2-yl)ethyl]-2*H*-1,2,3-triazol-4-amine (7f): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (t, J = 6.5 Hz, 2 H, CH_2), 3.59 (q, J = 6.5 Hz, 2 H, CH_2), 4.01 (t, J = 6.5 Hz, 1 H, NH), 6.89 (dd, J = 3.3, 0.8 Hz, 1 H, Ar-H), 6.98 (dd, J = 5.3, 3.3 Hz, 1 H, Ar-H), 7.18 (s, 1 H, Ar-H), 7.20 (t, J = 0.8 Hz, 1 H, Ar-H), 7.21 (dq, J = 5.3, 0.8 Hz, 1 H, Ar-H), 7.36 (t, J = 8.1 Hz, 1 H, Ar-H), 7.83 (dq, J = 8.1, 1.9 Hz, 1 H, Ar-H), 7.97 (t, J = 1.9 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.9, 46.0, 115.5, 117.8, 122.9, 124.0, 125.5, 125.8, 127.1, 130.2, 134.9, 140.8, 141.4, 154.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3403, 1568, 1483, 1105, 952, 781, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{14}ClN_4S$ [M + H]$^+$ 305.06277 (100%), 307.05982 (32%); found 305.06182 (100%), 307.05870 (32%).

2-[4-Methyl-2-(pyrrolidin-1-yl)thiazol-5-yl]ethanol (8a): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03 (dt, J = 3.6, 6.7 Hz, 4 H, 2 × CH_2), 2.22 (s, 3 H, CH_3), 2.84 (t, J = 6.2 Hz, 2 H, CH_2), 3.46 (dt, J = 3.6, 6.7 Hz, 4 H, 2 × CH_2), 3.76 (t, J = 6.2 Hz, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7, 25.7, 29.7, 49.7, 63.1, 113.6, 144.3, 165.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2926, 1542, 1123, 1054 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{17}N_2OS$ [M + H]$^+$ 213.10616; found 213.10543 (100%).

4,5-Dimethyl-2-(pyrrolidin-1-yl)thiazole (8b): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.00 (dt, J = 3.6, 6.6 Hz, 4 H, 2 × CH_2), 2.15 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 3.40 (dt, J = 3.6, 6.6 Hz, 4 H, 2 × CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 14.7, 25.6, 49.3, 112.2, 143.8, 164.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1543, 1359, 1301 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{15}N_2S$ [M + H]$^+$ 183.09559; found 183.09478 (100%).

4-(1-Methyl-5-phenyl-1*H*-imidazol-2-yl)morpholine (9a): Yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.21 (s, 4 H, 2 × CH_2), 3.50 (s, 3 H, NCH_3), 3.87 (s, 4 H, 2 × CH_2), 6.91 (s, 1 H, Ar-H), 7.31–7.45 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.7, 50.9, 66.7, 123.0, 127.2, 127.5, 127.7, 128.6, 128.8, 130.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1458, 1114, 762, 701 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{18}N_3O$ [M + H]$^+$ 244.14499; found 244.14378 (100%).

4-(1-Methyl-5-*p*-tolyl-1*H*-imidazol-2-yl)morpholine (9b): Yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 3.24 (s, 4 H, 2 × CH_2), 3.49 (s, 3 H, CH_3), 3.88 (t, J = 4.6 Hz, 4 H, 2 × CH_2), 6.89 (s, 1 H, Ar-H), 7.24 (d, J = 8.4 Hz, 2 H, Ar-H), 7.27 (d, J = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 31.8, 50.8, 66.7, 121.6, 127.0, 127.4, 127.8, 129.5, 132.0, 137.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1508, 1462, 1114, 818 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}N_3O$ [M + H]$^+$ 258.16064; found 258.15938 (100%).

4-[5-(4-Methoxyphenyl)-1-methyl-1*H*-imidazol-2-yl]morpholine (9c): Yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.19 (s, 4 H, 2 × CH_2), 3.46 (s, 3 H, NCH_3), 3.84 (s, 3 H, OCH_3), 3.86 (t, J = 4.8 Hz, 4 H, 2 × CH_2), 6.82 (s, 1 H, Ar-H), 6.96 (d, J = 8.6 Hz, 2 H, Ar-H), 7.29 (d, J = 8.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.5, 50.9, 55.3, 66.8, 113.7, 114.3, 122.1, 122.7, 129.3, 131.7, 159.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1510, 1465, 1210, 1118, 835 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}N_3O_2$ [M + H]$^+$ 274.15555; found 274.15425 (100%).

2-(3-Chlorophenyl)-2*H*-1,2,3-triazole (10): ^{1}H NMR (400 MHz, CD_3OD): δ = 7.35 (d, J = 8.0 Hz, 1 H, Ar-H), 7.47 (t, J = 8.0 Hz, 1 H, Ar-H), 7.92 (s, 2 H, Ar-H), 7.97 (d, J = 8.0 Hz, 1 H, Ar-H), 8.04 (d, J = 1.7 Hz, 1 H, Ar-H) ppm.

[D$_1$]-2-(3-Chlorophenyl)-2*H*-1,2,3-triazole *N*-Oxide (11-*d*$_1$): ^{1}H NMR (400 MHz, CD_3OD): δ = 7.57 (t, J = 7.7 Hz, 1 H, Ar-H), 7.59 (t, J = 7.7 Hz, 1 H, Ar-H), 7.88 (d, J = 7.7 Hz, 1 H, Ar-H), 7.95 (s, 1 H, Ar-H), 8.03 (s, 1 H, Ar-H) ppm.

Supporting Information (see footnote on the first page of this article): Experimental details and spectroscopic data for **2j**–**2n**; ^{1}H and ^{13}C NMR spectra.

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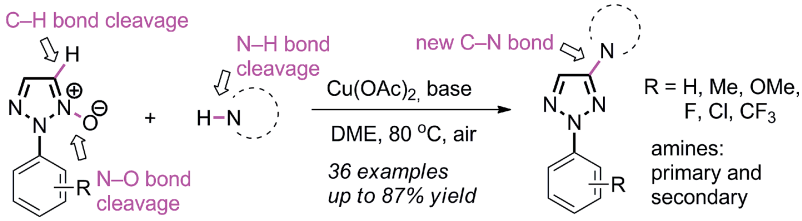
Amination



A facile, efficient, and practical method for the copper-catalyzed direct C–H amination of 2-aryl-1,2,3-triazole *N*-oxides with various amines, including primary and secondary aliphatic and aromatic amines, has been developed. Furthermore, the targeted N^+–O^- bond cleavage is observed during the reaction and, thus, an additional deoxygenation step is obviated.

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Copper-Catalyzed Direct Amination of 1,2,3-Triazole *N*-Oxides by C–H Activation and C–N Coupling

Keywords: Nitrogen heterocycles / C–H activation / Copper / Amination

