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# On reactions of triazinones: Synthesis of new 5-arylidene-4,5-dihydro-1,2,4-triazin-6-ones

**Hany M. Dalloul** * **and Ali Z. Al-Shorafa**

*Department of Chemistry, Faculty of Science, Al-Aqsa University of Gaza, P.O.Box 4051, Gaza 76888, PALESTINE*

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**Abstract:** 5-Benzylidene-, 5-(furan-2-ylmethylene)- and 5-(thiophen-2-ylmethylene)-4,5-dihydro-1,2,4-triazin-6-ones have been synthesized from the reaction of 4,5-dihydro-1,2,4-triazin-6-ones with appropriate aromatic aldehydes. All the products have been characterized by elemental analysis and their spectral data.

**Keywords**: Cyclocondensation, aromatic aldehydes; 4,5-dihydro-1,2,4-triazin-6-ones.

## 1. Introduction

The chemistry of triazinone derivatives have been the subject of much interest in recent years due to use of such ring system as the core structure in many heterocyclic compounds covering wide range of pharmacological applications.[1-9] Recently, 1,2,4-triazinone derivatives have gained great attention as ligands to transition metals. The reaction of 1,3,5-trisubstituted 4,5-dihydro-1,2,4-triazine oximes with metal acetates afforded different complexes according to the used reagent and conditions.[10-13] Quit recently, we have reported the synthesis of different 1,2,4-triazinones derivatives employing amidrazones and α-halo acid esters.[14] Cyclocondensation reactions of nitrilimines with 2-hydrazinoacetate or with α-amino esters represent an important synthetic route to prepare substituted 1,2,4-triazin-6-ones.[7,15,16] In continuation of our work on the reaction of five and six membered aza heterocyclic compounds, we wish to report the reactivity of 3-aroyl-1-aryl-4,5-dihydro-1,2,4-triazin-6-ones **2a-x** toward aromatic aldehydes.

## 2. Results and Discussion

Substituted 4,5-dihydro-1,2,4-triazin-6-ones **2a-x** employed in this study were prepared by direct interaction of hydrazonoyl halides **1A,** nitrilimines precursors, with α-amino esters in presence of

* Corresponding author: E-mail hanydallool@yahoo.com

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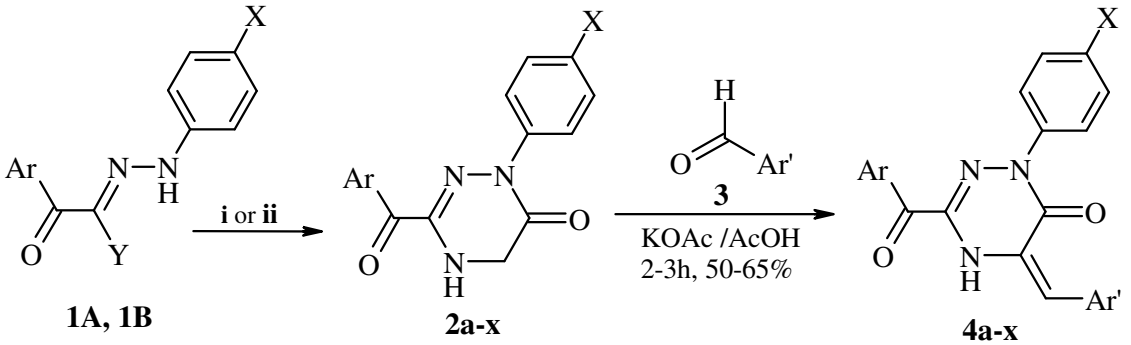
triethylamine as a base[16,17] or by treatment of amidrazones **1B** with α-haloesters.[14] Condensation of these triazinones **2a-x** with aromatic aldehydes **3** (benzaldehyde, 2-furaldehyde and thiophene-2-carboxaldehyde) in presence of potassium acetate/acetic acid at refluxing temperature afforded the corresponding 5-arylidene-4,5-dihydro-1,2,4-triazin-6-ones **4a-x** (Scheme 1) in moderate yields. The assignment of structures of obtained compounds is based on their analytical and spectral data.




**1A:** Y= Cl or Br and **i:** $H_2NCH_2CO_2Me$

**1B:** Y= $NH_2$ and **ii:** $ZCH_2CO_2R$ (Z= Cl,Br & R= Me,Et)

| Entry | Ar | X | Ar' |
|---|---|---|---|
| **a** | Me | H | Ph |
| **b** | Me | H | 2-Furyl |
| **c** | Me | Cl | Ph |
| **d** | Me | Cl | 2-Thienyl |
| **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' |
|---|---|---|---|
| **m** | PhNH | Cl | 2-Furyl |
| **n** | PhNH | Cl | 2-Thienyl |
| **o** | PhNH | Br | Ph |
| **p** | PhNH | Br | 2-Furyl |
| **q** | PhNH | Br | 2-Thienyl |
| **r** | PhNH | F | Ph |
| **s** | PhNH | F | 2-Furyl |
| **t** | PhNH | Me | Ph |
| **u** | PhNH | Me | 2-Furyl |
| **v** | PhNH | Me | 2-Thienyl |
| **w** | 2-Naphthyl | Cl | 2-Furyl |
| **x** | 2-Naphthyl | Cl | 2-Thienyl |

**Scheme 1**. Synthetic pathway for the preparation of compounds **4a-x**.

The IR spectra of the title compounds **4a-x** in KBr showed strong absorption band in the 3380-3320 $cm^{-1}$ region corresponding to NH of the ring. The absorption bands of the aroyl carbonyl groups appeared in the 1690-1640 $cm^{-1}$ region, and a lactam C=O band in the 1680-1670 $cm^{-1}$ region. The mass spectra of the synthesized triazinones displayed the correct molecular ions ($M^{+\cdot}$) in accordance with the proposed structures. Their main fragmentation was similar to the reported type.[7,18] The base peak for compounds containing benzylidene moiety was (M-117), for compounds containing furan-2-ylmethylene moiety was (M-108), and for compounds containing thiophen-2-ylmethylene moiety was (M-124). The $^1$H-NMR spectra of the title compounds **4a-x** showed the disappearance of the methylene protons (4.2-4.0 ppm) at C-5. Instead the methine proton (=CHAr') appeared as singlet in the range of 6.8-6.7 ppm. The signal at about 6.2 ppm was attributed to N-H proton of the triazinone ring. The $^{13}$C-NMR spectra of these adducts displayed the characteristic signals of the

different carbons of suggested structures. The signal of carbonyl carbon of lactam (C=O of ring) appeared in the range of 162-160 ppm, and that of methine carbon (=CHAr') resonated in the range of 112-109 ppm. The signal at about 139 ppm, was attributed to C=N of the triazinone ring. The detailed $^{13}$C-NMR data is shown in the experimental part.

## 3. Conclusion

The condensation of 4,5-dihydro-1,2,4-triazin-6-ones with appropriate aromatic aldehydes gave 5-arylidene-4,5-dihydro-1,2,4-triazin-6-ones in a yield of 50-65%.

## 4. Experimental

Melting points were determined on a Stuart Electrothermal Apparatus and are uncorrected. The IR spectra were obtained by using Satellite 3000 Mid infrared spectrophotometer in potassium bromide pellets. $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker spectrometer (400.13 MHz) at room temperature in DMSO-$d_6$, using tetramethylsilane (TMS) as internal reference and the chemical shifts (δ) were reported in ppm downfield from TMS. The electron impact (EI) mass spectra for selected compounds (**4a,c,f,h,i,k,m,o,q,s,u,w**) were run on Shimadzu GCMS-QP1000 EX spectrometer with an ionizing potential of 70 eV. Elemental analysis performed at Cairo University, Egypt and the results agreed with the calculated values within experimental errors. The 3-aroyl-1-aryl-4,5-dihydro-1,2,4-triazin-6-ones **2a-x** were prepared according to previous described methods.[15-17] Benzaldehyde, 2-furaldehyde and thiophene-2-carboxaldehyde were purchased from Avocado Research Chemicals, England, and used without further purification.

### *4.1. General method for the synthesis of adducts (4a-x):*

A compounds **2a-x** (0.01mol), appropriate aldehyde **3** (0.01 mol) and anhydrous potassium acetate (0.01 mol) were dissolved in glacial acetic acid (5 ml) at room temperature. The reaction mixture was heated to reflux temperature for 2-3h with efficient stirring. The reaction was monitored by thin layer chromatography (TLC) analysis until all the aldehyde had reacted. Upon cooling, the mixture gave a precipitate which was collected, washed several times with water and recrystallized from ethanol.

The following compounds were synthesized using this method:

**3-Acetyl-5-benzylidene-1-phenyl-4,5-dihydro-1,2,4-triazin-6-one (4a):**

Yield: 65%; mp: 208-210 °C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.78-6.95 (10H, m, Ar-H), 6.75 (1H, s, CH), 6.23 (1H, s, NH), 2.53 (3H, s, $CH_3$); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 189.5 (C=O), 160.3 (lactam C=O), 139.2 (C=N), 142.4, 137.0, 136.7, 129.5.2, 129.2.1, 128.8, 127.2, 125.6, 116.0, 111.6, 26.6 ($CH_3$); IR ($\nu$/cm$^{-1}$): 3330 (N-H), 1697 ($CH_3$C=O), 1675 (lactam C=O); MS: m/z = 305 [$M^{+\cdot}$]; Analysis for $C_{18}H_{15}N_3O_2$ (Mw 305.34): calcd. C, 70.81; H, 4.95; N, 13.76; found. C, 70.60; H, 5.10; N, 13.60.

**3-Acetyl-5-(furan-2-ylmethylene)-1-phenyl-4,5-dihydro-1,2,4-triazin-6-one (4b):**

Yield: 61%; mp: 149-151 °C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 8.20-7.15 (8H, m, Ar-H), 6.72 (1H, s, CH), 6.22 (1H, s, NH), 2.56 (3H, s, $CH_3$); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 189.7 (C=O), 160.2 (lactam C=O), 139.2 (C=N), 142.0, 134.6, 133.8, 132.2, 131.3, 129.2, 128.3, 125.6, 116.1, 109.5, 26.7 ($CH_3$); IR ($\nu$/cm$^{-1}$): 3325 (N-H), 1695 ($CH_3$C=O), 1677 (lactam C=O); Analysis for $C_{16}H_{13}N_3O_3$ (Mw 295.30): calcd. C, 65.08; H, 4.44; N, 14.23; found. C, 66.20; H, 4.30; N, 14.40.

**3-Acetyl-5-benzylidene-1-(4-chlorophenyl)-4,5-dihydro-1,2,4-triazin-6-one (4c):**

Yield: 63%; mp: 212-214 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.82-7.11 (9H, m, Ar-H), 6.80 (1H, s, CH), 6.25 (1H, s, NH), 2.55 (3H, s, $CH_3$); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 189.6 (C=O), 160.7 (lactam C=O), 139.4 (C=N), 142.3, 136.9, 134.6, 130.9, 129.2, 128.7, 128.3, 125.6, 116.8, 111.8, 26.6 ($CH_3$); IR ($\nu$/cm$^{-1}$): 3330 (N-H), 1698 ($CH_3$C=O), 1680 (lactam C=O); MS: m/z = 339/341 [$M^{+\cdot}$]; Analysis for $C_{18}H_{14}ClN_3O_2$ (Mw 339.78): calcd. C, 63.63; H, 4.15; N, 12.37; found. C, 63.50; H, 4.20; N, 12.40.

**3-Acetyl-1-(4-chlorophenyl)-5-(thiophen-2-ylmethylene)-4,5-dihydro-1,2,4-triazin-6-one (4d):**

Yield: 57%; mp: 177-179 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 8.28-7.18 (7H, m, Ar-H), 6.80 (1H, s, CH), 6.23 (1H, s, NH), 2.56 (3H, s, $CH_3$); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 189.5 (C=O), 160.8 (lactam C=O), 139.5 (C=N), 142.4, 138.2, 134.8, 133.7, 132.2, 131.3, 129.2, 125.3, 116.2, 110.3, 26.7 ($CH_3$); IR ($\nu$/cm$^{-1}$): 3336 (N-H), 1692 ($CH_3$C=O), 1682 (lactam C=O); Analysis for $C_{16}H_{12}ClN_3O_2S$ (Mw 345.81): calcd. C, 55.57; H, 3.50; N, 12.15; found. C, 55.70; H, 3.30; N, 12.00.

**3-Acetyl-5-benzylidene-1-(4-bromophenyl)-4,5-dihydro-1,2,4-triazin-6-one (4e):**

Yield: 55%; mp: 198-200 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 8.21-7.10 (9H, m, Ar-H), 6.70 (1H, s, CH), 6.20 (1H, s, NH), 2.58 (3H, s, $CH_3$); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 189.7 (C=O), 160.5 (lactam C=O), 139.6 (C=N), 141.6, 137.8, 136.4, 135.2, 130.9, 129.7, 129.2, 124.5, 117.2, 111.5, 26.6 ($CH_3$); IR ($\nu$/cm$^{-1}$): 3334 (N-H), 1696 ($CH_3$C=O), 1675 (lactam C=O); Analysis for $C_{18}H_{14}BrN_3O_2$ (Mw 384.24): calcd. C, 56.27; H, 3.67; N, 10.94; found. C, 56.40; H, 3.50; N, 11.10.

**3-Acetyl-1-(4-bromophenyl)-5-(furan-2-ylmethylene)-4,5-dihydro-1,2,4-triazin-6-one (4f):**

Yield: 54%; mp: 178-180 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 8.12-7.05 (7H, m, Ar-H), 6.73 (1H, s, CH), 6.22 (1H, s, NH), 2.57 (3H, s, $CH_3$); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 189.6 (C=O), 160.8 (lactam C=O), 139.4 (C=N), 141.8, 137.5, 135.2, 132.2, 131.2, 129.2, 128.7, 124.3, 118.4, 109.3, 26.7 ($CH_3$); IR ($\nu$/cm$^{-1}$): 3340 (N-H), 1698 ($CH_3$C=O), 1673 (lactam C=O); MS: m/z = 374/376 [$M^{+\cdot}$]; Analysis for $C_{16}H_{12}BrN_3O_3$ (Mw 374.20): calcd. C, 51.36; H, 3.23; N, 11.23; found. C, 51.20; H, 3.30; N, 11.40.

**3-Benzoyl-5-benzylidene-1-(4-chlorophenyl)-4,5-dihydro-1,2,4-triazin-6-one (4g):**

Yield: 62%; mp: 211-213 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 8.20-7.11 (14H, m, Ar-H), 6.65 (1H, s, CH), 6.18 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 185.4 (C=O), 162.2 (lactam C=O), 139.2 (C=N), 141.8, 138.2, 134.8, 133.7, 132.4, 131.3, 129.4, 129.1, 128.7, 128.3, 126.7, 124.6, 119.5, 111.9 ; IR ($\nu$/cm$^{-1}$): 3370 (N-H), 1678 (lactam C=O), 1650 (C=O); Analysis for $C_{23}H_{16}ClN_3O_2$ (Mw 401.86): calcd. C, 68.75; H, 4.01; N, 10.46; found. C, 68.90; H, 3.90; N, 10.40.

**3-Benzoyl-1-(4-chlorophenyl)-5-(furan-2-ylmethylene)-4,5-dihydro-1,2,4-triazin-6-one (4h):**

Yield: 60%; mp: 158-160 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 8.22-7.18 (12H, m, Ar-H), 6.67 (1H, s, CH), 6.20 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 185.5 (C=O), 162.1 (lactam C=O), 139.1 (C=N), 141.9, 138.1, 134.6, 133.7, 132.2, 131.1, 129.3, 129.1 128.7, 128.2, 126.7, 124.8, 119.4, 110.8 ; IR ($\nu$/cm$^{-1}$): 3371 (N-H), 1676 (lactam C=O), 1653 (C=O); MS: m/z = 391/393 [$M^{+\cdot}$]; Analysis for $C_{21}H_{14}ClN_3O_3$ (Mw 391.82): calcd. C, 64.38; H, 3.60; N, 10.72; found. C, 64.20; H, 3.40; N, 10.90.

**5-Benzylidene-1-phenyl-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-triazin-6-one (4i):**

Yield: 55%; mp: 218-220 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.62-7.12 (15H, m, Ar-H), 6.71 (1H, s, CH), 6.31 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 160.3 (lactam C=O), 157.3 (amide C=O), 139.0 (C=N), 140.8, 138.7, 137.5, 136.9, 132.3, 129.5, 129.2, 128.8, 127.3, 125.5, 125.1, 123.9, 119.7, 112.1 ; IR ($\nu$/cm$^{-1}$): 3363, 3258 (N-H), 1679 (lactam C=O), 1655 (amide C=O); MS: m/z = 382 [$M^{+\cdot}$]; Analysis for $C_{23}H_{18}N_4O_2$ (Mw 382.43): calcd. C, 72.24; H, 4.74; N, 14.65; found. C, 72.30; H, 5.60; N, 14.80.

**5-(furan-2-ylmethylene)-1-phenyl-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-triazin-6-one (4j):**

Yield: 51%; mp: 140-142 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.78-7.21 (13H, m, Ar-H), 6.73 (1H, s, CH), 6.33 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 160.6 (lactam C=O), 157.0 (amide C=O), 138.7 (C=N), 140.9, 136.2, 135.1, 133.9, 130.5, 129.4, 129.0, 128.7, 128.2, 127.1, 125.0, 123.5, 119.8, 110.9; IR ($\nu$/cm$^{-1}$): 3365, 3260 (N-H), 1676 (lactam C=O), 1650 (amide C=O); Analysis for $C_{21}H_{16}N_4O_3$ (Mw 372.39): calcd. C, 67.73; H, 4.33; N, 15.05; found. C, 67.90; H, 4.20; N, 14.90.

**1-Phenyl-3-phenylaminocarbonyl-5-(thiophen-2-ylmethylene)-4,5-dihydro-1,2,4-triazin-6-one (4k):**

Yield: 57%; mp: 170-172 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.76-7.15 (13H, m, Ar-H), 6.70 (1H, s, CH), 6.35 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 160.8 (lactam C=O), 157.2 (amide C=O), 139.1 (C=N), 140.8, 136.6, 135.4, 134.7, 130.3, 129.6, 129.1, 128.5, 128.1, 127.5, 125.3, 123.7, 119.8, 111.3; IR ($\nu$/cm$^{-1}$): 3365, 3255 (N-H), 1678 (lactam C=O), 1652 (amide C=O); MS: m/z = 388 [$M^{+\cdot}$]; Analysis for $C_{21}H_{16}N_4O_2S$ (Mw 388.45): calcd. C, 64.93; H, 4.15; N, 14.42; found. C, 65.10; H, 4.30; N, 14.30.

**5-Benzylidene-1-(4-chlorophenyl)-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-tri-azin-6-one (4l):**

Yield: 65%; mp: 201-203 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.55-7.13 (14H, m, Ar-H), 6.72 (1H, s, CH), 6.35 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 160.7 (lactam C=O), 156.6 (amide C=O), 138.9 (C=N), 140.6, 138.8, 136.4, 135.1, 132.5, 130.4, 129.3, 128.9, 128.7, 127.6, 126.2, 125.2, 119.9, 112.3; IR ($\nu$/cm$^{-1}$): 3362, 3257 (N-H), 1680 (lactam C=O), 1660 (amide C=O); Analysis for $C_{23}H_{17}ClN_4O_2$ (Mw 416.87): calcd. C, 66.27; H, 4.11; N, 13.44; found. C, 66.50; H, 3.90; N, 13.20.

**1-(4-Chlorophenyl)-5-(furan-2-ylmethylene)-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-tri-azin-6-one (4m):**

Yield: 59%; mp: 190-192 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.60-7.16 (12H, m, Ar-H), 6.76 (1H, s, CH), 6.34 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 160.6 (lactam C=O), 156.8 (amide C=O), 139.0 (C=N), 140.4, 138.6, 136.2, 133.8, 132.3, 130.5, 129.1, 128.4, 127.2, 126.7, 125.7, 123.1, 119.7, 110.9; IR ($\nu$/cm$^{-1}$): 3370, 3265 (N-H), 1682 (lactam C=O), 1665 (amide C=O); MS: m/z = 406/408 [$M^{+\cdot}$]; Analysis for $C_{21}H_{15}ClN_4O_3$ (Mw 406.83): calcd. C, 62.00; H, 3.72; N, 13.77; found. C, 61.80; H, 3.60; N, 13.90.

**1-(4-Chlorophenyl)-3-phenylaminocarbonyl-5-(thiophen-2-ylmethylene)-4,5-dihydro-1,2,4-triazin-6-one (4n):**

Yield: 53%; mp: 192-194 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.68-7.20 (12H, m, Ar-H), 6.74 (1H, s, CH), 6.37 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 160.6 (lactam C=O), 156.7 (amide C=O), 139.1 (C=N), 140.6, 138.7, 136.3, 134.1, 132.5, 130.3, 129.2,

128.4, 127.8, 126.7, 125.2, 123.7, 119.8, 111.5 ; IR ($\nu$/cm$^{-1}$): 3369, 3258 (N-H), 1679 (lactam C=O), 1660 (amide C=O); Analysis for $C_{21}H_{15}ClN_4O_2S$ (Mw 422.90): calcd. C, 59.64; H, 3.58; N, 13.25; found. C, 59.50; H, 3.40; N, 13.40.

**5-Benzylidene-1-(4-bromophenyl)-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-tri-azin-6-one (4o):**

Yield: 56%; mp: 200-202 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.58-7.15 (14H, m, Ar-H), 6.66 (1H, s, CH), 6.25 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 160.8 (lactam C=O), 158.0 (amide C=O), 139.7 (C=N), 140.0, 137.5, 136.4, 135.2, 131.0, 129.7, 128.7, 128.2, 126.6, 125.2, 124.5, 121.0, 118.5, 112.1; IR ($\nu$/cm$^{-1}$): 3360, 3246 (N-H), 1682 (lactam C=O), 1650 (amide C=O); MS: m/z = 461/463 [$M^{+\cdot}$]; Analysis for $C_{23}H_{17}BrN_4O_2$ (Mw 461.32): calcd. C, 59.88; H, 3.71; N, 12.14; found. C, 60.10; H, 3.80; N, 12.00.

**1-(4-Bromophenyl)-5-(furan-2-ylmethylene)-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-triazin-6-one (4p):**

Yield: 51%; mp: 188-190 $^{o}$C (from EtOH); $^{1}$H NMR (δ/ppm): 7.55-7.13 (12H, m, Ar-H), 6.65 (1H, s, CH), 6.24 (1H, s, NH); $^{13}$C NMR (δ/ppm): 160.9 (lactam C=O), 158.2 (amide C=O), 139.8 (C=N), 140.3, 137.7, 136.4, 134.2, 130.8, 129.3, 128.5, 127.6, 126.8, 124.3, 123.5, 120.9, 118.4, 110.3 ; IR ($\nu$/cm$^{-1}$): 3366, 3249 (N-H), 1683 (lactam C=O), 1655 (amide C=O); Analysis for $C_{21}H_{15}BrN_4O_3$ (Mw 451.28): calcd. C, 55.89; H, 3.35; N, 12.42; found. C, 55.70; H, 3.20; N, 12.60.

**1-(4-Bromophenyl)-3-phenylaminocarbonyl-5-(thiophen-2-ylmethylene)-4,5-dihydro-1,2,4-triazin-6-one (4q):**

Yield: 58%; mp: 150-152 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.58-7.14 (12H, m, Ar-H), 6.68 (1H, s, CH), 6.21 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 160.7 (lactam C=O), 158.1 (amide C=O), 139.7 (C=N), 140.1, 137.4, 136.9, 133.9, 130.9, 129.6, 128.5, 127.8, 126.6, 124.1, 123.7, 120.5, 118.5, 111.2 ; IR ($\nu$/cm$^{-1}$): 3363, 3245 (N-H), 1681 (lactam C=O), 1650 (amide C=O); MS: m/z = 467/469 [$M^{+\cdot}$]; Analysis for $C_{21}H_{15}BrN_4O_2S$ (Mw 467.35): calcd. C, 53.97; H, 3.24; N, 11.99; found. C, 54.10; H, 3.10; N, 12.10.

**5-Benzylidene-1-(4-fluorophenyl)-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-tri-azin-6-one (4r):**

Yield: 55%; mp: 243-245 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.83-7.16 (14H, m, Ar-H), 6.80 (1H, s, CH), 6.39 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 161.3 (lactam C=O), 157.3 (amide C=O), 139.3 (C=N), 140.0, 137.5, 136.9, 129.7, 128.8, 128.6, 128.2, 126.8, 124.4, 120.9, 125.2, 125.0, 119.8, 112.3 ; IR ($\nu$/cm$^{-1}$): 3347, 3240 (N-H), 1682 (lactam C=O), 1660 (amide C=O); Analysis for $C_{23}H_{17}FN_4O_2$ (Mw 400.42): calcd. C, 68.99; H, 4.28; N, 13.99; found. C, 69.20; H, 4.40; N, 13.10.

**1-(4-Fluorophenyl)-5-(furan-2-ylmethylene)-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-triazin-6-one (4s):**

Yield: 54%; mp: 187-189 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.80-7.11 (12H, m, Ar-H), 6.81 (1H, s, CH), 6.40 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 161.2 (lactam C=O), 157.4 (amide C=O), 139.2 (C=N), 140.2, 137.5, 136.9, 129.7, 128.8, 128.6, 128.2, 126.8, 124.4, 120.9, 125.2, 125.0, 119.2, 111.7 ; IR ($\nu$/cm$^{-1}$): 3342, 3232 (N-H), 1682 (lactam C=O), 1665 (amide C=O); MS: m/z = 390 [$M^{+\cdot}$]; Analysis for $C_{21}H_{15}FN_4O_3$ (Mw 390.38): calcd. C, 64.61; H, 3.87; N, 14.35; found. C, 64.40; H, 4.00; N, 14.40.

**5-Benzylidene-1-(4-methylphenyl)-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-tri-azin-6-one (4t):**

Yield: 52%; m.p. 200-203 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.75-7.12 (14H, m, Ar-H), 6.76 (1H, s, CH), 6.35 (1H, s, NH), 2.25 (3H, s, $CH_3$); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 161.4 (lactam C=O), 157.7 (amide C=O), 139.6 (C=N), 140.9, 138.7, 138.1, 136.9, 132.6, 129.5, 129.2, 128.8, 127.3, 125.3, 125.1, 123.7, 119.3, 111.9, 20.7 ($CH_3$); IR ($\nu$/cm$^{-1}$): 3356, 3233 (N-H), 1682 (lactam C=O), 1656 (amide C=O); Analysis for $C_{24}H_{20}N_4O_2$ (Mw 396.45): calcd. C, 72.71; H, 5.08; N, 14.13; found. C, 72.60; H, 5.10; N, 14.30.

**5-(furan-2-ylmethylene)-1-(4-methylphenyl)-3-phenylaminocarbonyl-4,5-dihydro-1,2,4-tri-azin-6-one (4u):**

Yield: 58%; mp: 145-147 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.76-7.16 (12H, m, Ar-H), 6.72 (1H, s, CH), 6.33 (1H, s, NH), 2.23 (3H, s, $CH_3$); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 161.3 (lactam C=O), 157.8 (amide C=O), 139.7 (C=N), 141.2, 138.7, 138.1, 136.9, 132.6, 129.5, 129.2, 128.8, 127.3, 125.3, 125.1, 124.63, 119.8, 110.9, 20.6 ($CH_3$); IR ($\nu$/cm$^{-1}$): 3350, 3247 (N-H), 1682 (lactam C=O), 1651 (amide C=O); MS: m/z = 386 [$M^{+\cdot}$]; Analysis for $C_{22}H_{18}N_4O_3$ (Mw 386.41): calcd. C, 68.38; H, 4.70; N, 14.50; found. C, 68.60; H, 4.60; N, 14.40.

**1-(4-Methylphenyl)-3-phenylaminocarbonyl-5-(thiophen-2-ylmethylene)-4,5-dihydro-1,2,4-triazin-6-one (4v):**

Yield: 50%; mp: 175-177 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 7.78-7.24 (12H, m, Ar-H), 6.75 (1H, s, CH), 6.35 (1H, s, NH), 2.22 (3H, s, $CH_3$); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 161.3 (lactam C=O), 157.7 (amide C=O), 139.3 (C=N), 140.8, 138.7, 138.1, 136.9, 132.6, 129.5, 129.2, 128.8, 127.3, 125.3, 125.1, 123.6, 119.7, 111.4, 20.7 ($CH_3$); IR ($\nu$/cm$^{-1}$): 3353, 3239 (N-H), 1682 (lactam C=O), 1656 (amide C=O); Analysis for $C_{22}H_{18}N_4O_2S$ (Mw 402.48): calcd. C, 65.65; H, 4.51; N, 13.92; found. C, 65.50; H, 4.70; N, 14.10.

**1-(4-Chlorophenyl)-5-(furan-2-ylmethylene)-3-(2-naphthoyl)-4,5-dihydro-1,2,4-triazin-6-one (4w):**

Yield: 61%; mp: 228-230 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 8.95-7.15 (14H, m, Ar-H), 6.71 (1H, s, CH), 6.30 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 185.0 (C=O), 160.7 (lactam C=O), 140.7 (C=N), 142.80, 138.7, 138.1, 136.9, 134.1, 132.6, 132.1, 130.0, 129.5, 129.2, 128.8, 128.5, 127.7, 127.3, 126.9, 126.6, 125.3, 125.1, 119.9, 109.6 ; IR ($\nu$/cm$^{-1}$): 3355 (N-H), 1682 (lactam C=O), 1642 (C=O); MS: m/z = 441/443 [$M^{+\cdot}$]; Analysis for $C_{25}H_{16}ClN_3O_3$ (Mw 441.88): calcd. C, 67.96; H, 3.65; N, 9.51; found. C, 68.10; H, 3.50; N, 9.40.

**1-(4-Chlorophenyl)-3-(2-naphthoyl)-5-(thiophen-2-ylmethylene)-4,5-dihydro-1,2,4-tri-azin-6-one (4x):**

Yield: 56%; m.p. 168-170 $^{o}$C (from EtOH); $^{1}$H NMR (DMSO-$d_6$) (δ/ppm): 8.96-7.17 (14H, m, Ar-H), 6.72 (1H, s, CH), 6.31 (1H, s, NH); $^{13}$C NMR (DMSO-$d_6$) (δ/ppm): 184.9 (C=O), 160.8 (lactam C=O), 140.6 (C=N), 142.8, 138.5, 137.6, 135.8, 134.0, 132.2, 132.5, 129.9, 129.1, 128.9, 128.6, 128.2, 127.8, 127.5, 126.9, 126.1, 125.5, 125.1, 119.4, 109.8 ; IR ($\nu$/cm$^{-1}$): 3350 (N-H), 1682 (lactam C=O), 1645 (C=O); Analysis for $C_{25}H_{16}ClN_3O_2S$ (Mw 343.39): calcd. C, 65.57; H, 3.52; N, 9.18; found. C, 65.30; H, 3.70; N, 9.00.

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