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Preparation of 2-Azido-1-Substituted-1*H*-Benzo[*d*]imidazoles Using a Copper-Promoted Three-Component Reaction and Their Further Conversion into 2-Amino and 2-Triazolyl Derivatives

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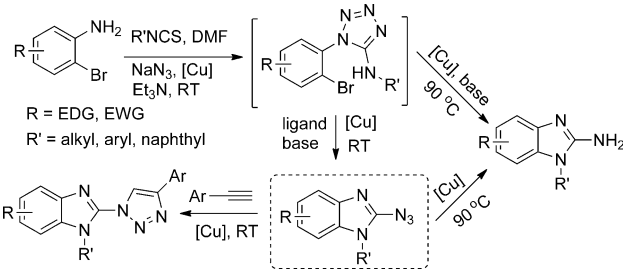
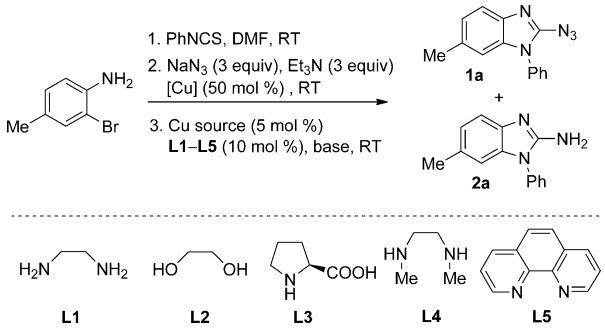
The conversion of a simple substrate into diverse libraries[1] of more complex molecules constitutes a great challenge in modern organic synthesis, both from an academic and an industrial standpoint.[2] The use of multicomponent reactions (MCRs) involving tandem processes has emerged as a powerful strategy to meet this challenge.[3] Herein, we wish to report a new room-temperature copper-promoted three-component reaction involving tandem addition, substitution, electrocyclization, N-arylation, and tautomerization;[4–6] specifically, a 2-bromoaniline derivative, an isothiocyanate, and sodium azide react to give 2-azido-1-substituted-1*H*-benzo[*d*]imidazoles. We also show that these compounds can be subsequently converted into 2-amino and 2-(1*H*-1,2,3-triazol-1-yl)-1-aryl-1*H*-benzo[*d*]-imidazoles, which are important in biological[7] and medicinal[8] sciences (Scheme 1).[9]

First, reaction conditions that could affect the above multicomponent reaction were identified and optimized using readily available 4-methyl-2-bromoaniline, sodium azide, and phenylisothiocyanate as model substrates, together with different copper sources, ligands, and bases; the reactions were carried out at room temperature (Table 1). We were pleased to observe that the substrates reacted to afford the corresponding tetrazole derivative with complete conversion when using 3 equivalents of Et_3N and 50 mol% of a copper source in DMF at room temperature (see the Supporting Information). Gratifyingly, when this tetrazole derivative was subsequently treated with 5 mol% CuI, 10 mol% 1,10-phenanthroline (**L5**), and 2 equivalents of $K_3PO_4{\cdot}3H_2O$, it gave a 19:1 mixture of 2-azido- and 2-amino-1*H*-benzo[*d*]imidazoles **1a** and **2a** in 100% conversion (Table 1, entry 1). The formation of the tetrazole derivative was more efficient when using Et_3N compared to the use of inorganic bases ($K_3PO_4{\cdot}3H_2O$, Cs_2CO_3, K_2CO_3, and KOH). However, the



Scheme 1. Possible method for the preparation of 2-azido-1-substituted-1*H*-benzo[*d*]imidazoles and their 2-amino and 2-(1*H*-1,2,3-triazo-1-yl) derivatives. DMF = *N*,*N*-dimethylformamide, EDG = electron-donating group. EWG = electron-withdrawing group.

Table 1. Optimization of the reaction conditions.[a]



Entry	Cu source	Base	Ligand	Conversion [%] (**1a**/**2a**)[b]
1	CuI	$K_3PO_4{\cdot}3H_2O$	**L5**	100 (19:1)
2	CuI	KOH	**L5**	16 (2:1)
3	CuI	K_2CO_3	**L5**	100 (9:1)
4	CuI	Cs_2CO_3	**L5**	45 (7:2)
5	CuI	$K_3PO_4{\cdot}3H_2O$	**L1**	15 (2:1)
6	CuI	$K_3PO_4{\cdot}3H_2O$	**L2**	16 (2:1)
7	CuI	$K_3PO_4{\cdot}3H_2O$	**L3**	18 (3:1)
8	CuI	$K_3PO_4{\cdot}3H_2O$	**L4**	20 (1:1)
9	CuBr	$K_3PO_4{\cdot}3H_2O$	**L5**	100 (19:1)
10	Cu_2O	$K_3PO_4{\cdot}3H_2O$	**L5**	100 (19:1)
11	$CuSO_4{\cdot}5H_2O$	$K_3PO_4{\cdot}3H_2O$	**L5**	100 (19:1)
12	$Cu(OAc)_2{\cdot}H_2O$	$K_3PO_4{\cdot}3H_2O$	**L5**	100 (19:1)
13[c]	$Cu(OAc)_2{\cdot}H_2O$	$K_3PO_4{\cdot}3H_2O$	**L5**	65 (10:3)
14[d]	$Cu(OAc)_2{\cdot}H_2O$	$K_3PO_4{\cdot}3H_2O$	**L5**	83 (13:3)
15	$Cu(OAc)_2{\cdot}H_2O$	$K_3PO_4{\cdot}3H_2O$	–	16 (2:1)
16	–	$K_3PO_4{\cdot}3H_2O$	–	n.d.

[a] Reaction conditions: phenylisothiocyanate (1 mmol), 4-methyl-2-bromoaniline (1 mmol), DMF (1.5 mL), 14 h, RT; then NaN_3 (3 mmol), Et_3N (3 mmol), $Cu(OAc)_2{\cdot}H_2O$ (50 mol%), 4 h, RT; then, catalyst (5 mol%), ligand (10 mol%), base (2 mmol), 30 h, RT. [b] Determined by ^1H NMR spectroscopy (400 MHz). [c] Cu source (2.5 mol%) used. [d] $K_3PO_4{\cdot}3H_2O$ (1.5 equiv) used. n.d. = not detected.

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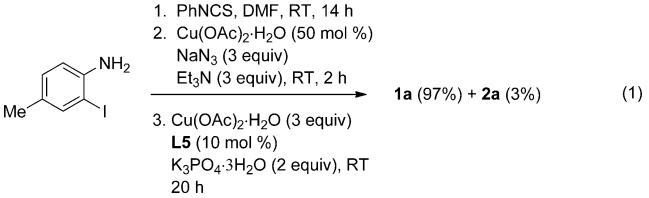
use of inorganic bases was found to be superior to the use of Et_3N for the N-arylation process. The use of $K_3PO_4 \cdot 3H_2O$ in the transformation of the tetrazole resulted in higher conversions and enhanced selectivity in favor of the 2-azido derivative **1a** compared to the use of Cs_2CO_3, K_2CO_3, and KOH (Table 1, entries 1–4). Among the ligands screened (**L1**–**L5**), **L5** was found to be the most effective (Table 1, entries 5–8). Copper(I) and copper(II) sources (CuBr, Cu_2O, CuI, $CuSO_4 \cdot 5H_2O$, and $Cu(OAc)_2 \cdot H_2O$) exhibited similar levels of activity and selectivity (Table 1, entries 1 and 9–12). For the N-arylation/tautomerization reaction, either lowering the amount of base (1.5 equivalents), lowering the amount of the copper source (2.5 mol%), or conducting the reaction in the absence of ligand gave lower conversions; for these reactions, **1a** and **2a** were obtained in less than 85% conversion (Table 1, entries 13–15). In a control reaction in which a copper source was absent, **1a** and **2a** were not formed (Table 1, entry 16).

2-Iodoaniline could also be used as a substrate and the reaction gave the target products **1a** and **2a** in a shorter reaction time [Eq. (1)]. In contrast, in the case of 2-chloroaniline, the N-arylation/tautomerization reaction did not occur and only the tetrazole derivative could be isolated (see the Supporting Information).



(1)

With optimized conditions established, the scope of the protocol was next explored (Scheme 2). The process was found to be generally applicable; various isothiocyanates and 2-bromoaniline derivatives in the presence of sodium azide gave the corresponding 2-azido-1-substituted-1*H*-benzo[*d*]imidazoles **1b**–**y** in moderate to good yield. Aryl isothiocyanates bearing electron-donating substituents on the aryl ring (4-Me, 4-OMe, 4-Et, 4-*i*Pr, 2,4-dimethyl, 3,4-dimethyl, 2,5-dimethyl, and 3,5-dimethyl groups) were more reactive than those bearing electron-withdrawing substituents on the aryl ring (4-Cl, 4-F and, 4-CF_3 groups). In addition, aryl isothiocyanates were more reactive than alkyl isothiocyanates. Regarding the scope of the 2-bromoaniline component, the use of both 2-bromoaniline (nonsubstituted) and the 4-Me, 4-*i*Pr, 4-Cl, 4-OMe, 2,4-dimethyl, and 3,4-dimethylbromoaniline derivatives gave good yields of the corresponding products. The structure of compound **1c** was confirmed by single-crystal X-ray analysis (see the Supporting information).

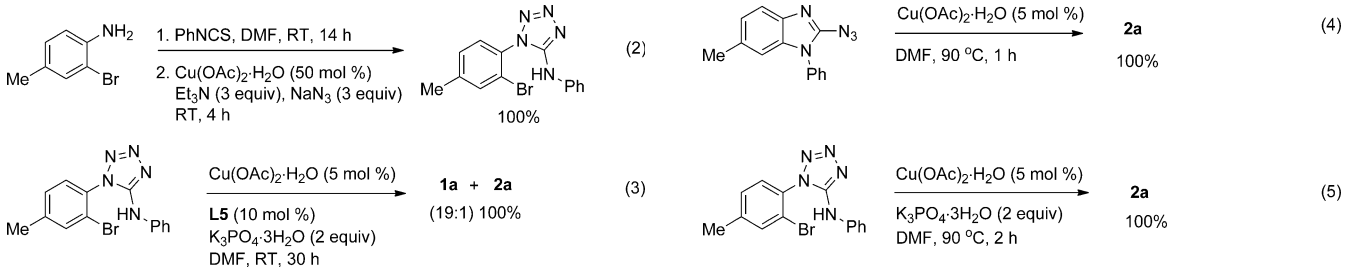
The above reactions gave 2-amino-1*H*-benzo[*d*]imidazoles as byproducts (5–10%). Because these compounds have a structure that is found as a motif in many medicinal compounds,[8] the selective transformation of **1a** into **2a** was next investigated (Scheme 3). When **1a** was treated with 5 mol% $Cu(OAc)_2 \cdot H_2O$ in DMF at 90°C for 1 h, it underwent reduction[10] to give **2a** with 100% conversion and selectivity.

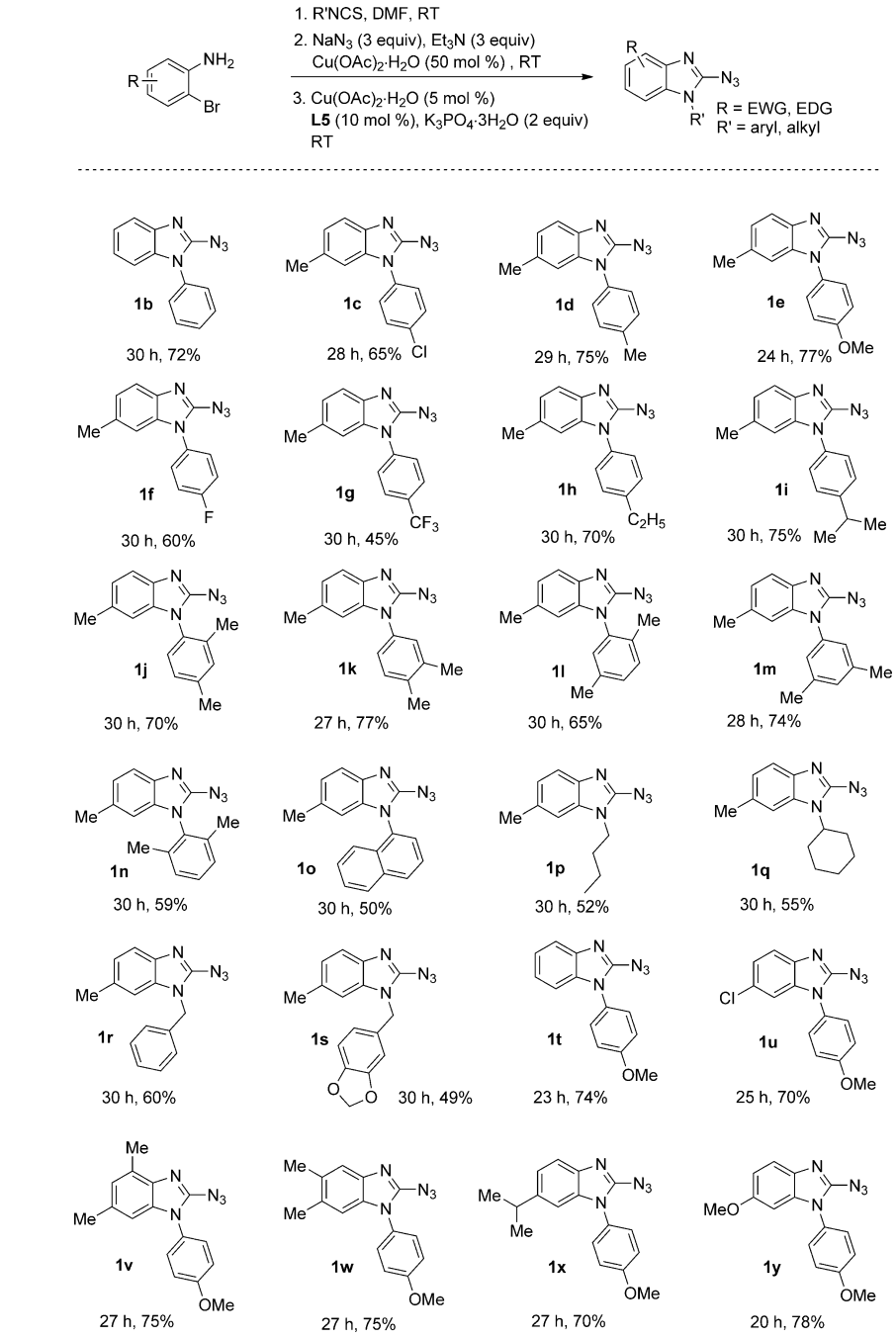
Alternatively, the tetrazole derivative can also be converted into **2a** via **1a** by using 5 mol% $Cu(OAc)_2 \cdot H_2O$ and 2 equivalents of $K_3PO_4 \cdot 3H_2O$ in DMF at 90°C for 2 h in the absence of ligand (Scheme 3). The reactions of 4-Me, 4-OMe and 2,4-dimethylphenylisothiocyanate with 4-Me- and 4,5-dimethyl-2-bromoaniline were investigated. The reactions gave the target compounds **2a**–**f** in 62–72% yield. The structure of **2e** was confirmed by single-crystal X-ray analysis (see the Supporting Information).

Finally, a click reaction of 2-azido-[1*H*]-benzo[*d*]imidazole and aryl alkynes to give substituted 2-(1*H*-1,2,3-triazo-1-yl)-1*H*-benzo[*d*]imidazoles was investigated (Scheme 4). Optimization studies revealed that the required products could be obtained when using reaction conditions developed by the research group of Sharpless (5 mol% CuI and 2 equivalents of Et_3N at room temperature).[11a] The click reactions of 2-azido-[1*H*]-benzo[*d*]imidazole (**1a**, **1m**, **1v** and **1w**) gave 2-(1*H*-1,2-3-triazo-1-yl)-1-aryl-1*H*-benzo[*d*]imidazoles **3a**—**d**, respectively, in high yields. Recrystallization of **3c** in MeOH gave crystals, which were used to confirm the structure of **3c** by single-crystal X-ray analysis (see the Supporting Information).

A proposed catalytic cycle is shown in Scheme 5. Toward determining the reaction pathway, a 1:1 mixture of 4-methyl-2-bromoaniline and phenylisothiocyanate was stirred in DMF at room temperature for 14 hours to afford the corresponding thiourea.[5k] When the thiourea derivative was added to a mixture of 3 equivalents of sodium azide, 3 equivalents of Et_3N, and 50 mol% $Cu(OAc)_2 \cdot H_2O$, the corresponding tetrazole derivative was obtained with 100% conversion [Eq. (2)]. Recrystallization of the tetrazole derivative in MeOH gave single crystals, which were used to determine the structure of the tetrazole by single-crystal X-ray analysis (see the Supporting Information). The tetrazole derivative underwent N-arylation followed by tautomerization[6] when treated with a mixture of 5 mol% $Cu(OAc)_2 \cdot H_2O$, 10 mol% **L5**, and 2 equivalents of $K_3PO_4 \cdot 3H_2O$ at room temperature; the reaction gave a 19:1 mixture of **1a** and **2a** in 100% conversion [Eq. (3)]. Furthermore, **1a** could be reduced to give **2a** in 100% conversion when the substrate was treated with 5 mol% $Cu(OAc)_2 \cdot H_2O$ in DMF at 90°C for 1 h [Eq. (4)]. In addition, when the tetrazole derivative was treated with 5 mol% $Cu(OAc)_2 \cdot H_2O$ and 2 equivalents of $K_3PO_4 \cdot 3H_2O$ in DMF at 90°C for 2 h it underwent sequential N-arylation, tautomerization, and reduction to afford **2a** directly in good yield [Eq. (5)].

These results clearly show that the reaction of 2-bromoaniline and isothiocyanate gives a thiourea, which in the presence of a copper source and Et_3N gives intermediate **a**. Nucleophilic substitution of **a** with sodium azide gives **b** with CuS and a sulfide as byproducts (see the Supporting Information). Electrocyclization of **b** could give tetrazole derivative **c**,[12] which could react with a copper(I) species (could be derived from a copper(II) species)[13] through oxi-





Scheme 2. Scope of the reaction for forming 2-azido-1-substituted-1*H*-benzo[*d*]imidazoles. Reaction conditions: Isothiocyanate (1 mmol), 2-bromoaniline (1 mmol), DMF (1.5 mL), RT, 14–22 h; then NaN_3 (3 mmol), Et_3N (3 mmol), $Cu(OAc)_2{\cdot}H_2O$ (50 mol%), RT, 3–6 h; then, $Cu(OAc)_2{\cdot}H_2O$ (5 mol%), **L5** (10 mol%), $K_3PO_4{\cdot}3H_2O$ (2 mmol), RT. The reactions gave 5–10% of 2-amino-1*H*-benzo[*d*]imidazoles as byproducts.

dative addition to give **d**. The transformation of **d** through N-arylation followed by tautomerization can give **e**, which upon reductive elimination of the target 1-substituted-2-azido-1*H*-benzo[*d*]imidazoles **1a–y** would complete the catalytic cycle. The copper(II)-catalyzed reduction of **1** could afford amines **2a–f** via **f**, a transformation that seems to require a relatively high temperature (90°C) to proceed (compare with the copper-catalyzed transformation of path a that proceeds at room temperature).[14] The click reaction of **1** with an aryl alkyne, as catalyzed by copper(I), to give 2-(1*H*-1,2,3-triazo-1-yl)-1*H*-benzo[*d*]imidazoles **3a-d** in high yield may proceed via **g** (path b).[11]

In conclusion, we have developed a room-temperature copper-catalyzed three-component reaction to prepare 1-substituted-2-azido-1*H*-benzo-[*d*]imidazoles. The reaction has a wide substrate scope and is conducted under mild reaction conditions. The 2-azido products were also transformed into 2-amino and 2-(1*H*-1,2,3-triazo-1-yl)-1*H*-benzo[*d*]imidazoles. Further studies towards determining the precise mechanism are currently underway.

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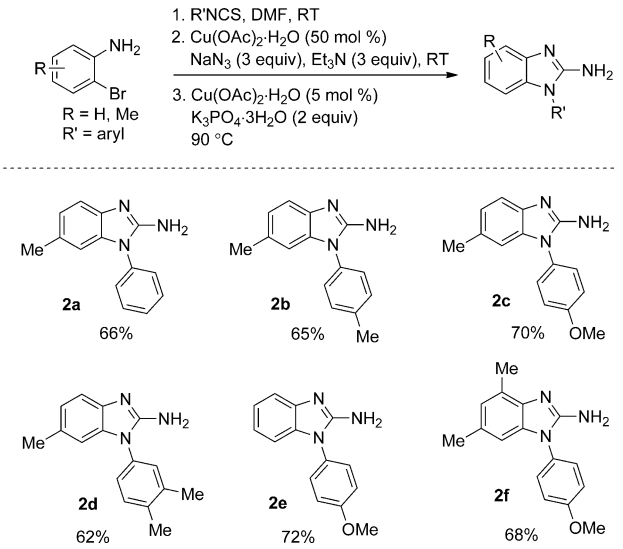
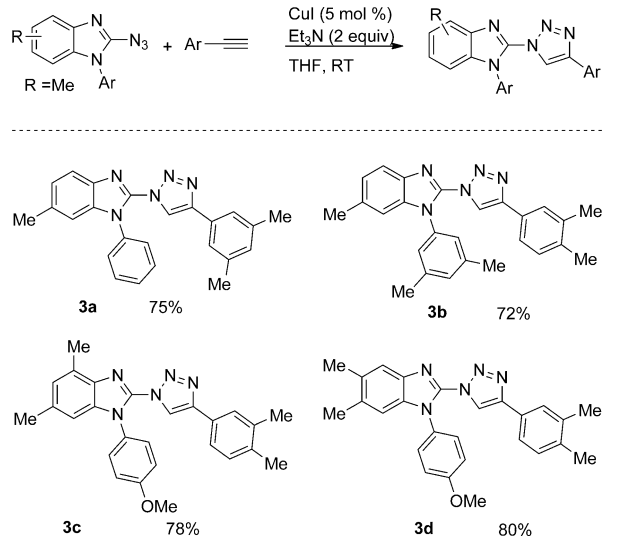
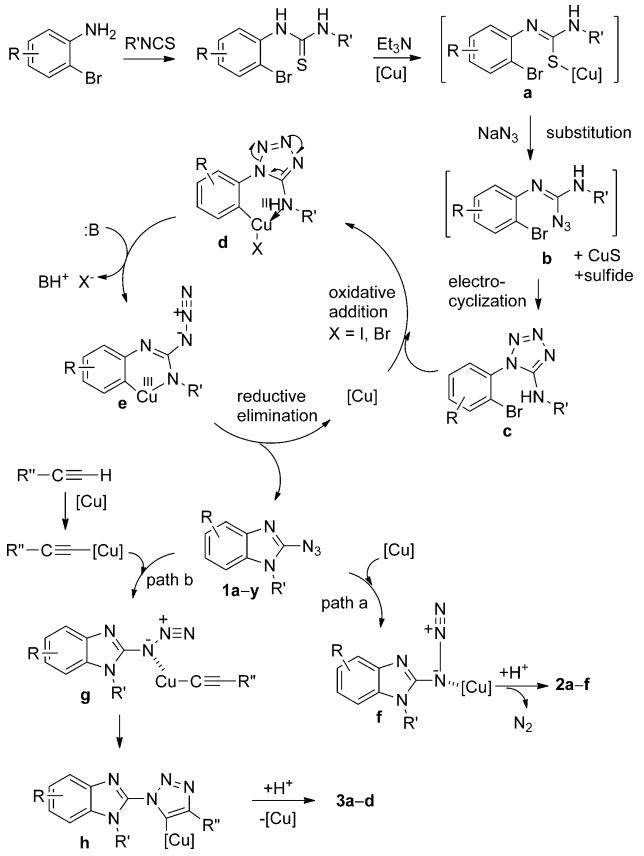


Scheme 3. Scope of the reaction for forming 2-amino-1-aryl-1*H*-benzo-[*d*]imidazoles. Reaction conditions: Isothiocyanate (1 mmol), 2-bromoaniline (1 mmol), DMF (1.5 mL), RT, 14–16 h; then NaN_3 (3 mmol), Et_3N (3 mmol), $Cu(OAc)_2{\cdot}H_2O$ (50 mol%), RT, 3–6 h; then, $Cu(OAc)_2{\cdot}H_2O$ (5 mol%), $K_3PO_4{\cdot}3H_2O$ (2 mmol), 90 °C, 2 h.



Scheme 4. Scope of the reaction for forming 2-(1*H*-1,2,3-triazo-1-yl)-1-aryl-1*H*benzo[*d*]imidazoles. Reaction conditions: 2-azido-1-aryl-1*H*-benzo[*d*]imidazole (1 mmol), aryl alkyne (1 mmol), CuI (5 mol%), Et_3N (2 mmol), THF (6 mL), RT, 5 h.



Scheme 5. Proposed catalytic cycle.

Keywords: benzimidazoles · copper · cycloaddition · multicomponent reactions · heterocycles

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Heterocycle Synthesis

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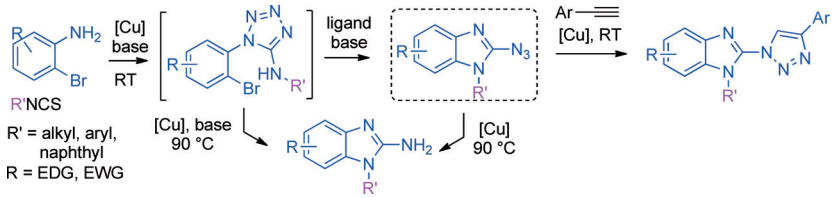
Preparation of 2-Azido-1-Substituted-1*H*-Benzo[*d*]imidazoles Using a Copper-Promoted Three-Component Reaction and Their Further Conversion into 2-Amino and 2-Triazolyl Derivatives



Multicomponent reaction: 2-azido-1-substituted-1*H*-benzo[*d*]imidazoles were prepared using a copper-catalyzed three-component reaction involving 2-bromoaniline derivatives, isothiocyanates, and sodium azide. The reaction conditions are mild and the scope is broad. The azido compounds were transformed into their 2-amino and 2-triazolyl derivatives using copper-mediated reduction and cycloaddition, respectively (see scheme).

