Synthesis of spiro(indenepyrazole) and indenotriazinone derivatives from 4-substituted thiosemicarbazides and (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile

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In a multistep reaction, *N*-substituted-5′-amino-4′-cyano-1,3-dioxo-1,3-dihydro-spiro[indene-2,3′-pyrazole]-2′(1*H*) carbothioamides (63–71 %) and 4-substituted-3-thioxo-3*H*-indeno[1,2-*e*][1,2,4] triazin-9(4*H*)-ones (17–26 %) have been formed, from a series of 4-substituted thiosemicarbazides **1a–f** with (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile **3** in aerated ethyl acetate. Rationales of these conversions involving the nucleophilic reactions and condensation are presented.

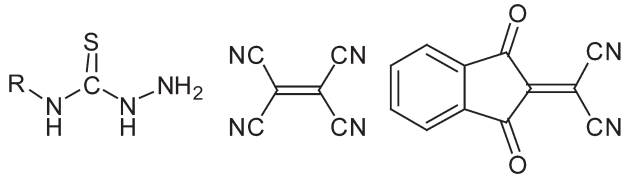
Keywords: 4-substituted thiosemicarbazides, spiro(indenepyrazoles), indenotriazines

Finding new methodologies for the synthesis of a family of biologically potent compounds by employing building blocks with multi-functional groups is a key issue for drug discovery.[1–6] Thiosemicarbazides **1** appear to be ideal candidates for the development of such processes, since they are the core feature in families of compounds known to display biological activities, *e.g.* pyrazoles,[7] 1,2,4-triazoles,[7–9] 1,3,4-oxadiazoles,[8] 1,3,4-thiadiazoles,[7] 1,3-thiazoles,[10] 1,2,4-triazepines,[11] 1,3,4-thiadiazines [12] and 1,3,4-thiadiazepines.[13]

Four-, five-, six- and seven-membered heterocyclic compounds were prepared by reaction of thiosemicarbazide derivatives with α- and β- haloketones.[14–16] The N^2 of thiosemicarbazide group is a softer nucleophilic centre than the harder and more powerful terminal nitrogen N^1. Thus, reagents susceptible to nucleophilic attack by N^1 may in a second step undergo cyclisation to give heterocycles even under mild reaction conditions.[14,15]

It has been reported that, 4-substituted thiosemicarbazides **1** reacted with ethenetetracarbonitrle (**2**,TCNE) to give pyrazole, thiadiazepine and pyrazolothiadiazole derivatives.[17] On the other hand, the reaction of 4-substituted thiosemicarbazides with (2,4,7-trinitro-4*H*-fluoren-9-ylidene)propanedinitrile in pyridine to form spiro[fluorene-9,3′-triazole] derivatives have been reported.[18]

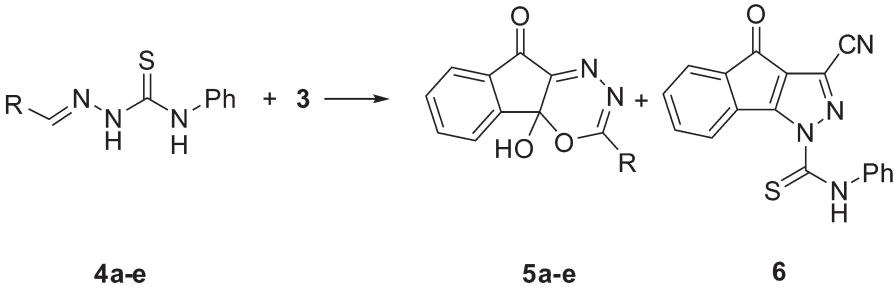
(1,3-Dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile **3** may be considered to be analogous to ethenetetracarbonitrile (**2**,TCNE) in its reactions (Fig. 1). Like the latter it readily adds *N*-nucleophiles such as secondary aliphatic[19,20] and primary aromatic amines at the dicyanomethylene carbon



1 **2** **3**

1a, R = C_6H_5-
b, R = C_6H_5-CH_2-
c, R = CH_2=CH-CH_2-
d, R = C_6H_4-4-F
e, R = C_6H_3-3,5-F
f, R = C_6H_4-4-CF_3

Fig. 1



4a-e **5a-e** **6**

4,5	R
a	C_6H_5
b	C_6H_4-*p*-CH_3
c	C_6H_5-*p*-Cl
d	2-Furyl
e	2-Thienyl

Scheme 1

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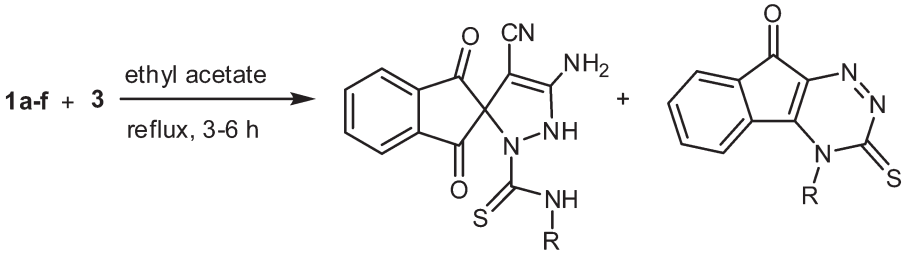


7a-f 8a-e

1,7	R	8	R
a	C_6H_5	a	C_6H_5
b	C_6H_5-CH_2	b	C_6H_5-CH_2
c	CH_2=CH-CH_2	c	CH_2=CH-CH_2
d	C_6H_4-4-F	d	C_6H_3-3,5-F
e	C_6H_3-3,5-F	e	C_6H_4-4-CF_3
f	C_6H_4-4-CF_3		

Scheme 2

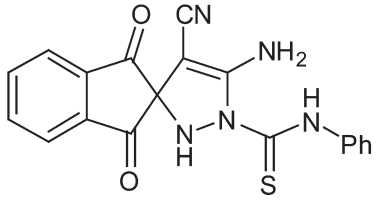
atom with release of hydrogen cyanide analogously to the corresponding reactions of TCNE.[21–23] Recently we reported an efficient transformation of aldehyde thiosemicarbazides **4a–e** with **3** into indeno[2,1-*e*][1,3,4]oxadiazine-9-ones **5a–e** and 4-oxoindeno[1,2-*c*] pyrazole-3-carbonitriles **6a–e** (Scheme 1).[24]

These intriguing transformations led us to investigate the reactions of 4-substituted thiosemicarbazides **1a–f** with **3**. The latter compound offer C/C multiple bonds and the electrophilic carbonyl and nitrile carbon atoms for attack by nucleophiles and compounds **1a–f** may react at least with N^1, N^2 and sulfur atoms as nucleophilic sites. Thus several options for interaction between **1a–f** and **3** may be envisaged, as will be outlined later. We chose thiosemicarbazides **1a–f** having aryl groups (unsubstituted benzene and aryl groups with electron withdrawing substituents on the benzene ring) as well as alkyl groups, in order to examine their effect on the course of the reaction.

Results and discussion

Solutions of **3** and substituted thiosemicarbazides **1a–f** in ethyl acetate in a molar ratio of 1:1 were refluxed. Concentration of the reaction mixture yielded a reddish brown crystals from *N*-substituted-5′-amino-4′-cyano-1,3-dioxo-1,3-dihydrospiro [indene-2,3′-pyrazole]-2′(1′*H*)- carbothioamide **7a–f** (63–71 %). The remaining soluble materials were subjected to preparative layer chromatography to give 4-substituted-3-thioxo-3H-indeno[1,2-*e*]triazine-9(4*H*)-one **8a–e** (17–26 %).

The structure of compounds **7a–f** and **8a–e** were assigned using spectroscopic tools such as IR, NMR (^{1}H, ^{13}C) and mass spectrometry, in addition to elemental analyses. Compounds



9

Fig. 2

7a–f showed IR absorption peaks at υ (cm^{-1}) = 3430–3150 (NH_2 and NH), 2220–2210 (CN) and carbonyl absorption at 1755–1735 as expected for indane-1,3-dione ring system, 1575–1565 (NH def. and C–N str.), 1365-1350, 1010–980 cm^{-1}(C=S and C–N). The mass spectra (EI mode) of compounds **7a–f** were characterised by molecular ions of low intensity and loss of 27 a.m.u (representing HCN) and 66 a.m.u (representing NC–C=C–NH_2). The resulting fragment ions undergo loss of 28 a.m.u. (dinitrogen or CO). Also, the mass spectra exhibited the loss of R–N=C=S and C_6H_4–CO fragments. The ^{1}H NMR spectrum of **7a** showed three broad signals at 6.97, 9.85 and 10.95 with the integration ratio 2:1:1 attributed to NH_2, NH attached to phenyl and pyrazole-NH, besides the aromatic protons. Distinctive signals appeared in the ^{13}C NMR spectrum of **7a** at δ = 194.56, 193.13 (C-1,3), 186.01 (C=S), 119.45 (CN), 106.76 (spiro-C-2,3′), pyrazole-C-4′ and C-5′ resonate at 59.73 and 174.68 ppm, respectively are in accordance with the observed trends in the δ values for C-atoms in Push–Pull alkenes.[25,26] The analytical data of **7** would also match other isomers of product **9–12** (Figs 2 and 3).

The alternative structures **10–12** could be ruled out on the basis of ^{1}H and ^{13}C NMR. Therefore, we will concentrate on the interplay between the formation of the products **7a–f** and the alternative structure **9** (Fig. 2). The *a priori* possible isomeric structures **9** were ruled on the basis of ^{1}H NMR, because in compounds **9**, the pyrazole-NH is isolated and not adjacent to C=C double bond and therefore, the δ value must be considerably lower. A value which should be expected for structure **9** is 4.5 ppm as given in the literature.[27] On the other hand, the ^{1}H- NMR spectrum of **7a** shows the presence of pyrazole-NH at (δ_H= 10.95 ppm) due to cojungation with π-system. Furthermore, in the ^{13}C NMR of **7a–f**, the pyrazole-C-5′ is regularly downfield shifted [**7a** (C-5′ = 174.68), **7b** (C-5′ = 173.66), **7c** (C-5′ = 170.31), **7d** (C-5′ = 173.65), **7e** (C-5′ = 173.54), **7f** (C-5′ = 172.82) compared to pyrazole-C-3′ in compounds **9** (which has been resonated with range 158.45–158.64).[28]

The IR spectra of **8a–e** showed strong absorption signals between 1720 and 1705 cm^{-1} for the carbonyl group, and between 1370 and 1355 cm^{-1} as well as 1010 and 995 cm^{-1} to strong vibration coupling of C=S and C–N entities.

The ^{1}H NMR spectrum of **8c** showed signals at 7.80–8.20 due to aryl protons of indanedione. The ^{1}H NMR of **8c** clearly indicated the presence of allyl group which appeared as three multiplets centred at 4.30, 5.20–5.30 and 5.85–5.92 ppm due to allyl-CH_2N, allyl-CH_2= and allyl-CH= respectively. The

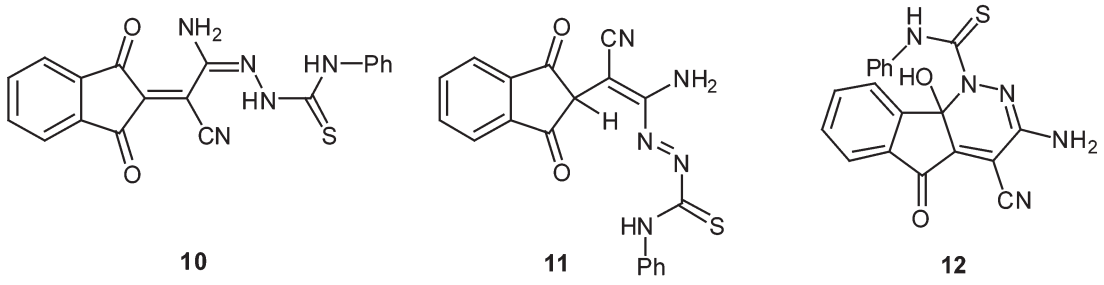


Fig. 3

presence of allyl group also evident from the ^{13}C-DEPT-NMR spectrum exhibiting positive signals at δ = 136.34 (allyl-CH=) and negative signals at 47.36 and 116.96 due to allyl-CH_2N and allyl-CH_2= respectively. Further peaks at 193.01 (CO) and 185.85 which clearly support a C=S group and not an isothiourea carbon as in **13**.

The gross formula $C_{13}H_9N_3OS$ of **8c** was confirmed by the mass spectrum, which exhibited the molecular ion at *m/z* 255 (14%). The fragmentation patterns of the mass spectra of **8** characterised by the loss of R–N=C=S and (N_2 or CO) giving rise to the ion *m/z* 128 common in the spectra of all compounds **8a–e**.

The formation of **7** and **8** indicate that thiosemicarbazides **1a–f** react with **3** through a nucleophilic attack of **1a–f** to the C≡N triple bond of **3** to form the intermediate **14**, compound **14** exerts its nucleophilic character and intramolecular nucleophilic attack of NH to the C=C douple bond, where the electron-withdrawing groups (two carbonyl and one nitrile groups) facilitate this reaction to form the product **7a–f**. On the other hand, nucleophilic attack of **1a–f** to C=C double bond of **3** and elimination a molecule of malononitrile afforded the formation of intermediate **15**. Nucleophilic attack of NH to the carbonyl group followed by elimination H_2O gave thioxoidenotriazines **8a–e**.

Experimental

The uncorrected melting points were determined on a Gallenkamp melting point apparatus; IR spectra were recorded using KBr disks on Shimadzu 408 instrument. ^{1}H NMR 400 MHz and 100 MHz ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer in $CDCl_3$ or DMSO-d_6 in 5mm tubes at RT, with the deuterium signal of the solvent as the lock and TMS as internal references, s = singlet, m = multiplet, br = broad. DEPT spectra 135/90 were run in a standard manner to separate the CH/CH_3 and CH_2 lines phased "up" and "down", respectively. The mass spectra (70 eV, electron impact mode) were recorded on a Finnigan MAT instrument. Combustion analyses were run at the Microanalytical Centre, Cairo University, Egypt. Preparative layer chromatography (PLC) was carried out using air dried 1.0 mm thick layers of slurry of Silica gel (Merck Pf 254) applied on 48 cm wide and 20 cm high glass plates using toluene/ethyl acetate as developing solvent. Zones were detected by their colour or by quenching of 254 nm light and extracted out with acetone.

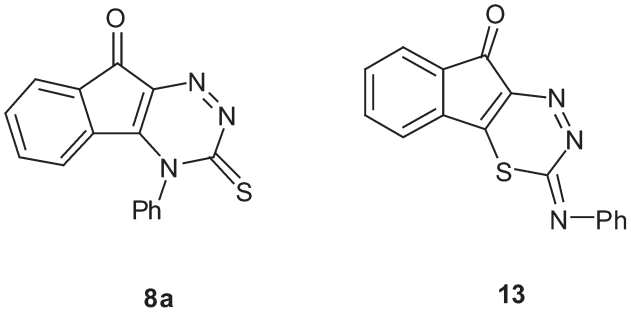


Fig. 4

4-Substituted thiosemicarbazides **1a–f** were synthesised by the reaction of hydrazine hydrate with the appropriate isothiocyanate according to the literature: 4-phenyl- thiosemicarbazide (**1a**),[29,30] 4-benzylthiosemicarbazide (**1b**),[30,31] 4-allylthiosemicarbazides (**1c**),[31,32] 4-(4-fluorophenyl)thiosemicarbazide (**1d**),[33] 4-(3,5-difluorophenyl)thiosemicarbazide (**1e**)[34] and 4-[4(trifluoromethyl)phenyl] thiosemicarbazide (**1f**).[34]

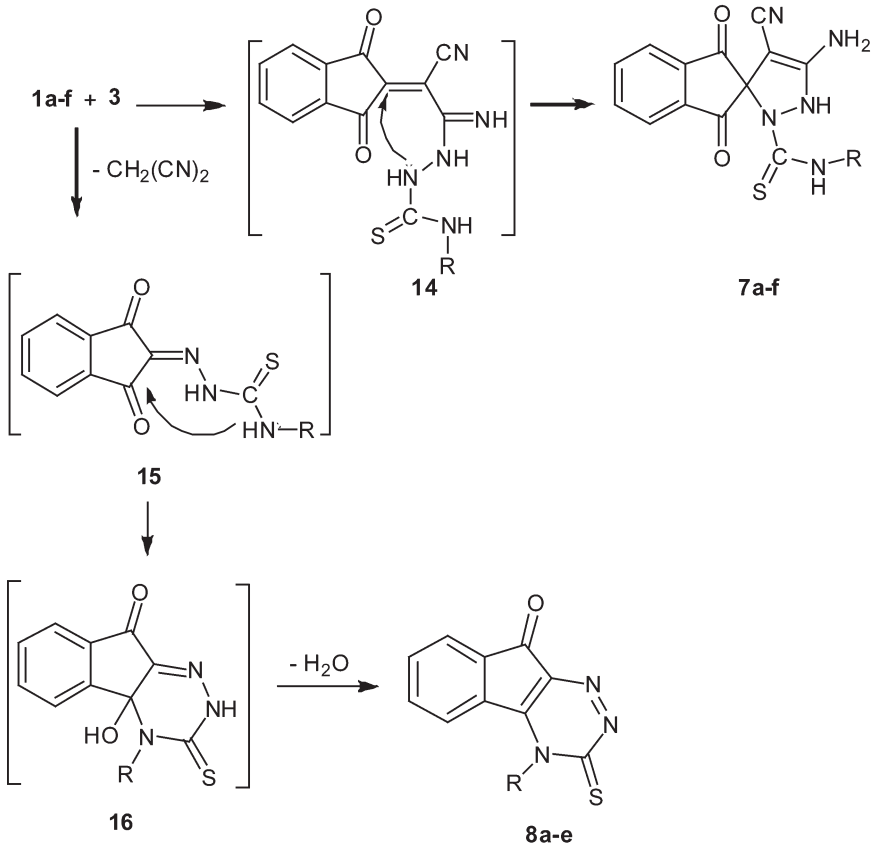
2-(1,3-Dioxo-2,3-dihydro-1*H*-indene-2-ylidene)propanedinitrile (dicyanomethylene indane-1,3-dione, **3**) was prepared according to Chaterjee.[35]

Reaction of 4-substituted thiosemicarbazides **1a–f** *with 2-(1,3-dioxo-2,3-dihydro-1*H*-inden-1-ylidene)propanedinitrile* (**3**): A solution of thiosemicarbazides **1a–f** (1.0 mmol) in 20 mL dry ethyl acetate was added dropwise to a solution of **3** (208 mg, 1 mmol) in 30 mL of dry ethyl acetate. The reaction mixture was magnetically stirred and heated under reflux for 3h with (**1a**), 4h with (**1b**), 6h with (**1c**,**d**,**e**) and 3h with (**1f**) (the reaction was followed by TLC analysis). Dark reddish brown crystals were precipitate, filtered and washed with ethanol to give compounds **7a–f**. The filtrate was concentrated and applied to 5 PLC-plates and developed with toluene/ethyl acetate (5:1) to give numerous coloured zones. The most intense of which was removed and extracted with acetone and recrystallised to give compounds **8a–e**.

*5′-Amino-4′-cyano-N-phenyl-1,3-dioxo-1,3-dihydrospiro[indene-2,3′-pyrazole]-2′(1′*H*)-carbothioamide* (**7a**): Dark reddish brown crystals (0.266 g, 71%), m.p. 280–282 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 6.97 (br, 2H, NH_2), 7.00–7.95 (m, 9H, ArH), 9.85 (br, 1H, NH-Ph), 10.95 (br, 1H, pyrazole-NH). ^{13}C NMR (DMSO-d_6): δ = 59.73 (C-4′), 106.76 (spiro-C-2,3′), 119.45 (CN), 126.79, 127.95, 128.04, 130.83 (ArCH), 138.11, 138.38, 139.04 (ArC), 174.68 (C-5′), 186.01(C=S), 193.13 and 194.56 (CO). IR (KBr): υ (cm^{-1}) = 3410-3150 (NH_2, NH), 2210 (CN), 1750 and 1740 (CO), 1600 (ArC=C), 1570 (NH-def. and C–N str.), 1365, 995 (C=S and C–N). MS, *m/z* (%) = 375 [M^+] (28), 348 (100), 282 (42), 254 (64), 135 (72), 91 (86), 77 (52). $C_{19}H_{13}N_5O_2S$ (375.40): Calcd: C, 60.79; H, 3.49; N, 18.66; S, 8.54. Found: C, 60.93; H, 3.41; N, 18.52; S, 8.69%.

*5′-Amino-4′-cyano-N-benzyl-1,3-dioxo-1,3-dihydrospiro[indene-2,3′-pyrazole]-2′(1′*H*)-carbothioamide* (**7b**): Dark reddish brown crystals (0.268 g, 69%), m.p. 292–294 °C (methanol). ^{1}H NMR (DMSO-d_6): δ = 4.80 (s, 2H, CH_2-Ph), 6.94 (br, 2H, NH_2), 7.10–7.95 (m, 9H, ArH), 8.80 (br, 1H, NH), 11.0 (br, 1H, pyrazole-NH). ^{13}C NMR (DMSO-d_6): δ = 46.51 (CH_2), 59.73 (C-4′), 106.76 (spiro-C-2,3′), 119.33 (CN), 126.79, 127.38, 127.91, 128.09, 131.69 (ArH), 137.57, 138.42, 139.39 (ArC), 173.66 (C-5′), 187.94 (C=S), 193.17, 194.36 (CO). IR (KBr): υ (cm^{-1}) = 3430-3220 (NH_2, NH), 2215 (CN), 1745 and 1735 (CO), 1610 (ArC=C), 1570 (NH-def. and C–N str.), 1350, 1000 (C=S, C–N). MS, m/z (%) = 389 [M^+] (17), 362 (76), 274 (25), 104 (28), 91 (100), 65 (47). $C_{20}H_{15}N_5O_2S$ (389.43): Calcd: C, 61.68; H, 3.88; N, 17.98; S, 8.23. Found: C, 61.85; H, 3.76; N, 18.12; S, 8.36%.

*N-Allyl-5′-amino-4′-cyano-1,3-dioxo-1,3-dihydrospiro[indene-2,3′-pyrazole]-2′(1′*H*)-carbothioamide* (**7c**): Dark reddish brown crystals (0.230 g, 68%), m.p. 240–242 °C (dec.) (ethanol). ^{1}H NMR (DMSO-d_6): δ = 4.35 (m, 2H, allyl-CH_2–N), 5.25 (m, 2H, allyl-CH_2=), 5.90 (m, 1H, allyl-CH=), 6.90 (br, 2H, NH_2), 7.15–7.90 (m, 5H, ArH and allyl-NH), 11.02 (br, 1H, pyrazole-NH). ^{13}C NMR (DMSO-d_6): δ = 56.62 (allyl-CH_2N), 59.72 (C-4′), 106.72 (spiro-C-2,3′), 114.62 (allyl-CH_2=), 116.68 (CN), 127.09, 130.04 (ArCH), 134.86, 137.56 (ArC), 170.31 (C-5′), 181.34 (C=S), 193.18, 194.40 (CO). IR (KBr): υ (cm^{-1}) = 3430–3210 (NH_2, NH), 2210 (CN), 1750 and 1735 (CO), 1620 (ArC=C), 1575 (NH-def. and C–N str.), 1360, 1010 (C=S, C–N). MS, *m/z* (%): 339 [M^+] (12), 312 (18), 273 (36), 245 (42), 99 (64),



Scheme 3

41 (100). $C_{16}H_{13}N_5O_2S$ (339.37): Calcd: C, 56.63; H, 3.86; N, 20.64; S, 9.45. Found: C, 56.76; H, 3.99; N, 20.46; S, 9.61%.

*5′-Amino-4′-cyano-N-(4-fluorophenyl)-1,3-dioxo-1,3-dihydrospiro [indene-2,3′-pyrazole]-2′(1′*H*)-carbothioamide* (**7d**): Dark brown crystals (0.247 g, 63%), m.p. 296–298 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 6.94 (br, 2H, NH_2), 7.21–7.94 (m, 8H, ArH), 9.84 (br, 1H, NH-Ph), 10.98 (br, 1H, pyrazole-NH). ^{13}C NMR (DMSO-d_6): δ = 60.26 (C-4′), 105.98 (spiro-C-2,3′), 119.11 (CN), 125.63, 128.55, 131.27, 132.15 (ArCH), 134.27, 137.92 (ArC), 162.86 (ArC-F), 173.65 (C-5′), 183.84 (C=S), 193.89, 195.12 (CO). IR (KBr): υ (cm^{-1}) = 3390-3205 (NH_2, NH), 2220 (CN), 1750 and 1735 (CO), 1610 (ArC=C), 1575 (NH-def. and C–N str.), 1350, 1000 (C=S and C–N). MS, *m/z* (%): 393 [M^+] (42), 366 (29), 338 (36), 304 (44), 234 (28), 219 (82), 166 (44), 154 (100), 110 (35), 91 (52). $C_{19}H_{12}FN_5O_2S$ (393.39): Calcd: C, 58.01; H, 3.07; N, 17.80; S, 8.15. Found: C, 57.84; H, 2.96; N, 17.92; S, 7.96%.

*5′-Amino-4′-cyano-N-(3,5-difluorophenyl)-1,3-dioxo-1,3-dihydrospiro [indene-2,3′-pyrazole]-2′(1′*H*)-carbothioamide* (**7e**): Dark brown crystals (0.263 g, 64%), m.p. 309–311 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 6.82 (br, 2H, NH_2), 7.02–7.86 (m, 7H, ArH), 9.62 (br, 1H, NH-Ph), 10.80 (br, 1H, pyrazole-NH). ^{13}C NMR (DMSO-d_6): δ = 60.74 (C-4′), 107.22 (spiro-C-2,3′), 118.87 (CN), 123.93, 126.77, 130.88, 132.22 (ArCH), 135.24, 138.17 (ArC), 160.12 (ArC-F), 173.54 (C-5′), 182.66 (C=S), 193.46, 194.85 (CO). IR (KBr): υ (cm^{-1}) = 3410-3190 (NH_2, NH), 2215 (CN), 1745 and 1725 (CO), 1615 (ArC=C), 1575 (NH-def. and C–N str.), 1355, 995 (C=S and C–N). MS, *m/z* (%): 411 [M^+] (6), 384 (17), 367 (19), 304 (100), 171 (22), 113 (26), 104 (35). $C_{19}H_{11}F_2N_5O_2S$ (411.38): Calcd: C, 55.47; H, 2.70; N, 17.02; S, 7.79. Found: C, 55.63; H, 2.59; N, 16.84; S, 7.71%.

*5′-Amino-4′-cyano-1,3-dioxo-N-[4-(trifluoromethyl)phenyl)-1,3-dihydrospiro[indene-2,3′-pyrazole]-2′(1′*H*)-carbothioamide* (**7f**): Reddish brown crystals (0.297 g, 67%), m.p. 326–328 °C (methanol). ^{1}H NMR ($CDCl_3$): δ = 7.02 (br, 2H, NH_2), 7.21–8.01 (m, 8H, ArH), 9.97 (br, 1H, NH-Ph), 11.07 (br, 1H, pyrazole-NH). ^{13}C NMR ($CDCl_3$): δ = 60.59 (C-4′), 106.27 (spiro-C-2,3′), 118.88 (CN), 125.17 (C-F_3), 126.83, 129.74, 130.82, 131.75 (ArCH), 133.22, 135.12, 137.66 (ArC), 172.82 (C-5′), 184.17 (C=S), 193.76, 194.95 (CO). IR (KBr): υ (cm^{-1}) = 3380–3220 (NH_2, NH), 2210 (CN), 1755 and 1740 (CO), 1620 (ArC=C), 1570 (NH-def. and C–N str.), 1360, 980 (C=S and C–N). MS, *m/z* (%): 443 [M^+] (12), 377 (100), 204 (47), 160 (18), 104 (23). $C_{20}H_{12}F_3N_5O_2S$ (443.40): Calcd: C, 54.18; H, 2.73; N, 15.79; S, 7.25. Found: C, 53.97; H, 2.85; N, 15.92; S, 7.08%.

*4-Phenyl-3-Thioxo-3*H*-indeno[1,2-e][1,2,4]-triazin-9(4*H*)-one* (**8a**): Yellowish brown crystals (0.070 g, 24%), m.p. 171–173 °C (ethanol). ^{1}H NMR (DMSO-d_6): δ = 7.05–7.50 (m, 7H, Ar), 7.65–7.90 (m, 2H, Ar), ^{13}C NMR (DMSO-d_6): δ = 127.37, 128.20, 128.76, 129.77, 129.90 (ArCH), 130.34, 134.50, 135.08 (ArC), 139.10 (C-9a), 140.43 (C-4a), 185.85 (C=S), 193.01 (CO). IR (KBr): υ (cm^{-1}) = 1715 (CO), 1610, 1585 (ArC=C), 1365,1005 (C=S and C–N). MS, *m/z* (%) = 291 [M^+] (16), 247 (66), 219 (61), 191 (53), 135 (22), 128 (41), 104 (46), 77 (100). $C_{16}H_9N_3OS$ (291.05): Calcd: C, 65.95; H, 3.11; N, 14.42; S, 11.01. Found: C, 66.12; H, 3.03; N, 14.28; S, 10.94%.

*4-Benzyl-3-Thioxo-3*H*-indeno[1,2-e][1,2,4]-triazin-9(4*H*)-one* (**8b**). Brown crystals (0.070 g, 23%), m.p. 188–190 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 4.95 (s, 2H, CH_2), 7.20–8.10 (m, 9H, ArH). ^{13}C NMR (DMSO-d_6): δ = 47.87 (CH_2), 127.68, 127.88, 128.18, 128.38, 128.63 (ArCH), 129.95, 135.98, 136.31 (ArC), 139.98 (C-9a), 142.09 (C-4a), 186.72 (C=S), 193.12 (CO). IR (KBr): υ (cm^{-1}) = 1710 (CO), 1620, 1580 (ArC=C), 1370, 1010(C=S and C–N). MS, *m/z* (%) = 305 [M^+] (9), 261 (21), 149 (24), 128 (36), 104 (56), 91 (100), 77 (58). $C_{17}H_{11}N_3OS$ (305.35): Calcd: C, 66.87; H, 3.63; N, 13.76; S, 10.50. Found: C, 67.02; H, 3.51; N, 13.88; S, 10.37%.

*4-Allyl-3-Thioxo-3*H*-indeno[1,2-e][1,2,4]-triazin-9(4*H*)-one* (**8c**). Brown crystals (0.066 g, 26%), m.p. 120–122 °C (ethanol). ^{1}H NMR (DMSO-d_6): δ = 4.30 (m, 2H, allyl-CH_2N), 5.22 (m, 2H, allyl-CH_2), 5.95 (m, 1H, allyl-CH=), 7.55–8.20 (m, 4H, ArH). ^{13}C NMR (DMSO-d_6): δ = 47.36 (allyl-CH_2-N), 118.31 (allyl CH_2=), 129.07, 131.97, 133.65 (ArCH), 134.28 (allyl-CH=), 136.32, 136.44 (ArC), 139.85 (C-9a), 141.70 (C-4a), 185.57 (C=S), 193.46 (CO). IR (KBr): υ (cm^{-1}) = 1720 (CO), 1595 (ArC=C), 1365, 995 (C=S and C–N). MS, *m/z* (%) = 255 [M^+] (14), 156 (26), 128 (52), 104 (33), 77 (47), 41 (100). $C_{13}H_9N_3OS$ (255.30): Calcd: C, 61.16; H, 3.55; N, 16.46; S, 12.56. Found: C, 60.97; H, 3.66; N, 16.63; S, 12.33%.

*4-(3,5-Difluorophenyl)-3-Thioxo-3H-indeno[1,2-e][1,2,4]-triazin-9(4*H*)-one* (**8d**). Orange crystals (0.056 g, 17%), m.p. 210–212 °C (dec.) (ethanol). ^{1}H NMR (DMSO-d_6): δ = 7.24–7.86 (m, 7H, ArH). ^{13}C NMR (DMSO-d_6): δ = 123.16, 124.27, 128.72, 129.83, 129.96

(ArCH), 134.87, 135.92, 136.12 (ArC), 139.37 (C-9a), 140.58 (C-4a), 160.27 (ArC-F), 185.76 (C=S), 193.16 (CO). IR (KBr): υ (cm^{-1}) = 1710 (CO), 1620, 1580 (ArC=C), 1360, 995 (C=S and C–N). MS, *m/z* (%) = 327 [M^+] (18), 299 (12), 283 (11), 171 (76), 128 (46), 104 (87), 76 (100). $C_{16}H_7F_2N_3OS$ (327.31): Calcd: C, 58.71; H, 2.16; N, 12.84; S, 9.80. Found: C, 58.56; H, 2.27; N, 13.03; S, 9.67%.

*3-Thioxo-4-[4-(trifluoromethyl)phenyl]-3*H-*indeno[1,2-e][1,2,4]-triazin-9(4*H*)-one* (**8e**): Reddish orange crystals (0.072 g, 20%), m.p. 270–272 °C (dec.) (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 7.18–8.02 (m, 8H, ArH). ^{13}C NMR (DMSO-d_6): δ = 127.27, 127.78, 128.28, 129.51, 129.86 (ArCH), 131.12, 135.84, 136.77, 137.46 (ArC), 140.26 (C-9a), 141.83 (C-4a), 185.81 (C=S), 193.42 (CO). IR (KBr): υ (cm^{-1}) = 1710 (CO), 1615, 1590 (ArC=C), 1355, 1010 (C=S and C–N). MS, *m/z* (%) = 359 [M^+] (12), 331 (16), 303 (10), 200 (51), 159 (27), 128 (27), 104 (81), 76 (100). $C_{17}H_8F_3N_3OS$ (359.33): Calcd: C, 56.82; H, 2.24; N, 11.69; S, 8.92. Found: C, 56.97; H, 2.18; N, 11.87; S, 9.07%.

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