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Regioselective Copper-Catalyzed Dicarbonylation of Imidazo[1,2-*a*]pyridines with N,N-Disubstituted Acetamide or Acetone: An Approach to 1,2-Diketones Using Molecular Oxygen

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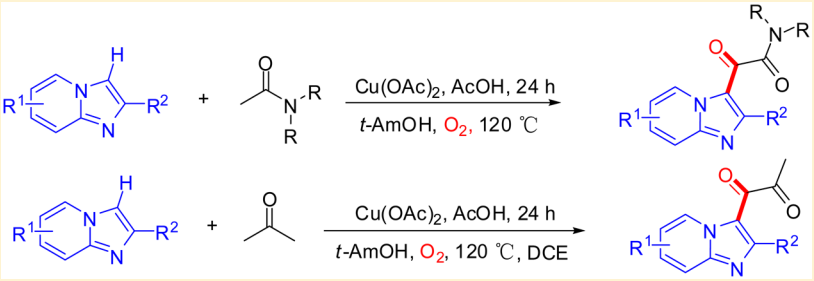
Supporting Information



ABSTRACT: A novel copper-catalyzed regioselective double carbonylation of imidazo[1,2-*a*]pyridines with N,N-disubstituted acetamide or acetone using molecular oxygen has been described. It has provided a new approach to synthesize 1,2-carbonyl imidazo[1,2-*a*]pyridines, which are important substrates and intermediates in preparation of fine chemicals. The product shares a skeleton similar to that of Zolpidem, one of the most prescribed drugs in the world. ^{18}O-labeling experiments unambiguously established that the oxygen source of products originated from O_2 rather than H_2O.

Transition-metal catalysis[1] is arguably the most fundamental subject for the formation of C−C bonds in modern organic chemistry because of its implications on both industrial and scientific levels. Catalysis reactions based on palladium, platinum, ruthenium, copper, etc., have been studied for more than a hundred years. Especially, transition-metal-catalyzed cross-coupling transformation is among the most important methods for C−C bond formation, such as Heck,[2] Suzuki,[3] Hiyama,[4] Stille,[5] and Negishi[6] et al. However, these cross-coupling reactions generally need functionalized substrates. Recently, transition-metal-catalyzed direct conversion of C−H bonds into C−C bonds[7] can potentially lead to a more convenient synthesis with a reduced number of synthetic operations and thus has attracted great interest due to its unique advantages, such as low cost, higher selectivity, atom-economical, and environmentally benign. Great and elegant progress has been achieved in the transition-metal-catalyzed direct C−H activation to synthesize carbonyl compounds.[8] In recent years, the oxidative cross-coupling of (hetero)arene C−H bonds with C_{sp3} C−H bonds has witnessed a remarkable transformation. In a challenging fashion,[9] our group has recently developed an efficient oxidative cross-coupling of imidazo[1,2-*a*]pyridines C−H bonds with C_{sp3} C−H bonds of DMSO for the formation of a new C_{sp2}−C_{sp2} bond to synthesize C3-formylation imidazo[1,2-*a*]pyridines.

1,2-Dicarbonyl derivatives are important starting materials and intermediates in preparation of fine chemicals. Classical routes to synthesize 1,2-dicarbonyl derivatives mainly relied on oxidation of 1,2-diols,[10] alkyne,[11] and alkene.[12] Recently, a successful and elegant process for the synthesis of C3-dicarbonyl indoles has been reported by Li,[13] Müller,[14] Wu,[15] and Li[16] et al., respectively. Although investigation in this field has been conducted, the development of a new method is still highly desirable for the direct introduction of dicarbonyl functional groups onto the (hetero)arene via C−H bond cleavage.

On the other hand, imidazo[1,2-*a*]pyridine and its derivatives are a fundamental class of heterocycles which have exhibited remarkable biological activities[17] and have been found to be key structural units in drugs, such as zolpidem, alpidem, zolimidine, olprinone, saripidem, and necopidem (Scheme 1). In the past few years, our group[18] and others[19] have reported many transformations for the synthesis of imidazo[1,2-*a*]pyridines. Our current interest is preparing C-3 1,2-dicarbonyl imidazo-[1,2-*a*]pyridine derivatives by direct C−H functionalization. Herein, a novel copper-catalyzed regioselective dicarbonylation of imidazo[1,2-*a*]pyridines with N,N-disubstituted acetamide or acetone has been developed using molecular oxygen.

The model reaction of imidazo[1,2-*a*]pyridines with DMA was examined with a variety of copper sources, additives, oxidants, and temperatures, and the results are summarized in Table 1. To our delight, using O_2 as the oxidant, AcOH as the

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Scheme 1. Imidazo[1,2-*a*]pyridines-Containing Drugs

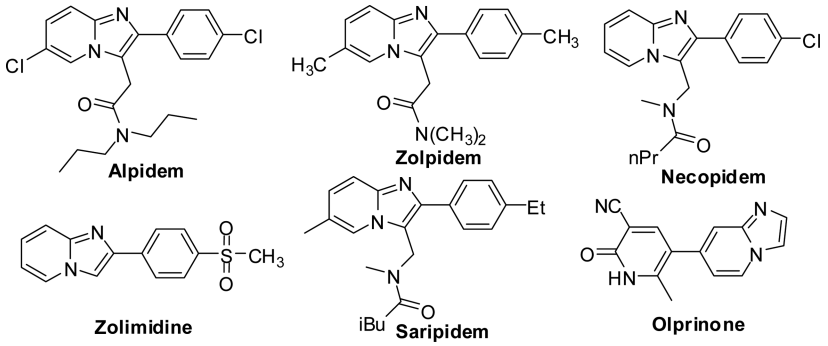
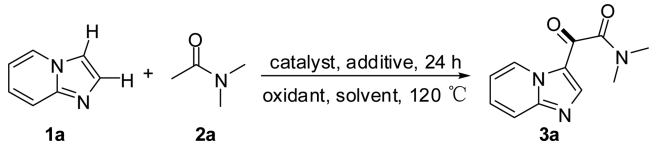


Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	additive	oxidant	T/°C	yield (%)[b]
1	$Cu(OAc)_2$	AcOH	O_2	120	65
2	$Cu(OAc)_2$	TfOH	O_2	120	53
3	$Cu(OAc)_2$	TFA	O_2	120	57
4	$Cu(OAc)_2$	PhCOOH	O_2	120	38
5	$Cu(OAc)_2$	K_2CO_3	O_2	120	N.P.
6[c]	$Cu(OAc)_2$	AcOH/*t*-AmOH	O_2	120	82
7	$CuCl_2$	AcOH/*t*-AmOH	O_2	120	20
8	CuF_2	AcOH/*t*-AmOH	O_2	120	trace
9	$CuBr_2$	AcOH/*t*-AmOH	O_2	120	14
10	$Cu(CF_3SO_3)_2$	AcOH/*t*-AmOH	O_2	120	78
11	$Cu(OAc)_2$	AcOH/*t*-AmOH	AgOAc	120	23
12	$Cu(OAc)_2$	AcOH/*t*-AmOH	AgOTf	120	26
13	$Cu(OAc)_2$	AcOH/*t*-AmOH	DDQ	120	trace
14	$Cu(OAc)_2$	AcOH/*t*-AmOH	TBHP	120	71
15	$Cu(OAc)_2$	AcOH/*t*-AmOH	air	120	12
16	$Cu(OAc)_2$	AcOH/*t*-AmOH	O_2	140	77
17	$Cu(OAc)_2$	AcOH/*t*-AmOH	O_2	100	68
18	$Cu(OAc)_2$	AcOH/*t*-AmOH	O_2	rt	N.P.
19	$Cu(OAc)_2$	AcOH/*t*-AmOH	O_2 (5 atm)	120	36
20[d]	$Cu(OAc)_2$	AcOH/*t*-AmOH	O_2	120	66
21[e]	$Cu(OAc)_2$	AcOH/*t*-AmOH	O_2	120	70
22[f]	$Cu(OAc)_2$	AcOH/*t*-AmOH	O_2	120	53
23[g]		AcOH/*t*-AmOH	O_2	120	N.P.
24	$FeCl_3$	AcOH/*t*-AmOH	O_2	120	N.P.

[a]Reaction conditions: **1a** (0.5 mmol), catalyst (10 mol %), additive (10 mol %), O_2/air (500 mL); other oxidant (1.0 mmol), DMA (3.0 mL). rt−140 °C, 24 h. [b]Yields determined by GC analysis using *n*-octadecane as internal standard. [c]*t*-AmOH (20 mol %). [d]Carried out in a sealed tube (25 mL). [e]Carried out for 18 h. [f]Carried out for 12 h. [g]Without $Cu(OAc)_2$.

additive, and 10 mol % of $Cu(OAc)_2$ as the catalyst provided the desired products in 65% yield (Table1, entry 1). The acidic reaction system brought about a beneficial effect and could promote the reaction. Other organic acids, such as TfOH, TFA, and $PhCO_2H$, were next employed, and the desired products **3a** were generated in 38−57% (Table1, entries 2−4). However, when K_2CO_3 was employed as the additive, no product **3a** was obtained (Table1, entry 5). Interestingly, when the reaction was carried out using *t*-AmOH and AcOH as the additives in the presence of $Cu(OAc)_2$ and O_2, the product **3a** was formed in 82% yield (Table 1, entry 6). The results indicated that copper as the catalyst can catalyze the C3-dicarbonylation of imidazo[1,2-*a*]pyridines with DMA. Then, other copper metal salts, such as $CuCl_2$, CuF_2, $CuBr_2$, and $Cu(CF_3SO_3)_2$, were tested (Table1, entries 7−10). The experiment indicated that $Cu(OAc)_2$ was most effective among the metal catalysts. Oxidants including AgOAc, AgOTf, DDQ, TBHP, and air were also probed in the reaction, which led to **3a** in the lower yields as compared to that of O_2 (Table 1, entries 11−15). Subsequently, various temperatures were examined (Table 1, entries 16−18), and the results indicated that 120 °C was the best choice. We then tried to improve the yield by increasing the oxygen pressure (5 atm), but the yield decreased to 36% (Table 1, entry 19). The product **3a** was obtained in 66% yield when the reaction was performed in a pressure tube (Table 1, entry 20). In addition, the reaction was carried out for 12 h or

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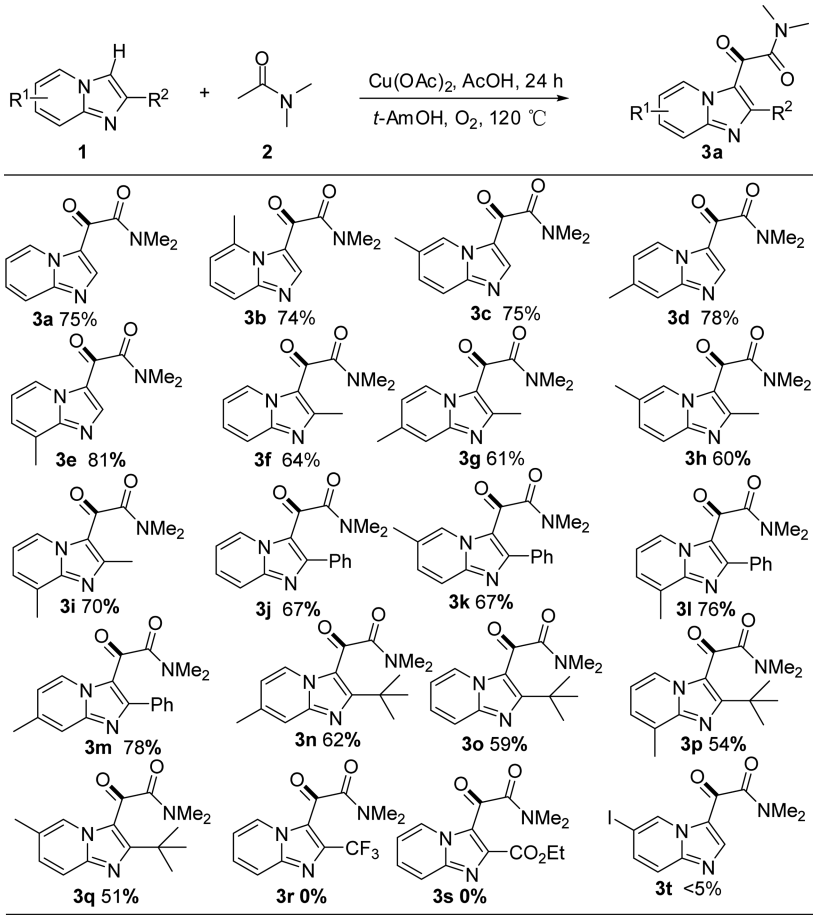
Table 2. Synthesis of 1,2-Dicarbonyl Imidazo[1,2-*a*]pyridines

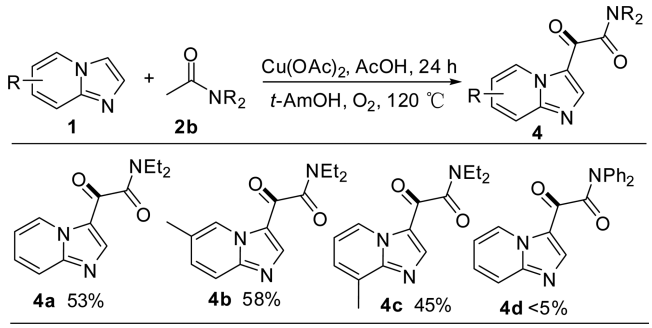


18 h, but the yield of **3a** was decreased (Table 1, entries 21−22). The control experiments indicated that product **3a** was not formed in the absence of $Cu(OAc)_2$ or using $FeCl_3$ as the catalyst (Table 1, entries 23−24).

The regioselective C3-dicarbonylation of imidazo[1,2-*a*]-pyridines with DMA was examined under the conditions of entry 6 in Table 1. As shown in Table 2, various imidazo[1,2-*a*]pyridine derivatives reacted with **2a** smoothly, and these reactions occurred in moderate to good yields. 2-Unsubstituted imidazo[1,2-*a*]pyridines were first employed under the optimized conditions. Different groups on the pyridine ring, having 5-CH_3, 6-CH_3, 7-CH_3, and 8-CH_3 substitution, smoothly participated in this C-3 dicarbonylation process to provide the corresponding 1,2-dicarbonyl imidazo[1,2-*a*]-pyridines **3a**−**3e** in satisfactory yields (74−81%). No regioisomeric products were observed by GC−MS and ^1H NMR spectroscopy. Selective C-3 cross-coupling products were obtained because the electron density distribution of C3(−0.125) was higher than that of C2(−0.054).[19j] Similar results[19f,j] were also reported in others. We were also pleased to find that this transformation was further found to be successfully applied to catalyze the C3-dicarbonylation of 2-CH_3, 2-Ph, or 2-$C(CH_3)_3$ substituted imidazo[1,2-*a*]pyridines, affording the corresponding products **3f**−**3p** in 51−78% yields. However, imidazo[1,2-*a*]pyridines with electron-withdrawing groups (CF_3, CO_2Et) at C2 could not perform the dicarbonylation with DMA. It was also noted that a trace amount of desired product **3t** was not formed using 6-iodoimidazo[1,2-*a*]pyridine as the substrate. We then tried to synthesize the Zolpidem or similar molecule, but the yield was not so good (<10%).

Extending the investigation further, *N*,*N*-diethylacetamide **2b** was also employed, and the results are presented in Scheme 2.

Scheme 2. Reaction of 1 with 2b



The transformation of **1a** with **2b** performed very well and formed the desired products C3-1,2-dicarbonyl imidazo[1,2-*a*]pyridines **4a**−**4c** in 45−58% yields under the optimized conditions. When *N*,*N*-diphenylacetamide as a substrate was used in the reaction, only trace amounts of **4d** were formed.

Next, acetone was investigated for further extending the substrate scope, and the results are summarized in Table 3. Interestingly, the desired product **5a** was formed in 63% yield with very good regioselectivity when the reaction was carried out in a sealed tube (25 mL) using $Cu(OAc)_2$ as catalyst,

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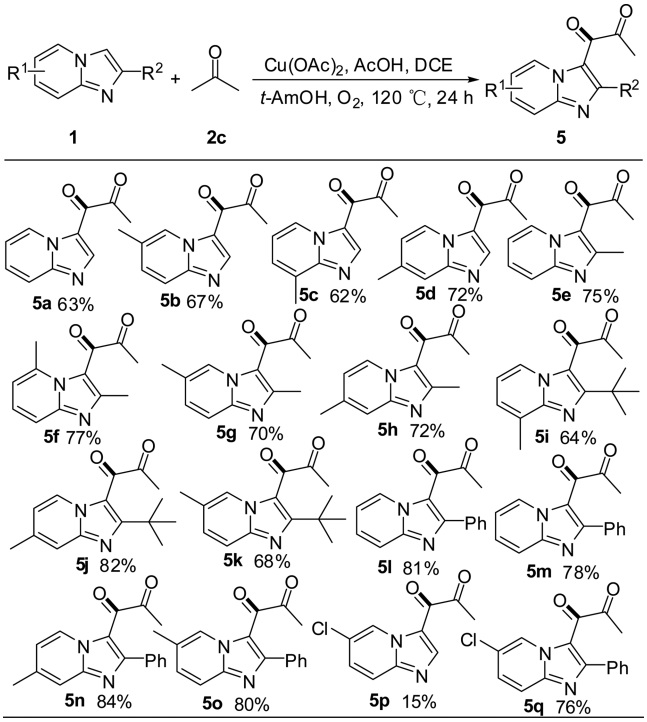
Table 3. Dicarbonylation of Imidazo[1,2-*a*]pyridines with Acetone[a]



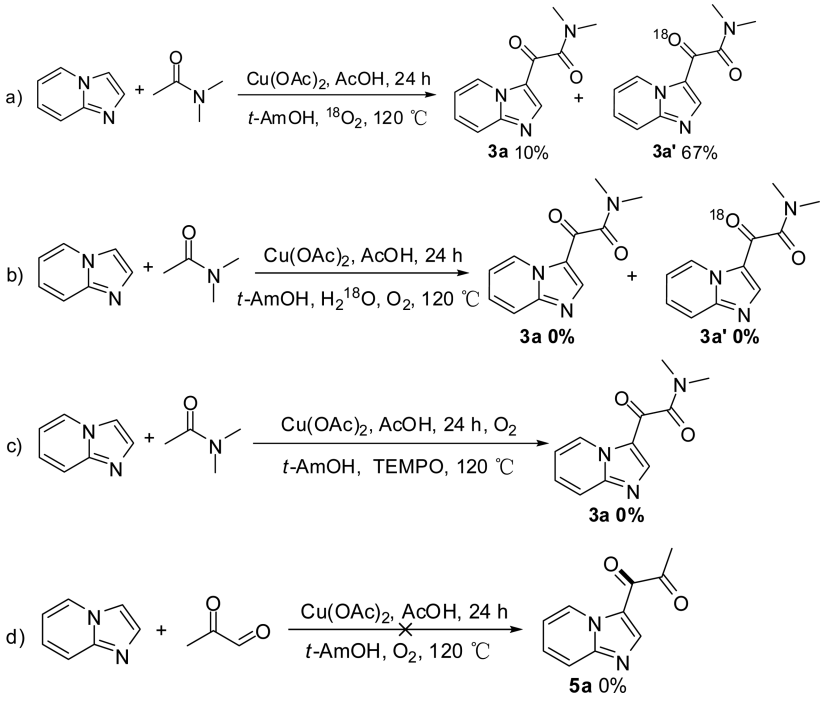
[a]Carried out in a sealed tube.

AcOH and *t*-AmOH as additives, O_2 as oxidant, in DCE. Subsequently, a series of imidazo[1,2-*a*]pyridines were examined. All the reactions proceeded smoothly in this C-3 dicarbonylation process to give the corresponding imidazo[1,2-*a*]pyridines in moderate to good yields. The results indicated that this new methodology was further found to be successfully applied to catalyze the carbonylation of substituted imidazo-[1,2-*a*]pyridines with acetone. For further investigation, 6-chloroimidazo[1,2-*a*]pyridine or 6-chloro-2-phenylimidazo[1,2-*a*]pyridine could also be used as the substrate in the reaction, and the products **5p** and **5q** were obtained in 15% and 76% yields, respectively.

To gain more insight into the mechanism of this Cu(II)-catalyzed dicarbonylation reaction, a series of control experiments were conducted to determine the source of the oxygen atom. ^{18}O-labeling experiments were first used to explore the potential role of O_2 in the reaction. The reaction of **1a** with **2a** gave the ^{18}O-labeled C3-dicarbonyl imidazo[1,2-*a*]pyridine **3a′**, which was confirmed by GC−MS analysis (Scheme 3a). However, the desired product **3a** and product **3a′** with ^{18}O in the carbonyl group were not detected in the presence of $H_2{}^{18}O$ under the standard reaction conditions(Scheme 3b). The ^{18}O-labeling experiments clearly showed that the oxygen atom of the carbonyl group in the product derived from the O_2 rather than H_2O. In addition, a radical inhibitor (e.g., TEMPO) was used to identify the reaction whether was a radical process in this transformation (Scheme 3c). The result showed that the reaction had been inhibited and a radical process was involved for this transformation. Furthermore, the desired product **5a** was not formed by using pyruvaldehyde as a substrate. As a result, the carbonyl compound coupling with imidazo[1,2-*a*]pyridine had first taken place and then the coupling product was oxygenated to give the final product (Scheme 3d).

On the basis of the above results, a plausible mechanism for this transformation is illustrated in Scheme 4. Initially, radical intermediate **I** is formed from **2a′** via a single electron transfer (SET) oxidation in the presence of Cu(II) species. Subsequently, radical **I** could directly add to the imidazo[1,2-*a*]pyridine **2a**, followed by another SET and proton transfer, to generate **II**, which is not isolated in the reaction. Intermediate **II** undergoes a single electron transfer oxidation to form intermediate radical intermediate **III**, which is trapped by

Scheme 3. Control Experiments for Investigation of the Mechanism



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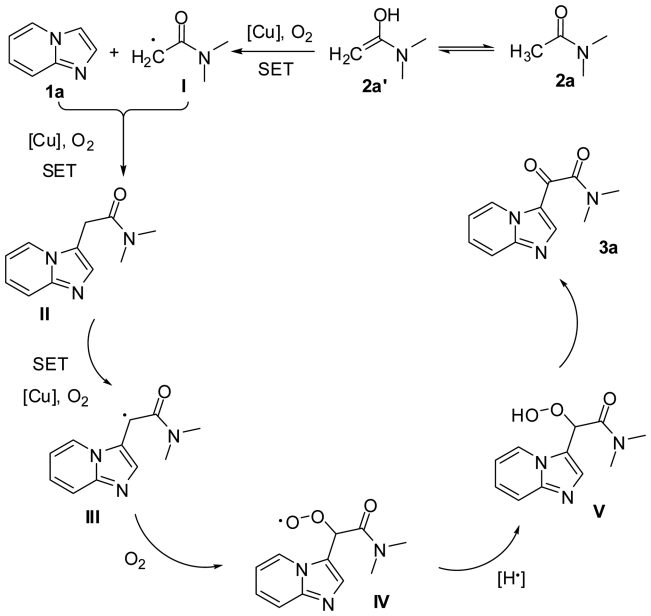
Scheme 4. Proposed Mechanism



dioxygen to give the radical intermediate **IV**. Intermediate **V**, generated by **IV** via capture of a hydrogen from the reaction medium, undergoes elimination of water to give the desired product **3a**. AcOH has played a key role in this transformation. It aids the formation of intermediate **2a′** and also promotes the transformation of product from intermediate **V**.

In conclusion, we have developed a versatile copper-catalyzed system for the dicarbonylation of imidazo[1,2-*a*]pyridine derivatives with DMA or acetone via a selectively direct oxidation coupling reaction. This process provided a new route to prepare 1,2-dicarbonyl imidazo[1,2-*a*]pyridines, which should be significant for the construction of imidazo[1,2-*a*]pyridine libraries. Imidazopyridine with an *N*,*N*-dimethylamide garnished carbon chain could be obtained through Cu-catalyzed C−H activation.

EXPERIMENTAL SECTION

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 Hz, respectively. Mass spectra were obtained on ESIMS. Elemental analyses were performed with an elemental analyzer. GC−MS was obtained using electron ionization. TLC was performed using commercially prepared 100−400 mesh silica gel plates.

Synthesis of 3a According to the Following Procedure. Under an oxygen atmosphere, a reaction tube was charged with imidazo[1,2-*a*]pyridine (**1a**, 59 mg, 0.5 mmol), $Cu(OAc)_2$ (18 mg, 10 mol %), AcOH (6 mg, 10 mol %), *t*-AmOH (17.6 mg, 20 mol %), and DMA (3 mL). The mixture was stirred at 120 °C for 24 h. After reaction completion, as monitored by TLC and GC−MS analysis, the solvent was then removed and the crude product was separated by column chromatography (eluted with petroleum ether:ethyl acetate = 1:1) to give a pure sample of **3a**.

Synthesis of 5a According to the Following Procedure. Under an oxygen atmosphere, a reaction tube was charged with imidazo[1,2-*a*]pyridine (**1a**, 59 mg, 0.5 mmol), acetone (**2c**, 145 mg, 2.5 mmol), $Cu(OAc)_2$ (18 mg, 10 mol %), AcOH (6 mg, 10 mol %), *t*-AmOH (17.6 mg, 20 mol %), and DCE (3 mL). The mixture was stirred at 120 °C for 24 h while adding acetone (**2c**, 2.5 mmol) for every 8 h. After reaction completion, the solvent was then removed and the crude product was separated by column chromatography (eluted with petroleum ether:ethyl acetate = 2:1) to give a pure sample of **5a**.

*2-(Imidazo[1,2-a]pyridin-3-yl)-N,N-dimethyl-2-oxoacetamide (**3a**).* Yield: 81.4 mg, 75%; white solid, m.p.: 121−122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, J = 6.8 Hz, 1H), 8.40 (s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 6.8 Hz, 1H), 3.14 (s, 3H), 3.10 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 179.5, 165.8,149.7, 147.0, 130.4, 128.9, 122.0, 118.0, 115.8, 37.5, 34.7. HRMS m/z (ESI+) calcd for $C_{11}H_{12}N_3O_2$ $[M + H]^+$: 218.0930, found: 218.0923.

*N,N-Dimethyl-2-(5-methyl-H-imidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**3b**).* Yield: 85.5 mg, 74%; brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 6.4 Hz, 1H), 3.06 (s, 3H), 3.00 (s, 3H), 2.85 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 117.7, 167.1, 152.6, 149.2, 141.2, 130.9, 124.5, 117.0, 115.5, 37.6, 34.6, 22.9. HRMS m/z (ESI+) calcd for $C_{12}H_{14}N_3O_2$ $[M + H]^+$: 232.1086, found: 232.1083.

*N,N-Dimethyl-2-(6-methylimidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**3c**).* Yield: 86.6 mg, 75%; white solid, m.p.: 113−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.33 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 3.13 (s, 3H), 3.09 (s, 3H), 2.46 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 179.4, 166.0, 148.7, 146.9, 133.2, 126.9, 126.1, 121.8, 117.1, 37.5, 34.7, 18.4. HRMS m/z (ESI+) calcd for $C_{12}H_{14}N_3O_2$ $[M + H]^+$: 232.1086, found: 232.1083.

*N,N-Dimethyl-2-(7-methylimidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**3d**).* Yield: 90.1 mg, 78%; yellow solid, m.p.: 198−199 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, J = 7.2 Hz, 1H), 8.27 (s, 1H), 7.51 (s, 1H), 6.94 (d, J = 6.8 Hz, 1H), 3.06 (s, 3H), 3.02 (s, 3H), 2.48 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 179.1, 166.0, 147.2, 142.3, 128.0, 127.9, 123.4, 118.2, 116.8, 37.5, 34.8, 21.7. HRMS m/z (ESI+) calcd for $C_{12}H_{14}N_3O_2$ $[M + H]^+$: 232.1086, found: 232.1083.

*N,N-Dimethyl-2-(8-methylimidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**3e**).* Yield: 93.6 mg, 81%; white solid, m.p.: 57−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, J = 6.4 Hz, 1H), 8.36 (s, 1H), 7.4 (d, J = 6.4 Hz, 1H), 7.09 (t, J = 6.4 Hz, 1H), 3.14 (s, 3H), 3.09 (s, 3H), 2.70 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 179.5, 166.0, 149.8, 146.2, 129.5, 128.0, 126.6, 122.3, 115.9, 37.5, 34.7, 16.9. HRMS m/z (ESI+) calcd for $C_{12}H_{14}N_3O_2$ $[M + H]^+$: 232.1086, found: 232.1083.

*N,N-Dimethyl-2-(2-methylimidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**3f**).* Yield: 73.9 mg, 64%; white solid, m.p.: 110−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, J = 6.0 Hz, 1H), 7.62(d, J = 8.4 Hz, 1H), 7.48 (q, J = 5.1 Hz, 1H), 7.04 (t, J = 6.4 Hz, 1H), 3.06 (s, 3H), 2.98 (s, 3H), 2.50 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 180.3, 166.9, 156.0, 148.1, 130.7, 129.1, 118.8, 116.8, 115.3, 37.1, 34.1, 15.6. HRMS m/z (ESI+) calcd for $C_{12}H_{14}N_3O_2$ $[M + H]^+$: 232.1086, found: 232.1083.

*2-(2,7-Dimethylimidazo[1,2-a]pyridin-3-yl)-N,N-dimethyl-2-oxoacetamide (**3g**).* Yield: 74.7 mg, 61%; brown solid, m.p.:113−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.460 (d, J = 6.8 Hz, 1H), 7.39(s, 1H), 6.87 (d, J = 6.8 Hz, 1H), 3.05 (s, 3H), 2.97 (s, 3H), 2.48 (s, 3H), 2.43 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 179.8, 167.0, 156.1, 148.5, 128.3, 117.7, 115.6, 37.1, 34.2, 21.7, 15.5. HRMS m/z (ESI+) calcd for $C_{13}H_{16}N_3O_2$ $[M + H]^+$: 246.1243, found: 246.1324.

*2-(2,6-Dimethylimidazo[1,2-a]pyridin-3-yl)-N,N-dimethyl-2-oxoacetamide (**3h**).* Yield: 73.5 mg, 60%; white solid, m.p.: 114−115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.34 (s, 1H), 7.72(d, J = 9.2 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 3.13 (s, 3H), 3.09 (s, 3H), 2.46 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 179.4, 166.0, 148.7, 146.9, 133.3, 126.9, 126.1, 121.8, 117.2, 37.5, 34.7, 18.4. HRMS m/z (ESI+) calcd for $C_{13}H_{16}N_3O_2$ $[M + H]^+$: 246.1243, found: 246.1234.

*2-(2,8-Dimethylimidazo[1,2-a]pyridin-3-yl)-N,N-dimethyl-2-oxoacetamide (**3i**).* Yield: 85.8 mg, 70%; white solid, m.p.: 132−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 6.8 Hz, 1H), 7.37 (d, J = 7.2 Hz, 1H), 7.02 (t, J = 6.8 Hz, 1H), 3.13 (s, 3H), 3.05 (s, 3H), 2.66 (s, 3H), 2.60 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 180.3, 167.0, 155.4, 148.2, 129.9, 126.9, 126.8, 119.1, 115.3, 37.1, 34.2, 16.9, 15.6. HRMS m/z (ESI+) calcd for $C_{13}H_{15}N_3NaO_2$ $[M + Na]^+$: 268.1062, found: 268.1056.

*N,N-Dimethyl-2-oxo-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)-acetamide (**3j**).* Yield: 98.2 mg, 67%; brown solid, m.p.: 129−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.56−7.32 (m, 6H), 7.10 (d, J = 6.4 Hz, 1H), 2.68 (s, 3H), 2.36 (s,

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3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 181.6, 165.7, 157.6, 148.1, 132.9, 130.9, 129.6, 129.5, 129.3, 127.8, 118.6, 117.5, 115.7, 36.9, 33.4. HRMS m/z (ESI+) calcd for $C_{17}H_{16}N_3O_2$ $[M + H]^+$: 294.1243, found: 294.1240.

*N,N-Diethyl-2-(6-methyl-2-phenyl-H-imidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**3k**).* Yield: 102.8 mg, 67%; white solid, m.p.: 162−163 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.72 (d, J = 9.2 Hz, 1H), 7.58−7.46 (m, 6H), 2.76 (s, 3H), 2.48 (s, 3H), 2.44 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 181.5, 165.8, 157.5, 147.1, 133.6, 133.1, 129.6, 129.4, 127.8, 127.4, 125.9, 118.5, 116.8, 36.9, 33.4, 18.5. HRMS m/z (ESI+) calcd for $C_{18}H_{18}N_3O_2$ $[M + H]^+$: 308.1399, found: 308.1396.

*N,N-Diethyl-2-(8-methyl-2-phenyl-H-imidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**3l**).* Yield: 116.7 mg, 76%; white liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, J = 6.8 Hz, 1H), 7.49 (t, J = 5.2 Hz, 2H), 7.36−7.28 (m, 4H), 6.99 (t, J = 6.8 Hz, 1H), 2.65 (s, 3H), 2.60 (s, 3H), 2.33 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 181.6, 165.8, 157.1, 148.2, 133.1, 130.0, 129.8, 129.4, 127.8, 127.6, 127.0, 119.0, 115.7, 36.9, 33.4, 17.0. HRMS m/z (ESI+) calcd for $C_{18}H_{18}N_3O_2$ $[M + H]^+$: 308.1399, found: 308.1396.

*N,N-Diethyl-2-(7-methyl-2-phenyl-H-imidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**3m**).* Yield: 119.7 mg, 78%; brown liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, J = 6.8 Hz, 1H), 7.57 (s, 3H), 7.46 (s, 3H), 7.01 (s, 1H), 2.75 (s, 3H), 2.52 (s, 3H), 2.44 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 181.2, 165.9, 157.9, 148.6, 142.7, 133.1, 129.6, 129.4, 128.5, 127.8, 118.4, 118.0, 116.3, 36.9, 33.4, 21.7. HRMS m/z (ESI+) calcd for $C_{18}H_{18}N_3O_2$ $[M + H]^+$: 308.1399, found: 308.1396.

*2-(2-tert-Butyl-7-methyl-H-imidazo[1,2-a]pyridin-3-yl)-N,N-dimethyl-2-oxoacetamide (**3n**).* Yield: 89.0 mg, 62%; white solid, m.p.: 138−139 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 7.2 Hz, 1H), 7.47 (s, 1H), 6.81 (d, J = 7.2 Hz, 1H), 3.07 (s, 3H), 2.99 (s, 3H), 2.42 (s, 3H), 1.47 (s, 9H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 180.0, 167.7, 167.5, 147.3, 141.1, 127.5, 119.1, 117.5, 116.4, 37.4, 35.3, 34.5, 29.6, 21.3. HRMS m/z (ESI+) calcd for $C_{16}H_{22}N_3O_2$ $[M + H]^+$: 288.1712, found: 288.1711.

*2-(2-tert-Butyl-H-imidazo[1,2-a]pyridin-3-yl)-N,N-dimethyl-2-oxoacetamide (**3o**).* Yield: 80.5 mg, 59%; Yellow solid, m.p.: 110−111 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 6.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 6.92 (t, J = 6.0 Hz, 1H), 3.02 (s, 3H), 2.95 (s, 3H), 1.43 (s, 9H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 180.4, 167.4, 166.9, 146.7, 129.3, 128.0, 119.3, 117.5, 115.1, 37.3, 35.2, 34.5, 29.6. HRMS m/z (ESI+) calcd for $C_{15}H_{19}N_3NaO_2$ $[M + Na]^+$: 296.1375, found: 296.1373.

*2-(2-tert-Butyl-8-methyl-H-imidazo[1,2-a]pyridin-3-yl)-N,N-dimethyl-2-oxoacetamide (**3p**).* Yield: 77.5 mg, 54%; white solid, m.p.: 114−115 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 6.8 Hz, 1H), 7.17 (d, J = 6.8 Hz, 1H), 6.82 (t, J = 6.8 Hz, 1H), 3.02 (s, 3H), 2.93 (s, 3H), 2.56 (s, 3H), 1.44 (s, 9H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 180.33, 167.7, 166.5, 146.9, 128.2, 127.8, 125.7, 119.7, 114.9, 37.3, 35.4, 34.5, 29.5, 16.8. HRMS m/z (ESI+) calcd for $C_{16}H_{22}N_3O_2$ $[M + H]^+$: 288.1712, found: 288.1711.

*2-(2-tert-Butyl-6-methyl-H-imidazo[1,2-a]pyridin-3-yl)-N,N-dimethyl-2-oxoacetamide (**3q**).* Yield: 73.2 mg, 51%; brown solid, m.p.: 168−169 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 9.6 Hz, 1H), 3.11 (s, 1H), 3.03 (s, 1H), 2.38 (s, 3H), 1.51 (s, 9H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 180.4, 167.6, 166.8, 145.7, 132.1, 126.2, 125.0, 121.0, 116.8, 37.3, 35.2, 34.4, 29.6, 18.6. HRMS m/z (ESI+) calcd for $C_{16}H_{22}N_3O_2$ $[M + H]^+$: 288.1712, found: 288.1711.

*N,N-Diethyl-2-(H-imidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**4a**).* Yield: 65.0 mg, 53%. ^1H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, J = 6.8 Hz, 1H), 8.35 (s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 6.8 Hz, 1H), 3.57 (q, J = 7.2 Hz, 2H), 3.38 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.0 Hz, 3H), 1.23 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 180.0, 165.6, 146.7, 136.3, 130.2, 128.9, 118.0, 115.8, 42.5, 39.4, 14.4, 12.8. ESI-MS m/z (%) 247(100) $[M + H]^+$; HRMS m/z (ESI+) calcd for $C_{13}H_{15}N_3NaO_2$ $[M + Na]^+$: 268.1057, found: 268.1062.

*N,N-diethyl-2-(6-methyl-H-imidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**4b**).* Yield: 75.2 mg, 58%. ^1H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.28 (s, 1H), 7.73 (d, J = 9.2 Hz, 1H), 7.44 (d, J = 9.2 Hz, 1H), 7.28 (s, 1H), 3.56 (q, J = 7.2 Hz, 2H), 3.37 (q, J = 6.8 Hz, 2H), 2.36 (s, 3H), 1.29 (t, J = 7.0 Hz, 3H), 1.22 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 179.8, 165.7, 148.5, 146.4, 133.2, 126.9, 121.7, 117.1, 42.5, 39.4, 14.4, 18.4, 14.4, 12.8. Anal. calcd for $C_{14}H_{17}N_3O_2$, $[M + Na]^+$: 282.1218, found: 282.1216.

*N,N-Diethyl-2-(8-methyl-H-imidazo[1,2-a]pyridin-3-yl)-2-oxoacetamide (**4c**).* Yield: 58.2 mg, 45%; brown solid, m.p.: 72−74 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, J = 6.8 Hz, 1H), 8.31 (s, 1H), 7.39 (d, J = 7.2 Hz, 1H), 7.08 (t, J = 6.2 Hz, 1H), 3.57 (q, J = 6.7 Hz, 2H), 3.37 (q, J = 7.1 Hz, 2H), 2.69 (s, 3H), 1.29 (t, J = 6.8 Hz, 3H), 1.22 (t, J = 6.4 Hz, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 179.9, 165.8, 149.7, 146.0, 129.4, 128.0, 126.6, 122.3, 115.8, 42.5, 39.4, 16.9, 14.4, 12.8. HRMS m/z (ESI+) calcd for $C_{14}H_{17}N_3NaO_2$ $[M + Na]^+$: 282.1218, found: 282.1213.

*1-(Imidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5a**).* Yield: 59.2 mg, 63%; yellow solid, m.p.: 49−51 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, J = 6.8 Hz, 1H), 8.84 (s, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.20 (t, J = 6.8 Hz, 1H), 2.57 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 198.9, 177.2, 148.1, 140.5, 130.6, 129.1, 120.5, 118.0, 115.9, 25.2. ESI-MS m/z (%) 189(100) $[M + H]^+$; Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.29; N, 14.89; Found: C, 63.52; H, 4.32; N, 14.97.

*1-(6-Methylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5b**).* Yield: 67.7 mg, 67%; brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.75 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 2.56 (s, 3H), 2.47 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 199.0, 177.0, 148.6, 147.9, 133.4, 127.1, 126.1, 120.2, 117.1, 25.2, 18.4. ESI-MS m/z (%) 203(100) $[M + H]^+$; Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85; Found: C, 65.01; H, 5.01; N, 13.94.

*1-(8-Methylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5c**).* Yield: 62.6 mg, 62%; yellow solid, m.p.: 85−88 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.53 (d, J = 6.4 Hz, 1H), 8.78 (s, 1H), 7.40 (d, J = 7.2 Hz, 1H), 7.09 (t, J = 6.4 Hz, 1H), 2.70 (s, 3H), 2.56 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 199.0, 177.2, 149.7, 147.5, 129.7, 128.1, 126.8, 120.8, 115.9, 25.3, 16.9. ESI-MS m/z (%) 203(100) $[M + H]^+$; Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85; Found: C, 65.62; H, 4.95; N, 13.79.

*1-(7-Methylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5d**).* Yield: 72.7 mg, 72%; yellow solid, m.p.: 139−142 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.51 (d, J = 7.2 Hz, 1H), 8.75 (s, 1H), 7.59 (s, 1H), 7.01 (d, J = 6.8 Hz, 1H), 2.55 (s, 3H), 2.52 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 199.1, 176.7, 150.0, 148.4, 142.5, 128.1, 120.2, 118.2, 116.8, 25.2, 21.6. ESI-MS m/z (%) 203(100) $[M + H]^+$; Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85; Found: C, 65.62; H, 4.95; N, 13.79.

*1-(2-Methylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5e**).* Yield: 75.8 mg, 75%; brown solid, m.p.: 40−42 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, J = 4.0 Hz, 1H), 7.72 (t, J = 3.6 Hz, 1H), 7.59 (t, J = 4.4 Hz, 1H), 7.14 (d, J = 5.2 Hz, 1H), 2.58 (s, 3H), 2.56 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 200.3, 182.6, 156.3, 148.3, 130.8, 129.2, 117.8, 116.8, 115.4, 26.2, 17.1. ESI-MS m/z (%) 203(100) $[M + H]^+$; Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85; Found: C, 65.06; H, 5.01; N, 13.79.

*1-(2,5-Dimethylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5f**).* Yield: 83.2 mg, 77%; brown solid, m.p.: 56−58 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.8 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 6.8 Hz, 1H), 2.60 (s, 3H), 2.53 (s, 3H),2.52 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 199.9, 180.4, 155.5, 150.1, 140.2, 130.4, 120.6, 116.5, 114.4, 25.5, 22.4, 16.9. ESI-MS m/z (%) 217(100) $[M + H]^+$; Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; Found: C, 66.32; H, 5.62; N, 13.02.

*1-(2,6-Dimethylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5g**).* Yield: 75.6 mg, 70%; brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 2.56 (s, 3H), 2.53 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 200.4, 182.5, 156.1, 147.2, 133.5, 127.4, 125.6, 117.6, 116.0, 26.2,

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18.3, 17.1. ESI-MS m/z (%) 217(100) $[M + H]^+$; Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; Found: C, 66.36; H, 5.61; N, 13.02.

1-(2,7-Dimethylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5h**). Yield: 77.8 mg, 72%; yellow solid, m.p.: 124−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, J = 6.8 Hz, 1H), 7.46 (s, 1H), 6.95 (d, J = 6.8 Hz, 1H), 2.56 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 200.5, 182.2, 156.6, 148.7, 142.8, 134.6, 128.4, 117.7, 115.7, 26.3, 21.6, 17.1. ESI-MS m/z (%) 217(100) $[M + H]^+$; Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; Found: C, 66.97; H, 5.56; N, 12.89.

1-(2-(tert-Butyl)-8-methylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5i**). Yield: 82.6 mg, 64%; yellow solid, m.p.: 71−73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 7.2 Hz, 1H), 7.22(d, J = 7.2 Hz, 1H), 6.86 (t, J = 7.0 Hz, 1H), 2.62 (s, 3H), 2.60 (s, 3H), 1.46 (s, 9H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 199.5, 184.9, 165.9, 147.1, 128.1, 127.6, 125.9, 117.6, 114.5, 35.2, 30.9, 25.9, 16.8. ESI-MS m/z (%) 259(100) $[M + H]^+$; Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84; Found: C, 69.42; H, 7.06; N, 10.89.

1-(2-(tert-Butyl)-7-methylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5j**). Yield: 105.8 mg, 82%; brown solid, m.p.: 49−51 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 7.2 Hz, 1H), 7.47 (s, 1H), 6.82 (d, J = 7.2 Hz, 1H), 2.60 (s, 3H), 2.45 (s, 3H), 1.45 (s, 9H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 199.5, 184.5, 166.9, 147.5, 141.5, 141.0, 127.5, 117.1, 116.1, 35.1, 30.9, 25.9, 21.4. ESI-MS m/z (%) 259(100) $[M + H]^+$; Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84; Found: C, 69.48; H, 7.05; N, 10.90.

1-(2-(tert-Butyl)-6-methylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5k**). Yield: 87.7 mg, 68%; yellow solid, m.p.: 41−43 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 9.6 Hz, 1H), 2.60 (s, 3H), 2.37 (s, 3H), 1.45 (s, 9H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 199.3, 184.9, 166.1, 145.9, 132.1, 126.2, 124.6, 117.1, 116.6, 35.0, 30.9, 25.8, 18.4. ESI-MS m/z (%) 259(100) $[M + H]^+$; Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84; Found: C, 69.98; H, 6.99; N, 10.78.

1-(2-Phenylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5l**). Yield: 106.9 mg, 81%; yellow solid, m.p.: 145−148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 6.8 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.54−7.44 (m, 5H), 7.17 (t, J = 7.2 Hz, 1H), 2.26 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 198.9, 184.5, 158.1, 148.4, 133.8, 130.8, 129.9, 129.9, 129.8, 128.9, 128.5, 117.7, 115.7, 25.9. ESI-MS m/z (%) 265(100) $[M + H]^+$; Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60; Found: C, 72.41; H, 4.61; N, 10.66.

1-(8-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5m**). Yield: 108.4 mg, 78%; yellow solid, m.p.: 119−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, J = 6.8 Hz, 1H), 7.55−7.40 (m, 6H), 7.07 (t, J = 7.0 Hz, 1H), 2.72 (s, 3H), 2.23 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 199.0, 184.6, 157.5, 148.4, 133.9, 130.1, 130.0, 129.9, 129.8, 128.5, 127.8, 126.5, 115.7, 25.9, 17.1. ESI-MS m/z (%) 279(100) $[M + H]^+$; Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07; Found: C, 73.01; H, 5.10; N, 10.13.

1-(7-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5n**). Yield: 116.8 mg, 84%; yellow solid, m.p.: 98−100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, J = 6.8 Hz, 1H), 7.60 (s, 1H), 7.54−7.43 (m, 5H), 7.00 (d, J = 7.2 Hz, 1H), 2.52 (s, 3H), 2.25 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 199.1, 184.1, 158.2, 148.7, 142.9, 133.7, 129.9, 129.8, 129.8, 128.5, 128.0, 118.1, 116.3, 26.0, 21.7. ESI-MS m/z (%) 279(100) $[M + H]^+$; Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07; Found: C, 73.56; H, 5.06; N, 10.01.

1-(6-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5o**). Yield: 111.2 mg, 80%; yellow solid, m.p.: 65−67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.54−7.46 (m, 6H), 2.47 (s, 3H), 2.26 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ198.7, 184.4, 156.7, 146.5, 134.1, 133.1, 130.0, 129.8, 128.6, 126.9, 126.4, 116.9, 116.5, 25.9, 18.5. ESI-MS m/z (%) 279(100) $[M + H]^+$; Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07; Found: C, 73.15; H, 5.09; N, 10.12.

1-(6-Chloroimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5p**). Yield: 16.7 mg, 15%; yellow solid, m.p.: 75−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (d, J = 1.6 Hz, 1H), 8.89 (s, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.66 (q, J = 3.7 Hz, 1H), 2.58 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 198.0, 177.2, 146.0, 135.5, 133.3, 132.6, 127.1, 125.1, 117.7, 29.7, 25.0. ESI-MS m/z (%) 223(100) $[M + H]^+$; Anal. Calcd for $C_{10}H_7ClN_2O_2$: C, 53.95; H, 3.17; N, 12.58; Found: C, 53.74; H, 3.19; N, 12.65.

1-(6-Chloro-2-phenylimidazo[1,2-a]pyridin-3-yl)propane-1,2-dione (**5q**). Yield: 113.2 mg, 76%; yellow solid, m.p.: 80−82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.45−7.58 (m, 6H), 2.76 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 198.3, 184.5, 158.2, 146.6, 133.4, 131.7, 130.0, 129.7, 128.5, 126.7, 123.8, 117.8,, 25.8. ESI-MS m/z (%) 299(100) $[M + H]^+$; Anal. Calcd for $C_{16}H_{11}ClN_2O_2$: C, 64.33; H, 3.71; N, 9.38; Found: C, C, 64.01; H, 3.72; N, 9.43.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02417.

Copies of ^{1}H and ^{13}CNMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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