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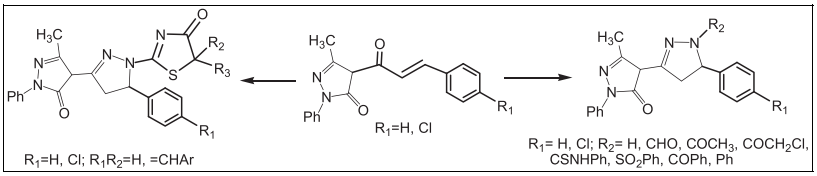

A novel series of pyrazoline and thiazole derivatives incorporating 2-pyrazolin-5-one moiety were synthesized starting from α,β-unsaturated ketones under the effect of hydrazine derivatives and thiosemicarbazide. The obtained pyrazolines **4a**,**b** were treated with different reagents to afford *N*-substituted pyrazolines **5a**,**b–8a**,**b**. *N*-Thiocarbamoyl pyrazolines **12a**,**b** were cyclized using phenacyl bromide, 2,3-dichloroquinoxaline, and monochloroacetic acid afforded the novel pyrazolinyl thiazoles **13a**,**b–16a–f**. The newly synthesized compounds were characterized by analytical and spectral data.

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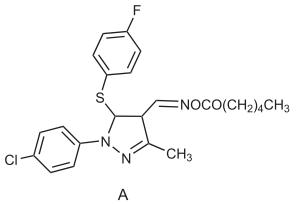
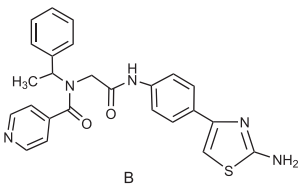
INTRODUCTION

2-Pyrazolin-5-one derivatives are an important class of heterocyclic compounds possessing wide variety in synthetic chemistry [1–5]. Derivatives of 2-pyrazolin-5-one are found to show remarkable anti-tubercular [6,7], antimicrobial [8–10], and anti-inflammatory [11] activities. On the other hand, the chemistry of thiazoles has received considerable attention in recent years owing to their synthetic [12–14] and biological [15,16] importance. Among the analogs, pyrazoline compound; A [17,18] and thiazole derivative especially BILS 179BS; B [19] were reported to exhibit a high antiviral activity against hepatitis A virus and hepatitis B virus HSV, respectively.

In view of these observations and in continuation of our research program on the synthesis of some novel heterocyclic compounds related to 2-pyrazolin-5-one [20–24], the present research concerns the synthesis of pyrazoline and thiazole derivatives related to 2-pyrazolin-5-one nucleus.



A



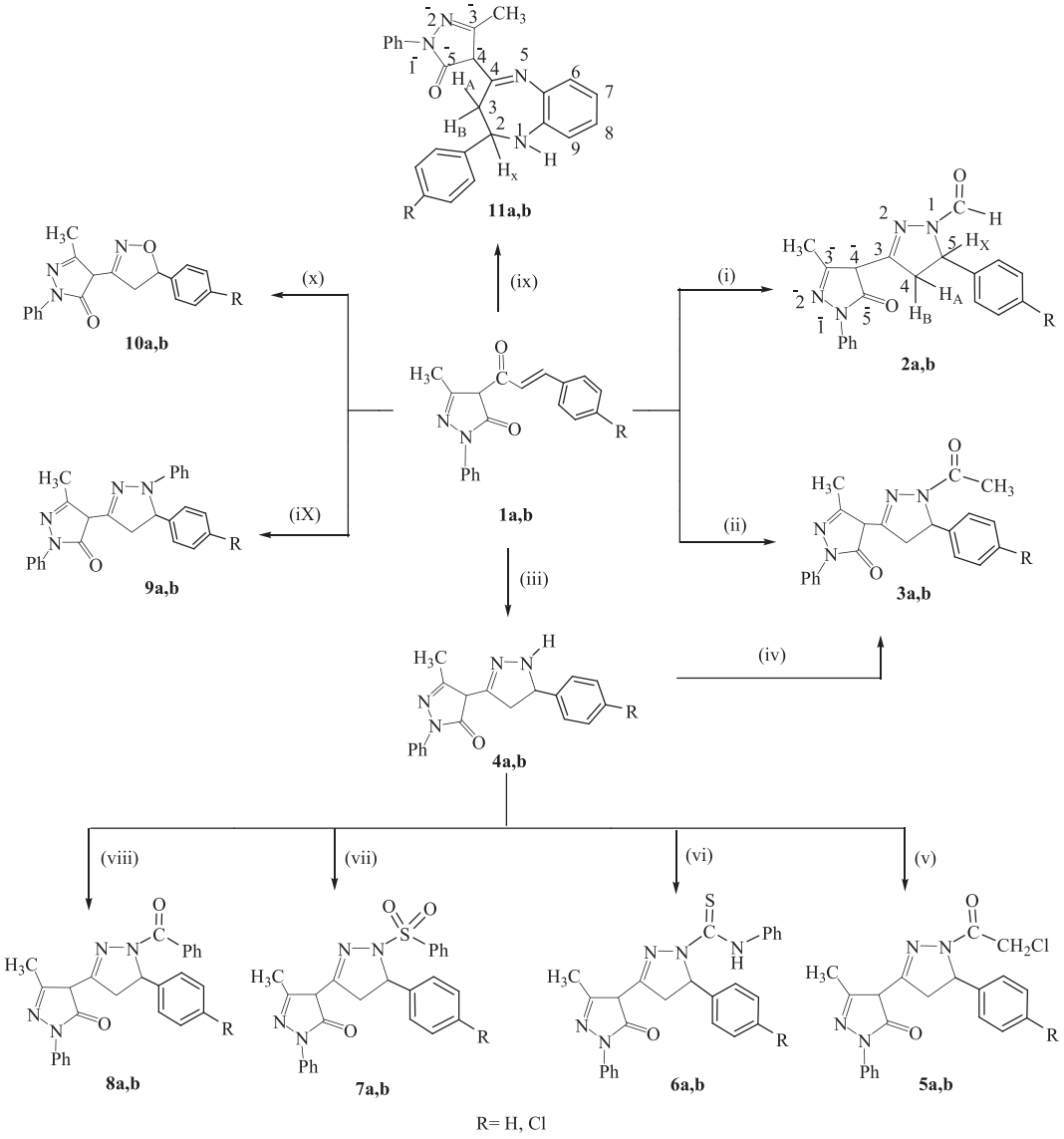
B

RESULTS AND DISCUSSION

The reaction sequences employed for synthesis of the target pyrazoline, diazepine, quinoxaline, and thiazole derivatives are illustrated in Schemes 1 and 2. The desired chalcones 3-aryl-1-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl) prop-2-en-1-ones **1a**,**b** were synthesized through condensation of equimolar amounts of 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one with benzaldehyde or *p*-chlorobenzaldehyde in accordance with the method described in the literature [25]. When chalcones **1a**,**b** treated with hydrazine hydrate in hot formic acid, *N*-formyl pyrazoline derivatives **2a**,**b** were obtained rather than the non formylated ones due to heating in formic acid for long periods of time. The presence of *N*-formyl group of **2a**, e.g., was established using IR, ^{1}H-NMR, and ^{13}C-NMR spectra whereas IR revealed a strong absorption band at ν 1721 cm^{-1} for the carbonyl group, meanwhile, its ^{1}H-NMR spectra presented the presence of singlet signal integrating one proton at δ 9.00 ppm due to the formyl group proton. Further evidence was obtained from ^{13}C-NMR spectra, which showed signal at δ 161.1 ppm owing to the formyl carbon. The evidence for the formation of pyrazoline ring in *N*-formyl pyrazolines **2a**,**b** was obtained from ^{1}H-NMR and ^{13}C-NMR spectra, which provide diagnostic tools for the positional elucidation of the protons. The geminal pyrazoline protons (H_A and H_B) at C4 appeared in the region of 3.41–3.46 and 3.79–3.85 ppm as doublet of doublets in compounds **2a**,**b**. The proton (H_X) at C5 also appears as doublet of doublets in the region of 4.76–4.81 ppm due to vicinal coupling with two non-magnetically equivalent germinal protons of C4 carbon. The signals obtained from ^{13}C-NMR spectra further confirmed the proposed structures; the C4 and C5 carbons of the pyrazoline ring resonate at 40.8–41.1 and 57.3–57.9 ppm, respectively. Furthermore, it presented signals at range of δ 147.1–147.4 ppm, which assignable to azomethine carbons of pyrazoline ring.

On the other hand, upon using acetic acid instead of formic acid in the previous reaction, the *N*-acetyl

Scheme 1. Reagents: (i) $NH_2NH_2.H_2O$/HCOOH; (ii) $NH_2NH_2.H_2O$/AcOH; (iii) $NH_2NH_2.H_2O$/EtOH; (iv) AcOH; (v) $ClCH_2COCl$/toluene; (vi) PhNCS/EtOH; (vii) $PhSO_2Cl$/pyridine; (viii) PhCOCl/pyridine; (ix) $PhNHNH_2$/EtOH; (x) $NH_2OH.HCl$/EtOH, AcONa; (xi) *o*-phenylenediamine/EtOH.



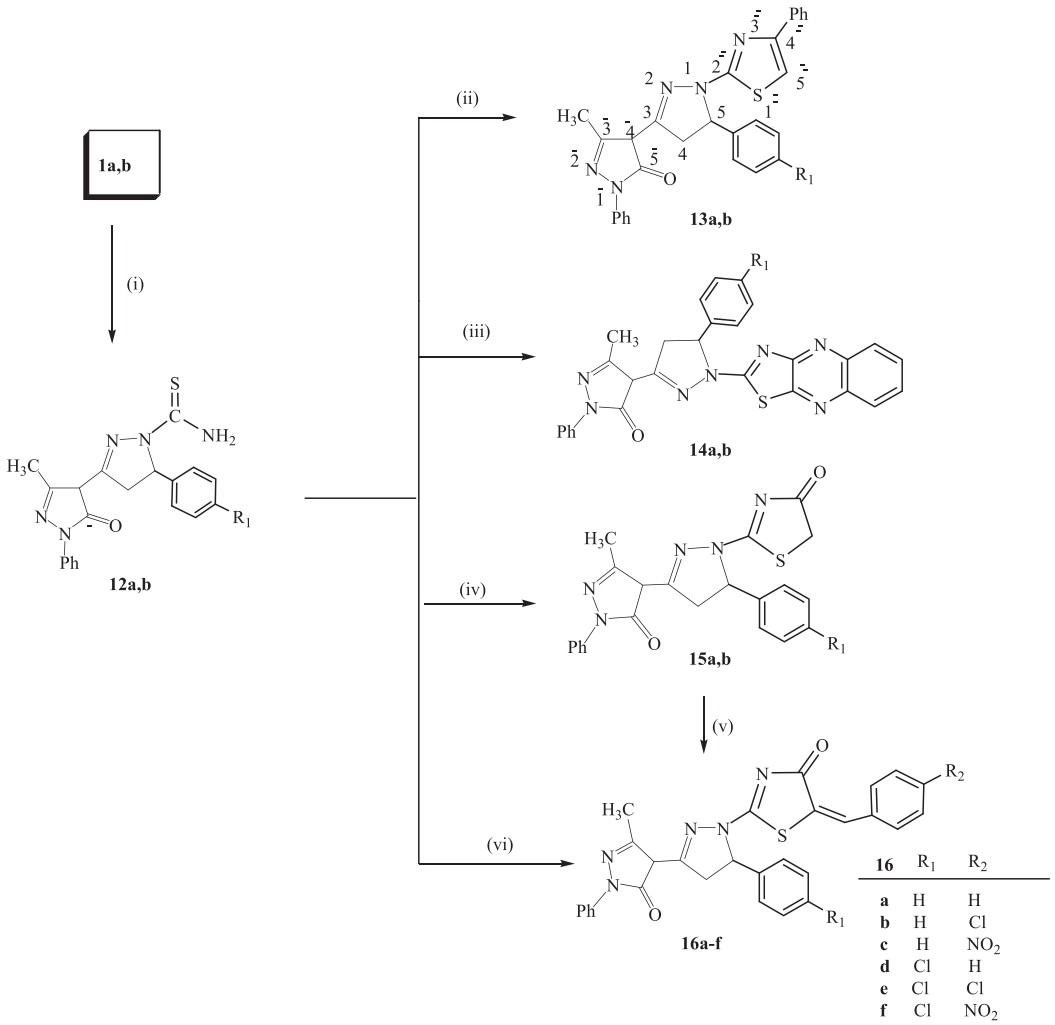
pyrazolines **3a**,**b** were formed. The presence of *N*-acetyl group was established using IR and ^{1}H-NMR spectra. While condensing **1a**,**b** with hydrazine hydrate in ethanol, 3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-aryl-2-pyrazolines **4a**,**b** were obtained. The reaction includes formation of hydrazones intermediate and then addition of NH_2 of hydrazones to the double bond. Upon acetylation of the pyrazolines **4a**,**b** by acetic acid, *N*-acetyl pyrazolines **3a**,**b** were obtained. Moreover, the aforementioned pyrazoline derivatives **4a**,**b** were converted into the corresponding substituted *N*-pyrazolines **5a**,**b–8a**,**b** through their reaction with various reagents such as chloroacetyl chloride, phenyl isothiocyanate, benzenesulfonyl chloride, and benzoyl chloride, respectively.

The structures of products **5a**,**b–8a**,**b** were evidenced by their spectra (IR, ^{1}H-NMR, ^{13}C-NMR, and MS) and elemental analyses (see Experimental section and Table 1).

N-phenyl pyrazolines **9a**,**b** were obtained upon condensing with phenyl hydrazine in hot ethanol. The presence of *N*-phenyl group in **9a** or **9b** was elucidated from spectral data and EIMS, which is in agreement with their molecular weights. The isooxazoline derivatives **10a**,**b** were obtained through condensation of **1a**,**b** with hydroxyl amine in hot ethanol containing anhydrous sodium acetate. The spectroscopic data and elemental analysis were constituent with the structures of compounds **10a**,**b**.

On the other hand, binucleophile compound like *o*-phenylenediamine was condensed with **1a**,**b** in ethanol

Scheme 2. Reagents: (i) $NH_2CSNHNH_2$/EtOH, NaOH; (ii) $PhCOCH_2Br$/EtOH; (iii) 2,3-dichloroquinoxaline/EtOH; (iv) $ClCH_2COOH$/AcOH, AcONa; (v) ArCHO/AcOH, AcONa; (vi) $ClCH_2COOH$, ArCHO/AcOH, AcONa.



containing few drops of TEA to give 4-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-aryl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepines **11a**,**b** with good yields (Scheme 1). IR spectra of **11a** showed a strong absorption band at ν 3343 cm^{-1} due to NH group; meanwhile, the ^{1}H-NMR spectra revealed three doublet signals at δ 3.40–3.42, 3.92–4.08, and 4.78–4.99 ppm due to H_A, H_B, and H_X of diazepine ring. Further evidence for the formation of diazepine ring was obtained from the ^{13}C-NMR spectrum, which presents nine signals of benzo[*b*]diazepine carbons at δ 121.2, 122.8, 125.5, 127.8, 129.8, 134.7, 135.9, 151.9, and 168.2. The novel key intermediates 1-thiocarbamoyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-aryl-2-pyrazolines **12a**,**b** were obtained by heating at reflux equimolar amounts of thiosemicarbazide and α,β-unsaturated ketones **1a**,**b** in hot ethanolic NaOH solution for 8 h. The structures of *N*-thiocarbamoyl pyrazolines **12a**,**b** were characterized using IR and ^{13}C-NMR spectra, whereas IR showed strong absorption bands at range of ν 3295–3401 cm^{-1} due to NH_2 group. Furthermore, ^{13}C-NMR spectra of **12a** or **12b** displayed a signal at δ 176.9 or 177.1 ppm assignable to thiocarbamoyl carbon (C═S). The *N*-thiocarbamoyl pyrazolines **12a**,**b** were cyclized to pyrazolinyl thiazole derivatives **13a**,**b** through their reaction with phenacyl bromide in hot ethanol for 1 h. The structures of the new thiazoles **13a**,**b** were confirmed using ^{1}H-NMR spectra, which revealed the appearance of singlet signals around δ = 6.80–6.83 ppm integrating one proton due to C_5-H of the thiazole ring. Further evidence for the formation of thiazole ring was obtained from the ^{13}C-NMR spectra of compound **13a**, which confirmed the proposed structure due to the appearance of characteristic signals at δ = 178.2 (azomethine carbon), 164.8 (C_2 of thiazole), 150.6 (C_4 of thiazole), and 105.7 ppm indicating the presence of thiazole ring.

3-(3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-aryl-1-(thiazolo[4,5-*b*]quinoxalin-2-yl)-2-pyrazolines **14a**,**b** were produced through treatment of *N*-thiocarbamoyl pyrazolines

Table 1

The elemental analyses of the prepared compounds **2a**,**b–10a**,**b**.

Compound no.	Formula	Molecular weight		Elemental analyses C	H	N	S	Cl
2a	$C_{20}H_{18}N_4O_2$	346.38	Calcd	69.35	5.24	16.17	—	—
			Found	69.33	5.26	16.15	—	—
2b	$C_{20}H_{17}ClN_4O_2$	380.83	Calcd	63.08	4.50	14.71	—	9.31
			Found	63.04	4.53	14.69	—	9.35
3a	$C_{21}H_{20}N_4O_2$	360.41	Calcd	69.98	5.59	15.55	—	—
			Found	69.96	5.56	15.53	—	—
3b	$C_{21}H_{19}ClN_4O_2$	394.85	Calcd	63.88	4.85	14.19	—	8.98
			Found	63.86	4.84	14.17	—	9.03
4a	$C_{19}H_{18}N_4O$	318.37	Calcd	71.68	5.70	17.60	—	—
			Found	71.65	5.72	17.58	—	—
4b	$C_{19}H_{17}ClN_4O$	352.82	Calcd	64.68	4.86	15.88	—	10.05
			Found	64.67	4.85	15.90	—	10.09
5a	$C_{21}H_{19}ClN_4O_2$	394.85	Calcd	63.88	4.85	14.19	—	8.98
			Found	63.85	4.87	14.16	—	8.94
5b	$C_{21}H_{18}Cl_2N_4O_2$	429.30	Calcd	58.75	4.23	13.05	—	16.52
			Found	58.73	4.26	13.03	—	16.50
6a	$C_{26}H_{23}N_5OS$	453.56	Calcd	68.85	5.11	15.44	7.07	—
			Found	68.82	5.14	15.47	7.03	—
6b	$C_{26}H_{22}ClN_5OS$	488.00	Calcd	63.99	4.54	14.35	6.57	7.26
			Found	63.96	4.56	14.32	6.59	7.30
7a	$C_{25}H_{22}N_4O_3S$	458.53	Calcd	65.48	4.84	12.22	6.99	—
			Found	65.51	4.87	12.18	6.96	—
7b	$C_{25}H_{21}ClN_4O_3S$	492.98	Calcd	60.91	4.29	11.36	6.50	7.19
			Found	60.93	4.26	11.39	6.47	7.15
8a	$C_{26}H_{22}N_4O_2$	422.48	Calcd	73.92	5.25	13.26	—	—
			Found	73.89	5.23	13.28	—	—
8b	$C_{26}H_{21}ClN_4O_2$	456.92	Calcd	68.34	4.63	12.26	—	7.76
			Found	62.36	4.65	12.23	—	7.72
9a	$C_{25}H_{22}N_4O$	394.47	Calcd	76.12	5.62	14.20	—	—
			Found	76.15	5.65	14.24	—	—
9b	$C_{25}H_{21}ClN_4O$	428.91	Calcd	70.01	4.93	13.06	—	8.27
			Found	70.03	4.90	13.08	—	8.31
10a	$C_{19}H_{17}N_3O_2$	319.36	Calcd	71.46	5.37	13.16	—	—
			Found	71.45	5.35	13.19	—	—
10b	$C_{19}H_{16}ClN_3O_2$	353.8	Calcd	64.50	4.56	11.88	—	10.02
			Found	64.53	4.53	11.85	—	10.06

12a,**b** with 2,3-dichloroquinoxaline in hot ethanol. On the other hand, the thiocarbamoyl pyrazolines **12a**,**b** were cyclized to pyrazolinyl thiazolones **15a**,**b** through their reaction with chloroacetic acid and anhydrous sodium acetate in acetic acid as a solvent. The structures of new thiazolones **15a**,**b** were confirmed using IR, which revealed strong absorption bands at range of ν 1715–1717 cm^{-1} due to carbonyl group of thiazole ring. In addition, ^{1}H-NMR showed the appearance of signals (two doublets) around δ = 3.98–4.22 ppm integrating two protons due to C_5-H of the thiazolone ring. ^{13}C-NMR spectra of **15a** established the proposed structure due to the appearance of signal at δ = 189.2 ppm due to carbonyl carbon as well as the presence of signal at δ = 35.3 ppm assignable to C_5 of thiazolone ring. Upon condensing thiazolone derivatives **15a**,**b** with a variety of aromatic aldehydes, the corresponding arylidenes **16a–f** were obtained. The latter compounds were directly synthesized through one-pot reaction of **12a**,**b** with the aromatic aldehydes and chloroacetic acid (Scheme 2). The structures of the products **16a–f** were confirmed based on their analytical and spectral data (Table 2).

EXPERIMENTAL

Melting points were determined on APP. Digital ST 15 melting point apparatus and are corrected. The time required for each reaction to complete was monitored by thin-layer chromatography . Elemental analysis (C, H, N, S) was conducted using a Vario EL C, H, N, S Analyzer; their results were found to be in good agreement (±0.3%) with the calculated values. FTIR spectra (KBr disk) were recorded on a Pye-Unicam SP3-100 spectrophotometer. The ^{1}H-NMR and ^{13}C-NMR spectra were measured on a JNM-LA Series 400 and a Varian 1H-Gemini 200 spectrometers with TMS as the internal standard and DMSO-d_6 as solvent. Mass spectra were recorded at 70 eV with JEOL JMS 600 spectrometer.

Table 2

The elemental analyses of the prepared compounds **11a**,**b–16a–f**.

Compound no.	Formula	Molecular weight		Elemental analyses C	H	N	S	Cl
11a	$C_{25}H_{22}N_4O$	394.47	Calcd	76.12	5.62	14.20	—	—
			Found	76.11	5.65	14.17	—	—
11b	$C_{25}H_{21}ClN_4O$	428.91	Calcd	70.01	4.93	13.06	—	8.27
			Found	70.04	4.90	13.04	—	8.30
12a	$C_{20}H_{19}N_5OS$	377.46	Calcd	63.64	5.07	18.55	8.49	—
			Found	63.61	5.09	18.58	8.50	—
12b	$C_{20}H_{18}ClN_5OS$	411.91	Calcd	58.32	4.40	17.00	7.78	8.61
			Found	58.30	4.41	17.04	7.76	8.58
13a	$C_{28}H_{23}N_5OS$	477.58	Calcd	70.42	4.85	14.66	6.71	—
			Found	70.40	4.87	14.70	6.68	—
13b	$C_{28}H_{22}ClN_5OS$	512.03	Calcd	65.68	4.33	13.68	6.26	6.92
			Found	65.90	4.30	13.67	6.23	6.97
14a	$C_{28}H_{21}N_7OS$	419.5	Calcd	66.78	4.20	19.47	6.37	—
			Found	66.75	4.17	19.50	6.35	—
14b	$C_{28}H_{20}ClN_7OS$	453.94	Calcd	62.51	3.75	18.22	5.96	6.59
			Found	62.48	3.72	18.20	5.92	6.63
15a	$C_{22}H_{19}N_5O_2S$	417.48	Calcd	63.29	4.59	16.78	7.68	—
			Found	63.26	4.57	16.76	7.71	—
15b	$C_{22}H_{18}ClN_5O_2S$	451.93	Calcd	58.47	4.01	15.50	7.10	7.84
			Found	58.49	4.02	15.53	7.14	7.83
16a	$C_{29}H_{25}N_5O_2S$	505.59	Calcd	68.89	4.59	13.85	6.34	—
			Found	68.89	4.59	13.85	6.34	—
16b	$C_{29}H_{22}ClN_5O_2S$	540.04	Calcd	64.50	4.11	12.97	5.94	6.56
			Found	64.52	4.14	12.94	5.96	6.60
16c	$C_{29}H_{22}N_6O_4S$	550.59	Calcd	63.26	4.03	15.26	5.82	—
			Found	63.28	4.06	15.27	5.84	—
16d	$C_{29}H_{22}ClN_5O_2S$	540.04	Calcd	64.50	4.11	12.97	5.94	6.56
			Found	64.51	4.15	12.95	5.91	6.53
16e	$C_{29}H_{21}Cl_2N_5O_2S$	574.48	Calcd	60.63	3.68	12.19	5.58	12.34
			Found	60.65	3.65	12.14	5.53	12.30
16f	$C_{29}H_{21}ClN_6O_4S$	585.03	Calcd	59.54	3.62	14.37	5.48	6.06
			Found	59.55	3.65	14.34	5.43	6.10

General procedure for the synthesis of 2a,b. The corresponding chalcones **1a**,**b** (5 mmol) were refluxed in formic acid (20 mL) with hydrazine hydrate (0.32 mL, 10 mmol) for 8 h. The mixture was cooled, poured into crushed ice, and then neutralized by ammonia. The obtained product was washed by cold water and crystallized from the proper solvent to give **2a** or **2b**, respectively.

1-Formyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-phenyl-2-pyrazoline (2a). Crystallized from ethanol to give white powder, yield 1.27 g (73 %), mp 225–226°C. IR (KBr): 3010 (Ar-H), 2933 (aliphatic-H), 1721 (C═O formyl), 1633 (C═O), 1610 (C═N), 1584, 1497 (C═C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 400 MHz): $\delta = 2.35$ (s, 3H, CH_3), 3.41–3.45 (dd, $J = 18.2$, 4.2 Hz, H_A, C4-H), 3.79–3.83 (dd, $J = 18.2$,11.3 Hz, H_B, C4-H), 4.76–4.80 (dd, $J = 11.3$, 4.2 Hz, H_X, C5-H), 7.05–7.40 (m, 6H, Ar-H + H4′), 7.49–7.51 (m, 5H, Ar-H), 9.00 (s, 1H, CHO) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.2$, 40.8, 57.9, 117.9, 118.8, 121.3, 122.3, 127.4, 129.7, 132.8, 135.8, 137.3, 138.4, 139.2, 140.2, 144.1, 145.8, 147.1, 161.1, 169.8 ppm. EI ms: *m/z*: 346.29 [M^+] (70).

1-Formyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-p-chlorophenyl-2-pyrazoline (2b). Crystallized from ethanol to afford white crystals, yield 1.44 g (76%), mp 220–221°C. IR (KBr): 3012 (Ar-H), 2991 (aliphatic-H), 1720 (C═O formyl), 1635 (C═O), 1615 (C═N), 1581, 1490 (C═C), 710 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 400 MHz): $\delta = 2.35$ (s, 3H, CH_3), 3.43–3.46 (dd, $J = 18.3$, 4.3 Hz, H_A, C4-H), 3.81–3.85 (dd, $J = 18.3$,11.3 Hz, H_B, C4-H), 4.77–4.81 (dd, $J = 11.3$, 4.3 Hz, H_X, C5-H), 7.07–7.41 (m, 6H, Ar-H + H4′), 7.48–7.53 (m, 4H, Ar-H), 9.10 (s, 1H, CHO) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.3$, 41.1, 57.3, 117.4, 118.7, 121.3, 122.3, 127.4, 129.7, 132.8, 135.9, 137.3, 138.4, 139.3, 140.3, 144.2, 145.8, 147.4, 161.2, 169.9 ppm. EI ms: *m/z*: 380.79 [M^+] (62), 382.86 [$M^+ + 2$] (16).

General procedure for the synthesis of 3a,b. A mixture of chalcones **1a**,**b** (5 mmol), hydrazine hydrate (0.32 mL, 10 mmol) and acetic acid (20 mL) was refluxed for 8 h. The resulting mixture was poured into crushed ice and then neutralized by ammonia. The obtained product was separated by filtration, washed with cold water and then crystallized from suitable solvent to give compounds **3a**,**b**.

1-Acetyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-phenyl-2-pyrazoline (3a). Crystallized from ethanol to give pale yellow powder, yield 1.22 g (68%), mp 200–202°C. IR (KBr): 3010 (Ar-H), 2944 (aliphatic-H), 1712 (C═O acetyl), 1640 (C═O), 1605 (C═N), 1588, 1497 (C═C) cm^{-1}.^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.30$ (s, 3H, $COCH_3$), 2.39 (s, 3H,

CH_3), 3.44–3.53 (dd, J = 17.5, 5.1 Hz, H_A, C4-H), 3.74–3.82 (dd, J = 17.5, 11.8 Hz, H_B, C4-H), 4.61–4.80 (dd, J = 11.8, 5.1 Hz, H_X, C5-H), 7.01–7.60 (m, 6H, Ar-H + H4′), 7.61–7.91 (m, 4H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 15.5, 29.4, 40.8, 57.8, 118.1, 118.7, 121.4, 122.5, 127.5, 129.8, 133.7, 135.7, 137.3, 138.3, 139.1, 141.4, 144.5, 145.8, 147.8, 169.1, 170.5 ppm. EI ms: *m/z*: 360.31 [M^+] (65).

1-Acetyl-3-(3-methyl-1-phenyl-5-oxo-2-pyrazolin-4-yl)-5-p-chlorophenyl-2-pyrazoline (3b). Crystallized from methanol to give yellow powder, yield 1.37 g (70%), mp 205–207°C. IR (KBr): 3013 (Ar-H), 2943 (aliphatic-H), 1710 (C=O acetyl), 1635 (C=O), 1605 (C=N), 1589, 1499 (C=C), 715 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): δ = 2.29 (s, 3H, $COCH_3$), 2.38 (s, 3H, CH_3), 3.45–3.54 (dd, J = 17.5, 5.1 Hz, H_A, C4-H), 3.72–3.81 (dd, J = 17.5,11.8 Hz, H_B, C4-H), 4.60–4.80 (dd, J = 11.8, 5.1 Hz, H_X, C5-H), 7.00–7.60 (m, 6H, Ar-H + H4′), 7.76–7.91 (m, 5H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 15.4, 29.2, 40.9, 58.1, 117.9, 118.8, 121.3, 122.3, 127.4, 129.7, 132.8, 135.8, 137.3, 138.4, 139.2, 141.1, 144.3, 145.9, 147.9, 169.3, 170.2 ppm. EI ms: *m/z*: 394.82 [M^+] (63), 396.81 [M^+ + 2] (20).

General procedure for the synthesis of 4a,b. To a solution of chalcones **1a**,**b** (2 mmol) in ethanol (25 mL), hydrazine hydrate (0.16 mL, 5 mmol) was added. The reaction mixture was refluxed for 6 h. Left to cool to room temperature, and the obtained product was filtered, dried and crystallized from an appropriate solvent to afford **4a**,**b**.

3-(3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-phenyl-2-pyrazoline (4a). Crystallized from ethanol to afford pale yellow crystals, yield 0.44 g (70%), mp 200°C. IR (KBr): 3370 (N–H), 3030 (Ar-H), 2990 (aliphatic-H), 1633 (C=O), 1595 (C=N), 1580, 1499 (C=C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 2.21 (s, 3H, CH_3), 3.40–3.42 (dd, J = 18.2, 4.2 Hz, H_A, C4-H), 3.77–3.79 (dd, J = 18.2, 11.3 Hz, H_B, C4-H), 4.76–4.78 (dd, J = 11.3, 4.2 Hz, H_X, C5-H), 7.03–7.36 (m, 6H, Ar-H + H4′), 7.42–7.47 (m, 5H, Ar-H), 7.99 (s, 1H, NH, D_2O exchangeable) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 15.2, 40.8, 57.9, 117.5, 118.9, 121.5, 123.7, 126.3, 128.1, 132.2, 135.4, 136.9, 138.2, 139.1, 140.7, 144.4, 145.9, 146.7, 169.6 ppm. EI ms: *m/z*: 318.33 [M^+] (83).

3-(3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-p-chlorophenyl-2-pyrazoline (4b). Crystallized from ethanol to give white crystals, yield 0.51 g (72%), mp 212°C. IR (KBr): 3372 (N–H), 3031 (Ar-H), 2993 (aliphatic-H), 1633 (C=O), 1590 (C=N), 1583, 1495 (C=C), 714 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): δ = 2.23 (s, 3H, CH_3), 3.41–3.43 (dd, J = 18.2, 4.2 Hz, H_A, C4-H), 3.77–3.79 (dd, J = 18.2, 11.3 Hz, H_B, C4-H), 4.76–4.79 (dd, J = 11.3, 4.2 Hz, H_X, C5-H), 7.05–7.40 (m, 6H, Ar-H + H4′), 7.47–7.51 (m, 4H, Ar-H), 7.99 (s, 1H, NH, D_2O exchangeable) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 15.4, 40.9, 57.7, 117.3, 118.8, 121.7, 123.5, 125.9, 127.9, 132.5, 134.9, 137.1, 138.4, 139.2, 140.9, 144.8, 146.1, 146.9, 169.1 ppm. EI ms: *m/z*: 352.51 [M^+] (63), 354.71 [M^+ + 2] (18).

General procedure for the synthesis of 5a,b. The pyrazoline derivatives **4a**,**b** (2 mmol) and triethyl amine (0.28 mL, 2 mmol) were dissolved in dry toluene (15 mL) with stirring. Later, the reaction mixture was cooled in an ice bath, and chloroacetyl chloride (0.16 mL, 2 mmol) was added dropwise with stirring. The reaction mixture thus obtained was further stirred for 2 h at room temperature. The pale yellow solid thus formed was collected and crystallized from suitable solvent to give products **5a**,**b**.

1-Chloroacetyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-phenyl-2-pyrazoline (5a). Crystallized from toluene to afford red powder, yield 0.54 g (68%), mp 225–226°C. IR (KBr): 3032 (Ar-H), 2988 (aliphatic-H), 1680 (C=O), 1638 (C=O), 1594 (C=N), 1582, 1495 (C=C), 718 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 2.30 (s, 3H, CH_3), 4.12 (s, 2H, CH_2), 3.41–3.44 (dd, J = 18.1, 4.3 Hz, H_A, C4-H), 3.76–3.78 (dd, J = 18.1, 11.2 Hz, H_B, C4-H), 4.74–4.79 (dd, J = 11.2, 4.3 Hz, H_X, C5-H), 7.04–7.42 (m, 6H, Ar-H + H4′), 7.53–7.79 (m, 5H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 15.3, 41.2, 58.2, 64.1, 117.4, 119.2, 121.2, 123.8, 126.2, 127.8, 132.7, 134.7, 136.8, 138.7, 139.4, 141.1, 144.1, 145.9, 146.8, 169.5, 171.4 ppm. EI ms: *m/z*: 394.79 [M^+] (71), 396.81 [M^+ + 2] (23).

1-Chloroacetyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-p-chlorophenyl-2-pyrazoline (5b). Crystallized from dioxane to give brown crystals, yield 0.60 g (70%), mp 241–243°C. IR (KBr): 3031 (Ar-H), 2991 (aliphatic-H), 1679 (C=O), 1637 (C=O), 1592 (C=N), 1580, 1490 (C=C), 712 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): δ = 2.32 (s, 3H, CH_3), 4.17 (s, 2H, CH_2), 3.40–3.43 (dd, J = 18.3, 4.5 Hz, H_A, C4-H), 3.69–3.77 (dd, J = 18.3, 11.1 Hz, H_B, C4-H), 4.75–4.79 (dd, J = 11.1, 4.5 Hz, H_X, C5-H), 7.10–7.52 (m, 6H, Ar-H + H4′), 7.64–7.81 (m, 4H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 15.5, 41.5, 57.9, 63.9, 117.8, 118.9, 121.7, 124.1, 125.9, 128.1, 133.1, 134.5, 136.7, 139.1, 139.6, 141.8, 144.2, 146.1, 147.1, 169.3, 171.6 ppm. EI ms: *m/z*: 429.25 [M^+] (69), 431.23 [M^+ + 2] (18), 433.25 [M^+ + 4] (10).

General procedure for the synthesis of 6a,b. A mixture of **4a**,**b** (2 mmol) and phenyl isothiocyanate (2 mmol, 0.27 g) in dry ethanol (25 mL) was refluxed for 5 h. Cool to the room temperature and the solid mass which separated out was filtered, dried, and crystallized from an appropriate solvent to afford products **6a**,**b**.

1-N-Phenylthiocarbamoyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-phenyl-2-pyrazoline (6a). Crystallized from ethanol to afford yellow crystals, yield 0.56 g (62%), mp 199–200°C. IR (KBr): 3550 (N–H), 3063 (Ar-H), 2993 (aliphatic-H), 1639 (C=O), 1615 (C=S), 1592 (C=N), 1540, 1499 (C=C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): δ = 2.36 (s, 3H, CH_3), 3.42–3.50 (dd, J = 18.0, 4.4 Hz, H_A, C4-H), 3.74–3.80 (dd, J = 18.0, 11.2 Hz, H_B, C4-H), 4.78–4.81 (dd, J = 11.2, 4.4 Hz, H_X, C5-H), 7.10–7.80 (m, 11H, Ar-H + H4′), 7.90–8.30 (m, 5H, Ar-H), 9.10 (s, 1H, NH D_2O exchangeable) ppm. ^{13}C-NMR (DMSO-*d6*, 100 MHz): δ = 15.5, 40.7, 43.9, 65.1, 120.8, 121.4, 123.5, 124.8, 125.6, 128.6, 130.4, 132.4, 133.7, 134.5, 135.8, 136.5, 137.8, 138.4, 140.8, 141.5, 142.9, 147.9, 155.5, 157.4, 169.9, 177.9 ppm. EI ms: *m/z*: 453.51 [M^+] (72).

1-N-Phenylthiocarbamoyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-p-chlorophenyl-2-pyrazoline (6b). Crystallized from toluene to give yellow powder, yield 0.61 g (63%), mp 203–304°C. IR (KBr): 3545 (N–H), 3062 (Ar-H), 2990 (aliphatic-H), 1640 (C=O), 1617 (C=S), 1590 (C=N), 1535, 1497 (C=C), 709 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): δ = 2.37 (s, 3H, CH_3), 3.43–3.51 (dd, J = 18.0, 4.4 Hz, H_A, C4-H4′), 3.73–3.81 (dd, J = 18.0, 11.2 Hz, H_B, C4-H), 4.78–4.82 (dd, J = 11.2, 4.4 Hz, H_X, C5-H), 7.11–7.82 (m, 11H, Ar-H + H4′), 7.90–8.31 (m, 4H, Ar-H), 9.06 (s, 1H, NH D_2O exchangeable) ppm. ^{13}C-NMR (DMSO-*d6*, 100 MHz): δ = 15.7, 40.9, 44.1, 64.9, 121.2, 122.1, 123.7, 124.9, 125.8, 128.1, 130.8, 132.9, 134.1, 135.9, 136.8, 137.9, 138.1, 139.2,

140.9, 142.1, 143.9, 147.5, 155.8, 160.1, 169.7, 177.9 ppm. EI ms: *m/z*: 487.95 [M^+] (63), 490.10 [$M^+ + 2$] (16).

General procedure for the synthesis of 7a,b. To solution of **4a**,**b** (2 mmol) in dry pyridine (15 mL) cooled in an ice bath, benzenesulfonyl chloride (2 mmol) was added. The reaction mixture was heated on a water bath for 3 h, cooled, and then poured into crushed ice. The solid product separated was filtered, dried, and crystallized from suitable solvent to give **7a**,**b**.

1-Benzenesulfonyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-phenyl-2-pyrazoline (7a). Crystallized from toluene to afford red crystals, yield 0.60 g (65%), mp 242–243°C. IR (KBr): 3053 (Ar-H), 2991 (CH aliphatic), 1640 (C═O), 1594 (C═N), 1530, 1498 (C═C), 1344 (anti-symmetric SO_2), 1090 (symmetric SO_2) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 400 MHz): $\delta = 2.40$ (s, 3H, CH_3), 3.42–3.54 (dd, $J = 18.1$, 4.6 Hz, H_A, H4′), 3.75–3.82 (dd, $J = 18.1$, 11.3 Hz, H_B, C4-H), 4.77–4.80 (dd, $J = 11.3$, 4.6 Hz, H_X, C5-H), 7.10–7.79 (m, 11H, Ar-H + H4′), 7.90–8.31 (m, 5H, Ar-H) ppm. ^{13}C-NMR (DMSO-*d6*, 100 MHz): $\delta = 15.4$, 40.7, 44.3, 65.2, 121.2, 122.5, 123.6, 124.8, 125.7, 128.2, 130.5, 132.8, 133.0, 135.4, 136.5, 137.7, 138.5, 139.4, 141.0, 142.3, 143.7, 147.9, 155.7, 157.8, 170.1 ppm. EI ms: *m/z*: 458.51 [M^+] (72).

1-Benzenesulfonyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-p-chlorophenyl-2-pyrazoline (7b). Crystallized from toluene to afford red powder, yield 0.66 g (67%), mp 235–336°C. IR (KBr): 3053 (Ar-H), 2991 (aliphatic-H), 1643 (C═O), 1594 (C═N), 1532, 1499 (C═C), 1349 (anti-symmetric SO_2), 1093 (symmetric SO_2), 710 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.39$ (s, 3H, CH_3), 3.41–3.54 (dd, $J = 18.1$, 4.6 Hz, H_A, C4-H), 3.76–3.82 (dd, $J = 18.1$, 11.3 Hz, H_B, C4-H), 4.76–4.81 (dd, $J = 11.3$, 4.6 Hz, H_X, C5-H), 7.11–7.79 (m, 11H, Ar-H + H4′), 7.90–8.30 (m, 4H, Ar-H) ppm. ^{13}C-NMR (DMSO-*d6*, 100 MHz): $\delta = 15.5$, 40.8, 44.5, 65.4, 120.9, 122.6, 123.7, 124.7, 125.8, 128.1, 130.7, 132.9, 133.4, 135.3, 136.7, 137.8, 138.4, 139.5, 141.2, 142.5, 143.8, 147.7, 155.6, 157.4, 170.3 ppm. EI ms: *m/z*: 492.95 [M^+] (74), 494.89 [$M^+ + 2$] (22).

General procedure for the synthesis of 8a,b. To compounds **4a**,**b** (2 mmol) in pyridine (10 mL), benzoyl chloride (0.47 mL, 4 mmol) was added. The reaction mixture was heated on water bath for 3 h and poured over crushed ice mixed with diluted hydrochloric acid. The solid separated out was filtered, washed with water, dried, and crystallized from suitable solvent to give compounds **8a**,**b**.

1-Benzoyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-phenyl-2-pyrazoline (8a). Crystallized from ethanol to afford white crystals, yield 0.61 g (72%), mp 274–276°C. IR (KBr): 3030 (Ar-H), 2990 (aliphatic-H), 1650 (C═O), 1639 (C═O), 1590 (C═N), 1580, 1491 (C═C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 400 MHz): $\delta = 2.38$ (s, 3H, CH_3), 3.40–3.53 (dd, $J = 18.2$, 4.6 Hz, 1 H_A, C4-H), 3.74–3.82 (dd, $J = 18.2$, 11.2 Hz, H_B, C4-H), 4.77–4.81 (dd, $J = 11.2$, 4.6 Hz, H_X, C5-H), 7.00–7.76 (m, 11H, Ar-H + H4′), 7.90–8.26 (m, 5H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.9$, 40.7, 44.3, 65.2, 121.1, 122.5, 123.8, 124.6, 125.9, 128.2, 130.8, 133.1, 133.3, 135.2, 136.8, 137.9, 138.3, 139.4, 141.5, 142.7, 143.9, 147.5, 155.4, 157.5, 170.7, 190.6 ppm. EI ms: *m/z*: 422.50 (M^+).

1-Benzoyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-p-chlorophenyl-2-pyrazoline (8b). Crystallized from methanol to afford gray powder, yield 0.68 g (74%), mp 262–263°C. IR (KBr): 3031 (Ar-H), 2998 (aliphatic-H), 1649 (C═O), 1640 (C═O), 1589 (C═N), 1581, 1490 (C═C), 715 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.39$ (s, 3H, CH_3), 3.41–3.54 (dd, $J = 18.2$, 4.6 Hz, H_A, C4-H), 3.73–3.82 (dd, $J = 18.2$, 11.2 Hz, H_B, C4-H), 4.76–4.81 (dd, $J = 11.2$, 4.6 Hz, H_X, C5-H), 7.02–7.76 (m, 11H, Ar-H + H4′), 7.91–8.26 (m, 4H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 16.1$, 40.5, 44.4, 65.6, 121.8, 122.2, 123.9, 124.7, 126.0, 128.0, 130.9, 133.2, 133.5, 135.4, 136.7, 137.8, 138.4, 139.5, 141.6, 142.4, 143.7, 147.6, 155.8, 157.9, 170.9, 190.5 ppm. EI ms: *m/z*: 456.89 [M^+] (76), 458.91 [$M^+ + 2$] (19).

General procedure for the synthesis of 9a,b. To a solution of the corresponding chalcones **1a**,**b** (2 mmol) in ethanol (25 mL), phenyl hydrazine (0.49 mL, 5 mmol) was added. The reaction mixture was refluxed for 6 h. Left to cool to room temperature, and the obtained product was filtered, dried, and crystallized from suitable solvent to give **9a**,**b**.

3-(3-Methyl-1-phenyl-5-oxo-2-pyrazolin-4-yl)-1,5-diphenyl-2-pyrazoline (9a). Crystallized from methanol to produce white crystals, yield 0.54 g (69%), mp 261–262°C. IR (KBr): 3029 (Ar-H), 2990 (aliphatic-H), 1639 (C═O), 1590 (C═N), 1580, 1495 (C═C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.40$ (s, 3H, CH_3), 3.42–3.52 (dd, $J = 18.1$, 4.5 Hz, H_A, C4-H), 3.72–3.83 (dd, $J = 18.1$, 11.3 Hz, H_B, C4-H), 4.76–4.82 (dd, $J = 11.3$, 4.5 Hz, H_X, C5-H), 7.10–7.77 (m, 11H, Ar-H + H4′), 7.90–8.20 (m, 5H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.7$, 41.1, 57.8, 117.9, 118.8, 121.7, 122.5, 123.7, 124.6, 126.3, 127.6, 128.1, 129.6, 130.7, 132.2, 133.9, 135.5, 136.8, 138.4, 139.2, 140.8, 144.5, 145.8, 146.9, 170.1 ppm. EI ms: *m/z*: 394.43 [M^+] (74).

3-(3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-p-chlorophenyl-1-phenyl-2-pyrazoline (9b). Crystallized from ethanol to afford white powder, yield 0.63 g (74%), mp 279–281°C. IR (KBr): 3031 (Ar-H), 2992 (aliphatic-H), 1640 (C═O), 1591 (C═N), 1582, 1490 (C═C), 709 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.41$ (s, 3H, CH_3), 3.41–3.54 (dd, $J = 18.2$, 4.5 Hz, H_A, C4-H), 3.72–3.84 (dd, $J = 18.2$, 11.3 Hz, H_B, C4-H), 4.77–4.82 (dd, $J = 11.3$, 4.5 Hz, H_X, C5-H), 7.11–7.76 (m, 11H, Ar-H + H4′), 7.91–8.21 (m, 4H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.8$, 41.3, 57.7, 117.5, 118.7, 121.5, 122.6, 123.8, 124.5, 125.9, 127.7, 128.5, 129.7, 130.8, 132.4, 133.8, 135.6, 136.7, 138.4, 139.1, 140.9, 144.7, 145.5, 146.8, 170.5 ppm. EI ms: *m/z*: 428.89 [M^+] (80), 430.90 [$M^+ + 2$] (26).

General procedure for the synthesis of 10a,b. A mixture of chalcones **1a**,**b** (2 mmol), hydroxylamine hydrochloride (0.35 g, 5 mmol), and sodium acetate (0.50 g) in ethanol (20 mL) was refluxed for 8 h. The mixture was concentrated by distilling out the solvent under reduced pressure and poured into crushed ice. The obtained solid was filtered, washed, and crystallized from suitable solvent to give **10a**,**b**.

3-(3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-phenylisooxazole (10a). Crystallized from ethanol to afford white crystals, yield 0.46 g (72%), mp 298–299°C. IR (KBr): 3058 (Ar-H), 2999 (aliphatic-H), 1639 (C═O), 1590 (C═N), 1580 (C═C), 1435 (CH_2 isoxazole), 1340 (C–N–C), 1120 (C–O–C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.40$ (s, 3H, CH_3), 3.58–3.61 (dd, $J = 17.9$, 3.5 Hz, isoxazoline-H4), 3.86–3.90 (dd, $J = 17.9$, 3.5 Hz, isoxazoline-H4), 5.90 (dd, $J = 17.9$, 3.5 Hz, isoxazoline-H5), 7.10–7.76 (m, 6H, Ar-H + H4′), 7.90–8.22 (m, 5H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.5$, 41.0, 58.0, 117.2, 118.5, 121.7, 123.8, 126.1, 128.5, 132.6, 135.5, 137.0, 138.1, 139.5, 140.8, 144.3, 146.0, 147.0, 169.8 ppm. EI ms: *m/z*: 319.29 [M^+] (71).

3-(3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-p-chlorophenyl-isooxazole (10b). Crystallized from ethanol to give white

powder, yield 0.54 g (76%), mp 304–305°C. IR (KBr): 3055 (Ar-H), 2990 (aliphatic-H), 1641 (C═O), 1589 (C═N), 1581 (C═C), 1433 (CH_2 isoxazole), 1335 (C–N–C), 1122 (C–O–C), 709 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.38$ (s, 3H, CH_3), 3.55–3.60(dd, $J = 17.9$, 3.4 Hz, isoxazoline-H_4), 3.85–3.90 (dd, $J = 17.9$, 3.4 Hz, isoxazoline-H_4), 5.91 (dd, $J = 17.9$, 3.4 Hz, isoxazoline-H_5), 7.10–7.76 (m, 6H, Ar-H + H4′), 7.90–8.22 (m, 5H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.8$, 41.1, 58.2, 117.3, 118.4, 121.9, 123.5, 126.2, 128.4, 132.3, 135.2, 137.1, 137.9, 139.4, 140.9, 144.1, 145.9, 147.1, 169.9 ppm. EI ms: *m/z*: 353.73 [M^+] (70), 455.76 [$M^+ + 2$] (27).

General procedure for the synthesis of 11a,b. A mixture of **1a**,**b** (2 mmol) and *o*-phenylenediamine (0.22 g, 2 mmol) in ethanol (15 mL) with a few drops of triethylamine was refluxed for 10 h. The progress of the reaction was monitored by using thin-layer chromatography. After completion of reaction, the reaction mixture was cooled to 0°C and let overnight. The crude solid product obtained was filtered, washed with water, and crystallized from suitable solvent to produce **11a**,**b**.

4-(3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-phenyl-2,3-dihydro-1H-benzo[b][1,4] diazepine (11a). Crystallized from ethanol to afford yellow crystals, yield 0.55 g (70%), mp 237–238°C. IR (KBr): 3343 (N–H), 3138 (Ar-H), 2992 (aliphatic-H), 1632 (C═O), 1599 (C═N), 1580, 1489 (C═C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.38$ (s, 3H, CH_3), 3.40–3.42 (dd, H_A, $J = 12.5$, 9.2 Hz, CH_2), 3.92–4.08 (dd, H_B, $J = 12.5$, 5.1 Hz, CH_2), 4.15 (s, 1H, N1-H, D2O exchangeable), 4.78–4.99 (dd, H_X, $J = 9.2$, 5.1 Hz, CH), 6.95–7.22 (m, 5H, [$H_6 + H_7 + H_8 + H_9 +$ H4′]), 7.42–8.30 (m, 10H, Ar-H) ppm; ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.4$, 41.5, 58.6, 65.2, 115.4, 118.2, 121.2, 122.8, 125.5, 126.5, 127.8, 129.8, 132.7, 134.7, 135.9, 136.8, 138.7, 139.4, 141.1, 142.3, 144.1, 145.1, 145.9, 151.9, 168.2, 170.3 ppm. EI ms: *m/z*: 394.49 [M^+] (82).

4-(3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-p-chlorophenyl-2,3-dihydro-1H-benzo[b][1,4]diazepine (11b). Crystallized from ethanol to give pale yellow crystals, yield 0.61 g (71%), mp 249–251°C. IR (KBr): 3345 (N–H), 3135 (Ar-H), 2990 (aliphatic-H), 1639 (C═O), 1595 (C═N), 1582, 1487 (C═C), 714 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.39$ (s, 3H, CH_3), 3.41–3.45 (dd, H_A, $J = 12.6$, 9.3 Hz, CH_2), 3.90–4.04 (dd, H_B, $J = 12.6$, 5.1 Hz, CH_2), 4.17 (s, 1H, N_1-H D_2O exchangeable), 4.80–5.00 (dd, H_X, $J = 9.3$, 5.1 Hz, CH), 6.95–7.23 (m, 5H, [$H_6 + H_7 + H_8 + H_9 +$ H4′]), 7.44–8.30 (m, 9H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.5$, 41.8, 58.7, 65.1, 115.5, 118.3, 121.5, 122.9, 125.4, 126.3, 127.9, 129.7, 132.8, 134.5, 135.6, 136.7, 138.8, 139.5, 141.0, 142.2, 144.3, 145.2, 145.8, 152.0, 168.3, 170.2 ppm. EI ms: *m/z*: 428.93 [M^+] (76), 430.86 [$M^+ + 2$] (26).

General procedure for the synthesis of 12a,b. To a suspension of chalcones **1a**,**b** (5 mmol) and sodium hydroxide (0.40 g, 10 mmol) in ethanol (25 mL), thiosemicarbazide (0.46 g, 5 mmol) was added. The mixture was refluxed for 8 h. The products were poured into crushed ice, and the solid mass that separated was filtered, dried, and crystallized from suitable solvent to give compounds **12a**,**b**.

1-Thiocarbamoyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-phenyl-2-pyrazoline (12a). Crystallized from benzene to afford orange powder, yield 0.52 g (69%), mp 291–292°C. IR (KBr): 3400, 3295 (NH_2), 3031 (Ar-H), 2900 (aliphatic-H), 1639 (C═O), 1593 (C═N), 1511, 1485 (C═C), 1325 (C═S) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.35$ (s, 3H, CH_3), 3.40–3.52 (dd, $J = 17.5$, 5.1 Hz, H_A, CH_2), 3.76–3.84 (dd, $J = 17.5$,11.8 Hz, H_B, CH_2), 4.97–5.05 (dd, $J = 11.8$, 5.1 Hz, H_X, CH), 7.01–7.62 (m, 6H, Ar-H + H4′), 7.75–7.92 (m, 5H, Ar-H), 8.85 (s, 2H, NH_2 D_2O exchangeable) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.2$, 42.9, 60.5, 117.9, 119.8, 120.3, 121.5, 122.3, 127.4, 129.7, 130.5, 132.8, 133.8, 135.8, 138.4, 139.2, 147.1, 154.2, 169.9, 176.9 ppm. EI ms: *m/z*: 377.43 [M^+] (81).

1-Thiocarbamoyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-5-p-chlorophenyl-2-pyrazoline (12b). Crystallized from benzene to afford orange powder, yield 0.58 g (71%), mp 280–281°C. IR (KBr): 3401, 3296 (NH_2), 3030 (Ar-H), 2910 (aliphatic-H), 1640 (C═O), 1595 (C═N), 1513, 1486 (C═C), 1328 (C═S), 716 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.37$ (s, 3H, CH_3), 3.41–3.52 (dd, $J = 17.5$, 5.1 Hz, H_A, CH_2), 3.74–3.84 (dd, $J = 17.5$,11.8 Hz, H_B, CH_2), 4.96–5.07 (dd, $J = 11.8$, 5.1 Hz, H_X, CH), 7.00–7.62 (m, 6H, Ar-H + H4′), 7.76–7.92 (m, 4H, Ar-H), 8.85 (s, 2H, NH_2 D_2O exchangeable) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.4$, 42.9, 63.1, 117.9, 119.7, 120.2, 121.6, 122.3, 127.3, 129.8, 130.4, 132.7, 133.8, 135.3, 138.2, 139.3, 147.2, 154.3, 169.8, 177.1 ppm. EI ms: *m/z*: 411.87 [M^+] (61), 413.88 [$M^+ + 2$] (19).

General procedure for the synthesis of 13a,b. A mixture of **12a**,**b** (2 mmol) and phenacyl bromide (0.99 g, 2 mmol) in absolute ethanol (20 mL) was refluxed for 1 h. After cooling, the obtained product was collected by filtration, dried, and crystallized from suitable solvent to afford compounds **13a**,**b**.

2-(5-Phenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl)-4-phenylthiazole (13a). Crystallized from dioxane afford pale brown powder, yield 0.68 g (71%), mp 270–271°C. IR (KBr): 3031 (Ar-H), 2940 (aliphatic-H), 1638 (C═O), 1598 (C═N), 1510, 1484 (C═C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.40$ (s, 3H, CH_3), 3.39–3.42 (dd, $J = 17.8$, 3.9 Hz, H_A, CH_2), 3.80–3.83 (dd, $J = 17.8$, 11.2 Hz, H_B, CH_2), 4.75–4.79 (dd, $J = 11.2$, 3.9 Hz, H_X, CH), 6.83 (s, 1H, C_5-H of thiazole), 7.15–8.20 (m, 16H, Ar-H + H4′) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.4$, 42.9, 60.4, 105.7, 117.9, 118.8, 119.6, 120.8, 121.3, 122.3, 124.3, 125.5, 127.5, 129.6, 130.7, 132.6, 134.1, 135.7, 136.4, 137.3, 138.1, 138.9, 140.5, 147.3, 150.6, 154.2, 164.8, 169.7, 178.2 ppm. EI ms: *m/z*: 477.54 [M^+] (86).

2-(5-p-Chlorophenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl)-4-phenylthiazole (13b). Crystallized from dioxane to afford brown crystals, yield 0.75 g (73%), mp 245–247°C. IR (KBr): 3035 (Ar-H), 2946 (aliphatic-H), 1641 (C═O), 1597 (C═N), 1515, 1489 (C═C), 713 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.41$ (s, 3H, CH_3), 3.38–3.41 (dd, $J = 16.1$, 3.5 Hz, H_A, CH_2), 3.70–3.80 (dd, $J = 16.1$, 11.0 Hz, H_B, CH_2), 4.70–4.80 (dd, $J = 11.0$, 3.5 Hz, H_X, CH), 6.80 (s, 1H, C_5-H of thiazole), 7.10–8.20 (m, 15H, Ar-H + H4′) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.7$, 42.8, 60.7, 105.2, 117.8, 118.9, 119.7, 120.9, 121.5, 122.7, 124.5, 125.4, 127.6, 129.7, 130.8, 132.7, 134.2, 135.8, 136.5, 137.4, 138.2, 138.8, 140.7, 147.4, 150.7, 154.3, 164.9, 170.0, 178.3 ppm. EI ms: *m/z*: 512.00 [M^+] (81), 514.01 [$M^+ + 2$] (27).

General procedure for the synthesis of 14a,b. A mixture of **12a**,**b** (2 mmol) and 2,3-dichloroquinoxaline (0.4 g, 2 mmol) in ethanol (10 mL) was heated under reflux for 8 h. The solvent was evaporated under reduced pressure. The residue was crystallized to give **14a**,**b**.

3-[3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl]-5-phenyl-1-(thiazolo[4,5-b]qunixalin-2-yl)-2-pyrazoline (14a). Crystallized from toluene to afford red powder, yield 0.57 g (68%), mp 284–286°C. IR (KBr): 3100 (Ar-H), 2986 (aliphatic-H), 1633 (C═O), 1590

(C=N), 1517, 1490 (C=C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.35$ (s, 3H, CH_3), 3.39–3.50 (dd, $J = 17.4$, 5.1 Hz, H_A, CH_2), 3.77–3.84 (dd, $J = 17.4$, 11.8 Hz, H_B, CH_2), 4.96–5.06 (dd, $J = 11.8$, 5.1 Hz, H_X, CH), 7.00–7.60 (m, 6H, Ar-H + H4′), 7.74–7.92 (m, 9H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.5$, 40.9, 58.1, 117.7, 118.5, 121.9, 122.5, 123.8, 125.1, 126.6, 128.2, 129.7, 130.5, 132.8, 134.6, 135.7, 137.1, 138.6, 139.3, 140.9, 143.5, 144.5, 145.7, 146.6, 147.9, 148.3, 163.8, 170.1 ppm. EI ms: *m/z*: 503.61 [M^+] (70).

3-[3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl]-5-p-chlorophenyl-1-(thiazolo[4,5-b] qunixalin-2-yl)-2-pyrazoline (14b). Crystallized from toluene to give brown powder, yield 0.61 g (67%), mp 270–272°C. IR (KBr): 3099 (Ar-H), 2985 (aliphatic-H), 1633 (C=O), 1598 (C=N), 1515, 1494 (C=C), 715 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.39$ (s, 3H, CH_3), 3.38–3.50 (dd, $J = 17.3$, 5.2 Hz, H_A, CH_2), 3.75–3.83 (dd, $J = 17.3$, 11.8 Hz, H_B, CH_2), 4.95–5.02 (dd, $J = 11.8$, 5.2 Hz, H_X, CH), 7.00–7.65 (m, 6H, Ar-H + H4′), 7.72–7.99 (m, 8H, Ar-H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.7$, 41.1, 58.5, 117.8, 118.7, 121.5, 122.9, 123.7, 125.5, 126.7, 128.1, 129.8, 131.0, 132.9, 134.8, 135.6, 137.0, 138.8, 139.7, 141.0, 143.8, 144.7, 145.9, 146.7, 147.2, 148.4, 163.9, 170.0 ppm. EI ms: *m/z*: 537.98 [M^+] (59), 540.01 [$M^+ + 2$] (18).

General procedure for the synthesis of 15a,b. A mixture of **12a**,**b** (2 mmol), chloroacetic acid (0.29 g, 3 mmol), and anhydrous sodium acetate (0.27 g) was refluxed in acetic acid (15 mL) for 3 h. The mixture was poured into crushed ice, and the solid mass that separated out was filtered, dried, and crystallized from an appropriate solvent to afford **15a**,**b**.

2-(5-Phenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl)thiazol-4(5H)-one (15a). Crystallized from ethanol to afford yellow powder, yield 0.58 g (70%), mp 246–248°C. IR (KBr): 3090 (Ar-H), 2980 (aliphatic-H), 1715 (C=O thiazole), 1636 (C=O), 1594 (C=N), 1540, 1489 (C=C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.39$ (s, 3H, CH_3), 3.37–3.42 (dd, $J = 17.8$, 3.9 Hz, H_A, CH_2), 3.81–3.83 (dd, $J = 17.8$, 11.2 Hz, H_B, CH_2), 4.75–4.78 (dd, $J = 11.2$, 3.9 Hz, H_X, CH), 3.99–4.22 (2 dd, 2H, C_5-H of thiazolone), 7.11–8.23 (m, 11H, Ar-H + H4′) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.6$, 35.3, 40.9, 60.5, 117.8, 119.5, 121.8, 122.3, 124.3, 129.6, 131.4, 134.3, 135.7, 136.4, 138.1, 138.9,140.5, 147.3, 150.3, 154.2, 173.8, 189.2 ppm. EI ms: *m/z*: 417.43 [M^+] (79).

2-(5-p-Chlorophenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl) thiazol-4(5H)-one (15b). Crystallized from ethanol to give red crystals, yield 0.65 g (72%), mp 259–260°C. IR (KBr): 3100 (Ar-H), 2990 (aliphatic-H), 1717 (C=O thiazole), 1640 (C=O), 1598 (C=N), 1541, 1487 (C=C), 708 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.39$ (s, 3H, CH_3), 3.35–3.42 (dd, $J = 17.7$, 3.9 Hz, H_A, CH_2), 3.83–3.85 (dd, $J = 17.7$, 11.2 Hz, H_B, CH_2), 4.75–4.79 (dd, $J = 11.2$, 3.9 Hz, H_X, CH), 3.98–4.22 (2 dd, 2H, C_5-H of thiazolone), 7.10–8.20 (m, 10H, Ar-H + H4′) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.7$, 35.4, 41.1, 61.1, 118.2, 119.4, 122.1, 123.0, 124.5, 129.7, 131.5, 134.4, 135.9, 136.2, 137.9, 139.0, 140.7, 148.1, 150.5, 154.6, 173.1, 189.1 ppm. EI ms: *m/z*: 451.90 [M^+] (76), 453.92 [$M^+ + 2$] (27).

General procedure for the synthesis of 16a–f. A mixture of **12a**,**b** (2 mmol), chloroacetic acid (0.29 g, 3 mmol), various aromatic aldehydes (2 mmol), and anhydrous sodium acetate (0.27 g) was refluxed in acetic acid (20 mL) for 6 h. The mixture was poured into crushed ice, and the precipitate was collected by filtration, dried, and crystallized from suitable solvent to afford products **16a–f**.

Another route for the synthesis of compounds 16a–f. A mixture of **15a**,**b** (2 mmol), aromatic aldehydes (2 mmol), and anhydrous sodium acetate (0.27 g) was refluxed in acetic acid (10 mL) for 6 h. The mixture was cooled and poured into ice water. The resulting solid was collected by filtration, dried, and crystallized to give products identical in all aspects (mp, mixed mp, IR, and ^{1}H-NMR) with **16a–f**.

5-Benzylidene-2-(5-phenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl) thiazol-4-one (16a). Crystallized from methanol to afford orange crystals, yield 0.73 g (72%), mp 212–213°C. IR (KBr): 3102 (Ar-H), 2996 (aliphatic-H), 1715 (C=O), 1641 (C=O), 1598 (C=N), 1545, 1489 (C=C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.41$ (s, 3H, CH_3), 3.30–3.40 (dd, $J = 15.4$, 4.3 Hz, H_A, CH_2), 3.80–3.90 (dd, $J = 15.4$, 11.6 Hz, H_B, CH_2), 4.70–4.80 (dd, $J = 11.6$, 4.3 Hz, H_X, CH), 7.10–8.20 (m, 17H, 15 Ar-H + H4′ + CH=) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.7$, 40.9, 60.8, 117.9, 119.7, 121.6, 122.4, 123.8, 124.5, 125.9, 127.6, 129.7, 131.8, 132.8, 134.5, 135.6, 136.5, 137.7, 138.2, 139.9, 140.6, 142.8, 144.4, 147.5, 150.4, 152.9, 154.3, 170.3, 189.5 ppm. EI ms: *m/z*: 505.53 [M^+] (79).

5-p-Chlorobenzylidene-2-(5-phenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl) thiazol-4-one (16b). Crystallized from ethanol to afford yellow crystals, yield 0.80 g (74%), mp 215–217°C. IR (KBr): 3105 (Ar-H), 2996 (aliphatic-H), 1717 (C=O), 1639 (C=O), 1598 (C=N), 1547, 1480 (C=C), 710 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.40$ (s, 3H, CH_3), 3.32–3.41 (dd, $J = 15.4$, 4.3 Hz, H_A, CH_2), 3.80–3.92 (dd, $J = 15.4$, 11.6 Hz, H_B, CH_2), 4.72–4.80 (dd, $J = 11.6$, 4.3 Hz, H_X, CH), 7.10–8.20 (m, 16H, 14 Ar-H + H4′ + CH=) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.6$, 40.8, 60.9, 117.5, 119.8, 121.7, 122.5, 123.9, 124.6, 125.8, 127.7, 129.5, 131.7, 132.6, 134.9, 135.7, 136.6, 137.9, 138.4, 140.2, 141.6, 142.9, 144.5, 147.7, 150.6, 152.8, 154.5, 170.8, 189.6 ppm. EI ms: *m/z*: 540.01 [M^+] (79), 542.00 [$M^+ + 2$] (28).

5-p-Nitrobenzylidene-2-(5-phenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl) thiazol-4-one (16c). Crystallized from ethanol to afford pale yellow powder, yield 0.77 g (70%), mp 223–225°C. IR (KBr): 3100 (Ar-H), 2990 (aliphatic-H), 1718 (C=O), 1641 (C=O), 1598 (C=N), 1545, 1482 (C=C) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.40$ (s, 3H, CH_3), 3.31–3.40 (dd, $J = 15.3$, 4.3 Hz, H_A, CH_2), 3.80–3.91 (dd, $J = 15.3$, 11.6 Hz, H_B, CH_2), 4.71–4.78 (dd, $J = 11.6$, 4.3 Hz, H_X, CH), 7.10–8.22 (m, 16H, 14 Ar-H + H4′ + CH=) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.8$, 41.1, 61.2, 117.4, 120.1, 121.8, 122.4, 123.8, 124.7, 125.9, 127.8, 129.4, 131.9, 132.7, 135.1, 136.1, 137.0, 138.0, 139.1, 140.5, 141.7, 142.8, 144.6, 147.8, 150.9, 152.9, 154.8, 170.7, 189.8 ppm. EI ms: *m/z*: 550.55 [M^+] (81).

5-Benzylidene-2-(5-p-chlorophenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl) thiazol-4-one (16d). Crystallized from toluene to afford white crystals, yield 0.77 g (71%), mp 237–238°C. IR (KBr): 3108 (Ar-H), 2994 (aliphatic-H), 1715 (C=O), 1643 (C=O), 1599 (C=N), 1544, 1481 (C=C), 711 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.38$ (s, 3H, CH_3), 3.31–3.38 (dd, $J = 15.3$, 4.2 Hz, H_A, CH_2), 3.80–3.88 (dd, $J = 15.3$, 11.6 Hz, H_B, CH_2), 4.70–4.78 (dd, $J = 11.6$, 4.3 Hz, H_X, CH), 7.12–8.22 (m, 16H, 14 Ar-H + H4′ + CH=) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.4$, 41.0, 61.1, 117.4, 120.1, 121.8, 122.4, 123.8, 124.8, 125.9, 127.5, 129.8, 131.4, 132.8,

134.6, 135.4, 136.7, 137.6, 138.7, 140.9, 141.8, 142.7, 144.6, 147.9, 150.8, 152.9, 154.7, 170.8, 189.8 ppm. EI ms: *m/z*: 540.00 [M^+] (82), 542.01 [$M^+ + 2$] (23).

5-p-Chlorobenzylidene-2-(5-p-chlorophenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl)thiazol-4-one (16e). Crystallized from ethanol to give white powder, yield 0.83 g (72%), mp 241–243°C. IR (KBr): $\nu = 3101$ (Ar-H), 2995 (aliphatic-H), 1718 (C═O), 1640 (C═O), 1598 (C═N), 1544, 1480 (C═C), 714 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.40$ (s, 3H, CH_3), 3.30–3.38 (dd, $J = 15.3$, 4.2 Hz, H_A, CH_2), 3.82–3.88 (dd, $J = 15.3$, 11.6 Hz, H_B, CH_2), 4.70–4.76 (dd, $J = 11.6$, 4.3 Hz, H_X, CH), 7.10–8.23 (m, 15H, 13 Ar-H + H4′ + CH═) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 16.0$, 41.5, 61.3, 117.8, 121.0, 121.9, 122.8, 123.9, 124.9, 126.2, 127.8, 129.9, 131.6, 133.5, 134.7, 135.6, 136.8, 137.9, 138.8, 141.1, 141.9, 143.2, 144.8, 148.2, 150.9, 153.1, 155.0, 170.4, 188.9 ppm. EI ms: *m/z*: 574.42 [M^+] (67), 576.41 [$M^+ + 2$] (21), 578.38 [$M^+ + 4$] (11).

5-p-Nitrobenzylidene-2-(5-p-chlorophenyl-3-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-yl)-2-pyrazolin-1-yl) thiazol-4-one (16f). Crystallized from ethanol afford yellow powder, yield 0.82 g (70%), mp 239–240°C. IR (KBr): 3100 (Ar-H), 2991 (aliphatic-H), 1720 (C═O), 1638 (C═O), 1598 (C═N), 1546 (C═C), 1514, 1370 (NO_2), 710 (C–Cl) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 200 MHz): $\delta = 2.41$ (s, 3H, CH_3), 3.32–3.36 (dd, $J = 15.3$, 4.4 Hz, H_A, CH_2), 3.80–4.00 (dd, $J = 15.3$, 11.6 Hz, H_B, CH_2), 4.72–4.76 (dd, $J = 11.6$, 4.3 Hz, H_X, CH), 7.12–8.40 (m, 15H, 13 Ar-H + H4′ + CH═) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): $\delta = 15.9$, 41.4, 60.9, 118.2, 121.4, 121.5, 122.9, 123.7, 125.2, 126.6, 127.9, 130.1, 131.9, 133.8, 134.6, 135.5, 136.7, 137.6, 138.9, 141.4, 141.4, 143.6, 144.7, 148.3, 150.6, 153.0, 155.2, 170.3, 189.0 ppm. EI ms: *m/z*: 585.00 [M^+] (76), 587.09 [$M^+ + 2$] (27).

CONCLUSION

In conclusion, 2-pyrazolines **4a**,**b** and *N*-thiocarbamoyl-2-pyrazolines **12a**,**b** incorporating 2-pyrazolin-5-one moiety were used as efficient precursors for the synthesis of new heterocycles including the 2-pyrazolin- 5-one moiety with expected biological activities.

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