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Sulfonamide-functionalized covalent organic framework ($COF\text{-}SO_3H$): an efficient heterogeneous acidic catalyst for the one-pot preparation of polyhydroquinoline and 1,4-dihydropyridine derivatives

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Abstract

Herein, we report the sulfonamide-functionalized covalent organic framework ($COF\text{-}SO_3H$) prepared from melamine and terephthalaldehyde and subsequent sulfonation, as an acidic porous catalyst for the one-pot preparation of polyhydroquinoline and 1,4-dihydropyridine derivatives. $COF\text{-}SO_3H$ was characterized by FT-IR, EDX, TGA, SEM, XRD, and BET. This methodology offers several advantages including high yield, short reaction time, simple workup procedure, solvent-free conditions, ease of separation, and recyclability.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11164-020-04322-5) contains supplementary material, which is available to authorized users.

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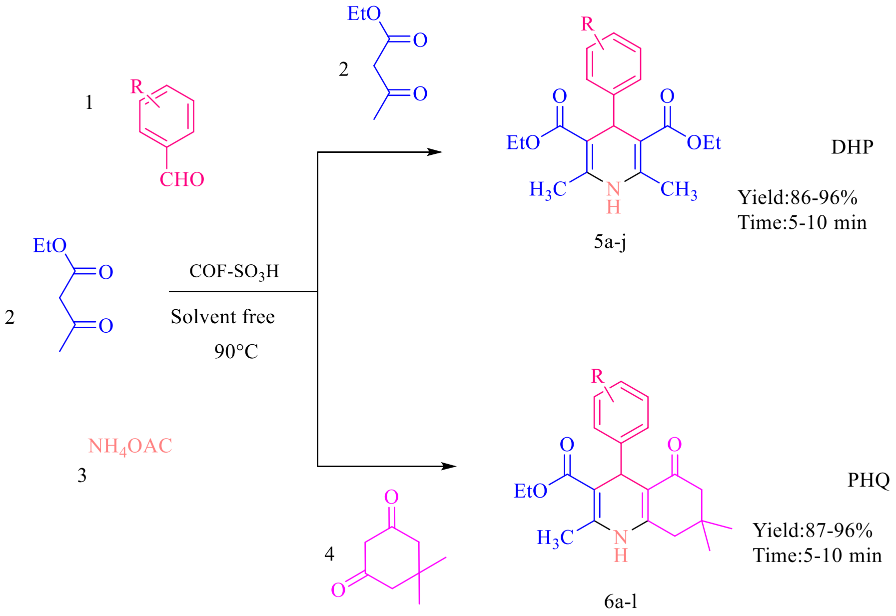
Graphic abstract

One-pot preparation of polyhydroquinoline and 1, 4-dihydropyridinederivatives



Keywords Covalent organic framework (COF) · Nanoporous · Melamine · Terephthalaldehyde · Acidic catalyst · Chlorosulfonic acid

Introduction

Over the past decade, interest in the field of nanoporous materials as regular organic or inorganic frameworks has grown tremendously because of their excellent porous properties and broad applications [1]. As an emerging kind of crystalline porous materials, covalent organic frameworks (COFs) pioneered by Yaghi and co-workers in 2005 are composed of two organic moieties via strong covalent bonds between light atoms (e.g., H, B, C, N, O, Si) to generate long-range ordered two-dimensional (2D) or three-dimensional (3D) network structures [2–5]. A wide range of porous organic polymers (POPs), which are also called porous organic materials [6], have been introduced in the past two decades, such as COFs and various amorphous networks, such as hypercrosslinked polymers (HCPs), covalent triazine frameworks (CTFs), porous aromatic frameworks (PAFs), and conjugated microporous polymers (CMPs) [7–9]. Due to their fascinating properties, such as high surface area, viscous cavities, and high porosity, low-density economical materials are obtained due to the low-cost starting materials and the easy way of synthesis. High thermal and chemical stability endows COFs with a wide application potential in the fields of energy storage, gas adsorption, drug delivery, catalysis, sensing, and optoelectronics

[10–15]. Functionalization in the course of synthesis and/or post-functionalization of COFs endows their framework with specific active sites, which could further improve their catalytic activity or enhance their dispersion stability. Thus, it is of great applicability to prepare a functionalized COF and to further investigate its catalytic potential [16, 17].

Heterocyclic compounds containing nitrogen have attracted considerable attention due to their wide pharmaceutical activity range acting as antitumour, antiatherosclerotic, vasodilator, hepatoprotective, bronchodilator, antidiabetic activity. 1,4-Dihydropyridine (DHP) and polyhydroquinoline (PHQ) as nitrogen heterocycles occupy a unique position in medicinal chemistry according to their widespread range of biological applications [18–22]. Therefore, the development of facile synthetic methodologies for preparation of these nitrogen-containing heterocycles is of much importance. Experimentally the straightforward route for this goal was first reported by Hantzsch in 1882 via the reaction of an aldehyde, *β*-ketoester, and ammonia in acetic acid or by refluxing ethanol for long reaction times, which typically leads to low yields [23–25].

Several more efficient and alternative methods have been introduced due to the biological importance of DHP and PHQ derivatives for the synthesis of various drug sources. Several catalysts have been reported for the synthesis of these compounds such as cyanuric chloride [26], ionic liquids [27, 28], $Yb(OTf)_3$ [29], silica gel/$NaHSO_4$ [30], PSA [31], L-proline [32], $Sc(OTf)_3$ [33], p-TSA [34], ZnO [35], and TMSCl [18].

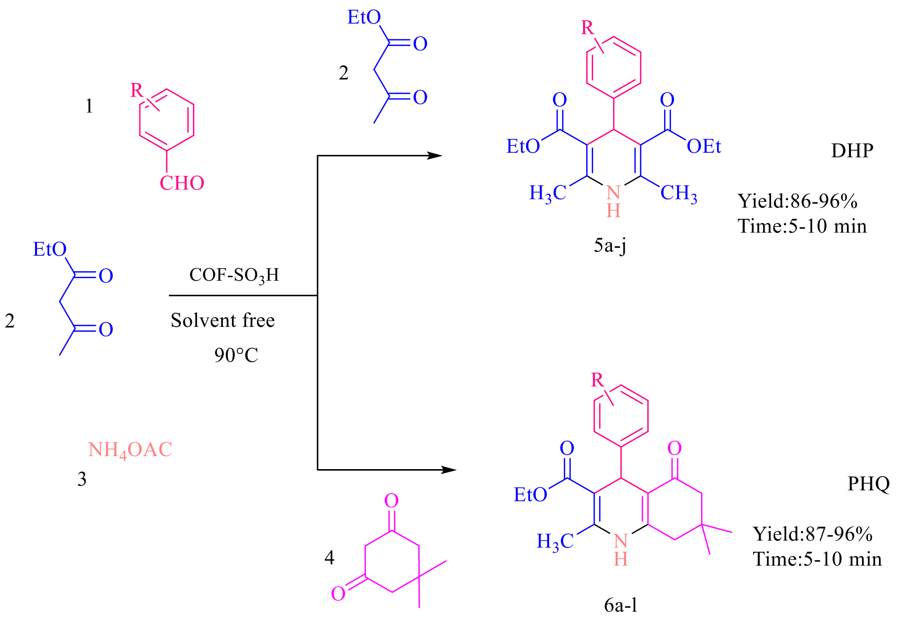
However, most of these methods suffer from certain drawbacks such as long reaction time, low yields of product, hard operation, high reaction temperatures, toxic solvents, and utilization of expensive or unavailable catalysts. Furthermore, catalysts are destroyed and cannot be recovered or reused in the majority of the proposed methodologies.

Therefore, considering the above-mentioned weaknesses, and in continuation of our pioneering research on preparation and application of new catalysts in the field of organic methodology [36, 37], we wish to report a facile and efficient synthesis of DHP and PHQ derivatives through one-pot Hantzsch condensation reaction in the presence of COF-SO_3H under solvent-free neat conditions (Scheme 1).

Experimental

General

Chemicals were purchased from Chemical Companies with at least for synthesis grade and were used without further purification. All yields refer to isolated products. Products were characterized by comparison of their physical data such as IR, ^1H NMR and ^{13}C NMR spectra with authentic samples. By using TMS as an internal standard, NMR spectra were recorded in $CDCl_3$ on a Bruker Advance DPX 250 MHz spectrometer. Determination of the products' purity in the course of the reaction was monitored by TLC on silica gel polygram SILG/UV 254 plates. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrophotometer



Scheme 1 One-pot preparation of 1,4-dihydropyridine (DHP) and polyhydroquinoline (PHQ) derivatives via Hantzsch reaction

as KBr disks. The melting points were recorded in open capillary tubes and were uncorrected. The SEM images and EDX-Map were recorded by TESCAN MIRA III FESEM. The BET diagrams were recorded via BELSORP MINI II.

A general procedure for the synthesis of 1,4 -dihydropyridines derivatives catalyzed by COF-SO$_3$H nanoparticles under solvent-free conditions

A mixture of ethyl acetoacetate (0.26 g, 2 mmol), ammonium acetate (0.154 g, 2 mmol), aryl aldehyde (1 mmol) in the presence of COF-SO$_3$H (0.02 g) as acid catalyst was mixed in a test tube on the oil bath at 90 °C for adequate times under solvent-free conditions as embedded in Table 3. The reaction monitoring was checked by TLC. After the completion of the reaction as witnessed by TLC, ethanol was added to the reaction mixture and the catalyst was filtered. The filtrate was collected as crude product after cooling to room temperature. The product was recrystallized from water–ethanol mixtures.

General procedure for synthesis of polyhydroquinoline derivatives catalyzed by COF-SO$_3$H nanoparticles under solvent-free conditions

A mixture of aryl aldehyde (1 mmol), dimedone (0.14 g, 1 mmol), ethyl acetoacetate (0.13 g, 1 mmol), ammonium acetate (0.115 g, 1.5 mmol), in the presence of COF (0.02 g) as acid catalyst was heated on the oil bath at 90 °C for adequate times under solvent-free conditions as embedded in Table 4. The reaction mixture was checked by TLC. After the completion of the reaction as witnessed by TLC, ethanol was added to the reaction mixture and the catalyst was filtered. The filtrate was collected as crude product after cooling to room temperature. The product was recrystallized from water–ethanol mixtures.

Synthesis of melamine-based covalent organic framework (COF)

Via a typical solvothermal method, according to a recent literature [1], melamine (470 mg, 3.73 mmol) and terephthalaldehyde (750 mg, 5.59 mmol) were dissolved in DMSO (23 mL) in a Teflon-lined laboratory autoclave, which was heated at 180 °C for 14 h. Subsequently, the product was washed thoroughly, with excess acetone (30 mL × 2) and dichloromethane (30 mL × 2). Finally, a white powder was obtained, which was dried in an oven at 60 °C for 12 h.

Synthesis of COF-SO_3H

Sulfonation of the COF was carried out using chlorosulfonic acid. In a typical synthesis, 0.5 g of the COF was suspended in 20 ml chloroform in a 25-mL round-bottomed flask. Then, 5 ml of chlorosulfonic in CH_2Cl_2 (10 mL) was added dropwise over a period of 2 h at room temperature. Finally, the prepared catalyst was washed several times with chloroform and dried in oven for 24 h at 60 °C. The acidity of catalyst was determined by adding 0.02 g of the catalyst to 25 mL of NaCl (1 M) which the pH of the solution was decreased from 6.5 to 2.48 after 1 h of stirring. Accordingly, the acidity of the catalyst was determined to be 4.1 mmol H^+/g.

Spectral data for selected compounds

***4-(3-nitro-phenyl)-2,6-dimethyl-1,4-dihydro-pyridine-3,5-dicarboxylic acid diethyl ester*(5j).** (Table 3 entry 10): Yield: 94%; m.p 166–168 °C (Lit. 166–168 °C) [45]; IR (KBr) ν_{max}: 3342, 2988, 1705, 1645, 1207, 1109, 774. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.21 (t, 6H, *J 7* Hz), 2.35(s, 6H, $2CH_3$), 4.07 (q, 4H, *J 3.3 Hz*), 5.08 (s, 1H), 5.98 (s, 1H, NH), 7.26–8.11 (Aromatic). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 15.22, 20.57, 40.95, 60.95, 104.29, 109.7, 117.6, 128.8, 131.8, 146.6, 150.9, 168.1.

2,7,7-*Trimethyl*-5-*oxo*-4-(4-*Boromophenyl*)-1,4,5,6,7,8-*hexahydroquinoline*-3-*carboxylic acid* *ethyl ester* (**6e**) (Table 4 entry 5): Yield: 95%; m.p 249–251 °C (Lit. 252–254 °C)[48];IR (KBr) ν_{max}: 3273, 3203, 3074, 1703, 1648, 1279, 1213.; ^{1}HNMR (250 MHz, $CDCl_3$) δ 0.91 (s, 3H), 1.05 (s, 3H), 1.18 (t, *J 7* Hz, 3H), 2.09–2.26 (m, 4H), 2.34 (m, 3H), 4.06 (q, *J6.9* Hz, 2H), 5.00 (s, 1H), 6.54 (s, 1H), 7.15 (d, *J 8* Hz, 2H),7.33 (d, *J 8* Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 15.2, 20.3, 28.0, 30.4, 33.6, 37.3, 41.9, 51.6, 60.9, 106.6, 112.6, 120.8, 130.8, 131.9, 144.8, 147.1, 149.6, 168.2, 196.6.

Catalyst recycling and reuse

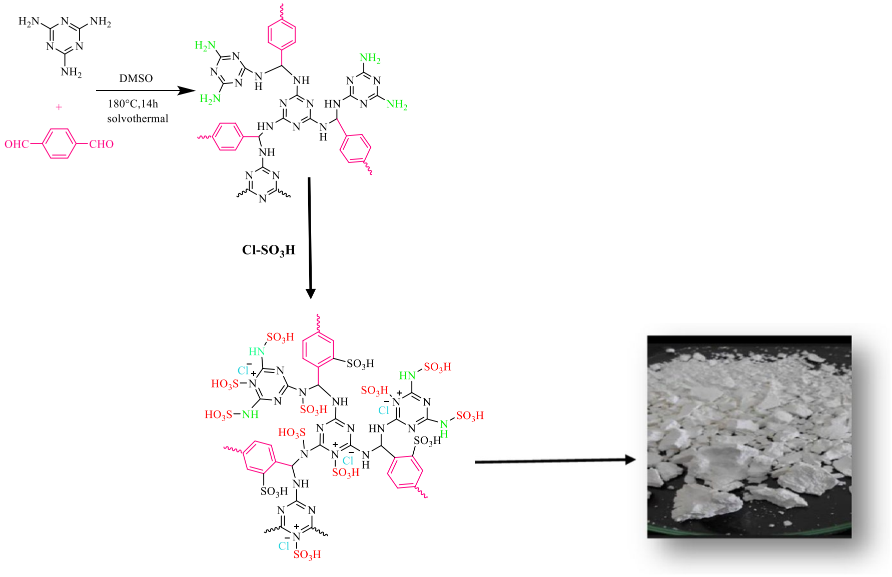
The acidic catalyst, COF-SO_3H, was recycled and reused as follows: After the completion of the reaction as witnessed with TLC, the catalyst was separated from the reaction mixture, and after washing thoroughly with hot ethanol, it was reused for the next run. The recycling efficiency of the COF-SO_3H catalyst was determined by using benzaldehyde, dimedone, and ethyl acetoacetate as the representative reactant molecules. Following this recycling procedure, COF-SO_3H catalyst was reused for five consecutive cycles.

Results and discussion

COF-SO_3H was easily prepared in two steps by using melamine and terephthalaldehyde through aminal formation reaction, which enables outstanding properties such as high surface area, good thermal stability, low density, and acidification in the next step (Scheme 2).

The Fourier transformed infrared (FTIR) spectra of the synthesized COF and its COF-SO_3H are shown in Fig. 1. In the IR spectrum of the COF (Fig. 1a), the stretching vibration of N–H bond is observed at 3408 cm^{-1}, which is wide due to the presence of numerous N–H bonds in the COF. The characteristic aromatic rings are observed at 1548 and 1474 cm^{-1} (C=C and also C=N vibration).

In COF-SO_3H spectrum, bands around 1018–1200 cm^{-1} can be attributed to –SO_3H stretching vibrations. These results suggest the successful introduction of –SO_3H groups onto the main polymeric framework of COF. It is also noteworthy



Scheme 2 Synthesis of COF and COF-SO_3H

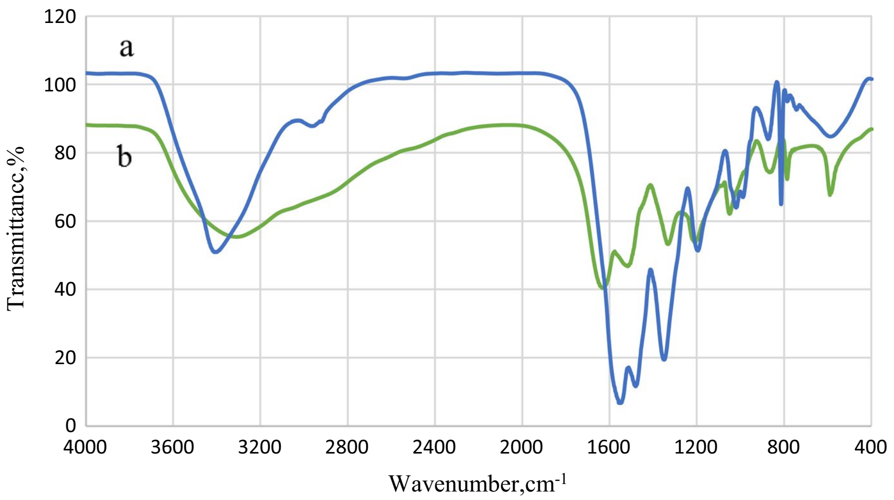


Fig. 1 FTIR spectra of **a** COF (blue) and **b** COF-SO_3H (green). (Color figure online)

that the successful functionalization of COF with –SO_3H groups can be confirmed via EDX analysis.

The thermal stability for the synthesized COF polymers and sulfonated materials COF-SO_3H has been determined by TGA measurement in the temperature range of 0 to 1000 °C. The TG plots of the samples are shown in Fig. 2. For COF, there is no structural decomposition up to 432 °C, but afterwards the cleavages of polymeric framework of the COF get started. In the COF-SO_3H therogravimetric diagram, below 200 °C a 20% weight loss was observed, which is attributed to intercalated and adsorbed water molecules in the sample. Afterward, COF-SO_3H structure was stable up to 294 °C which the weight loss gradually occurs subsequently due to the breaking of sulfonic acid group first and finally for the decomposition of organic structure of the COF.

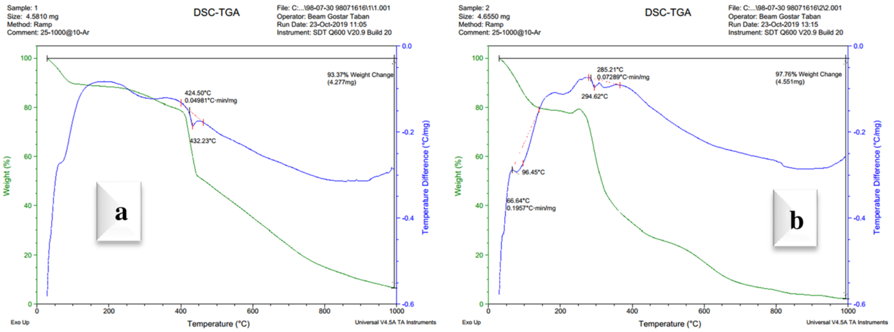


Fig. 2 The TGA curve of COF (**a**); and COF-SO_3H (**b**)

Table 1 Surface area, average pore width, and total pore volume (V_{total}) of COF and COF-SO_3H

Sample	BET surface area ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	Pore size (nm)
COF	166.11	0.4352	10.48
COF-SO_3H	79.327	0.4474	22.562

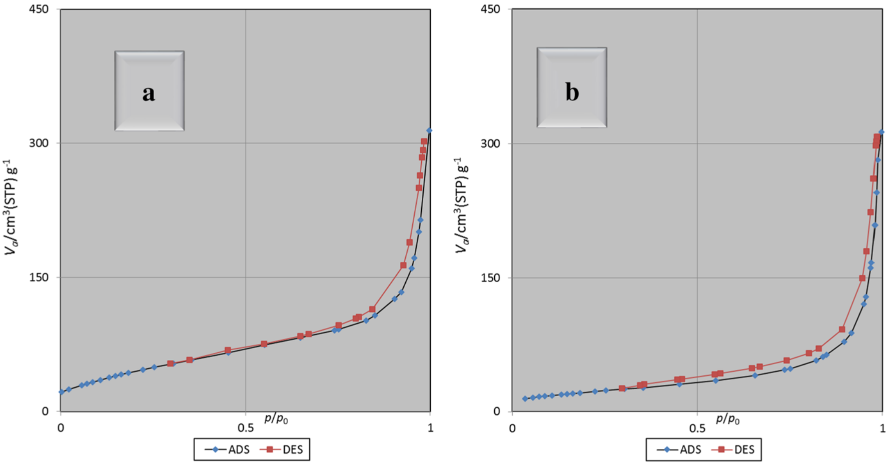


Fig. 3 The BET curve of COF (**a**); and COF-SO_3H (**b**)

The Brunauer–Emmett–Teller (BET) surface area of COF was 166.11 m^2g^{-1} with total pore volume of around 0.4352 cm^3g^{-1} (Table 1 and Fig. 3). Upon sulfonation of the sufonated polymer, COF-SO_3H, the BET surface area is decreased to 79.327 m^2g^1 with a total pore volume of 0.4474 cm^3g^{-1}. Surprisingly, although the surface area has decreased, the pore volume and pore size were increased. It can be attributed to the flexible bonds, which can be broken and reformed in the acidic medium (e.g., aminal bonds) so that the pore can breathe. And also, it is an indication of more external functionalization than internal.

The morphological and structural properties of the COF and COF-SO_3H materials were carried out using SEM analysis (Fig. 4). It can be visualized that the COF and COF-SO_3H have nano-sized structure with an average size of about 10 nm.

Figure 5 shows the results of energy-dispersive X-ray spectroscopy (EDX). The presence of, O, N, C and S species in the obtained COF-SO_3H is confirmed. The EDS mapping images of COF-SO_3H (Fig. 6) revealed the homogeneous dispersion of C, N, O, and S within the polymer network. The loading content of sulfur is 5.56 wt%, and this can be used as a verification criteria for the successful sulfonic acid functionalization of the catalyst.

The catalytic application of COF-SO_3H was studied in Hantzsch condensation reaction for the preparation of polyhydroquinoline and 1,4-dihydropyridine derivatives. The reaction of benzaldehyde, ethyl acetoacetate and ammonium

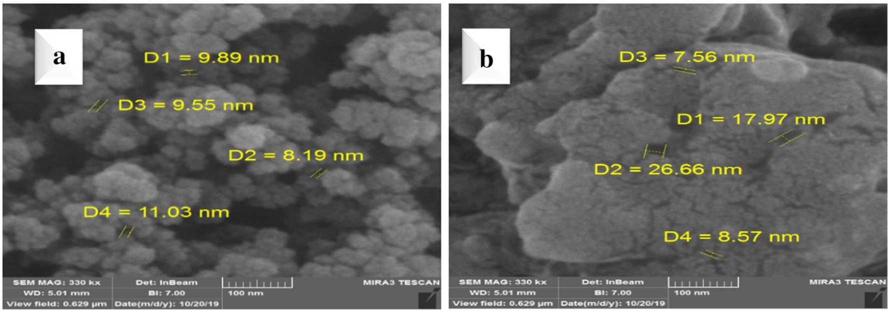
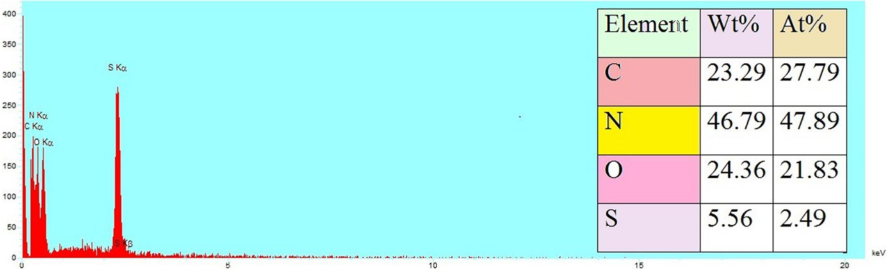


Fig. 4 SEM images of COF (**a**) and COF-SO_3H (**b**)



Element	Wt%	At%
C	23.29	27.79
N	46.79	47.89
O	24.36	21.83
S	5.56	2.49

Fig. 5 SEM image of COF-SO_3H and corresponding quantitative EDX element mapping of O, C, N, and S

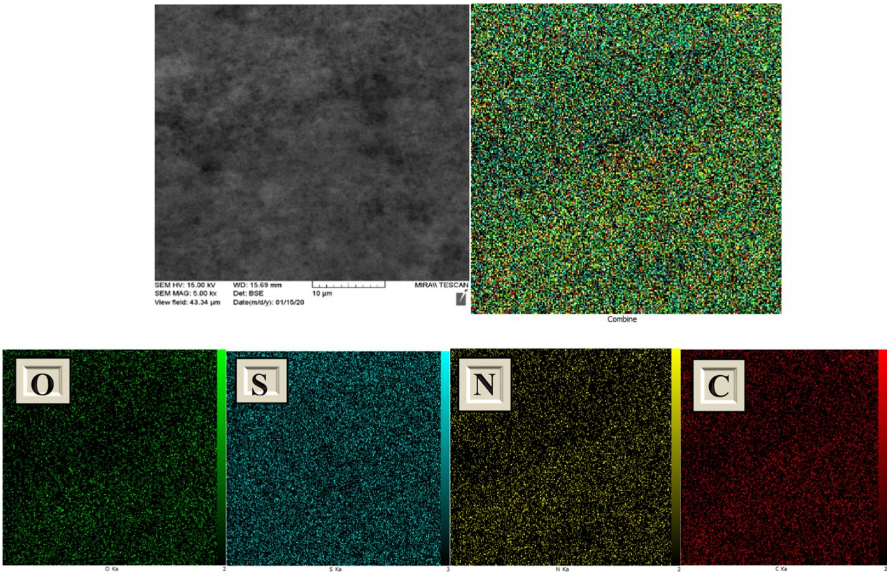


Fig. 6 SEM image of COF-SO_3H and corresponding quantitative EDX element mapping of O, C, N, and S

acetate (1, 2, 2) was chosen as the model reaction to optimize the reaction condition in the presence of different amounts of the catalyst in a range of temperatures (Table 2).

Using this optimized condition, we probed the generality of our methodology by reacting with various other aldehydes, ammonium acetate, and ethyl acetoacetate (1, 2, 2) under solvent-free conditions at 90 °C (Scheme1). It is noteworthy to mention that the structural variation relating to the aldehyde and substituents on the aromatic ring had no significant impact on this change, as 1,4-dihydropyridine derivatives were obtained in high-to-excellent efficiencies with rather short reaction times (Table 3).

It can be postulated that the reaction is proceeded via a hydrogen abstraction and a Knoevenagel condensation reaction. After nucleophilic attack of another ethylacetoacetate molecule, the subsequent imine formation occurs with the liberated ammonia from ammonium acetate. After dehydration, the target 1,4-dihydropyridine will be prepared (Scheme 3).

After successful preparation of Hantzsch 1,4-dihydropyridine derivatives in good-to-excellent yields and also as a next step to benchmark the catalyst, we decided to synthesize polyhydroquinoline derivatives (PHQs) via Hantzsch reaction under optimal reaction conditions (Scheme 1). The products were acquired with high yields (87–96%). The obtained outcomes are summarized in Table 4.

It can be proposed that the reaction proceeds as 1,4-dihydropyridines with the difference that in the first step, the Knoevenagel condensation occurs with dimedone and aromatic aldehyde; afterward, a Michael addition occurs and after cyclization, the target polyhydroquinolines are prepared (Scheme 4).

The wide-angle powder X-ray diffraction (PXRD) of COF, fresh COF-SO_3H, and reused COF-SO_3H was obtained (Fig. 7). The appearance of broad peaks between 2θ value of 15 to 30 degree in the PXRD pattern could be attributed to the amorphous nature of this porous organic polymer.

The FT-IR spectrum of the reused catalyst was obtained and was compared with the fresh catalyst (Fig. 8). There was no considerable change in the spectrum, which is an indication of the stability of the catalyst structure in the reaction medium.

Table 2 Optimization of conditions for the condensation reaction of benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol) and ammonium acetate under solvent-free conditions

Entry	NH_4OAc (mmol)	Catalyst (gr)	Temp (°C)	Time (min)	Yield (%)
1	2	0.02	80	15	91
2	1.5	0.02	80	20	89
3	2	0.01	80	30	76
5	2	0.02	90	10	93
6	2	0.02	100	10	91
7	1	0.02	80	45	62
8	1.5	0.02	90	15	90
9	2	0.03	90	10	86

Table 3 Synthesis of 1,4-dihydropyridine derivatives catalyzed by COF-SO_3H under solvent-free thermal conditions

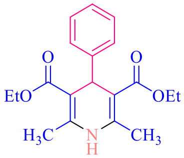
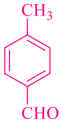
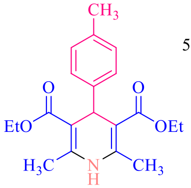
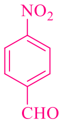
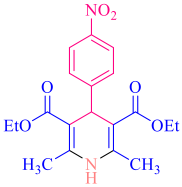
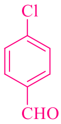
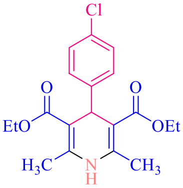
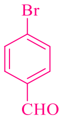
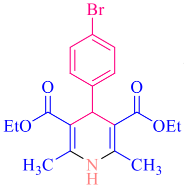
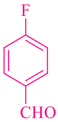
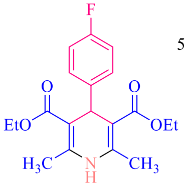
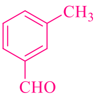
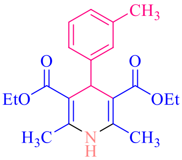
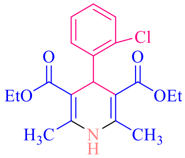
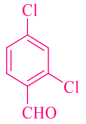
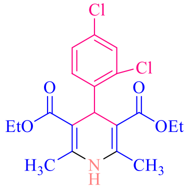
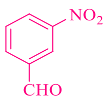
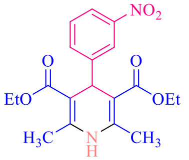
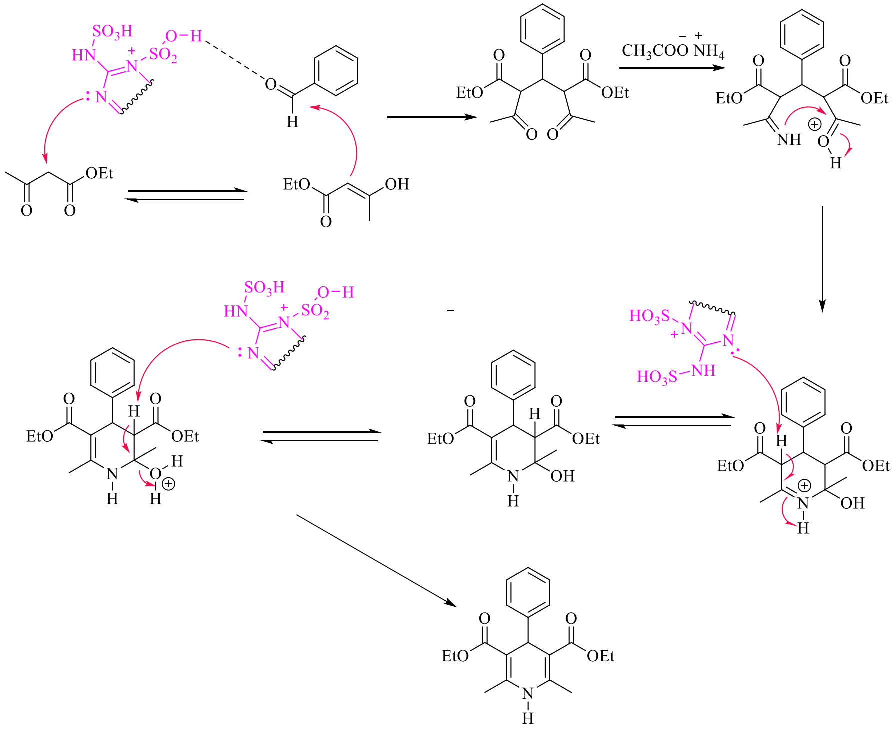
Entry	R	Product	Time (min)	Yeild (%)	Melting point (°C) Found	Melting point (°C) Lit
1		 5a	10	93	157-159	158-160[38]
2		 5b	10	95	136-138	135-137[38]
3		 5c	5	95	128-130	130-132[39]
4		 5d	5	95	142-144	144-145[39]
5		 5e	5	96	162-164	160-162[40]
6		 5f	10	92	155-157	153-156[40]
7		 5g	10	92	123-125	122-124[41]

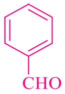
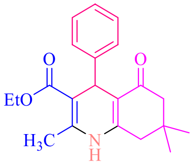
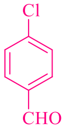
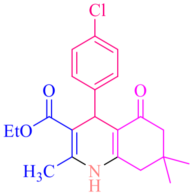
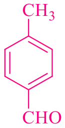
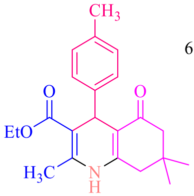
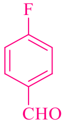
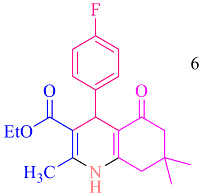
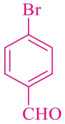
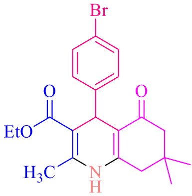
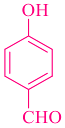
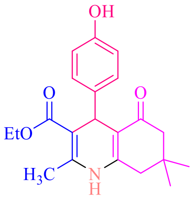
Table 3 (continued)

Entry	R	Product	Time (min)	Yeild (%)	Melting point (°C) Found	Melting point (°C) Lit
8		 5h	10	87	214-216	216-218[42]
9		 5i	10	90	108-110	108-110[42]
10		 5j	5	94	165-167	166-168[43]



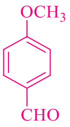
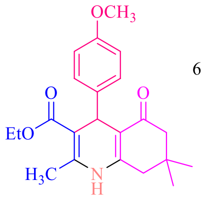
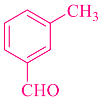
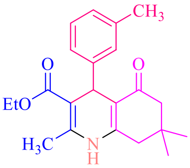
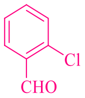
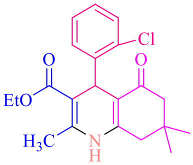
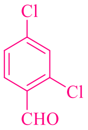
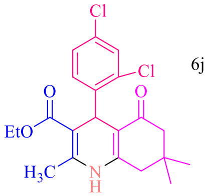
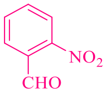
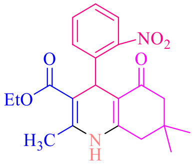
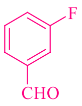
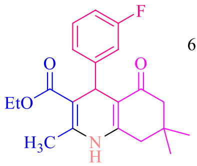
Scheme 3 Proposed mechanism of COF-SO_3H-catalyzed synthesis of 1,4-dihydropyridine

Table 4 Synthesis of polyhydroquinoline derivatives catalyzed by COF-SO_3H under solvent-free thermal conditions

Entry	R	Product	Time (min)	Yeild (%)	Melting point (°C) Found	Melting point (°C) Lit
1		 6a	5	96	201-203	202-204[44]
2		 6b	5	95	242-244	244-246[44]
3		 6c	5	96	262-264	260-262[45]
4		 6d	5	96	186-188	185-187[45]
5		 6e	5	95	249-251	252–254[46]
6		 6f	10	88	234-236	232-234[46]

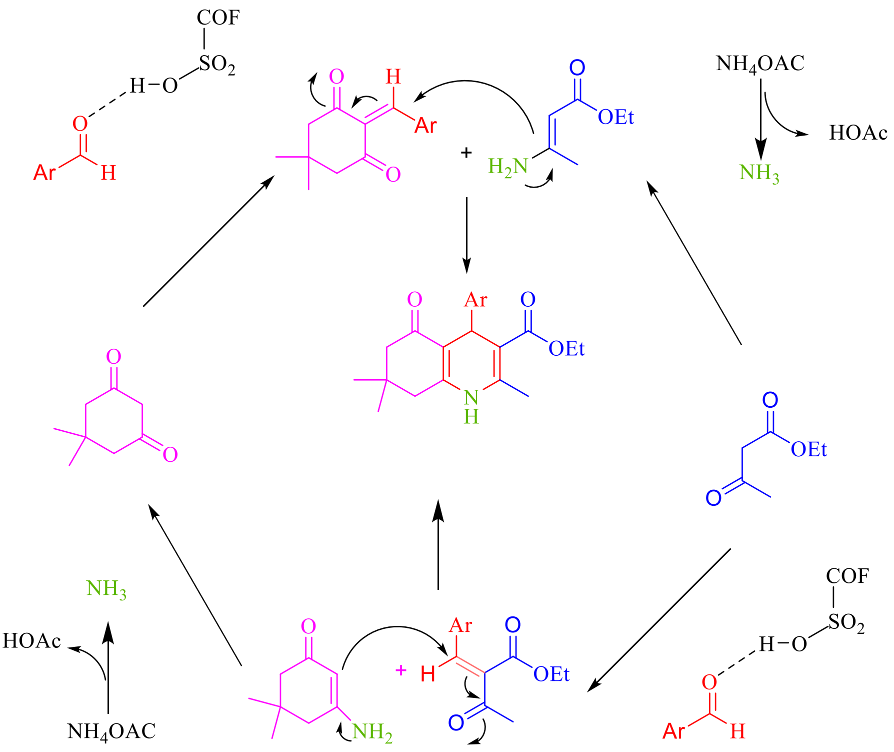
According to the green chemistry principles and also sustainable chemistry remarks, the catalyst reusability in the reaction of ethyl acetoacetate, benzaldehyde, and ammonium acetate was evaluated. In this case, after the completion of reaction, the reaction mixture was cooled to room temperature and the catalyst was removed,

Table 4 (continued)

Entry	R	Product	Time (min)	Yeild (%)	Melting point (°C) Found	Melting point (°C) Lit
7		 6g	10	87	251-253	254-255[47]
8		 6h	5	90	257-259	256-258[47]
9		 6i	10	92	207-209	208-210[48]
10		 6j	5	94	242-244	240-242[48]
11		 6k	5	92	204-206	204-206[49]
12		 6l	10	93	241-243	242-245[49]

washed with ethanol and dried; subsequently, it was reused for the similar reaction. The results illustrated in Fig. 9 indicate that the catalyst could be reused at least for five cycles with only slight reduction in catalytic activity.

With the same method, the reusability of the catalyst in the reaction of benzaldehyde, ethyl acetoacetate, dimedone and ammonium acetate at 90 °C under solvent-free conditions was evaluated. As it is shown in Fig. 10 that the catalyst could be reused at least five times without significant decrease in this nanoporous catalyst.



Scheme 4 Proposed mechanism of COF-SO_3H-catalyzed polyhydroquinolines synthesis

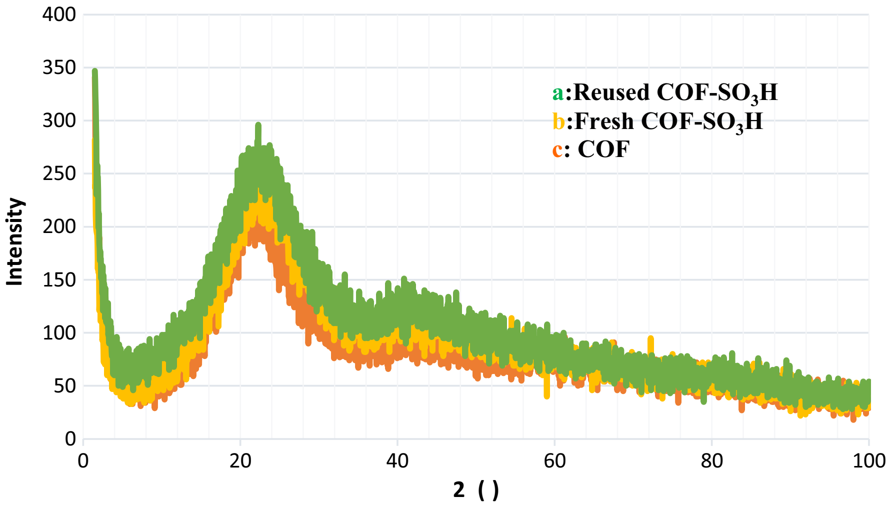


Fig. 7 Powder X-ray diffraction (PXRD) of COF, fresh COF-SO_3H, and reused COF-SO_3H

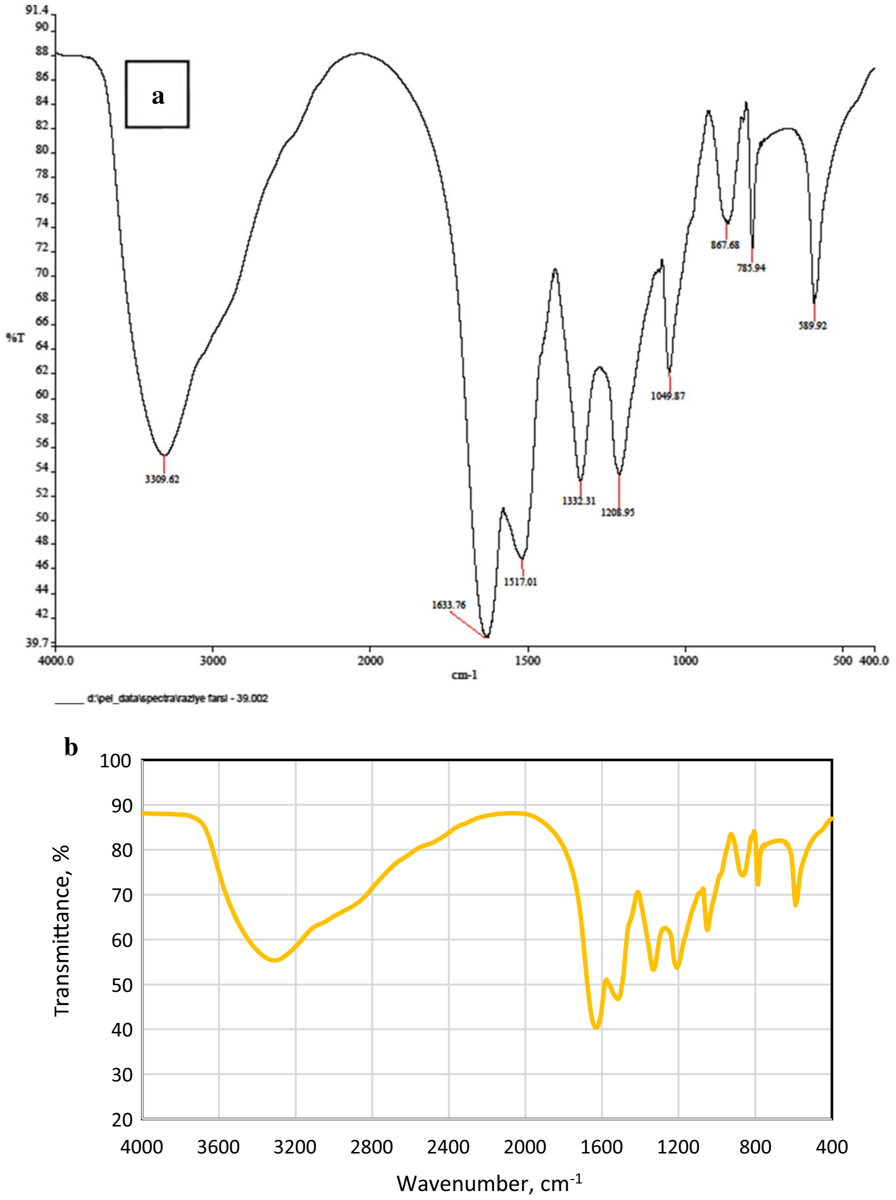


Fig. 8 FT-IR spectra of fresh (**a**) and reused (**b**) catalyst

At last, to show the superiority of the present approach in comparison with other catalysts, we compared our results with the reported results in the literature for the synthesis of DHP and PHQ (Table 5). Results showed that while in most of these cases comparative yields of the desired product were obtained following the COF-SO_3H-catalyzed procedure, some of the previous procedures required

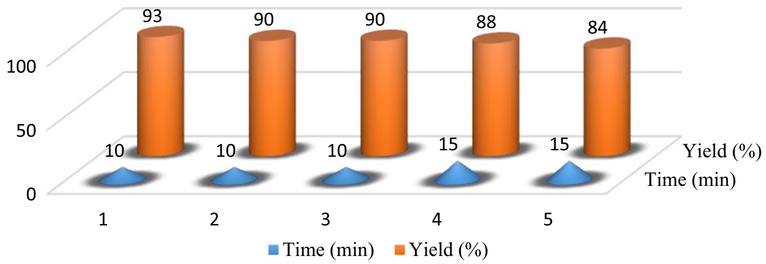


Fig. 9 Reusability of the catalyst in the reaction of benzaldehyde, ethyl acetoacetate, and ammonium acetate at 90 °C under solvent-free conditions

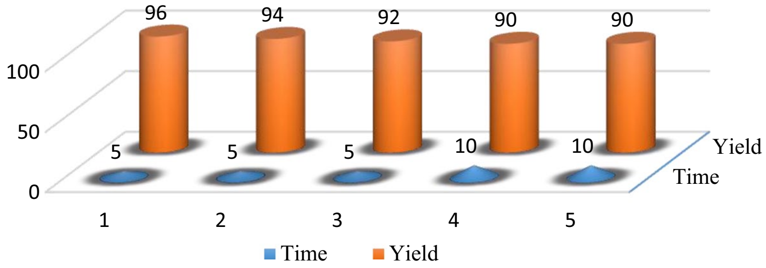


Fig. 10 Catalyst reusability in the reaction of benzaldehyde, dimedone, ethyl acetoacetate, and ammonium acetate

Table 5 Comparison of catalytic activity of COF-SO_3H nanostructures with some other catalysts

Entry	Catalyst	Conditions		Time (min)	Yield (%)	Catalyst loading (mol %)	Ref
		Solvent	T/°C				
1	2,4,6-Trichloro (1,3,5)triazine	Solvent-free	25	30	94	10	[26]
2	$InCl_3$	[bmim]Cl	Reflux	240–360	92	5	[27]
3	$Yb(OTf)_3$	EtOH	r.t	300	90	5	[29]
4	Silica gel/$NaHSO_4$	Solvent-free	r.t	360	85	5	[30]
5	L-proline	EtOH	Reflux	360–420	81–92	10	[32]
6	$Sc(OTf)_3$	EtOH	r.t	120–360	86–95	5	[33]
7	ZnO	EtOH	80	60	92	10	[35]
8	COF-SO_3H	Solvent-free	90	5–10	87–96	8.2	This work

long reaction time (Entries 2, 3, 4, 5, 6), or high catalyst loading (Entry 1, 5, 7). These results clearly demonstrate that the presented procedure can be utilized as a useful acidic catalyst in organic methodology.

Conclusion

In conclusion, we have prepared an efficient organic solid acid catalyst by post-modification of the COF, which was prepared via reaction of melamine and terephthalaldehyde. The COF-SO_3H was shown to be porous with a surface area of 79.327 $m^2 g^{-1}$. After characterization of the catalyst, it was used as an effective solid acid catalyst for the synthesis of various 1,4-dihydropyridine and polyhydroquinoline derivatives via an one-pot multicomponent Hantzsch reaction in the presence of COF-SO_3H as the catalyst with high isolated yields. This methodology offers several advantages including high yield, short reaction time, simple workup procedure, solvent-free conditions, and recyclability of the catalyst.

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