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ARTICLE

Cu(II)-promoted Tandem Decarboxylative Halogenation and Oxidative Diamination Reaction of 2-Aminopyridines with Alkynoic Acids for the Synthesis of 2-Haloimidazo[1,2-*a*]pyridines

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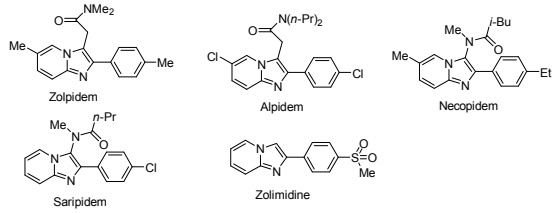
A copper-promoted cascade decarboxylative halogention and oxidative diamination reaction sequence of 2-aminopyridines with alkynoic acids has been developed for the synthesis of 2-haloimidazo[1,2-*a*]pyridines. In this reaction, two C-N bonds and one C-halogen bond are formed in one pot, generating the desired products in good yields. This is the first report for the synthesis of 2- haloimidazo [1,2-*a*]pyridine derivatives from alkynoic acids.

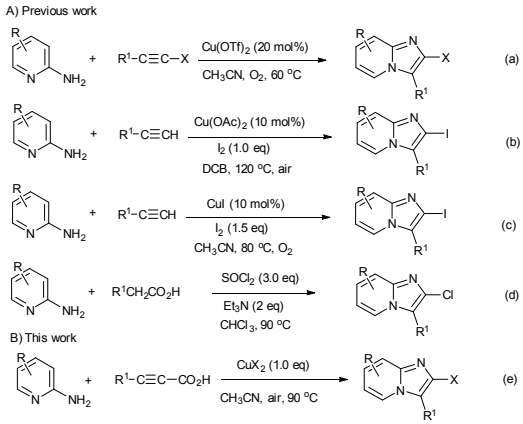
Introduction

Imidazo[1,2-*a*]pyridines are privileged heterocycles[1] due to their remarkable diversified biological activities and their widespread pharmaceutical use as inhibitors of virus,[2] cyclin-dependent kinase,[3] and human rhinovirus[4] et al.[5] Some of the representative imidazo[1,2-*a*]pyridine drugs in current use are shown in Scheme 1 and it is seen that all of them are 2-arylated derivatives. Furthermore, imidazo[1,2-*a*]pyridines have wide application in material science field.[6] Consequently, the synthesis of imidazo[1,2-*a*] pyridine derivatives has drawn much attention in the past decades.[7]



Scheme 1 Representative Imidazo[1,2-*a*]pyridine Drugs

2-Haloimidazo[1,2-*a*]pyridines represent an important class of imidazo[1,2-*a*]pyridine derivatives and can be transformed into the much interested 2-arylated derivatives via cross coupling reactions. However, there are only a few current synthetic protocols to these compounds and they mainly involve three routes: (i) copper-catalyzed oxidative cyclization of 2-aminopyridines with halogenated alkynes preprepared by oxidative halogenation of the terminal alkynes (Scheme 2a);[8] (ii) copper salt catalyzed cyclization of 2-aminopyridines with terminal alkynes in the presence of an equimolar amount of molecular iodine to afford 2-iodoimidazo[1,2-*a*]pyridines (Scheme 2b and 2c);[9] (iii) chlorocyclization of 2-aminopyridines with carboxylic acid under metal-free conditions (Scheme 2d).[10] However, there are some limitations and inconveniences to these protocols, such as the necessity of using prefunctionalized haloalkynes, restricted substituent type at C3 position of the imidazo[1,2-*a*]pyridine core, as well as limited halogen kinds. Therefore, more general synthetic protocols to these compounds are highly desired.



Scheme 2 Synthesis of 2-Haloimidazo[1,2-*a*]pyridines.

In recent years, transition metal-catalyzed decarboxylative coupling reaction has become a powerful tool to construct organic molecules.[11,12] Among this, alkynoic acid is a common coupling partner.[13] Herein, we report an efficient synthesis of 2-haloimidazo[1,2-*a*]pyridines via copper-promoted sequential decarboxylative halogenation and oxidative diamination

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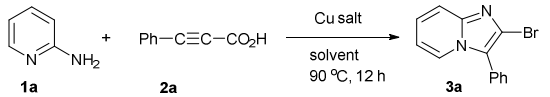
reaction of 2-aminopyridines with alkynoic acids (Scheme 2e). To the best of our knowledge, this is the first report for the synthesis of 2-haloimidazo[1,2-*a*]pyridines using alkynoic acids as the starting materials.

Results and Discussion

To begin our work, we chose 2-aminopyridine **1a** and phenylpropiolic acid **2a** as the model reactants for the optimization of reaction conditions (Table 1). Initially, by heating **1a** (0.5 mmol), **2a** (0.5 mmol), pyridine (1.0 mmol) and $CuBr_2$ (0.5 mmol) in 1,2-dichloroethane (DCE) at 90 °C in a sealed tube for 12 h, we got only trace amount of **3a** (entry 1). Using Et_3N, K_2CO_3 or Cs_2CO_3 as base respectively instead of pyridine in this reaction did not give any improvement. However, we found that when the amount of **1a** was increased to 3.0 equiv without adding additional base, **3a** was formed in 70% yield (entry 2). Based on this result, other solvents including DMF, benzene, dioxane and acetonitrile were tried, and acetonitrile provided the best result (entry 3-6). With acetonitrile as solvent, we employed 1.0 equiv of CuBr in place of $CuBr_2$ in the reaction, but only trace amount of **3a** was isolated (entry 7). To reduce the loading of copper salt, we attempted to use NaBr as bromine source in combination with 0.2 equiv of copper salts, but did not get satisfied result (entry 8-11). Carrying out the reaction without $CuBr_2$, no **3a** was formed (entry 12). Under O_2 atmosphere, **3a** was obtained in similar yield as that in the air, while using other oxidants as TBHP or DTBP led to decreased yields (entry 13-15). Besides, no better results were obtained by increasing the amount of $CuBr_2$ or lowering the reaction temperature (entry 16-17).

Table 1 Optimization of Reaction Conditions[a]



1a 2a 3a

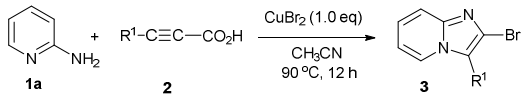
Entry	Solvent	Copper (eq.)	Oxidant (eq.)	Yield (%)[b]
1[c]	DCE	$CuBr_2$ (1)	air	trace
2	DCE	$CuBr_2$ (1)	air	70
3	DMF	$CuBr_2$ (1)	air	48
4	C_6H_6	$CuBr_2$ (1)	air	62
5	Dioxane	$CuBr_2$ (1)	air	51
6	CH_3CN	$CuBr_2$ (1)	air	78
7	CH_3CN	CuBr (1)	air	trace
8[d]	CH_3CN	$CuBr_2$ (0.2)	air	72
9[d]	CH_3CN	$CuCl_2$ (0.2)	air	70
10[d]	CH_3CN	$Cu(OAc)_2$ (0.2)	air	55
11[d]	CH_3CN	$Cu(OTf)_2$ (0.2)	air	61
12	CH_3CN	none	air	0
13	CH_3CN	$CuBr_2$ (1)	O_2	77
14	CH_3CN	$CuBr_2$ (1)	TBHP (2)	28
15	CH_3CN	$CuBr_2$ (1)	DTBP (2)	25
16	CH_3CN	$CuBr_2$ (1.2)	air	78
17[e]	CH_3CN	$CuBr_2$ (1)	air	53

[a] Conditions: **1a** (1.5 mmol), **2a** (0.5 mmol), copper salt, oxidant, heating in solvent (5 mL) at 90 °C for 12 h in a sealed tube. [b] Isolated yield. [c] Using 0.5 mmol of **1a**, adding 1.0 mmol of pyridine. [d] Adding 2.0 equiv of NaBr. [e] Heating at 60 °C.

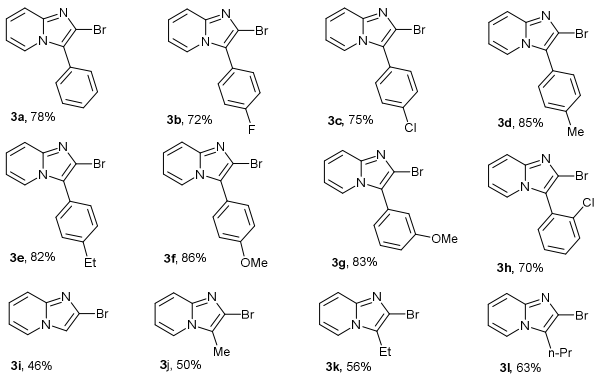
Therefore, the optimal reaction conditions were set to heating **1a** (1.5 mmol) and **2a** (0.5 mmol) in acetonitrile at 90 °C for 12 h in the presence of 1.0 equiv of $CuBr_2$.

With the optimal conditions in hand, we then investigated the scope of alkynoic acids (Table 2). It showed that either steric or electronic effect is not important to this reaction and various alkynoic acids **2** reacted with **1a** well. For instance, aryl alkynoic acids attached with F, Cl, Me, Et or OMe group at *para*-position of benzene ring led to **3b**-**3f** in 72%-86% yields. Similarly, aryl alkynoic acids bearing *meta*- or *ortho*-substituent on the benzene ring afforded **3g** and **3h** in good yields. Additionally, aliphatic alkynoic acids afforded 3-unsubstituted and 3-alkylated 2-haloimidazo[1,2-a]pyridines **3i**-**3l** in moderate to good yields which are difficultly prepared before. Compared to previous examples using terminal alkynes or halogenated alkynes as reactants which generally led to 2-haloimidazo[1,2-*a*]pyridines with aryl or bulky alkyl at C3 position,[8,9] this protocol showed more broad product scope mainly due to the fact that alkynoic acids have higher boiling point than the corresponding terminal alkynes and haloalkynes, and are easy to handle at higher reaction temperature.

Table 2 Scope of Alkynoic acids[a,b]



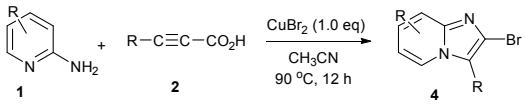
1a 2 3



[a] Conditions: **1a** (1.5 mmol), **2** (0.5 mmol), $CuBr_2$ (0.5 mmol), heating in CH_3CN (5 mL) at 90 °C for 12 h in a sealed tube. [b] Isolated yield.

Next, the scope of 2-aminopyridines was examined. As shown in table 3, a range of 2-aminopyridine derivatives with different substituents (F, Cl or Me) on the pyridine ring were compatible with this reaction, furnishing products **4a**-**4g** in 76% to 87% yields. 2-Aminoquinoline was also proven to be good reactant and afforded **4h** in 82% yield. Besides, the reactions of 2-aminopyridine derivatives with aliphatic alkynoic acids resulted in products **4i**-**4p** in 48% to 71% yields.

Table 3 Scope of 2-Aminopyridines[a,b]



1 2 4

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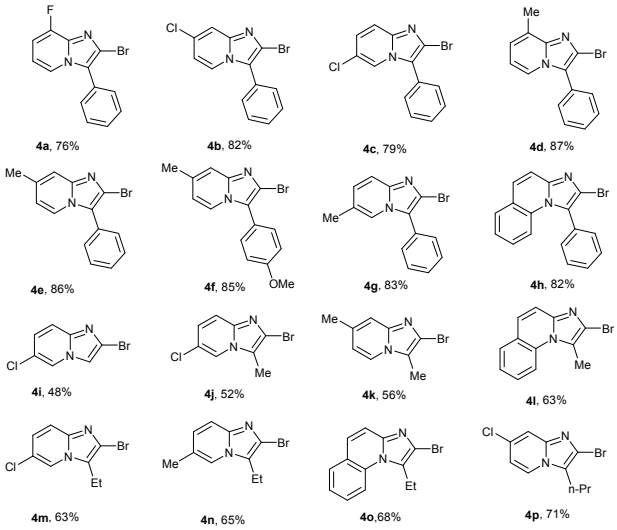
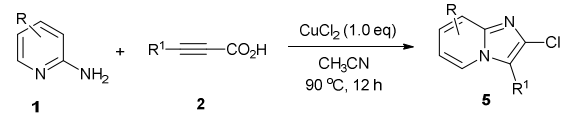
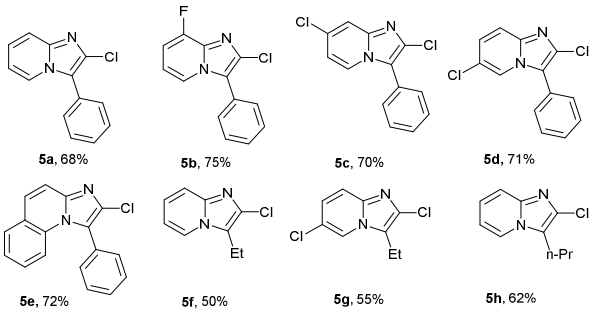


[a] Conditions: **1** (1.5 mmol), **2** (0.5 mmol), $CuBr_2$ (0.5 mmol), heating in CH_3CN (5 mL) at 90 °C for 12 h in a sealed tube. [b] Isolated yield.

To expand the reaction scope further, we subsequently surveyed $CuCl_2$-promoted reaction of 2-aminopyridines **1** with alkynoic acids **2**, to synthesize chlorinated products (Table 4). Pleasingly, aryl propionic acids participating in this reaction smoothly, resulting in 2-chloroimidazo[1,2-*a*]pyridines **5a**-**5e** in 68% to 75% yields. Meanwhile, aliphatic propiolic acids gave the chlorinated products **5f**-**5h** in good yields under the standard conditions.

Table 4 Synthesis of 2-Chloroimidazo[1,2-*a*]pyridines[a,b]

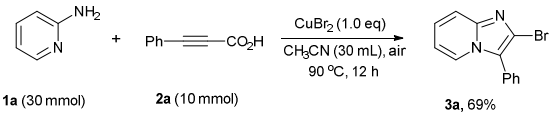




[a] Conditions: **1** (1.5 mmol), **2** (0.5 mmol), $CuCl_2$ (0.5 mmol), heating in CH_3CN (5 mL) at 90 °C for 12 h in a sealed tube. [b] Isolated yield.

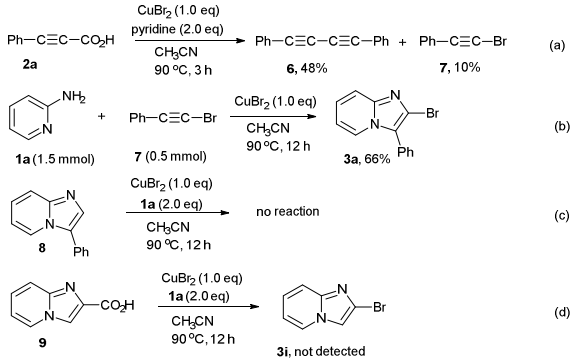
Noteworthily, this reactions could be carried out on enlarged gram scale. For example, the reaction of **1a** (30 mmol, 2.82 g), **2a** (10 mmol, 1.46 g) and $CuBr_2$ (10 mmol, 2.21 g) under the optimal conditions resulted in 1.87 g **3a**, that is, a 69% yield (Scheme 3).

To shed light on the reaction mechanism, we carried out several control experiments. First, exposing **2a** with $CuBr_2$ and



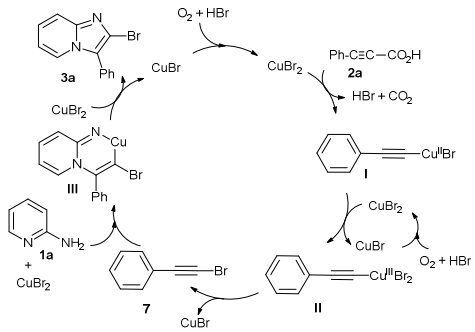
Scheme 3 Gram Scale Synthesis

pyridine in acetonitrile for 3 h afforded alkyne dimerization product **6** and bromoalkyne **7** stimutanously (Scheme 4a). Meanwhile, **7** could generate **3a** in 66% yield under the optimal conditions (Scheme 4b). These result raised the possibility of bromoalkyne **7** as the reaction intermediate. Second, no reaction occurred by prolonged heating of 3-phenylimidazo[1,2-*a*]pyridine **8**[14] with 2-aminopyridine **1a** and $CuBr_2$ in acetonitrile (Scheme 4c). This illustrated that the reaction did not proceed via bromination of an intermediate product **8**. Finally, the reaction of imidazo[1,2-*a*]pyridine-2-carboxylic acid **9** with $CuBr_2$ and **1a** did not lead to **3i**, which dispelled the pathway of first diamination of alkynoic acid followed by decarboxylative bromination (Scheme 4d).



Scheme 4 Control Experiments.

Based on these experimental results and previous literature,[8,15] a plausible mechanism was suggested (Scheme 5). At first, the reaction of alkynoic acid **2a** with $CuBr_2$ leads to intermediate **I**, dispelling HBr and CO_2 molecules. Next, intermediate **I** is oxidized to the Cu^{III} species **II,** which undergoes reductive elimination to afford bromoalkyne **7** in situ.[16] A $CuBr_2$-promoted diamination of **7** generates intermediate **III**, which occurs oxidation to Cu^{III} and reductive elimination again to give the final product **3a**.



Scheme 5 Possible Mechanism.

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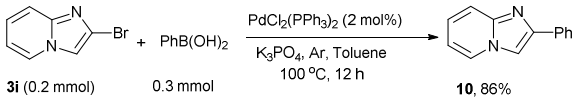
To demonstrate the utility of these halogenated imidazo[1,2-*a*]pyridines, we attempted to synthesize 2-phenylimidazo[1,2-*a*]pyridine **10** from **3i** via Suzuki reaction. As we expected, by heating **3i**, phenyl boronic acid (1.5 equiv) at 100 °C under Ar atmosphere with 2 mol% of $PdCl_2(PPh_3)_2$ as catalyst, we obtained product **10** in 86% yield (Scheme 6).



Scheme 6 Synthesis of 2-Phenylimidazo[1,2-*a*]pyridine

Conclusions

In summary, we have developed a versatile Cu(II)-promoted reaction of 2-aminopyridines with alkynoic acids for the synthesis of 2-haloimidazo[1,2-*a*]pyridines. In this reaction, two C-N bond and one C-halogen bond are formed in one pot and 2-haloimidazo[1,2-*a*]pyridines were formed in moderate to high yields. With this protocol, 2-bromo and 2-chloro imidazo[1,2-*a*]pyridines with diversified 3-aryl or alkyl group can be selectively synthesized. We believed that this protocol may open up a new way to the synthesis of other halogenated heterocycles using alkynoic acids as coupling partner and copper halide as halogen source.

Experimental

General: Melting points are uncorrected. ^{1}H NMR spectra were measured on 400 MHz with $CDCl_3$ as solvent. The chemical shifts (δ) are reported in parts per million relative to the residual deuterated solvent signal, and coupling constants (J) are given in Hertz. ^{13}C NMR spectra were measured on 100 MHz with $CDCl_3$ as solvent. HRMS (ESI) data were obtained in the electron impact (EI) mode.

Alkynoic acids 2 were prepared according to literature 13c.

3-(4-Fluorophenyl)propiolic acid (2b) Yellow solid, mp 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, J = 8.4 Hz, 2H), 7.60–7.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (d, J = 253 Hz), 158.0, 135.6 (d, J = 9 Hz), 116.2 (d, J = 22 Hz), 115.3 (d, J = 3 Hz), 87.8, 80.1. HRMS (ESI) *m/z* calcd for $C_9H_4FO_2$ [M-H]$^-$ 163.0196, found 163.0195.

3-(4-Chlorophenyl)propiolic acid (2c) Yellow solid, mp 169–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 137.3, 134.3, 129.0, 117.7, 86.7, 80.9. HRMS (ESI) *m/z* calcd for $C_9H_4ClO_2$ [M-H]$^-$ 178.9900, found 178.9893.

3-(*p*-Tolyl)propiolic acid (2d) Yellow solid, mp 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 7.19 (d, J = 8.0 Hz, 2H), 8.50 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 141.9, 133.3, 129.4, 116.0, 89.5, 79.9, 21.8. HRMS (ESI) *m/z* calcd for $C_{10}H_7O_2$ [M-H]$^-$ 159.0446, found 159.0430.

3-(4-Ethylphenyl)propiolic acid (2e) Yellow solid, mp 104–106 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J = 7.6 Hz, 3H), 2.68 (q, J = 7.6 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 148.0, 133.4, 128.3, 116.2, 89.4, 79.8, 29.0, 15.1. HRMS (ESI) *m/z* calcd for $C_{11}H_9O_2$ [M-H]$^-$ 173.0603, found 173.0603.

3-(4-Methoxyphenyl)propiolic acid (2f) Yellow solid, mp 140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.89 (d, J = 9.2 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 158.2, 135.3, 114.4, 110.9, 89.8, 79.7, 55.4. HRMS (ESI) *m/z* calcd for $C_{10}H_7O_3$ [M-H]$^-$ 175.0395, found 175.0406.

3-(3-Methoxyphenyl)propiolic acid (2g) Yellow solid, mp 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 7.01–7.04 (m, 1H), 7.1–7.12 (m, 1H), 7.20 (td, J = 7.6, 1.2 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 158.2, 129.8, 125.8, 120.0, 118.1, 117.6, 88.8, 79.8, 55.4. HRMS (ESI) *m/z* calcd for $C_{10}H_7O_3$ [M-H]$^-$ 175.0395, found 175.0395.

3-(2-Chlorophenyl)propiolic acid (2h) Yellow solid, mp 127–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (td, J = 7.6, 1.2 Hz, 1H), 7.40–7.45 (m, 2H), 7.63 (dd, J = 7.6, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 137.6, 134.8, 131.9, 129.6, 126.6, 119.4, 84.7, 84.1. HRMS (ESI) *m/z* calcd for $C_9H_4ClO_2$ [M-H]$^-$ 178.9900, found 178.9899.

General Procedure for the Preparation of 2-Bromo- imidazo[1,2-*a*]pyridine 3:

2-Aminopyridine **1a** (1.5 mmol), alkynoic acid **2** (0.5 mmol) and $CuBr_2$ (0.5 mmol) were mixed in 5 mL of CH_3CN and heated at 90 °C for 12 h in a sealed tube. After completion of the reaction, the mixture was cooled and separated by flash column chromatography (ethyl acetate/hexane) on silica gel to afford product **3**.

2-Bromo-3-phenylimidazo[1,2-*a*]pyridine (3a) White solid, mp 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (td, J = 6.8, 1.6 Hz, 1H), 7.20–7.24 (m, 1H), 7.47–7.48 (m, 1H), 7.55–7.60 (m, 5H), 8.11 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 129.7, 129.3, 129.0, 127.6, 125.2, 123.2, 122.3, 117.3, 113.0. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}BrN_2$ [M+H]$^+$ 273.0027, found 273.0020.

2-Bromo-3-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (3b) White solid, mp 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (d, J = 6.8 Hz, 1H), 7.23–7.27 (m, 3H), 7.52–7.61 (m, 3H), 8.04 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J = 248 Hz), 144.6, 131.7 (d, J = 8.0 Hz), 125.2, 123.6, 123.5, 123.0, 122.4, 121.3, 117.4, 116.5 (d, J = 21.7 Hz), 113.2. HRMS (ESI) *m/z* calcd for $C_{13}H_9BrFN_2$ [M+H]$^+$ 290.9933, found 290.99218.

2-Bromo-3-(4-chlorophenyl)imidazo[1,2-*a*]pyridine (3c) White solid, mp 178–179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (dd, J = 7.2, 2.0 Hz, 1H), 7.48–7.60 (m, 6H), 8.07 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 134.6, 131.8, 129.6, 129.4, 129.3, 129.2, 126.7, 123.6, 120.1, 116.2, 114.7. HRMS (ESI) *m/z* calcd for $C_{13}H_8BrClN_2Na$ [M+Na]$^+$ 328.9457, found 328.9456.

2-Bromo-3-*p*-tolylimidazo[1,2-*a*]pyridine (3d) Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 6.79 (t, J = 6.8 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 9.2 Hz, 1H), 8.09 (d, J =7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 139.1, 129.9, 129.6, 125.0, 124.6, 123.3, 122.3, 122.1, 117.3, 112.9, 21.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2$ [M+H]$^+$ 287.0184, found 287.0182.

2-Bromo-3-(4-ethylphenyl)imidazo[1,2-*a*]pyridine (3e) Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J = 7.6 Hz, 3H), 2.73 (q, J = 7.6 Hz, 2H), 6.77 (td, J = 6.8, 0.8 Hz, 1H), 7.19 (td, J = 7.6, 0.8 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 144.3, 129.5, 128.6, 124.9, 124.6, 123.3, 122.2,

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121.9, 117.1, 112.8, 28.7, 15.3. HRMS (ESI) *m/z* calcd for $C_{15}H_{14}BrN_2$ $[M+H]^+$ 301.0340, found 301.0348.

2-Bromo-3-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (3f) White solid, mp 111–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 6.79 (td, J = 6.8, 1.2 Hz, 1H), 7.08 (d, J = 6.8 Hz, 2H), 7.18–7.23 (m, 1H), 7.47 (d, J = 6.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 1H), 8.05 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 144.4, 131.2, 124.9, 123.2, 122.1, 119.6, 117.2, 114.7, 112.9, 55.4. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2O$ $[M+H]^+$ 303.0133, found 303.0139.

2-Bromo-3-(3-methoxyphenyl)imidazo[1,2-*a*]pyridine (3g) White solid, mp 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.89 (td, J = 6.8, 0.8 Hz, 1H), 7.00 (dd, J = 8.0, 2.4 Hz, 1H), 7.10–7.15 (m, 2H), 7.19–7.24 (m, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 8.15 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 144.6, 130.3, 128.8, 125.2, 123.4, 122.2, 122.1, 121.7, 117.3, 115.3, 114.5, 113.0, 55.4. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2O$ $[M+H]^+$ 303.0133, found 303.0132.

2-Bromo-3-(2-chlorophenyl)imidazo[1,2-*a*]pyridine (3h) White solid, mp 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (td, J = 6.8, 0.8 Hz, 1H), 7.25–7.29 (m, 1H), 7.43–7.52 (m, 3H), 7.58–7.67 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 135.4, 133.9, 131.2, 130.2, 127.4, 126.7, 125.4, 124.3, 123.3, 120.3, 117.1, 112.8. HRMS (ESI) *m/z* calcd for $C_{13}H_9BrClN_2$ $[M+H]^+$ 306.9638, found 306.9646.

2-Bromoimidazo[1,2-*a*]pyridine (3i) White solid, mp 80–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (t, J = 6.8 Hz, 1H), 7.19–7.23 (m, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.57 (s, 1H), 8.06 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 125.4, 125.0, 122.1, 117.0, 113.2, 111.5. HRMS (ESI) *m/z* calcd for $C_7H_6BrN_2$ $[M+H]^+$ 196.9714, found 196.9717.

2-Bromo-3-methylimidazo[1,2-*a*]pyridine (3j) White solid, mp 100–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 6.87 (t, J = 6.8 Hz, 1H), 7.19 (dd, J = 8.0, 0.8 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 124.0, 122.8, 121.7, 117.5, 117.0, 112.7, 8.8. HRMS (ESI) *m/z* calcd for $C_8H_8BrN_2$ $[M+H]^+$ 210.9871, found 201.9879.

2-Bromo-3-ethylimidazo[1,2-*a*]pyridine (3k) Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J = 7.6 Hz, 3H), 2.94 (q, J = 7.6 Hz, 2H), 6.85 (t, J = 6.8 Hz, 1H), 7.17 (td, J = 8.0, 1.2 Hz, 1H), 7.54 (d, J = 9.2 Hz, 1H), 7.90 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 123.9, 122.9, 122.7, 121.0, 117.2, 112.6, 16.8, 11.6. HRMS (ESI) *m/z* calcd for $C_9H_{10}BrN_2$ $[M+H]^+$ 225.0027, found 225.0029.

2-Bromo-3-propylimidazo[1,2-*a*]pyridine (3l) Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.6 Hz, 3H), 1.68 (q, J = 7.6 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 6.85 (td, J = 6.8, 0.8 Hz, 1H), 7.15–7.19 (m, 1H), 7.54 (d, J = 9.2 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 123.9, 122.8, 121.9, 121.6, 117.2, 112.6, 25.1, 20.5, 13.7. HRMS (ESI) *m/z* calcd for $C_{10}H_{12}BrN_2$ $[M+H]^+$ 239.0184, found 239.0181.

General Procedure for the Preparation of 2-Bromoimidazo[1,2-*a*]pyridine 4:

2-Aminopyridine **1** (1.5 mmol), alkynoic acid **2** (0.5 mmol) and $CuBr_2$ (0.5 mmol) were mixed in 5 mL of CH_3CN and heated at 90 °C for 12 h in a sealed tube. After completion of the reaction, the mixture was cooled and separated by flash column chromatography (ethyl acetate/hexane) on silica gel to afford product **4**.

2-Bromo-8-fluoro-3-phenylimidazo[1,2-*a*]pyridine (4a) White solid, mp 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74–6.76 (m, 1H), 6.92–6.96 (m, 1H), 7.49–7.58 (m, 5H), 7.93 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9 (d, J = 254 Hz), 137.2 (d, J = 28.2 Hz), 129.7, 129.4, 129.3, 127.2, 124.0, 122.3, 119.7, 119.6, 112.2, 112.1, 107.8 (d, J = 26.1 Hz). HRMS (ESI) *m/z* calcd for $C_{13}H_9BrFN_2$ $[M+H]^+$ 290.9933, found 290.9922.

2-Bromo-7-chloro-3-phenylimidazo[1,2-*a*]pyridine (4b) White solid, mp 127–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (dd, J = 7.6, 2.0 Hz, 1H), 7.47–7.60 (m, 6H), 8.03 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 131.8, 129.6, 129.4, 129.3, 127.1, 123.6, 122.9, 122.7, 116.1, 114.7. HRMS (ESI) *m/z* calcd for $C_{13}H_9BrClN_2$ $[M+H]^+$ 306.9638, found 306.9639.

2-Bromo-6-chloro-3-phenylimidazo[1,2-*a*]pyridine (4c) White solid, mp 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J = 9.6, 1.6 Hz, 1H), 7.51–7.60 (m, 6H), 8.13 (d, J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 129.6, 129.5, 129.4, 127.0, 126.5, 123.0, 122.9, 121.6, 121.1, 117.7. HRMS (ESI) *m/z* calcd for $C_{13}H_9BrClN_2$ $[M+H]^+$ 306.9638, found 306.9646.

2-Bromo-8-methyl-3-phenylimidazo[1,2-*a*]pyridine (4d) White solid, mp 147–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H), 6.72 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 6.8 Hz, 1H), 7.46–7.56 (m, 5H), 7.98 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 129.7, 129.2, 128.9, 127.9, 127.2, 124.1, 122.6, 121.6, 121.1, 113.0, 17.0. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2$ $[M+H]^+$ 287.0184, found 287.0188.

2-Bromo-7-methyl-3-phenylimidazo[1,2-*a*]pyridine (4e) White solid, mp 142–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 6.63 (d, J = 7.2 Hz, 1H), 7.35 (s, 1H), 7.46–7.56 (m, 5H), 8.00 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 136.4, 129.6, 129.2, 128.8, 127.8, 122.5, 121.8, 121.6, 115.7, 115.6, 21.3. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2$ $[M+H]^+$ 287.0184, found 287.0181.

2-Bromo-3-(4-methoxyphenyl)-7-methylimidazo[1,2-*a*]pyridine (4f) White solid, mp 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.88 (s, 3H), 6.61 (dd, J = 6.8, 1.2 Hz, 1H), 7.06 (dt, J = 8.8, 2.0 Hz, 2H), 7.32 (s, 1H), 7.46 (dt, J = 8.8, 2.0 Hz, 2H), 7.93 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 144.8, 136.0, 131.1, 122.5, 121.6, 119.9, 115.6, 115.4, 114.7, 55.4, 21.3. HRMS (ESI) *m/z* calcd for $C_{15}H_{14}BrN_2O$ $[M+H]^+$ 317.0290, found 317.0281.

2-Bromo-6-methyl-3-phenylimidazo[1,2-*a*]pyridine (4g) White solid, mp 107–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 7.06 (dd, J = 6.8, 1.2 Hz, 1H), 7.47–7.50 (m, 2H), 7.55–7.56 (m, 4H), 7.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 129.7, 129.2, 128.9, 128.3, 127.9, 122.8, 121.9, 121.8, 120.9, 116.6, 18.3. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}BrN_2$ $[M+H]^+$ 287.0184, found 287.0189..

2-Bromo-1-phenylimidazo[1,2-*a*]quinoline (4h) White solid, mp 129–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (td, J = 8.4, 1.2 Hz, 1H), 7.33–7.36 (m, 2H), 7.47–7.59 (m, 7H), 7.73 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 133.3, 131.2, 130.8, 129.6, 129.3, 129.2, 128.2, 127.2, 125.5, 124.9, 124.3, 122.8, 116.6. HRMS (ESI) *m/z* calcd for $C_{17}H_{12}BrN_2$ $[M+H]^+$ 323.0184, found 323.0180.

2-Bromo-6-chloroimidazo[1,2-*a*]pyridine (4i) White solid, mp 173–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 9.6, 2.0 Hz, 1H), 7.51 (d, J = 9.6 Hz, 1H), 7.53 (s, 1H), 8.12 (d, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 126.7, 123.3, 122.8, 121.5, 117.4, 112.0. HRMS (ESI) *m/z* calcd for $C_7H_5BrClN_2$ $[M+H]^+$ 230.9325, found 230.9324.

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2-Bromo-6-chloro-3-methylimidazo[1,2-*a*]pyridine (4j) White solid, mp 181–183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.14 (dd, J = 9.2, 2.0 Hz, 1H), 7.48 (d, J = 9.2 Hz, 1H), 7.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 125.6, 123.0, 121.5, 121.0, 118.6, 117.6, 9.1. HRMS (ESI) *m/z* calcd for $C_8H_7BrClN_2$ $[M+H]^+$ 244.9481, found 244.9481.

2-Bromo-3,7-dimethylimidazo[1,2-*a*]pyridine (4k) White solid, mp 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.42 (s, 3H), 6.70 (dd, J = 6.8, 1.2 Hz, 1H), 7.29 (s, 1H), 7.70 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 135.2, 122.1, 121.0, 116.9, 115.4, 115.3, 21.3, 8.8. HRMS (ESI) *m/z* calcd for $C_9H_{10}BrN_2$ $[M+H]^+$ 225.0027, found 225.0029.

2-Bromo-1-methylimidazo[1,2-*a*]quinoline (4l) White solid, mp 105–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (s, 3H), 7.47–7.51 (m, 3H), 7.60–7.64 (m, 1H), 7.80 (dd, J = 8.0, 1.6 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 134.3, 129.3, 128.3, 126.3, 124.8, 124.4, 122.0, 121.6, 116.7, 115.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{12}H_{10}BrN_2$ $[M+H]^+$ 261.0027, found 261.0027.

2-Bromo-6-chloro-3-ethylimidazo[1,2-*a*]pyridine (4m) White solid, mp 129–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J = 7.6 Hz, 3H), 2.91 (q, J = 7.6 Hz, 2H), 7.12 (dd, J = 9.6, 2.0 Hz, 1H), 7.87 (d, J = 9.6 Hz, 1H), 7.92 (d, J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 125.3, 123.7, 121.2, 120.6, 117.6, 16.8, 11.6. HRMS (ESI) *m/z* calcd for $C_9H_9BrClN_2$ $[M+H]^+$ 258.9638, found 258.9630.

2-Bromo-3-ethyl-6-methylimidazo[1,2-*a*]pyridine (4n) White solid, mp 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, J = 7.6 Hz, 3H), 2.35 (d, J = 0.8 Hz, 3H), 2.90 (q, J = 7.6 Hz, 2H), 7.01 (dd, J = 9.2, 1.6 Hz, 1H), 7.43 (d, J = 9.2 Hz, 1H), 7.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 127.0, 122.6, 122.3, 120.6, 120.5, 116.5, 18.4, 16.8, 11.7. HRMS (ESI) *m/z* calcd for $C_{10}H_{12}BrN_2$ $[M+H]^+$ 239.0184, found 239.0189.

2-Bromo-1-ethylimidazo[1,2-*a*]quinoline (4o) White solid, mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, J = 7.6 Hz, 3H), 3.35 (q, J = 7.6 Hz, 2H), 7.46–7.50 (m, 3H), 7.62–7.66 (m, 1H), 7.80 (dd, J = 8.0, 1.6 Hz, 1H), 8.22 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 133.7, 129.4, 128.5, 127.1, 126.3, 124.8, 124.4, 121.6, 116.8, 115.6, 20.4, 12.9. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}BrN_2$ $[M+H]^+$ 275.0184, found 275.0194.

2-Bromo-7-chloro-3-propylimidazo[1,2-*a*]pyridine (4p) Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.6 Hz, 3H), 1.67 (q, J = 7.6 Hz, 2H), 2.88 (t, J = 7.6 Hz, 2H), 6.85 (dd, J = 7.2, 2.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.82 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 130.7, 123.1, 122.6, 122.1, 116.0, 114.3, 25.1, 20.5, 13.7. HRMS (ESI) *m/z* calcd for $C_{10}H_{11}BrClN_2$ $[M+H]^+$ 272.9794, found 272.9793.

General Procedure for the Preparation of 2-Chloroimidazo[1,2-*a*]pyridine 5:

2-Aminopyridine **1** (1.5 mmol), alkynoic acid **2** (0.5 mmol) and $CuCl_2$ (0.5 mmol) were mixed in 5 mL of CH_3CN and heated at 90 °C for 12 h in a sealed tube. After completion of the reaction, the mixture was cooled and separated by flash column chromatography (ethyl acetate/hexane) on silica gel to afford product **5**.

2-Chloro-3-phenylimidazo[1,2-*a*]pyridine (5a) Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (td, J = 6.8, 1.2 Hz, 1H), 7.22–7.26 (m, 1H), 7.47–7.60 (m, 6H), 8.16 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 133.9, 129.4, 129.2, 128.9, 127.3, 125.2, 123.2, 119.7, 117.4, 113.0. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}ClN_2$ $[M+H]^+$ 229.0533, found 229.0531. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}ClN_2$ $[M+H]^+$ 229.0533, found 229.0521.

2-Chloro-8-fluoro-3-phenylimidazo[1,2-*a*]pyridine (5b) White solid, mp 137–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74–6.79 (m, 1H), 6.93–6.98 (m, 1H), 7.47–7.57 (m, 5H), 7.97 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (d, J = 253 Hz), 135.7 (d, J = 28.4 Hz), 134.0, 129.4, 129.3, 129.2, 126.8, 121.4, 119.7 (d, J = 5.0 Hz), 112.2 (d, J = 6.7 Hz), 108.1, 107.9. HRMS (ESI) *m/z* calcd for $C_{13}H_9ClFN_2$ $[M+H]^+$ 247.0438, found 247.0449.

2,7-Dichloro-3-phenylimidazo[1,2-*a*]pyridine (5c) White solid, mp 186–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (t, J = 6.8 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.51–7.61 (m, 5H), 8.11 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 134.9, 134.2, 130.6, 129.6, 125.7, 125.5, 123.0, 118.5, 117.5, 113.3. HRMS (ESI) *m/z* calcd for $C_{13}H_9Cl_2N_2$ $[M+H]^+$ 263.0143, found 263.0140.

2,6-Dichloro-3-phenylimidazo[1,2-*a*]pyridine (5d) White solid, mp 126–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J = 9.6, 2.0 Hz, 1H), 7.48–7.60 (m, 6H), 8.17 (dd, J = 2.0, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 134.7, 129.4, 129.3, 129.2, 126.6, 121.6, 121.1, 120.4, 117.7. HRMS (ESI) *m/z* calcd for $C_{13}H_9Cl_2N_2$ $[M+H]^+$ 263.0143, found 263.0136.

2-Chloro-1-phenylimidazo[1,2-*a*]quinoline (5e) Color-less oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.28 (m, 1H), 7.36–7.41 (m, 2H), 7.51–7.59 (m, 7H), 7.78 (dd, J = 8.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 134.2, 133.5, 131.3, 131.1, 130.2, 129.5, 129.3, 129.1, 128.2, 127.2, 124.9, 124.4, 122.9, 116.7, 116.6. HRMS (ESI) *m/z* calcd for $C_{17}H_{12}ClN_2$ $[M+H]^+$ 279.0689, found 279.0682.

2-Chloro-3-ethylimidazo[1,2-*a*]pyridine (5f) Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.6 Hz, 3H), 2.96 (q, J = 7.6 Hz, 2H), 6.89 (td, J = 6.8, 0.8 Hz, 1H), 7.19–7.24 (m, 1H), 7.56 (d, J = 9.2 Hz, 1H), 7.90 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 124.9, 122.9, 120.6, 116.9, 113.2, 16.1, 11.5. HRMS (ESI) *m/z* calcd for $C_9H_{10}ClN_2$ $[M+H]^+$ 181.0533, found 181.0533.

2,6-Dichloro-3-ethylimidazo[1,2-*a*]pyridine (5g) White solid, mp 140–142 °C.. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.6 Hz, 3H), 2.93 (q, J = 7.6 Hz, 2H), 7.16 (dd, J = 9.6, 2.0 Hz, 1H), 7.48 (d, J = 9.6 Hz, 1H), 7.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 133.5, 125.2, 121.1, 120.6, 117.5, 16.1, 11.4. HRMS (ESI) *m/z* calcd for $C_9H_9Cl_2N_2$ $[M+H]^+$ 215.0143, found 215.0143.

2-Chloro-3-propylimidazo[1,2-*a*]pyridine (5h) Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.6 Hz, 3H), 1.69 (q, J = 7.6 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 6.87 (td, J = 6.8, 0.8 Hz, 1H), 7.18–7.22 (m, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 133.3, 124.1, 122.8, 119.0, 117.1, 112.7, 24.5, 20.5, 13.7. HRMS (ESI) *m/z* calcd for $C_{10}H_{12}ClN_2$ $[M+H]^+$ 195.0689, found 195.0699.

Compound 8 was prepared according to literature 14:

3-Phenylimidazo[1,2-*a*]pyridine (8) Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (td, J = 6.8, 1.2 Hz, 1H), 7.17–7.21 (m, 1H), 7.41 (tt, J = 7.2, 1.6 Hz, 1H), 7.49–7.56 (m, 4H), 7.67 (dt, J = 8.8, 1.2 Hz, 1H), 7.69 (s, 1H), 8.33 (dt, J = 7.2, 1.2 Hz, 1H). ^{3}C NMR (100 MHz, $CDCl_3$) δ 145.6, 132.0, 128.8, 127.7, 127.6, 125.3, 123.8, 122.9, 117.8, 112.1.

Procedure for the Preparation of 10:

Imidazo[1,2-*a*]pyridine **3i** (0.2 mmol), phenyl boronic acid (0.3 mmol), $PdCl_2(PPh_3)_2$ (0.004 mmol) and K_3PO_4 (0.4 mmol) were

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mixed in 2.0 mL of toluene and heated at 100 °C under Ar atmosphere for 12 h. After completion of the reaction, the mixture was cooled and separated by flash column chromatography (ethyl acetate/hexane) on silica gel to afford product **10**.

2-Phenylimidazo[1,2-*a*]pyridine (10) White solid, mp 125–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (td, J = 6.8, 1.2 Hz, 1H), 7.13–7.17 (m, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.62 (d, J = 9.2 Hz, 1H), 7.84 (s, 1H), 7.94–7.96 (m, 2H), 8.09 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 134.0, 129.0, 128.3, 126.3, 125.9, 125.0, 117.8, 112.7, 108.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}N_2$ $[M+H]^+$ 195.0922, found 195.0917.

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