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# Fe<sub>3</sub>O<sub>4</sub> nanoparticles stabilized on mmt: An efficient magnetically recoverable heterogeneous Catalyst for the synthesis of Dihydropyrimidinones

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## ABSTRACT

 $Fe_3O_4$  magnetic nanoparticles supported on modified montmorillonite clay, were utilized for catalytic performance for the synthesis of different 3,4-dihydropyrimidin-2(1H)-ones under green reaction condition. The modification of Montmorillonite K10 clay was carried out with HCl under controlled conditions for generating a high surface area porous matrix which acts as support for the in situ generation of Fe<sub>3</sub>O<sub>4</sub>-nanoparticles. The synthesized nanocomposite material was characterized by powder XRD, TEM, N<sub>2</sub> adsorption-desorption and XPS analysis. The catalysts can be recycled and reused several times without significant loss of their catalytic activity.

Keywords: Modified montmorillonite, Fe<sub>3</sub>O<sub>4</sub>@mmt, 3,4-dihydropyrimidin-2(1H)-ones, Heterogeneous catalyst.

#### INTRODUCTION

Environmentally benign, efficient, economical and green synthesis of nanocatalysts as well as green conditions during catalysis has become more important to address industrial and environmental concerns [1-4]. In this connection, various multicomponent reactions have been designed for the synthesis of different complex molecules through a combination of three or more starting materials under one-pot conditions [5-6]. Among them, one-pot three component condensation reactions of ethylacetoacetate, aldehydes and urea known as Biginelli reaction is one of the best examples where Dihydropyrimidinones (DHPMs) are obtained as main product. Pyrimidinones or Dihydropyrimidinones (DHPMs) are versatile intermediates in various nitrogen containing organic compounds having pharmaceutical and therapeutic activities such as anticancer, anti-inflammatory, antibacterial, antifungal activities [7-16]. The clinically important antiretroviral agents like AZT, DDC and DDI possess the pyrimidine scaffold [7-9]. Some marine natural products such as the alkaloid Batzlladine B are found to be potent HIV gp-120-CD4 inhibitors which contain the dihydropyrimidine-5-carboxylate as a sole unit [11-13]. The Biginelli reaction involves one-pot three component condensation of  $\beta$ -ketoester, aldehyde and urea to give dihydropyrimidinone derivative [16]. One major drawback of this reaction, however, is the low to moderate yield that is often encountered when substituted aromatic or aliphatic aldehyde is used [17-18]. In recent years, various homogeneous and heterogeneous catalysts were developed for efficient synthesis of dihydropyrimidinones [16-29]. Although both homogeneous and heterogeneous catalysts were used in this reaction, heterogeneous catalysts have more advantages than homogenous ones, because of facile separation and reusability of the catalyst and simple isolation of the product.

Moreover, due to stringent and growing environmental regulations, the chemical industry needs the development of ecofriendly and sustainable synthetic methods [1, 6]. The strategy of magnetic separation of the catalysts attracted much attention over filtration or centrifugation as it prevents the loss of catalyst. Herein, we have reported a well-defined heterogeneous catalytic system by preparing  $Fe_3O_4$  magnetic nanoparticles supported on modified montmorillonite clay and their catalytic activities for the one pot synthesis of Dihydropyrimidinones (DHPMs). Montmorillonite K10 clay is environmentally benign, cheap, which is purchased from M/S Sigma Aldrich, USA. The K10 clay was modified by treatment with mineral acid (HCl) under controlled conditions to generate a matrix having high surface area and contain micro-and mesopores. The modified montmorillonite clay acts as a support for the *in situ* generation of Fe<sub>3</sub>O<sub>4</sub>-manoparticles (Fe<sub>3</sub>O<sub>4</sub>@mmt). Fe<sub>3</sub>O<sub>4</sub>@mmt catalyses the one pot three component condensation of aldehyde,  $\beta$ -ketoester (or  $\beta$ -diketone) and urea (or substituted urea) to give the Dihydropyrimidinones (DHPMs) (85 - 98% yield) with 100% selectivity under mild reaction condition.

#### **EXPERIMENTAL SECTION**

**Material:** Montmorillonite K-10, FeCl<sub>3</sub>, FeCl<sub>2</sub>. 4H<sub>2</sub>O were purchased from M/S Sigma Aldrich, USA. NH<sub>3</sub> solution was purchased from Merck Chemicals. All aldhydes, urea and active methylene compounds (ethyacetoacetate, acetylacetone) were purchased from M/S Sigma Aldrich. All the chemicals were used without further purification.

**Support preparation:** Montmorillonite K10 (10 g) was dispersed in 200 ml 2M HCl and refluxed for 2 hour. After cooling, the supernatant liquid was discarded and the activated montmorillonite was repeatedly washed with deionised water until no Cl ions could be detected by the AgNO<sub>3</sub> test. The activated clay was dried in air oven at  $50^{\circ}$ C over for 12 h and the solid product was designated as modified montmorillonite.

**Catalyst preparation:** 0.5 g of modified montmorillonite was dispersed in 50 ml double distilled water and 0.5 mmol of FeCl<sub>2</sub>.4H<sub>2</sub>O and 1 mmol FeCl<sub>3</sub> were added to this solution. The solution mixture was vigorously stirred and degassed with nitrogen. After that 10 ml of aqueous NH<sub>3</sub> solution was added drop wise to the stirring solution. The solution became black immediately and stirring continued for another 1 h. The black reaction product was recovered and washed with deionised water several times and then dried in a desiccators for 15 h. The composite was designated as Fe<sub>3</sub>O<sub>4</sub>@mmt.

#### General procedure for the one-pot synthesis of Dihydropyrimidinones (DHPMs):

Aldehyde (2 mmol),  $\beta$ -ketoester (or  $\beta$ -diketone) (2 mmol), urea (or substituted urea) (3 mmol), 20 mg catalyst (Fe<sub>3</sub>O<sub>4</sub>@mmt) and 5 ml ethanol were taken in a 25 ml round bottom flask and reaction mixture was refluxed at 78 °C for stipulated time period. The progress of the reactions was monitored by TLC. After completion of the reaction, the solid catalyst was recovered magnetically with the help of a magnetic needle retriever. Then the soluble product was evaporated to dryness under reduced pressure to obtain a solid residue. It was finally recrystallized to give the pure product. The isolated pure product was characterized by <sup>1</sup>H and <sup>13</sup>C NMR and CHNS analysis and all gave satisfactory results.

#### **RESULTS AND DISCUSSION**

**Characterization of Support and Catalyst:** The characterization of modified montmorillonite was thoroughly carried out with the help of different sophisticated analytical instruments like Powder-XRD, N<sub>2</sub> adsorption-desorption etc. The parent montmorillonite K10 exhibited an intense basal reflection at  $7.07^{\circ}$  20 corresponding to a basal spacing of 12.6 Å (Fig. 1 a). During acid activation, the reflection intensity decreased with time and no basal reflection was seen after 2h acid activation. The modified montmorillonite contained micro- (< 2 nm) and mesopores (> 2 nm), a high specific surface area of 416 m<sup>2</sup>/g and a large specific pore volume of ~ 0.65 cm<sup>3</sup>/g (Table 1).

	Specific Surface Area $(m/g)$	Specific Pore <sup>3</sup> Volume (c m /g)
Modified montmorillonite	416	0.65
Fe <sub>3</sub> O <sub>4</sub> @mmt (fresh)	308	0.51
Fe <sub>3</sub> O <sub>4</sub> @mmt (after 1 <sup>st</sup> run)	265	0.42
Fe <sub>3</sub> O <sub>4</sub> @mmt ( after 2 <sup>nd</sup> run)	225	0.36
Fe <sub>3</sub> O <sub>4</sub> @mmt (after 3 <sup>rd</sup> run)	204	0.32

Table 1: Surface properties of Fe<sub>3</sub>O<sub>4</sub>@mmt and modified montmorillonite



Fig. 1: (a) Powder XRD pattern of Parent and Modified Mont, (b) Powder XRD pattern of Fe<sub>3</sub>O<sub>4</sub>@mmt, (c) TEM image of Fe<sub>3</sub>O<sub>4</sub>@mmt, (d) Representative HRTEM image and corresponding SAED pattern (inset) of Fe<sub>3</sub>O<sub>4</sub>@mmt, (e) XPS spectrum of Fe<sub>3</sub>O<sub>4</sub>@mmt

The evidence for the formation of  $Fe_3O_4$ -nanoparticles was obtained from powder XRD analysis. The powder XRD suggests face centred cubic lattice (fcc) type arrangement of Fe<sub>3</sub>O<sub>4</sub>-nanoparticles. The seven reflections were assigned to the (111), (220), (311), (400), (422), (511) and (440) diffraction of a cubic face-centered (fcc) lattice of Fe<sub>3</sub>O<sub>4</sub> (Fig. 1 b) [30]. TEM image (Fig.1 c) shows the Fe<sub>3</sub>O<sub>4</sub> nanoparticles form a magnetic nanocluster with particle size below 20 nm. The HRTEM (Fig. 1 d) and SAED (Selected Area Electron Diffraction) pattern [Fig. 1d(inset)] of Fe<sub>3</sub>O<sub>4</sub>-nanoparticles corresponds to crystalline nature of the magnetic nanoparticles. XPS experiment was performed to determine the chemical state of iron in the nanocomposite material. Figure 1(e) gives the broad and narrow scan XPS spectra of  $Fe_3O_4$  nanoparticles. For Fe<sub>3</sub>O<sub>4</sub>, the peaks at 710.8 eV and 724.1 eV are the characteristic doublets of  $Fe_{2p_{3/2}}$  and  $Fe_{2p_{1/2}}$  from iron oxide. The peak at 529.4 is assigned to O1s [Fig. 1e (inset)]. No satellite peak at 719 eV is observed indicating  $Fe^{3+}$  in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. This confirms that the peaks shift to high binding energy and broaden for Fe<sub>3</sub>O<sub>4</sub> due to the appearance of  $Fe2p_{3/2}$  and  $Fe2p_{1/2}$  and it does not contain any impurity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> [31-32]. From surface area study, it is observed that there is an appreciable decrease of the specific surface area and the specific pore volume after supporting Fe<sub>3</sub>O<sub>4</sub>-nanoparticles (Table1), but it exhibits a similar type of isotherm and hysteresis loop to that of modified montmorillonite (Fig. 2). This might be due to clogging of some pores by Fe<sub>3</sub>O<sub>4</sub>-nanoparticles. The Fe contents in Fe<sub>3</sub>O<sub>4</sub>@mmt as analyzed by ICP-AES, reveals the presence of 16.47 mg of Fe per 100 mg Fe<sub>3</sub>O<sub>4</sub>@mmt catalyst.



Fig. 2: (a) N<sub>2</sub> adsorption/desorption isotherm and (b) BJH pore size distribution curve of Modified Mont. and Fe<sub>3</sub>O<sub>4</sub>@mmt

**Catalytic activity:** In order to introduce an efficient, robust and eco-friendly heterogeneous catalyst under mild conditions, the synthesized  $Fe_3O_4@$ mmt was utilized as catalyst precursor for the well-known Biginelli reaction. A series of three-component reactions were carried out using benzaldehyde, urea and ethylacetoacetate ( $\beta$ -ketoester) as the model substrates to determine the best reaction condition (i.e. solvent, reaction time etc.) which is required to afford excellent yields of DHPMs. The reaction without solvent was the first choice, where about 60% of the DHPMs product was obtained in 3 h in presence of  $Fe_3O_4@$ mmt catalyst. The use of water as a solvent increased the yield of the desired product to 68% in 3 h. When ethanol was used as a solvent at 78°C, surprisingly, the yield of the product increased to 98% in 2 h. The use of other solvents was also tested, but no encouraging results were obtained (Table 2). Therefore, ethanol is used as the solvent of for the synthesis of DHPMs by considering its high yield and selectivity. The results of the reactions are represented in Table 3. A control reaction was carried out to test the requirement of a catalyst by stirring the model substrates in the absence of the catalyst. Only 6% yield of the product was obtained in 5 h. The use of only modified clay as a catalyst gave only 55% yield in 2 h.

The effect of various catalyst amounts was also studied to optimize catalyst amount for the synthesis of DHPMs. The effect of catalyst amount was studied with 5, 10, 15, 20 and 25 mg of the catalyst in the model reaction (Table 2). With increased in the amount of catalyst, the yield of the reaction increased. But, almost same yields were observed for 20 and 25 mg catalyst which was maximum for the model reaction. Thus, all the reactions were performed using 20 mg catalyst (contains 0.059 mmol Fe).

Sl no	Solvent	Catalyst amount (mg)	Temperature ( <sup>0</sup> C)	Time (h)	Isolated Yield (%)			
I	Effect of solvent:							
1	Solvent free	20	90	3	60			
2	Water	20	90	3	68			
3	Methanol	20	65	3	66			
4	Ethanol	20	78	2	98			
5	DMF	20	110	3	28			
6	Acetonitrile	20	80	3	35			
Effect of catalyst amount								
7	Ethanol	5	78	2	65			
8	Ethanol	10	78	2	76			
9	Ethanol	15	78	2	86			
10	Ethanol	20	78	2	98			
11	Ethanol	25	78	2	98			

Table 2: Effect of solvent and Fe<sub>3</sub>O<sub>4</sub>@mmt catalyst

\*\*Reaction conditions: Benzaldehyde (2 mmol), Ethylacetoacetate (2 mmol), Urea (3 mmol), and solvent (5 ml).

The presence of electron donating or withdrawing group on the aldehyde has no significant effect on the yield of the product (entry S1, S2 and S4) but aliphatic aldehyde (entry S9, S10) gives slightly lower yield than aromatic aldehyde (S1, S2 in Table 3). A variation in the reaction was done by using substituted urea such as 1,3-dimethyl urea, thiourea and acetylacetone (\beta-diketone) instead of ethylacetoacetate for the synthesis of different DHPMs (Table 3). The use of thiourea and 1,3-dimethyl urea as substrate also run the reaction smoothly but thiourea gives slightly lower yield of product compared to urea and 1,3-dimethyl urea (entry S1, S14 and S15). Both the active methylene compound i.e. ethylacetoacetate and acetylacetone run the reaction without any difficulty (entry S1 and S18). All the reactions give a very good yield (85-98%) with 100% selectivity. One of the advantages of our catalytic system is that the separation of the catalyst from the product is done simply by magnetic separation. The products were purified by recrystallization. The recyclability of our catalyst was investigated in the synthesis of DHPMs (Table 3). The catalyst was recovered by magnetic separation technique after each experiment. The recovered catalyst was washed with acetone, dried in a desiccator and reused directly with fresh reaction mixture without further purification for the desired DHPMs synthesis upto the 4<sup>th</sup> run and showed only a slight decrease in activity (Table 3). The recovered catalyst was further investigated through N<sub>2</sub> adsorption-desorption, HRTEM analysis. The specific surface areas of the recovered catalysts decrease compared to the fresh catalyst with surface area of 308 m<sup>2</sup>g<sup>-1</sup> (Table 1) which may be due to blockage of the pores by the reactant molecules after each reaction. In the HRTEM analysis of the recovered catalyst (after 3rd run), it was found the sizes of Fe<sub>3</sub>O<sub>4</sub> nanoparticles are still below 20 nm (Fig. 3).



Fig. 3: HRTEM image of recovered Fe<sub>3</sub>O<sub>4</sub>@mmt clay after 3<sup>rd</sup> run

	O	o o		2 mmt
	H <sub>2</sub> N <sup>N</sup> NH <sub>2</sub>	+	Ethanc	a, 78⁰C, 2 h
Entry	(Urea/ Substituted urea)	(Ethylacetoacetate/ Acetylacetone)	Aldehyde	H Product Yield <sup>*</sup> (%)
S1	H <sub>2</sub> N NH <sub>2</sub>		СНО	
<u>S2</u>				
\$3			сно	
S4			CHO CH <sub>3</sub>	CH <sub>3</sub> NH NH NH 98
S5	0 H <sub>2</sub> N NH <sub>2</sub>		СНО	
S6	H <sub>2</sub> N NH <sub>2</sub>		СНО	
S7	$H_2N $ $NH_2$		CHO	Pr NH NH NH 95
<b>S</b> 8	H <sub>2</sub> N NH <sub>2</sub>		СНО	
<b>S</b> 9			0	

Table 3: Fe $_{3}O_{4}@mmt$  catalyzed three-component condensation reaction to synthesize DHPMs \*\*

S10	$H_2N M_2$	0~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		
			но-	
<b>S</b> 11	$H_2N M_2$			
S12	$H_2N MH_2$	0		
\$13	$H_2N$ $NH_2$	0	NH NH NH NH NH NH NH NH NH NH NH NH NH N	1
S14		СНО	NH NH NH S 94	
S15		СНО		
S16		сно		
S17	H <sub>2</sub> N NH <sub>2</sub>	CHO OCH <sub>3</sub>		
S18	$H_2N$ $NH_2$	СНО		
S19				
S20				
S21		СНО		



<sup>\*</sup>Yields are isolated products based on the aldehyde after recrystallization.

\*\*Reaction conditions: Aldehyde (2 mmol), Ethylacetoacetate (2 mmol), Urea (3 mmol), Catalyst (20 mg, contains 0.059 mmol Fe) and Ethanol (5 ml); Refluxing temp. 78°C, Time 2 h.

A hot filtration test was carried out to investigate whether any leaching of  $Fe_3O_4$  occurs during the course of the reaction. Here, the three component condensation reaction of benzaldehyde, ethylacetoacetate and urea was carried out in ethanol at 78°C for 1 h using our  $Fe_3O_4$ @mmt catalyst. At this stage, the yield of the product is 64%. The  $Fe_3O_4$ @mmt catalyst was the filtered off in hot conditions and with the filtrate the reaction was continued for another 1 h. But no further increase in the yield of the product was observed. Again, the Fe content in  $Fe_3O_4$ @mmt before the catalytic reaction was 16.47 mg Fe per 100 mg  $Fe_3O_4$ @mmt catalyst. After 3<sup>rd</sup> run, Fe content in the catalyst was found to be 16.43 mg Fe per 100 mg catalyst which was marginally decreased. Thus, the catalyst maintains its heterogeneous nature and no leaching of  $Fe_3O_4$  occurs during the course of the reaction. For comparison, we have screened wide range of iron catalysts known in the literature for the reaction of urea, ethylacetoacetate and benzaldehyde (Table 4) and the result showed that our protocol is better than other previous protocols.

Catalyst	Solvent	Temperature	Time	Isolated Yield	Reference
		$(^{0}C)$	(h)	(%)	
FeCl <sub>3</sub>	Ethanol	78	5	38	
FeCl <sub>2</sub> .4H <sub>2</sub> O	Ethanol	78	5	31	
Nano-Fe <sub>3</sub> O <sub>4</sub>	Ethanol	78	5	48	
γ-Fe <sub>2</sub> O <sub>3</sub> -SO <sub>3</sub> H	Ethanol	60	5	91	[29]
Fe <sub>3</sub> O <sub>4</sub> @SBA15	Ethanol	100	6	85	[16]
Fe <sub>3</sub> O <sub>4</sub> @mmt	Ethanol	78	2	98	Present work

Table 4: Screening of different iron catalyst for the reaction of urea, ethylacetoacetate and benzaldehyde

The possible reaction pathway for the synthesis of DHPMs catalysed by  $Fe_3O_4@mmt$  is given in Scheme 1. The electrophilicity of the carbonyl carbon of the active methylene compound (ethylacetoacetate) increases due to coordination with the highly porous  $Fe_3O_4@mmt$  catalyst. After that the aromatic aldehyde and ethyl acetoacetate undergo aldol type condensation to offer the corresponding aldol-type product. Then the urea molecule coordinates with aldol type product through one of its N-atom and undergoes 1,4-addition reaction of urea.



Scheme 1: Proposed mechanism for the synthesis of DHMPs

This leads to the aldol type intermediate (A) to generate ureides (B) that ultimately cyclize to give the desired product and the catalyst is regenerated. The theoretical byproduct obtained from the reaction is only water. The regenerated catalyst continues the catalytic cycles till the completion of the reaction.

### CONCLUSION

In conclusion, we have developed an economical and practical protocol for the synthesis of DHPMs through an  $Fe_3O_4@mmt$  catalyzed three-component condensation reaction of Aldehyde,  $\beta$ -ketoester (or  $\beta$ -diketone) and Urea (or substituted urea) using ethanol as solvent. The specific surface area and the pore size of Montmorillonite K10 were tuned by controlled acid activation. Further, the catalysts retained its magnetic property after several runs and were reused for new batch of reactions (upto 4<sup>th</sup> run) without significant loss of their activity under the same conditions. The operational simplicity, mild reaction condition and robustness of the catalyst, make it attractive for the large scale synthesis of biologically active dihydropyrimidinones.

## <sup>1</sup>H and <sup>13</sup>C NMR data along with C, H, N percentage of some of the products:

#### S1. Ethyl-1,2,3,4-tetrahydro-6-methyl-2-oxo-4-phenylpyrimidine-5-carboxylate

<sup>1</sup>H NMR (300 MHz, DMSO-d6):  $\delta$  1.09 (t, 3H),  $\delta$  2.25 (s, 3H),  $\delta$  3.94-4.02 (q, 2H),  $\delta$  5.15 (d, 1H),  $\delta$  7.22-7.35 (m, 5H),  $\delta$  7.74 (s, 1H),  $\delta$  9.2 (s, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-d6):  $\delta$  14.53, 18.24, 54.41, 59.66, 99.71, 126.70, 127.73, 128.86, 145.31, 148.82, 152.50, 165.80; C: 64.60%, H: 6.18%, N: 10.76%.

#### S2. Ethyl-1,2,3,4-tetrahydro-6-methyl-4-(4-nitrophenyl)-2-oxopyrimidine-5-carboxylate

<sup>1</sup>H NMR (300 MHz, DMSO-d6):  $\delta$  1.09 (t, 3H),  $\delta$  2.50 (s, 3H),  $\delta$  3.95-4.04 (q, 2H),  $\delta$  5.26 (d, 1H),  $\delta$  7.49-7.52 (m, 1H),  $\delta$  7.90 (s, 1H),  $\delta$  8.15-8.44 (m,3H),  $\delta$  9.37 (s, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-d6):  $\delta$  14.50, 18.33, 54.12, 98.62, 124.75, 128.12, 131.11, 147.16, 149.86, 152.45, 165.51, 192.83; C: 55.10%, H: 4.95%, N: 13.75%.

#### S3. Ethyl-1,2,3,4-tetrahydro-4-(4-methoxyphenyl)-6-methyl-2-oxopyrimidine-5-carboxylate

<sup>1</sup>H NMR (300 MHz, DMSO-d6):  $\delta$  1.12 (t, 3H),  $\delta$  2.23 (s, 3H),  $\delta$  3.71 (s, 3H),  $\delta$  3.94-4.01 (q, 2H),  $\delta$  5.09 (d, 1H),  $\delta$  6.86-6.89 (m, 2H),  $\delta$  7.12-7.15 (m, 2H),  $\delta$  7.68 (s, 1H),  $\delta$  9.16 (s, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-d6):  $\delta$  14.55, 18.21, 53.78, 55.49, 59.62, 100.02, 114.14, 127.86, 137.49, 148.47, 152.64, 158.89, 165.83; C: 62.06%, H: 6.23%, N: 9.63%.

S4. Ethyl-1,2,3,4-tetrahydro-6-methyl-2-oxo-4-p-tolylpyrimidine-5-carboxylate

<sup>1</sup>H NMR (300 MHz, DMSO-d6): δ 1.11 (t, 3H), δ 2.25 (s, 3H), δ 2.50 (s, 3H), δ 3.93-4.0 (q, 2H), δ 5.10 (s, 1H), δ 6.86-6.89 (m, 2H), δ 7.11 (m, 4H), δ 7.69 (s, 1H), δ 9.16 (s, 1H); <sup>13</sup>C NMR (75 MHz, 10.15) (s, 10.15)

DMSO-d6): δ 14.50, 18.18, 21.05, 54.07, 59.71, 99.96, 126.60, 129.36, 136.93, 142.29, 148.56, 152.74, 165.87; C: 65.70%, H: 6.61%, N: 10.19%.

S5. Ethyl 1,2,3,4-tetrahydro-4-(2-hydroxyphenyl)-6-methyl-2-oxopyrimidine-5-carboxylate <sup>1</sup>H NMR (300 MHz, DMSO-d6):  $\delta$  1.19 (t, 3H),  $\delta$  1.69 (s, 3H),  $\delta$  4.15 (q, 2H),  $\delta$  4.43 (s, 1H),  $\delta$  5.38 (s, 1H),  $\delta$  6.72-7.12 (m, 4H),  $\delta$  7.14 (s, 1H),  $\delta$  7.57 (s, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-d6):  $\delta$  14.54, 24.48, 44.1, 48.1, 61.03, 83.61, 117.06, 121.0, 125.92, 129.13, 129.83, 151.15, 155.07, 168.92; C: 60.86%, H: 5.82%, N: 10.12%.

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