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Abstract

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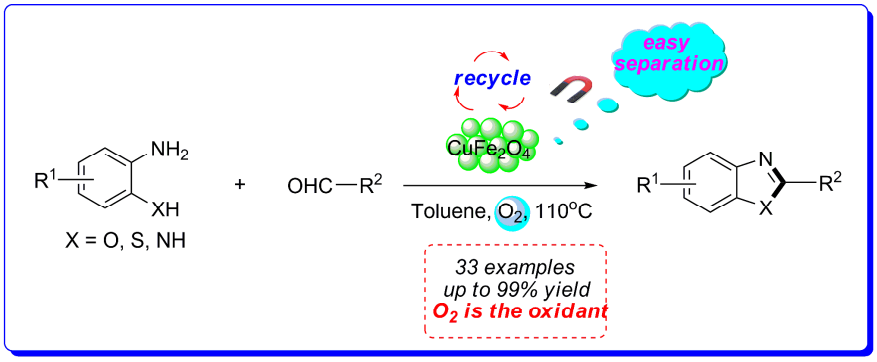

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ARTICLE TYPE

Magnetically recoverable and reusable $CuFe_2O_4$ nanoparticles-catalyzed synthesis of benzoxazoles, benzothiazoles and benzimidazoles using dioxygen as oxidant

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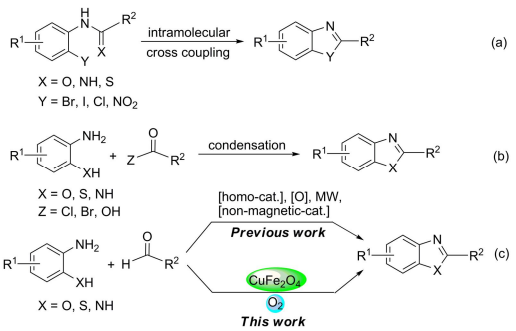
A green and efficient strategy for the synthesis of benzoxazoles, benzothiazoles and benzimidazoles has been developed by using inexpensive, readily available, dioxygen-stable and recyclable $CuFe_2O_4$ as the nanocatalyst, and *o*-substituted aminobenzene and various aldehydes as the starting materials. The $CuFe_2O_4$ nanoparticles is dioxygen insensitive and easily recoverable with an external magnet from the reaction medium. The catalyst can be reused ten times without significant loss of catalytic activity.

Introduction

N-Heterocycles widely occur in nature products, biologically active molecules and organic materials, especially they play an important role in the design and discovery of new drugs. Therefore, the development of novel, efficient and practical methods for heterocycles synthesis is an important goal in modern organic synthesis. Benzoxazoles, benzothiazoles and benzimidazoles are now known to have a wide range of useful biological and medicinal properties, such as polymers [1], enzyme inhibitors [2], antibacterial [3], anticancer agents [4], antimicrobial [5], anti-inflammatory [6], antiparkinson [7], antioxidants [8], and antiallergy activities [9], so their synthesis is attracting much attention. Consequently, a lot of significant methods for the synthesis of these important building blocks have been developed. The conventional methods for the synthesis of these important compounds typically involve two approaches. One is the metal-catalyzed intramolecular condensation of *o*-haloanilides or their analogues (Scheme 1, a) [10]. The second approach mainly involves the coupling of *o*-substituted aminoaromatics with carboxylic acids or acyl halides (Scheme 1, b) [11]. Despite these methods have made various successes, the uneasily available precursors and undesired by-products limit their wide applications. Therefore, a more effective process is needed.

Aldehydes are important and common building blocks, and they are easily prepared from readily available materials. Using *o*-substituted aminoaromatics and aldehyde as the starting materials to construct these heterocycles have caught considerable attention (Scheme 1, c). In this regard, several examples of aerobic oxidation pathways have been reported with various transition metal salts or oxidants, such as $ZrOCl_2{\cdot}8H_2O$ [12], $Pd(OAc)_2/O_2$ [13], $CuCl_2$ [14], $Sc(OTf)_3$ [15], $Yb(OTf)_3$ [16], $FeCl_3{\cdot}6H_2O$ [17], $HAuCl_4{\cdot}4H_2O/O_2$ [18], DDQ [19], $PhI(OAc)_2$ [20], H_2O_2-HCl [21], TEMPO [22], activated carbon [23] and cyanide [24]. However, in some cases, most of these methods might suffer from some drawbacks such as undesirable stoichiometric oxidants, noble transition metal catalyst, long reaction times, toxic reaction reagents, and residual metal catalysts in the end products, which should still impede their applications for the heterocycle synthesis on a large scale.



Scheme 1 Strategies for the synthesis of benzoxazoles, benzothiazoles and benzimidazoles.

In recent years, heterogeneous catalysts have attracted much attention in organic transformations due to their interesting reactivity as well as for economic and environmental reasons. A large number of recyclable supported catalytic systems have been developed (Scheme 1, c) [25-27]. For example, Satyanarayana's group reported an efficient method for the synthesis of

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benzoxazoles using silica-supported sodium hydrogen sulphate [25]. Recently, Kidwai and co-workers reported an efficient CuO nanoparticles catalyzed coupling aromatic or heteroaromatic aldehydes with 2-aminophenol to construct benzoxazoles in the presence of K_2CO_3 in MeOH. [26]. Gracefully excellent as these works could be, the small size of catalyst particles might often make their separation and recyclization difficult, especially the catalysis efficiency of the recovered catalysts might be somewhat reduced through a filtration step.

Recently, magnetic nanoparticles (MNPs) have been extensively used in organic transformations owing to their easy preparation, large surface area ratio, low toxicity, high dispersion property in organic solvents, facile separation by using an external magnetic force and without the need for filtration step [28]. Very recently, Brahmachari *et al*. reported an elegant work for the synthesis of 2-substituted benzimidazoles and quinoxalines using $MnFe_2O_4$ as a heterogeneous catalyst [29]. However, challenges still remain, magnetic-nanoparticles catalyzed direct coupling of 2-aminophenol or 2-aminobenzenethiol with aldehyde has not been reported to date. Additionally, we couldn't get benzoxazoles and benzothiazoles under the standard conditions reported by lit.[28]. We therefore set out to look for an improved catalyst system for this transformation and to demonstrate the generality with which it can be employed. Recently, for economical and environmental reasons, there is an increasing demand for the use of dioxygen as an oxidant for many oxidation reactions, because water is the only waste when dioxygen is used as oxidant. Inspired by the utilization of magnetically separable $CuFe_2O_4$ nanoparticles as a powerful and excellent catalyst for many organic transformations[30]. Herein, we report a simple, practical and efficient method for the synthesis of substituted benzoxazoles, benzothiazoles and benzimidazoles by using the cheap, dioxygen-stable $CuFe_2O_4$ nanoparticles as a magnetically recoverable catalyst and O_2 as a green oxidant.

Results and Discussion

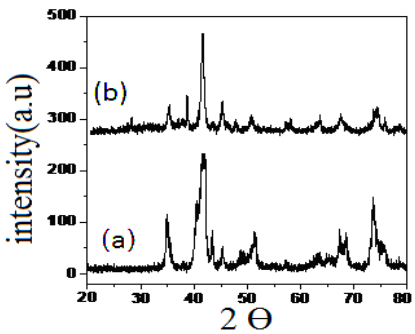


Figure 1 (a) XRD spectrum of native $CuFe_2O_4$ catalyst. (b) XRD spectrum of reused $CuFe_2O_4$ catalyst after 3th cycle.

The $CuFe_2O_4$ nanoparticles were synthesis by reaction of Cu^{2+} ions and Fe^{3+} in alkaline condition according to the literature procedure[31] and characterized by X-ray diffraction (Fig. 1), TEM spectrum (Fig. 2) and EDX spectrum (Fig. 1, ESI†). The diffraction patterns of all the peaks are in agreement with the standard XRD pattern (JCPDS34-0425). The XRD pattern of the $CuFe_2O_4$ nanoparticles before reaction (Fig. 1, a) and after reaction in the 3th cycle (Fig. 1, b) showed that the Cu remains in the +2 oxidation state. Additionally, the TEM and SEM images analysis of the recovered nano $CuFe_2O_4$ particles revealed that the morphology of the catalyst remains unchanged, even after three cycles under dixoygen atomshpere (Fig. 2 and Fig. 3).

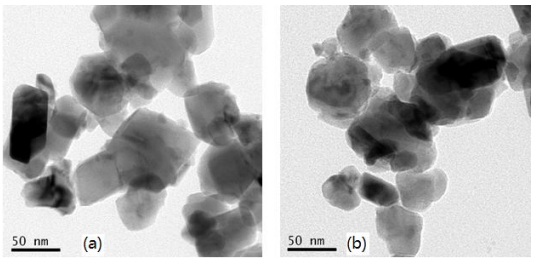


Figure 2. (a) TEM image of the fresh $CuFe_2O_4$ nanoparticles. (b) TEM image of the $CuFe_2O_4$ nanoparticles after 3th cycle.

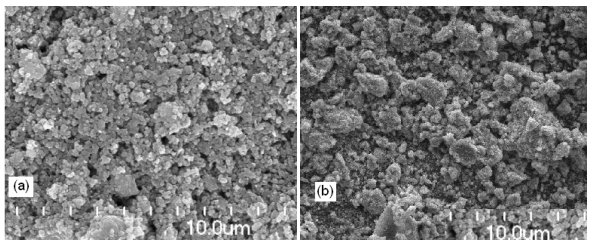
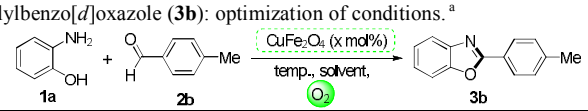


Figure 3 SEM images of $CuFe_2O_4$ nanoparticles before (a) and after (b) 3th cycle.

Table 1. Magnetic $CuFe_2O_4$-catalyzed condensation of 2-aminophenol (**1a**) with 4-methylbenzaldehyde (**2b**) leading to 2-*p*-tolylbenzo[*d*]oxazole (**3b**): optimization of conditions. [a]



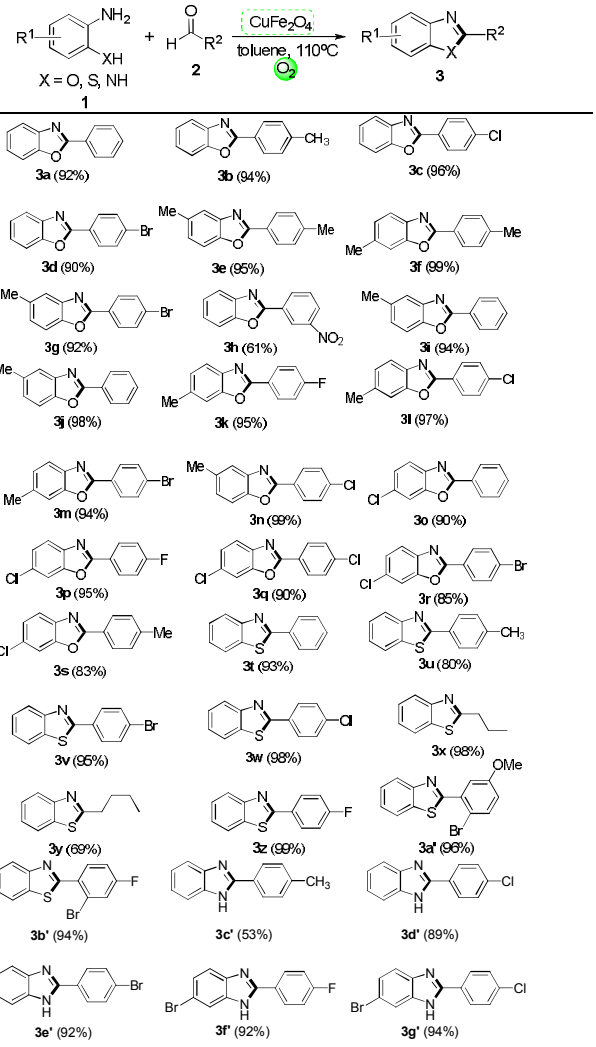
1a 2b 3b

Entry	Solvent	Temp.[°C]	Yield [%][b]
1	H_2O	100	0
2	EtOH	80	0
3	CH_3CN	80	0
4	THF	80	0
5	**toluene**	**110**	**94**
6	--	110	45
7	toluene	110	trace[c]
8	toluene	110	30[d]
9	toluene	110	45[e]
10	toluene	110	65[f]
11	toluene	25	0
12	toluene	60	0
13	toluene	90	58
14	toluene	100	78
15	toluene	110	76[g]

[a] Reaction conditions: 2-aminophenol (**1a**) (0.75 mmol), benzaldehyde (**2b**) (0.5 mmol), catalyst (0.1 mmol), solvent (0.5 mL) under oxygen atmosphere. [b] Isolated yield. [c] Without catalyst. [d, e] and [f] In the presence of catalyst (0.005 mmol; 0.0125 mmol; 0.05 mmol, respectively). [g] Under air conditions

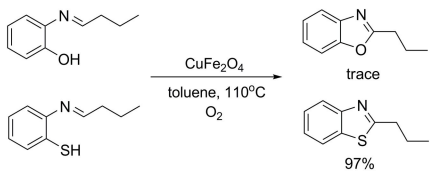
At first, 2-aminophenol (**1a**) and 4-methylbenzaldehyde (**2b**) were chosen as the model substrates to optimize reaction conditions including the amount of catalysts, solvents and reaction temperatures under oxygen atmosphere. First, five solvents were tested in the presence of 0.2 equiv. of $CuFe_2O_4$ nanoparticles, and toluene gave the highest yiled (94%), interestingly, without solvent, also afforded the target product (3a) in 45% yield (entries 1-6). Furthermore, when the amount of the catalyst was changed from 20 mol% to 1 mol%, the reaction yield decreased, providing only 30% yield. (entries 5, 8-10). Control experiments confirmed that the product was not formed in the absence of the catalyst (entries 8). We attempted different temperature (compare entries 5 and 11-14), and 110 °C was optimal. The reaction under air also gave a good yield (76%) (entry 15). Therefore, the standard reaction condition for the $CuFe_2O_4$-catalyzed synthesis of benzoxazole derivatives is as follows: 20 mol% of $CuFe_2O_4$ as the catalyst and toluene as the solvent under oxygen atmosphere.

Table 2. Magnetic $CuFe_2O_4$-catalyzed synthesis of benzoxazoles, benzothiazoles and benzimidazoles.[a]



[a] Reaction conditions: *o*-substituted aminobenzene (**1**) (0.75 mmol), benzaldehyde **(2)** (0.5 mmol), catalyst (0.1 mmol), solvent (0.5 mL) under oxygen atmosphere. [b] Isolated yield.

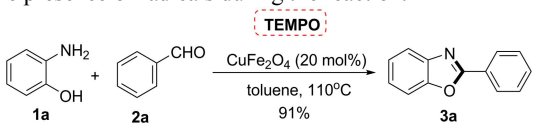
We then investigated the scope of $CuFe_2O_4$-catalyzed reactions of substituted 2-aminophenol (**1**) with benzaldehyde (**2**) under the optimized catalytic conditions determined above. As shown in Table 2, most of the examined substrates provided good to excellent yields. For the substituted 2-aminophenol and benzaldehyde the electronic effect of the substituted groups including electron-rich, -neutral, and -deficient substituents did not display evident difference in reactivity as shown in Table 2. For the substituted benzaldehyde, the substrates containing nitro groups gave moderate yields. Under a similar condition, the methodology was extended to the synthesis of various benzothiazoles and benzimidazoles from other building blocks like *o*-aminothiophenol and *o*-phenyldiamine. The results are also summarized in Table 2. The $CuFe_2O_4$-catalyzed domino reactions could tolerate some functional groups such as alkyl group, C-F bonds, C-Cl bonds, C-Br bonds , and nitro groups . Although aromatic aldehyde showed high reactivity, unfortunately, aliphatic ones were poor substrates, they are suitable for 2-aminobenzenethiol but unactived for *o*-aminophenols or *o*-phenylenediamines. In order to explain this, two control experiments were performed under the standard conditions as shown in Scheme 2. Treatment of (*E*)-2-(butylideneamino)phenol and (*E*)-2-(butylideneamino)benzenethiol under the standard conditions provided 2-propylbenzo[d]thiazole (**3x**) in 97% yield and no 2-propylbenzo[*d*]oxazole was observed. This result indicate an weaker nucleophilicity of the hydroxyl group under the $CuFe_2O_4$ catalyzed conditions.



Scheme 2 Control experiments

We also studied the recyclability of the catalyst. For this, we investigated the $CuFe_2O_4$-catalyzed cyclization of 2-aminophenol (**1a**) with benzaldehyde (**2a**) under the optimized conditions. After completion of the reaction, the reaction mixture was cooled to room temperature, and the catalyst was magnetically separated from the reaction mixture, washed with ethanol and dried at 100 °C for 2 h and then used directly for further catalytic reactions. The catalyst could be reused ten times without significant loss in catalytic activity (average yields in 90%).

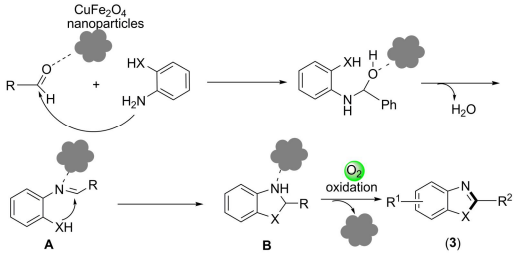
Finally, we investigated the formation mechanism of benzoxazole derivatives. As shown in Scheme 3, when one equivalent of TEMPO (2, 2, 6, 6-tetramethyl-1-piperidinyloxy, a well known radical-capturing species) was added to the reaction system, no significant difference was observed in the yield, ruling out the presence of radicals during the reaction.



Scheme 3 Reactions of *o*-aminophenol with benzaldehyde in the presence of TEMPO under the optimized reaction condition.

On the basis of these results above, a possible mechanism is thus proposed as illustrated in Scheme 4. Initially, $CuFe_2O_4$ nanoparticles could act as a Lewis acid which activates the aldehyde and promote the imine (**A**) formation. The resulting imine could further undergo the ring closure by the intramolecular attack of hydroxyl, sulfydryl and amino group on

the C=N double bond to give intermediate (**B**) that subsequently could proceed the aromatization by aerial oxidation under the reaction conditions so as to afford the desired products (**3**).



Scheme 4 Possible mechanism for $CuFe_2O_4$-catalyzed synthesis of Benzoxazoles, Benzimidazoles and Benzothiazoles.

Experimental Section

General: All reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. Flash chromatography was performed on silica gel (200 ~ 300 mesh). ^{1}H and ^{13}C NMR data were recorded at 400 and 100 MHz on a BRUKER 400 spectrometer. Chemical shifts (d) are expressed in parts per million (ppm) coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.24 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm) or were recorded using tetramethylsilane (TMS) in the solvent of DMSO-D6 as the internal standard (^{1}H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; ^{13}C NMR: DMSO at 40.0 ppm).

General procedure for $CuFe_2O_4$-catalyzed synthesis of Benzoxazoles, Benzimidazoles and Benzothiazoles: (3): A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with $CuFe_2O_4$ nanoparticles (0.05 mmol, 12 mg), substituted *o*-substituted aminobenzene (**1**) (0.5 mmol). The tube was evacuated twice and backfilled with oxygen, and toluene (0.5 mL) was added to the tube under oxygen atmosphere. The tube was sealed with a balloon and then the mixture was allowed to stir under oxygen atmosphere at 110 °C for 24 h. After completion of the reaction, the resulting solution was cooled to room temperature, and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product (**3**).

2-Phenylbenzo[*d*]oxazole (3a) [32]**.** Eluent petroleum ether/ethyl acetate (30:1). White solid. mp 94-95 °C (lit. [32] 94-96 °C). (petroleum ether/ethyl acetate = 40:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.29 (d, 2H, J = 7.6 Hz), 7.81 (d, 1H, J = 3.3 Hz), 7.61 (d, 1H, J = 3.4 Hz), 7.62-7.54 (m, 3H), 7.38 (d, 2H, J = 6.0 Hz) ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 163.1, 150.8, 142.1, 131.5, 128.9, 127.6, 127.2, 125.1, 124.6, 120.0, 110.6. ESI-MS $[M+H]^+$ m/z 196.4.

2-*p*-Tolylbenzo[*d*]oxazole (3b) [33]**.** Eluent petroleum ether/ethyl acetate (30:1). White solid. mp 116-117 °C (lit. [33] 118-119 °C). (petroleum ether/ethyl acetate = 40:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.15 (d, 2H, J = 8.0Hz), 7.78 (d, 1H, J = 4.8 Hz), 7.59 (d, 1H, J = 5.2 Hz), 7.37-7.34 (m, 4H), 2.46(s, 3H) ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 163.3, 150.7, 142.2, 142.1, 129.7, 127.6, 124.9, 124.5, 124.4, 119.9, 110.5, 21.7. ESI-MS $[M+H]^+$ m/z 210.4.

2-(4-chlorophenyl)benzo[*d*]oxazole (3c) [34]**.** Eluent petroleum ether/ethyl acetate (30:1). White solid. mp 157-159 °C (lit. [34]155-156 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.21 (d, 2H, J = 4.0 Hz), 7.79 (d, 1H, J = 6.4 Hz), 7.60 (d, 1H, J = 4.0Hz), 7.57-7.41 (m, 2H), 7.36-7.36 (m, 2H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 162.1, 150.8, 142.0, 137.8, 129.3, 128.9, 125.7, 124.7, 120.1, 124.8, 110.6. ESI-MS $[M+H]^+$ m/z 230.5.

2-(4-bromophenyl)benzo[*d*]oxazole (3d) [35]**.** Eluent petroleum ether/ethyl acetate (15:1). White solid. mp 158-160 °C (lit. [35] 156-158 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.14 (d, 2H, J = 8.8 Hz), 7.79 (d, 1H, J = 3.2 Hz), 7.69 (d, 2H, J = 8.8 Hz), 7.60 (d, 1H, J = 5.6Hz), 7.42-7.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 162.2, 150.8, 142.0, 132.3,129.0, 126.3, 125.4, 124.8, 120.1, 110.7. ESI-MS $[M+H]^+$ m/z 273.5, 275.4.

5-methyl-2-*p*-tolylbenzo[*d*]oxazole (3e) [36]**.** Eluent petroleum ether/ethyl acetate (30:1). White solid. mp 104-105°C (lit.[36] 103-104°C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.4). ^{1}H NMR (CDCl3, 400 MHz, ppm) δ 8.15 (d, 2H, J = 8.4Hz), 7.56 (d, 1H, J = 0.8Hz), 7.45 (d, 1H, J = 8.4Hz), 7.35-7.33 (m, 2H), 7.16 (m, 1H), 2.52 (s, 1H), 2.46(s, 1H). ^{13}C NMR (CDCl3, 200 MHz, ppm) δ 163.4, 148.9, 142.4, 142.9, 127.5, 126.0, 109.9, 21.7, 21.6. ESI-MS $[M+H]^+$ m/z 223.6.

6-methyl-2-*p*-tolylbenzo[*d*]oxazole (3f) [37]**.** Eluent petroleum ether/ethyl acetate (30:1). White solid. mp 90-92 °C (lit. [37] 89-91°C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.14 (d, 2H, J = 8.4Hz), 7.64 (d, 1H, J = 8.4Hz), 7.39-7.33 (m, 3H), 7.17 (d, 1H, J = 8.4Hz), 2.52 (s, 1H), 2.46(s, 1H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 162.8, 151.0, 141.8, 140.0, 135.3, 129.6, 127.4, 125.7, 124.6, 119.2, 110.7, 21.8, 21.6. ESI-MS $[M+H]^+$ m/z 223.7.

2-(4-bromophenyl)-5-methylbenzo[*d*]oxazole (3g). Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 190-191 °C. (petroleum ether/ethyl acetate = 20:1, Rf= 0.5). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.12 (d, 2H, J = 8.4 Hz), 7.66 (d, 1H, J = 8.4 Hz), 7.57 (s, 1H), 7.46 (d, 1H, J = 8.4 Hz), 7.18 (d, 1H, J = 8.4 Hz), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 162.2, 149.0, 128.9, 126.5, 126.3, 126.1, 120.0, 110.0, 21.6. ESI-MS $[M+H]^+$ m/z 287.2, 289.1. HR-MS: m/z calcd for C14H11BrON: 288.0024; found: 288.0027, 290.0006. IR: max(thin film) (cm^{-1}) = 3078, 2919, 1592, 1548, 1455, 1398, 1068, 838, 796, 7283.

(R)-2-(3-nitrophenyl)benzo[*d*]oxazole (3h) [38]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 210-212 °C (lit. [38] 210 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.4).^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.10 (s, 1H), 8.59 (d, 1H, J = 7.6 Hz), 8.40 (d, 1H, J = 7.6 Hz), 7.83 (d, 1H, J = 8.4 Hz), 7.77-7.64 (m, 2H), 7.43 (d, 2H, J = 8.4). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 160.6, 150.9, 148.7, 141.8, 133.0, 130.1, 129.5, 128.6, 126.1, 125.1, 122.5, 120.5, 110.9. ESI-MS $[M+H]^+$ m/z 240.6.

6-methyl-2-phenylbenzo[*d*]oxazole (3i) [39]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 100-101 °C (lit. [39] 99-102 °C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.26 (d, 2H, J = 5.6 Hz), 7.58-7.52 (m, 4H), 7.47 (d, 1H, J = 8.4 Hz), 7.17 (d, 1H, J = 8.4 Hz), 2.5 (s, 1H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 163.1, 149.0, 142.3, 134.4, 131.4, 128.9, 127.6, 127.3, 126.2, 119.9, 109.9, 21.6. ESI-MS $[M+H]^+$ m/z 209.6.

5-methyl-2-phenylbenzo[*d*]oxazole (3j) [39]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 112-114°C (lit. [39] 112-114 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.29-8.26 (m, 2H), 7.58 (s, 1H), 7.56-7.53 (m, 3H), 7.62-7.55 (m, 3H), 7.19(d, 1H, J = 7.6 Hz), 7.17 (d, 1H, J = 6.0 Hz), 2.51 (s, 1H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 163.1, 149.0, 142.3, 134.4, 131.4, 128.9, 127.6, 127.3, 126.2, 119.9, 109.9, 21.6. ESI-MS $[M+H]^+$ m/z 210.2.

2-(4-fluorophenyl)-6-methylbenzo[*d*]oxazole (3k) [40]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 112-113 °C (lit. [40] 113-116 °C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.5). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.27-8.24 (m, 2H), 7.56 (s, 1H), 7.45 (d, 1H, J = 8.4 Hz), 7.24-7.17 (m, 3H), 2.5 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 160.0, 163.5, 162.2, 149.0, 142.3, 134.5, 129.8, 129.7, 126.3, 123.7, 123.6, 119.9, 116.3, 116.0, 109.9, 21.5. ESI-MS $[M+H]^+$ m/z 227.7.

2-(4-chlorophenyl)-6-methylbenzo[*d*]oxazole (3l) [36]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 149-152 °C (lit. [36] 151-152 °C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.4).^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.17 (d, 1H, J = 8.4 Hz), 7.55 (s, 1H), 7.51-7.44 (m, 3H), 7.17 (s, 1H, J = 8.0 Hz), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 162.1, 148.9, 142.2, 137.6, 134.6, 129.2, 128.8, 120.0, 110.0, 21.5. ESI-MS $[M+H]^+$ m/z 243.6.

2-(4-bromophenyl)-6-methylbenzo[*d*]oxazole (3m). Eluent petroleum ether/ethyl acetate (30:1). White solid. mp 171-173 °C. (petroleum ether/ethyl acetate = 20:1, Rf= 0.5).^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.10 (d, 2H, J = 8.4 Hz), 7.68-7.64 (m, 3H), 7.39 (s, 1H), 7.19 (d, 1H, J = 8.0 Hz), 2.53 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 161.6,151.0, 139.8, 135.9, 132.2, 128.9, 126.3, 126.0, 125.9, 119.4, 110.8, 21.9. ESI-MS $[M+H]^+$ m/z 288.2, 290.4. HR-MS: m/z calcd for C14H11BrON: 288.0024; found: 288.0026, 290.0010. IR: max(thin film) (cm^{-1}) = 3086, 2920, 1612, 1588, 1548, 1480, 1397, 1068, 835, 813, 726.

2-(4-chlorophenyl)-5-methylbenzo[*d*]oxazole (3n) [35]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 149-151 °C (lit. [35] 150-151 °C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.15 (d, 2H, J = 8.4Hz), 7.55(s, 1H), 7.49 (d, 2H, J = 8.4Hz), 7.44 (d, 1H, J = 8.4 Hz), 7.16 (d, 1H, J = 8.2 Hz), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 162.1, 149.0, 142.1, 137.6, 134.6, 129.2, 128.8, 126.5, 125.8, 120.0, 109.9, 21.5. ESI-MS $[M+H]^+$ m/z 243.7.

6-chloro-2-phenylbenzo[*d*]oxazole (3o) [41]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 108-110 °C (lit. [41] 107-108 °C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.25 (d, 2H, J = 5.6 Hz), 7.69 (d, 1H, J = 8.4 Hz), 7.62 (s, 1H), 7.61-7.53 (m, 3H), 7.34 (d, 1H, J = 5.6 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 163.7, 150.9, 140.9, 131.8, 130.7, 129.0, 127.7, 126.7, 125.3, 120.5, 111.3,. ESI-MS $[M+H]^+$ m/z 229.5.

6-chloro-2-(4-fluorophenyl)benzo[*d*]oxazole (3p) [42]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 130-131 °C (lit. [42] 132-133 °C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.5). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.26-8.21 (m, 2H), 7.67 (d, 1H, J = 8.4 Hz), 7.59 (s, 1H), 7.36 (d, 1H, J = 8.4 Hz), 7.33-7.20 (m, 2H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 166.2, 163.7, 162.8, 150.9, 140.8, 130.7, 130.0, 129.9, 125.4, 123.1, 123.0, 120.4, 116.4, 116.2, 111.2. ESI-MS $[M+H]^+$ m/z 247.7.

6-chloro-2-(4-chlorophenyl)benzo[*d*]oxazole (3q) [41]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 149-150 °C (lit. [41] 148-149 °C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.5). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.18-8.15 (m, 2H), 7.68 (d, 1H, J = 8.4 Hz), 7.60 (s, 1H), 7.54-7.50 (m, 2H), 7.36 (d, 1H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 162.7, 150.9, 140.8, 138.1, 131.0, 129.4, 128.9, 125.5, 125.2, 120.6, 111.3. ESI-MS $[M+H]^+$ m/z 263.4.

2-(4-bromophenyl)-6-chlorobenzo[*d*]oxazole (3r) [42]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 168-170 °C (lit. [42] 168-170 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.09 (d, 2H, J = 8.4 Hz), 7.69-7.66 (m, 3H), 7.59 (s, 1H), 7.36 (d, 2H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 162.8, 151.0, 140.8, 132.3, 131.0, 129.0, 126.6, 125.6, 125.5, 120.6, 111.3. ESI-MS $[M+H]^+$ m/z 308.4, 310.3.

6-chloro-2-*p*-tolylbenzo[*d*]oxazole (3s) [43]**.** Eluent petroleum ether/ethyl acetate (20:1). White solid. mp 126-128 °C (lit. [43] 126-127 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.12 (d, 2H, J = 8.0 Hz), 7.67 (d, 2H, J = 8.4 Hz), 7.58 (s, 1H), 7.34-7.33 (m, 3H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 164.0, 150.9, 142.5, 141.0, 130.4, 129.7, 127.6, 125.2, 123.9, 120.3, 111.2, 21.7. ESI-MS $[M+H]^+$ m/z 243.7.

2-phenylbenzo[*d*]thiazole (3t) [43]**.** Eluent petroleum ether/ethyl acetate (10:1). White solid. mp 113-115 °C (lit. [43] 112-114 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.14-8.11 (m, 3H), 7.93 (d, 2H, J = 8.0 Hz), 7.55-7.51 (m, 4H), 7.42 (t, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 168.1, 154.2, 135.1, 133.6, 131.0, 129.1, 127.6, 126.3, 125.2, 123.3, 121.7. ESI-MS $[M+H]^+$ m/z 211.7.

2-*p*-tolylbenzo[*d*]thiazole (3u) [44]**.** Eluent petroleum ether/ethyl acetate (30:1). White solid. mp 83-85 °C (lit. [44] 85-86 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.09 (d, 1H, J = 8.0 Hz), 8.01 (d, 2H, J = 8.0 Hz), 7.92 (d, 2H, J = 8.0 Hz), 7.51 (m, 1H), 7.41 (t, 1H, J = 8.0 Hz), 7.37-7.31 (m, 2H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 168.2, 154.2, 141.4, 135.0, 131.0, 129.7, 127.5, 126.2, 125.0, 123.1, 121.6, 21.5. ESI-MS $[M+H]^+$ m/z 225.6.

2-(4-bromophenyl)benzo[*d*]thiazole (3v) [45]**.** Eluent petroleum ether/ethyl acetate (10:1). White solid. mp 130-131 °C (lit. [45]132-133 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.10 (d, 1H, J = 8.0 Hz), 7.97 (d, 2H, J = 8.0 Hz), 7.92 (d, 2H, J = 8.0 Hz), 7.51 (m, 1H), 7.65 (t, 2H, J = 8.0 Hz), 7.54 (t, 1H, J = 8.0 Hz), 7.43 (t, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 166.7, 154.1, 135.1, 132.6, 132.2, 128.9, 126.5, 125.5, 125.4, 123.3, 121.7. ESI-MS $[M+H]^+$ m/z 290.4, 291.3.

2-(4-chlorophenyl)benzo[*d*]thiazole (3w) [46]**.** Eluent petroleum ether/ethyl acetate (10:1). White solid. mp 116-117 °C (lit. [46] 115-116 °C). (petroleum ether/ethyl acetate = 30:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.08 (d, 1H, J = 8.0 Hz), 8.01 (d, 2H, J = 8.0 Hz), 7.92 (d, 1H, J = 7.6 Hz), 7.52 (t, 1H, J = 7.6 Hz), 7.45 (t, 2H, J = 8.4 Hz), 7.39 (t, 1H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 166.6, 154.1, 137.0, 135.1, 132.1, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7. ESI-MS $[M+H]^+$ m/z 245.5.

2-propylbenzo[*d*]thiazole (3x). Eluent petroleum ether/ethyl acetate (10:1). Yellow oil. (petroleum ether/ethyl acetate = 30:1, Rf= 0.2). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.98 (d, 1H, J = 8.4 Hz), 7.83 (d, 2H, J = 8.4 Hz), 7.43 (t, 1H, J = 8.0 Hz), 7.31 (t, 1H, J = 8.0 Hz), 3.09 (t, 2H, J = 7.6 Hz) , 1.91 (dt, 2H, J = 7.2 Hz), 1.05 (t, 2H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 172.1, 153.3, 135.2, 125.9, 124.6, 122.5, 121.5, 36.3, 23.1, 13.7.

ESI-MS $[M+H]^+$ m/z 177.6. HR-MS: m/z calcd for C10H11NS: 178.0690; found: 178.0687. IR: max(thin film) (cm^{-1}) = 3414, 2968, 1617, 1560, 1518, 1455, 1405, 1381, 1068, 879, 759.

2-butylbenzo[*d*]thiazole (3y). Eluent petroleum ether/ethyl acetate (10:1). yellow oil. (petroleum ether/ethyl acetate = 30:1, Rf= 0.2). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.90 (d, 1H, J = 8.0 Hz), 7.85 (d, 2H, J = 8.0 Hz), 7.47 (t, 1H, J = 6.8 Hz), 7.34 (t, 1H, J = 6.8 Hz), 7.45 (t, 2H, J = 8.4 Hz), 7.39 (t, 1H, J = 7.6 Hz), 3.14 (t, 2H, J = 7.2 Hz) , 1.88 (t, 2H, J = 6.8 Hz), 1.50 (t, 2H, J = 7.2 Hz), 0.99 (t, 3H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 172.4, 153.3, 135.1, 125.9, 124.6, 122.5, 121.5, 34.1, 31.8, 22.3, 13.8. ESI-MS $[M+H]^+$ m/z 191.6. HR-MS: m/z calcd for C11H15NS: 192.0847; found: 192.0850. IR: max(thin film) (cm^{-1}) = 3436, 3306, 2957, 2871, 1630, 1561, 1520, 1456, 1436, 1381, 1127, 855, 758.

2-(4-fluorophenyl)benzo[*d*]thiazole (3z) [47]**.** Eluent petroleum ether/ethyl acetate (10:1). White solid. mp 98-99 °C (lit.[47] 100-102 °C). (petroleum ether/ethyl acetate = 20:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.16-8.07 (m, 3H), 8.05 (d, 2H, J = 8.0 Hz), 7.57 (t, 1H, J = 7.2 Hz), 7.55-7.38 (m, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 172.4, 153.3, 135.1, 125.9, 124.6, 122.5, 121.5, 34.1, 31.8, 22.3, 13.8. ESI-MS $[M+H]^+$ m/z 229.5.

(R)-2-(2-bromo-5-methoxyphenyl)benzo[*d*]thiazole (3a'). Eluent petroleum ether/ethyl acetate (10:1). White solid. mp 252-254 °C. (petroleum ether/ethyl acetate =20:1, Rf= 0.3).^{1}H NMR (DMSO-D_6, 400 MHz, ppm) δ 8.16 (d, 2H, J = 8.4 Hz), 7.97 (d, 2H, J = 7.6 Hz), 7.64-7.54 (m, 3H), 7.47 (t, 1H, J = 8.0 Hz), 7.47 (d, 1H, J = 8.4 Hz), 3.90 (s, 3H). ^{13}C NMR (DMSO-D_6, 200 MHz, ppm) δ 165.6, 158.9, 152.6, 136.2, 135.1, 134.8, 126.3, 125.5, 123.6, 121.5, 118.2, 116.6, 112.5, 55.7. ESI-MS $[M+H]^+$ m/z 319.5, 321.4. HR-MS: m/z calcd for C14H11BrNOS: 319.9745; found: 319.9745, 321.9725. IR: max(thin film) (cm^{-1}) = 3064, 3005, 2939, 2834, 1593, 1564, 1484, 1380, 1316, 853, 759, 603.

(R)-2-(2-bromo-4-fluorophenyl)benzo[*d*]thiazole (3b'). Eluent petroleum ether/ethyl acetate (10:1). White solid. mp 246-248 °C. (petroleum ether/ethyl acetate = 5:1, Rf= 0.4). ^{1}H NMR (DMSO-D_6, 400 MHz, ppm) δ 8.15 (d, 2H, J = 8.0 Hz), 8.06 (t, 1H, J = 8.8 Hz), 7.97 (d, 2H, J = 8.0 Hz), 7.58-7.45 (m, 3H), 7.20 (t, 1H, J = 8.8 Hz). ^{13}C NMR (DMSO-D_6, 200 MHz, ppm) δ 164.6, 164.3, 161.8, 152.7, 136.1, 133.6, 133.5, 131.0, 130.9, 126.4, 125.6, 123.6, 122.6, 122.5, 121.4, 121.2, 115.2, 115.0. ESI-MS $[M+H]^+$ m/z 307.5, 309.4. HR-MS: m/z calcd for C13H8BrFNS: 307.9545; found: 307.9557, 308.9547. IR: max(thin film) (cm^{-1}) = 3084, 2971, 2900, 1614, 1490, 1464, 1241, 1042, 857, 750.

2-p-tolyl-1H-benzo[*d*]imidazole (3c') [48]**.** Eluent petroleum ether/ethyl acetate (3:1). White solid. mp 276-277 °C (lit. [48] 275-276 °C). (petroleum ether/ethyl acetate = 5:1, Rf= 0.3).^{1}H NMR (DMSO-D_6, 400 MHz, ppm) δ 12.83 (s, br, 1H), 8.07 (d, 2H, J = 8.4 Hz), 7.58 (m, 2H), 7.36 (d, 2H, J = 8.0 Hz), 7.20 (d, 2H, J = 8.5 Hz). ^{13}C NMR (DMSO-D_6, 200 MHz, ppm) δ 168.2, 151.8, 140.0, 130.0, 127.9, 126.9, 21.4. ESI-MS $[M+H]^+$ m/z 209.6.

2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole (3d') [49]**.** Eluent petroleum ether/ethyl acetate (3:1). White solid. mp 300-301 °C (lit.[49] 303 °C). (petroleum ether/ethyl acetate = 5:1, Rf= 0.4).^{1}H NMR (DMSO-D_6, 400 MHz, ppm) δ 13.00 (s, br, 1H), 8.20 (d, 2H, J = 8.8 Hz), 7.69-7.54 (m, 4H), 7.23 (t, 2H, J = 8.0 Hz), 7.20 (d, 2H, J = 8.5 Hz). ^{13}C NMR (DMSO-D_6, 200 MHz, ppm) δ 150.6, 144.2, 135.5, 134.9, 129.5, 128.6, 123.2, 122.3, 119.4, 111.9. ESI-MS $[M+H]^+$ m/z 228.7.

2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole (3e') [50]**.** Eluent petroleum ether/ethyl acetate (5:1). White solid. mp 300-301 °C (lit.[50] 299-300 °C). (petroleum ether/ethyl acetate = 5:1, Rf= 0.5).^{1}H NMR (DMSO-D_6, 400 MHz, ppm) δ 13.00 (s, br, 1H), 8.12 (d, 2H, J = 8.8 Hz), 7.77 (d, 2H, J = 6.8 Hz), 7.61 (m, 2H), 7.22 (d, 2H, J = 8.8 Hz). ^{13}C NMR (DMSO-D_6, 200 MHz, ppm) δ 150.6, 135.5, 132.4, 129.9, 123.7, 122.3, 119.4, 111.9. ESI-MS $[M+H]^+$ m/z 272.7, 274.6.

6-bromo-2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (3f'). Eluent petroleum ether/ethyl acetate (5:1). White solid. mp 320-321 °C. (petroleum ether/ethyl acetate = 5:1, Rf= 0.4).^{1}H NMR (DMSO-D_6, 400 MHz, ppm) δ 13.10 (s, br, 1H), 8.23-8.21(m, 2H), 7.86-7.49 (m, 2H), 7.43-7.34 (m, 3H). ^{13}C NMR (DMSO-D_6, 200 MHz, ppm) δ 164.9, 165.2, 134.6, 129.4, 125.5, 116.5, 114.4, 113.6. ESI-MS $[M+H]^+$ m/z 290.4, 292.3. HR-MS: m/z calcd for C13H9BrFN2: 290.9933; found: 290.9936, 292.9911. IR: max(thin film) (cm^{-1}) = 3445, 2965, 1628, 1600, 1464, 1430, 1383, 1233, 915, 805, 734.

6-bromo-2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole (3g'). Eluent petroleum ether/ethyl acetate (2:1). White solid. mp 336-337 °C. (petroleum ether/ethyl acetate = 1:1, Rf= 0.5). ^{1}H NMR (DMSO-D_6, 400 MHz, ppm) δ 13.17 (s, br, 1H), 8.17 (d, 2H, J = 8.8 Hz), 7.79 (m, 1H), 7.62-7.55 (m, 3H), 7.34 (d, 1H, J = 8.4 Hz). ^{13}C NMR (DMSO-D_6, 200 MHz, ppm) δ 152.1, 132.5, 129.4, 129.0,125.8, 125.3, 124.1, 121.8, 121.1, 114.5, 113.6. ESI-MS $[M+H]^+$ m/z 306.4, 308.3. HR-MS: m/z calcd for C13H9BrClN2: 306.9638; found: 306.9634, 308.9604. IR: max(thin film) (cm^{-1}) = 3271, 2900, 1629, 1507, 1393, 1241, 1015, 1233, 879, 732.

Conclusions

In conclusion, We have developed a simple, green and efficient strategy for the synthesis of benzoxazoles, benzothiazoles and benzimidazoles. The couplings were performed using readily available starting materials (*o*-substituted aminobenzene and various aldehydes), magnetically separable and reusable $CuFe_2O_4$ nanoparticles as the catalyst and dioxygen as the green oxidant, importantly, organic oxidizing agents, stong acids or bases were not necessary. The present method shows eco-friendly, economical, broad scope of substrates and practical advantages over the previous methods. Further applications of $CuFe_2O_4$ magnetic nanoparticles in the synthesis of other useful heterocycles is underway in our laboratory.

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