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A piperidinium triflate catalyzed Biginelli reaction

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ABSTRACT

A piperidinium triflate, 1,1,3,5-tetramethyl-4-oxo-2,6-diphenylpiperidinium triflate, in acetonitrile efficiently catalyzes one synthetic operational construction of biopertinent hydropyrimidines from respective aldehyde, β-dicarbonyl, and urea/thiourea building blocks.

1. Introduction

The one-pot assembly of an aldehyde with β-keto ester and urea pioneered by Biginelli allows the direct formation of hydropyrimidines.[1] Although this enabling technology is appealing because of its simplicity, the demerits, however, associated with this synthetic protocol are represented by the modest yield and/cumbersome method of product isolation. Despite the significant developments,[2] the catalytic one-pot Biginelli reaction for the construction of hydropyrimidine frame works has recently been the subject of numerous investigations since six-membered pyrimidine heterocycles are ubiquitous structural components of several unnatural and natural products that possess multifaceted biological profiles.[3–6] A plethora of useful methodologies involving various types of catalysts has been elaborated in order to keep the simplicity of the classical Biginelli protocol and to simultaneously overcome its undesirable features.[7–10] Asymmetric[11] and chemo-/regioselective synthesis[12] of Biginelli products with high enantioselectivity and regioselectivity using organocatalysts have been developed. Ammonium chloride,[13] ammonium, and tetrabutylammonium bromides,[14] polymer-supported aminoformoyldiphenylammonium triflate,[15] sodium chloride[16] have also been utilized as efficient catalysts for the Biginelli reaction.

The catalysis using metal triflate/triflimide as catalysts is found to be one of the elegant methods for the construction of hydropyrimidines as these catalysts not only possess non-nucleophilic anion but also generally have high thermal stability and compatibility especially with water.[17] Suzuki et al. have reported that pyrazolidine dihydrochloride worked efficiently for the Biginelli reaction to provide hydropyrimidines under mild conditions.[18] In view of developing new synthetic methodologies for novel organic compounds, we envisioned that an organotriflate catalyzed Biginelli reaction would occupy an unique place, featuring many advantages including operational simplicity, non-metal containing catalyst, and environmental consciousness. Although there are other quaternary ammonium PTC (Phase Transfer Catalyst) type catalysts available for this reaction as mentioned above, it is obvious that finding a new PTC type catalyst is also important as for as a fundamental organic transformation is concerned. Furthermore, it is known that chiral quaternary ammonium PTC type catalysts play an important role in asymmetric synthesis/catalysis.[19] Unlike the success of the Biginelli reaction using other quaternary ammonium PTC type catalysts,[13–15] the success using piperidinium triflates, which we used herein opens up a possibility of utilizing either/both of its enantiomer/enantiomers in asymmetric synthesis/catalysis as a new family of chiral catalysts in the near future as the piperidinium core of the catalysts is a single diastereomer and optical resolution of these diastereomers into enatiomers could be achieved using an appropriate chiral stationary phase (Chiral HPLC). In this article, we outline an organotriflate, piperidinium triflate, catalyzed Biginelli reaction that allows the production of a diverse range of new hydropyrimidines from respective aldehydes, β-dicarbonyl compounds, and urea/thiourea.

2. Results and discussion

The schematic representation for the synthesis of piperidinium triflate catalysts (**6a**–**6c**) is depicted in Scheme 1. Benzaldehyde (**1**) on a very straightforward Mannich type condensation with propan-2-one (**2a**) and ammonium acetate followed by methylation using methyl iodide in the presence of a base produced the heterocyclic ketone, 2,6-diphenyl piperidin-4-one (**4a**),[20] and its corresponding 1-methylated derivative (**5a**),[21] respectively. The 1-methyl derivative (**5a**) was then treated with methyl triflate at 0 °C to ambient temperature to afford 1,1-dimethyl-4-oxo-2,6-diphenylpiperidinium triflate (**6a**) in excellent yield. Organotriflates **6b** and **6c** were synthesized in a similar manner using pentan-3-one (**2b**) and

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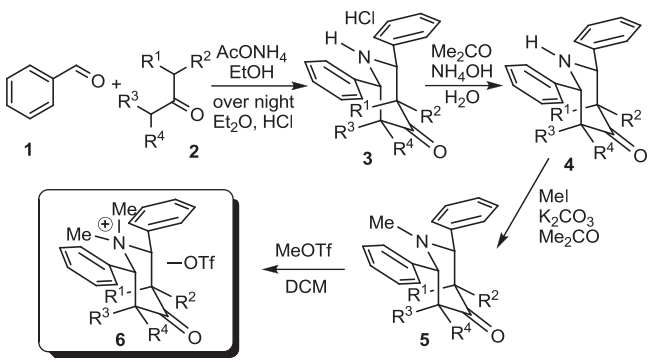
butan-2-one (**2c**), respectively, in place of **2a** in the initial Mannich type condensation reaction under similar conditions.

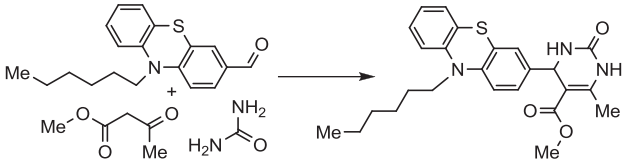


2a, 3a, 4a, 5a, 6a; R^1 = H, R^2 = H, R^3 = H, R^4 = H
2b, 3b, 4b, 5b, 6b; R^1 = H, R^2 = Me, R^3 = H, R^4 = Me
2c, 3c, 4c, 5c, 6c; R^1 = H, R^2 = Me, R^3 = H, R^4 = H

Scheme 1. Synthesis of piperidinium triflate catalysts **6a**–**6c**.

In our continuous effort to the synthesis of novel chemical entities possessing hydropyrimidine with various heterocyclic cores, we used 10-hexyl-10*H*-phenothiazine-3-carbaldehyde as one of the model substrates along with methyl acetoacetate and urea. The piperidinium triflate **6a** (10 mol %) was then used as a catalyst for the three component one synthetic operational fusion of 10-hexyl-10*H*-phenothiazine-3-carbaldehyde, [22–24] methyl acetoacetate, and urea (1:1:1.2, respectively) in acetonitrile at ambient temperature. When the reaction was performed at 70 °C for 24 h, the desired new hydropyrimidine heterocycle was obtained although proved as an unsuccessful catalysis, with product formation in low yield. In contrast, the use of organotriflates **6b** and **6c** as catalysts (10 mol %) in the model reaction afforded in good to excellent yields of the hydropyrimidine heterocycle as outlined in Table 1. Although the better catalytic activity of **6b**/**6c** over **6a** is unclear at this moment, it might be due to the presence of bulky substituents around the nucleophilic carbonyl carbon of the catalyst **6b**/**6c**, which is less reactive toward the urea nucleophile than that of **6a**. Further, the slightly lower catalytic activity of **6c** compared to **6b** is probably due to poor solubility of the former over the later.

Table 1
Optimization of the model Biginelli reaction

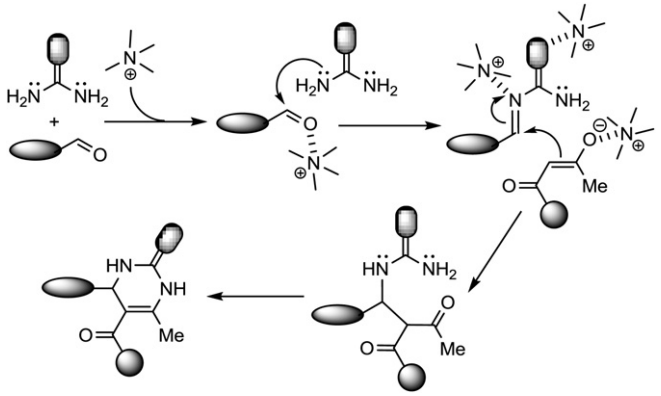


Entry	Cat.	Solvent	Temp (°C)	Time (h)	Yield (%)
1	**6a**	MeCN	70	24	28
2	**6b**	MeCN	70	24	85
3	**6c**	MeCN	70	24	60
4	**6b**	MeOH/DMF (3:1)	70	24	42
5	**6b**	MeOH	Reflux	24	48
6	**6b**	*i*-PrOH	70	24	53
7	**6b**	MeOH/*i*-PrOH (2:1)	70	24	49
8	**6b**	DMF	70	24	40
9	**6b**	MeCN/*i*-PrOH (1:3)	70	24	61
10	**6b**	MeCN	RT	60	44

The better catalytic efficiency exhibited by **6b** prompted us to prefer this organotriflate for further examination. After screening various proportions of the substrates and catalyst loading, it was found that treatment of respective aldehydes (1 equiv) with β-ketoesters (1.2 equiv), and ureas (1.2 equiv) in the presence of the catalyst **6b** (10 mol %) in acetonitrile at 70 °C for 24 h afforded the desired hydropyrimidine heterocycle in highest yield. Further, acetonitrile as solvent proved to be superior to methanol–DMF (3:1), methanol, isopropanol, methanol–isopropanol (2:1), *N*,*N*-dimethylformamide (DMF), and acetonitrile–isopropanol (1:3) as the use of these solvents provided the model in lower yields. It is noteworthy that the reaction proceeded at ambient temperature as well although the fused hydropyrimidine was obtained in moderate yield after 60 h.

The present catalytic Biginelli reaction in the presence of piperidinium triflate **6b** (10 mol %) in acetonitrile tolerated the various aldehydes synthesized using either known or modified methods [23,25–27] and thus the corresponding new hydropyrimidines were obtained in good to excellent yields as listed in Table 2. The ubiquitous aldehydes, such as benzaldehyde and *p*-tolualdehyde also provided their corresponding known hydropyrimidines in excellent yields (90% and 81%, respectively; ^{1}H and ^{13}C NMR spectra are identical with the authentic samples, see Ref. 28d). On the other hand, use of yet another β-keto ester (ethyl acetoacetate) and β-diketone (acetylacetone) in place of methyl acetoacetate in the one-step operation with various aldehydes and urea also provided their corresponding new hydropyrimidines in good to excellent yields, expanding the utility of this synthetic protocol as a practical tool for accessing a variety of hydropyrimidine building blocks. It was eventually found that the catalyst is not only suitable for the synthesis of a diverse range of new hydropyrimidones but also suitable for the synthesis of a diverse range of new hydropyrimidine thiones as it efficiently catalyzes the one-step fusion of respective aldehydes, methyl acetoacetate/ethyl acetoacetate/acetylacetone, and thiourea.

A plausible reaction pathway for the catalytic Biginelli reaction, which is consistent with the one proposed by Folkers et al. via *N*-acylimine intermediate,[2a,14b,28] is shown in Scheme 2. The catalyst



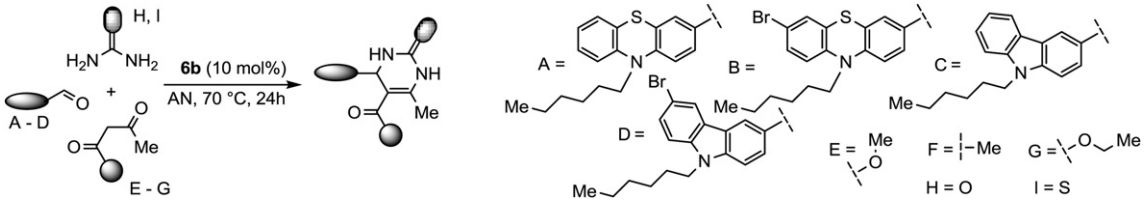
Scheme 2. Plausible reaction pathway of a piperidinium triflate catalyzed Biginelli reaction.

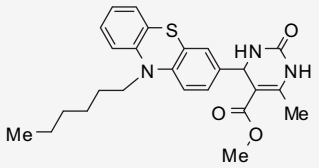
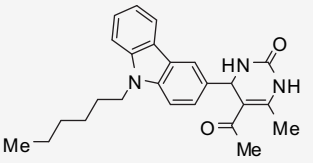
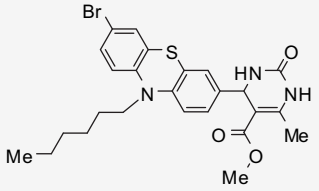
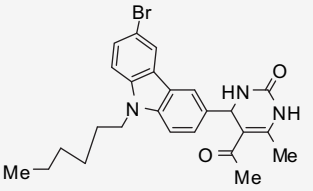
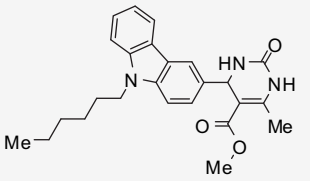
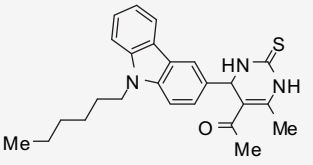
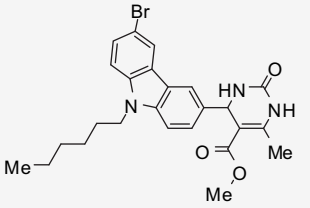
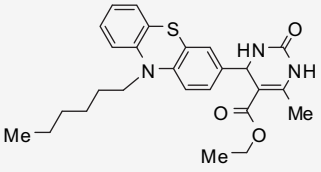
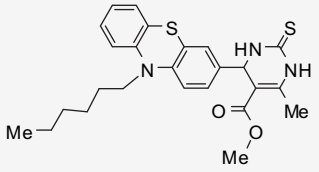
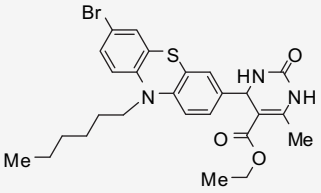
activates the nucleophilicity of carbonyl carbon of 10-hexyl-10*H*-phenothiazine-3-carbaldehyde toward a urea/thiourea nucleophile through the interaction between the positively charged quaternary piperidinium ion and the carbonyl oxygen atom of the aldehyde. The subsequent addition of urea/thiourea followed by elimination of water produces the *N*-acylimine intermediate. A simultaneous attack of β-dicarbonyl compound, activated by the piperidinium group of the catalyst, on the imine carbon of the active intermediate affords the open chain intermediate. The intramolecular nucleophilic addition of this intermediate followed by an eventual dehydration generates the hydropyrimidine heterocycles. When 10-hexyl-10*H*-phenothiazine-3-carbaldehyde without a β-dicarbonyl compound, such as methyl acetoacetate was treated with urea (1:1.2 ratio) in the presence of the catalyst **6b** in acetonitrile at 70 °C for 12 h, the corresponding *N*-acylimine was formed in an excellent NMR yield (80%) while in the absence of the catalyst **6b** provided the *N*-acylimine in

lower NMR yield (32%). [Yields are based on NMR using nitromethane as an internal standard; unfortunately, attempts for the isolation of the intermediate in pure form were unsuccessful]. This observation supports the proposed reaction pathway of the Biginelli reaction. In addition, experiments to prove the stability of the catalysts **6a–6c** were also performed as the catalysts may decompose via Hoffmann type elimination pathway under reaction conditions to give stable enones and triflic acid dimethyl amine that could also act as an acid catalyst in the reaction. When the catalysts **6a–6c** (0.025 mmol) in acetonitrile (3 mL) were independently stirred at 70 °C for 24 h, there were no changes in the catalysts observed after removal of the solvent under reduced pressure indicating that the catalysts are stable under the experimental conditions.

In conclusion, 1,1,3,5-tetramethyl-4-oxo-2,6-diphenylpiperidinium triflate (**6b**) has successfully been utilized as an efficient organotriflate catalyst to access new hydropyrimidine heterocycles in a single operation. This one-step catalytic protocol

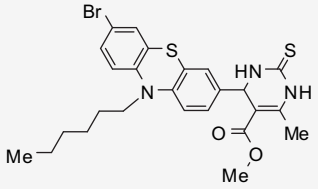
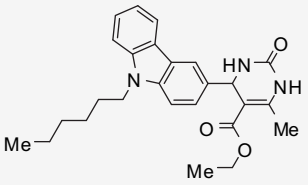
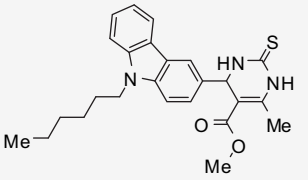
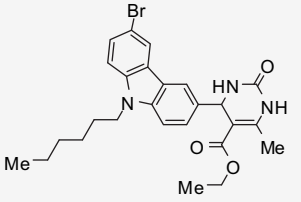
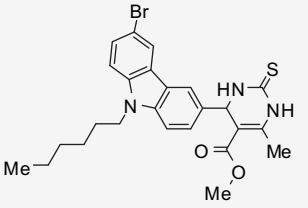
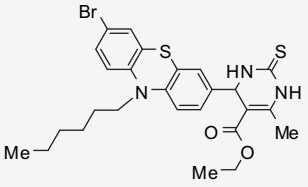
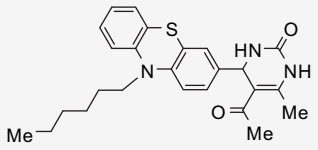
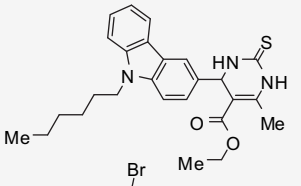
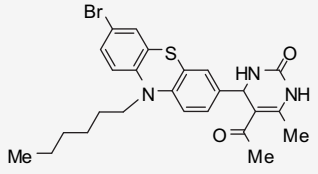
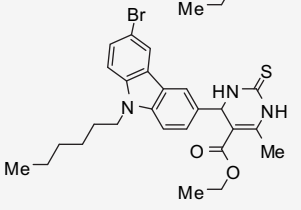
Table 2
Piperidinium triflate catalyzed Biginelli reactions leading to hydropyrimidines



Entry	Reactants	Product	Yield (%)	Entry	Reactants	Product	Yield (%)
1	A+E+H		85	11	C+F+H		93
2	B+E+H		88	12	D+F+H		94
3	C+E+H		92	13	C+F+I		84
4	D+E+H		94	14	A+G+H		87
5	A+E+I		76	15	B+G+H		88

(*continued on next page*)

Table 2 (*continued*)

Entry	Reactants	Product	Yield (%)	Entry	Reactants	Product	Yield (%)
6	B+E+I		80	16	C+G+H		91
7	C+E+I		87	17	D+G+H		94
8	D+E+I		88	18	B+G+I		77
9	A+F+H		82	19	C+G+I		79
10	B+F+H		86	20	D+G+I		82

allows various aldehydes, β-ketoesters/β-diketone, and urea/thiourea for the efficient construction of their respective hydropyrimidine heterocycles, reflecting its versatility.

3. Experimental section

3.1. General

All the reported melting points were measured in open capillaries with a Laboratory Devices-Mel-Temp II apparatus. Freshly distilled solvents were used for all the experiments. All the reagents are reagent grade and were used without further purification. Thin layer chromatography (TLC) was performed on Silica gel 60 F plates eluting with the solvents indicated. Column chromatography was performed on Silica gel 70–230 mesh slurry packed in glass columns with eluent system as indicated. ^{1}H NMR and ^{13}C NMR spectra were acquired on a Bruker Avance 400 Spectrometer at 298 K using either DMSO-d_6 or $CDCl_3$ as a solvent and TMS as an internal standard. Infrared spectra were measured on a Mattson Galaxy 7020A (KBr pellet). Mass spectra were measured on a Shimadzu QP5000. Elemental analyses were acquired on a Fisone, EA 1106. The abbreviations s, d, t, dd, dt, br s, br d, br t and m stand for the resonance multiplicities singlet, doublet, triplet, doublet of doublet, doublet of triplet, broad singlet, broad doublet, broad triplet and multiplet, respectively.

3.2. Synthesis of 10-hexyl-10*H*-phenothiazine[22]

A slightly modified method. To a stirring suspension of sodium hydroxide (50 mmol), 10*H*-phenothiazine (25 mmol) in dimethyl sulfoxide (75 mL) at ambient temperature under nitrogen atmosphere was added tetrabutylammoniumhydrogen sulfate (5 mol%). After stirring vigorously for 30 min, 1-bromohexane (35 mmol) was added and the stirring was continued for 24 h at the same temperature. The reaction mixture, after removal of three-fourth of the solvent under reduced pressure, was extracted with dichloromethane and water. The organic layer was separated and dried over magnesium sulfate. The crude thus obtained, after removal of the solvent under vacuum, was subjected to column chromatography over silica gel using hexane/ethyl acetate (100:5) as an eluent system to afford the title compound (Yield 80%).

3.3. Synthesis of 10-hexyl-10*H*-phenothiazine-3-carbaldehyde[23]

A modified method. To a cooled (ice-water bath) mixture of 10-hexyl-10*H*-phenothiazine (20 mmol) and *N*-methylformanilide (23 mmol) in 1,2-dichlorobenzene (10 mL), was added phosphorous oxychloride (20.5 mmol) in a dropwise fashion. Then the temperature of the reaction was allowed to reach 90 °C while stirring after removing the ice-water bath. After 24 h, it was cooled to attain ambient temperature and aqueous sodium acetate (approximately 20 g in 50 mL) was added in a dropwise fashion. The combined organic layers, after extracted with dichloromethane, were dried over sodium sulfate and concentrated under reduced pressure. After silica gel column chromatographic separation of the residual mass thus obtained using hexane/dichoromethane (80:20 followed by 15:85) eluent system, the pure title compound was obtained (yield 73%).

3.4. Synthesis of 9-hexyl-9*H*-carbazole[24]

This compound was synthesized in a similar method as that of the synthesis of 10-hexyl-10*H*-phenothiazine using 9*H*-carbazole in place of 10*H*-phenothiazine under otherwise identical conditions (yield 87%).

3.5. Synthesis of 9-hexyl-9*H*-carbazole-3-carbaldehyde[25]

Synthesis of this compound was achieved in a similar method as that of the synthesis of 10-hexyl-10*H*-phenothiazine-3-carbaldehyde using 9-hexyl-9*H*-carbazole in place of 10-hexyl-10*H*-phenothiazine under otherwise identical conditions (yield 76%).

3.6. Synthesis of 7-bromo-10-hexyl-10*H*-phenothiazine-3-carbaldehyde[26]

In a two neck flask equipped with condenser and dropping funnel, were taken 10-hexyl-10*H*-phenothiazine-3-carbaldehyde (14 mmol) and glacial acetic acid (20 mL). Bromine in glacial acetic acid (14 mmol in 5 mL) was then added in a dropwise fashion while stirring after the flask was cooled (15–20 °C). The temperature of the reaction was raised to ambient and was stirred further for 48 h. The organic ethereal layer was then separated, after the addition of water (150 mL) and diethyl ether (300 mL), and evaporated under vacuum, after dried over sodium sulfate. The residue thus obtained was subjected to column chromatography over silica gel using hexane/dichloromethane (100:20 followed by 100:40) eluent to afford the title compound (yield 84%).

3.7. Synthesis of 6-bromo-9-hexyl-9*H*-carbazole-3-carbaldehyde[27]

This compound was synthesized in a similar method as that of the synthesis of 7-bromo-10-hexyl-10*H*-phenothiazine-3-carbaldehyde using 9-hexyl-9*H*-carbazole-3-carbaldehyde in place of 10-hexyl-10*H*-phenothiazine-3-carbaldehyde under otherwise identical conditions (yield 79%).

3.8. General method for the synthesis of catalysts (6a–6c)

In a two-necked flask under nitrogen atmosphere, was taken **5a–5c** (5.0 mmol) and dry dichloromethane (25 mL). After the complete dissolution, it was cooled to 0–5 °C and then methyl trifluoromethanesulfonate (7.0 mmol) was added while stirring. After 15 min, the temperature of the reaction mixture was allowed to raise upto ambient and the stirring was continued at the same temperature for further 8 h. After completion of the reaction, the mixture was concentrated under reduced pressure and the solid thus obtained was recrystallized from hexane/ethyl acetate mixture.

*3.8.1. 1,1-Dimethyl-4-oxo-2,6-diphenylpiperidinium triflate (**6a**).* Yield, 92%. Mp 204–205 °C; ^{1}H NMR (400 MHz, in CD_3CN) δ 7.62–7.50 (m, 10H), 5.25 (d, J=14.0 Hz, 2H), 3.72 (t, J=17.0 Hz, 2H), 3.03 (s, 3H), 2.82 (d, J=17.0 Hz, 2H), 2.64 (s, 3H); ^{13}C NMR (400 MHz, in CD_3CN) δ 198.10, 131.20, 130.84, 130.47, 130.18, 129.40, 127.84, 73.90, 48.96, 39.89, 36.05; Anal. Calcd for $C_{20}H_{22}F_3NO_4S$: C, 55.93; H, 5.16; N, 3.26; S, 7.47. Found: C, 56.11; H, 5.21; N, 3.29; S, 7.54.

*3.8.2. 1,1,3,5-Tetramethyl-4-oxo-2,6-diphenylpiperidinium triflate (**6b**).* Yield, 93%. Mp 197–198 °C; ^{1}H NMR (400 MHz, in CD_3CN) δ 7.69–7.59 (m, 10H), 4.92 (d, J=13.2 Hz, 2H), 3.74–3.63 (m, 2H), 3.14 (s, 3H), 2.57 (s, 3H), 0.87 (d, J=6.6 Hz, 6H); ^{13}C NMR (400 MHz, in CD_3CN) δ 202.82, 133.99, 132.40, 130.76, 130.15, 129.33, 129.20, 129.02, 128.54, 80.17, 51.64, 42.67, 39.51, 11.26; Anal. Calcd for $C_{22}H_{26}F_3NO_4S$: C, 57.76; H, 5.73; N, 3.06; S, 7.01. Found: C, 57.80; H, 5.78; N, 3.03; S, 7.08.

*3.8.3. 1,1,3-Trimethyl-4-oxo-2,6-diphenylpiperidinium triflate (**6c**).* Yield, 87%. Mp 266–267 °C; ^{1}H NMR (400 MHz, in CD_3CN) δ 7.63–7.56 (m, 10H), 5.24 (dd, 14.3; 3.2 Hz, 1H), 4.95 (d, J=12.9 Hz, 1H), 3.79 (dd, J=16.8; 14.5 Hz, 1H), 3.67–3.58 (m, 1H), 3.07 (s, 3H), 2.84 (dd, J=16.8; 3.2 Hz, 1H), 2.61 (s, 3H), 0.87 (d, J=6.6 Hz, 3H); ^{13}C NMR (400 MHz, in CD_3CN) δ 200.90, 133.97, 130.95, 130.78, 129.92, 129.34, 129.28, 129.04, 129.01, 128.22, 80.21, 74.41, 50.98, 43.26, 40.71, 37.42, 10.93; Anal. Calcd for $C_{21}H_{24}F_3NO_4S$: C, 56.87; H, 5.45; N, 3.16; S, 7.23. Found: C, 56.95; H, 5.40; N, 3.22; S, 7.26.

3.9. General procedure for a piperidinium triflate catalyzed Biginelli reaction

To a solution of catalyst **6b** (0.025 mmol) in acetonitrile (3 mL), were added respective aldehyde (0.25 mmol) and urea/thiourea (0.30 mmol). The reaction mixture was stirred at ambient temperature for 20 min and then β-dicarbonyl compound (0.30 mmol) was added. The temperature of the reaction was raised to 70 °C and was maintained at the same temperature for 24 h while stirring. Water (7 mL) was added after cooling the mixture, and the mixture was extracted three times with ethyl acetate (7 mL×3). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue thus obtained was purified by silica gel column chromatography (pet-ether/ethyl acetate, 10:3.5) to afford their respective pure title compounds. The characterization data for all the synthesized new compounds are given below.

3.9.1. Methyl 4-(10-hexyl-10H-phenothiazin-3-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 1). Mp 189–190 °C; IR (υ cm^{-1}, KBr) 3442.6, 3329.7, 2930.0, 2856.4, 1697.4, 1668.3, 1651.7, 1463.3, 1431.4, 1339.1, 1238.7, 1092.7, 813.4, 748.2, 673.9; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.25 (s, 1H), 7.72 (s, 1H), 7.18 (dt, J=7.2; 1.0 Hz, 1H), 7.13 (dd, J=7.6; 1.0 Hz, 1H), 7.03 (dd, J=8.6; 1.8 Hz, 1H), 7.00 (d, J=8.3 Hz, 1H), 6.97–6.91 (m, 3H), 5.05 (d, J=3.3 Hz, 1H), 3.82 (t, J=6.8 Hz, 2H), 3.52 (s, 3H), 2.25 (s, 3H), 1.65 (quintet, J=7.1 Hz, 2H), 1.36 (br t, J=6.8 Hz, 2H), 1.24–1.19 (m, 4H), 0.81 (t, J=6.8 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 166.16, 152.48, 149.12, 144.97, 144.34, 139.22, 127.99, 127.48, 125.79, 125.18, 123.71, 123.50, 122.78, 116.06, 99.10, 53.31, 51.21, 46.78, 31.19, 26.54, 26.22, 22.43, 18.23, 14.18; GC/MS (m/z) 451 (M^+); Anal. Calcd for $C_{25}H_{29}N_3O_3S$: C, 66.49; H, 6.47; N, 9.31; S, 7.10. Found: C, 66.61; H, 6.55; N, 9.22; S, 6.92.

3.9.2. Methyl 4-(7-bromo-10-hexyl-10H-phenothiazin-3-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate (entry 2). Mp 185–187 °C; IR (υ cm^{-1}, KBr) 3310.7, 3111.5, 2928.4, 2855.5, 1696.4,

1645.6, 1461.0, 1339.2, 1233.2, 1095.0, 799.7, 767.1, 467.9; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.26 (s, 1H), 7.73 (s, 1H), 7.35–7.32 (m, 2H), 7.05 (dd, J=8.5; 1.9 Hz, 1H), 6.99–6.92 (m, 3H), 5.06 (d, J=3.0 Hz, 1H), 3.80 (t, J=6.8 Hz, 2H), 3.53 (s, 3H), 2.25 (s, 3H), 1.63 (quintet, J=7.2 Hz, 2H), 1.35 (br s, 2H), 1.24–1.22 (m, 4H), 0.81 (t, J=7.0 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 166.14, 152.45, 149.19, 144.38, 143.93, 139.59, 130.49, 129.32, 126.08, 125.29, 122.96, 117.69, 116.32, 113.99, 99.02, 53.26, 51.22, 46.88, 31.16, 26.39, 26.14, 22.42, 18.24, 14.19; GC/MS (m/z) 529 (M^+); Anal. Calcd for $C_{25}H_{28}BrN_3O_3S$: C, 56.60; H, 5.32; N, 7.92; S, 6.04. Found: C, 56.49; H, 5.33; N, 7.77; S, 5.88.

3.9.3. Methyl 4-(9-hexyl-9H-carbazol-3-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 3). Mp 202–204 °C; IR (υ cm^{-1}, KBr) 3435.0, 3338.8, 2929.6, 2854.3, 1698.2, 1667.3, 1646.6, 1489.9, 1467.2, 1434.2, 1338.7, 1238.8, 1091.9, 812.3, 776.8, 747.9, 674.1, 630.3, 459.8; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.24 (s, 1H), 8.11 (d, J=7.8 Hz, 1H), 7.93 (s, 1H), 7.79 (s, 1H), 7.56 (2d, J=8.3; 8.6 Hz, 2H), 7.44 (t, J=8.3 Hz, 1H), 7.35 (dd, J=8.6; 1.5 Hz, 1H), 7.18 (t, J=7.4 Hz, 1H), 5.33 (d, J=3.3 Hz, 1H), 4.36 (t, J=6.9 Hz, 2H), 3.52 (s, 3H), 2.31 (s, 3H), 1.74 (quintet, J=6.8 Hz, 2H), 1.27–1.19 (m, 6H), 0.80 (t, J=7.1 Hz, 3H); ^{13}C NMR (400 MHz, in $CDCl_3$) δ 166.80, 154.14, 146.66, 141.20, 140.49, 134.89, 126.13, 124.82, 123.17 123.08, 120.87, 119.22, 118.83, 109.37, 109.14, 102.06, 56.50, 51.51, 43.56, 31.99, 29.36, 27.38, 22.96, 19.09, 14.45; GC/MS (m/z) 419 (M^+); Anal. Calcd for $C_{25}H_{29}N_3O_3$: C, 71.57; H, 6.97; N, 10.02. Found: C, 71.37; H, 7.15; N, 9.96.

3.9.4. Methyl 4-(6-bromo-9-hexyl-9H-carbazol-3-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 4). Mp 106–107 °C; IR (υ cm^{-1}, KBr) 3399.8, 3243.1, 3116.0, 2930.0, 2857.3, 1701.9, 1645.3, 1484.8, 1448.5, 1344.8, 1316.4, 1281.6, 1230.4, 1189.7, 1092.2, 870.6, 795.0, 674.2, 636.2, 569.6; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.24 (d, J=1.3 Hz, 1H), 8.39 (d, J=1.5 Hz, 1H), 7.98 (d, J=1.2 Hz, 1H), 7.79 (s, 1H), 7.59–7.55 (m, 3H), 7.41 (dd, J=8.6; 1.5 Hz, 1H), 5.32 (d, J=3.3 Hz, 1H), 4.36 (t, J=6.9 Hz, 2H), 3.51 (s, 3H), 2.33 (s, 3H), 1.73 (br t, J=6.4 Hz, 2H), 1.25–1.18 (m, 6H), 0.79 (t, J=6.9 Hz, 3H); ^{13}C NMR (400 MHz, in $CDCl_3$) δ 166.71, 154.14, 146.78, 140.72, 139.78, 135.37, 128.72, 125.56, 124.78, 123.55, 122.15, 118.95, 111.99, 110.54, 109.65, 101.92, 56.31, 51.55, 43.67, 31.92, 29.28, 27.31, 22.92, 19.11, 14.41; GC/MS (m/z) 497 (M^+); Anal. Calcd for $C_{25}H_{28}BrN_3O_3$: C, 60.24; H, 5.66; N, 8.43. Found: C, 59.99; H, 5.71; N, 8.32.

3.9.5. Methyl 4-(10-hexyl-10H-phenothiazin-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 5). Mp 90–91 °C; IR (υ cm^{-1}, KBr) 3419.6, 3191.6, 2952.0, 2928.1, 2855.5, 1712.7, 1696.8, 1651.1, 1575.0, 1464.3, 1318.5, 1250.2, 1180.1, 1110.8, 1039.4, 821.2, 786.6, 748.0, 638.5, 546.6, 502.9; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 10.37 (s, 1H), 9.62 (s, 1H), 7.18 (t, J=7.8 Hz, 1H), 7.13 (d, J=7.6 Hz, 1H), 7.04–6.91 (m, 5H), 5.10 (d, J=3.3 Hz, 1H), 3.82 (t, J=6.7 Hz, 2H), 3.55 (s, 3H), 2.31 (s, 3H), 1.64 (quintet, J=7.0 Hz, 2H), 1.35 (br t, J=6.3 Hz, 2H), 1.22 (br d, J=3.3 Hz, 4H), 0.81 (t, J=6.4 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 174.46, 165.96, 145.79, 144.82, 144.69, 137.82, 128.04, 127.50, 126.01, 125.29, 123.84, 123.37, 122.86, 116.15, 100.49, 53.41, 51.51, 46.82, 31.19, 26.54, 26.22, 22.43, 17.63, 14.19; GC/MS (m/z) 467 (M^+); Anal. Calcd for $C_{25}H_{29}N_3O_2S_2$: C, 64.21; H, 6.25; N, 8.99; S, 13.71. Found: C, 64.10; H, 6.38; N, 8.80; S, 13.54.

3.9.6. Methyl 4-(7-bromo-10-hexyl-10H-phenothiazin-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate (entry 6). Mp 99–100 °C; IR (υ cm^{-1}, KBr) 3390.9, 3187.8, 2951.8, 2928.1, 2855.3, 1712.7, 1695.1, 1650.9, 1562.0, 1461.5, 1318.6, 1270.8, 1251.7, 1179.3, 1110.4, 868.5, 806.6, 768.2; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 10.39 (s, 1H), 9.60 (d, J=1.8 Hz, 1H), 7.33–7.31 (m, 2H), 7.03 (dd, J=8.5; 1.9 Hz, 1H), 6.98 (d, J=8.4 Hz, 1H), 6.94 (d, J=2.0 Hz, 1H), 6.90 (d, J=9.4 Hz, 1H), 5.09 (d, J=3.5 Hz, 1H), 3.79 (t, J=6.8 Hz, 2H), 3.55 (s, 3H), 2.30 (s, 3H), 1.61 (quintet, J=7.1 Hz, 2H), 1.36–1.29 (m, 2H), 1.22–1.20 (m, 4H), 0.80 (t, J=6.8 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 174.46, 165.95, 145.85, 144.29, 144.23, 138.17, 130.53, 129.34, 126.26, 125.95, 125.39, 123.11, 117.74, 116.41, 114.10, 100.42, 53.36, 51.53, 46.91, 31.16, 26.38, 26.14, 22.42, 17.63, 14.19; GC/MS (m/z) 545 (M^+); Anal. Calcd for $C_{25}H_{28}BrN_3O_2S_2$: C, 54.94; H, 5.16; N, 7.69; S, 11.73. Found: C, 54.84; H, 5.20; N, 7.59; S, 11.65.

3.9.7. Methyl 4-(9-hexyl-9H-carbazol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 7). Mp 94–96 °C; IR (υ cm^{-1}, KBr) 3380.5, 3191.4, 2952.2, 2929.0, 2856.6, 1697.1, 1651.4, 1562.3, 1490.1, 1468.0, 1382.9, 1332.3, 1277.0, 1243.3, 1186.6, 1165.6, 1112.1, 1024.3, 889.6, 769.9, 747.7, 642.9, 567.2; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 10.40 (s, 1H), 9.75 (s, 1H), 8.12 (d, J=7.6 Hz, 1H), 7.95 (s, 1H), 7.57 (dd, J=7.8; 3.2 Hz, 2H), 7.45 (t, J=7.6 Hz, 1H), 7.36 (d, J=8.4 Hz, 1H), 7.20 (t, J=7.3 Hz, 1H), 5.39 (d, J=3.3 Hz, 1H), 4.34 (t, J=6.7 Hz, 2H), 3.54 (s, 3H), 2.38 (s, 3H), 1.73 (br t, J=6.6 Hz, 2H), 1.24–1.19 (m, 6H), 0.79 (t, J=6.7 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 174.16, 166.19, 145.39, 140.75, 139.86, 134.46, 126.19, 124.80, 122.19, 122.08, 120.53, 119.12, 118.44, 109.91, 109.73, 101.27, 54.80, 51.41, 42.66, 31.34, 28.86, 26.51, 22.38, 17.68, 14.22; GC/MS (m/z) 435 (M^+); Anal. Calcd for $C_{25}H_{29}N_3O_2S$: C, 68.93; H, 6.71; N, 9.65; S, 7.36. Found: C, 69.24; H, 6.91; N, 9.42; S, 7.29.

3.9.8. Methyl 4-(6-bromo-9-hexyl-9H-carbazol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate (entry 8). Mp 104–105 °C; IR (υ cm^{-1}, KBr) 3399.7, 3188.4, 2952.0, 2928.8, 2856.6, 1697.6, 1651.3, 1562.4, 1484.7, 1455.9, 1381.4, 1344.3, 1315.7, 1281.1, 1242.0, 1186.2, 1161.7, 1112.8, 1022.0, 794.1, 763.9, 643.9, 571.3, 503.3; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 10.40 (s, 1H), 9.75 (d, J=1.5 Hz, 1H), 8.40 (s, 1H), 7.99 (d, J=1.2 Hz, 1H), 7.61–7.56 (m, 3H), 7.42 (dd, J=8.6; 1.5 Hz, 1H), 5.38 (d, J=3.8 Hz, 1H), 4.34 (t, J=6.9 Hz, 2H), 3.54 (s, 3H), 2.40 (s, 3H), 1.72 (br t, J=6.4 Hz, 2H), 1.22 (br s, 6H), 0.79 (t, J=6.9 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 174.07, 166.13, 145.69, 140.19, 139.46, 134.92, 128.49, 125.90, 124.15, 123.19, 121.05, 118.92, 111.81, 111.27, 110.33, 100.93, 54.73, 51.43, 42.83, 31.30, 28.81, 26.45, 22.35, 17.71, 14.22; GC/MS (m/z) 513 (M^+); Anal. Calcd for $C_{25}H_{28}BrN_3O_2S$: C, 58.36; H, 5.49; N, 8.17; S, 6.23. Found: C, 58.31; H, 5.58; N, 8.03; S, 6.13.

3.9.9. 5-Acetyl-4-(10-hexyl-10H-phenothiazin-3-yl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (entry 9). Mp 174–176 °C; IR (υ cm^{-1}, KBr) 3347.4, 3271.5, 2953.5, 2927.4, 2854.7, 1712.1, 1675.5, 1599.7, 1463.7, 1442.9, 1381.0, 1364.0, 1328.4, 1232.8, 1133.9, 1105.0, 1000.8, 964.1, 822.0, 763.7, 742.4, 579.0, 547.5; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.20 (s, 1H), 7.77 (s, 1H), 7.20–7.11 (m, 2H), 7.05 (d, J=7.0 Hz, 1H), 7.00–6.90 (m, 4H), 5.18 (br s, 1H), 3.82 (br s, 2H), 2.29 (s, 3H), 2.09 (s, 3H), 1.64 (br s, 2H), 1.35 (br s, 2H), 1.22 (br t, J=3.3 Hz, 4H), 0.81 (br t, J=3.3 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 194.62, 152.47, 148.54, 144.98, 144.34, 138.84, 127.98, 127.48, 125.99, 125.48, 123.79, 123.50, 122.78, 116.07, 109.68, 53.35, 46.79, 31.18, 30.67, 26.54, 26.21, 22.43, 19.29, 14.19; GC/MS (m/z) 435 (M^+); Anal. Calcd for $C_{25}H_{29}N_3O_2S$: C, 68.93; H, 6.71; N, 9.65; S, 7.36. Found: C, 68.80; H, 6.86; N, 9.55; S, 7.22.

3.9.10. 5-Acetyl-4-(7-bromo-10-hexyl-10H-phenothiazin-3-yl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (entry 10). Mp 105–106 °C; IR (υ cm^{-1}, KBr) 3395.5, 3239.8, 3125.0, 2954.3, 2928.5, 2855.9, 1702.2, 1617.3, 1461.6, 1381.4, 1358.4, 1328.1, 1235.7, 1194.6, 1107.9, 944.0, 867.8, 805.2, 720.5, 583.2, 548.3; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.23 (s, 1H), 7.80 (s, 1H), 7.34–7.32 (m, 2H), 7.07 (dd, J=8.3; 1.8 Hz,

1H), 7.01–6.96 (m, 2H), 6.92 (d, *J*=9.4 Hz, 1H), 5.19 (d, *J*=3.3 Hz, 1H), 3.80 (t, *J*=6.7 Hz, 2H), 2.30 (s, 3H), 2.11 (s, 3H), 1.62 (br t, *J*=6.9 Hz, 2H), 1.37–1.32 (m, 2H), 1.23–1.21 (m, 4H), 0.81 (t, *J*=6.6 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 194.58, 152.46, 148.61, 144.39, 143.91, 139.22, 130.48, 129.30, 126.25, 126.09, 125.57, 123.05, 117.67, 116.31, 113.98, 109.68, 53.28, 46.90, 31.16, 30.70, 26.39, 26.14, 22.42, 19.31, 14.19; GC/MS (*m*/*z*) 513 (M^+); Anal. Calcd for $C_{25}H_{28}BrN_3O_2S$: C, 58.36; H, 5.49; N, 8.17; S, 6.23. Found: C, 58.50; H, 5.51; N, 8.10; S, 6.34.

3.9.11. 5-Acetyl-4-(9-hexyl-9H-carbazol-3-yl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (entry 11). Mp 97–98 °C; IR (υ cm^{-1}, KBr) 3391.2, 3242.5, 3120.6, 2929.5, 2857.4, 1702.0, 1601.5, 1490.3, 1467.6, 1382.0, 1331.0, 1263.8, 1235.8, 1152.7, 1105.4, 1064.7, 1024.0, 943.6, 785.2, 748.8, 628.1, 556.1; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.25 (s, 1H), 8.11 (d, *J*=7.8 Hz, 1H), 7.99 (s, 1H), 7.89 (s, 1H), 7.56 (dd, *J*=8.1; 5.8 Hz, 2H), 7.46–7.39 (m, 2H), 7.19 (t, *J*=7.5 Hz, 1H), 5.47 (d, *J*=3.0 Hz, 1H), 4.35 (t, *J*=6.8 Hz, 2H), 2.37 (s, 3H), 2.11 (s, 3H), 1.74 (br s, 2H), 1.26–1.18 (m, 6H), 0.79 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 194.98, 152.39, 148.13, 140.73, 139.75, 135.33, 126.08, 124.99, 122.27, 122.11, 120.51, 119.02, 118.47, 110.08, 109.85, 109.69, 54.95, 42.64, 31.34, 30.58, 28.84, 26.50, 22.37, 19.29, 14.21; GC/MS (*m*/*z*) 403 (M^+); Anal. Calcd for $C_{25}H_{29}N_3O_2$: C, 74.41; H, 7.24; N, 10.41. Found: C, 74.31; H, 7.32; N, 10.30.

3.9.12. 5-Acetyl-4-(6-bromo-9-hexyl-9H-carbazol-3-yl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (entry 12). Mp 103–105 °C; IR (υ cm^{-1}, KBr) 3399.7, 3242.9, 2954.8, 2929.3, 2857.3, 1702.0, 1617.4, 1483.5, 1449.1, 1381.1, 1356.7, 1280.3, 1235.2, 1153.1, 1105.9, 1022.0, 943.8, 794.7, 767.4, 635.0, 554.9; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.24 (s, 1H), 8.39 (s, 1H), 8.01 (s, 1H), 7.89 (s, 1H), 7.60–7.56 (m, 3H), 7.46 (dd, *J*=8.6; 1.2 Hz, 1H), 5.45 (d, *J*=3.0 Hz, 1H), 4.34 (t, *J*=6.8 Hz, 2H), 2.38 (s, 3H), 2.12 (s, 3H), 1.72 (br t, *J*=6.2 Hz, 2H), 1.22 (br s, 6H), 0.78 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 194.89, 152.34, 148.37, 140.07, 139.43, 135.82, 128.36, 126.10, 124.22, 123.13, 121.08, 118.83, 111.73, 111.17, 110.24, 109.85, 54.87, 42.79, 31.30, 30.60, 28.79, 26.43, 22.35, 19.36, 14.19; GC/MS (*m*/*z*) 481 (M^+); Anal. Calcd for $C_{25}H_{28}BrN_3O_2$: C, 62.24; H, 5.85; N, 8.71. Found: C, 62.05; H, 5.89; N, 8.62.

3.9.13. 1-(4-(9-Hexyl-9H-carbazol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethanone (entry 13). Mp 99–100 °C; IR (υ cm^{-1}, KBr) 3420.3, 3216.8, 2954.8, 2928.5, 2856.8, 1678.7, 1599.8, 1567.0, 1490.1, 1467.5, 1381.5, 1330.8, 1243.6, 1187.6, 1165.2, 1116.5, 1023.0, 963.5, 809.7, 770.8, 748.1, 650.6, 508.5; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 10.31 (s, 1H), 9.83 (s, 1H), 8.12 (d, *J*=7.8 Hz, 1H), 7.97 (s, 1H), 7.58 (d, *J*=8.3 Hz, 2H), 7.45 (t, *J*=7.6 Hz, 1H), 7.38 (d, *J*=8.3 Hz, 1H), 7.20 (t, *J*=7.5 Hz, 1H), 5.50 (d, *J*=3.3 Hz, 1H), 4.35 (t, *J*=6.6 Hz, 2H), 2.41 (s, 3H), 2.15 (s, 3H), 1.74 (br t, *J*=6.0 Hz, 2H), 1.25–1.19 (m, 6H), 0.79 (t, *J*=6.7 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 195.47, 173.89, 144.55, 140.76, 139.88, 134.03, 126.20, 125.10, 122.19, 122.14, 120.55, 119.12, 118.73, 110.88, 109.99, 109.76, 54.93, 42.67, 31.33, 30.65, 28.85, 26.50, 22.37, 18.62, 14.22; GC/MS (*m*/*z*) 419 (M^+); Anal. Calcd for $C_{25}H_{29}N_3OS$: C, 71.56; H, 6.97; N, 10.01; S, 7.64. Found: C, 71.68; H, 7.16; N, 9.91; S, 7.56.

3.9.14. Ethyl 4-(10-hexyl-10H-phenothiazin-3-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 14). Mp 83–85 °C; IR (υ cm^{-1}, KBr) 3234.3, 3108.0, 2954.7, 2929.1, 2856.0, 1702.2, 1644.9, 1602.7, 1576.6, 1493.3, 1464.3, 1368.4, 1330.7, 1288.4, 1226.1, 1196.7, 1092.5, 1039.6, 878.7, 795.2, 748.3, 670.1, 515.4; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.22 (s, 1H), 7.71 (s, 1H), 7.18 (br t, *J*=7.7 Hz, 1H), 7.12 (d, *J*=7.6 Hz, 1H), 7.05 (dd, *J*=8.2; 1.9 Hz, 1H), 7.00–6.90 (m, 4H), 5.07 (d, *J*=3.3 Hz, 1H), 3.99 (q, *J*=7.1 Hz, 2H), 3.82 (t, *J*=6.8 Hz, 2H), 2.26 (s, 3H), 1.65 (quintet, *J*=7.1 Hz, 2H), 1.35 (br t, *J*=6.9 Hz, 2H), 1.24–1.22 (m, 4H), 1.11 (t, *J*=7.1 Hz, 3H), 0.81 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 165.66, 152.48, 148.74, 145.01, 144.24, 139.46, 127.98, 127.46, 125.82, 125.26, 123.66, 123.52, 122.75, 116.07, 116.02, 99.43, 59.59, 53.48, 46.79, 31.19, 26.53, 26.19, 22.43, 18.18, 14.45, 14.17; GC/MS (*m*/*z*) 465 (M^+); Anal. Calcd for $C_{26}H_{31}N_3O_3S$: C, 67.07; H, 6.71; N, 9.02; S, 6.89. Found: C, 66.92; H, 6.89; N, 8.92; S, 6.80.

3.9.15. Ethyl 4-(7-bromo-10-hexyl-10H-phenothiazin-3-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 15). Mp 95–96 °C; IR (υ cm^{-1}, KBr) 3238.9, 3114.4, 2955.0, 2929.5, 2856.4, 1702.1, 1645.0, 1462.2, 1330.1, 1226.6, 1092.3, 803.2, 670.1, 544.8, 469.1; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.24 (s, 1H), 7.72 (s, 1H), 7.35–7.33 (m, 2H), 7.06 (dd, *J*=8.5; 1.9 Hz, 1H), 6.99–6.96 (m, 2H), 6.93 (d, *J*=9.6 Hz, 1H), 5.06 (d, *J*=3.3 Hz, 1H), 3.98 (q, *J*=7.1 Hz, 2H), 3.80 (t, *J*=6.8 Hz, 2H), 2.25 (s, 3H), 1.62 (quintet, *J*=7.1 Hz, 2H), 1.36–1.31 (m, 2H), 1.23–1.20 (m, 4H), 1.11 (t, *J*=7.1 Hz, 3H), 0.81 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (400 MHz, in DMSO-d_6) δ 165.63, 152.45, 148.82, 144.41, 143.83, 139.82, 130.48, 129.29, 126.09, 125.35, 122.90, 117.68, 116.29, 113.97, 99.35, 59.61, 53.44, 46.87, 31.15, 26.37, 26.11, 22.41, 18.19, 14.45, 14.17; GC/MS (*m*/*z*) 543 (M^+); Anal. Calcd for $C_{26}H_{30}BrN_3O_3S$: C, 57.35; H, 5.55; N, 7.72; S, 5.89. Found: C, 57.21; H, 5.60; N, 7.63; S, 5.80.

3.9.16. Ethyl 4-(9-hexyl-9H-carbazol-3-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 16). Mp 84–86 °C; IR (υ cm^{-1}, KBr) 3235.6, 3109.3, 2930.0, 2857.7, 1701.8, 1645.1, 1490.5, 1467.8, 1331.4, 1225.6, 1093.0, 771.5, 747.3, 674.0, 627.3, 462.8; ^{1}H NMR (400 MHz, in DMSO-d_6) δ 9.22 (s, 1H), 8.09 (d, *J*=7.6 Hz, 1H), 7.94 (d, *J*=1.2 Hz, 1H), 7.78 (s, 1H), 7.56 (2d, *J*=8.1; 8.6 Hz, 2H), 7.43 (t, *J*=8.3 Hz, 1H), 7.37 (dd, *J*=8.6; 1.5 Hz, 1H), 7.18 (t, *J*=7.5 Hz, 1H), 5.34 (d, *J*=3.0 Hz, 1H), 4.35 (t, *J*=6.9 Hz, 2H), 3.97 (q, *J*=7.1 Hz, 2H), 2.30 (s, 3H), 1.74 (quintet, *J*=6.7 Hz, 2H), 1.26–1.19 (m, 6H), 1.09 (t, *J*=7.1 Hz, 3H), 0.79 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (400 MHz in DMSO-d_6) δ 165.84, 152.45, 148.18, 140.66, 139.65, 136.02, 126.00, 124.68, 122.24, 121.86, 120.35, 119.00, 118.29, 109.65, 100.24, 59.45, 54.86, 42.58, 31.31, 28.81, 26.47, 22.34, 18.18, 14.40, 14.17; GC/MS (*m*/*z*) 433 (M^+); Anal. Calcd for $C_{26}H_{31}N_3O_3$: C, 72.03; H, 7.21; N, 9.69. Found: C, 72.26; H, 7.34; N, 9.58.

3.9.17. Ethyl 4-(6-bromo-9-hexyl-9H-carbazol-3-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 17). Mp 88–89 °C; IR (υ cm^{-1}, KBr) 3238.7, 3112.7, 2955.4, 2930.1, 2857.8, 1701.8, 1645.4, 1482.0, 1448.7, 1345.1, 1316.1, 1281.6, 1226.0, 1152.7, 1092.5, 1022.3, 869.3, 795.0, 731.8, 674.0, 635.7, 569.6; ^{1}H NMR (400 MHz in DMSO-d_6) δ 9.23 (s, 1H), 8.36 (s, 1H), 7.99 (d, *J*=0.8 Hz, 1H), 7.79 (s, 1H), 7.57–7.54 (m, 3H), 7.42 (dd, *J*=8.6; 1.3 Hz, 1H), 5.34 (d, *J*=2.8 Hz, 1H), 4.33 (t, *J*=6.8 Hz, 2H), 3.95 (q, *J*=7.1 Hz, 2H), 2.32 (s, 3H), 1.70 (br t, *J*=6.2 Hz, 2H), 1.21–1.16 (m, 6H), 1.06 (t, *J*=7.0 Hz, 3H), 0.77 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (400 MHz in DMSO-d_6) δ 165.82, 152.37, 148.45, 140.04, 139.40, 136.56, 128.33, 125.79, 124.23, 123.00, 120.91, 118.83, 111.71, 111.16, 110.03, 99.97, 59.45, 54.90, 42.76, 31.30, 28.78, 26.43, 22.35, 18.25, 14.43, 14.18; GC/MS (*m*/*z*) 511 (M^+); Anal. Calcd for $C_{26}H_{30}BrN_3O_3$: C, 60.94; H, 5.90; N, 8.20. Found: C, 60.79; H, 5.97; N, 8.08.

3.9.18. Ethyl 4-(7-bromo-10-hexyl-10H-phenothiazin-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 18). Mp 93–95 °C; IR (υ cm^{-1}, KBr) 3395.1, 3192.2, 2955.1, 2928.8, 2856.0, 1694.4, 1651.8, 1561.9, 1462.1, 1329.7, 1270.6, 1251.9, 1180.4, 1106.3, 867.9, 806.7, 768.0, 630.9, 543.5; ^{1}H NMR (400 MHz in DMSO-d_6) δ 10.27 (s, 1H), 9.53 (d, *J*=2.0 Hz, 1H), 7.24–7.22 (m, 2H), 6.96–6.88 (m, 2H), 6.85–6.81 (m, 2H), 4.99 (d, *J*=3.5 Hz, 1H), 3.94–3.88 (m, 2H), 3.70 (t, *J*=6.8 Hz, 2H), 2.20 (s, 3H), 1.52 (quintet, *J*=7.1 Hz, 2H), 1.27–1.20 (m, 2H), 1.13–1.11 (m, 4H), 1.01 (t, *J*=7.1 Hz, 3H), 0.70 (t, *J*=6.7 Hz, 3H); ^{13}C NMR (400 MHz in DMSO-d_6) 174.46, 165.43, 145.49, 144.27, 144.20, 138.43, 130.54, 129.32, 126.30, 125.95,

125.43, 123.05, 117.74, 116.38, 114.08, 100.78, 60.00, 53.50, 46.90, 31.14, 26.35, 26.10, 22.41, 17.58, 14.39, 14.18; GC/MS (m/z) 559 (M^+); Anal. Calcd for $C_{26}H_{30}BrN_3O_2S_2$: C, 55.71; H, 5.39; N, 7.50; S, 11.44. Found: C, 55.83; H, 5.40; N, 7.62; S, 11.52.

3.9.19. Ethyl 4-(9-hexyl-9H-carbazol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 19). Mp 88–89 °C; IR (υ cm^{-1}, KBr) 3420.1, 3191.9, 2955.6, 2929.1, 2856.9, 1694.3, 1651.7, 1567.0, 1490.1, 1468.1, 1383.2, 1368.6, 1331.0, 1275.9, 1243.7, 1187.7, 1166.4, 1104.9, 1024.3, 769.9, 747.5, 642.9, 503.7; ^{1}H NMR (400 MHz in DMSO-d_6) δ 10.37 (s, 1H), 9.74 (d, J=1.3 Hz, 1H), 8.10 (d, J=7.6 Hz, 1H), 7.95 (d, J=1.3 Hz, 1H), 7.57 (d, J=8.6 Hz, 2H), 7.45 (t, J=7.7 Hz, 1H), 7.35 (dd, J=8.6; 1.5 Hz, 1H), 7.19 (t, J=7.4 Hz, 1H), 5.38 (d, J=3.3 Hz, 1H), 4.35 (t, J=6.8 Hz, 2H), 4.00 (q, J=7.1 Hz, 2H), 2.37 (s, 3H), 1.74 (br t, J=6.8 Hz, 2H), 1.25–1.16 (m, 6H), 1.09 (t, J=7.1 Hz, 3H), 0.79 (t, J=6.9 Hz, 3H); ^{13}C NMR (400 MHz in DMSO-d_6) δ 174.16, 165.66, 144.97, 140.74, 139.85, 134.72, 126.16, 124.81, 122.22, 121.97, 120.43, 119.14, 118.57, 109.87, 109.75, 101.65, 59.85, 54.98, 42.66, 31.34, 28.84, 26.50, 22.37, 17.59, 14.37, 14.20; GC/MS (m/z) 449 (M^+); Anal. Calcd for $C_{26}H_{31}N_3O_2S$: C, 69.46; H, 6.95; N, 9.35; S, 7.13. Found: C, 69.28; H, 7.11; N, 9.24; S, 7.01.

3.9.20. Ethyl 4-(6-bromo-9-hexyl-9H-carbazol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate (entry 20). Mp 101–103 °C; IR (υ cm^{-1}, KBr) 3289.2, 3188.0, 2955.5, 2929.0, 2857.0, 1694.2, 1651.6, 1562.3, 1484.7, 1456.1, 1368.9, 1345.5, 1313.7, 1280.5, 1187.3, 1162.3, 1106.4, 1022.1, 869.0, 794.1, 763.7, 643.3, 574.4; ^{1}H NMR (400 MHz in DMSO-d_6) δ 10.36 (s, 1H), 9.73 (d, J=1.5 Hz, 1H), 8.38 (s, 1H), 7.99 (d, J=1.0 Hz, 1H), 7.61–7.56 (m, 3H), 7.41 (dd, J=8.4; 1.4 Hz, 1H), 5.37 (d, J=3.5 Hz, 1H), 4.34 (t, J=6.8 Hz, 2H), 3.99 (q, J=7.1 Hz, 2H), 2.38 (s, 3H), 1.72 (br t, J=6.4 Hz, 2H), 1.21 (br s, 6H), 1.08 (t, J=7.1 Hz, 3H), 0.78 (t, J=6.8 Hz, 3H); ^{13}C NMR (400 MHz in DMSO-d_6) δ 174.06, 165.60, 145.26, 140.19, 139.44, 135.20, 128.46, 125.92, 124.17, 123.06, 120.97, 119.07, 111.79, 111.28, 110.23, 101.31, 59.82, 54.95, 42.80, 31.30, 28.79, 26.43, 22.35, 17.64, 14.37, 14.19; GC/MS (m/z) 527 (M^+); Anal. Calcd for $C_{26}H_{30}BrN_3O_2S$: C, 59.09; H, 5.72; N, 7.95; S, 6.07. Found: C, 59.03; H, 5.85; N, 7.77; S, 5.93.

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