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Visible-Light-Induced Dehydrogenative Imidoylation of Imidazo[1,2-*a*]pyridines with α-Amino Acid Derivatives and α-Amino Ketones

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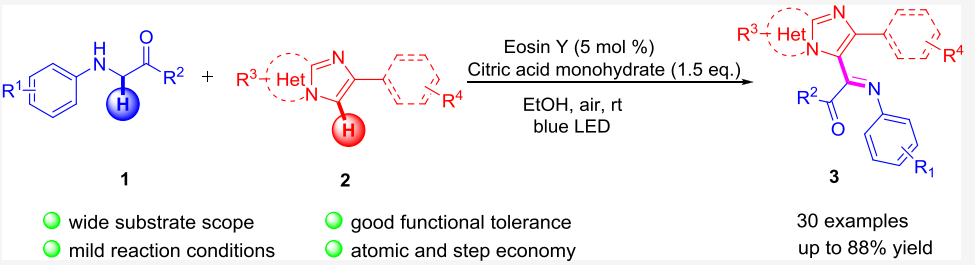

ABSTRACT: A new and efficient visible-light-promoted dehydrogenative cross-coupling reaction of imidazo[1,2-*a*]pyridines with α-amino carbonyl compounds toward imidoyl imidazo[1,2-*a*]pyridines is developed. A diverse range of imidazo[1,2-*a*]pyridines undergoes the dehydrogenative imidoylation smoothly with α-amino carbonyl compounds to access the corresponding products in satisfactory yields. We have also proposed the possible reaction mechanism based on preliminary mechanistic studies. The synthetic method has the advantages of wide substrate scope, good functional tolerance, and mild reaction conditions, which make this transformation more practical and sustainable.

INTRODUCTION

As an important "privileged scaffold", an imidazo[1,2-*a*]-pyridine core is prevalent in a large number of bioactive pharmaceuticals and nature products.[1] Among them, C-3 functionalized imidazo[1,2-*a*]pyridines possess various biological and pharmaceutical activities, like antibacterial,[2] anti-inflammatory,[3] anti-viral,[4] and anti-cancer.[5] Several commercially available drugs such as alpidem, zolpidem, necopidem, and saripidem contain the imidazo[1,2-*a*]pyridine moiety in their core structure.[6] In addition, imidazo[1,2-*a*]pyridine derivatives have been found to be useful as charge transporters in materials science.[7] Owing to their importance and utilizations, tremendous efforts have been made for direct C−H functionalization of imidazo[1,2-*a*]pyridines, and significant progress has been achieved in the past few years.[8] Despite these achievements, selective imidoylation of imidazo-[1,2-*a*]pyridines with α-amino carbonyl compounds leading to imidoyl imidazo[1,2-*a*]pyridines by using a C−H oxidation strategy has not been established. Therefore, the development of new and efficient methods toward the synthesis of potentially useful organic molecules is still highly desired.

Direct dehydrogenative cross-coupling has been considered as a promising ideal synthetic tool to construct new chemical bonds because this type of reaction avoids functional group interconversion and has the advantages of high atomic and step economy.[9] Much attention has been paid for direct α-functionalization of the C−H bond in α-amino carbonyl compounds with various coupling partners to deliver α-substituted α-amino carbonyl derivatives in the past decade.[10,11] However, the use of α-amino carbonyl compounds to produce a new C−C or C−heteroatom bond and a C−N double bond has been rarely studied.[12] For example, in 2012, Li's group reported an oxidative α-arylation of α-amino carbonyl compounds with indoles to produce 2-(1*H*-indol-3-yl)-2-iminocarbonyls using a CuCl/TBHP catalytic system.[12a] In 2013, Yang and co-workers described a selective α-phosphonation of α-amino ketones with diphenylphosphine oxide to furnish imidoylphosphonates by copper catalysis with TBHP as an oxidant.[12b] Recently, Huang et al. and Xiang et al. disclosed copper-catalyzed oxidative cross-coupling reactions of α-amino carbonyl compounds with amines to obtain 2-amino-2-iminocarbonyl compounds.,[12c12d] Visible-light sensitization to facilitate various organic transformations has recently emerged as a reliable and attractive synthetic technology due to its intrinsic characteristics of sustainability and green chemistry.[13] In consideration of the biological

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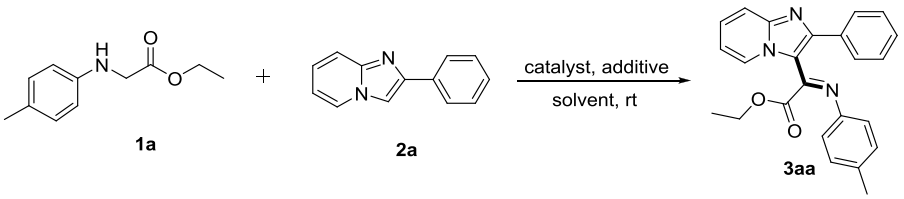
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	additive	solvent	yield (%)[b]
1[c]	eosin Y		CH_3CN	14
2	eosin Y	$C_6H_8O_7·H_2O$	CH_3CN	69
3	Acr^+-Mes-ClO_4^-	$C_6H_8O_7·H_2O$	CH_3CN	40
4	$Ir(ppy)_3$	$C_6H_8O_7·H_2O$	CH_3CN	trace
5	$Ru(bpy)_3Cl_2·6H_2O$	$C_6H_8O_7·H_2O$	CH_3CN	trace
6	eosin Y	HCOOH	CH_3CN	41
7	eosin Y	CH_3COOH	CH_3CN	15
8	eosin Y	PhCOOH	CH_3CN	27
9	eosin Y	$C_6H_8O_7$[d]	CH_3CN	45
10[e]	eosin Y	$C_6H_8O_7·H_2O$	CH_3CN	0
11	eosin Y	$C_6H_8O_7·H_2O$	DMF	40
12	eosin Y	$C_6H_8O_7·H_2O$	EtOH	78
13[f]	eosin Y	$C_6H_8O_7·H_2O$	EtOH	65
14[g]	eosin Y	$C_6H_8O_7·H_2O$	EtOH	0
15[h]		$C_6H_8O_7·H_2O$	EtOH	19
16[c]	eosin Y		EtOH	26

[a]Reaction conditions: **1a** (0.15 mmol), **2a** (0.18 mmol), catalyst (5 mol %), oxidant (2 equiv), additive (1.5 equiv), solvent (2 mL) at room temperature under the irradiation of 18 W blue LED light for 18−24 h. [b]Isolated yield based on **1a**. [c]No additive. [d]Citric acid ($C_6H_8O_7$). [e]Under a nitrogen atmosphere. [f]Citric acid monohydrate ($C_6H_8O_7·H_2O$, 1 equiv). [g]Without irradiation of visible light. [h]In the absence of a catalyst, 37% yield of product **C** was isolated.

importance of imidazo[1,2-*a*]pyridines and as the continuation of our interest in the dehydrogenative cross-coupling reaction,[14] we herein present our recent work on a green and novel visible-light-mediated dehydrogenative imidoylation of imidazo[1,2-*a*]pyridines with α-amino acid derivatives and α-amino ketones for imidoyl imidazo[1,2-*a*]pyridines.

RESULTS AND DISCUSSION

Our initial study began with *N*-(4-methylphenyl)glycine ethyl ester **1a** and 2-phenylimidazo[1,2-*a*]pyridine **2a** under the catalysis of 10 mol % eosin Y in MeCN at room temperature (entry 1, Table 1). To our delight, the desired product **3aa** was formed, albeit in a yield of 14% under illumination of 18 W blue LED light. Interestingly, product **3aa** was isolated in 69% yield when citric acid monohydrate ($C_6H_8O_7·H_2O$) was used as an additive (entry 2, Table 1). The structure of **3aa** was confirmed by single-crystal X-ray diffraction analysis (CCDC 1951464).[15] Encouraged by these results, several common sensitizers like Acr^+-Mes-ClO_4^-, $Ru(bpy)_3Cl_2·6H_2O$, and $Ir(ppy)_3$ were investigated, and inferior yields of product **3aa** were displayed (compare entries 3−5 with entry 2, Table 1). Replacing citric acid monohydrate with other additives such as HCOOH, CH_3COOH, PhCOOH, and $C_6H_8O_7$ resulted in lower yields of **3aa** (compare entries 6−9 with entry 2, Table 1). A series of oxidants were also examined, and lower yields of product **3aa** were obtained (see the Supporting Information). No reaction occurred when the reaction was performed in a nitrogen atmosphere (entry 10, Table 1). Among the solvents screened, EtOH was proved to be the best for the yield of product **3aa** (compare entries 2 and 11 with entry 12, Table 1; also see the Supporting Information). A reduction in the amount of $C_6H_8O_7·H_2O$ led to low yield of **3aa** (entry 13, Table 1). Without the irradiation of visible light, no desired product **3aa** was detected (entry 14, Table 1). Screening revealed that lower yields of **3aa** were isolated in the absence of a photosensitizer or an additive (entries 15 and 16, Table 1).

After exploring different parameters, the optimized reaction should be carried out with eosin Y (10 mol %) and citric acid monohydrate (1.5 equiv) in EtOH under irradiation of 18 W blue LED light at room temperature. Under the optimized conditions, various α-amino carbonyl compounds **1** were investigated in this reaction with 2-phenylimidazo[1,2-*a*]-pyridine **2a** (Table 2). Initially, steric and electronic variations in the benzene rings of *N*-arylglycine ethyl esters **1a−1f** were tested with **2a**, and it was observed that the electron-donating substituents on the benzene rings of *N*-arylglycine ethyl esters **1a−1d** led to better yields than the electron-deficient substituents on the benzene rings of *N*-arylglycine ethyl esters **1g** and **1h**. Changing the position of the methyl group on the benzene ring of *N*-arylglycine ester from the *para* position **1a** to the *meta* position **1d** resulted in diminished yield. The synthetically valuable functional groups, Cl and Br, could be well tolerated under the current conditions. Furthermore, *N*-arylglycine esters **1i−1l** including a series of alkyl substituents in the ester moiety, like methyl, isopropyl, *tert*-butyl, and benzyl, were also able to deliver the desired products **3ia−3la** in satisfactory yields. Moreover, the current dehydrogenative coupling reaction was found to be efficient for α-amino ketones **1m** and **1n**, albeit providing the desired products **3ma** and **3na** with relatively lower yields. Unfortunately, when α-amino alkyl ketone, 1-(*p*-tolylamino)propan-2-one, was used instead of **1a** with **2a**, no desired product was detected by GC−MS analysis. To demonstrate the practicability of this protocol, the reaction of glycine ester **1a** (5.3 mmol, 1.02 g)

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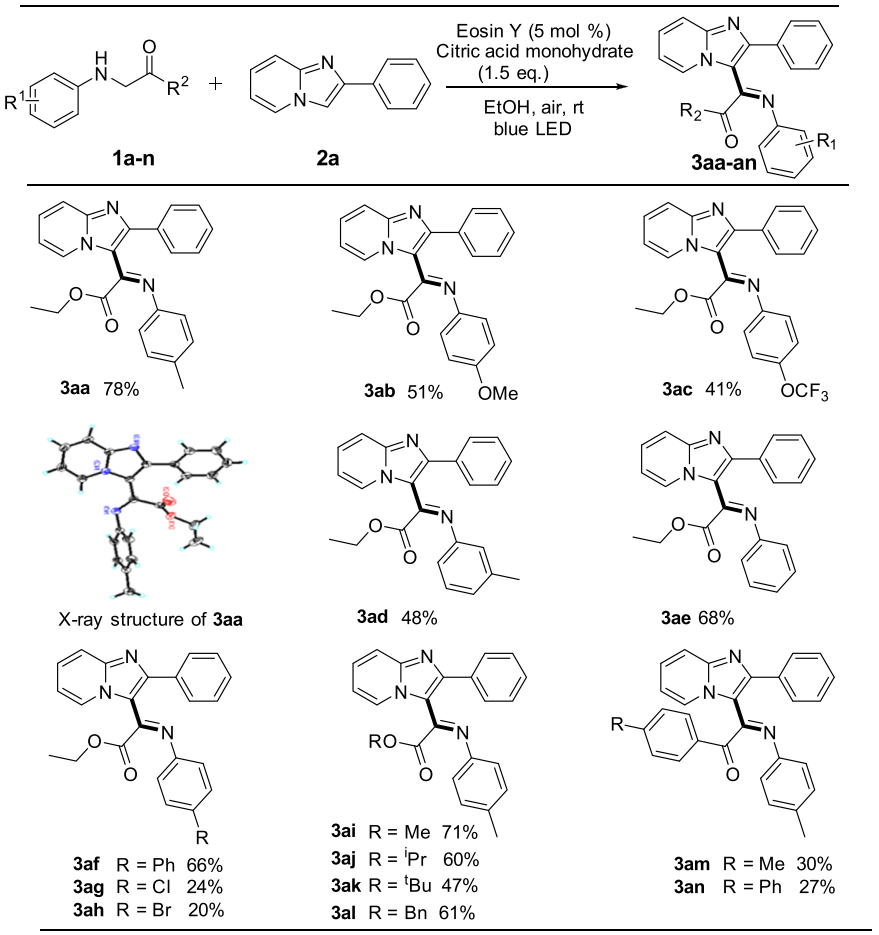
Table 2. Reaction Scope of α-Amino Carbonyl Compounds 1[a,b]



[a]Reaction conditions: **1** (0.15 mmol), **2a** (0.18 mmol), eosin Y (5 mol %), $C_6H_8O_7 \cdot H_2O$ (1.5 equiv), EtOH (2 mL) in air at room temperature under the irradiation of 18 W blue LED light for 18−24 h. [b]Isolated yield based on **1**.

with 2-phenylimidazo[1,2-*a*]pyridine **2a** was carried out in a gram scale, and the desired product **3aa** was isolated in 71% yield (1.45 g).

To evaluate the scope and limitations of the present protocol, various imidazoheterocycles **2** were examined with *N*-(4-methylphenyl)glycine ethyl ester **1a** under the current conditions. As expected, a wide range of imidazoheterocycles **2a**−**2p** could be readily transformed into the desired coupling products **3aa**−**3pa** with **1a** in 40−88% yields (Table 3). Imidazo[1,2-*a*]pyridines **2b**−**2f** possessing either an electron-donating group or electron-withdrawing group on benzene rings reacted efficiently with **1a**, giving the corresponding products **3ba**−**3fa** in good to excellent yields. The results showed that the reactivity of the electron-rich substituent was superior to that of the electron-deficient substituent on the benzene rings of imidazo[1,2-*a*]pyridines, and some halogen substituents could be tolerated by the reaction. However, when imidazo[1,2-*a*]pyridines **2f**−**2h** were utilized under the standard conditions, products **3af**−**3ah** were isolated in relatively low yields, and a complex mixture of unidentified compounds was formed. On the other hand, imidazo[1,2-*a*]pyridines including electron-rich groups on the pyridine rings **2i**−**2k** displayed better efficiency than electron-deficient groups on the pyridine rings **2g** and **2h**. The experimental results also revealed that imidazo[1,2-*a*]pyridines **2l**−**2n** bearing substituents on both the benzene ring and pyridine ring were suitable for this transformation, leading to the corresponding coupling products **3la**−**3na** in good to excellent yields. Expectedly, 2-methylimidazo[1,2-*a*]pyridine **2o** reacted with **1a** smoothly, affording the coupling product **3oa** in a yield of 50%. 2-Phenyl imidazothiazole **2p** was also compatible under the current conditions, producing the corresponding product **3pa** in 58% yield.

To better understand the mechanism of this transformation, some control experiments were carried out and the results are listed in Scheme 1. Firstly, when TEMPO (2,2,6,6-tetramethylpiperidinyloxy, a radical inhibitor) was subjected to the model reaction, no formation of the desired **3aa** was observed (Scheme 1a). The result suggested that a radical process was possibly involved in the coupling reaction. Next, we found that *N*-(4-methylphenyl)glycine ethyl ester **1a** could be converted into imine intermediate **4a**, albeit in 15% yield, as well as a yield of 12% self-cyclization product **5a** and other byproducts (Scheme 1b). Furthermore, when the reaction of imine **4a** with 2-phenylimidazo[1,2-*a*]pyridine **2a** was conducted under the standard conditions, product **3aa** and **C** were obtained in 21% and 62% yields, respectively (Scheme 1c). Low yield or a trace amount of **3aa** was formed in the absence of citric acid monohydrate or eosin Y. Moreover, intermediate **C** could be transformed into **3aa** in 86% yield under the standard conditions (Scheme 1d). Decreased yields of **3aa** were obtained without the use of citric acid

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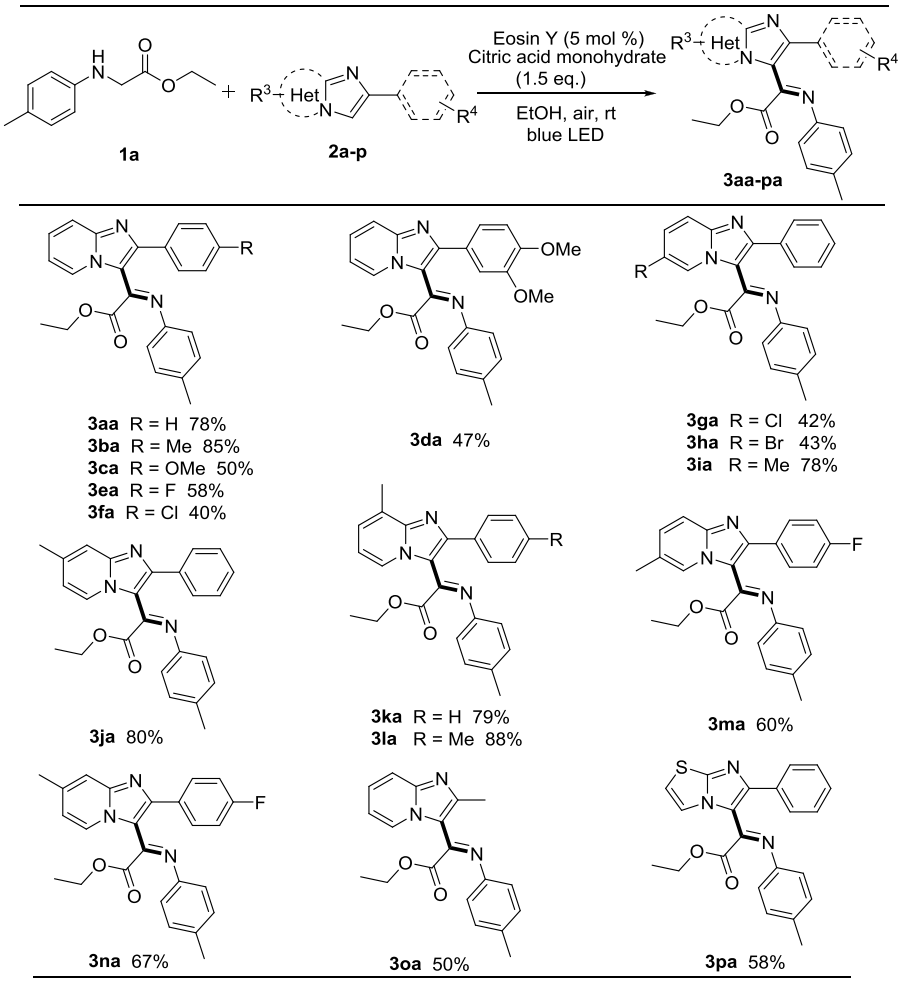
Table 3. Reaction Scope of Imidazoheterocycles 2[a,b]



[a]Reaction conditions: **1a** (0.15 mmol), **2** (0.18 mmol), eosin Y (5 mol %), $C_6H_8O_7{\cdot}H_2O$ (1.5 equiv), EtOH (2 mL) in air at room temperature under the irradiation of 18 W blue LED light for 18−24 h. [b]Isolated yield based on **1a**.

monohydrate or eosin Y. The abovementioned results indicated that both eosin Y and citric acid monohydrate played an important role in this coupling reaction. In addition, fluorescence quenching experiments with the eosin Y photoredox catalyst as well as cyclic voltammetry (CV) experiments to study the redox potential of substrates were also performed (see the Supporting Information). The experimental results revealed that the reaction might proceed through a reductive quenching pathway.

On the basis of the control experiments and precedent literature,[16−18] a plausible reaction pathway for the visible-light-induced dehydrogenative imidoylation of imidazo[1,2-*a*]pyridine is depicted in Scheme 2. Initially, upon irradiation, eosin Y was excited to produce the excited eosin Y, and a single electron transfer (SET) from *N*-arylglycine ethyl ester **1a** (+0.81 V vs SCE) to the excited eosin Y (eosin Y*/eosin $Y^{\cdot-}$: +0.83 V vs SCE) gave radical cation **A** and eosin $Y^{\cdot-}$.[16] At the same time, eosin $Y^{\cdot-}$ was oxidized by molecular oxygen to generate the ground-state eosin Y and superoxide radical anion ($O_2^{\cdot-}$). Subsequently, radical cation **A** was converted into iminium ion intermediate **B** by interacting with the superoxide radical anion ($O_2^{\cdot-}$).[17] Next, intermediate **B** underwent electrophilic addition with imidazo[1,2-*a*]pyridine **2a** to generate **C**. On the other hand, intermediate **C** could be formed, albeit in a low yield, by the auto-oxidation-promoted cross-coupling of **1a** with **2a** through an acid-catalyzed process,[18] which is followed by further oxidation to afford the desired product **3aa**.

CONCLUSIONS

In conclusion, we have developed a novel and efficient visible-light-induced dehydrogenative imidoylation of imidazo[1,2-*a*]pyridines with *α*-amino carbonyl compounds for the synthesis of imidoyl imidazo[1,2-*a*]pyridines. A series of imidazo[1,2-*a*]pyridines undergo the dehydrogenative imidoylation well with *α*-amino carbonyl compounds, affording the corresponding imidoyl imidazo[1,2-*a*]pyridines in satisfactory yields. The synthetic method has the advantages of broad substrate scope, good functional tolerance, and mild reaction conditions, thus making this conversion more sustainable and practical.

EXPERIMENTAL SECTION

General Information. Unless otherwise indicated, all reagents were purchased from commercial distributors and used without further purification. ^{1}H NMR and ^{13}C NMR were recorded at 400 or 500 MHz and 100 or 125 MHz, respectively, using tetramethylsilane as an internal reference and $CDCl_3$ as a solvent (unless otherwise stated). High-resolution mass spectra (HRMS) were measured on a

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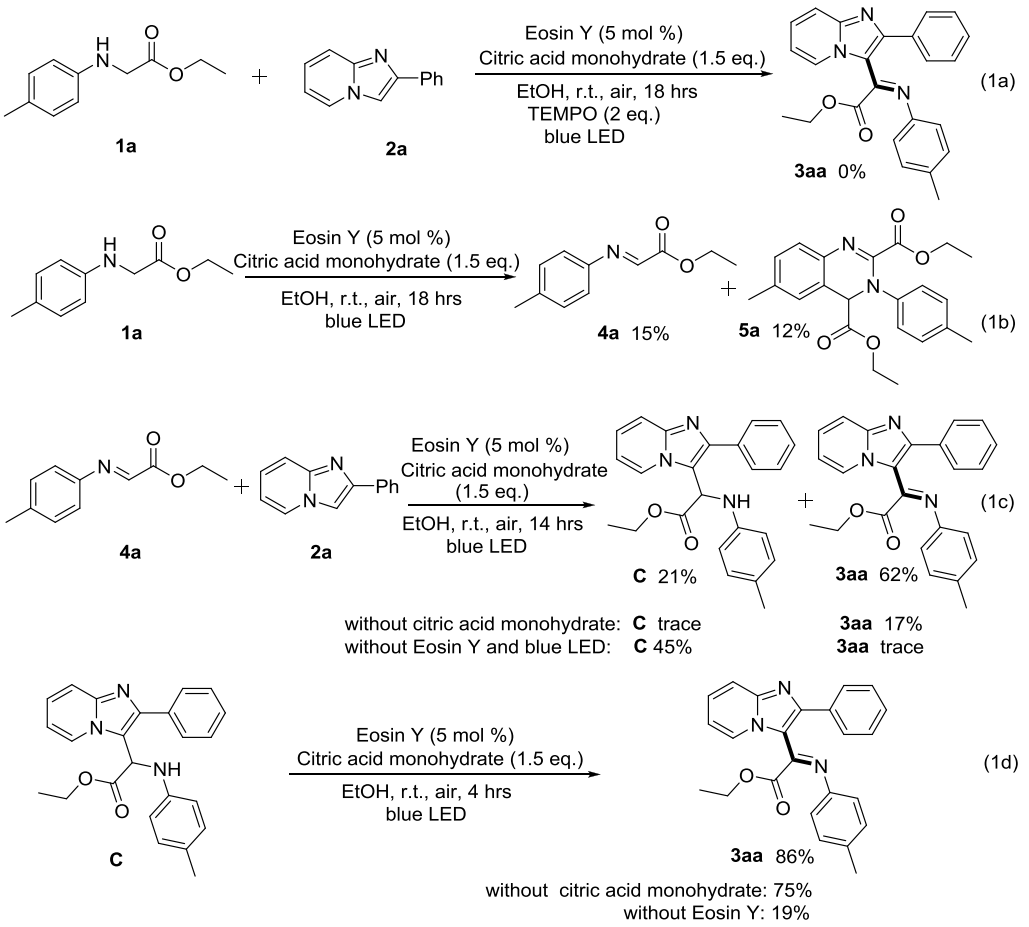
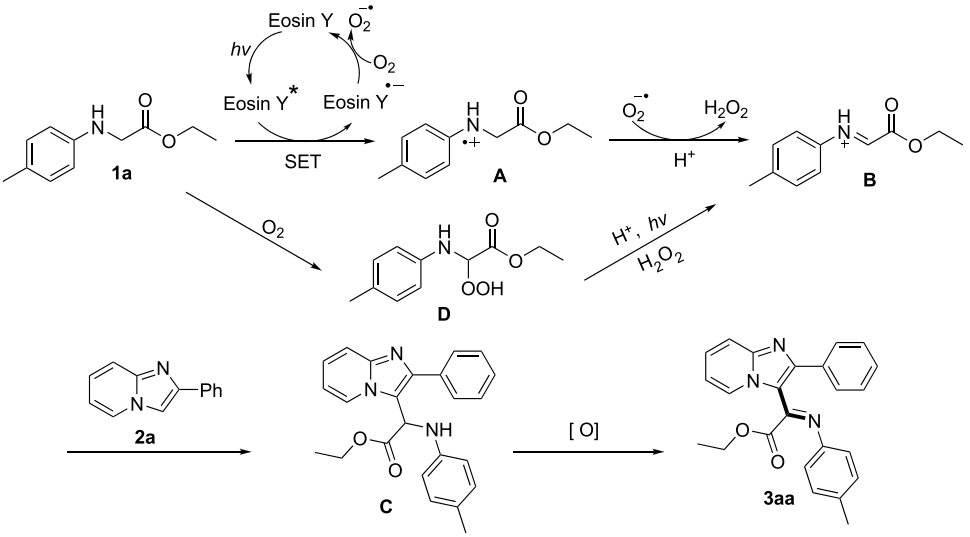
Scheme 1. Control Experiments



Scheme 2. Plausible Mechanism



quadrupole time-of-flight (Q-TOF) mass spectrometer instrument with an electrospray ionization (ESI) source. Cyclic voltammograms were obtained on a CHI 600E potentiostat. Melting points were uncorrected. Flash column chromatography was performed over silica gel 200−300 mesh. α-Amino carbonyl compounds **1** and imidazoheterocycles **2** were prepared according to the previous reported protocols.[14]

General Procedure for the Synthesis of 3. To a mixture of α-amino carbonyl compounds **1** (0.15 mmol) and imidazo[1,2-*a*]pyridines **2** (0.18 mmol) in EtOH (2 mL) were added eosin Y (0.0075 mmol, 5.1 mg) and citric acid monohydrate (0.225 mmol, 47.2 mg). Then, the reaction mixture was stirred at room temperature under air by the irradiation of a single LED light (Ouying Lighting Co., Ltd., 18 W/5313 A/455 nm) for the time indicated through the bottom of the vial at a distance of 15 cm. After the reaction was finished, the resulting mixture was concentrated under vacuum and the residue was subjected to column chromatography (silica gel,

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petroleum ether/ethyl acetate 4:1 as an eluent) to afford the desired coupling products **3**.

*Ethyl 2-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylamino)-acetate (**3aa**).* Yield 78% (44.8 mg); light yellow solid; mp: 164.4−168.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (d, J = 6.8 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.61−7.59 (m, 2H), 7.48−7.44 (m, 1H), 7.42−7.38 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 7.00 (td, J = 6.8, 0.8 Hz, 1H), 6.83 (d, J = 8.4 Hz, 2H), 3.36 (q, J = 7.2 Hz, 2H), 2.32 (s, 3H), 0.76 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.3, 153.2, 151.9, 147.3, 147.1, 134.3, 134.1, 130.0, 129.3, 128.9, 128.7, 128.2, 127.9, 119.8, 117.3, 116.7, 114.0, 61.2, 20.9, 13.2; HRMS (ESI) calcd for $C_{24}H_{22}N_3O_2$ (M + H)$^+$ 384.1707, found 384.1703.

*Ethyl-2-((4-methoxyphenyl)imino)-2-(2-phenylimidazo[1,2-a]-pyridin-3-yl)acetate (**3ab**).* Yield 51% (30.5 mg); light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (d, J = 7.2 Hz, 1H), 7.82−7.76 (m, 1H), 7.61−7.58 (m, 2H), 7.46−7.43 (m, 1H), 7.40−7.36 (m, 3H), 7.03−7.00 (m, 1H), 6.91−6.85 (m, 4H), 3.79 (s, 3H), 3.37 (q, J = 6.8 Hz, 2H), 0.79 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.6, 157.2, 153.1, 151.7, 147.1, 143.1, 134.1, 130.0, 128.9, 128.7, 128.1, 127.9, 121.2, 117.3, 116.8, 114.1, 114.0, 61.3, 55.5, 13.3; HRMS (ESI) calcd for $C_{24}H_{21}N_3O_3$ (M + H)$^+$ 400.1656, found 400.1653.

*Ethyl-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-((4-(trifluoromethoxy)phenyl)imino)acetate (**3ac**).* Yield 41% (27.8 mg); light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.60−7.57 (m, 2H), 7.54−7.49 (m, 1H), 7.42−7.40 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.06 (td, J = 7.2, 1.2 Hz, 1H), 6.95−6.91 (m, 2H), 3.36 (q, J = 7.2, 1.2 Hz, 2H), 0.73 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.7, 154.0, 152.9, 148.5, 147.2, 146.0, 133.7, 129.9, 129.6, 129.0, 128.7, 128.5, 128.3, 127.9, 121.5, 121.0, 117.4, 114.3, 61.4, 13.0; HRMS (ESI) calcd for $C_{24}H_{18}F_3N_3O_3$ (M + H)$^+$ 454.1373, found 454.1365.

*Ethyl 2-(2-Phenylimidazo[1,2-a]pyridin-3-yl)-2-(m-tolylimino)-acetate (**3ad**).* Yield 48% (27.6 mg); light yellow solid; mp: 161.4−164.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (d, J = 5.6 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.61 (dd, J = 6.0, 3.2 Hz, 2H), 7.48−7.42 (m, 1H), 7.40−7.39 (m, 3H), 7.19 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 6.4 Hz, 1H), 6.94 (d, J = 5.6 Hz, 1H), 6.77 (s, 1H), 6.72 (d, J = 6.4 Hz, 1H), 3.36 (q, J = 6.4 Hz, 2H), 2.32 (s, 3H), 0.75 (t, J = 5.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.3, 153.4, 152.0, 149.8, 147.1, 138.6, 134.0, 129.9, 129.0, 128.7, 128.6, 128.3, 128.0, 125.4, 120.6, 117.4, 116.7, 116.6, 114.2, 61.3, 21.4, 13.3; HRMS (ESI) calcd for $C_{24}H_{22}N_3O_2$ (M + H)$^+$ 384.1701, found 384.1711.

*Benzyl 2-(2-Phenylimidazo[1,2-a]pyridin-3-yl)-2-(phenylimino)-acetate (**3ae**).* Yield 68% (37.6 mg); light yellow solid; mp: 162.9−164.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.62−7.59 (m, 2H), 7.48 (dd, J = 11.6, 4.2 Hz, 1H), 7.40−7.38 (m, 3H), 7.31 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 7.2 Hz, 1H), 7.05−7.01 (m, 1H), 6.93 (d, J = 7.6 Hz, 2H), 3.35 (q, J = 7.2 Hz, 2H), 0.73 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2, 153.4, 152.1, 149.9, 147.1, 133.9, 129.9, 129.0, 128.8, 128.7, 128.4, 128.0, 124.7, 119.8, 117.4, 116.5, 114.2, 61.4, 13.2; HRMS (ESI) calcd for $C_{23}H_{20}N_3O_2$ (M + H)$^+$ 370.1550, found 370.1554.

*Benzyl 2-([1,1′-Biphenyl]-4-ylimino)-2-(2-phenylimidazo[1,2-a]-pyridin-3-yl)acetate (**3af**).* Yield 66% (44.1 mg); light yellow solid; mp: 141.8−142.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.81 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 9.2 Hz, 1H), 7.64−7.54 (m, 6H), 7.51−7.47 (m, 1H), 7.44−7.39 (m, 5H), 7.33 (t, J = 7.4 Hz, 1H), 7.06−7.00 (m, 3H), 3.38 (q, J = 7.2 Hz, 2H), 0.76 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2, 153.6, 152.1, 149.1, 147.2, 140.7, 137.6, 134.0, 129.9, 129.0, 128.8, 128.6, 128.4, 128.0, 127.5, 127.1, 126.8, 120.4, 117.4, 116.7, 114.2, 61.4, 13.2; HRMS (ESI) calcd for $C_{29}H_{24}N_3O_2$ (M + H)$^+$ 446.1863, found 446.1869.

*Ethyl 2-((4-Chlorophenyl)imino)-2-(2-phenylimidazo[1,2-a]-pyridin-3-yl)acetate (**3ag**).* Yield 24% (14.5 mg); light yellow solid; mp: 170.4−173.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.77 (d, J = 6.8 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.60−7.58 (m, 2H), 7.53−7.48 (m, 1H), 7.41−7.40 (m, 3H), 7.28 (d, J = 8.4 Hz, 2H), 7.07 (td, J = 6.8, 0.8 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 3.36 (q, J = 7.2 Hz, 2H), 0.78 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 161.9, 154.0, 152.5, 148.9, 147.3, 133.9, 129.9 (d, J = 8.3 Hz, 2C), 129.1, 128.7 (d, J = 11.8 Hz, 2C), 128.6, 128.0, 121.6, 117.5, 116.4, 114.4, 61.6, 13.3; HRMS (ESI) calcd for $C_{23}H_{18}ClN_3O_2$ (M + H)$^+$ 404.1160, found 404.1157.

*Ethyl 2-((4-Bromophenyl)imino)-2-(2-phenylimidazo[1,2-a]-pyridin-3-yl)acetate (**3ah**).* Yield 20% (13.4 mg); light yellow solid; mp: 181.9−184.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (d, J = 7.2 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.60−7.58 (m, 2H), 7.52−7.48 (m, 1H), 7.43−7.40 (m, 5H), 7.07−7.04 (m, 1H), 6.81 (d, J = 8.8 Hz, 2H), 3.36 (q, J = 7.2 Hz, 2H), 0.78 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 161.9, 153.9, 152.5, 148.9, 147.3, 133.8, 131.8, 129.9, 129.1, 128.8, 128.7, 128.1, 121.6, 117.7, 117.4, 116.5, 114.4, 61.6, 13.3; HRMS (ESI) calcd for $C_{23}H_{18}BrN_3O_2$ (M + H)$^+$ 448.0655, found 448.0651.

*Methyl 2-(2-Phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)-acetate (**3ai**).* Yield 71% (39.3 mg); light yellow solid; mp: 171.3−173.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.79 (d, J = 7.0 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.60−7.58 (m, 2H), 7.49−7.45 (m, 1H), 7.43−7.39 (m, 3H), 7.13 (d, J = 8.0 Hz, 2H), 7.02 (td, J = 7.0 Hz, J = 1.5 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 2.96 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.9, 153.4, 151.2, 147.1 (d, J = 5.7 Hz, 2C), 134.5, 134.0, 129.9, 129.6, 128.9, 128.7, 128.3, 128.1, 119.7, 117.4, 116.8, 114.2, 51.6, 21.0; HRMS (ESI) calcd for $C_{23}H_{20}N_3O_2$ (M + H)$^+$ 370.1550, found 370.1562.

*Isopropyl 2-(2-Phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3aj**).* Yield 60% (35.7 mg); light yellow solid; mp: 173.4−174.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.77 (d, J = 7.0 Hz, 1H), 7.78 (d, J = 9.5 Hz, 1H), 7.64−7.62 (m, 2H), 7.49−7.45 (m, 1H), 7.42−7.39 (m, 3H), 7.12 (d, J = 8.5 Hz, 2H), 7.02 (td, J = 7.0, 1.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H), 4.19−4.17 (m, 1H), 2.33 (s, 3H), 0.69 (d, J = 6.5 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 161.9, 153.0, 152.3, 147.3, 147.0, 134.2, 134.0, 130.1, 129.3, 128.9, 128.6, 128.1, 120.8, 119.7, 117.3, 116.5, 114.0, 70.3, 20.9, 20.8; HRMS (ESI) calcd for $C_{25}H_{23}N_3O_2$ (M + H)$^+$ 398.1863, found 398.1860.

*tert-Butyl 2-(2-Phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3ak**).* Yield 47% (29.0 mg); light yellow solid; mp: 176.5−177.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (d, J = 7.2 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.67 (dd, J = 8.0, 1.6 Hz, 2H), 7.47−7.34 (m, 4H), 7.13 (d, J = 7.6 Hz, 2H), 6.99−6.96 (m, 1H), 6.85 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 0.82 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.9, 152.9, 152.5, 147.4, 146.9, 134.1, 134.0, 130.3, 129.3, 129.0, 128.4, 128.1, 127.9, 119.6, 117.3, 116.7, 113.9, 84.1, 27.1, 21.0; HRMS (ESI) calcd for $C_{26}H_{25}N_3O_2$ (M + H)$^+$ 412.2020, found 412.2021.

*Benzyl 2-(2-Phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)-acetate (**3al**).* Yield 61% (40.7 mg); light yellow solid; mp: 161.4−162.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (d, J = 6.8 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.65−7.62 (m, 2H), 7.47−7.40 (m, 4H), 7.25−7.19 (m, 3H), 7.04 (d, J = 8.4 Hz, 2H), 7.00 (td, J = 6.8, 0.8 Hz, 1H), 6.83−6.78 (m, 4H), 4.26 (s, 2H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.4, 153.3, 151.3, 147.3, 147.1, 134.4, 134.1, 134.0, 130.0, 129.5, 129.0, 128.8, 128.7, 128.6, 128.4, 128.4, 128.1, 119.8, 117.3, 116.7, 114.1, 67.3, 21.0; HRMS (ESI) calcd for $C_{29}H_{24}N_3O_2$ (M + H)$^+$ 446.1863, found 446.1867.

*2-(2-Phenylimidazo[1,2-a]pyridin-3-yl)-1-(p-tolyl)-2-(p-tolylimino)ethan-1-one (**3am**).* Yield 30% (19.3 mg); light yellow solid; mp: 169.2−171.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (d, J = 6.8 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.52−7.48 (m, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.11−7.06 (m, 4H), 6.99 (t, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 4H), 6.78 (d, J = 8.4 Hz, 2H), 2.29 (s, 3H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.7, 158.3, 153.7, 147.1, 146.3, 144.5, 133.9, 133.4, 132.9, 130.5, 129.9, 129.4, 129.2, 129.1, 128.8, 128.4, 128.2, 127.2, 120.7, 118.0, 117.3, 114.1, 20.8; HRMS (ESI) calcd for $C_{29}H_{23}N_3O$ (M + H)$^+$ 430.1914, found 430.1917.

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*1-([1,1′-Biphenyl]-4-yl)-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)-ethan-1-one (**3an**).* Yield 27% (19.9 mg); light yellow solid; mp: 176.1−177.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (d, *J* = 6.8 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 3H), 7.46−7.36 (m, 7H), 7.15−7.08 (m, 4H), 7.01−6.93 (m, 4H), 6.81 (d, *J* = 8.0 Hz, 2H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.8, 158.1, 153.8, 147.1, 146.3, 146.0, 139.6, 134.0, 133.9, 133.4, 130.6, 129.5, 129.4, 129.3, 129.0, 128.5, 128.4, 128.3, 127.3, 127.2, 126.7, 120.7, 118.0, 117.4, 114.2, 20.8; HRMS (ESI) calcd for $C_{34}H_{25}N_3O$ (M + H)$^+$ 492.2070, found 492.2074.

*Ethyl 2-(2-(p-Tolyl)imidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)-acetate (**3ba**).* Yield 85% (50.6 mg); light yellow solid; mp: 139.1−141.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44−7.41 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.00−6.97 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 3.40 (q, *J* = 6.8 Hz, 2H), 2.37 (s, 3H), 2.33 (s, 3H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.4, 153.4, 151.9, 147.4, 147.1, 138.8, 134.2, 131.2, 129.8, 129.3, 128.6, 128.1, 120.7, 119.8, 117.3, 116.6, 113.9, 61.2, 21.4, 20.9, 13.2; HRMS (ESI) calcd for $C_{25}H_{22}N_3O_2$ (M + H)$^+$ 398.18660, found 398.18630.

*Ethyl 2-(2-(4-Methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3ca**).* Yield 50% (30.9 mg); light yellow solid; mp: 141.8−143.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.46−7.42 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.99−6.97 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 3.45 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.4, 160.3, 153.1, 151.9, 147.4, 147.1, 134.2, 131.3, 129.4, 128.6, 128.1, 126.5, 119.8, 117.2, 116.5, 113.9, 113.5, 61.3, 55.4, 20.9, 13.3; HRMS (ESI) calcd for $C_{25}H_{24}N_3O_3$ (M + H)$^+$ 414.1812, found 414.1810.

*Ethyl 2-(2-(3,4-Dimethoxyphenyl)imidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3da**).* Yield 47% (31.2 mg); light yellow solid; mp: 134.4−136.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.79 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 9.5 Hz, 1H), 7.49−7.45 (m, 1H), 7.19−7.12 (m, 4H), 7.01 (td, *J* = 7.0 Hz, *J* = 0.8 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.92 (d, *J* = 11.0 Hz, 6H), 3.47 (d, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 0.78 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.6, 153.1, 151.8, 149.6, 148.5, 147.3, 147.1, 134.4, 129.4, 128.6, 128.3, 126.7, 122.8, 119.8, 117.2, 116.5, 114.0, 112.6, 110.5, 61.4, 56.0, 55.9, 21.0, 13.3; HRMS (ESI) calcd for $C_{26}H_{26}N_3O_4$ (M + H)$^+$ 444.1918, found 444.1919.

*Ethyl 2-(2-(4-Fluorophenyl)imidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3ea**).* Yield 58% (34.9 mg); light yellow solid; mp: 151.9−155.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.59 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.13−7.07 (m, 4H), 7.02 (t, *J* = 6.8 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.45 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.3, 162.2 (d, *J* = 258.8 Hz, 2C), 152.0, 151.6, 147.2, 147.0, 134.4, 131.8 (d, *J* = 8.3 Hz, 2C), 130.1 (d, *J* = 3.0 Hz, 2C), 129.4, 128.7, 128.4, 119.7, 117.3, 116.7, 115.1 (d, *J* = 21.5 Hz, 2C), 114.2, 61.4, 21.0, 13.3; HRMS (ESI) calcd for $C_{24}H_{21}FN_3O_2$ (M + H)$^+$ 402.1612, found 402.1608.

*Ethyl 2-(2-(4-Chlorophenyl)imidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3fa**).* Yield 40% (25.0 mg); light yellow solid; mp: 142.6−145.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.57−7.49 (m, 3H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08−7.04 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.45 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.3, 151.5, 151.1, 147.1, 146.7, 135.4, 134.6, 132.0, 131.3, 129.4, 128.8, 128.7, 128.3, 119.7, 117.2, 116.8, 114.5, 61.5, 20.9, 13.3; HRMS (ESI) calcd for $C_{24}H_{21}ClN_3O_2$ (M + H)$^+$ 418.1317, found 418.1314.

*Ethyl 2-(6-Chloro-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3ga**).* Yield 42% (26.3 mg); light yellow solid; mp: 137.0−137.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 7.72 (d, *J* = 9.6 Hz, 1H), 7.59−7.57 (m, 3H), 7.44−7.39 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.36 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.1, 153.6, 151.6, 147.0, 145.3, 134.7, 133.6, 129.8, 129.4, 129.1, 128.1, 126.5, 122.3, 119.8, 117.5, 117.0, 61.4, 29.7, 21.0, 13.2; HRMS (ESI) calcd for $C_{24}H_{20}ClN_3O_2$ (M + H)$^+$ 418.1317, found 418.1313.

*Ethyl 2-(6-Bromo-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3ha**).* Yield 43% (29.7 mg); light yellow solid; mp: 130.4−132.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.67 (d, *J* = 9.6 Hz, 1H), 7.59−7.57 (m, 2H), 7.54 (dd, *J* = 9.2, 1.2 Hz, 1H), 7.40−7.39 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.36 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.1, 153.4, 151.7, 147.1, 145.5, 134.7, 133.6, 131.6, 129.9, 129.4, 129.1, 128.6, 128.1, 119.8, 117.9, 116.9, 108.9, 61.5, 20.9, 13.1; HRMS (ESI) calcd for $C_{24}H_{20}BrN_3O_2$ (M + H)$^+$ 462.0812, found 462.0810.

*Ethyl 2-(6-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3ia**).* Yield 78% (46.4 mg); light yellow solid; mp: 152.4−155.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.60−7.58 (m, 2H), 7.39−7.34 (m, 3H), 7.33 (dd, *J* = 9.2, 1.6 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.37 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.4, 153.2, 152.0, 147.5, 146.1, 134.2, 134.1, 131.1, 130.0, 129.3, 128.8, 127.9, 126.4, 124.0, 119.8, 116.6, 116.5, 61.2, 20.9, 18.6, 13.2; HRMS (ESI) calcd for $C_{25}H_{22}N_3O_2$ (M + H)$^+$ 398.18660, found 398.18639.

*Ethyl 2-(7-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3ja**).* Yield 80% (47.6 mg); light yellow solid; mp: 166.7−170.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (d, *J* = 7.2 Hz, 1H), 7.60−7.57 (m, 2H), 7.52 (s, 1H), 7.41−7.37 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.84−6.81 (m, 3H), 3.35 (q, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 2.32 (s, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.4, 153.4, 151.8, 147.6, 147.5, 139.6, 134.2, 134.1, 129.9, 129.3, 128.7, 128.0, 127.9, 119.8, 116.5, 116.4, 116.0, 61.2, 21.5, 20.9, 13.2; HRMS (ESI) calcd for $C_{25}H_{24}N_3O_2$(M + H)$^+$ 398.1863, found 398.1860.

*Ethyl 2-(8-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3ka**).* Yield 79% (47.1 mg); light yellow solid; mp: 128.9−132.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (d, *J* = 6.8 Hz, 1H), 7.62−7.59 (m, 2H), 7.41−7.37 (m, 3H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.33 (q, *J* = 7.2 Hz, 2H), 2.71 (s, 3H), 2.32 (s, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.4, 152.8, 152.0, 147.4, 147.3, 134.3, 134.1, 130.2, 129.3, 128.7, 127.9, 127.3, 127.1, 126.4, 119.8, 117.1, 114.0, 61.1, 21.0, 17.2, 13.2; HRMS (ESI) calcd for $C_{25}H_{24}N_3O_2$ (M + H)$^+$ 398.1863, found 398.1859.

*Ethyl 2-(8-Methyl-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)acetate (**3la**).* Yield 88% (54.3 mg); light yellow solid; mp: 144.3−145.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.36 (q, *J* = 7.2 Hz, 2H), 2.70 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.5, 152.9, 152.1, 147.5, 147.4, 138.6, 134.1, 131.4, 130.0, 129.3, 128.6, 127.2, 127.1, 126.4, 119.8, 117.0, 113.9, 61.1, 21.3, 20.9, 17.2, 13.2; HRMS (ESI) calcd for $C_{26}H_{26}N_3O_2$ (M + H)$^+$ 412.2020, found 412.2017.

*Ethyl 2-(2-(4-Fluorophenyl)-6-methylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)-acetate (**3ma**).* Yield 60% (37.3 mg); light yellow solid; mp: 167.7−168.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (s, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.60−7.56 (m, 2H), 7.34 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.15−7.07 (m, 5H), 6.84 (d, *J* = 6.8 Hz, 2H), 3.43 (q, *J* = 5.6 Hz, 2H), 2.40 (s, 3H), 2.34 (s, 3H), 0.78 (t, *J* = 5.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.5 (d, *J* = 246.2 Hz, 2C), 162.4, 147.4, 146.0, 134.3, 131.8 (d, *J* = 7.9 Hz, 2C), 131.2, 130.3 (d, *J* = 2.7 Hz, 2C), 129.3, 126.4, 124.1, 119.7, 116.6, 115.0 (d, *J* = 21.5 Hz, 2C), 61.3, 20.9, 18.6, 13.2; HRMS (ESI) calcd for $C_{25}H_{22}FN_3O_2$ (M + H)$^+$ 416.1769, found 416.1765.

*Ethyl 2-(2-(4-Fluorophenyl)-7-methylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)-acetate (**3na**).* Yield 67% (41.7 mg); light yellow solid; mp: 165.6−167.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (d, *J* = 5.6 Hz, 1H), 7.59−7.56 (m, 2H), 7.53 (s, 1H), 7.13−7.07 (m,

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4H), 6.86−6.81 (m, 3H), 3.43 (q, J = 5.6 Hz, 2H), 2.49 (s, 3H), 2.33 (s, 3H), 0.78 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.5 (d, J = 246.2 Hz, 2C) 162.5, 152.2, 151.6, 147.5, 147.3, 139.8, 134.5, 131.8 (d, J = 8.5 Hz, 2C), 130.3 (d, J = 2.7 Hz, 2C), 129.3, 127.9, 119.8, 116.6, 116.3, 115.9, 115.0, 114.8, 61.3, 21.5, 20.9, 13.2; HRMS (ESI) calcd for $C_{25}H_{22}FN_3O_2$ $(M + H)^+$ 416.1769, found 416.1772.

*Ethyl 2-(2-Methylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolylimino)-acetate (**3oa**).* Yield 50% (24.1 mg); light yellow solid; mp: 128.4−131.1 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.81 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 8.4 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 2.52 (s, 3H), 2.35 (s, 3H), 1.08 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.7, 151.8, 150.4, 147.2, 147.0, 134.1, 129.3, 129.1, 127.8, 120.1, 116.5, 116.2, 113.7, 61.7, 20.9, 15.4, 13.7; HRMS (ESI) calcd for $C_{19}H_{20}N_3O_2$ $(M + H)^+$ 322.1550, found 322.1548.

*Ethyl 2-(6-Phenylimidazo[2,1-b]thiazol-5-yl)-2-(p-tolylimino)-acetate (**3pa**).* Yield 58% (33.9 mg); light yellow solid; mp: 169.3−169.9 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 4.4 Hz, 1H), 7.56−7.54 (m, 2H), 7.39−7.37 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 4.4 Hz, 1H), 6.81 (d, J = 8.0 Hz, 2H), 3.43 (q, J = 7.2 Hz, 2H), 2.32 (s, 3H), 0.77 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.4, 153.4, 153.2, 150.6, 147.2, 134.3, 134.0, 129.6, 129.3, 128.8, 128.0, 122.4, 120.0, 119.9, 112.8, 61.3, 20.9, 13.2; HRMS (ESI) calcd for $C_{22}H_{19}N_3O_2S$ $(M + H)^+$ 390.1271, found 390.1275.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01940.

Optimization of the reaction conditions, X-ray crystallography data of **3aa**, and copies of ^1H NMR and ^{13}C NMR spectra of all products (PDF)

Accession Codes

CCDC 1951464 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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