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Sulfonation of Carbonized Xylan-type Hemicellulose: A Renewable and Effective Biomass-based Biocatalyst for the Synthesis of O- and N-Heterocycles

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Abstract

The application of biomass-based carbonaceous solid acid in catalysis is attracting more and more attention in the field of chemistry. In this work, a heterogeneous carbon-based solid acid biocatalyst (CXH-SO_3H) with regular spherical structure was synthesized from xylan-type hemicellulose (XH) by a simple two-step method. The catalyst was successfully applied in the synthesis of O- and N-heterocycles with yields of 80-96%, 98-99% and 60-97%, respectively. In the view of environment and economy, the CXH-SO_3H shows the merits of environmental friendliness, easy operation, simple work-up, excellent yields and the avoidance of organic solvents and inexpensive catalysts. Moreover, the as-synthesized solid acid catalyst could be used for several cycles without significant loss of its catalytic activity. The results of FT-IR, XRD and SEM showed that no obvious difference in physico-chemical structures of CXH-SO_3H were observed. Thus, the eco-friendly CXH-SO_3H catalyst is promising for green synthesis of O- and N-heterocycles from low-cost feed-stocks and has good prospect in partially substituting commercially available solid acid, liquid acid catalysts and precious metal catalysts.

Keywords: Carbon-based solid acid, Xylan-type hemicelluloses, O- and N-Heterocycles, Benzoxanthenes, 4-Aryl-*NH*-1,2,3-triazoles

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1. Introduction

Oxygen and nitrogen heterocycles are structures frequently found in a large number of biologically active products.[1] The interest of the scientific community in synthesis of oxygen and nitrogen heterocycles has been enormous. As important components of these heterocycles, xanthenes and 1,2,3-triazoles attract significant attention for their important biological activities.[2] Furthermore, xanthenes and its derivatives can also be employed as brilliant fluorescent dyes,[3] pH-sensitive fluorescent materials,[4] and antagonists in photodynamic therapy.[5] Thus, synthesis of these two compounds are of great importance. To this end, great efforts have been devoted to synthesizing these heterocycles with different catalysts, such as [CTA]Fe/MCM-41,[2b] proline triflate,[6] ionic liquids,[7] $[Ir(cod)Cl]_2$,[2d] $Rh_2(Oct)_4$,[8] CuI,[2e] $AgSbF_6$.[9] Currently, acid catalysts were frequently used in these heterocycles synthesis based on their mild acidity.[10] However, most of these protocols suffer from undesirable employment of harsh reaction conditions, long reaction time, tedious work-ups, toxic organic solvents and using transition-metal catalysts. Hence, developing a mild and practical catalytic system for the preparation of xanthenes and 1,2,3-triazoles remains a challenge.

Recently, developing metal-free catalysts is of great relevance for industry-university-research cooperation in the view of green and sustainable chemistry point.[11] In this scenario, functional carbon materials have became a focus of whole society.[12] They can serve as “green” and efficient options for catalytic transformations. To this end, great efforts have been devoted to synthesizing novel carbon materials that have an excellent catalysis activity. Among these processes, biopolymers as raw materials to produce high-performance and environmentally friendly

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catalysts have attracted considerable amount of attentions due to their low cost, abundance and renewability. Since the biomass-based carbonaceous solid acid catalyst from D-glucose was first reported by Toda et al.,[13] much efforts have been devoted to developing a variety of carbon-based catalysts from raw biomass with a high cellulose/hemicellulose content[14] by thermal or hydrothermal carbonization. Although cellulose is a good biodegradable material in the synthesis of carbon-based catalyst, this process is not an economical and advisable option for utilization of cellulose when compared with the present applications of cellulose (Fig. S1).[15]

Hemicelluloses are the second most abundant renewable polymers in lignocellulosic biomass.[16] Unlike cellulose, in which the monomer unit is chemically homogeneous, hemicelluloses are a series of heterogeneous polysaccharides with diverse structures. In addition, these polysaccharides are different from each other in the light of structure, physical and physicochemical properties.[17] Therefore, how to use the hemicelluloses to develop functional materials is a challenge. In the early reports, hemicelluloses can be converted to many value-added chemicals, such as ethanol, furfural, levulinivic acid, 5-hydroxymethylfurfural (HMF) and xylitol.[18] Similarly, many hemicelluloses-based materials have been reported in literature.[19] The US Department of Energy estimated that about 400 million tons of hemicelluloses are available in the USA each year.[20] Moreover, it is reported that about 15 million tons of hemicelluloses are produced annually from the USA pulp and paper industry.[19] However, many of these hemicelluloses are not utilized for value-added applications. The partial carbonization of hemicelluloses to produce carbons is a promising way for the utilization of hemicelluloses. These functional carbons are rich in oxygen and hydrogen that are

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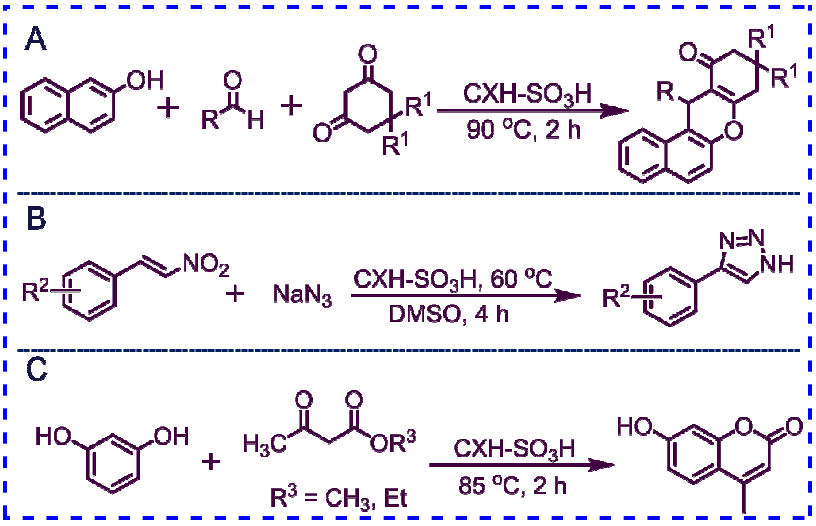
beneficial for the further sulfonation.[11d, 13] The sulfonated carbons are promising candidates for synthesis,[21] biomass conversion[11d] and biodiesel production.[13]

In the present work, we report a simple and eficient procedure for one-pot synthesis of oxygen and nitrogen heterocycles using CXH-SO_3H as an effective, neutral, heterogeneous, and reusable acidic catalyst under mild conditions (Scheme 1). The preparation method of CXH-SO_3H is quite simple and suit for mass product with low cost. The established process represents a new protocol for rational utilization of the waste hemicellulose from the pulp and paper industry biomass, which may hold great potential in industrial applications.



Scheme 1 The CXH-SO_3H was applied in the synthesis of benzoxanthenes (A), 4-aryl-*NH*-1,2,3-triazoles (B), and 7-hydroxy-4-methylcoumarin (C).

2. Results and discussion

The functional group of CXH-SO_3H was detected by FT-IR. As illustrated in Fig. 1A-a, the broad band observed at 3430 cm^{-1} is assigned to -OH group linked with the neighbor oxygen or sulfuric acid by hydrogen bonds, indicating that these acidic groups are located in close

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proximity.[22] The peaks at around 1177 cm^{-1} and 1037 cm^{-1} are ascribed to the stretching of O=S=O in -SO_3H groups.[23]

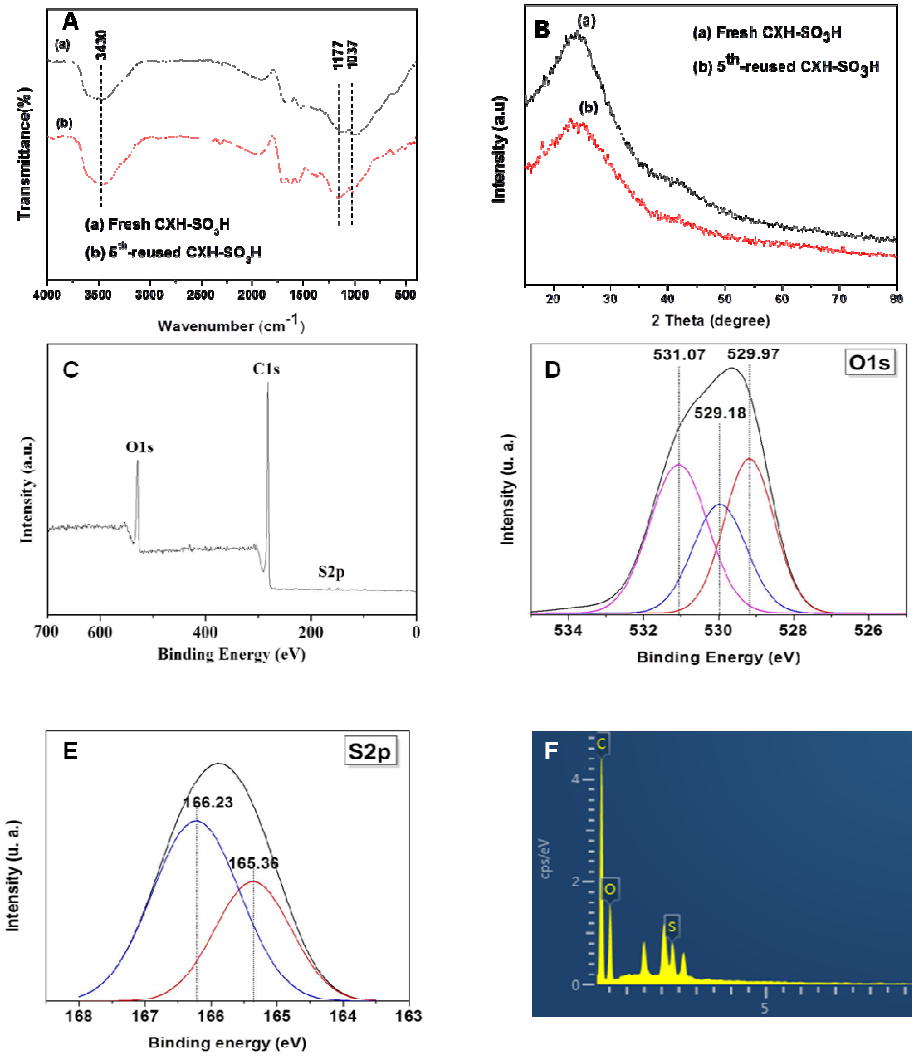

Fig. 1 The characterization of fresh CXH-SO_3H and the fifth reused CXH-SO_3H: (A) FT-IR spectra, (B) XRD patterns, (C) XPS spectra of CXH-SO_3H, (D) O_{1S}, (E) S_{2P}, and (F) EDX.

As can be seen from the XPS results, the elements C, O and S are observed in the low-resolution XPS spectrum of CXH-SO_3H (Fig. 1C). The high-resolution O_{1S} and S_{2P} are shown in Fig. 1D and 1E, respectively. In addition, the presences of the above-mentioned elements

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are also observed from EDX (Fig. 1F), which well agrees with the results of XPS and FT-IR.

In order to quantify the sulfonic group in CXH-SO_3H, acid-base titration and EA experiments were performed and the results are shown in Table 1. The content of sulfur determined by EA is about 3.55 wt%, indicating that 1.10 mmol/g -SO_3H in CXH-SO_3H. This value was slightly higher than that from acid-base titration, suggesting that some sulfur species are probably not in the acidic form.

Table 1 Acid density of CXH-SO_3H

Sample	S content[a] (wt%)	SO_3H density[b] (mmol/g)	SO_3H density[c] (mmol/g)
CXH-SO_3H	3.55	1.10	1.08

[a] Determined by EA. [b] Calculated from the S content. [c] Determined by acid-base titration.

In addition, acetic acid lignin, alkali lignin and industrial lignin were also treated via the same step to obtain sulfonation of carbonized acetic acid lignin (CAAL-SO_3H), sulfonation of carbonized alkali lignin (CAL-SO_3H) and sulfonation of carbonized industrial lignin (CIL-SO_3H). As shown in Fig. 2, the as-prepared three types of lignin-based solid acids show a smooth surface and irregular block morphology (Fig. 2A-2F), while CXH-SO_3H exhibites regular spherical morphology (from 8 to 30 μm) with smooth surface (Fig. 2G and 2H). Meanwhile, EA results (Table S1) show that the content of sulfur element in CXH-SO_3H is significantly higher than those of lignin-based solid acids. This result demonstrates that CXH-SO_3H has more acide sites.

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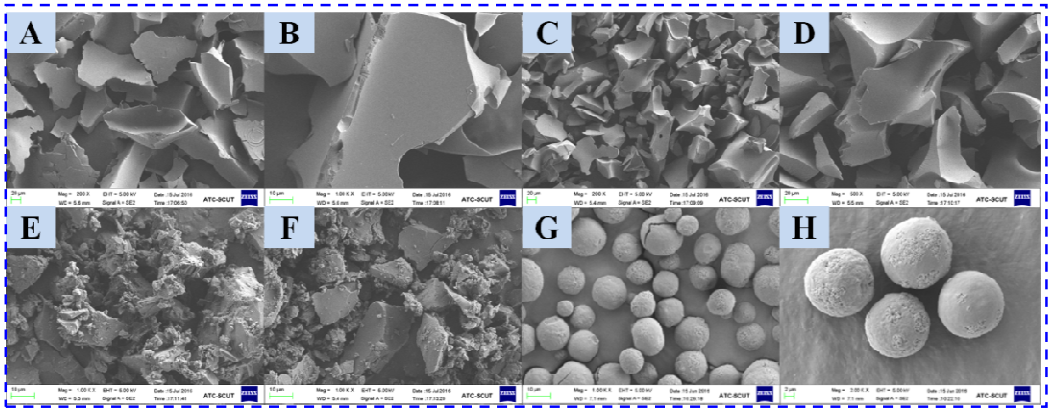
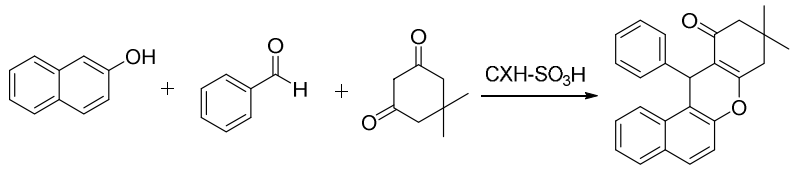


Fig. 2 SEM spectra of CAAL-SO_3H (A and B), CAL-SO_3H (C and D), CIL-SO_3H (E and F) and CXH-SO_3H (G and H).

Table 2 Effect of biocatalyst dosage on the one-pot condensation of benzaldehyde with 2-naphthol and dimedone [a]



Entry	Catalyst (mol%)	Temperature (^oC)	Time (h)	Yield (%)[b]
1	0	90	2	trace
2	2.16	90	2	74
3	3.24	90	2	85
4	4.32	90	2	88
5	5.40	90	2	89

[a]Typical reaction conditions: benzaldehyde (0.5 mmol), 2-naphthol (0.5 mmol), dimedone (0.6 mmol). [b]Isolated yield.

The feasibility for the green synthesis of benzoxanthenes catalyzed by CXH-SO_3H was investigated. Initially, the experiments were performed by using benzaldehyde (0.5 mmol), 2-naphthol (0.5 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (0.6 mmol) as substrates at 90 ^oC for 2 h under solvent-free condition. The results are summarized in Table 2. Only trace product was detected in the absence of biocatalyst (Table 2, entry 1). However, a yield of 74% could be obtained by using

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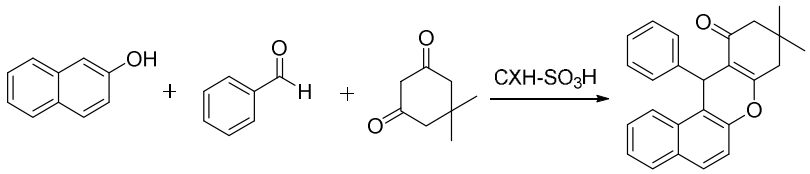
CXH-SO_3H (2.16 mol%) as a biocatalyst, indicating a good catalytic performance of CXH-SO_3H. Encouraged by the result, the effect of amount of CXH-SO_3H on the synthesis of benzoxanthene was explored. The results showed that the yield of 2a increased with the increasing amount of CXH-SO_3H (Table 2, entries 2-5); however, an increase in the amount of CXH-SO_3H from 4.32 to 5.40 mol% did not lead to significant change in the yield (Table 2, entries 4-5). Thus, 4.32 mol% CXH-SO_3H was optimal for this reaction from atom economy.

Table 3 Effects of reaction time and temperature on the synthesis of benzoxanthenes [a]



Entry	Catalyst (mol %)	Temperature(^{o}C)	Time (h)	Yield (%)[b]
1	4.32	70	3	64
2	4.32	80	3	81
3	4.32	80	2	80
4	4.32	90	2	88
5	4.32	90	1	84
6	4.32	110	1	85

[a]Typical reaction conditions: benzaldehyde (0.5 mmol), 2-naphthol (0.5 mmol), dimedone (0.6 mmol). [b]Isolated yield.

Thereafter, the effects of temperature and time on the reaction were also investigated. The results are given in Table 3. As the temperature rises, the yield of 2a shows an increasing trend (Table 3, entries 1-2, 3-4). In addition, the output of 2a increased along with the extension of reaction time under the same condition (Table 3, entries 2-3, 4-5). According to the above results, 2 h and 90 ^{o}C were chosen as the optimum reaction time and temperature for sequent reactions.

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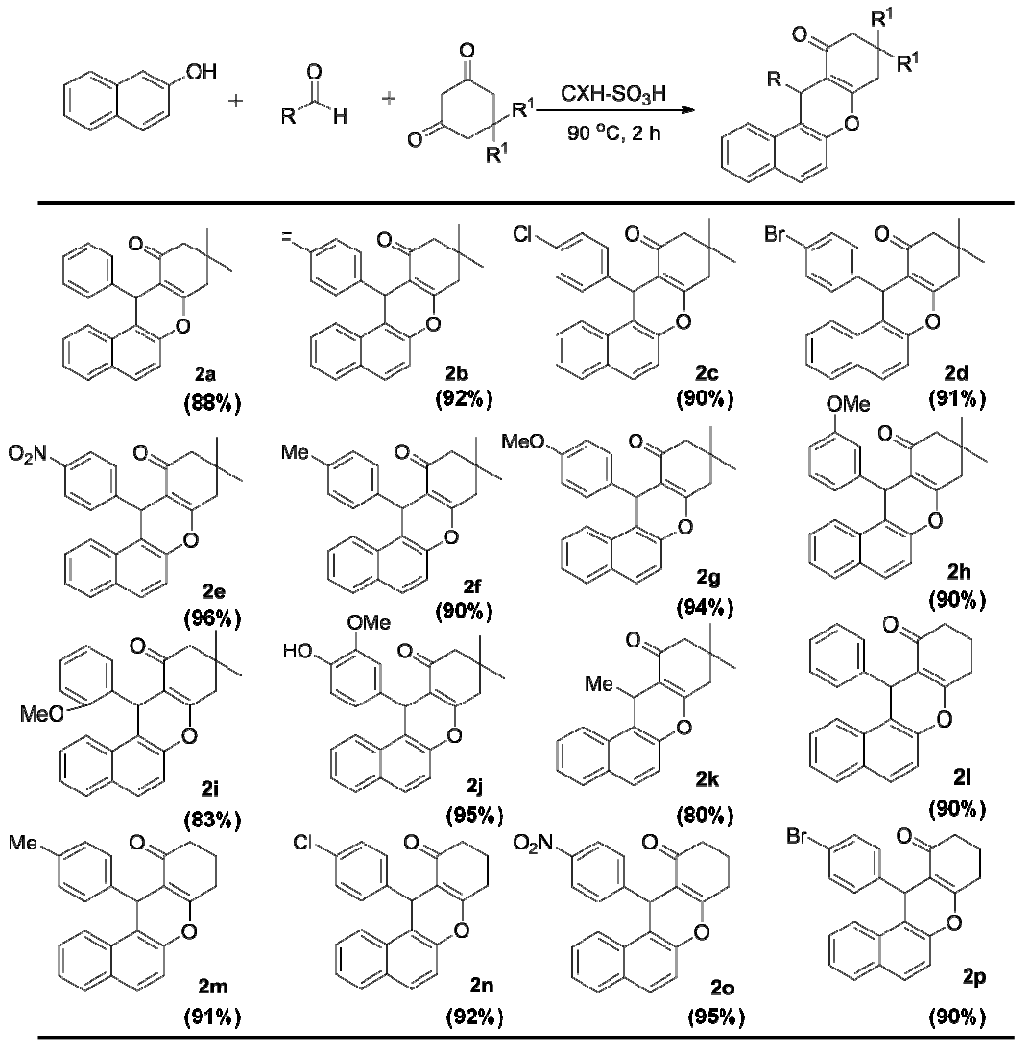

Reaction conditions: aldehudes (0.5 mmol), 2-naphthol (0.5 mmol), cyclic 1,3-dicarbonyl (0.6 mmol), CXH-SO_3H (4.32 mol %), 90 ^oC, 2 h.

Scheme 2 One-pot synthesis of benzoxanthenes catalyzed by CXH-SO_3H.

To examine the extent of the application of biocatalyst in this condensation reaction, the three-component reaction of a variety of aldehydes, 2-naphthol and cyclic 1,3-dicarbonyl compounds in the presence of CXH-SO_3H was also investigated in the optimal condition (Scheme 2). The procedure was highly effective for the synthesis of benzoxanthene. Most importantly, aromatic aldehydes having either electron donating or withdrawing substituents reacted efficiently and gave good to excellent yields (83-96%). Aliphatic aldehydes could also react

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smoothly to afford a good yield under the same reaction condition. On the other hand, 1,3-cyclohexanedione could also achieve good results. Thus, CXH-SO_3H could act as an efficient biocatalyst for the synthesis of benzoxanthene.

Table 4 Brief comparison of yields for the one-pot reaction of benzaldehyde, 2-naphthol and dimedone from various methods

Entry	Catalyst	Solvent	Temperature (^oC)	Time	Yield (%)	Reference
1	$CeCl_3 \cdot 7H_2O$	MeOH	50	2 h	90	34a
2	$Sr(OTf)_2$	MeOH	50	5 h	85	34b
3	TPPMS/CBr_4[a]	neat	100	80 min	84	34c
4	$[Cu(bpdo)_2 \cdot 2H_2O]^{2+}$/SBA-15[b]	neat	150	55 min	85	34d
5	PVPP.OTf[c]	toluene	110	5 h	85	34e
6	$B(HSO_4)_3$	neat	120	10 min	87	34f
7	Trityl Chloride	neat	110	50 min	89	32d
8	*p*-TSA	neat	120	45 min	88	34g
9	$NaHSO_4 \cdot SiO_2$	DCE	reflux	4	87	32e
10	n-WSA[d]	neat	100	90 min	90	34h
11	Fe_3O_4/CS-Ag NPs	water	80	30 min	94	32c
12	CXH-SO_3H	neat	90	2 h	88	This work

[a]TPPMS/CBr_4: Triphenylphosphine-*m*-sulfonate/carbon tetrabromide. [b]bpdo: 2,2' bipyridine, 1,1'-dioxide. [c]PVPP.OTf: Polyvinylpolypyrrolidoniume triflate. [d]n-WSA: nano-WO_3-SO_3H.

To have a better understanding of our catalytic system, the effectiveness of CXH-SO_3H was compared to those of catalysts reported previously for the synthesis of 12-phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one, as shown in Table 4. Generally, the yield in this work is similar to those

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reported previously. Although some of them have excellent yields, additional solvents (MeOH, toluene, and DCE et al.) were used (Table 4, entries 1, 5, 9), or the reaction time was relatively long (Table 4, entry 9). Although Fe_3O_4/CS-Ag NPs could obtain a higher yield than CXH-SO_3H within a short time, but the synthesis of the catalyst was very tedious and required additional solvent (Table 4, entry 11). Furthermore, the catalytic activity of XH source for the prepararion of CXH-SO_3H catalyst was also investigated. In this work, the xylan-type hemicellulose obtained from bamboo, eucalyptus, and pulping and papermaking industry were used to prepare CXH-SO_3H catalysts under the same conditions. All the CXH-SO_3H catalysts showed a good catalytic activity for the eco-friendly synthesis of 12-Phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (Table S2). Therefore, the source of raw materials of CXH-SO_3H catalysts doesn't influence the catalytic activity.

The excellent catalysis activity of CXH-SO_3H inspired us to explore its catalytic activity for synthesis of coumarins. Coumarin and their derivatives are important oxygen heterocycles in the realm natural and synthetic organic chemists mainly due to their various biological properities and pharmaceuticals applications such as antilipoperoxidant,[24] antimicrobial,[25] antithrombotic,[26] anticancer,[27] anti-HIV[28] and antioxidant,[29] etc. Moreover, they have been commercialized as lasers for fluorescent labels, fluorescent probes[30] and enzymatic measurements.[31] Therefore, synthesis of coumarins is of great importance. For coumarins synthesis, the condensation reaction was carried out by mixing resorcinol and ethyl acetoacetate or methyl acetoacetate with the yield of 98% and 99%, respectively (Scheme 1C).

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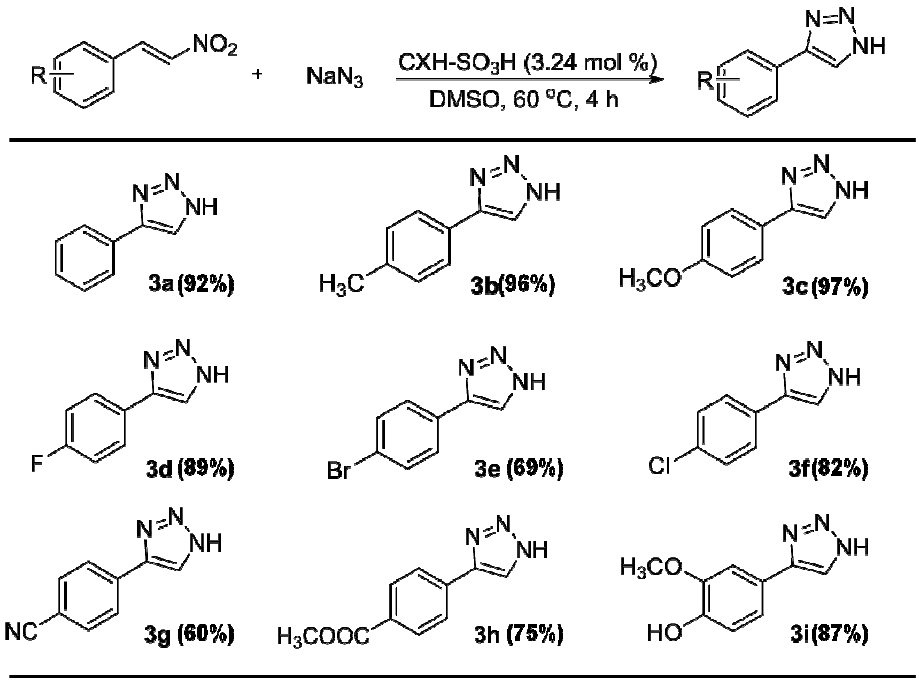

Reaction conditions: nitroolefin (0.3 mmol), NaN_3 (0.45 mmol), CXH-SO_3H (3.24 mol %), DMSO (1.5 mL), 60 ^oC, 4 h.

Scheme 3 One-pot synthesis of 4-aryl-*NH*-1,2,3-triazoles catalyzed by CXH-SO_3H

The model reaction of synthesis of nitrogen heterocycles was carried out by mixing trans-3-nitrostyrene, NaN_3, and CXH-SO_3H in DMSO and gave a yield of 72% (Table S3, entry 1). Encouraged by this result, the experimental condition was optimized and the corresponding results were shown in Table S3 and Table S4. From the perspective of green chemistry, the optimal results for the transformation were observed when trans-3-nitrostyrene (0.3 mmol) and NaN_3 (0.45 mmol) reacted in DMSO at 60 ^oC for 4 h in the presence of CXH-SO_3H (3.24 mol%). Subsequently, a series of nitroolefin and NaN_3 were explored in the presence of CXH-SO_3H. As seen from Scheme 3, the catalysis of CXH-SO_3H was highly effective for the synthesis of 4-aryl-*NH*-1,2,3-triazoles. A variety of nitroolefins with either electron-donating or electron-withdrawing groups were converted to 4-aryl-*NH*-1,2,3-triazoles in excellent yields (60-97%). It is found that, as

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compared with the nitroolefin with electron-donating groups in Scheme 3, the yield of nitroolefin with electron-withdrawing groups was lower.

The recyclability and reusability of catalysts are key factors for green synthesis. In this work, the reusability of CXH-SO_3H was explored by using benzaldehyde, 2-naphthol and dimedone as model substrates under the optimized condition. As depicted in Fig. 3, CXH-SO_3H exhibited an excellent catalytic stability, and it could be reused for five times without a significant loss in catalytic activity. After reaction, the biocatalyst could be reused by simple filtration, washing and drying. In addition, the structural characteristic of the reused biocatalyst was checked by FT-IR (Fig. 1A-b), XRD (Fig. 1B-b), and SEM (Fig. 4C, 4D). The characteristic peaks of the fifth reused biocatalyst show no significant difference from that of fresh CXH-SO_3H (Fig. 1A), indicating that the reuse of CXH-SO_3H did not change the chemical structure of CXH-SO_3H.

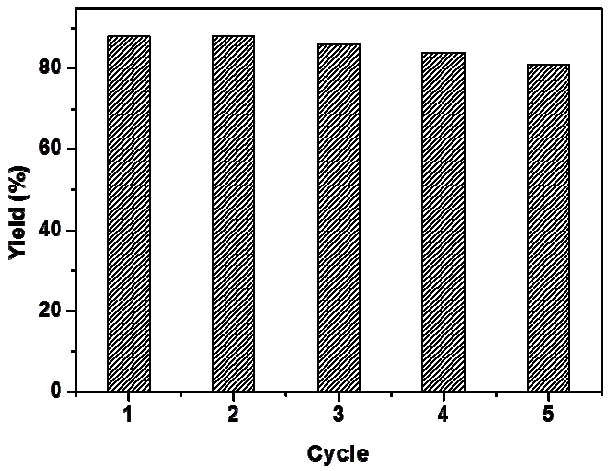

Fig. 3 Recycle of CXH-SO_3H

The phase structure of the fresh CXH-SO_3H and the recycled CXH-SO_3H after five cycles were determined by XRD. As indicated in Fig. 1B-a, the fresh biocatalyst exhibited a broad diffraction peak at 2θ = 20-30°, which

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is assigned to the amorphous carbon structure of CXH-SO_3H. The broad diffraction peak of the fifth reused biocatalyst showed little difference (Fig. 1B-b), indicating that the reuse of CXH-SO_3H did not change the crystallographic property of CXH-SO_3H.

The morphologies of fresh CXH-SO_3H and the recycled CXH-SO_3H after five cycles were observed by SEM, and the results are presented in Fig. 4. Both the fresh CXH-SO_3H and the reused CXH-SO_3H are regular spherical particles, demonstrating the good stability of CXH-SO_3H during catalysis.

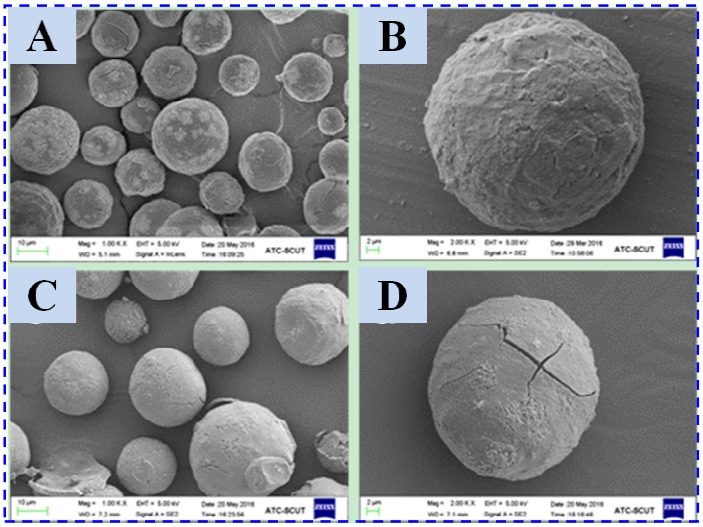

Fig. 4. SEM images of fresh CXH-SO_3H (A and B) and the fifth reused of CXH-SO_3H (C and D)

A plausible mechanism for the synthesis of 12-phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one catalyzed by CXH-SO_3H is shown in Fig. 5. According to literatures[32] we suppose that the reaction might proceed via the initial formation of *ortho*-quinone methides (**4**),[32e, 33] which was formed by the nucleophilic addition of activated 2-naphthol (**2**) to the activation of the carbonyl group of benzaldehyde (**1**), in the presence of CXH-SO_3H. Then, the

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intermediate **4** was activated as a Michael acceptor, which was attacked by nuclephile dimedone in the presence of CXH-SO_3H. Finally, the condensation process resulte in the formation of **7** which was cyclyzed to **8** and subsequently produced target product **9** upon dehydration.

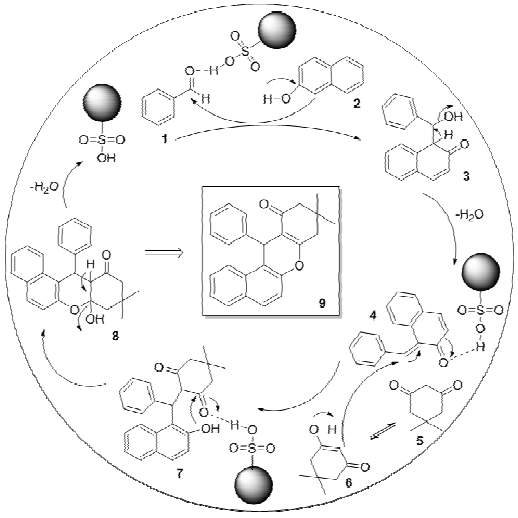

Fig. 5 A plausible mechanism for synthesis of 12-phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one catalyzed by CXH-SO_3H

3. Conclusions

The present work describes the synthesis and characterization of a novel heterogeneous CXH-SO_3H biocatalyst that exhibited an excellent catalytic activity. The biocatalyst showed a high catalytic potential for the eco-friendly multicomponent synthesis of oxygen and nitrogen heterocycles. Furthermore, the procedure had several advantages, such as ease of preparation and handling of the biocatalyst, simple work-up procedure, mild reaction conditions, high product yield and the use of inexpensive, environmentally friendly, and renewable biomass. Compared with the commercially available solid acid catalysts and liquid acid catalysts, CXH-SO_3H showed much better performance. Therefore, CXH-SO_3H is promising to partially replace commercially available solid

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acid catalysts and liquid acid catalysts in the synthesis of oxygen and nitrogen heterocycles.

4. Experimental

4.1 General information

Xylan-type hemicelluloses were obtained from by-product of pulping and papermaking industry. Aldehyde, 2-naphthol, cyclic 1,3-dicarbonyl compounds and NaN_3 used were analysis grade and were purchased from Aladdin Industrial Corporation. Nitromethane, sodium chloride, magnesium sulfate anhydrous and other reagents used were analysis grade and were provided by Guangzhou Chemical Reagent Factory, China. All chemicals were used without further purification. X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Focus Diffractometer equipped with Cu Kα radiation (λ = 0.15418 nm). The voltage and current were 40 kV and 40 mA, respectively. Scanning electron microscope (SEM) images were derived on a Zeiss EVO 18 (Jena, Germany) operated at a 10 kV acceleration voltage. XPS measurements were conducted on a Kratos Axis Ultra DLD spectrometer employing amonochromated Al Kα X-ray source (hν = 1486.6 eV). IR spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer using KBr pellets. Element analysis (EA) was performed on a Vario EI III elementar.

4.2 Preparation of Sulfonation of Carbonized Xylan-type Hemicelluloses (CXH-SO_3H)

3 g of XH was carbonized at 350 ^oC for 90 min under nitrogen atmosphere to produce the incomplete carbonization product CXH. Thereafter, the CXH was added into concentrated H_2SO_4 with a ratio of solid to liquid = 1: 30 (g: mL), and heated at 150 ^oC for 15 h under

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nitrogen atmosphere to introduce -SO_3H groups. The mixture was immediately cooled to room temperature and diluted with 2000 mL deionized water, followed by filtrating and washing with hot deionized water (> 80 ^oC) until no sulfate ions were detected in the washed water. Finally, the resulting biocatalyst CXH-SO_3H was collected and dried in a vacuum oven at 80 ^oC for 24 h to remove excess moisture.

4.3 General Procedure for the Synthesis of Benzoxanthenes

In a typical experimental procedure, CXH-SO_3H (4.32 mol%) was added to a mixture of aldehyde (0.5 mmol), 2-naphtol (0.5 mmol), and 1,3-cyclohexadione (0.6 mmol) in a 15 mL pressure flask with a magnetic stirring bar. The reaction processed at 90 ^oC for 2 h, as indicated by TLC for a complete reaction. Upon the completion of the reaction, ethyl acetate (10 mL) was added when the reaction system was cooled to room temperature, and fully crushed, rested for a period of time, and then filtered. The solid biocatalyst was washed with ethyl acetate (10 mL) for two times and used for subsequent cycles after drying under vacuum. Finally, the combined filtrate was evaporated under reduced pressure and the target products were obtained by column chromatography on silica gel using ethyl acetate/hexane as an eluent. All products were characterized by NMR spectroscopy.

12-Phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (2a): ^1H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, J = 12.0 Hz, 1H), 7.79-7.76 (m, 2H), 7.45-7.34 (m, 5H), 7.21-7.18 (m, 2H), 7.09-7.06 (m, 1H), 5.75 (s, 1H), 2.57 (s, 2H), 2.28 (dd, J_1 = 18.0 Hz, J_2 = 36.0 Hz, 2H), 1.12 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.74, 163.77, 147.67, 144.68, 131.41, 131.33, 128.74, 128.34, 128.30, 128.15,

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126.91, 126.15, 124.80, 123.59, 117.62, 116.95, 114.19, 50.81, 41.31, 34.63, 32.14, 26.21, 27.05.

12-(4-Fluorinephenyl)-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2b): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77 (d, J = 6.0 Hz, 1H), 7.39-7.34 (m, 2H), 7.32-7.26 (m, 5H), 6.88-6.85 (m, 2H), 5.71 (s, 1H), 2.57 (s, 2H), 2.27 (dd, J_1 = 18.0 Hz, J_2 = 36.0 Hz, 2H), 1.12 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.85, 163.87, 161.96, 160.34, 147.70, 140.52, 131.21, 129.83 (d, J = 7.55.0 Hz), 128.96, 128.43, 127.02, 124.94, 123.49, 117.34, 117.01, 115.06, 114.92, 114.06, 50.84, 41.37, 33.95, 32.20, 29.27, 27.04.

12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2c): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, J = 6.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.42-7.24 (m, 5H), 7.13-7.12 (m, 2H), 5.68 (s, 1H), 2.55 (s, 2H), 2.24 (dd, J_1 = 18.0 Hz, J_2 = 36.0 Hz, 2H), 1.10 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.87, 164.06, 147.67, 143.19, 131.87, 131.46, 131.15, 129.75, 129.05, 128.43, 128.34, 127.06, 124.97, 123.39, 116.99, 116.98, 113.75, 50.76, 41.32, 34.08, 32.13, 29.25, 27.04.

12-(4-Bromophenyl)-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2d): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88 (d, J = 12.0 Hz, 1H), 7.77-7.74 (m, 2H), 7.42-7.27 (m, 5H), 7.24-7.20 (m, 2H), 5.66 (s, 1H), 2.54 (s, 2H), 2.24 (dd, J_1 = 12.0 Hz, J_2 = 36.0 Hz, 2H), 1.10 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.76, 164.07, 147.68, 143.72, 131.45, 131.29, 131.15, 130.15, 129.06, 128.44, 127.08, 124.98, 123.39, 120.06, 116.98, 116.92, 113.68, 50.79, 41.33, 34.22, 32.18, 29.25, 27.09.

12-(4-Nitrophenyl)-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2e): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, J = 12.0 Hz, 2H),

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7.84-7.80 (m, 3H), 7.53-7.51 (m, 2H), 7.44-7.26 (m, 3H), 5.82 (s, 1H), 2.59 (s, 2H), 2.27 (dd, J_1 = 18.0 Hz, J_2 = 48.0 Hz, 2H), 1.13 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.66, 164.57, 151.80, 147.69, 146.24, 131.49, 130.93, 129.55, 129.28, 128.59, 127.29, 125.15, 123.53, 123.02, 116.98, 115.94, 112.88, 50.68, 41.31, 34.79, 32.16, 29.22, 26.96.

12-(p-Tolyl)-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2f): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, J = 6.0 Hz, 1H), 7.75-7.71 (m, 2H), 7.41 (m, 1H), 7.34-7.31 (m, 2H), 7.23-7.21 (m, 2H), 6.97-6.95 (m, 2H), 5.66 (s, 1H), 2.54 (s, 2H), 2.24 (dd, J_1 = 18.0 Hz, J_2 = 36.0 Hz, 2H), 2.18 (s, 3H), 1.09 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.91, 163.79, 147.73, 141.91, 135.68, 131.53, 131.47, 128.97, 128.74, 128.40, 128.31, 126.99, 124.88, 123.72, 117.93, 117.07, 114.43, 50.97, 41.45, 34.34, 32.29, 29.30, 27.30, 21.01.

12-(4-Methoxyphenyl)-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2g): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, J = 12.0 Hz, 1H), 7.76-7.72 (m, 2H), 7.41-7.24 (m, 5H), 6.70-6.69 (m, 2H), 5.65 (s, 1H), 3.66 (s, 3H), 2.54 (s, 2H), 2.25 (dd, J_1 = 18.0 Hz, J_2 = 30.0 Hz, 2H), 1.10 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.93, 163.62, 157.73, 147.63, 137.12, 131.44, 131.34, 129.31, 128.60, 128.32, 126.89, 124.80, 123.64, 117.83, 116.98, 114.36, 113.53, 55.00, 50.87, 41.33, 33.77, 32.19, 29.24, 27.13.

12-(3-Methoxyphenyl)-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2h): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, J = 6.0 Hz, 1H), 7.75-7.72 (m, 2H), 7.42-7.23 (m, 3H), 7.08-7.06 (m, 1H), 6.93-6.90 (m, 2H), 6.59-6.57 (m, 1H), 5.69 (s, 1H), 3.68 (s, 3H), 2.53 (s, 2H), 2.25 (dd, J_1 = 18.0 Hz, J_2 = 30.0 Hz, 2H), 1.09 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.76, 163.86, 159.38, 147.68, 146.26, 131.41, 131.37, 129.02, 128.77, 128.30, 126.92, 124.82, 123.60, 120.92, 117.49,

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116.97, 114.57, 114.07, 111.19, 54.91, 50.84, 41.33, 34.57, 32.16, 29.18, 27.16.

12-(2-Methoxyphenyl)-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2i): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.28 (d, J = 6.0 Hz, 1H), 7.72-7.66 (m, 2H), 7.43-7.23 (m, 4H), 7.03-7.00 (m, 1H), 6.79-6.72 (m, 2H), 5.96 (s, 1H), 3.93 (s, 3H), 2.57 (s, 2H), 2.20 (dd, J_1 = 12.0 Hz, J_2 = 36.0 Hz, 2H), 1.10 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.76, 164.21, 156.30, 147.63, 133.30, 131.84, 131.22, 130.56, 128.29, 128.14, 127.57, 126.69, 124.60, 123.95, 120.68, 118.28, 116.91, 113.61, 111.48, 55.84, 50.87, 41.43, 32.17, 29.40, 26.96.

12-(3-Methoxy-4-hydroxylphenyl)-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2j): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 (d, J = 12.0 Hz, 1H), 7.79-7.75 (m, 2H), 7.45-7.31 (m, 3H), 7.01 (m, 1H), 6.68-6.64 (m, 2H), 5.65 (s, 1H), 3.83 (s, 3H), 2.56 (s, 2H), 2.28 (dd, J_1 = 18.0 Hz, J_2 = 30.0 Hz, 2H), 1.12 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 197.07, 163.73, 147.74, 146.08, 143.81, 136.97, 131.47, 131.42, 128.73, 128.36, 126.92, 124.86, 123.67, 121.01, 117.76, 116.98, 114.44, 114.09, 111.33, 55.88, 50.91, 41.40, 34.14, 32.24, 29.28, 27.12.

12-Methyl-9,9-dimethyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2k): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.08 (d, J = 6.0 Hz, 1H), 7.81 (d, J = 6.0 Hz, 1H), 7.69 (d, J = 6.0 Hz, 1H), 7.57-7.54 (m, 1H), 7.45-7.43 (m, 1H), 7.19 (d, J = 6.0 Hz, 1H), 4.60-4.57 (m, 1H), 2.52 (s, 2H), 2.36 (s, 2H), 1.36 (d, J = 6.0 Hz, 3H), 1.17 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 197.50, 164.94, 147.28, 131.39, 131.14, 128.55, 128.00, 126.81, 124.78, 123.03, 119.96, 117.03, 114.63, 51.01, 41.34, 32.21, 29.44, 27.17, 23.33, 22.97.

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12-Phenyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (2l): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 6.0 Hz, 1H), 7.79-7.76 (m, 2H), 7.44-7.35 (m, 5H), 7.21-7.18 (m, 2H), 7.09-7.07 (m, 1H), 5.78 (s, 1H), 2.76-2.63 (m, 2H), 2.48-2.35 (m, 2H), 2.05-1.94 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.92, 165.49, 147.70, 144.98, 131.41, 131.31, 128.75, 128.41, 128.29, 128.19, 126.90, 126.17, 124.80, 123.60, 117.62, 116.89, 115.47, 36.96, 34.56, 27.64, 20.18.

12-(p-Tolyl)-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2m): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 6.0 Hz, 1H), 7.73-7.70 (m, 2H), 7.39-7.29 (m, 3H), 7.22-7.20 (m, 2H), 6.96 (d, *J* = 6.0 Hz, 1H), 5.69 (s, 1H), 2.70-2.57 (m, 2H), 2.44-2.30 (m, 2H), 2.17 (s, 3H), 2.00-1.89 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 197.12, 165.53, 147.61, 142.07, 135.62, 131.39, 131.29, 128.88, 128.63, 128.25, 128.23, 126.86, 124.75, 123.58, 117.75, 116.85, 115.58, 36.89, 34.11, 27.60, 20.88, 20.14.

12-(4-Chlorophenyl)-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2n): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 6.0 Hz, 1H), 7.80-7.77 (m, 2H), 7.45-7.28 (m, 5H), 7.16-7.14 (m, 2H), 5.73 (s, 1H), 2.76-2.63 (m, 2H), 2.49-2.36 (m, 2H), 2.08-1.93 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 197.20, 165.89, 147.65, 143.44, 131.90, 131.45, 131.11, 129.80, 129.05, 128.41, 128.36, 127.05, 124.96, 123.40, 116.97, 115.03, 36.86, 34.06, 27.64, 20.17.

12-(4-Nitrophenyl)-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (2o): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 6.0 Hz, 2H), 7.81-7.78 (m, 3H), 7.52-7.48 (m, 2H), 7.43-7.35 (m, 3H), 5.83 (s, 1H), 2.78-2.66 (m, 2H), 2.48-2.36 (m, 2H), 2.10-1.92 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.76, 166.19, 152.02, 147.63, 146.18, 131.42, 130.86, 129.48, 129.30, 128.52, 127.20, 125.07, 123.47, 122.99, 116.91, 115.88, 114.07, 36.80, 34.70, 27.61, 20.08.

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12-(4-Bromophenyl)-8,9,10,12tetrahydrobenzo[a]xanthen-11-one (2p): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 12.0 Hz, 1H), 7.74-7.71 (m, 2H), 7.39-7.25 (m, 5H), 7.21-7.19 (m, 2H), 5.68 (s, 1H), 2.69-2.56 (m, 2H), 2.43-2.30 (m, 2H), 2.00-1.86 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.84, 165.61, 147.59, 143.93, 131.36, 131.22, 131.04, 130.15, 128.99, 128.35, 126.98, 124.88, 123.31, 120.01, 116.84, 116.81, 114.85, 36.84, 34.09, 27.55, 20.10.

4.4 General Procedure for the Synthesis of 7-Hydroxy-4-methylcoumarin

In a typical procedure, a mixture of resorcinol (1 mmol), ethyl acetoacetate or methyl acetoacetate (1 mmol), and CXH-SO_3H (3.24 mol%) was successively charged into a 15 mL pressure flask with a magnetic stirring bar. Then the reaction system was placed in an oil-bath (85 ^{o}C) for the desired reaction time with magnetic stirring, and the progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was cooled to room temperature and added with cold ethanol (10 mL). The biocatalyst was then separated by filtration and ice-cold distilled water was poured into the reaction mixture to precipitate the crude product. The collected crude product was recrystallized from ethanol, producing high quality 7-hydroxy-4-methylcoumarin. The product was confirmed by NMR spectroscopy.

7-Hydroxy-4-methylcoumarin

^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.54 (s, 1H), 7.56 (d, *J* = 6.0 Hz, 1H), 6.81 (d, *J* = 12.0 Hz, 1H), 6.73 (s, 1H), 6.12 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6): δ = 161.25, 160.39, 154.94, 153.47, 126.54, 112.93, 112.10, 110.35, 102.29, 18.14.

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4.5 General Procedure for the Synthesis of 4-Aryl-*NH*-1,2,3-triazoles

CAUTION: All the experiments were performed in a well-ventilated fume hood and behind a blast shield. CXH-SO_3H (3.24 mol%) was carefully added to a mixture of nitroolefin (0.3 mmol) and NaN3 (0.45 mmol) in DMSO (1.5 mL) under stirring. Thereafter, the mixture was stirred at 60 ^oC for 2 h, and the progress of the reaction was monitored by TLC. After the completion of reaction, the solid biocatalyst was removed by filtration and washed with ethyl acetate for several times, and used for subsequent cycles after drying under vacuum. The filtrate was extracted with saturated NaCl solution, and then the organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. Finally, the target products were obtained by column chromatography on silica gel using ethyl acetate/hexane as an eluent. All products were characterized by NMR spectroscopy.

4-Phenyl-*NH*-1,2,3-triazole (3a): ^{1}H NMR (600 MHz, DMSO-d_6), 1 drop TFA: δ = 14.95 (s, 1H), 8.25 (s, 1H), 7.86 (s, 2H), 7.45 (s, 2H), 7.35 (s, 1H); ^{13}C NMR (151 MHz, DMSO-d_6), 1 drop TFA: δ = 145.9, 130.5, 128.9, 128.1, 127.2, 125.5.

4-(p-Tolyl)-*NH*-1,2,3-triazole (3b): ^{1}H NMR (600 MHz, DMSO-d_6), 1 drop TFA: δ = 14.94 (s, 1H), 8.23 (s, 1H), 7.75 (s, 2H), 7.26 (d, J = 6.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6), 1 drop TFA: δ = 146.2, 137.5. 130.5, 129.5, 127.8, 125.5, 20.8.

4-(4-Methoxyphenyl)-*NH*-1,2,3-triazole (3c): ^{1}H NMR (600 MHz, DMSO-d_6), 1 drop TFA: δ = 14.98 (s, 1H), 8.21 (s, 1H), 7.79 (d, J = 12.0 Hz, 2H), 7.02 (d, J = 6.0 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6), 1 drop TFA: δ = 159.2, 126.9, 122.7, 114.3, 55.1.

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4-(4-Fluorinephenyl)-*NH*-1,2,3-triazole (3d): ^{1}H NMR (600 MHz, DMSO-d_6), 1 drop TFA: δ = 14.98 (s, 1H), 8.24 (s, 1H), 7.91 (s, 2H), 7.29 (s, 2H); ^{13}C NMR (151 MHz, DMSO-d_6), 1 drop TFA: δ = 162.8, 161.2, 145.5, 130.7, 127.7 (J_{CF} = 58.89 Hz), 119.3, 115.9 (J_{CF} = 19.63 Hz).

4-(4-Bromophenyl)-*NH*-1,2,3-triazole (3e): ^{1}H NMR (600 MHz, DMSO-d_6), 1 drop TFA: δ = 15.06 (s, 1H), 8.30 (s, 1H), 7.83 (d, J = 6.0 Hz, 2H), 7.66 (d, J = 6.0 Hz, 2H); ^{13}C NMR (151 MHz, DMSO-d_6), 1 drop TFA: δ = 145.2, 131.6, 131.0, 130.0, 127.6, 121.2.

4-(4-Chlorophenyl)-*NH*-1,2,3-triazole (3f): ^{1}H NMR (600 MHz, DMSO-d_6), 1 drop TFA: δ = 15.05 (s, 1H), 8.29 (s, 1H), 7.90 (d, J = 6.0 Hz, 2H), 7.53 (d, J = 12.0 Hz, 2H); ^{13}C NMR (151 MHz, DMSO-d_6), 1 drop TFA: δ = 145.2, 132.7, 131.0, 129.0, 127.3, 119.8.

4-(*NH*-1,2,3-Triazol-4-yl)benzonitrile (3g): ^{1}H NMR (600 MHz, DMSO-d_6), 1 drop TFA: δ = 15.24 (s, 1H), 8.43 (s, 1H), 8.08 (d, J = 6.0 Hz, 2H), 7.93 (s, 2H); ^{13}C NMR (151 MHz, DMSO-d_6), 1 drop TFA: δ = 143.9, 133.0, 132.3, 131.9, 126.3, 121.3, 118.8.

Methyl-4-(*NH*-1,2,3-triazol-4-yl)benzoate (3h): ^{1}H NMR (600 MHz, DMSO-d_6), 1 drop TFA: δ = 15.19 (s, 1H), 8.38 (s, 1H), 8.03 (s, 4H), 3.86 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6), 1 drop TFA: δ = 142.7, 133.3, 129.4, 127.6, 120.6, 111.8, 55.5.

4-(3-Methoxy-4-hydroxylphenyl)-*NH*-1,2,3-triazole (3i): ^{1}H NMR (600 MHz, DMSO-d_6), 1 drop TFA: δ = 14.76 (s, 1H), 9.19 (s, 1H), 8.13 (s, 1H), 7.38 (s, 1H), 7.28 (s, 1H), 6.82 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6), 1 drop TFA: δ = 148.4, 147.2, 130.6, 122.3, 118.7, 116.3, 110.2, 56.1, 29.50.

4.6 Recyclability experiments

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A mixture of benzaldehyde (0.5 mmol), 2-naphtol (0.5 mmol), dimedone (0.6 mmol), and CXH-SO_3H (4.32 mol%) was charged into a 15 mL pressure flask with a magnetic stirring bar. The reaction system was then stirred at 90 ^oC for 2 h. Upon the completion of the reaction, ethyl acetate (10 mL) was added when the reaction system was cooled to room temperature to precipitate CXH-SO_3H. The CXH-SO_3H was filtered off and washed with ethyl acetate for several times. The recovered CXH-SO_3H was then dried under vacuum at 80 ^oC for 24 h and used directly for the next run. Finally, pure product was obtained by evaporation of the solvent, followed by column chromatography on silica gel using ethyl acetate/hexane as an eluent. The product was confirmed by NMR spectroscopy.

Conflicts of interest

There are no conflicts to declare.

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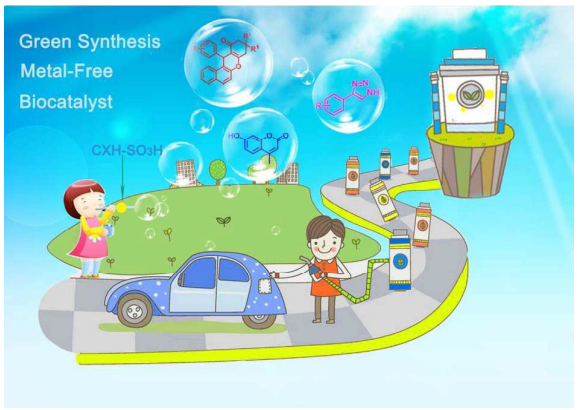

Sulfonation of Carbonized Xylan-type Hemicellulose: A Renewable and Effective Biomass-based Biocatalyst for the Synthesis of O- and N-Heterocycles