Molecular Catalysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Editor's choice paper

Multilinker phosphorous acid anchored En/MIL-100(Cr) as a novel nanoporous catalyst for the synthesis of new *N*-heterocyclic pyrimido[4,5-*b*] quinolines

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ARTICLE INFO

Keywords:
En/MIL-100(Cr)
MIL (Matérial Institut Lavoisier)
Metal-organic frameworks (MOFs)
Multilinker phosphorous acid catalyst
Octahydropyrimido[4,5-*b*]quinoline-6(1*H*)-one
Tetrahydropyrimido[4,5-*b*]quinolone
Tetrahydropyrimido[4,5-*b*]quinoline-4,6(3*H*,7*H*)-dione

ABSTRACT

A novel ethylenediamine (En) based metal-organic frameworks (MOFs) of Cr-MOFs, En/MIL-100(Cr), containing phosphorous acid tags was prepared. MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ characterized by a variety of techniques, including fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), elemental mapping and energy dispersive X-ray (EDS), transmission electron microscopy (TEM), Thermal gravimetric (TG), differential thermal gravimetric (DTG), N_2 adsorption-desorption isotherms (BET) and elemental analysis. MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ successfully applied for the synthesis of new categories of *N*-heterocyclic compounds such as tetrahydropyrimido[4,5-*b*]quinoline-2,4,6(1*H*,3*H*,7*H*)-trione, tetrahydropyrimido[4,5-*b*]quinoline-4,6(3*H*,7*H*)-dione and octahydropyrimido[4,5-*b*]quinolin-6(1*H*)-one derivatives. More specifically, this paper has explored new tetrahydropyrimido[4,5-*b*]quinolone based on uracil (X = S, O). The major advantages of this work are high yields, short reaction times, high stability thermal, facile workup and reusability of the MOFs catalyst.

1. Introduction

Nowadays, solid compounds with crystalline structure were prepared by inorganic clusters or metal ions (generally transition metal) which linked to two or multifunctional organic units to give metal-organic frameworks (MOFs) [1]. In recent years, Metal-organic frameworks (MOFs) are valuable materials because of their applications on the preparation of various catalysts, sensors, electronics, fuel cells and industrial products in large scale and other applications of them in adsorption, petrochemistry, selective separation, and drug delivery [2–4].

Some advantages of nanoscopic materials and porous materials are high surface area, high thermal stability of their chemical structure [5]. Multivariate MOFs (MTV-MOFs), in which numerous nuclei, organic and linker features are merged into a framework, have introduced with many chances for modeling the complexity of the porous of MOFs in a logical method [6–8]. Among the many developments which made in this field and nanoscale properties of MOFs can be modified with organic linker groups for target reactions with biological molecules builds them appealing to motivation enzymes for catalytic processes. Therefore, nanoarchitecture with the goal apply changes in surface area, pore size, stability thermal and chemical improve the performance of the structure of metal-organic frameworks (MOFs) [9]. The catalytic activities of MOFs were also reported in cases of oxidation reactions, C−C bond formation and organic synthesis [10–11]. Recently, the facility of the design and modification of MOFs, as a significant system, have developed to produce new functionalized frameworks for other applications [12–15]. The synthesis of MIL-100(Cr) was reported by Férey et al. for the first time [16]. Some MOFs such as [$MoO(O_2)_2$@En/MIL-100(Cr)], Pd@En/MIL-100(Cr) and MIL-100(Cr)One, as a category of metal-organic frameworks (MOFs) containing of Cr nuclei, has post-modification ability and increases the flexibility and compatibility of the compound and can be used as bifunctional catalysts for the oxidation of selective thioether, Knoevenagel condensation reaction, Friedel-Crafts reaction, Aldol condensation, coupling reaction, ring opening of epoxides, 1,3-Dipolar cycloaddition, multicomponent reactions (MCRs)

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https://doi.org/10.1016/j.mcat.2019.01.023
Received 14 October 2018; Received in revised form 28 December 2018; Accepted 22 January 2019
2468-8231/

and CO_2 adsorption respectively [17–20].

Multi component reactions (MCRs) are one of the most important methods for the synthesis of products in organic and medicinal chemistry. At first, the synthesis of amino acids was reported as a multi component reaction, by Strecker in 1850 [21]. In last few years, MCRs were developed in three, four or more component reactions and reported so many researches for developing of new MCRs [22]. It is necessary to reduce toxic waste and time of reaction process in industrials and experimental studies for environmental protection. Furthermore, high yield in the synthesis of products is remarkable.

N-Heterocyclic compounds such as uracil derivatives are one of the important categories of compounds in organic synthesis. Quinoline and pyrimidines derivatives containing uracil in their structure are interesting classes of organic compounds because of their pharmacological activity including antitumour [23], cardiotonic [24], hepatoprotactive [24], antihypertensive [24], antibronchitic [25] and antifungal activity [26]. Pyrimido[4,5-*b*]quinolone derivatives are a category of fused quinolines which separated from the marine bacteria having antibacterial and antifungal activities. There is extensive information about synthesis of these biological molecules for the synthesis of uracil-based derivatives [27–31]. In the present research, we have explored MOFs chemically modified by organophosphonic acid MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ based on En/MIL-100(Cr) by heterogeneous synthesis method, and used it as task-specific and reusable catalyst for the operational and one-pot synthetic method of new *N*-heterocyclic compounds such as tetrahydropyrimido[4,5-b]quinoline-2,4,6(1*H*,3*H*,7*H*)-trione, tetrahydropyrimido[4,5-*b*]quinoline-4,6(3*H*,7*H*)-dione and octahydropyrimido[4,5-*b*]quinolin-6(1*H*)-one derivatives (Scheme 1).

2. Experimental

2.1. Instrumental details

All of chemicals were prepared from Merck Chemical Company. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were run on a BRUKER BioSpin GmbH or Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Fourier transforms infrared (FT-IR) spectra of derivatives and catalyst were recorded on a FT-IR spectrometer (Perkin-Elmer spectrum 65) using KBr disk. Transmission electron microscopy (TEM) images were performed using a Zeiss-EM10C-100 microscope. Scanning electron microscopy (SEM), SEM-EDS elemental mapping studies were performed using a SIGMA VP-500. Thermogravimetric analyses were carried out on a METTLER TOLEDO apparatus (models Pyris 1) under nitrogen atmosphere at 25 °C and using a heating rate of 20 °C min^{-1} up to 550 °C. Nitrogen adsorption-desorption isotherm (BET) was performed using a BELSORP MINI II.

2.2. Preparation of MIL-100(Cr)

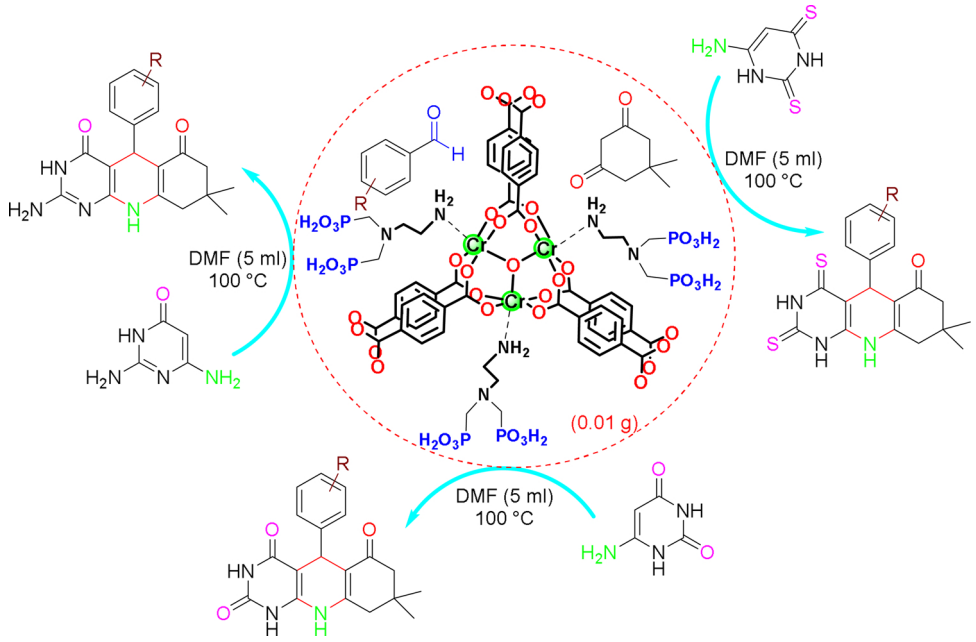
According to previous reports [17], In a teflon-lined stainless steel autoclave, a mixture of chromium trioxide (12 mmol, 1.2 g), terephthalic acid (11.99 mmol, 1.99 g), hydrofluoric acid (12 mmol) (HF, 40%) and deionized water 58 mL were mixed and stirred at 25 °C during two hours and then kept at 220 °C for four days. The obtained green solid was washed with water and dried at room temperature.

2.3. Grafting ethylenediamine onto the MIL-100(Cr) [En/MIL-100(Cr)]

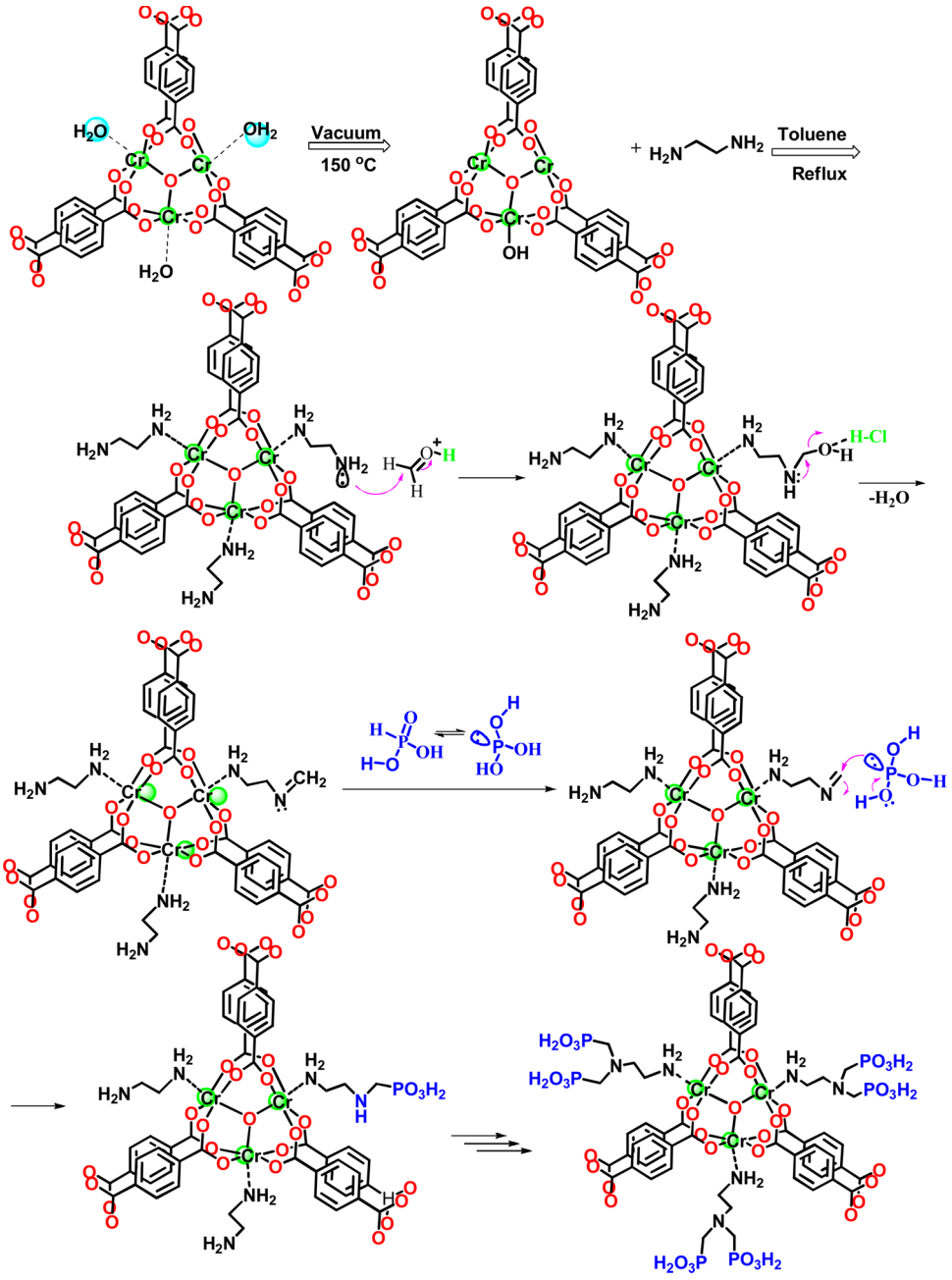
After synthesis of MOFs, 0.1 g of MIL-100(Cr), activated at 200 °C for 2 h. Then it was suspended in 10 mL of ultra-dry toluene and 1 mL of ethylene diamine was added to this suspension, and the mixture was stirred under argon atmosphere of for 16 h to facilitate amine grafting. The resulting En/MIL-100(Cr) solid was collected by filtration and washed with acetone for several times [17].

2.4. Preparation of MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$

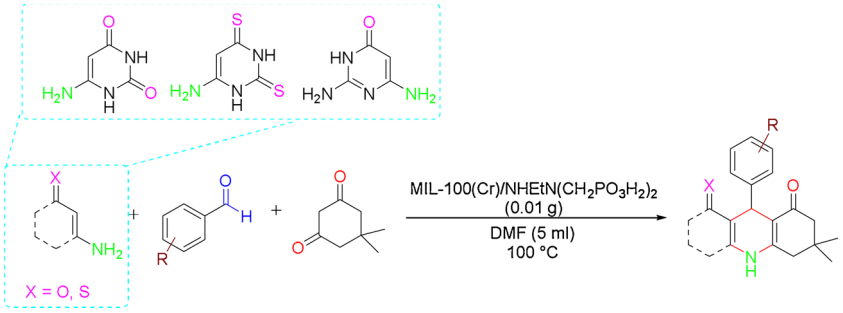
In a 100 mL round-bottomed flask, a mixture of En/MIL-100(Cr) [MIL-100(Cr)/NHEtNH$_2$] (1 g), paraformaldehyde (28 mmol, 0.840 g), phosphorous acid (28 mmol, 2.296 g), HCl (2 ml, 37%) and 50 ml of ethanol was refluxed for 18 h [32]. After this time, a green precipitated appeared which was filtered and dried under vacuum to obtain MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ (Scheme 2).



Scheme 1. Synthesis of *N*-heterocyclic compounds catalyzed by MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$.



Scheme 2. Preparation of MIL-100(Cr)/NHEtN($CH_2PO_3H_2$)$_2$.



Scheme 3. Synthesis of pyrimido[4,5-*b*]quinolone derivatives using MIL-100(Cr)/NHEtN($CH_2PO_3H_2$)$_2$.

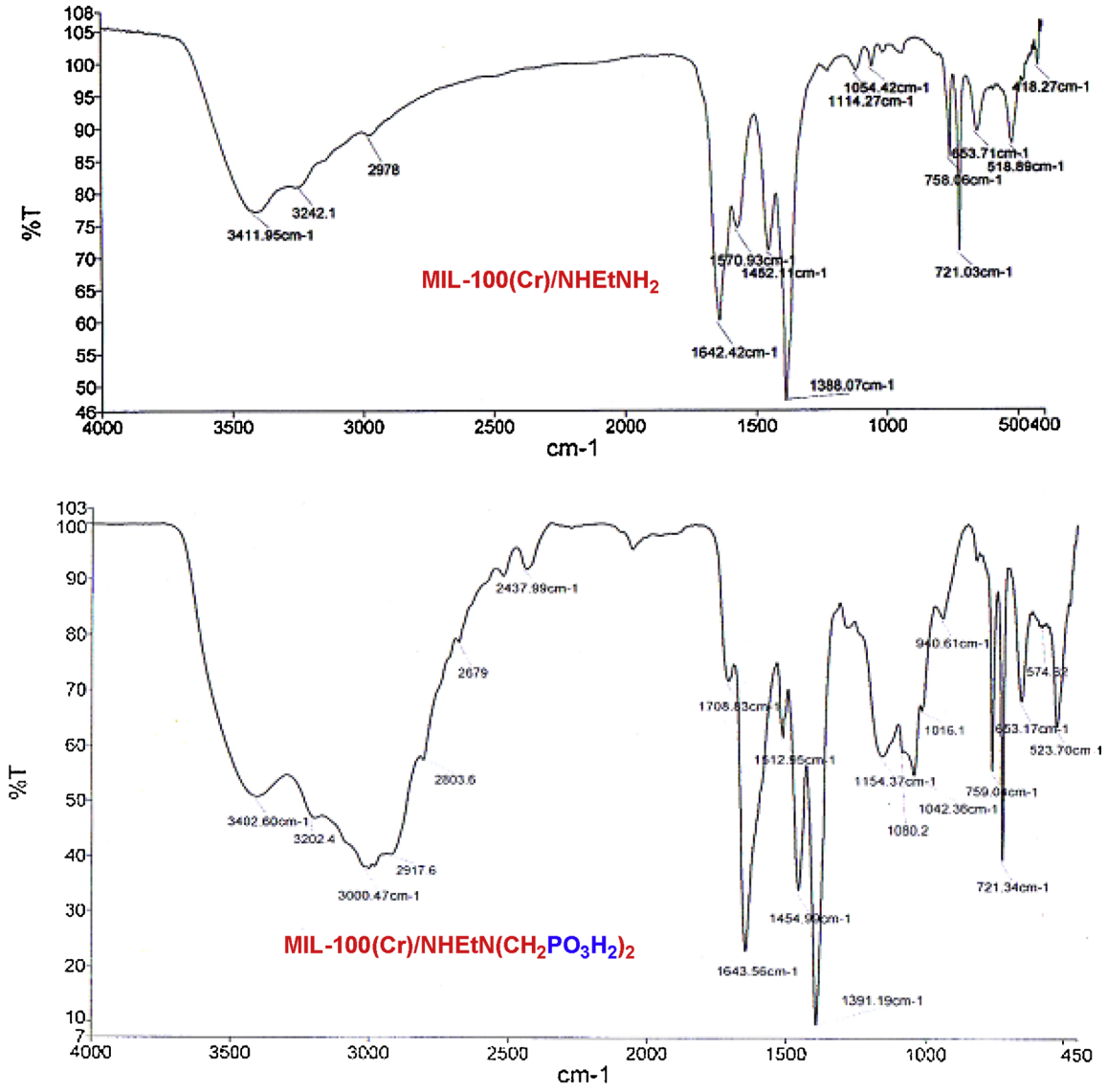


Fig. 1. FT-IR spectrum of a) MIL-100(Cr)/$NHEtNH_2$ b) MIL-100(Cr)/$NHEtN(CH_2PO_3H_2)_2$.

2.5. General procedure for the preparation of pyrimido[4,5-b]quinolone derivatives

In a 10 mL round-bottomed flask, a mixture of aldehyde (1 mmol), uracil derivatives (1 mmol), dimedone (1 mmol, 0.14 g) and MIL-100(Cr)/$NHEtN(CH_2PO_3H_2)_2$ (0.01 g) were stirred at 100 °C in DMF (5 ml) as solvent. After completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature. Then, the catalyst was separated from the solution of reaction mixture by centrifugation (1000 rpm). Then, H_2O (5 ml) was added to reaction mixture to give the solid sediment. The prepared solid was collected by simple filtration. The crude product was purified by recrystallization from EtOAc (Scheme 3). The pure products were identified by FT-IR, ^1H, ^{13}C NMR and mass spectra.

2.5.1. 4-(2-Amino-8,8-dimethyl-4,6-dioxo-3,4,5,6,7,8,9,10-octahydropyrimido[4,5-b]quinolin-5-yl)benzonitrile (1S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.6; IR (KBr, cm^{-1}): 3436, 3244, 2931, 2230, 1692, 1651; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm):10.49 (s, 1 H), 9.52 (s, 1 H), 7.72 (d, J = 8.3 Hz, 2 H), 7.42 (d, J = 8.3 Hz, 2 H), 6.46 (s, 2 H), 4.92 (s, 1 H), 2.53- 2.44 (m, 2 H), 2.25 (d, J = 16.1 Hz, 1 H), 2.06 (d, J = 16.1 Hz, 1 H), 1.08 (s, 3 H), 0.95 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.78, 161.43, 157.06, 153.75, 151.01, 139.95, 128.26, 112.87, 109.92, 92.38, 54.84, 50.22, 32.45, 32.04, 29.07, 26.70, 18.54. MS *m/z* (%); found for $C_{20}H_{19}N_5O_2$: 361.4.

2.5.2. 2-Amino-5-(furan-2-yl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7H)-dione (2S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.8; IR (KBr, cm^{-1}): 3480, 3249, 3045, 2886, 1665, 1620; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm):10.44 (s, 2 H), 9.41 (s, 2 H), 7.20 (dt, J = 10.5, 8.5 Hz, 3 H), 7.08 (ddd, J = 11.6, 8.0, 1.8 Hz, 3 H), 6.99-6.87 (m, 3 H), 6.38 (s, 2 H), 4.78 (s, 3 H), 2.46- 2.33 (m, 2 H), 2.15 (d, J = 16.1 Hz, 1 H), 1.99 (d, J = 16.0 Hz, 1 H), 0.98 (s, 3 H), 0.87 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.9, 161.4, 154.1, 153.9, 153.8, 151.7, 151.6, 149.9, 149.8, 148.7, 148.5, 147.5, 147.4, 146.2, 146.1, 145.1, 123.6, 123.6, 123.6, 123.5, 116.5, 116.4, 116.0, 115.9, 108.9, 108.8, 91.2, 91.2, 50.0, 33.2, 32.0, 28.8, 26.7. MS *m/z* (%); found for $C_{17}H_{18}N_4O_3$: 326.3.

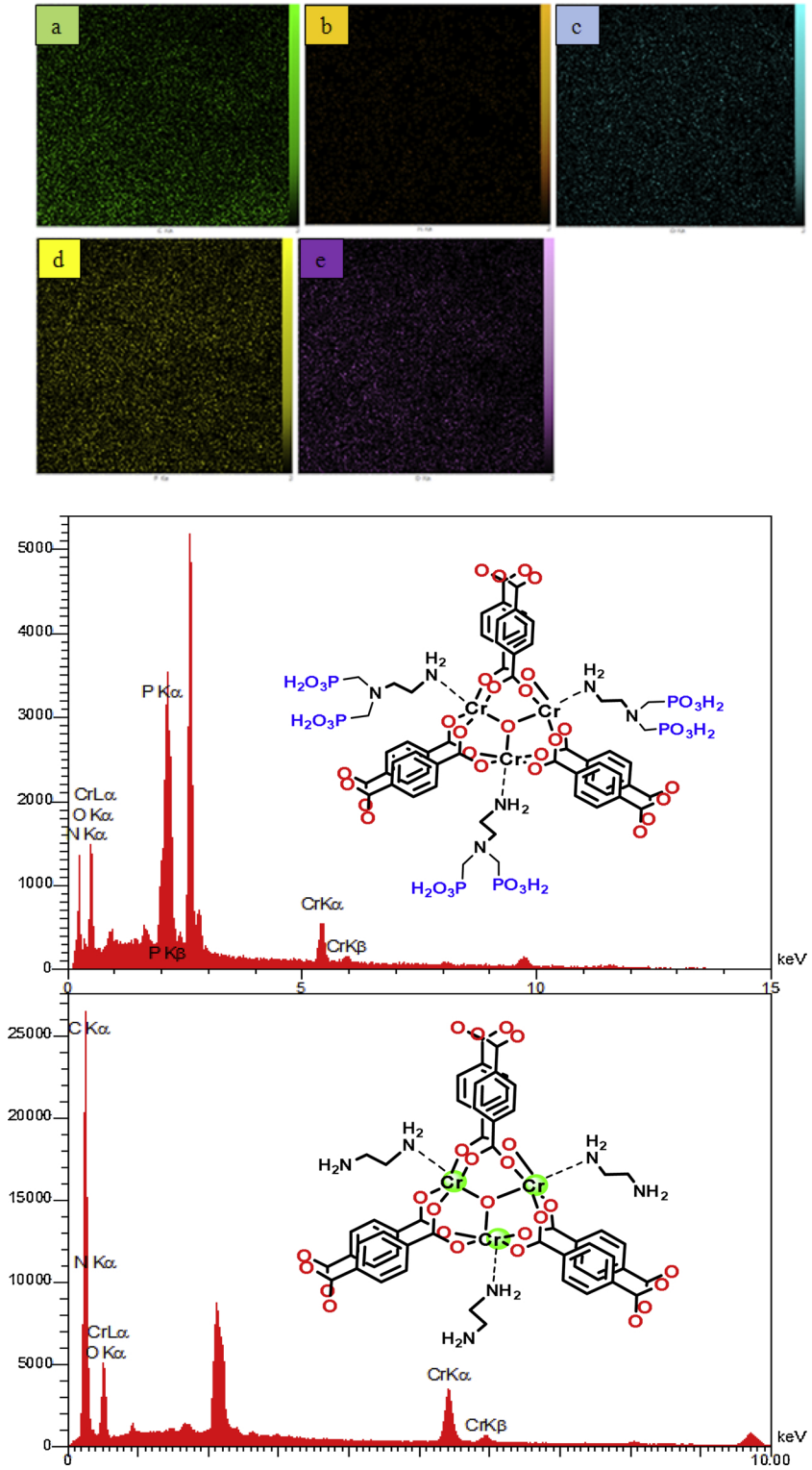


Fig. 2. Elemental maps (EDX) of C (green, a); N (orange, b); Cr (blue, c); P (yellow, d) and O (violet, e) atoms for MIL-100(Cr)/NHEtN($CH_2PO_3H_2$)$_2$. SEM-EDS analysis f) MIL-100(Cr)/NHEtN($CH_2PO_3H_2$)$_2$ g) MIL-100(Cr)/$NHEtNH_2$ (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

2.5.3. 2-Amino-5-(dimethylamino)phenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (3S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1): 0.8; IR (KBr, cm^{-1}): 3420, 3249, 3188, 2932, 2607, 1671, 1614; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.34 (s, 1 H), 9.24 (s, 1 H), 6.99 (d, J = 8.6 Hz, 2 H), 6.53 (d, J = 8.7 Hz, 2 H), 6.28 (s, 2 H), 4.70 (s, 1 H), 2.43 (d, J = 17.2 Hz, 1 H), 2.36 (d, J = 17.2 Hz, 1 H), 2.16 (d, J = 16.1 Hz, 1 H), 1.97 (d, J = 16.0 Hz, 1 H), 1.00 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm):193.8, 161.4, 153.7, 153.6, 150.7, 148.5, 136.1, 127.8, 112.0, 110.1, 92.7, 50.2, 32.1, 32.0, 29.1, 26.7. MS *m/z* (%); found for $C_{21}H_{25}N_5O_2$: 379.4.

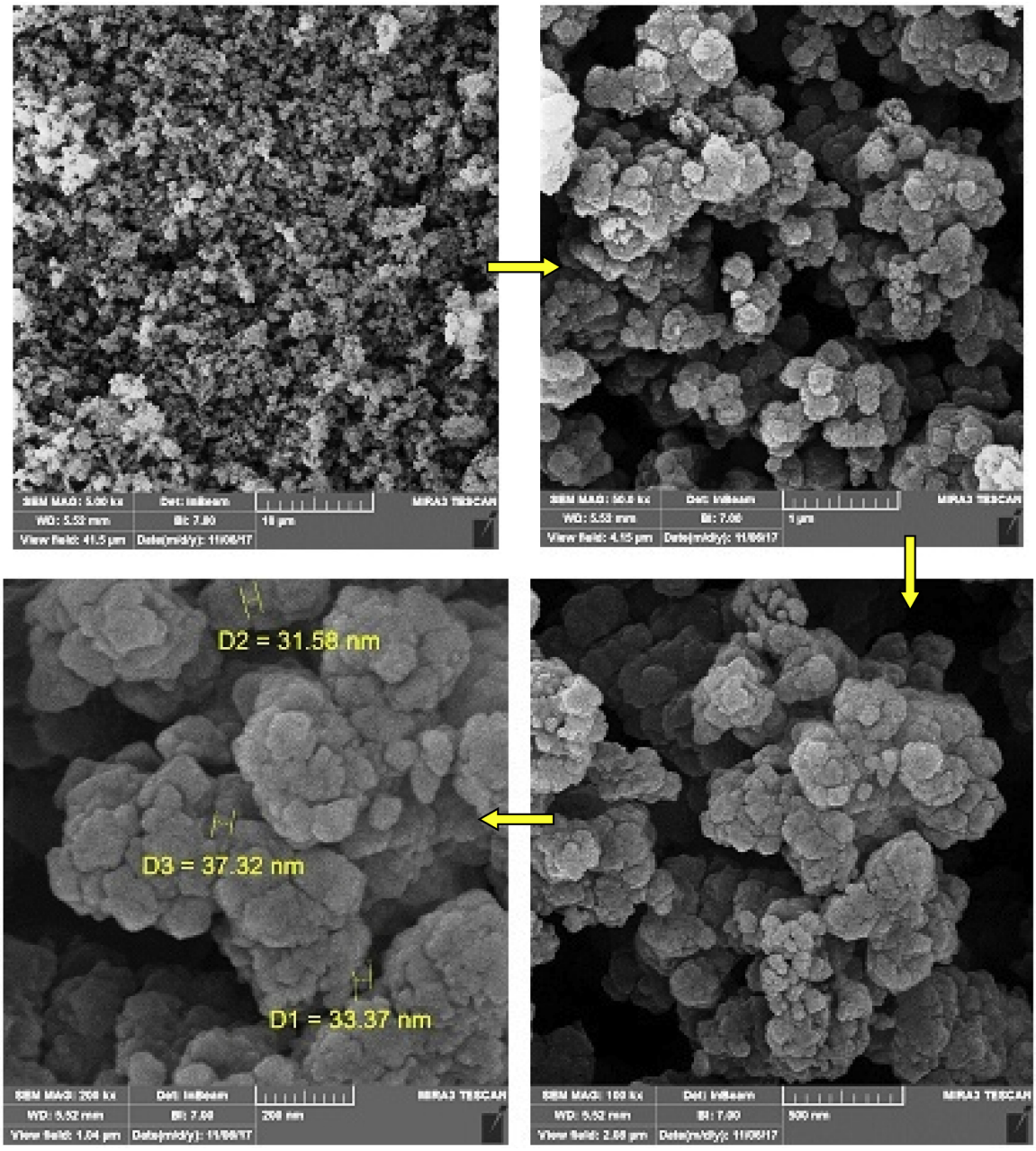


Fig. 3. SEM of MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$.

2.5.4. 2-Amino-5-(3,5-difluorophenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (4S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.65; IR (KBr, cm^{-1}): 3487, 3356, 3273, 2963, 2893, 1664; 1625; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm):10.55 (s, 1 H), 9.61 (s, 1 H), 7.90 (s, 1 H), 7.80 (s, 2 H), 6.55 (s, 2 H), 4.99 (s, 1 H), 2.60 (s, 1 H), 2.48 (d, *J* = 17.3 Hz, 1 H), 2.28 (d, *J* = 16.1 Hz, 1 H), 2.03 (d, *J* = 16.1 Hz, 1 H), 1.08 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.9, 161.4, 154.3, 153.9, 153.8, 152.5, 152.4, 150.5, 129.6, 129.3, 128.9, 127.7, 127.4, 124.7, 122.0, 119.4, 108.1, 108.1, 90.6, 90.6, 49.8, 34.5, 32.0, 29.2, 25.9. MS *m/z* (%); found for $C_{19}H_{18}Cl_2N_4O_2$: 405.2.

2.5.5. 2-Amino-5-(2-hydroxynaphthalen-1-yl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (5S)

White solid; Mp: 280–282 °C; (*n*-hexane: acetone 1:1) = 0.6; IR (KBr, cm^{-1}): 3396, 3317, 3191, 2926, 2874, 1644; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 9.48 (s, 1 H), 8.01 (d, *J* = 8.3 Hz, 1 H), 7.89 (d, *J* = 7.9 Hz, 1 H), 7.78 (d, *J* = 8.8 Hz, 1 H), 7.50 (t, *J* = 7.3 Hz, 1 H), 7.43 (t, *J* = 7.3 Hz, 1 H), 7.27 (d, *J* = 8.8 Hz, 1 H), 6.27 (s, 1 H), 6.05 (s, 1 H), 5.09 (s, 1 H), 2.73-2.59 (m, 2 H), 2.39 (d, *J* = 16.3 Hz, 1 H), 2.23 (d, *J* = 16.3 Hz, 1 H), 1.13 (s, 3 H), 1.04 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm):197.5, 164.9, 160.9, 148.1, 131.44, 130.5, 128.2, 127.3, 126.3, 124.1, 123.4, 117.2, 116.6, 110.3, 93.0, 50.2, 31.8, 29.0, 26.2, 25.3. MS *m/z* (%); found for $C_{23}H_{22}N_4O_3$: 402.2.

2.5.6. 2-Amino-5-(3,5-dimethoxyphenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (6S)

White solid; Mp: > 350 °C; (*n*-hexane: acetone 1:1) = 0.6; IR (KBr, cm^{-1}): 3572, 3447, 3272, 2934, 1656, 1620; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.40 (s, 1 H), 9.31 (s, 1 H), 6.83 (d, *J* = 1.8 Hz, 1 H), 6.74 (d, *J* = 8.3 Hz, 1 H), 6.63 (dd, *J* = 8.3, 1.8 Hz, 1 H), 6.33 (s, 2 H), 4.76 (s, 1 H), 3.66 (s, 3 H), 3.65 (s, 3 H), 2.45 (d, *J* = 17.2 Hz, 1 H), 2.38 (d, *J* = 17.2 Hz, 1 H), 2.18 (d, *J* = 16.1 Hz, 1 H), 1.99 (d,

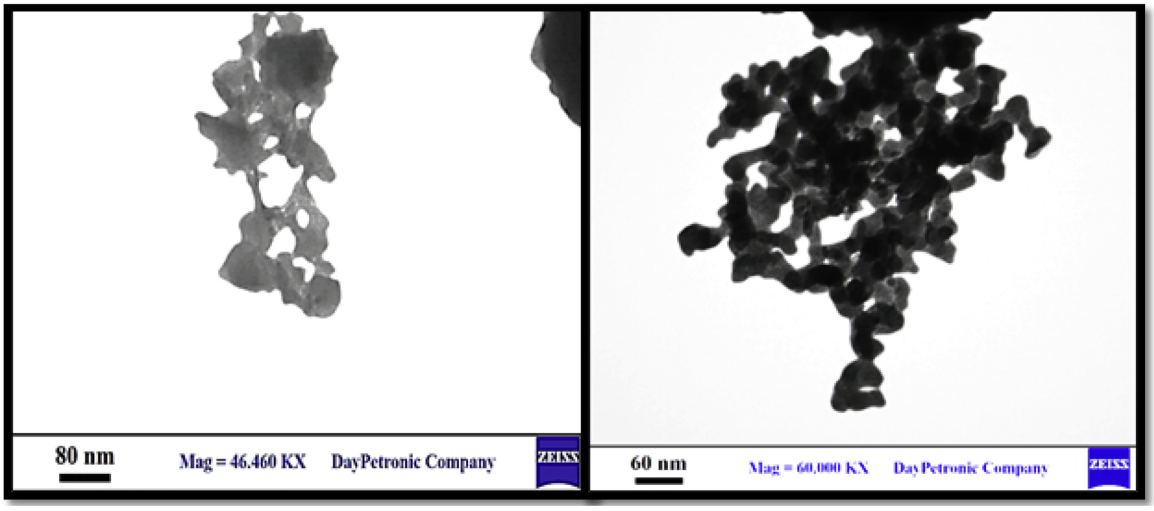


Fig. 4. TEM images of MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$.

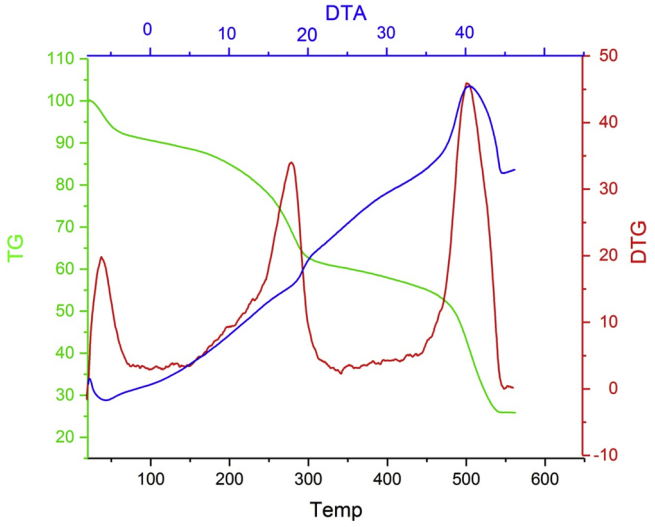


Fig. 5. The thermogravimetric (TG), derivative thermogravimetric (DTG), as well as the differential thermal (DTA) analysis of MIL-100(Cr)/NHEtN $(CH_2PO_3H_2)_2$.

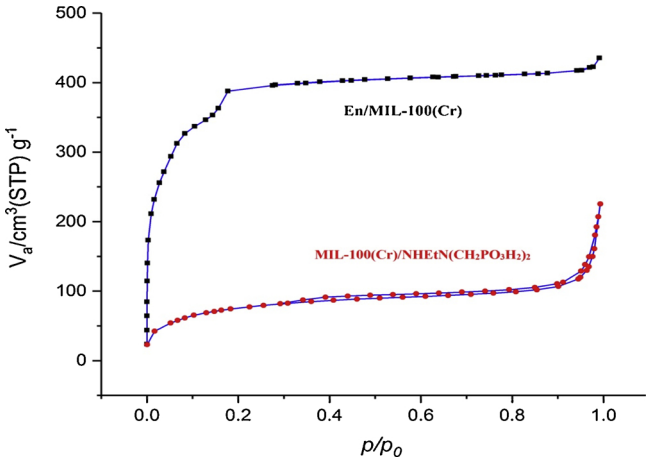


Fig. 6. N_2 adsorption/desorption isotherm of En/MIL-100(Cr) and MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$.

J = 16.0 Hz, 1 H), 1.01 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.9, 161.5, 153.8, 153.7, 153.6, 151.2, 151.1, 147.8, 146.7, 140.3, 119.0, 111.7, 111.2, 109.7, 109.6, 92.2, 92.2, 55.4, 55.2, 50.2, 40.3, 32.6, 32.0, 29.1, 26.5. MS m/z (%); found for $C_{21}H_{24}N_4O_4$: 396.4.

2.5.7. 2-Amino-8,8-dimethyl-5-phenyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (7S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.4; IR (KBr, cm^{-1}): 3437, 3244, 3029, 2967, 1623, 1590; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.46 (s, 1 H), 9.41 (s, 1 H), 7.29- 7.18 (m, 4 H), 7.15- 7.04 (m, 1 H), 6.41 (s, 2 H), 4.88 (s, 1 H), 2.53 (d, J = 17.2 Hz, 1 H), 2.45 (d, J = 17.2 Hz, 1 H), 2.24 (d, J = 16.1 Hz, 1 H), 2.05 (d, J = 16.1 Hz, 1 H), 1.08 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.8, 161.4, 153.9, 153.8, 151.3, 151.2, 147.5, 131.5, 128.64, 127.5, 127.4, 125.3, 109.6, 92.0, 65.0, 50.1, 33.3, 32.0, 29.9, 29.0, 26.6, 18.6, 13.5. MS m/z (%); found for $C_{19}H_{20}N_4O_2$: 336.4.

2.5.8. 2-Amino-5-(2-chlorophenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dion (8S)

White solid; Mp: 270–272 °C; R_f: (*n*-hexane: acetone 1:1) = 0.7; IR (KBr, cm^{-1}): 3621, 3164, 3466, 3422, 2872, 1657; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.26 (s, 1 H), 9.37 (s, 1 H), 7.27 (dd, J = 7.7, 1.5 Hz, 1 H), 7.18 (dd, J = 7.9, 1.0 Hz, 1 H), 7.13 (td, J = 7.5, 1.1 Hz, 1 H), 7.04 (td, J = 7.6, 1.6 Hz, 1 H), 6.32 (s, 2 H), 5.10 (s, 1 H), 2.44 (d, J = 17.1 Hz, 1 H), 2.33 (d, J = 17.1 Hz, 1 H), 2.13 (d, J = 16.1 Hz, 1 H), 1.90 (d, J = 16.1 Hz, 1 H), 0.99 (s, 3 H), 0.87 (s, 3 H);^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.5, 161.1, 154.0, 153.9, 151.5, 151.4, 144.6, 132.3, 131.8, 128.8, 126.7, 126.1, 108.9, 91.4, 50.1, 33.5, 31.8, 29.1, 26.4. MS m/z (%); found for $C_{19}H_{19}ClN_4O_2$: 370.8.

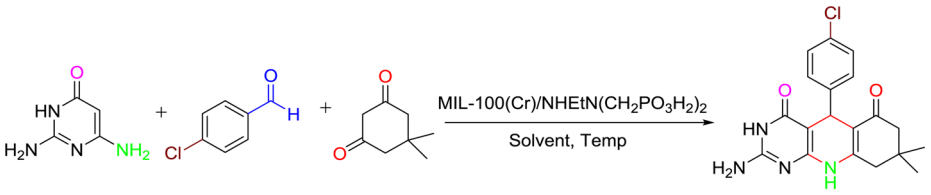
2.5.9. 2-Amino-8,8-dimethyl-5-(4-nitrophenyl)-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (9S)

Yellow solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.7; IR (KBr, cm^{-1}): 3470, 3336, 3257, 3194, 1665, 1618, 1517, 1348; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.46 (s, 1 H), 9.49 (s, 1 H), 8.08 (d, J = 8.7 Hz, 2 H), 7.43 (d, J = 8.7 Hz, 2 H), 6.41 (s, 2 H), 4.91 (s, 1 H), 2.46 (s, 1 H), 2.40 (d, J = 17.2 Hz, 1 H), 2.18 (d, J = 16.1 Hz, 1 H), 1.98 (d, J = 16.1 Hz, 1 H), 1.00 (s, 3 H), 0.88 (s, 3 H);^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.8, 161.3, 155.1, 154.2, 154.0, 153.96, 152.0, 151.9, 145.3, 128.6, 122.9, 108.6, 108.5, 90.9, 90.8, 50.0, 34.4, 32.0, 28.9, 26.7. MS m/z (%); found for $C_{19}H_{19}N_5O_4$: 381.3.

2.5.10. 2-Amino-8,8-dimethyl-5-(thiophen-2-yl)-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (10S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.8; IR (KBr, cm^{-1}): 3322, 3163, 2971, 1717, 1640;^{1}H NMR (400 MHz, DMSO-

Table 1
Effect of different amounts of catalyst, temperature and solvent on the synthesis of 2-amino-5-(4-chlorophenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-*b*]quinoline-4,6(3*H*,7*H*)-dione.



Entry	Solvent	Catalyst (g)	Temp. (°C)	Time (min)	Yield[a] (%)
1	DMF	0.02	100	20	80
2	DMF	0.01	25	120	20
3	DMF	0.01	50	90	35
4	DMF	0.01	80	90	50
5	DMF	0.01	100	15	85
6	DMF	0.01	Reflux	300	70
7	DMF	0.005	100	300	35
8	DMF	–	Reflux	300	–
9	DMF	0.02	100	120	50
10	H_2O	0.01	Reflux	300	10
11	EtOH	0.01	Reflux	300	15
12	CH_2Cl_2	0.01	Reflux	300	–
13	$CHCl_3$	0.01	Reflux	300	–
14	EtOAc	0.01	Reflux	300	15
15	CH_3CN	0.01	Reflux	300	–
16	–	0.01	100	120	–

[a] Reaction conditions: 2,6-diamino pyrimidin-4(3*H*)-one(1 mmol, 0.126 g), 4-chloro benzaldehyde (1 mmol, 0.14 g) and dimedone (1 mmol, 0.14 g).

d_6): δ (ppm): 10.54 (s, 1 H), 9.53 (s, 1 H), 7.00 (tt, J = 9.2, 2.3 Hz, 1 H), 6.86 (dd, J = 8.5, 2.0 Hz, 2 H), 6.38 (d, J = 89.5 Hz, 2 H), 4.92 (s, 1 H), 2.52 (s, 2 H), 2.26 (d, J = 16.1 Hz, 1 H), 2.12 (d, J = 16.1 Hz, 1 H), 1.14- 1.04 (m, 3 H), 1.04- 0.93 (m, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.9, 163.1, 163.0, 161.4, 160.7, 160.6, 154.2, 154.0, 152.1, 110.2, 110.0, 108.4, 90.8, 50.0, 33.7, 32.0, 28.8, 26.7. MS *m/z* (%); found for $C_{17}H_{18}N_4O_2S$: 342.4.

2.5.11. 2-Amino-8,8-dimethyl-5-(p-tolyl)-5,8,9,10-tetrahydropyrimido [4,5-b]quinoline-4,6(3H,7 H)-dione (11S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.5; IR (KBr, cm^{-1}): 3472, 3257, 2931, 2748, 1659, 1620; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.39 (s, 1 H), 9.32 (s, 1 H), 7.07 (d, J = 8.0 Hz, 2 H), 6.97 (d, J = 7.9 Hz, 2 H), 6.34 (s, 2 H), 4.78 (s, 1 H), 2.46 (d, J = 17.1 Hz, 1 H), 2.38 (d, J = 17.4 Hz, 1 H), 2.20 (s, 3 H), 2.16 (s, 1 H), 1.98 (d, J = 16.0 Hz, 1 H), 1.02 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.8, 161.4, 153.8, 153.8, 151.1, 144.7, 134.1, 128.0, 127.3, 109.8, 109.8, 92.2, 50.1, 32.9, 32.0, 29.0, 26.6, 20.5.MS *m/z* (%); found for $C_{20}H_{22}N_4O_2$: 350.4.

2.5.12. 2-Amino-5-(4-chlorophenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (12S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.6; IR (KBr, cm^{-1}): 3399, 3257, 3170, 2967, 1641, 1621; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.41 (s, 1H, NH), 9.37 (s, 1H, NH), 7.20 (q, J = 8.5 Hz, 4 H), 6.35 (s, 2H, NH_2), 4.79 (s, 1 H), 2.45 (d, J = 17.2 Hz, 1 H), 2.38 (d, J = 17.2 Hz, 1 H), 2.17 (d, J = 16.1 Hz, 1 H), 1.98 (d, J = 16.1 Hz, 1 H), 1.00 (s, 3 H), 0.88 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.8, 161.3, 154.0, 153.9, 153.8, 151.5, 151.3, 146.5, 129.8, 129.2, 127.4, 109.2, 109.2, 91.6, 91.6, 50.1, 33.2, 32.0, 28.9, 26.6. MS *m/z* (%); found for $C_{19}H_{19}ClN_4O_2$: 370.8.

2.5.13. 2-Amino-5-(4-hydroxyphenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (13S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.45; IR (KBr, cm^{-1}): 3276, 3193, 3088, 1720, 1669, ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.38 (s, 1 H), 9.24 (s, 1 H), 9.00 (s, 1 H), 6.95 (d, J = 6.6 Hz, 2 H), 6.53 (d, J = 6.8 Hz, 2 H), 6.30 (s, 2 H), 4.70 (s, 1 H), 2.43 (d, J = 17.4 Hz, 1 H), 2.36 (d, J = 17.3 Hz, 1 H), 2.15 (d, J = 16.1 Hz, 1 H), 1.97 (d, J = 16.0 Hz, 1 H), 1.00 (s, 3 H), 0.89 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.8, 155.0, 153.7, 150.88, 150.7, 138.3, 128.2, 114.1, 114.1, 110.1, 92.5, 50.2, 32.2, 32.0, 29.0, 26.6. MS *m/z* (%); found for $C_{19}H_{20}N_4O_3$: 352.3.

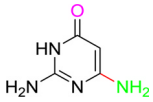
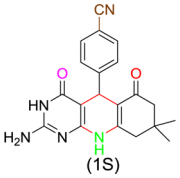
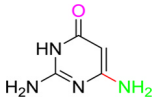
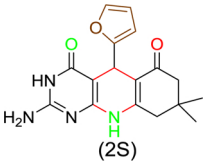
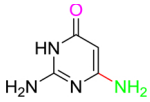
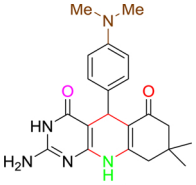
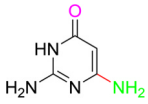
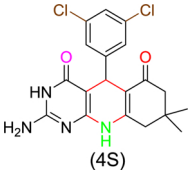
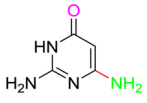
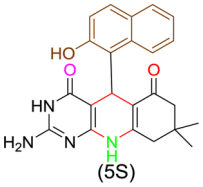
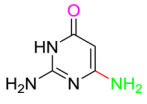
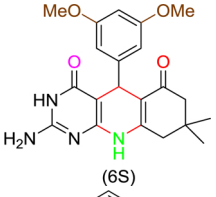
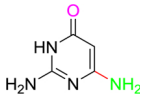
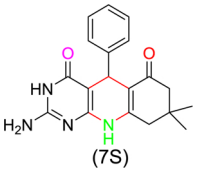
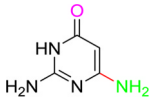
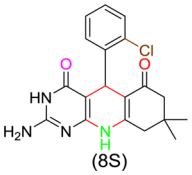
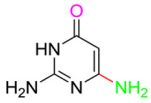
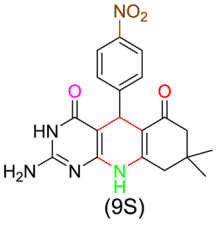
2.5.14. 2-Amino-5-(4-methoxyphenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (14S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.6; IR (KBr, cm^{-1}): 3404, 3250, 3194, 2937, 1657; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.43 (s, 1 H), 9.36 (s, 1 H), 7.15 (d, 2 H), 6.80 (d, 2 H), 6.37 (s, 2 H), 4.82 (s, 1 H), 3.75 (s, 3 H), 2.52 (d, J = 17.3 Hz, 1 H), 2.45 (d, J = 17.3 Hz, 1 H), 2.24 (d, J = 16.1 Hz, 1 H), 2.06 (d, J = 16.1 Hz, 1 H), 1.09 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.7, 161.4, 157.0, 153.8, 153.7, 151.0, 150.8, 139.9, 128.2, 112.8, 109.9, 92.3, 77.5, 54.8, 50.2, 32.45, 32.0, 29.0, 26.7, 18.5. MS *m/z* (%); found for $C_{20}H_{22}N_4O_3$: 366.4.

2.5.15. 2-Amino-5-(3,4-dimethoxyphenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (15S)

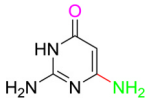
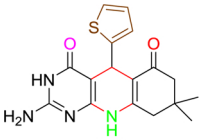
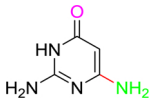
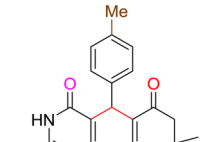
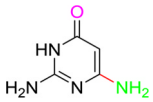
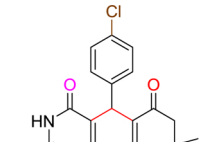
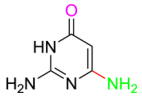
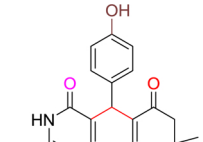
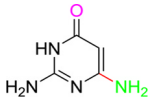
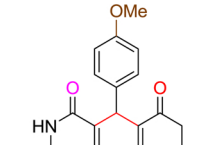
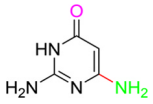
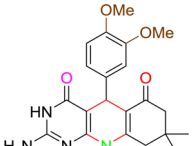
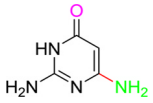
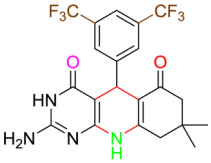
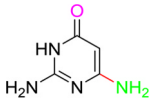
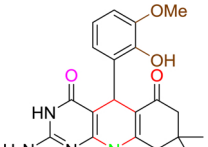
White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.7; IR (KBr, cm^{-1}): 3426, 3269, 3176, 2957, 1670, 1638; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.42 (s, 1 H), 9.35 (s, 1 H), 6.89 (d, J = 1.9 Hz, 1 H), 6.80 (d, J = 8.3 Hz, 1 H), 6.69 (dd, J = 8.3, 1.9 Hz, 1 H), 6.36 (s, 2 H), 4.82 (s, 1 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 2.52 (d, J = 17.2 Hz, 1 H), 2.47- 2.38 (m, 1 H), 2.24 (d, J = 16.0 Hz, 1 H), 2.06 (d, J = 16.0 Hz, 1 H), 1.07 (s, 3 H), 0.99 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.8, 161.5, 153.8, 153.7, 151.2, 147.8, 146.7, 140.3, 119.0, 111.7, 111.2, 109.6, 92.2, 55.4, 55.2, 50.2, 32.6, 32.0, 29.1, 26.6. MS *m/z* (%); found for $C_{21}H_{24}N_4O_4$: 396.4.

Table 2
Synthesis of *N*-heterocyclic compounds in DMF at 100 °C.

Entry	Uracil	Product	Time (min)	Yield (%)	M.p (°C)
1		 (1S)	15	88	> 350
2		 (2S)	15	76	> 350
3		 (3S)	20	84	> 350
4		 (4S)	15	82	> 350
5		 (5S)	15	79	280-282
6		 (6S)	15	88	> 350
7		 (7S)	15	85	> 350
8		 (8S)	15	87	270-272
9		 (9S)	15	91	> 350

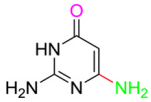
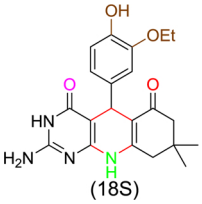
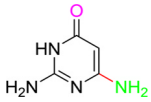
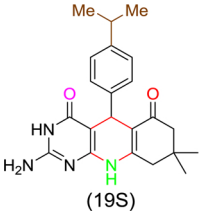
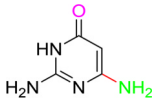
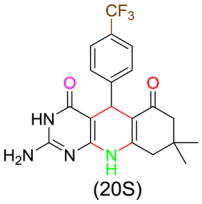
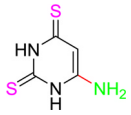
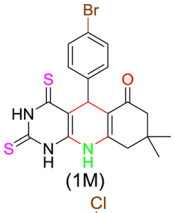
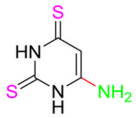
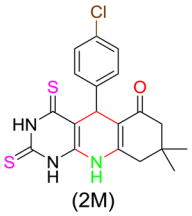
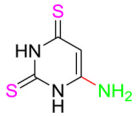
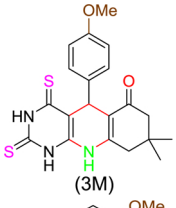
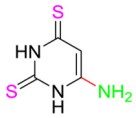
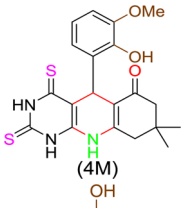
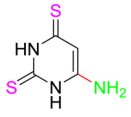
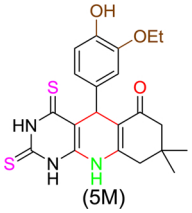
(*continued on next page*)

Table 2 (*continued*)

Entry	Uracil	Product	Time (min)	Yield (%)	M.p (°C)
10		 (10S)	15	78	> 350
11		 (11S)	15	84	> 350
12		 (12S)	15	90	> 350
13		 (13S)	15	83	> 350
14		 (14S)	15	90	> 350
15		 (15S)	20	84	> 350
16		 (16S)	20	86	> 350
17		 (17S)	15	81	> 350

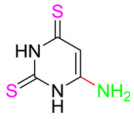
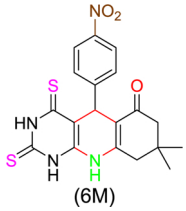
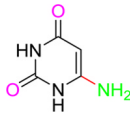
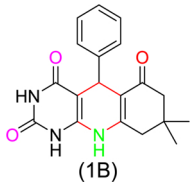
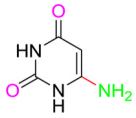
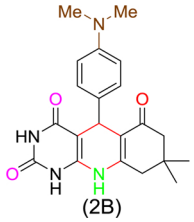
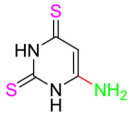
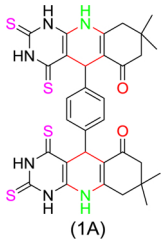
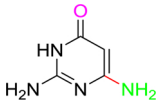
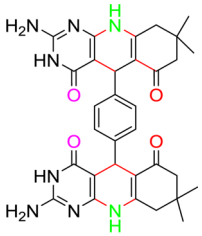
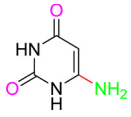
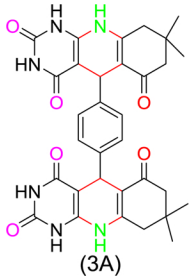
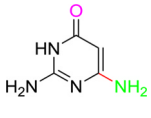
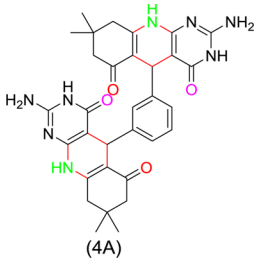
(*continued on next page*)

Table 2 (*continued*)

Entry	Uracil	Product	Time (min)	Yield (%)	M.p (°C)
18		 (18S)	15	83	> 350
19		 (19S)	20	86	> 350
20		 (20S)	20	88	> 350
21		 (1M)	20	87	> 350
22		 (2M)	15	93	> 350
23		 (3M)	15	85	> 350
24		 (4M)	15	83	> 350
25		 (5M)	15	84	> 350

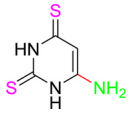
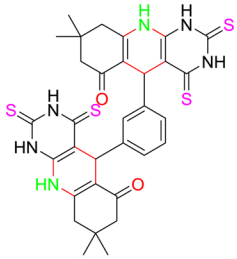
(*continued on next page*)

Table 2 (*continued*)

Entry	Uracil	Product	Time (min)	Yield (%)	M.p (°C)
26		 (6M)	15	92	> 350
27		 (1B)	15	87	> 350
28		 (2B)	20	82	> 350
29		 (1A)	15	77[a]	> 350
30		 (2A)	15	81[a]	> 350
31		 (3A)	20	80[a]	> 350
32		 (4A)	20	73[a]	> 350

(*continued on next page*)

Table 2 (*continued*)

Entry	Uracil	Product	Time (min)	Yield (%)	M.p (°C)
33		 (5A)	20	79[a]	> 350

[a] These products were purified by plate chromatography.

Table 3
Evaluation of various catalyst for the synthesis of *N*-heterocyclic compounds in comparison with MIL-100(Cr)/NHEtN($CH_2PO_3H_2$)$_2$.

Entry	Catalyst	(mol%)	Time (min)	Yield (%)
1	SSA	5 mg	60	trace
2	$NaHSO_4$	5	60	–
3	GTBSA [35]	5	60	45
4	$Al(HSO_4)_3$	5	60	–
5	*p*-TSA	5	60	–
6	[Py-SO_3H]Cl [36]	5	60	–
7	[Fe_3O_4@SiO_2@Pr-DABCO-SO_3H]Cl_2 [37]	5 mg	60	trace
8	$FeCl_3$	5	60	–
9	H_2SO_4	5	60	–
10	$Mg(NO_3)_2.6H_2O$	5	60	–
11	$Zn(NO_3)_2.6H_2O$	5	60	–
12	NH_4NO_3	5	60	–
13	Fe_3O_4	5 mg	60	–
14	$H_3[p(W_3O_{10})_4].XH_2O$	5	60	–
15	$H_3[p(Mo_3O_{10})_4].XH_2O$	5	60	–
16	Trichloroisocyanuric acid	5	60	–
17	CF_3SO_3H	5	60	–

2.5.16. 2-Amino-5-(3,5-bis(trifluoromethyl)phenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (16S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.3; IR (KBr, cm^{-1}): 3416, 3323, 3173, 3035, 1731, 1671; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.55 (s, 1 H), 9.61 (s, 1 H), 7.90 (s, 1 H), 7.80 (s, 2 H), 6.56 (s, 2 H), 4.99 (s, 1 H), 2.61 (d, *J* = 3.9 Hz, 1 H), 2.48 (d, *J* = 17.5 Hz, 1 H), 2.28 (d, *J* = 16.1 Hz, 1 H), 2.03 (d, *J* = 16.2 Hz, 1 H), 1.08 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): δ 194.0, 153.9, 153.8, 152.6, 152.4, 150.5, 129.6, 129.3, 127.81, 122.0, 119.5, 108.2, 90.6, 49.8, 34.5, 32.0, 29.2, 25.8. MS *m/z* (%); found for $C_{21}H_{18}F_6N_4O_2$: 472.3.

2.5.17. 2-Amino-5-(2-hydroxy-3-methoxyphenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (17S)

Brown solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.8; IR (KBr, cm^{-1}): 3453, 3354, 3196, 3962, 1648, 1626;^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm):11.01 (s, 1 H), 10.19 (s, 1 H), 9.65 (s, 1 H), 6.70 (dd, *J* = 17.5, 7.9 Hz, 3 H), 6.51 (s, 2 H), 5.04 (s, 1 H), 3.75 (s, 3 H), 2.27 (d, *J* = 15.9 Hz, 1 H), 2.09 (d, *J* = 16.2 Hz, 1 H), 1.09 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 194.3, 152.6, 152.5, 149.4, 149.3, 142.9, 142.7, 135.6, 119.4, 119.3, 119.2, 109.9, 109.1, 91.8, 55.3, 49.9, 32.0, 28.9, 27.0, 26.9. MS *m/z* (%); found for $C_{20}H_{22}N_4O_4$: 382.4.

2.5.18. 2-Amino-5-(3-ethoxy-4-hydroxyphenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (18S)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.5; IR (KBr, cm^{-1}): 3457, 3280, 2962, 2930, 1670, 1619; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm):9.31 (s, 1 H), 8.57 (s, 1 H), 8.01 (s, 1 H), 6.82 (d, *J* = 1.8 Hz, 1 H), 6.61 (d, *J* = 8.1 Hz, 1 H), 6.56 (dd, *J* = 8.2, 1.9 Hz, 1 H), 6.36 (s, 2 H), 4.76 (s, 1 H), 3.95 (qd, *J* = 6.9, 1.4 Hz, 2 H), 2.49 (d, *J* = 17.0 Hz, 1 H), 2.42 (d, *J* = 17.0 Hz, 1 H), 2.22 (d, *J* = 16.1 Hz, 1 H), 2.04 (d, *J* = 16.0 Hz, 1 H), 1.34 (t, *J* = 7.0 Hz, 3 H), 1.06 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.9, 162.3, 153.6, 151.0, 150.9, 145.6, 144.4, 138.7, 119.4, 114.6, 113.5, 109.8, 92.4, 63.7, 50.2, 35.7, 32.4, 32.0, 29.1, 26.5, 14.7. MS *m/z* (%); found for $C_{21}H_{24}N_4O_4$: 396.4.

2.5.19. 2-Amino-5-(4-isopropylphenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (19S)

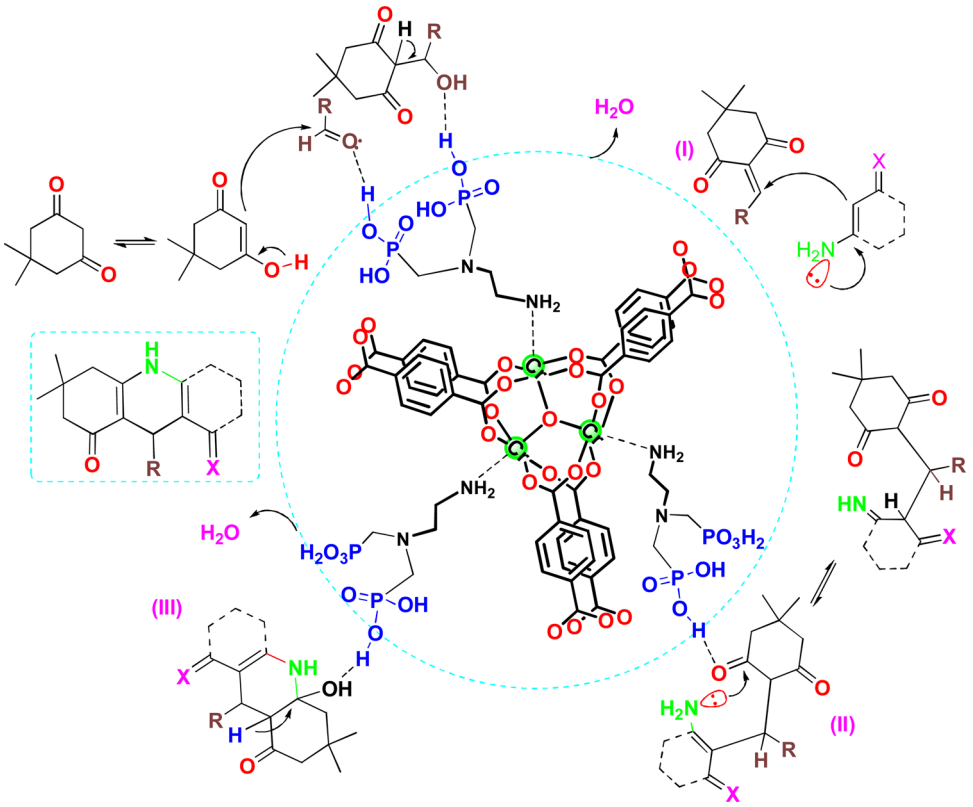
White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.6; IR (KBr, cm^{-1}): 3441, 3258, 2960, 2925, 1670, 1625; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.43 (s, 1 H), 9.38 (s, 1 H), 7.16 (d, *J* = 8.2 Hz, 2 H), 7.10 (d, *J* = 8.2 Hz, 2 H), 6.40 (s, 2 H), 4.84 (s, 1 H), 2.85 (dt, *J* = 13.8, 6.9 Hz, 1 H), 2.53 (d, *J* = 17.3 Hz, 1 H), 2.47 (d, *J* = 17.2 Hz, 1 H), 2.24 (d, *J* = 16.1 Hz, 1 H), 2.07 (d, *J* = 16.1 Hz, 1 H), 1.22 (s, 3 H), 1.21 (s, 3 H), 1.08 (s, 3 H), 1.00 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.9, 153.7, 153.7, 151.3, 151.2, 145.2, 145.0, 127.2, 125.4, 109.7, 109.6, 92.3, 50.1, 32.9, 32.8, 32.0, 28.9, 26.8, 23.9, 23.8. MS *m/z* (%); found for $C_{22}H_{26}N_4O_2$: 378.4.

2.5.20. 2-Amino-8,8-dimethyl-5-(4-(trifluoromethyl)phenyl)-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione (20S)

Brown solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.4; IR (KBr, cm^{-1}): 3487, 3353, 3272, 2962, 1663, 1624; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.45 (s, 1 H), 9.45 (s, 1 H), 7.54 (d, *J* = 8.1 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 6.41 (s, 2 H), 4.87 (s, 1 H), 2.48-2.35 (m, 2 H), 2.18 (d, *J* = 16.1 Hz, 1 H), 1.98 (d, *J* = 16.0 Hz, 1 H), 1.00 (s, 3 H), 0.88 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.8, 161.3, 154.1, 154.0, 153.9, 152.0, 151.8, 151.7, 128.2, 124.5, 124.4, 108.9, 108.9, 91.32, 91.2, 50.0, 34.0, 32.0, 28.9, 26.6. MS *m/z* (%); found for $C_{20}H_{19}F_3N_4O_2$: 404.3.

2.5.21. 5-(4-Bromophenyl)-8,8-dimethyl-2,4-dithioxo-2,3,4,5,7,8,9,10-octahydropyrimido[4,5-b]quinolin-6(1 H)-one (1 M)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.6; IR (KBr, cm^{-1}): 3248, 3166, 2930, 2867, 1638; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.27 (s, 1 H), 9.53 (S, 1 H), 8.03 (S, 1 H), 7.41 (d, 2 H), 7.06 (d, 2 H), 4.85 (s, 1 H), 2.52- 2.36 (m, 2 H), 2.23 (d, 1 H), 2.04 (d, *J* = 10.2 Hz, 1 H), 1.07 (S, 3 H), 0.95 (S, 3 H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.5, 162.3, 152.0, 147.3, 130.2, 129.7, 118.1, 108.6, 50.1, 35.7, 32.0, 30.7, 28.9, 26.7. MS *m/z* (%); found for $C_{19}H_{18}BrN_3OS_4$: 448.4.



Scheme 4. Plausible mechanism for the synthesis *N*-heterocyclic compounds using MIL-100(Cr)/NHEtN($CH_2PO_3H_2$)$_2$.

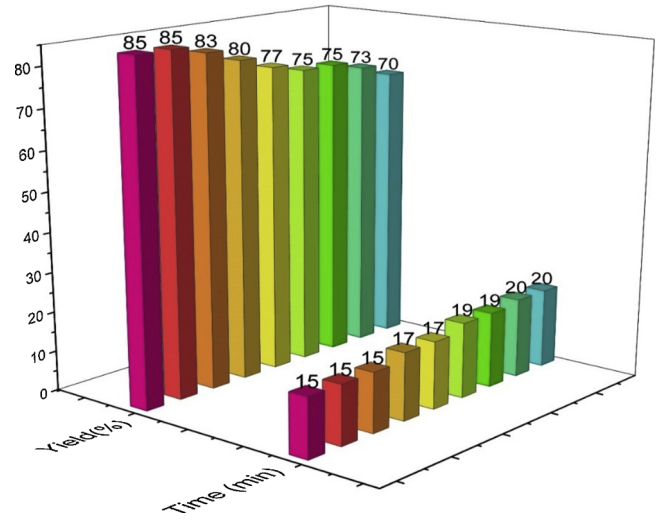


Fig. 7. Recyclability of MIL-100(Cr)/NHETN($CH_2PO_3H_2$)$_2$ as catalyst in the synthesis of tetrahydropyrimido[4,5-*b*]quinolone.

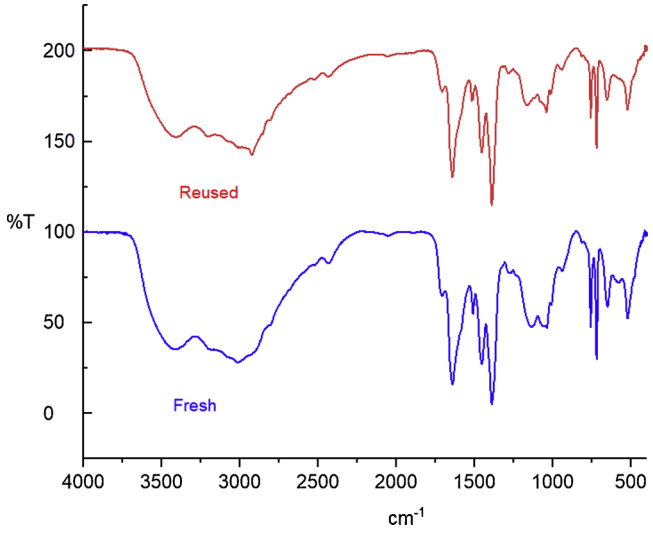


Fig. 8. FT-IR of MIL-100(Cr)/NHETN($CH_2PO_3H_2$)$_2$ in a) reused (red) b) fresh (blue) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

2.5.22. 5-(4-Chlorophenyl)-8,8-dimethyl-2,4-dithioxo-2,3,4,5,7,8,9,10-octahydropyrimido[4,5-b]quinolin-6(1 H)-one (2 M)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.75; IR (KBr, cm^{-1}): 3433, 3329, 3090,2928, 1660, 1649; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 12.23 (s, 1 H), 11.79 (s, 1 H), 8.67 (s, 1 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 4.78 (s, 1 H), 2.53- 2.41 (m, *J* = 13.9 Hz, 2 H), 2.25 (d, *J* = 16.1 Hz, 1 H), 2.08 (d, *J* = 16.1 Hz, 1 H), 1.07 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 194.2, 173.4, 160.1, 148.9, 144.7, 143.7, 130.5, 129.4, 127.7, 110.5, 93.6, 50.0, 32.8, 32.1, 28.7, 26.4. MS *m/z* (%); found for $C_{19}H_{18}ClN_3OS_4$: 403.9.

2.5.23. 5-(4-Methoxyphenyl)-8,8-dimethyl-2,4-dithioxo-2,3,4,5,7,8,9,10-octahydropyrimido[4,5-b]quinolin-6(1 H)-one (3 M)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.7; IR (KBr, cm^{-1}): 3458, 3275, 2958, 1642, 1612; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 12.12 (s, 1 H), 8.66 (s, 1 H), 8.03 (s, 1 H), 7.16 (d, 2 H), 6.83 (d, 2 H), 4.76 (s, 1 H), 3.76 (s, 3 H), 2.56- 2.45 (m, 2 H), 2.28 (d, *J* = 16.1, 3.0 Hz, 1 H), 2.09 (d, 1 H), 1.10 (s, 3 H), 0.98 (s, 3 H) ;^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 194.2, 173.3, 162.2, 160.1, 157.4, 148.5, 143.6, 142.8, 138.1, 128.5, 113.1, 111.1, 94.3, 54.8, 50.0, 35.7, 32.1, 30.7, 28.8, 26.4. MS *m/z* (%); found for $C_{20}H_{21}N_3O_2S_2$: 399.3.

2.5.24. 5-(2-Hydroxy-3-methoxyphenyl)-8,8-dimethyl-2,4-dithioxo-2,3,4,5,7,8,9,10-octahydropyrimido[4,5-b]quinolin-6(1 H)-one (4 M)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.8; IR (KBr, cm^{-1}): 3660, 3314, 2896, 1640, 1622; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 11.62 (s, 1 H), 11.50 (s, 1 H), 7.02 (t, *J* = 7.9 Hz, 1 H), 6.92 (d, *J* = 7.4 Hz, 1 H), 6.70 (s, 1 H), 6.67 (d, *J* = 7.2 Hz, 1 H), 4.78 (s, 1 H), 3.88 (s, 3 H), 2.63 (d, 1 H), 2.48 (d, 1 H), 2.32 (d, 1 H), 2.18 (d, *J* = 13.0, 7.7 Hz, 1 H), 1.13 (s, 3 H), 1.06 (s, 3 H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 196.2, 172.8, 165.3, 159.8, 150.3, 146.5, 139.4, 124.8, 123.7, 119.8, 109.8, 109.1, 94.6, 55.4, 50.3, 40.5, 31.7, 28.8, 26.4. MS *m/z* (%); found for $C_{20}H_{21}N_3O_3S_2$: 415.5.

2.5.25. 5-(3-Ethoxy-4-hydroxyphenyl)-8,8-dimethyl-2,4-dithioxo-2,3,4,5,7,8,9,10-octahydropyrimido[4,5-b]quinolin-6(1 H)-one (5 M)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.65; IR (KBr, cm^{-1}): 3391, 3173, 2856, 1638; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 12.04 (s, 1 H), 9.36 (s, 1 H), 8.67 (s, 1 H), 8.52 (s, 1 H), 8.01 (s, 1 H), 6.84 (s, 1 H), 6.70- 6.39 (m, 2 H), 4.76 (s, 1 H), 3.95 (q, *J* = 6.9 Hz, 2 H), 2.56 – 2.31 (m, 2 H), 2.21 (d, *J* = 16.1 Hz, 1 H), 2.03 (d, *J* = 16.1 Hz, 1 H), 1.34 (t, *J* = 12.6, 6.2 Hz, 3 H), 1.01 (d, *J* = 33.9 Hz, 6 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.7, 146.2, 145.6, 144.2, 119.3, 118.7, 115.0, 114.7, 113.5, 112.6, 109.30, 76.4, 63.9, 63.7, 50.3, 35.7, 32.0, 29.1, 26.6, 14.8, 14.7. MS *m/z* (%); found for $C_{21}H_{23}N_3O_3S_2$: 429.5.

2.5.26. 8,8-Dimethyl-5-(4-nitrophenyl)-2,4-dithioxo-2,3,4,5,7,8,9,10-octahydropyrimido[4,5-b]quinolin-6(1 H)-one(6 M)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.5; IR (KBr, cm^{-1}): 3331, 2974, 2934, 1639, 1601; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.26 (s, 1 H), 9.65 (s, 1 H), 8.14 (d, J = 8.7 Hz, 2 H), 8.05 (s, 1 H), 7.51 (d, *J* = 8.7 Hz, 2 H), 4.97 (s, 1 H), 2.53 (d, *J* = 17.1 Hz, 1 H), 2.44 (d, *J* = 16.3 Hz, 1 H), 2.25 (d, *J* = 16.0 Hz, 1 H), 2.05 (d, *J* = 16.0 Hz, 1 H), 1.09 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.2, 162.3, 155.6, 152.8, 145.3, 128.4, 123.3, 107.8, 50.0, 35.7, 34.3, 32.2, 29.0, 26.5, 18.4. MS *m/z* (%); found for $C_{19}H_{18}N_4O_3S_2$: 414.5.

2.5.27. 8,8-Dimethyl-5-phenyl-5,8,9,10-tetrahydropyrimido[4,5-b] quinoline-2,4,6(1H,3H,7 H)-trione (1B)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.5; IR (KBr, cm^{-1}): 3322, 3163, 2971,1717, 1640; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.81-10.53 (m, 1 H), 10.51-10.24 (m, 1 H), 7.28- 7.18 (m, 4 H), 7.10 (s, 1 H), 6.73 (s, 1 H), 4.71 (s, 1 H), 2.48 – 2.38 (m, 2 H), 2.21 (d, *J* = 16.4 Hz, 1 H), 2.02 (d, *J* = 14.8 Hz, 1 H), 1.02 (s, 3 H), 0.88 (s, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 194.2, 162.7, 149.7, 145.5, 138.6, 130.2, 129.4, 128.5, 127.6, 127.4, 110.6, 89.1, 59.7, 50.02, 32.8, 32.1, 28.8, 26.4, 20.7, 14.0. MS *m/z* (%); found for $C_{19}H_{19}N_3O_3$: 337.3.

2.5.28. 5-(4-(Dimethylamino)phenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,7 H)-trione (2B)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.6; IR (KBr, cm^{-1}): 3416, 3323, 3055, 1731, 1642; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.73 (s, 1 H), 10.14 (d, *J* = 9.7 Hz, 1 H), 7.04 (d, *J* = 8.7 Hz, 2 H), 6.61 (d, *J* = 8.7 Hz, 2 H), 6.24 (s, 1 H), 4.68 (s, 1 H), 4.47 (s, 1 H), 2.86 (s, 6 H), 2.53- 2.40 (m, 2 H), 2.25 (d, *J* = 16.1 Hz, 1 H), 2.06 (d, *J* = 16.1 Hz, 1 H), 1.08 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 194.3, 164.2, 162.7, 155.0, 150.9, 148.7, 148.6, 134.8, 127.9, 112.0, 111.6, 90.1, 74.0, 50.1, 40.3, 32.1, 31.7, 29.0, 26.4. MS *m/z* (%); found for $C_{21}H_{24}N_4O_3$: 380.4.

2.5.29. 5,5′-(1,4-Phenylene)bis(8,8-dimethyl-2,4-dithioxo-2,3,4,5,7,8,9,10-octahydropyrimido[4,5-b]quinolin-6(1 H)-one) (1 A)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.7; IR (KBr, cm^{-1}): 3473, 3232, 2938, 1683; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 12.12 (s, 1 H), 11.65 (s, 1 H), 8.48 (s, 1 H), 7.96 (s, 2 H), 7.01 (s, 1 H), 2.41 (d, *J* = 24.2 Hz, 2 H), 2.13 (dd, *J* = 32.3, 16.3 Hz, 2 H), 1.01 (s, 3 H), 0.90 (s, 3 H).^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 194.3, 173.2, 162.2, 160.1, 148.8, 143.2, 126.8, 110.9, 93.8, 50.0, 35.7, 32.2, 32.0, 30.7, 28.4, 26.9. MS *m/z* (%); found for $C_{32}H_{32}N_6O_2S_4$: 660.8.

2.5.30. 5,5′-(1,4-Phenylene)bis(2-amino-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione)(2A)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.65; IR (KBr, cm^{-1}): 3451, 3326, 2956, 2934, 1620; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.36 (s, 2 H), 9.33 (s, 2 H), 7.01 (d, *J* = 2.7 Hz, 4 H), 6.36 (s, 4 H), 4.80 (d, *J* = 4.2 Hz, 2 H), 2.45 (d, *J* = 16.0 Hz, 4 H), 2.21- 2.05 (m, 4 H), 1.07 (d, *J* = 11.2 Hz, 6 H), 0.99 (s, 3 H), 0.95 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.8, 161.3, 153.8, 151.4, 151.2, 144.6, 144.5, 126.5, 109.8, 109.6, 92.1, 50.1, 32.5, 32.1, 28.7, 28.5, 27.4, 27.0. MS *m/z* (%); found for $C_{32}H_{34}N_8O_4$: 594.6.

2.5.31. 5,5′-(1,4-Phenylene)bis(8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-2,4,6(1H,3H,7 H)-trione) (3 A)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.7, IR (KBr, cm^{-1}): 3191, 2959, 1731, 1659; ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 192.0, 165.7, 162.4, 149.8, 135.7, 125.8, 84.8, 74.4, 47.7, 42.1, 31.9, 22.8, 22.4. MS *m/z* (%); found for $C_{32}H_{32}N_6O_4$: 596.6.

2.5.32. 5,5′-(1,3-Phenylene)bis(2-amino-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-b]quinoline-4,6(3H,7 H)-dione) (4 A)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.65; IR (KBr, cm^{-1}): 3422, 3337, 3187, 2955, 1655; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.23 (d, *J* = 11.5 Hz, 2 H), 9.21 (s, 1 H), 9.16 (s, 1 H), 7.07 (s, 1 H), 6.98 – 6.93 (m, 1 H), 6.93- 6.82 (m, 3 H), 6.25 (s, 2 H), 6.20 (s, 2 H), 4.77 (s, 1 H), 4.67 (s, 1 H), 2.38 (dd, *J* = 28.4, 18.0 Hz, 4 H), 2.15- 2.00 (m, 3 H), 1.86 (d, *J* = 15.9 Hz, 1 H), 1.03- 0.93 (m, 9 H), 0.82 (s, 3 H).^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 193.8, 193.6, 161.3, 153.9, 153.6, 153.6, 151.4, 151.1, 147.3, 146.7, 125.5, 124.4, 109.6, 109.4, 92.4, 92.0, 50.3, 50.2, 33.3, 32.5, 32.0, 31.8, 29.2, 28.5, 27.7, 26.6. MS *m/z* (%); found for $C_{32}H_{34}N_8O_4$: 594.60.

2.5.33. 5,5′-(1,3-phenylene)bis(8,8-dimethyl-2,4-dithioxo-2,3,4,5,7,8,9,10-octahydropyrimido[4,5-b]quinolin-6(1 H)-one) (5 A)

White solid; Mp: > 350 °C; R_f: (*n*-hexane: acetone 1:1) = 0.8; IR (KBr, cm^{-1}): 3331, 3176, 2955, 1670, 1640; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 10.52 (s, 1 H), 9.51 (s, 1 H), 6.98 (s, 1 H), 6.91 (s, 1 H), 4.60 (s, 1 H), 2.44 (d, *J* = 23.9 Hz, 1 H), 2.30 (d, *J* = 17.0 Hz, 1 H), 2.16 (d, *J* = 16.1 Hz, 1 H), 1.88 (d, *J* = 16.0 Hz, 1 H), 0.97 (s, 3 H), 0.77 (s, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 194.0, 162.7, 162.7, 146.9, 125.8, 125.5, 125.4, 111.0, 90.1, 49.9, 32.8, 32.0, 31.7, 29.2, 28.6, 27.0, 25.8.MS *m/z* (%); found for $C_{32}H_{32}N_6O_2S_4$: 660.8.

3. Results and discussion

Initially, MIL-100(Cr)/NHEtN($CH_2PO_3H_2$)$_2$ was prepared as MOFs catalyst by the condensation reaction of MIL-100(Cr)/$NHEtNH_2$, paraformaldehyde, phosphorous acid, HCl and EtOH as solvent under reflux condition (path method [32,33]) (Scheme 2). The structure of MOFs linker phosphorous acid was confirmed by several techniques such as, fourier transform infrared spectroscopy (FT-IR), EDX, elemental mapping, scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2 adsorption-desorption isotherms (BET), thermal gravimetric (TG), differential thermal gravimetric (DTG) and differential thermal analysis (DTA).

The comparison FT-IR spectrum of catalyst and MIL-100(Cr)/$NHEtNH_2$ were showed in Fig. 1. As it is shown in Fig. 1, a broad peak was displayed at about 2679–3402 cm^{-1} related to OH of PO_3H_2 groups in the structure of the catalyst. The peaks between 2800–2940 cm^{-1} can be attributed to the presence of C–H of alkyl chain of propyl group and C–H of other methylenes besides of PO_3H_2 groups. The peak related

to P−O bond was observed at about 1080 cm^{-1}. Furthermore, two peaks related to Cr-O of octahedral CrO_6 were appeared at 523 and 663 cm^{-1} respectively. Two peaks at about 1393 and 1642 cm^{-1} were corresponded to asymmetric and symmetric vibrations of C=C [34].

SEM-EDS analysis of the catalyst was studied in comparison with MIL-100(Cr)/$NHEtNH_2$. The structure of MIL-100(Cr)/NHEtN $(CH_2PO_3H_2)_2$ was verified the existence of Cr, C, O, N and P atoms whereas the structure of MIL-100(Cr)/$NHEtNH_2$ which is contained Cr, C, O and N atoms. Then, SEM-elemental mapping (Cr, C, N, O and P) in the MOFs-catalyst with a well-dispersed over the catalyst surface was confirmed (Fig. 2). Elemental analysis of the catalyst was verified C: 43.09, N: 12.85 and P: 11.16.

To distinguish the surface morphology of the synthesized MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ SEM was studied. SEM micrographs of the MOFs-catalyst showed that the particles have not completely agglomerated. Moreover, particles of the MOFs-catalyst were observed in average size of 35 nm (Fig. 3).

In another investigation, we have studied transmission electron microscopy (TEM) to verify the structure of MOFs-catalyst in Fig. 4. The TEM images of MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ showed that the particles prepared in nano size with proper dispersion.

In the direction study of thermal stability of the MOFs-catalyst, the thermal gravimetric (TG), derivative thermal gravimetric (DTG), as well as the differential thermal analysis (DTA) were investigated (Fig. 5). The first weight loss, was happened between 25 and 100 °C, associated with the removal of possible solvents (organic and water). The main stage of weight loss, disrupts the structure of MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$, was happened after 200 °C, and includes about 40% weight loss. Therefore, this catalyst can be used up to 200 °C.

Nitrogen adsorption-desorption isotherm (BET) of En/MIL-100(Cr) and MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ were compared in Fig. 6. These isotherms reveal that the hysteresis loop progressively shifts to lower relative pressures with grafting of PO_3H_2 group ($-CH_2PO_3H_2$) indicative of decreasing pore size and surface area decreased from 460 to 100 m^2/g. BET surface area, and total pore volume of En/MIL-100(Cr) are 223.5 $m^2\,g^{-1}$ and 0.19 $cm^3\,g^{-1}$ and for MIL-100(Cr)/NHEtN $(CH_2PO_3H_2)_2$ are 84.0 $m^2\,g^{-1}$ and 0.24 $cm^3\,g^{-1}$ respectively.

In addition, the catalytic activity of MIL-100(Cr)/NHEtN $(CH_2PO_3H_2)_2$ was tested in one-pot synthesis of 2-amino-5-(4-chlorophenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-*b*]quinoline-4,6(3*H*,7*H*)-dione by the reaction of 4-chloro benzaldehyde (1 mmol, 0.14 g), 2,6-diaminopyrimidin-4(3*H*)-one (1 mmol, 0.126 g) and dimedone (1 mmol, 0.14 g) as a model reaction and optimized (Table 1). In the first experiment, model reaction was tested using DMF as a solvent, 0.01 (g) MOFs-catalyst at 25–100 °C which was obtained greatest yield at 100 °C (Table 1, entry 4). By testing different amounts MOFs-catalyst, the highest yield was obtained in the presence of 0.01 (g) MOFs-catalyst (Table 1, entry 5–7). Different solvents including DMF, H_2O, EtOH, CH_2Cl_2, $CHCl_3$, EtOAc, CH_3CN in comparison with solvent-free condition were tested on the model reaction which the best result was observed in the presence of DMF as a solvent (Table 1, entry 8–14).

After the optimization of the reaction conditions, the efficiency and applicability of MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ were studied by the reaction of dimedone and uracil derivatives compound such as 6-aminopyrimidine-2,4(1*H*,3*H*)-dione, 6-aminopyrimidine-2,4(1*H*,3*H*)-dithione and 2,6-diaminopyrimidin-4(3*H*)-one with various aldehydes. The results are depicted in Table 2. As Table 2 indicates that, all aldehydes including benzaldehyde as well as other aromatic aldehydes possessing electron-releasing substituents, electron withdrawing substituents, basic groups or halogens afforded the desired *N*-heterocyclic compounds such as tetrahydropyrimido[4,5-*b*]quinoline-2,4,6(1*H*,3*H*,7*H*)-trione, tetrahydropyrimido[4,5-*b*]quinoline-4,6(3H,7 *H*)-dione and octahydropyrimido[4,5-*b*]quinolin-6(1*H*)-one derivatives with short reaction times in high to excellent yields (73–93%) (5–30 min) (Table 2).

To compare the efficiency of the prepared catalyst for the preparation of 2-amino-5-(4-chlorophenyl)-8,8-dimethyl-5,8,9,10-tetrahydropyrimido[4,5-*b*]quinoline-4,6(3*H*,7*H*)-dione by the reaction of 4-chloro benzaldehyde (1 mmol, 0.14 g), 2,6-diaminopyrimidin-4(3*H*)-one (1 mmol, 0.126 g) and dimedone (1 mmol, 0.14 g), we have used different organic and inorganic acid catalysts for the condensation reaction between 4-chloro benzaldehyde (1 mmol, 0.14 g), 2,6-diaminopyrimidin-4(3*H*)-one (1 mmol, 0.126 g) and dimedone (1 mmol, 0.14 g), in Table 3. As Table 3 indicates, MIL-100(Cr)/NHEtN $(CH_2PO_3H_2)_2$ is the best catalyst for the synthesis of *N*-heterocyclic compounds.

A proposed mechanism for the synthesis of *N*-heterocyclic compounds was displayed in Scheme 4. Firstly, dimedone, in enol form, was reacted with aldehyde which is activated by MIL-100(Cr)/NHETN $(CH_2PO_3H_2)_2$ to give **I** as a Michael acceptor after removing of one molecule of H_2O. Then, uracil derivative compound was reacted with **I** to prepare **II** which converted to **III** after cyclization reaction. Finally, by removing of one molecule of H_2O, the desired product was obtained.

According to the results in Fig. 7, MIL-100(Cr)/NHETN$(CH_2PO_3H_2)_2$ can be separated by centrifugation and reused without significantly reducing of catalytic activity, for this purpose recyclability of the catalyst was tested on the reaction of 2,6-diamino pyrimidin-4(3*H*)-one (1 mmol, 0.126 g) with 4-chloro benzaldehyde (1 mmol, 0.14 g) and dimedone (1 mmol, 0.14 g) as a model reaction. Therefore, MIL-100(Cr)/NHETN$(CH_2PO_3H_2)_2$ can be reused up to eight runs without noticeable changes in the catalytic activity. The reused catalyst was also characterized by FT-IR after its catalytic application in the reaction. The FT-IR spectra of the fresh catalyst and reused catalyst were compared with each other in Fig. 8.

4. Conclusion

In this work, we have reported a new multifunctional of the MIL-100(Cr)/En metal-organic framework with phosphorous acid namely MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ as an efficient nanoporous catalyst. MIL-100(Cr)/NHEtN$(CH_2PO_3H_2)_2$ was fully characterized by FT-IR, SEM-Elemental Mapping., EDX, TEM, TGA and BET and successfully used for the synthesis of some new biological *N*-heterocyclic compounds containing uracil moiety such as tetrahydropyrimido[4,5-*b*]quinoline-2,4,6(1*H*,3*H*,7*H*)-trione, tetrahydropyrimido[4,5-*b*]quinoline-4,6(3*H*,7*H*)-dione and octahydropyrimido[4,5-*b*]quinolin-6(1*H*)-one derivatives. Major advantages of this work are high yield of products, short reaction times, facile workup and reusability of the catalyst.

Acknowledgements

We thank Bu-Ali Sina University, Sayyed Jamaleddin Asadabadi University, National Elites Foundation and Iran National Science Foundation (INSF) (grant number:96003376) for financial support to our research group.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.01.023.

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