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Michael additions of dihydropyrimidines and 2-amino-1,3,4-thiadiazoles to α,β-ethylenic compounds: using polyethylene glycols as a green reaction media

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Abstract—Polyethylene glycol (PEG) was found to be an inexpensive, non-toxic, and effective medium for the Michael additions of 3,4-dihydropyrimidines to α,β-ethylenic compounds to provide *N*3-functionalized dihydropyrimidines in the presence of K_2CO_3 as the catalyst. Under similar reaction conditions, 2-amino-5-aryloxymethyl-1,3,4-thiadiazoles reacted with methyl acrylate to give unexpected products 5*H*,6*H*-[1,3,4]thiadiazolo[1,2-*a*]pyrimidine-7-ones through tandem Michael addition and intramolecular cyclization.

1. Introduction

The Michael reaction has been one of the most important reactions in organic chemistry.[1] While most of them are performed in organic solvents, therefore this synthetic methodology does not meet the requirement of green chemistry. To address some of these issues, there are three main methods to eliminate the threat of organic solvents to environment. Firstly, solvent-free processes have been developed,[2] which to some extent have succeeded in some Michael addition reactions. But in performing the majority of organic transformations, solvents play a critical role in mixing the ingredients to allow molecular interactions to be more efficient. Meanwhile using water as green solvent has also been well documented,[3] but the practical utilization is limited due to the hydrophobic nature of organic compounds and the sensitivity of catalysts to moisture. Another alternative has been reported where ionic liquid has been used as reaction media instead of water and organic solvents.[4] However, ionic liquids require tedious preparation and their environment safety is still debatable.

Recently, polyethylene glycol (PEG) and its monomethyl ethers have emerged as alternative green reaction media with unique properties such as thermal stability, commercial availability, non-volatility, immiscibility with a number of organic solvents, and recyclability. On the other hand, PEGs are inexpensive, completely non-halogenated, easily degradable, and possess low toxicity.[5] The use of PEGs as a reaction solvent has received considerable attention in synthetic organic chemistry. It has previously been suggested that PEGs could be used as complexing solvents of inorganic salts, in order to enhance the reactivity of the anion with the organic substrate.[6] In these systems, where the anion could be brought into solution with higher reactivity. Additionally, it may be possible by utilizing the unique physicochemical properties of PEGs to realize reactivity and/or selectivity that cannot be attained in organic solvents.[7] However, it is surprised that Michael additions in PEGs are relatively scarce.[8]

3,4-Dihydropyrimidines (DHPMs) have received considerable attention in the past decades due to their heterocyclic scaffold[9] and their interesting pharmacological properties.[10] Among the DHPM derivatives, most of the pharmacologically attractive DHPM derivatives are *N*3 substituted analogues.[9b,9c] It has already been pointed out that *N*3-monoalkylated DHPMs cannot be obtained either by alkylation of unsubstituted derivatives or by classical Biginelli condensation using alkylureas. In both cases, only *N*1-alkylated products are formed.[11] Previously we reported an alternative synthetic pathway to *N*3-functionalized DHPMs: by treatment of DHPMs with α,β-ethylenic compounds using KF/Al_2O_3 as the catalyst under mild reaction conditions.[12] At that time we noted that these aza-Michael reactions carried out in DMF were not efficient when using K_2CO_3 as the catalyst.

Keywords: 3,4-Dihydropyrimidines; 5*H*,6*H*-[1,3,4]Thiadiazolo[1,2-*a*]pyrimidine-7-ones; Polyethylene glycol; Michael additions.
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Herein, we report the aza-Michael additions of DHPMs and 2-amino-5-aryloxymethyl-1,3,4-thiadiazoles to α,β-ethylenic compounds where PEG-400 is used as solvent and applying K_2CO_3 as the catalyst (Schemes 1 and 2). Consequently, cumbersome isolation is avoided, and good yield of desired products are obtained, and mild reaction condition is of significant contribution to synthetic convenience.

2. Results and discussion

In a model reaction, we employed DHPM **1a** and methyl acrylate **2a** as reactants with PEG-400 as solvent and found that *N*3-functionalized 3,4-dihydropyrimidine **3a** could be produced in the presence of inorganic bases such as K_2CO_3, Na_2CO_3, KF, NaOH, and KOH. However, the reaction would be failed if Et_3N was applied as catalyst. From Table 1, we can see that the best yield of **3a** (80%) was obtained by carrying out the reaction in PEG-400 at room temperature for 18 h using DHPM **1a** (1 mmol), methyl acrylate **2a** (1 mmol), and K_2CO_3 (0.2 mmol) (entry 1). The reaction could also be conducted at more elevated temperature for 4 h to give **3a** with good yield of 80% (entry 6). It has been reported that water has unusual effects on the rate and outcome of many organic reactions. We then mixed **1a** and **2a** in the combination solvent system of equal amount of PEG-400 and H_2O, and the Michael reaction occurred to give **3a**. However, the higher temperature and prolonged reaction time were required and the yield of **3a** was unsatisfied. When using water as reaction medium the Michael adduct could not be detected (entry 12).

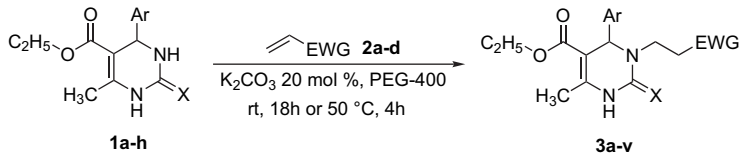
After experimentation with a variety of material molars, bases, reaction times, and temperature, we quickly arrived at the optimized reaction conditions: equivalent amounts of **1a** and **2a**, 20 mol % of K_2CO_3, 2.0 g of PEG-400, and stirring for 18 h at room temperature.

Under the optimal conditions, the Michael additions were extended to a series of substrates **1a–g** and **2b–c** with various substituents. The results are presented in Table 2. Generally, the reactions between DHPMs **1a–g** and **2b–d** proceeded efficiently and furnished excellent isolated yields of desired products (entries 1–22). After completion of the reaction, the mixture was diluted with H_2O and filtered to give the adduct product. And PEG was recyclized from the solution by extraction with CH_2Cl_2 and could be reused without obvious losses of its high activity and regioselectivity. For the reaction of **1a** with **2a**, over 70% yield for **3a** was obtained after recycling three times (78%, 74%, and 71%).

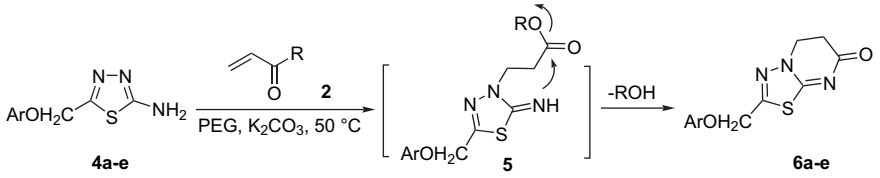
PEGs can be regarded as open-chain crown ethers as they are able to form complexes with alkaline and alkaline-earth cations in protic and aprotic solvents.[13] We postulated that in the PEG/K_2CO_3 system, where the CO_3^{2-} anion could be brought into solution through coordination of the cationic center of K_2CO_3 with the oxygen atom of the PEG. Thus the reactivity of CO_3^{2-} anion with dihydropyrimidines was elevated through enhancing the nucleophilicity of nitrogen for addition to electron-deficient alkenes.

We next planned to establish the generality of the reaction media of PEG/K_2CO_3 for reactions of 2-amino-5-aryloxymethyl-1,3,4-thiadiazoles with α,β-unsaturated carbonyl compounds (Scheme 2). The mixture of 2-amino-5-aryloxymethyl-1,3,4-thiadiazole **4a** and methyl acrylate **2a** was warmed in PEG/K_2CO_3 system at 50 °C for 12 h, resulting in an unexpected compound. Extensive analysis of this compound was performed to elucidate the structure. To our surprise, mass spectrometry indicated that this compound resulted from the elimination of one equivalent of methanol between 2-amino-5-aryloxymethyl-1,3,4-thiadiazole **4a** and methyl acrylate **2a**. Elemental analysis confirmed this finding. The IR (KBr) spectrum of this compound exhibited a strong absorption at 1690 cm^{-1}, which indicated that the carbonyl group (C═O) was conjugate with the π-conjugate of C═N or nitrogen atom, respectively. And the disappearance of the absorption of NH_2 confirmed the previous findings. The ^1H NMR spectrum was clean and exhibited two triplicate signals derived from methylene groups. These facts along with the ^{13}C NMR spectrum led us to hypothesize that **4a** reacted with **2a** to afford 5*H*,6*H*-[1,3,4]thiadiazolo[1,2-*a*]pyrimidine-7-one **6a** through tandem Michael addition and intramolecular cyclization by losing methanol.

In order to verify the hypothesis, ethyl acrylate **2b** was employed as substrate under above mentioned conditions, the same product **6a** was obtained. These results promoted us to utilize other 2-amino-5-aryloxymethyl-1,3,4-thiadiazoles **4b–e** as substrates and all the reactions were smoothly

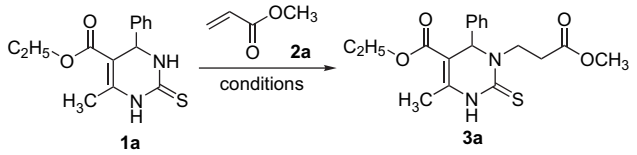


Scheme 1.



Scheme 2. Ar=C_6H_5, **4a**, **6a**; Ar=2-$CH_3C_6H_4$, **4b**, **6b**; Ar=3-$CH_3C_6H_4$, **4c**, **6c**; Ar=4-$CH_3C_6H_4$, **4d**, **6d**; Ar=4-$CH_3OC_6H_4$, **4e**, **6e**. R=CH_3 **2a** or C_2H_5 **2b**.

Table 1. Optimization of Michael reaction conditions[a]



Entry	Base (mol)	Solvent[b]	T (°C)	Time[c] (h)	Yield[d] (%)
1	20% K_2CO_3	PEG-400	rt	18	80
2	20% Na_2CO_3	PEG-400	rt	18	68
3	20% KF	PEG-400	rt	18	58
4	20% NaOH	PEG-400	rt	18	68
5	20% KOH	PEG-400	rt	18	62
6	20% K_2CO_3	PEG-400	50	4	80
7	30% K_2CO_3	PEG-400	rt	18	80
8	20% Et_3N	PEG-400	50	18	0
9	None	PEG-400	50	18	0
10	20% K_2CO_3	1:1 PEG/H_2O	50	18	40
11	20% K_2CO_3	2:1 PEG/H_2O	50	12	50
12	20% K_2CO_3	H_2O	rt	72	0

[a] Equivalent amounts of starting material **1a** (1 mmol), methyl acrylate **2a** (1 mmol), K_2CO_3, and PEG-400 were used for the reaction.
[b] Amount of solvents (in 2.0 g) used for the reaction.
[c] Time required for complete disappearance of starting compounds by TLC.
[d] Isolated yield of purified Michael product after recrystallization.

completed affording the corresponding products **6b–e** (Scheme 2). It should be emphasized that it is the first example of one-pot procedure for 5*H*,6*H*-[1,3,4]thiadiazolo-[3,2-*a*]pyrimidine-7-one through the addition/elimination reaction of 2-amino-5-aryloxymethyl-1,3,4-thiadiazoles and α,β-unsaturated carbonyl compounds.

Some previous searches on the reactions of 2-amino-5-substituted-1,3,4-thiadiazoles with α-halo carbonyl compounds have revealed that the amino group (NH_2) of 2-amino-5-substituted-1,3,4-thiadiazoles showed poor reactivity to electrophilic compounds.[14,15] Comparatively, the nitrogen atom on thiadiazole cycle has a good reactivity to electrophilic agent. So the probable mechanism for the reactions of 2-amino-5-aryloxymethyl-1,3,4-thiadiazoles with alkyl acrylate may be described as Scheme 2. Herein, the *N*3 of thiadiazole **4** attacked β-carbon of alkyl acrylate to give the intermediate **5**. Then a nucleophilic addition and elimination reactions occurred to give the product **6** (Scheme 2).

Table 2. Aza-Michael reactions of DHPMs **1** with α,β-ethylenic compounds **2** in PEG

Entry[a]	Ar	1	X	EWG	2	Product	Yield[b] (%)
1	C_6H_5	**1a**	S	COOMe	**2a**	**3a**	80
2	4-$CH_3OC_6H_4$	**1b**	S	COOMe	**2a**	**3b**	70
3	4-ClC_6H_4	**1c**	S	COOMe	**2a**	**3c**	83
4	C_6H_5	**1a**	S	$COOC_2H_5$	**2b**	**3d**	86
5	4-$CH_3OC_6H_4$	**1b**	S	$COOC_2H_5$	**2b**	**3e**	70
6	4-ClC_6H_4	**1c**	S	$COOC_2H_5$	**2b**	**3f**	86
7	C_6H_5	**1a**	S	CN	**2c**	**3g**	80
8	4-$CH_3OC_6H_4$	**1b**	S	CN	**2c**	**3h**	79
9	4-ClC_6H_4	**1c**	S	CN	**2c**	**3i**	80
10	C_6H_5	**1d**	O	COOMe	**2a**	**3j**	82
11	4-$CH_3OC_6H_4$	**1e**	O	COOMe	**2a**	**3k**	74
12	4-ClC_6H_4	**1f**	O	COOMe	**2a**	**3l**	87
13	C_6H_5	**1d**	O	$COOC_2H_5$	**2b**	**3m**	82
14	4-$CH_3OC_6H_4$	**1e**	O	$COOC_2H_5$	**2b**	**3n**	83
15	4-ClC_6H_4	**1f**	O	$COOC_2H_5$	**2b**	**3o**	79
16	C_6H_5	**1d**	O	CN	**2c**	**3p**	78
17	4-$CH_3OC_6H_4$	**1e**	O	CN	**2c**	**3q**	71
18	4-ClC_6H_4	**1f**	O	CN	**2c**	**3r**	80
19	C_6H_5	**1a**	S	$CONH_2$	**2d**	**3s**	90
20	2-ClC_6H_4	**1g**	S	$CONH_2$	**2d**	**3t**	86
21	4-ClC_6H_4	**1c**	S	$CONH_2$	**2d**	**3u**	92
22	2-$CH_3OC_6H_4$	**1h**	S	$CONH_2$	**2d**	**3v**	80

[a] Equivalent amounts of starting material **1a** (1 mmol), methyl acrylate **2a** (1 mmol), K_2CO_3 (0.2 mmol), and PEG-400 (2.0 g) were used for the reaction.
[b] Isolated yield of purified Michael product after recrystallization from 80% ethanol.

In summary, we have developed a novel and efficient protocol for the *N*3-functionalized DHPMs by Michael additions using K_2CO_3 as the catalyst in PEG under mild reaction conditions with excellent yields. Under similar reaction conditions, treatment of 2-amino-5-aryloxymethyl-1,3,4-thiadiazoles with methyl/ethyl acrylate led to a tandem Michael addition and elimination reaction, to provide 5*H*,6*H*-[1,3,4]thiadiazolo[3,2-*a*]pyrimidine-7-ones. The advantages of this protocol are the simplicity of operation, the high regioselectivity of products, the utilization of inexpensive and mild basic catalyst, and without using volatile organic solvents as reaction media.

3. Experimental

3.1. General experimental procedures

All reagents were obtained commercially and used without further purification. Melting points were determined on an XT-4 electrothermal micromelting point apparatus and are uncorrected. IR spectra were recorded using KBr pellets on a Digilab Merlin FT-IR spectrophotometer. NMR spectra were recorded at 400 (^{1}H) and 100 (^{13}C) MHz, respectively, on a Varian Mercury plus-400 instrument using $CDCl_3$ or DMSO-d_6 as solvent and TMS as an internal standard. Elemental analyses were performed on a Carlo-Erba 1106 Elemental Analysis instrument. Mass spectra were recorded on a TRACE DSQ instrument. Compounds **1a–h**[16] and **4a–e**[17] were prepared by following the reported methods.

3.2. Synthesis of compounds 3a–v: general procedure

To a suspension of 3,4-dihydropyrimidine **1** (1.00 mmol) and α,β-ethylenic compound **2** (1.00 mmol) in PEG-400 (2.0 g), K_2CO_3 (20 mol %, 0.26 g) was added in one portion. The mixture was stirred at room temperature for 18 h and poured onto ice-water. The resulting product was purified by recrystallization from ethanol and water (EtOH/H_2O=4:1).

3.2.1. 3-(2-Methoxycarbonyl-ethyl)-6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3a). Mp 175–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (br s, 1H), 7.29–7.24 (m, 5H), 5.55 (s, 1H), 4.32–4.25 (m, 1H), 4.19–4.08 (m, 2H), 3.76–3.69 (m, 1H), 3.61 (s, 3H), 2.96–2.89 (m, 1H), 2.59–2.52 (m, 1H), 2.29 (s, 3H), 1.25–1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 171.8, 165.2, 142.4, 141.0, 128.8, 128.4, 126.9, 102.8, 62.1, 60.4, 50.8, 48.4, 31.7, 18.0, 14.2. FT-IR (KBr) ν (cm^{-1}) 3298, 3076, 2992, 2938, 1722, 1704, 1644, 1245, 1221, 1194, 1101. MS: m/z=362 (M^+). Anal. Calcd for $C_{18}H_{22}N_2O_4S$: C, 59.65; H, 6.12; N, 7.73. Found: C, 59.38; H, 6.19; N, 7.96.

3.2.2. 3-(2-Methoxycarbonyl-ethyl)-6-methyl-2-thioxo-4-(4-methoxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3b). Mp 170–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (br s, 1H), 6.80 (d, J=8.8 Hz, 2H), 6.49 (d, J=8.8 Hz, 2H), 5.91 (s, 1H), 4.35–4.24 (m, 1H), 4.07–4.02 (m, 2H), 3.78–3.70 (m, 1H), 3.75 (s, 3H), 3.60 (s, 3H), 2.94–2.86 (m, 1H), 2.61–2.54 (m, 1H), 2.30 (s, 3H), 1.22–1.19 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 171.8, 165.7, 153.6, 146.3, 136.1, 127.8, 113.9, 101.5, 62.1, 59.9, 55.2, 55.3, 48.4, 31.8, 16.6, 14.1. FT-IR (KBr) ν (cm^{-1}) 3278, 3098, 2992, 2938, 1723, 1707, 1644, 1245, 1221, 1194, 1101. Anal. Calcd for $C_{19}H_{24}N_2O_5S$: C, 58.15; H, 6.16; N, 7.14. Found: C, 58.41; H, 6.31; N, 7.01.

3.2.3. 3-(2-Methoxycarbonyl-ethyl)-6-methyl-2-thioxo-4-(4-chlorophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3c). Mp 126–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (br s, 1H), 7.29–7.22 (m, 4H), 5.57 (s, 1H), 4.32–4.25 (m, 1H), 4.18–4.10 (m, 2H), 3.67–3.60 (m, 4H), 2.97–2.89 (m, 1H), 2.62–2.55 (m, 1H), 2.29 (s, 3H), 1.26–1.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 171.8, 165.2, 142.4, 141.0, 128.8, 128.4, 126.9, 102.8, 62.1, 60.4, 50.8, 48.4, 31.8, 18.1, 14.2. FT-IR (KBr) ν (cm^{-1}) 3304, 3064, 2986, 2950, 1725, 1707, 1650, 1260, 1215, 1194, 1098. Anal. Calcd for $C_{18}H_{21}ClN_2O_4S$: C, 54.47; H, 5.33; N, 7.06. Found: C, 54.79; H, 5.49; N, 7.30.

3.2.4. 3-(2-Ethoxycarbonyl-ethyl)-6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3d). Mp 150–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (br s, 1H), 7.33–7.25 (m, 5H), 5.27 (s, 1H), 4.33–4.26 (m, 1H), 4.17–4.05 (m, 4H), 3.70–3.63 (m, 1H), 2.94–2.86 (m, 1H), 2.59–2.52 (m, 1H), 2.14 (s, 3H), 1.25–1.19 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 171.2, 165.2, 142.3, 141.0, 128.8, 128.4, 126.9, 102.9, 62.0, 60.8, 60.4, 53.4, 48.4, 32.0, 18.2, 14.2, 14.1. FT-IR (KBr) ν (cm^{-1}) 3298, 3082, 2992, 2938, 1704, 1644, 1245, 1215, 1197, 1098. MS: m/z=376 (M^+). Anal. Calcd for $C_{19}H_{24}N_2O_4S$: C, 60.62; H, 6.43; N, 7.44. Found: C, 60.80; H, 6.30; N, 7.60.

3.2.5. 3-(2-Ethoxycarbonyl-ethyl)-6-methyl-2-thioxo-4-(4-methoxylphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3e). Mp 114–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (br s, 1H), 6.85 (d, J=8.8 Hz, 2H), 6.51 (d, J=8.8 Hz, 2H), 5.56 (s, 1H), 4.36–4.25 (m, 1H), 4.11–4.06 (m, 4H), 3.77 (s, 3H), 3.75–3.68 (m, 1H), 3.26–3.19 (m, 1H), 2.60–2.55 (m, 1H), 2.28 (s, 3H), 1.23–1.18 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 171.4, 165.4, 153.6, 145.4, 136.1, 127.8, 113.8, 102.4, 62.1, 59.9, 55.4, 55.3, 48.4, 32.1, 18.2, 14.2, 14.1. FT-IR (KBr) ν (cm^{-1}) 3302, 3098, 2992, 2938, 1700, 1648, 1240, 1218, 1200, 1098. Anal. Calcd for $C_{20}H_{26}N_2O_5S$: C, 59.09; H, 6.45; N, 6.89. Found: C, 59.33; H, 6.59; N, 6.74.

3.2.6. 3-(2-Ethoxycarbonyl-ethyl)-6-methyl-2-thioxo-4-(4-chlorophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3f). Mp 160–161 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (br s, 1H), 7.31–7.23 (m, 4H), 5.58 (s, 1H), 4.32–4.26 (m, 1H), 4.18–4.10 (m, 4H), 3.67–3.60 (m, 1H), 2.97–2.85 (m, 1H), 2.59–2.55 (m, 1H), 2.27 (s, 3H), 1.27–1.24 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 171.4, 165.2, 142.3, 141.0, 128.8, 128.4, 126.9, 102.9, 62.0, 60.3, 53.4, 48.4, 32.0, 18.2, 14.2, 14.1. FT-IR (KBr) ν (cm^{-1}) 3305, 3091, 2962, 2948, 1733, 1715, 1682, 1265, 1246, 1215, 1096. Anal. Calcd for $C_{19}H_{23}ClN_2O_4S$: C, 55.54; H, 5.64; N, 6.82. Found: C, 55.27; H, 5.50; N, 6.95.

3.2.7. 3-(2-Cyanoethyl)-6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3g). Mp 154–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (br s, 1H), 7.32–7.24 (m, 5H), 5.53 (s, 1H), 4.31–4.24 (m, 1H), 4.17–4.07 (m, 2H), 3.71–3.64 (m, 1H), 3.11–3.01 (m, 1H), 2.44–2.32 (m, 1H), 2.27 (s, 3H), 1.25–1.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 164.8, 142.3, 140.6, 129.1, 128.8, 127.0, 117.42, 103.2, 62.8, 60.6, 48.3, 17.9, 15.6, 14.2. FT-IR (KBr) ν (cm^{-1}) 3208, 3058, 2992, 2944, 2260, 1701, 1653, 1266, 1239, 1200. MS: m/z=329 (M^+). Anal. Calcd for $C_{17}H_{19}N_3O_2S$: C, 61.98; H, 5.81; N, 12.76. Found: C, 62.15; H, 5.85; N, 12.68.

3.2.8. 3-(2-Cyanoethyl)-6-methyl-2-thioxo-4-(4-methoxylphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3h). Mp 86–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (br s, 1H), 6.89 (d, J=8.8 Hz, 2H), 6.50 (d, J=8.8 Hz, 2H), 5.55 (s, 1H), 4.30–4.25 (m, 1H), 4.17–4.08 (m, 2H), 3.76 (s, 3H), 3.73–3.65 (m, 1H), 3.11–3.02 (m, 1H), 2.45–2.33 (m, 1H), 2.29 (s, 3H), 1.23–1.18 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 164.8, 153.6, 142.3, 140.6, 127.2, 117.3, 103.5, 62.8, 60.6, 55.4, 48.2, 17.9, 15.6, 14.1. FT-IR (KBr) ν (cm^{-1}) 3222, 3090, 2962, 2938, 2264, 1705, 1655, 1265, 1246, 1213. Anal. Calcd for $C_{18}H_{21}N_3O_3S$: C, 60.15; H, 5.89; N, 11.69. Found: C, 60.28; H, 5.86; N, 11.65.

3.2.9. 3-(2-Cyanoethyl)-6-methyl-2-thioxo-4-(4-chlorophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3i). Mp 121–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (br s, 1H), 7.28–7.21 (m, 4H), 5.56 (s, 1H), 4.32–4.23 (m, 1H), 4.18–4.10 (m, 2H), 3.73–3.62 (m, 1H), 3.11–3.01 (m, 1H), 2.39–2.30 (m, 1H), 2.30 (s, 3H), 1.23–1.19 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 164.8, 142.3, 140.6, 139.5, 129.1, 128.4, 116.8, 102.8, 62.7, 60.6, 48.3, 17.8, 15.6, 14.1. FT-IR (KBr) ν (cm^{-1}) 3302, 3093, 2965, 2946, 2259, 1708, 1655, 1265, 1245, 1208. Anal. Calcd for $C_{17}H_{18}ClN_3O_2S$: C, 56.12; H, 4.99; N, 11.55. Found: C, 56.37; H, 5.06; N, 11.71.

3.2.10. 3-(2-Methoxycarbonyl-ethyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3j). Mp 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (br s, 1H), 7.34–7.22 (m, 5H), 5.34 (s, 1H), 4.12–4.03 (m, 2H), 3.77–3.70 (m, 1H), 3.62 (s, 3H), 3.30–3.23 (m, 1H), 2.71–2.63 (m, 1H), 2.48–2.36 (m, 1H), 2.29 (s, 3H), 1.22–1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 165.5, 153.1, 146.3, 142.1, 128.6, 128.0, 127.2, 101.6, 61.3, 59.9, 51.7, 42.1, 32.6, 18.5, 14.2. FT-IR (KBr) ν (cm^{-1}) 3208, 3088, 2956, 1737, 1713, 1683, 1263, 1242, 1086. Anal. Calcd for $C_{18}H_{22}N_2O_5$: C, 62.42; H, 6.40; N, 8.09. Found: C, 62.70; H, 6.32; N, 7.96.

3.2.11. 3-(2-Methoxycarbonyl-ethyl)-6-methyl-2-oxo-4-(4-methoxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3k). Mp 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (br s, 1H), 6.91–6.50 (m, 4H), 5.83 (s, 1H), 4.15–4.04 (m, 2H), 3.79–3.71 (m, 1H), 3.75

(s, 3H), 3.63 (s, 3H), 3.31–3.22 (m, 1H), 2.77–2.64 (m, 1H), 2.48–2.35 (m, 1H), 2.30 (s, 3H), 1.25–1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 165.6, 153.6, 153.2, 146.4, 142.2, 136.6, 127.8, 113.9, 101.5, 61.3, 59.9, 51.7, 42.0, 32.6, 18.5, 14.2. FT-IR (KBr) ν (cm^{-1}) 3258, 3092, 2956, 1747, 1708, 1683, 1260, 1243, 1086. Anal. Calcd for $C_{19}H_{24}N_2O_6$: C, 60.63; H, 6.43; N, 7.44. Found: C, 60.46; H, 6.52; N, 7.31.

3.2.12. 3-(2-Methoxycarbonyl-ethyl)-6-methyl-2-oxo-4-(4-chloroxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3l). Mp 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br s, 1H), 7.30–7.21 (m, 4H), 5.39 (s, 1H), 4.17–4.06 (m, 2H), 3.59–3.54 (m, 1H), 3.63 (s, 3H), 3.31–3.22 (m, 1H), 2.73–2.64 (m, 1H), 2.50–2.37 (m, 1H), 2.28 (s, 3H), 1.23–1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 165.6, 153.2, 146.4, 144.1, 128.6, 128.1, 127.2, 101.8, 61.3, 59.9, 51.6, 42.1, 32.6, 18.4, 14.2. FT-IR (KBr) ν (cm^{-1}) 3266, 3059, 2956, 1743, 1710, 1680, 1260, 1245, 1086. Anal. Calcd for $C_{18}H_{21}ClN_2O_5$: C, 56.77; H, 5.56; N, 7.36. Found: C, 56.52; H, 5.68; N, 7.50.

3.2.13. 3-(2-Ethoxycarbonyl-ethyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3m). Mp 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (br s, 1H), 7.35–7.23 (m, 5H), 5.34 (s, 1H), 4.12–4.03 (m, 4H), 3.78–3.71 (m, 1H), 3.28–3.20 (m, 1H), 2.70–2.62 (m, 1H), 2.42–2.32 (m, 1H), 2.30 (s, 3H), 1.23–1.18 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 165.5, 153.0, 146.2, 142.1, 128.6, 128.1, 127.2, 101.6, 61.2, 60.6, 59.9, 53.4, 42.0, 32.93, 18.5, 14.2, 14.1. FT-IR (KBr) ν (cm^{-1}) 3255, 3096, 2956, 1742, 1705, 1683, 1260, 1242, 1089. Anal. Calcd for $C_{19}H_{24}N_2O_5$: C, 63.32; H, 6.71; N, 7.77. Found: C, 63.66; H, 6.45; N, 7.52.

3.2.14. 3-(2-Ethoxycarbonyl-ethyl)-6-methyl-2-oxo-4-(4-methoxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3n). Mp 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (br s, 1H), 7.01–6.84 (m, 4H), 5.42 (s, 1H), 4.11–4.01 (m, 4H), 3.78 (s, 3H), 3.77–3.70 (m, 1H), 3.29–3.20 (m, 1H), 2.71–2.63 (m, 1H), 2.43–2.31 (m, 1H), 2.30 (s, 3H), 1.25–1.19 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 165.6, 153.6, 153.0, 146.2, 142.2, 136.1, 127.8, 113.9, 102.0, 61.3, 60.6, 59.9, 55.3, 51.6, 42.1, 32.6, 18.5, 18.4, 14.2, 14.1. FT-IR (KBr) ν (cm^{-1}) 3268, 3104, 2956, 1746, 1707, 1683, 1260, 1246, 1090. Anal. Calcd for $C_{20}H_{26}N_2O_6$: C, 61.53; H, 6.71; N, 7.18. Found: C, 61.81; H, 6.57; N, 7.03.

3.2.15. 3-(2-Ethoxycarbonyl-ethyl)-6-methyl-2-oxo-4-(4-chlorophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3o). Mp 119–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (br s, 1H), 7.33–7.22 (m, 4H), 5.40 (s, 1H), 4.19–4.05 (m, 4H), 3.75–3.69 (m, 1H), 3.30–3.20 (m, 1H), 2.73–2.64 (m, 1H), 2.45–2.33 (m, 1H), 2.29 (s, 3H), 1.22–1.16 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 165.6, 153.0, 146.3, 142.1, 128.6, 128.1, 127.2, 102.0, 61.3, 60.0, 53.5, 42.1, 32.9, 18.6, 14.3, 14.2. FT-IR (KBr) ν (cm^{-1}) 3275, 3096, 2936, 1722, 1711, 1683, 1260, 1240, 1081. Anal. Calcd for $C_{19}H_{23}ClN_2O_5$: C, 57.80; H, 5.87; N, 7.09. Found: C, 58.25; H, 5.63; N, 6.85.

3.2.16. 3-(2-Cyanoethyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3p). Mp 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (br s, 1H), 7.34–7.26 (m, 5H), 5.34 (s, 1H), 4.12–4.03 (m, 2H), 3.73–3.66 (m, 1H), 3.35–3.27 (m, 1H), 2.71–2.63 (m, 1H), 2.44–2.32 (m, 1H), 2.25 (s, 3H), 1.75–1.69 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 153.1, 146.0, 141.6, 128.8, 128.4, 127.1, 117.6, 101.7, 61.9, 60.1, 42.3, 18.4, 16.4, 14.1. FT-IR (KBr) ν (cm^{-1}) 3202, 3094, 2956, 2266, 1668, 1641, 1272, 1248, 1119. Anal. Calcd for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.35; H, 5.97; N, 13.55.

3.2.17. 3-(2-Cyanoethyl)-6-methyl-2-oxo-4-(4-methoxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3q). Mp 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (br s, 1H), 6.93 (d, J=8.8 Hz, 2H), 6.82 (d, J=8.8 Hz, 2H), 5.45 (s, 1H), 4.15–4.06 (m, 2H), 3.76 (s, 3H), 3.72–3.64 (m, 1H), 3.34–3.25 (m, 1H), 2.70–2.62 (m, 1H), 2.44–2.36 (m, 1H), 2.24 (s, 3H), 1.75–1.69 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 153.6, 153.0, 146.1, 141.6, 128.5, 127.2, 117.6, 102.0, 62.0, 60.5, 55.4, 42.4, 18.5, 16.4, 14.2. FT-IR (KBr) ν (cm^{-1}) 3213, 3099, 2954, 2265, 1668, 1641, 1272, 1241, 1098. Anal. Calcd for $C_{18}H_{21}N_3O_4$: C, 62.96; H, 6.16; N, 12.24. Found: C, 63.02; H, 6.13; N, 12.19.

3.2.18. 3-(2-Cyanoethyl)-6-methyl-2-oxo-4-(4-chlorophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3r). Mp 77–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (br s, 1H), 7.33–7.26 (m, 4H), 5.35 (s, 1H), 4.10–4.05 (m, 2H), 3.75–3.69 (m, 1H), 3.39–3.28 (m, 1H), 2.70–2.61 (m, 1H), 2.45–2.35 (m, 1H), 2.23 (s, 3H), 1.81–1.72 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 153.1, 146.0, 139.6, 134.3, 129.1, 128.4, 117.6, 101.8, 62.0, 60.2, 42.4, 18.4, 16.4, 14.2. FT-IR (KBr) ν (cm^{-1}) 3209, 3090, 2956, 2267, 1668, 1641, 1272, 1248, 1124. Anal. Calcd for $C_{17}H_{18}ClN_3O_3$: C, 58.71; H, 5.22; N, 12.08. Found: C, 59.02; H, 5.03; N, 12.25.

3.2.19. 3-(2-Aminocarbonyl-ethyl)-6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3s). Mp 192–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (br s, 1H), 7.33–7.27 (m, 5H), 5.78 (br s, 1H), 5.70 (br s, 1H), 5.59 (s, 1H), 4.26–4.19 (m, 1H), 4.18–4.08 (m, 2H), 3.84–3.77 (m, 1H), 2.86–2.79 (m, 1H), 2.49–2.42 (m, 1H), 2.32 (s, 3H), 1.22 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 172.7, 165.1, 142.2, 141.1, 128.8, 128.4, 127.1, 103.0, 62.2, 60.4, 49.1, 33.5, 18.1, 14.1. FT-IR (KBr) ν (cm^{-1}) 3376, 3178, 3070, 2986, 1695, 1668, 1554, 1233. MS: m/z=347 (M^+). Anal. Calcd for $C_{17}H_{21}N_3O_3S$: C, 58.77; H, 6.09; N, 12.09. Found: C, 58.52; H, 6.23; N, 12.27.

3.2.20. 3-(2-Aminocarbonyl-ethyl)-6-methyl-2-thioxo-4-(2-chlorophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3t). Mp 149–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (br s, 1H), 7.32–7.28 (m, 4H), 5.79 (br s, 1H), 5.70 (br s, 1H), 5.61 (s, 1H), 4.28–4.21 (m, 1H), 4.19–4.08 (m, 2H), 3.91–3.80 (m, 1H), 2.86–2.79 (m, 1H), 2.51–2.43 (m, 1H), 2.33 (s, 3H), 1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 172.6, 164.6, 150.6, 143.4, 142.2, 136.5, 136.1, 130.6, 128.8, 104.3, 61.9, 60.8,

48.6, 35.2, 18.1, 14.2. FT-IR (KBr) ν (cm^{-1}) 3376, 3196, 3070, 2980, 1713, 1653, 1545, 1242. Anal. Calcd for $C_{17}H_{20}ClN_3O_3S$: C, 53.47; H, 5.28; N, 11.00. Found: C, 53.58; H, 5.38; N, 11.25.

3.2.21. 3-(2-Aminocarbonyl-ethyl)-6-methyl-2-thioxo-4-(4-chlorophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3u). Mp 195–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (br s, 1H), 7.33–7.23 (m, 4H), 5.77 (br s, 1H), 5.71 (br s, 1H), 5.41 (s, 1H), 4.25–4.20 (m, 1H), 4.18–4.06 (m, 2H), 3.62–3.54 (m, 1H), 2.74–2.65 (m, 1H), 2.48–2.41 (m, 1H), 2.31 (s, 3H), 1.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 171.8, 165.2, 142.4, 141.0, 136.5, 128.8, 128.4, 102.9, 62.1, 60.4, 50.7, 32.4, 18.1, 14.2. FT-IR (KBr) ν (cm^{-1}) 3400, 3208, 3064, 2998, 1675, 1668, 1548, 1239. Anal. Calcd for $C_{17}H_{20}ClN_3O_3S$: C, 53.47; H, 5.28; N, 11.00. Found: C, 53.70; H, 5.61; N, 10.79.

3.2.22. 3-(2-Aminocarbonyl-ethyl)-6-methyl-2-thioxo-4-(2-methoxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid ethyl ester (3v). Mp 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (br s, 1H), 7.37–7.23 (m, 1H), 7.03–7.00 (m, 1H), 6.90–6.87 (m, 2H), 5.78 (br s, 1H), 5.71 (br s, 1H), 5.61 (s, 1H), 4.24–4.18 (m, 1H), 4.08–4.03 (m, 2H), 3.78–3.73 (m, 1H), 3.61 (s, 3H), 2.86–2.80 (m, 1H), 2.52–2.43 (m, 1H), 2.41 (s, 3H), 1.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 172.3, 166.1, 158.4, 150.2, 142.3, 128.8, 127.4, 111.8, 102.6, 62.3, 60.3, 56.8, 49.5, 33.3, 18.1, 14.2. FT-IR (KBr) ν (cm^{-1}) 3436, 3394, 3166, 3064, 2998, 1707, 1659, 1548, 1242. Anal. Calcd for $C_{18}H_{23}N_3O_4S$: C, 57.28; H, 6.14; N, 11.13. Found: C, 57.52; H, 6.26; N, 11.34.

3.3. Synthesis of compounds 6a–e: general procedure

To a suspension of methyl acrylate **2** (1.2 mmol, 0.10 g) and 2-amino-5-aryloxymethyl-1,3,4-thiadiazole **5** (1.0 mmol) in PEG-400 (2.0 g), K_2CO_3 (0.2 mmol, 0.26 g) was added in one portion. After the mixture was stirred at 50 °C for 12 h, the mixture was poured onto ice and neutralized by 2 N HCl. The precipitate formed was isolated by filtration. The crude product was purified by column chromatography on silica gel (EtOAc).

3.3.1. 5*H*,6*H*-2-Phenyloxymethylene-[1,3,4]thiadiazolo[1,2-*a*]pyrimidine-7-one 6a. Yield 65%, mp 180 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H), 7.07–7.00 (m, 3H), 5.47 (s, 2H), 3.77 (t, J=6.5 Hz, 2H), 2.90 (t, J=6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 160.6, 159.3, 157.5, 129.8, 121.7, 115.1, 64.1, 48.7, 32.8. FT-IR (KBr) ν (cm^{-1}) 2920, 2870, 1689, 1570, 1250, 1122. MS: m/z=261 (M^+). Anal. Calcd for $C_{12}H_{11}N_3O_2S$: C, 55.16; H, 4.24; N, 16.08. Found: C, 55.02; H, 4.19; N, 16.15.

3.3.2. 5*H*,6*H*-2-(2-Methylphenyloxymethylene)-[1,3,4]thiadiazolo[1,2-*a*]pyrimidine-7-one 6b. Yield 68%, mp 156 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.07 (m, 1H), 6.90 (s, 2H), 5.42 (s, 2H), 3.76 (t, J=6.4 Hz, 2H), 2.87 (t, J=6.5 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 160.8, 155.5, 130.8, 127.1, 126.1, 121.4, 112.1, 69.8, 48.7, 33.0, 16.0. FT-IR (KBr) ν (cm^{-1}) 2909, 2873, 1690, 1569, 1251, 1118. MS: 275 (M^+). Anal. Calcd for $C_{13}H_{13}N_3O_2S$: C, 56.71; H, 4.76; N, 15.26. Found: C, 56.87; H, 4.73; N, 15.21.

3.3.3. 5*H*,6*H*-2-(3-Methylphenyloxymethylene)-[1,3,4]thiadiazolo[1,2-*a*]pyrimidine-7-one 6c. Yield 65%, mp 185 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02–6.98 (m, 1H), 6.87–6.83 (m, 3H), 5.46 (s, 2H), 3.67 (t, J=6.4 Hz, 2H), 2.90 (t, J=6.5 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 162.3, 157.2, 132.4, 129.2, 126.1, 122.8, 112.0, 65.9, 48.6, 32.2, 16.0. FT-IR (KBr) ν (cm^{-1}) 2914, 2884, 1695, 1614, 1260, 1158. MS: m/z=275 (M^+). $C_{13}H_{13}N_3O_2S$: C, 56.71; H, 4.76; N, 15.26. Found: C, 56.62; H, 4.73; N, 15.20.

3.3.4. 5*H*,6*H*-2-(4-Methylphenyloxymethylene)-[1,3,4]thiadiazolo[1,2-*a*]pyrimidine-7-one 6d. Yield 70%, mp 166 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–7.09 (m, 2H), 6.95–6.90 (m, 3H), 5.42 (s, 2H), 3.76 (t, J=6.4 Hz, 2H), 2.87 (t, J=6.5 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 160.6, 155.0, 130.4, 114.9, 64.2, 48.7, 32.9, 20.2. FT-IR (KBr) ν (cm^{-1}) 2922, 2872, 1691, 1595, 1247, 1174. MS: m/z=275 (M^+). Anal. Calcd for $C_{13}H_{13}N_3O_2S$: C, 56.71; H, 4.76; N, 15.26. Found: C, 56.59; H, 4.74; N, 15.33.

3.3.5. 5*H*,6*H*-2-(4-Methoxylphenyloxymethylene)-[1,3,4]thiadiazolo[1,2-*a*]pyrimidine-7-one 6e. Yield 70%, mp 175 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J=8.6 Hz, 2H), 6.0 (d, J=8.6 Hz, 2H), 5.42 (s, 2H), 3.78 (s, 3H), 3.75 (t, J=6.4 Hz, 2H), 2.85 (t, J=6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 160.6, 158.3, 158.0, 115.4, 64.0, 55.35, 48.7, 32.8. FT-IR (KBr) ν (cm^{-1}) 2914, 1695, 1629, 1569, 1239, 1170. MS: m/z=291 (M^+). Anal. Calcd for $C_{13}H_{13}N_3O_3S$: C, 53.60; H, 4.50; N, 14.42. Found: C, 53.72; H, 4.57; N, 14.34.

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