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RESEARCH PAPER

# $SnCl_4$/Nano-Sawdust as an Efficient Bio-based Catalyst for the Synthesis of 2-Substituted Benzimidazoles and Benzothiazoles

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**ABSTRACT**

$SnCl_4$/nano-sawdust was prepared as a carbohydrate-based catalyst containing of tin bearing cellulose units. The catalyst was characterized by X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDS). The catalyst was applied successfully as a readily available, inexpensive, biodegradable and environmentally benign heterogeneous bio-based solid acid for the one pot synthesis of 2-substituted benzimidazoles and benzothiazoles.

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## INTRODUCTION

Benzimidazoles and benzothiazoles are among the most important N-containing five-membered heterocyclic compounds. They exhibit a wide range of biological activities [1] and have also been applied in dyes [2], liquid crystals [3], chemosensing [4], radioactive amyloid imaging agents [5], ligands for asymmetric transformations [6] and corrosion science [7]. Due to the wide range application of these compounds, their synthesis is an area of interest in synthetic chemistry. Therefore, a number of synthetic protocols have been developed for the synthesis of these class compounds [8-10]. The most common method for their synthesis is condensation of 1,2-phenylenediamine [11,12] or 2-aminothiphenols [13,14] with aldehydes in the presence of acid catalyst (Fig. 1).

Development of new solid acids with numerous advantages such as cost-effectiveness, environmentally benign, easy workup and good stability for one-pot synthesis of these heterocyclic compounds is still required. In this regard, our aim is developing cheap and bio- based solid acid catalysts for these condensation.

Sawdust is a natural, cheap, renewable and readily available source of cellulose with OH groups. In this work, we have investigated the synthesis of bio-based catalyst by bonding Lewis acids to OH groups of D-glucose units in sawdust. Pectin, lignin, proteins, minerals and tannin in sawdust which caused leaching in organic mediums must be removed. For this purpose, the pine sawdust was treated with NaOH, NaOCl, and $H_2O_2$, respectively. For preparation of nano-sawdust, the sawdust has been treated with concentrated $H_2SO_4$ for partial hydrolysis of its cellulose [15]. Then, in continuation of our previous efforts about supported catalysts [15-20] and $BF_3$/nano-sawdust

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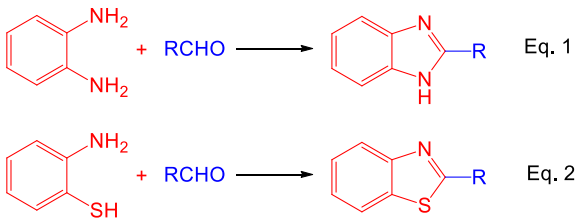



Fig. 1.The most common method for synthesis of 2-substituted benzimidazoles (Eq. 1) and 2-substituted benzothiazoles (Eq. 2)

[21], the nano-sawdust was used to synthesis of $SnCl_4$/nano-sawdust as a new, bio-based and green catalyst.

We have examined its catalytic behaviour for the synthesis of benzimidazoles and benzothiazoles under various conditions.

## MATERIALS AND METHODS

All chemicals and solvents were buy from the Merck and Fluka chemical companies in high purity. FT-IR spectra were obtained on an attenuated total reflectance fourier transform infrared (ATR-FTIR) spectrophotometer (Bruker, Eqinox 55). $^1$H NMR and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, on a Bruker DXR-400 spectrometer. Melting points were determined with a Buchi melting point B-540 B.V.CHI apparatus. X-ray diffraction (XRD) pattern was obtained in the 2θ range from 10 to 80° by a Philips Xpert MPD diffractometer equipped with a Cu Kα anode (k = 1.54 A°). Field emission scanning electron microscopy (FESEM) image was obtained on a Mira 3-XMU. Quantitative elemental information (EDS) of $SnCl_4$/nano-sawdust was obtained by SEM/EDS instrument, Phenom pro X.

*Preparation of nano-sawdust*

4 g of pine sawdust was treated with a solution of 17.5% w/v sodium hydroxide and refluxed for 12 hours, filtered and washed with water. The resulted fibres was then bleached with 100 ml of 1:1 diluted 5% w/v sodium hypochlorite and refluxed for 8 hours, filtered and washed with water. Then, the fibres were treated with 10 ml of 20% v/v hydrogen peroxide at 50 °C for 2 hours, filtered and washed with water. A mixture of the obtained fibres and sulphuric acid (65% $H_2SO_4$ with fibre to liquor ratio of 1:20) was mixed strongly for 2 hours at 60 °C. The resulted mixture was cooled to room temperature and diluted by distilled water. Then, the suspension was repeatedly centrifuged at 12000 rpm for 8 minutes using a refrigerated centrifuge (Appendorf Centrifuge 5417R). After each run, the nano-sawdust, as white powder, was washed with distilled water and centrifuged repeatedly till neutralization of the product.

*Preparation of $SnCl_4$/nano-sawdust*

In a ventilated room, by dropping funnel, $SnCl_4$ (1 mL) was charged drop wise in to a suspension of 1 g nano-sawdust and 10 mL of chloroform. The mixture was stirred for one hour at room temperature. The resulted mixture was filtered and the obtained white solid was washed with chloroform and dried at room temperature.

*Typical procedure for synthesis of 2-arylbenzimidazoles or 2-arylbenzothiazoles*

To a mixture of 1,2-phenylendiamine or 2-aminobenzothiazole (1mmol) and aldehyde (1.1mmol) in ethanol (10 ml), $SnCl_4$/nano-sawdust (0.08 g) was added. The reaction mixture was refluxed and the progress of the reaction was monitored by TLC (n-hexane/EtOAc, 7:3). After completion of reaction, the reaction mixture was filtered and washed with acetone. By addition of water to the concentrated filtrated, the solid product was appeared. The product was re-crystallized in ethanol to obtain pure product as a white solid.

## RESULTS AND DISCUSSION

For investigation of catalyst structure, we have studied the FT-IR (ATR) spectra of pine sawdust and $SnCl_4$/nano-sawdust (Fig. 2). In sawdust FT-IR spectrum, three strong bands at 3323, 2889 and 1025 $cm^{-1}$ were observed. In $SnCl_4$/nano-sawdust, in addition to the sawdust FTIR bands, one band also appeared at 1108 which verify the C-O-Sn group on the catalyst. The our proposed structure for $SnCl_4$/nano-sawdust is similar to the reported structure for cellulose triphosphate gels

(Fig. 3) [22].

The FESEM image of nano-sawdust and $SnCl_4$/nano-sawdust are shown in Fig. 4. According to the FESEM data, the particle size of catalyst is below 50 nm. Quantitative elemental information (EDS) of $SnCl_4$/nano-sawdust was measured by SEM/EDS instrument (Fig. 5). According to this data, the weight percentage of Sn, Cl and C are 45.4, 41.0 and 13.5 respectively.

The X-ray diffraction (XRD) pattern of $SnCl_4$/nano-sawdust is shown in Fig. 6. The values of 2θ and FWHM are shown in table 1. According to XRD pattern, the three signals in 2Θ equal to 15.13, 16.74 and 22.93 with FWHM equal to 0.472, 0.944, and 0.472 respectively, show the existence of sawdust. Other signals in 2Θ equal to 20.55, 28.56, 34.63 and 41.84 prove the bonding of Sn to sawdust backbone.

In this study, we have investigated the catalytic efficiency of $SnCl_4$/nano-sawdust for the synthesis of 2-substituted benzimidazoles and benzothiazoles via reaction of 1,2-phenylendiamine or 2-aminothiophenol with aromatic aldehydes. Synthesis of 2-phenyl-1H-benzimidazole (I) was examined under various condition for finding suitable condition for this preparation. As shown in table 2, entry 6, the most yield of reaction in condensation of benzaldehyde (1.1 mmol) and 1, 2-phenylenediamine (1 mmol) was achieved in the presence of 0.08 g $SnCl_4$/nano-sawdust and ethanol after 25 minutes reflux. Reusability of catalyst was investigated for three cycles (Table 2, entries 13–15). For this purpose after each run the reaction mixture was diluted with acetone and

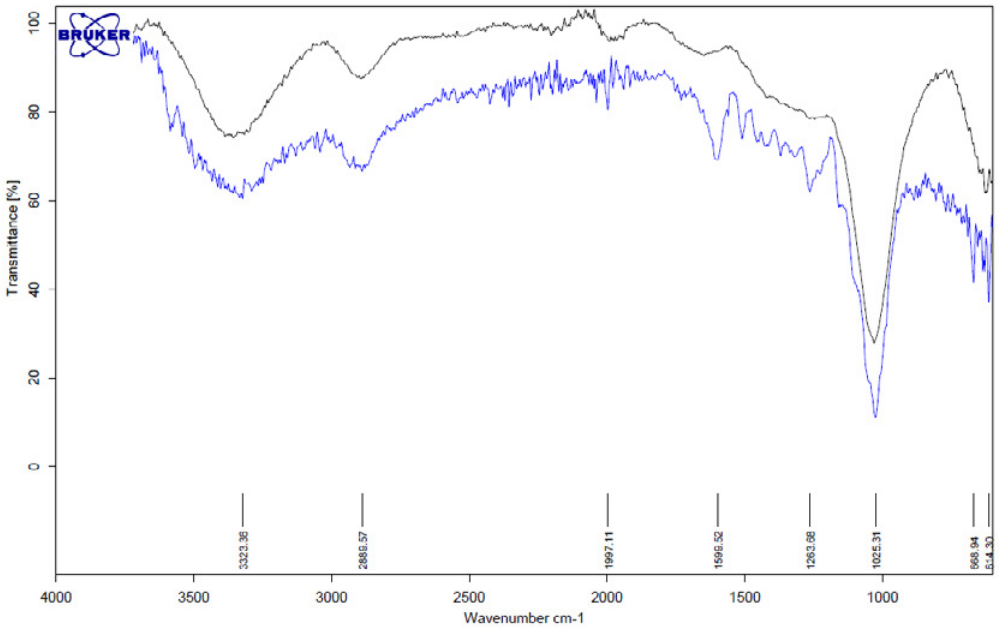



Fig. 2. FT-IR (ATR) spectra of (a) pine sawdust and (b) $SnCl_4$/nano-sawdust.

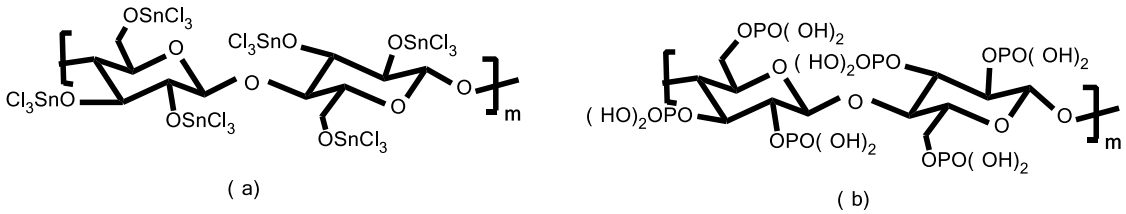



Fig. 3. Proposed structure for (a) $SnCl_4$/nano-sawdust and (b) cellulose triphosphate.

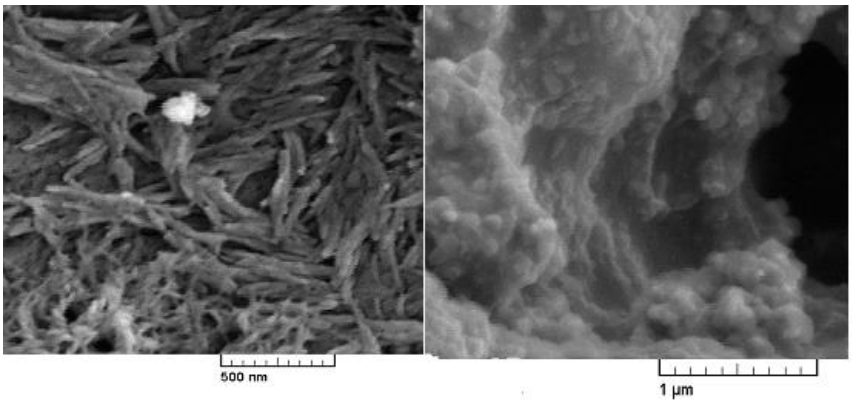



Fig. 4. The FESEM image of (a) nano-sawdust and (b) $SnCl_4$/nano-sawdust.

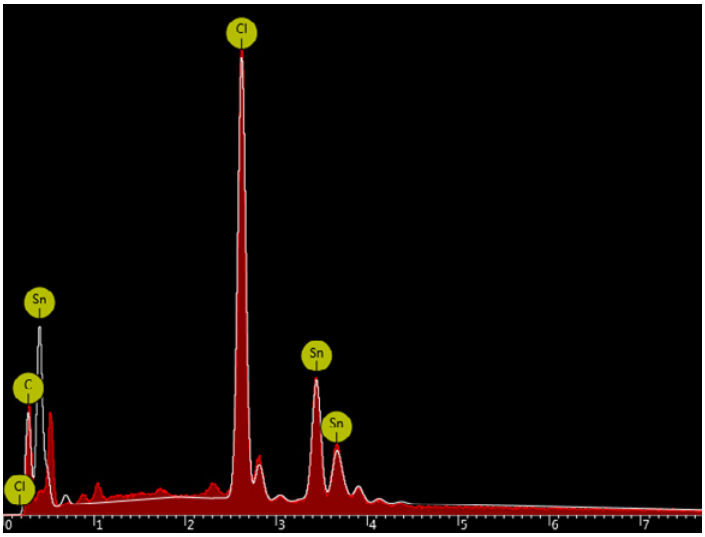



Fig. 5. EDS analysis diagram of $SnCl_4$/nano-sawdust.

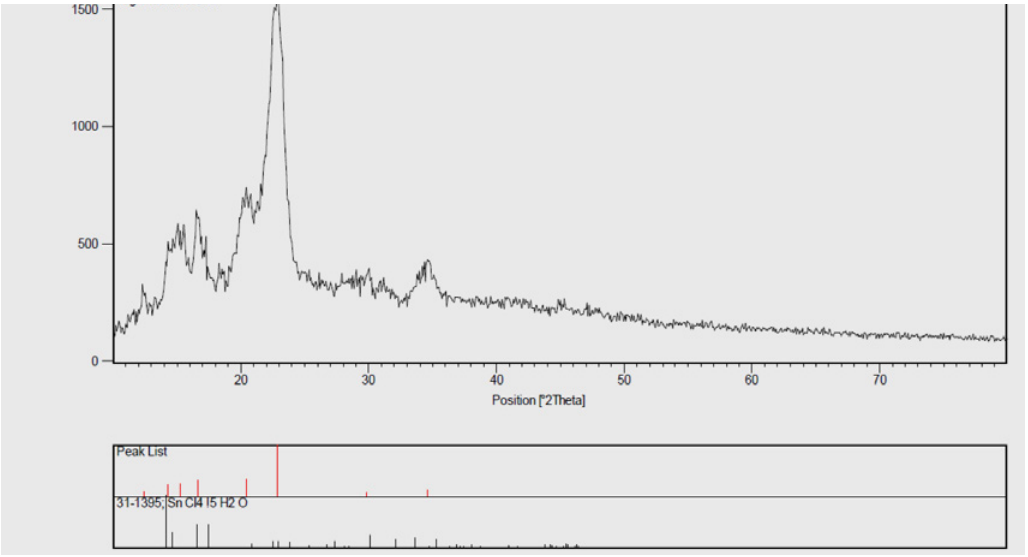
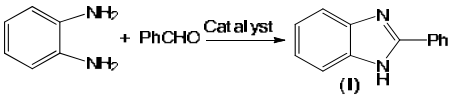



Fig. 6. XRD pattern of $SnCl_4$/nano-sawdust

Table 1. $SnCl_4$/nano-sawdust reflexes in XRD diffract gram

| No | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Pos. [°2Θ] | 15.130 | 16.748 | 20.553 | 22.935 | 28.563 | 34.634 | 41.846 |
| FWHM [°2Θ] | 0.472 | 0.944 | 0.472 | 0.472 | 0.708 | 0.295 | 1.728 |

Table 2. Optimization of reaction conditions for the synthesis of 2-phenyl-1*H*-benzimidazole [a]

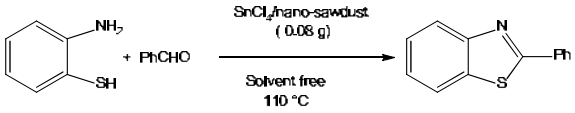



(I)

| Entry | Cat (g) | Solvent | Temp (°C)/ Time (min) | Yield[b](%) |
|---|---|---|---|---|
| 1 | - | EtOH | RT/60 | trace |
| 2 | $SnCl_4$/nano-sawdust (0.02) | EtOH | RT/60 | 25 |
| 3 | $SnCl_4$/nano-sawdust (0.02) | EtOH | Reflux/60 | 48 |
| 4 | $SnCl_4$/nano-sawdust (0.05) | EtOH | Reflux/60 | 65 |
| 5 | $SnCl_4$/nano-sawdust (0.08) | EtOH | Reflux/60 | 92 |
| 6 | $SnCl_4$/nano-sawdust (0.08) | EtOH | Reflux/25 | 92 |
| 7 | $SnCl_4$/nano-sawdust (0.08) | n-Hexan | Reflux/25 | 25 |
| 8 | $SnCl_4$/nano-sawdust (0.08) | MeOH | Reflux/25 | 80 |
| 9 | $SnCl_4$/nano-sawdust (0.08) | THF | Reflux/25 | 33 |
| 10 | $SnCl_4$/nano-sawdust (0.08) | EtOAc | Reflux/25 | 40 |
| 11 | $SnCl_4$/nano-sawdust (0.08) | DMF | 80/25 | 65 |
| 12 | $SnCl_4$/nano-sawdust (0.08) | S. F | 90/25 | N. R |
| 13 | $SnCl_4$/nano-sawdust (0.08), 2nd run | EtOH | Reflux/25 | 88 |
| 14 | $SnCl_4$/nano-sawdust (0.08), 3nd run | EtOH | Reflux/25 | 84 |
| 15 | $SnCl_4$/nano-sawdust (0.08), 4nd run | EtOH | Reflux/25 | 82 |

[a]Themmol amount of benzaldehyde and 1,2-phenylendiamine is 1.1:1
[b] Isolated yield after re-crystallized in ethanol.

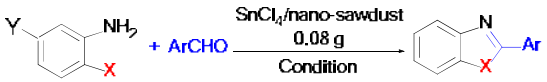
Table 3. Optimization of reaction conditions for the synthesis of 2-phenylbenzothiazole [a]




| Entry | Solvent | Temp (°C) | Time (min) | Yield[b] |
|---|---|---|---|---|
| 1 | EtOH | Reflux | 25 | 65% |
| 2 | EtOH | Reflux | 60 | 75% |
| 3 | EtOH | Reflux | 90 | 75% |
| 4 | MeOH | Reflux | 90 | 68% |
| 5 | THF | Reflux | 90 | 35% |
| 6 | DMF | 90 | 90 | 79% |
| 7 | S. F | 90 | 90 | 75% |
| 8 | S. F | 110 | 90 | 94% |

[a]The mmol amount of benzaldehyde and 2-aminothiophenol is 1:1.1
[b]Isolated yield.

Table 4. $SnCl_4$/nano-sawdust catalyzed synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles




Condition X=$NH_2$ Ethanol, Reflux
X=SH Solvent free, 110 °C

| Ent. | X | Y | Ar | Time (min) | Yield[a] | m.p. (°C) | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | NH | H | $C_6H_5$ | 25 | 92 | 292–294[9] | [9] |
| 2 | NH | H | 4-$ClC_6H_4$ | 25 | 88 | 289–291[9] | [9] |
| 3 | NH | $NO_2$ | 2, 4-$Cl_2C_6H_3$ | 25 | 90 | 214-215[17] | [23] |
| 4 | NH | H | 4-$MeC_6H_4$ | 30 | 90 | 275–277[9] | [9] |
| 5 | NH | H | 4-$NO_2C_6H_4$ | 35 | 85 | 259–260[9] | [9] |
| 6 | NH | H | 4-$OHC_6H_4$ | 30 | 87 | 240-242[17] | [23] |
| 7 | NH | H | 2,3-$(OH)_2C_6H_3$ | 40 | 86 | 201-202[17] | [23] |
| 8 | NH | H | $CH_2CH_2Ph$ | 30 | 88 | 246-247[17] | [23] |
| 9 | NH | $CH_3$ | 4-$NO_2C_6H_4$ | 25 | 92 | 234-236[17] | [23] |
| 10 | NH | $NO_2$ | 4-$NO_2C_6H_4$ | 25 | 88 | 255-256[17] | [23] |
| 11 | NH | $NO_2$ | 2,3-$(OH)_2C_6H_3$ | 35 | 86 | 206-207[17] | [23] |
| 12 | NH | H | 4-$BrC_6H_4$ | 27 | 89 | 250-252[17] | [23] |
| 13 | S | H | $C_6H_5$ | 90 | 94 | 98-100[10] | [10] |
| 14 | S | H | 4-$ClC_6H_4$ | 90 | 95 | 110-112[10] | [10] |
| 15 | S | H | 2, 4-$Cl_2C_6H_3$ | 90 | 92 | 150-152[13] | [13] |
| 16 | S | H | 4-$NO_2C_6H_4$ | 110 | 85 | 226-228[14] | [14] |
| 17 | S | H | 3-$NO_2C_6H_4$ | 110 | 87 | 180-182[13] | [13] |
| 18 | S | H | 2-OH $C_6H_4$ | 100 | 92 | 130-131[14] | [14] |
| 19 | S | H | 2, 3-$(OH)_2C_6H_3$ | 110 | 85 | 186-188[13] | [13] |
| 20 | S | H | 3, 4-$(OH)_2C_6H_3$ | 110 | 82 | 190-192[14] | [14] |
| 21 | S | H | 4-$((CH_3)_2CH)$ $C_6H_4$ | 90 | 94 | 115-117[14] | [14] |
| 22 | S | H | 4-$N(CH_3)_2$ $C_6H_4$ | 120 | 83 | 173-175[18] | [24] |
| 23 | S | H | H | 120 | 89 | 80-81[18] | [24] |

[a]Isolated yield

subsequently centrifuged to get the catalyst. The obtained catalyst was then washed with acetone followed by drying in oven at 100 ˚C for 4 h. It was found that the reactivity of the recovered catalyst decreases slightly for the next run (approx 4%).

According to above mentioned protocol, the best condition for synthesis of 2-phenylbenzothiazole was achieved using 0.08 g catalyst under solvent free condition at 110 °C after 90 min.

We have applied the previous method for the modification of 2-phenylbenzothiazole synthesis. We have found that using 0.08 g $SnCl_4$/nano-sawdust under solvent free condition at 110 °C and 90 min is the best condition (Table 3, Entry 8).

Finally, The above mentioned optimized conditions were used for synthesis of 2-aryl-1H-benzimidazoles and 2-arylbenzothiazoles (Table 4).

## CONCLUSION

In summary, $SnCl_4$/nano-sawdust as a new carbohydrate based solid acid catalyst was prepared and characterized. This catalyst was successfully applied for synthesis of various 2-arylbenzimidazoles and 2-arylbenzothiazoles via condensation of 1,2-phenylendiamine or 2-aminothiophenol with aldehydes. This protocol has many advantages including high conversions, eco-friendly, low-cost and easy workup which makes this method more attractive.


## ACKNOWLEDGMENTS

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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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