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Recyclable Heterogeneous Copper(II)-Catalyzed Oxidative Cyclization of 2-Pyridine Ketone Hydrazones Towards [1,2,3]Triazolo[1,5-*a*]pyridines

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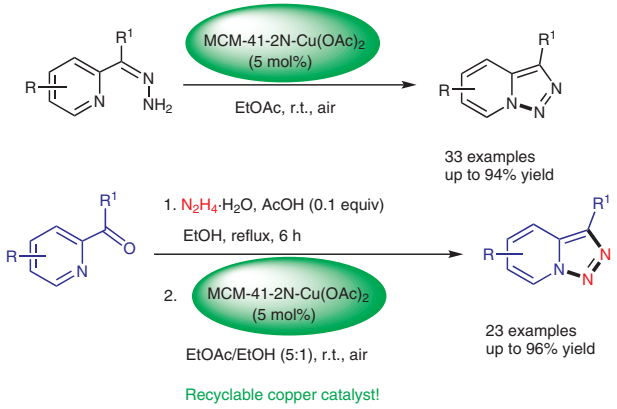

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Abstract The heterogeneous copper(II)-catalyzed oxidative cyclization of 2-pyridine ketone hydrazones was achieved in ethyl acetate at room temperature in the presence of an MCM-41-anchored bidentate 2-aminoethylamino copper(II) catalyst [MCM-41-2N-Cu(OAc)$_2$], in the presence of air as the oxidant, yielding a wide variety of [1,2,3]triazolo[1,5-*a*]pyridines in mostly good to high yields. The present method was also applied to the direct one-pot synthesis of [1,2,3]triazolo[1,5-*a*]pyridines from 2-acylpyridine derivatives and hydrazine monohydrate. Importantly, this supported copper(II) catalyst could be conveniently obtained via a simple procedure from easily available and inexpensive reagents, recovered by filtration of the reaction mixture, and reused at least seven times without a significant loss of catalytic activity.

Key words copper catalysis, [1,2,3]triazolo[1,5-*a*]pyridines, oxidative cyclization, heterogeneous catalysis, N–N coupling

Triazolopyridine structures are important building blocks for many pharmaceutical and functional materials. Among various triazolopyridine derivatives, [1,2,3]triazolo[1,5-*a*]pyridines have been investigated by the Jones[1] and Abarca[2] groups since the early 1980s. Although pharmacological studies of [1,2,3]triazolo[1,5-*a*]pyridine derivatives are rare,[3] their unique fluorescent properties and coordination chemistry have been extensively explored and applied to materials science.[4] Additionally, they are frequently used as useful synthetic intermediates in organic synthesis.[5] Because of the versatility of [1,2,3]triazolo[1,5-*a*]pyridines, considerable effort has been devoted to developing efficient synthetic routes for their preparation. The most commonly used synthesis of [1,2,3]triazolo[1,5-*a*]pyridines involves the oxidative cyclization of 2-pyridylcarboxaldehyde or 2-pyridyl ketone hydrazones by using at least a stoichiometric amount of an oxidant such as Ag_2O,[6] nickel peroxide,[7] $Pb(OAc)_2$,[8] MnO_2,[9] copper salts,[10] or hypervalent iodine.[11]

Copper-catalyzed organic reactions are particularly important in modern organic synthesis owing to low cost and low toxicity of copper catalysts. To develop economic and environmentally benign catalytic oxidative reactions, employment of a copper salt as a catalytic oxidant is highly desirable. As a result, copper-catalyzed oxidative C–H bond functionalization[12] and C–N bond-forming reaction have received much attention.[13] In spite of significant progress made in N–N bond formation reactions,[14] there are very few reports on catalytic methods for the construction of the N–N bond.[15] Recently, Nagasawa and coworkers reported a copper(I)-catalyzed tandem addition/oxidative cyclization of nitriles with 2-aminopyridines towards 3-substituted [1,2,4]triazolo[1,5-*a*]pyridines and a copper(II)-catalyzed oxidative cyclization of 2-pyridine ketone hydrazones for the construction of [1,2,3]triazolo[1,5-*a*]pyridines.[16] Although these copper-catalyzed N–N bond formation reactions are highly efficient for the construction of triazolopyridines, the use of 5–10 mol% of copper salts with or without a ligand was required to obtain high yields, and these homogeneous copper catalysts are difficult to recover from the reaction mixture and cannot be recycled. Furthermore, homogeneous catalysis might lead to unacceptable contamination of the product by copper, because triazolopyridines as strong ligands could easily coordinate with copper salts to produce the corresponding stable complexes,[17] thus restricting their applications in the synthesis of drug molecules containing triazolopyridines, which must be free of any residual metal. Anchoring of homogeneous copper catalysts on various insoluble supports with high surface areas is usually the strategy of choice for the solution to these

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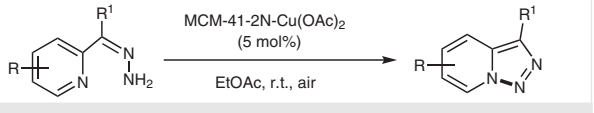
problems, because the supported catalysts can be easily separated from the reaction product via a simple filtration process after reactions and reused several times.[18] Recently, application of supported copper catalysts in various carbon–heteroatom bond-forming reactions has attracted considerable interest.[19] However, to the best of our knowledge, heterogeneous copper-catalyzed oxidative N–N bond formation for the construction of [1,2,3]triazolo[1,5-*a*]pyridines has not been explored until now.

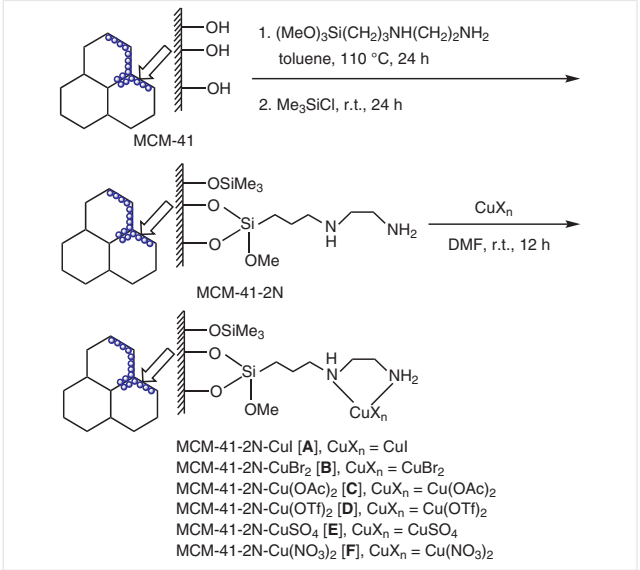
Recently, the mesoporous silica material MCM-41 has been widely employed as an ideal solid support for anchoring homogeneous metal catalysts due to its advantageous properties over other solid supports, including an extremely high surface area, large pore volume, tunable and uniform pore size, and excellent thermal stability.[20] To date, palladium,[21] rhodium,[22] molybdenum,[23] gold,[24] and copper[19f–h] complexes anchored onto MCM-41 have been prepared and applied to various organic reactions as recyclable heterogeneous catalysts. In continuation of our interest in developing green and sustainable catalytic systems for organic transformations,[19f–j,21e–g,24d] herein we report a heterogeneous copper(II)-catalyzed oxidative cyclization of 2-pyridine ketone hydrazones leading to [1,2,3]triazolo[1,5-*a*]pyridines by using an MCM-41-anchored bidentate 2-aminoethylamino copper(II) complex [MCM-41-2N-Cu(OAc)$_2$] as the catalyst and air as the oxidant (Scheme 1).



Scheme 1 Heterogeneous copper(II)-catalyzed synthesis of [1,2,3]triazolo[1,5-*a*]pyridines

MCM-41-anchored bidentate 2-aminoethylamino copper(I) or (II) complexes [MCM-41-2N-CuX$_n$] were facilely synthesized via a simple procedure from easily available and inexpensive [3-(2-aminoethylamino)propyl]trimethoxysilane according to our previous method (Scheme 2).[19f] The condensation reaction of the mesoporous material MCM-41[20a] with [3-(2-aminoethylamino)propyl]trimethoxysilane at 110 °C in toluene for 24 hours, followed by treatment with Me$_3$SiCl in toluene at room temperature provided the MCM-41-anchored bidentate 2-aminoethylamino ligand (MCM-41-2N). Subsequent reaction of MCM-41-2N with various copper salts [CuX$_n$ = CuI, CuBr$_2$, Cu(OAc)$_2$, Cu(OTf)$_2$, CuSO$_4$, and Cu(NO$_3$)$_2$] at room temperature in DMF afforded a series of MCM-41-anchored bidentate 2-aminoethylamino copper(I) or (II) complexes [MCM-41-2N-CuX$_n$] as pale blue powders.

In our initial screening experiments, the oxidative cyclization of 2-benzoylpyridine hydrazone (**1a**) was selected as the model reaction to determine the optimal reaction conditions, and the results are summarized in Table 1. First,



Scheme 2 Synthesis of the MCM-41-2N-CuX$_n$ catalysts

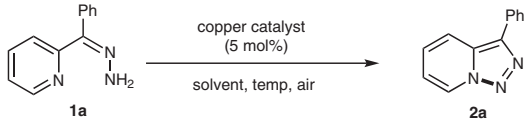
the effect of various heterogeneous copper catalysts on the model reaction was examined with DMF as the solvent at 60 °C under air (entries 1–6). The best result was obtained by using MCM-41-2N-Cu(OAc)$_2$ (**C**) as catalyst, to give 3-phenyl[1,2,3]triazolo[1,5-*a*]pyridine (**2a**) in 90% yield (entry 3). The use of MCM-41-2N-CuI (**A**) and MCM-41-2N-CuBr$_2$ (**B**) as catalyst provided the desired **2a** in 67 and 78% yield (entries 1 and 2), while other heterogeneous copper catalysts such as MCM-41-2N-Cu(OTf)$_2$ (**D**), MCM-41-2N-CuSO$_4$ (**E**), and MCM-41-2N-Cu(NO$_3$)$_2$ (**F**) were ineffective (entries 4–6). The reaction did not work without any copper catalyst, revealing the catalytic role of copper in this transformation (entry 7). Next, the effect of the solvent on the model reaction was explored with MCM-41-2N-Cu(OAc)$_2$ (**C**) as the catalyst at 60 °C (entries 8–12). The reaction also proceeded smoothly in acetonitrile, toluene, and ethyl acetate, yielding the desired **2a** in 84–88% yield (entries 8–10). In the case of EtOAc as solvent, the starting material **1a** was completely converted into **2a** within 0.5 h, because EtOAc could accelerate the reaction (entry 10). The use of 1,2-dimethoxyethane and ethanol as solvents led to decreased yields due to the hydrolytic decomposition of starting material **1a** (entries 11 and 12). To our delight, the reaction in EtOAc could also proceed efficiently at room temperature to give the target product **2a** in 87% yield within 0.5 h (entry 13). In contrast, complete consumption of **1a** was not observed with MeCN or toluene as solvent even after 3 h (entries 14 and 15). Therefore, EtOAc was selected as the solvent, because of the high reaction rate at room temperature (entry 13). Reducing the loading of the copper catalyst to 2.5 mol% resulted in a decreased yield and required a longer reaction time (entry 16). Increasing the loading of the copper catalyst to 10 mol% did not increase the yield of

2a significantly (entry 17). When homogeneous $Cu(OAc)_2$ (5 mol%) was used as catalyst, the desired **2a** was isolated in 88% yield (entry 18), indicating that the catalytic efficiency of MCM-41-2N-$Cu(OAc)_2$ was comparable to that of $Cu(OAc)_2$. When the reaction was carried out under argon, the desired **2a** was not detected, confirming that the oxidative N–N bond formation reaction did not occur in the absence of air or oxygen (entry 19). The use of 2 mmol of **1a** as substrate also gave **2a** in high yield (entry 20). Thus, the optimized reaction conditions for this oxidative cyclization are the use of MCM-41-2N-$Cu(OAc)_2$ (5 mol%) with EtOAc as solvent at room temperature under air for 0.5 hours (entry 13).

With this promising result in hand, we started to examine the substrate scope of this heterogeneous copper-catalyzed oxidative cyclization reaction under the optimized conditions; the results are summarized in Scheme 3. A variety of substituted 2-benzoylpyridine hydrazones **1b–j** bearing various substituents on the phenyl group, regardless of their electronic properties or substitution positions, were converted into the corresponding triazolopyridines **2b–j** in mostly good to excellent yields within 0.5 h. Methoxy-substituted 2-benzoylpyridine hydrazones **1c** and **1i** with a strongly electron-donating group furnished the target product **2c** and **2i** in relatively low yields of 40 and 59% due to the presence of competitive hydrolytic decomposition of the hydazones to the ketones, since the stability of the hydrazone strongly depends on the basicity of its imino nitrogen atom. The cyclization reactions of the hydrazones **1k–m** having a rigid biphenyl or a bulky naphthalene group also worked well, providing the desired products **2k–m** in 78–85% yields, but the reaction of hydrazone **1k** with a rigid biphenyl group required heating at 60 °C for a longer reaction time to achieve complete consumption of **1k**. 2,2′-Dipyridylketone hydrazone **1n** showed similar reactivity with aryl pyridyl ketone hydrazones and gave the expected product **2n** in 89% yield within 0.5 h. In addition to aryl pyridyl ketone hydrazones, alkyl pyridyl ketone hydrazones **1o** and **1p** were also compatible with the standard conditions and afforded the corresponding products **2o** and **2p**, respectively, in 83 and 85% yield. Notably, substitution on the pyridine ring was also tolerated in this transformation. For example, aryl (5-bromopyridyl) ketone hydrazones **1q–y** bearing various substituents on the benzene ring could undergo the cyclization reaction smoothly to give the corresponding triazolopyridines **2q–y** in mostly good to high yields. Cyclohexyl (5-bromopyridyl) ketone hydrazone **1z** also gave the desired **2z** in 82% yield. Additionally, hydrazones **1a′–d′** having 5-fluoro or 3-methyl groups on the pyridine ring also reacted well, providing the corresponding products **2a′–d′** in good yields. However, (6-bromopyridyl) methyl ketone hydrazone **1e′** and (6-methylpyridyl) methyl ketone hydrazone **1f′** displayed a relatively lower reactivity, and the reactions required a higher temperature (60 °C) and a longer reaction time, giving **2e′** and **2f′** in only 63 and 65% yield. Interestingly, quinoline hydrazone **1g′** could undergo the oxidative cyclization at 60 °C to give the corresponding triazoloquinoline **2g′** in 52% yield. The relatively lower reactivity of substrates **1e′–g′** may be due to the steric hindrance resulting from substitution at the 6-position on the pyridine ring.

Because the pyridine ketone hydrazones could be easily obtained by the reaction of the corresponding 2-acylpyridines with hydrazine monohydrate, we next attempted the one-pot synthesis of [1,2,3]triazolo[1,5-*a*]pyridines to improve the convenience of the present reaction; the results are listed in Scheme 4. Optimization of the reaction conditions indicated that the treatment of 2-benzoylpyridine **3a** with hydrazine monohydrate (1.5 equiv) in EtOH in the presence of acetic acid (0.1 equiv) under reflux for 6 hours, followed by oxidative cyclization in EtOAc/EtOH (5:1) in the

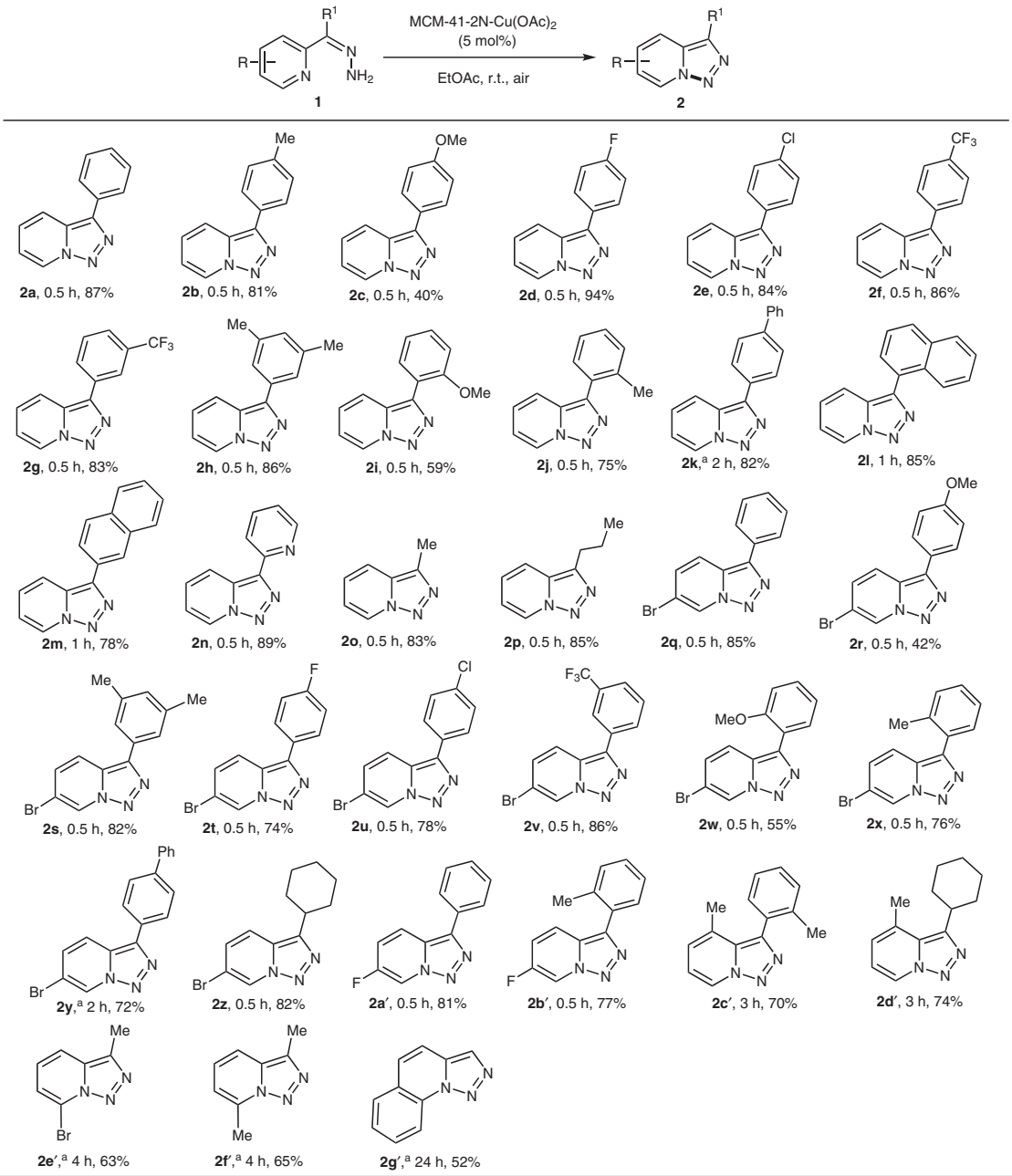
Table 1 Optimization of the Reaction Conditions[a]



1a **2a**

Entry	Copper catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	**A**	DMF	60	3	67
2	**B**	DMF	60	3	78
3	**C**	DMF	60	3	90
4	**D**	DMF	60	12	0
5	**E**	DMF	60	12	0
6	**F**	DMF	60	12	0
7	–	DMF	60	12	0
8	**C**	MeCN	60	3	84
9	**C**	toluene	60	3	88
10	**C**	EtOAc	60	0.5	85
11	**C**	DME	60	3	72
12	**C**	EtOH	60	3	74
13	**C**	EtOAc	r.t.	0.5	87
14	**C**	MeCN	r.t.	3	71
15	**C**	toluene	r.t.	3	75
16[c]	**C**	EtOAc	r.t.	1	80
17[d]	**C**	EtOAc	r.t.	0.5	89
18	$Cu(OAc)_2$	EtOAc	r.t.	0.5	88
19[e]	**C**	EtOAc	r.t.	12	0
20[f]	**C**	EtOAc	r.t.	0.5	86

[a] Reaction conditions: **1a** (0.2 mmol), copper catalyst (5 mol%), solvent (1.5 mL), under air.
[b] Isolated yield.
[c] Catalyst (2.5 mol%) was used.
[d] Catalyst (10 mol%) was used.
[e] The reaction was performed under argon.
[f] Modified conditions: **1a** (2 mmol), **C** (0.1 mmol), EtOAc (10 mL).



Scheme 3 Heterogeneous copper(II)-catalyzed synthesis of substituted [1,2,3]triazolo[1,5-*a*]pyridines. *Reagents and conditions*: **1** (0.2 mmol), MCM-41-2N-Cu(OAc)$_2$ (5 mol%), EtOAc (1.5 mL), r.t. (unless indicated otherwise), under air; isolated yields given. [a] Reaction was conducted at 60 °C.

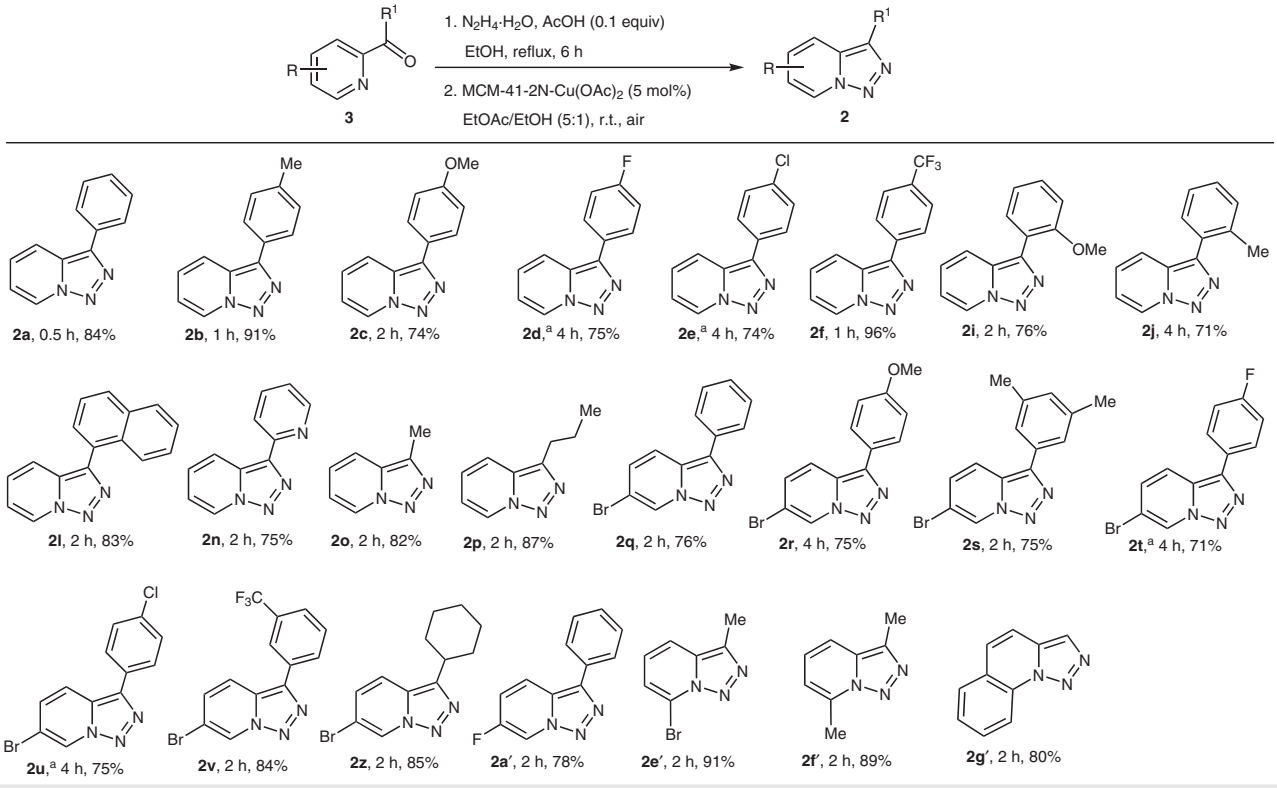
presence of MCM-41-2N-Cu(OAc)$_2$ (5 mol%) at room temperature under air for 0.5 hours afforded the desired **2a** in 84% yield. Subsequently, a variety of 2-acylpyridines were applied to the one-pot construction of [1,2,3]triazolo[1,5-*a*]pyridine derivatives. As shown in Scheme 4, 2-(4-methylbenzoyl)pyridine (**3b**), 2-(4-trifluoromethylbenzoyl)pyridine (**3f**), and 2-acetyl-6-bromopyridine (**3e′**) afforded the corresponding triazolopyridines **2b**, **2f**, and **2e′** in excellent yields. Substituted 2-benzoylpyridines **3c–e**, **3i**, and **3j** bearing either an electron-donating or electron-withdrawing group on the benzene ring underwent the one-pot reaction smoothly to give the corresponding products **2c–e**, **2i**, and **2j** in good yields. The other 2-acylpyridines also reacted well in this transformation, thus providing triazolopyridines **2l**, **2n-v**, **2z**, **2a′**, and **2f′–g′** in good yields. Notably, the yields of products **2c**, **2i**, **2r**, and **2e′–g′** were significantly improved to 74, 76, 75, 91, 89, and 80%, respectively, through the one-pot reaction compared with the direct

synthesis from the corresponding hydrazones. The improvements in the yields may be due to inhibition of the hydrolytic decomposition of the intermediate hydrazones in the presence of excess hydrazine monohydrate. Thus, we have developed a general, efficient and practical one-pot route to [1,2,3]triazolo[1,5-*a*]pyridine derivatives from 2-acylpyridines.

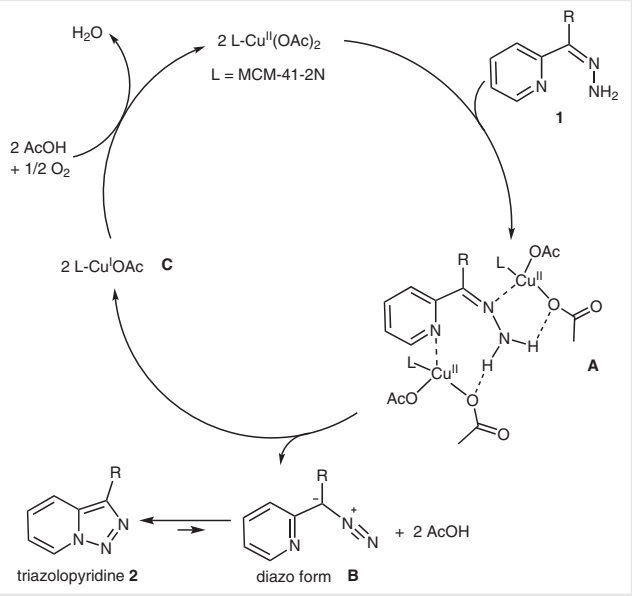
To ensure that the observed catalysis arises from the heterogeneous catalyst MCM-41-2N-Cu(OAc)$_2$ and not from the leached copper species in solution, we focused on the oxidative cyclization of 2-benzoylpyridine hydrazone (**1a**). The reaction was carried out until an approximately 50% conversion of **1a**. Then the copper catalyst was removed by filtration of the reaction solution and the catalyst-free filtrate was allowed to react further under air for 0.5 h. We found that after removal of the catalyst, no increase in the conversion of 2-benzoylpyridine hydrazone (**1a**) was observed. The copper content in the filtrate was also determined by ICP-AES analysis, and no copper was detected in the clear solution. These results rule out any contribution to the observed conversion from the leached copper species, indicating that MCM-41-2N-Cu(OAc)$_2$ was stable during the oxidative cyclization and the observed cyclization reaction was intrinsically heterogeneous.

A possible reaction mechanism for this heterogeneous copper(II)-catalyzed synthesis of [1,2,3]triazolo[1,5-*a*]pyridines is illustrated in Scheme 5.[16b] Firstly, coordination of the pyridine ketone hydrazone **1** to MCM-41-2N-Cu(OAc)$_2$ provides intermediate **A**. Then two electrons from the hydrazone immediately transfer to each of the two copper(II) ions in intermediate **A**, to generate MCM-41-2N-CuOAc **C** and the diazo intermediate **B**. The formation of the diazo intermediate was also suggested by a previous report on diazoketone formation from ketohydrazone by Cu(acac)$_2$ oxidation.[25] The formed diazo intermediate **B** easily converts into the triazolopyridine product **2** since the cyclized structure is highly dominant in the equilibrium between the diazo form and product **2**.[9c,25] Finally, the resulting MCM-41-2N-CuOAc **C** is oxidized by atmospheric oxygen to regenerate the MCM-41-2N-Cu(OAc)$_2$ complex and complete the catalytic cycle.

For the practical application of a supported metal catalyst, its ease of separation and recyclability are important factors to be examined. The MCM-41-2N-Cu(OAc)$_2$ catalyst can be facilely separated and recovered by a simple filtration of the reaction mixture. We next studied the recycling of the catalyst by using the one-pot reaction of 2-(4-trifluoromethylbenzoyl)pyridine (**3f**) with hydrazine monohy-



Scheme 4 Heterogeneous copper(II)-catalyzed one-pot synthesis of [1,2,3]triazolo[1,5-*a*]pyridine derivatives. *Reagents and conditions*: 1. **3** (0.2 mmol), $N_2H_4{\cdot}H_2O$ (0.3 mmol), AcOH (0.02 mmol), EtOH (1.0 mL), 80 °C, 6 h; 2. MCM-41-2N-Cu(OAc)$_2$ (5 mol%), EtOAc (5 mL) r.t. (unless indicated otherwise), under air, 0.5–4 h; isolated yields given. [a] Reaction was conducted at 60 °C.



Scheme 5 Proposed catalytic cycle

drate for the synthesis of 3-(4-trifluoromethylphenyl)[1,2,3]triazolo[1,5-*a*]pyridine **2f**. After the reaction was carried out, the reaction mixture was diluted with ethyl acetate, and the catalyst was recovered by simple filtration and washed with distilled water and acetone. After being air-dried, it can be reused directly without further purification. The recovered copper catalyst was employed in the next run, and the yield of the target product **2f** was found to be 95, 96, 95, 94, 94, 93, and 92% in seven consecutive cycles, respectively. Compared with the fresh catalyst (96% yield), only a slight decrease in activity was observed for the recovered catalyst. In addition, the copper leaching in the supported catalyst was also examined by ICP analysis. The copper content of the catalyst after eight consecutive runs was determined to be 0.62 mmol/g, indicating that only 3.1% of copper had been lost from the MCM-41 support.

In conclusion, we have developed a highly efficient heterogeneous copper(II)-catalyzed oxidative cyclization of 2-pyridyl ketone hydrazones for the construction of [1,2,3]triazolo[1,5-*a*]pyridine derivatives. The present approach was also applied to the direct synthesis of [1,2,3]triazolo[1,5-*a*]pyridines from 2-acylpyridines and hydrazine monohydrate by using a one-pot reaction. In contrast to the classical synthetic route to these compounds, the present heterogeneous oxidative cyclization method shows many attractive features, including: (a) the starting materials are easily available, and a wide range of 2-acylpyridine derivatives are allowed; (b) a wide variety of [1,2,3]triazolo[1,5-*a*]pyridines could be produced in mostly good to high yields; (c) the reaction conditions were mild and atmospheric oxygen was used as the oxidant, producing water as the sole side-product; and (d) this heterogeneous copper(II) catalyst can facilely be obtained via a simple procedure from easily available and cheap reagents and recovered by filtration of the reaction mixture, and reused at least seven times with only a slight decrease in activity. Thus, the present method is an attractive alternative to prepare [1,2,3]triazolo[1,5-*a*]pyridine derivatives.

All chemicals were purchased from different commercial suppliers and used as received without purification. All solvents were dried and distilled before use. MCM-41-2N-CuI (**A**), MCM-41-2N-$CuBr_2$ (**B**), MCM-41-2N-$Cu(OAc)_2$ (**C**), MCM-41-2N-$Cu(OTf)_2$ (**D**), MCM-41-2N-$CuSO_4$ (**E**), and MCM-41-2N-$Cu(NO_3)_2$ (**F**) were prepared according to our previous procedure;[19f] the copper content was determined to be 0.57, 0.59, 0.64, 0.66, 0.61, and 0.62 mmol/g, respectively. 2-Acylpyridine derivatives[26] and 2-pyridyl ketone hydrazones[16b] were prepared according to literature methods. The products were isolated by flash column chromatography on 100–200 mesh silica gel with a mixture of light petroleum ether and ethyl acetate as eluent. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer (400 MHz or 100 MHz, respectively); $CDCl_3$ was used as solvent with TMS as internal reference. Melting points were determined on an X-5 Data microscopic melting point apparatus and are uncorrected. The copper content was determined on a Perkin-Elmer Optima 3100 XL ICP-AES spectrometer. High-resolution mass spectra (HRMS) were obtained with a GCT-TOF instrument with an EI source.

Heterogeneous Copper(II)-Catalyzed Synthesis of [1,2,3]Triazolo[1,5-*a*]pyridines 2a–g′ from Hydrazones 1a–g′; General Procedure

A dried reaction tube was charged with hydrazone **1** (0.2 mmol), MCM-41-2N-$Cu(OAc)_2$ (16 mg, 0.01 mmol), and EtOAc (1.5 mL). The reaction mixture was stirred at room temperature or 60 °C for the indicated time. The mixture was diluted with EtOAc (15 mL) and filtered. The copper catalyst was washed with acetone (2 × 5 mL), air-dried for 2 h, and reused in the next run. The filtrate was washed with brine (10 mL) and dried over $MgSO_4$. Then the organic phase was concentrated under vacuum and the residue was purified by column chromatography (silica gel, light PE/EtOAc, 3:1) to afford the desired product **2**.

3-Phenyl[1,2,3]triazolo[1,5-*a*]pyridine (2a)

Yield: 34.1 mg (87%); white solid; mp 113–114 °C (Lit.[16b] 112–113 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, *J* = 7.2 Hz, 1 H), 8.01–7.94 (m, 3 H), 7.51 (t, *J* = 7.8 Hz, 2 H), 7.39 (t, *J* = 7.6 Hz, 1 H), 7.32–7.25 (m, 1 H), 7.00 (t, *J* = 6.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 131.5, 130.5, 129.0, 127.9, 126.7, 125.6, 125.5, 118.4, 115.2.

3-(4-Methylphenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2b)

Yield: 33.9 mg (81%); white solid; mp 138–139 °C (Lit.[7b] 137–138 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 6.4 Hz, 1 H), 7.99 (d, *J* = 8.4 Hz, 1 H), 7.86 (d, *J* = 7.2 Hz, 2 H), 7.35–7.26 (m, 3 H), 7.00 (t, *J* = 5.6 Hz, 1 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 137.8, 130.3, 129.7, 128.6, 126.6, 125.6, 125.3, 118.5, 115.2, 21.3.

3-(4-Methoxyphenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2c)

Yield: 18.1 mg (40%); white solid; mp 133–134 °C (Lit.[5c] 134–135 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 6.8 Hz, 1 H), 7.95 (d, *J* = 9.2 Hz, 1 H), 7.88 (d, *J* = 8.4 Hz, 2 H), 7.27 (t, *J* = 7.8 Hz, 1 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 6.98 (t, *J* = 6.8 Hz, 1 H), 3.88 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 138.0, 130.1, 128.0, 125.6, 125.2, 124.1, 118.5, 115.3, 114.5, 55.4.

3-(4-Fluorophenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2d)

Yield: 40.1 mg (94%); white solid; mp 133–134 °C (Lit.[16b] 134–135 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 7.2 Hz, 1 H), 7.94–7.88 (m, 3 H), 7.29 (t, *J* = 7.8 Hz, 1 H), 7.18 (t, *J* = 8.8 Hz, 2 H), 7.00 (t, *J* = 6.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 245.9 Hz), 137.0, 130.2, 128.3 (d, *J* = 8.1 Hz), 127.6 (d, *J* = 3.3 Hz), 125.8, 125.6, 118.1, 116.0 (d, *J* = 21.6 Hz), 115.4.

3-(4-Chlorophenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2e)

Yield: 38.6 mg (84%); white solid; mp 158–159 °C (Lit.[16b] 159–160 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 7.2 Hz, 1 H), 7.97 (d, *J* = 8.8 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H), 7.34 (dd, *J* = 8.8, 6.8 Hz, 1 H), 7.04 (t, *J* = 6.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.9, 133.7, 130.4, 130.0, 129.2, 127.8, 126.0, 125.8, 118.2, 115.4.

3-[4-(Trifluoromethyl)phenyl][1,2,3]triazolo[1,5-*a*]pyridine (2f)

Yield: 45.3 mg (86%); white solid; mp 184–185 °C (Lit.[5a] 178–179 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 6.8 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 2 H), 8.00 (d, *J* = 8.8 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.38 (dd, *J* = 8.8, 6.8 Hz, 1 H), 7.05 (t, *J* = 6.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.3, 135.0, 130.8, 129.6 (q, *J* = 32.1 Hz), 126.6, 126.5, 125.9 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.4 Hz), 118.0, 115.5.

3-[3-(Trifluoromethyl)phenyl][1,2,3]triazolo[1,5-*a*]pyridine (2g)

Yield: 43.7 mg (83%); white solid; mp 144–145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 7.2 Hz, 1 H), 8.23 (s, 1 H), 8.15 (t, *J* = 3.6 Hz, 1 H), 8.00 (d, *J* = 9.2 Hz, 1 H), 7.65–7.62 (m, 2 H), 7.38 (dd, *J* = 9.0, 6.6 Hz, 1 H), 7.06 (t, *J* = 7.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4, 132.3, 131.5 (q, *J* = 32.2 Hz), 130.6, 129.6, 129.5, 126.4, 125.9, 124.4 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270.8 Hz), 123.2 (q, *J* = 3.7 Hz), 118.0, 115.5.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_9F_3N_3$: 264.0749; found: 264.0744.

3-(3,5-Dimethylphenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2h)

Yield: 38.4 mg (86%); white solid; mp 113–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 6.8 Hz, 1 H), 7.99 (d, *J* = 8.8 Hz, 1 H), 7.57 (s, 2 H), 7.30–7.25 (m, 1 H), 7.03 (s, 1 H), 6.98 (t, *J* = 6.4 Hz, 1 H), 2.41 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6, 138.2, 131.2, 130.4, 129.7, 125.5, 125.4, 124.5, 118.6, 115.3, 21.4.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{14}H_{14}N_3$: 224.1188; found: 224.1191.

3-(2-Methoxyphenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2i)

Yield: 26.6 mg (59%); white solid; mp 103–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 7.2 Hz, 1 H), 7.86 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.82 (d, *J* = 9.2 Hz, 1 H), 7.42–7.37 (m, 1 H), 7.22–7.17 (m, 1 H), 7.11 (t, *J* = 7.6 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 6.94 (t, *J* = 6.4 Hz, 1 H), 3.85 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 135.7, 131.8, 131.1, 129.6, 125.1, 124.3, 121.2, 120.5, 120.4, 115.1, 111.3, 55.4.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_{12}N_3O$: 226.0980; found: 226.0981.

3-(2-Methylphenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2j)

Yield: 31.4 mg (75%); white solid; mp 105–106 °C (Lit.[2f] 106–107 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 6.8 Hz, 1 H), 7.67 (d, *J* = 8.8 Hz, 1 H), 7.48–7.45 (m, 1 H), 7.38–7.28 (m, 3 H), 7.27–7.22 (m, 1 H), 7.00 (t, *J* = 6.8 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 137.5, 131.5, 131.0, 130.1, 130.0, 128.4, 125.9, 125.4, 125.2, 118.3, 115.2, 20.5.

3-Biphenyl-4-yl[1,2,3]triazolo[1,5-*a*]pyridine (2k)

Yield: 44.5 mg (82%); white solid; mp 178–179 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 6.8 Hz, 1 H), 8.03 (d, *J* = 8.0 Hz, 2 H), 8.01–7.98 (m, 1 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 7.6 Hz, 2 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.36 (t, *J* = 7.2 Hz, 1 H), 7.31–7.26 (m, 1 H), 6.97 (t, *J* = 6.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 140.5, 137.6, 130.5, 128.9, 127.7, 127.5, 127.0, 126.9, 125.7, 125.6, 118.5, 115.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{18}H_{14}N_3$: 272.1188; found: 272.1179.

3-Naphthalen-1-yl[1,2,3]triazolo[1,5-*a*]pyridine (2l)

Yield: 41.7 mg (85%); white solid; mp 122–123 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 7.2 Hz, 1 H), 8.22 (d, *J* = 8.4 Hz, 1 H), 7.92–7.89 (m, 2 H), 7.69 (d, *J* = 6.8 Hz, 1 H), 7.61 (d, *J* = 9.2 Hz, 1 H), 7.56 (t, *J* = 7.6 Hz, 1 H), 7.53–7.45 (m, 2 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 6.96 (t, *J* = 6.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 134.1, 132.2, 131.7, 129.0, 128.4, 128.1, 127.9, 126.6, 126.2, 125.9, 125.5, 125.4, 118.4, 115.5.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{16}H_{12}N_3$: 246.1031; found: 246.1036.

3-Naphthalen-2-yl[1,2,3]triazolo[1,5-*a*]pyridine (2m)

Yield: 38.3 mg (78%); yellow solid; mp 158–159 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 3.6 Hz, 1 H), 8.30 (s, 1 H), 8.09 (dd, *J* = 8.4, 1.2 Hz, 1 H), 8.02–7.80 (m, 4 H), 7.50–7.42 (m, 2 H), 7.24–7.15 (m, 1 H), 6.93–6.86 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8, 133.6, 132.8, 130.6, 128.9, 128.8, 128.1, 127.8, 126.5, 126.2, 125.9, 125.6, 125.1, 124.7, 118.4, 115.4.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{16}H_{12}N_3$: 246.1031; found: 246.1029.

3-Pyridin-2-yl[1,2,3]triazolo[1,5-*a*]pyridine (2n)

Yield: 34.9 mg (89%); white solid; mp 127–128 °C (Lit.[16b] 126–127 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 7.2 Hz, 1 H), 8.70 (d, *J* = 8.8 Hz, 1 H), 8.65 (d, *J* = 4.4 Hz, 1 H), 8.35 (d, *J* = 8.0 Hz, 1 H), 7.78 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.38–7.32 (m, 1 H), 7.22–7.18 (m, 1 H), 7.03 (td, *J* = 6.8, 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 149.3, 137.4, 136.6, 132.0, 126.4, 125.2, 122.0, 121.2, 120.4, 115.9.

3-Methyl[1,2,3]triazolo[1,5-*a*]pyridine (2o)

Yield: 22.1 mg (83%); white solid; mp 81–82 °C (Lit.[5b] 78–80 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 6.8 Hz, 1 H), 7.62 (d, *J* = 8.8 Hz, 1 H), 7.17 (dd, *J* = 8.2, 6.6 Hz, 1 H), 6.95–6.90 (m, 1 H), 2.63 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 131.6, 125.1, 123.6, 117.5, 114.9, 10.3.

3-Propyl[1,2,3]triazolo[1,5-*a*]pyridine (2p)

Yield: 27.4 mg (85%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 6.8 Hz, 1 H), 7.64 (d, *J* = 9.2 Hz, 1 H), 7.16 (dd, *J* = 8.8, 6.8 Hz, 1 H), 6.92 (t, *J* = 6.8 Hz, 1 H), 2.98 (t, *J* = 7.6 Hz, 2 H), 1.89–1.82 (m, 2 H), 1.00 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8, 131.4, 125.2, 123.6, 117.6, 114.9, 27.3, 22.9, 13.9.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_9H_{12}N_3$: 162.1031; found: 162.1026.

6-Bromo-3-phenyl[1,2,3]triazolo[1,5-*a*]pyridine (2q)

Yield: 46.6 mg (85%); white solid; mp 161–162 °C (Lit.[16b] 162–163 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (s, 1 H), 7.91 (d, *J* = 7.2 Hz, 2 H), 7.88 (d, *J* = 9.2 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.35 (dd, *J* = 9.4, 1.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7, 130.8, 129.3, 129.1, 129.0, 128.3, 126.7, 125.8, 118.8, 110.8.

6-Bromo-3-(4-methoxyphenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2r)

Yield: 25.5 mg (42%); white solid; mp 168–169 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (s, 1 H), 7.84–7.79 (m, 3 H), 7.29 (d, *J* = 9.2 Hz, 1 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 138.6, 128.7, 128.6, 128.0, 125.7, 123.4, 118.8, 114.6, 110.6, 55.4.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_{11}BrN_3O$: 304.0085; found: 304.0082.

6-Bromo-3-(3,5-dimethylphenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2s)

Yield: 49.5 mg (82%); white solid; mp 141–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (s, 1 H), 7.87 (d, *J* = 9.6 Hz, 1 H), 7.52 (s, 2 H), 7.32 (d, *J* = 9.2 Hz, 1 H), 7.04 (s, 1 H), 2.40 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 138.7, 130.6, 130.0, 129.0, 125.7, 124.5, 119.0, 110.6, 21.4.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{14}H_{13}BrN_3$: 302.0293; found: 302.0299.

6-Bromo-3-(4-fluorophenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2t)

Yield: 43.2 mg (74%); white solid; mp 159–160 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (s, 1 H), 7.88 (dd, *J* = 8.4, 5.6 Hz, 2 H), 7.82 (d, *J* = 9.2 Hz, 1 H), 7.36 (d, *J* = 9.6 Hz, 1 H), 7.20 (t, *J* = 8.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, *J* = 246.8 Hz), 137.8, 129.4, 128.8, 128.4 (d, *J* = 8.1 Hz), 127.0 (d, *J* = 3.2 Hz), 125.8, 118.5, 116.2 (d, *J* = 21.6 Hz), 110.8.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{12}H_8BrFN_3$: 291.9886; found: 291.9881.

6-Bromo-3-(4-chlorophenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2u)

Yield: 48.1 mg (78%); white solid; mp 178–179 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (s, 1 H), 7.87–7.79 (m, 3 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 9.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 134.2, 129.6, 129.3, 128.9, 127.8, 125.9, 118.5, 110.8.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{12}H_8BrClN_3$: 307.9590; found: 307.9593.

6-Bromo-3-[3-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-*a*]pyridine (2v)

Yield: 58.8 mg (86%); white solid; mp 164–165 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 1 H), 8.19 (s, 1 H), 8.11 (d, *J* = 6.4 Hz, 1 H), 7.88 (d, *J* = 9.6 Hz, 1 H), 7.66–7.61 (m, 2 H), 7.43 (dd, *J* = 9.4, 1.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1, 131.7, 131.6 (q, *J* = 32.3 Hz), 130.1, 129.7, 129.6, 129.2, 126.1, 124.8 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 270.8 Hz), 123.3 (q, *J* = 3.7 Hz), 118.3, 111.0.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_8BrF_3N_3$: 341.9854; found: 341.9857.

6-Bromo-3-(2-methoxyphenyl)[1,2,3]triazolo[1,5-*a*]pyridine (2w)

Yield: 33.4 mg (55%); white solid; mp 112–113 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (s, 1 H), 7.87 (d, *J* = 7.2 Hz, 1 H), 7.75 (d, *J* = 9.2 Hz, 1 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.27 (d, *J* = 8.4 Hz, 1 H), 7.12 (t, *J* = 7.4 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 136.4, 131.1, 130.3, 129.9, 128.0, 125.3, 121.3, 121.0, 119.9, 111.3, 110.6, 55.5.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_{11}BrN_3O$: 304.0085; found: 304.0078.

6-Bromo-3-*o*-tolyl[1,2,3]triazolo[1,5-*a*]pyridine (2x)

Yield: 43.8 mg (76%); white solid; mp 120–121 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (s, 1 H), 7.57 (d, *J* = 9.6 Hz, 1 H), 7.42 (d, *J* = 7.2 Hz, 1 H), 7.39–7.27 (m, 4 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 137.6, 131.1, 130.1, 130.0, 129.4, 128.9, 128.8, 126.0, 125.6, 118.7, 110.7, 20.5.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_{11}BrN_3$: 288.0136; found: 288.0139.

3-Biphenyl-4-yl-6-bromo[1,2,3]triazolo[1,5-*a*]pyridine (2y)

Yield: 50.4 mg (72%); white solid; mp 201–202 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (s, 1 H), 7.99 (d, *J* = 8.0 Hz, 2 H), 7.90 (d, *J* = 9.2 Hz, 1 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.65 (d, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.41–7.33 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 140.4, 138.3, 129.8, 129.3, 129.0, 128.9, 127.8, 127.6, 127.1, 127.0, 125.9, 118.8, 110.8.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{18}H_{13}BrN_3$: 350.0293; found: 350.0298.

6-Bromo-3-cyclohexyl[1,2,3]triazolo[1,5-*a*]pyridine (2z)

Yield: 45.9 mg (82%); white solid; mp 85 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 1 H), 7.60 (d, *J* = 9.2 Hz, 1 H), 7.20 (d, *J* = 9.6 Hz, 1 H), 3.09–3.01 (m, 1 H), 2.06–2.01 (m, 2 H), 1.96–1.86 (m, 2 H), 1.82–1.69 (m, 3 H), 1.51–1.32 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 129.1, 127.2, 125.4, 118.3, 110.3, 35.9, 32.8, 26.5, 26.0.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{12}H_{15}BrN_3$: 280.0449; found: 280.0451.

6-Fluoro-3-phenyl[1,2,3]triazolo[1,5-*a*]pyridine (2a')

Yield: 34.5 mg (81%); white solid; mp 117–118 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (s, 1 H), 8.01–7.97 (m, 1 H), 7.92 (d, *J* = 7.2 Hz, 2 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.25 (t, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7 (d, *J* = 243.8 Hz), 138.8, 130.9, 129.1, 128.4, 128.3, 126.7, 119.0 (d, *J* = 9.3 Hz), 118.3 (d, *J* = 26.0 Hz), 112.7 (d, *J* = 39.9 Hz).

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{12}H_9FN_3$: 214.0781; found: 214.0789.

6-Fluoro-3-*o*-tolyl[1,2,3]triazolo[1,5-*a*]pyridine (2b')

Yield: 34.9 mg (77%); white solid; mp 106–107 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1 H), 7.67 (dd, *J* = 9.6, 5.2 Hz, 1 H), 7.43 (d, *J* = 7.6 Hz, 1 H), 7.40–7.28 (m, 3 H), 7.23–7.17 (m, 1 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8 (d, *J* = 243.5 Hz), 139.2, 137.6, 131.1, 130.0, 129.5, 128.8, 126.0, 118.9 (d, *J* = 9.4 Hz), 118.0 (d, *J* = 26.1 Hz), 112.4 (d, *J* = 39.9 Hz). 20.5.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_{11}FN_3$: 228.0937; found: 228.0931.

4-Methyl-3-*o*-tolyl[1,2,3]triazolo[1,5-*a*]pyridine (2c')

Yield: 31.3 mg (70%); white solid; mp 84–85 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 6.4 Hz, 1 H), 7.39–7.23 (m, 4 H), 6.96–6.87 (m, 2 H), 2.18 (s, 3 H), 2.14 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5, 131.8, 131.6, 131.5, 129.9, 129.6, 128.9, 125.3, 124.4, 123.2, 115.4, 20.3, 18.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{14}H_{14}N_3$: 224.1188; found: 224.1186.

3-Cyclohexyl-4-methyl[1,2,3]triazolo[1,5-*a*]pyridine (2d')

Yield: 31.9 mg (74%); white solid; mp 93 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 7.2 Hz, 1 H), 6.85 (d, *J* = 6.0 Hz, 1 H), 6.77 (t, *J* = 6.8 Hz, 1 H), 3.17–3.11 (m, 1 H), 2.64 (s, 3 H), 2.01–1.88 (m, 6 H), 1.81–1.77 (m, 1 H), 1.47–1.35 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 130.6, 128.7, 123.5, 123.1, 114.8, 36.4, 33.9, 26.8, 26.0, 18.9.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_{18}N_3$: 216.1501; found: 216.1509.

7-Bromo-3-methyl[1,2,3]triazolo[1,5-*a*]pyridine (2e')

Yield: 26.7 mg (63%); white solid; mp 101–102 °C (Lit.[16b] 102–103 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.8 Hz, 1 H), 7.21 (d, *J* = 6.8 Hz, 1 H), 7.10 (t, *J* = 7.8 Hz, 1 H), 2.64 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.2, 133.1, 124.3, 119.1, 116.5, 115.0, 10.7.

3,7-Dimethyl[1,2,3]triazolo[1,5-*a*]pyridine (2f')

Yield: 19.2 mg (65%); yellow solid; mp 94–95 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.6 Hz, 1 H), 7.63 (t, *J* = 7.8 Hz, 1 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 2.60 (s, 3 H), 2.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 157.4, 155.2, 136.4, 123.4, 118.2, 24.6, 13.9.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_8H_{10}N_3$: 148.0875; found: 148.0871.

[1,2,3]Triazolo[1,5-*a*]quinoline (2g')

Yield: 17.6 mg (52%); white solid; mp 111–113 °C (Lit.[16b] 112–114 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 8.4 Hz, 1 H), 8.12 (s, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.77 (t, *J* = 7.6 Hz, 1 H), 7.61 (t, *J* = 7.6 Hz, 1 H), 7.58–7.50 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.9, 131.8, 130.1, 128.6, 127.6, 127.1, 126.7, 123.9, 116.4, 114.8.

Heterogeneous Copper(II)-Catalyzed One-Pot Synthesis of [1,2,3]Triazolo[1,5-*a*]pyridines; General Procedure

A dried reaction tube was charged with 2-acylpyridine **3** (0.2 mmol), hydrazine monohydrate (0.3 mmol), acetic acid (0.02 mmol), and ethanol (1.0 mL) at room temperature. The reaction mixture was stirred at 80 °C for 6 h, and then EtOAc (5.0 mL) and MCM-41-2N-Cu(OAc)$_2$ (16 mg, 0.01 mmol) were added. After stirring at room temperature or 60 °C for the indicated time, the resulting mixture was diluted with EtOAc (15 mL) and filtered. The copper catalyst was washed with distilled water (2 × 5 mL), acetone (2 × 5 mL), and air-dried for 2 h, and reused in the next run. The filtrate was washed with water (10 mL) and dried over $MgSO_4$. Then the organic phase was concentrated in vacuum and the residue was purified by column chromatography (silica gel, light PE/EtOAc, 3:1) to afford the desired product **2**.

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Supporting Information

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