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Heterogeneous copper-catalyzed decarboxylative cyclization of 2-benzoylpyridines with α-amino acids leading to imidazo[1,5-*a*]pyridines

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ABSTRACT

The heterogeneous decarboxylative cyclization reaction between 2-benzoylpyridines and α-amino acids was achieved in toluene at 120 °C in the presence of 15 mol% of L-proline-functionalized MCM-41-supported copper(II) complex [L-Proline-MCM-41-Cu(OTf)$_2$] and iodine with di-*tert*-butyl peroxide (DTBP) as oxidant, yielding a variety of 1,3-disubstituted imidazo[1,5-*a*]pyridines in good to excellent yields. The new supported copper catalyst can be prepared from commercially available and inexpensive reagents, and recovered from the reaction mixture by a simple filtration and recycled up to eight times with almost consistent activity.

1. Introduction

Imidazo[1,5-*a*]pyridines are important scaffolds present in natural products and synthetic compounds of high utility and have been widely used in many areas of research such as pharmaceutical and materials chemistry [1–3]. However, only a few synthetic routes mainly relied on conventional Vilsmeier-type cyclizations [4,5] and other alternative methods [6,7] are available for these compounds so far, in spite of their wide range of biological and photophysical activities. Therefore, the development of more efficient and practical synthetic approaches for construction of imidazo[1,5-*a*]pyridines from readily available starting materials is highly desirable.

Transition-metal-catalyzed intermolecular or intramolecular direct oxidative aminations of the C–H bonds have been developed into a powerful tool for the construction of C–N bonds with high atom and step economy and have been widely applied for the preparation of azaheterocycles [8–15]. Various transition metal catalysts such as ruthenium [16–18], rhodium [19–22] and palladium [23–27] based catalytic systems have been used for C–H bond amination. Recently, copper-catalyzed construction of imidazo[1,5-*a*]pyridines *via* oxidative aminations of C(sp^3)–H bonds has attracted considerable interest due to their high efficiency and low cost of copper catalysts, which included Cu(I)-catalyzed transannulation of *N*-heteroaryl aldehydes or ketones with alkylamines [28], Cu(I) or Cu(II)-catalyzed annulation of 2-(pyridine-2-yl)acetates or 2-benzoylpyridines with benzylamines [29,30], Cu(II)-catalyzed decarboxylative annulation between 2-benzoylpyridines and α-amino acids [31], and Cu(I)-catalyzed denitrogenative transannulation of pyridotriazoles with benzylamines or α-amino acids [32]. Although these copper-catalyzed oxidative amination/annulation protocols were highly efficient for construction of imidazo[1,5-*a*]pyridines, high loading of copper salts (typically 10–20 mol%) were used to obtain high yields, and they are difficult to separate from the reaction mixture and not recyclable, which is of particular environmental and economic concerns in large-scale syntheses and in industry. Furthermore, homogeneous copper catalysis might cause unacceptable copper contamination of the desired product because of the formation of complexes of imidazo[1,5-*a*]pyridines with copper, which restricts the application of such catalytic systems in electronics and biomedicine. The heterogenization of the existing homogeneous

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copper catalysts could be a logical solution to these problems; the use of immobilized catalysts could give rise to facile removal, recovery, and reusability of the copper catalysts, thereby minimizing both copper contamination of the desired isolated product and waste derived from reaction workup [33–37]. In recent years, heterogeneous copper-catalyzed carbon-carbon [38–41] and carbon-heteroatom [42–49] bond formation reactions have received much attention. However, to the best of our knowledge, no examples of heterogeneous copper-catalyzed oxidative aminations of C(sp^3)–H bonds for construction of C–N bonds have been described until now.

Mesoporous MCM-41 materials have recently emerged as promising supports for immobilization of homogeneous catalysts because of their remarkable advantages such as ultrahigh surface areas, large and defined pore sizes, big pore volumes and the existence of a large number of Si–OH groups on the inner surface, in comparison with other solid supports [50–52]. Recently, various MCM-41-supported transition metal catalysts such as palladium [53–58], rhodium [59], molybdenum [60,61], gold [62–66] and copper [40,41,47–49] based catalytic systems have been successfully employed in many organic reactions as recyclable catalysts. In continuation of our effort to develop economical and eco-friendly synthetic routes for organic transformations from the viewpoint of green and sustainable chemistry [40,41,47–49,66], herein we report the synthesis of L-proline-functionalized MCM-41-supported copper(II) complex [L-Proline-MCM-41-Cu(OTf)$_2$] and its successful application to the decarboxylative cyclization between 2-benzoylpyridines and α-amino acids leading to a variety of 1,3-disubstituted imidazo[1,5-*a*]pyridines in good to excellent yields (Scheme 1).

2. Results and discussion

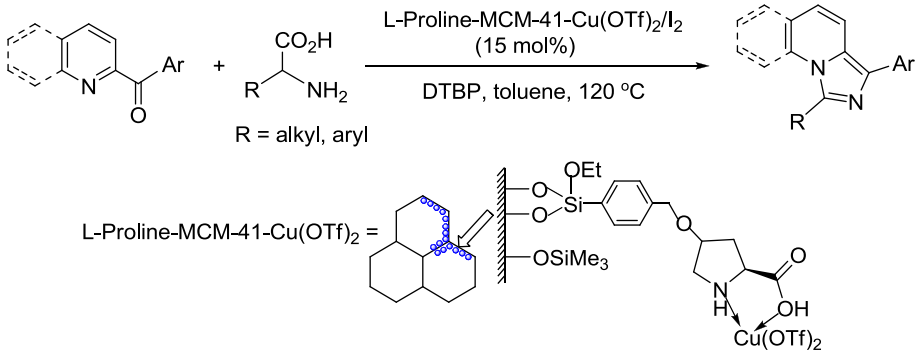
2.1. Preparation and characterization of L-Proline-MCM-41-CuX$_n$ complexes

A series of L-proline-functionalized MCM-41-supported copper(I) or (II) complexes [L-Proline-MCM-41-CuX$_n$] were easily prepared from commercially available and inexpensive reagents according to the procedure as shown in Scheme 2. Firstly, the mesoporous MCM-41 was condensed with 4-(chloromethyl)phenyltrichlorosilane in toluene, followed by the treatment with anhydrous ethanol and then the silylation with Me_3SiCl to generate the chloromethyl-functionalized MCM-41 ($ClCH_2$-MCM-41). The latter was then treated with *N*-Boc-*trans*-4-hydroxy-L-proline in THF with NaH as base, followed by deprotection with TFA in CH_2Cl_2 to afford the L-proline-functionalized MCM-41 (L-Proline-MCM-41). Finally, the reaction of L-Proline-MCM-41 with various copper salts [CuX$_n$ = CuI, CuBr, $CuCl_2$, $CuBr_2$, Cu(OAc)$_2$, Cu(OTf)$_2$] in acetone afforded a series of L-proline-functionalized MCM-41-supported copper(I) or (II) complexes [L-Proline-MCM-41-CuX$_n$] as light yellow or pale blue powders.

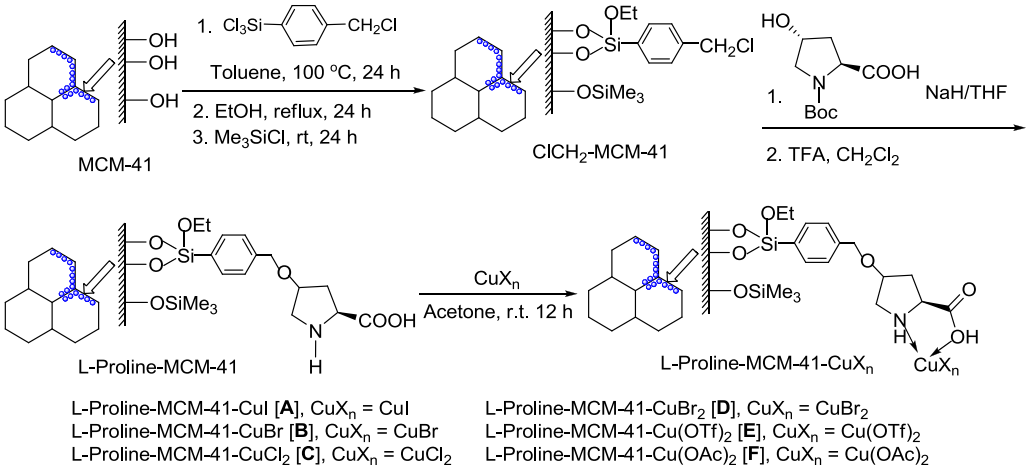
The small angle X-ray diffraction (XRD) patterns of the parent MCM-41 and L-Proline-MCM-41-Cu(OTf)$_2$ are shown in Fig. 1. The pattern of the parent MCM-41 exhibits an intense (100) diffraction peak at 2.32 2-theta and two additional high order peaks (110 and 200) with lower intensities at 3.91 and 4.46 2-theta, respectively [50]. The diffraction pattern of L-Proline-MCM-41-Cu(OTf)$_2$ was similar to that of parent MCM-41, the (100) diffraction peak of L-Proline-MCM-41-Cu(OTf)$_2$ with decreased intensity was observed after introduction of the copper complex, while the (110) and (200) diffraction peaks became weak and diffuse. The decrease in intensity may be mainly due to contrast matching between the silica walls and organic moieties located inside the channels of MCM-41. These results indicate that the basic structure of the mesoporous MCM-41 remains unchanged after grafting the copper complex and the copper complex is well dispersed on the inner channel walls.

FT-IR spectra of MCM-41, L-Proline-MCM-41, L-Proline-MCM-41-Cu(OTf)$_2$ and the recovered L-Proline-MCM-41-Cu(OTf)$_2$ are shown in Fig. 2. The FT-IR spectrum (Fig. 2a) of MCM-41 shows the Si–O stretching absorption at 1080 and 805 cm^{-1}. In the FT-IR spectrum (Fig. 2b) of L-Proline-MCM-41 absorptions at 3435 cm^{-1} (N–H), 1631 and 1414 cm^{-1} (COOH) were observed indicating the presence of silylated L-Proline groups. After the complexion of Cu ions with MCM-41-ligand, the N–H stretching frequency is shifted to a higher frequency 3447 cm^{-1}, while the two absor-ption bands of COOH are red shifted and appear at 1617 and 1395 cm^{-1}, respectively, demonstrating that –NH and –OH coordinate with the metal Cu (Fig. 2c). Finally, the FT-IR spectrum (Fig. 2d) of the eighth reused catalyst indicated that the structure of the catalyst was maintained during the reaction.

The N_2 adsorption-desorption isotherms for MCM-41 and L-Proline-MCM-41-Cu(OTf)$_2$ recorded at 77 K are illustrated in Fig. 3. The isotherms in Fig. 3 have remarkable changes as expected before and after grafting the copper complex because the organic moieties entered the channels of MCM-41, but both samples gave similar adsorption-desorption isotherms of type IV (definition by IUPAC), indicating that the mesoporous structure was remained. Fig. 4 shows pore size distributions for MCM-41 and L-Proline-MCM-41-Cu(OTf)$_2$. Compared to MCM-41, the obvious decreases in pore volume and size were observed for L-Proline-MCM-41-Cu(OTf)$_2$ owing to the incorporation of organic moieties into the channels of MCM-41, but L-Proline-MCM- 41-Cu(OTf)$_2$ still exhibited a narrow pore size distribution. After the anchoring the L-Proline-Cu(OTf)$_2$ complex onto MCM-41, the BET specific surface area and pore diameter decreased from 912 m^2/g and 2.7 nm to 583 m^2/g and 2.5 nm, respectively. The energy dispersive spectroscopy (EDS) analysis carried out with fresh L-Proline-MCM-41-Cu(OTf)$_2$



Scheme 1. Heterogeneous copper(II)-catalyzed synthesis of imidazo[1,5-*a*]pyridines.



Scheme 2. Preparation of L-Proline-MCM-41-CuX_n complexes.

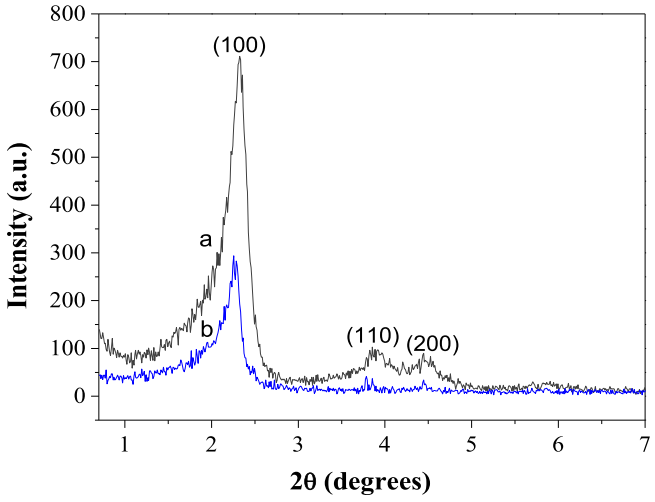


Fig. 1. XRD patterns of MCM-41 (a) and L-Proline-MCM-41-$Cu(OTf)_2$ (b).

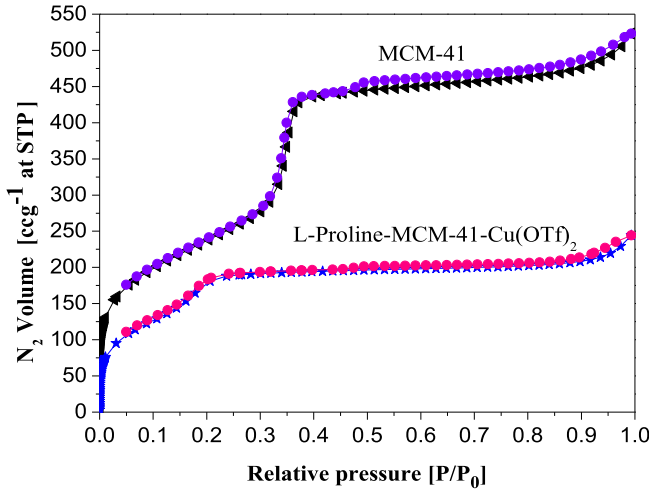


Fig. 3. N_2 adsorption/desorption isotherms of MCM-41 and L-Proline-MCM-41-$Cu(OTf)_2$.

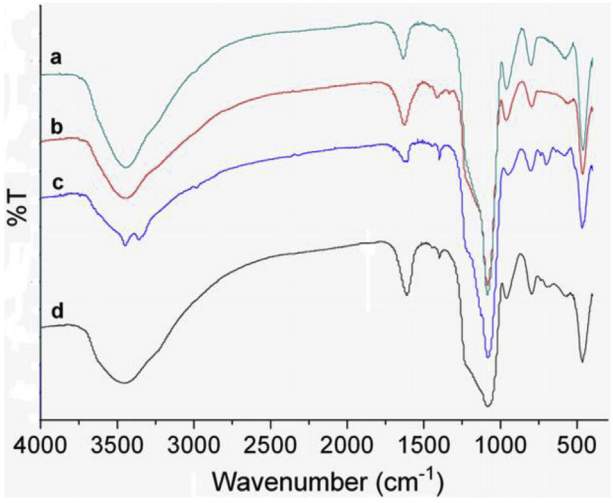


Fig. 2. FT-IR spectra of MCM-41 (a), L-Proline-MCM-41 (b), L-Proline-MCM-41-$Cu(OTf)_2$ (c) and the recovered L-Proline-MCM-41-$Cu(OTf)_2$ after the eighth cycle (d).

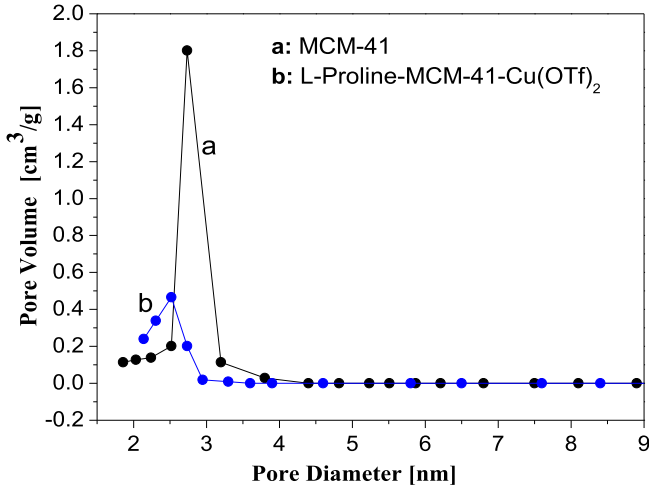


Fig. 4. Pore size distributions of MCM-41 and L-Proline-MCM-41-$Cu(OTf)_2$.

complex showed the presence of Si, O, C, N, S, F and Cu elements (Fig. 5), which further confirming the successful anchoring of the L-Proline-Cu(OTf)$_2$ complex onto MCM-41.

The TGA curves of MCM-41, L-Proline-MCM-41-Cu(OTf)$_2$ and the recovered L-Proline-MCM-41-Cu(OTf)$_2$ show the mass loss of the organic materials as they decompose upon heating (Fig. 6). TGA curve (Fig. 6a) of MCM-41 showed only one mass loss step between 120 and 200 °C due to the loss of physically adsorbed water, indicating its outstanding thermal stability. For L-Proline-MCM-41-Cu(OTf)$_2$, two weight loss steps were observed (Fig. 6b). The first weight loss step occurs in the temperature range of 120–300 °C, which is related to the loss of physically and chemically adsorbed water and solvents. The second one occurs in the temperature range of 300–800 °C corresponding to the thermal decomposition of organic moieties in the catalytic material. TGA analysis indicated that this supported copper catalyst was stable up to 280 °C. TGA curve (Fig. 6c) of the eighth reused catalyst showed that the catalyst still remained high thermal stability even after eight consecutive cycles.

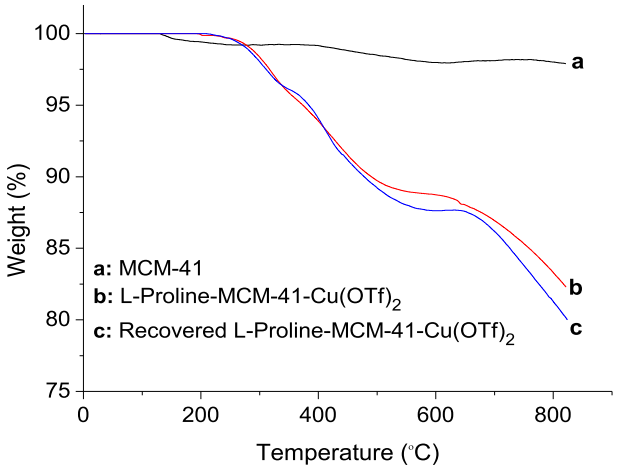


Fig. 6. TGA curves of MCM-41, L-Proline-MCM-41-Cu(OTf)$_2$ and the recovered L-Proline-MCM-41-Cu(OTf)$_2$ after the eighth cycle.

2.2. Heterogeneous copper-catalyzed decarboxylative cyclization reaction between 2-benzoylpyridines and α-amino acids

In our initial screening experiments, the decarboxylative cyclization reaction between 2-benzoylpyridine **1a** and leucine **2a** was investigated to optimize the reaction conditions, and the results are listed in Table 1. First, the efficiency of various heterogeneous copper catalysts was screened with molecular iodine as a co-catalyst and di-*tert*-butyl peroxide (DTBP) as oxidant in toluene. The results showed that L-Proline-MCM-41-Cu(OTf)$_2$ [**E**] was the most efficient catalyst for this reaction (entry 5), whilst other heterogeneous copper catalysts such as L-Proline-MCM-41-CuI [**A**], L-Proline-MCM-41-CuBr [**B**], L-Proline-MCM-41-CuCl$_2$ [**C**], L-Proline-MCM-41-CuBr$_2$ [**D**] and L-Proline-MCM-41-Cu(OAc)$_2$ [**F**] afforded low yields (entries 1–4 and 6). When a homogeneous Cu(OTf)$_2$ was used as the catalyst, the desired product **3a** was also isolated in 92% yield (Table 1, entry 7), which indicating that catalytic activity of L-Proline-MCM-41-Cu(OTf)$_2$ was comparable to that of Cu(OTf)$_2$. In the absence of any copper catalyst, the reaction generated the target product **3a** in only 38% yield (entry 8). Then, the effect of different oxidants on this transformation was examined. When *tert*-butyl hydroperoxide (TBHP) or dibenzoyl peroxide (BPO) was used as oxidant, the desired **3a** was obtained in lower yields (entries 9 and 10), so DTBP as oxidant was the best choice (entry 5). With L-Proline-MCM-41-Cu(OTf)$_2$ in other solvents, the yields of **3a** were 86%, 69%, 67%, and 55%, respectively, in dioxane, DCE, MeCN, and DMF (entries 11–14), which indicating that toluene was the optimal solvent. By raising or lowering the reaction temperature, no improvement in yield of **3a** was observed (entries 15 and 16). When the amount of leucine **2a** was decreased from 3.0 equiv to 2.0 equiv, a remarkable decrease in the yield of **3a** was observed (entry 17). Finally, reducing the amount of the catalyst to 8 mol% resulted in a lower yield and required a long reaction time (entry 18). Increasing the amount of the catalyst to 30 mol% could shorten the reaction time, but did not improve the yield significantly (entry 19). Thus, the optimized conditions for this decarboxylative cyclization are the use of leucine **2a** (3.0 equiv), L-Proline-MCM-41-Cu(OTf)$_2$ (15 mol%), I_2 (15 mol%) as cocatalyst with DTBP as oxidant in toluene at 120 °C for 12 h (Table 1, entry 5).

With this promising result in hand, we started to investigate the substrate scope of this heterogeneous copper(II)-catalyzed decarboxylative cyclization reaction under the optimized conditions. First, the substrate scope of pyridine ketones was examined by evaluating a variety of 2-benzoylpyridine derivatives and the results are listed in Table 2. As shown in Table 2, *para*-substituted 2-benzoylpyridines **1b-1j** bearing electron-donating or electron-withdrawing groups could undergo the decarboxylative cyclization with leucine (**2a**) smoothly to give the corresponding 3-

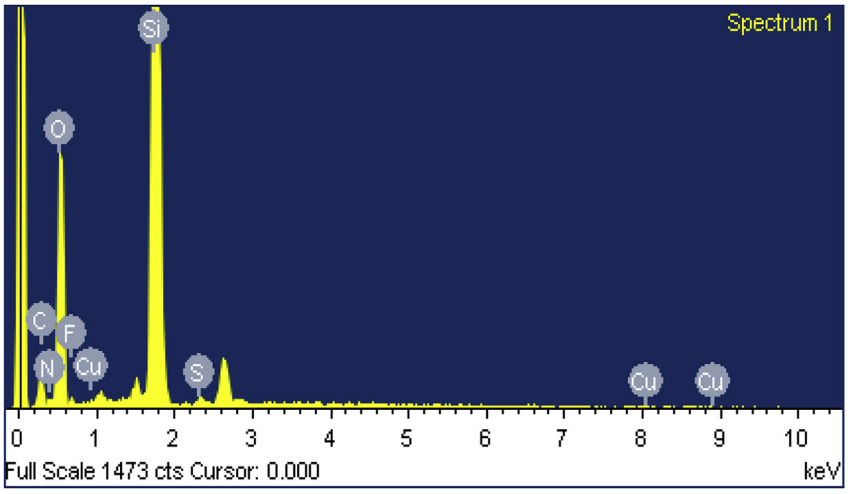
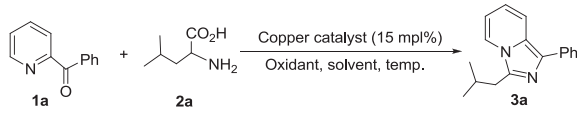


Fig. 5. EDS analysis of L-Proline-MCM-41-Cu(OTf)$_2$.

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



Entry	Copper catalyst	Oxidant	Solvent	Temp. (°C)	Yield (%)[b]
1	**A**	DTBP	Toluene	120	30
2	**B**	DTBP	Toluene	120	28
3	**C**	DTBP	Toluene	120	36
4	**D**	DTBP	Toluene	120	38
5	**E**	DTBP	Toluene	120	91
6	**F**	DTBP	Toluene	120	46
7	$Cu(OTf)_2$	DTBP	Toluene	120	92
8	–	DTBP	Toluene	120	38
9	**E**	TBHP	Toluene	120	67
10	**E**	BPO	Toluene	120	54
11	**E**	DTBP	dioxane	120	86
12	**E**	DTBP	DCE	120	69
13	**E**	DTBP	MeCN	120	67
14	**E**	DTBP	DMF	120	55
15	**E**	DTBP	Toluene	100	85
16	**E**	DTBP	Toluene	130	88
17[c]	**E**	DTBP	Toluene	120	79
18[d]	**E**	DTBP	Toluene	120	76
19[e]	**E**	DTBP	Toluene	120	92

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), copper catalyst (0.045 mmol), I_2 (0.045 mmol), oxidant (0.75 mmol) in solvent (2 mL), 120 °C, 12 h.
[b] Isolated yield.
[c] **2a** (0.6 mmol) was used.
[d] 8 mol% copper catalyst was used for 24 h.
[e] 30 mol% copper catalyst was used for 8 h.

isobutyl-1-arylimidazo[1,5-a]pyridines **3b-3j** in moderate to excellent yields. These results indicate that the electronic nature of the substituents on the benzene ring has limited influence on the heterogeneous copper(II)-catalyzed decarboxylative cyclization reaction. When *meta*-substituted 2-benzoylpyridines **1k-1l** or 3,5-disubstituted 2-benzoylpyridines **1m-1n** were used as substrates, the decarboxylative cyclization reaction also worked well to afford the desired products **3k-3n** in high yields. However, *ortho*-substituted 2-benzoylpyridine **1o** showed a relatively lower reactivity and gave the expected **3o** in only 75% yield. Notably, a heteroaryl containing pyridine ketone **1p** was compatible with the standard conditions and afforded the target product **3p** in 62% yield. Bulky naphthalene-1-yl(pyridine-2-yl)methanone **1q** proved to be also a good substrate and produced the cyclized product **3q** in 82% yield. In addition, when 2-benzoylquinoline **1r** was used as the substrate, the desired product **3r** was isolated in 81% yield. Unfortunately, when 1-(pyridin-2-yl)ethanone **1s** was employed as the substrate, no desired cyclized product was detected. Various functional groups such as methyl, methoxy, fluoro, chloro, trifluoromethyl, cyano, hydroxy, amide, ester and heteroaryl were tolerated well in this reaction.

Under the optimized reaction conditions, we next examined the scope of α-amino acids by using various aliphatic α-amino acids and α-aryl-substituted amino acids as substrates and the results are summarized in Table 3. The decarboxylative cyclization reactions of linear or branched aliphatic α-amino acids **2b-2d** with 2-benzoylpyridine **1a** proceeded effectively to give the corresponding cyclized products **3t-3v** in 73–83% yields. The reaction of phenylglycine **2e** with **1a** furnished the expected product **3w** in excellent yield. In addition, *para*- and *meta*-halogenated phenylglycines **2f-2h** were all compatible with the standard conditions and the reactions with **1a** afforded the desired products **3x-3z** in high yields. To further extend the utility of this heterogeneous copper(II)-catalyzed decarboxylative cyclization reaction, we next turned our attention to the reaction of phenylglycine **2e** with a variety of 2-benzoylpyridine derivatives. As shown in Table 3, the reactions of phenylglycine **2e** with 2-benzoylpyridines (**1b**, **1c**, **1f**, **1h**, **1k**, **1l** and **1o**) bearing various substituents, regardless of their electronic properties and substitution positions, generated the corresponding cyclized products **3a'-3g'** in 82–91% yields. 3,5-Disubstituted 2-benzoylpyridines proved to be also suitable substrates and the reactions with **2e** furnished the desired products **3h'-3l'** in high yields. Besides, the reaction of bulky naphthalene-1-yl(pyridine-2-yl)methanone **1q** with **2e** could give the cyclized product **3m'** in 89% yield. Finally, 2-benzoylquinoline **1r** was also successfully employed as a substrate to yield the corresponding product **3n'** in 84% yield. We also carried out the reaction of α-amino acids bearing a heteroaryl ring such as tryptophan and histidine with 2-benzoylpyridine **1a**, unfortunately, the formation of a complex mixture was observed.

2.3. Leaching test for L-Proline-MCM-41-Cu(OTf)$_2$

To determine whether the supported copper catalyst is actually functioning in a heterogeneous manner, or whether it is merely a reservoir for more active soluble forms of Cu, the heterogeneity of L-Proline-MCM-41-Cu(OTf)$_2$ was tested by hot filtration [67]. For this, the decarboxylative cyclization reaction of 2-benzoylpyridine **1a** with leucine **2a** was carried out until an approximately 30% conversion of **1a**. Then L-Proline-MCM-41-Cu(OTf)$_2$ was removed by filtration of the reaction mixture at 120 °C and the filtrate was allowed to react further at 120 °C for 10 h. In this case, no significant increase in conversion was observed, confirming that leached copper species from L-Proline-MCM-41-Cu(OTf)$_2$ (if any) are not responsible for the observed conversion. The determination of the copper content in the filtrate by ICP-AES analysis showed that no copper could be detected in the solution. These results indicated that L-Proline-MCM-41-Cu(OTf)$_2$ was stable during the decarboxylative cyclization reaction and is actually functioning in a heterogeneous manner.

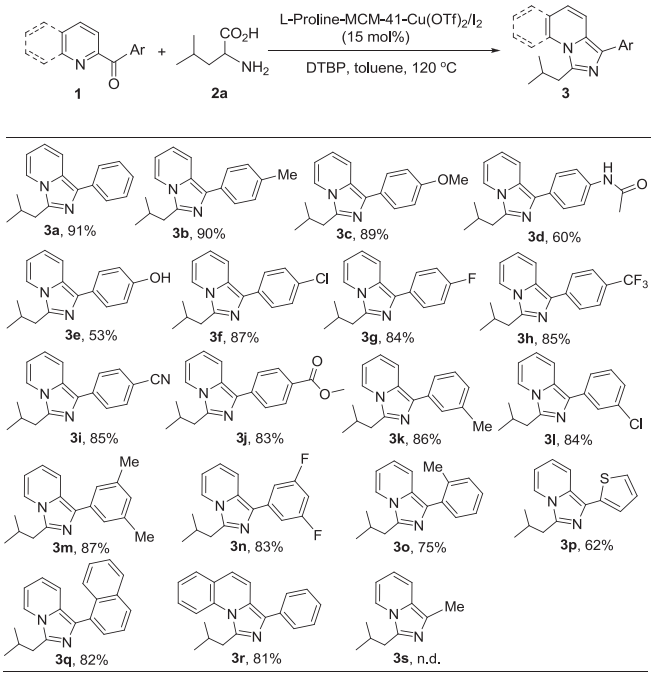
2.4. Possible mechanism for the heterogeneous copper-catalyzed decarboxylative cyclization reaction

A possible mechanism for the heterogeneous copper(II)-catalyzed decarboxylative cyclization reaction between 2-benzoylpyridines and α-amino acids is shown in Scheme 3. First, 2-benzoylpyridine **1a** undergoes a condensation reaction with α-amino acid **2** to give imine **A.** The deprotonation of the imine **A** in the presence of a nitrogen source as the base produces an organic acid anion, which then reacts with L-Proline-MCM-41-Cu(OTf)$_2$ to forms an MCM-41-immobilized L-Proline-Cu(II) carboxylate intermediate **B**. Subsequent decarboxylation of intermediate **B** generates intermediate **C**, which then undergoes an oxidative iodination to produce intermediate **D**. The C–Cu bond in intermediate **D** could dissociate by the aid of triflate anion to give the azomethine ylide-type intermediate **E** [68,69] and regenerate the L-Proline-MCM-41-Cu(OTf)$_2$ complex. Subsequently, the elimination of iodide anion from intermediate **E** provides intermediate **F** [30,32], which further isomerizes into intermediate **G**. Finally, the intramolecular cyclization of intermediate **G** happens to afford the cyclized intermediate **H** [70], which then undergoes an oxidative dehydrogenation and rearrangement to give 1,3-disubstituted imidazo[1,5-*a*]pyridine **3**.

2.5. Recycling of the catalyst

In order to check the stability and recyclability of L-Proline-MCM-41-Cu(OTf)$_2$, the decarboxylative cyclization between 2-

Table 2
Heterogeneous copper(II)-catalyzed decarboxylative cyclization of 2-benzoylpyridine derivatives **1** with leucine (**2a**).[a,b].



[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.9 mmol), L-Proline-MCM-41-Cu(OTf)$_2$ (0.045 mmol), I_2 (0.045 mmol), DTBP (0.75 mmol) in toluene (2 mL), 120 ºC, 12 h. [b] Isolated yield.

benzoylpyridine **1a** and phenylglycine **2e** as model reaction was investigated under the optimized conditions, and the results are summarized in Table 4. After carrying out the reaction, the reaction mixture was diluted with ethyl acetate. Filtration of the reaction mixture followed by washing of the resulting solid with ethanol allowed the easy recovery of L-Proline-MCM-41-Cu(OTf)$_2$. The recovered catalyst could be reused at least seven times, and almost consistent activity was observed. Besides, the copper content of the recovered catalyst after eight consecutive runs was determined to be 0.63 mmol g^{-1} by ICP-AES analysis, which showing almost the same Cu content as the fresh catalyst. In our opinion, the excellent catalytic behavior of the supported copper catalyst should be attributed to the efficient site isolation, to the optimal dispersion of the active sites on the inner channel walls and to the relatively strong interaction between bidentate L-Proline ligand and the copper centre anchored on the MCM-41.

3. Conclusions

In conclusion, we have developed an efficient heterogeneous copper(II)-catalyzed decarboxylative cyclization reaction between 2-benzoylpyridines and α-amino acids for construction of 1,3-disubstituted imidazo[1,5-*a*]pyridines, which are found in a number of drug-relevant molecules and biologically active agents. This heterogeneous decarboxylative cyclization has many attractive features, such as: (1) the substrate scope is broad, and a wide range of α-amino acids and 2-benzoylpyridine derivatives are allowed; (2) a variety of 1,3-disubstituted imidazo[1,5-*a*]pyridines were obtained in good to excellent yields; (3) the reaction has opened a new route to construct 3-alkyl-1-arylimidazo[1,5-*a*]pyridines, which are difficult to obtain by the existing protocols; (4) this new heterogeneous copper(II) catalyst can easily be prepared from commercially readily available and inexpensive reagents, and recovered from the reaction mixture by a simple filtration, and recycled up to eight times with almost consistent activity.

4. Experimental

4.1. General remarks

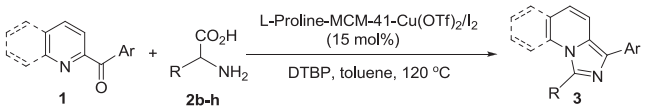
All chemicals were reagent grade and used as received without further purification. All solvents were dried and distilled before use. The products were purified by flash column chromatography on 230–400 mesh silica gel. A mixture of petroleum ether (60–90 °C) and ethyl acetate was generally used as eluent. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 NMR spectrometer (400 MHz or 100 MHz, respectively) in $CDCl_3$ as solvent. Melting points are uncorrected. X-ray powder diffraction patterns were recorded on Damx-rA (Riguka). Copper content was determined with a Jarrell-Ash 1100 ICP. The BET surface areas and pore analysis were performed using a ASAP2010 analyzer by nitrogen adsorption/desorption at 77.4 K. Samples were degassed at 413 K overnight before measurements. Energy dispersive X-ray spectroscopy (EDS) was obtained using a microscope. HRMS spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electrospray mode (ES). Mesoporous material MCM-41 [50] and pyridine ketones **1** [30] were prepared according to literature methods.

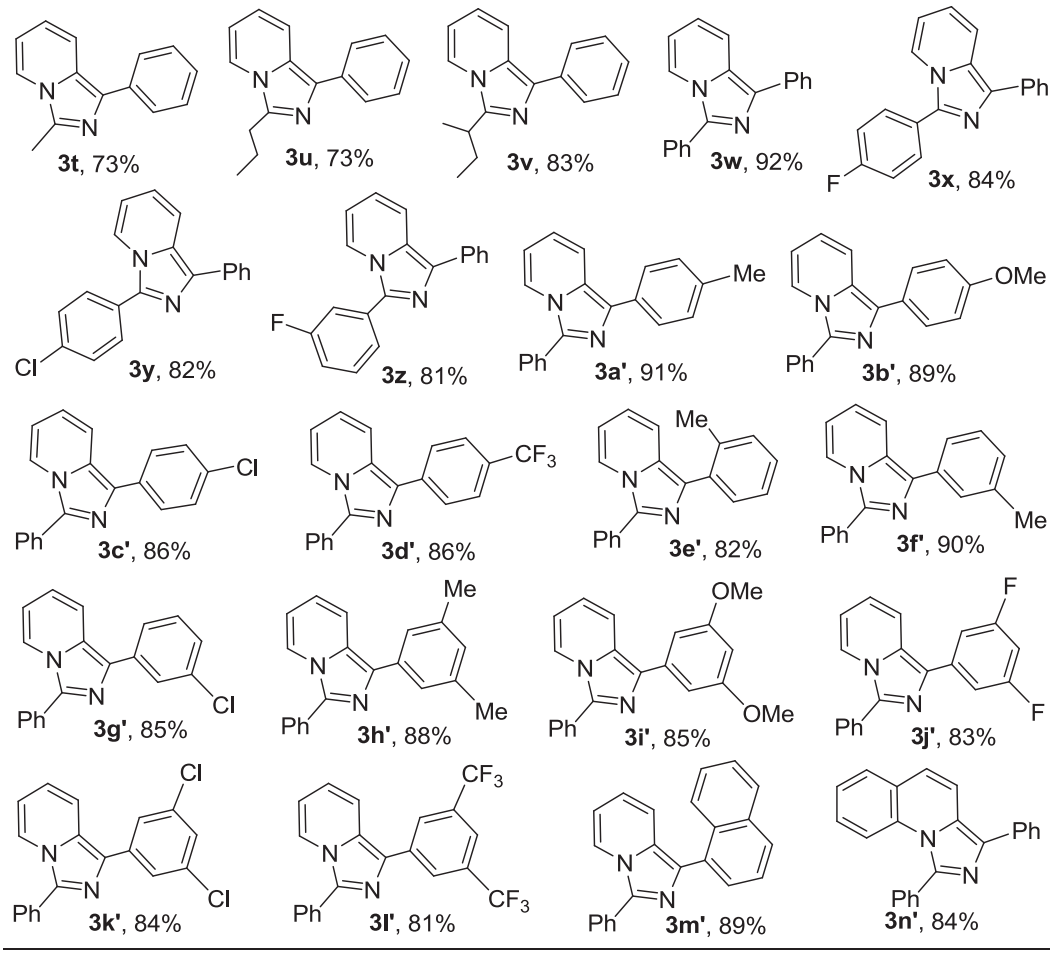
4.2. Synthesis of supported copper catalysts

4.2.1. Preparation of $ClCH_2$-MCM-41

To a suspension of 5.5 g of the MCM-41 in 140 mL of dry toluene was added a solution of 5.0 g of 4-(chloromethyl)phenyltrichlorosilane in 10 mL of dry toluene. The mixture was stirred for 24 h at 100 °C under Ar. The solid product was filtered and washed

Table 3
Heterogeneous copper(II)-catalyzed decarboxylative cyclization of 2-benzoylpyridine derivatives **1** with various α-amino acids.[a,b].





[a] Reaction conditions: **1** (0.3 mmol), **2** (0.9 mmol), L-Proline-MCM-41-Cu(OTf)$_2$ (0.045 mmol), I_2 (0.045 mmol), DTBP (0.75 mmol) in toluene (2 mL), 120 ºC, 12 h. [b] Isolated yield.

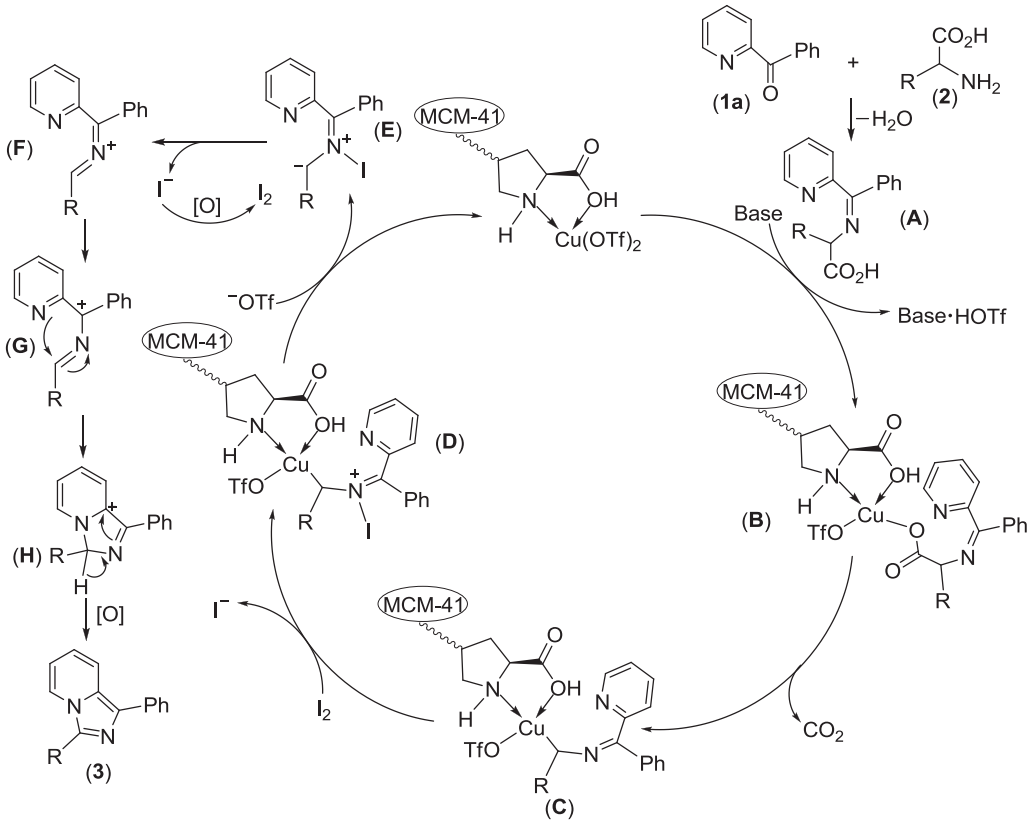
by $CHCl_3$ (20 mL), and dried in vacuum at 110 °C for 3 h. The dried white solid was then treated with dry ethanol (50 mL) at 80 °C for 5 h under Ar. The resulting solid was filtered, washed with diethyl ether (3 × 20 mL), and then soaked in a solution of 5.0 g of Me_3SiCl in 100 mL of dry toluene at 25 °C with stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried in vacuum at 130 °C for 5 h to obtain 7.45 g of hybrid material $ClCH_2$-MCM-41. The chlorine content was found to be 1.66 mmol/g by elemental analysis.

4.2.2. Preparation of L-Proline-MCM-41

To a solution of *N*-Boc-*trans*-4-hydroxy-L-proline (1.27 g, 5.5 mmol) in 100 mL of dry THF was added NaH (0.28 g, 11.6 mmol) and the reaction mixture was stirred at 25 °C for 2 h under Ar. Then 2.23 g of $ClCH_2$-MCM-41 was added and the mixture was refluxed for 24 h. After being cooled to room temperature, the solid product was filtered, washed with distilled water (2 × 20 mL), ethanol (2 × 20 mL), and dried in vacuum at 110 °C for 4 h. The dried white solid (1.553 g) was treated with TFA (8 mL) in CH_2Cl_2 (10 mL) at reflux for 3 h, then filtered, and washed with Et_3N (6 mL), CH_2Cl_2 (10 mL) and Et_2O (10 mL), and dried in vacuum at 110 °C for 4 h to afford 1.278 g of hybrid material L-Proline-MCM-41. The nitrogen content was found to be 1.08 mmol/g by elemental analysis.

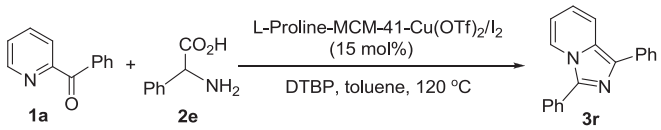
4.2.3. Preparation of L-Proline-MCM-41-Cu(OTf)$_2$

In a small Schlenk tube, 1.121 g of the above-functionalized MCM-41 (L-Proline-MCM-41) was mixed with 0.362 g (1.0 mmol) of $Cu(OTf)_2$ in 20 mL of acetone. The reaction mixture was stirred at room temperature for 12 h under Ar. The solid product was filtered by suction, washed with distilled water and acetone, and dried at 70 °C/26.7 Pa under Ar for 4 h to give 1.382 g of a pale blue powder copper complex [L-Proline-MCM-41-Cu(OTf)$_2$]. The nitrogen and copper contents were found to be 0.75 mmol/g and 0.64 mmol/g, respectively.



Scheme 3. Proposed catalytic cycle.

Table 4
The recycle of L-Proline-MCM-41-Cu(OTf)$_2$.[a]



Entry	Catalyst cycle	Time (h)	Yield [b] (%)	Entry	Catalyst cycle	Time (h)	Yield[b] (%)
1	1st (fresh)	12	92	5	5th	14	91
2	2nd	12	92	6	6th	14	90
3	3rd	12	91	7	7th	16	89
4	4th	12	90	8	8th	16	88

[a] Reaction conditions: **1a** (0.3 mmol), **2e** (0.9 mmol), L-Proline-MCM-41-Cu(OTf)$_2$ (0.045 mmol), I_2 (0.045 mmol), DTBP (0.75 mmol) in toluene (2 mL), 120 °C.
[b] Isolated yield.

The L-Proline-MCM-41-CuI [**A**], L-Proline-MCM-41-CuBr [**B**], L-Proline-MCM-41-$CuCl_2$ [**C**], L-Proline-MCM-41-$CuBr_2$ [**D**] and L-Proline-MCM-41-Cu(OAc)$_2$ [**F**] were also prepared by using L-Proline-MCM-41 (1.12 g) and the corresponding copper salts (1.0 mmol) as the starting materials in the same manner, the copper contents were determined to be 0.57 mmol g^{-1}, 0.53 mmol g^{-1}, 0.60 mmol g^{-1}, 0.59 mmol g^{-1}, and 0.66 mmol g^{-1}, respectively.

4.3. General procedure for the heterogeneous copper(II)-catalyzed synthesis of 1,3-disubstituted imidazo[1,5-a]pyridines

To a 10 mL reaction tube were added L-Proline-MCM-41-Cu(OTf)$_2$ (71 mg, 0.045 mmol), 2-benzoylpyridine **1** (0.3 mmol), amino acid **2** (0.9 mmol), molecular iodine (0.045 mmol), DTBP (0.75 mmol), and toluene (2 mL). The reaction tube was sealed and placed in an oil bath at room temperature. The reaction mixture was stirred at 120 °C for 12 h. After being cooled to room temperature, the reaction mixture was diluted with 15 mL of EtOAc, and filtered. The L-Proline-MCM-41-Cu(OTf)$_2$ complex was washed with EtOAc (2 × 5 mL) and ethanol (2 × 5 mL), and reused in the next run. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether: EtOAc = 15:1–20:1) to provide the desired product **3**.

4.3.1. 3-Isobutyl-1-phenylimidazo[1,5-a]pyridine (**3a**) [32]

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 7.2 Hz, 2H), 7.75–7.70 (m, 2H), 7.43 (t, J = 7.2 Hz, 2H), 7.25 (t, J = 7.0 Hz, 1H), 6.67 (t, J = 7.4 Hz, 1H), 6.51 (t, J = 6.4 Hz, 1H), 2.91 (d, J = 6.8 Hz, 2H), 2.30–2.23 (m, 1H), 1.01 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 135.2, 130.1, 128.7, 126.6, 126.4, 126.2, 121.1, 119.0,

118.6, 112.4, 35.5, 27.9, 22.7.

*4.3.2. 3-Isobutyl-1-(p-tolyl)imidazo[1,5-a]pyridine (**3b**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H), 7.72–7.68 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.66–6.62 (m, 1H), 6.50–6.46 (m, 1H), 2.89 (d, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.31–2.20 (m, 1H), 1.01 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 135.7, 132.5, 130.4, 129.4, 126.5, 126.1, 121.0, 119.1, 118.1, 112.2, 35.6, 27.9, 22.7, 21.2.

*4.3.3. 3-Isobutyl-1-(4-methoxyphenyl)imidazo[1,5-a]pyridine (**3c**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J = 6.8, 2.0 Hz, 2H), 7.71–7.65 (m, 2H), 6.98 (dd, J = 6.8, 2.0 Hz, 2H), 6.64–6.60 (m, 1H), 6.50–6.46 (m, 1H), 3.83 (s, 3H), 2.89 (d, J = 7.2 Hz, 2H), 2.29–2.22 (m, 1H), 1.01 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 138.2, 130.2, 128.1, 127.8, 125.7, 120.9, 119.1, 117.9, 114.2, 112.2, 55.3, 35.6, 27.9, 22.7.

*4.3.4. N-(4-(3-Isobutylimidazo[1,5-a]pyridin-1-yl)phenyl) acetamide (**3d**)*

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.0 Hz, 2H), 7.75–7.69 (m, 2H), 7.59 (d, J = 8.0 Hz, 2H), 6.73–6.68 (m, 1H), 6.55 (t, J = 6.6 Hz, 1H), 2.92 (d, J = 7.2 Hz, 2H), 2.29–2.22 (m, 1H), 2.18 (s, 3H), 1.01 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 138.5, 137.5, 136.2, 131.3, 129.7, 127.1, 121.1, 120.2, 119.1, 118.6, 112.5, 35.6, 27.9, 24.7, 22.7. HRMS calcd for $C_{19}H_{21}N_3O^+$ [M^+]: 307.1685, found 307.1677.

*4.3.5. 4-(3-Isobutylimidazo[1,5-a]pyridin-1-yl)phenol (**3e**)*

Light yellow solid. Mp 105–106 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.39 (s, 1H), 8.16 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.76–6.72 (m, 1H), 6.62 (t, J = 6.6 Hz, 1H), 2.89 (d, J = 7.2 Hz, 2H), 2.21–2.11 (m, 1H), 0.96 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.3, 138.1, 129.3, 127.5, 126.6, 125.0, 122.6, 119.0, 118.9, 116.0, 112.6, 34.8, 27.7, 22.8. HRMS calcd for $C_{17}H_{18}N_2O^+$ [M^+]: 266.1419, found 266.1413.

*4.3.6. 1-(4-Chlorophenyl)-3-isobutylimidazo[1,5-a]pyridine (**3f**)*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 9.2 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 6.73–6.68 (m, 1H), 6.54 (t, J = 7.4 Hz, 1H), 2.89 (d, J = 7.2 Hz, 2H), 2.29–2.22 (m, 1H), 1.02 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 133.9, 131.6, 129.0, 128.8, 127.6, 126.5, 121.2, 119.0, 118.7, 112.4, 35.6, 27.8, 22.7. HRMS calcd for $C_{17}H_{17}ClN_2^+$ [M^+]: 284.1080, found 284.1076.

*4.3.7. 1-(4-Fluorophenyl)-3-isobutylimidazo[1,5-a]pyridine (**3g**)*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.78 (m, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 9.6 Hz, 1H), 7.12 (t, J = 8.8 Hz, 2H), 6.71–6.67 (m, 1H), 6.53 (t, J = 6.6 Hz, 1H), 2.90 (d, J = 7.6 Hz, 2H), 2.30–2.23 (m, 1H), 1.02 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6 (d, $^1J_{C\text{-}F}$ = 243.5 Hz), 138.5, 131.5 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 129.3, 128.1 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 126.1, 121.1, 118.8, 118.6, 115.5 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 112.4, 35.6, 27.8, 22.6. HRMS calcd for $C_{17}H_{17}FN_2^+$ [M^+]: 268.1376, found 268.1385.

*4.3.8. 3-Isobutyl-1-(4-(trifluoromethyl)phenyl)imidazo[1,5-a] pyridine (**3h**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 2H), 7.78–7.74 (m, 2H), 7.66 (d, J = 8.0 Hz, 2H), 6.80–6.76 (m, 1H), 6.58 (t, J = 6.8 Hz, 1H), 2.91 (d, J = 7.6 Hz, 2H), 2.31–2.25 (m, 1H), 1.03 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 138.9, 128.5, 127.6 (q, $^2J_{C\text{-}F}$ = 32.1 Hz), 127.3, 126.2, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.5 (q, $^1J_{C\text{-}F}$ = 269.9 Hz), 121.4, 119.7, 118.6, 112.6, 35.5, 27.8, 22.6.

*4.3.9. 4-(3-Isobutylimidazo[1,5-a]pyridin-1-yl)benzonitrile (**3i**)*

Pale green solid. Mp 101–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 6.87–6.82 (m, 1H), 6.63 (t, J = 6.8 Hz, 1H), 2.91 (d, J = 7.2 Hz, 2H), 2.33–2.23 (m, 1H), 1.03 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 139.5, 132.4, 127.9, 127.8, 126.2, 121.7, 120.5, 119.6, 118.5, 112.8, 108.5, 35.5, 27.7, 22.6. HRMS calcd for $C_{18}H_{17}N_3^+$ [M^+]: 275.1422, found 275.1423.

*4.3.10. Methyl 4-(3-isobutylimidazo[1,5-a]pyridin-1-yl)benzoate (**3j**)*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.80–7.76 (m, 2H), 6.80–6.76 (m, 1H), 6.60–6.56 (m, 1H), 3.92 (s, 3H), 2.91 (d, J = 7.2 Hz, 2H), 2.33–2.22 (m, 1H), 1.02 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 139.9, 139.2, 130.7, 128.8, 127.5, 127.1, 125.8, 121.5, 119.8, 118.8, 112.6, 51.9, 35.5, 27.8, 22.6. HRMS calcd for $C_{19}H_{20}N_2O_2^+$ [M^+]: 308.1525, found 308.1520.

*4.3.11. 3-Isobutyl-1-(m-tolyl)imidazo[1,5-a]pyridine (**3k**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.70 (m, 3H), 7.63 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.70–6.65 (m, 1H), 6.51 (t, J = 6.8 Hz, 1H), 2.91 (d, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.30–2.22 (m, 1H), 1.01 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.3, 135.2, 130.4, 128.5, 127.4, 127.0, 126.4, 123.7, 121.1, 119.2, 118.3, 112.3, 35.6, 27.9, 22.7, 21.6.

*4.3.12. 1-(3-Chlorophenyl)-3-isobutylimidazo[1,5-a]pyridine (**3l**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (t, J = 1.8 Hz, 1H), 7.75–7.70 (m, 3H), 7.34 (t, J = 7.8 Hz, 1H), 7.22–7.18 (m, 1H), 6.75–6.71 (m, 1H), 6.56–6.52 (m, 1H), 2.89 (d, J = 7.2 Hz, 2H), 2.30–2.23 (m, 1H), 1.02 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 137.2, 134.6, 129.8, 128.6, 126.8, 126.3, 125.9, 124.4, 121.3, 119.3, 118.7, 112.5, 35.6, 27.8, 22.7.

*4.3.13. 1-(3,5-Dimethylphenyl)-3-isobutylimidazo[1,5-a]pyridine (**3m**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.70 (m, 2H), 7.48 (s, 2H), 6.91 (s, 1H), 6.68–6.63 (m, 1H), 6.50 (t, J = 6.8 Hz, 1H), 2.91 (d, J = 7.6 Hz, 2H), 2.38 (s, 6H), 2.29–2.22 (m, 1H), 1.01 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 138.1, 135.1, 130.5, 128.0, 126.3, 124.5, 121.1, 119.3, 118.2, 112.3, 35.6, 27.9, 22.6, 21.5.

*4.3.14. 1-(3,5-Difluorophenyl)-3-isobutylimidazo[1,5-a]pyridine (**3n**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 7.2 Hz, 1H), 7.74 (d, J = 9.6 Hz, 1H), 7.41–7.38 (m, 2H), 6.83–6.78 (m, 1H), 6.70–6.64 (m, 1H), 6.60 (t, J = 6.4 Hz, 1H), 2.90 (d, J = 7.2 Hz, 2H), 2.31–2.24 (m, 1H), 1.03 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4 (dd, $^1J_{C\text{-}F}$ = 244.9, 13.4 Hz), 138.9, 127.1, 121.4, 119.9, 118.5, 112.6, 108.7 (dd, $^2J_{C\text{-}F}$ = 18.7, 7.3 Hz), 101.0 (t, $^2J_{C\text{-}F}$ = 25.6 Hz), 35.5, 27.7, 22.6.

*4.3.15. 3-Isobutyl-1-(o-tolyl)imidazo[1,5-a]pyridine (**3o**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.2 Hz, 1H), 7.44–7.41 (m, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.31–7.28 (m, 1H), 7.26–7.22 (m, 2H), 6.63–6.58 (m, 1H), 6.52 (t, J = 6.2 Hz, 1H), 2.91 (d, J = 7.2 Hz, 2H), 2.40 (s, 3H), 2.32–2.26 (m, 1H), 1.03 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 137.3, 134.0, 130.8, 130.7, 130.3, 127.2, 127.0, 125.5, 120.7, 119.0, 117.6, 112.2, 35.6, 27.7, 22.7, 20.5.

*4.3.16. 3-Isobutyl-1-(thiophen-2-yl)imidazo[1,5-a]pyridine (**3p**)*

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.71 (m, 2H), 7.41–7.39 (m, 1H), 7.24–7.22 (m, 1H), 7.12–7.09 (m, 1H), 6.75–6.71 (m, 1H), 6.55 (t, J = 7.0 Hz, 1H), 2.90 (d, J = 7.6 Hz, 2H), 2.31–2.20 (m, 1H), 1.01 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 132.1, 128.8, 128.3, 127.5, 122.8, 121.7, 121.1, 119.0, 118.7, 112.5, 35.4, 27.9, 22.6. HRMS calcd for $C_{15}H_{16}N_2S^+$ [M^+]: 256.1034, found 256.1029.

*4.3.17. 3-Isobutyl-1-(naphthalen-1-yl)imidazo[1,5-a]pyridine (**3q**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31–8.28 (m, 1H), 7.90–7.87 (m, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 6.8 Hz, 1H), 7.67 (d, J = 6.8 Hz, 1H), 7.55–7.51 (m, 1H), 7.48–7.43 (m, 2H), 7.39 (d, J = 9.2 Hz, 1H), 6.63–6.53 (m, 2H), 2.98 (d, J = 7.2 Hz, 2H), 2.38–2.31 (m, 1H), 1.07 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 134.3, 132.2, 132.1, 129.7, 128.2, 127.9, 127.6, 127.5, 126.6, 126.0, 125.7, 125.4, 120.9, 119.1, 118.0, 112.4, 35.7, 27.8, 22.8.

*4.3.18. 1-Isobutyl-3-phenylimidazo[1,5-a]quinoline (**3r**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.59–7.53 (m, 2H), 7.50–7.41 (m, 3H), 7.36–7.26 (m, 2H), 6.90 (d, J = 9.2 Hz, 1H), 3.28 (d, J = 6.8 Hz, 2H), 2.46–2.40 (m, 1H), 1.10 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 135.0, 133.3, 132.3, 128.7, 128.5, 127.8, 127.4, 126.7, 126.3, 126.0, 124.8, 121.1, 117.7, 116.6, 41.1, 26.6, 22.6.

*4.3.19. 3-Methyl-1-phenylimidazo[1,5-a]pyridine (**3t**) [32].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 9.2 Hz, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 6.74–6.70 (m, 1H), 6.59–6.55 (m, 1H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$: δ 135.1, 134.9, 129.9, 128.7, 126.4, 126.2, 121.0, 119.0, 118.6, 112.6, 12.5.

*4.3.20. 1-Phenyl-3-propylimidazo[1,5-a]pyridine (**3u**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 8.2, 1.0 Hz, 2H), 7.75 (d, J = 9.2 Hz, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.27–7.23 (m, 1H), 6.71–6.66 (m, 1H), 6.54–6.50 (m, 1H), 3.00 (t, J = 7.6 Hz, 2H), 1.93–1.84 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 135.3, 130.1, 128.7, 126.5, 126.4, 126.1, 121.0, 119.1, 118.6, 112.4, 28.7, 20.7, 14.0.

*4.3.21. 3-(sec-Butyl)-1-phenylimidazo[1,5-a]pyridine (**3v**) [31].*

Pale green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 8.2, 1.0 Hz, 2H), 7.75–7.71 (m, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 6.68–6.63 (m, 1H), 6.51–6.47 (m, 1H), 3.15–3.06 (m, 1H), 2.07–1.97 (m, 1H), 1.83–1.69 (m, 1H), 1.45 (d, J = 7.2 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 135.5, 130.2, 128.7, 126.7, 126.4, 126.1, 120.9, 119.1, 118.4, 112.2, 33.1, 28.2, 18.3, 12.1.

*4.3.22. 1,3-Diphenylimidazo[1,5-a]pyridine (**3w**) [30].*

Yellow solid. Mp 111–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 7.2 Hz, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.85–7.82 (m, 3H), 7.53 (t, J = 7.4 Hz, 2H), 7.49–7.44 (m, 3H), 7.30 (t, J = 7.4 Hz, 1H), 6.80–6.76 (m, 1H), 6.56 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 135.0, 132.1, 130.2, 129.0, 128.8, 128.7, 128.4, 127.7, 126.8, 126.5, 121.8, 119.7, 119.2, 113.2.

*4.3.23. 3-(4-Fluorophenyl)-1-phenylimidazo[1,5-a]pyridine (**3x**) [32].*

Yellow solid. Mp 168–169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 6.8 Hz, 1H), 7.92 (d, J = 7.6 Hz, 2H), 7.84–7.76 (m, 3H), 7.46 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.21 (t, J = 8.0 Hz, 2H), 6.76 (t, J = 7.6 Hz, 1H), 6.56 (t, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, $^1J_{C\text{-}F}$ = 247.6 Hz), 137.2, 134.9, 132.0, 130.3 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 128.8, 127.7, 126.8, 126.6, 126.4 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 121.5, 119.7, 119.2, 116.1 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 113.4.

*4.3.24. 3-(4-Chlorophenyl)-1-phenylimidazo[1,5-a]pyridine (**3y**) [30].*

Yellow solid. Mp 172–173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 6.8 Hz, 2H), 7.83 (d, J = 9.2 Hz, 1H), 7.78 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.45 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 6.81–6.76 (m, 1H), 6.59 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 134.8, 134.7, 132.4, 129.5, 129.3, 128.8, 128.7, 127.9, 126.8, 126.7, 121.5, 119.8, 119.3, 113.6.

*4.3.25. 3-(3-Fluorophenyl)-1-phenylimidazo[1,5-a]pyridine (**3z**) [32].*

Yellow solid. Mp 150–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 9.2 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.59–7.56 (m, 1H), 7.52–7.44 (m, 3H), 7.31 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 8.8 Hz, 1H), 6.83–6.78 (m, 1H), 6.61 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (d, $^1J_{C\text{-}F}$ = 245.4 Hz), 136.7 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 134.8, 132.4, 132.3 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 130.6 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 128.8, 128.0, 126.9, 126.7, 123.7 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 121.6, 119.9, 119.3, 115.7 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 115.3 (d, $^2J_{C\text{-}F}$ = 22.8 Hz), 113.7.

*4.3.26. 3-Phenyl-1-(p-tolyl)imidazo[1,5-a]pyridine (**3a'**) [30].*

Yellow solid. Mp 133–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 7.2 Hz, 1H), 7.84–7.77 (m, 5H), 7.51 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 6.75–6.71 (m, 1H), 6.52 (t, J = 6.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 136.2, 132.2, 132.1, 130.3, 129.4, 129.0, 128.8, 128.3, 127.4, 126.8, 121.7, 119.4, 119.3, 113.2, 21.3.

*4.3.27. 1-(4-Methoxyphenyl)-3-phenylimidazo[1,5-a]pyridine (**3b'**) [30].*

Yellow solid. Mp 115–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 7.2 Hz, 1H), 7.86–7.81 (m, 4H), 7.76 (d, J = 9.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 6.74–6.70 (m, 1H), 6.52 (t, J = 6.2 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 137.8, 132.1, 130.3, 129.0, 128.7, 128.3, 128.1, 127.8, 127.1, 121.6, 119.2, 119.1, 114.3, 113.2, 55.4.

*4.3.28. 1-(4-Chlorophenyl)-3-phenylimidazo[1,5-a]pyridine (**3c'**)*

Yellow solid. Mp 138–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 7.2 Hz, 1H), 7.90–7.86 (m, 2H), 7.83–7.76 (m, 3H), 7.54 (t, J = 7.6 Hz, 2H), 7.48–7.40 (m, 3H), 6.83–6.79 (m, 1H), 6.59 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 133.6, 132.1, 130.8, 130.0, 129.1, 129.0, 128.9, 128.3, 127.9, 127.8, 121.9, 120.1, 118.9, 113.3. HRMS calcd for $C_{19}H_{13}ClN_2^+$ [M^+]: 304.0767, found 304.0769.

*4.3.29. 3-Phenyl-1-(4-(trifluoromethyl)phenyl)imidazo[1,5-a] pyridine (**3d'**) [32].*

Yellow solid. Mp 184–185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26–8.24 (m, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.85–7.80 (m, 3H), 7.70 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 8.0 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 6.88–6.84 (m, 1H), 6.61 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 138.6, 130.9, 130.3, 129.9, 128.8, 128.5, 128.4, 128.0 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 126.5, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.5 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 122.1, 120.8, 118.7, 113.4.

*4.3.30. 3-Phenyl-1-(o-tolyl)imidazo[1,5-a]pyridine (**3e'**) [32].*

Yellow solid. Mp 118–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 7.2 Hz, 2H), 7.54–7.48 (m, 3H), 7.45–7.41 (m, 2H), 7.35–7.31 (m, 1H), 7.30–7.26 (m, 2H), 6.73–6.68 (m, 1H), 6.57 (t, J = 6.8 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 137.5, 137.4, 133.6, 132.8, 130.8, 130.4, 129.0, 128.6, 128.5, 128.1, 127.5, 125.6, 121.5, 119.2, 118.9, 113.2, 20.6.

*4.3.31. 3-Phenyl-1-(m-tolyl)imidazo[1,5-a]pyridine (**3f'**) [32].*

Yellow solid. Mp 112–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 7.2 Hz, 1H), 7.84–7.78 (m, 4H), 7.70 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.46–7.41 (m, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.78–6.73 (m, 1H), 6.54 (t, J = 6.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.1, 134.9, 132.2, 130.3, 129.0, 128.8, 128.6, 128.4, 127.7, 127.6, 127.4, 123.9, 121.7, 119.5, 119.3, 113.2, 21.6.

*4.3.32. 1-(3-Chlorophenyl)-3-phenylimidazo[1,5-a]pyridine (**3g'**) [30].*

Yellow solid. Mp 131–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 7.2 Hz, 1H), 7.95 (t, J = 1.8 Hz, 1H), 7.83–7.80 (m, 4H), 7.54 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.26–7.23 (m, 1H), 6.85–6.81 (m, 1H), 6.59 (t, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 136.9, 134.7, 130.4. 130.0, 129.9, 129.1, 129.0, 128.4, 128.0, 126.6, 126.4, 124.6, 122.0, 120.4, 118.8, 113.4.

*4.3.33. 1-(3,5-Dimethylphenyl)-3-phenylimidazo[1,5-a]pyridine (**3h'**) [30].*

Yellow solid. Mp 125–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 7.2 Hz, 1H), 7.85–7.81 (m, 3H), 7.57–7.51 (m, 4H), 7.44 (t, J = 7.2 Hz, 1H), 6.95 (s, 1H), 6.77 (t, J = 7.4 Hz, 1H), 6.55 (t, J = 6.4 Hz, 1H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 138.0, 134.8, 132.3, 130.3, 129.0, 128.8, 128.4, 127.6, 124.7, 121.7, 119.4, 113.2, 21.5.

*4.3.34. 1-(3,5-Dimethoxyphenyl)-3-phenylimidazo[1,5-a]pyridine (**3i'**) [30].*

Yellow solid. Mp 178–179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 7.2 Hz, 1H), 7.86–7.81 (m, 3H), 7.53 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 2.0 Hz, 2H), 6.80–6.75 (m, 1H), 6.56 (t, J = 6.4 Hz, 1H), 6.44 (t, J = 2.2 Hz, 1H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 138.0, 136.9, 131.9, 130.2, 129.0, 128.9, 128.4, 127.9, 121.8, 119.9, 119.2, 113.3, 104.9, 99.2, 55.5.

*4.3.35. 1-(3,5-Difluorophenyl)-3-phenylimidazo[1,5-a]pyridine (**3j'**) [30].*

Yellow solid. Mp 164–165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27–8.25 (m, 1H), 7.84–7.81 (m, 3H), 7.56 (t, J = 7.6 Hz, 2H), 7.50–7.46 (m, 3H), 6.92–6.87 (m, 1H), 6.74–6.69 (m, 1H), 6.65–7.62 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5 (dd, $^1J_{C\text{-}F}$ = 244.8, 13.4 Hz), 138.6, 138.2, 129.8, 129.6, 129.2, 129.1, 128.4, 128.3, 122.2, 121.0, 118.6, 113.4, 109.0 (dd, $^2J_{C\text{-}F}$ = 18.8, 7.3 Hz), 101.5.

*4.3.36. 1-(3,5-Dichlorophenyl)-3-phenylimidazo[1,5-a]pyridine (**3k'**) [30].*

Yellow solid. Mp 188–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 7.2 Hz, 1H), 7.85–7.80 (m, 5H), 7.55 (t, J = 7.4 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.26–7.24 (m, 1H), 6.92–6.87 (m, 1H), 6.63 (t, J = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 138.0, 135.2, 129.7, 129.2, 129.1, 129.0, 128.4, 126.0, 124.6, 122.2, 121.1, 118.6, 113.5.

*4.3.37. 1-(3,5-Bis(trifluoromethyl)phenyl)-3-phenylimidazo[1,5-a] pyridine (**3l'**) [30].*

Yellow solid. Mp 134–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 2H), 8.29 (d, J = 7.2 Hz, 1H), 7.85–7.80 (m, 3H), 7.75 (s, 1H), 7.59–7.48 (m, 3H), 6.96 (t, J = 7.8 Hz, 1H), 6.68 (t, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 137.2, 132.0 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 129.6, 129.4, 129.2, 128.7, 128.4, 126.0, 123.6 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 122.4, 121.7, 119.4 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 118.2, 113.6.

*4.3.38. 1-(Naphthalen-1-yl)-3-phenylimidazo[1,5-a]pyridine (**3m'**) [30].*

Yellow solid. Mp 118–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.92–7.85 (m, 4H), 7.74 (d, J = 6.8 Hz, 1H), 7.57–7.51 (m, 3H), 7.49–7.41 (m, 4H), 6.71–6.67 (m, 1H), 6.57 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 134.3, 132.2, 131.8, 131.7, 130.4, 129.3, 129.0, 128.8, 128.3, 127.9, 127.8, 126.6, 126.1, 125.8, 125.5, 121.6, 119.3, 119.2, 113.4.

*4.3.39. 1,3-Diphenylimidazo[1,5-a]quinoline (**3n'**) [30].*

Yellow solid. Mp 136–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.2 Hz, 2H), 7.69–7.63 (m, 3H), 7.58 (d, J = 7.6 Hz, 1H), 7.54–7.42 (m, 6H), 7.34–7.23 (m, 2H), 7.14 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 134.6, 133.9, 133.8, 132.6, 129.8, 129.5, 128.9, 128.7, 128.5, 127.5, 127.0, 126.5, 125.8, 125.2, 122.0, 117.6, 117.5.

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