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THE SYNTHESIS OF 3,4-DIHYDROPYRIMIDIN-2(1H)-ONE/THIONE DERIVATIVES USING SILICA-SUPPORTED 3-(TRIETHOXYSILYL) PROPAN-1-AMMONIUM CHLORIDE AS REUSABLE HETEROGENEOUS CATALYST UNDER SOLVENT-FREE CONDITIONS AND MICROWAVE

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ABSTRACT: Silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride was prepared and used as an effective catalyst for the efficient synthesis of 3,4-dihydropyrimidin-2(1H)-ones or thiones by three-component Biginelli reaction, one-pot condensation of aromatic aldehydes, β-dicarbonyl compounds, and urea (thiourea) derivatives under solvent-free conditions. The reactions were carried out at 100 °C under microwave and thermal conditions. This catalyst was characterized by XRD, ^{1}H, ^{13}C NMR and FT-IR. The short reaction times, good recyclability and reusable of the catalyst, consistent yields of products, non-toxic and clean reaction conditions and minimum environmental effects were important features of this protocol which make it a useful process for the synthesis of these important heterocyclic compounds.

KEYWORDS: Silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride, reusable catalyst, biginelli reaction, 3,4-Dihydropyrimidin-2(1H)-ones or thiones, solvent-free conditions, heterocyclic compounds

INTRODUCTION

In 1893, Italian chemist Pietro Biginelli reported reaction of an aldehyde, a β-ketoester, and urea (or thiourea) in the presence of either Lewis or mineral acids, a procedure known as the biginelli reaction in the history of MCRs [i,ii], is receiving increased attention. The result of the three-component reaction was a new product that was correctly characterized as a substituted 3,4-dihydropyrimidine-2(1*H*)-one (DHPM). Over the past decade, dihydropyrimidin-2(1*H*)-ones and their derivatives have attracted considerable attention in organic and medicinal chemistry as the dihydropyrimidine scaffold displays a fascinating array of pharmacological and therapeutic properties.[iii] They have emerged as integral backbones of several calcium channel blockers, antihypersentive agents, α-1a-antagonists, and neuropeptide Y (NPY) antagonists.[iv] Moreover, several alkaloids containing the dihydropyrimidine core unit have been isolated from marine sources, which also exhibit interesting biological properties.[v] The original biginelli protocol for the preparation of the DHPMs consisted of heating a mixture of the three components (aldehyde **1**, β-dicarbonyl compound **2**, and urea (thiourea) derivatives **3** in ethanol containing a catalytic amount of HCl. [iii] This procedure leads in one step-one pot to the desired DHPM. The major

drawback associated with this protocol is the low yields, particularly for substituted aromatic and aliphatic aldehydes.[vi] This has led to the development of multi-step synthetic strategies involving combinations of Lewis acids and transition metal salts, e.g. $BF_3.OEt_2$, polyphosphate esters, and reagents like $InCl_3$, $Mn(OAc)_3$, $LaCl_3.7H_2O$, $CeCl_3.7H_2O$, $LiClO_4$, $Yb(OTf)_3$, trimethylsilyltriflate, clays,[vii] phase-transfer catalyst,[viii] etc. However, many of these methods involve expensive reagents, toxic and strongly acidic conditions, long reaction times, and stoichiometric amount of catalysts, and difficult to handle especially on a large scale. Therefore, the discovery of a new and an inexpensive catalyst for the preparation of dihydropyrimidin-2-(1*H*)-ones under mild conditions is of prime importance. For the increasing environmental and economical concerns in recent years, it is now essential for chemists to search environmentally benign catalytic reactions as many as possible. Herein, we wish to report the use of silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride as an efficient and new heterogeneous catalyst for biginelli reaction under microwave irradiation and solvent-free conditions (Scheme 1). The silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride catalyst was used solid, recyclable, non-corrosive and inexpensive.

Scheme 1. Biginelli condensation

For identification of the structure of silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride (J) as catalyst, the XRD, ^1H, ^{13}C NMR, IR spectra of this catalyst was studied. Figure **1** shows X-Ray diffraction patterns of the silica gel sample and silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride sample synthesized. No peaks are observed in the silica gel sample except for the harrow like pattern at 2θ degree between 15 °C and 24 °C attributed to amorphous silica gel. XRD patterns of silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride showed a high intensity peak at 2θ = 20.7˚ with a basal spacing of 4.3 Å and broad hump in the region of 2θ = 8-11˚. This spacing indicated that 3-(triethoxysilyl) propan-1-ammonium chloride can enter the interlayer space and link with silica.

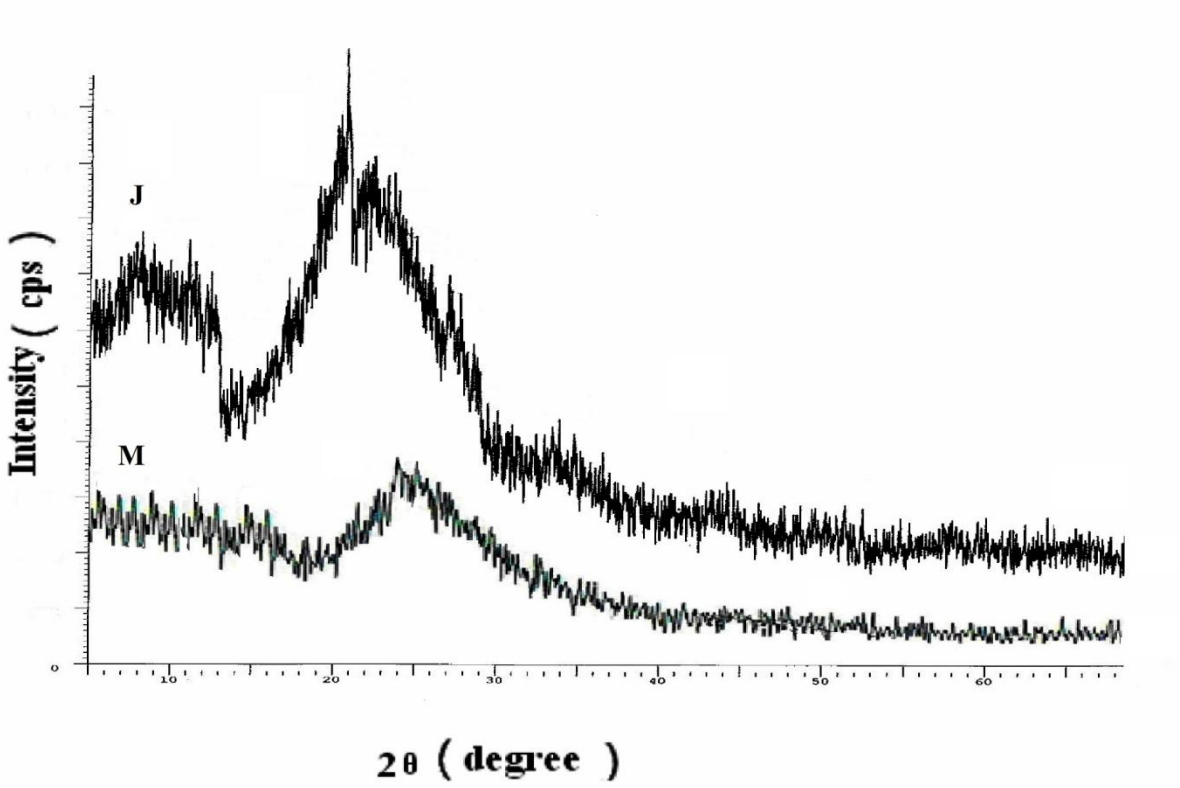


Figure 1. The powder XRD patterns of silica gel (**M**), silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride (**J**)

In the IR spectra of dry silica gel (**M**), silica gel-supported propylamine (**N**), silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride (**J**) (**Fig.2**), all samples showed the absorption bands for Si-OH and Si-O-Si in ~800 cm^{-1} and ~1100 cm^{-1}, respectively. OH stretching band is observed at 3300-3500 $cm^{-1}$and strong intermolecular hydrogen bonding occurs in the hydroxyl groups or NH group. Therefore, the resulting O-H absorption is very broad. In IR spectrum of catalyst (**J**) showed absorption bands for Si-CH_2 at 2900 and 3000cm^{-1}. The ^1H NMR spectra of catalyst which taken at 400 MHz, exhibited main triplet signals at δ= 1.27, 3.84 ppm ($^3J_{HH}$= 7.2 Hz), which arises from protons of two CH_2 groups, a 2-H quintuplet signal for other CH_2 groups of propylamine (δ= 2.58 ppm, $^3J_{HH}$=7.1 Hz). The OH protons of compound **J** showed characteristic signals at δ= 7.30-8.10 and δ= 10.00-11.20 ppm. The NH_3^+ protons appeared as a broad signal at δ= 11.2 ppm. The ^{13}C NMR spectrum of catalyst showed 3 significant signals, in agreement with the proposed structure. The three signals were observed at 16.46, 24.80, 56.70 for methylene carbon (CH_2). The ninhydrine solution in ethyl acetate (solvent) added to this catalyst (**J**) and the color change was not observed. This test showed that catalyst (**J**) is a form of ammonium salt. Based on these results, we suggest the following structure for silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride (J) (**Scheme 2**).

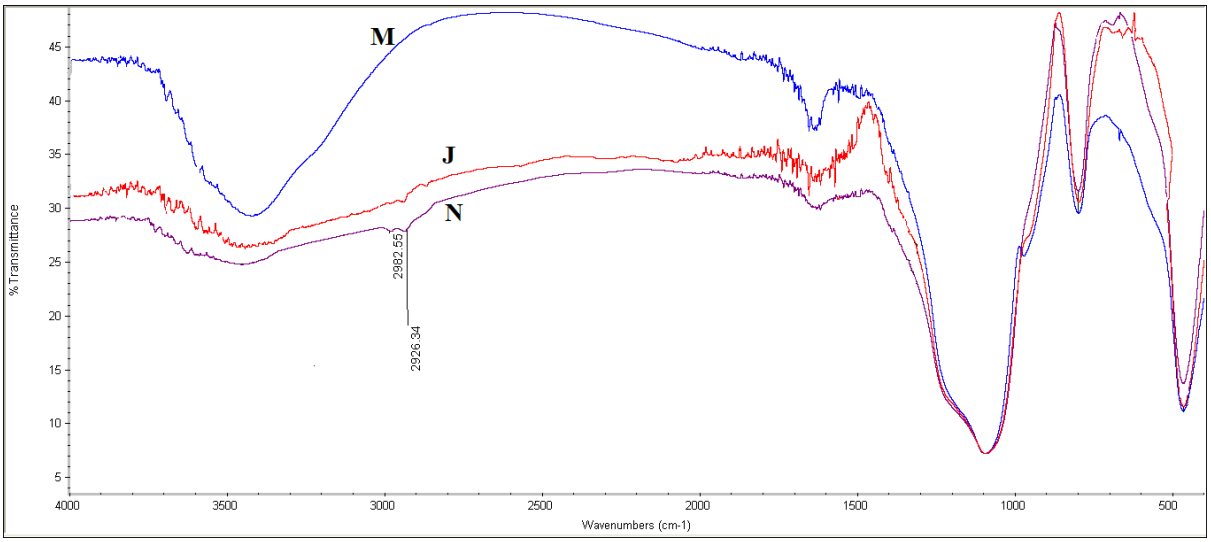
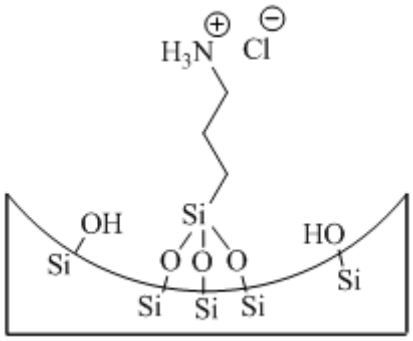


Figure 2. FT-IR spectrum of dry silica gel (**M**), silica gel-supported propylamine (**N**), silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride (**J**)



Scheme 2. Suggestion structure for silica gel-supported ammonium salt as catalyst

Efficiency of this reaction (**scheme 1**) is mainly affected by the amount of catalyst and reaction time. No product was formed in the condensation of 4-chloro benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and urea (1.5 mmol) in absence of the catalyst even after extending reaction time (**Table 1**, **entry 1**) indicating that the catalyst is necessary for the reaction. For getting the best conditions in the presence of catalyst, we started the condensation of 4-chloro benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and urea (1.5 mmol) in the presence of silica gel-supported 3-(triethoxysilyl) propan-1-ammonium chloride (**J**) (0.01 gr) as a catalyst at 100 ˚C for 3 h, which led to low yield (45%) of product 3 (**entry 2**). The yield of dihydropyrimidinones increased with increasing the amounts of the catalyst from 0.01 to 0.02 g (**entry 3**). Higher amounts of the catalyst did not improve the yield (**entry 4**). Varying the amount of reactants, the best result was obtained when the molar ratio of 4-chloro benzaldehyde, ethyl acetoacetate and urea was 1.0:1.0:1.5.

Table 1. Effect of the amounts of catalyst on the model reaction [a]

Entry	Catalyst (gr)	Yield (%)
1	None	None

2	0.01	45
3	0.02	89
4	0.03	60

[a] reaction condition: 4-chloro benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and urea (1.5 mmol) in solvent-free and thermal.

After optimizing the amount of catalyst, we applied this catalyst in condensation of ethyl acetoacetate (or acetylacetone), urea (or thiourea) and wide range of aromatic aldehydes under solvent-free conditions (**Table 2**). In all cases, the three-component reaction proceeded smoothly to give the corresponding 3, 4-dihydropyrimidin-2(1H)-ones/thiones in moderate to good yields. The reaction with aromatic aldehydes carrying either electron-donating or electron-withdrawing substituents in the *ortho*, *meta* and *para*-positions gave the corresponding product in good yields and high purity. Thiourea also reacts under similar reaction conditions to provide the biginelli products in good yields (**Table 2, entries 14–24**). The structures of all the products were confirmed by comparing melting point and spectral data with those in the literature.

Table 2. Synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones using silica gel supported 3-(triethoxysilyl) propan-1-ammonium chloride under Thermal solvent-free conditions (at 100°C in an oil bath).

DHPM	R^1	R^2	R^3	R^4	R^5	X	Time (h)	Yield[a] (%)	M.p.(°C)	
									Found	Reported[ref]
1	4-NO_2	Me	OEt	H	H	O	3	85	204-206	205-207[b]
2	3-NO_2	Me	OEt	H	H	O	3	80	223-225	225-226[c]
3	4-Cl	Me	OEt	H	H	O	3	89	210-212	210-212[b]
4	4-OH	Me	OEt	H	H	O	2	90	236-238	236-238[b]
5	4-Br	Me	OEt	H	H	O	2.75	84	219-221	220-222[d]
6	4-F	Me	OEt	H	H	O	2	86	176-179	179-180[d]
7	4-Me	Me	OEt	H	H	O	3	92	210-212	212-214[c]
8	4-OMe	Me	OEt	H	H	O	3	90	200-202	199-201[b]
9	2,4-Cl_2	Me	OEt	H	H	O	3	78	247-249	248-250[c]
10	4-Cl	Me	Me	H	H	O	2	85	211-214	212-213[e]
11	4-NO_2	Me	Me	H	H	O	2.75	86	above 400	above 400[g]
12	4-OMe	Me	Me	H	H	O	3	89	168-170	169-170[g]
13	4-Br	Me	Me	H	H	O	2.5	87	240-242	242-244[g]
14	3-NO_2	Me	OEt	H	H	S	3	76	206-208	205-207[c]
15	4-Cl	Me	OEt	H	H	S	2.5	91	177-179	176-177[e]
16	4-Me	Me	OEt	H	H	S	3	84	190-192	191-193[e]
17	4-OMe	Me	OEt	H	H	S	3	89	142-145	141-143[e]
18	4-F	Me	OEt	H	H	S	2.5	85	208-210	-
19	4-OH	Me	OEt	H	H	S	2	87	197-199	199-200[d]
20	2-Cl	Me	OEt	H	H	S	1.15	79	167-168	168-169[g]
21	4- Br	Me	OEt	H	H	S	3	75	180-182	182-183[d]
22	4- Cl	Me	Me	H	H	S	1.5	92	207-209	208-209[e]
23	4-OMe	Me	Me	H	H	S	1.5	88	163-165	161-163[e]
24	2-Cl	Me	Me	H	H	S	1	94	175-176	173-175[e]

25	4-NO_2	Me	OEt	H	Me	O	3	82	105-107	107-109[d]
26	3-NO_2	Me	OEt	H	Me	O	3	79	128-130	130-131[f]
27	4-Br	Me	OEt	H	Me	O	3	93	149-150	150-151[d]
28	4-NO_2	Me	OEt	Me	Me	O	2.5	78	106-108	105-107[f]
29	4-OMe	Me	OEt	Me	Me	O	2.5	78	86-87	84-86[f]

[a]Isolated Yield.[b]Ref. [ix].[c]Ref. [x].[d]Ref. [xi]. [e]Ref. [xii].[f]Ref. [xiii]. [g]Ref. [xiv].

In order to decrease the reaction time, microwave irradiation under solvent-free condition was used. The reaction time decreased from 3 hours to 3 minutes. Moreover, the yields of products increased in all cases that were examined (**Table 3**).

Table 3. Synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones using silica gel supported 3-(triethoxysilyl) propan-1-ammonium chloride under Microwave-Assisted[b] solvent-free conditions

DHPM	R^1	R^2	R^3	R^4	R^5	X	Time(min)	Yeild(%)
1	4-NO_2	Me	OEt	H	H	O	3	94
3	4-Cl	Me	OEt	H	H	O	3	95
4	4-OH	Me	OEt	H	H	O	3	97
8	4-OMe	Me	OEt	H	H	O	3	97
10	4-Cl	Me	Me	H	H	O	3	95
11	4-NO_2	Me	Me	H	H	O	3	93
17	4-OMe	Me	OEt	H	H	S	3	92
19	4-OH	Me	OEt	H	H	S	3	93

[m] with a power of 1200 W.

The two procedures give the products in good yields and avoid problems associated with solvent use (cost, handling, safety and pollution). Decreased reaction times are also realized because of the increased reactivity of the reactant in the solid state and the fact that the other reaction product, water, evaporates at the reaction temperature of 100°C.
As can be seen from **Table 4**, silica gel-supported 3-(triethoxysilyl) propan-1-ammonium chloride catalyst was recovered and recycled by a simple filtration of the reaction solution and reused for several times without significant decreases in activity.

Table 4. Results of reusability of the catalyst

Catalyst	Product yield (%)
Fresh	89
Cycle 1	88
Cycle 2	88

Cycle 1, 2 indicate the reusability of the catalyst recovered from experiment 3.
Reaction condition: 4-chloro benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.5 mmol) and catalyst (0.02 gr) in solvent-free and Thermal.

In Conclusion, Silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride is an efficiency catalyst for the synthesis of DHPMs without any solvent at 100 °C and Microwave irradiation. The simplicity of the system, easy separation of catalyst and products from the reaction mixture, purification of compound by crystallization method, high yields and shorter reaction times make

this an improved protocol than existing methods. Further silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride catalysts can be easily recovered and reused without loss in their activities. Therefore, the use of this catalysts not only makes the process economical viable but also help to reduce environmental pollution to achieve environmentally friendly processes.

EXPERIMENTAL

All materials and solvents were purchased from Sigma-Aldrich and Merck and were used without any additional purification. The X-ray powder diffraction (XRD) was carried out on a Bruker D8Advance X-ray diffractometer using nickel filtered Cu Kα radiation at 40 kV and 20 mA. The instruments used for spectroscopic data are; FT-IR spectra of all the final products were recorded on a Bruker instrument by using the KBr self-supported pellet technique. All ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz Bruker FT-NMR spectrometers. Microwave reactions were performed on LG MS2022H -microwave synthesizer. The melting points of the products were determined by using BAMSTEAB Electrothermal apparatus model 9002. The purity of the compounds was routinely checked by thin layer chromatography (TLC) with Silica Gel (Merck). All the products are known compound, which were characterized by IR, FT-NMR spectral data, their melting points and physical properties with literature reports.

Procedure for preparation of the silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride catalyst (J)

A mixture of dry silica gel (10 gr, 70-230 mesh) and 3-(triethoxysilyl) propylamine (5 ml) in dry toluene (20 ml) was stirred and refluxed for 20 h. The precipitate was filtered. The obtained solid was washed with dry toluene and dried at 120 ˚C for 10 h under reduced pressure, and then a mixture of 2 gr of silica gel-propylamine and 10 ml of HCl (2 N) was stirred for 20 h at room temperature. The resulted suspension was filtered by centrifuges. The obtained solid was washed with water and dried at 80 ˚C under reduced pressure for 10 h.

Spectral data this catalyst: IR (KBr) υ_{max}: 3400-3600, 2900, 1100, 800, 500 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.27 (t, J=7.2 Hz, 2H), 2.58 (quintuplet, J=7.1 Hz, 2H), 3.84 (t, J=7.2 Hz, 2H), 7.30 (s, 1H, OH), 7.78 (s, 1H, OH), 8.10 (s, 1H, OH), 9.30 (s, 3H, NH_3^+), 10.00-11.20 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 16.46, 24.80, 56.70 ppm.

General procedure for synthesis of 3,4-dihydropyrimidin-2(1H)-ones or thiones (1-29) under Thermal Solvent-free conditions in the Presence of Catalyst J

A mixture of aromatic aldehyde (1 mmol), ethyl acetoacetate or acetylacetone (1 mmol), urea or thiourea (1.5 mmol) and silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride as catalyst (0.02 g) was heated with stirring for 1-3 h at 100°C, in an oil bath. After completion of the reaction (indicated by TLC), the reaction was cooled to room temperature and water (5 mL) was added. The crude product containing the catalyst was collected on a Buchner funnel by filtration and heated in boiling ethanol (10 mL). The undissolved catalyst was removed by filtration and washed with hot ethanol. Concentrating the filtrate in vacuum yielded the product. The pure dihydropyrimidin-2(1H)-ones was obtained by recrystallization from hot ethanol. The isolated catalyst was dried at 80 °C overnight and was reused in the next runs without further purification. The yields, time reaction and melting points of the products are reported in **Table 2**.

5-(Ethoxycarbonyl)-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1*H*)-one (1).

M.P: 204–206°C; IR (KBr): υ_{max}: 3233, 3000, 1710, 1675, 1630, 1613, 1560, 1524, 1309 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.30(br. s, 1H), 8.25(d, J = 8.2 Hz, 2H), 7.90 (br. s, 1H), 7.50 (d,

J = 8.3 Hz, 2H), 5.15 (d, J = 2.8 Hz, 1H), 3.90 (q, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d6) δ: 164.7, 151.3, 149.3, 146.4, 126.8, 123.7, 59.3, 52.8,17.8, 13.7 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-Chlorophenyl)-3,4-dihydropyrimidin-2(1H)-one (3). M.P: 210-212^{o}C; IR (KBr) υ_{max}: 3240, 1723, 1643 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.3 (s, 1H), 7.8 (s, 1H), 7.40–7.30 (m, 4H, arom CH), 5.1 (s, 1H), 3.9 (q, J=7.5 Hz, 2H), 2.3 (s, 3H), 1.0 (t, J=7.5 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.0, 151.4, 148.9, 141.2, 131.7, 129.2, 128.7, 98.2, 58.9, 51.9, 17.9 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (4). M.P: 236-238^{o}C; IR (KBr) υ_{max}: 3274, 3232, 1714, 1681, 1506–1614 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.3 (s, 1H), 9.1 (s, 1H), 7.6 (s, 1H), 7.0 (d, J=8.4 Hz, 2H), 6.7 (d, J=8.4 Hz, 2H), 5.0 (d, J=3.2 Hz, 1H), 3.9 (q, J=7.2 Hz, 2H), 2.2 (s, 3H), 1.1(t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.4, 156.6, 152.2, 147.8, 135.5, 127.4, 115.0, 99.8, 59.1, 53.5, 17.8, 14.3 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (8). M.P: 200-202^{o}C; IR (KBr) υ_{max}: 3242, 2956, 1704, 1681, 1504 cm^{-1};^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.1 (s, 1H), 7.7 (s, 1H), 7.1 (d, J=8.4 Hz, 2H), 6.9 (d, J=8.4 Hz, 2H), 5.1 (d, J=2.8 Hz, 1H), 3.9 (q, J=7.2 Hz, 2H), 3.7 (s, 3H), 2.2 (s, 3H), 1.1 (t, J=7.2 Hz, 3H).

5-acetyl-4-(4-chlorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (10): M.P: 211–214 °C; IR (KBr): υ_{max}: 3231, 1700, 1641 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.2 (s, 1H), 7.8 (s, 1H), 7.3-7.2 (m, 5H, arom CH), 5.2 (d, 1H), 3.5 (s, 3H), 2.2 (s, 3H) ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1*H*)-thione (15). M.P: 177-179°C; IR(KBr): υ_{max}: 3258, 1661, 1566 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.0 (br-s, 1H), 9.3 (br-s, 1H), 7.2 (m, 4H), 5.3 (s, 1H) 4.1 (q, J =7.1 Hz, 2H), 2.5 (s, 3H), 1.2 (t, J =7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 174.8, 165.3, 145.5, 142.7, 132.0, 127.9, 128.9, 100.4, 59.3, 53.4, 17.2, 14.2 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione (17): M.P: 151-152°C; IR (KBr): υ_{max}: 3256, 1659, 1595, 1569 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.89 (br. s, 1H), 9.3 (br. s, 1H), 7.2 (d, J = 8.1 Hz, 2H), 6.7 (d, J = 8.1 Hz, 2H), 5.2 (s, 1H), 4.1 (q, J = 7.1 Hz, 2H), 2.3 (s, 3H), 1.2 (t, J = 7.2 Hz, 3H); ^{13}C NMR (300 MHz, DMSO-d6) δ: 173.9, 174.3, 165.9, 126.8, 158.5, 145.2, 135.9, 128.0, 114.0, 101.5, 59.8, 55.3, 53.6, 17.4, 14.3 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-fluorophenyl)-3,4-dihydropyrimidin-2(1*H*)-thione (18). M.P: 208-210°C; IR (KBr): υ_{max}: 3276, 1657, 1569 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.4 (s, 1H), 9.7(s, 1H), 7.4-7.2 (m, 5H), 5.2 (d, J = 3.5 Hz, 1H) 4.0 (q, J = 7.0 Hz, 2H), 2.3 (s, 3H), 1.1 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.8, 151.0, 142.0, 125.9, 124.9, 125.0, 95.9, 57.0, 51.8, 16.3, 12.0 ppm.

5-Ethoxycarbonyl-1,6-dimethyl-4-(4-bromophenyl)-3,4-dihydropyrimidin-2(1*H*)-one (27): M.P: 1549-150 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.0 (d, J = 3.7 Hz, 1H), 7.5 (d, J = 8.4 Hz, 2H), 7.2 (d, J = 8.06, 2H), 5.2 (d, J = 3.7 Hz, 1H), 4.0 (q, J = 6.7, 14.3 Hz, 2H), 3.1 (s, 3H), 2.5 (s, 3H), 1.1 (t, , J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.4, 152.8, 150.9, 143.4, 131.3, 128.3, 120.3, 101.9, 59.5, 51.9, 29.7, 15.9, 13.9 ppm.

Typical procedure for synthesis of compound 1-29 under microwave-assisted conditions in the Presence of Catalyst J.

A mixture of aromatic aldehyde (1 mmol), ethyl acetoacetate or acetylacetone (1 mmol), urea or thiourea (1.5 mmol) and silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride as catalyst (0.02 g) were finely mixed together. The reaction mixture was placed in a screw-capped

vial and irradiated for 3 min with a power of 1200 W. After completion of the reaction and cooling, water (5 mL) was added to the reaction mixture. The crude product containing the catalyst was collected on a Buchner funnel by filtration and heated in boiling ethanol (10 mL). The undissolved catalyst was removed by filtration and washed with hot ethanol. Concentrating the filtrate in vacuum yielded the product. The pure dihydropyrimidin-2(1H)-ones was obtained by recrystallization from hot ethanol. The isolated catalyst was dried at 80 °C overnight and was reused in the next runs without further purification. The yields and time reaction of the products are reported in **Table 3.**

Acknowledgments

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