Gallium(III) Triflate: an efficient catalyst for solvent-free synthesis of dihydropyrimidinone derivates

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Dihydropyrimidione derivates were successfully synthesized by Gallium(III) triflate($Ga(OTf)_3$) catalyzed Biginelli-type reaction using ethyl acetoacetate (or cycloketone) , aldehyde and urea as reactant, respectively. The samples were characterized by ^1H NMR (400 MHz), HRMS, and Electrothermal Digital Melting-point. The results showed that the dihydropyrimidione derivates could be effectively catalyzed by using $Ga(OTf)_3$ to give the corresponding adducts in good to excellent yields under solvent-free condition.

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Keywords: $Ga(OTf)_3$, Biginelli reaction, Dihydropyrimidinone derivates

1. Introduction

The synthesis of 3, 4-dihydropyrimidin-2(1H)-ones (DHPMs) has gained much attention in organic and medicinal chemistry. DHPMs have interesting pharmacological properties, such as efficacy as calcium channel modulators and α_{1a} adrenoaceptor-selective antagonists [1]; use as an anticancer drug capable of inhibiting kinesin motor protein [2]; Rho-kinase inhibitors [3] and anti-HIV activity in some marine natural products, containing the DHPM skeleton. The first report was by the Italian chemist Pietro Biginelli in 1893 [4]. In the past several years, many improvements in the process using Lewis acids such as $BF_3.OEt_2$ [5], $Zr(NO_3)_3$ [6], $BiCl_3$ [7], $FeCl_3{\cdot}6H_2O$ [8], $Yb(OTf)_3$ [9], $Cu(OTf)_2$ [10], $InBr_3$ [11], I_2 [12], $ZrOCl_2$ [13], $CaCl_2$ [14], and LiBr [15] etc.

$Ga(OTf)_3$ is a water-tolerant strong Lewis acid catalyst, which has been used in organic reactions such as Beckmann rearrangement [16], Thiolysis reaction [17], Friedel – Crafts reactions [18], synthesis of Heterocycles [19], dehydration of aldoximes [20], aqueous asymmetric Mukaiyama aldol reactions [21], reduction of ketones [22], constructions of fused-bicyclolactones [23], reaction of 3-Hydroxyoxindolesand [24] and Multicomponent Reactions [25].

Herein, we report a new application of gallium(III) triflate catalyst for neat Biginelli-type reaction. Compared to other methods reported in the literature, gallium(III)-promoted reactions are straightforward, give good to excellent yields, expand the reactant to cycloketones, and lead to the discovery of a novel transformation for dihydropyrimidinones in solvent-free condition.

2. Experimental

2.1 General procedure for the synthesis of DHPMs

To a mixture of ethyl acetoacetate (or cycloketone) (1mmol), aldehyde (1mmol) and urea (1.2mmol) , $Ga(OTf)_3$ (10mol%) was added. The mixture was stirred at 90℃ for appropriate time. After reaction completed (TLC analysis), water was added and the product was extracted with ethyl acetate. The organic layer was dried (Na_2SO_4) and evaporated, the residue was recrystallized by methanol or ethanol to obtain pure products.

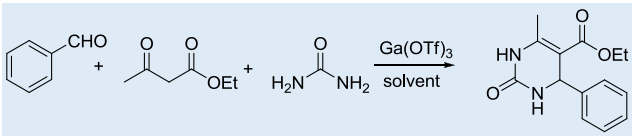
2.2 Characterization

Melting points were recorded on an electrothermal digital melting-point apparatus and are uncorrected. ^1H NMR (400 MHz) spectra were recorded on a Varian Mercury MHz spectrometer in $CDCl_3$ or DMSO-d_6. High-resolution mass spectra (HRMS) were obtained using a GCT-TOF instrument

3. Results and discussion

Initially, we explored the typical Biginelli reaction of ethyl acetoacetate, benzaldehyde and urea (Scheme 1). We have tried varieties of reaction conditions with the Biginelli model reaction using $Ga(OTf)_3$ as a catalyst. The results are

summarized in Table 1. It seems that EtOH is a better solvent (85%) than other solvents, such as toluene (25%), CH_3CN (45%). The best result was achieved by carrying out the reaction at 90℃ in the presence of catalytic amount (10mol%) of $Ga(OTf)_3$ without any solvent. And the yield became lower (90%) when the catalytic amount dropped to 5mol%.



Scheme 1 $Ga(OTf)_3$ catalyzed the typical Biginelli reaction

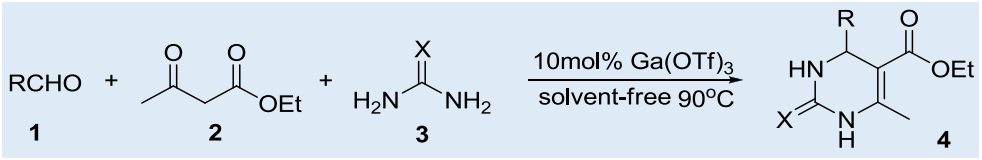
Table 1. Effect of reaction conditions on the $Ga(OTf)_3$ catalyzed the typical Biginelli reaction

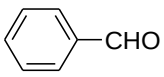
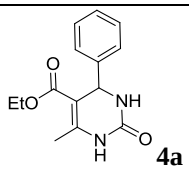
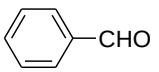
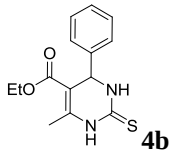
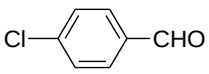
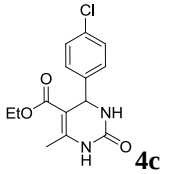
Entry [a]	Solvent	Amount of $Ga(OTf)_3$ (mol%)	Reflux time/h	Yield [b] /%
1	THF	10	10	trace
2	Toluene	10	10	25
3	CH_2Cl_2	10	10	trace
4	CH_3CN	10	10	45
5	EtOH	10	10	85
6	Solvent-free	10	0.5	98
7	Solvent-free	5	1	90

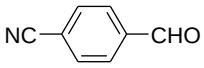
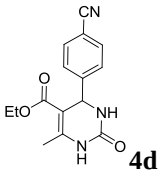
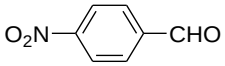
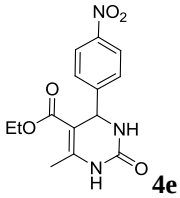
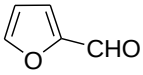
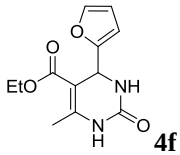
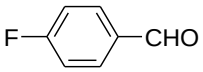
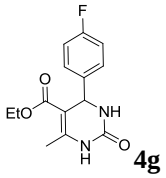
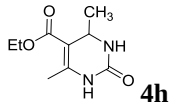
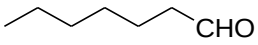
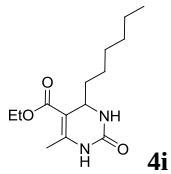
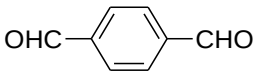
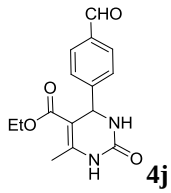
[a] Benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol), $Ga(OTf)_3$ (10 mol%) were used
[b] Isolated yield

Under the optimized conditions described above, a series of aldehydes were used to evaluate the scope of $Ga(OTf)_3$ catalyzed typical Biginelli reaction (Table 2). Aromatic aldehydes containing either electron-donating or electron-withdrawing substituents or aliphatic aldehydes all produced well. And in most case, the reaction took place smoothly to give the corresponding DHPMs in good to excellent yields and the reaction time is shorter.

Table 2. $Ga(OTf)_3$ catalyzed the typical Biginelli reaction under solvent-free condition



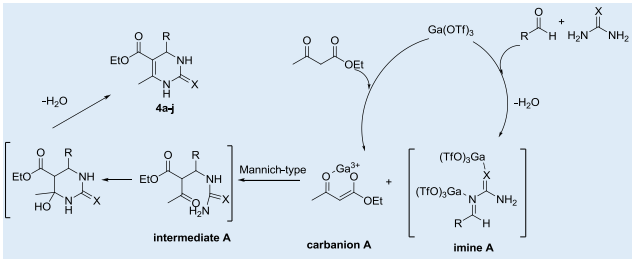
Entry	Aldehyde	X	Time (h)	Yield [a] (%)	Product [c]
1		O	0.3	98	 **4a**
2		S	0.5	91	 **4b**
3		O	0.5	95	 **4c**

4		O	0.3	94	 **4d**
5		O	0.25	96	 **4e**
6		O	0.75	90	 **4f**
7		O	0.5	92	 **4g**
8	CH_3CHO [b]	O	0.5	84	 **4h**
9		O	1	82	 **4i**
10		O	0.5	83	 **4j**

. [a] Isolated yield; [b] From 40% acetaldehyde solution; [c] All compounds were characterized by ^{1}H NMR and HRMS spectra

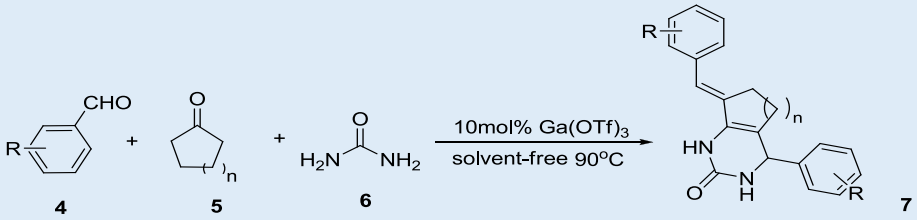
According to the mechanism suggested by Folkers, Johnson and Kappe [26-27], we thought the reaction may proceed through imine formation from the aldehyde and urea (or thiourea), which is activated by $Ga(OTf)_3$. Then the addition of the carbanion A derived from β-keto ester to the imine A to form intermediate A and followed by cyclodehydration and dehydration to afford 3, 4-dihydropyrimidin-2(1H)-ones (Scheme 2)

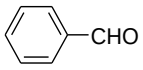
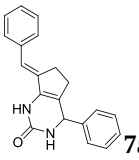
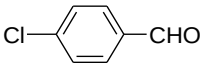
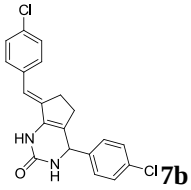
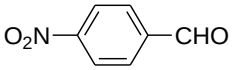
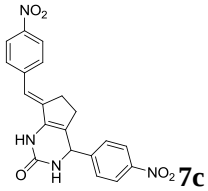
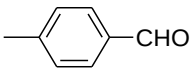
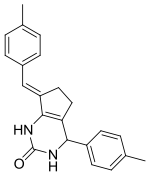
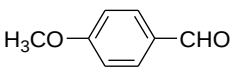
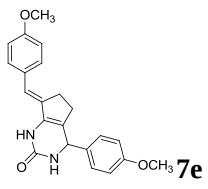
Scheme 2. Proposed mechanism for $Ga(OTf)_3$ catalyzed the Biginelli reaction under solvent-free condition

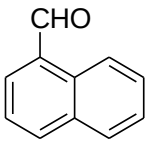
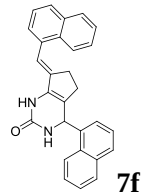
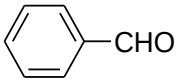
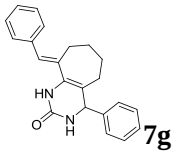


The good results above (Table 2) prompted us to explore new substrate for the extension of the versatile Biginelli reaction by using other substituted 3, 4-dihydropyrimidin-2(1H)-ones. We assumed whether cycloketones can be used, instead of β-keto-ester. Pan etc have reported one-pot multicomponent Biginelli reactions between cycloalkanones, urea or thiourea, and aldehydes [28]. Fortunately, we found that only 10mol% $Ga(OTf)_3$ can also efficiently catalyzed this reaction under solvent-free condition to give exciting results (Table 3). All the product was characterized by ^{1}HNMR and HRMS spectra. According to the experimental results, a possible mechanism for the Biginelli-type reaction was proposed in (Scheme 3). It also came through a mannich-type addition route to form intermediate B. The intermediates B created the target moleculars through the processes of cyclodehydration, dehydration and urea elimination.

Table 3. $Ga(OTf)_3$ catalyzed the Biginelli-type reaction of cycloketone, aldehydes and urea under solvent-free condition

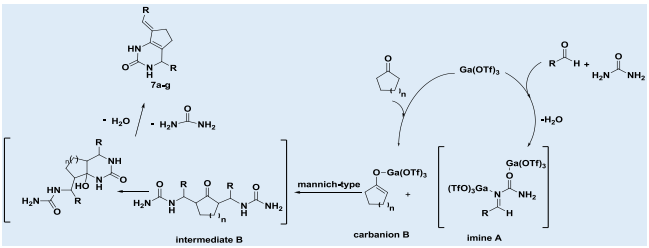


Entry	Aldehyde	n	Time (h)	Yield [a] (%)	Product [b]
1		1	0.5	94	 **7a**
2		1	0.75	88	 **7b**
3		1	0.25	86	 **7c**
4		1	0.75	88	 **7d**
5		1	0.5	89	 **7e**

6		1	1	86	 **7f**
7		3	1	89	 **7g**

[a] Isolated yield; [b] All compounds were characterized by ^{1}H NMR and HRMS spectra

Scheme 3. Proposed mechanism for $Ga(OTf)_3$ catalyzed the Biginelli-type reaction in solvent-free condition



4. Conclusion

In conclusion, We found that 10mol% $Ga(OTf)_3$ could effectively catalyzed the Biginelli-type reaction of ethyl acetoacetate or cycloketone, aldehyde and urea under solvent-free condition which were heated to 90℃. It's a new catalyst in the formation of DHPM skeletons. The neat reaction conditions, shorter reaction times and high yields are the great advantage of the method

Spectral data of products

2,2-Dimethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepine (**4a**): mp. 150–152℃. (Lit. [9] 150– 152℃). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.81-7.62 (m, 14H, ArH), 3.51 (s, 1H, NH), 2.96-3.15 (d, 2H, J = 13.2 Hz), 1.76 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100M Hz): δ 168.1 (C=N), 147.0, 140.5, 139.9, 130.2, 127.8, 128.5, 127.5, 126.7, 124.9, 122.1, 121.9, 74.2, 42.5, 30.3.

Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4b**): mp 205-206℃ (lit.[8] 208-210℃) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (s, 1H, NH), 7.27-7.25 (m, 5H, ArH), 5.37 (s, 1H, NH), 4.06-4.05 (d, 2H, J = 0.4Hz, CH_2O), 2.34 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), HRMS: *m/z* (%) calcd for $C_{14}H_{16}N_2O_2S$ (M^+) 276.0932, found 276.0940 (M^+, 84.33)

2,2,4-Trimethyl-2,3-dihydro-1H-1,5-benzodiazepine (**4c**): mp. 136–138℃ (Lit. [9] 137–138℃). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.11-7.14 (m, 1H, ArH), 6.96-7.01 (m, 2H, ArH), 6.72-6.73 (m, 1H, ArH), 2.96 (s, 1H, NH), 2.35 (s, 3H, CH_3), 2.21 (s, 2H, CH_2), 1.34 (s, 6H, $2CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.1 (C=N), 141.1, 138.3, 127.1, 125.9, 122.5, 122.2, 68.9, 45.4, 30.8, 30.2.

4-(4-Chlorophenyl)-2,2-dimethyl-2,3-dihydro-1H-1,5-benzodiazepine (**4d**): mp. 147–149℃ (Lit. [8] 143–144℃). ^{1}H NMR ($CDCl_3$, 400MHz): δ 6.84-7.53 (m, 12H, ArH), 3.45 (s, 1H, NH), 2.88-3.10 (dd, 2H, J_1 = 12 Hz, J_2 = 12.8 Hz), 1.74(s, 3H, CH_3).

2,2-Dimethyl-4-(4-nitrophenyl)-2,3-dihydro-1H-1,5-benzodiazepine (**4e**): mp. 154–155℃ (Lit. [12] 156–158℃). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.90-8.07 (m, 12H, ArH), 3.63 (s, 1H, NH), 2.99-3.31 (m, 2H, CH_2), 1.84 (s, 3H, CH_3). $C_{22}H_{18}N_4O_4$ (402.13) calcd: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.37; H, 4.47; N, 14.01.

2,2-Dimethyl-4-p-tolyl-2,3-dihydro-1H-1,5-benzodiazepine (**4f**): mp. 99–101℃ (Lit. [12] 98–99℃). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.81-7.59 (m, 12H, ArH), 3.52 (s, 1H, NH), 2.95-3.12 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.31 (s, 3H CH_3), 1.74 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.0 (C=N), 144.5, 140.8, 140.5, 136.7, 137.4, 137.2, 129.5, 129.3, 129.0, 127.6, 126.6, 125.7, 122.1, 122.0, 73.9, 43.3, 30.3, 21.8, 21.4.

2,2-Dimethyl-4-(3-nitrophenyl)-2,3-dihydro-1H-1,5-benzodiazepine (**4g**): mp. 164–166℃ (Lit.[8] 151–153℃). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.92-8.48 (m, 12H, ArH), 3.56 (s, 1H, NH), 2.99-3.28 (m, 2H, CH_2), 1.87 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.6 (C=N), 149.6, 148.7, 141.0, 139.8, 137.6, 133.0, 132.4, 130.0, 129.7, 129.4, 127.9, 124.9, 122.9, 122.7, 122.0, 121.3, 104.0, 74.6, 43.3, 37.6, 30.4. HRMS (*m/z*): calcd for $C_{22}H_{18}N_4O_4$ 402.1328, found 402.1295.

Ethyl 4,6-dimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4h**): mp 168-169℃ (lit.[8] 194-195℃) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (s, 1H, NH), 5.71 (s, 1H, NH), 4.44-4.42 (m, 1H, CH), 4.21-4.17 (m, 2H, CH_2), 2.29 (s, 3H, CH_3), 1.30-1.27 (t, 6H, J=7.2Hz, 2×CH_3) HRMS: *m/z* (%)

calcd for $C_8H_{11}N_2O_3$ (M+) 183.0743, found 183.0740 (M^+, 100.00).

Ethyl 4-hexyl-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4i**): mp 205-206℃(lit.[8] 208-210℃) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (brs, 1H, NH), 5.85 (brs, 1H, NH), 4.31 (s, 1H, CH), 4.23-4.14 (m, 2H CH_2O), 2.29 (s, 3H, CH_3), 1.54 (s, 2H, CH_2), 1.27 (*d*, 10H, *J* = 8.8Hz, 5× CH_2), 0.87 (s, 3H, CH_3), HRMS: *m/z* (%) calcd for $C_{14}H_{16}N_2O_2S$ (M^+) 276.0940, found 276.0932 (M^+, 84.33).

Ethyl 4-(4-formylphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4j**): mp 215-216 ℃ (lit.[8] 216-218℃) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.15 (s, 1H, CHO), 8.31 (s, 2H, ArH+NH), 7.67 (s, 1H, ArH), 7.17 (s, 2H, ArH), 5.13 (s, 1H, NH), 3.97 (d, 2H, *J* = 9.2Hz, CH_2), 2.29 (s, 3H, CH_3), 1.09 (t, 3H, *J* = 9.2Hz, CH_3)

7-benzylidene-4-phenyl-3,4,6,7-tetrahydro-1H-cyclopenta[d]pyrimidin-2(5H)-one (**7a**) : mp 236-2387℃ ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.77 (s, 1H, NH), 7.40-7.21 (m, 11H, ArH+CH), 6.63 (s, 1H, NH), 5.15 (s, 1H, CH), 2.83-2.79 (m, 2H, CH_2), 2.38-2.37 (m, 1H, CH), 2.03-1.97 (m, 1H, CH), HRMS: m/z (%) calcd for $C_{20}H_{18}N_2O$ (M^+) 302.1419, found 302.1418 (M^+, 100)

7-(4-chlorobenzylidene)-4-(4-chlorophenyl)-3,4,6,7-tetrahydro-1H cyclopenta[d]pyrimidin-2(5H)-one (**7b**): mp 252-253℃ ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.83 (s, 1H, NH), 7.46-7.27 (m, 9H, ArH+CH), 6.63 (s, 1H, NH), 5.19 (s, 1H, CH), 2.81-2.77 (m, 2H, CH2), 2.43-2.37 (m, 1H, CH), 2.02-1.96 (m, 1H, CH), ^{13}C NMR (100 MHz, DMSO- d_6): δ 28.1, 28.2, 56.6, 79.1, 115.6, 118.6, 128.3, 128.4, 128.5, 129.4, 130.3, 131.9, 135.9, 136.5, 139.9, 142.1, 152.9;

7-(4-nitrobenzylidene)-4-(4-nitrophenyl)-3,4,6,7-tetrahydro-1H-cyclopenta[d]pyrimidin-2(5H)-one (**7c**): mp 280-282℃ ^{1}H NMR (400 MHz, DMSO- d_6): δ 8.87 (s, 1H, NH), 8.35- 8.19 (m, 4H, ArH), 7.65-7.39 (m, 4H, ArH), 6.89-6.77 (m, 2H, NH+CH), 5.39 (s, 1H, CH), 2.91-2.86 (m, 2H, CH_2), 2.26-2.18 (m, 1H, CH), 2.05-2.01 (m, 1H, CH), HRMS: m/z (%) calcd for $C_{20}H_{16}N_4O_5$ (M^+) 392.1121, found 392.1121 (M^+, 83.64)

7-(4-methylidene)-4-(4-methyl)-3,4,6,7-tetrahydro-1H-cyclopenta[d]pyrimidin-2(5H)-one (**7d**): mp 238-239℃ ^{1}H NMR (400 MHz, DMSO- d_6): δ 9.00 (s, 1H, NH), 7.41-7.26 (m, 9H, ArH+CH), 6.92 (s, 1H, NH), 5.20 (s, 1H, CH), 2.84-2.83 (m, 2H, CH_2), 2.45-2.37 (m, 1H, CH), 2.09 (s, 7H, 2 ×CH_3+CH), HRMS: m/z(%) calcd for $C_{22}H_{22}N_2O$ (M^+) 330.1732, found 330.1723 (M^+, 57.81)

7-(4-methoxybenzylidene)-4-(4-methoxyphenyl)-3,4,6,7-tetrahydro-1H-cyclopenta[d]pyrimidin-2(5H)-one (**7e**): mp 250-251℃ ^{1}H NMR (300 MHz, DMSO- d_6): δ 8.64 (s, 1H, NH), 7.26 (d, 2H, J = 8.4Hz, ArH), 7.17 (d, 2H, J= 8.4Hz, ArH), 7.06 (s, 1H, ArH), 6.92 (d, 4H, J = 7.5Hz, ArH+CH), 6.56 (s, 1H, NH), 5.08 (s, 1H, CH), 3.75 (s, 6H, 2×OCH_3), 2.77 (s, 2H, CH2), 2.38-2.33 (m, 1H, CH), 2.02-1.96 (m, 1H, CH), HRMS: m/z(%) calcd for $C_{22}H_{22}N_2O_3$ (M^+) 362.1630, found 362.1626 (M^+, 100)

4-(naphthalen-1-yl)-7-(naphthalen-1-ylmethylene)-3,4,6,7-tetrahydro-1H-cyclopenta[d]pyrimidin-2(5H)-one (**7f**): mp 260-261℃ ^{1}H NMR (300 MHz, DMSO- d_6): δ 9.19 (s, 1H, NH), 8.38- 6.74 (m, 15H, ArH+CH), 7.06 (s, 1H, ArH), 6.04 (s, 1H, NH), 5.28 (s, 1H, CH), 2.79- 2.71 (m, 2H, CH_2), 2.43-2.41 (m, 1H, CH), 1.81-1.73 (m, 1H, CH), HRMS: m/z (%) calcd for $C_{28}H_{22}N_2O$ (M^+) 402.1732, found 402.1726 (M^+, 100)

9-benzylidene-4-phenyl-3,4,6,7,8,9-hexahydro-1H-cyclohepta[d]pyrimidin-2(5H)-one (**7g**): mp 286-287℃ ^{1}H NMR (400 MHz, DMSO- d_6): δ 9.01 (s, 1H, NH), 7.41- 7.24 (m, 11H, ArH+CH), 6.92 (s, 1H, NH), 5.21 (s, 1H, CH), 2.84-2.83 (m, 2H, CH_2), 2.43-2.42 (m, 1H, CH), 2.08 (s, 5H, CH+2CH_2)

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