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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.202000999

Link to VoR: https://doi.org/10.1002/ejoc.202000999

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10.1002/ejoc.202000999

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FULL PAPER

Consecutive oxidation/condensation/cyclization/aromatization sequences catalyzed by nanostructured iron(III)-porphyrin complex toward benzoxazole derivatives

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Abstract: A facile, efficient, and eco-friendly strategy to access benzoxazole heterocyclic products has been accomplished through oxidation of catechols followed by condensation/cyclization/aromatization sequences. This process is catalyzed by nanostructured iron(III)-porphyrin complex to form desired benzoxazole derivatives at room temperature under air condition. The procedure is widely applicable to diverse amines, and can provide the heterocyclic products in a scalable fashion, as well. One of the most significant types of oxidizing agents in nature is the iron-porphyrin complexes (0.1 mol%), existing in the structure of hemoglobin. They have benefits such as low toxicity and high oxidation potential for many substrates.

Introduction

Heterocycles are cyclic compounds composed of carbon, hydrogen, and heteroatom (including oxygen, or nitrogen, or both O and N).[1-8] Benzoxazoles contain O and N heteroatoms and are a significant class of benzo-fused heterocyclic products. Among diverse fused-ring heterocyclic compounds, the benzoxazole scaffold broadly exists in numerous compounds with many and various biological activities including antibacterial, anticancer, anti-measles virus and anti-HIV activities.[9,10]

A survey of the literature reveals that the benzoxazole scaffold is an excellent template for anti-inflammatory activity,[10] with low side effects and considerable gastric safety margins. On the other hand, a range of cytotoxic natural products such as natural antimycobacterial pseudopteroxazole,[11,12] salvianen,[13] AJI9561,[14] and UK-1(bisbenzoxazole)[15] holds benzoxazole moiety (Figure 1).

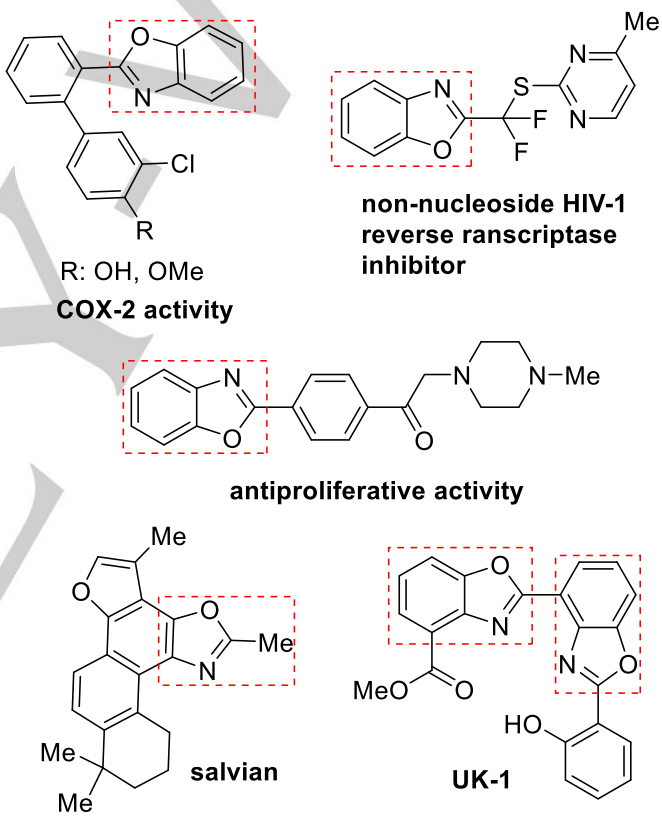

Figure 1. Chemical structures of some bioactive benzoxazole derivatives.

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Moreover, the synthesis of metal-benzoxazole complexes has attracted much attention in recent years, awning to their extensive applications in catalysis, synthesis, medicinal chemistry, and materials science. In general, compounds containing *N*-donor azole groups can bind to first-row transition metals. They have also exhibited excellent coordination ability through a strong σ–donation and poor π–back donation from the metal to form NHC-complexes with almost every transition metals.[16]

Furthermore, there is a remarkable interest to develop new strategies for the efficient and more applicable synthesis of 2-substituted benzoxazole derivatives in recent years.[17-19] In this regard, numerous synthetic protocols for 2-substituted benzoxazole derivatives have been described in the literature (Figure 2).[20-32].

While the strategies as mentioned above enriched approaches to 2-substituted benzoxazole derivatives, their applicability is often compromised by the use of expensive metals, utilization of harsh reaction conditions, high catalyst loading, and use of volatile and toxic organic solvents.

In this aspect, the aerobic oxidative reaction of catechol with amine derivatives is a reliable pathway towards the corresponding benzoxazole derivatives. Firstly, Yin and Zhou coworkers reported that CuBr (10 mol%) catalyzed aerobic oxidative reaction of catechol derivatives with amine derivatives in DCE for 6 h or 12 h at room temperature under air condition affords 2-substituted benzoxazole derivatives with good efficiency.[33]

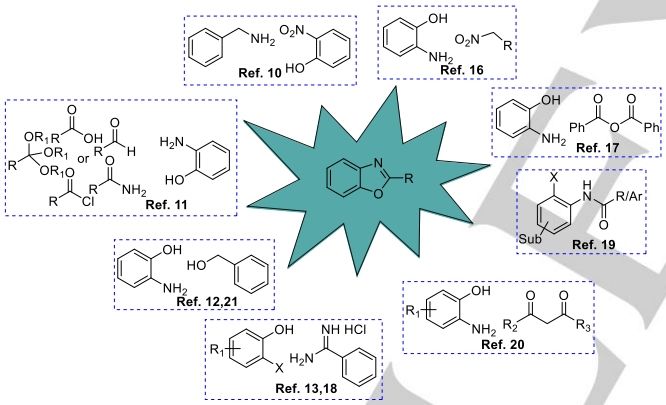

Figure 2. Some routes for synthesis of 2-substituted benzoxazole derivatives from different starting materials.

Later, the domino oxidation/cyclization reaction of catechol derivatives (0.2 mmol) with amine derivatives (0.24 mmol) catalyzed by OMS-2-supported Cu hydroxide (2 mol % Cu) was used to form a variety of 2-substituted benzoxazole derivatives in EtOH (1.0 mL) for 2 h at room temperature under air condition.[34]

Our research group has reported the synthetic procedure for the synthesis of benzoxazole from the reaction of 3,5-di-*tert*-butylbenzene-1,2-diol and primary amines.[1a] Although these methods are very significant, the search for a better catalytic system should be continued for the synthesis of 2-substituted benzoxazole derivatives in terms of operational simplicity, higher selectivity, reaction rate, and reaction yield.

One of the appealing options for the construction of green and efficient catalysts is to use the porphyrin family. Recently, various metalloporphyrins have been prepared and used in organic reactions.[35-41]

As part of our longstanding interests in the catalytic synthesis of heterocyclic products under mild conditions, we report a novel modification for the consecutive oxidation/condensation/cyclization/aromatization sequences catalyzed by nanostructured iron(III)-porphyrin complex as a highly efficient catalyst toward benzoxazole derivatives that previously developed by Yin and Zhou[33] and later by Zhao[34]. Moreover, all reactions were performed for short reaction times in room temperature under air condition.

Results and Discussion

We sought to perform the reaction pathway by synthesizing the nanostructured iron(III)-porphyrin complex, and investigating its competence in the aerobic oxidation of C(aryl)-OH bonds of catechols and then cyclization of resulted intermediates with amine derivatives. Since metalo-porphyrin complexes have exhibited diverse applications in organic synthesis and chemical processes, these biomimetic catalysts have been the subject of several types of research.[42] On the other hand, they are stable in different conditions and they can tolerate many biological and synthetic reactions. More importantly, these catalysts can perform the oxidation of substrates, as well.[43]

Initially, the nanostructured iron(III)-porphyrin was synthesized according to the literature with slight modification.[44-45] In a typical procedure, benzaldehyde and pyrrole were magnetically stirred in CH_2Cl_2 in the presence of CF_3SO_2Cl at room temperature under nitrogen atmosphere to produce tetraphenylporphyrin. In the next step, tetraphenylporphyrin and anhydrous $FeCl_3$ were refluxed in DMF for 2 h at 165 °C to prepare iron-porphyrin complex. The nanostructured iron(III)-porphyrin was characterized by FESEM and EDX analysis.

The morphology of the iron(III)-porphyrin complex was evaluated by FESEM. The FESEM image of the iron(III)-porphyrin complex displays that the complex particles have a nanostructured shape. The EDX spectrum of the obtained nanostructured iron(III)-porphyrin complex confirmed the presence of the expected elements in its structure namely iron, chlorine, oxygen, nitrogen, and carbon (Figure S1-S2).

To establish the optimal process conditions for the reaction of catechols with structurally diverse amines, different metal-porphyrin complexes were screened in a standard reaction between 3,5-di-*tert*-butylcatechol and 2-methylpropan-1-amine in various solvents at room temperature using atmospheric air as a green oxidant.

In the first step, a range of metal-porphyrin complexes, such as CdTPP, Sn(II)TPP, Pb(II)TPP, ZnTPP, Cu(II)TPP, NiTPP, and FeTPPCl were tested in the reaction (Table 1, entries 1-7). Under CdTPP, Sn(II)TPP, Pb(II)TPP, and ZnTPP catalysis, comparably poor results were observed (Table 1, entries 1-4). When the reaction was performed using the Cu(II)TPP catalyst, approximately good yield of the compound was achieved (Table 1, entry 5). The NiTPP catalyst showed a good yield of the product (Table 1, entry 6). The nanostructured iron-porphyrin complex was proved to be highly active in terms of yield, selectivity, and time for the synthesis of 2-substituted benzoxazole derivatives in ethanol solvent (Table 1, entry 7). $FeCl_3$ and $FeCl_2$ were used as

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commercial catalysts in place of iron-porphyrin complex in EtOH at room temperature, and the results demonstrated that iron-porphyrin complex exhibits highly efficient catalytic behavior (Table 1, entries 8-9). The iron-based catalyst was vital for the aerobic oxidative reaction of 3,5-di-*tert*-butylcatechol with amine derivatives and only a trace amount of desired product was detected in the absence of the catalyst (Table 1, entry 10). As previously reported in the literature, iron-based complexes have been reported as the active catalysts in the oxidative reactions.[46] To achieve the minimum catalyst loading, the iron-porphyrin complex loading was reduced to 0.1 mol% (Table 1, entry 11).

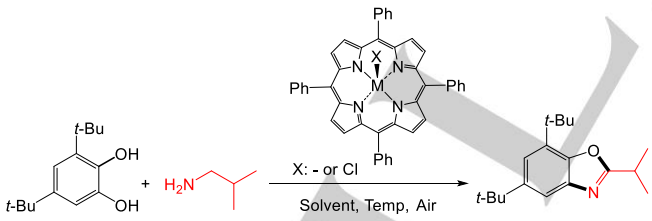
In the next step, the effect of a range of organic solvents was also explored for the model reaction. PEG as solvent was ineffective for this transformation (Table 1, entry 13). Under solvent-free conditions only 30 % of desired 2-substituted benzoxazole was detected (Table 1, entry 14). Using the $CHCl_3$, EtOAC, and Et_2O as solvent, the reaction gave the desired product in only moderate yields (Table 1, entries 15-17). Changing the solvent to CH_3CN slightly increased the yield (Table 1, entry 18), whereas using MeOH, DCE, and DCM highly increased the yield (Table 1, entries 19-21). Ethanol was proved to be the best option for the reaction (Table 1, entry 11).

The reaction was also tested at 70 °C using the catalyst and it was found that the temperature has a reverse effect on the yield of model reaction (Table 1, entry 22).

On the other hand, when the model reaction was carried out under argon, only 10% of product was detected; this result indicated that the air atmosphere is necessary for this reaction (Table 1, entry 23).

With the optimized conditions in hand, catechols were reacted with structurally diverse amines in 2.0 mL of ethanol at room temperature using 0.1 mol% of the iron(III)-porphyrin complex under air condition to determine the scope, versatility and the efficiency of our strategy for consecutive oxidation/condensation/cyclization/aromatization sequences towards structurally diverse benzoxazole derivatives (Table 2).

Table 1. Investigation of different conditions for the reaction between 3,5-di-*tert*-butylcatechol and 2-methylpropan-1-amine.



Entry	Catalyst	Mol%	Solvent	Temp	Time (h)	Yield %[a]
1	CdTPP	0.5	EtOH	25 °C	13	25
2	Sn(II)TPP	0.5	EtOH	25 °C	8	50
3	Pb(II)TPP	0.5	EtOH	25 °C	10	45
4	ZnTPP	0.5	EtOH	25 °C	12	40
5	Cu(II)TPP	0.5	EtOH	25 °C	7	65
6	NiTPP	0.5	EtOH	25 °C	4	90
7	FeTPPCl-NP	0.5	EtOH	25 °C	1.2	98
8	$FeCl_3$	0.5	EtOH	25 °C	12	53
9	$FeCl_2$	0.5	EtOH	25 °C	12	42
10	-	-	EtOH	25 °C	24	trace
11	**FeTPPCl-NP**	**0.1**	**EtOH**	**25 °C**	**1.2**	**98**
12	FeTPPCl-NP	0.05	EtOH	25 °C	1.8	92
13[b]	FeTPPCl-NP	0.1	PEG	25 °C	24	-
14	FeTPPCl-NP	0.1	-	25 °C	12	30
15	FeTPPCl-NP	0.1	$CHCl_3$	25 °C	12	38
16	FeTPPCl-NP	0.1	EtOAC	25 °C	10	45
17	FeTPPCl-NP	0.1	Et_2O	25 °C	12	10
18	FeTPPCl-NP	0.1	CH_3CN	25 °C	8	70
19	FeTPPCl-NP	0.1	MeOH	25 °C	2	87
20	FeTPPCl-NP	0.1	DCE	25 °C	1.5	90
21	FeTPPCl-NP	0.1	DCM	25 °C	2	83
22	FeTPPCl-NP	0.1	EtOH	70 °C	1	90
23[c]	FeTPPCl-NP	0.1	EtOH	25 °C	2	10

[a] Isolated yield. [b] Polyethylene glycol 200 was applied as a solvent. [C] the reaction was performed under the argon atmosphere.

Electron-donating and electron-withdrawing groups (-Me, -OH, -OMe, and -CN) at the para position of benzylamines worked well and produced the corresponding benzoxazoles in good to excellent yields. Electron-donating groups showed better reactivity than electron-withdrawing groups (Table 2, entries 2-5). The halogen groups such as –Cl and –F could afford the corresponding products in excellent yields, as well (Table 2, entries 6-7). The ortho-substituted benzylamines underwent the consecutive oxidation/condensation/cyclization/aromatization sequences to afford desired benzoxazole heterocyclic products in excellent yields (Table 2, entries 8-9). Aliphatic amines without aromatic ring also worked well to afford benzoxazole heterocyclic products (Table 2, entries 10-18, 22-28, 32). The 2-(1-(2-aminoethyl)cyclohexyl)acetic acid was a successful reaction partner, as well. This produced acid containing benzoxazole can take part in many organic reactions that require acid (Table 2, entry 15).

The reaction also afforded excellent results in the case of amino alcohol derivatives (Table 2, entry 16-17). It is worth noting that allylic amine can be transformed to the corresponding product in good yield (Table 2, entry 18).

Aliphatic propane-amine with 3,4-dimethoxyphenyl substitution was tolerated to provide corresponding product in good yield (Table 2, entry 19). Then, we turned our attention towards the synthesis of benzoxazoles containing five-membered and six-membered heterocyclic substitutions (Table 2, entries 20, 21).

We were also pleased to find that amines containing aliphatic heterocycle including (tetrahydrofuran-2-yl)methanamine, 2-(piperazin-1-yl)ethan-1-amine, and 3-morpholinopropan-1-amine can efficiently lead to the corresponding products (Table 2, entries 22-24). This protocol could then be extended to the synthesis of benzoxazole containing morpholine moiety (Table 2, entry 23).

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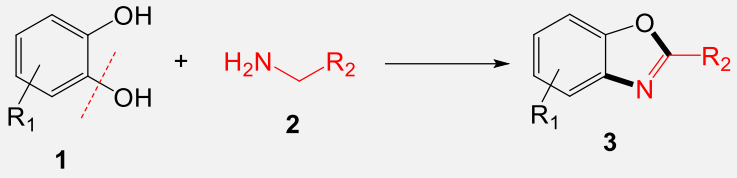
The morpholine is a potential substituent to impart remarkable biological property to organic molecules. In addition, this procedure allows the synthesis of the benzoxazole containing secondary amine moiety (Table 2, entry 24).

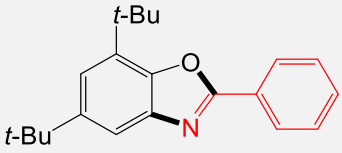
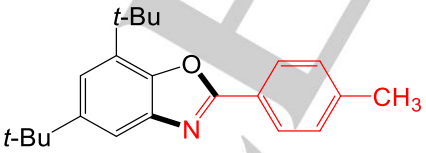
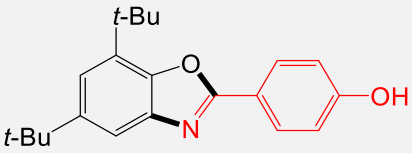
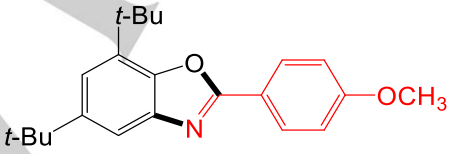
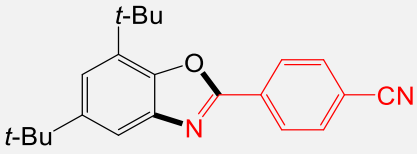
Encouraged by these results, bis aliphatic amines were employed in the reaction for the synthesis of bis products. Interestingly, bis products were isolated with moderate to good yields and times (Table 2, entries 25-28). Surprisingly, when long chain aliphatic amines were involved in this process, only desired products were formed in high yields (Table 2, entry 14, 25, and 28).

To further highlight the usefulness of this protocol, catechol derivatives carried out using benzyl and aliphatic amines. 4-*tert*-butylcatechol reacted with benzyl amines substituted at *ortho* and *para* positions to afford excellent yields of products (Table 2, entries 29, 30). When 4-metylcatechol was subjected, the reaction underwent this process to provide desired products, as well (Table 2, entriy 31). The 3-methoxycatechol treated with amine substrate under optimized reaction conditions to give moderate yield of product (Table 2, entry 32). Finally, no yield of product was detected by using other types of catechol derivatives (Table 2, entries 33-36). A secondary amine (isopropylamine) was checked for the reaction. We found the reaction stops at E intermediate (Table 2, entry 33).

According to literature reports,[33-34] a plausible mechanism can be proposed on the basis of consecutive oxidation/condensation/cyclization/aromatization sequences. The oxidation of catechol using the catalyst is the initial step. A nucleophilic attack of NH_2 group in a primary amine to the carbonyl group on ortho-quinone intermediate (**A**) efforts intermediate (**B**). Afterward, intermediate (**B**) is dehydrated to produce imine (**C**). Subsequently, the Schiff base (**D**) is formed *via* the tautomerization process of imine (**C**). Then, intermediate (**D**) transforms to benzoxazoline intermediate (**E**) through addition–cyclization sequences. Finally, the benzoxazoline intermediate (**E**) converts to benzoxazole product *via* an aerobic oxidative dehydrogenation process (Scheme1).

Table 2. Consecutive oxidation/condensation/cyclization/aromatization sequences catalyzed by nanostructured iron(III)-porphyrin complex toward benzoxazole derivatives.[a]



Entry	Product	Time (h)	Yield (%)[b]
1	 **3a**	2	91
2	 **3b**	1.2	96
3	 **3c**	2	83
4	 **3d**	1	96
5	 **3e**	2.5	77

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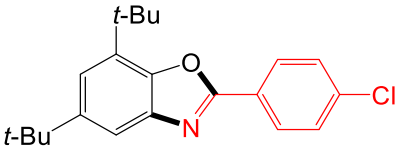
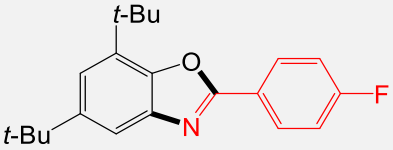
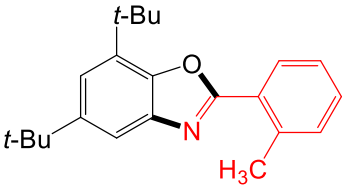
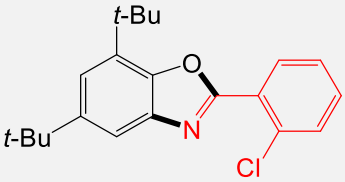
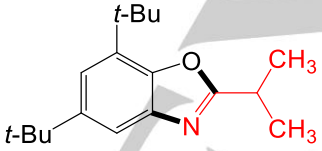
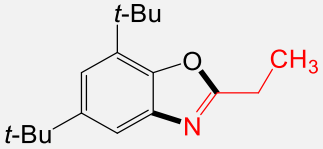
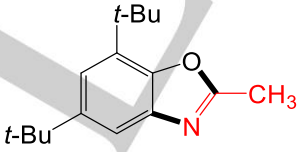
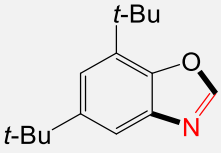
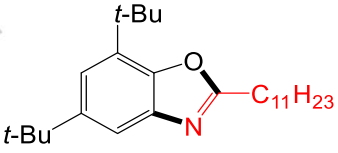
6	 **3f**	1.5	95
7	 **3g**	2	85
8	 **3h**	1.5	94
9	 **3i**	1.7	92
10	 **3j**	1.2	98
11 [c]	 **3k**	2.5	91
12 [d]	 **3l**	4	90
13	 **3m**	4.5	75
14	 **3n**	1.8	93

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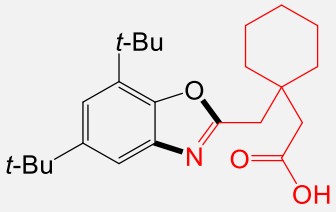
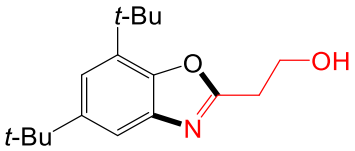
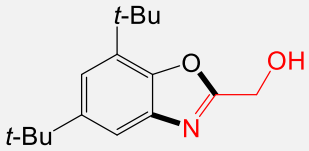
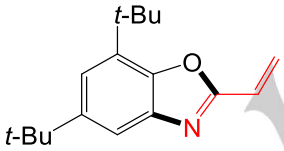
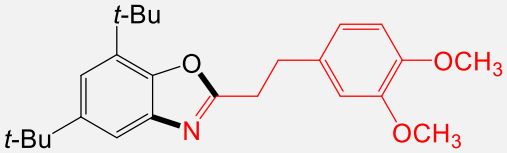
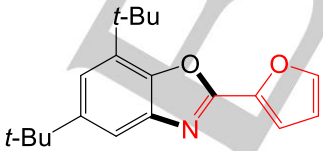
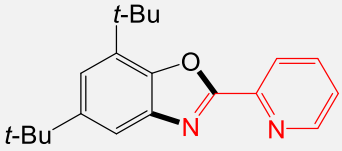
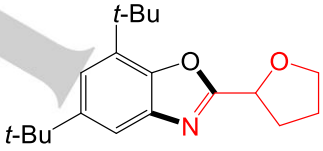
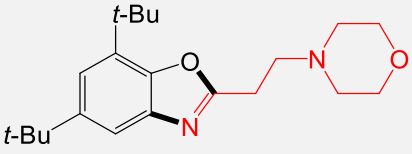
15	 **3o**	3.5	90
16	 **3p**	2	94
17	 **3q**	2.5	91
18	 **3r**	4	80
19	 **3s**	3	85
20	 **3t**	2	93
21	 **3u**	1.7	95
22	 **3v**	2.5	88
23	 **3w**	2.5	89

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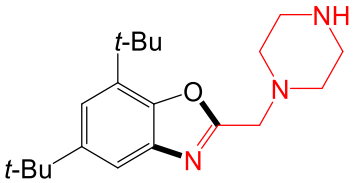
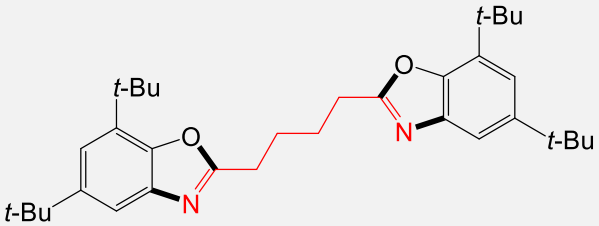
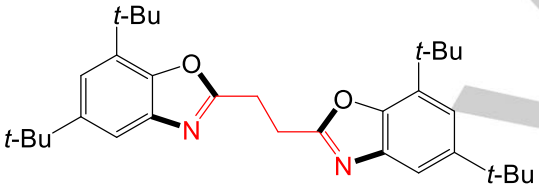
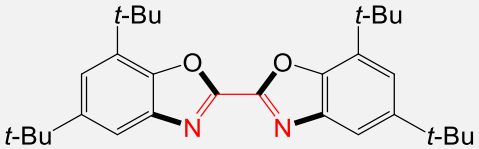
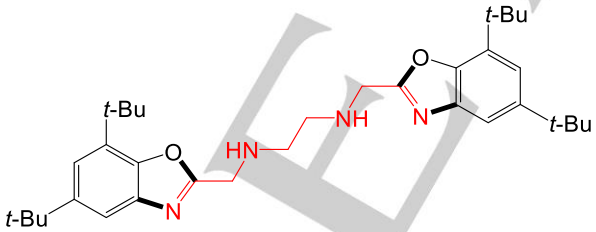
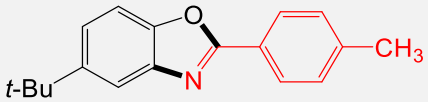
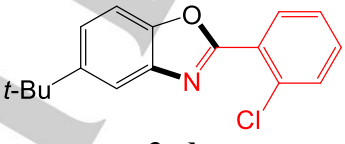
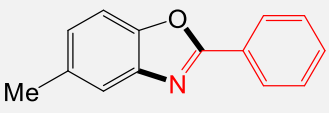
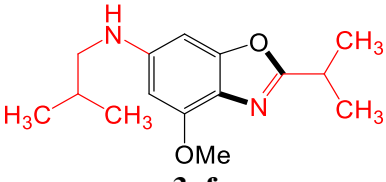
24	 **3x**	1.6	95
25 [e]	 **3y**	3	85
26 [e]	 **3z**	3	85
27 [e]	 **3aa**	4	80
28 [e]	 **3ab**	6	65
29	 **3ac**	2.7	92
30	 **3ad**	3	87
31	 **3ae**	4	83
32	 **3af**	5	75

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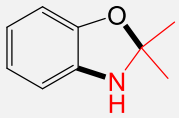
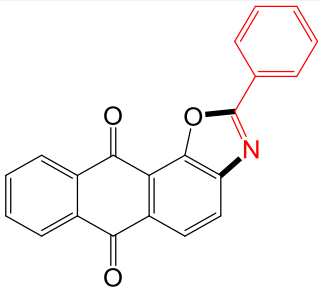
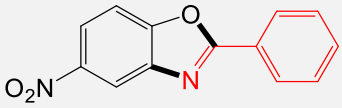
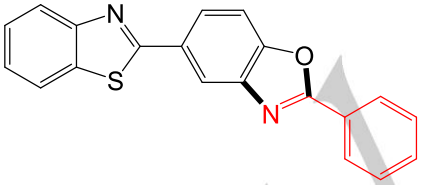
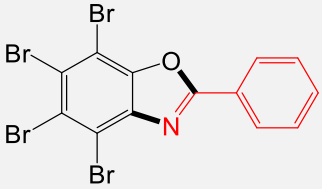
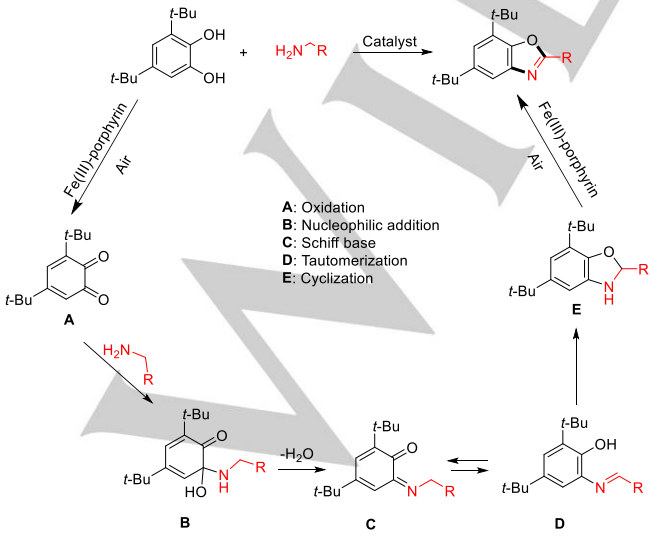
33 [f]	 **3ag**	3	74
34	 **3ah**	24	0
35	 **3ai**	24	0
36	 **3aj**	24	0
37	 **3ak**	24	0

[a] Isolated yield. [b] reaction conditions, amine (1.0 mmol), catechol (1.0 mmol), catalyst loading (0.1 mol%), and ethanol (2.0 mL). [c] A 70% aqueous solution of ethylamine was used. [d] A 40% aqueous solution of methylamine was used. [e] 2 mmol of 3,5-di-tert-butylbenzene-1,2-diol has been applied. [f] A secondary amine (isopropylamine) was used.



Scheme 1. A plausible mechanism for consecutive oxidation/condensation/cyclization/aromatization sequences catalyzed by nanostructured iron(III)-porphyrin complex toward benzoxazole derivatives.

Conclusions

A highly efficient and environmental friendly nanostructured iron(III)-porphyrin complex was prepared. Its actual structure and morphology were characterized by FE-SEM and EDX. The efficiency of this catalyst was achieved for a consecutive oxidation/condensation/cyclization/aromatization sequences toward benzoxazole derivatives. We have shown that only 2.0 mL of solvent and 0.1 mol% of catalyst can be used for the synthesis of target products in good to excellent yields at room temperature under air condition (32 different products were prepared). On the other hand, our strategy is associated with the lowest amounts of solvent and catalyst as well as the lowest generation of waste. More importantly, porphyrin structures exist in animals and plants.

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So, they are considered as green oxidizing agents in many organic reactions.

Experimental

Reagents and solvents were purchased from Merck, Fluka or Sigma-Aldrich. Melting points were determined in capillary tubes in a Büchi B-545 apparatus. The progress of the reaction and the purity of compounds were monitored by thin layer chromatography (TLC) analytical silica gel plates (Merck 60 F250). All known compounds were identified by comparison of their melting points and proton nuclear magnetic resonance (^{1}H-NMR) data with those in the authentic samples. The ^{1}H-NMR (400, 300 and 250 MHz) and ^{13}C-NMR (100, 75 and 62.5 MHz) were run on a Bruker Avance DPX-250 and Bruker Avance DPX-400 fourier transform (FT)-NMR spectrometers respectively. Chemical shifts are given as δ values against tetramethylsilane (TMS) as the internal standard and J values are given in Hz. The elemental analysis was performed on a Perkin-Elmer 240-B microanalyzer.

General procedure for the synthesis of benzoxazoles

In a 10 mL round-bottom flask contained a suspension of nanostructured iron(III)-porphyrin complex (0.1 mol%) in ethanol (2.0 mL), catechol (1.0 mmol) and primary amine (1.0 mmol) were added and resulting mixture was stirred at room temperature under the air atmosphere. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, water (10 mL) was added to the solution and products was extracted with EtOAc (5 mL) dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel to give the pure products.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully appreciate the Shiraz University Research Councils and the Iran National Elite Foundation for the financial support of this work.

Keywords: Benzoxazole derivatives • Catechol oxidation • Diverse scope • Green conditions • Porphyrin catalyst

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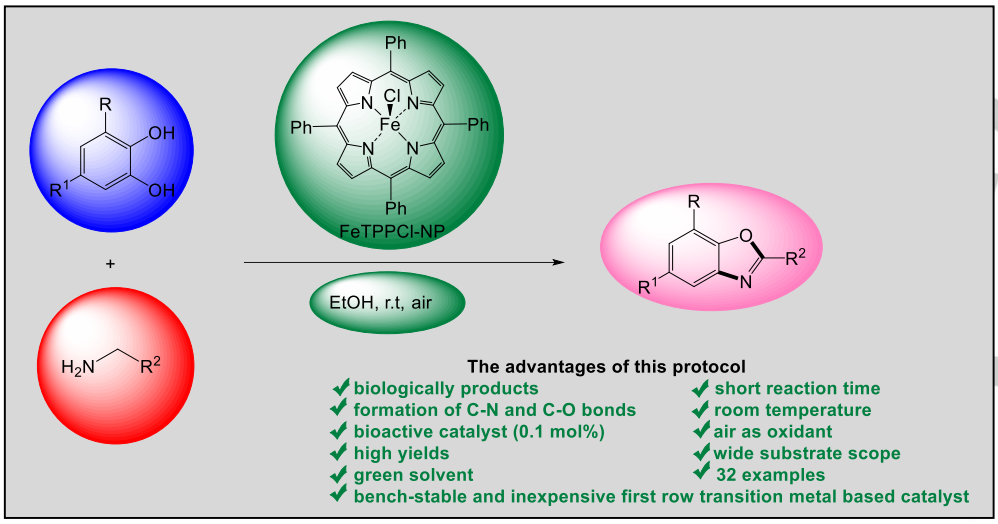

Divers benzoxazole heterocyclic products have been synthesized by a facile, efficient, and eco-friendly strategy. The synthesis of benzoxazoles was catalyzed by nanostructured iron(III)-porphyrin complex at room temperature under green conditions.

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