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Copper-Catalyzed Three-Component Reaction: Solvent-Controlled Regioselective Synthesis of 4-Amino- and 6-Amino-2-iminopyridines

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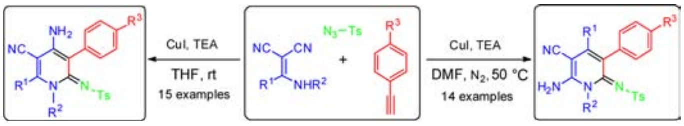
ABSTRACT



Regioselective synthesis of multisubstituted 4-amino- and 6-amino-2-iminopyridines has been developed *via* the copper-catalyzed three-component reaction based on the reaction conditions selection. The reaction of sulfonyl azides, alkynes, and 2-[(amino)methylene]malononitriles catalyzed by copper(I) iodide in tetrahydrofuran at room temperature afforded substituted 4-amino-2-iminopyridines, whereas, in *N,N*-dimethylformamide at 50 °C under N$_2$, it generated substituted 6-amino-2-iminopyridines as predominant products.

Functionalized 2-iminopyridines are known to have diverse biological and pharmacological activities,[1,2] such as antimicrobial,[2a] antiulcer,[2b] anticancer,[2c] antipyretic,[2d] and anti-inflammatory activity.[2d] In addition, 2-iminopyridines are versatile intermediates for the synthesis of many functionalized aza-heterocycles, such as pyridin-2(1*H*)-ones,[3] pyrido[2,3-*b*]indoles,[4] and imidazo[1,2-*a*]pyridines.[5] The pharmaceutical importance of 2-iminopyridines and their utilization in organic transformations have directed great research activity toward the construction of the skeletons of different kinds of heterocycles. To date, a variety of synthetic approaches are already available, based on either the modification of pyridines by alkylation reactions of *o*-aminopyridines[6] and amination reactions of *o*-halopyridine salts,[7] or intramolecular aza-cyclization of nitriles,[8] metal mediated cycloaddtion of alkynes to carbodiimides,[9] and

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the four-component reaction of malononitrile, acetophenone, aldehyde, and ammonium acetate.[10] Each of these approaches represents an important advance toward the objective of general methods for the synthesis of 2-iminopyridines; however, each of them suffers from significant limitations, such as a narrow scope of precursors, requirement for harsh conditions, or low yields along with less selectivity. Therefore, to match the increasing scientific and practical demands, it is still of continued interest and great importance to explore simple and efficient synthetic approaches for the construction of 2-iminopyridines, especially those with wide applicability to achieve more elaborate and flexible substitution patterns.

Multicomponent reactions (MCRs) are convergent reactions of three or more starting materials to obtain the product, emerging as an efficient method in rapidly generating complex molecules with diverse functional substituents.[11] In recent years, a copper-catalyed three-component reaction of sulfonyl azides, alkynes, and different nucleophiles have drawn special interest; by this protocol a variety of heterocycles, including benzimidazoles,[12a] pyrimidines,[12b] iminodihydro-coumarins,[12c] 2-benzoxazolineamidine,[12d] azetidin-2-imines,[12e] 2-iminooxetanes,[12f] imidazolidin-4-ones,[12g] 2- iminopyrrolines,[12h] pyrazoles[12i] and dihydroquinolines,[12j] have been synthesized.

During the course of our studies on the synthetic utilization of malononitrile and its derivatives, we developed an efficient synthesis of highly substituted benzenes from malononitrile and chalcones in ionic liquids[13a] and further achieved the synthesis of multisubstituted pyridines *via* MCR of malonitrile, β-oxo amides, and aromatic aldehydes in alcohols.[13b] Very recently, we reported a facile synthetic route to 2-aminopyridines by [5C + 1N] annulation of 2,4-pentadienenitriles and hydroxylamine under very mild conditions.[13c] In connection with this previous work, we prepared a series of 2-[(amino)methylene]-malononitriles and investigated their reaction behavior under different reaction conditions. As a result, we achieved regioselective synthesis of 4-amino- and 6-amino-2-imino-pyridines *via* an MCR of 2-[(amino)methylene]malononitriles, sulfonyl azide, and alkynes by conditions selection. Herein, we wish to report our experimental results and a proposed mechanism involved.

The substrates, 2-[(amino)methylene]malononitriles **1a**–**i**, were prepared *via* a three-component reaction of malononitrile, triethyl orthoformate, and varied amines according to a reported procedure.[14] We then selected 2- [(phenylamino)methylene]malononitrile **1a** as the model compound to examine its reaction with *p*-toluenesulfonyl azide (TsN_3) and phenylacetylene **2a** at room temperature in the presence of CuI (0.1 equiv) and DBU (1.0 equiv) in THF. The reaction formed a complex mixture as indicated by the TLC results (Table 1, entry 1). In the presence of triethylamine (1.0 equiv), the reaction could proceed to afford a product along with some starting material recovered. The product was characterzied as *N*-[4-amino-5-cyano-1,3-diphenyl-pyridin-2(1*H*)-ylidene]-4-methylbenzenesulfonamide **3aa** based on its spectral and analytical data (Table 1, entry 2).

To optimize the yield of **3aa**, the reaction conditions, including bases, amount of bases, solvents, copper salts, and reaction temperature, were then investigated. The reaction could be completed in 1.0 h when the added amount of Et_3N was increased to 2.0 equiv (Table 1, entry 3). A decrease in the amount of CuI would prolong the reaction time (Table 1, entry 4). In the presence of pyridine, K_2CO_3 or Cs_2CO_3, the conversion was quite low (Table 1, entries 5–7). It was noted that CuBr showed an efficient catalytic effect as in the case of CuI on the reaction (Table 1, entry 8); however, a copper(II) salt would result in a low yield of **3aa** in comparison to a copper(I) salt (Table 1, entries 9 and 10). The reaction performed in CH_2Cl_2 could furnish **3aa** in 80% yield (Table 1, entry 11). In the case of acetonitrile, **3aa** was obtained in 61% yield along with a byproduct that was characterzied as *N*-[6-amino-5-cyano-1,3-diphenylpyridin-2(1*H*)-ylidene]-4-methylbenzenesulfonamide **4aa** based on its spectral and analytical data (Table 1, entry 12). Similar results were obtained when other polar solvents, DMF or DMSO, were employed (Table 1, entries 13 and 14). When **1a**, **2a**, and TsN_3 were subjected to DMF at room temperature under N_2, the yield of **4aa** significantly increased (Table 1, entry 15), suggesting N_2 efficiently inhibits the formation of **3aa**. To our delight, the yield of **4aa** could reach 76% when the reaction was performed at 50 °C (Table 1, entry 16).

After establishing the optimized reaction conditions, a range of reactions for the synthesis of **3** were carried out with varied substrates **1**, **2**, and TsN_3, and some of the results are summarized in Table 2. It was observed that the three-component reactions of **1a**–**g** (R^1 = H, R^2 = aryl), aryl acetylenes, and TsN_3 could proceed smoothly to afford **3aa**–**ga** in good to high yields, which revealed that

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Table 1. Three-Component Reaction of 2-[(Amino)-methylene]malononitriles, Sulfonyl Azide, and Alkynes[a]

					yield (%)[c]	
entry	base (equiv)	copper salt	solvent	time (h)	**3aa**	**4aa**
1	DBU (1.0)	CuI	THF	12	mixture	
2	TEA (1.0)	CuI	THF	10	48	–
3	**TEA (2.0)**	**CuI**	**THF**	**1**	**87**	–
4	TEA (2.0)	CuI[b]	THF	8	85	–
5	pyridine (2.0)	CuI	THF	12	5	–
6	K_2CO_3 (2.0)	CuI	THF	12	9	–
7	Cs_2CO_3 (2.0)	CuI	THF	12	21	–
8	TEA (2.0)	CuBr	THF	2	84	–
9	TEA (2.0)	$Cu(OAc)_2$	THF	5	62	–
10	TEA (2.0)	$CuBr_2$	THF	5	28	–
11	TEA (2.0)	CuI	CH_2Cl_2	2	80	–
12	TEA (2.0)	CuI	CH_3CN	12	61	15
13	TEA (2.0)	CuI	DMF	12	38	40
14	TEA (2.0)	CuI	DMSO	12	33	35
15	TEA (2.0)	CuI	DMF	12	15	65
16	**TEA (2.0)**	**CuI**	**DMF**	**12**	**5**	**76**

[a] Reaction conditions: **1a** (1.0 mmol), TsN_3 (1.1 mmol), **2a** (1.1 mmol), copper salt (0.1 mmol), solvent (10.0 mL), for entries 1–14, under air, rt; for entry 15, under N_2, rt; for entry 16, under N_2, 50 °C. [b] 0.05 mmol. [c] Isolated yields.

the 4-amino-2-iminopyridine synthesis proved to be suitable for substrates **1** and **2** bearing electron withdrawing or donating substituents in their aromatic rings (Table 2, entries 2–13). The versatility of this 4-amino-2-iminopyridine synthesis was further evaluated by performing **1h** (R^1 = H, R^2 = Bn) and **1i** (R^1 = Me, R^2 = Ph) under identical conditions (Table 2, entries 14 and 15). The relatively low yields of **3ha** and **3ia** might be attributed to the electronic and steric effects of the substrates.

Table 2. Multicomponent Reactions for the Synthesis of 4-Amino-2-iminopyridines **3**[a]

entry	1	R^1/ R^2	2	R^3	3	yield (%)[b]
1	**1a**	H/Ph	**2a**	H	**3aa**	87
2	**1a**	H/Ph	**2b**	Me	**3ab**	82
3	**1a**	H/Ph	**2c**	MeO	**3ac**	80
4	**1b**	H/*p*-MeC_6H_4	**2a**	H	**3ba**	88
5	**1b**	H/*p*-MeC_6H_4	**2b**	Me	**3bb**	85
6	**1b**	H/*p*-MeC_6H_4	**2c**	MeO	**3bc**	79
7	**1c**	H/*p*-$MeOC_6H_4$	**2a**	H	**3ca**	89
8	**1c**	H/*p*-$MeOC_6H_4$	**2b**	Me	**3cb**	86
9	**1c**	H/*p*-$MeOC_6H_4$	**2c**	MeO	**3cc**	82
10	**1d**	H/*o*-MeC_6H_4	**2a**	H	**3da**	83
11	**1e**	H/*o*-ClC_6H_4	**2a**	H	**3ea**	82
12	**1f**	H/*m*-ClC_6H_4	**2a**	H	**3fa**	81
13	**1g**	H/*p*-ClC_6H_4	**2a**	H	**3ga**	81
14	**1h**	H/$PhCH_2$	**2a**	H	**3ha**	54
15	**1i**	Me/Ph	**2a**	H	**3ia**	59

[a] Reaction condition: **1** (1.0 mmol), TsN_3 (1.1 mmol), **2** (1.0 mmol), CuI (0.1 mmol), TEA (2.0 mmol), THF (10 mL), air, 25 °C. [b] Isolated yields.

The substrate diversity for the synthesis of **4** was also surveyed, and the results are listed in Table 3. It was found that all the reactions of varied substrates **1a**–**g** (R^1 = H, R^2 = aryl), **2**, and TsN_3 could procced under the conditions used for **4aa** in Table 1 (entry 16) to afford 6-amino-2-iminopyridines **4aa**–**gb** in moderate to good yields (Table 3, entries 2–14). It should be mentioned that the corresponding 4-amino-2-iminopyridines **3** were simultaneously formed within this reaction system as indicated by TLC results. In the case of aryl acetylene **2c**, the reaction could only furnish 4-amino-2-iminopyridine **3ac** in 38% yield along with the recovery of some starting material, and 6-amino-2-iminopyridine **4ac** was not even detected (Table 3, entry 15). For the substrates **1h** (R^1 = H, R^2 = Bn) and **1i** (R^1 = Me, R^2 = Ph), the conversion was very low, with only a trace of **3** detected and most of the starting materials remaining intact (Table 3, entries 16 and 17). The structure of **4fa** was further elucidated by X-ray single crystal analysis as shown in Figure 1.

Table 3. Multicomponent Reactions for the Synthesis of 6-Amino-2-iminopyridines **4**[a]

							yield(%)[b]	
entry	1	R^1/R^2	2	R^3	3	4	3	4
1	**1a**	H/Ph	**2a**	H	**3aa**	**4aa**	5	76
2	**1a**	H/Ph	**2b**	Me	**3ab**	**4ab**	10	71
3	**1b**	H/*p*-MeC_6H_4	**2a**	H	**3ba**	**4ba**	12	65
4	**1b**	H/*p*-MeC_6H_4	**2b**	Me	**3bb**	**4bb**	8	58
5	**1c**	H/*p*-$MeOC_6H_4$	**2a**	H	**3ca**	**4ca**	11	58
6	**1c**	H/*p*-$MeOC_6H_4$	**2b**	Me	**3cb**	**4cb**	9	51
7	**1d**	H/*o*-MeC_6H_4	**2a**	H	**3da**	**4da**	5	75
8	**1d**	H/*o*-MeC_6H_4	**2b**	Me	**3db**	**4db**	–	68
9	**1e**	H/*o*-ClC_6H_4	**2a**	H	**3ea**	**4ea**	–	79
10	**1e**	H/*o*-ClC_6H_4	**2b**	Me	**3eb**	**4eb**	–	72
11	**1f**	H/*m*-ClC_6H_4	**2a**	H	**3fa**	**4fa**	–	70
12	**1f**	H/*m*-ClC_6H_4	**2b**	Me	**3fb**	**4fb**	–	66
13	**1g**	H/*p*-ClC_6H_4	**2a**	H	**3ga**	**4ga**	–	67
14	**1g**	H/*p*-ClC_6H_4	**2b**	Me	**3gb**	**4gb**	–	56
15	**1a**	H/Ph	**2c**	MeO	**3ac**	**4ac**	38	–
16	**1h**	H/$PhCH_2$	**2a**	H	**3ha**	**4ha**	–	–
17	**1i**	Me/Ph	**2a**	H	**3ia**	**4ia**	–	–

[a] Reaction conditions: **1** (1.0 mmol), TsN_3 (1.1 mmol), **2** (1.0 mmol), CuI (0.1 mmol), TEA (2.0 mmol), DMF (10 mL), N_2, 50 °C. [b] Isolated yields.

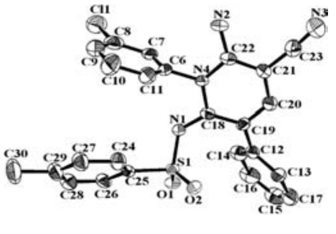
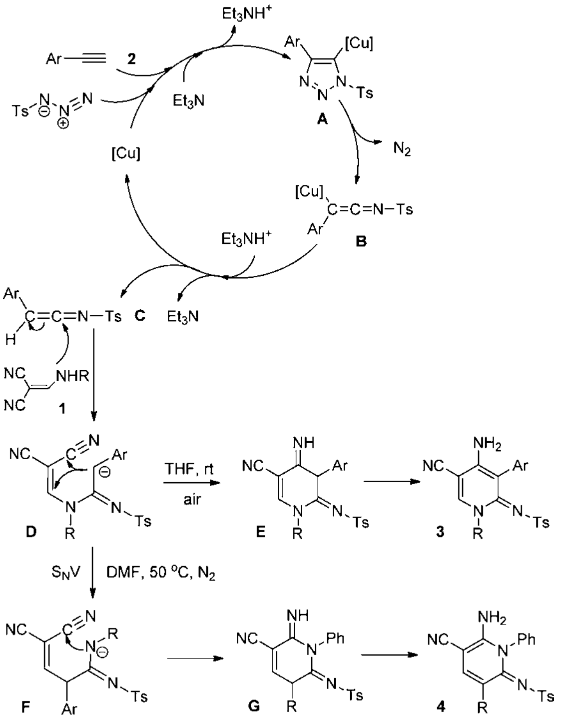


Figure 1. ORTEP drawing of **4fa**.

Scheme 1. Proposed Mechanism for the Regioselective Synthesis of 4-Amino- and 6-Amino-2-iminopyridines **3** and **4**



On the basis of all the results obtained and the literature, a plausible mechanism for the regioselective synthesis of 4-amino- and 6-amino-2-iminopyridines **3** and **4** *via* MCR is proposed as depicted in Scheme 1. In the presence of triethylamine, the reaction of **2** and TsN_3 is triggered by CuI to form a *N*-sulfonyl triazolyl copper species **A**,[12,15] which then undergoes a ring-opening reaction giving rise to a ketenimine species **B** upon the release of a N_2 molecule.[15b,c] A highly reactive ketenimine **C** is generated *via* protonation of **B** promoted by a triethylamine salt, which is quickly attacked by the nucleophilic nitrogen of **1** to form an anionic species **D**.[12,15] In THF at room temperature, an intramolecular cyclization of **D** occurs directly leading to the formation of the intermediate **E**, which is finally converted into 4-amino-2-iminopyridine **3**.[16] While in DMF at 50 °C under N_2, an intramolecular nucleophilic vinylic substitution (S_NV)[17] takes place to generate the intermediate **F**, which is eventually transformed to 6-amino-2-iminopyridine **4** upon intramolecular cyclization.

In summary, a facile and efficient solvent-controlled regioselective synthesis of multisubstituted 4-amino- and 6-amino-2-iminopyridines *via* the copper-catalyzed three-component reaction of sulfonyl azides, alkynes, and 2-[(amino)methylene]malononitriles has been develveped under very mild conditions. By this three-component reaction, 4-amino-2-iminopyridines **3** are synthesized in moderate to good yield in THF at room temperature, whereas 6-amino-2-iminopyridines **4** are dominantly obtained in DMF at 50 °C under N_2. This protocol is associated with readily available starting materials, mild conditions, high selectivity, flexible substitution patterns, and a wide range of synthetic potential of products. Investigation on the reaction mechanism and application of the as-synthesized 2-iminopyridines **3** and **4** in pharmacology are currently underway in our laboratory.

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Supporting Information Available. Experimental details, full characterization data, and copies of NMR spectra for compounds **3** and **4**, and crystallographic data for compound **4fa** (CIF). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.