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One-Pot Multicomponent Coupling Reaction of Catechols, Benzyl Alcohols/Benzyl Methyl Ethers, and Ammonium Acetate toward Synthesis of Benzoxazoles

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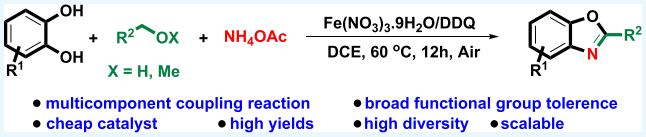
ABSTRACT: The multicomponent coupling reaction of catechol, ammonium acetate, and benzyl alcohol/benzyl methyl ether in the presence of a Fe(III) catalyst precursor afforded benzoxazole derivatives in good to excellent yields. The notable features of this protocol are abundant availability of the catalyst system, large-scale synthesis, high diversity, and high yields of products.



INTRODUCTION

Benzoxazoles are among the most important heterocyclic rings, which are widely found in natural products, advanced materials, pharmaceuticals, and biologically active compounds.[1−3] For example, benzoxazole alkaloids, which are isolated from marine sponges or plants, showed potent pharmaceutical activities (Figure 1).[4−8]

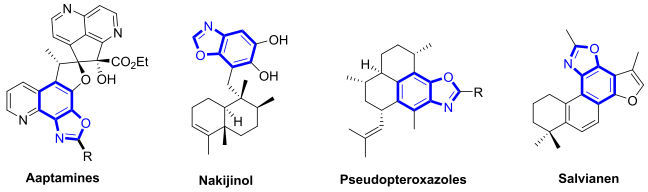
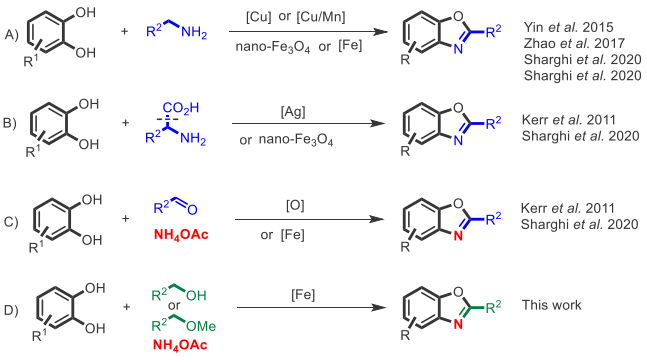


Figure 1. Chemical structure of some biologically important benzoxazole alkaloids.

One of the proposed biosynthetic precursors in the plausible biogenetic pathway to generate benzoxazole alkaloids is catechol, which is highly matched to the isolated metabolites.[4,9] Accordingly, the catechol precursor undergoes a domino oxidation/cyclization process to afford the final benzoxazole product.[4] Taking into consideration these biosynthetic pathways, the preparation of benzoxazole derivatives via the oxidation of catechols has received considerable attention. The coupling reaction of catechols with amines using a copper or iron catalyst system to produce the corresponding benzoxazoles was well developed (Scheme 1A).[10−13] In other approaches, amino acids were used as a precursor in a silver- or iron-catalyzed process to obtain benzoxazoles containing the R-backbone of amino acids (Scheme 1B).[12,14] The chemical structures of aaptodines A−D showed that their difference related to a part of molecule which is originated to the amino acid backbone, confirming the importance of this transformation in the biosynthesis of

Scheme 1. Background and Summary of Oxidative Functionalization of Catechols toward the Synthesis of Benzoxazoles



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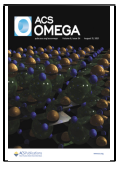

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benzoxazoles.[4] These approaches not only permit expedient synthesis of various benzoxazoles but also make possible the construction of structurally complex derivatives. Interestingly, a one-pot multicomponent coupling reaction of catechols, ammonium acetate, and aldehydes afforded benzoxazole derivatives in high yields (Scheme 1C).[14,15]

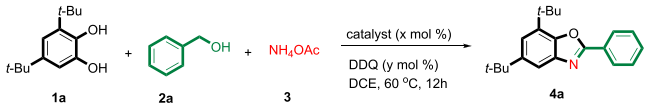
Because the oxidation of benzyl alcohols and benzyl methyl ethers to the corresponding aldehydes is common,[16−18] we envisioned that benzyl alcohols and benzyl methyl ethers might be used directly instead of aldehydes (Scheme 1D).

To the best of our knowledge, one-pot multicomponent coupling reaction of catechols, benzyl alcohols/benzyl methyl ethers, and ammonium acetate toward the synthesis of benzoxazoles has not been reported yet. Based on the applications of Fe(III) as a catalyst,[19,20] herein, we describe an efficient method for the synthesis of 2-substituted benzoxazoles with this multicomponent reaction using Fe(III) as the catalyst.

RESULTS AND DISCUSSION

In our initial experiment, the reaction of 3,5-di-*tert*-butylbenzene-1,2-diol (**1a**), benzyl alcohol (**2a**), and ammonium acetate (**3**) in the presence of 10 mol % of $Fe(NO_3)_3.9H_2O$ as the catalyst in the 1,2-dichloroethane (DCE) solvent at 60 °C after 12 h resulted in a trace amount of the benzoxazole product (**4a**) under air conditions (Table 1, entry 1). While using the same reaction conditions and only the addition of 5 mol % of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as the additive, benzoxazole **4a** was obtained in 80% isolated yield (Table 1, entry 2). The catalyst loading (Table S1) was investigated, and 15 mol % of $Fe(NO_3)_3.9H_2O$ was found to be optimum, exhibiting high yields of 86% (Table 1, entry 3). Different additives were tested (Table S2), and 5 mol % of DDQ was efficient for providing a high product yield. In addition, we did not observe increase in yields with a higher amount of DDQ (Table 1, entry 4).

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst (x)	y	yield **4a** (%)[b]
1	$Fe(NO_3)_3.9H_2O$ (10)	0	trace
2	$Fe(NO_3)_3.9H_2O$ (10)	5	80
3	$Fe(NO_3)_3.9H_2O$ (15)	5	86
4	$Fe(NO_3)_3.9H_2O$ (15)	10	85
5	none	5	0
6	$Fe(NO_3)_3.9H_2O$ (15)	5	10[c]
7	$Fe(NO_3)_3.9H_2O$ (15)	5	80[d]
8	$Mg(NO_3)_2.4H_2O$ (10)	5	33
9	$Zn(NO_3)_2.6H_2O$ (10)	5	27
10	$Cd(NO_3)_2.6H_2O$ (10)	5	20
11	$FeCl_3.6H_2O$ (15)	5	45

[a]Reaction condition: **1a** (1.0 mmol), **2a** (1.0 mmol), **3** (1.0 mmol), solvent (3.0 mL), open air. [b]Isolated yield. [c]Reaction was performed at RT. [d]Reaction was performed under reflux conditions.

Two blank tests were performed in order to show the role of the catalyst and additive. In the absence of both the catalyst and additive, no product was observed. Also, in the presence of only DDQ, no product yield was detected (Table 1, entry 5). Different solvents including toluene, xylene, tetrahydrofuran (THF), dimethylformamide (DMF), EtOH, H_2O, and CH_3CN were checked, and only in the case of acetonitrile, the yield of more than 50% was observed (Table S3). Our results showed that lower or elevated temperatures have a negative effect on the reaction yield (Table S4).

Other metal catalyst sources (Mn, Zn, Cd, Cu, Mo, Co, and Bi) were also checked, and it was found that Fe is the best catalyst in this transformation (Table S5). Also, other iron sources were employed, and among them, nitrate salt was the best (Table S6). For example, in the presence of $FeCl_3.6H_2O$ as the catalyst, only 45% of the product was produced (Table 1, entry 11). Finally, different sources of ammonia were checked, and ammonium acetate was found to be the preferred nitrogen source (Table S7).

Having optimized conditions in hand, we started to show the generality and scope of the reaction. Thus, different benzyl alcohols and catechols were reacted with ammonium acetate, and different benzoxazole derivatives were synthesized in good to excellent yields (Scheme 2).

The reaction tolerates a wide variety of functional groups, including ether (**4b,l,q,u**), alkyl (**4c,d,j**), halogen (**4e,f,g,k**), nitro (**4h**), and hydroxy (**4i**) (Scheme 2) groups. Both electron-rich and electron-poor benzyl alcohols worked well with this methodology. Heterocyclic substrates including furan, thiophene, and pyridine were used successfully in this process, and benzoxazoles (**4m,n,o**) were obtained in a high yield of more than 80%. In the case of non-benzylic substrates, satisfactory yields of the products were observed (**4p,q**). An alkene-functionalized benzoxazole was synthesized using allyl alcohol in 41% isolated yield (**4r**).1-Naphthalenemethanol was subjected to the Fe-catalyzed multicomponent coupling reaction, resulting in the corresponding benzoxazole in 77% yield (**4s**). Sterically hindered substrates gave benzoxazoles in good yields (**4j,k**). Two other commercially available catechols successfully afforded products (**4t,u**). No benzoxazole product was obtained using catechol with electron-poor groups such as $-NO_2$, $-CO_2H$, and -Br as well as using unsubstituted catechol (**4v,w,x,y**). To prove the large-scale applicability of this new method, compound **4a** was fruitfully synthesized in gram-scale (5.0 mmol), and 82% (1.26 g) of the product was isolated under optimized conditions. In order to show the applicability of this new methodology further, benzyl methyl ether was used as the substrate instead of benzyl alcohol (Scheme 3).

To gain insights into the reaction mechanism, several control experiments were conducted (Scheme 4). When 4-methoxybenzyl alcohol (**2b**) was subjected to the optimized condition in the absence of catechol, 4-methoxybenzaldehyde was obtained in a quantitative yield, representing the oxidative capability of the catalyst system to produce aldehyde from benzyl alcohol (Scheme 4A).[16,17] When the model reaction was carried out under N_2, only 15% yield of benzoxazole **4b** was achieved, confirming the necessity of the air atmosphere to complete the reaction (Scheme 4B). In an experiment, **2b** was reacted with ammonium acetate first; then, **1a** was added to the reaction media, and benzoxazole **4b** was isolated in 87% yield, confirming the formation of imine and reaction with catechol according to the proposed reaction mechanism (Scheme 4C). The imine formation under this condition was strongly confirmed by previous studies.[21−24] In other experiments, 3,5-di-*tert*-butylcyclohexa-3,5-diene-1,2-dione (**1aa**) was used instead of catechol, and surprisingly, benzimidazole

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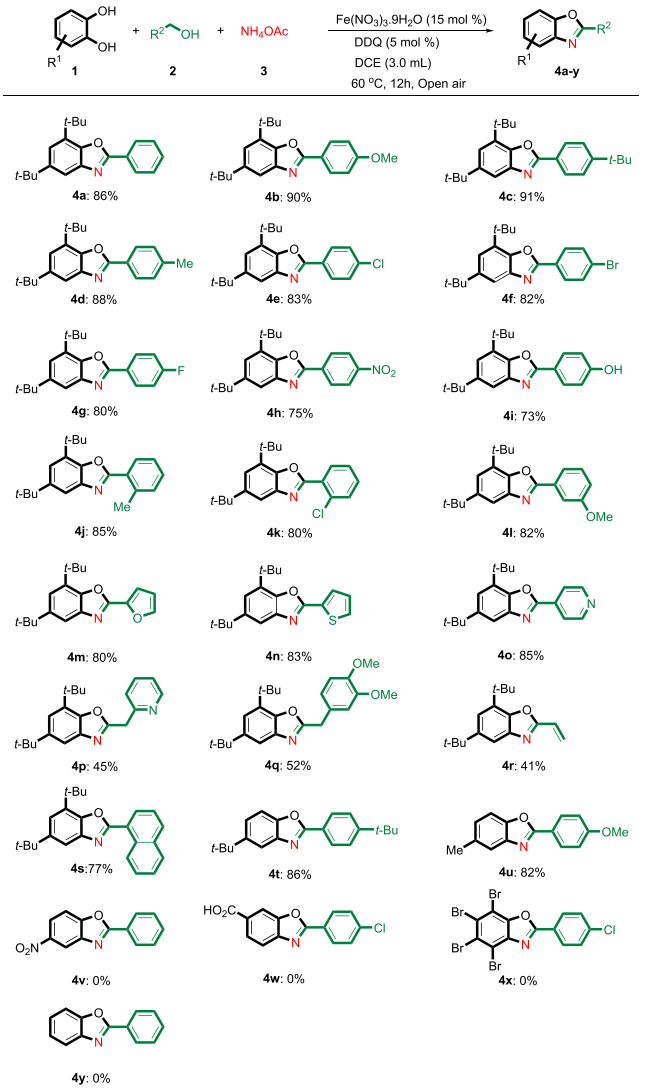
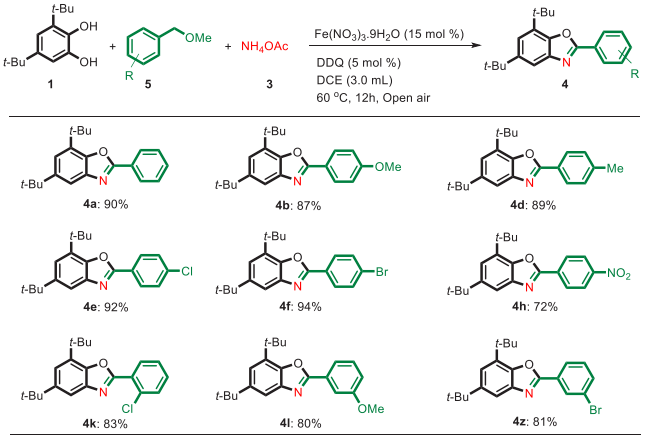
ACS Omega 2021, 6, 22395−22399

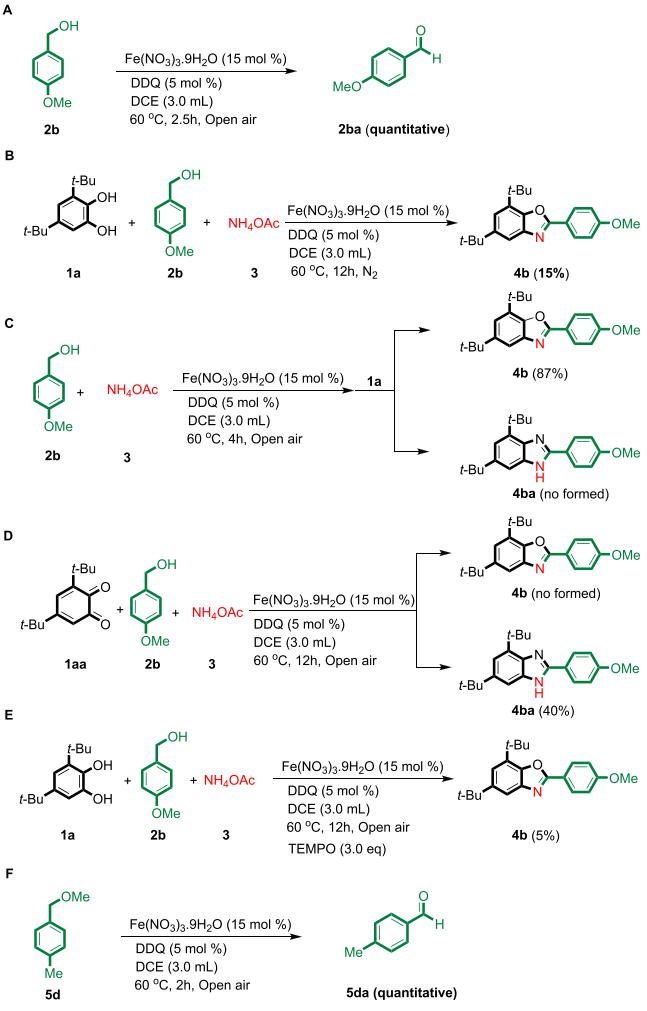
Scheme 2. Scope of Benzoxazoles. Reaction Conditions: Catechol (1.0 mmol), Alcohol (1.0 mmol), Ammonium Acetate (1.0 mmol), $Fe(NO_3)_3.9H_2O$ (15 mol %), DDQ (5 mol %), DCE (3.0 mL), Open Air. All Yields are Isolated



Scheme 3. Synthesis of Benzoxazoles via Catechol, Benzyl Methyl Ethers, and Ammonium Acetate. Reaction Conditions: Catechol (1.0 mmol), Benzyl Methyl Ether (1.0 mmol), Ammonium Acetate (1.0 mmol), $Fe(NO_3)_3.9H_2O$ (15 mol %), DDQ (5 mol %), DCE (3.0 mL), Open Air. All Yields Correspond to the Isolated Product



Scheme 4. Control Experiments



(**4ba**) was obtained (Scheme 4D). This result demonstrates that this process does not undergo the formation of the **1aa** intermediate and a radical pathway is most likely. Using 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) as the radical inhibitor, only 5% of the desired product was obtained, confirming again that the reaction mechanism proceeds radically (Scheme 4E). In addition, under standard conditions, 4-methylbenzyl methyl ether (**5d**) quantitatively converted to the corresponding aldehyde, representing that benzyl methyl ether derivatives also worked via aldehyde formation (Scheme 4F).[17]

On the basis of the experimental observations and previous literature, a possible reaction mechanism has been proposed for the multicomponent coupling reaction of 3,5-di-*tert*-butylbenzene-1,2-diol, benzyl alcohol or benzyl methyl ether, and ammonium acetate in the presence of Fe(III)/DDQ (Scheme 5).

First, benzyl alcohol or benzyl methyl ether (**III**) is converted to benzaldehyde (**IV**) in the presence of Fe(III)/DDQ.[16,17,25−28] Then, NH_4OA attacks benzaldehyde for imine intermediate (**V**) formation.[21−24] The reaction of radical intermediate (**II**) generated from substrate (**I**) reacted with intermediate (**V**), leading to the formation of imine

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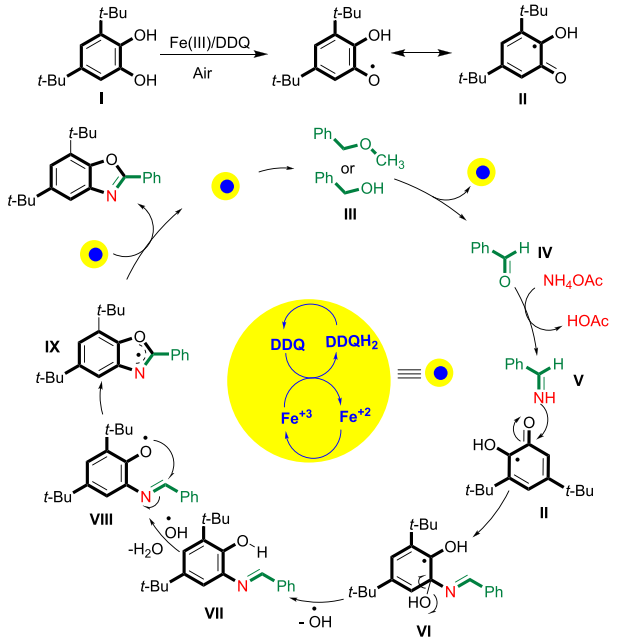
Scheme 5. Proposed Reaction Mechanism for the Synthesis of Benzoxazoles



intermediate (**VI**).[29] Afterward, the elimination of the hydroxyl radical from intermediate (**VI**) afforded 2-(benzylideneamino)-4,6-di-*tert*-butylphenol (**VII**) as an imine intermediate. Single-electron transfer (SET) causes the formation of intermediate (**VIII**) from intermediate (**VII**) likely by hydroxyl radicals.[30] The intramolecular cyclization of **VIII** resulted in the production of intermediate (**IX**). Finally, aromatization of the intermediate (**IX**) with SET and the oxidative dehydrogenation process produce the final benzoxazole product.[15,31]

CONCLUSIONS

In conclusion, we have developed an efficient multicomponent coupling reaction involving catechol, benzyl alcohols/benzyl methyl ethers, and ammonium acetate for the synthesis of benzoxazoles using the Fe(III)/DDQ catalyst system. Using this new protocol, a variety of benzylic, aliphatic, and allylic alcohols (and benzyl methyl ethers) was converted to benzoxazoles under air conditions. This work provides a powerful alternative protocol for the efficient synthesis of this important class of heterocycles using the abundantly available and cheap catalyst system. More importantly, in this protocol, we used ammonium acetate as the nitrogen source in the synthesis of benzoxazole derivatives. Some experimental studies were conducted in order to prove the suggested reaction mechanism.

EXPERIMENTAL SECTION

General Information. All chemicals, materials, reagents, and solvents used in this work were purchased from Sigma-Aldrich, Merck, and Fluka Companies. All known products were identified by comparison of their spectral data and melting points with those of the valid samples. ^{1}H NMR and ^{13}C NMR spectra were determined using 250, 300, and 400 MHz in dimethyl sulfoxide-d_6 (DMSO-d_6) or $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Melting points were checked using a Büchi B-545 apparatus in open capillary tubes. Using thin-layer chromatography (TLC) analytical silica gel plates 60 F250 (Merck chemical company), the purity of the products was investigated.

Typical Experimental Procedure for the Preparation of Benzoxazole Derivatives via Benzyl Alcohol/Benzyl Methyl Ether. Under air, the mixture of alcohols or benzyl methyl ethers (1.0 mmol), $Fe(NO_3)_3.9H_2O$ (15 mol %), DDQ (5 mol %), and DCE as the solvent (3.0 mL) was added to a tube in an oil bath at 60 °C and stirred for 30 min. Next, catechol (1.0 mmol) and NH_4OAc (1.0 mmol) were added to the reaction mixture. After the reaction, DCE was removed under vacuum and extracted with ethyl acetate. Eventually, the crude mixtures were purified by column chromatography using an eluent to obtain the pure benzoxazoles **4**.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03207.

Optimization of loading; different additives and different amounts of additives; investigation of different types of solvent; effect of temperature on the reaction; different metal catalyst sources; Fe sources employed in the reaction; various sources of ammonia; spectral data; and copies of ^{1}H and ^{13}C NMR spectra for the synthesized compounds (PDF).

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Notes

The authors declare no competing financial interest.

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