

**ON REACTIONS OF THIADIAZINONES:
SYNTHESIS OF NEW 6-ARYLIDENE-
1,3,4-THIADIAZIN-5-ONES**

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6-Benzylidene-, 6-(furan-2-ylmethylene)-, and 6-(thiophen-2-ylmethylene)-1,3,4-thiadiazin-5-ones have been synthesized by condensation of 1,3,4-thiadiazin-5-ones with appropriate aromatic aldehydes.

Keywords: aromatic aldehydes, 1,3,4-thiadiazin-5-ones, condensation.

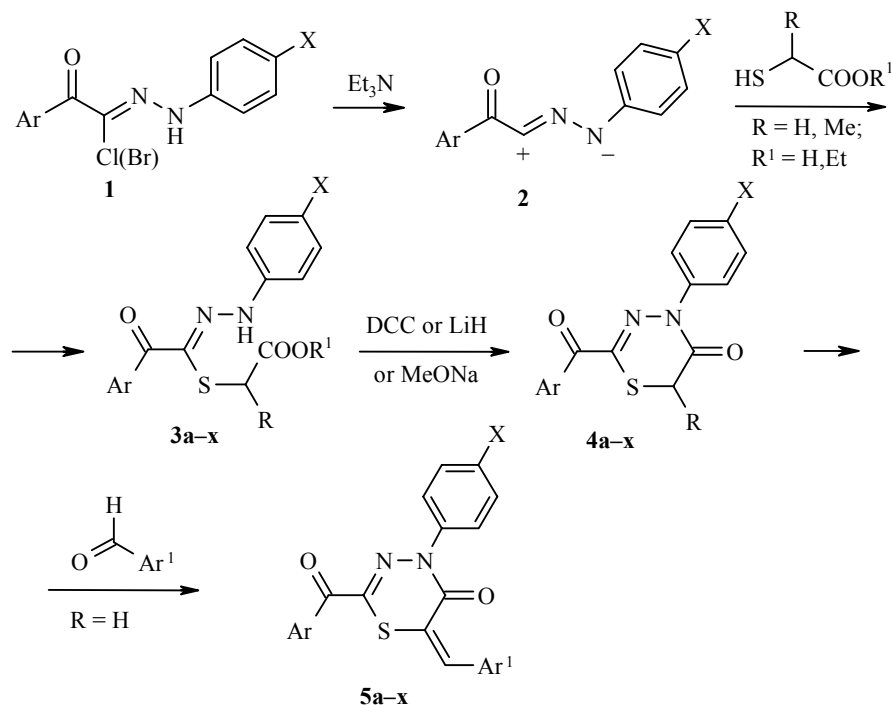
Heterocycles containing nitrogen and sulfur constitute the core structure of a number of biologically interesting compounds. 1,3,4-Thiadiazine derivatives are known to possess various biological and medicinal activities such as bactericidal [1], fungicidal [2], insecticidal [3], pesticidal [4], herbicidal [5, 6], plant-growth regulator activity [7], anti-inflammatory [8], antithrombotic [9], antiplatelet [10], anti-arrhythmic [11], spasmolytic [12, 13], cardiotoxic [14, 15], and metalloproteinase inhibitor activity [16]. They have been proposed for the treatment of heart failures [17]. Moreover, 1,3,4-thiadiazinone derivatives have been used for prevention and/or treatment of anemia [18], as phosphodiesterase III/IV inhibitors [19, 20], and also for the treatment of tumors and acquired immune deficiency syndrome (AIDS) [20, 21]. Different methods were used to synthesize the 1,3,4-thiadiazin-5-one derivatives, some of which employed thiosemicarbazide [22], thiocarbohydrazide [23], thiooxamic acid derivatives [24] and α -halocarbonyl compounds. Recently, the reactions of 1,3,4-thiadiazine derivatives have been reviewed [25].

In continuation of our work on the reaction of six-membered thiazia heterocyclic compounds we report on the reactivity of 2-aryl-4-aryl-6H-1,3,4-triazin-5-ones **4a-x** towards aromatic aldehydes (see Scheme). The N-aryl-substituted hydrazoneyl halides **1** are found to react with 2-sulfanyl alkanolic acids [26] or ethyl sulfanylacetate [27] *via* reactive nitrilimines **2** yielding acyclic adducts **3a-x** which underwent cyclization to 1,3,4-thiadiazinone rings **4a-x** in the presence of dicyclohexylcarbodiimide (DCC) or lithium hydride, or methanolic sodium methoxide. Condensation of these thiadiazinones with benzaldehyde, 2-furaldehyde, and thiophene-2-carboxaldehyde in the presence of potassium acetate/acetic acid afforded the corresponding 6-benzylidene-, 6-(furan-2-ylmethylene)-, and 6-(thiophen-2-yl-methylene)-1,3,4-thiadiazin-5-ones **5a-x** in moderate yields (Table 1).

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The IR spectra of compounds **5a-x** in KBr showed strong absorption bands of the aroyl carbonyl group in the 1690-1640 region, a lactam C=O band in the 1680-1670 region, and C-S band in the 1220-1200 cm^{-1} region. The ^1H NMR spectra of compounds **5a-x** showed the disappearance of methylene protons (3.9-3.8 ppm) at C-6 (present in compounds **4a-x**), the methine proton (=CHAr') signal appeared as a singlet in the range of 6.2-6.1 and the signal at about 9.0 ppm was attributed to amide N-H proton in compounds **5i-q**. The ^{13}C NMR spectra of these adducts displayed characteristic signals of the different carbons of the structures suggested. The signal of carbonyl carbon of lactam (C=O of ring) appeared in the range of 161-160 ppm and that of methine carbon (=CHAr') resonated in the range of 111-109 ppm. The signal in the range of 147-143 ppm was attributed to C=N of the thiadiazinone ring.



Entry	Ar	X	Ar ¹
a	Me	H	Ph
b	Me	H	2-Furyl
c	Me	Cl	Ph
d	Me	Cl	2-Furyl
e	Me	Br	Ph
f	Me	Br	2-Furyl
g	Ph	Cl	Ph
h	Ph	Cl	2-Furyl
i	PhNH	H	Ph
j	PhNH	H	2-Furyl
k	PhNH	H	2-Thienyl
l	PhNH	Cl	Ph

Entry	Ar	X	Ar ¹
m	PhNH	Cl	2-Furyl
n	PhNH	Cl	2-Thienyl
o	PhNH	Br	Ph
p	PhNH	Br	2-Thienyl
q	PhNH	F	2-Furyl
r	2-Furyl	Cl	Ph
s	2-Furyl	Cl	2-Furyl
t	2-Thienyl	Cl	Ph
u	2-Thienyl	Cl	2-Thienyl
v	2-Naphthyl	H	Ph
w	2-Naphthyl	Me	Ph
x	2-Naphthyl	Me	2-Furyl

In conclusion, the condensation of 2-aryol-4-aryl-6H-1,3,4-triazin-5-ones with appropriate aromatic aldehydes gave 6-arylidene-1,3,4-triazin-5-ones in 60-70% yield.

TABLE 1 Physical Characteristics and Elemental Analysis Data of Compounds **5a-x**

Compound	Empirical formula	Found, %			mp, °C	Yield, %
		Calculated, %				
		C	H	N		
5a	C ₁₈ H ₁₄ N ₂ O ₂ S	66.80	4.20	8.60	218-220	65
		67.06	4.38	8.69		
5b	C ₁₆ H ₁₂ N ₂ O ₃ S	61.20	4.00	9.10	145-147	61
		61.53	3.87	8.97		
5c	C ₁₈ H ₁₃ ClN ₂ O ₂ S	60.80	3.50	7.70	198-200	63
		60.59	3.67	7.85		
5d	C ₁₆ H ₁₁ ClN ₂ O ₃ S	55.70	3.30	7.90	147-149	61
		55.42	3.20	8.08		
5e	C ₁₈ H ₁₃ BrN ₂ O ₂ S	53.50	3.40	7.10	190-191	65
		53.88	3.27	6.98		
5f	C ₁₆ H ₁₁ BrN ₂ O ₃ S	49.40	2.60	7.40	170-172	64
		49.12	2.83	7.16		
5g	C ₂₃ H ₁₅ ClN ₂ O ₂ S	66.20	3.50	6.60	190-192	62
		65.95	3.61	6.69		
5h	C ₂₁ H ₁₃ ClN ₂ O ₃ S	61.40	3.40	6.70	150-152	60
		61.69	3.20	6.85		
5i	C ₂₃ H ₁₇ N ₃ O ₂ S	69.40	4.60	10.70	110-112	65
		69.15	4.29	10.52		
5j	C ₂₁ H ₁₅ N ₃ O ₃ S	64.90	4.10	10.90	164-166	61
		64.77	4.88	10.79		
5k	C ₂₁ H ₁₅ N ₃ O ₂ S ₂	62.00	3.60	10.20	123-125	67
		62.20	3.73	10.36		
5l	C ₂₃ H ₁₆ ClN ₃ O ₂ S	63.50	3.90	9.50	136-138	65
		63.67	3.72	9.68		
5m	C ₂₁ H ₁₄ ClN ₃ O ₃ S	59.80	3.60	10.10	190-192	69
		59.51	3.38	9.91		
5n	C ₂₁ H ₁₄ ClN ₃ O ₂ S	57.50	3.40	9.40	174-176	63
		57.33	3.21	9.55		
5o	C ₂₃ H ₁₆ BrN ₃ O ₂ S	57.90	3.60	8.50	146-148	66
		57.75	3.37	8.78		
5p	C ₂₁ H ₁₄ BrN ₂ O ₂ S ₂	51.80	3.10	8.50	128-130	61
		52.07	2.90	8.67		
5q	C ₂₁ H ₁₄ FN ₃ O ₃ S	62.10	3.30	10.20	144-146	68
		61.91	3.46	10.31		
5r	C ₂₁ H ₁₃ ClN ₂ O ₃ S	61.50	3.40	7.00	212-214	65
		61.69	3.20	6.85		
5s	C ₁₉ H ₁₁ ClN ₂ O ₄ S	57.50	2.60	6.90	158-160	64
		57.22	2.78	7.02		
5t	C ₂₁ H ₁₃ ClN ₂ O ₂ S ₂	59.60	2.90	6.30	207-209	62
		59.36	3.08	6.59		
5u	C ₁₉ H ₁₁ ClN ₂ O ₂ S ₃	53.15	2.75	6.40	196-197	68
		52.95	2.57	6.50		
5v	C ₂₇ H ₁₈ N ₂ O ₂ S	74.50	4.25	6.35	216-218	60
		74.63	4.18	6.45		
5w	C ₂₈ H ₂₀ N ₂ O ₂ S	75.20	4.30	6.10	188-190	61
		74.98	4.49	6.25		
5x	C ₂₆ H ₁₈ N ₂ O ₃ S	71.40	4.30	6.50	168-170	60
		71.22	4.14	6.39		

EXPERIMENTAL

Melting points were determined on a Stuart electrothermal apparatus and are uncorrected. The IR spectra were obtained by using Satellite 3000 Mid IR spectrophotometer in KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Bruker spectrometer (400 and 100 MHz, respectively) at room temperature in DMSO-d₆, using TMS as an internal reference, and the chemical shifts (δ) were reported in ppm downfield from TMS. The elemental analysis was performed at Cairo University, Egypt, and the results agreed with the calculated values within experimental errors.

2-Aroyl-4-aryl-1,3,4-thiadiazin-5-ones **4a-x** were prepared according to the previous by described procedures [25, 26]. Benzaldehyde, 2-furaldehyde, and thiophene-2-carboxaldehyde were purchased from Avocado Research Chemicals, England.

Synthesis of adducts 5a-x (General Method). Molar equivalents of 1,3,4-thiadiazin-5-ones **4a-x** and appropriate aldehyde (1:1 adducts), anhydrous potassium acetate, and glacial acetic acid were dissolved together at room temperature, and the reaction mixture was heated to reflux temperature with efficient stirring. The reactions were monitored by thin layer chromatography (TLC) analysis until all the aldehydes reacted. Upon cooling, the mixture gave a precipitate, which was collected, washed several times with water, and recrystallized from ethanol.

2-Acetyl-6-benzylidene-4-phenyl-1,3,4-thiadiazin-5-one (5a). IR spectrum, ν , cm^{-1} : 1692 ($\text{CH}_3\text{C}=\text{O}$), 1675 (lactam $\text{C}=\text{O}$), 1215 ($\text{C}-\text{S}$). ^1H NMR spectrum, δ , ppm: 7.81-7.05 (10H, m, H Ar); 6.15 (1H, s, CH); 2.58 (3H, s, CH_3). ^{13}C NMR spectrum, δ , ppm: 192.5 ($\text{C}=\text{O}$); 160.3 (lactam $\text{C}=\text{O}$); 145.2 ($\text{C}=\text{N}$); 142.4; 140.8; 135.2; 130.7; 128.8; 128.2; 127.7; 125.2; 115.2 (8 arom. carbons and C-6); 111.6 ($=\text{CH}$); 26.6 (CH_3).

2-Acetyl-6-(furan-2-ylmethylene)-4-phenyl-1,3,4-thiadiazin-5-one (5b). IR spectrum, ν , cm^{-1} : 1695 ($\text{CH}_3\text{C}=\text{O}$), 1677 (lactam $\text{C}=\text{O}$), 1217 ($\text{C}-\text{S}$). ^1H NMR spectrum, δ , ppm: 8.20-7.15 (8H, m, H Ar); 6.22 (1H, s, CH); 2.60 (3H, s, CH_3). ^{13}C NMR spectrum, δ , ppm: 192.7 ($\text{C}=\text{O}$); 160.2 (lactam $\text{C}=\text{O}$); 145.7 ($\text{C}=\text{N}$); 142.0; 140.6; 134.8; 132.2; 128.9; 128.4; 127.8; 125.1; 115.4 (8 arom. carbons and C-6); 109.5 ($=\text{CH}$); 26.7 (CH_3).

2-Acetyl-6-benzylidene-4-(4-chlorophenyl)-1,3,4-thiadiazin-5-one (5c). IR spectrum, ν , cm^{-1} : 1694 ($\text{CH}_3\text{C}=\text{O}$), 1680 (lactam $\text{C}=\text{O}$), 1219 ($\text{C}-\text{S}$). ^1H NMR spectrum, δ , ppm: 7.84-7.16 (9H, m, H Ar); 6.18 (1H, s, CH); 2.56 (3H, s, CH_3). ^{13}C NMR spectrum, δ , ppm: 192.6 ($\text{C}=\text{O}$); 160.7 (lactam $\text{C}=\text{O}$); 146.3 ($\text{C}=\text{N}$); 142.9; 139.1; 135.0; 133.5; 129.0; 127.4; 126.4; 121.0; 116.6 (8 arom. carbons and C-6); 111.8 ($=\text{CH}$), 26.6 (CH_3).

2-Acetyl-4-(4-chlorophenyl)-6-(furan-2-ylmethylene)-1,3,4-thiadiazin-5-one (5d). IR spectrum, ν , cm^{-1} : 3336 ($\text{N}-\text{H}$), 1692 ($\text{CH}_3\text{C}=\text{O}$), 1682 (lactam $\text{C}=\text{O}$), 1214 ($\text{C}-\text{S}$). ^1H NMR spectrum, δ , ppm: 7.82-7.18 (7H, m, H Ar); 6.20 (1H, s, CH); 2.55 (3H, s, CH_3). ^{13}C NMR spectrum, δ , ppm: 192.5 ($\text{C}=\text{O}$); 160.8 (lactam $\text{C}=\text{O}$); 146.9 ($\text{C}=\text{N}$); 142.4; 139.1; 135.3; 133.4; 129.1; 128.2; 127.9; 126.3; 116.2 (8 arom. carbons and C-6); 110.3 ($=\text{CH}$), 26.7 (CH_3).

2-Acetyl-6-benzylidene-4-(4-bromophenyl)-1,3,4-thiadiazin-5-one (5e). IR spectrum, ν , cm^{-1} : 1695 ($\text{CH}_3\text{C}=\text{O}$), 1675 (lactam $\text{C}=\text{O}$), 1221 ($\text{C}-\text{S}$). ^1H NMR spectrum, δ , ppm: 8.49-7.10 (9H, m, H Ar); 6.17 (1H, s, CH); 2.57 (3H, s, CH_3). ^{13}C NMR spectrum, δ , ppm: 192.7 ($\text{C}=\text{O}$); 160.5 (lactam $\text{C}=\text{O}$); 146.6 ($\text{C}=\text{N}$); 142.6; 139.7; 135.2; 132.0; 128.9; 128.1; 126.6; 121.4; 117.0 (8 arom. carbons and C-6); 111.5 ($=\text{CH}$); 26.6 (CH_3).

2-Acetyl-4-(4-bromophenyl)-6-(furan-2-ylmethylene)-1,3,4-thiadiazin-5-one (5f). IR spectrum, ν , cm^{-1} : 1693 ($\text{CH}_3\text{C}=\text{O}$), 1673 (lactam $\text{C}=\text{O}$), 1219 ($\text{C}-\text{S}$). ^1H NMR spectrum, δ , ppm: 8.22-7.05 (7H, m, H Ar); 6.23 (1H, s, CH); 2.54 (3H, s, CH_3). ^{13}C NMR spectrum, δ , ppm: 192.6 ($\text{C}=\text{O}$); 160.8 (lactam $\text{C}=\text{O}$); 146.4 ($\text{C}=\text{N}$); 142.8; 139.6; 135.5; 131.9; 128.1; 127.6; 126.4; 121.1; 117.2 (8 arom. carbons and C-6); 109.3 ($=\text{CH}$), 26.7 (CH_3).

2-Benzoyl-6-benzylidene-4-(4-chlorophenyl)-1,3,4-thiadiazin-5-one (5g). IR spectrum, ν , cm^{-1} : 1678 (lactam $\text{C}=\text{O}$), 1650 ($\text{C}=\text{O}$), 1205 ($\text{C}-\text{S}$). ^1H NMR spectrum, δ , ppm: 8.27-7.16 (14H, m, H Ar); 6.28 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 185.6 ($\text{C}=\text{O}$); 161.2 (lactam $\text{C}=\text{O}$); 142.9 ($\text{C}=\text{N}$); 141.3; 140.6; 138.3; 137.9; 135.3; 134.8; 132.4; 129.5; 127.9; 127.5; 126.1; 125.6; 124.6 (12 arom. carbons and C-6); 111.9 ($=\text{CH}$).

2-Benzoyl-4-(4-chlorophenyl)-6-(furan-2-ylmethylene)-1,3,4-thiadiazin-5-one (5h). IR spectrum, ν , cm^{-1} : 1676 (lactam $\text{C}=\text{O}$), 1653 ($\text{C}=\text{O}$), 1207 ($\text{C}-\text{S}$). ^1H NMR spectrum, δ , ppm: 8.24-7.12 (12H, m, H Ar); 6.27 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 185.4 ($\text{C}=\text{O}$); 161.1 (lactam $\text{C}=\text{O}$); 142.8 ($\text{C}=\text{N}$); 141.5; 140.4; 138.7; 137.9; 135.1; 134.8; 130.9; 129.4; 128.0; 127.6; 125.2; 124.4; 120.6 (12 arom. carbons and C-6); 110.4 ($=\text{CH}$).

6-Benzylidene-4-phenyl-2-phenylaminocarbonyl-1,3,4-thiadiazin-5-one (5i). IR spectrum, ν , cm^{-1} : 3258 ($\text{N}-\text{H}$), 1679 (lactam $\text{C}=\text{O}$), 1655 (amide $\text{C}=\text{O}$), 1205 ($\text{C}-\text{S}$). ^1H NMR spectrum, δ , ppm: 9.20 (1H, s, NH); 7.59-7.12 (15H, m, H Ar); 6.11 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 160.3 (lactam $\text{C}=\text{O}$); 157.7 (amide $\text{C}=\text{O}$); 145.0 ($\text{C}=\text{N}$); 141.5; 138.7; 137.6; 135.2; 135.0; 128.9; 128.6; 127.9; 127.5; 125.1; 124.5; 121.0; 113.7 (12 arom. carbons and C-6); 111.1 ($=\text{CH}$).

6-(Furan-2-ylmethylene)-4-phenyl-2-phenylaminocarbonyl-1,3,4-thiadiazin-5-one (5j). IR spectrum, ν , cm^{-1} : 3260 (N–H), 1676 (lactam C=O), 1650 (amide C=O), 1208 (C–S). ^1H NMR spectrum, δ , ppm: 9.15 (1H, s, NH); 7.72-7.16 (13H, m, H Ar); 6.13 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 160.6 (lactam C=O); 158.2 (amide C=O); 144.7 (C=N); 141.3; 138.9; 137.9; 135.2; 134.8; 130.4; 128.7; 128.5; 127.6; 126.5; 124.3; 123.3; 114.4 (12 arom. carbons and C-6); 110.9 (=CH).

4-Phenyl-2-phenylaminocarbonyl-6-(thiophen-2-ylmethylene)-1,3,4-thiadiazin-5-one (5k). IR spectrum, ν , cm^{-1} : 3255 (N–H), 1678 (lactam C=O), 1652 (amide C=O), 1202 (C–S). ^1H NMR spectrum, δ , ppm: 9.17 (1H, s, NH); 7.76-7.20 (13H, m, H Ar); 6.10 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 160.8 (lactam C=O); 158.5 (amide C=O); 145.1 (C=N); 141.5; 138.2; 134.7; 131.4; 129.1; 128.8; 128.0; 127.8; 127.2; 124.5; 121.8; 114.7 (12 arom. carbons and C-6); 110.3 (=CH).

6-Benzylidene-4-(4-chlorophenyl)-2-phenylaminocarbonyl-1,3,4-thiadiazin-5-one (5l). IR spectrum, ν , cm^{-1} : 3257 (N–H), 1680 (lactam C=O), 1660 (amide C=O), 1207 (C–S). ^1H NMR spectrum, δ , ppm: 9.33 (1H, s, NH); 7.50-7.05 (14H, m, H Ar); 6.12 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 160.7 (lactam C=O); 157.9 (amide C=O); 143.9 (C=N); 141.0; 139.0; 138.6; 135.0; 130.4; 129.1; 128.6; 128.3; 126.4; 124.2; 123.3; 120.1; 115.8 (12 arom. carbons and C-6); 111.3 (=CH).

4-(4-Chlorophenyl)-6-(furan-2-ylmethylene)-2-phenylaminocarbonyl-1,3,4-thiadiazin-5-one (5m). IR spectrum, ν , cm^{-1} : 3265 (N–H), 1682 (lactam C=O), 1665 (amide C=O), 1205 (C–S). ^1H NMR spectrum, δ , ppm: 9.25 (1H, s, NH); 7.64-7.13 (12H, m, H Ar); 6.16 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 160.1 (lactam C=O); 157.7 (amide C=O); 144.5 (C=N); 140.2; 139.5; 138.9; 135.2; 130.5; 128.7; 128.5; 127.7; 125.8; 124.4; 123.2; 120.2; 116.5 (12 arom. carbons and C-6); 110.9 (=CH).

4-(4-Chlorophenyl)-2-phenylaminocarbonyl-6-(thiophen-2-ylmethylene)-1,3,4-thiadiazin-5-one (5n). IR spectrum, ν , cm^{-1} : 3258 (N–H), 1679 (lactam C=O), 1660 (amide C=O), 1204 (C–S). ^1H NMR spectrum, δ , ppm: 9.23 (1H, s, NH); 7.68-7.20 (12H, m, H Ar); 6.14 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 160.2 (lactam C=O); 158.1 (amide C=O); 144.1 (C=N); 140.6; 139.6; 138.6; 135.0; 130.2; 129.6; 128.9; 128.2; 127.9; 124.2; 123.0; 120.8; 116.8 (12 arom. carbons and C-6); 110.5 (=CH).

6-Benzylidene-4-(4-bromophenyl)-2-phenylaminocarbonyl-1,3,4-thiadiazin-5-one (5o). IR spectrum, ν , cm^{-1} : 3246 (N–H), 1682 (lactam C=O), 1650 (amide C=O), 1211 (C–S). ^1H NMR spectrum, δ , ppm: 9.19 (1H, s, NH); 7.49-7.11 (14H, m, H Ar); 6.16 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 160.8 (lactam C=O); 158.0 (amide C=O); 144.7 (C=N); 141.0; 139.9; 138.4; 137.5; 135.1; 131.4; 128.8; 127.8; 127.6; 125.8; 124.5; 121.1; 118.5 (12 arom. carbons and C-6); 111.1 (=CH).

4-(4-Bromophenyl)-2-phenylaminocarbonyl-6-(thiophen-2-ylmethylene)-1,3,4-thiadiazin-5-one (5p). IR spectrum, ν , cm^{-1} : 3249 (N–H), 1683 (lactam C=O), 1655 (amide C=O), 1210 (C–S). ^1H NMR spectrum, δ , ppm: 9.26 (1H, s, NH); 7.51-7.13 (12H, m, H Ar); 6.15 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 160.9 (lactam C=O); 158.2 (amide C=O); 144.3 (C=N); 141.3; 139.1; 138.6; 137.7; 135.3; 131.2; 129.1; 128.4; 127.1; 126.6; 124.1; 120.9; 118.4 (12 arom. carbons and C-6); 110.3 (=CH).

4-(4-Fluorophenyl)-6-(furan-2-ylmethylene)-2-phenylaminocarbonyl-1,3,4-thiadiazin-5-one (5q). IR spectrum, ν , cm^{-1} : 3245 (N–H), 1681 (lactam C=O), 1650 (amide C=O), 1213 (C–S). ^1H NMR spectrum, δ , ppm: 9.12 (1H, s, NH); 7.48-7.14 (12H, m, H Ar); 6.18 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 160.7 (lactam C=O); 158.1 (amide C=O); 144.1 (C=N); 140.6; 139.4; 138.4; 135.5; 132.2; 129.3; 128.7; 128.2; 127.4; 125.4; 120.2; 116.6; 115.7 (12 arom. carbons and C-6); 110.2 (=CH).

6-Benzylidene-4-(4-chlorophenyl)-2-furoyl-1,3,4-thiadiazin-5-one (5r). IR spectrum, ν , cm^{-1} : 1682 (lactam C=O), 1660 (C=O), 1213 (C–S). ^1H NMR spectrum, δ , ppm: 7.84-7.16 (12H, m, H Ar); 6.20 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 173.5 (C=O); 161.3 (lactam C=O); 145.3 (C=N); 142.9; 139.7; 134.9; 130.4; 129.8; 129.0; 128.9; 128.6; 127.3; 125.1; 123.7; 120.6; 115.0 (12 arom. carbons and C-6); 111.3 (=CH).

4-(4-Chlorophenyl)-6-(furan-2-ylmethylene)-2-(2-furoyl)-1,3,4-thiadiazin-5-one (5s). IR spectrum, ν , cm^{-1} : 1682 (lactam C=O), 1665 (C=O), 1215 (C–S). ^1H NMR spectrum, δ , ppm: 7.82-7.14 (10H, m, H Ar); 6.21 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 173.4 (C=O); 161.0 (lactam C=O); 145.7 (C=N); 142.3; 139.6; 135.2; 132.2; 130.9; 129.8; 129.1; 128.8; 127.6; 125.3; 123.7; 120.8; 114.9 (12 arom. carbons and C-6); 110.7 (=CH).

6-Benzylidene-4-(4-chlorophenyl)-2-thenoyl-1,3,4-thiadiazin-5-one (5t). IR spectrum, ν , cm^{-1} : 1682 (lactam C=O), 1660 (C=O), 1217 (C–S). ^1H NMR spectrum, δ , ppm: 7.76-7.12 (12H, m, H Ar); 6.16 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 174.7 (amide C=O); 161.1 (lactam C=O); 144.6 (C=N); 141.5; 140.2; 138.9; 135.2; 135.0; 130.4; 128.7; 128.5; 126.7; 124.3; 123.5; 120.2; 115.9 (12 arom. carbons and C-6); 111.3 (=CH).

4-(4-Chlorophenyl)-6-(thiophen-2-ylmethylene)-2-(2-thenoyl)-1,2,4-thiadiazin-5-one (5u). IR spectrum, ν , cm^{-1} : 1682 (lactam C=O), 1651 (C=O), 1216 (C–S). ^1H NMR spectrum, δ , ppm: 7.78-7.16 (10H, m, H Ar); 6.12 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 174.8 (C=O); 161.3 (lactam C=O); 144.1 (C=N); 141.3; 139.9; 138.6; 135.4; 135.1; 130.2; 128.9; 128.2; 126.1; 124.6; 123.9; 120.3; 115.8 (12 arom. carbons and C-6); 110.6 (=CH).

6-Benzylidene-2-(2-naphthoyl)-4-phenyl-1,3,4-thiadiazin-5-one (5v). IR spectrum, ν , cm^{-1} : 1682 (lactam C=O), 1646 (C=O), 1201 (C–S). ^1H NMR spectrum, δ , ppm: 8.85-7.24 (17H, m, H Ar); 6.15 (1H, s, CH). ^{13}C NMR spectrum, δ , ppm: 184.7 (C=O); 161.0 (lactam C=O); 147.7 (C=N); 142.4; 140.8; 138.7; 137.5; 135.6; 134.9; 132.6; 132.4; 129.9; 128.9; 128.6; 128.0; 127.7; 127.2; 126.6; 125.5; 124.5; 121.0; 115.6 (18 arom. carbons and C-6); 111.4 (=CH).

6-Benzylidene-4-(4-methylphenyl)-2-(2-naphthoyl)-1,3,4-thiadiazin-5-one (5w). IR spectrum, ν , cm^{-1} : 1682 (lactam C=O), 1642 (C=O), 1204 (C–S). ^1H NMR spectrum, δ , ppm: 8.83-7.25 (16H, m, H Ar); 6.11 (1H, s, CH); 2.27 (3H, s, CH_3). ^{13}C NMR spectrum, δ , ppm: 184.4 (C=O); 160.7 (lactam C=O); 147.3 (C=N); 142.2; 140.4; 139.7; 138.7; 137.5; 135.6; 132.9; 132.6; 130.4; 129.7; 128.9; 128.6; 128.0; 127.7; 127.3; 126.6; 125.5; 124.5; 114.0 (18 arom. carbons and C-6); 111.6 (=CH), 21.7 (CH_3).

6-(Furan-2-ylmethylene)-4-(4-methylphenyl)-2-(2-naphthoyl)-1,3,4-thiadiazin-5-one (5x). IR spectrum, ν , cm^{-1} : 1682 (lactam C=O), 1645 (C=O), 1202 (C–S). ^1H NMR spectrum, δ , ppm: 8.86-7.27 (14H, m, H Ar); 6.12 (1H, s, CH); 2.26 (3H, s, CH_3). ^{13}C NMR spectrum, δ , ppm: 184.5 (C=O); 160.8 (lactam C=O); 146.9 (C=N); 142.2; 140.8; 138.7; 137.5; 135.6; 132.9; 132.6; 132.4; 129.9; 128.9; 128.6; 128.0; 127.7; 127.4; 126.6; 125.5; 124.5; 121.0; 113.8 (18 arom. carbons and C-6); 109.9 (=CH), 21.9 (CH_3).

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