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Sulfonic Acid and Ionic Liquid Functionalized Covalent Organic Framework for Efficient Catalysis of the Biginelli Reaction

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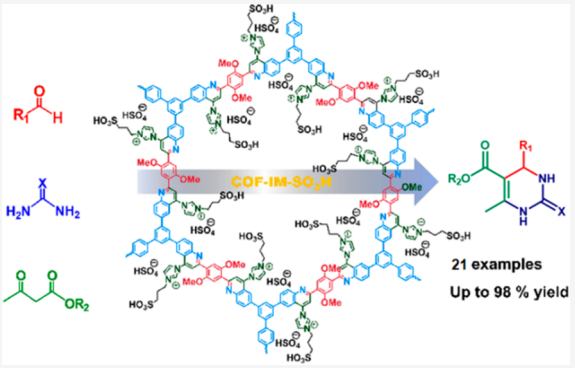
ABSTRACT: A quinoline-linked and ionic liquid-decorated covalent organic framework was prepared by incorporation of a multicomponent Povarov reaction and postsynthetic modification. The imidazolium and sulfonic acid-decorated COF-IM-SO_3H can be a highly efficient Brønsted acid catalyst to promote the Biginelli reaction under solvent-free conditions in a heterogeneous way. In addition, a scaled-up Biginelli reaction has been readily realized over a COF-IM-SO_3H@chitosan aerogel-based cup reactor.



Owing to the high degree of atom economy, multicomponent reactions (MCRs) have attracted intense attention in organic and medicinal chemistry.[1] Among various MCRs, the Biginelli reaction,[2] which is derived from aldehyde, *β*-keto ester, and urea or thiourea with a catalytic amount of acid, is one of the most important one-pot multicomponent reactions due to the important pharmacological functionality of the generated dihydropyrimidine derivatives (DHPMs).[3] For pursuing a "greener synthesis" of DHPMs in a facial, clean, and atomic economic manner, metal-free organocatalysis has been recognized as one of the feasible synthetic methodologies.[4] However, the homogeneous organocatalysts faced some problems such as catalyst separation and recycling, involved hazardous organic solvents, and sometimes a long reaction time.[5] To address these issues, heterogeneous organocatalysis should be an effective way to realize the green synthesis of DHPMs.[6] To meet the multifaceted requirements of good stability, high activity, simplified product separation, facile catalyst recycling, and so on, the design and synthesis of new types of heterogeneous organocatalysts for the Biginelli reaction are highly imperative.

As a result of their permanent porosity, highly ordered and extended structure, good chemical stability, and tunable functionality, covalent organic frameworks (COFs)[7] have emerged as a new type of organic material that can be excellent candidates for the construction of heterogeneous organocatalysts.[8] In this context, the most reported COFs, however, are connected via imine linkage, which suffers from poor chemical stability against strong acidic or reducing reagents.[9] In order to expand linkage type and improve the chemical stability of COFs, we and others recently developed a multicomponent one-pot in situ polymerization methodology, which can be an alternative way to synthesize the robust linkage connected COFs.[10]

In this contribution, we report herein a new quinoline-linked COF-IM with an imidazole group via a three-component one-pot in situ Povarov reaction. After postsynthetic modification (PSM) with 1,3-propane sultone, both sulfonic acid and ionic liquid (IL)-decorated COF-IM-SO_3H, which can be a highly active heterogeneous Brønsted acid type catalyst for the Biginelli reaction, were generated. In addition, a scaled-up Biginelli reaction was realized via a COF-IM-SO_3H@chitosan aerogel based fixed-bed model reactor.

Based on the model multicomponent Povarov reaction,[11] among aniline, benzaldehyde (Ba), and 1-vinylimidazole (VIM) (Scheme S1, Figures S1−S3), the three-component one-pot in situ polymerization of 1,3,5-tri(4-aminophenyl)-benzene (TAPB), 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMTPA), and VIM in the presence of $Yb(OTf)_3$ and 2,3-dicyano-5,6-dichloroben-quinone (DDQ) under solvothermal conditions (MeCN, 80 °C, 3 days) afforded COF-IM as the brick red crystalline solids in 87% yield (Scheme 1). Formation of the quinoline linkage was verified by FTIR and solid-state NMR spectroscopy (Figure S4), and the assignments were made based on the molecular model compounds.

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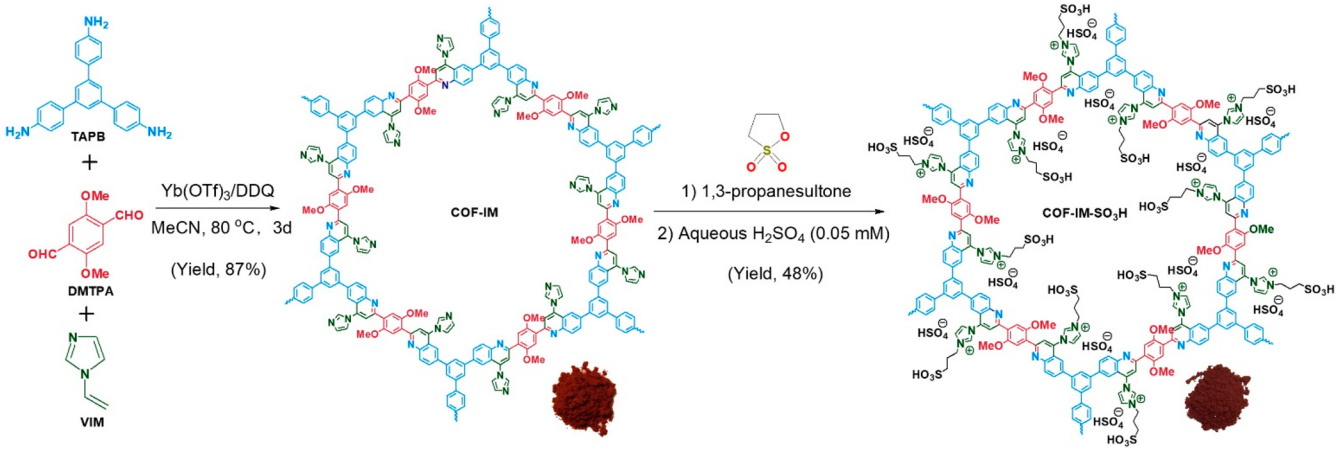
Scheme 1. Synthesis of COF-IM and COF-IM-SO_3H



As revealed by the measured powder X-ray diffraction (PXRD) patterns, the obtained COF-IM exhibited good crystallinity (Figure 1a). The simulation of its PXRD patterns

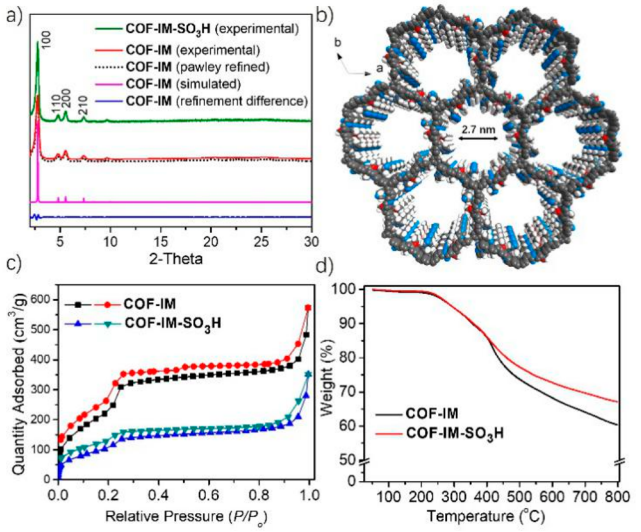


Figure 1. (a) Simulated and measured PXRD patterns of COF-IM and COF-IM-SO_3H: comparison between the experimental (red and green lines) and Pawley refined profile (black dots), the simulated pattern for eclipsed (AA) stacking mode (purple line), and the refinement difference (blue line). (b) Crystal structure viewed down the crystallographic *c* axis. (c) N_2 adsorption isotherms of COF-IM and COF-IM-SO_3H at 77 K. (d) TGA traces of COF-IM and COF-IM-SO_3H.

with Materials Studio (version 2018)[12] suggested that COF-IM possesses preferably the 2D eclipsed AA-type stacking arrangement using the space group *P*3 with the lattice parameters $a = b = 36.9554$ Å, $c = 3.9068$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, residuals $R_{wp} = 4.33\%$ and $R_p = 3.36\%$ (Table S1). Pawley refinement showed a negligible difference between the simulated and experimental PXRD pattern, and COF-IM displayed prominent peaks at 2.77, 4.80, 5.56, and 7.37 corresponding to (100), (110), (200), and (210) facets, respectively. Figure 1b showed that the eclipsed 2D structure contains hexagonal pores with a diameter of ~2.7 nm based on crystal structural analysis.

The porosity of COF-IM was examined by N_2 adsorption–desorption measurements at 77 K. As shown in Figure 1c, the N_2 adsorption capacity and Brunauer–Emmett–Teller (BET) surface area of COF-IM was 598 $cm^3\ g^{-1}$ and 1203 $m^2\ g^{-1}$, respectively, and the total pore volume was calculated to be 0.615 $cm^3\ g^{-1}$. The average pore size distribution is centered at ca. 2.7 nm based on Barrett–Joyner–Halenda analysis, which is in good agreement with that calculated from its crystal structure (Figure S5). As expected, COF-IM is chemically stable, and it can tolerate various conditions such as HCl, NaOH, and $NaBH_4$ aqueous solutions (Figure S6).

The excellent chemical stability allowed COF-IM to be further modified. As shown in Scheme 1, sulfonic acid could be easily decorated on the framework via PSM. Upon reaction of COF-IM with 1,3-propane sultone in acetone for 24 h, together with subsequent protonation, sulfonic acid-functionalized COF-IM-SO_3H was obtained as a brick red crystalline powder in 48% yield. As indicated in Figure 1a, the crystallinity and structural integrality of COF-IM was well maintained after PSM. Besides IR and solid-state NMR spectra characterizations (Figure S4), the N_2 adsorption isotherm of COF-IM-SO_3H indicated that its N_2 adsorption capacity and BET surface area, respectively, decreased to 351.5 $cm^3\ g^{-1}$ and 504.6 $m^2\ g^{-1}$ (Figure 1c), which is undoubtedly caused by the partial channel occupation after PSM. Accordingly, the pore volume and size of COF-IM-SO_3H decreased to 0.319 $cm^3\ g^{-1}$ and 2.5 nm (Figure S5), respectively.

Thermogravimetric analysis (TGA, Figure 1d) revealed that both COF-IM and COF-IM-SO_3H were thermally stable at 250 °C, indicating their sufficient stability for catalytic applications. The SEM and TEM images showed COF-IM and COF-IM-SO_3H, which were highly crystalline, and nanoscale spherical particles with good phase purity (Figure S7). In addition, the energy-dispersive X-ray spectra (EDX-mapping) of COF-IM and COF-IM-SO_3H clearly indicated the required elemental composition (Figure S8).

In addition, COF-IM-SO_3H is stable against organic (DMSO, DMF, toluene, MeCN, CH_2Cl_2, THF, acetone) and aqueous media (Figure S6), which would ensure the safety in the catalysis with different media. More importantly, the coexistence of SO_3H and ILs would allow COF-IM-SO_3H to promote MCRs efficiently.[13]

As shown in Figure 2a, the reaction of benzaldehyde, ethyl acetoacetate, and urea was chosen as the model Biginelli reaction to examine the catalytic activity of COF-IM-SO_3H.

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J. Org. Chem. 2021, 86, 3024–3032

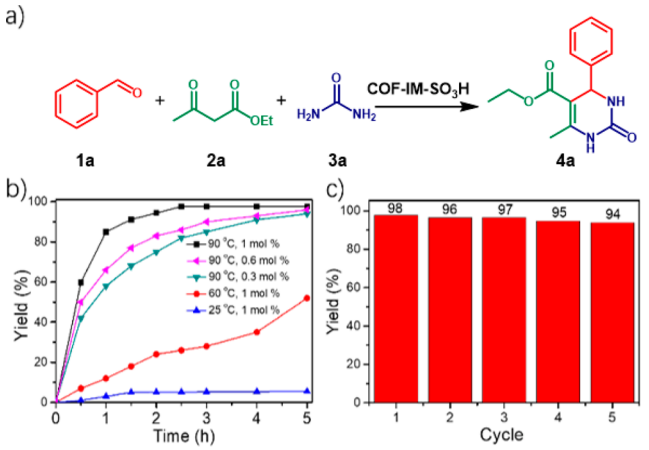


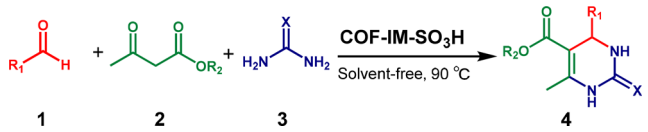
Figure 2. (a) Model Biginelli reaction. (b) Effect of temperature, reaction time, and catalyst amount on the catalytic Biginelli reaction over COF-IM-SO_3H. Reaction conditions: solvent-free, benzaldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), urea (1.0 mmol), COF-IM-SO_3H (0.3–1.0 mol %, 2.59–8.64 mg), 25–90 °C. (c) Catalytic cycles.

Compared with organic and aqueous media such as EtOH, MeOH, toluene, and water (Figure S9), the solvent-free was confirmed to be the best condition for the reaction (Figure 2b). In addition, the reaction temperature was screened, and Figure 2b showed that the best reaction temperature was 90 °C, and the maximum isolated yield of 98% was achieved within ~2.5 h. When the catalyst loading was switched to 0.3 and 0.6 mol % at 90 °C, it gave reasonable isolated yields (80–84%), and higher yields of 93 and 95% can be reached by extending the reaction time to 5.0 h. When the reaction was conducted at 25 and 60 °C over 1.0 mol % of the catalyst, it turned into the Biginelli adducts in the yield of 4 and 23% within 2.5 h, respectively, indicating the positive correlation between catalytic efficiency and temperature. Thus, the best reaction conditions herein were determined as 1.0 mol % COF-IM-SO_3H, 90 °C, solvent-free, and 2.5 h. Based on each sulfonic acid unit present in COF-IM-SO_3H, the corresponding turnover number (TON) and turnover frequency (TOF) were 98 and 39 h^{-1}, respectively. By comparison, sulfonic acid-functionalized ionic liquids containing the HSO_4^- counteranion would enhance the Brønsted acidity of the catalyst (Table S2), which is well consistent with the previous work.[14] Of note, COF-IM-SO_3H herein is one of the best catalysts for the Biginelli reaction among the reported heterogeneous catalysts (Table S3),[15−37] which may be attributed to its high density of sulfonic acid moiety and high surface area.

The hot leaching test demonstrated that COF-IM-SO_3H is a typical heterogeneous catalyst (Figure S10), and the isolated yield of the desired Biginelli adducts was still up to 94% even after five catalytic cycles (Figure 2c). The crystallinity and structural integrity of COF-IM-SO_3H, however, were intact after multiple catalytic runs (Figures S10 and S11), indicating the robust nature of the quinoline linkage. In addition, the SEM-EDX mapping (Figure S10) and elemental analysis (Table S4) revealed that no changes in morphology or chemical composition occurred. Thus, COF-IM-SO_3H herein is an ideal platform for loading of Brønsted acid and task-specific ILs for the catalysis of the Biginelli reaction.

The Biginelli reaction can be readily extended to various other substrates with 100% selectivity. Under the optimized conditions, the reactions gave excellent yields (90–98%) for different aromatic aldehydes with a wide range of functional groups, such as −OH, $-NO_2$, $-CH_3$, −Cl, and $-OCH_3$, at different substituted positions on substituted benzaldehydes (Table 1, entries 1–8). For heterocyclic aldehydes, such as 3-pyridine carboxaldehyde and furfural, the corresponding product was obtained in 75 and 89% yields, respectively (Table 1, entries 9 and 10). The reaction worked well for aliphatic aldehydes: cyclohexanealdehyde and hexaldehyde gave 90 and 92% yields, respectively (Table 1, entries 11 and 12). The large substrates of 2-naphthaldehyde and 4-phenylbenzaldehyde gave a moderate 60% yield (Table 1, entries 13 and 14), and the decrease in yield might result from their limited diffusion within the COF framework. In the case of using methyl acetoacetate instead of ethyl acetoacetate, the target products of benzaldehyde, 4-chlorobenzaldehyde, and 4-methylbenzaldehyde were isolated in excellent yields of 96, 94, and 93%, respectively (Table 1, entries 15–17).

Table 1. Scope of the Biginelli Reaction Catalyzed by COF-IM-SO_3H[a]



EN	R_1	R_2	X	yield (%)[b]
1	Ph	Et	O	98 (**4a**)
2	2-ClPh	Et	O	90 (**4b**)
3	4-ClPh	Et	O	92 (**4c**)
4	4-NO_2Ph	Et	O	94 (**4d**)
5	4-MePh	Et	O	93 (**4e**)
6	2-MeOPh	Et	O	90 (**4f**)
7	4-MeOPh	Et	O	96 (**4g**)
8	4-OHPh	Et	O	92 (**4h**)
9	3-pyridine	Et	O	75 (**4i**)
10	2-fural	Et	O	89 (**4j**)
11	cyclohexyl	Et	O	90 (**4k**)
12	hexyl	Et	O	92 (**4l**)
13	(1,1′-biphenyl)-4-yl	Et	O	60 (**4m**)
14	2-naphtyl	Et	O	60 (**4n**)
15	Ph	Me	O	96 (**4o**)
16	4-ClPh	Me	O	94 (**4p**)
17	4-MePh	Me	O	93 (**4q**)
18	Ph	Et	S	93 (**4r**)
19	4-ClPh	Et	S	89 (**4s**)
20	4-MeOPh	Et	S	91 (**4t**)
21	Ph	Me	S	86 (**4u**)

[a]Reaction conditions: solvent-free, aromatic aldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), urea or thiourea (1.0 mmol), COF-IM-SO_3H (8.64 mg, 1.0 mol %), 90 °C, 2.5 h. [b]Isolated yields. Compounds **4a–u** were characterized by ^1H NMR, ^{13}C NMR, and MS spectra (Figures S12–S32).

Additionally, the reactions of thiourea with different benzaldehydes and ethyl acetoacetate were also examined, and they could afford corresponding products in 89–93% yields (Table 1, entries 18–20). Moreover, the reaction between benzaldehyde, methyl acetoacetate, and thiourea gives the corresponding product in 86% yield (Table 1, entry 21).

The mechanism of this COF-IM-SO_3H-catalyzed Biginelli reaction was proposed under solvent-free conditions, which is believed to be the same as suggested by Kappe (Figure S33).[38]

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J. Org. Chem. 2021, 86, 3024−3032

For practical application, we designed and fabricated a COF-IM-SO_3H@chitosan aerogel-based cup-like reactor[39] (Figure 3a,b), which was used as a fixed-bed model to realize the scaled-up Biginelli reaction. The COF-IM-SO_3H content in porous aerogel is up to 80 wt %. SEM images indicated that the COF-IM-SO_3H nanoparticles are homogeneously blended in the macropores aerogel with no detectable interface boundary (Figure 3c). PXRD patterns indicated that the structural integrity and crystallinity of COF-IM-SO_3H were well retained (Figure S34). As the ice-template-generated macropore aerogel did not significantly contribute to the surface area, the COF-IM-SO_3H@chitosan showed a decreased N_2 adsorption capacity (221.5 $cm^3\ g^{-1}$) and a lower BET specific surface area (160.6 $m^2\ g^{-1}$) (Figure S34).

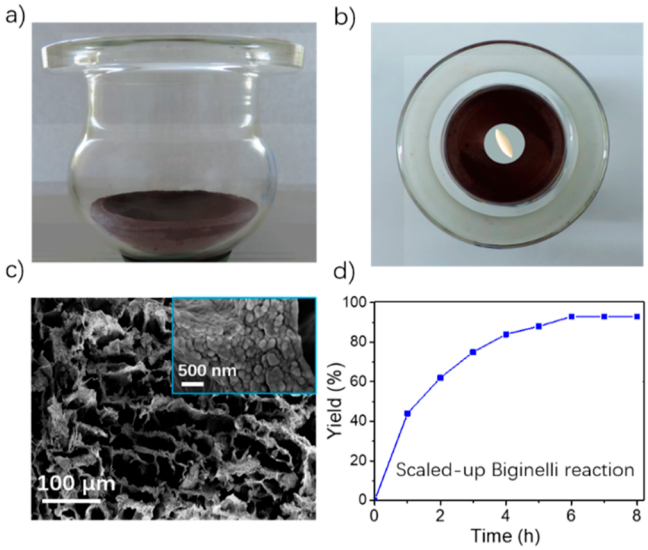


Figure 3. (a) Side and (b) top views and (c) SEM images of the COF-IM-SO_3H@chitosan cup reactor. (d) Reaction monitoring. Reaction conditions: solvent-free, benzaldehyde (305.6 mmol), ethyl acetoacetate (305.6 mmol), urea (305.6 mmol), COF-IM-SO_3H@chitosan (1.65 g, 0.5 mol % COF-IM-SO_3H equiv), 90 °C.

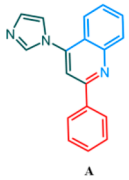
As shown in Figure 3d, when 31.2 mL of (305.6 mmol) benzaldehyde, 38.7 mL of ethyl acetoacetate (305.6 mmol), and 18.35 g of urea (305.6 mmol) were used to perform the reaction in a cup-like reactor (1.65 g of COF-IM-SO_3H@chitosan, 0.5 mol % COF-IM-SO_3H equiv), a 93% isolated yield (73.9 g) of the desired product was obtained within 6 h. After the reaction, the product−catalyst separation was easily achieved by simply washing with hot ethanol, and the cup-like reactor was directly used for the next catalytic cycle after vacuum drying. The COF-IM-SO_3H@chitosan reactor was very stable under the given conditions, and it could be reused at least five times without loss of its catalytic activity (yield ≥ 92%) (Figure S34). Thus, the aerogel monolith used herein is highly efficient, versatile, maneuverable toward organic catalytic conversion, and it could effectively overcome the issues of catalyst regeneration and product separation.

In conclusion, we report a robust quinoline-linked COF with SO_3H and ILs moieties. Due to its strong acidity and high porosity, the obtained COF-IM-SO_3H can be an efficient Brønsted acid type catalyst to promote the Biginelli reaction under solvent-free conditions in a heterogeneous way. Besides, an ice-templated COF-IM-SO_3H@chitosan aerogel with remarkably high COF loading (up to 80 wt %) was prepared, and its cup-like reactor can act as a highly efficient and reusable fixed-bed model to realize the scaled-up Biginelli reaction. The potential utility of this strategy is highlighted by the preparation of many more new COF-based multifunctional heterogeneous organocatalysts to promote various organic transformations in a green and facile way.

EXPERIMENTAL SECTION

All chemicals were obtained from commercial sources and used without further purification. Proton nuclear magnetic resonance (^1H NMR) data were obtained on a Bruker Avance 400 HD spectrometer with tetramethylsilane (TMS) as the internal standard. Fourier transform infrared (FT-IR) spectroscopy was performed on a Bruker ALPHA spectrometer in the range of 400−4000 cm^{-1}. High-resolution mass spectrometry (HRMS) analysis was carried out on a Bruker maXis ultrahigh-resolution-TOF mass spectrometer. Elemental analysis was performed on an Elemental UNICUBE elemental analyzer. The solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectra were obtained on a Bruker AVANCE II 400 spectrometer. Scanning electron microscopy (SEM) was conducted on a Gemini Zeiss SUPRA scanning electron microscope equipped with an energy-dispersive X-ray detector. The Powder X-ray diffraction patterns were measured on a D8 Advance X-ray powder diffractometer (Cu Kα radiation λ = 1.5405 Å). N_2 adsorption−desorption isotherms were obtained on an ASAP 2020/TriStar 3000 (Micromeritics). Thermogravimetric analyses (TGA) were performed on a TA Instrument Q5 simultaneous TGA at a heating rate of 10 °C min^{-1} from 25 to 800 °C under 60 mL min^{-1} with flowing nitrogen. Melting points were measured on a X-4 Digital display microscopic melting point tester. Differential thermal scanning (DSC) was performed on a METTLER TOLEDO DSC^{3+} instrument.

Synthesis Model Compounds A and B. *Synthesis of A.* A mixture of aniline (149 mg, 1.6 mmol), benzaldehyde (170 mg, 1.6 mmol), 1-vinylimidazole (151 mg, 1.6 mmol), $Yb(OTf)_3$ (50 mg, 5 mol %), and DDQ (25.6 mg, 0.096 mmol) in 30 mL of MeCN was sealed in a Pyrex tube. The tube was flash frozen in a liquid nitrogen bath and evacuated to an internal pressure of 0.5 mbar and flame-sealed. After the mixture was heated at 80 °C (oil bath) in N_2 for 72 h, the crude product was purified via column chromatography (eluent: dichloromethane/petroleum ether = 4:1) to afford A as a yellow powder in 94% yield (407.8 mg): mp 125−126 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 8.41 (d, 1H), 8.33 (q, J = 6.3 Hz, 2H), 8.21 (d, J = 8.4 Hz, 1H), 8.16 (t, J = 7.0 Hz, 1H), 7.91 (t, J = 7.0 Hz, 1H), 7.77 (t, J = 7.3 Hz, 1H), 7.65 (m, J = 6.7 Hz, 3H), 7.55 (m, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 156.8, 148.8, 142.8, 137.9, 135.5 (2C), 131.7, 131.1, 130.2 (2C), 129.4, 128.5 (2C), 127.9, 125.0, 124.0, 120.8, 119.4; IR (KBr, cm^{-1}) 3106 (s), 1589 (m), 1488 (m), 1405 (w), 1325 (m), 1210 (m), 1210 (w), 1054 (m), 937 (s), 841 (w), 758 (m), 693 (w), 658 (m); HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{13}N_3$ 272.1182, found 272.1186.



A

Synthesis of B. A mixture of A (271 mg, 1 mmol) and 1,3-propane sultone (134 mg, 1.1 mmol) in 10 mL of acetone was stirred at room temperature for 24 h. Then, the precipitated solid product was collected by filtration, washed with acetone, and then dried under a vacuum at room temperature. The solids were mixed with 10 mL of H_2SO_4 aqueous solution (0.05 mM, pH = 4) and stirred for 1 h at room temperature. After rotary evaporation, washing with ethyl acetate (3 × 5 mL), and vacuum drying, B was generated in 78% yield (307.7 mg): T_g −58.3 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 8.43 (d, 1H), 8.33 (q, J = 6.3 Hz, 2H), 8.22 (d, J = 8.4 Hz, 1H), 8.17 (t, J = 7.0 Hz, 1H), 7.92 (t, J = 7.0 Hz, 1H), 7.81 (q, J = 7.3 Hz, 2H), 7.69 (m, J

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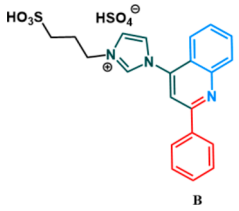
J. Org. Chem. 2021, 86, 3024−3032

= 6.7 Hz, 2H), 7.56 (m, J = 7.2 Hz, 3H), 4.33 (t, J = 6.9 Hz, 2H), 2.40 (t, J = 6.9 Hz, 2H), 2.10 (m, J = 6.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 156.8, 148.6, 143.0, 137.8, 135.9, 131.7, 130.7, 130.0, 129.4 (2C), 128.5, 128.0 (2C), 125.1, 124.1, 122.5, 120.3, 119.4, 48.0, 47.8, 26.7; IR (KBr, cm^{-1}) 3113 (m), 1590 (m), 1497 (w), 1358 (w), 1210 (m), 1108 (w), 1027 (s), 977 (m),775 (w), 522 (m); HRMS (ESI) m/z $[M]^+$ calcd for $C_{21}H_{20}N_3O_3S^+$ 394.1220, found 394.1294; $[M]^-$ calcd for HSO_4^- 96.9601, found 96.9649; $[M - H]^-$ calcd for $C_{21}H_{21}N_3O_7S_2$ 490.0748, found 490.0877.



B

Synthesis COF-IM and COF-IM-SO_3H. *Synthesis of COF-IM.* The synthetic procedure refers to our reported work with modification.[10b] In brief, a mixture of 1,3,5-tri(4-aminophenyl)-benzene (TAPB) (56.2 mg, 0.16 mmol), 2,5-dimethoxy terephthaladehyde (DMTPA) (46.5 mg, 0.24 mmol), 1-vinylimidazole (VIM) (226.4 μL, 2.50 mmol), Yb(OTf)$_3$ (15.0 mg, 0.024 mmol), and DDQ (8 mg, 0.03 mmol) in 3 mL of MeCN was sealed in a Pyrex tube. The tube was flash frozen in a liquid nitrogen bath, evacuated to an internal pressure of 0.5 mbar, and flame-sealed. Upon warming to room temperature, it was heated under N_2 at 80 °C (oil bath) for 3 days. The obtained solids were completely washed with THF (15 mL × 6) and dried in a vacuum at 120 °C for 24 h to produce COF-IM as brick red solids in 87% yield (120.3 mg). Elemental Analysis (%) calcd for $(C_{18}H_{13}N_3O)_n$ (desolvated) (%): C, 75.22; H, 4.56; N, 14.63; O, 5.57. Found (%): C, 75.45; H, 4.52; N, 14.59; O, 5.35. FT-IR (KBr, cm^{-1}): 3359 (w), 1592 (m), 1500 (s), 1408 (m), 1288 (w), 1210 (m), 1035 (w), 828 (m). Solid-state ^{13}C $\{^1H\}$ MAS NMR (δ, ppm): 157, 150, 144, 137, 132, 124, 120, 116, 110, 56.

Synthesis of COF-IM-SO_3H. COF-IM (287 mg, 1 mmol) was dispersed in 20 mL of acetone solution of 1,3-propane sultone (1.1 mmol, 134 mg). After the mixture was stirred at room temperature for 24 h, the precipitate was collected by centrifugation and completely washed with acetone (5 mL). After drying under a vacuum, the solids were mixed with 10 mL of H_2SO_4 aqueous solution (0.05 mM, pH = 4), and the mixture was stirred for 1 h at room temperature to afford COF-IM-SO_3H as brick red solids. According to the elemental analysis of sulfur content (3.75 wt %), the postsynthetic modification yield was ca. 48% (197.2 mg). FT-IR (KBr, cm^{-1}): 3359 (w), 1592 (m), 1500 (s), 1408 (w), 1288 (w), 1210 (m), 1108 (w), 1035 (m), 824 (m). Solid-state ^{13}C $\{^1H\}$ MAS NMR (δ, ppm): 157, 150, 142, 137, 134, 124, 120, 117, 112, 56, 50, 23.

Catalytic Biginelli Reaction over COF-IM-SO_3H. *General Procedure.* In a typical procedure, a mixture of aromatic aldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), and urea (1.0 mmol) was stirred at 90 °C (oil bath), utilizing COF-IM-SO_3H (8.64 mg, 1.0 mol %) under solvent-free conditions for the appropriate time until the reaction was complete (monitored by TLC). After the addition of hot ethanol (5 mL, 60 °C) and after the mixture was centrifuged and filtrated, the formed precipitate was collected. The crude product was purified by recrystallization in ethanol, and the structure of the desired Biginelli adduct (3,4-dihydopyrimidin-2(1*H*)-ones) was confirmed by ^1H NMR, ^{13}C NMR, and MS spectra.

*5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-(1H)-one (**4a**).* The compound was prepared according to the general procedure: white powder (255 mg, 98%); mp 202−204 °C;[40a] ^1H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 7.74 (s, 1H), 7.32 (t, 2H), 7.25 (d, 3H), 5.15 (d, J = 3.2 Hz, 1H), 3.97 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.8, 152.6, 148.8, 145.3, 129.2, 127.7, 126.7, 99.7, 59.6, 54.4, 18.2, 14.5; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{16}N_2O_3$ 261.1234, found 261.1234.

*5-(Ethoxycarbonyl)-6-methyl-4-(2-chlorophenyl)-3,4-dihy-dropyrimidin-2(1H)-one (**4b**).* The compound was prepared according to the general procedure: white powder (265 mg, 90%); mp 223−224 °C;[40a] ^1H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 7.71 (s, 1H), 7.41−7.24 (m, 4H), 5.63 (d, J = 2.7 Hz, 1H), 3.86 (q, J = 7.1 Hz, 2H), 2.30 (s, 3H), 0.97 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.4, 151.7, 149.8, 142.2, 132.1, 129.8, 129.5, 129.2, 128.2, 98.4, 59.5, 51.9, 18.1, 14.4; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{15}ClN_2O_3$ 295.0844, found 295.0842.

*5-(Ethoxycarbonyl)-6-methyl-4-(4-chlorophenyl)-3,4-dihydro-pyrimidin-2(1H)-one (**4c**).* The compound was prepared according to the general procedure: white powder (271 mg, 92%); mp 217−218 °C;[40a] ^1H NMR (400 MHz, DMSO-d_6) δ 9.26 (s, 1H), 7.78 (s, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 5.15 (d, J = 3.2 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.7, 152.4, 149.2, 144.3, 132.2, 128.9, 128.6, 99.3, 59.7, 53.9, 18.3, 14.5; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{15}ClN_2O_3$ 295.0844, found 295.0848.

*5-(Ethoxycarbonyl)-6-methyl-4-(4-nitrophenyl)-3,4-dihydr-opyri-midin-2(1H)-one (**4d**).* The compound was prepared according to the general procedure: yellow powder (287 mg, 94%); mp 201−202 °C;[40a] ^1H NMR (400 MHz, DMSO-d_6) δ 9.38 (s, 1H), 8.22 (d, J = 8.7 Hz, 2H), 7.91 (s, 1H), 7.51 (d, J = 8.7 Hz, 2H), 5.29 (d, J = 3.3 Hz, 1H), 3.99 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.5, 152.5, 152.2, 149.9, 147.2, 128.1, 124.3, 98.6, 59.9, 54.1, 18.3, 14.5; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{15}N_3O_5$ 306.1084, found 306.1082.

*5-(Ethoxycarbonyl)-6-methyl-4-(4-methylphenyl)-3,4-dihydro-pyrimidin-2(1H)-one (**4e**).* The compound was prepared according to the general procedure: white powder (255 mg, 93%); mp 216−217 °C;[40a] ^1H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 1H), 7.68 (s, 1H), 7.11 (s, 4H), 5.10 (d, J = 3.2 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 2.23 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.8, 152.6, 148.6, 142.4, 136.8, 129.3, 126.6, 99.9, 59.6, 54.5, 21.1, 18.2, 14.6; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{18}N_2O_3$ 275.1390, found 275.1391.

*5-(Ethoxycarbonyl)-6-methyl-4-(2-methoxyphenyl)-3,4-dihydro-pyrimidin-2(1H)-one (**4f**).* The compound was prepared according to the general procedure: white powder (262 mg, 90%); mp 264−268 °C;[40b] ^1H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 7.27 (s, 1H), 6.85−7.25 (m, 4H,), 5.49 (d, J = 3.1 Hz, 1H), 3.91 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 2.28 (s, 3H), 1.00 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.8, 157.0, 152.6, 149.3, 132.1, 129.6, 127.6, 120.6, 111.6, 59.4, 55.8, 49.7, 18.2, 14.5; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{18}N_2O_4$ 291.1339, found 291.1336.

*5-(Ethoxycarbonyl)-6-methyl-4-(4-methoxyphenyl)-3,4-dihydro-pyrimidin-2(1H)-one (**4g**).* The compound was prepared according to the general procedure: white powder (279 mg, 96%); mp 204−206 °C;[40a] ^1H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 1H), 7.70 (s, 1H), 7.13 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.09 (d, J = 3.1 Hz, 1H), 3.97 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 2.24 (s, 3H),1.10 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.8, 158.9, 152.6, 148.5, 137.5, 127.9, 114.2, 100.0, 59.6, 55.5, 53.8, 18.2, 14.6; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{18}N_2O_4$ 291.1339, found 291.1335.

*5-(Ethoxycarbonyl)-6-methyl-4-(4-hydroxyphenyl)-3,4-dihydro-pyrimidin-2(1H)-one (**4h**).* The compound was prepared according to the general procedure: white powder (255 mg, 92%); mp 225−226 °C;[40c] ^1H NMR (400 MHz, DMSO-d_6) δ 9.32 (s, 1H), 9.10 (s, 1H), 7.57 (s, 1H), 7.01(d, J = 8.1 Hz, 2H), 6.67 (d, J = 8.1 Hz, 2H), 5.03 (d, J = 3.0 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.23 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 166.3, 157.0, 152.6, 148.6, 136.3, 128.4, 115.4, 100.7, 59.6, 53.4, 18.9, 15.1; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{16}N_2O_4$ 277.1183, found 277.1187.

*5-(Ethoxycarbonyl)-6-methyl-4-(3-pyridine)-3,4-dihydropy-rimidin-2(1H)-one (**4i**).* The compound was prepared according to the general procedure: white powder (196 mg, 75%); mp 205−206 °C;[40d] ^1H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 8.45 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.7 Hz, 1H), 7.60 (s, 1H), 7.36 (t, J = 8.7 Hz, 1H), 5.20 (d, J = 3.1 Hz, 1H), 3.97 (q, J = 7.1 Hz, 2H), 2.27 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6)

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J. Org. Chem. 2021, 86, 3024−3032

δ 166.0, 152.3, 149.6, 141.0, 134.4, 124.3, 98.8, 59.8, 53.8, 18.2, 14.5; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{15}N_3O_3$ 262.1186, found 262.1185.

*5-(Ethoxycarbonyl)-6-methyl-4-(2-furaldehyde)-3,4-dihydropyrimidin-2(1H)-one (**4j**).* The compound was prepared according to the general procedure: white powder (223 mg, 89%); mp 203−205 °C;[40c] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (s, 1H), 7.75 (s, 1H), 7.55 (d, 1H), 6.35 (t, 1H), 6.09 (d, 1H), 5.20 (s, 1H), 4.03 (q, J = 7.1 Hz, 2H), 2.23 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.5, 156.8, 152.5, 150.2, 142.6, 110.8, 106.2, 97.6, 59.7, 49.1, 18.2, 14.6; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{12}H_{14}N_2O_4$ 251.1026, found 251.1022.

*5-(Ethoxycarbonyl)-6-methyl-4-cyclohexyl-3,4-dihydropyrimidin-2(1H)-one (**4k**).* The compound was prepared according to the general procedure: white powder (240 mg, 90%); mp 233−234 °C;[40a] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (s, 1H), 7.34 (s, 1H), 4.08−3.89 (m, 3H), 2.16 (s, 3H), 1.07−1.14 (t, J = 7.1 Hz, 3H), 0.84−0.9, 1.16−1.73 (m, 11H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.3, 153.7, 149.0, 98.4, 59.5, 55.4, 45.3, 29.0, 26.7, 26.5, 26.4, 26.1, 18.2, 14.6; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{22}N_2O_3$ 267.1703, found 267.1727.

*5-(Ethoxycarbonyl)-6-methyl-4-hexyl-3,4-dihydropyrimidin-2(1H)-one (**4l**).* The compound was prepared according to the general procedure: white powder (234 mg, 92%); mp 227−228 °C;[40a] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 1H), 7.34 (s, 1H), 4.00−4.08 (q, J = 7.1 Hz, 3H), 2.14 (s, 3H), 1.19−1.37(m, 11H), 0.81−0.88 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.9, 153.3, 148.8, 99.8, 59.5, 50.5, 37.1, 31.5, 23.8, 22.5, 18.2, 14.7, 14.3; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{22}N_2O_3$ 255.1703, found 255.1706.

*5-(Ethoxycarbonyl)-6-methyl-4-(4-biphenylyl)-3,4-dihydro-pyrimidin-2(1H)-one (**4m**).* The compound was prepared according to the general procedure: white powder (202 mg, 60%); mp 216−217 °C;[40e] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 1H), 7.80 (s, 1H), 7.65−7.33 (m, 9H), 5.21 (s, 1H), 4.02 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.8, 152.5, 149.2, 140.9, 133.9, 130.5, 128.9, 128.4, 126.5, 126.2, 126.1, 124.7, 124.1, 119.5, 100.2, 60.1, 50.2, 18.2, 14.3; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{20}N_2O_3$ 337.1547, found 337.1542.

*5-(Ethoxycarbonyl)-6-methyl-4-(2-Naphthyl)-3,4-dihydropy rimidin-2(1H)-one (**4n**).* The compound was prepared according to the general procedure: white powder (186 mg, 60%); mp 253−254 °C;[40a] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 1H), 8.31−7.83 (m, 3H), 7.74 (d, J = 8.2 Hz, 1H), 7.60−7.40 (m, 3H), 6.05 (d, J = 3.0 Hz,1H), 3.79 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 0.81 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.7, 152.1, 149.6, 140.9, 130.7, 128.9, 128.4, 126.5, 126.2, 124.7, 124.1, 123.0, 99.6, 59.5, 49.8, 18.2, 14.3; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{18}N_2O_3$ 311.1390, found 311.1394.

*5-(Methoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrim-idin-2(1H)-one (**4o**).* The compound was prepared according to the general procedure: pink powder (237 mg, 96%); mp 238−239 °C;[40b] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.23 (s, 1H), 7.76 (s, 1H), 7.34−7.22 (m, 5H), 5.14 (d, J = 3.4 Hz, 1H), 3.53 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.3, 152.6, 149.1, 145.1, 129.4, 127.8, 127.2, 100.0, 54.3, 51.3, 18.3; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{13}H_{14}N_2O_3$ 269.0897, found 269.0894.

*5-(Methoxycarbonyl)-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-one (**4p**).* The compound was prepared according to the general procedure: pink powder (264 mg, 94%); mp 202−204 °C;[40b] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 7.80 (s, 1H), 7.40−7.24 (m, 4H), 5.14 (d, J = 3.4 Hz, 1H), 3.53 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.2, 152.4, 149.5, 144.5, 132.3, 129.4, 99.05, 53.7, 50.9, 18.3; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{13}ClN_2O_3$ 281.0687, found 281.0685.

*5-(Methoxycarbonyl)-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2(1H)-one (**4q**).* The compound was prepared according to the general procedure: pink powder (242 mg, 93%); mp 207−211 °C;[40b] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 7.70 (s, 1H), 7.11 (s, 4H), 5.10 (d, J = 3.4 Hz, 1H), 3.52 (s, 3H), 2.25 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.3, 152.6, 149.0, 142.2, 136.9, 129.4, 126.6, 99.6, 53.6, 21.1, 18.3; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{16}N_2O_3$ 261.1234, found 261.1237.

*5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione (**4r**).* The compound was prepared according to the general procedure: white powder (257 mg, 93%); mp 209−210 °C;[40b] ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.34 (s, 1H), 9.65 (s, 1H), 7.37−7.21 (m, 5H), 5.17 (d, J = 3.4 Hz, 1H), 4.00 (q, J = 7.1 Hz, 2H), 2.29 (s, 3H), 1.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 174.7, 166.0, 145.5, 144.0, 129.0, 128.2, 126.9, 101.2, 60.6, 54.5, 18.1, 14.5; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{16}N_2O_2S$ 277.1005, found 277.1004.

*5-(Ethoxycarbonyl)-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-thione (**4s**).* The compound was prepared according to the general procedure: white powder (276 mg, 89%); mp 192−193 °C;[40f] ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.39 (s, 1H), 9.67 (s, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 5.17 (d, J = 3.4 Hz, 1H), 4.00 (q, J = 7.1 Hz, 2H),2.29 (s, 3H), 1.10 (t, J = 6.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 174.7, 165.5, 145.9, 142.9, 132.7, 129.1, 128.8, 100.8, 60.1, 53.9, 17.7, 14.0; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{15}ClN_2O_2S$ 311.0616, found 311.0612.

*5-(Ethoxycarbonyl)-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione (**4t**).* The compound was prepared according to the general procedure: white powder (279 mg, 91%); mp 155−157 °C;[40g] ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.29 (s, 1H), 9.60 (s, 1H), 7.13 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.11 (d, J = 3.4 Hz, 1H), 4.01 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 2.28 (s, 3H), 1.11 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 174.5, 166.1, 159.8, 145.2, 136.7, 127.7, 114.4, 101.4, 60.0, 55.0, 53.9, 17.6, 14.0; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{18}N_2O_3S$ 307.1111, found 307.1114.

*5-(Methoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrim-idin-2(1H)-thione (**4u**).* The compound was prepared according to the general procedure: white powder (226 mg, 86%); mp 233−235 °C;[40h] ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 9.67 (s, 1H), 7.37−7.21 (m, 5H), 5.17 (d, J = 3.4 Hz, 1H), 3.56 (s, 2H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 174.7, 166.1, 145.8, 143.2, 129.1, 127.8, 126.8, 100.9, 54.4, 51.6, 17.0; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{14}N_2O_2S$ 285.0668, found 285.0665.

Leaching Test. The solvent-free reaction system is relatively viscous, and it is difficult to directly separate the catalyst and the reactants without adding a solvent. For easy handling, the alternative leaching test was conducted and assessed in an ethanol system. The solid catalyst of COF-IM-SO_3H was separated from the hot reaction solution right after the reaction for 3.0 h. The reaction was continued with the residual filtrate in the absence of COF-IM-SO_3H for an additional 5.0 h.

Catalyst Regeneration. After each catalytic cycle, a certain amount of hot ethanol was added to the reaction system to dissolve the reaction product, and the COF-IM-SO_3H was recovered by centrifugation. After the product was completely washed with THF and dried overnight under a vacuum at 60 °C, the regenerated catalyst was used for the next catalytic run under the same reaction conditions.

Scaled-up Synthesis. *Preparation of COF-IM-SO_3H@chitosan.* Chitosan powder (0.33 g) of was dissolved in 10 mL of deionized water added with 120 μL of acetic acid. Once the transparent solution formed, 1.32 g of COF-IM-SO_3H powder was added inside. Then, 500 μL of 1,4-butanediol diglycidyl ether was added as the cross-linker with strong stirring and ultrasonic shaking. The obtained solution was immediately transferred into the "split-flask" mold and allowed to stand for ca. 12 h until a stable hydrogel was formed. Then, the obtained hydrogel was transferred into a cooler for 12 h to generate the ice crystals. Finally, the frozen sample was freeze-dried at −50 °C for 24 h in a freeze-dryer to form the dry COF-chitosan aerogel monolith with 80 wt % of COF-IM-SO_3H loading. After thorough washing with ethanol to remove residual acetic acid, the obtained COF-IM-SO_3H@chitosan aerogel was applied to catalysis.

Scaled-up Model Biginelli Reaction. A mixture of benzaldehyde (31.2 mL, 305.6 mmol), ethyl acetoacetate (38.7 mL, 305.6 mmol),

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J. Org. Chem. 2021, 86, 3024−3032

and urea (18.35 g, 305.6 mmol) was heated at 90 °C (oil bath) for 6 h in a split-flask (250 mL) equipped with a COF-IM-SO_3H@chitosan aerogel (1.65 g, 0.5 mol % COF-IM-SO_3H equiv) (monitored by TLC). After the reaction, the system was diluted with hot ethanol (1 L, 60 °C), and the crude product was purified by recrystallization in ethanol. The amount of the product obtained was 73.9 g (93%). After the product was thoroughly washed with THF and dried overnight in a vacuum at 80 °C, the COF-IM-SO_3H@chitosan aerogel was used for the next catalytic cycle under the same reaction conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02423.

Characterization of model compounds, COF-IM, COF-IM-SO_3H, and COF-IM-SO_3H@chitosan; general catalytic products characterization; catalyst hot leaching, catalytic cycles, and proposed mechanism; crystallographic information for COF-IM; abbreviations (PDF)

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Notes

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