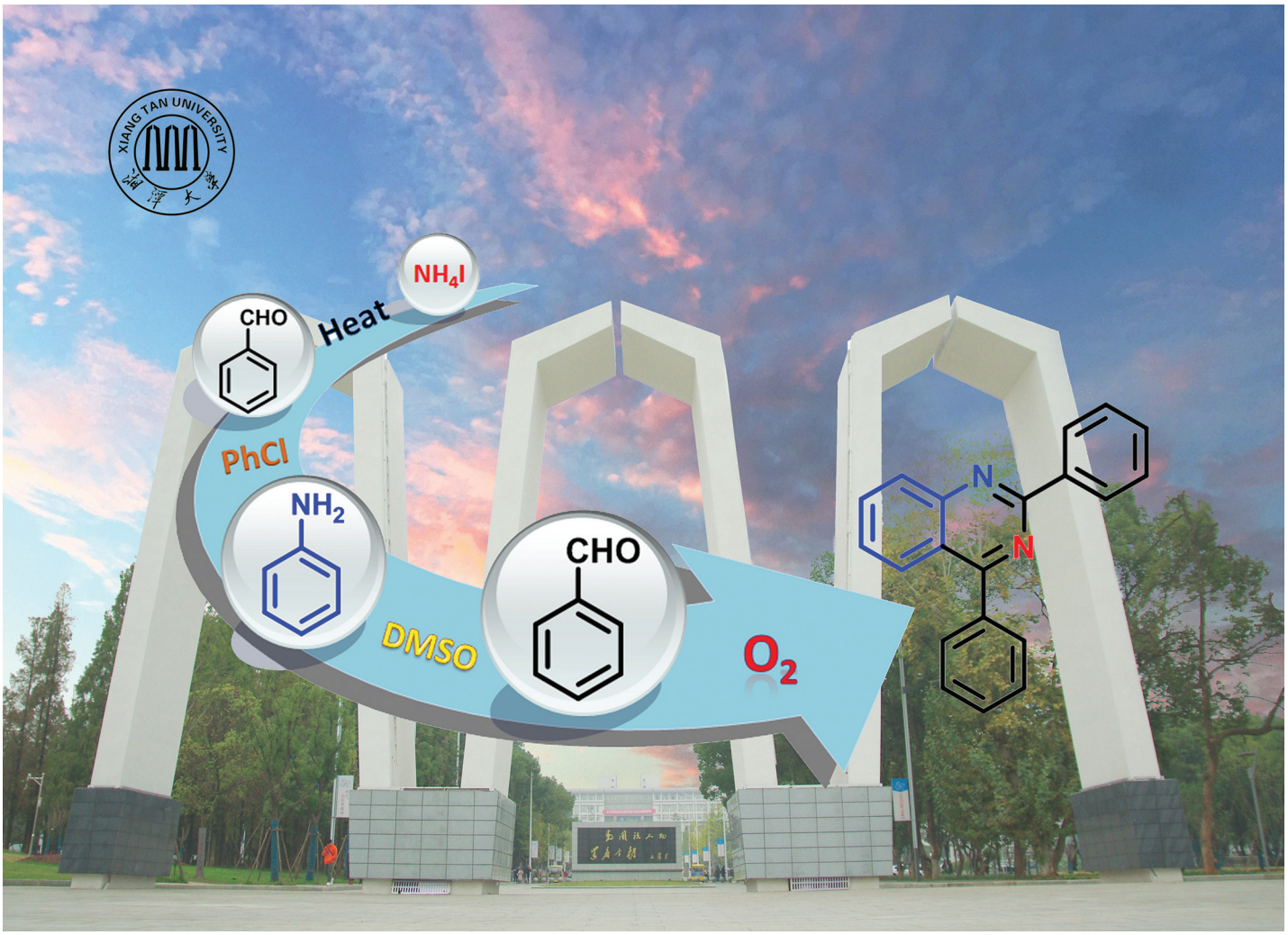

An article presented by Prof. Guo-Jun Deng *et al.* of Xiangtan university, Xiangtan, China.

Four-component quinazoline synthesis from simple anilines, aromatic aldehydes and ammonium iodide under metal-free conditions

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As featured in:

See Fuhong Xiao, Guo-Jun Deng *et al.*, *Green Chem.*, 2018, **20**, 5459.

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Cite this: *Green Chem.*, 2018, **20**, 5459

Received 21st August 2018,
Accepted 15th October 2018

DOI: 10.1039/c8gc02654h

rsc.li/greenchem

Four-component quinazoline synthesis from simple anilines, aromatic aldehydes and ammonium iodide under metal-free conditions†

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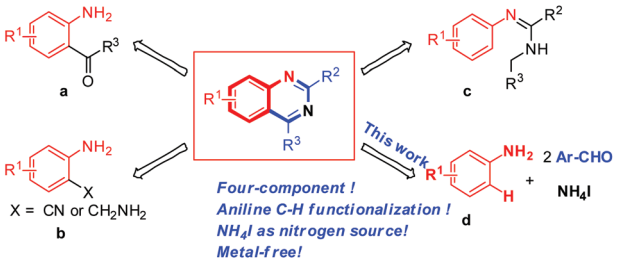
A four-component procedure for the preparation of substituted quinazolines from anilines, aromatic aldehydes and ammonium iodide is described. The C–H bond *ortho* to the amino group in anilines was directly functionalized under metal-free conditions. Two aldehydes were involved in this reaction and ammonium iodide was used as one of the nitrogen sources. This reaction provides a strategy for the facile construction of substituted quinazolines from simple anilines and other readily available reactants.

As an important class of fused six-membered heterocycles, quinazolines are widespread in natural products and pharmaceuticals.[1] In particular, multi-substituted quinazolines display a wide range of biological activities such as anticancer,[2] anti-HIV,[3] anti-inflammatory,[4] antibacterial[5] and antitubercular.[6] Some of them are known to act as selective inhibitors of the tyrosine kinase activity of the epidermal growth factor receptor (EGFR).[7] Because of the many pharmaceutical applications as well as the biological values of quinazoline derivatives, the efficient construction of these compounds has attracted considerable interest. Among the various reported procedures, substituted quinazoline synthesis from *ortho*-functionalized anilines and derivatives is undoubtedly the most popular method. Various *ortho*-functionalized anilines such as 2-carbonyl anilines,[8] 2-aminobenzylamines[9] and 2-aminobenzonitriles[10] were successfully used as the starting materials to provide the corresponding benzo-heterocyclic products *via* a condensation procedure with aldehydes, benzyl amines, benzylic acids or benzonitriles (Scheme 1a and b). Besides *ortho*-functionalized anilines, we and others found that more stable *o*-nitroacetophenones also could be used as raw materials for the synthesis of substituted quinazolines *via* a hydrogen-transfer strategy.[11] Alternatively, *N*-arylamides were used as the starting materials for quinazoline synthesis *via* an intramolecular cyclization process, in which preactivation at the *ortho*-position of the aniline ring is unnecessary (Scheme 1c).[12] In recent years, other activated nitrogen-containing reagents such 2-ethynylanilines,[13] aryl diazonium salts,[14] 2-alkylaminobenzonitriles,[15] *N*-sulfinylimines,[16] imines[17] and amidines[18] were proved to be alternative substrates for the synthesis of various substituted quinazoline derivatives.



Scheme 1 Synthesis of substituted quinazolines from aniline derivatives.

There is no doubt that the aforementioned methods can be effectively used to prepare a wide variety of quinazoline derivatives. However, most of them need to use highly functionalized aniline derivatives or other activated intermediates, which often require multi-steps for their preparation, thus increasing the difficulty of synthesis and limiting the substrate scope. Although in some cases the use of metal-catalysts can improve the reaction efficiency,[19] metal contamination remains an issue, especially when the products are destined for human consumption or when trace metal contamination can affect the product performance, such as in organic electronics. Anilines can be easily prepared by nitroarene reduction and are widely used as key synthons in drug synthesis as well as other nitrogen-containing functional molecular synthesis.[20] Therefore, it is highly desirable to use cheap and readily available anilines as the raw materials for the preparation of

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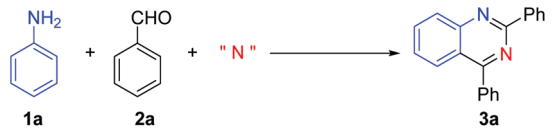
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c8gc02654h

nitrogen-containing heterocycles *via* direct functionalization of the C–H bond *ortho* to the amino group. Although some functional groups could be directly introduced into the *ortho* position of the free amino group,[21] protection and de-protection procedures are usually required in most cases. It is challenging to use anilines as the starting materials for substituted quinazoline synthesis in one pot without tedious preactivation, purification or protection–deprotection process, which can provide the target products in a more direct and convenient way. As part of our continuing efforts on heterocycle formation using readily available starting materials under metal-free conditions,[22] herein we describe a general four-component reaction for multi-substituted quinazoline synthesis from anilines, aromatic aldehydes and an ammonium salt under very simple reaction conditions. In this strategy, two equiv. of aromatic aldehydes were involved in the cyclization process and ammonium iodide was used as one of the nitrogen sources (Scheme 1d). The four components could be selectively assembled into the target products in one-pot without the use of any expensive reagents or metal-catalysts.

To find the optimized reaction conditions, we initiated our investigation using aniline (**1a**) and benzaldehyde (**2a**) as the model substrates (Table 1). Firstly, several ammonium salts were screened in toluene to find the suitable nitrogen source (entries 1–7). Among them, ammonium iodide showed the best efficiency to provide the desired product **3aa** in 50% yield, whereas the use of ammonium bromide as the nitrogen source only provided the product in trace amounts. The yield could be improved to 23% when NH_4OAc was used as the nitrogen source in the presence of I_2 (entry 4). It shows that iodine can promote this transformation. Solvent plays an important role in this kind of transformation and the use chlorobenzene as the solvent could further improve the reaction yield to 67% (entry 8). Other organic solvents such as *o*-dichlorobenzene and NMP were less efficient (entries 9 and 10). When an equal amount of ammonium iodide was used, the reaction yield decreased to 53% (entry 11). To our delight, a high reaction yield could be achieved when an equal amount of DMSO was added to the reaction mixture (entry 12). Encouraged by this result, various oxidants such as $K_2S_2O_8$, H_2O_2, TBHP and DTBP were investigated (entries 13–16) and DMSO showed the best activity. When two equiv. of DMSO were used, the yield was not improved obviously (entry 17). Decreasing the reaction temperature decreased the reaction yield (entry 18). The reaction was less efficient when the reaction was carried out under an air atmosphere (entry 19).

With the optimized reaction conditions in hand, the scope and generality of the four-component reaction was explored by using various aromatic amines (Table 2). Good to high yields were obtained when electron-donating substituents were present at the *para* position in anilines (**3ba–3fa**). When 4-*tert*-butylaniline was used as the coupling partner, the desired product **3ea** was obtained in 95% yield. Halogen functional

Table 1 Optimization of the reaction conditions[a]

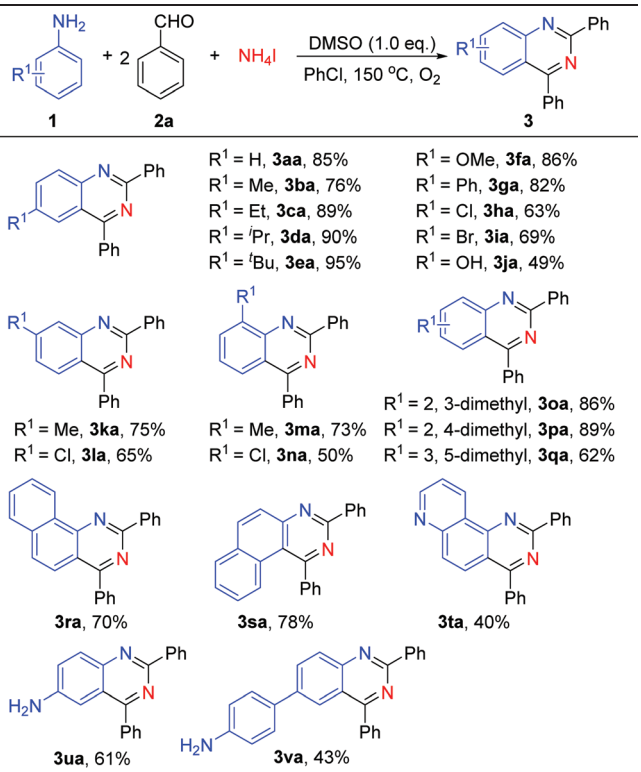


1a **2a** **3a**

Entry	"N"	Oxidant	Solvent	Yield[b] (%)
1	NH_4I		Toluene	50
2	NH_4Br		Toluene	Trace
3	NH_4CI		Toluene	Trace
4	NH_4OAc		Toluene	7 (23)[c]
5	$NH_3{\cdot}H_2O$		Toluene	5
6	NH_4HCO_3		Toluene	6
7	$(NH_4)_2CO_3$		Toluene	Trace
8	NH_4I		PhCl	67
9	NH_4I		*o*-DCB	45
10	NH_4I		NMP	20
11[d]	NH_4I		PhCl	53
12	NH_4I	DMSO	PhCl	97
13	NH_4I	$K_2S_2O_8$	PhCl	26
14	NH_4I	H_2O_2	PhCl	72
15	NH_4I	TBHP	PhCl	44
16	NH_4I	DTBP	PhCl	46
17[e]	NH_4I	DMSO	PhCl	95
18[f]	NH_4I	DMSO	PhCl	86
19[g]	NH_4I	DMSO	PhCl	70

[a] Conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), "N" (0.24 mmol), oxidant (0.2 mmol), solvent (0.5 mL), 150 °C, 12 h, under oxygen unless otherwise noted. [b] GC yield. [c] I_2 (0.2 mmol) was added. [d] NH_4I (0.2 mmol). [e] DMSO (0.4 mmol). [f] 140 °C. [g] Under air.

Table 2 Scope of aromatic amines (**1**)[a]



[a] Conditions: **1** (0.2 mmol), **2a** (0.6 mmol), NH_4I (0.24 mmol), DMSO (0.2 mmol), PhCl (0.5 mL), 150 °C, 12 h, under oxygen unless otherwise noted, and the isolated yield is based on **1**.

groups such as chloro and bromo were well tolerated to give the corresponding products **3ha** and **3ia** in good yields, respectively. To our delight, a free hydroxy group also could be used to give the desired product **3ja** in moderate yield. No obvious steric effect was observed and good yields were obtained even when the methyl group was located at the *ortho* position (**3ka** and **3ma**). High yields were obtained when anilines with two methyl substituents were used as the substrate (**3oa–3qa**). Analogously, the desired products **3ra** and **3sa** were obtained in 70% and 78% yields when naphthalen-1-amine and naphthalen-2-amine were used as the substrates. When naphthalen-2-amine was used, the C–H functionalization selectively occurred at the α position. Heteroaromatic amines such as quinolin-5-amine could smoothly couple with benzaldehyde and ammonium iodide to give the corresponding product **3ta** in 40% yield. Notably, the free amino group was well tolerated in the present system, delivering the corresponding products **3ua** and **3va** in 61% and 43% yields, respectively.

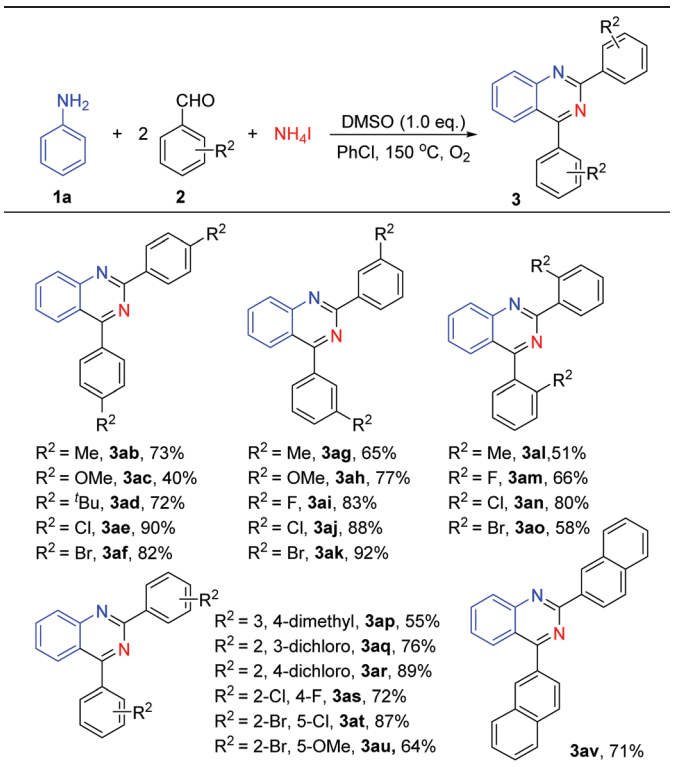
To further investigate the scope and limitation of this four-component system, various aromatic aldehydes were examined under the optimized reaction conditions (Table 3). In general, the reactions with benzaldehydes bearing electron-donating groups such as methyl and *tert*-butyl and withdrawing groups such as chloro and bromo worked smoothly to give the corresponding substituted quinazoline products in good to high yields. High yields were obtained with benzaldehydes with the fluoro, chloro and bromo substituents at the *para* or *meta* positions (**3ae–3af** and **3ai–3ak**). A steric effect was observed when the substituents were located at the *ortho* position, in which the desired products were obtained in lower yields (**3al–3ao**). Various benzaldehydes with two substituents were investigated in this system and most of them regioselectively afforded the corresponding products in good to high yields (**3ap–3au**). Substituted quinazoline **3ar** was obtained in 89% yield when 2,4-dichlorobenzaldehyde was employed. Remarkably, **3av** was obtained in 71% yield when the steric substrate 2-naphthaldehyde was used. Unfortunately, when two different aldehydes are used, four products are detected. The result shows that the reaction displays no chemical selectivity.

To our surprise, stable and readily available nitroarenes also could be directly used for this kind of reaction when 2 equiv. of iron were used as the reductant (Scheme 2). Nitroarenes with methyl, *tert*-butyl and 2,4-dimethyl substituents were able to smoothly react with benzaldehyde to give the corresponding products **3ba**, **3ea** and **3pa** in 66%, 75% and 73% yields, respectively. Interestingly, 2,4-diphenylquinazolin-6-amine (**3ua**) with a free amino group was achieved in 43% yield when 4-nitroaniline was used. Furthermore, monosubstituted 2-phenylquinazoline (**6**) was obtained in moderate yield when 2-aminobenzaldehyde (**5**) was used as the substrate under the current system.

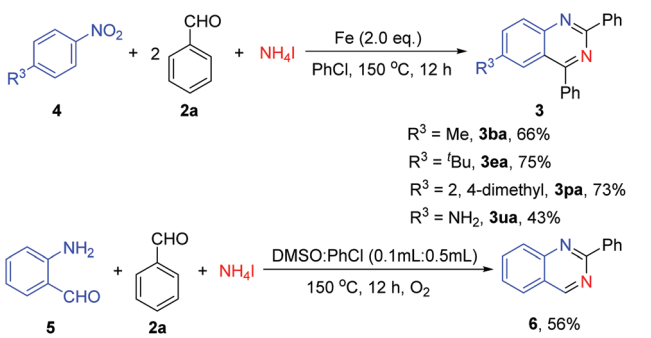
Based on the aforementioned results and some related research, a plausible mechanistic pathway is depicted in Scheme 3. The condensation of aniline with benzaldehyde generates an imine intermediate **A**, which can be detected during the reaction. Meanwhile, the condensation reaction of benzaldehyde and ammonium iodide affords an imine intermediate **B**.[8a,e,l,23] The cyclization reaction of **A** and **B** yields an intermediate **D** according to a two-step domino reaction.[24] Oxidative dehydrogenation of the intermediate **D** affords the final product 2,4-diphenylquinazoline **3aa**.

In summary, we have developed a four-component strategy for substituted quinazoline synthesis from readily available anilines, aromatic aldehydes and ammonium iodide under simple reaction conditions. The *ortho* C–H bond in anilines

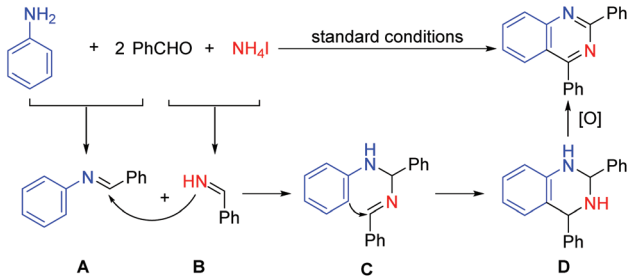
Table 3 Scope of aromatic aldehydes (**2**)[a]



[a] Conditions: **1a** (0.2 mmol), **2** (0.6 mmol), NH_4I (0.24 mmol), DMSO (0.2 mmol), PhCl (0.5 mL), 150 °C, 12 h, under oxygen unless otherwise noted, and the isolated yield is based on **1a**.



Scheme 2 Synthesis of quinazolines from nitroarenes (**4**) or 2-aminobenzaldehyde (**5**).



Scheme 3 Possible reaction pathway.

was directly functionalized and used for a further cyclization process under metal-free conditions. Two equiv. of aldehydes were involved in this reaction to provide two C1 sources and ammonium iodide was used as one of the nitrogen sources. The reaction showed good functional group tolerance and wide substrate scope. The four-component mixture could be selectively assembled into the target products in one-pot without the use of any expensive reagents or metal-catalysts. This method provides an efficient approach to various substituted quinazolines under simple reaction conditions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21871226, 21572194), the Collaborative Innovation Center of New Chemical Technologies for Environmental Benignity and Efficient Resource Utilization, the Hunan Provincial Innovative Foundation for Postgraduate (CX2018B046), and the China Postdoctoral Science Foundation (2018M632976).

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