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Magnetically separable $MnFe_2O_4$ nano-material: an efficient and reusable heterogeneous catalyst for the synthesis of 2-substituted benzimidazoles and the extended synthesis of quinoxalines at room temperature under aerobic conditions†

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A simple and efficient protocol has been developed for the synthesis of biologically relevant 2-substituted benzimidazoles and quinoxalines using magnetically separable manganese ferrite ($MnFe_2O_4$) nanopowder for the first time as a reusable heterogeneous catalyst at room temperature under aerobic conditions. $MnFe_2O_4$ nanoparticles were prepared by a simple sol–gel method using starch as a bio-polymeric matrix, and characterized by XRD, TEM, EDAX and VSM analyses.

Introduction

Benzimidazole and quinoxaline scaffolds are widely distributed heterocyclic units in pharmaceutical and bioactive natural products. Benzimidazole-privileged scaffolds exhibit versatile pharmacological properties and thus find useful clinical applications.[1] Compounds bearing diverse substituents in the benzimidazole motif are associated with a wide range of biological activities.[2] The benzimidazole unit is found to be present in many marketed drugs (Fig. 1)[3–6] being used in different therapeutic areas, and remarkably effective both with respect to their corresponding inhibitory activity and favorable selectivity ratio.[7,8] Compounds bearing diverse substituents in the benzimidazole motif are associated with a wide range of biological activities that include antiulcer, antiviral, antifungal, anticancer, antimalarial, antihistaminic, anti-helmintic, anti-oxidant and many more.[8] In addition, benzimidazoles have recently been used in the treatment of diseases such as ischemia-reperfusion injury,[9] hypertension,[10] and obesity.[11] Quinoxaline, another *N*-heterocyclic scaffold, is well-known for being a key structural motif in many biocides,[12a] pharmaceuticals[12b] and various bio-functional molecules.[12c] Besides, quinoxalines find useful applications in the field of organic semiconductor materials[13] and organic synthons.[14]

Such promising pharmacological properties of benzimidazole and quinoxaline scaffolds have motivated synthetic chemists to synthesize them, and as a result of which a plenty of synthetic methods are currently available for both of the *N*-heterocycles.[15–20] However, one-pot synthesis of 2-substituted benzimidazoles starting from *o*-phenylenediamines and aldehydes using a condensation-aromatization strategy under oxidative conditions have recently attained considerable interest; various oxidative and catalytic reagents, both homo- and heterogeneous, are already reported for the synthesis of such important moiety.[21–62] Although these methods have certain merits, still most of them are associated with notable shortcomings such as usage of stoichiometric amounts of catalysts, harsh reaction conditions, high temperature, costly catalysts, operational difficulty, and strong oxidizing nature of the reagents. In addition, a major concern in the reaction between *o*-phenylenediamine and an aldehyde is to attain 2-substituted benzimidazole selectively; in most of the cases, a mixture of products including 1,2-disubstituted benzimidazoles is also obtained. Very few methods are concerned with the

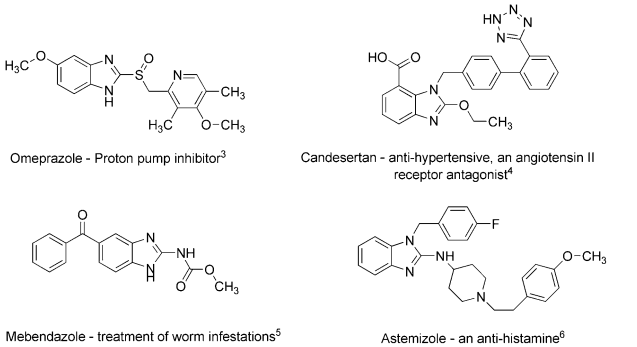

Fig. 1 Some of the marketed approved drugs bearing benzimidazole scaffolds.[3–6]

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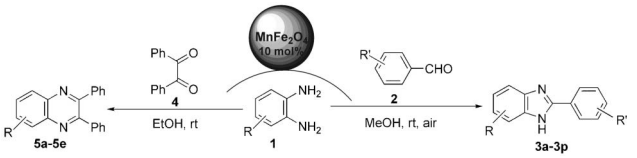
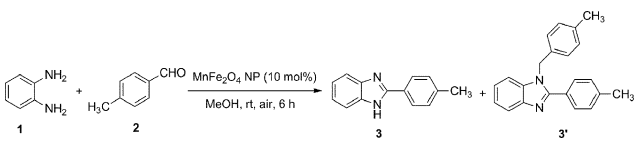
† Electronic supplementary information (ESI) available: General methods including preparation, characterization and magnetic evaluation of $MnFe_2O_4$ nano-material are described in detail in the ESI. See DOI: 10.1039/c3ra41457d



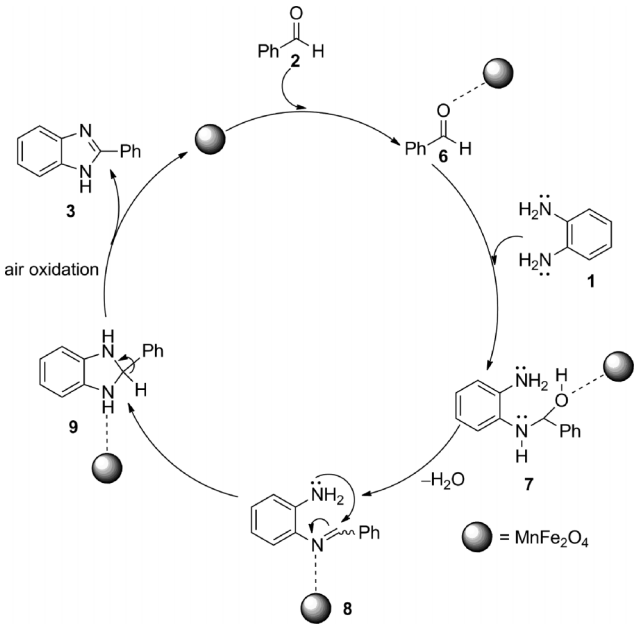
Scheme 1 Synthesis of benzimidazoles (**3a–p**) and quinoxalines (**5a–e**).

selective formation of 2-substituted benzimidazoles at room temperature.[21f,53,60,61] Looking at the importance of both benzimidazole and quinoxaline motifs, there is still an essential need for the development of mild and recyclable, cost-effective and eco-friendly heterogeneous catalysts for the facile and efficient synthesis of such significant biologically relevant *N*-heterocycles at room temperature.

Very recently, development of recyclable heterogeneous catalysts based on magnetic nanoparticles has invoked tremendous interest among synthetic chemists due to their emerging applications in organic synthesis coupled with their effective catalytic performance under mild reaction conditions and easy re-cyclization.[63–67] Manganese ferrite ($MnFe_2O_4$) is one of the most important spinel ferrite magnetic oxides where oxygen has fcc close packing and Mn^{2+} and Fe^{3+} ions can occupy either tetrahedral (A) or octahedral (B) interstitial sites.[68] Due to its good magnetic characteristics coupled with simple preparative methods,[69–75] it finds immense applications in various technological fields;[75–79] hence, synthesis of this spinel ferrite from readily available non-toxic starting materials using bio-polymeric matrix as a green template is of interest in material industry as well. To the best of our knowledge, still there is no report on the direct application of manganese ferrite ($MnFe_2O_4$) as catalyst in organic synthesis. In continuation of our efforts to develop green synthetic methodologies for organic transformations,[80] we herein wish to report for the first time on the development of a facile and efficient synthesis of 2-substituted benzimidazoles and quinoxalines at room temperature under aerobic conditions using manganese ferrite as a magnetically reusable catalyst (Scheme 1). $MnFe_2O_4$ has been prepared with a very low-cost green method using starch as a bio-polymeric matrix. The present method is not only selective to 2-substituted benzimidazoles, but also is experimentally safe and simple, clean and efficient, environmentally benign, and robust as a whole. The results are summarized in Schemes 1–3 and Tables 1–3.



Scheme 2 $MnFe_2O_4$ NP-catalyzed selective synthesis of 2-substituted benzimidazole (**3**) at room temperature under open air.



Scheme 3 Proposed mechanism for the catalytic synthesis of benzimidazoles.

Results and discussion

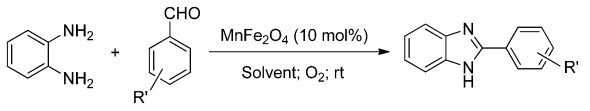
We prepared a magnetically separable catalyst of manganese ferrite ($MnFe_2O_4$) nano-materials by a simple sol–gel method from

Table 1 Optimization of reaction conditions for the synthesis of 2-substituted benzimidazole[a]

Entry	Catalyst	Solvent	Time (h)	%Yield[b]
1	TBATB	EtOH	24	51
2	$CuCl_2$	EtOH	24	50
3	Cu dust	EtOH	24	52
4	CuBr	EtOH	24	54
5	SiO_2–$HClO_4$	EtOH	24	trace
6	ZnO NP	EtOH	24	59
7	ZnO NP	CH_3CN	24	63
8	$NiCl_2$	EtOH	24	49
9	Fe_3O_4 NP	CH_3CN	24	70
10	$CuFe_2O_4$ NP	EtOH	24	59
11	$MnFe_2O_4$ NP	EtOH	24	83
12	$MnFe_2O_4$ NP	CH_3CN	24	91
14	$MnFe_2O_4$ NP	Toluene	24	52
15	$MnFe_2O_4$ NP	THF	24	53
16	$MnFe_2O_4$ NP	DCM	24	48
17	$MnFe_2O_4$ NP	DMF	24	50
18	$MnFe_2O_4$ NP	H_2O	24	trace
19	No catalyst	MeOH	24	31
20	**$MnFe_2O_4$ NP**	**MeOH**	**4**	**92**
21[c]	$MnFe_2O_4$ NP	MeOH	24	trace

[a] Catalyst (10 mol%), *o*-phenylenediamine (1 mmol), benzaldehyde (1 mmol), solvent (3–5 mL), rt, in the presence of air. [b] Isolated yield. [c] Under nitrogen atmosphere.

Table 2 The influence of oxygen on the condensation reaction of *o*-phenylenediamine and benzaldehyde catalyzed by $MnFe_2O_4$ nanopowder[a]



Entry	Aldehyde	Solvent	Time (h)	Yield (%)[b]
1	Benzaldehyde	MeOH	1.33	91
		CH_3CN	4.0	89
2	4-Methylbenzaldehyde	MeOH	1.75	93
		CH_3CN	4.0	87
3	4-Fluorobenzaldehyde	MeOH	1.33	92
		CH_3CN	4.0	90
4	4-Chlorobenzaldehyde	MeOH	1.5	85
		CH3CN	4.0	83
5[c]	4-Fluorobenzaldehyde	MeOH	4.5	41
		CH_3CN	4.5	36

[a] $MnFe_2O_4$ nano-catalyst (10 mol%), *o*-phenylenediamine (1 mmol), aldehyde (1 mmol), MeOH/CH_3CN (3–5 mL), rt, in the presence of O_2 atmosphere. [b] Isolated yield. [c] Without catalyst.

the reaction between $FeCl_3{\cdot}6H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$ in a stoichiometric ratio of 2 : 1 using starch as a cost-effective and green biopolymeric matrix; the modified methodology is discussed in detail in the experimental and ESI.† Characterization and magnetic measurement of the catalyst prepared by this method was evaluated by XRD, TEM, EDAX and VSM (Fig. 2 and 3; ESI†). All the diffraction peaks of the XRD pattern can readily be indexed to face-centred cubic phase [space group *Fd3m*(227)] of spinel $MnFe_2O_4$ [JCPDS 00-073-1964] as shown in Fig. 2. The particle size as obtained from XRD is ~50 nm. The TEM image (Fig. 3a) indicates the average size of the nanocrystals in the range of 50–100 nm. The matrix of the EDAX shows strong Mn, Fe and O peaks. No trace of other element is evident. The molar ratios of Mn : Fe : O is 1 : 1.75 : 3.27. This is almost in accordance with the theory formula of $MnFe_2O_4$. The coercive fields (H_c) and saturation magnetizations (M_s) were calculated from the curves (ESI†). The $MnFe_2O_4$ nanoparticles possess saturation magnetization of 30.03 emu g^{-1} and coercivity of 168 (−193) G.

To optimize the reaction conditions, we initially attempted the synthesis of 2-phenylbenzimidazole (**3a**) from the reaction of *o*-phenylenediamine (**1**; 1 mmol) and benzaldehyde (**2**; 1 mmol) in the presence of various catalysts and solvents as summarized in Table 1. It was revealed that solvent plays a crucial role in this reaction. From the experimental results (Table 1), use of 10 mol% $MnFe_2O_4$ appeared to be the most facile and efficient catalyst in the series for the synthesis of 2-phenylbenzimidazole (**3a**) under open air at room temperature in methanol. Reactions with supermagnetic Fe_3O_4@NP and $CuFe_2O_4$@NP were observed to furnish just moderate yields of **3a** of 70% and 59%, respectively (entries 9 and 10; Table 1). The catalyst-free reaction provided only 28% yield of **3a** in methanol under open air (entry 19; Table 1). Control experiment using 10 mol% $MnFe_2O_4$ under nitrogen atmosphere (in the absence of open air) was found not to proceed much, giving a very low yield of 2-phenylbenzimidazole at 24 h under the optimized conditions. Thus the presence of oxygen appeared to be mandatory for carrying out the transformation. A detailed mechanistic study on oxygen-catalyzed coupling for this reaction was reported earlier by Smith and Ho.[81]

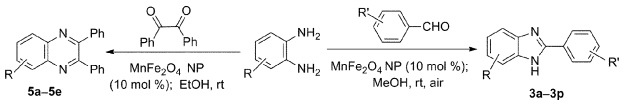
Then we checked the activity of the catalyst in the presence of oxygen atmosphere. For this purpose, 1 mmol of *o*-phenylenediamine was reacted with 1 mmol of benzaldehyde in the presence of 10 mol% of $MnFe_2O_4$ at room temperature under oxygen atmosphere using both methanol and acetonitrile as solvents. The result showed that reaction under oxygen atmosphere (balloon) underwent at a faster rate and was completed within 1.33–1.75 h and 4–4.5 h, respectively, affording almost similar yield of the product **3a** (entry 1; Table 2). To generalize the observation, we carried out few more reactions with varying benzaldehydes; in all the cases the reaction proceeded at faster rate under oxygen atmosphere giving similar kind of yields. The results were summarized in Table 2. Hence, it appeared clearly that the present catalyst $MnFe_2O_4$ nano-materials can efficiently use up aerial oxygen for effecting the transformation.

It is worthy to mention that the present method showed excellent selectivity in furnishing 2-substituted benzimidazole (**3**) even when the reaction was carried out with 1 equiv. of *o*-phenylenediamine (**1**) and 2 equiv. of 4-methylbenzaldehyde (**2**) using $MnFe_2O_4$ (10 mol%) in methanol under open air in 90% yield at 6 h along with a trace amount of **3′** (Scheme 2). Such selectivity is seldom observed in literature;[21f] in most of the cases 1,2-disubstituted benzimidazole (**3′**) was found to be the major product under Lewis acidic conditions.

Encouraged by the above results, we examined the applications and scope of our method with varying diamines and aldehydes. By using methanol as solvent at room temperature, 2-substituted benzimidazoles with various functional groups were obtained in excellent yields (Table 3, entries 1–16) under $MnFe_2O_4$ NP-catalysis in open air. The aromatic aldehydes containing both electron-donating and electron-withdrawing groups such as F, Cl, Br, CN, OH, OMe, tri-OMe, Me underwent the reaction smoothly affording the corresponding 2-substituted benzimidazoles (**3a–n**) in 59–94% yields within reasonable time frames (4–20 h) at room temperature. It is also noteworthy that the bulky anthracene-9-carboxylaldehyde substrate underwent smooth reaction to afford the corresponding 2-substituted benzimidazole derivative (**3m**) in good yield (63%) following this protocol (Table 3, entry 13). The aliphatic aldehyde, butyraldehyde was also found to take part in the reaction (Table 3, entry 15, 16). To our delight, the present methodology is further extended for the synthesis of quinoxaline derivatives (**5a–e**) in ethanolic medium with good yields (Table 3, entries 17–21). The results are summarized in Table 3.

We herein propose a plausible mechanism (Scheme 3) for the facile formation of 2-substituted benzimidazoles (**3**) under the reaction conditions where $MnFe_2O_4$ acts as a bifunctional-like Lewis acid as well as an oxidative agent. It is supposed that the reaction proceeds *via* activation of aldehyde (**2**) by $MnFe_2O_4$ followed by condensation with diamine (**1**) leading to the formation of imine derivative (**8**) stabilized by $MnFe_2O_4$. The resulting imine eventually undergoes ring closure by the intramolecular attack of second amino group on C=N double bond (**8**) to give hydrobenzimidazole (**9**) that subsequently

Table 3 $MnFe_2O_4$ nano-catalyzed synthesis of 2-substituted benzimidazoles (**3a–p**)[a] and quinoxalines (**5a–e**)[b] at room temperature[c]



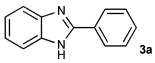
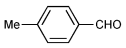
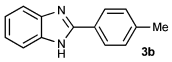
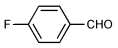
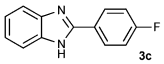
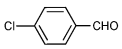
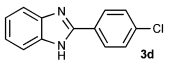
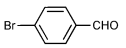
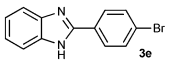
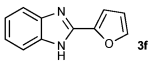
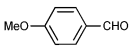
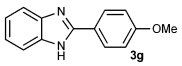
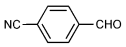
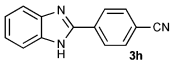
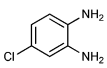
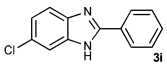
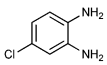
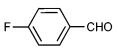
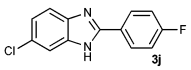
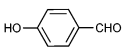
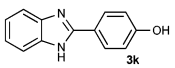
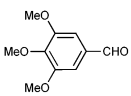
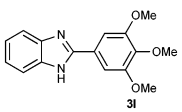
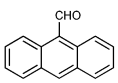
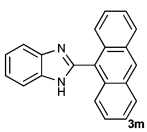
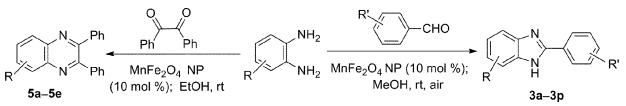
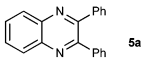
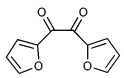
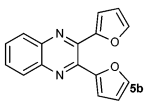
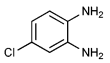
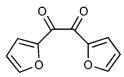
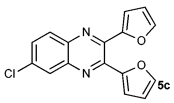
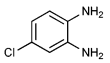
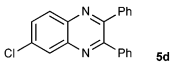
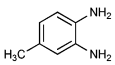
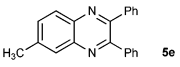
Entry	Diamine	Carbonyl Compound	Time (h)	Product	Yield (%)
1			4	 **3a**	92
2			6	 **3b**	94
3			4	 **3c**	94
4			5	 **3d**	87
5			7	 **3e**	88
6			20	 **3f**	59
7			5	 **3g**	82
8			20	 **3h**	67
9			15	 **3i**	76
10			15	 **3j**	75
11			4	 **3k**	87
12			5	 **3l**	91
13			18	 **3m**	63
14			6	**3n**	85
15			20	**3o**	62
16			15	**3p**	65

Table 3 (*Continued*)



Entry	Diamine	Carbonyl Compound	Time (h)	Product	Yield (%)
17			2.5	 5a	91
18			2.5	 5b	83
19			2.5	 5c	81
20			2.5	 5d	80
21			2.5	 5e	70

[a] aldehyde (1 mmol), diamine (1 mmol), $MnFe_2O_4$ NP (10 mol%), MeOH (3–5 mL), air, rt. [b] diketone (1 mmol), diamine (1 mmol), $MnFe_2O_4$ NP (10 mol%), EtOH (3 mL), air, rt for 2.5 h. [c] Isolated yield.

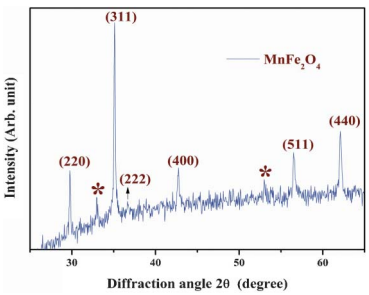


Fig. 2 X-ray diffraction patterns of the $MnFe_2O_4$ nanoparticles.

undergoes aromatization by aerial oxidation under the reaction conditions to afford the desired 2-substituted benzimidazole (**3**). The proposed mechanism is supported by the control experiment under nitrogen atmosphere which leads to a trace of final product.

Another major advantage of the protocol is simple recovery and easy reusability of the heterogeneous catalyst. Upon completion of the reactions, the catalyst was recovered from the reaction mixture simply by applying a strong external permanent magnet (as shown in Fig. 5) followed by washing with ethanol/acetone and dried at 100 °C for 2 h. The recovered $MnFe_2O_4$ was reused successfully in subsequent reactions without significant loss of catalytic performance as illustrated in Fig. 4. We also examined the feasibility of the present method for a somewhat scaled-up (on the gram scale) experiment with 1,2-phenylenediamine (1.08 g; 10 mmol) and

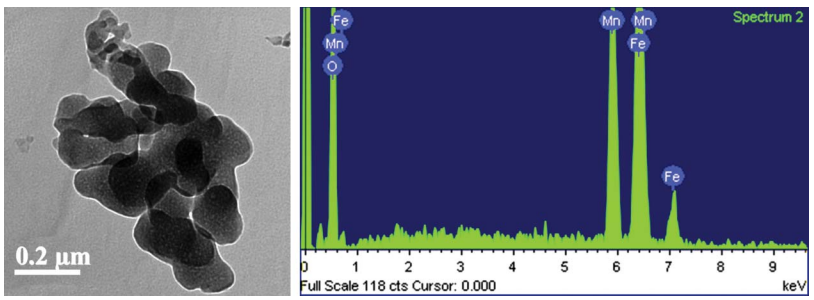


Fig. 3 (a) Bright field Transmission Electron Micrographs and (b) EDAX obtained by HRTEM of $MnFe_2O_4$ nanoparticles.

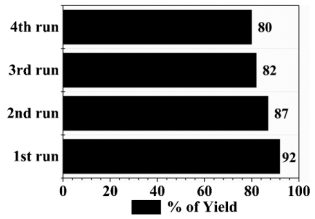


Fig. 4 Recyclability chart.

Fig. 5 Magnetic separation of $MnFe_2O_4$ nano-materials by an external magnet.

4-methylbenzaldehyde (1.2 g; 10 mmol) using 10 mol% of $MnFe_2O_4$ nano-catalyst at room temperature in methanol; the reaction was found to proceed smoothly affording the desired product, 2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole (**3b**) 90% yield within 6 h, almost similarly in all respects with 1 mmol scale entry (Table 3, entry 2). This experiment demonstrated the efficiency of the catalyst for large scale production as well.

Experimental

General methods and instrumentations are described in the ESI.†

Preparation of $MnFe_2O_4$ catalyst

$MnFe_2O_4$ nanoparticles were prepared by a simple sol–gel method. $FeCl_3{\cdot}6H_2O$ (6 mmol) and $Mn(CH_3COO)_2{\cdot}4H_2O$ (3 mmol) were used in a stoichiometric ratio of 2 : 1. A homogeneous aqueous solution of starch was prepared by stirring for 30 min at 90 °C. $Mn(CH_3COO)_2{\cdot}4H_2O$ was then added to the starch solution under N_2 atmosphere on vigorous stirring. Subsequently, $FeCl_3{\cdot}6H_2O$ was added to the solution; the reaction temperature was kept between 90–100 °C in an oil bath for 2 h. After then aqueous ammonium hydroxide was added into the reaction mixture to maintain the pH of 13–14, and the resulting solution was magnetically stirred for another 2 h. On completion of the reaction, the flask was allowed to cool down to room temperature. The black precipitate obtained was washed with deionised water and then dried at 100 °C for 12 h. The dried black-powder was then placed into clean alumina crucibles and annealed in the presence of air at a temperature of 900 °C for 4 h to get rid of the excess carbon and the unreacted organic residues and also to obtain a pure $MnFe_2O_4$ phase (yield 90% based on the calculation of $FeCl_3{\cdot}6H_2O$). Characterization and magnetic measurement of the prepared catalyst was evaluated by XRD, TEM, EDAX and VSM analyses (ESI†).

Representative experimental procedure for the synthesis of 2-substituted benzimidazoles and quinoxalines

Synthesis of 2-(4-fluorophenyl)-1*H*-benzimidazole (3c). In a typical reaction, 4-fluorobenzaldehyde (124 mg; 1 mmol) and *o*-phenylenediamine (108 mg; 1 mmol) were dissolved in 3–5 mL of MeOH in a 10 mL reaction tube. To this solution, $MnFe_2O_4$ (23 mg; 10 mol%) was added and stirred vigorously for 24 h at room temperature under open atmosphere with the aid of an external bar magnet. The progress of the reaction was monitored by TLC. After the completion of reaction, the solvent was evaporated and the reaction mixture was extracted with dichloromethane/ethyl acetate (3 × 10 mL) for 7–10 h and allowed the mixture to settle the catalyst which was then separated by the simple application of a strong external magnet. The organic extract was dried in sodium sulphate and the product was finally obtained after chromatographic purification. The product was characterized by elemental analyses and spectral studies including FT-IR, ^{1}H-NMR, and ^{13}C-NMR data. These data for the known entries are in good agreement with those reported in literature.[21*fg*,53,60] The residual catalyst was further washed with ethanol followed by acetone, dried under vacuum at 100 °C and reused.

Characterization data for new entries

4-(1*H*-Benzo[*d*]imidazol-2-yl)benzonitrile (3h). Creamy white solid, m.p.: 235–236 °C; IR (KBr): ν_{max} = 3045, 2228, 1608, 1517, 1493, 1441, 1277, 966, 840, 746, 573 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 13.19 (1H, s, NH), 8.34 (2H, d, J = 8.4 Hz, Ar–H), 8.0 (2H, d, J = 8 Hz, Ar–H), 7.71–7.59 (2H, m, Ar–H), 7.26 (2H, br s, Ar–H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 149.83, 134.72, 133.39, 127.43, 123.80, 122.68, 119.82, 119.07, 112.33, 112.15. Anal. Calcd. for $C_{14}H_9N_3$: C, 76.70; H, 4.14; N, 19.17; Found: C, 76.72; H, 4.13; N, 19.15.

6-Chloro-2-phenyl-1*H*-benzo[*d*]imidazole (3i). Off-white solid, m.p.: 184 °C; IR (KBr): ν_{max} = 3068, 3042, 1616, 1568, 1510, 1441, 1223, 964, 839, 700, 571 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 13.12 (very weak, br s, NH), 8.18 (2H, dd, J = 7.6 Hz & 1.2 Hz, Ar–H), 7.66 (1H, br s, Ar–H), 7.62–7.49 (4H, m, Ar–H), 7.23 (1H, dd, J = 8.4 Hz, 2.4 Hz, 2 Hz, Ar–H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 153.10, 130.16, 130.15, 129.46, 127.05, 126.89, 122.83. Anal. Calcd. for $C_{13}H_9ClN_2$: C, 68.28; H, 3.97; N, 12.25; Found: C, 68.26; H, 3.98; N, 12.28.

6-Chloro-2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (3j). Off-white solid, m.p.: 204–206 °C; IR (KBr): ν_{max} = 3082, 3040, 1609, 1534, 1491, 1234, 962, 839, 808, 571, 504 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 13.12 (bs, s, NH), 8.22(2H, dd, J = 8.4 Hz & 5.6 Hz, Ar–H), 7.76–7.66 (2H, m, Ar–H), 7.40 (2H, t, J = 8.4 Hz & 7.6 Hz, Ar–H), 7.22 (1H, d, J = 7.2 Hz, Ar–H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 164.90, 162.43, 152.32, 145.10, 134.25, 129.36, 126.75, 122.98, 120.43, 118.64, 116.57, 113.01, 111.44; Anal. Calcd. for $C_{13}H_8ClFN_2$: C, 63.30; H, 3.27; N, 11.36; Found: C, 63.29; H, 3.29; N, 11.39.

2-(2-Chlorophenyl)-1*H*-benzo[*d*]imidazole (3n). Off-white solid, m.p.: 179–182 °C; IR (KBr): ν_{max} = 3051, 3005, 1625, 1568, 1433, 1272, 973, 854, 565 cm^{-1};^{1}H-NMR (400 MHz, DMSO-d_6): δ = 12.76 (br, s, NH), 7.92 (1H, dd, J = 7 Hz, 2.4 Hz & 2 Hz, Ar–H), 7.71–

7.60 (3H, m, Ar–H), 7.57–7.5 (2H, m, Ar–H), 7.26–7.24 (2H, m, Ar–H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 149.52, 132.50, 132.06, 131.61, 130.76, 130.39, 127.85, 127.58, 122.70, 120.03; Anal. Calcd. for $C_{13}H_9ClN_2$: C, 68.28; H, 3.97; N, 12.25; Found: C, 68.26; H, 3.95; N, 12.29.

6-Chloro-2-propyl-1*H*-benzo[*d*]imidazole (3p). White amorphous powder; IR (KBr): ν_{max} = 3003, 2922, 1612, 1544, 1528, 1450, 1035, 746, 513 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 12.39 (br, s, NH), 7.52–7.47 (2H, m, Ar–H), 7.12 (1H, d, J = 8 Hz, Ar–H), 2.78 (2H, t, J = 7.6, 7.2 Hz, –CH_2–), 1.82–1.79 (2H, q, J = 7.2, 5.2 Hz, –CH_2–), 1.17 (3H, t, J = 7.2 Hz, –CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 170.72, 157.03, 125.85, 121.62, 117.83, 112.39, 30.85, 21.24, 14.44. Anal. Calcd. for $C_{10}H_{11}ClN_2$: C, 61.70; H, 5.70; N, 14.39; Found: C, 61.73; H, 5.71; N, 14.36.

Synthesis of 2,3-diphenylquinoxaline (5a). In a typical procedure, benzil (1 mmol), 1,2-phenylenediamines (1 mmol), and the catalyst $MnFe_2O_4$ (10 mol%) were placed in a 10 mL glass tube previously charged with a external bar magnet containing 3 mL aqueous ethanol. The reaction mixture was stirred for 2.5 h vigorously. The progress of the reaction was monitored by TLC. The mixture was allowed to settle the catalyst which was then removed by the application of a simple magnetic environment; the resulting reaction mixture was extracted with dichloromethane/ethyl acetate (3 × 10 mL). The extract was dried in sodium sulphate and the product was finally obtained after chromatographic purification. The product was characterized by elemental analyses and spectral studies including FT-IR, ^{1}H-NMR, ^{13}C-NMR data. These data for the known entries are in good agreement with those reported in literature.[20]

Characterization data for new entries

2,3-Di(furan-2-yl)quinoxaline (5b). IR (KBr): Pale yellow solid, m.p. 135 °C; ν_{max} = 3109, 1622, 1570, 1485, 1329, 1225, 1150, 1067, 1007, 760, 663 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.36 (2H, d, J = 7.5 Hz, Ar–H), 8.52 (2H, d, J = 7.5 Hz, Ar–H), 8.30 (2H, dd, J = 6 Hz & 3 Hz, Ar–H), 7.84 (2H, dd, J = 6 Hz & 3.9 Hz, 3.6 Hz, Ar–H), 7.79–7.69 (2H, m, Ar–H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 142.41, 142.15, 132.02, 130.28, 129.75, 129.44, 127.92, 126.24, 122.90. Anal. Calcd. for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68; Found: C, 73.29; H, 3.81; N, 10.67.

6-Chloro-2,3-di(furan-2-yl)quinoxaline (5c). Dark brownish solid, m.p. 120–125 °C; IR (KBr): ν_{max} = 3119, 2959, 1628, 1599, 1507, 1072, 750, 594 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.24–7.67 (6H, m, Ar–H), 6.71 (3H, br s, Ar–H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 151.31, 150.46, 150.38, 145.69, 145.51, 143.12, 142.55, 140.58, 138.90, 135.45, 131.62, 130.79, 127.68, 113.98, 113.68, 112.64. Anal. Calcd. for $C_{16}H_9ClN_2O_2$: C, 64.77; H, 3.06; N, 9.44; Found: C, 64.72; H, 3.09; N, 9.43.

Conclusions

In conclusion, we have developed an energy-efficient green procedure for the facile synthesis of selectively 2-substituted benzimidazoles at room temperature from the reaction between *ortho*-phenylenediamines and aldehydes on the surface of a magnetically separable and reusable heterogeneous $MnFe_2O_4$ nano-catalyst under aerobic conditions in methanol. The present protocol offers an easy access for a wide spectrum of diverse 2-substituted benzimidazoles. The catalytic system could also be extended successfully for the synthesis of quinoxaline derivatives. The significant features of this newly developed eco-friendly green procedure are easy separation of the heterogeneous catalyst from reaction mixture, just by the application of an external magnet, and its reusability, operational simplicity, room temperature condition, energy-efficiency, clean reaction profiles, high selectivity and good yields.

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