



Research article

A green approach for the synthesis of 2-substituted benzoxazoles and benzothiazoles *via* coupling/cyclization reactionsHai Truong Nguyen^{a,b}, Trinh Hao Nguyen^{a,b}, Dung Duc Pham^{c,**}, Cong Tien Nguyen^c,
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ABSTRACT

We have developed the green method for the synthesis of benzoxazoles and benzothiazoles with moderate to good yields using imidazolium chlorozincate (II) ionic liquid supported into Fe₃O₄ nanoparticles (LAIL@MNP) under solvent-free sonication. The reaction was performed under mild conditions and only produced water as a sole byproduct. The reactions under solvent-free sonication showed advantages of faster reaction rate (30 min) and high yields of the products (up to 90%). Moreover, the LAIL@MNP material was easily separated from the reaction mixture and can be recycled for five consecutive runs with a slight decrease in its catalytic performance (from 82 to 73%).

1. Introduction

Azoles scaffolds have been associated with biological activities such as antitumor, antihypertensive, anti-histaminic, and antimicrobial activities (Figure 1) (Aiello et al., 2008; Boyer et al., 2011; Daletos et al., 2014; He et al., 2017; Johnson et al., 2008; Ko et al., 2001; Leventhal et al., 2006; Mishra et al., 2019; Oksuzoglu et al., 2008; Sun et al., 2004; Wang et al., 2014). The synthesis of benzoxazoles has been studied extensively *via* different pathways, including (a) cyclization of 2-amino-phenols with β -diketones (Mayo et al., 2014; Miao et al., 2019), carboxylic acids (Dev et al., 2016; Yuan et al., 2018), aldehydes (Layek et al., 2020; Matloubi Moghaddam et al., 2006; Sirgamalla et al., 2020), acyl chloride (Tian et al., 2019; Zheng et al., 2019), isocyanides (Akbay et al., 2003), alcohols (Doan et al., 2019; Kaldhi et al., 2019), (b) oxidative intramolecular C–O coupling, (c) C–H arylation reaction, and (d) oxidative cyclization of phenolic Schiff base (Chang et al., 2002). However, the condensation and aromatization of *o*-aminophenol was the most popular method for the synthesis of benzoxazoles. Moreover, Yanling Tang et al. have reported the synthesis of azole derivatives through the intramolecular *O*-arylation using DPPAP, Cu(OAc)₂ from *N*-(2-bromophenyl) benzamide in the presence of Et₃N and H₂O (Tang et al., 2020). Furthermore, the intramolecular *O*-arylation were improved by using

more metal sources such as CuI/1,10-phenanthroline (Evindar and Batey, 2006), cobalt(II)/1,10-phenanthroline (Saha et al., 2010), CuI (Wu et al., 2014), FeCl₃/Cs₂CO₃ (Bonnamour and Bolm, 2008), (IPr)CuCl for the synthesis of azoles (Urzúa et al., 2016). Efficient methods for the synthesis of thiazole frames have been developed by using Pd/Cu (Kamali et al., 2009a, 2009b), Cu/Fe₃O₄ nanoparticles (Nezafat and Nasrollahzadeh, 2021) or ultrasonic power (Habibi et al., 2013), H₂SO₄/SiO₂ (Maleki et al., 2010), and 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) (Hojati et al., 2011).

Ionic liquids (ILs) have been known as green solvents/catalysts for organic synthesis for over two decades for their unique properties of high thermal stability, negligible vapor pressure, tunable acidity, and selective dissolvability (Singh and Savoy, 2020). Although ionic liquids are potential green catalysts with promising advantages, their practical applications are still restricted by some drawbacks such as high viscosity and difficulty for product separation. Magnetic nanoparticles (MNPs) have been considered a new type of catalyst with many outstanding properties such as recyclable catalysts, good stability, and high surface area (Polshettiwar et al., 2011). Thus, the synthesis of ionic liquids supported on magnetic nanoparticles has been studied extensively in organic synthesis (González-Izquierdo et al., 2020; Nasrollahzadeh et al., 2018; Zhang et al., 2009; Zheng et al., 2009). Zhang and Xia reported γ -Fe₂O₃

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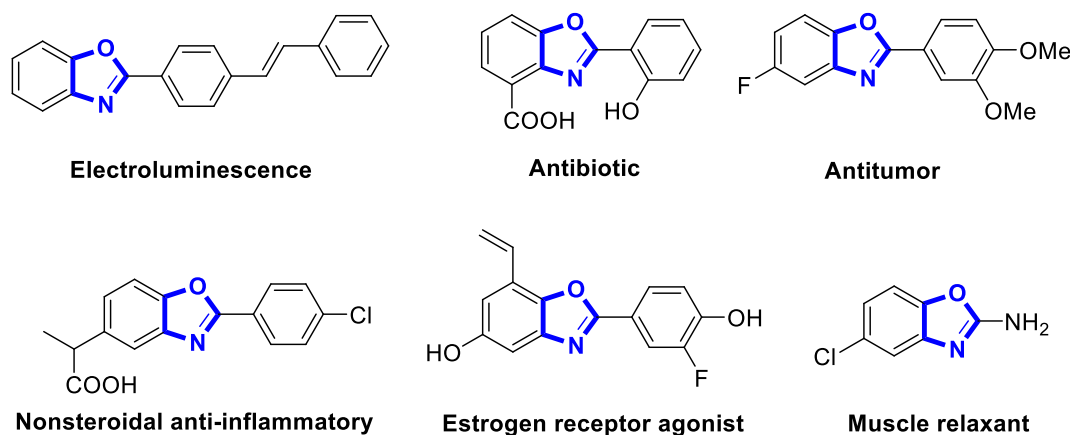


Figure 1. Some azole structures with known biological activity.

nanoparticles functionalized with basic ionic liquids for aqueous Knoevenagel condensation, which showed the quantitative conversion of the reactants under mild conditions and easy recycling of the catalyst through convenient magnetic decantation (Zhang and Xia, 2009). Zhang et al. investigated the magnetic nanoparticle-supported dual acidic ionic liquid as a “quasi-homogeneous” catalyst for the one-pot synthesis of benzoxanthenes through a three-component condensation of dimedone with aldehyde and 2-naphthol under solvent-free conditions (Zhang et al., 2012). Kong et al. developed l-proline supported ionic liquid-modified magnetic nanoparticles as a highly efficient and reusable organocatalyst for direct asymmetric aldol reaction in water (Kong et al., 2013).

In this research, we reported the magnetic nanomaterial Fe_3O_4 -supported Lewis acidic ionic liquid (LAIL@MNP) as the green catalyst for preparing benzoxazoles and benzothiazoles through the condensation reaction between 2-aminophenols and aromatic aldehydes under solvent-free ultrasound irradiation. This is the first time the Fe_3O_4 -supported Lewis acidic ionic liquid was used as a recyclable catalyst to synthesize azole under solvent-free sonication. The prominent feature of the present method is that the reactions are conducted in the green condition, such as recyclable catalyst, solvent-free reaction, ultrasound activation, mild temperature, and short reaction time.

2. Result and discussion

The LAIL@MNP was synthesized according to our previous literature (Nguyen et al., 2018, 2020), and the procedure was summarized in Figure 2. LAIL@MNP was then applied for condensation/cyclization

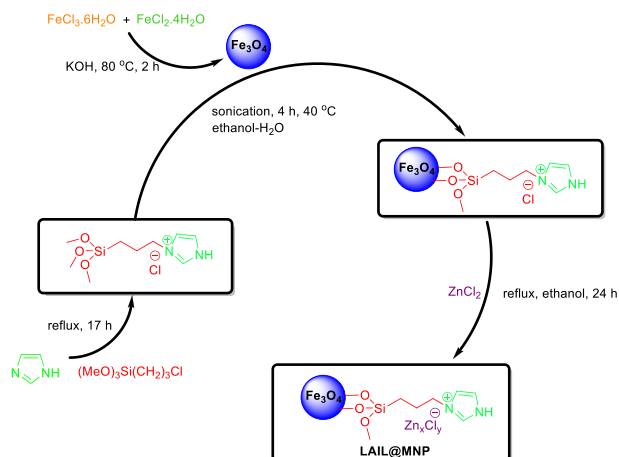
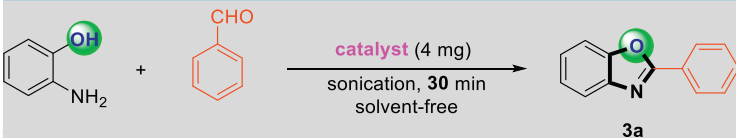


Figure 2. Synthesis of LAIL@MNP.

reaction to synthesize benzoxazole, benzothiazole derivatives from 2-aminophenols/2-aminothiophenols and aromatic aldehydes under solvent-free ultrasound irradiation. As shown in Table S1, the reaction was carried out between 2-aminophenol and benzaldehyde to form 2-phenylbenzoxazole in the presence of LAIL@MNP as the catalyst under ultrasound irradiation. The reaction conditions, including reaction time, the catalyst loading, and solvents, were investigated in the current method. Among these tested conditions, the highest conversion was obtained by treating LAIL@MNP (4.0 mg) for 30 min under solvent-free conditions (Entry 12, Table S1). Next, control experiments using only Fe_3O_4 , 3-(3-(trimethoxysilyl)propyl)-1H-imidazole-3-ium chloride or ZnCl_2 under solvent-free sonication for 30 min were performed. In these cases, the desired product was formed in lower yields than that noted with the use of LAIL@MNP (Entries 1–3, Table 1). Besides, the conversions were also decreased when FeCl_3 or choline chloride was employed. The conversion percentage was not good (Entries 4–5, Table 1), and the reaction did not proceed in the absence of the catalyst. Moreover, ionic liquids such as EMIM]Cl, and [BMIM]BF₄ were also studied, and the conversion was obtained in only 31% and 43% (Entries 7–8, Table 1). As we expected, the best conversion was obtained by using LAIL@MNP, presumably due to the high area surface of the nanoparticle catalyst.

The comparison of our work with previous literature was described in Table 2, and the results indicated that LAIL@MNP was good catalytic performance for the synthesis of benzoxazole. In general, although the product yield of the current method was not comparable with some previous papers, recyclable catalyst, mild conditions, short reaction time, and solvent-free conditions rendered this method more attractive from the viewpoint of green chemistry.

With the optimized conditions in hand, the substrate scope and limitations were explored with benzaldehydes bearing various substituents and 2-aminophenol derivatives under solvent-free sonication (Figure 3). The reactions of benzaldehydes bearing the electron-donating substituent including *tert*-butyl, methoxy, or the electron-withdrawing substituent such as chloro at the *para* position afforded the desired products in moderate to good yields. The higher yield of *p*-chlorobenzaldehyde could be explained by the effect of electron-withdrawing chlorine atoms on the carbonyl group. Next, these conditions were then applied to 2-aminothiophenol derivatives. The reactions were found to be successful for *o*-aminothiophenol with benzaldehyde and 4-methoxybenzaldehyde to provide the benzothiazoles up to 90%. The reaction of pyridine-4-carbaldehyde with *o*-aminothiophenol resulted in 44% yield of the corresponding product under the current method, presumably because the reaction of Lewis base (nitrogen on pyridine-4-carbaldehyde) and Lewis acidic sites on catalyst produced the coordinate covalent bond led to deactivate the catalyst. The synthesis of benzoxazole derivatives from 2-aminophenol derivatives containing methyl group at the 4-position provided desired products in moderate yields. Next, the examination of 2-amino-4-chlorophenol with a series of benzaldehyde derivatives led to

Table 1. Effect of various catalysts for the preparation of 2-phenylbenzoxazole.^a


Entry	Catalyst	Conversion ^b (%)
1	Fe ₃ O ₄	26
2	3-(3-(Trimethoxysilyl)propyl)-1 <i>H</i> -imidazole-3-ium chloride	44
3	ZnCl ₂	35
4	FeCl ₃	30
5	Choline chloride	41
6	LAIL@MNP	82
7	[EMIM]Cl	31
8	[BMIM]BF ₄	43

^a Reaction conditions: 2-Aminophenol (1.0 mmol), benzaldehyde (1.0 mmol), catalysts (4 mg) under solvent-free sonication at 70 °C for 30 min.

^b Conversion was reported by GC-MS.

Table 2. Comparison of the present work with the previous literature for the synthesis of 2-phenylbenzoxazole.

Entry	Catalyst	Temp. (°C)	Time (h)	Yield (%)
1	FeCl ₃ (5%), Toluene, O ₂ (1 atm)	110	24	70 (Cao et al., 2010)
2	CeCl ₃ (15 mol%), NaI (10 mol%), Toluene/O ₂	100	36	73 (Zhu and Wei, 2012)
3	Sm(OTf) ₃ (10 mol%), EtOH-H ₂ O (4:2)	50–60	2	92 (Gorepatil et al., 2013)
4	[BMIm] ₂ [WO ₄], air, 1,4-Dioxane (5 mL)	100	5	82 (Zhou et al., 2020)
5	MIL-101(Cr) (10 mg) Xylene	120	9	87 (Niknam et al., 2018)
6	Present work: LAIL@MNP (4 mg), solvent-free, sonication	70	0.5	82

the formation of the corresponding benzoxazole products with acceptable yields. However, isonicinaldehyde was not reactive in the current method gave the low to moderate yields with 2-aminothiophenol, 2-amino-4-methylphenol, and 2-amino-4-chlorophenol, presumably due to the effect of the basic pyridine ring.

During the reaction course, the active species could migrate from the LAIL@MNP to the liquid phase, and the leaching acted as a homogeneous catalyst. To explore the catalyst leaching, the reaction of 2-aminophenol and benzaldehyde using LAIL@MNP was carried out under optimized conditions. When the reaction time reached 10 min, acetone (15 mL) was added, and the LAIL@MNP was separated by an external magnet. The reaction mixture was divided into two parts. Part 1 was analyzed by GC-MS, and the conversion of benzaldehyde was 55%. Part 2 was concentrated to remove the acetone and then sonicated under the above conditions for another 20 min to give 58% conversion of benzaldehyde (less than 82% in the typical procedure).

Consequently, the leaching test exhibited no contribution from homogeneous leached species of the catalyst. Remarkably, the optimized reaction was readily scaled up to 10 mmol for the synthesis of 2-phenylbenzoxazole. The typical reaction was performed with 10 mmol of 2-aminophenol and 10 mmol of benzaldehyde in the presence of LAIL@MNP (40 mg), and the mixture was activated by ultrasound for 30 min under solvent-free conditions (Figure 4). The desired product was obtained in a slightly lower yield of 1 mmol scale 75% illustrating that this process can be applied in large-scale synthesis. Finally, LAIL@MNP was recovered and reused five times under optimized conditions, which was not significantly reduced in catalytic activity (Figure 5). The structure of the recovered catalyst has remained after the fifth run (checked by FTIR, please see in supporting information, Figure S1). Two FTIR spectra were

in good agreement between two, which peaks at ~3400 cm⁻¹ (Si–OH), ~2900 cm⁻¹ (aliphatic C–H), 1600 cm⁻¹ (C=N), ~1100 cm⁻¹ and ~1000 cm⁻¹ (Si–O–Si), and ~580 cm⁻¹ (Fe–O–Fe). These results demonstrated that the recovered catalyst was retained the structure after the fifth run.

The plausible mechanism was proposed for the formation of 2-phenylbenzoxazole over LAIL@MNP, which was presented in Figure 6. First, the carbonyl group of aldehyde was activated by LAIL@MNP and reacted with 2-aminophenol to form [A]. Next, [A] eliminated a water molecule to form the imine [B] (detected by GCMS). Next, the OH group in the intermediate [B] attacked the imine groups to obtain the intermediate [C]. Finally, the corresponding product was made up of an intermediate [C] through the oxidation with oxygen in the air to give the 2-phenylbenzoxazole (detected by GCMS).

3. Experimental section

3.1. Chemicals and instrumentation

2-Aminophenol (assay 99%), 2-aminothiophenol (assay 99%), 4-*tert*-butylbenzaldehyde (assay 97%), 4-fluorobenzaldehyde (assay 98%), 4-chlorobenzaldehyde (assay 97%), 4-pyridinecarboxaldehyde (assay 97%), 2-amino-4-methylphenol (assay 97%), 2-amino-4-chlorophenol (assay 97%) were obtained from Sigma-Aldrich. Benzaldehyde (for synthesis), 4-methylbenzaldehyde (for synthesis), 4-methoxybenzaldehyde (for synthesis), 4-nitrobenzaldehyde (for synthesis), TLC (silica gel 60 F₂₅₄), and zinc chloride (ZnCl₂) were obtained from Merck. Silica gel 230–400 mesh (for flash chromatography) was obtained from HiMedia Laboratories Pvt. Ltd. (India). Ethyl acetate (purity ≥99.5%), *n*-hexane

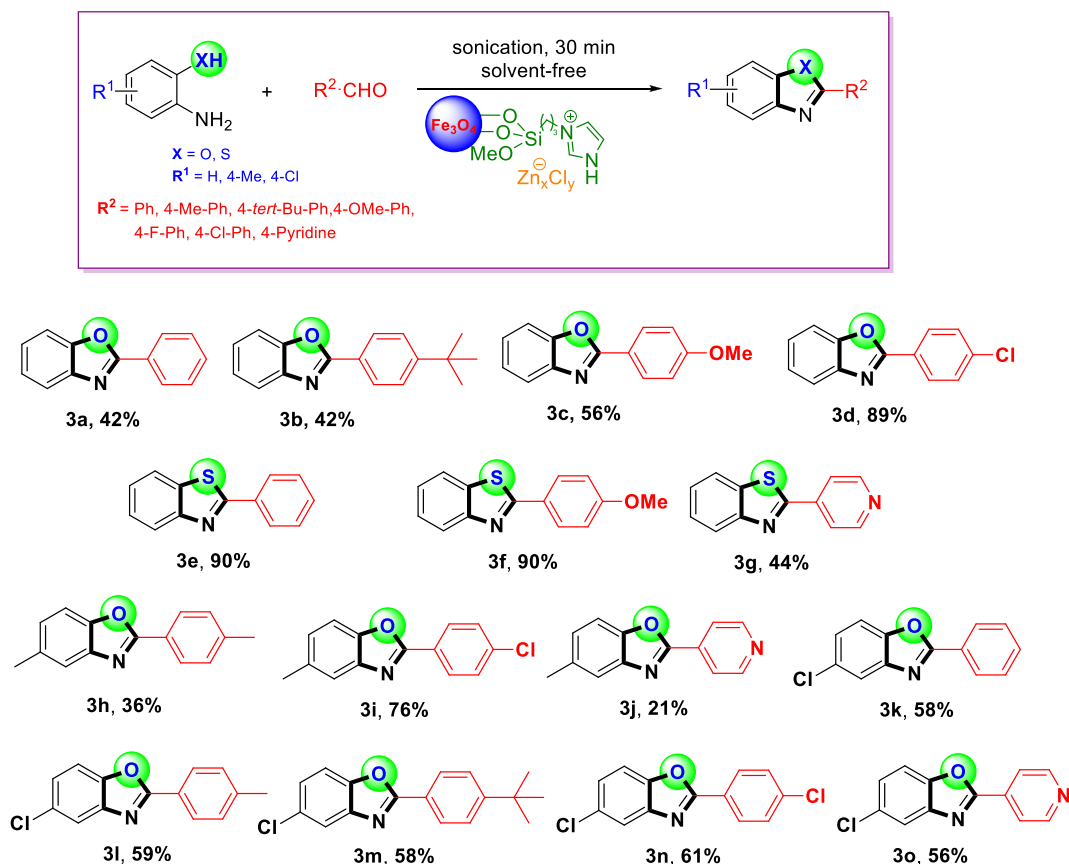


Figure 3. The condensation of 2-aminophenols with various aldehydes. Reaction condition: Substrates (1.0 mmol) and aldehydes (1.0 mmol), LAIL@MNP (4 mg).

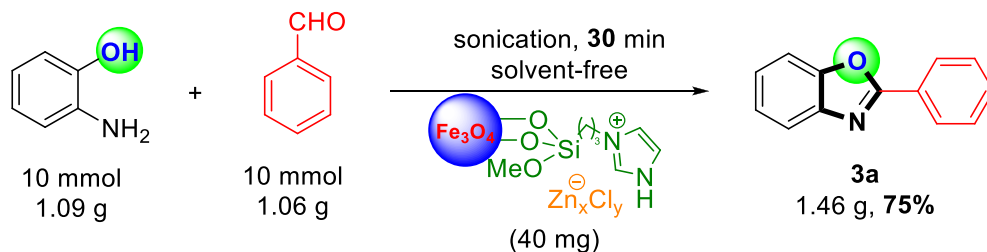


Figure 4. Gram-scale synthesis of 2-phenylbenzoxazole.

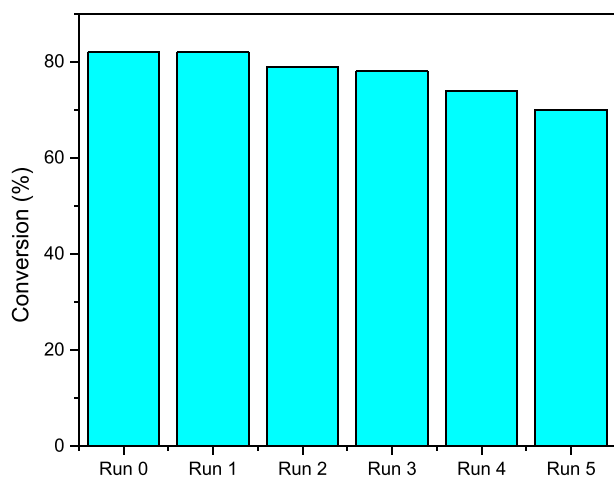


Figure 5. Reuse of LAIL@MNP in the preparation of 2-phenylbenzoxazole.

(purity $\geq 99.5\%$), ethanol (water $\leq 0.10\%$), and chloroform (purity $\geq 99\%$) were obtained from Xilong Chemical Co., Ltd (China). Sulfuric acid, hydrochloric acid, acetic acid, FeCl_3 , choline chloride, $[\text{EMIM}]\text{Cl}$, and $[\text{BMIM}]\text{BF}_4$ were purchased from Merck and used without any further purification.

Gas chromatography-mass spectrometry measurements were carried out on an Agilent GC System 7890 equipped with a mass selective detector (Agilent 5973N) and a capillary DB-5MS column ($30\text{ m} \times 250\ \mu\text{m} \times 0.25\ \mu\text{m}$) with NIST 2014. The ^1H spectra were recorded on a Bruker Advance 500 instruments using CDCl_3 as solvent and solvent peaks or TMS as internal standards. Ultrasonic irradiation-assisted reactions were performed on an Elma sonic S30H at the frequency of 37 kHz.

3.2. General procedure for the synthesis of LAIL@MNP

The LAIL@MNP was synthesized according to our previous literature (Nguyen et al., 2018, 2020) and checked by FT-IR, Raman, TGA, SEM, TEM, ICP-OES, and EDS before LAIL@MNP was used for condensation/cyclization reaction to synthesize benzoxazole, benzothiazole

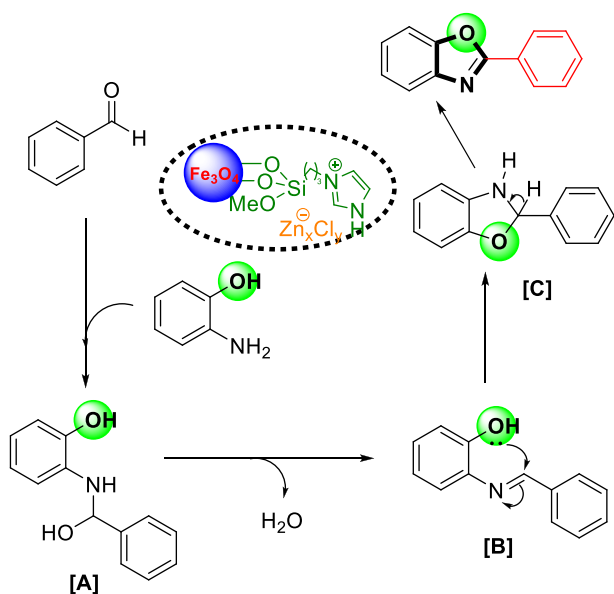


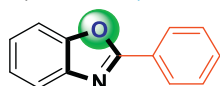
Figure 6. Possible mechanism of the synthesis of 2-phenylbenzoxazole.

derivatives from 2-aminophenols/2-aminothiophenols and aromatic aldehydes under solvent-free ultrasound irradiation.

3.3. General procedure for the synthesis of benzoxazole

A mixture of 2-aminophenol (0.109 g, 1.0 mmol), benzaldehyde (0.106 g, 1.0 mmol), and LAIL@MNP (4.0 mg) was sonicated at 70 °C in 30 min. After completing the reaction (monitored by GCMS), ethyl acetate (15 mL) was added to the reaction mixture, and the catalyst was recovered from the reaction mixture by an external magnet. The organic layer was dried with magnesium sulfate, and the solvent was removed under a vacuum. The conversion based on the consumption of benzaldehyde was reported by GCMS analysis. The magnetic catalyst was washed organic solvent and was dried under 80 °C for reuse in the next run. The purification of the product was carried out by column chromatography using silica and acetone/*n*-hexane (10:90). The identity of the product was confirmed by melting point, ¹H NMR, and GC-MS spectra in comparison with the previous literature. The other derivatives were prepared using the same procedure.

2-Phenylbenzoxazole (3a) (Sirgamalla et al., 2020; Tang et al., 2020; Zhou et al., 2020)

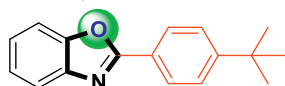


White solid, mp = 102–103 °C

¹H NMR (500 MHz, CDCl₃): δ = 8.10–8.08 (m, 2H), 7.60–7.58 (m, 1H), 7.41–7.38 (m, 1H), 7.36–7.33 (m, 3H), 7.21–7.18 (m, 2H).

GC-MS (EI, 70 eV) *m/z*: 51, 63, 77, 92, 103, 115, 139, 167, 195.

2-(4-*tert*-Butylphenyl)benzoxazole (3b) (Layek et al., 2020; Sirgamalla et al., 2020)

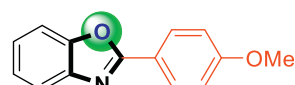


White solid, mp = 107–108 °C

¹H NMR (500 MHz, CDCl₃): δ = 8.19 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 7.78–7.76 (m, 1H), 7.59–7.57 (m, 1H), 7.55 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 7.35–7.34 (m, 2H), 1.38 (s, 9H).

GC-MS (EI, 70 eV) *m/z*: 51, 63, 77, 89, 104, 116, 128, 140, 152, 167, 180, 196, 208, 220, 236, 251.

2-(4-Methoxyphenyl)benzoxazole (3c) (Sirgamalla et al., 2020; Tang et al., 2020; Zhou et al., 2020)

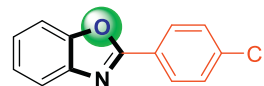


White solid, mp = 98–100 °C

¹H NMR (500 MHz, CDCl₃): δ = 8.20 (d, *J* = 9.0 Hz, 2H), 7.75–7.72 (m, 1H), 7.57–7.55 (m, 1H), 7.35–7.30 (m, 2H), 7.04 (dt, *J* = 2.5 Hz, 9.0 Hz, 2H), 3.90 (s, 3H).

GC-MS (EI, 70 eV) *m/z*: 51, 63, 77, 90, 102, 112, 127, 140, 153, 182, 194, 210, 225.

2-(4-Chlorophenyl)benzoxazole (3d) (Sirgamalla et al., 2020; Tang et al., 2020; Yang, 2020; Zhou et al., 2020)

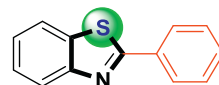


White solid, mp = 146–147 °C

¹H NMR (500 MHz, Acetone-*d*₆): δ = 8.25 (d, *J* = 9.0 Hz, 2H), 7.80 (d, *J* = 1.5 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 9.0 Hz, 2H), 7.46 (dd, *J* = 2.0 Hz, 1H).

GC-MS (EI, 70 eV) *m/z*: 50, 63, 75, 92, 100, 111, 137, 166, 194, 201, 209, 229.

2-Phenylbenzothiazole (3e) (Choi et al., 2020; Zhang et al., 2019)

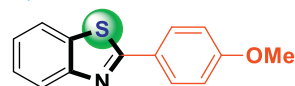


White solid, mp = 124–125 °C

¹H NMR (500 MHz, CDCl₃): δ = 8.12–8.08 (m, 3H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.51–7.48 (m, 4H), 7.40–7.37 (m, 1H).

GC-MS (EI, 70 eV) *m/z*: 51, 58, 69, 82, 92, 108, 121, 139, 152, 167, 184, 196, 211.

2-(4-Methoxyphenyl)benzothiazole (3f) (Choi et al., 2020; Zhang et al., 2019)



White solid, mp = 123–124 °C

¹H NMR (500 MHz, CDCl₃): δ = 8.05–8.02 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.49–7.45 (m, 1H), 7.37–7.34 (m, 1H), 7.00 (dt, *J* = 3.0 Hz, 9.0 Hz, 2H), 3.89 (s, 3H).

GC-MS (EI, 70 eV) *m/z*: 69, 198, 226, 241.

2-(Pyridin-4-yl)benzothiazole (3g) (Nale and Bhanage, 2015)

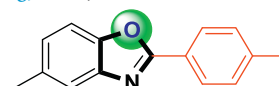


White solid, mp = 127–128 °C

¹H NMR (500 MHz, CDCl₃): δ = 7.17–7.14 (m, 4H), 7.72–7.70 (m, 2H), 6.59 (td, *J* = 1.5 Hz, 8.0 Hz, 2H).

GC-MS (EI, 70 eV) *m/z*: 51, 69, 82, 92, 108, 122, 141, 160, 186, 197, 212.

5-Methyl-2-(*p*-tolyl)benzoxazole (3h) (Sirgamalla et al., 2020; Yang, 2019, 2020)

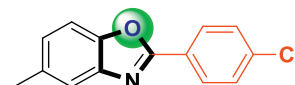


White solid, mp = 134–135 °C

¹H NMR (500 MHz, CDCl₃): δ = 8.13 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 3.0 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H).

GC-MS (EI, 70 eV) *m/z*: 51, 63, 78, 91, 111, 120, 152, 165, 180, 194, 208, 223

5-Methyl-2-(4-chlorophenyl)benzoxazole (3i) (Sirgamalla et al., 2020)

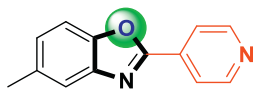


White solid, mp = 124–125 °C

$^1\text{H NMR}$ (500 MHz, Acetone- d_6): δ = 8.17 (d, J = 8.0 Hz, 2H), 7.54 (s, 1H), 7.49 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 2.49 (s, 3H).

GC-MS (EI, 70 eV) m/z : 51, 63, 78, 87, 106, 121, 139, 152, 180, 206, 214, 243

5-Methyl-2-(pyridin-4-yl)benzoxazole (3j) (Sirgamalla et al., 2020)

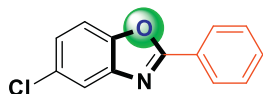


White solid, mp = 129–130 °C

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 8.81 (d, J = 5.5 Hz, 2H), 8.08 (d, J = 6.0 Hz, 2H), 7.61 (s, 1H), 7.50 (d, J = 8.5 Hz, 1H), 2.51 (s, 3H).

GC-MS (EI, 70 eV) m/z : 51, 63, 78, 91, 106, 132, 154, 166, 181, 195, 210.

5-Chloro-2-phenylbenzoxazole (3k) (Ge et al., 2020; Sirgamalla et al., 2020; Zhou et al., 2020)

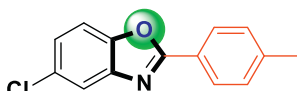


White solid, mp = 102–104 °C

$^1\text{H NMR}$ (500 MHz, Acetone- d_6): δ = 8.26 (dd, J = 1.5 Hz, 8.0 Hz, 2H), 7.80 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.66–7.61 (m, 3H), 7.44 (dd, J = 2.0 Hz, 8.5 Hz, 1H).

GC-MS (EI, 70 eV) m/z : 98, 126, 166, 201, 229.

5-Chloro-2-(*p*-tolyl)benzoxazole (3l) (Sirgamalla et al., 2020; Yang, 2020)

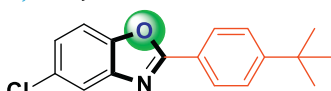


White solid, mp = 138–140 °C

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 8.12 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.30 (dd, J = 2.0 Hz, 8.5 Hz, 1H), 2.44 (s, 3H).

GC-MS (EI, 70 eV) m/z : 51, 63, 76, 91, 98, 116, 126, 152, 180, 208, 215, 243.

5-Chloro-2-(4-*tert*-butylphenyl)benzoxazole (3m) (Sirgamalla et al., 2020)

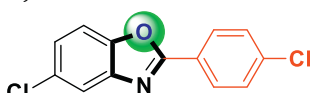


White solid, mp = 140–142 °C

$^1\text{H NMR}$ (500 MHz, Acetone- d_6): δ = 8.19 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 2.0 Hz, 1H), 7.68 (d, J = 8.5 Hz, 2H), 7.43 (dd, J = 2.0 Hz, 8.5 Hz, 1H), 1.39 (s, 9H).

GC-MS (EI, 70 eV) m/z : 51, 63, 77, 89, 98, 121, 135, 144, 164, 178, 191, 207, 230, 242, 254, 270, 285.

5-Chloro-2-(4-chlorophenyl)benzoxazole (3n) (Sirgamalla et al., 2020)

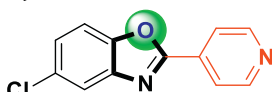


White solid, mp = 190–192 °C

$^1\text{H NMR}$ (500 MHz, Acetone- d_6): δ = 8.26 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.67 (td, J = 2.0 Hz, 8.5 Hz, 2H), 7.46 (dd, J = 2.0 Hz, 8.5 Hz, 1H).

GC-MS (EI, 70 eV) m/z : 50, 63, 75, 87, 98, 111, 126, 137, 164, 175, 200, 235, 263.

5-Chloro-2-(pyridin-4-yl)benzoxazole (3o) (Sirgamalla et al., 2020)



White solid, mp = 152–153 °C

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 8.84 (d, J = 5.0 Hz, 2H), 8.07 (d, J = 5.5 Hz, 2H), 7.81 (s, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H).

GC-MS (EI, 70 eV) m/z : 51, 63, 78, 88, 98, 115, 126, 140, 167, 177, 204, 230.

4. Conclusions

We have developed a green method for the synthesis of benzoxazoles and benzothiazoles in the presence of a catalytic amount of the LAIL@MNP under solvent-free ultrasound irradiation. Using this protocol, 15 derivatives of benzoxazoles and benzothiazoles were synthesized with moderate to good yields (from 21 to 90%). The LAIL@MNP catalyst could be separated easily from the reaction mixture by a magnet and reused several times to synthesize benzoxazole without a considerable decline in catalytic activity. The work-up simplicity, mild reaction conditions, and recyclability of the LAIL@MNP are the outstanding features of the current work.

Declarations

Author contribution statement

Hai Truong Nguyen: Performed the experiments; Wrote the paper.

Trinh Hao Nguyen: Performed the experiments.

Dung Duc Pham; Phuong Hoang Tran: Conceived and designed the experiments; Wrote the paper.

Cong Tien Nguyen: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at <https://doi.org/10.1016/j.heliyon.2021.e08309>.

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