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RESEARCH ARTICLE

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N-alkyl imidazole-based homonuclear coordination complex as a neutral organocatalyst for the faster and efficient construction of 3,4-dihydro-2*H*-1,3-oxazine scaffold

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Abstract

In the present work, homonuclear coordination complex including Zn (II) and *N*-hexadecylimidazole ligand was used for the first time as a highly efficient homogeneous neutral organocatalyst for the synthesis of 3,4-dihydro-2*H*-1,3-benzoxazine monomers. Therefore, *N*-alkyl or *N*-aryl substituted, both mono-benzoxazine and bis-benzoxazine, were successfully synthesized (21 examples) via Mannich-type condensation reactions. Effortlessly obtaining the pure product with high yields and the short reaction time makes this method more useful and advantageous than the common existing benzoxazine synthesis methods.

KEYWORDS

1,3-benzoxazines, metal complex catalyst, multicomponent synthesis, *N*-alkylimidazole, two-component synthesis

1 | INTRODUCTION

Compounds bearing the dihydro-1,3-benzoxazine ring system exhibit a wide range of biological activity.[1–5] The recently synthesized nonionic, cationic, and anionic polybenzoxazine surfactants draw attention with their alternative more advanced properties in comparison with conventional surfactants.[6–8] On the other hand, polybenzoxazines exhibit superior properties than previously well-known phenol-based resins.[9–11] Recently, Yildirim et al. reported thermally curable benzoxazine-modified renewable bio-resource based on triglyceride oils[12] and Raicopol et al. also reported triglyceride based polybenzoxazine derivatives as coatings on Zn–Mg–Al alloy coated steel which can act as a corrosion protection layer.[13] It can be concluded that benzoxazine-based monomeric compounds can play a key role in the development of advanced multifunctional polymeric materials with unique advantages. Since these compounds can be synthesized from large varieties of phenolic compounds and amines containing different substituents, they can have very different molecular structures.[10,14] Therefore, the two most general approaches for the preparation of compounds having this fused ring system are syntheses based on three-component and two-component Mannich-type condensation reactions (Figure 1). In order to achieve the synthesis via the three-component and the two-component condensation reactions, the most commonly used reagents are shown in Figure 1. As seen in the figure, naphthols or phenols, alkyl or arylamines are reacting with formaldehyde (*Route I*), and secondary alkyl or arylamines bearing naphthol or phenol moiety are reacting with formaldehyde (*Route II*). Noncatalyzed reactions, including both of these routes, usually require quite long reaction times, and in some cases no product was obtained.[15]

Many approaches in the literature, revealing the synthesis methods of this class of compounds, often have some disadvantages, such as long condensation time, high temperatures, and consequent formation of by-products through polymerization and low product yields.[5,8,9,16–21] On the other hand, a comprehensive

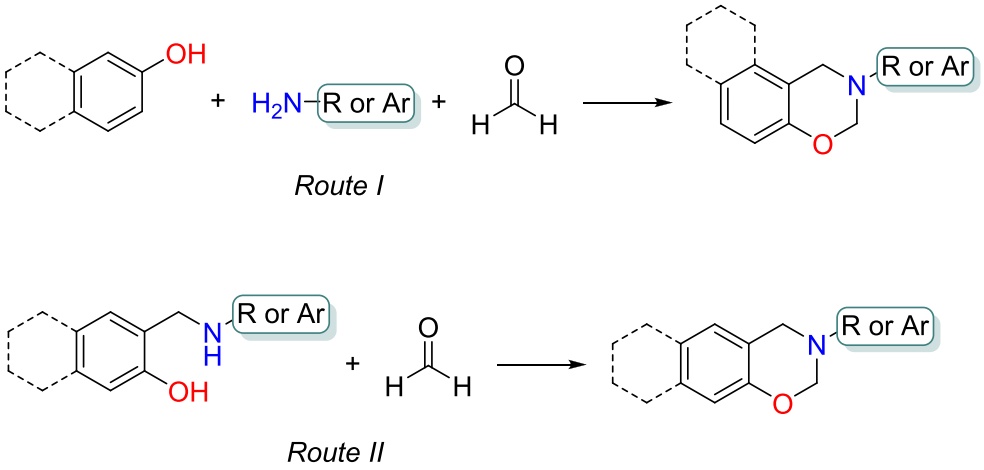


FIGURE 1 Routes of multicomponent and two-component construction of dihydro-1,3-oxazine ring system

literature review reveals that many different compounds have been investigated to catalyze these multicomponent condensation reactions.[2,15,22,23]

Many green methods have also been developed for the synthesis of 1,3-oxazines.[1,20,23–29] Unfortunately, in some of these studies, acidic catalysts are used, while in some cases it is necessary to interact with strong bases during product isolation and laborious techniques such as extraction and column chromatography that are applied. According to Tang et al., no product was formed although a secondary amine and formaldehyde were refluxed in chloroform for 5 h in the presence of Et_3N or in the absence of any catalyst.[15] In addition, very low yields of benzoxazines were obtained in the presence of different acidic catalysts. In the case of metal salts, overloading of the catalyst and long reaction times is required for higher product yields. The use of acids or bases, either as catalysts or in product isolation stages, may cause structural changes in starting compounds and products which have functional groups with high tendency toward effects of strong acids and bases. Therefore, for the preparation of benzoxazines, the development of mild and neutral catalysts, without such undesirable side-effects, is gaining importance. In addition, some different synthesis strategies for the preparation of these compounds continue to be developed. Multicomponent synthesis of bio-based benzoxazines from cardanol by using a deep eutectic solvent[30] and a modified method based on arylboronic acids has also been described.[31] Vengatesan et al. reported ultrasound-assisted synthesis of benzoxazine monomers.[32]

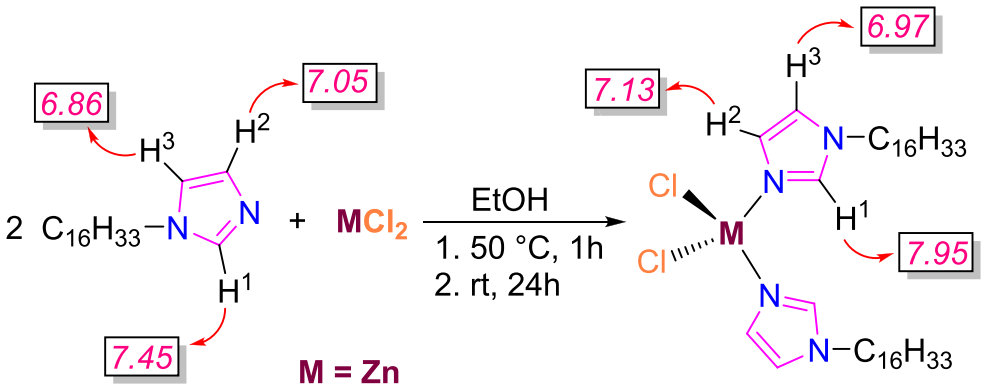
N-alkyl and/or *N*, *N*-dialkylated imidazoles and their modified derivatives have been used as catalysts in the synthesis of 1,3-oxazines and variety of organic compounds.[23,33–37] Some transition metal complexes of *N*-alkylated imidazoles have been used as catalyst in several different organic synthesis reactions.[38–41] In continuation of our focus on the *N*-alkylated imidazole-based organocatalyst systems and to the best of our knowledge, metal complexes of higher *N*-alkylated imidazoles have not yet been used as catalysts for the producing of 3,4-dihydro-2*H*-1,3-benzoxazines. Therefore, in the present study, symmetric metal complex compound was prepared by reacting Zn (II) chloride with *N*-hexadecylimidazole ligand, and thus, synthesized neutral compound was used as a catalyst for the preparation of a series of 3,4-dihydro-2*H*-1,3-benzoxazines via two-component or multicomponent Mannich-type condensation reaction.

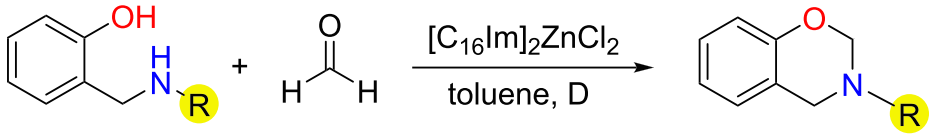
2 | RESULTS AND DISCUSSION

2.1 | Synthesis of catalyst ($[C_{16}Im]_2MCl_2$)

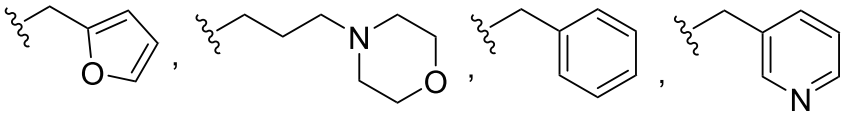
The neutral organocatalyst used in this study was synthesized easily under the reaction conditions[42,43] shown in Scheme 1, and for this purpose, the required starting ligand, 1-hexadecyl-1*H*-imidazole was prepared in accordance to previously published procedure.[44] As seen in the figure, the metal complex compound was prepared by the reaction of two equivalents of 1-hexadecyl-1*H*-imidazole with one equivalent of anhydrous zinc chloride in EtOH and the complex product precipitates, whose solubility decreases in EtOH due to the long alkyl side chains. Complexation between zinc metal and 1-hexadecyl-1*H*-imidazole ligand caused changes in the ^{1}H NMR chemical shift of ligand (Scheme 1). The imidazole ring protons which correspond to the protons in carbon atoms of the heterocyclic system appeared as singlet, and each singlet corresponds to a single proton (three protons in total). On the other hand, a *triplet* peak and a *quintet* peak belonging to two protons located on the –$NC\underline{H}_2CH_2$– and –$NCH_2C\underline{H}_2$– carbon atoms of the

SCHEME 1 Synthesis of catalyst $[C_{16}Im]_2ZnCl_2$



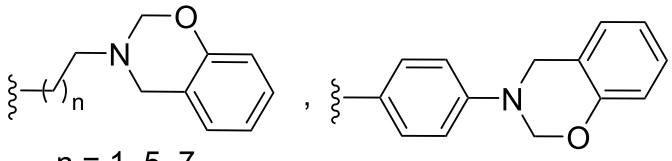


R *Ph*, *p*-CH_3*Ph*, *p*-CH_3O*Ph*, *p*-EtOPh, *p*-Cl*Ph*, *p*-Br*Ph*, **1a-n**
p-NO_2*Ph*, *p*-COOEtPh, CH_2CH_2*Ph*, 2-Cl-6-CH_3*Ph*
optimum reaction conditions: catalyst (2 mmol%), time (10 min), temperature (90 °C)



optimum reaction conditions: catalyst (2.5 mmol%), time (15 min), temperature (90 °C)

R



2a-d

n = 1, 5, 7

optimum reaction conditions: catalyst (2.5 mmol%), time (15 min), temperature (90 °C)

R $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ **3a-c**
optimum reaction conditions: catalyst (2.5 mmol%), time (15 min), temperature (90 °C)

SCHEME 2 Two-component synthesis of benzoxazine monomers

hexadecyl alkyl side chain attached to the N atom in the imidazole ring were observed at 3.96 and 1.78 ppm, respectively. Because of decrease in the electron, density of the imidazole ring yields downfield shifts at all ring positions. Thus, the downfield shifts of imidazole ring protons in the complex, compared with free 1-hexadecyl-1*H*-imidazole ligand, confirm the successful synthesis of the desired complex compound.

2.2 | Synthesis of benzoxazine monomers

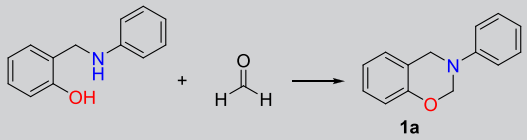
A series of 3,4-dihydro-2*H*-1,3-benzoxazines (21 examples) were synthesized based on 2-((alkylamino)methyl)phenols or 2-((arylamino)methyl)phenols as secondary amines with the assistance of $[C_{16}Im]_2ZnCl_2$ as presented in Scheme 2. The starting secondary amines (Mannich

bases) were prepared readily and with good yields, via common two step reactions from salicylaldehyde and different primary amines. For this, the corresponding Schiff bases were first obtained and then reduced with $NaBH_4$ to give secondary amines. The 1,3-benzoxazine ring formation was achieved by reacting the corresponding 2-((arylamino)methyl)phenols or 2-((alkylamino)methyl)phenols with 2 equivalent of paraformaldehyde in the presence of appropriate amount of the catalyst, $[C_{16}Im]_2ZnCl_2$ in toluene for 10 to 15 min (Tables 1 and 2). After the reaction is complete, the solvent was removed and the remaining residue was crystallized from the appropriate solvent mixture to obtain the corresponding benzoxazines with good to excellent yields. As can be seen from Table 1, when using the imidazole complex containing the cobalt transition metal as the catalyst, the corresponding benzoxazine **1a** was obtained with lower yield than the reaction carried out with the catalyst containing the zinc metal. Therefore, in the present paper, optimization studies and the synthesis reactions of all benzoxazine compounds were carried out with the catalyst containing zinc as metal.

When the reaction temperature is increased by 10°C, the yields of benzoxazines decrease slightly, most likely due to the formation of polymeric by-products during the condensation between paraformaldehyde and 2-((arylamino)methyl)phenols or 2-(alkylamino)methyl) phenols (Table 1, Entry 3, and Table 2, Entry 5). In addition, it was observed that the increase in the amount of catalyst in the condensation reaction with 2-((phenylamino)methyl)phenol significantly reduced the yield of the corresponding benzoxazine (Table 1, Entry 4). Thus, it is concluded that the optimum reaction conditions for condensation paraformaldehyde with 2-((arylamino)methyl)phenols or 2-((alkylamino)methyl) phenols are as indicated in Table 1, Entry 1, and Table 2, Entry 4, respectively.

In the case of preparation of benzoxazines in aqueous medium, the oxazine ring is usually opened and unwanted oligomeric side products are formed in the

TABLE 1 Optimization of reaction conditions for the synthesis of benzoxazines from 2-((arylamino)methyl)phenols



Entry	Catalyst	Catalyst loading (mmol%)	Time (min)	Temperature (°C)	Yield (%)[a]
1	ImZn	2	10	90	96
2	ImZn	2	15	90	75
3	ImZn	2	10	100	43
4	ImZn	2.5	10	90	59
5	ImCo	2	10	90	41

[a]Yields after crystallization from MeOH/H_2O.

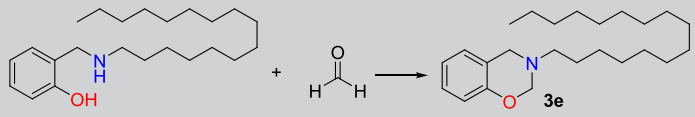
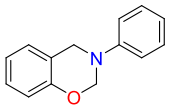
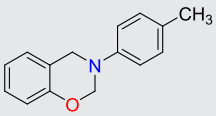
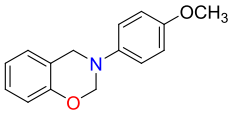
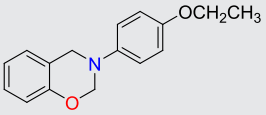
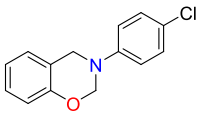
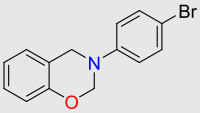
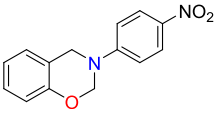
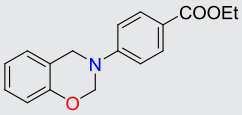


TABLE 2 Optimization of reaction conditions for the synthesis of benzoxazines from 2-((alkylamino) methyl)phenols

Entry	Catalyst loading (mmol%)	Time (min)	Temperature (°C)	Yield (%)[a]
1	2	10	90	92
2	2	15	90	90
3	2	20	90	87
4	2.5	15	90	97
5	2.5	15	100	83

[a]Yields after crystallization from MeOH/H_2O.

TABLE 3 Structures of benzoxazines synthesized in the presence of $[C_{16}Im]_2ZnCl_2$ catalyst

Entry	Compound	Structure	Yield (%)[a]
1	**1a**		85
2	**1b**		89
3	**1c**		89
4	**1d**		76
5	**1e**		64
6	**1f**		77
7	**1g**		76
87	**1h**		69

(Continues)

TABLE 3 (Continued)

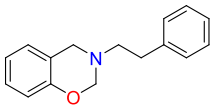
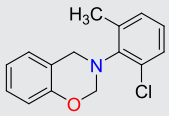
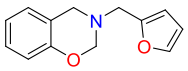
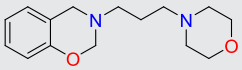
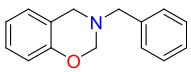
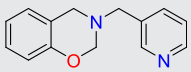
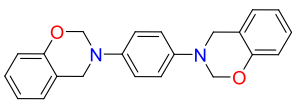
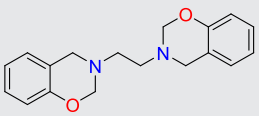
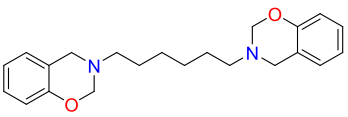
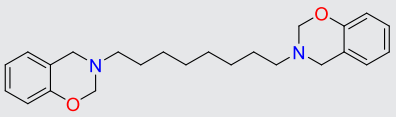
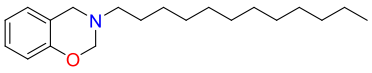
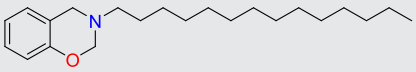
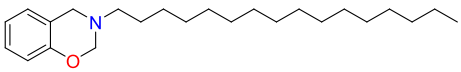
Entry	Compound	Structure	Yield (%)[a]
9	**1i**		89
10	**1j**		70
11	**1k**		89
12	**1l**		76
13	**1m**		89
14	**1n**		90
15	**2a**		75
16	**2b**		92
17	**2c**		95

TABLE 3 (Continued)

Entry	Compound	Structure	Yield (%)[a]
18	**2d**		95
19	**3a**		96
20	**3b**		96
21	**3c**		97

[a]Yields after crystallization from MeOH/H_2O.

reaction medium.[45] Therefore, to increase the benzoxazine yield, paraformaldehyde is preferred instead of formalin, and nonpolar solvents such as toluene are generally preferred as solvents. Therefore, we preferred to perform condensation reactions between secondary amines and paraformaldehyde in toluene as a most reliable method for the synthesis of 1,3-benzoxazine monomers. In order to evaluate the substrate scope of the condensation procedure developed in the present work, we used a variety of secondary amines for the synthesis of 1,3-benzoxazine monomers. All of these attempts showed that either aryl or alkyl substituted secondary amine as starting compounds can provide the corresponding 1,3-benzoxazines with good to excellent yields in the presence of $[C_{16}Im]_2ZnCl_2$ as an efficient organocatalyst. The structures of all the benzoxazines synthesized within the scope of this work are given in Table 3. As can be seen from the table, the (2-((alkylamino)methyl)phenols) formed the related benzoxazines with higher yields than (2-((arylamino)methyl)phenols) (Entries 15–20). On the other hand, generally, the (2-((arylamino)methyl)phenols) with electron-withdrawing groups on the amine-based aryl ring gave slightly lower yields than those with electron-donating groups. The reason for these higher benzoxazine yields can be attributed to the fact that the nucleophilic characters of the amino groups in (2-((alkylamino)methyl)phenols) are higher than that of the *N*-aryl substituted amines.

The molecular structures of all the synthesized 1,3-benzoxazines were established on the basis of their spectroscopic data (^{1}H NMR, ^{13}C NMR, and Fourier Transform Infrared (FTIR)) and elemental analysis. For the benzoxazine **1a**, representative ^{1}H NMR and ^{13}C NMR spectra are given in Figure 2. The ^{1}H NMR spectrum of **1a** showed characteristic two clear singlet signals at 4.62 and 5.35 ppm, corresponding to the two protons each in the 1,3-oxazine ring (Ar$C\underline{H}_2$N– and –N$C\underline{H}_2$O–, respectively). On the other hand, when the ^{13}C NMR spectrum of this compound is examined, it is seen that the characteristic signals of the C atoms in the Ar$C\underline{H}_2$N– and –N$C\underline{H}_2$O– groups appear at 50.4 and 79.5 ppm, respectively.

The fact that the $[C_{16}Im]_2ZnCl_2$ catalyst facilitates the synthesis of 1,3-benzoxazines via the two-component condensation reaction has encouraged us to investigate the catalytic activity of this complex compound for the synthesis of abovementioned compounds through the three-component condensation reaction. For this purpose, hexadecyl amine, phenol, and paraformaldehyde were reacted under the reaction conditions shown in Table 4. As can be seen from the table, with the assistance of this catalyst, benzoxazines can also be successfully synthesized following a three-component reaction strategy. For instance, the benzoxazine **3e** was obtained in good yield by using this synthesis strategy. (Table 4, Entry 6).

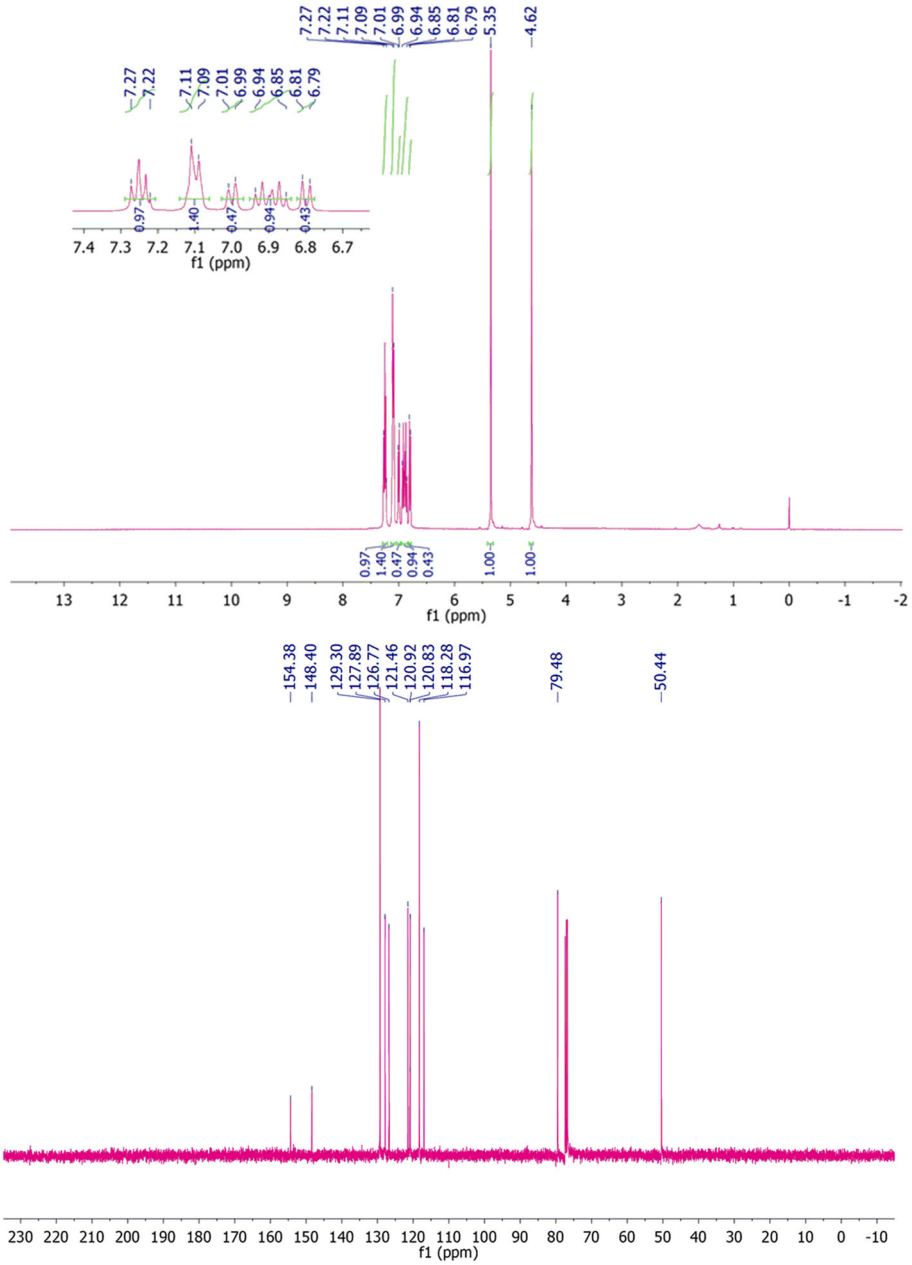


FIGURE 2 ^{1}H NMR and ^{13}C NMR spectra of benzoxazine **1a**

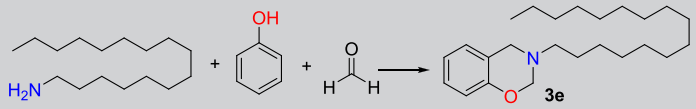
2.3 | Reusing of the reaction medium

In order to investigate reusability of the catalyst, 2-((phenylamino)methyl)phenol and paraformaldehyde were treated under the optimum condensation reaction conditions given in Table 1, Entry 1. After the reaction was complete, the solvent was removed and the residue was crystallized from the MeOH/H_2O system. After isolation of the desired product, the resulting filtrate was evaporated to dryness and the remaining crude catalyst was used directly in the next similar runs without further purification. The results obtained are given in Table 5. According to the yields obtained, it can be concluded that the synthesized catalyst is convenient to use two times without a significant loss in its activity.

2.4 | Plausible mechanism of $[C_{16}Im]_2ZnCl_2$ catalyzed two-component condensation reaction

The catalytic two-component condensation reaction between paraformaldehyde and (2-((hexadecylamino)methyl)phenol) is considered to proceed through the mechanism shown in Figure 3. Formaldehyde molecule interacts via its unpaired electrons on the carbonyl oxygen atom with the zinc atom of catalyst $[C_{16}Im]_2ZnCl_2$ which act as an electron pair acceptor. Thus, the amino group on the Mannich base readily makes a nucleophilic attack on the carbonyl group of the aldehyde molecule to form a tetrahedral intermediate. Following a proton migration, the related

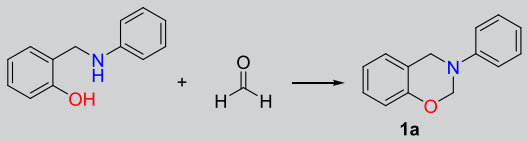
TABLE 4 Optimization of reaction conditions for the three-component synthesis of benzoxazines



Entry	Catalyst loading (mmol%)	Time (h)	Temperature (°C)	Yield (%)[a]
1	2	3	110	83
2	2.5	3	110	75
3	2	4	110	75
4	2	3	120	Polymerization occurs, and product isolation is difficult
5	1	3	110	56
6	2	4	100	85
7	2	2	110	64
8	2	3	100	83
9	2	4	90	56

[a]Yields after crystallization from MeOH/H_2O.

TABLE 5 Catalyst reuse studies



Entry	Catalyst cycle	Catalyst loading (mmol%)	Time (min)	Temperature (°C)	Yield (%)[a]
1	1	2	10	90	96
2	2	2	10	90	94
3	3	2	10	90	69
4	4	2	10	90	57

[a]Yields after crystallization from MeOH/H_2O.

benzoxazine compound is formed via an intramolecular cyclization of *N*-(2-hydroxybenzyl)-*N*-methylenehexadecan-1-aminium intermediate.

In order to explain the catalytic effect of $[C_{16}Im]_2ZnCl_2$ in the condensation reaction, a different mechanistic approach was adopted and some simple theoretical calculations were also made. Geometry optimizations of the 2-(hexadecylamino)methyl)phenol, formaldehyde and $[C_{16}Im]_2ZnCl_2$ molecules were performed using the MM2 force field option through the Chem3D. The calculated Frontier Molecular Orbital (FMO) energetics of the abovementioned molecules with their optimized geometries are given in Figure 4. In Figure 4a, the energies of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) orbitals of the 2-(hexadecylamino) methyl)phenol and formaldehyde molecules are given, respectively, and the electron flow from the 2-(hexadecylamino)methyl)phenol molecule to formaldehyde molecule is also shown. On the other hand, in Figure 4b the energies of the LUMO and HOMO orbitals of the catalyst and formaldehyde molecules are given, respectively, and the electron flow from formaldehyde molecule to the catalyst molecule is also shown. As can be seen from Figure 4, the $LUMO_{catalyst}$ - $HOMO_{formaldehyde}$ energy gap is lower than the $HOMO_{2\text{-(hexadecylamino)methyl)phenol}}$ - $LUMO_{formaldehyde}$ (4.461 and 6.656 eV, respectively). Thus, after this favorable interaction with the catalyst, the formaldehyde molecule is more easily subjected to nucleophilic attack by

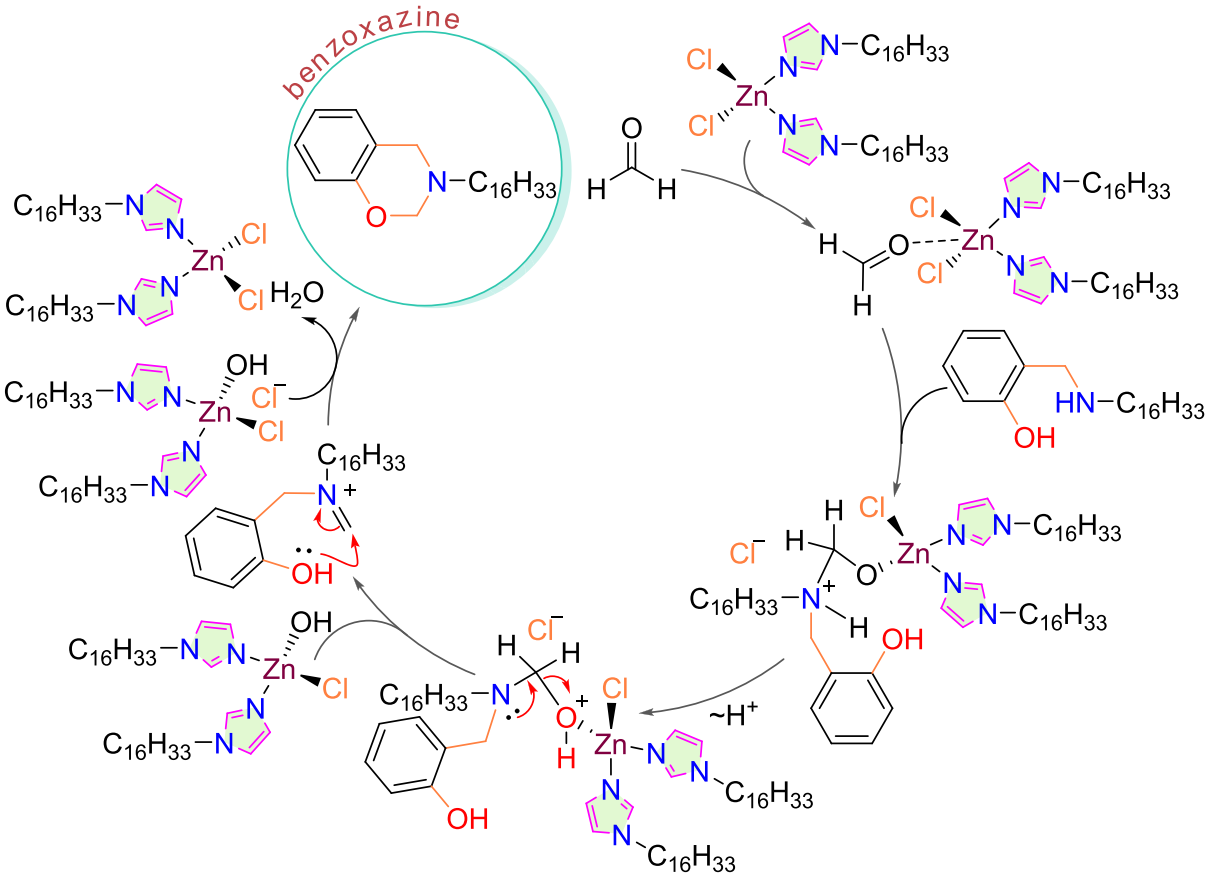


FIGURE 3 Proposed mechanistic pathway for the production of benzoxazines via the two-component condensation reaction

the 2-(hexadecylamino)methyl)phenol molecule as shown previously in Figure 3.

3 | CONCLUSIONS

As a result, the catalyst $[C_{16}Im]_2ZnCl_2$, prepared from *N*-alkylimdazole and anhydrous zinc chloride, is a highly efficient catalyst for the two- or three-component synthesis of many different types of 3,4-dihydro-2*H*-1, 3-benzoxazines. In this study, for the first time, an imidazole-based metal-containing compound was successfully used as a catalyst in the synthesis of 1,3-benzoxazines. This compound is very stable at room conditions and is not hygroscopic, so it can be stored easily and its use in condensation reactions is quite simple. The most important factors that make this invented practical method more considerable are its simplicity and very short reaction times (10–15 min). The condensation reaction can proceed at fairly low catalyst load (down to 2 mmol%) under mild reaction conditions.

4 | EXPERIMENTAL

4.1 | Reagents and analyses

All reagents and solvents were purchased from Merck (Merck, Darmstadt, Germany), Sigma-Aldrich (St. Louis, MO), or Acros Organics (Thermo Fisher Scientific, Geel, Belgium) and used without further purification. Thin layer chromatography was performed using silica gel (60 F_{254}, Merck, Darmstadt, Germany) plates. Melting points were recorded by BÜCHI melting pointB-540 apparatus (BÜCHI Labortechnik AG in Flawil, Switzerland). A Bruker Tensor II Fourier transform infrared (FT-IR) spectrometer (Billerica, MA, USA) was used for acquisition of the FT-IR spectra. The NMR spectra were measured using A600a Agilent DD2 600-MHz NMR spectrometer (Santa Clara, California, USA) and chloroform-d ($CDCl_3$) as a solvent. Chemical shifts (δ) are reported in ppm and *J* values in Hertz. The elemental analyses were performed using an LECO CHNS-932 elemental analyzer (Saint Joseph, MI, USA).

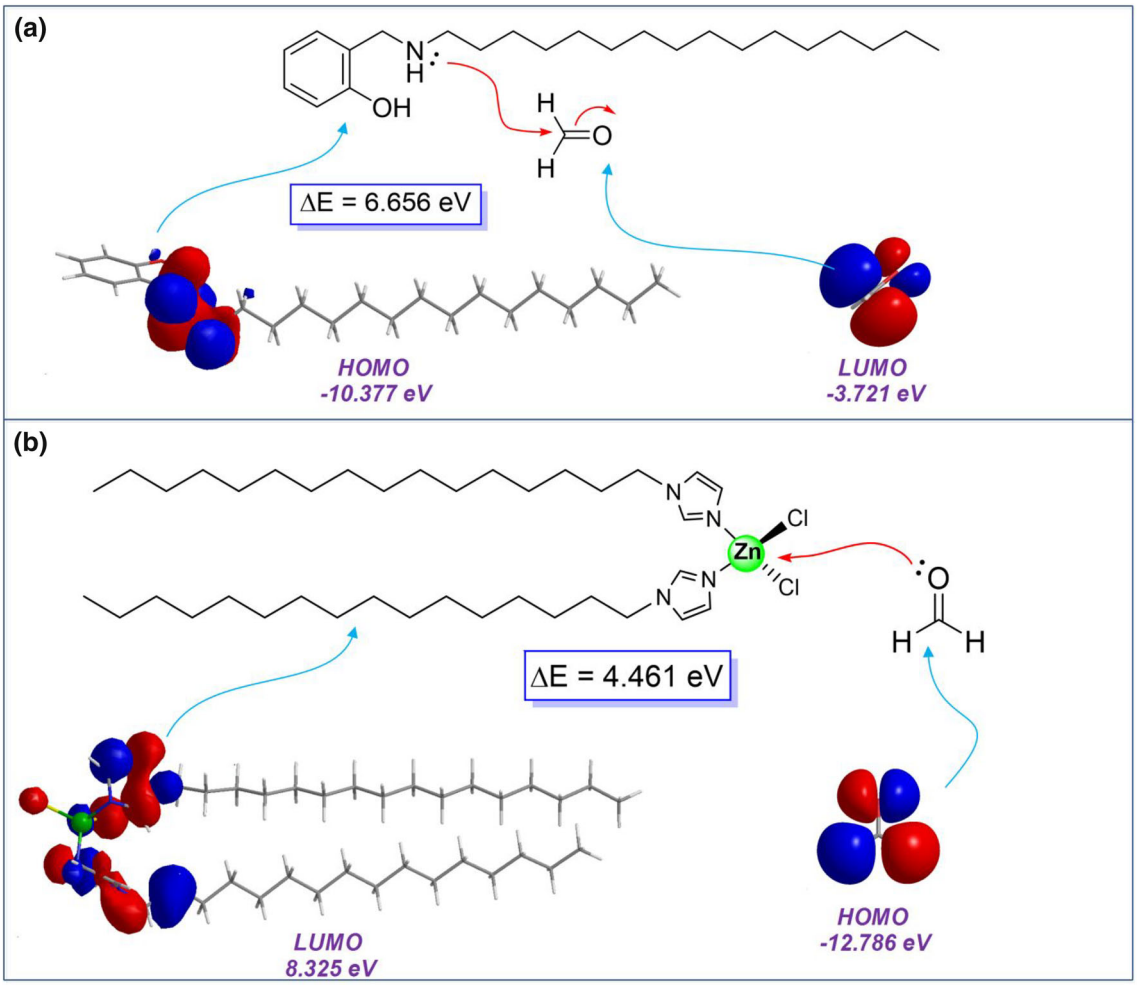


FIGURE 4 FMO orbitals of 2-(hexadecylamino)methyl)phenol, formaldehyde, catalyst, and energy gap

4.2 | Preparation of catalyst

Into a 50-ml flat bottom reaction flask anhydrous $ZnCl_2$ (0.12 g, 0.88 mmol) was added and dissolved in 10 ml of EtOH. With stirring at room temperature, 0.5 g of 1-hexadecyl-1*H*-imidazole dissolved in 10 ml of ethanol was added slowly and heated at 50°C for 1 h. The resulting mixture was then left at room temperature overnight, and the precipitated yellowish solid was filtered and washed with ether. The yield of the product was 0.5 g (41%) with mp: 102.4–103.2°C.

4.3 | Typical experimental procedure for the preparation of 1,3-benzoxazines from 2-((alkylamino)methyl)phenols

To a 50-ml round-bottomed flask containing 2 ml of toluene were added 2-((hexadecylamino)methyl)phenol (0.20 g, 0.58 mmol), paraformaldehyde (0.035 g, 1.16 mmol, 2 equivalent), and 2.5 mmol% of the catalyst. The flask was attached to a reflux condenser and heated under atmospheric conditions in an oil bath at 90°C for 15 min. Thereafter, the solvent was removed by rotary evaporator and the resulting solid product was crystallized from acetone–water solvent mixture to give pure 1,3-benzoxazine as a white crystalline solid.

4.4 | Typical experimental procedure for the three-component preparation of 1,3-benzoxazines

To a single-necked 50-ml reaction flask, 0.2 g, 0.83 mmol of hexadecylamine, 0.078 g, 0.83 mmol of phenol, 0.050 g, 1.66 mmol of paraformaldehyde, 2 mmol% of the catalyst, and 2-ml toluene were added. The flask was attached to a reflux condenser and heated under atmospheric conditions in an oil bath at 100°C for 4 h. Thereafter, the solvent was removed by rotary evaporator and the resulting solid product was crystallized from acetone–water solvent mixture to give pure 1,3-benzoxazine as a

white crystalline solid with sufficient purity for further spectroscopic analysis. (Supporting information includes characterization data and FTIR, ^{1}HNMR, ^{13}CNMR spectra of all the synthesized benzoxazines).

DATA AVAILABILITY STATEMENT

Data openly available in a public repository that issues datasets with DOIs.

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