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Synthesis of 2-aryl quinazolinones *via* iron-catalyzed cross-dehydrogenative coupling (CDC) between N–H and C–H bonds†

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Herein, we describe the direct synthesis of quinazolinones *via* cross-dehydrogenative coupling between methyl arenes and anthranilamides. The C–H functionalization of the benzylic sp^3 carbon is achieved by di-*t*-butyl peroxide under air, and the subsequent amination–aerobic oxidation process completes the annulation process. Iron catalyzed the whole reaction process and various kinds of functional groups were tolerated under the reaction conditions, providing 31 examples of 2-aryl quinazolinones using methyl arene derivatives in yields of 57–95%. The synthetic potential has been demonstrated by the additional synthesis of aryl-containing heterocycles.

Introduction

Quinazolinones, widely found in natural products and synthetic pharmaceuticals,[1] are a significant class of annulated six-membered nitrogen heterocycles. They are key structural motifs with a wide range of biological properties, including anticancer,[2] antihypertensive,[3] anti-inflammatory,[4] and antimalarial activity.[5] Recently, some synthetic drugs based on quinazolinone such as raltitrexed, ispinesib, and halofuginone have been used in clinical trials for cancer treatment. Additionally, quinazolinones are important building blocks for the synthesis of bioactive quinazoline derivatives.[6]

The attractive biological profile and synthetic importance of quinazolinones have encouraged researchers to develop efficient synthetic methods for these heterocycles and their structural analogs.[7] The simplest synthetic approach for preparing 2-aryl quinazolinone would be starting from anthranilamide **1a** and an electrophilic benzyl carbon synthon. Depending on the benzyl carbon synthon, various synthetic methods have already been reported (Fig. 1). The most classical synthetic approach is oxidative condensation with carbonyl derivatives (path a).[8] Besides the use of carbonyl substrates, recent studies report the development of various alternative methods using benzylic carbon as the one-carbon synthon, attached with hydroxy,[9] amine,[10] and halogen[11] groups (path b). Another synthetic method is palladium-catalyzed carbonylative annulation using an aryl halide, with carbon monoxide as a carbon source (path c).[12] Although all of the synthetic methods mentioned above provided various strategies for the synthesis of quinazolinones, they required a specific functional group on the electrophilic carbon synthon.

Recently, oxidative cross-dehydrogenative coupling (CDC) reactions have become a topic of interest because the couplings avoid the tedious and time-consuming prefunctionalization of substrates.[13] In CDC reactions, direct functionalization of C–H bonds builds C–C or C–heteroatom bonds and offers substantial benefits owing to the remarkable potential for atom economy and environmental sustainability. Thus, the oxidative CDC reaction is an attractive synthetic tool for estab-

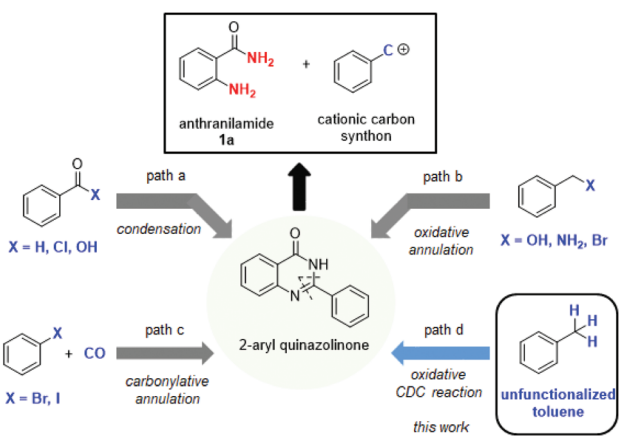

Fig. 1 Diverse syntheses of quinazolinones from anthranilamide (**1a**).

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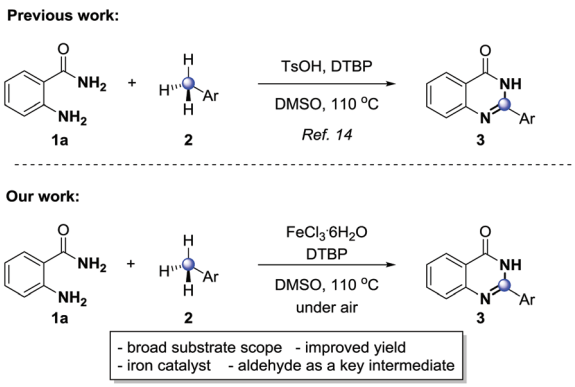
lishing quinazolinone structures (path d in Fig. 1 and Scheme 1). Li *et al.* reported the oxidative CDC annulation between **1a** and an unfunctionalized benzylic sp^3 carbon to synthesize 2-aryl quinazolinones **3** with the assistance of *p*-toluenesulfonic acid.[14] The oxidant activated the benzylic C–H bond, and this carbon synthon participated in annulation with **1a**. Although the authors explored various types of substrates, the substrate scope is limited because of acidic reaction conditions, and low yields are observed with most substrates. Recently, similar transformations have also been reported by several groups using solid-supported heterogeneous catalysts with mild oxidants (air or O_2 gas).[15] The advantage of heterogeneous catalysis is obvious, but these catalysts have the drawback of the need to be prepared in advance. Thus, a more convenient and general method for the synthesis of quinazolinones using readily available catalysts and reagents is desirable. In particular, iron is an inexpensive, nontoxic and environmentally benign transition metal.[16] Therefore, an increasing number of reactions using iron metal have recently been reported. As part of our program related to the development of a new approach for the synthesis of N-heterocycles, we wish to develop a synthetic method for 2-aryl quinazolinones **3** *via* CDC reactions using iron catalysts.

Results and discussion

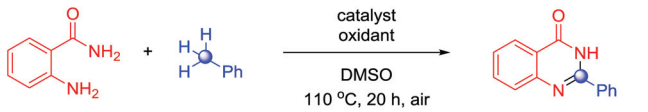
First, we employed $FeCl_3$ as a preliminary catalyst in the reaction of 2-anthranilamide **1a** with toluene **2a**, and 2-phenyl quinazolinone **3aa** was obtained in 29% yield (Table 1, entry 1). When we used the hydrated catalyst $FeCl_3{\cdot}6H_2O$, an improved yield was observed (entry 2). Interestingly, exposure of the reaction mixture to air was a crucial factor for a high yield (entry 3). We supposed that oxygen gas plays an important role in this reaction. As expected, the desired product was obtained in a high yield of 95% with an O_2 balloon (entry 4). However, because we obtained an adequate yield without an O_2 balloon, we focused on optimizing our reaction under aerobic conditions. In the absence of the iron catalyst, the yield was significantly decreased (entry 5). An attempt to reduce the amount of the oxidant also resulted in a low yield (entry 6). Upon screening various types of catalysts and oxidants, we could not find more efficient ones. Therefore, $FeCl_3{\cdot}6H_2O$ and di-*t*-butyl peroxide (DTBP) were chosen as the optimal catalyst and oxidant, respectively.

As shown in Table 2, we further optimized the reaction conditions using $FeCl_3{\cdot}6H_2O$ and DTBP. High temperatures over 110 °C were required for sufficient conversion (entries 1–3). Therefore, we could not use a solvent with a boiling point



Scheme 1 Synthesis of 2-aryl quinazolinones **3** *via* the CDC strategy.

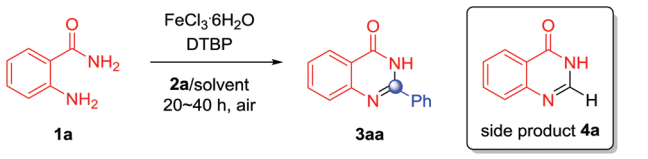
Table 1 Screening of catalysts and oxidants[a]



Entry	Catalyst	Oxidant	Yield[b] (%)
1[c]	$FeCl_3$	DTBP	29
2[c]	$FeCl_3{\cdot}6H_2O$	DTBP	46
3	**$FeCl_3{\cdot}6H_2O$**	**DTBP**	**88**
4[d]	$FeCl_3{\cdot}6H_2O$	DTBP	95
5	No catalyst	DTBP	48
6	$FeCl_3{\cdot}6H_2O$	DTBP[e]	60
7	$FeCl_2{\cdot}4H_2O$	DTBP	77
8	$Fe(OTf)_3$	DTBP	62
9	$CuCl_2$	DTBP	31
10	$FeCl_3{\cdot}6H_2O$	TBHP[f]	68
11	$FeCl_3{\cdot}6H_2O$	H_2O_2[g]	40
12	$FeCl_3{\cdot}6H_2O$	DDQ	No reaction

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (18 mmol, 1.9 mL), catalyst (10 mol%) and oxidant (0.9 mmol) in DMSO (2 mL) at 100 °C under air for 20 h. [b] Isolated yield. [c] The reaction was performed in a sealed tube. [d] The reaction vessel was recharged with O_2 gas and connected with an O_2 balloon. [e] 0.6 mmol DTBP was used. [f] 70% aqueous solution. [g] 35% aqueous solution.

Table 2 Optimization of the reaction conditions[a]



Entry	**2a**/solvent (mL)	*T* (°C)	Time (h)	Yield[b] (%)
1	**2a**/DMSO (1.9/2)	110	20	88
2	**2a**/DMSO (1.9/2)	100	20	30
3	**2a**/DMSO (1.9/2)	90	20	9
4	**2a**/DMF (1.9/2)	110	20	12
5	**2a**/HMPA (1.9/2)	110	20	Trace
6	**2a**/DMSO (1.9/1)	110	40	90
7	**2a/DMSO (1.9/0.5)**	**110**	**40**	**95**
8	**2a**/DMSO (1.9/0.2)	110	40	64
9	**2a**/DMSO (0.95/0.5)	110	40	74
10	**2a/DMSO (0.95/0.5)**	**120**	**40**	**93**
11	**2a**/diphenyl sulfoxide (0.95/0.5)	120	40	68

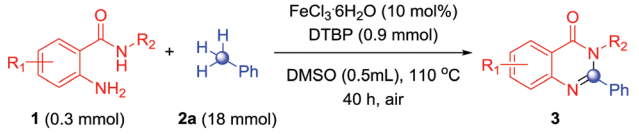
[a] Reaction conditions: **1a** (0.3 mmol), $FeCl_3{\cdot}6H_2O$ (10 mol%) and DTBP (0.9 mmol) in **2a**/solvent under air. [b] Isolated yield.

lower than 110 °C in the open-air reaction system. Among the screened solvents, DMSO gave the best results (entries 1, 4 and 5). In the reaction system, side product **4a** was always observed. However, we could not calculate the exact mass of **4a** at this stage because of the low solubility of **4a** in organic solvents. **4a** might be formed through the cleavage of the sp^3 C–heteroatom bond of the solvent followed by the formation of a C–N bond with **1a**. With this hypothesis, we tried to reduce the amount of the solvent to increase the **2a**/solvent ratio. The increased amount of **2a** caused more substrate **1a** to convert into the desired product **3aa** (entries 1, 6 and 7), although a longer reaction time was needed. We expected a decrease in the formation of **4a** to result in this tendency. However, a minimum amount of DMSO was necessary to achieve clean conversion (entries 7 and 8). We could reduce the number of equivalents of **2a** by half at increased temperature to obtain a sufficient yield (entry 10). We also employed diphenyl sulfoxide to suppress the formation of **4a**. Although **4a** was not observed in the reaction mixture as we expected, these solvents did not afford better yields than DMSO (entries 7 and 11).

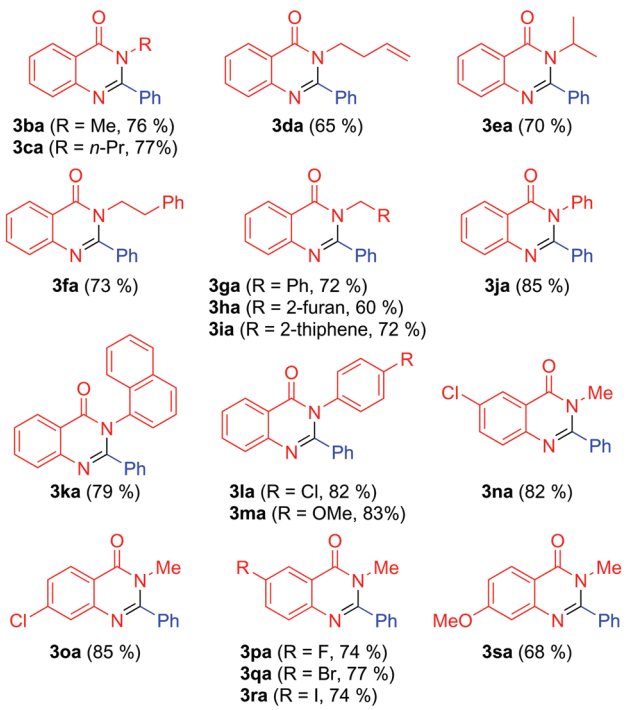
After the optimization of the reaction conditions, a wide range of anthranilamides **1** were employed for annulation with **2a** (Table 3). Under the developed conditions, 2-phenyl quinazolinones **3** bearing *N*-substituents were successfully synthesized from the corresponding 2-amino *N*-substituted benzamides (**3ba–3ma**). Not only a sterically hindered amide substituted with an i-propyl group (**3ea**) but also less nucleophilic amides substituted with an aryl group (**3ja–3ma**) afforded good yields. The *N*-substituted homo-allyl group was tolerated under the reaction conditions (**3da**). In addition to benzyl, other heteroarene methyl substituted amides also provided the desired products in good yields (**3ga–3ia**). Moreover, there was no significant difference with regard to the substituents on the aromatic ring of the substrate (**3na–3sa**). Bromide and iodide were also retained in the annulated product, representing efficient functional groups for further transformation (**3qa** and **3ra**).

Next, we applied various types of methyl arenes **2** to synthesize 2-aryl quinazolinones under the same conditions (Table 4). Because of the low solubility of 2-phenyl quinazolinone **3aa** in organic solvents, we used 2-amino *N*-methyl benzamide **1b** as a starting material. A diverse array of methyl arenes bearing electron-withdrawing and electron-donating groups could smoothly react with **1b**, and the corresponding quinazolinones could be obtained in moderate to good yields. Generally, better results were achieved with methyl arenes with electron-donating groups, such as methyl groups, than those with electron-withdrawing groups (**3bb–3be** *vs.* **3bf–3bj**), except for the methoxy group (**3bk**). The steric effect slightly influenced the formation of the desired product, depending on the

Table 3 Scope of 2-anthranilamide analog substrates

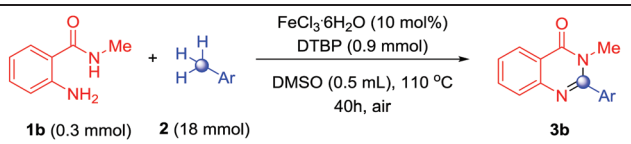


1 (0.3 mmol) **2a** (18 mmol) **3**

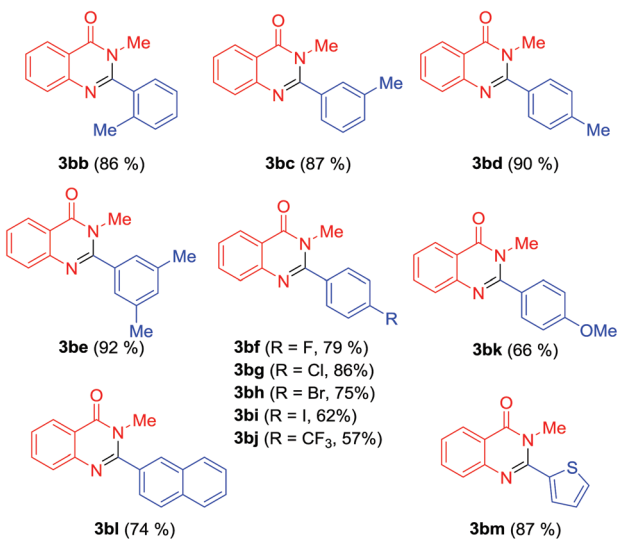


All of the presented yields are isolated yields.

Table 4 Scope of methyl arene analog substrates



1b (0.3 mmol) **2** (18 mmol) **3b**



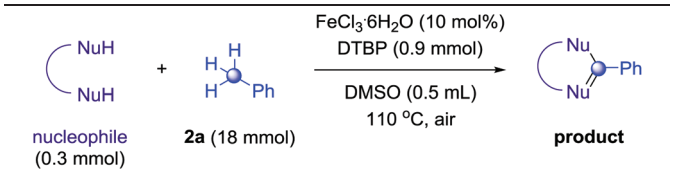
All of the presented yields are isolated yields.

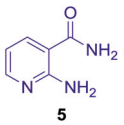
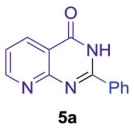
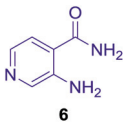
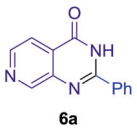
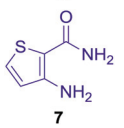
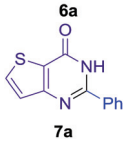
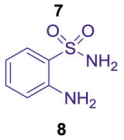
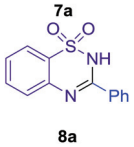
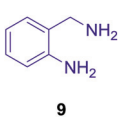
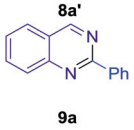
position of the substituent (**3bb–3bd**). Based on these results, we assumed that the activation process of the benzylic C–H bond usually would be the rate-determining step instead of the annulation process. The electron-donating group could stabilize the benzyl cationic charge that is generated during benzylic carbon activation by the oxidant. In the case of the methoxy-substituted methyl arene, the reaction proceeded smoothly until annulation with **1b**, but the final oxidation to afford the quinazolinone moiety was quite slow. Additionally, naphthalene and thiophene could be substituted at the 2-position of the quinazolinones (**3bl** and **3bm**).

As shown in Table 5, we also explored other nucleophiles that have structural similarity with 2-anthranilamide to obtain other aryl-containing heterocycles. First, nicotinamide substrates **5** and **6**, which have a pyridine moiety instead of the phenyl group of **1**, were subjected to the reaction conditions, and the desired product was obtained in a high yield. However, similar to the case of **3bk** shown in Table 4, the final oxidation process to generate **5a** and **6a** was slow. We assumed that a longer reaction time is needed for the final oxidation step depending on the substrate. In the case of 2-amino thiophen-3-amide **7**, the annulation and oxidation processes were easily achieved under the standard conditions. We could control the final oxidation step depending on the reaction time with 2-amino benzenesulfonamide **8**. A long reaction time gave the fully oxidized product **8a**, and a short reaction time gave the unoxidized annulation product **8a′**. Quinazoline derivative **9a** was also well synthesized using the developed conditions, even though more oxidant and solvent were needed. Under the previous Li's conditions, basic nitrogen containing substrates (**5a** and **9**) failed to afford the corresponding annulated products (the failure examples are given in the ESI of ref. 14). Moreover, only **8a′** was reported as a product which could be obtained from sulfonamide substrate **8** under Li's conditions. These examples showed that our conditions are more efficient for the CDC annulation with methyl arene.

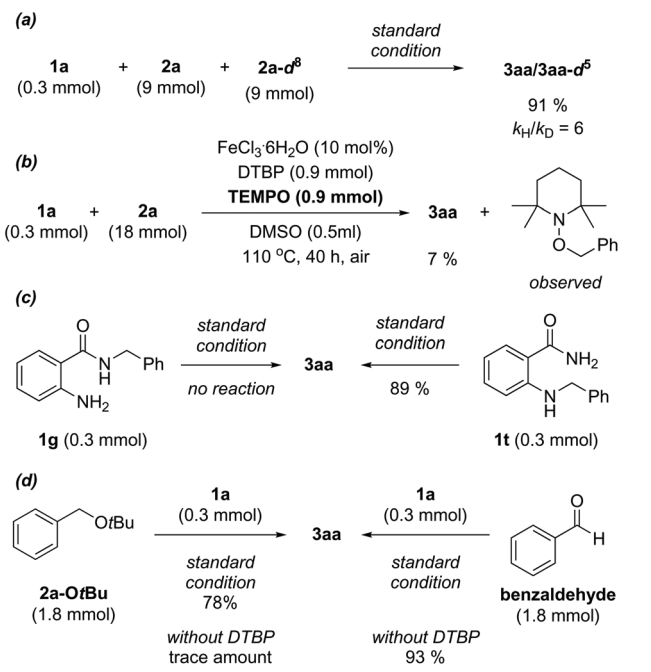
Then, we carried out several control experiments to understand the mechanism (Scheme 2). We focused on the formation of benzaldehyde during the reaction because the corresponding benzaldehyde could be observed in most reactions (see the details in the ESI†). This observation contrasts with the previous mechanistic study, although the transformation and reaction conditions were similar.[14] In the competition reaction with toluene and toluene-d^8, a significant kinetic isotope effect (KIE, k_H/k_D = 6/1) was observed, so the activation of the C–H bond was suggested to be the rate-determining step (*a*). A well-known radical scavenger, TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxide), quenched the reaction. Benzylated TEMPO was observed during the reaction, so we supposed that the reaction involved a benzyl radical intermedi-

Table 5 Screening of other types of nucleophiles



Nucleophile	Product	Time (h)	Yield[a] (%)
 **5**	 **5a**	65	>99
 **6**	 **6a**	65	76
 **7**	 **7a**	40	69
 **8**	 **8a**	65	92
	 **8a'**	20	59
 **9**	 **9a**	40	54[b]

[a] Isolated yield. [b] DMSO (0.7 mL) and DTBP (1.2 mmol).

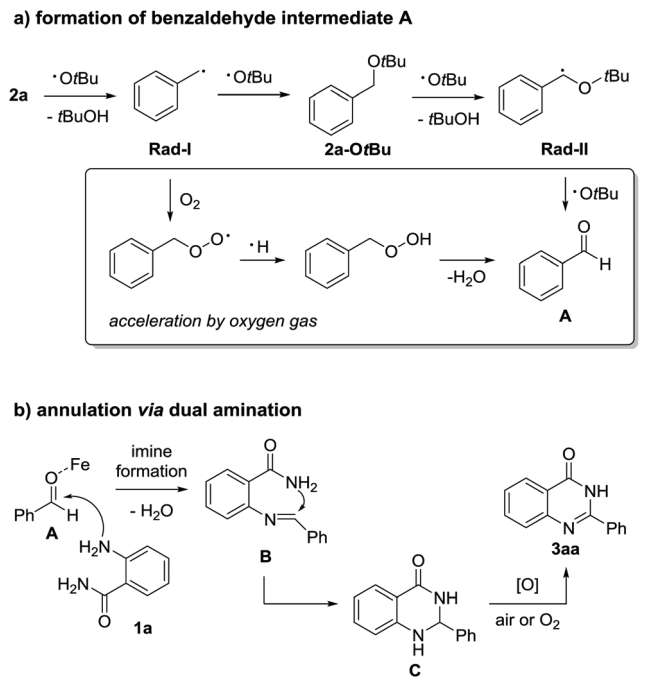


Scheme 2 Investigation of the reaction mechanism.

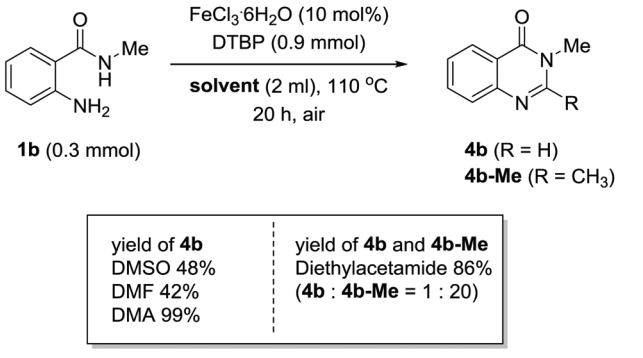
ate (*b*). On comparing the experiments using 2-amino *N*-benzylbenzamide **1g** and 2-(benzylamino) benzamide **1t** in the absence of toluene, **1g** is supposed to be an intermediate in the reaction, so the activated benzylic carbon coupled with the anilinic amine prior to coupling with the amide (*c*). We supposed that first, *t*-butoxy benzyl ether was generated from toluene, and then, it was converted to benzaldehyde in the presence of DTBP. Imine formation from benzaldehyde and amine **1** would be catalyzed by an iron catalyst, and the quinazolinone would be formed *via* an intramolecular amination–oxidation process. As expected, when *t*-butoxy benzyl ether was reacted with **1a**, annulated product **3aa** was obtained under the standard conditions (left side of (*d*)). However, without DTBP, only a trace amount of **3aa** was detected by TLC. Based on this result, we could exclude the direct nucleophilic attack of the amine on the benzyl ether intermediate. After the annulation between **1a** and benzaldehyde, the ensuing oxidation process readily occurred under aerobic conditions. Therefore, the quinazolinone structure of **3aa** could be adequately constructed in the absence of DTBP (right side of (*d*)).

Based on the results of the control experiments, we suggested a possible mechanism (Scheme 3). First, *t*-butoxy radicals were generated by the homolysis of DTBP under the reaction conditions. The benzyl radical **Rad-I** was formed by the abstraction of H$^{\bullet}$ from the benzylic carbon of toluene by the *t*-butoxy radical. The coupling of these two radicals gave *t*-butoxy benzyl ether **2a-O*t*Bu** as an intermediate. Another *t*-butoxy radical abstracted H$^{\bullet}$ from **2a-O*t*Bu**, and its subsequent autolysis produced benzaldehyde **A**. The iron(III) salt might be involved in the oxidation process of **2a** through single-electron transfer, especially in the formation of radical species. After the formation of benzaldehyde **A**, it reacted with 2-anthranilamide **1a**, and imine **B** was generated with the assistance of the iron catalyst. Subsequently, annulation of imine **B** through intramolecular nucleophilic amination followed by aerobic oxidation gave the final product **3aa**. However, we could not exclude direct amination of **1a** by radical species **Rad-I** or **Rad-II**. We supposed that exposure to air accelerated the formation of benzaldehyde **A** through another pathway. In the presence of oxygen gas, benzyl hydrogen peroxide was generated *via* the coupling of **Rad-I** with O_2, followed by the abstraction of H$^{\bullet}$ from the solvent (**2a** or DMSO). Then, benzyl hydrogen peroxide could be converted to benzaldehyde **A** under the reaction conditions. Through this pathway, not only the formation of aldehydes but also the overall reaction was accelerated by oxygen gas.

As mentioned in Table 2, we always observed another annulated quinazolinone **4a** as a side product under the reaction conditions. To investigate the significant formation of **4a**, we carried out several control experiments (Scheme 4). We assumed that one carbon atom comes from the solvent based on a related research study.[17] The methyl carbon adjacent to a heteroatom is activated by an oxidant or radical intermediate, and this activated carbon reacts with the amine group of **1** instead of benzaldehyde **A**. After sequential cleavage of the C–heteroatom bond, annulated product **4a** was formed following a similar process as that shown in Scheme 3. Due to the solubility problem of **4a**, we used the methyl-substituted amide substrate **1b**. Based on the results shown in Table 2, we supposed that the reactivity of DMSO was lower than that of toluene. Therefore, the reaction was carried out in the absence of toluene and side product **4b** was obtained in 48% yield. Among the similar types of solvents, we found that dimethylacetamide (DMA) is the most efficient solvent to serve as a methyl carbon source. To verify that the carbon atom comes from the solvent, diethylacetamide, which has an ethyl substituent, was used under the same conditions. As a result, **4b-Me** was obtained as a major product (**4b** : **4b-Me** = 1 : 20), which means that the solvent serves as the carbon source (see the details in the ESI†). The trace amount of **4b** might be attributed to the methyl radicals of DTBP.[18]



Scheme 3 Proposed mechanism.



Scheme 4 Annulation of **1b** without toluene.

Conclusions

In summary, we have developed an efficient synthetic method for the synthesis of 2-aryl quinazolinones from unreactive methyl arenes *via* an iron-catalyzed CDC reaction. During the reaction, C–H bond activation on a benzylic sp^3 carbon occurs in the presence of DTBP, and the annulated product is obtained followed by dual amination with anthranilamides **1** with the assistance of an iron catalyst. The reaction was performed under air, and we found that oxygen gas plays a crucial role in the oxidative process of the reaction. Compared with the previous CDC conditions, our conditions improved the yields with most substrates and provided a broad substrate scope to obtain various N-heterocycles. The developed method also tolerates various functional groups allowing further functionalization. And all of the reagents and catalysts used are inexpensive and readily available. Based on the results and control experiments, we suggested a possible radical mechanism, with benzaldehyde as a key intermediate. Further extension of this methodology to access other types of N-heterocycles is under investigation in our research group.

Conflicts of interest

There are no conflicts to declare.

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