# Humin-sulfuric acid as a novel recoverable biocatalyst for pyrrole synthesis in water

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## Abstract

Humin-sulfuric acid (Humin-$SO_3H$) as a novel efficient biobased sulfonic acid was easily prepared by adding chlorosulfuric acid (Cl$SO_3H$) to Humin and characterized by potentiometric titration and FT-IR spectrum. Humin-$SO_3H$ is an eco-friendly, heterogeneous biobased, and efficient catalyst for Paal-Knorr and Clauson-Kaas pyrrole synthesis. The catalyst is easily recovered by simple filtration and has excellent turnover efficiency even after 4 cycles. Besides, due to the clearance of the biocatalyst away from the reaction media, the desired highly pure products can be achieved in high to excellent yields. Due to high water dispersibility, Humin-$SO_3H$ can be utilized as a highly efficient green catalyst for pyrrole synthesis.

**Keywords**  Humin-$SO_3H$, Pyrrole, Biocatalyst, Eco-friendly, Recoverable, Water

## Introduction

Pyrrole is a five-membered heterocycle with one nitrogen atom most commonly found in biologically active molecules, natural products, and drugs. Several of its derivatives/natural products show antibacterial, anti-viral, anti-inflammatory, anti-tumoral, and antioxidant activities [1]. Owing to their importance, a plethora of methods/reactions is available in the literature for the synthesis of pyrroles, including the more popular reactions such as Paal–Knorr [2], Clauson-Kaas [3], Hantzsch process [4], and several other methods such as conjugate addition reactions [5], transition metal-mediated reactions [6], reductive couplings [7], Aza-Wittig [8], as well as multicomponent reactions [9]. Amongst these, Clauson-Kaas and Paal–Knorr are the most commonly used reactions for synthesizing pyrroles as they use simple and readily available precursors. These reactions were reported with several catalysts such as Ionic liquid [10], β-cyclodextrin sulfuric acid (β-CD-$SO_3H$) [11, 12], silica sulfuric acid ($SiO_2$–$OSO_3H$) [13], phosphorus pentoxide ($P_2O_5$) [14], copper(II) chloride ($CuCl_2$) [15], ferric chloride pentahydrate ($FeCl_3 \cdot 7H_2O$) [16], montmorillonite K-10 ($Al_2H_2O_{12}SiO_4$) [17], cerium(III) chloride ($CeCl_3$) [18], bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) [19], nano sulfated titania (Nano-sulfate $TiO_2$) [20], zinc trifluoromethane sulfonate ($Zn(OTf)_2$) [21], magnesium iodide etherate ($MgI_2 \cdot (Et_2O)_n$) [22], iodine ($I_2$) [23], scandium(III) trifluoromethane sulfonate ($Sc(OTf)_3$) [24], ultrasound irradiation [25], nano-organocatalyst [26], sulfonic acid-functionalized magnetite-coated maghemite ($Fe_3O_4@\gamma$–$Fe_2O_3$–$SO_3H$) [27], and polyethylene glycol sulfuric acid (PEG-$SO_3H$) [28].

Despite the advances, many of them suffer from certain drawbacks such as harsh reaction conditions, use of expensive reagents, toxic solvents, strongly acidic conditions, costly catalysts, longer reaction times, non-recyclability, tedious workup procedures, and use of extra energy sources such as microwaves or ultrasounds. Therefore, in this context, developing an efficient, simple, economical, and environmentally friendly protocol using a recyclable catalyst and a green solvent for synthesizing pyrrole derivatives is highly desirable.

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Organic synthesis in aqueous media has gained widespread attention on account of several advantages as water is more environmentally friendly, affordable, and benign [29].

Biocatalysis for organic transformations has become a common tool in organic synthesis, which is also frequently applied in industry. The generally high activity and outstanding stereo-, regio-, and chemoselectivity observed in many biotransformations result from precise control of the reaction in the active site of the biocatalyst [30].

Functionalization of different materials by sulfuric acid improves their property as a catalyst for a variety of applications, such as sulfonic acid functionalized ionic liquid for the protection of aldehydes, phenol, and alcohols with acetic anhydride under neat conditions [17], Phosphosulfonic acid (PSA) as a highly effective and environmentally benign catalyst for the production of biodiesel through the esterification of long-chain fatty acids at room temperature [31] and an environmentally safe and efficient solid acid catalyst, for the synthesis of several 2-disubstituted benzimidazoles, 2-substituted benzoxazoles, and 2-substituted quinoxalines in ethanol as a green solvent at ambient temperature [32], thiocyanation of electron-rich arenes in the presence of sulfonic acid functionalized imidazolium thiocyanate solid acid catalyst ((Imidazole-$SO_3H$)/SCN) in water [33] and isoquinolinium-N-sulfonic acid thiocyanate (Isoquinoline-$SO_3H$) SCN as efficient reagent for thiocyanation of N-bearing (hetero)aromatic compounds [34].

Considering the high abundance and accessibility of Humin, a renewable source of carbon material, which has a lot of functional groups on its surface including phenolic, carboxylic, hydroxylic, and amid groups causing high efficiency in organic synthesis, here in this study, we reported a novel preparation and application of Humin-$SO_3H$ in pyrrole synthesis. We successfully presented it as a highly efficient recoverable biocatalyst, a non-toxic natural substance, in mild, with an eco-friendly method readily accessible to catalyze pyrrole synthesis under mild conditions efficiently. The organic part of Humin affects the solubility of the substrates in water and the acidic part activates the substrate molecules simultaneously to conduct pyrrole synthesis in water efficiently.

## Experimental section
### Materials
Raw materials were purchased from Merck and Fluka and were used without any further purification. The reaction progress was followed by using TLC. The reaction product was conformed from IR, 1H NMR, and 13C NMR analysis. The whole process was performed with TLC-Card Silica Gel-G/UV 254 nm; analytical balance Miller/Colleg 150; OVEN/Model: U30/W:800-Shimaz CO; FTIR: Spectrometer-Spectrum RX 1 Perkin–Elmer AVE (4000–400 cm$^{-1}$); 1H NMR and 13C NMR: Bruker Avance 400 MHz spectrometer; pH meter: Horiba model: f-IIE.

### Preparation of Humin-$SO_3H$
The solution of $ClSO_3H$ (5.0 mmol, 0.58 g) in dichloromethane (6 mL) was added to dispersed Humin (1 g) in dichloromethane (10 mL) and stirred for 12 h. The mixture was filtered off, washed with $CH_2Cl_2$ (20 mL), and dried at 60 ℃ in a vacuum oven to produce Brown powder of Humin-$SO_3H$.

### Synthesis of N-aryl-2, 5-dimethyl pyrrole catalyzed by Humin-$SO_3H$
Humin-$SO_3H$ (0.01 g) was added to the mixture of 2, 5-hexadione (1.2 mmol, 0.14 mL) and amine (1 mmol) in water (4 mL) and was stirred at room temperature. After completing the reaction, ethanol was added to the reaction mixture, and the catalyst was separated with a simple filtration and washed with ethanol. The solid corresponding pyrrole product was separated after a reduced solvent volume and filtered off. The pure N-aryl-2, 5-dimethyl pyrrole was achieved after recrystallizing in an $H_2O$/EtOH mixture in 80–98% isolated yield.

### Synthesis of N-aryl pyrrole catalyzed by Humin-$SO_3H$
Humin-$SO_3H$ (0.01 g) was added to the mixture of 2,5-dimethoxy tetrahydrofuran (1.2 mmol, 0.14 mL) and amin (1 mmol) in water, and the reaction was stirred at 80 ℃. After the reaction, ethanol was added to the reaction mixture, and the catalyst was separated with a simple filtration. The solid corresponding pyrrole product was separated after a reduced solvent volume and filtered off. The pure N-aryl pyrrole was achieved after recrystallizing in an $H_2O$/EtOH mixture in 85–98% isolated yield.

## Results and discussion
Humin-$SO_3H$ was prepared by adding drop by drop of $ClSO_3H$ to dispersed Humin in dichloromethane and let it be stirred for 12 h. The solid product was filtered off, washed with $CH_2Cl_2$, and dried under a vacuum oven at 60 ℃ to achieve Humin-$SO_3H$ powder in brown color (Fig. 1). There are many hydroxyls functional groups in the Humin structure to react with $ClSO_3H$. The FTIR spectra and potentiometric titration chart of sulfonated Humin were compared with the basic Humin to confirm of –$SO_3H$ functional group in the Humin structure (Humin-$SO_3H$).

The strong acidity of the potentiometric titration chart of Humin and Humin-$SO_3H$ was shown in Fig. 2 and a remarkable difference in acid strength can be seen. The
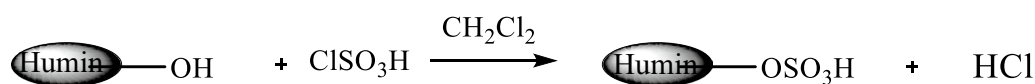
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$$Humin-OH \ + \ ClSO_3H \xrightarrow{CH_2Cl_2} \ Humin-OSO_3H \ + \ HCl$$

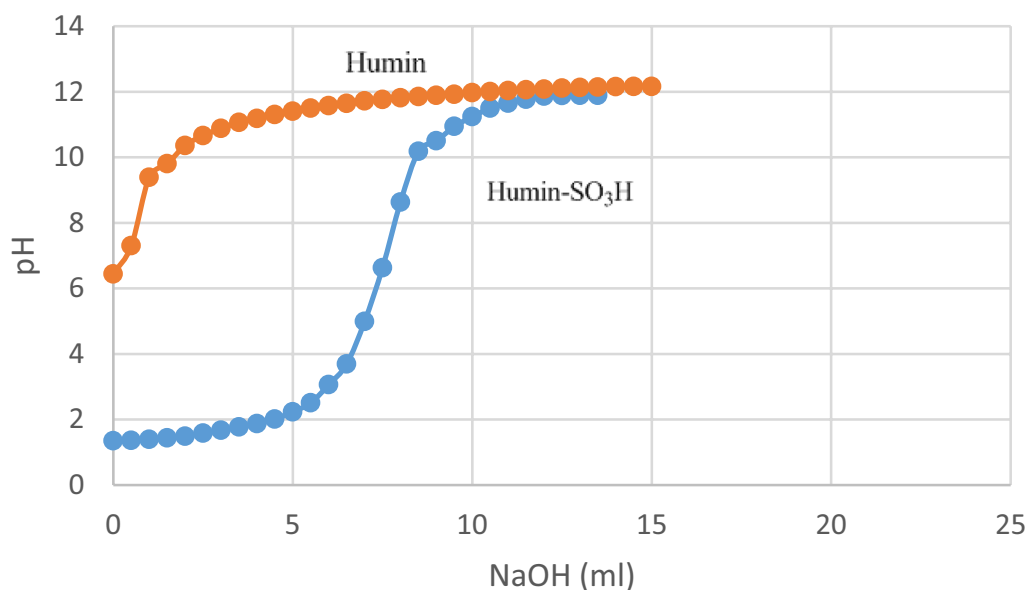**Fig. 1** The synthesis process of Humin-SO$_3$H



**Fig. 2** Potentiometric titration chart of Humin and Humin-SO$_3$H for equilateral point calculation

number of sulfonic acid groups on the Humin was calculated by using the neutralization titration method and was found to be at 3.7 mmolg$^{-1}$.

The FTIR spectroscopy is an important tool to show the structural characterization of the units of Humin and Humin-SO$_3$H as shown in Fig. 3. In FTIR spectra of Humin, the wide pic that appeared in 2600–3600 cm$^{-1}$ is related to hydroxyl and carboxyl groups, and a pic in 1023 cm$^{-1}$ is related to the C–O bond. In the FTIR spectrum of Humin-SO$_3$H, the pic in 2600–3600 cm$^{-1}$ has been wider and three new appeared pics in frequencies of 1285, 1172, and 578 cm$^{-1}$, are related to symmetrical and asymmetrical tensile vibrations of O=S=O and tensile vibrations of S–O respectively [27]. FTIR spectra confirm the presence of the sulfuric acid group on the surface of Humin.

Humin-SO$_3$H was used as a catalyst in the Paal–Knorr pyrrole synthesis reactions to show its catalytic activity. The reaction of 2,5-hexadione with aniline was considered a model reaction to optimized reaction conditions (Table 1).

By screening loading of the catalyst and considering the effect of the solvent and temperature on the reaction rate, it was found that only 0.01 g of Humin-SO$_3$H was sufficient for Paal-Knorr pyrrole synthesis at room

temperature in water (Table 1, entry 5). The organic part of the catalyst affects the solubility of the substrates in water and the acidic part activates the substrate molecules at the same time. When these two factors are in play together, a drastic enhancement is observed in the products' rates and yields.

To check the recyclability of the catalyst, after completion of the model reaction, ethanol was added to the reaction mixture to solve N-phenyl-2,5-dimethyl pyrrole, and the solid Humin-SO$_3$H was separated by a simple filtration, washed with ethanol, dried at 100 ℃ and reused in a subsequent reaction. The results show, that the recycled catalyst can be reused up to at least 3 times with a slight loss of catalytic activity under optimal conditions (Table 2).

After this success, to show the general applicability of the method, the reaction of structurally diverse amines with hexane-2,5-dione was studied under optimized reaction conditions. Aromatic and aliphatic amines easily reacted with hexane-2,5-dione to produce N-substituted pyrroles in high to excellent yields. Aliphatic amines reacted more efficiently than aromatic ones to give N-alkyl pyrroles in excellent yields (Table 3). Also, the polyaromatic substrates, 1-amino naphthalene, and 4,4′-methylenedianiline reacted efficiently to afford the
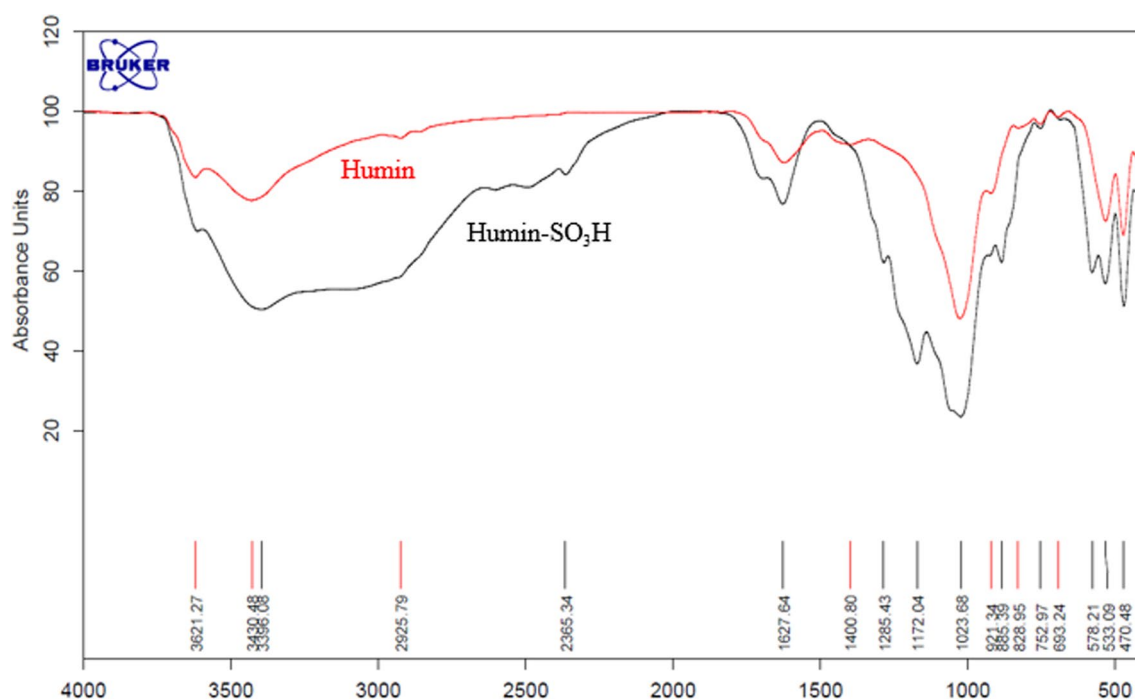
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**Fig. 3** FTIR spectroscopy of Humin and Humin-SO$_3$H

**Table 1** Optimization of reaction of 2,5-hexadione with aniline

| Entry | Cat. (g) | Solvent (mL) | Temp. (°C) | Time (h) | Conv. (%) |
|---|---|---|---|---|---|
| 1 | Humin-SO$_3$H (0.01) | – | 30 | 2.5 | 100 |
| 2 | Humin-SO$_3$H (0.01) | – | 50 | 2.5 | 100 |
| 3 | Humin-SO$_3$H (0.03) | H$_2$O (4 mL) | R.T | 1 | 100 |
| 4 | Humin-SO$_3$H (0.02) | H$_2$O (4 mL) | R.T | 1 | 100 |
| 5 | Humin-SO$_3$H (0.01) | H$_2$O (4 mL) | R.T | 1 | 100 |
| 6 | Humin-SO$_3$H (0.005) | H$_2$O (4 mL) | R.T | 3 | 100 |
| 7 | Humin (0.01) | H$_2$O (4 mL) | R.T | 2.5 | 100 |
| 8 | Humin-SO$_3$H (0.01) | EtOH (4 mL) | R.T | 3 | 30 |
| 9 | Humin-SO$_3$H (0.01) | CH$_3$CN (4 mL) | R.T | 3 | 5 |

**Table 2** Reusability of Humin-SO$_3$H

| Reusability time | First | Second | Third |
|---|---|---|---|
| Time (h) | 1 | 1.25 | 1.25 |
| Yield (%) | 95 | 92 | 91 |

desired products in good yields of 95% and 94% respectively (Table 3, entries 5 and 12). In all the cases, at the end time, EtOH was added to the reaction mixture to solve precipitated pyrrole and filter off the solid catalyst. The pure solid product was isolated by the reduced value of solvent by a simple filtration, recrystallizing in an H$_2$O/EtOH mixture without using any chromatography or cumbersome reaction workup.

Due to the success of the Humin-SO$_3$H in green Paal-Knorr pyrrole synthesis, we decided to develop its catalytic activity for the Clauson-Kaas another common method for the synthesis of pyrrole, too. In this regard, the reaction of 2,5-dimethoxy tetrahydrofuran with aniline was chosen as the model substrate for the optimization reaction conditions. The model reaction was performed under Paal-Knorr optimized conditions. The reaction proceeded sluggishly at room temperature and after 12 h, N-phenyl pyrrole was produced in only a 50% yield. To improve the yield of the model reaction, the effect of temperature, loading of catalyst, and solvent was screened (Table 4). The best yields of the products and reaction rate were obtained when the reaction was performed in the presence of Humin-SO$_3$H (0.01 g) in water at 80 °C (Table 4, entry 3) rather than using organic solvents or under solvent-free conditions.

Encouraged by this result, we have performed the reactions of various amines with 2,5-dimethoxy tetrahydrofuran to probe the scope and reactivity of the new

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**Table 3** Paal–Knorr Pyrrole Synthesis catalyzed by Humin-SO$_3$H in water at room temperature



| Entry | Amine | Product | Time (h) | Yield (%) | TON | TOF (h$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | | | 1 | 98 | 26.48 | 26.48 |
| 2 | | | 1 | 98 | 26.48 | 26.48 |
| 3 | | | 2 | 98 | 26.48 | 13.24 |
| 4 | | | 1 | 94 | 25.40 | 25.40 |
| 5 | | | 3 | 95 | 25.67 | 8.89 |
| 6 | | | 1.15 | 96 | 25.94 | 22.55 |
| 7 | | | 3 | 83 | 22.43 | 7.47 |
| 8 | | | 0.5 | 97 | 26.21 | 52.42 |

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**Table 3** (continued)



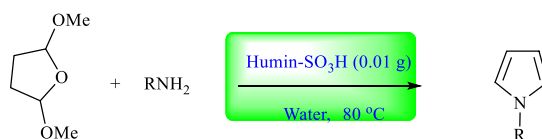| Entry | Amine | Product | Time (h) | Yield (%) | TON | TOF (h$^{-1}$) |
|-------|-------|---------|----------|-----------|-----|----------------|
| 9 |  |  | 4 | 87 | 23.51 | 5.87 |
| 10 |  |  | 1.5 | 90 | 24.32 | 16.21 |
| 11 |  |  | 3 | 93 | 25.13 | 8.37 |
| 12 |  |  | 2.5 | 94 | 25.40 | 1.016 |

Reaction conditions: 2,5-Hexadion (1.2 mmol), amine (1 mmol), Water (4 mL), Humin-SO$_3$H

(0.01 g), were mixed and stirred at room temperature

**Table 4** Optimization of the reaction of Aniline with 2,5-dimethoxy tetrahydrofuran

| Entry | Cat. (g) | Solvent (mL) | Temp. (℃) | Time (h) | Conv. (%) |
|-------|----------|--------------|-----------|----------|-----------|
| 1 | Humin-SO$_3$H (0.01) | H$_2$O | R.T | 12 | 50 |
| 2 | Humin-SO$_3$H (0.01) | H$_2$O | 60 | 3 | 60 |
| 3 | Humin-SO$_3$H (0.01) | H$_2$O | 80 | 1 | 100 |
| 4 | Humin-SO$_3$H (0.02) | H$_2$O | 80 | 1.45 | 100 |
| 5 | Humin-SO$_3$H (0.005) | H$_2$O | 80 | 3 | 70 |
| 6 | Humin-SO$_3$H (0.01) | – | 80 | 3 | 70 |
| 7 | Humin-SO$_3$H (0.01) | EtOH | 80 | 3.5 | 70 |
| 8 | Humin-SO$_3$H (0.01) | CH$_3$Cl | 80 | 4.5 | 60 |

catalyst, and the results are summarized in Table 5. Aromatic amine with electron-donating and withdrawing group quickly produces corresponding pyrrole product in high to excellent yield. Also, the polyaromatic substrates, 4,4′-methylenedianiline, and 4,4′-Oxydianiline reacted efficiently to afford the desired products in good yields of 97% and 88% respectively (Table 5, entries 4 and 6).

To realize the efficacy and potency of Humin-SO$_3$H, the present catalytic system was compared with several previously reported methods for Clauson-Kaas reaction of aniline with 2,5-dimethoxy tetrahydrofuran (Table 6). The Humin-SO$_3$H exhibits high catalytic activity as compared to other reports, which is attributed to the availability of more active and stable sites on the catalyst surface. The results clearly show that Humin-SO$_3$H is a renewable carbon source, environmentally friendly, and efficient biocatalyst for synthesizing pyrrole in mild conditions.

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**Table 5** Synthesis of Pyrrole derivations with Humin-SO$_3$H



| Entry | Amine | Product | Time (h) | Yield (%) | TON | TOF (h$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 |  |  | 1 | 98 | 26.48 | 26.48 |
| 2 |  |  | 1.5 | 98 | 26.48 | 17.65 |
| 3 |  |  | 1.5 | 98 | 26.48 | 17.65 |
| 4 |  |  | 1.5 | 97 | 26.21 | 17.48 |
| 5 |  |  | 2.5 | 97 | 26.21 | 10.48 |
| 6 |  |  | 3 | 88 | 23.78 | 7.92 |
| 7 |  |  | 5 | 85 | 22.97 | 4.59 |

Reaction conditions: 2,5-Dimethoxy tetrahydrofuran (1.2 mmol), amine (1 mmol), water (4 mL), and Humin-SO$_3$H (0.01 g) were stirred at 80 ℃

**Table 6** Comparison of the activity of Humin-SO$_3$H with another recent catalyst used for the reaction of 2,5-dimethoxy tetrahydrofuran with aniline

| Entry | Catalyst | Solvent (mL) | Temp. (℃) | Time (h) | Yield (%) | References |
|---|---|---|---|---|---|---|
| 1 | P$_2$O$_5$ | Toluene | 110 | 45 | 87 | [14] |
| 2 | Sc (OTf)$_3$ | Dioxane | 100 | 0.6 | 91 | [24] |
| 3 | MgI$_2$·(OEt$_2$)$_n$ | CH$_3$CN | 80 | 6 | 85 | [22] |
| 4 | FeCl$_3$·7H$_2$O | H$_2$O | 60 | 1 | 95 | [16] |
| 5 | β-CD-SO$_3$H | H$_2$O | 80 | 3.5 | 96 | [11] |
| 6 | Nano-solfate TiO$_2$ | – | 120 | 0.5 | 98 | [20] |
| 7 | Zn (OTf)$_2$ | – | 70 | 8 | 94 | [21] |
| 8 | Humin-SO$_3$H | H$_2$O | 80 | 1 | 98 | This work |

## Conclusion

This work presented a new green method for two general routes, Paal-Knorr and Clauson-Kaas reactions, to be approved for synthesizing pyrrole. The advantages of this reaction include using water as a solvent and introducing waste Humin to a valuable supported biocatalyst (Humin-SO$_3$H). The high stability, efficiency,

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eco-friendliness, and reusability are the advantages of Humin-SO₃H biocatalyst in pyrrole synthesis.

### Availability of data and materials
The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

## Declarations

### Ethics approval and consent to participate
Not applicable.

### Consent for publication
Not applicable.

### Competing interests
The authors declare no competing interests.

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