

Introduction of sulfonated bamboo (bamboo-SO₃H) as a new catalyst for the facile synthesis of bis(indolyl)methanes

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ABSTRACT

Bamboo is one of the important biopolymers which is used in chemistry. In this work, for the first time, a solid acid catalyst from bamboo was prepared from the reaction of sawdust bamboo and chlorosulfonic acid. Relevant properties of catalyst were investigated by FT-IR, XRD, SEM and TGA. The sulfonated bamboo (bamboo-SO₃H) with several acid functional groups was utilized as highly efficient, heterogeneous and reusable catalyst for synthesis of bis(indolyl)methanes in short reaction times with excellent yields. Also, the novel solid acid catalyst was reused without any appreciable loss in activity.

Keywords: Sawdust bamboo, Chlorosulfonic acid, Bis(indolyl)methanes, Solid acid catalyst.

1. Introduction

Indoles and their derivatives are one of the important classes of heterocyclic compounds [1] because of their broad range of biological activity. Among them, bis(indolyl)methanes (BIMS) have received considerable attention in recent years due to their applications in pharmaceuticals such as anticancer [2], anti-hyperglycemic, antiviral, antimicrobial activities, and tranquilizer [3]. The simple and straightforward method for the synthesis of bis(indolyl)methanes involves the electrophilic substitution reaction of indoles with aldehydes in the presence of a variety of catalysts such as Lewis acid ZrOCl₂ · 8H₂O [4], CuBr₂ [5], ZrCl₄ [6], ZnO [7] or heterogeneous acidic catalysts poly (4-vinyl pyridinium) perchlorate [8], H₆P₂W₁₈O₆₂ [9] and Zn-Y Zeolite [10]. Although these mentioned catalysts improved the synthesis of bis(indolyl)methanes, some of them suffer from disadvantages such as: no eco-friendly catalyst, requirement of stoichiometric amount of catalyst, expensive catalyst, low yields, toxic solvent, long reaction times, tedious work-up and un-reusable catalyst. Therefore, development of a green mild and efficient procedure for synthesis of these compounds with the use of a recyclable heterogeneous catalyst is still in demand.

Nowadays, bioenergy and bio-based materials have attracted researchers' attention. Bamboo is recognized as one of the most popular biomass resources because of its abundance, short growth cycle, renewability, simple production and low price [11].

In addition, in recent years, there has been further interest in the synthesis of solid acid catalyst for organic reactions. Solid acid catalysts have many advantages in comparison with traditional liquid acids including operational simplicity, easy recoverability, non-corrosive and environmentally friendly nature and their efficiency [12-16], which are very important factors for industrial applications. So, the solid acid catalysts play a main role in the development of clean industrial technologies.

In this study, a novel solid acid catalyst, sulfonated bamboo (bamboo-SO₃H) is prepared and used for the preparation of bis(indolyl)methanes successfully.

2. Experimental

2.1. General

All chemicals were purchased from Merck or Fluka chemical companies. Products were characterized by their physical constant and through a comparison with authentic samples. The reactions were monitored by TLC using silica gel IL G/UV 254 TLC plates (Germany). Bamboo wood materials (*Dendrocalamus*

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baandissi), four-year-old, were collected from the north forest of Iran.

2.2. Instrumentation

X-ray diffraction (XRD) measurements were performed at room temperature on a D8-Bruker Advanced X-ray powder diffractometer, using Ni filter and Cu-K α radiation ($k=1.542 \text{ \AA}$). The FT-IR spectra were recorded on a run on a VERTEX 70 Bruker company (Germany) spectrometer. Melting points were recorded on a Büchi B-545 apparatus (Germany) in open capillary tubes.

2.3. Preparation of bamboo-SO₃H

The bamboo was ground to produce sawdust. The bamboo sawdust was washed with distilled water repeatedly to remove dust and any impurities and dried at 100 °C in an oven for overnight. Then chlorosulfonic acid (5 ml) was added to a suspension of bamboo sawdust (5.00 g) in dry CH₂Cl₂ (10 ml) over a period of 20 min while the reaction mixture was stirred in an ice bath. The mixture was stirred for 2 hours at room temperature. The solid powder was filtered and washed with methanol (20 ml) and dried at 60 °C overnight to obtain bamboo-SO₃H as a black powder [17].

2.4. General procedure for the Synthesis of bis(indolyl)methanes

A mixture of indole (2 mmol), aldehyde (1 mmol) and bamboo-SO₃H (20 mg) was magnetically stirred under solvent-free conditions at 80 °C for the appropriate time. The progress of the reaction was monitored by TLC (using a 1:6 mixture of EtOAc/*n*-hexane). After the reaction was completed, ethanol (10 ml) was added to the mixture and the catalyst was collected by filtration. Then, water was added and precipitated and product was collected by filtration in high purity [18].

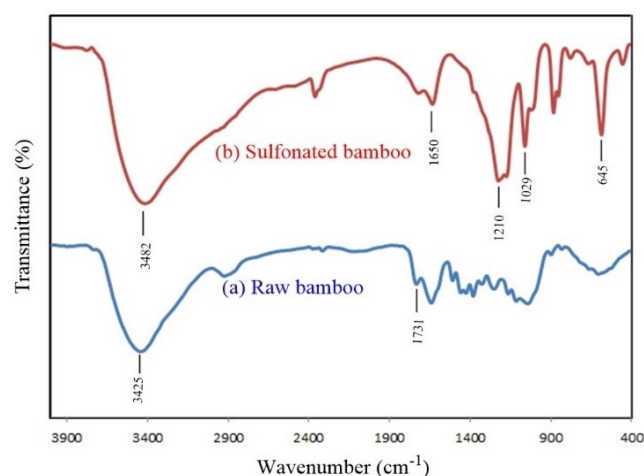


Fig. 1. FT-IR spectra of raw bamboo (a) and bamboo-SO₃H (b).

3. Results and Discussion

3.1. Catalyst characterization

FT-IR spectra of raw bamboo and bamboo-SO₃H are shown in Fig. 1. In the case of raw bamboo (Fig. 1a), a wide absorption peak at 3425 cm⁻¹ is assigned to -OH groups and the absorption peak at 1731 cm⁻¹ is assigned as unconjugated carbonyl vibration [19]. Fig. 1b is related to bamboo-SO₃H, a broad band at 3482 cm⁻¹ is attributed to -OH stretching vibrations. The absorption bands at 1210 and 1029 cm⁻¹ are assigned to stretching vibration of O=S=O. Since the prepared catalyst has an amorphous carbon structure; it probably consists of polycyclic aromatic of carbon sheets that randomly attached with -SO₃H, -COOH, and phenolic -OH groups. Therefore, the peak at 1650 cm⁻¹ is related to carbonyl group in -COOH. Also, the absorption band which is observed at 645cm⁻¹ is attributed to C-S band, this indicated incorporation of -SO₃H groups [20].

Fig. 2 shows the X-ray diffraction (XRD) patterns of raw bamboo and bamboo-SO₃H. Sulfonation of bamboo led to the increase of the intensity and some changes in the diffractogram of raw bamboo. The XRD pattern of raw bamboo exhibits broad bands at $2\theta=16^\circ$ and 23.5° and a weak peak at $2\theta=35^\circ$ which indicates amorphous feature of raw bamboo [21], whereas, for bamboo-SO₃H, a broad peak at $2\theta = 10-30^\circ$ was observed with more intensity. These results imply that raw bamboo keeps its primary structure after sulfonation with chlorosulfonic acid.

As can be seen from the TGA curves (Fig. 3), when the temperature reached 700 °C, 15.99% of the raw bamboo and 24.85% of the bamboo-SO₃H remained in form of solid residues. These results indicated that the bamboo-SO₃H remained more than raw bamboo at the of end of analysis.

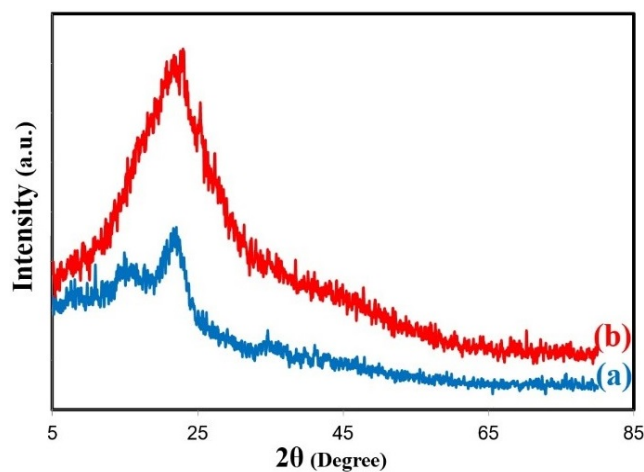


Fig. 2. XRD patterns of raw bamboo (a) and bamboo-SO₃H (b).

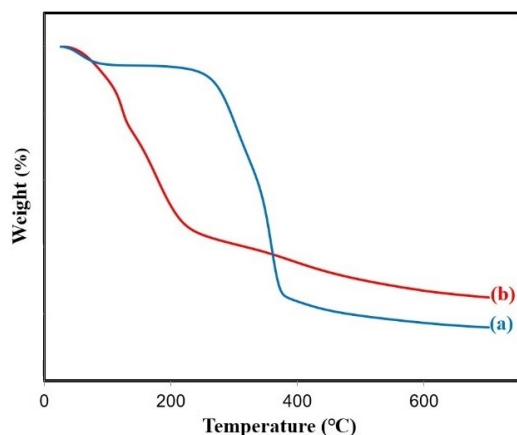


Fig. 3. TGA curves for raw bamboo (a) and bamboo-SO₃H (b) under N₂ flow.

In general, there were three stages of degradation in the TGA curves of the two samples. In the TGA curves, the slight mass loss below 150 °C is attributed to adsorption water and CO₂. In the second stage at around 250-400 °C, for raw bamboo material, the weight loss in this stage resulted from the decomposition of carboxylic groups and the elimination of hydroxyl groups in the material. However, for bamboo-SO₃H, the mass loss at the second stage may be attributed to not only the two processes mentioned above, but also the elimination of sulfur groups. This made the bamboo-SO₃H lose its weight at lower temperature than the raw bamboo. The last stage of mass losses appeared at around 400-700 °C, this was due to the aromatization of the structural network [22].

Fig. 4 shows the SEM images of raw bamboo (Fig. 4a and b) and bamboo-SO₃H (Fig. 4c and d). The SEM

images show that the primal morphology of raw bamboo was changed due to acidification process. These images showed that bamboo-SO₃H mainly consisted of aggregates of irregular particles with several micrometers diameters and was much smaller than that of the raw bamboo. By using this method and also the Debye-Sherrer method for calculation it was clarified that these particles size are at 240 nm -1 μm. The structure of carbon was damaged after the sulfonation treatment, while the raw bamboo has the porous structure and the pore diameter is greater than the bamboo-SO₃H [21].

The Hammett acidity function (H_0) is a measure of acidity which is used for very concentrated solutions of strong acids using UV-Vis technique [23]. It can be calculated by the equation below:

$$H_0 = \text{p}K(\text{I})_{\text{aq}} + \log \left(\frac{[\text{I}]_{\text{s}}}{[\text{IH}^+]_{\text{s}}} \right)$$

Where $\text{p}K(\text{I})_{\text{aq}}$ is the $\text{p}K_{\text{a}}$ value of the indicator referred to an aqueous solution, $[\text{IH}^+]_{\text{s}}$ and $[\text{I}]_{\text{s}}$ are the molar concentrations of the protonated and unprotonated forms of the indicator in the solvents, respectively.

According to Lambert-Beer's law, the value of $[\text{I}]_{\text{s}}/[\text{IH}^+]_{\text{s}}$ can be calculated through UV-Vis spectrum. For this purpose, 4-nitroaniline ($\text{p}K(\text{I})_{\text{aq}}=0.99$) was chosen as the basic indicator and CCl₄ as solvent. The maximal absorbance of the deprotonated form of the indicator was observed at 340 nm in CCl₄. As can be seen in Fig. 5 in comparison with blank solution, when bamboo-SO₃H as acid catalyst was added to the indicator solution, the absorbance of the deprotonated form of the indicator decreased. Table 1 shows the strength acidity of the bamboo-SO₃H [24].

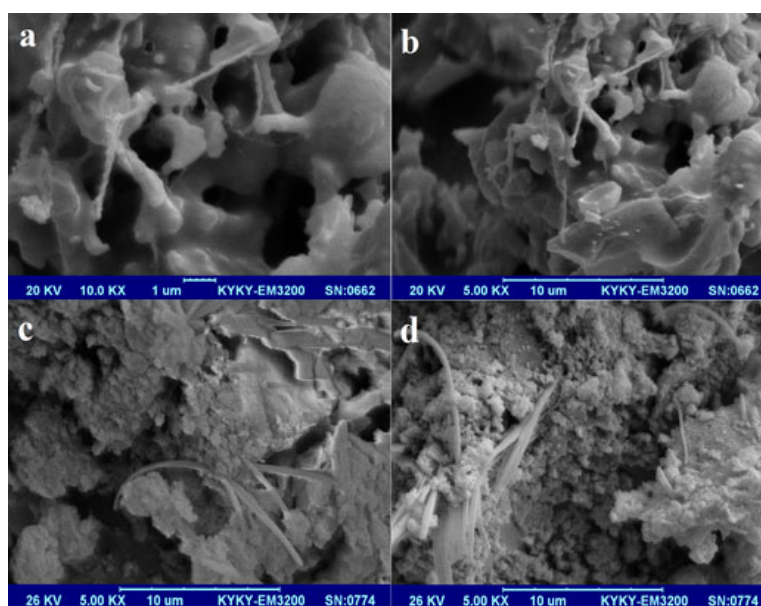


Fig. 4. SEM images of raw bamboo (a and b) and bamboo-SO₃H (c and d).

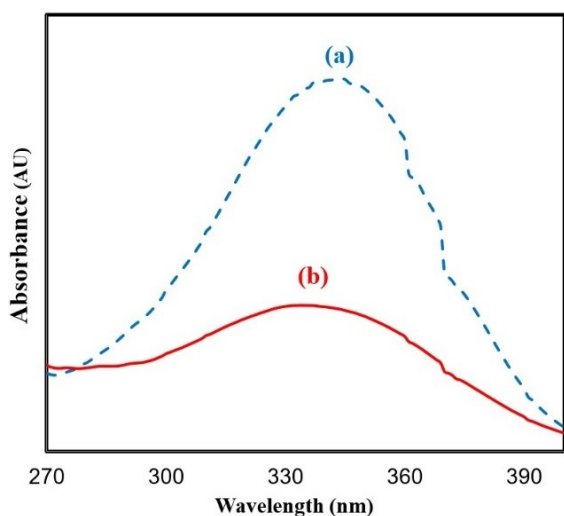


Fig. 5. Absorption spectra of 4-nitroaniline (indicator) (a) and bamboo-SO₃H (b) in CCl₄.

3.2. Catalyst activity

To investigate the catalytic activity of prepared catalyst and considering the growing interest in the use of indole derivatives in medicinal chemistry, the bamboo-SO₃H was used for the synthesis of bis(indolyl)methanes compounds. First, the reaction between 4-chloro benzaldehyde and indole was chosen as a model for optimization of the reaction conditions.

The effects of various solvents on the yield and time of the reaction were examined. As it is shown in Table 2, the best result was obtained under solvent-free conditions.

The influence of the amount of the catalyst was also tested. The results are summarized in Table 3 and it was clarified that any further increase in the amount of the catalyst (more than 20 mg) did not improve the reaction times or yields.

Second, the best result was obtained by using aldehyde (1 mol) and indole (2 mol) in the presence of 20 mg of bamboo-SO₃H in solvent-less media, as shown in Scheme 1.

After optimization of reaction conditions and in order to establish the successfulness and acceptability of this produce, we explored the reaction of the various aldehydes with indole under the optimized reaction

conditions (Table 3). The results showed that benzaldehyde and the other aromatic aldehydes containing electron-withdrawing (Cl and NO₂) and electron-donating (OCH₃ and OH) groups in presence of the bamboo-SO₃H can be easily converted to the corresponding 3,3'(4-chlorophenylmethylene)-bis-(1*H*-indole) in short reaction times with excellent yields (Table 4, entries 1–18).

Table 1. Calculation of Hammett acidity function (H_0) for bamboo-SO₃H.

| Catalyst | A_{\max} | $[I]_s\%$ | $[IH^+]_s\%$ | H_0 |
|--------------------------|------------|-----------|--------------|-------|
| - | 2.548 | 100 | 0 | - |
| bamboo-SO ₃ H | 0.998 | 39.16 | 60.84 | 0.79 |

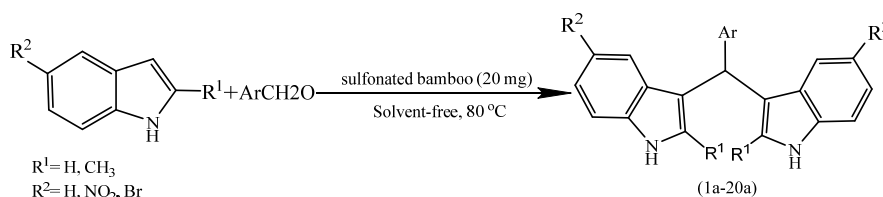
Condition for UV-Vis spectrum measurement: solvent: CCl₄, indicator: 4-nitroaniline [$pK(I)_{\text{aq}} = 0.99$], 1.44×10^{-4} mol/L (10 mL); catalyst: bamboo-SO₃H (5 mg), 25 °C.

Table 2. The effect of different solvents (5 ml) on the condensation of indole with 4-chlorobenzaldehyde in the presence of bamboo-SO₃H at 80 °C.

| Entry | Solvent | Time (min) | Yield (%) |
|-------|--------------------|------------|-----------|
| 1 | - | 4 | 96 |
| 2 | H ₂ O | 45 | 25 |
| 3 | CHCl ₃ | 15 | 55 |
| 4 | EtOH | 20 | 80 |
| 5 | CH ₃ CN | 25 | 83 |
| 6 | EtOAc | 80 | 86 |

Table 3. The effect of amount of catalyst on the condensation of indole with 4-chlorobenzaldehyde under solvent-free conditions at 80 °C.

| Entry | Amount of catalyst (mg) | Time (min) | Yield (%) |
|-------|-------------------------|------------|-----------|
| 1 | 10 | 20 | 49 |
| 2 | 15 | 12 | 83 |
| 3 | 20 | 4 | 98 |
| 4 | 25 | 4 | 98 |



Scheme 1. Synthesis of bis(indolyl)methane derivatives in the presence of bamboo-SO₃H.

For more investigation the selectivity of the catalyst was examined in the presence of a ketone (acetophenone) under the optimized conditions. The result showed that no product was obtained and this indicates the chemoselectivity of the catalyst. Since aldehydes are more reactive than ketones, this chemoselectivity can be related to higher electrophilicity of aldehydes rather than ketones (Table 4, entry 19), [25].

In order to show the superiority of the developed method, our result for the synthesis of 3,3'-(4-chlorophenylmethylene)-bis-(1*H*-indole) was compared with the results of other catalysts that were reported in the literature for this reaction (Table 5). As it is clear that bamboo-SO₃H as an acidic catalyst, improved the reaction effectively and gave the desired products in short reaction times. This catalyst is prepared easily and a very low amount of the catalyst is used for the promotion of the required reactions.

During a separate investigation for evaluation of the ability of the prepared catalyst, the acidic catalysts were also synthesized using different mineral acids such as HClO₄, H₂SO₄ and HNO₃. As the results showed in Table 6, among these catalysts, the bamboo-SO₃H is superior in term of yields and reaction times under the optimized reaction conditions. So chlorosulfonic acid as a sulfonation agent is more effective than others.

Finally, the reusability of the catalyst was examined. The model reaction was studied under the optimized reaction conditions. After completion of reaction, the catalyst was separated by filtration and washed with acetone, dried and re-used in the model reactions under the optimized reaction conditions. This process was repeated for at least three cycles without changes in activity. The yields for these three cycles at the reaction times 4, 6 and 10 minutes was 96, 93 and 89%, respectively.

Table 4. Preparation of bis(indolyl)methane derivatives catalyzed by bamboo-SO₃H^a.

| Entry | Ar | R ¹ | R ² | Product | Time (min) | Yield (%) ^b | m.p. (°C) | | Ref. |
|-------|--|-----------------|-----------------|---------|------------|------------------------|-----------|----------|------|
| | | | | | | | Found | Reported | |
| 1 | C ₆ H ₅ - | H | H | 1a | 8 | 94 | 126-128 | 126-127 | [28] |
| 2 | 2-Cl-C ₆ H ₄ - | H | H | 2a | 7 | 91 | 74-77 | 75-76 | [29] |
| 3 | 4-Cl-C ₆ H ₄ - | H | H | 3a | 4 | 98 | 78-80 | 78-80 | [4] |
| 4 | 4-Br-C ₆ H ₄ - | H | H | 4a | 5 | 96 | 113-115 | 116-117 | [30] |
| 5 | 3-MeO-C ₆ H ₄ - | H | H | 5a | 9 | 89 | 163-166 | 165 | [31] |
| 6 | 4-MeO-C ₆ H ₄ - | H | H | 6a | 8 | 93 | 184-186 | 186-187 | [27] |
| 7 | 2-NO ₂ -C ₆ H ₄ - | H | H | 7a | 10 | 95 | 138-140 | 140-142 | [34] |
| 8 | 3-NO ₂ -C ₆ H ₄ - | H | H | 8a | 5 | 95 | 218-222 | 219-221 | [29] |
| 9 | 4-NO ₂ -C ₆ H ₄ - | H | H | 9a | 5 | 98 | 300-302 | 304-306 | [26] |
| 10 | 4-Me-C ₆ H ₄ - | H | H | 10a | 11 | 96 | 91-93 | 89-91 | [29] |
| 11 | 4-(CH ₃) ₂ CH-C ₆ H ₄ | H | H | 11a | 7 | 94 | 155-157 | 153-154 | [32] |
| 12 | 4-OH-C ₆ H ₄ - | H | H | 12a | 11 | 91 | 122-124 | 124-126 | [4] |
| 13 | C ₆ H ₅ - | CH ₃ | H | 14a | 5 | 95 | 252-255 | 250-253 | [33] |
| 14 | 4-Cl-C ₆ H ₄ - | CH ₃ | H | 15a | 3 | 97 | 245-247 | 247-248 | [29] |
| 15 | 4-NO ₂ -C ₆ H ₄ - | CH ₃ | H | 16a | 3 | 98 | 242-244 | 241-243 | [33] |
| 16 | 4-MeO-C ₆ H ₄ | CH ₃ | H | 17a | 5 | 94 | 103-106 | 101-103 | [33] |
| 17 | 4-MeO-C ₆ H ₄ - | H | NO ₂ | 18a | 15 | 94 | 315-317 | 316-318 | [18] |
| 18 | 4-MeO-C ₆ H ₄ - | H | Br | 19a | 11 | 92 | 253-255 | 254-256 | [18] |
| 19 | Acetophenone | | | 20a | 120 | - | - | - | |

^aReaction condition: Aldehyde (1 mmol), indole (2 mmol), bamboo-SO₃H (20 mg) at 80 °C under solvent-free conditions.

^bIsolated yields.

Table 5. Comparison of the results obtained from the synthesis of 3,3'-(4-chlorophenylmethylene)-bis-(1*H*-indole) in the presence of bamboo-SO₃H with these obtained using other catalysts.

| Product | Catalyst (loading) | Reaction conditions | Time (min) | Yields (%) | Ref. |
|---------|--|-----------------------------|------------|------------|-----------|
| | (PhCH ₂ PPh ₃) ⁺ Br ³⁻ / SiO ₂ (5 mol) | solvent-free, 90 °C | 16 | 80 | [25] |
| | FeCl ₃ -RiH (150 mg) | EtOH, 80 °C | 10 | 96 | [26] |
| | ZrOCl ₂ .8H ₂ O (5 mol%) | H ₂ O-EtOH, r.t. | 540 | 89 | [4] |
| | H ₆ P ₂ W ₁₈ O ₆₂ (0.7mol%,0.04g) | solvent-free,110 °C | 25 | 98 | [9] |
| | Bamboo-SO ₃ H (20mg) | solvent-free, 80 °C | 4 | 96 | This work |

4. Conclusions

In conclusion, we have prepared and identified bamboo-SO₃H at a size of 270-290 nm as a novel acid catalyst. The solid catalyst was used for the simple and efficient synthesis of bis(indolyl)methanes. The most significant advantages of this procedure are using an inexpensive re-useable catalyst, high yields, short reaction times, being low cost, avoiding of organic solvents and easy work-up. Further work to explore this catalyst in other reactions is in progress.

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Table 6. Comparison of the results obtained from the synthesis of 3,3'-(4-chlorophenylmethylene)-bis-(1*H*-indole) in the presence of various mineral acids with bamboo.

| Entry | Catalyst | Time (min) | Conversion (%) |
|-------|--------------------------|------------|----------------|
| 1 | bamboo-HSO ₃ | 4 | 96 |
| 2 | bamboo-HClO ₄ | 17 | 53 |
| 3 | bamboo-HSO ₄ | 23 | 43 |
| 4 | bamboo-HNO ₃ | 25 | 40 |

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