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ARTICLE

Photocatalytic Regeneration of Brominating Agent in the Visible Light-Mediated Synthesis of Imidazo[1,2-*a*]pyridines

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A wide array of imidazo[1,2-*a*]pyridines are available from the coupling of 1,3-dicarbonyls with 2-aminopyridines under visible-light mediated photocatalysis. The inexpensive and commercially available fluorescein dye, erythrosine B, is employed as the photoredox catalyst and KBr as halogenating agent for *in situ* bromination. This protocol features the use of catalytic amounts of the halogenating agent which is regenerated by the photocatalyst under visible light irradiation. Cyclic voltammetry studies provide supporting evidence of reductive quenching pathway. The avoidance of stoichiometric excess of the halogen or peroxide oxidants for halide regeneration makes this protocol an environmentally-friendly synthesis with low E-factor.

Introduction

Electrophilic activation by *in-situ* halogenation is an attractive strategy to employ as a great variety of readily available starting materials can be used, thereby saving costs and time needed to prepare the required halogenated substrates. In recent years, *in-situ* halogenation has attracted significant attention in the synthesis of nitrogen-containing heterocyclic ring systems. Electrophilic activation of carbon by *in-situ* halogenation facilitates nucleophilic attack by nitrogen, thereby allowing the rapid and selective formation of C-N bonds. This synthetic strategy has allowed for the efficient preparation of indoles,[1-3] pyrazoles,[4, 5] imidazoles,[6-8] indolizines,[9] pyrroles,[10-12] quinolones,[13-15] and other nitrogen containing heterocycles.[16-19]

Imidazo[1,2-*a*]pyridines are nitrogen-containing heterocycles that are ubiquitous in pharmaceuticals and biologically active molecules.[20, 21] Compounds with the imidazo[1,2-*a*]pyridine motif have been used as organic functional materials and as ligands in organometallic chemistry.[22-26] Thus, efficient synthetic methodologies for imidazo[1,2-*a*]pyridines remain an interest to synthetic chemists. Imidazo[1,2-*a*]pyridines are traditionally constructed via a condensation reaction between 2-aminopyridines and α-halo ketones.[27-30] Over the years, alkynyl(phenyl) iodonium salts, nitroolefins, α-diazoketones, arylglyoxal hydrates and 1-bromo-2-phenylacetylenes were also paired with 2-aminopyridines,[31-35] including a few multicomponent reactions.[36-43]

In-situ halogenation has also been used to couple 2-aminopyridines with alkenes, alkynes and ketones.[44-53] In particular, the coupling of 2-aminopyridines with 1,3-dicarbonyls is popular due to the ready availability of both substrates. Early work required overstoichiometric amounts of halogenating agents such as CBr_4, $CBrCl_3$, *N*-bromosuccinimide, or $PhI(OAc)_2$ (Scheme 1a).[54-58] However, it is an environmental as well as economical disadvantage to use the halogenating agent in excess. To overcome this problem, Yu *et al.* developed a protocol with catalytic amounts of tetra-*n*-butylammonium iodide (TBAI) as the halogenating agent, and two equivalents of *tert*-butylhydroperoxide (TBHP) as oxidant to regenerate the iodide (Scheme 1b).[59] This regeneration strategy using peroxides has also been applied for *in situ* iodination in the synthesis of other heterocycles.[60, 61]

Using excess amounts of highly reactive peroxide oxidants is also not atom-economical and makes the reactions unsuitable for large-scale synthesis. With these limitations in mind, we devised a strategy to regenerate the halide using photoredox catalysis instead. Herein, we report a visible light-mediated synthesis of imidazo[1,2-*a*]pyridines with the fluorescein dye, erythrosine B, as a photoredox catalyst and KBr as the halogenating agent. Fluorescein dyes are frequently used as biological stains in cellular biology. They are also applied as dyes for inks, paints, cosmetics, papers and food. Thus, they are abundant, commercially available and inexpensive. Eosin Y (EY) in particular has been employed for a wide spectrum of organic reactions.[62-64] Erythrosine B and its acidic derivative tetraiodofluorescein on the other hand are less explored. They are currently employed in cyclization reactions,[65, 66] photoinitiated radical polymerization,[67] photodehydrogenation,[68] and as sensitizers for cis/trans isomerization of alkenes.[69, 70] The ability to regenerate the

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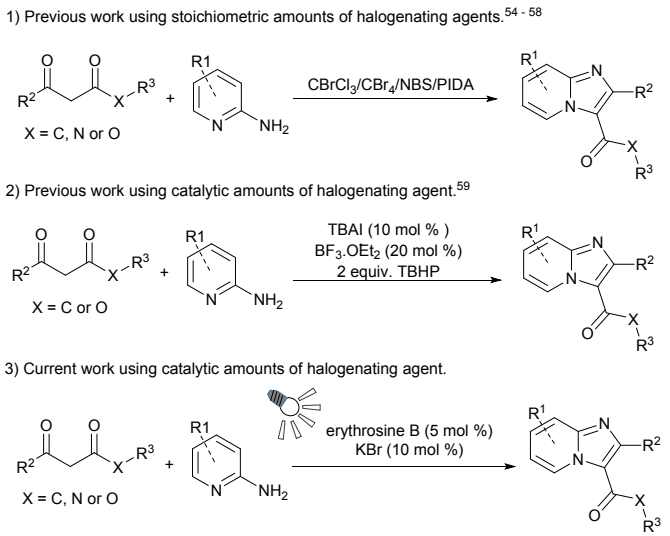


Scheme 1. Previous and current work on imidazopyridines using *in situ* halogenation strategies. Abbr. PIDA: (diacetoxyiodo)benzene; NBS: *N*-bromosuccinimide; TBAI: tetra *n*-butyl ammonium iodide; TBHP: *tert*-butyl hydroperoxide.

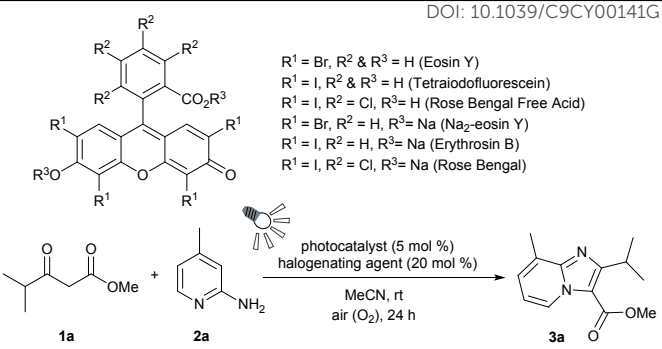
reduced erythrosine B by molecular oxygen is an important feature of our protocol as it results in a closed catalytic cycle. Aerobic oxidative coupling reactions have received increasing attention recently.[71-76] In these reactions, molecular oxygen is employed as an oxidizing agent[77, 78] or as part of the desired product itself.[79-81]

Results and Discussions

Optimization studies

We began our optimization studies by reacting 1 mmol of methyl isobutyrylacetate **1a** with 1.2 mol of 2-amino-3-methylpyridine **2a** for 24 h using 5 mol % of eosin Y and 20 mol % of KBr in acetonitrile at room temperature. The system was open to air and a 15 W compact fluorescent lamp (CFL) was used as the visible light source (Table 1). **3a** was obtained in a poor yield of 12 % (Table 1, entry 1). Slightly higher yields were obtained with tetraiodofluorescein, rose Bengal free acid and phloxin B (Table 1, entries 2-3). The disodium salt of eosin Y and rose Bengal performed significantly better with moderate to good yields, respectively, while erythrosine B gave the best result with 89 % yield (Table 1, entries 4-6). Product **3a** was not formed in the absence of photocatalyst or when the reaction was carried out in the dark, confirming the photocatalytic nature of the reaction (Table 1, entries, 7 and 8). Next, the amount of erythrosine B was varied from 1 to 10 mol % (Table 1, entries 9-11). While 10 mol % gave similar results to that of 5 mol % photocatalyst, there were significant drops in yields when 1 and 2 mol % of erythrosine B were used instead. Other alkali halide salts were also screened during the optimization process. Reaction with KI was messy with many unidentifiable side products whereas that with KCl proceeded sluggishly (Table 1, entries 12-13). On the other hand, tetra *n*-butyl ammonium bromide (TBAB) and NaBr gave moderate yields of **3a** (Table 1, entries 14-15). CsBr gave comparable yields to KBr (Table 1, entry 16). In the absence of KBr, product **3a** was not formed, suggesting that the reaction proceeded via *in situ* bromination of

Table 1. Optimization of parameters[a]



Entry	Photocatalyst	Hal. Agent	Yield **3a** (%)[b]
1	Eosin Y	KBr	12
2	Rose Bengal Free Acid	KBr	35
3	Phloxine B	KBr	39
4	Na_2-eosin Y	KBr	60
5	Erythrosine B	KBr	89
6	Rose Bengal	KBr	81
7	—	KBr	0
8[c]	Erythrosine B	KBr	0
9[d]	Erythrosine B	KBr	53
10[e]	Erythrosine B	KBr	69
11[f]	Erythrosine B	KBr	85
12	Erythrosine B	KI	n.d.
13	Erythrosine B	KCl	10
14	Erythrosine B	TBAB	67
15	Erythrosine B	NaBr	73
16	Erythrosine B	CsBr	91
17	Erythrosine B	—	0
18[g]	Erythrosine B	KBr	73
19[h]	Erythrosine B	KBr	89
20[i]	Erythrosine B	KBr	93
21[h,j]	Erythrosine B	KBr	0
22[h,k]	Erythrosine B	KBr	0
23[h,l]	Erythrosine B	KBr	0
24[h,m]	Erythrosine B	KBr	83
25[h,n]	Erythrosine B	KBr	91

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), halogenating agent (20 mol %), photocatalyst (5 mol %), solvent (10 mL), 24 h, rt in open air and under irradiation of 15 W compact fluorescence lamp (CFL). [b]Isolated yield. [c]Reaction performed in the dark. [d,e,f]1, 2 and 10 mol % photocatalyst. [g,h,i]5, 10 and 40 mol % of KBr used. [j]Under argon. [k]1 equiv. of 2,2,6,6-tetramethylpiperidin-1-yl oxyl (TEMPO) added. [l]1 equiv. of hydroquinone added. [m]1 equiv. of 2,3-dimethyl-2-butene added. [n]Scale-up to 10 mmol w.r.t **1a**. Abbr. n.d: not determined. TBAB: *n*-tetrabutyl ammonium bromide.

the β-ketoester moiety (Table 1, entry 17). The amount of KBr was varied from 5 to 40 mol % (Table 1, entries 18 to 20). Gratifyingly, the amount of KBr could be reduced to 10 mol % without a significant drop in yield of **3a** (Table 1, entries 5 and 19). However, when only 5 mol % of KBr were used, the yield decreased to 73 %. Hence, 10 mol % KBr was optimum. This is a first example involving the use of a catalytic amount of halogenating agent which is regenerated by the photocatalyst. Hence, the protocol benefits from reduced waste which translates to a smaller E-factor (mass of waste to mass of product). A scaled-up synthesis also produced

excellent yields of **3a**, 91 %, highlighting the potential of this protocol for large scale synthesis (Table 1, entry 25).

Scope of Reaction

Using the optimized conditions, a wide array of *β*-ketoesters with various alkyl or aryl substituents at the keto moiety were screened for their suitability in this reaction. With a methyl substituent, the reaction proceeded with a moderate yield of 72 % whereas ethyl, *n*-propyl and *tert*-butyl substituted building blocks fared significantly better (Table 2, **3b**-**3e**). A cyclopropyl ring or the trifluoromethyl group were also well tolerated (Table 2, **3f**-**3g**). Phenyl groups were less suitable as the reaction proceeded with low yield (Table 2, **3h**). Phenyl groups carrying the electron withdrawing NO_2 group were less tolerated compared to electron donating methoxy group (Table 2, **3i** and **3j**). Various acetoacetates were also screened for the reaction, including ethyl, isopropyl, *tert*-butyl, isopentyl, 2-methoxyethyl and allyl derivatives, proceeding with moderate to good yields of 72 % to 82 % (Table 2, **3k**-**3p**). Gratifyingly, with *N*,*N*-diethylacetoacetamide and acetylacetone, the reaction proceeded smoothly to form the corresponding products **3q** and **3r**.

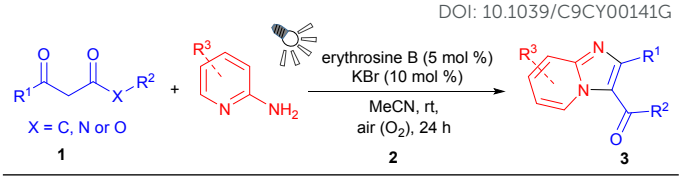
We also tested the reaction with a variety of 2-aminopyridine derivatives. 2-Aminopyridines with 4-methyl and 5-methyl substituents were well tolerated under the optimized conditions whereas only traces of product were observed with the 6-methyl derivative (Table 2, **3s**-**3u**). Chloro- and bromo-substituted 2-aminopyridines as well as 2-aminopyridines without any substituents were also suitable substrates for the reaction (Table 2, **3v**-**3x**). Only trace amounts of **3y** was observed when 2-aminopyridine with the electron withdrawing NO_2 group was used, with majority of the aminopyridine moiety not converted whereas a moderate yield of 59 % of **3z** was obtained in the case of an electron donating methoxy group.

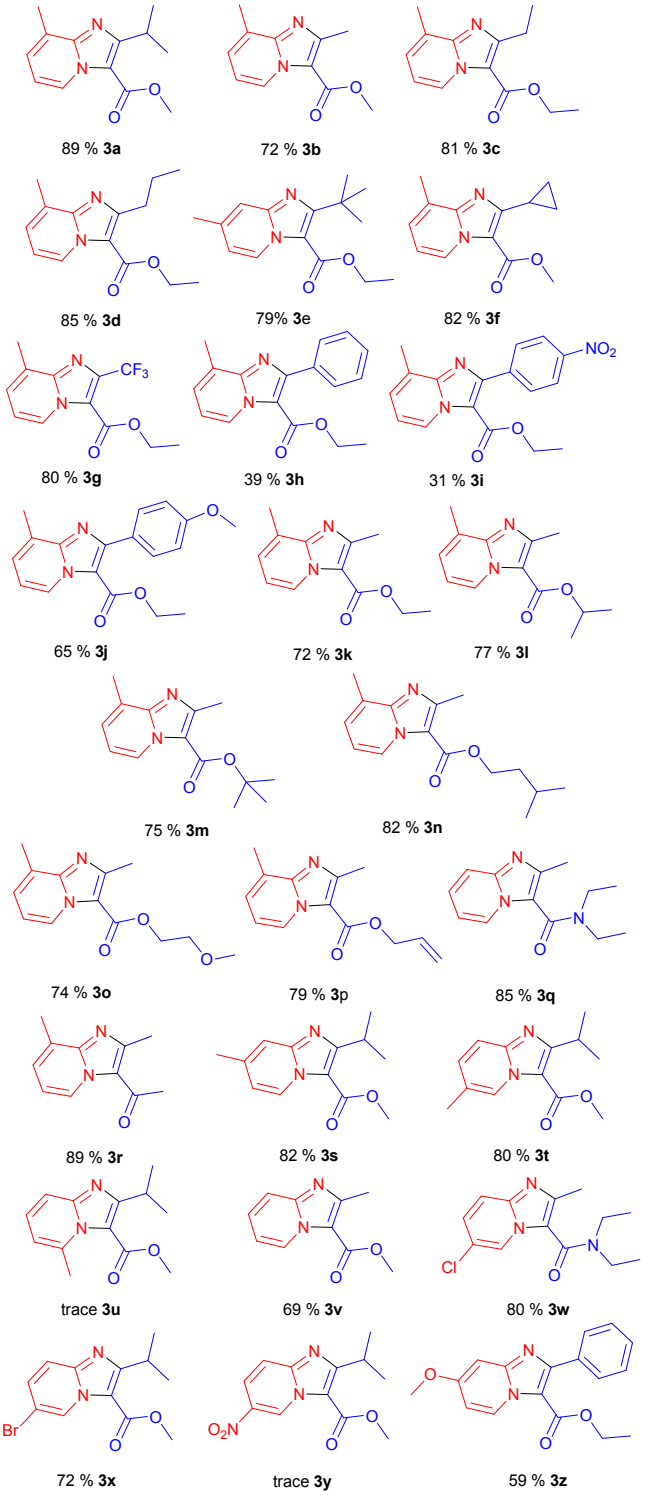
Mechanistic studies

To obtain some insight into the photocatalytic nature of the reaction, an experiment was conducted under argon. No formation of **3a** was observed, implying that O_2 is necessary (Table 1, entry 21). When 1 equivalent of the radical scavengers 2,2,6,6-tetramethylpiperidin-1-yl oxyl (TEMPO) and hydroquinone were added to two separate reaction mixtures, production of **3a** was suppressed, suggesting that free radicals are involved (Table 1, entries 22-23). However, the singlet O_2 scavenger 2,3-dimethyl-2-butane did not interfere with the reaction, and **3a** was obtained in 83 % yield (Table 1, entry 24). This supports the hypothesis that the reaction involves triplet O_2 rather than singlet O_2,[82] and that the photocatalytic step is the generation of $Br^{\cdot}$ radicals.

To better understand the role of the photoredox catalyst erythrosine B in the reaction, cyclic voltammetry (CV) was conducted to obtain the reduction potentials in the ground and the various excited states (Figure S1, supporting information). Four different samples of 1 mM erythrosine B in acetonitrile were subjected to visible light irradiation for 0 to 4 h. A standard three-electrode system was used with a glassy carbon working electrode and Ag/AgCl as the reference. Without irradiation, the CV of erythrosine B shows a peak at -1.05 V which is due to the reduction

Table 2. Scope of reaction.[a]





[a]Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), erythrosine B (5 mol %), KBr (10 mol %), MeCN (10 mL), 24 h, rt in open air and under irradiation of 15 W compact fluorescence lamp (CFL).

of EB to $EB^{\bullet-}$.[83, 84] Upon visible light irradiation, another peak at -1.87 V was observed which became more pronounced with increasing irradiation time. This value corresponds to the energy of the triplet state of erythrosine B which is formed by intersystem crossing from the singlet. The energy involved in the deactivation of the excited $^3EB^*$ to $EB^{\bullet-}$ is calculated to be 0.82 eV (Figure S2, supporting information). Similar values have been found for erythrosine B[85, 86] and its derivatives eosin Y and rose Bengal.[86-89] With 1 mM KBr in acetonitrile, the electrochemical oxidation of Br^- to $Br^\bullet$ occurs at 0.89 V vs Ag/AgCl.[87, 88] This potential matches well with the value of 0.82 V obtained for the reduction of EB to $EB^{\bullet-}$ anion radical. These results provide an insight into the role of the phototocatalyst EB in the formation of $Br^\bullet$ from Br^-. This agrees with the work of Najmar and Mac who reported the reductive quenching of fluorescein dyes using KBr.[89]

Proposed Mechanism

The proposed mechanism for the synthesis of imidazo[1,2-*a*]pyridines using photoredox catalysis is shown in Figure 1. The reductive quenching cycle starts with visible light irradiation to promote the photoredox catalyst, erythrosine B (EB), to its excited state (EB*). Single electron transfer (SET) from the bromide ion to EB* generates a $Br^\bullet$ radical and the radical anion $EB^{\bullet-}$. Aerobic oxygen regenerates the photocatalyst in a dark reaction, hence completing the reductive quenching cycle by generating a superoxide radical anion $O_2^{\bullet-}$.[63, 90] Simultaneously, the condensation reaction between 1,3-dicarbonyl **1** and 2-aminopyridine **2** affords enamine **A** and its corresponding tautomer **A'**. This is followed by the addition of $Br^\bullet$ and proton abstraction by $O_2^{\bullet-}$, forming the α-bromo intermediate **B** and regenerating a Br^- in the process. Subsequently, electron transfer to $HO_2^\bullet$ forms the HO_2^- anion. Intramolecular nucleophilic attack of **B** then gives the intermediate

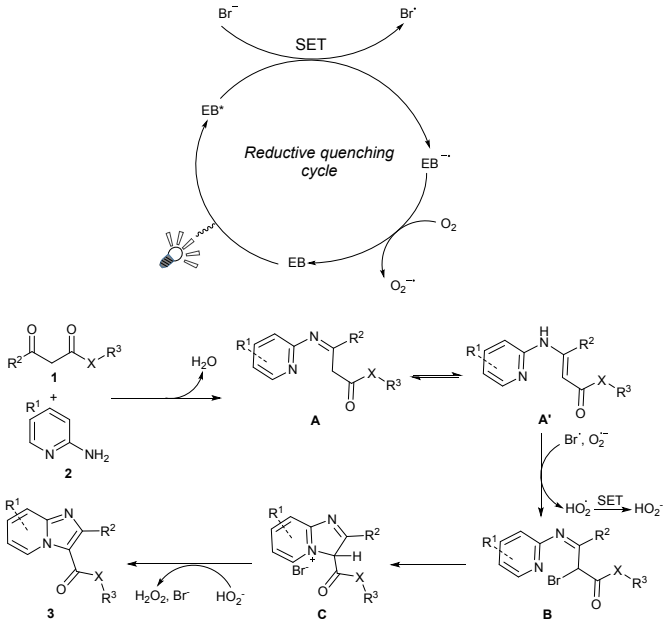


Figure 1. Proposed mechanism.

C which loses a proton to HO_2^-, resulting in the desired product **3** and regenerating the second bromide ion in the process together with H_2O_2.[63, 90] H_2O_2 likely decomposed immediately to H_2O and O_2 as no H_2O_2 could be detected by NMR[90] or KI/starch paper.[66, 82]

Conclusions

In summary, we have developed a green synthetic methodology for the construction of imidazo[1,2-*a*]pyridines by coupling of 2-aminopyridines and 1,3-dicarbonyls using visible light-mediated photoredox catalysis. This protocol requires only catalytic amounts of photocatalyst erythrosine B and the halogenating agent KBr, reducing its E-factor and making it extremely environmentally friendly. The bromide anion is regenerated in the reaction, without the need for overstoichiometric amounts of chemicals for regeneration such as peroxide oxidants. Cyclic voltammetry studies was conducted to give further evidence of the reductive quenching mechanism in the reaction. The protocol also has a wide scope of reaction and proceeds under ambient reaction conditions.

Experimental

General information

Thin layer chromatography (TLC) was performed using TLC silica gel 60 F_{254} glass plates and silica gel 60 (230 – 400 mesh) was used for column chromatography. ^1H NMR and ^{13}C NMR were measured in $CDCl_3$ using a Bruker Avance 500 (AV500) spectrometer with tetramethylsilane as an internal standard. For ^1H NMR spectra, chemical shifts were reported in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant (Hz). The signals at approximately *δ* 1.23 (^1H NMR) and *δ* 29.6 (^{13}C NMR) correspond to trace amounts of long-chained alkane impurity from technical grade hexane used in column chromatography. Mass spectra measurements were recorded on Bruker micrOTOFQII under electrospray ionization (ESI) mode. The cyclic voltammograms were recorded using an Iviumstat electrochemical interface and employing a three-electrode system consisting of glassy carbon electrodes as working and counter electrodes and Ag/AgCl as the reference electrode. The scan rate was 10 mV/s and current range of 100 µA and E step of 10 mV was employed.

Materials

The following chemicals were obtained from Alfa-Aesar, Sigma-Aldrich, and TCI and used as received: organic dyes, KBr, MeCN, 1,3-dicarbonyls and their derivatives, 2-aminopyridines and their derivatives and silica gel 60 (230 – 400 mesh). A commercially available Philips Tornado 15 W compact fluorescent lamp (CFL) was used as the visible light source.

Typical procedure for the synthesis of imidazo[1,2-a]pyridines via photoredox catalysis

A test tube was charged with methyl isobutyrylacetate **1a** (143 µL, 1.0 mmol), 2-amino-3-methylpyridine **2a** (121 µL, 1.2 mmol), potassium bromide (11.9 mg, 0.1 mmol) and erythrosine B (44 mg, 0.05 mmol) in 10 mL of MeCN. The test

tube was placed in the 8-port sample holder of the photoreactor (Figure S3, supporting information). The reaction mixture was stirred in open air under irradiation from the fluorescent lamp at room temperature. After 24 h, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were dried with anhydrous Na_2SO_4. After filtration, the solvent was removed by rotary evaporation and the residue was purified by column chromatography (hexane/ ethyl acetate, 10:1 (v/v) to afford **3a** in 89 % yield.

Methyl 2-isopropyl-8-methylimidazo[1,2-*a*]pyridine-3-carboxylate (3a) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (d, J = 7.0 Hz, 1H), 7.14 (d, J = 7.0 Hz, 1H), 6.85 (t, J = 7.0 Hz, 1H), 3.95 (s, 3H), 3.86-3.76 (m, 1H), 2.63 (s, 3H), 1.38 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 161.7, 147.4, 127.0, 126.3, 125.8, 113.4, 111.4, 51.1, 28.1, 22.1, 17.0. HRMS (ESI) calcd for $C_{13}H_{17}N_2O_2$ $[M+H]^+$: 233.1285; found 233.1287.

Conflicts of interest

There are no conflicts of interests to declare.

Acknowledgements

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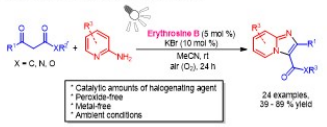
Regenerating the brominating agent by Erythrosine B closes a catalytic cycle for the construction of the imidazo[1,2-*a*]pyridine framework



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