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A Facile $FeCl_3/I_2$-Catalyzed Aerobic Oxidative Coupling Reaction: Synthesis of Tetrasubstituted Imidazoles from Amidines and Chalcones

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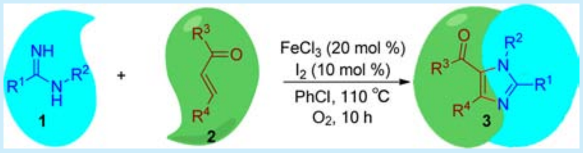
Supporting Information

ABSTRACT: A facile and efficient route for the synthesis of tetrasubstituted imidazoles from amidines and chalcones via $FeCl_3/I_2$-catalyzed aerobic oxidative coupling has been developed. This new strategy is featured by high regioselectivity and yields, good functional group tolerance, and mild reaction conditions.



Imidazoles, one of the most valuable heterocyclic compounds, have been found in many natural products[1] and widely applied in functional materials.[2] In particular, they also have good pharmacological activities,[3] such as antifungal,[4] antitumor,[5] antibacterial,[6] antiplasmodium,[7] and anti-inflammatory.[8] Current synthesis methods for imidazole derivatives are mainly restricted to less-substituted imidazoles,[9] while only a handful of them provided access to tetrasubstituted imidazoles.[10] Particularly during the last decades, several new methodologies have emerged, such as cross-coupling of aldimines,[11] the coupling reaction of 2-azido acrylates and nitrones,[12] Cu-catalyzed cycloaddition of amidines and nitroolefins,[13] the three-component reaction,[14] Ni-catalyzed dehydrogenation of benzylic-type imines,[15] and Zn-catalyzed cyclization of 2-(tetrazol-5-yl)-2*H*-azirines and imines.[16] However, most approaches encounter some drawbacks, including high catalyst loading, substrates unavailable, limited applications, long reaction time or low yields under harsh reaction conditions. Moreover, most substrates are limited to 1,2-diketone, aldehydes and primary amines,[17] so those procedures restrict the synthesis of tetrasubstituted imidazoles and usually involve poor regioselectivity. Therefore, a novel, practical and efficient protocol for a straightforward construction of tetrasubstituted imidazoles remains highly desirable.

Recently, the direct oxidative C–H bond functionalization by iron and iodine has gained considerable attention, and is an excellent way to form various heterocycles from the readily available reactants.[18] This research shows that, compared to rare metal catalyst, the iron and iodine not only are available, inexpensive, and environmentally benign catalysts, but also can offer complementary selectivity and impressive reactivity. Therefore, these results encouraged us to hypothesize that it may be a new protocol for the synthesis of tetrasubstituted imidazoles through iron and iodine cocatalyzed oxidative C–H functionalization of amidines with chalcones. On the basis of the above hypothesis, we present here the first successful attempt on a $FeCl_3/I_2$-catalyzed aerobic oxidative coupling of amidines with chalcones for synthesizing tetrasubstituted imidazoles.

We began our study by taking *N*-phenylbenzamidine (**1a**) and chalcone (**2a**) as the model substrates. The results are summarized in Table 1. Delightedly, when the reaction was carried out employing a combination of $FeCl_3$ (20 mol %) and I_2 (10 mol %) in toluene at 110 °C under air atmosphere, the desired product was obtained in 56% (Table 1, entry1). Control experiments showed the necessities of both $FeCl_3$ and I_2 for this reaction, without any resulting in the lack of reactivity (Table 1, entries 2–3). Lower yields were obtained by use of $Fe(NO_3)_3{\cdot}9H_2O$, $FeBr_3$, $CuCl_2$, and $Cu(OAc)_2$ instead of $FeCl_3$ (Table 1, entries 4–7). Other iodide ion sources, such as NaI, KI, and ZnI_2 were also examined, resulting in a sharp decrease of yield (Table 1, entries 8–10). Other common solvents, such as DMSO, DMF, DMA, chlorobenzene, 1,2-dichloroethane (1,2-DCE) and dioxane, were also screened, and the results showed that chlorobenzene was the most suitable solvent for this reaction (Table 1, entries 11–16). After further elaboration of the reaction conditions (Table 1, entries 17–20), including varying temperature and catalyst loading, the yield of desired product was improved to 85% when oxygen gas was used as a oxidant (Table 1, entry 17).

With the optimized conditions in hand, the scope of various *N*-arylbenzamidines with different substituents on one or both phenyl rings were tested (Scheme 1). With regard to the electronic effects, it was found that electron-donating substituents arylamidines (**3ba**, **3ea**, **3ia** and **3ja**) showed better reactivities and gave higher yields than electron-

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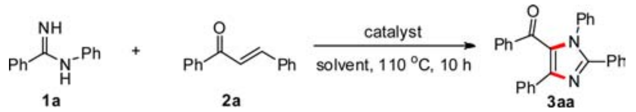
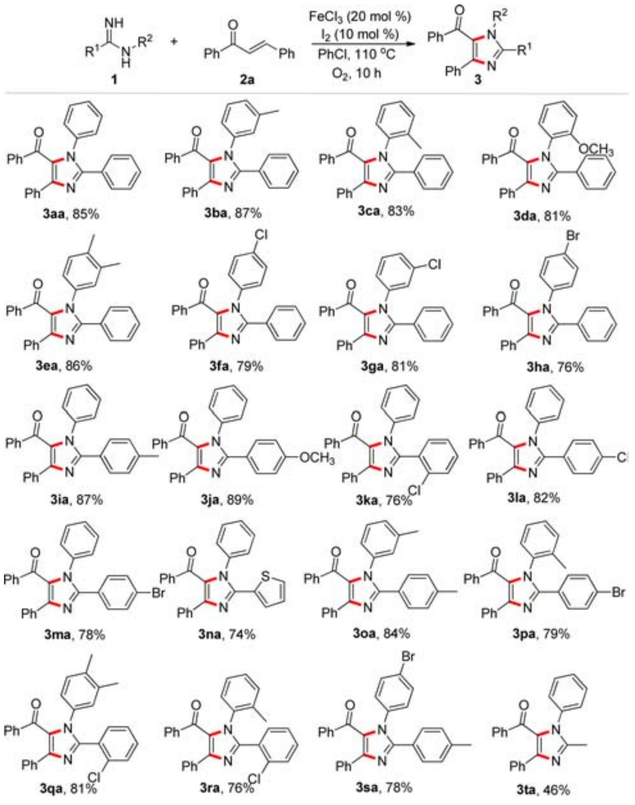
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (mol %)	solvent	yield[b] (%)
1	$FeCl_3$ (20), I_2 (10)	toluene	56
2	I_2 (10)	toluene	0
3	$FeCl_3$ (20)	toluene	0
4	$Fe(NO_3)_3{\cdot}9H_2O$ (20), I_2 (10)	toluene	51
5	$FeBr_3$ (20), I_2 (10)	toluene	48
6	$CuCl_2$ (20), I_2 (10)	toluene	37
7	$Cu(OAc)_2$ (20), I_2 (10)	toluene	53
8	$FeCl_3$ (20), NaI (20)	toluene	32
9	$FeCl_3$ (20), KI (20)	toluene	43
10	$FeCl_3$ (20), ZnI_2 (10)	toluene	39
11	$FeCl_3$ (20), I_2 (10)	DMSO	21
12	$FeCl_3$ (20), I_2 (10)	DMF	23
13	$FeCl_3$ (20), I_2 (10)	DMA	27
14	$FeCl_3$ (20), I_2 (10)	PhCl	72
15	$FeCl_3$ (20), I_2 (10)	1,2-DCE	37
16	$FeCl_3$ (20), I_2 (10)	dioxane	33
17[c]	$FeCl_3$ (20), I_2 (10)	PhCl	85
18[c]	$FeCl_3$ (10), I_2 (5)	PhCl	53
19[c,d]	$FeCl_3$ (20), I_2 (10)	PhCl	81
20[c,e]	$FeCl_3$ (20), I_2 (10)	PhCl	58

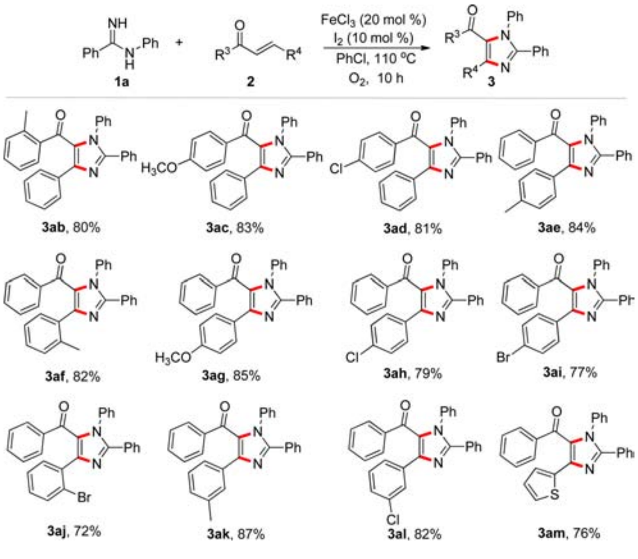
[a] Reaction conditions: 0.6 mmol of **1a** and 0.5 mmol of **2a** in the presence of catalyst in solvent (2 mL) for 10 h in air. [b] Isolated yields. [c] Reaction performed under O_2 balloon. [d] The reaction was carried out at 120 °C. [e] The reaction was carried out at 90 °C.

Scheme 1. Substrate Scope of Amidines[a]



[a] Reaction conditions: **1** (0.6 mmol), **2a** (0.5 mmol), $FeCl_3$ (20 mol %), I_2 (10 mol %), PhCl (2 mL), O_2 balloon, 110 °C, 10 h; isolated yields.

Scheme 2. Substrate Scope of Chalcones[a]



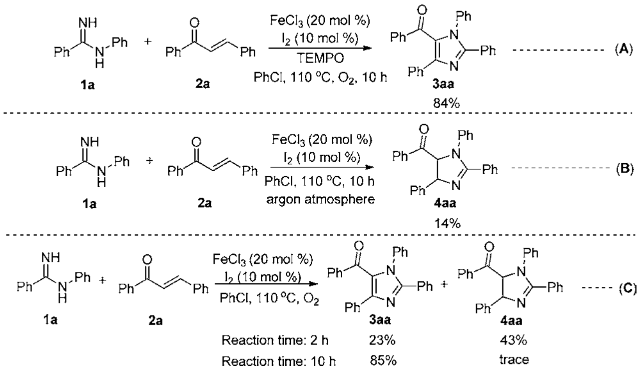
[a] Reaction conditions: **1a** (0.6 mmol), **2** (0.5 mmol), $FeCl_3$ (20 mol %), I_2 (10 mol %), PhCl (2 mL), O_2 balloon, 110 °C,10 h; isolated yields.

withdrawing ones (**3ga**, **3ha**, **3la** and **3ma**). It should benoted that the steric hindrance of the substrates almostly have no effect on the yields (**3ca**, **3da**, **3pa** and **3ra**). Notably, *N*-phenylthiophene-2-carboximidamide could also be well tolerated, and the yield of the corresponding product (**3na**) is 74%. And substrate scope not limited to arylated benzamidines, *C*-alkylimidazole **3ta** was isolated in reasonable yields by using this new methodology. To our delight, the structure of **3na** and **3sa** were unambiguously confirmed by X-ray diffraction analysis. On the whole, for *N*-arylbenzamidines, these reactions displayed high functional group tolerance and gave the desired products in moderate to high yields.

Furthermore, chalcones with different substituents were also investigated, and satisfactorily, imidazoles could be obtained smoothly with good results (Scheme 2). When the similar groups are located on the phenyl rings whatever adjacent to carbonyl groups or connected to C−C double bond, they groups had no significant impact on the yields which are high (from 72 to 85%). But the substrates with electron-donating group substituted on phenyl rings (**3ae**, **3af**, **3ag**, and **3ak**) show better reactivities and give higher yields than those with electron-withdrawing group ones (**3ah**, **3ai**, **3aj**, and **3al**). Besides, chalcones bearing aromatic heterocycles are also suitable for the oxidative coupling reactions, such as **3am** in 76% yield.

Following our synthetic studies, some controlled experiments were carried out to gain insight into the reaction mechanism (Scheme 3). No significant decrease in yield was observed when a radical scavenger TEMPO (1.5 equiv) was added to the reaction, thus a radical process is probably unlikely to be involved (Scheme 3, eq A). The reaction under argon atmosphere delivered imidazolidine **4aa** in 14% yield as the only product, which indicates that the oxygen is critical to the formation of imidazole and the turnover of the catalytic cycle (Scheme 3, eq B). Furthermore, when the reactions were quenched at 2 h, imidazoline **4aa** was isolated as the major

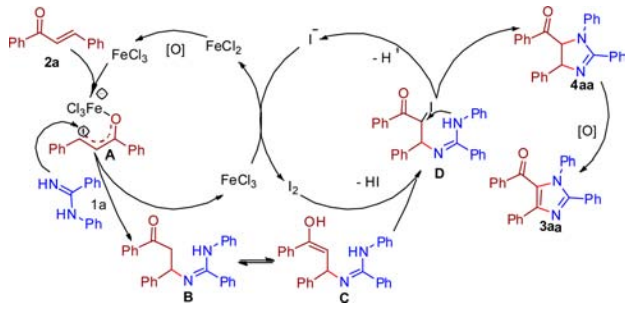
Scheme 3. Controlled Experiments



product (43% yield, eq C), along with 23% of imidazole **3aa**. Extending the reaction time to 10 h, imidazoline **4aa** was almost disappeared and the desired imidazole **3aa** was obtained in 85% yield. These results suggest that the reaction proceeds through the cyclization of the amidines and chalcones to form the imidazoline first, followed by dehydrogenative oxidation of the tetrasubstituted imidazoline to the imidazole.

On the basis of the aforementioned results and the literature reports,[19] a plausible mechanism concerning the iron and iodine cocatalyzed coupling between **1a** and **2a** is proposed in Scheme 4. The reaction is initiated by the activation of chalcone (**2a**) by FeCl$_3$, in the next step, the addition of *N*-arylbenzamidines (**1a**) to **A** forming the Michael adduct **B**, which was observed by HRMS. The Michael adduct **B** is in tautomerization with the enol form **C**. Then, **C** reacts with I$_2$ to produce intermediate **D**, followed by a subsequently intramolecular cyclization to afford **4aa**, which is oxidated to the desired product **3aa** under aerobic conditions. In the end, iodide anion is oxidized to iodine by FeCl$_3$, and Fe(II) is further oxidized to Fe(III) in the oxygen atmosphere to complete the catalytic cycle. As part of our ongoing effort, we also calculated Fukui function $f^{-}_{(r)}$ of compound **B** (Figure 1). The $f^{-}_{(r)}$ calculation result indicates that the nitrogen atom that connected to the benzene ring is the strongest site for electrophilic attack. However, it is still difficult for this nitrogen atom to direct attack the α-carbon of the ketone. When the hydrogen on the α-carbon of the ketone is substituted by iodine, which as a good leaving group, it will become very easy to undergo cyclization. This result also proved the tentative mechanism.

Scheme 4. Plausible Reaction Mechanism



In summary, a new facile and efficient route for the synthesis of tetrasubstituted imidazoles from amidines and chalcones via FeCl$_3$/I$_2$-catalyzed aerobic oxidative coupling has been developed. The reaction employs easily available amidines and chalcones as the starting materials and tolerates a wide range of functional groups. This operationally practical protocol might be a useful and widely applicable method in medicinal, organic, and material chemistry.

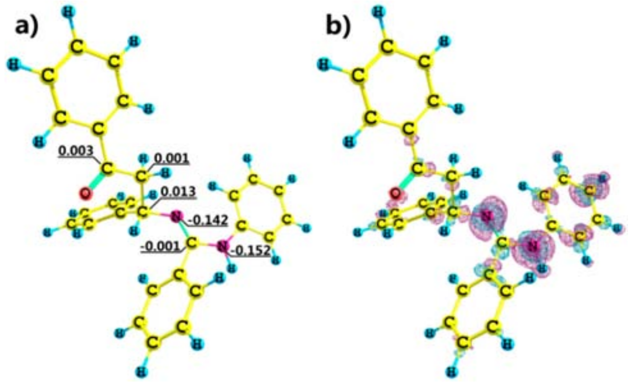


Figure 1. (a) The condensed Fukui function $f^{-}_{(r)}$ of nitrogen and other surrounding atoms in compound **B**. (b) The 3D representation of the Fukui function $f^{-}_{(r)}$ of the iso-value of 0.003 a.u. for compound **B** (positive for red color and negative for green color).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental procedure, characterization data of the compounds, and CIF data for **3na** and **3sa**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01854.

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Notes

The authors declare no competing financial interest.

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