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One-pot, three-component, iron-catalyzed synthesis of benzimidazoles *via* domino C–N bond formation†

Jasem Aboonajmi,^a Masoumeh Mohammadi,^a Farhad Panahi,^{ID}*^{ab} Mahdi Aberi^c and Hashem Sharghi^{ID}^a

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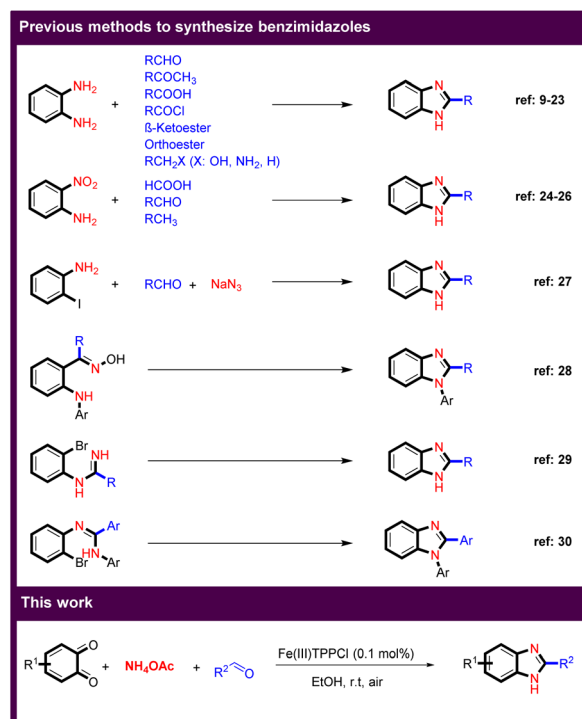
An efficient one-pot, three-component process for the synthesis of benzimidazole derivatives using a catalytic amount of Fe(III) porphyrin has been developed. The reaction proceeds *via* domino C–N bond formation and cyclization reactions of benzo-1,2-quinone, aldehydes and ammonium acetate as a nitrogen source to selectively produce benzimidazole. A number of benzimidazole derivatives have been synthesized using this method in high yields under mild reaction conditions.

Introduction

Multicomponent reactions (MCRs) play an essential role in the pharmaceutical industry and in modern organic synthesis, as they provide a powerful tool for the cost and time-efficient synthesis of advanced drugs and target compounds by generating a complex structure from multiple reactants in a single step.^{1–5} Imidazole derivatives are one of the most important groups in heterocyclic compounds that have attracted much attention because they are found in a variety of natural products. In addition, benzimidazoles are the core structure of many pharmaceuticals, ionic liquids (ILs) as more environmentally friendly solvents, and *N*-heterocyclic carbenes as valuable ligands in transition-metal catalysis.^{3,6–8} There are several known routes to benzimidazole derivatives (Scheme 1). Reaction between *o*-phenylenediamine and carbonyl compounds such as aldehydes,^{9–13} ketones,¹⁴ acids,¹⁵ acyl chlorides,¹⁶ and as well as β -ketoesters,^{17,18} or orthoesters,^{19,20} or and benzylic including benzyl alcohols,²¹ benzyl amines,²² and toluene derivatives²³ are the main methods for the synthesis of a large number of benzimidazole derivatives. Another important approach is the reaction of 2-aminonitrobenzenes with acids,²⁴ aldehydes,²⁵ and activated methyl groups.²⁶ In another strategy, benzimidazoles were obtained by coupling of 2-iodoaniline with aldehydes.²⁷ Arylamino oximes also led to benzimidazoles in the presence of a base.²⁸ The synthesis of benzimidazoles by

intramolecular *N*-arylation using copper catalysts was developed.²⁹ The intramolecular cyclization of *o*-bromoaryl derivatives also resulted in benzimidazoles.³⁰

Despite numerous advances in the synthesis of benzimidazoles, the development of new synthetic methods is strongly considered because the existing methods have many drawbacks, such as low yields, complicated reaction conditions, use



Scheme 1 Different methods for the synthesis of benzimidazole scaffolds.

^aDepartment of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran. E-mail: Panahi@shirazu.ac.ir; Fax: +98 7132280926; Tel: +98 7136137136

^bInstitut für Organische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstraße 21, 79104 Freiburg im Breisgau, Germany

^cDepartment of Chemical and Materials Engineering, Faculty of Shahid Rajaei, Technical and Vocational University (TVU), Shiraz Branch, Shiraz, Iran

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of toxic reagents and solvents. On the other hand, there is a high demand for efficient and clean synthesis of benzimidazole derivatives from other sources. Continuing our program on the synthesis of benzoxazoles,^{4,5,31,32} we would like to present here a novel and efficient protocol for the synthesis of benzimidazole derivatives. In this work, MCR of benzo-1,2-quinones, aryl aldehydes and ammonium acetate in the presence of catalytic amount of an Fe(III)-porphyrin catalyst at room temperature resulted in a benzimidazole core.

Metalloporphyrins have been used as catalyst in many organic reactions such as the hydroxylation and epoxidation of hydrocarbon compounds,^{33,34} the hydroxylation of aromatic compounds,³⁵ the aziridination of olefins,³⁶ oxidation of sulfides to sulfones,³⁷ the ring-opening of epoxides,³⁸ and the synthesis of heterocyclic compounds.^{10,39,40}

Results and discussion

To optimize the new method for the synthesis of benzimidazoles, the reaction of 3,5-di-*tert*-butylcyclohexa-3,5-diene-1,2-dione (**1**), ammonium acetate (**2**), and 4-methoxybenzaldehyde (**3a**) was selected as a model reaction (Table 1). In the absence of catalyst, in ethanol as solvent and at 80 °C, only 5% product was observed

(Table 1, entry 1). In an attempt to improve the reaction yield, some transition metals such as Fe, Zn, Ni, Cu, Cd and Mn were tested as catalysts (Table 1, entries 2–7). Among the catalysts tested, an increase of the reaction yield to 65% was observed using FeCl₃. However, a benzoxazole by-product was also isolated using these catalysts (Table 1, entries 2–7). To enhance the yield and selectivity, different iron sources were tested (Table 1, entries 8–10). Surprisingly, the maximum product was obtained with a Fe^{III}-porphyrin complex (Fe^{III}TPPCL) at room temperature after only 2 h without the formation of the benzoxazole **5a** side-product (Table 1, entry 11).

Since the porphyrin complex was found to be the best catalyst for this reaction, the porphyrin complexes of other metals were also synthesized^{10,40} and tested to verify that iron was the best catalyst for this reaction (Table 1, entries 12–17). In the presence of Sn^{II}TPP, about 65% of the product was isolated after 7 hours at room temperature (Table 1, entry 12). With Pb^{II}TPP, **4a** was prepared in 60% yield after 8 hours (Table 1, entry 13). Good yield was obtained with Zn^{II}TPP (Table 1, entry 14). Cd^{II}TPP worked the same way as Pb^{II}TPP and 60% of the product was isolated (Table 1, entry 15). Interestingly, Ni^{II}TPP and Cu^{II}TPP gave comparable yields of product (Table 1, entries 16 and 17). The interesting thing is that with the use of porphyrin complexes as catalysts, we have high selectivity for the formation of the benzimidazole product. Among the tested metal complexes, Fe^{III}TPPCL showed high catalytic activity and was therefore selected as catalyst for this multicomponent synthesis of benzimidazoles.

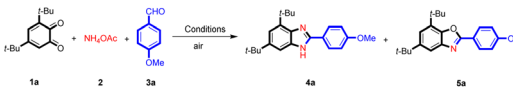
For further optimization, different catalyst loadings were used for the reaction, and no further improvements were found (Table 1, entries 18 and 19). Different solvents were also investigated and no superiority was found (Table 1, entries 20–23). For example, in the solvents acetonitrile and methanol, 70% and 86% of the product were isolated respectively, albeit with a slight loss of selectivity. In addition, the reaction was carried out under N₂ and a yield of 55% was obtained (Table 1, entry 24).

After optimizing the reaction conditions, various aryl aldehydes with electron donor and electron withdrawing groups were first investigated under optimized conditions to test the generality and scope of the method (Scheme 2).

Aryl aldehydes with electron-donating groups in *para* position such as –OMe, –Me, –Cl, –iPr, and –^tBu gave benzimidazoles **4a–e** in more than 90% yield. Electron withdrawing groups such as –F, –CN, and –CF₃ were tested in this reaction and gave good yields of benzimidazoles **4f–h**. The *ortho*- or *meta*-substituted benzaldehyde worked well and provided the desired products in good to excellent yields, regardless of their electronic nature (Scheme 2, **4i–m**).

To further investigate the reaction possibilities, aryl aldehydes with two substituents such as 3,4-dimethoxybenzaldehyde, 2,3-dimethoxybenzaldehyde and 2,6-dichlorobenzaldehyde were tested (Scheme 2, **4n–p**). Remarkably, various heteroaryl aldehydes such as 2-thiophene carboxaldehyde and 3-thiophene carboxaldehyde gave good yields of the desired products (Scheme 2, **4r,s**). Encouragingly, 1-naphthaldehyde, and phenanthrene-9-carbaldehyde were subjected to Fe(III)-catalyzed domino C–N bond formation as polyaromatic

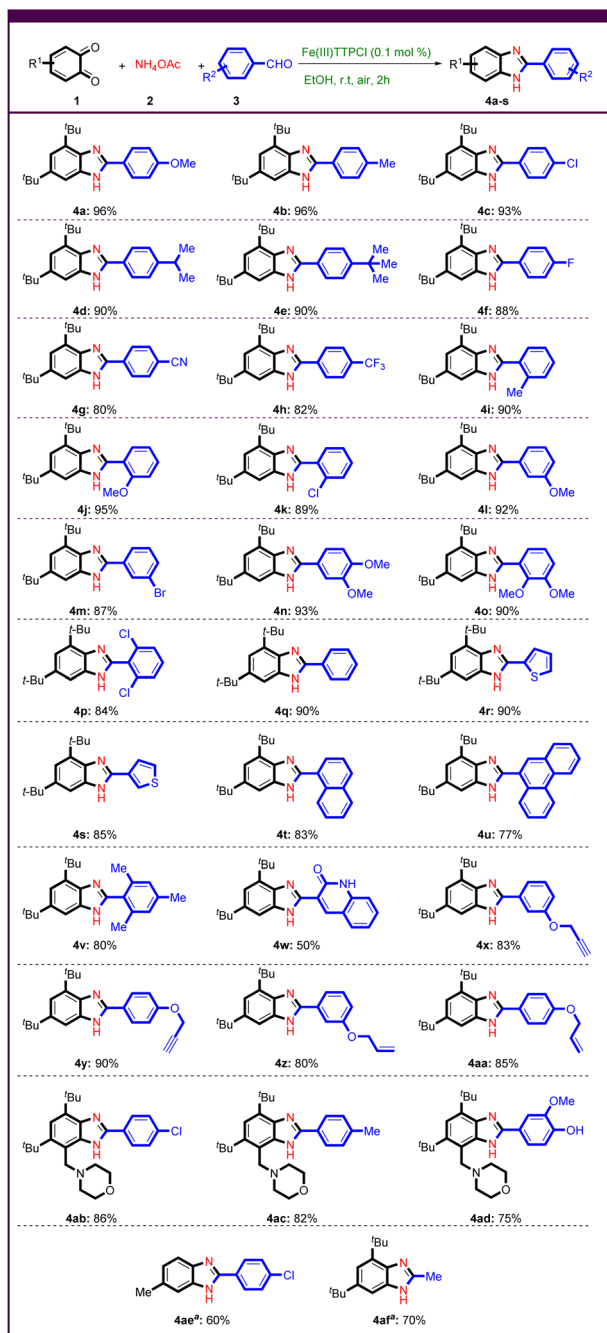
Table 1 Optimization of the reaction conditions for the synthesis of benzimidazoles via a one-pot multicomponent reaction^a



#	Cat. (mol%)	Solv.	T (°C)	Time (h)	Yield 4a/5a ^b (%)
1	—	EtOH	80	12	5/—
2	FeCl ₃ (5)	EtOH	rt	12	65/15
3	ZnCl ₂ (5)	EtOH	rt	12	28/5
4	NiCl ₂ (5)	EtOH	rt	12	36/10
5	CuCl ₂ (5)	EtOH	rt	12	45/8
6	CdCl ₂ (5)	EtOH	rt	12	25/5
7	MnCl ₂ (5)	EtOH	rt	12	50/20
8	Fe(NO ₃) ₃ (5)	EtOH	rt	12	45/20
9	FeBr ₃ (5)	EtOH	rt	12	22/18
10	Fe(acac) ₃ (5)	EtOH	rt	12	20/10
11	Fe ^{III} TPPCL (0.1)	EtOH	rt	2	96/0
12	Sn ^{II} TPP (0.1)	EtOH	rt	7	65/0
13	Pb ^{II} TPP (0.1)	EtOH	rt	8	60/0
14	Zn ^{II} TPP (0.1)	EtOH	rt	5	70/0
15	Cd ^{II} TPP (0.1)	EtOH	rt	9	60/0
16	Ni ^{II} TPP (0.1)	EtOH	rt	3	77/0
17	Cu ^{II} TPP (0.1)	EtOH	rt	4	80/0
18	Fe ^{III} TPPCL (0.05)	EtOH	rt	12	78/0
19	Fe ^{III} TPPCL (0.15)	EtOH	rt	2	94/0
20	Fe ^{III} TPPCL (0.1)	MeCN	rt	3	70/10
21	Fe ^{III} TPPCL (0.1)	H ₂ O	rt	9	45/5
22	Fe ^{III} TPPCL (0.1)	MeOH	rt	3	86/5
23	Fe ^{III} TPPCL (0.1)	PhMe	rt	7	67/0
24	Fe ^{III} TPPCL (0.1)	EtOH	rt	5	^c 55/0

^a Reaction conditions: **1a** (1.0 mmol), **2a** (2.2 mmol), **3a** (1.0 mmol), and solvent (5.0 mL) at r. t. ^b Isolated yield. ^c Under nitrogen atmosphere.





Scheme 2 Synthesis of benzimidazole derivatives. Reaction conditions: 1 (1.0 mmol), 2 (2.2 mmol) and 3 (1.0 mmol) in the presence of FeTPPCl (0.1 mol %) in EtOH (5.0 mL) at room temperature under air condition for 2 h. All yields are isolated. ^a The reaction was performed at 60 °C, 6 h.

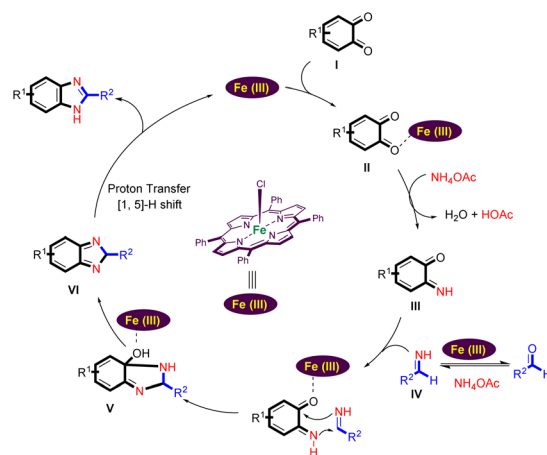
substrates, resulting in the corresponding benzimidazoles in 83%, and 77% yields, respectively (Scheme 2, **4t,u**). Sterically hindered substrates were found to lead to the corresponding benzimidazoles in good yields (Scheme 2, **4p,v**).

The use of quinoline-3-carbaldehyde as substrate gave a bis-heterocyclic product **4w** in 50% yield.

Alkene and alkyne functional groups tolerated the reaction conditions well, giving allyl- and propargyl-functionalized



Scheme 3 Gram-scale Synthesis.



Scheme 4 The proposed mechanism.

benzimidazoles in high yields (Scheme 2, **4x-aa**). To expand the scope of this method, we attempted to synthesize poly-substituted benzo-1,2-quinone derivative with heterocycle.⁴¹ The synthetic benzo-1,2-quinone derivative derived from morpholine worked quite well and yielded benzimidazoles in good yields (Scheme 2, **4ab-ad**). The desired product **4ae** was also successfully prepared from other benzo-1,2-quinones. Remarkably, acetaldehyde as an aliphatic substrate led to the synthesis of benzimidazole **4af** in 70% yield.

To demonstrate the efficiency of the synthesis, we performed a large-scale reaction producing compound **4a** in 90% yield (Scheme 3).

A plausible reaction mechanism for the Fe(III)-porphyrin-catalyzed formation of the benzimidazoles from benzo-1,2-quinone, ammonium acetate, and aldehydes is shown in Scheme 4.

Coordination of the carbonyl group of benzo-1,2-quinone (**I**) with the Lewis acid site of Fe(III) porphyrin leads to its activation. It now reacts with ammonium acetate to form the imine intermediate (**III**).^{42,43} At the same time, aldehyde can react with an excess of ammonium acetate to form a Schiff base **IV**.⁴⁴⁻⁴⁸ Schiff base **IV** is able to react with intermediate (**III**) by intermolecular cyclization to form intermediate **V**. When the intermediate **V** is formed, a dehydration process could take place to obtain the intermediate (**VI**). Finally, the desired benzimidazole is generated by [1,5]-*H* shift (**VI**) and the Fe(III) porphyrin catalyst is regenerated to start the next cycle.^{2,49}

Conclusions

In summary, we have demonstrated an efficient, novel, green and simple procedure for the multicomponent one-pot



synthesis of benzimidazoles in the presence of Fe(III) porphyrin complexes of benzo-1,2-quinone, NH_4OAc as nitrogen source and aldehydes. Key features of this process include mild reaction conditions, large-scale synthesis and the use of environmentally friendly organic solvents in the reaction process, providing an efficient method for the preparation of benzimidazoles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- 1 T. Meng, Y. Zou, O. Khorev, Y. Jin, H. Zhou, Y. Zhang, D. Hu, L. Ma, X. Wang and J. Shen, Simple and Efficient Copper(I)-Catalyzed Access to Three Versatile Aminocoumarin-Based Scaffolds Using Isocynoacetate, *Adv. Synth. Catal.*, 2011, **353**, 918–924.
- 2 H. Sharghi, M. Aberi and M. M. Doroodmand, A Mild, Three-Component One-Pot Synthesis of 2,4,5-Trisubstituted Imidazoles Using Mo(IV) Salen Complex in Homogeneous Catalytic System and Mo(IV) Salen Complex Nanoparticles onto Silica as a Highly Active, Efficient, and Reusable Heterogeneous Nanocatalyst, *Mol. Diversity*, 2015, **19**, 77–85.
- 3 M. A. Zolfigol, A. Khazaei, A. R. Moosavi-Zare, A. Zare, Z. Asgari, V. Khakyzadeh and A. Hasaninejad, Design of Ionic Liquid 1,3-Disulfonic Acid Imidazolium Hydrogen Sulfate as a Dual-Catalyst for the One-Pot Multi-Component Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles, *J. Ind. Eng. Chem.*, 2013, **19**, 721–726.
- 4 H. Sharghi, J. Aboonajmi and M. Aberi, One-Pot Multicomponent Reaction of Catechols, Ammonium Acetate, and Aldehydes for the Synthesis of Benzoxazole Derivatives Using the Fe(III)-Salen Complex, *J. Org. Chem.*, 2020, **85**, 6567–6577.
- 5 J. Aboonajmi, F. Panahi and H. Sharghi, One-Pot Multicomponent Coupling Reaction of Catechols, Benzyl Alcohols/Benzyl Methyl Ethers, and Ammonium Acetate toward Synthesis of Benzoxazoles, *ACS Omega*, 2021, **6**, 22395–22399.
- 6 R. Bansal, P. Soni, M. Ahirwar and A. Halve, One-Pot Multi-Component Synthesis of Some Pharmacologically Significant 2,4,5-Tri and 1,2,4,5-Tetrasubstituted Imidazoles: A Review, *Int. Res. J. Pure Appl. Chem.*, 2016, **11**, 1–26.
- 7 A. Nakhaei and A. Davoodnia, Application of a Keplerate Type Giant Nanoporous Isopolyoxomolybdate as a Reusable Catalyst for the Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles, *Chin. J. Catal.*, 2014, **35**, 1761–1767.
- 8 I. Beltran-Hortelano, V. Alcolea, M. Font and S. Pérez-Silanes, The Role of Imidazole and Benzimidazole Heterocycles in Chagas Disease: A Review, *Eur. J. Med. Chem.*, 2020, **206**, 112692.
- 9 E. Niknam, F. Panahi, F. Daneshgar, F. Bahrami and A. Khalafi-Nezhad, Metal-Organic Framework MIL-101(Cr) as an Efficient Heterogeneous Catalyst for Clean Synthesis of Benzoazoles, *ACS Omega*, 2018, **3**, 17135–17144.
- 10 H. Sharghi, M. H. Beyzavi and M. M. Doroodmand, Reusable Porphyrinatoiron(III) Complex Supported on Activated Silica as an Efficient Heterogeneous Catalyst for a Facile, One-Pot, Selective Synthesis of 2-Arylbzenzimidazole Derivatives in the Presence of Atmospheric Air as a “Green” Oxidant at Ambient Temperature, *Eur. J. Org. Chem.*, 2008, **2008**, 4126–4138.
- 11 H. Kottayil, S. Machingal, S. Mole Parackal, B. S. Alungal, M. L. V. Theresa, A. Govindan and S. Krishnapillai, Development of Homogeneous Polyamine Organocatalyst for the Synthesis of 2-Aryl-Substituted Benzimidazole and Benzoxazole Derivatives, *J. Heterocycl. Chem.*, 2020, **57**, 3310–3317.
- 12 H. Sharghi, M. Aberi and M. M. Doroodmand, Reusable Cobalt(III)-Salen Complex Supported on Activated Carbon as an Efficient Heterogeneous Catalyst for Synthesis of 2-Arylbzenzimidazole Derivatives, *Adv. Synth. Catal.*, 2008, **350**, 2380–2390.
- 13 H. Sharghi, S. F. Razavi, M. Aberi, F. Tavakoli and M. Shekouhy, The Co^{2+} Complex of [7-Hydroxy-4-Methyl-8-Coumarinyl]Glycine as a Nanocatalyst for the Synthesis and Biological Evaluation of New Mannich Bases of Benzimidazoles and Benzothiazoles, *ChemistrySelect*, 2020, **5**, 2662–2671.
- 14 O. Ravi, A. Shaikh, A. Upare, K. K. Singarapu and S. R. Bathula, Benzimidazoles from Aryl Alkyl Ketones and 2-Amino Anilines by an Iodine Catalyzed Oxidative C(CO)-C(Alkyl) Bond Cleavage, *J. Org. Chem.*, 2017, **82**, 4422–4428.
- 15 S. B. Bhagat, Y. B. Sutar, Y. Manohar and V. N. Telvekar, Diphosphorus Tetraiodide (P_2I_4): An Efficient Catalyst for Synthesis of 2-Aryl-1,3-Benzazoles via Cyclocondensation of o-Amino/Mercaptan/Hydroxy Anilines with Aryl Acids, *Asian J. Chem.*, 2018, **30**, 376–380.
- 16 V. K. Tandon and M. Kumar, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ Promoted One-Pot Expeditious and Convenient Synthesis of 2-Substituted Benzimidazoles and 3,1,5-Benzoxadiazepines, *Tetrahedron Lett.*, 2004, **45**, 4185–4187.
- 17 Z. Li, J. Dong, X. Chen, Q. Li, Y. Zhou and S. F. Yin, Metal- and Oxidant-Free Synthesis of Quinazolinones from β -Ketoesters with o-Aminobenzamides via Phosphorous Acid-Catalyzed Cyclocondensation and Selective C–C Bond Cleavage, *J. Org. Chem.*, 2015, **80**, 9392–9400.
- 18 M. S. Mayo, X. Yu, X. Zhou, X. Feng, Y. Yamamoto and M. Bao, Convenient Synthesis of Benzothiazoles and Benzimidazoles through Brønsted Acid Catalyzed Cyclization of 2-Amino Thiophenols/Anilines with β -Diketones, *Org. Lett.*, 2014, **16**, 764–767.



- 19 H. Sharghi, M. Mozaffari, J. Aboonajmi, M. M. Doroodmand, P. Shiri and M. Aberi, Synergetic Effect of Iron-Doped Acidic Multi-Walled Carbon Nanotubes in the Synthesis of Diverse Substituted Five-Membered Heterocyclic Compounds, *ChemistrySelect*, 2018, **3**, 13534–13540.
- 20 G. Bastug, C. Eviolitte and I. E. Markó, Functionalized Orthoesters as Powerful Building Blocks for the Efficient Preparation of Heteroaromatic Bicycles, *Org. Lett.*, 2012, **14**, 3502–3505.
- 21 A. J. Blacker, M. M. Farah, M. I. Hall, S. P. Marsden, O. Saidi and J. M. J. Williams, Synthesis of Benzazoles by Hydrogen-Transfer Catalysis, *Org. Lett.*, 2009, **11**, 2039–2042.
- 22 R. Zhang, Y. Qin, L. Zhang and S. Luo, Oxidative Synthesis of Benzimidazoles, Quinoxalines, and Benzoxazoles from Primary Amines by Ortho-Quinone Catalysis, *Org. Lett.*, 2017, **19**, 5629–5632.
- 23 A. Dandia, D. K. Mahawar, R. Sharma, R. S. Badgoti, K. S. Rathore and V. Parewa, Graphene Oxide-Catalyzed C_{sp3}-H Activation of Methylarenes in Aqueous Medium: A Unified Metal-Free Access to Amides and Benzimidazoles, *Appl. Organomet. Chem.*, 2019, **33**(11), e5232.
- 24 E. J. Hanan, B. K. Chan, A. A. Estrada, D. G. Shore and J. P. Lyssikatos, Mild and General One-Pot Reduction and Cyclization of Aromatic and Heteroaromatic 2-Nitroamines to Bicyclic 2H-Imidazoles, *Synlett*, 2010, 2759–2764.
- 25 D. Yang, D. Fokas, J. Li, L. Yu and C. M. Baldino, A Versatile Method for the Synthesis of Benzimidazoles from O-Nitroanilines and Aldehydes in One Step *via* a Reductive Cyclization, *Synthesis*, 2005, 47–56.
- 26 T. B. Nguyen, L. Ermolenko and A. Al-Mourabit, Iron Sulfide Catalyzed Redox/Condensation Cascade Reaction between 2-Amino/Hydroxy Nitrobenzenes and Activated Methyl Groups: A Straightforward Atom Economical Approach to 2-Hetaryl-Benzimidazoles and -Benzoxazoles, *J. Am. Chem. Soc.*, 2013, **135**, 118–121.
- 27 Y. Kim, M. R. Kumar, N. Park, Y. Heo and S. Lee, Copper-Catalyzed, One-Pot, Three-Component Synthesis of Benzimidazoles by Condensation and C–N Bond Formation, *J. Org. Chem.*, 2011, **76**, 9577–9583.
- 28 B. C. Wray and J. P. Stambuli, Synthesis of N-Arylindazoles and Benzimidazoles from a Common Intermediate, *Org. Lett.*, 2010, **12**, 4576–4579.
- 29 J. Peng, M. Ye, C. Zong, F. Hu, L. Feng, X. Wang, Y. Wang and C. Chen, Copper-Catalyzed Intramolecular C–N Bond Formation: A Straightforward Synthesis of Benzimidazole Derivatives in Water, *J. Org. Chem.*, 2011, **76**, 716–719.
- 30 P. Saha, T. Ramana, N. Purkait, M. A. Ali, R. Paul and T. Punniyamurthy, Ligand-Free Copper-Catalyzed Synthesis of Substituted Benzimidazoles, 2-Aminobenzimidazoles, 2-Aminobenzothiazoles, and Benzoxazoles, *J. Org. Chem.*, 2009, **74**, 8719–8725.
- 31 J. Aboonajmi, F. Panahi, M. A. Hosseini, M. Aberi and H. Sharghi, Iodine-Catalyzed Synthesis of Benzoxazoles Using Catechols, Ammonium Acetate, and Alkenes/Alkynes/Ketones *via* C–C and C–O Bond Cleavage, *RSC Adv.*, 2022, **12**, 20968–20972.
- 32 H. Sharghi, M. Aali Hosseini, J. Aboonajmi and M. Aberi, Use of Vitamin B₁₂ as a Nontoxic and Natural Catalyst for the Synthesis of Benzoxazoles *via* Catechols and Primary Amines in Water under Aerobic Oxidation, *ACS Sustain. Chem. Eng.*, 2021, **9**, 11163–11170.
- 33 H. Srour, P. Le Maux and G. Simonneaux, Enantioselective Manganese-Porphyrin-Catalyzed Epoxidation and C–H Hydroxylation with Hydrogen Peroxide in Water/Methanol Solutions, *Inorg. Chem.*, 2012, **51**, 5850–5856.
- 34 J. C. Barona-Castaño, C. C. Carmona-Vargas, T. J. Brocksom, K. T. De Oliveira, M. Graça, P. M. S. Neves, M. Amparo and F. Faustino, Porphyrins as Catalysts in Scalable Organic Reactions, *Molecules*, 2016, **21**, 310.
- 35 M. Asaka and H. Fujii, Participation of Electron Transfer Process in Rate-Limiting Step of Aromatic Hydroxylation Reactions by Compound i Models of Heme Enzymes, *J. Am. Chem. Soc.*, 2016, **138**, 8048–8051.
- 36 R. Vyas, G. Y. Gao, J. D. Harden and X. P. Zhang, Iron(III) Porphyrin Catalyzed Aziridination of Alkenes with Bromamine-T as Nitrene Source, *Org. Lett.*, 2004, **6**, 1907–1910.
- 37 A. Ghaemi, S. Rayati, S. Zakavi and N. Safari, Highly Efficient Oxidation of Sulfides to Sulfones with Tetra-*n*-Butylammonium Hydrogen Monopersulfate Catalyzed by β -Tri- and Tetra-Brominated Meso-Tetraphenylporphyrinatomanganese(III) Acetate, *Appl. Catal., A*, 2009, **353**, 154–159.
- 38 K. Venkatasubbaiah, X. Zhu, E. Kays, K. I. Hardcastle and C. W. Jones, Co(III)-Porphyrin-Mediated Highly Regioselective Ring-Opening of Terminal Epoxides with Alcohols and Phenols, *ACS Catal.*, 2011, **1**, 489–492.
- 39 J. Aboonajmi, H. Sharghi, M. Aberi and P. Shiri, Consecutive Oxidation/Condensation/Cyclization/Aromatization Sequences Catalyzed by Nanostructured Iron(III)-Porphyrin Complex towards Benzoxazole Derivatives, *Eur. J. Org. Chem.*, 2020, **2020**, 5978–5984.
- 40 H. Sharghi, M. H. Beyzavi, A. Safavi, M. M. Doroodmand and R. Khalifeh, Immobilization of Porphyrinatocopper Nanoparticles onto Activated Multi-Walled Carbon Nanotubes and a Study of Its Catalytic Activity as an Efficient Heterogeneous Catalyst for a Click Approach to the Three-Component Synthesis of 1,2,3-Triazoles in Water, *Adv. Synth. Catal.*, 2009, **351**, 2391–2410.
- 41 Y. A. Sayapin, I. O. Tupaeva, V. V. Tkachev and G. V. Shilov, 6,6'-[Piperazine-1,4-Diylbis(Methylene)]Bis[3,5-Di(*tert*-Butyl)-1,2-Benzoquinone]: Synthesis and Properties, *Russ. J. Org. Chem.*, 2016, **52**, 214–218.
- 42 M. Baltrun, F. A. Watt, R. Schoch, C. Wölper, A. G. Neuba and S. Hohloch, A New Bis-Phenolate Mesoionic Carbene Ligand for Early Transition Metal Chemistry, *Dalton Trans.*, 2019, **48**, 14611–14625.
- 43 V. I. Lodyato, I. L. Yurkova, V. L. Sorokin, O. I. Shadyro, V. I. Dolgopalets and M. A. Kisel, Synthesis and Properties of 11-(3,5-Di-*tert*-Butyl-2-Hydroxyphenylcarbonyl) Undecanoic Acid, a New Amphiphilic Antioxidant, *Bioorg. Med. Chem. Lett.*, 2003, **13**, 1179–1182.



- 44 M. Zhou, K. Li, D. Chen, R. Xu, G. Xu, G. Xu, W. Tang, W. Tang and W. Tang, Enantioselective Reductive Coupling of Imines Templated by Chiral Diboron, *J. Am. Chem. Soc.*, 2020, **142**, 10337–10342.
- 45 L. Villar, N. V. Orlov, N. S. Kondratyev, U. Uria, J. L. Vicario and A. V. Malkov, Kinetic Resolution of Secondary Allyl Boronates and Their Application in the Synthesis of Homoallylic Amines, *Chem.–Eur. J.*, 2018, **24**, 16262–16265.
- 46 T. G. Elford and D. G. Hall, Imine Allylation Using 2-Alkoxy carbonyl Allylboronates as an Expedient Three-Component Reaction to Polysubstituted α -Exo-Methylene- γ -Lactams, *Tetrahedron Lett.*, 2008, **49**, 6995–6998.
- 47 S. Sen, S. R. Kamma, R. Gundla, U. Adepally, S. Kuncha, S. Thirunathi and U. V. Prasad, A Reagent Based DOS Strategy *via* Evans Chiral Auxiliary: Highly Stereoselective Michael Reaction towards Optically Active Quinolizidinones, Piperidinones and Pyrrolidinones, *RSC Adv.*, 2013, **3**, 2404–2411.
- 48 Y. Chen, R. Yang, F. Xiao, T. Li, G. Mao and G. J. Deng, Four-Component Synthesis of 9*H*-Pyrimido[4,5-*b*]Indoles Using Ammonium Iodide as the Nitrogen Source, *Catalysts*, 2023, **13**, 623.
- 49 N. L. Higuera, D. Peña-Solórzano and C. Ochoa-Puentes, Urea-Zinc Chloride Eutectic Mixture-Mediated One-Pot Synthesis of Imidazoles: Efficient and Ecofriendly Access to Trifenagrel, *Synlett*, 2019, **30**, 225–229.

