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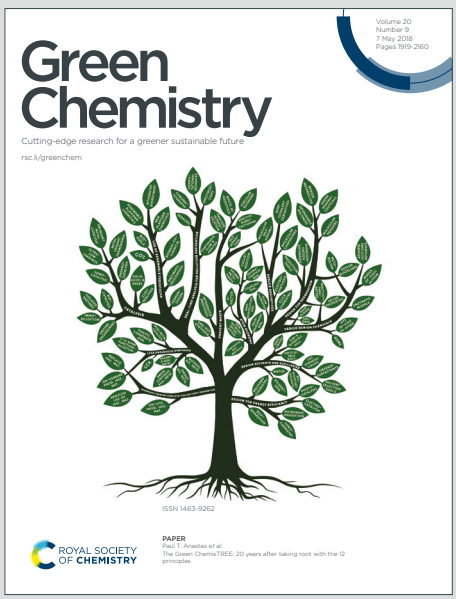




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COMMUNICATION

# Base-promoted aerobic oxidative synthesis of fused 1,3,5-triazines under metal-free conditions

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**An efficient base-promoted aerobic oxidation procedure for the synthesis of fused 1,3,5-triazines from 2-aminobenzimidazoles, aromatic aldehydes and ammonium iodide has been developed. In this multi-component protocol, ammonium iodide served as a convenient nitrogen source and four C−N bonds were formed in one-pot under metal-free conditions.**

Triazines, an important class of six-membered rich-nitrogen heterocycles, have received widespread application in pharmaceuticals, agricultures, organic synthesis and function materials.[1] Notably, 1, 3, 5-triazines have become the important isomers of triazines due to their special structures and chemical properties.[2] Among them, as privileged scaffolds in medicinal chemistry, the fused 1,3,5-triazines have been used as enzyme inhibitors, receptor ligands, anti-lung and breast cancer agents (Figure 1).[3] In addition, benzimidazole-fused 1,3,5-triazines were proved to possess significant antioxidant and anticancer activity.[4] Owing to the significant pharmaceutical applications and the biological values of fused 1,3,5-triazine derivatives, the synthesis of these heterocycles has recently attracted considerable interest.

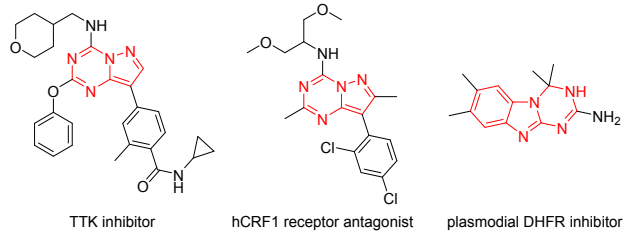
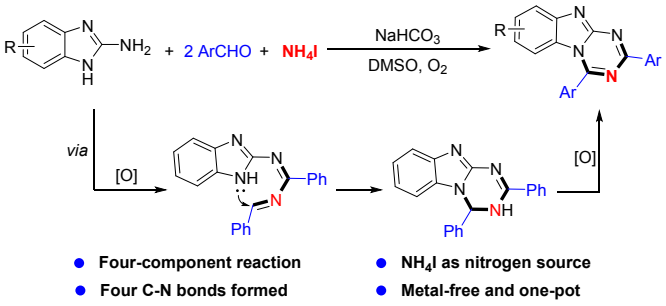



**Figure 1** Important bioactive fused 1,3,5-triazines

Gradual increases in the strategies of constructing fused 1,3,5-triazine bicyclic skeletons with pyridines,[5] imidazoles,[6] pyrazoles,[7] triazoles,[8] tetrazoles[9] and thiazoles[10] have been reported. However, efficient methods for the synthesis of benzimidazole-fused 1,3,5-triazines from readily available starting materials are rare. Traditionally, *N*-benzimidazol-2-yl imidates,[11] benzimidazol-guanidines[12] and *N*-benzimidazolyl amidines[13] were mainly used as the starting materials to provide the corresponding benzimidazole-fused 1,3,5-triazine products. For example, Bazgir et al. developed the first cobalt-catalyzed benzimidazo[1,2-*a*]-1,3,5-triazines synthesis from benzimidazol-guanidines and isocyanides *via* isocyanide insertion cyclization.[12a] In 2018, Chang and co-workers reported the multi-step synthesis of benzimidazo[1,2-*a*]-1,3,5-triazines by copper(I) iodide/iodine catalyzed annulation reaction of *N*-benzimidazolyl amidines with aldehydes.[13] In spite of the methods can be effectively used to prepare benzimidazo[1,2-a]-1,3,5-triazines, long synthetic routes, transition-metal catalysts and strong oxidant (DDQ) were still being used in most cases. Therefore, a simple, effective and metal-free route to synthesize the title compounds is urgently needed.

2-Aminobenzimidazoles were widely existed in biologically active natural products and pharmaceuticals, as well as frequently employed as viable building blocks in synthetic chemistry. Normally, 2-aminobenzimidazoles could provide a structurally feasible N-C-N splicing unit to construct diverse nitrogen-containing heterocycles including fused imidazoles,[14] pyrimidines[15] and thiadiazoles.[16] To our knowledge, 2-aminobenzimidazoles were also employed as starting materials for benzimidazo[1,2-*a*]-1,3,5-triazines formation.[4,17] However, these methods mainly rely on highly functionalized coupling partners, harsh reaction conditions and only a handful of substrates were commercially available, which not only increases the difficulty of operations but also limits the applications. Thus, efficient methods for the synthesis of diverse benzimidazo[1,2-*a*]-1,3,5-triazine compounds from readily available raw materials under simple one-pot and metal-




**Scheme 1** New strategy for the synthesis of benzimidazo[1,2-*a*]-1,3,5-triazines.

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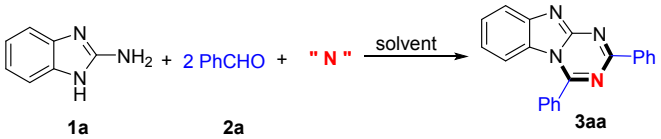
free conditions are highly desirable. Ammonium iodide is cheap and easy to handle, therefore, it would be an ideal nitrogen source to prepare various nitrogen-containing heterocycles. Besides, multicomponent reactions (MCRs) are a powerful tool for constructing diverse and complex compounds with featured productivity, atom economy and facile execution, which usually employ simple and readily available starting materials as the reaction substrates.[18] Within our continue efforts on utilizing ammonium salts and simple substrates to synthesize *N*-heterocycles *via* MCRs,[19] herein, we described an efficient base-promoted aerobic oxidative four-component reaction for multi-substituted fused 1,3,5-triazines synthesis from 2-aminobenzimidazoles, aromatic aldehydes and ammonium iodide under metal-free conditions (Scheme 1). In this multicomponent strategy, ammonium iodide was used as one of the nitrogen sources and four C−N bonds were formed in one-pot.

**Table 1** Optimization of the reaction conditions[a]



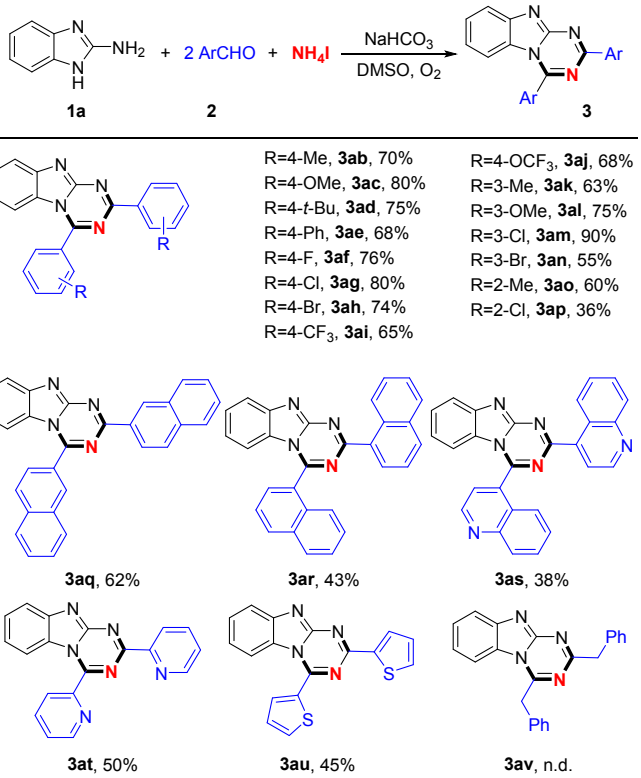

**1a** **2a** **3aa**

| entry | base | " N " | additive | solvent | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | | $NH_4I$ | DMSO | PhCl | 41 |
| 2 | | $NH_4Br$ | DMSO | PhCl | 20 |
| 3 | | $NH_4HCO_3$ | DMSO | PhCl | 8 (17)[c] |
| 4 | | $NH_4OAc$ | DMSO | PhCl | 6 |
| 5 | $NaHCO_3$ | $NH_4I$ | DMSO | PhCl | 69 |
| 6 | $Na_2CO_3$ | $NH_4I$ | DMSO | PhCl | 57 |
| 7 | NaOH | $NH_4I$ | DMSO | PhCl | 53 |
| 8 | $NaHCO_3$ | $NH_4I$ | DMSO | toluene | 51 |
| 9 | $NaHCO_3$ | $NH_4I$ | DMSO | *o*-DCB | 67 |
| 10 | $NaHCO_3$ | $NH_4I$ | DMSO | o-xylene | 55 |
| 11 | $NaHCO_3$ | $NH_4I$ | DMSO | NMP | trace |
| 12 | $NaHCO_3$ | $NH_4I$ | methyl phenyl sulfoxide | PhCl | 60 |
| 13 | $NaHCO_3$ | $NH_4I$ | diphenyl sulfoxide | PhCl | 45 |
| 14 | $NaHCO_3$ | $NH_4I$ | $K_2S_2O_8$ | PhCl | 29 |
| 15 | $NaHCO_3$ | $NH_4I$ | TBHP | PhCl | 16 |
| 16 | $NaHCO_3$ | $NH_4I$ | | PhCl | 57 (5)[h] |
| 17[d] | $NaHCO_3$ | $NH_4I$ | DMSO | PhCl | 66 |
| 18[e] | $NaHCO_3$ | $NH_4I$ | DMSO | PhCl | 67 |
| 19[f] | $NaHCO_3$ | $NH_4I$ | DMSO | PhCl | 68 |
| 20[g] | $NaHCO_3$ | $NH_4I$ | DMSO | PhCl | 79 |
| 21[g,h] | $NaHCO_3$ | $NH_4I$ | DMSO | PhCl | 11 |

[a] Conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), "N" (0.3 mmol), base (0.2 mmol), additive (0.2 mmol), solvent (0.6 mL), 140 °C, 16 h, under oxygen unless otherwise noted. [b] Isolated yield based on **1a**. [c] KI (0.2 mmol) was added. [d] DMSO (0.4 mmol). [e] $NaHCO_3$ (0.4 mmol). [f] 150 °C. [g] 4Å molecular sieves (100 mg) was added. [h] Under nitrogen.

To obtain the optimized reaction conditions, 2-aminobenzimidazole (**1a**), benzaldehyde (**2a**) and ammonium iodide were used as the model substrates (Table 1). Firstly, several ammonium salts were screened to find the matching nitrogen source in the absence of base (entries 1-4). Among them, ammonium iodide showed the most effective reactivity to afford the target benzimidazo[1,2-*a*]-1,3,5-triazine product **3aa** in 41% yield (entry 1). When $NH_4HCO_3$ was used as nitrogen source, the introduction of KI could increase the yield (entry 3), which showed that iodine ion could promote this transformation. Fortunately, we found that enhanced yields were obtained when various bases were used (entries 5-7) and the reaction yield could improve to 69% in the presence of $NaHCO_3$ (entry 5). Encouraged by these exciting results, we continuously investigated the influence of some organic solvents such as toluene, *o*-dichlorobenzene, *o*-xylene and NMP, it was found that no increase in yield was observed (entries 8-11). Sulfoxide reagents, $K_2S_2O_8$ and TBHP were also investigated as additives to improve the yield (entries 12-15). When DMSO was not used, the target compound can also be obtained with 57% yield (entry 16). Furthermore, there was no distinct improvement in yield by increasing the amount of DMSO or $NaHCO_3$ (entries 17 and 18). Meanwhile, increasing the reaction temperature, the yield was also not improved obviously (entry 19). To our delight, we accidentally discovered that 79% yield could be achieved upon the introduction of 4Å molecular sieves to the reaction mixture (entry 20). Lower yields were obtained when the reaction were performed under nitrogen (entries 16 and 21), which indicated that an oxygen atmosphere was required to ensure good conversion of the reaction.

**Table 2** Scope of aromatic aldehydes[a]




**1a** **2** **3**

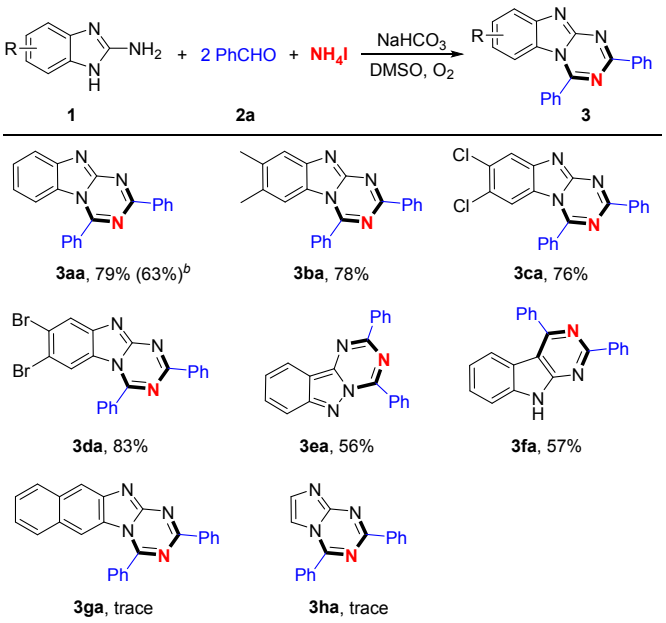
[a] Conditions: **1a** (0.2 mmol), **2** (0.6 mmol), $NH_4I$ (0.3 mmol), $NaHCO_3$ (0.2 mmol), DMSO (0.2 mmol), PhCl (0.6 mL), 4Å MS (100 mg), 140 °C, 16 h, under oxygen, and isolated yields based on **1a**.

With the optimized reaction conditions in hand, we first explored the scope and generality of aromatic aldehydes for the four-component benzimidazo[1,2-*a*]-1,3,5-triazines synthesis (Table 2). In general, the desired products **3ab-3ap** were synthesized in moderate to good yields when the reactions were carried out under the given conditions. Moreover, no significant electric effect and steric hindrance effect were observed when the substituents located at different positions. Thereinto, halogen functional groups were well tolerated to give the corresponding products (**3af-3ag** and **3am-3an**) in good yields. In particular, benzaldehydes with chloro

substituent at the *para* and *meta* positions were high reactive in the optimized system, delivering **3ag** and **3am** in 80% and 90% yields, respectively. Lower yield was obtained when the chloro group was located at the *ortho*-position of benzaldehyde. In addition, the target products **3aq** and **3ar** were obtained in 62% and 43% yields when sterically hindered 2-naphthaldehyde and 2-naphthaldehyde were used as the substrates. It is worth noting that heteroaromatic aldehydes, such as 4-quinolinealdehyde, 2-pyridinealdehyde and 2-thiophenealdehyde, could smoothly involve in this kind reaction and afforded the anticipated products in moderate yields (**3as-3au**). No target product was detected when aliphatic aldehyde was used as substrate (**3av**). Unsurprisingly, when two different aldehydes were used, four products were generally generated with poor chemoselectivity.

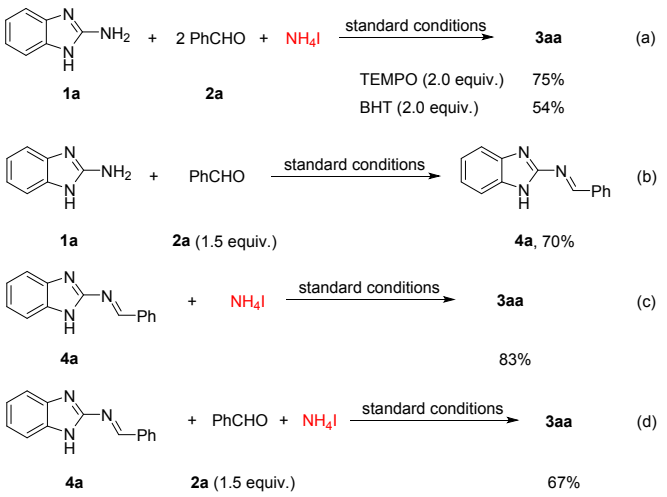
In order to further investigate the scope and limitation of this four-component system, a series of 2-aminobenzimidazoles were explored under the optimized reaction conditions (Scheme 3). For the benzimidazo[1,2-*a*]-1,3,5-triazine formation, a gram-scale reaction gave **3aa** in 63% yield. Meanwhile, it was found that 2-aminobenzimidazole with two methyl groups could be suitable substrate to give the desired product **3ba** in 78% yield. Analogously, good yields were also obtained when using 2-aminobenzimidazoles with two halogen functional groups as substrates (**3ca-3da**). Notably, 1*H*-indazol-3-amine also reacted well to afford the indazole fused 1,3,5-triazine **3ea** in moderate yield. Moreover, as an unexpected product, 2,4-diphenyl-9*H*-pyrimido[4,5-*b*]indole **3fa** instead of the desired indole fused 1,3,5-triazine product was obtained. This phenomenon could be attributed to the fact that the C3 position in indole is more active, which directly leads to the formation of C-C bond rather than C-N bond. Unfortunately, trace amounts of products **3ga** and **3ha** were detected when 1*H*-naphtho[2,3-*d*]imidazol-2-amine and 2-aminoimidazole were used in the present system.

**Table 3** Scope of 2-aminobenzimidazoles[a]

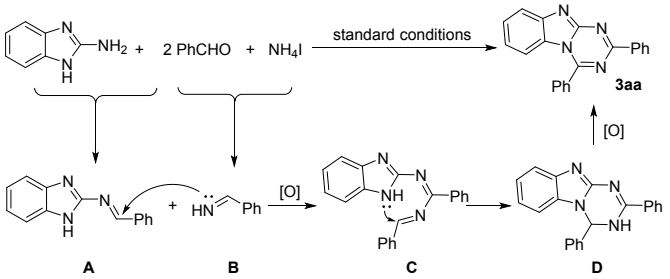



[a] Conditions: **1** (0.2 mmol), **2a** (0.6 mmol), $NH_4I$ (0.3 mmol), $NaHCO_3$ (0.2 mmol), DMSO (0.2 mmol), PhCl (0.6 mL), 4Å MS (100 mg), 140 °C, 16 h, under oxygen, and isolated yield based on **1**. [b] Isolated yield from 5 mmol scale reaction.

In order to understand the mechanism of the reaction, some control experiments were carried out (Scheme 2). It was found that the addition of radical scavenger such as TEMPO and BHT into the systems had no obvious prohibiting effect on the yield (Scheme 2, a), suggesting that the four-component reaction might not proceed through a radical pathway. When the model reaction was performed in the absence of $NH_4I$, the imine **4a** was generated *via* condensation of 2-aminobenzimidazole and benzaldehyde in 70% isolated yield. Subsequently, by using the newly formed **4a** as a substrate under standard conditions without benzaldehyde, the target benzimidazo[1,2-*a*]-1,3,5-triazine **3aa** was obtained in 83% yield, (Scheme 2, c). The result revealed that the imine **4a** might break down into 2-aminobenzimidazole and benzaldehyde in the system. This might be the reason why the reaction had no chemical selectivity when two different aldehydes were used. Furthermore, the imine **4a** could convert into the final product in moderate yield under the optimized reaction conditions (Scheme 2, d).




**Scheme 2** Control experiments




**Scheme 3** Possible reaction pathway

Based on aforementioned experimental results and related literatures,[13,19a,c,20] a plausible reaction mechanistic pathway was proposed in Scheme 3. Taking the formation of product **3aa** for example, first of all, the condensation of benzaldehyde with 2-aminobenzimidazole and ammonium iodide affords imine intermediates **A** and **B**, respectively. Then intermediate **D** is generated *via* two-step cyclization reaction of **A** and **B** under the aerobic condition. Subsequently, intermediate **D** undergoes an oxidative dehydrogenation reaction affords the final product **3aa**.

In summary, we developed a base-promoted four-component reaction for substituted benzimidazo[1,2-*a*]-1,3,5-triazines synthesis from 2-aminobenzimidazoles, aromatic aldehydes and ammonium iodide under metal-free conditions. Various indazole fused 1,3,5-triazines and pyrimido[4,5-b]indoles were selectively formed in the simple system. In this multi-component strategy, aldehydes and ammonium iodide were employed to provide two C1 sources and one nitrogen source, respectively. Besides, the synthetic approach

was operationally simple and four C−N bonds were formed in one-pot. This method provided an efficient approach to various substituted fused 1,3,5-triazines under simple reaction conditions and an alternative strategy for the construction of other fused heterocyclic frameworks from readily available raw materials.

## Acknowledgements

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