

# Sulfonic Acid-Functionalized Solid Polymer Catalyst from Crude Cashew Nut Shell Liquid: Synthesis of Tetra(indolyl)methanes and Bis(indolyl)methanes from Xylochemicals

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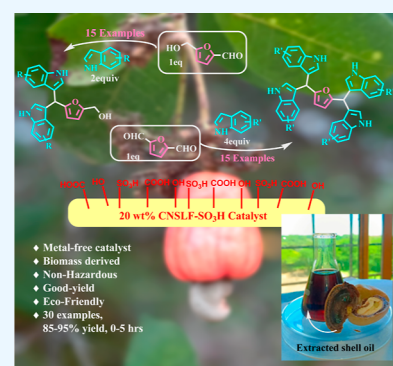
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**ABSTRACT:** Xylochemistry presents a sustainable solution to the depletion of petroleum resources, contributing to the success of the circular economy. The development of reusable carbonaceous materials as heterogeneous acid catalysts has garnered significant attention in both research community and industry. Catalysis research has an intrinsic connection with low-cost synthetic routes, sustainable raw materials, and chemical and thermal stability. We designed and made a solid acid catalyst that can be used more than once from cheap, naturally occurring, crude cashew nut shell liquid (CNSL). Identification of practical applications for waste biomass is a component of the objectives of sustainable development. We treated the black-colored crude CNSL with varying amounts of formaldehyde and further sulfonated the resulting crude resins with chlorosulfonic acid. The solid with the most sulfonic acid groups was used as a Bronsted acid catalyst (CNSLF-SO<sub>3</sub>H) for the Friedel–Craft reactions of indoles and furfuraldehydes. We synthesized 15 novel di[bis(indolyl)methane] derivatives from secondary xylochemical 2,5-diformylfuran (DFF) and 15 bis(indolyl)methanes from 5-hydroxymethylfurfural (5-HMF).



## 1. INTRODUCTION

Sustainability and circular economy are buzzwords of the modern world. The growing need for dwindling fossil fuels, as well as the environmental repercussions of their use, has compelled people to develop greener technology and ‘clean’ chemicals. Mother Nature, which turns harmful CO<sub>2</sub> into biomass, is the best source of inspiration for future generations. In this setting, the utilization of renewable biomass feedstocks has gained prominence. Lignocellulosic biomass, food waste, municipal solid waste, and so on can be valuable resources for creating alternative technologies to manufacture the chemicals that humans require.<sup>1</sup>

The industrial sector demands sustainable and efficient routes for important acid-catalyzed reactions such as esterification, transesterification, etherification, hydrolysis, Friedel–Craft, etc. Researchers in the field of catalysis are particularly interested in developing efficient heterogeneous catalysts. For practical applications, the preference for using a heterogeneous catalyst over a homogeneous one arises from its lower level of sophistication. Other factors that support this are easy catalyst recovery, potential reuse, and easy disposal, resulting in less pollution.<sup>2</sup>

One of the most important aspects of green chemistry is the synthesis of a catalyst that is both environmentally friendly and sustainable. To develop an acidic heterogeneous catalyst, it is necessary to introduce an acidic functionality onto the surface of a robust material. Such material could be an organic or inorganic polymer.<sup>3</sup> We need these polymeric support materials to be

environmentally sustainable, benign, and robust. The addition of an acidic functionality, such as the SO<sub>3</sub>H group, to the surface of such a support material can impart acidity, thereby transforming it into a heterogeneous acid catalyst. Organic sulfonated polymers are a promising heterogeneous acid catalyst that has been documented in the literature.<sup>4</sup> Production of sulfonated chars and their propensity to act as acidic catalysts is also a topic of interest among the researchers working in the field of sustainable chemistry.<sup>5</sup> However, there are very few reports of sulfonated biomass, or sulfonated polymer of biomass, being used as a Bronsted acid catalyst.<sup>6</sup>

Cashew nut shell (CNS) and its pericarp fluid CNS liquid (CNSL) are agricultural wastes with promising prospects due to their distinctive structural characteristics as raw materials for the development of valuable chemicals and goods.<sup>7</sup> There are four main parts that make up CNSL: cardanol, anacardic acid, cardol, and 2-methylcardol. The alkyl chain is also 1–3° unsaturated. The extraction procedure allows for the highest concentration of the two critical components, namely, anacardic acid and cardanol. The phrases “natural CNSL” and “technical CNSL” denote the presence of major constituents anacardic acid and

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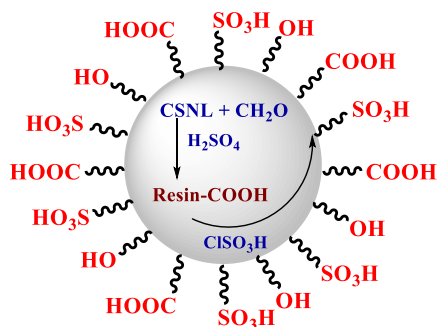
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cardanol, respectively.<sup>8</sup> Extensive studies are reported on the “technical CNSL”, which primarily consists of cardanol and lacks any anacardic acid. Considerable study has been carried out on cardanol–formaldehyde resin, derived from the original concept of phenol–formaldehyde resin.<sup>9</sup> These biomass-derived cardanol–formaldehyde polymeric materials are studied in the material sector. Researchers have also subjected the cardanol to other chemical modifications for further polymerization. The obtained resins demonstrate a wide range of applications, including flame retardant,<sup>10</sup> surface coating and painting,<sup>11</sup> adhesives,<sup>12</sup> antiaging/anticorrosive agents,<sup>13</sup> plasticizers,<sup>14</sup> and surfactants.<sup>15</sup> Research also demonstrates the potential of cardanol as a substitute for petroleum-based industrial raw materials. There are also few reports of the use of anacardic acid in natural product synthesis. While the phenol–formaldehyde polymer has already found applications as a support material for heterogeneous catalysts,<sup>16</sup> there have been no reports yet on the use of CNSL-based materials for this purpose. Further to our knowledge, there are no useful reports on the polymerization of natural or crude CNSL, which is rich in anacardic acid.

As Goa is a cashew hub, we conceived the idea of utilizing this economically viable and renewable resource as a basis for developing a solid acid catalyst and demonstrating its utility in organic transformations. Most small-scale industries follow the roasting process for processing cashew nuts. This technique produces a dark CNSL oil rich in anacardic acid. Traditionally, people painted wooden boats with this oil to prolong their shelf life. Nowadays, people either use this oil as fuel during the roasting process or sell it to CNSL enterprises for a throwaway price. Therefore, we contemplated utilizing this crude material directly to synthesize a polymer akin to phenol–formaldehyde resin, which can be sulfonated to obtain a solid acid catalyst. Further, our interest was to retain the carboxylic acid group of the anacardic acid, which is a major constituent of the crude CNSL. This method of making a solid acid catalyst not only ensures sustainability but also reduces CO<sub>2</sub> emissions in the environment by preventing the decarboxylation of CNSL, a process that produces cardanol. Such a catalyst (Figure 1) has the potential to substitute for numerous organic transformations that use inorganic or organic acids as catalysts.



**Figure 1.** Representation of the prepared CNSL/formaldehyde-SO<sub>3</sub>H catalyst.

The investigation of novel compounds incorporating physiologically active indoles and their derivatives has garnered significant interest across various academic fields, particularly within the realm of medicinal chemistry.<sup>17</sup> Di[bis(indolyl)-methane] [DBIM]-based compounds, also known as tetra-(indolyl)methane compounds, have received a lot of attention

from medicinal chemists. The compound 1,4-di[bis(3-indolyl)-methyl]benzene has shown promise in the treatment of fibromyalgia, chronic tiredness, and irritable bowel syndrome.<sup>18</sup> Figure 2 illustrates the varied DBIM compounds synthesized from different dialdehyde scaffolds with the aim of discovering improved pharmaceutical compounds for a range of biological functions and different applications. According to these investigations' findings, DBIM derivatives have the potential to be effective anticancer agents.<sup>19</sup> These structures display various aromatic or heterocyclic rings embedded between two bis(indolyl)methanes. A review of the literature showed that these DBIM compounds do not have a furan ring. Instead, they do have the important five-membered heterocycles, pyrrole and thiophene. This made us think of introducing a furan core between the two bis(indolyl)methanes. We envisaged that the furan ring, due to the presence of ethereal oxygen, could be beneficial for the potential interactions with the target proteins studied for cancer studies. Furthermore, the easy availability of the xylochemical 5-hydroxymethylfurfural (5-HMF) makes it easy to procure the required diformylfuran (DFF) (Figure 3). The use of xylochemicals such as furan, 5-HMF, ferulic acid, veratrole, and so on to synthesize value-added products is important from a sustainability perspective. 5-HMF has gained attention as a future sustainable replacement for many petroleum-derived chemicals.<sup>20</sup>

The synthesis of bis(indolyl)methane involves the fusion of reagents in a 1:2 equiv ratio, consisting of either cyclic or acyclic aldehyde/ketone and indole in the presence of an acidic medium. In a similar vein, the conventional method for synthesizing di[bis(indolyl)methane] compounds involve the condensation of one equivalent of cyclic or acyclic dialdehyde or diketone with four equivalents of indole (Scheme 1).

## 2. RESULTS AND DISCUSSION

**2.1. Catalyst Synthesis and Characterization.** The required CNSL/formaldehyde resin was synthesized by employing sulfuric acid.<sup>21</sup> Altering the mole ratio of crude CNSL to formaldehyde, eight CNSL/formaldehyde resin samples were prepared. It was observed that the amount of resin production increased linearly with the formaldehyde concentration. The preparation of the resin of crude CNSL was carried out at 80 °C to avoid decarboxylation and retain the carboxylic acid group of anacardic acid. Low-temperature heating had no effect on the resin's propensity to form. In order to facilitate substitution with SO<sub>3</sub>H groups over the heterogeneous polymer, an excess of chlorosulfonic acid was added. It was found that the yield of the sulfonation product linearly increased to a specific formaldehyde to CNSL (1:1) ratio and then eventually declined as the formaldehyde content increased. A higher proportion of formaldehyde causes extensive cross-linkage in the polymer, which affects substitution with SO<sub>3</sub>H groups. A plausible polymeric structure of the catalyst is given in Scheme 2 below. The catalyst obtained from mixing 1:1 formaldehyde/CNSL was chosen for further study as it showed a maximum increase in weight after sulfonation. Furthermore, this composition also showed a maximum sulfur content in elemental analysis (Table S1).

All of the synthesized CNSL/formaldehyde polymers and CNSL/formaldehyde-SO<sub>3</sub>H (CNSLF-SO<sub>3</sub>H) catalysts were structurally characterized by the Shimadzu Fourier transform infrared (FTIR) Prestige-21 spectrophotometer. The samples were ground with KBr and then filled in a sample cell. All of the samples were scanned from 4000 to 400 cm<sup>-1</sup>. The broad band

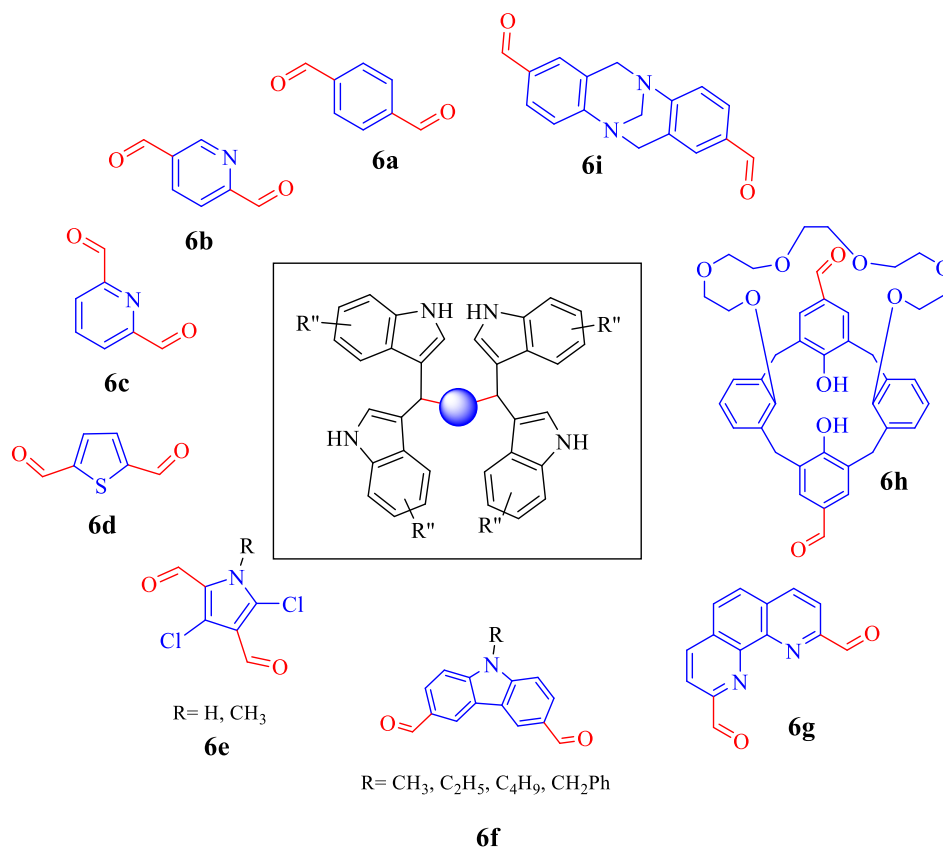


Figure 2. Different scaffolds employed in the formation of di[bis(indolyl)methane] derivatives for various applications.

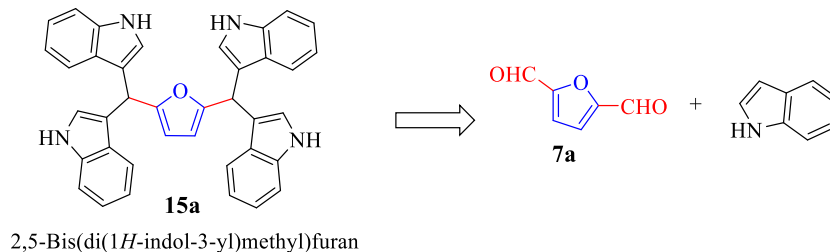
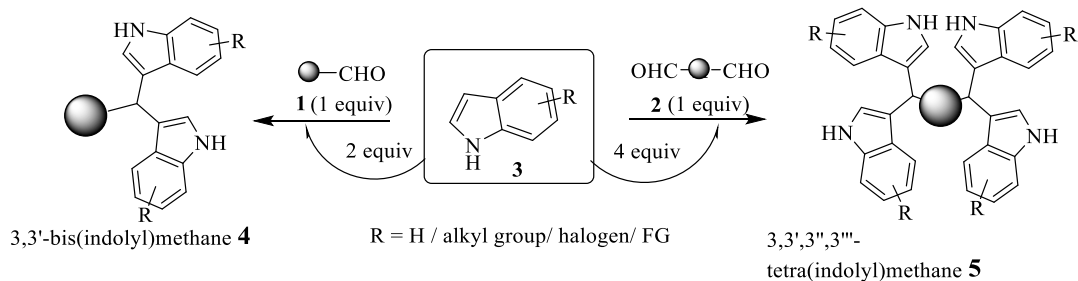


Figure 3. DBIM to be derived from xylochemical DFF.

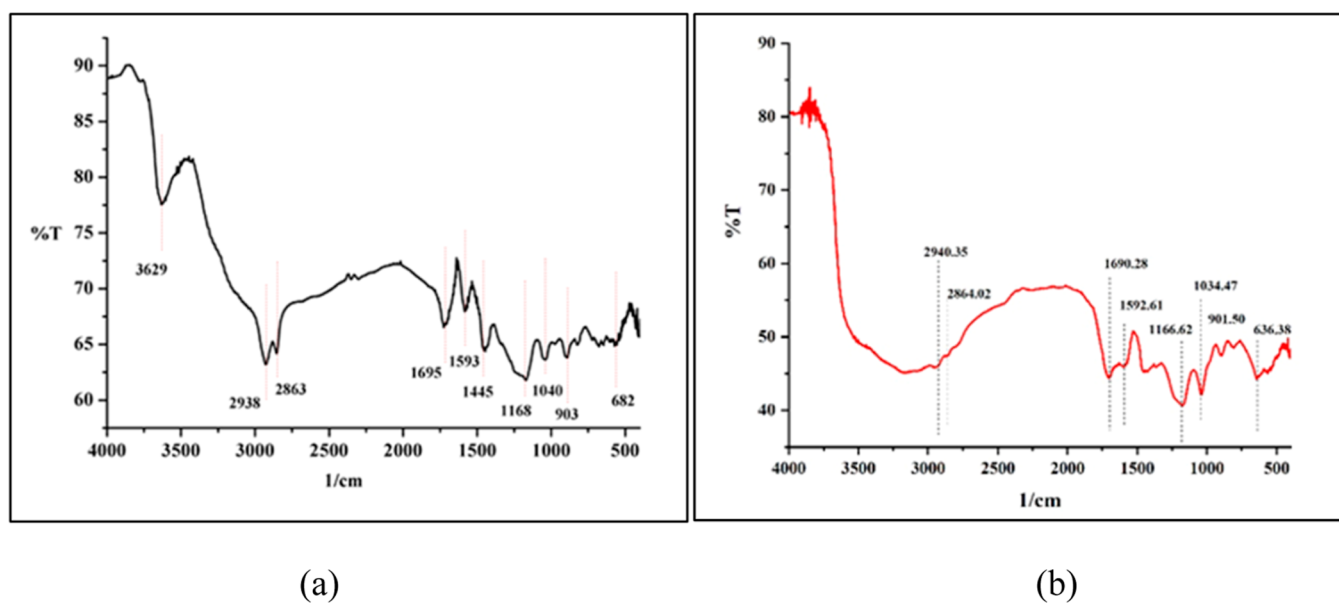
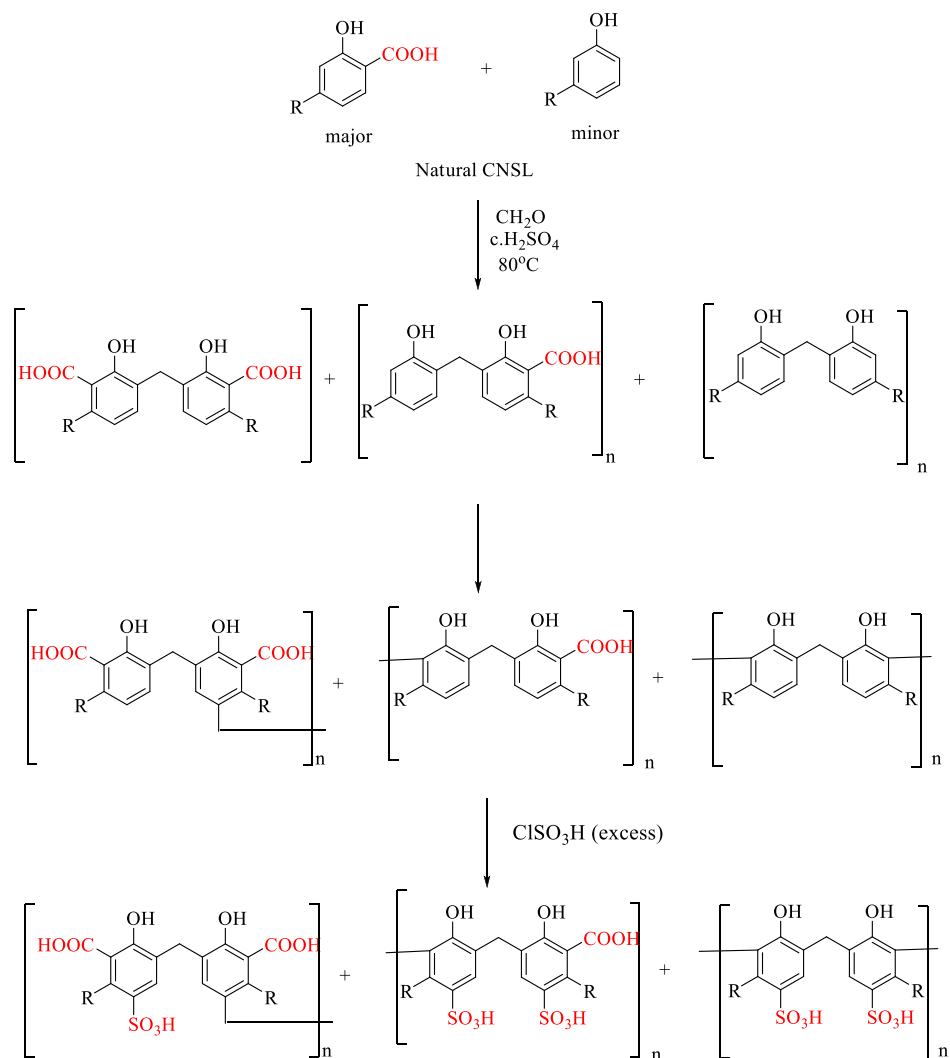
### Scheme 1. General Scheme for the Synthesis of Bis(indolyl)methane and Di[bis(indolyl)methane] Compounds



at 3485 cm<sup>-1</sup> depicts the presence of phenolic and carboxylic acid OH groups and bands at 2906 and 2864 cm<sup>-1</sup> account for the presence of -CH<sub>2</sub> linkage in the CNSL/formaldehyde polymer. The presence of the C=O asymmetric stretching peak at 1726 cm<sup>-1</sup> indicates the retention of the carboxylic group. Furthermore, the FTIR spectrum of CNSLF-SO<sub>3</sub>H shows characteristic IR bands of the polymer and the inserted SO<sub>3</sub>H group. The broad band at 3000–3500 cm<sup>-1</sup> shows the presence

of OH in the carboxylic acid and sulfonic acid. The strong band at 3629 cm<sup>-1</sup> confirms the presence of the phenol functionality. The band at 1695 cm<sup>-1</sup> depicts the carbonyl group of the COOH groups in the polymer. The bands at 1168 and 1040 cm<sup>-1</sup> depict SO<sub>3</sub>H stretching, as well as SO stretching at 682 cm<sup>-1</sup> (Figure 4). Figure 4b displays all of the visible bands from Figure 4a, demonstrating the retention of catalytic sites following three reuses of the catalyst.

## Scheme 2. Plausible Polymeric Reaction and Structure of Expected Mixture of Polymers

Figure 4. IR-spectrum polymer: (a) CNSLF-SO<sub>3</sub>H and (b) recycled CNSLF-SO<sub>3</sub>H.

The chemical compositions of CNSLF-SO<sub>3</sub>H were determined by elemental analysis using an Elementar Vario Micro Cube CHNS Analyzer (Table 1, Supporting Information). The

**Table 1. Qcfit Peak Analysis Distribution Functions through NH<sub>3</sub>-TPD**

peak	height (mV)	area (sig*t)	time (sec)	temp (°C)	% total area
1	28972.00	76451711.71	329	186.36	66.84
2	8042.31	7893033.40	1713	533.41	6.90
3	22718.90	30035931.55	2509	743.78	26.26

data reveal a significant sulfur percentage, which directly correlates with the number of acidic groups. The selected composition (1:1) had the highest sulfur percentile, 9.50, out of all of the compositions. After the third cycle, the recovered catalyst showed 8.54% sulfur, indicating the retention of the sulfonic acid group. We further investigated the acidity of the sulfonic acid-functionalized samples by FTIR, using pyridine as a probe molecule. The bands between 1400 cm<sup>-1</sup> and 1700 cm<sup>-1</sup> are known for the Bronsted acidity.<sup>22</sup> Sharp bands at 1439, 1482, and 1581 cm<sup>-1</sup> are seen, indicating strong interaction of pyridine with the Bronsted acid sites of the catalyst resulting from pyridinium ions [Figure 5a]. The availability of a high catalytic surface area has a significant impact on the catalyst's activity in a specific reaction. Giving importance to the same, we evaluated its surface area through the BET surface Quantachrome Autosorb IQ system and the Autosorb IQ QUA 211011 analyzer by gas adsorption. It is found to have 7.93 m<sup>2</sup>/g surface area for the catalyst. In addition, the structural characteristics of the CNSLF-SO<sub>3</sub>H catalyst was analyzed by *p*-XRD on the Rigaku SmartLab instrument. Figure 5b shows a broad Bragg reflection suggesting the amorphous nature of the polymer without any crystallinity.

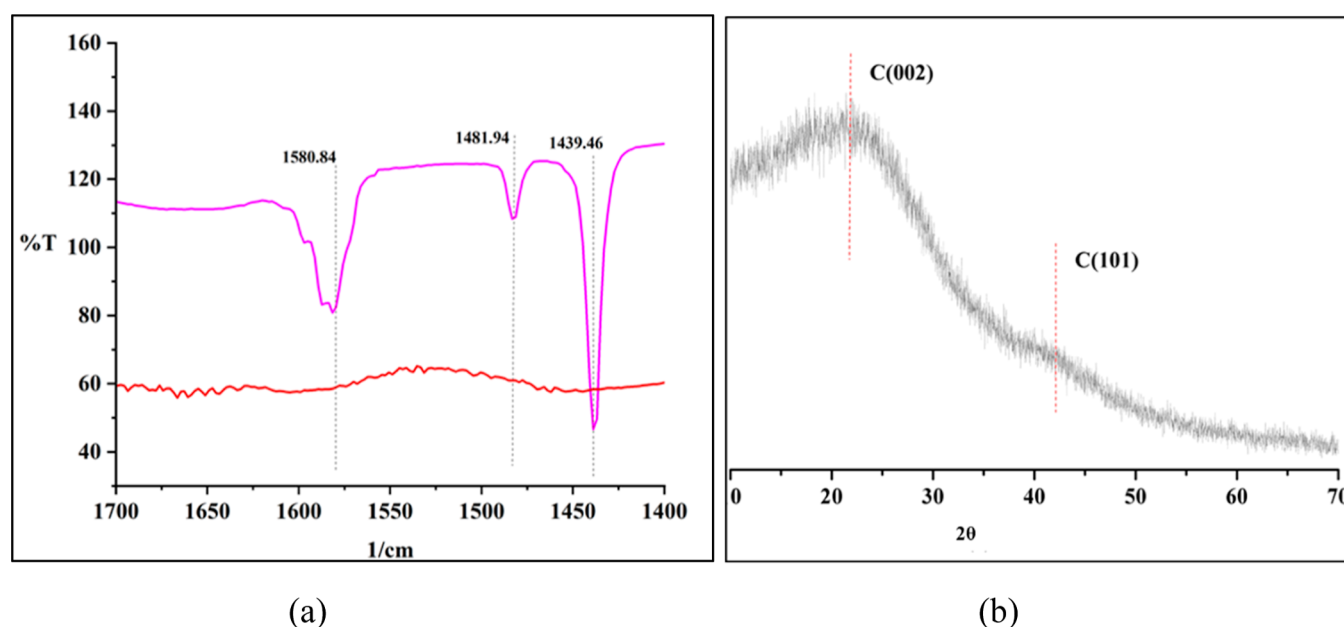
We also checked the acidity of the synthesized CNSLF-SO<sub>3</sub>H solid acid catalyst by using the inverse titration method. This method is highly beneficial for examining the surface acidic groups of carbonaceous material,<sup>23</sup> as it involves titrating with

Boehm-suggested bases that have different basicities, such as NaOH and NaHCO<sub>3</sub>. We obtained a pH value of 1.38 when we used NaOH as a base and 2.68 when we used NaHCO<sub>3</sub>. The presence of the phenolic hydroxyl group on the catalyst could be the cause of the difference in pH for the different bases.

The temperature-programmed desorption studies with ammonia (NH<sub>3</sub>-TPD) were obtained for the CNSLF/SO<sub>3</sub>H sample of 1:1 composition with the Quantachrome Autosorb IQ system model. On comparing the simulated TPD profiles, three peaks are obtained at 186 °C, 533 °C, and 744 °C. The significant peaks at lower temperatures, 186 °C, and higher temperatures, 533 and 744 °C, indicate mild to strong acid sites (Table 1). The introduction of the SO<sub>3</sub>H functionality on the aromatic ring containing phenolic hydroxy and carboxylic acid groups makes these groups more acidic, which in turn also makes the SO<sub>3</sub>H functionality more acidic. This is reflected in the peak of phenolic functionality appearing at 186 °C, the COOH functionality at 533 °C, and the -SO<sub>3</sub>H functionality at 744 °C. This is also reflected in pyridine desorption studies in IR, where pyridinium ion formation due to the phenolic OH is seen at 1439 cm<sup>-1</sup>, the COOH is seen at 1482 cm<sup>-1</sup>, and the SO<sub>3</sub>H is seen at 1581 cm<sup>-1</sup>. All of these studies suggest the significant presence of strong acid functionality SO<sub>3</sub>H on the catalyst surface.

The SEM image provided information about the microstructure and morphology of the CNSLF-SO<sub>3</sub>H catalyst [Figure 6a]. The image was recorded with a Carl-Zeiss scanning electron microscope. It indicated that the catalyst is amorphous and loose. Figure 6b presents the EDS survey of CNSLF-SO<sub>3</sub>H. The clear and strongest peak of the S-element in EDS showed that the SO<sub>3</sub>H group had been successfully attached to the polymer.

The thermogravimetric analysis evaluated the thermal stability of the prepared polymeric CNSLF-SO<sub>3</sub>H materials. We used a TG-DTA thermal analyzer of the NETZSCH STA 409PC (LUXX) to study the thermogravimetry (TGA) of the polymer at a heating rate of 10 °C/min in zero air between 30 and 800 °C. Figure 7 shows that the TGA curve of the solid acid



**Figure 5.** (a) FTIR spectra of the CNSLF-SO<sub>3</sub>H catalyst (red) and pyridine-absorbed CNSLF-SO<sub>3</sub>H catalyst (pink). (b) *p*-XRD pattern of the sulfonated catalyst (CNSLF-SO<sub>3</sub>H).



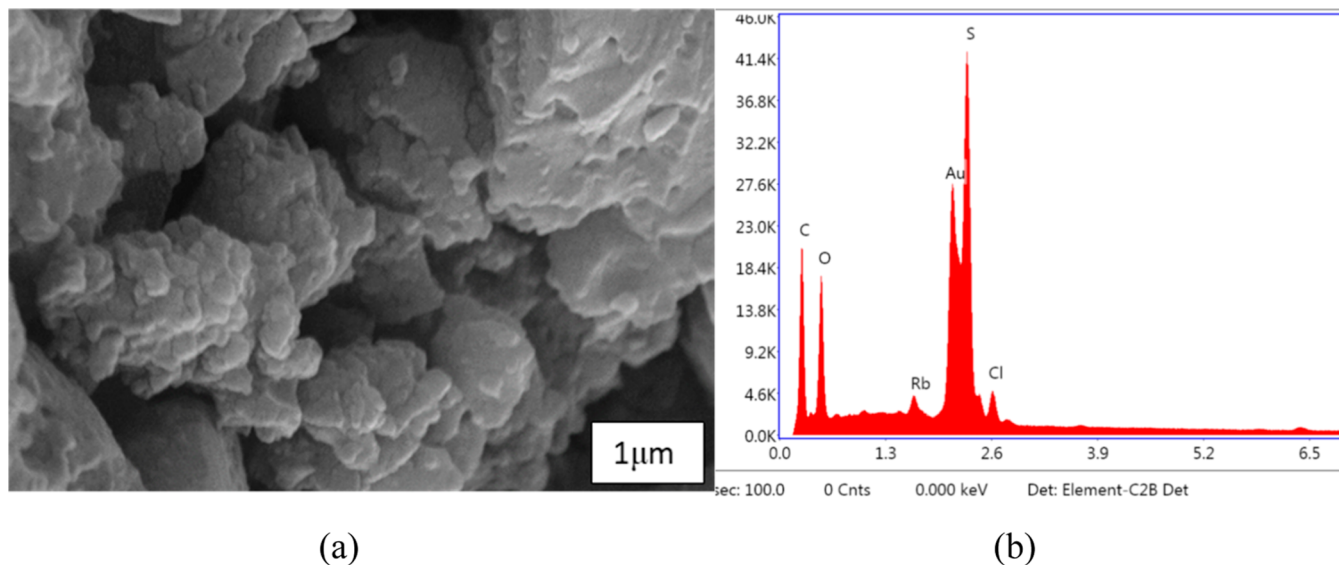


Figure 6. “a” depicts the SEM image of CNSLF-SO<sub>3</sub>H and “b” depicts EDS data.

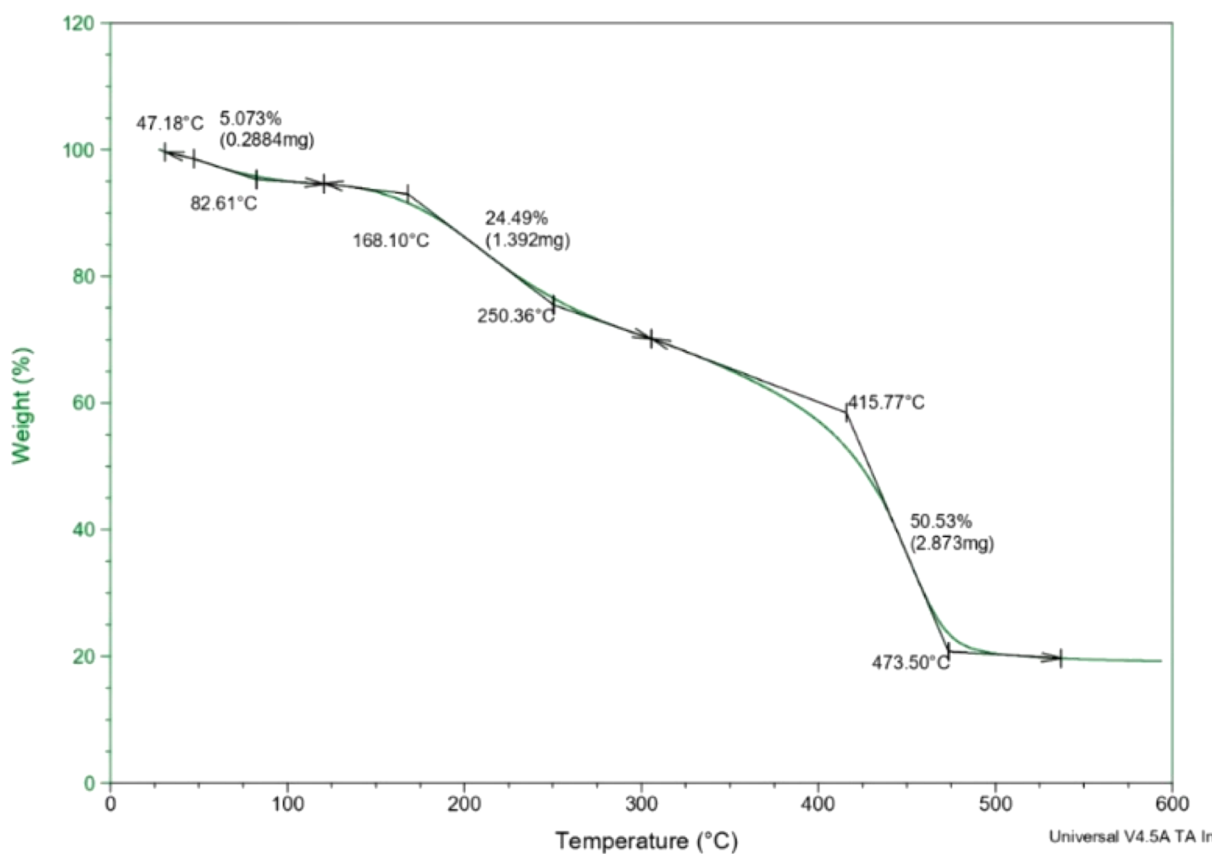


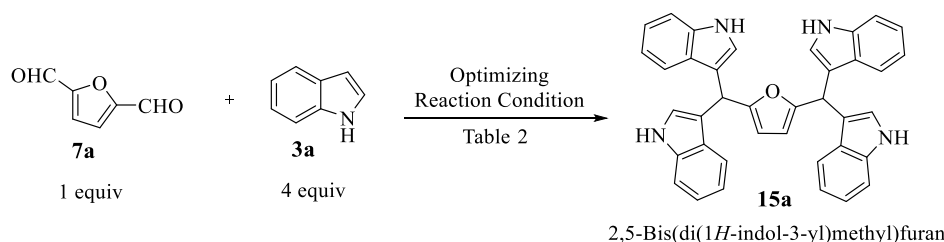
Figure 7. Thermal stability studies of the CNSLF-SO<sub>3</sub>H acid polymer.

polymer CNSLF-SO<sub>3</sub>H sample with a 1:1 mix revealed three weight losses in different areas. The first loss of ~5% is due to the desorption of water molecules from the hydrophilic surface of the SO<sub>3</sub>H-functionalized polymer surface. A weight loss of ~24% was observed at >160 °C to ~300 °C, which may correspond to loss of the carboxylic acid group and partly SO<sub>3</sub>H group. More than 51% weight loss above 300 °C indicates that the SO<sub>3</sub>H groups on the polymer surface and the alkyl side chain are completely broken down. These studies suggest that the

prepared solid acid can serve as a convenient catalyst for reactions of up to 160 °C, beyond which it begins to degrade.

**2.2. Catalyst Application.** We focused our initial studies on synthesizing di[bis(indolyl)methane] compounds from various indoles and DFF because these compounds were unknown. Researchers have reported numerous methods for the synthesis of bis(indolyl)methanes, and they have also extended some of these methods to the synthesis of di[bis(indolyl)methyl]-benzene from terephthalaldehyde. The methods include microwave synthesis, mechanochemical synthesis, conventional

## Scheme 3. Optimization of Reaction Parameters for 15a



heating, photoredox, and solventless, among others. Researchers have developed and employed a diverse array of catalysts to enhance product yield and minimize reaction time.<sup>23–31</sup>

Our first attempts to make di[bis(indolyl)methane] (Scheme 3) using our previous solventless and mechanochemical methods did not go well (condition 3, Table 2).<sup>32</sup> As a result,

**Table 2. Optimization of Scheme 3 by Solvent and Mechanochemical Condition Using CNSLF-SO<sub>3</sub>H Acid Catalyst**

solvent	condition 1 <sup>a</sup>			condition 2 <sup>a</sup>		
	temp (°C)	time (h)	% yield	temp (°C)	time (h)	% yield
toluene	room temperature	24	5	110	>24	25
1,4-dioxane			NPF	101	14	71
ethanol			8	78	8	77
ethyl acetate			NPF	77	28	69
THF			NPF	66	16	74
methanol			16	65	5	77
DCM			6	40	10	66
water			5	100	24	42
condition 3 <sup>b</sup>						
sr. no	catalyst (mole %)		time	% yield		
1			24	24		
2	50		16	48		

<sup>a</sup>Condition 1 and 2: indole (0.5 mmol), DFF (2 mmol), and CNSLF-SO<sub>3</sub>H catalyst (20 wt %). <sup>b</sup>Condition 3: entry 1:1 g silica, ball milling at 400 rpm; entry 2:1 g silica, 50 mol % sulfamic acid ball milling at 400 rpm; NPF: no product formed; Temp: temperature.

we constructed the present novel CNSLF-SO<sub>3</sub>H catalyst from natural waste material. Table 2 displays the CNSLF-SO<sub>3</sub>H catalyst's application results. Initially, we studied the effects of different solvents by varying them. We studied the solvents dichloromethane (DCM), 1,4-dioxane, ethanol, ethyl acetate (EA), methanol, tetrahydrofuran (THF), toluene, and water, using a 1:4 mol ratio of the reactants and a 20 weight % catalyst. We studied the reactions at room temperature and under refluxing conditions (conditions 1 and 2, Table 2).

Among the solvents studied, protic solvents, such as methanol and ethanol, yielded the highest yield. Methanol required less time than ethanol, possibly due to its ability to polarize. Water, a benign green solvent, was not helpful, because of the low solubility of the reactants. We chose ethanol for further studies because it is more environmentally friendly than methanol. The catalyst concentration was varied from 10 wt % to 60 wt % to explore the optimal conditions (Table 3). Interestingly, the product yield remained relatively constant, ranging from 76% to 81%, even as the reaction time varied. The increase in the concentration varied inversely with time. We chose conditions

**Table 3. Optimization of Catalyst Concentration**

conc. of catalyst (wt %)	time (h)	% yield
10	11	76
20	8	77
30	6	80
40	4	80
50	4	81
60	3	81

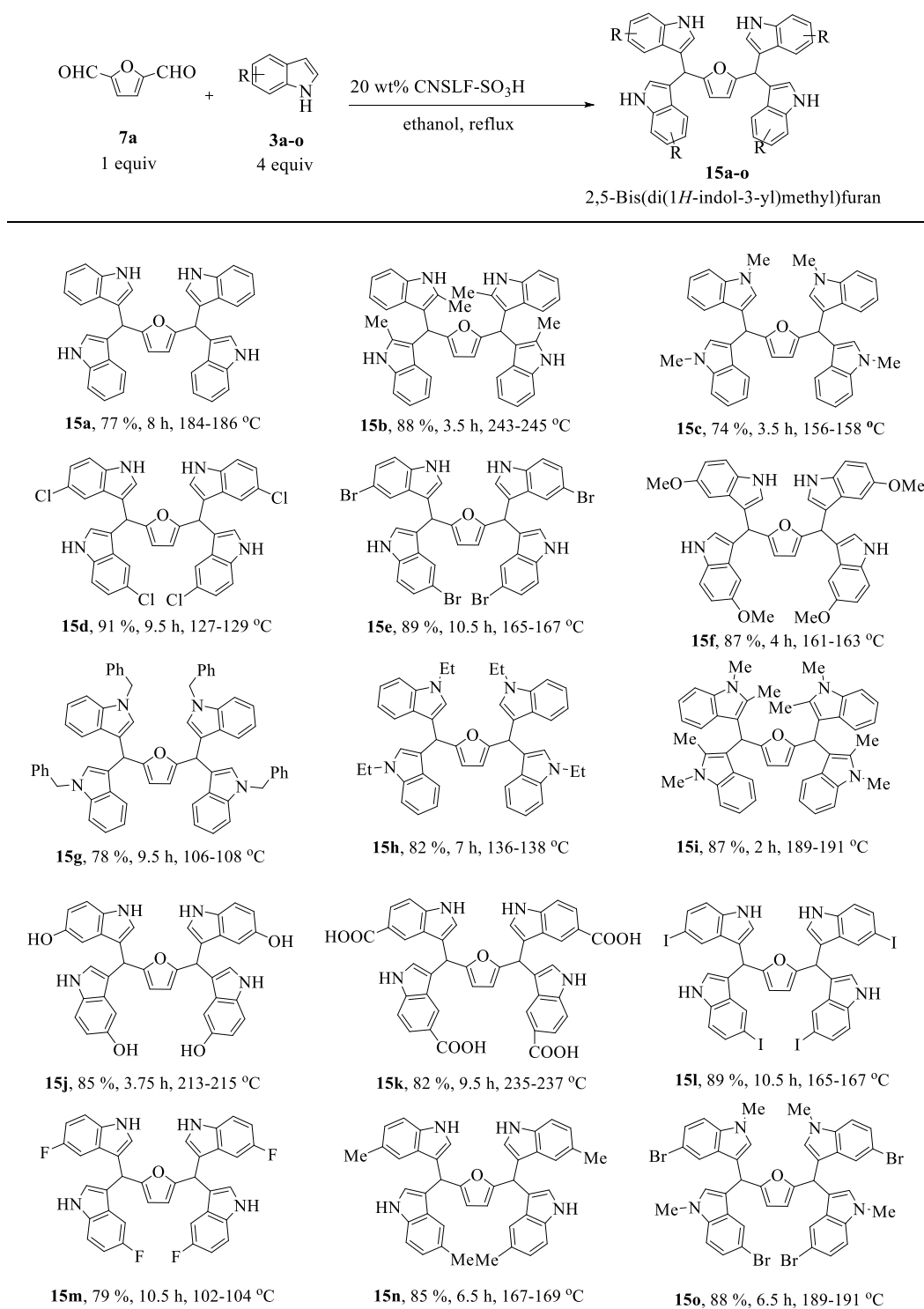
with 20 wt % of the catalyst as the optimal conditions for further applications.

Table 4 depicts the various novel di[bis(indolyl)methane] compounds 8a–o synthesized using the optimized protocol. The electron-rich indoles reacted faster than the electron-deficient ones, as expected in electrophilic substitution reactions. Also, sterically crowded indoles reacted at a slightly lower rate. Following the successful synthesis of di[bis(indolyl)methane] derivatives, the successful synthesis of 15 derivatives of bis(indolyl)methanes 10a–o further demonstrated the utility of catalyst CNSLF-SO<sub>3</sub>H (Table 5).

The reusability of the CNSLF-SO<sub>3</sub>H catalyst was another important aspect to study. To evaluate reusability, we performed Scheme 3 for 8 cycles. The activity remained almost unchanged for three cycles, and for the fourth cycle, a slight drop (~4%) was observed (Figure 8). We evaluated four additional cycles and observed a yield drop of 18%. This showed that after the fourth cycle, the catalyst lost catalytic activity by ~4–5% in every cycle. These observations suggested that the novel CNSLF-SO<sub>3</sub>H catalyst has high activity and good stability up to the fifth cycle. Therefore, the CNSLF-SO<sub>3</sub>H catalyst holds significant potential as a sulfuric acid substitute in various industrial processes. The decrease in activity could be attributed to the loss of some catalyst during the filtration process.

**Proposed Mechanism for the Synthesis of 5-HMF-Bis(indolyl)methane 16a and 5-HMF-Di[bis(indolyl)methane] 15a.** An acid-catalyzed electrophilic substitution reaction mechanism (Figure 9) explains the synthesis of bis(indolyl)methane and di[bis(indolyl)methane]. In the first step, an acid-catalyzed attack of the aldehyde on the indole occurs. The loss of water leads to the formation of azafulvaline-type intermediates 34 and 35. The second indole molecule reacts in a Michael fashion, resulting in the formation of 5-HMF-bis(indolyl)methane 33a from intermediate 34. In the case of DFF, it results in the formation of aldehyde 36, which reacts with two more molecules of indoles via azafulvaline-type intermediate 37 to yield di[bis(indolyl)methane] product 32a.

We also tested the CNSLF-SO<sub>3</sub>H catalyst to synthesize di[bis(indolyl)methyl]benzene from terephthalaldehyde, comparing it with some of the green reagents documented in the literature, as shown in Table 6. From Table 6, it is clear that,

Table 4. Substrate Scope of Di[bis(indolyl)methane] Derivatives<sup>a</sup>

<sup>a</sup>All reactions were carried out by refluxing DFF **7a** (0.48 mmol), indole **3a–o** (1.92 mmol), and 20 wt % of the CNSLF-SO<sub>3</sub>H catalyst (w.r.t DFF) in 5 mL of ethanol for appropriate time. The reaction mixture was filtered and washed with ethanol. The filtrate was concentrated and then subjected to flash column chromatography using the EA-pet ether eluent system to get **16a–o**.

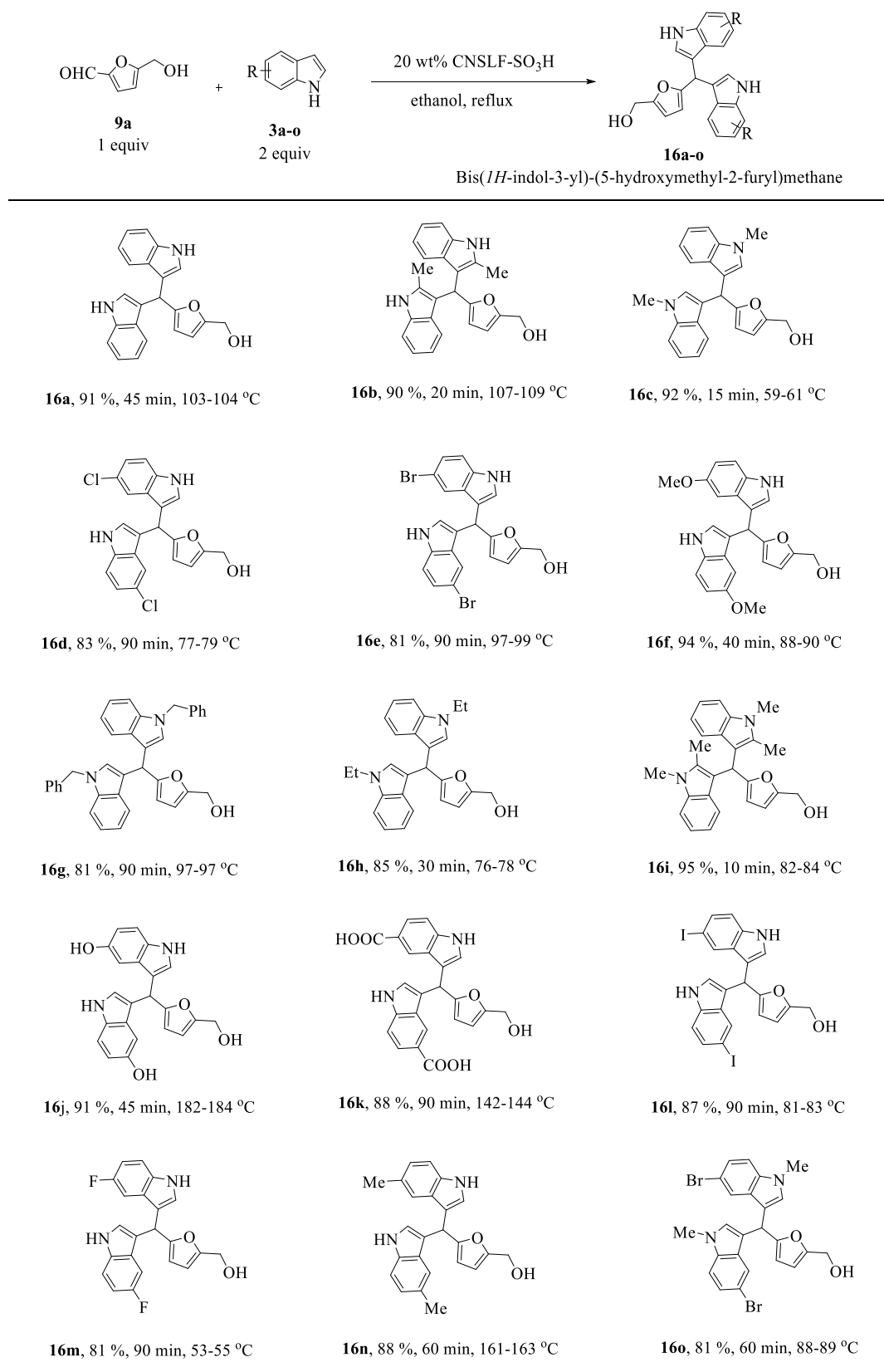
compared to terephthalaldehyde, HMF and DFF are less

electrophilic.

### 3. CONCLUSIONS

In conclusion, we have successfully developed a new sustainable heterogeneous polymeric solid catalyst with sulfonic-carboxylic acid functionalities from the crude CNSL. We prepared CNSL formaldehyde polymers with varying formaldehyde proportions



Table 5. Substrate Scope of Bis[di(indolyl)methane] Derivatives (BIMs)<sup>b</sup>

<sup>b</sup>All reactions were carried out by refluxing 5-HMF **9a** (1 mmol), indole **3a–o** (2 mmol), and 20 wt % of the CNSLF-SO<sub>3</sub>H catalyst (w.r.t 5-HMF) in 5 mL of ethanol for appropriate time. The reaction mixture was filtered and washed with ethanol.

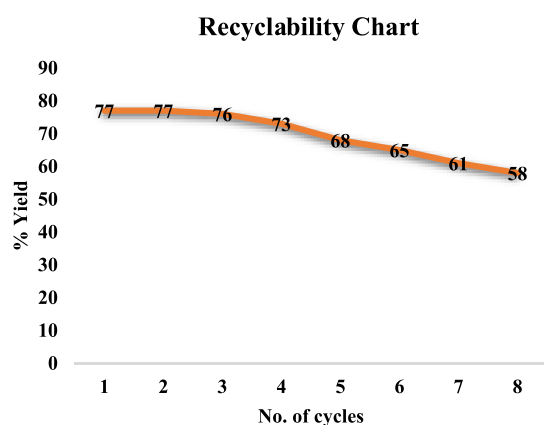


Figure 8. Recyclability chart of the CNSLF-SO<sub>3</sub>H catalyst.

and sulfonated them with chlorosulfonic acid. Among them, the composition prepared from 1:1 had the maximum number of sulfonic acid groups. Back titration and elemental analysis confirmed this. Pyridine absorption studies and NH<sub>3</sub>-TPD further confirmed the Bronsted acidity of the CNSLF-SO<sub>3</sub>H catalyst. TG studied the catalyst's thermal stability and found it to be stable up to 160 °C. The synthesis of a library of DBIMs from secondary xylochemical DFF successfully demonstrated the effectiveness of the prepared CNSLF-SO<sub>3</sub>H catalyst. The

utility of the catalyst was further demonstrated by the efficient synthesis of a library of BIMs known for their biological activities from xylochemical 5-HMF. The catalyst also demonstrated excellent recyclability for three cycles. The catalyst and molecular scaffolds synthesized exhibit typical attributes associated with sustainability and the implementation of Green Chemistry principles. Future studies will aim to determine strategies to improve the catalyst's thermal stability and the biological activities of synthesized DBIMs.

#### 4. EXPERIMENTAL SECTION

**4.1. Materials.** The crude black CNSL was procured from a local industry. Indole derivatives were purchased from TCI (India) Pvt., Ltd., and Spectrochem Pvt., Ltd. Conc. H<sub>2</sub>SO<sub>4</sub>, formaldehyde (40% solution), and other solvents were purchased from Thermo Fisher Scientific India Pvt., Ltd. Silica-coated alumina TLC plates were purchased from Merk Pvt., Ltd.

**4.2. Procedure for Catalyst Preparation.** CNSL/formaldehyde polymer preparation: Crude CNSL (2 g) was weighed in a round-bottom flask fitted with a Liebig condenser. Formaldehyde (40% solution, 0.44 mL) was added, followed by conc. H<sub>2</sub>SO<sub>4</sub> (1.2 mL). The reaction mixture was then heated to 80 °C for 2 h. After cooling to room temperature, ice cold water (10 mL) was added followed by EA (10 mL). The organic

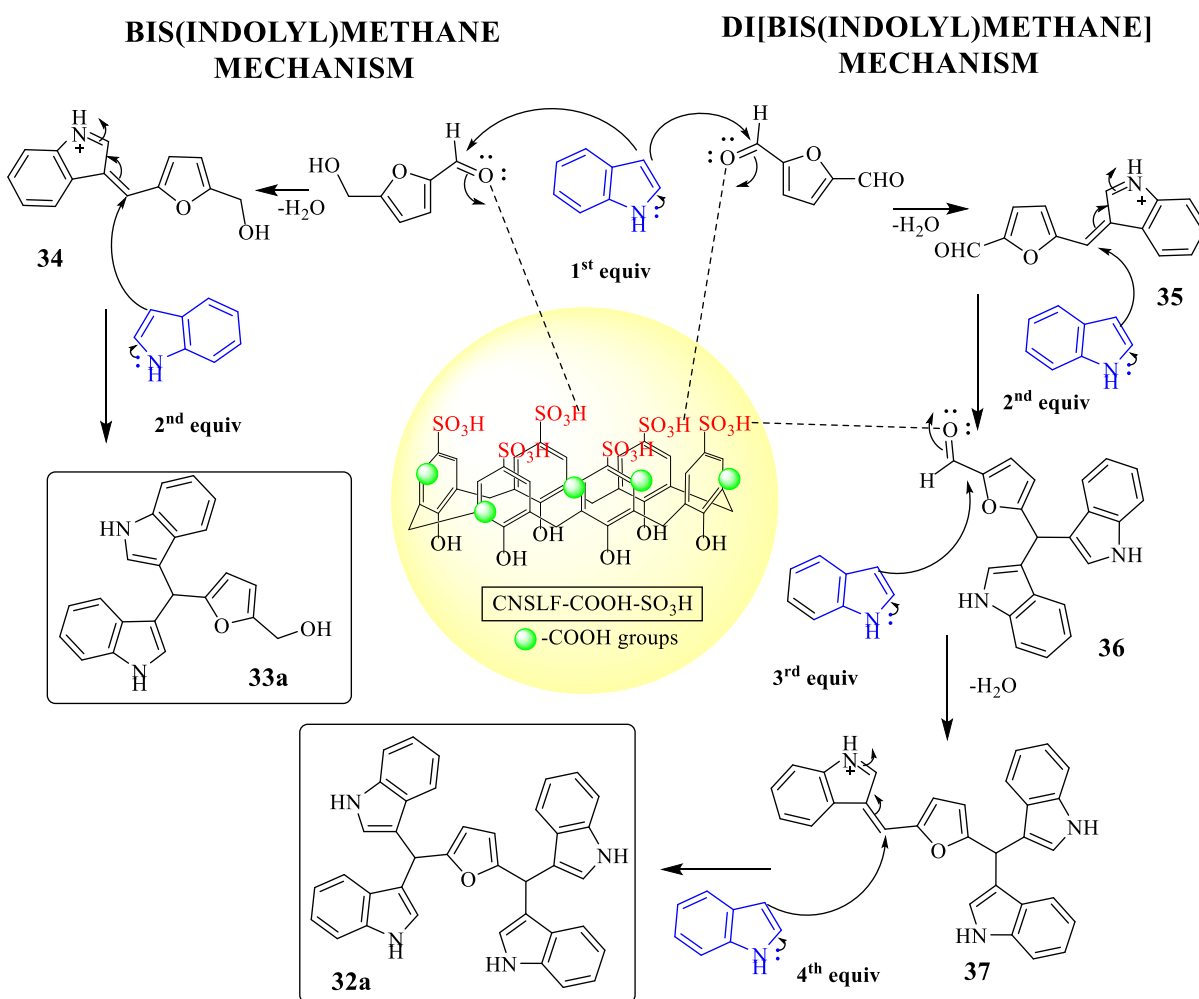
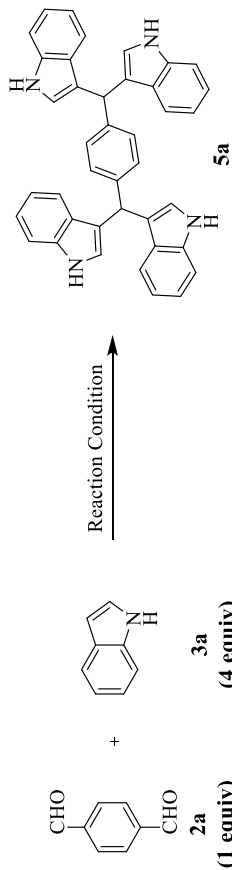


Figure 9. Proposed mechanism for bis(indolyl)methane and di[bis(indolyl)methane] compound using the CNSLF-SO<sub>3</sub>H catalyst.

Table 6. Literature Methods for the Synthesis of Di[bis(indolyl)methyl]benzene from Terephthalaldehyde

	reaction condition	solvent	catalyst conc	temp (°C)	time (min)	% yield	ref
1	sulfuric acid (silica supported)	acetonitrile	20 mol %	rt	10	95	23
2	lithium hydrogen sulfate (silica supported)	mortar and pestle grinding	20 mol %	rt	50	92	24
3	thiosulfuric acid, <i>S</i> -[3-(trimethoxysilyl) propyl] ester (silica supported)	acetonitrile	20 mol %	rt	210	89	25
4	1,1'-biphenyl, 4,4'-bis(bromomethyl)-, polymer with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (oxidized)carboxylic acid-functionalized cross-linked organic polymer (COP-A)	ethanol	30 mol %	rt	360	88	26
5	tetrabutylammonium bromide and 4,4'-(dihydroxysilylene)bis[benzenesulfonic acid] (silica gel-bound)	water	10 mol %	rt	20	85	27
6	boric acid-SiO <sub>2</sub> supported	50 °C, solvent free <sup>1</sup>	1.5 mol %	50	60	78	28
7	alumina supported-Citrus limon	solvent free	1 mL	MW 480 w	3	78	29
8	pyridine, 4-ethenyl-, homopolymer, chlorosulfate N-sulfonic acid poly(4-vinylpyridinium) chloride	mortar and pestle grinding	5 mol %	rt	180	67	30
9	KHSO <sub>4</sub> -SiO <sub>2</sub>	solvent free <sup>1</sup>	5 mol %	rt	15	65	31
10	CNSLF-SO <sub>3</sub> H	ethanol	10 wt %	refluxing	10	98	
11		ethanol	10 wt %	rt	75	97	
12	CNSLF-SO <sub>3</sub> H	ethanol	20 wt %	refluxing	480	87	



layer was separated and then washed with water ( $2 \times 10$  mL). The organic layer was dried (anhydrous  $\text{Na}_2\text{SO}_4$ ) and concentrated under vacuum to obtain a thick liquid (2.38 g).

**CNSLF- $\text{SO}_3\text{H}$  acid polymer catalyst:** To the above thick liquid, 25 mL of DCM was added. The solution was then ultrasonicated for 30 min. The flask was then kept in an ice-cold bath. An excess of  $\text{ClSO}_3\text{H}$  (3 mL) was added with constant stirring at 800 rpm. Stirring continued on the magnetic stirrer until fumes disappeared. The DCM was removed by evaporation, and the solid obtained was washed with a 50% ethanol solution, dried in an oven at  $80^\circ\text{C}$ , and stored in a closed container in the desiccator (3.41 g).

**4.3. Acidity Measurements.** Measurements of acidic active sites ( $-\text{SO}_3\text{H}$ ): Acid–base titration was conducted to determine the acid strength of the fresh catalyst in two different ways.

**4.3.1. Titration of HCl vs NaOH.** 0.05 g of the catalyst was stirred in 10 mL of 0.1 N NaOH solution at room temperature for 1 h. Then, the obtained aqueous solution was separated from the mixture, and the solution was titrated with a 0.1 N HCl solution with phenolphthalein as an indicator. The procedure was repeated three times (Table S1).<sup>33</sup>

**4.3.2. Titration of HCl vs  $\text{NaHCO}_3$ .** 0.05 g portion of the catalyst was stirred in 10 mL of 3 N  $\text{NaHCO}_3$  solution at room temperature for 1 h. Then, the obtained aqueous solution was separated from the mixture and solution was titrated with a 0.1 N HCl solution with methyl orange as an indicator. The procedure was repeated in triplicates.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c06337>.

General procedure of DFF-TIMs and 5-HMF-BIMs; optimization results of prepared catalyst CNSLF- $\text{SO}_3\text{H}$ : back titration, summary of characterization (BET, CHNS, and pH) data,  $p$ -XRD data, IR data, and TGA curve; and characterization interpreted data including M.P., IR, % yield, HRMS, and the spectra of  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR of all compounds (BIMs and TIMs) (PDF)

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### Author Contributions

Gayatri D. Kotkar: Methodology, investigation, data curation, and writing—original draft. Santosh G. Tilve: Conceptualization, project administration, resources, and writing—original draft.

### Notes

The authors declare no competing financial interest.

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