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# Metal-free C-3 selective C(sp<sup>2</sup>)–C(sp<sup>3</sup>) heteroarylation of anilines with imidazo[1,2-*a*]pyridine derivatives *via* cross-dehydrogenative coupling†

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A general and straightforward method for the regioselective construction of C-3 heteroaryl-containing imidazo[1,2-*a*]pyridines *via* cross-dehydrogenative coupling under transition-metal-free conditions has been reported, utilizing *N,N*-dimethylaniline as the methylenation source and furnishing the C(sp<sup>2</sup>)–C(sp<sup>3</sup>) functionalized products in good to excellent yields. Mechanism studies indicate that a radical pathway is responsible for this transformation.

## Introduction

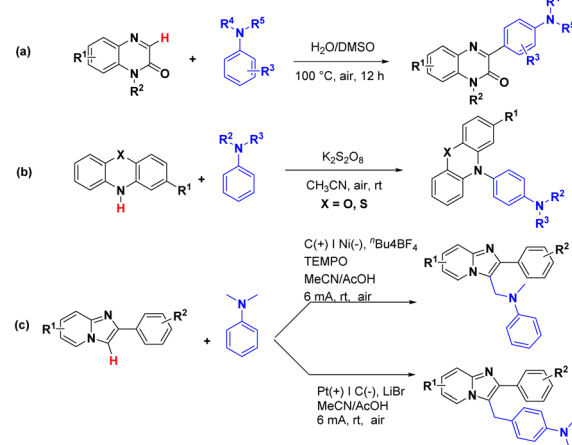
As classical N-heterocyclic compounds, imidazopyridine and its derivatives have always been present in organic synthesis, materials and pharmaceuticals.<sup>1</sup> Among which, imidazo[1,2-*a*]pyridines are considered to be privileged scaffolds due to their pharmaceutical activities,<sup>2</sup> like antiherpes,<sup>2a</sup> antifungal,<sup>2b,c</sup> antiinflammatory,<sup>2d</sup> and antiviral.<sup>2i</sup> All these unparalleled characteristics make the development of efficient synthetic methods for the characteristic compounds receive more attention than ever before. Thus, sustained efforts toward functionalized imidazo[1,2-*a*]pyridine derivatives have been developed, particularly on the C-3 position.<sup>3</sup>

Besides, the introduction of anilines has also obtained significant attention due to their specific bioactives in pharmaceuticals, natural products and advanced materials.<sup>4</sup> Therefore, substantial investigations have been committed to the exploring of novel methods for aniline-containing compounds *via* direct C–H functionalization.<sup>5</sup> Despite all the efforts, pre-functionalized substrates, transition metal catalysts and organic ligands are always inevitable, resulting in poor synthesis efficiency and low atom economy.

Taking all the above into account, cross-dehydrogenative coupling,<sup>6</sup> which with hydrogen as the main by-product, have

successfully attracted the attention of chemists and been applied into the construction of C–C,<sup>7</sup> C–X (X = N, O, S),<sup>8–10</sup> and N–X (X = N, O, S) bonds.<sup>11–13</sup> With the help of the efficient strategy, in 2021, the direct C–C heteroarylation on C-3 position of quinoxalinones with anilines was reported by Li's group (Scheme 1b).<sup>7c</sup> Same year, Lei and Zhang's group declared a novel direct C–H amination reaction for the preparation of triarylamine derivatives (Scheme 1c).<sup>7d</sup> The next year, Li, Wang and Cheng's group achieved a switchable progress for the C3-aminomethylation and C3-arylmethylation of imidazo[1,2-*a*]pyridines using *N*-methylanilines under electro-chemical conditions.<sup>7e</sup>

Previous work:



Scheme 1 Direct C–C cross-dehydrogenative coupling of anilines.

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Herein, we achieve a metal-free method for the synthesis of C-3 heteroarylation-containing imidazo[1,2-*a*]pyridine *via* direct cross-dehydrogenative coupling, affording the desired products in good to excellent yields under mild conditions.

## Results and discussion

Initially, 2-phenylimidazo[1,2-*a*]pyridine **1a** and *N,N*-dimethylaniline **2a** were selected as the model substrates. Delightfully, 27% of the cross-coupling product **3a** was generated in presence of 2.0 equivalents  $K_2S_2O_8$  in DCE (Table 1, entry 1). Encouraged by the results, solvents including DMSO, THF,  $CH_3CN$ ,  $H_2O$  and 1,4-dioxane were then investigated, and DMSO exhibited the optimal activity, giving the best yields at 65% (entries 2–6). Follow researches on the screening of oxidants manifested that  $K_2S_2O_8$  was superior to other oxidants including  $(NH_4)_2S_2O_8$ ,  $Na_2S_2O_8$ , Oxone,  $PhI(OAc)_2$ , DTBP, TBHP and *m*-CPBA (entries 7–13). At the same time, shortening the reaction time to 18 hours, the yield was descended to 58% (entry 14). Similarly, when the reaction was implemented under an oxygen atmosphere and prolonged the reaction time to 36 h, the yield was reduced to 45% (entry 15). Finally, with the amount of  $K_2S_2O_8$  declined to 1.5 equivalent or been removed, the yields dropped to 54% and 37%, respectively (entry 2, 15).

With the aforementioned optimized reaction protocol in hand, the generality and limitations of this transformation were then inspected (Table 2). Substrates containing electron-donating or electron-withdrawing groups ( $-Me$ ,  $-OMe$  and  $-OBn$ ) on both aryl ring and imidazo[1,2-*a*]pyridine ring ( $-F$ ,  $-Cl$  and  $-Br$ ) could take place this transformation smoothly and furnish the desired products from 38% to 68% yields (**3a–3n**).

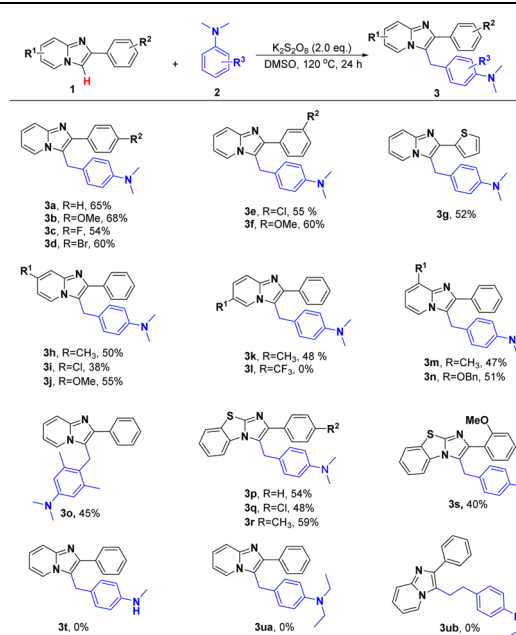
Table 1 Optimization of reaction conditions<sup>a,b</sup>

| Entry | Solvent     | Oxidant          | Yield <sup>b</sup> [%] |
|-------|-------------|------------------|------------------------|
| 1     | DCE         | $K_2S_2O_8$      | 27                     |
| 2     | DMSO        | $K_2S_2O_8$      | 65 (54) <sup>c</sup>   |
| 3     | THF         | $K_2S_2O_8$      | Trace                  |
| 4     | $CH_3CN$    | $K_2S_2O_8$      | 13                     |
| 5     | $H_2O$      | $K_2S_2O_8$      | nr                     |
| 6     | 1,4-Dioxane | $K_2S_2O_8$      | 20                     |
| 7     | DMSO        | $(NH_4)_2S_2O_8$ | 54                     |
| 8     | DMSO        | $Na_2S_2O_8$     | 48                     |
| 9     | DMSO        | Oxone            | 52                     |
| 10    | DMSO        | $PhI(OAc)_2$     | Trace                  |
| 11    | DMSO        | DTBP             | 50                     |
| 12    | DMSO        | TBHP             | 43                     |
| 13    | DMSO        | <i>m</i> -CPBA   | 40                     |
| 14    | DMSO        | $K_2S_2O_8$      | 58 <sup>d</sup>        |
| 15    | DMSO        | —                | 37 (45) <sup>e</sup>   |

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (2.0 eq.), oxidant (2.0 eq.), solvent (3.0 mL), stirred at 120 °C, under air, 24 h. <sup>b</sup> Isolated yields.

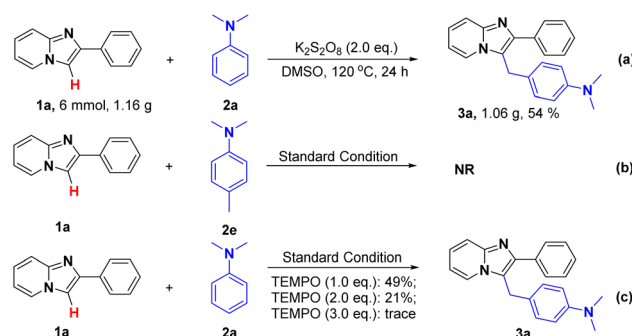
<sup>c</sup>  $K_2S_2O_8$  (1.5 eq.). <sup>d</sup>  $K_2S_2O_8$  (2.0 eq.), 18 h. <sup>e</sup> Under  $O_2$ , 36 h.

Table 2 Scope of substrates<sup>a,b</sup>



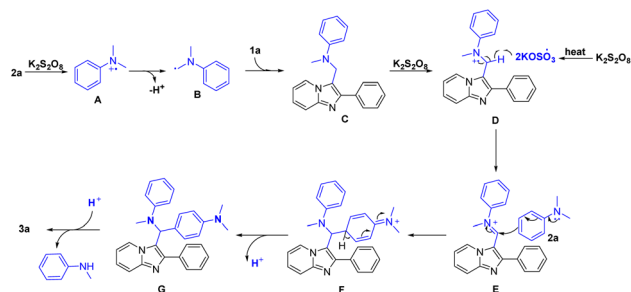
<sup>a</sup> Reaction conditions: **1** (0.3 mmol), **2** (2.0 eq.),  $K_2S_2O_8$  (2.0 eq.), DMSO (3.0 mL), stirred at 120 °C, under air, 24 h. <sup>b</sup> Isolated yields.

Ultimately, the electron-donating ones showed superior to the electron-withdrawing ones. Furthermore, with the electron-absorbent getting strong, the reaction would be less favorable. And no product could be obtained when 2-phenyl-6-(trifluoromethyl)imidazo[1,2-*a*]pyridine was employed as beginning material (**3l**). To our satisfaction, this transformation could be smoothly implemented with series of *N,N*-dimethyl-4-((2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazol-3-yl)methyl)aniline derivatives, and resulted the coupling products in 40–59% yields (**3p–3s**). At the same time, substrates with large hindrance substituents showed poor reactivity and gave the desired products up to 45% yields, which indicating that steric effect had an obvious influence on the reaction activity (**3o**, **3s**). Follow investigation of *N*-methylaniline and *N,N*-diethylaniline manifested that the changes in the source of methylene have a decisive effect on the reaction (**3t–3ub**).



Scheme 2 Gram-scale reaction and mechanistic studies.





Scheme 3 Plausible mechanistic pathway.

Next, a gram-scale reaction was conducted and the desired product could be obtained in 54% yields (Scheme 2a). Then, to gain more insights into the reaction mechanism, several control experiments were then conducted. Firstly, 4-methyl-*N,N*-dimethylaniline (**2e**) was utilized to replace **2a** as the starting material (Scheme 2b) and no desired product was detected. Next, in all of these cases, the yield of **3a** had a significantly decrease with the addition of 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO), suggesting a radical pathway may be included for this transformation (Scheme 2c).

Based on the aforementioned experiments and previous reports,<sup>7c,8d,e,14,15</sup> a plausible radical pathway mechanism was proposed (Scheme 3). Initially, *N,N*-dimethylaniline-radical-cation (**A**) was generated in the presence of  $K_2S_2O_8$ . Then, hydrogen transfer from (**A**) to furnish the crucial iminium species (**B**). Next, (**B**) attacked **1a** at C3 position to produce intermediate (**C**), which underwent further oxidation to generate (**D**). Next, the sulfate radical anion was generated from  $K_2S_2O_8$  under thermolysis and absorbed a hydrogen radical from (**D**) to give intermediate (**E**). Subsequently, species (**F**) was obtained from (**E**) *via* the nucleophilically attacked of **2a** and deprotonated to provide (**G**). Finally, the target product **3a** was furnished by eliminating *N*-methylaniline under the addition of hydrogen proton.

## Conclusions

In summary, we have developed a practical and metal-free method for the preparation of C-3 heteroarylation of anilines with imidazo[1,2-*a*]pyridine derivatives *via* cross-dehydrogenative coupling under mild conditions, exhibiting excellent functional group tolerance and giving the desired products in good to excellent yields with highly atom economic. Herein, *N,N*-dimethylaniline was utilized as the methylation source, which further enriched the content of methylation reaction. Control experiments revealed that a radical pathway was included in this transformation, and the gram-scale reaction showed that the ideal method possessed further application value.

## Experimental section

### General information

All the chemicals were obtained commercially and used without any prior purification.  $^1H$  NMR,  $^{13}C$  NMR and  $^{19}F$  NMR spectra

were recorded on a BrukerAvanceII 400 spectrometer. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C) and ethyl acetate. Unless otherwise noted. All compounds were characterized by  $^1H$  NMR,  $^{13}C$  NMR,  $^{19}F$  NMR and HRGC-HRMS, which are consistent with those reported in the literature.

### General procedure for the synthesis of 1a

A dried round-bottom flask was charged with 2-aminopyridine (3.0 mmol) and 2-bromoacetophenone (3.0 mmol) placed in a glass tube under neat conditions were added methanol (3.0 mL), the mixture was sonicated at 30 °C for 1 hour and then dried under vacuum. The solution of PE/AcOEt was added, the mixture was filtered under reduced pressure, and the residue was washed with PE and gave **1a** as white solid.

### General procedure for synthesis of 3a

A mixture of the **1a** (0.3 mmol), **2a** (2.0 eq.),  $K_2S_2O_8$  (2.0 eq.) in DMSO (3.0 mL) was placed in a Schlenk tube and stirred at 120 °C under air atmosphere for 24 h. Then the mixture was then allowed to reach room temperature and poured into water (5.0 mL). The mixture was extracted with ethyl acetate (5.0 mL  $\times$  3) and the combined organic layer was washed with brine (10.0 mL), dried with  $Na_2SO_4$ , and the solvent was removed under reduced pressure. The product **3a** was purified by flash column chromatography using PE/AcOEt as an eluent.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

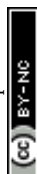
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