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Reactions with hydrazonoyl halides 65: Synthesis of some new 1,3,4-thiadiazoles and triazolino[4,3-*a*]pyrimidines containing pyrazole moiety

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ABSTRACT

2,3-Dihydro-1,3,4-thiadiazoles, and triazolino[4,3-*a*]pyrimidines containing pyrazole moieties were prepared from the reaction of alkyl 2-[1-(4-cyano-1,5-diphenyl-1*H*-pyrazol-3-yl)ethylidene]hydrazinecarbodithioate and pyrimidine-2-thione derivatives with appropriate hydrazonoyl halides. The structures of all the newly synthesized compounds were confirmed by elemental analyses, spectral data, and alternative route of synthesis whenever possible.

1. Introduction

1,3,4-Thiadiazoles have been screened for their antibacterial and antifungal activities [1-4], anti-inflammatory [5], anti-tuberculosis [6] and anticancer [7] activity. Also, pyrazoles and annelated pyrazoles have long been known to exhibit diverse biological activities [8, 9, 10-13]. These activities include their use as cAMP phosphodiesterase inhibitors, antipyretic, antitumor, hypnotic and herbicidal agents. It was of value to combine the two moieties in a series of derivatives with the objective of investigating their expected biological activities. As an extension of our study [14-20] and as a part of our program aiming at the synthesis of different heterocyclic derivatives, we report here the convenient synthesis of 2,3-dihydro-1,3,4-thiadiazoles and triazolino[4,3-*a*]pyrimidines containing pyrazole moiety.

2. Experimental

2.1. Instrumentation

All melting points were determined on an Electrothermal melting point apparatus and are uncorrected. IR spectra were recorded (KBr discs) on a Shimadzu FT-IR 8201 PC spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ solutions on a Varian Gemini 200 MHz and 300 MHz spectrometer and chemical shifts are expressed in δ units using TMS as internal reference. Mass spectra were recorded on a Shimadzu GCMS-QP1000 EX mass spectrometer, operating at 70 eV. Elemental analyses were carried out at Microanalytical Center of Cairo University, Giza 12613, Egypt.

2.2. Synthesis of alkyl 2-[1-(4-cyano-5-diphenyl-1-substituted-1H-pyrazol-3-yl)ethylidene]hydrazine-carbodithioate (3a and 3b)

A mixture of the appropriate of **1a** or **1b** [23] (10 mmol) and the appropriate alkyl hydrazinecarbodithioates **2a** or **b** [24] (10 mmol) in 2-propanol (10 mL) was boiled under reflux for 30 minutes. The resulting solid so formed after cooling was collected and crystallized from ethanol to give yellow crystals **3a-d** (Scheme 1)

Methyl 2-[1-(4-cyano-1,5-diphenyl-1H-pyrazol-3-yl) ethylidene]hydrazinecarbo-dithioate (**3a**): Yellow solid. Yield: 76%. M.p.: 180-182 °C. IR (KBr, cm^{-1}): 3039 (CH, aromatic), 2922 (CH, aliphatic), 2225 (CN), 1596 (C=C), 1364 (CH_3) cm^{-1}. ^{1}H NMR (300 MHz, $(CD_3)_2SO$, δ, ppm): 2.09 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 7.45-7.49 (m, 10 H, ArH's), 7.96 (s, br., 1H, NH). Anal. Calcd. for $C_{20}H_{17}N_5S_2$ (391.51): C, 61.36; H, 4.38; N, 17.89; S, 16.38. Found: C, 61.58; H, 4.12; N, 18.01; S, 16.15%.

Benzyl 2-[1-(4-cyano-1,5-diphenyl-1H-pyrazol-3-yl)ethylidene]hydrazinecarbo-dithioate (**3b**): Yellow solid. Yield: 81%. M.p.: 192-194 °C. IR (KBr, cm^{-1}): 3038 (CH, aromatic), 2921 (CH, aliphatic), 2224 (CN), 1609 (C=C), 1433 (CH_2), 1364 (CH_3) cm^{-1}. ^{1}H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.33 (s, 3H, CH_3), 4.37 (s, 2H, CH_2), 7.27-7.49 (m, 15 H, ArH's), 7.96 (s, br., 1H, NH). Anal. Calcd. for $C_{26}H_{21}N_5S_2$ (467.61): C, 66.78; H, 4.53; N, 14.98; S, 13.71. Found: C, 66.89; H, 4.62; N, 14.75; S, 13.55%.

Methyl 2-{1-[4-cyano-1-(4-methylphenyl)-5-phenyl-1H-pyrazol-3-yl]ethylidene}-hydrazinecarbodithioate (**3c**): Yellow solid. Yield: 85%. M.p.: 198-200 °C. IR (KBr, cm^{-1}): 3044 (CH, aromatic), 2922 (CH, aliphatic), 2227 (CN), 1612 (C=C), 1375 (CH_3) cm^{-1}. ^{1}H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.33 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 7.27-7.47 (m, 9 H, ArH's), 7.48 (s, br., 1H, NH).

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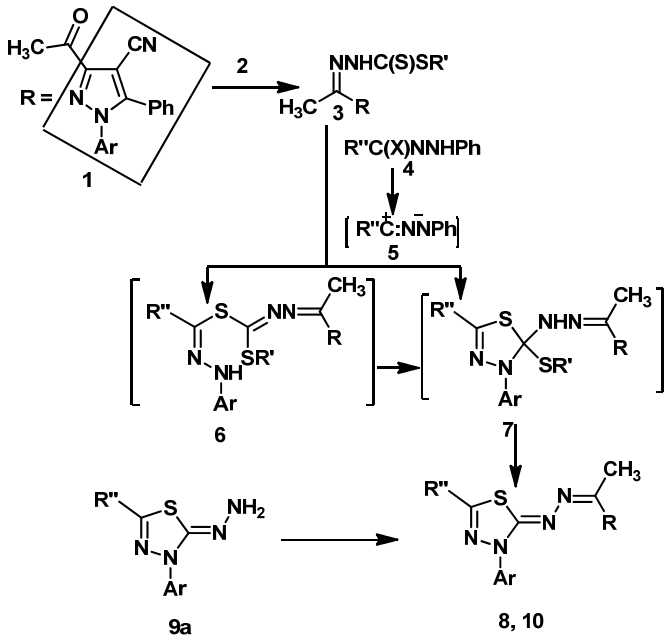


1a, Ar = C_6H_5,
1b, Ar = 4-$CH_3C_6H_4$
2a, $H_2NNHCSSCH_3$
2b, $H_2NNHCSSCH_2C_6H_5$
3a, R' = CH_3, Ar = C_6H_5
3b, R' = $CH_2C_6H_5$, Ar = C_6H_5
3c, R' = CH_3, Ar = 4-$CH_3C_6H_4$
3d, R' = $CH_2C_6H_5$,, Ar = 4-$CH_3C_6H_4$

4a, R'' = $CO_2C_2H_5$
b, R'' = $COCH_3$
c, R'' = COC_6H_5
d, R'' = $CONHC_6H_5$
e, R'' = 3-carbonyl-5-phenyl-1-*p*-tolyl-1*H*-pyrazole-4-carbonitrile

8a, R'' = $CO_2C_2H_5$; Ar = C_6H_5
b, R'' = $COCH_3$; Ar = C_6H_5
c, R'' = COC_6H_5; Ar = C_6H_5
d, R'' = $COHNC_6H_5$; Ar = C_6H_5
e, R'' = 3-carbonyl-5-phenyl-1-*p*-tolyl-1*H*-pyrazole-4-carbonitrile ; Ar = C_6H_5

10a, R'' = $CO_2C_2H_5$; Ar = 4-$CH_3C_6H_4$
b, R'' = $COCH_3$; Ar = 4-$CH_3C_6H_4$
c, R'' = COC_6H_5; Ar = 4-$CH_3C_6H_4$
d, R'' = $COHNC_6H_5$; Ar = 4-$CH_3C_6H_4$
e, R'' = 3-carbonyl-5-phenyl-1-*p*-tolyl-1*H*-pyrazole-4-carbonitrile ; Ar = 4-$CH_3C_6H_4$

Scheme 1

Anal. Calcd. for $C_{21}H_{19}N_5S_2$, (405.54): C, 62.19; H, 4.72; N, 17.27; S, 15.81. Found: C, 62.00; H, 4.94; N, 17.35; S, 15.62%.

Benzyl 2-{1-[4-cyano-1-(4-methylphenyl)-5-phenyl-1H-pyrazol-3-yl]ethylidene}-hydrazinecarbodithioate (**3d**): Yellow solid. Yield: 88%. M.p.: 208-210 °C. IR (KBr, cm^{-1}): 3052 (CH, aromatic), 2924 (CH, aliphatic), 2224 (CN), 1612 (C=C), 1438 (CH_2), 1375 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.30 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 4.54 (s, 2H, CH_2), 7.27-7.46 (m, 14 H, ArH's), 7.47 (s, br., 1H, NH). Anal. Calcd. for $C_{27}H_{23}N_5S_2$ (481.64): C, 67.33; H, 4.81; N, 14.54; S, 13.32. Found: C, 67.42; H, 5.01; N, 14.38; S, 13.51%.

2.3. Synthesis of 5-{[1-(4-cyano-1,5-diphenyl-1H-pyrazol-3-yl)-ethylidene]-hydrazono}-4-phenyl-2-substituted 4,5-dihydro-[1,3,4]thiadiazole (8a-e) and 5-{[1-(4-Cyano-5-phenyl-1-p-tolyl-1H-pyrazol-3-yl)-ethylidene]-hydrazono}-4-phenyl-2-substituted 4,5-dihydro-[1,3,4]thiadiazole (10a-e)

A mixture of the alkyl carbodithioate **3a**, **3b** or **3c**, **3d** (5 mmol), the appropriate hydrazonoyl halides **4a-e** (5 mmoles), and triethylamine (0.75 mL, 0.005 mol) in ethanol (20 mL) was stirred for 2 h at room temperature. The resulting solid was collected and recrystallized to give 2,3-dihydro-1,3,4-thiadiazoles **8a-e** and **10a-e**, respectively (Scheme 1).

Alternative Method: A mixture of ethyl 2-hydrazino-3-phenyl-1,3,4-thiadiazoline-5-carboxylate [25] (**9a**) (1.32 g, 5 mmol) and the appropriate 3-acetylpyrazole **1a** or **1b** (5 mmol) in 2-propanol (10 mL) was stirred for 2 h at room temperature. The resulting solids were collected and recrystallized from ethanol to give product identical with **8a** and **10a**, which were obtained by the above method).

Ethyl 5-{[1-(4-cyano-1,5-diphenyl-1H-pyrazol-3-yl)-ethylidene]-hydrazono}-4-phenyl-4,5-dihydro-[1,3,4]thiadiazole-2-carboxylate (**8a**): Yellow solid. Yield: 76 %. M.p.: 329-331 °C. IR (KBr, cm^{-1}): 3059 (CH, aromatic), 2922 (CH, aliphatic), 2225 (CN), 1734 (CO, ester), 1671 (CO), 1596 (C=C), 1433 (CH_2), 1364 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 1.25 (t, 3H, *J* = 7 Hz, CH_2CH_3), 2.49 (s, 3H, CH_3), 4.37 (q, 2H, *J* = 7 Hz, CH_2CH_3), 7.45-7.95 (m, 15 H, ArH's). ^{13}C NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 13.34, 15.41, 62.72, 99.21, 120.25, 125.56, 126.12, 127.23, 129.23, 129.67, 130.42, 130.83, 140.58, 143.56, 144.24, 147.31, 151.11, 160.56, 161.62, 177.83. MS (m/e, %): 534 (M+1, 100%), 519 (5.4%), 501 (3.7%), 434 (27.5%), 401 (4.21%), 372 (6.7%), 272 (8%), 243 (22%), 189 (11%), 179 (15%), 140 (14%), 134 (13%), 1o2 (10%), 90 (34%), 77 (43%), 64 (10%). Anal. Calcd. for $C_{29}H_{23}N_7O_2S$ (533.16): C, 65.28; H, 4.34; N, 18.37; S, 6.01. Found: C, 65.41; H, 4.28; N, 18.29; S, 6.21%.

3-{1-[(5-Acetyl-3-phenyl-3H-[1,3,4]thiadiazol-2-ylidene)-hydrazono]-ethyl}-1,5-diphenyl-1H-pyrazole-4-carbonitrile (**8b**): Pale yellow solid. Yield: 75%. M.p.: 298-300 °C. IR (KBr, cm^{-1}): 3054 (CH, aromatic), 2924 (CH, aliphatic), 2230 (CN), 1665 (CO), 1596 (C=C), 1428 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.08 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 7.42-7.98 (m, 15 H, ArH's). MS (m/e, %): 502 (M-1, 9.7%), 437 (9.87%), 363 (10.36.7%), 301 (10.17%), 286 (18%), 284 (13.56), 272 (21%), 271 (23%), 270 (30%), 259 (14.8%), 244 (20.6%), 233 (11%), 232 (11%), 210 (11.7%), 191 (20%), 180 (22%), 169 (13.3), 163 (11.5%), 151 (19.5%), 149 (24.8%), 140 (20%), 136 (17.2%), 126 (27.0%), 111 (32.8%), 109 (36%), 90 (100%), 77 (97.3%), 65 (36.1%). Anal. Calcd. for $C_{28}H_{21}N_7OS$ (503.58): C, 66.78; H, 4.20; N, 19.47; S, 6.37. Found: C, 66.92; H, 4.00; N, 19.13; S, 6.52%.

3-{1-[(5-Benzoyl-3-phenyl-3H-[1,3,4]thiadiazol-2-ylidene)-hydrazono]-ethyl}-1,5-diphenyl-1H-pyrazole-4-carbonitrile (**8c**): Brown solid. Yield: 73%. M.p.: 311-13°C (DMF). IR (KBr, cm^{-1}): 3059 (CH, aromatic), 2925 (CH, aliphatic), 2225 (CN), 1660 (CO), 1596 (C=C), 1395 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.49 (s, 3H, CH_3), 7.42-7.98 (m, 20 H, ArH's). MS (m/e, %): 566 (M+1, 1.1%), 407 (1%), 357 (67%), 340 (20.5%), 149 (7.3%), 135 (13.8), 105 (84.3%), 271 (23%), 98 (36.7, 912 (34.8%), 77 (100%), 68 (39.6%), 65 (22.56%). Anal. Calcd. for $C_{33}H_{23}N_7OS$, (565.17): C, 70.07; H, 4.10; N, 17.33; S, 5.67. Found: C, 69.81; H, 3.82; N, 17.25; S, 5.82%.

5-{[1-(4-Cyano-1,5-diphenyl-1H-pyrazol-3-yl)-ethylidene]-hydrazono}-4-phenyl-2-phenylcarbamoyl-4,5-dihydro-[1,3,4] thiadiazole (**8d**): Pale yellow solid. Yield: 78%. M.p.: 322-324 °C. IR (KBr, cm^{-1}): 3380 (NH), 3060 (CH), 2923 (CH, aliphatic), 2225 (CN), 1663 (CO), 1596 (C=C), 1346 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.72 (s, 3H, CH_3), 7.42-7.98 (m, 20 H, ArH's), 9.82 (s, br., 1H, NH). Anal. Calcd. for $C_{33}H_{24}N_8OS$ (580.66): C, 68.26; H, 4.17; N, 19.30; S, 5.52. Found: C, 68.43; H, 4.31; N, 19.12; S, 5.34%.

3-({2-[1,2-diaza-3-(4-cyano-1,5-diphenyl(2-pyrazolin-3-yl)but-2-enylidene]-3-phenyl(1,3,4-thiadiazolin-5-yl)}carbonyl)-1-(4-methylphenyl)-5-phenylpyrazole-4-carbonitrile (**8e**): Deep red solid. Yield: 78 %. M.p.: 243-245 °C. IR (KBr, cm^{-1}): 3032 (CH, aromatic), 2926 (CH, aliphatic), 2228 (CN), 1665 (CO), 1600 (C=C), 1378 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.33 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 7.07-7.95 (m, 24 H, ArH's). MS (m/e, %): 747 (M+1, 0.12%), 716 (0.45%), 688 (0.14%), 556 (6%), 542 (0.8%), 483 (0.2%), 286 (10%), 270 (34%), 258 (6.5%), 243 (20.8%), 216 (10.9%), 180 (16.2%), 155 (7.4%), 127 (11%), 114 (6%), 103 (24.6%), 91 (46%), (77 (100%), 65 (29.6%). Anal. Calcd. for $C_{44}H_{30}N_{10}OS$ (746.84): C, 70.76; H, 4.05; N, 18.75; S, 4.29. Found: C, 70.46; H, 3.82; N, 18.58; S, 4.12%.

Ethyl 5-{[1-(4-cyano-5-phenyl-1-p-tolyl-1H-pyrazol-3-yl)-ethylidene]-hydrazono}-4-phenyl-4,5-dihydro-[1,3,4]thiadiazole-2-carboxylate (**10a**): Yellow solid. Yield: 77%. M.p.: 322-324 °C. IR (KBr, cm^{-1}): 3044 (CH, aromatic), 2922 (CH, aliphatic), 2225 (CN), 1670 (CO), 1611 (C=N), 1545 (C=C), 1439 (CH_2), 1375 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 1.33 (t, 3H, *J* = 7 Hz, CH_2CH_3), 2.73 (s, 3H, CH_3), 2.89 (s, 3H, CH_3), 4.41 (q, 2H, *J* = 7 Hz, CH_2CH_3), 7.42-7.98 (m, 14 H, ArH's). MS (m/e, %): 548 (M+1, 17.8%), 547 (M^+, 34.4%), 496 (13.3.7%), 284 (35.6%), 135 (35.3%), 91 (100%), 77 (78%), 65 (46.7%). Anal. Calcd. for $C_{30}H_{25}N_7O_2S$, 547.63, C, 65.80; H, 4.60; N, 17.90; S, 5.86. Found: C, 66.02; H, 4.72; N, 17.82; S, 6.00%.

3-{1-[(5-Acetyl-3-phenyl-3H-[1,3,4]thiadiazol-2-ylidene)-hydrazono]-ethyl}-5-phenyl-1-p-tolyl-1H-pyrazole-4-carbonitrile (**10b**): Yellow solid. Yield: 76%. M.p.: 312-314 °C. IR (KBr, cm^{-1}): 3044 (CH, aromatic), 2922 (CH, aliphatic), 2227 (CN), 1676 (CO), 1609 (C=N), 1375 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.33 (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 2.89 (s, 3H, CH_3), 7.26-7.48 (m, 14 H, ArH's). MS (m/e, %): 518 (M+1, 4.4%), 437 (1.6%), 390 (1.8%), 358 (1.2%), 301 (4%), 284 (19.5%), 269 (13%), 242 (9.5%), 215 (4.9%), 194 (7.25), 154 (5.8%), 135 (17%), 103 (10.7%), 91 (100%), 76 (48%), 65 (34%). Anal. Calcd. for $C_{29}H_{23}N_7OS$ (517.6): C, 67.29; H, 4.48; N, 18.94; S, 6.19. Found: C, 67.02; H, 4.62; N, 18.72; S, 5.95%.

3-{1-[(5-Benzoyl-3-phenyl-3H-[1,3,4]thiadiazol-2-ylidene)-hydrazono]-ethyl}-5-phenyl-1-p-tolyl-1H-pyrazole-4-carbonitrile (**10c**): Orange solid. Yield: 73%. M.p.: 326-328 °C. IR (KBr): 3040 (CH, aromatic), 2924 (CH, aliphatic), 2223 (CN), 1663 (CO), 1612 (C=N), 1370 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.33 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 7.03-7.78 (m, 19 H, ArH's). Anal. Calcd. for $C_{34}H_{25}N_7OS$ (579.67): C, 70.45; H, 4.35; N, 16.91; S, 5.53. Found: C, 70.12; H, 4.42; N, 17.22; S, 5.52%.

5-{[1-(4-Cyano-5-phenyl-1-p-tolyl-1H-pyrazol-3-yl)-ethylidene]-hydrazono}-4-phenyl-2-phenylcarbamoyl-4,5-dihydro-[1,3,4]thiadiazole (**10d**): Yellow solid. Yield: 78%. M.p.: 240-242 °C.. IR (KBr, cm^{-1}): 3428 (NH), 3060 (CH), 2922 (CH, aliphatic), 2227 (CN), 1675 (CO), 1609 (C=N), 1371 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.33 (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 7.26-7.48 (m, 19 H, ArH's), 11.72 (s, br., 1H, NH). MS (m/e, %): 595 (M^+, 2.7%), 571 (0.8%), 225 (5.7%), 194 (6.8%), 150 (5.1%), 119 (14.3%), 103 (33.14), 91 (89%), 77 (100%), 65 (49.8%). Anal. Calcd. for $C_{34}H_{26}N_8OS$ (594.69), C, 68.67; H, 4.41; N, 18.84; S, 5.39. Found: C, 67.02; H, 4.62; N, 18.72; S, 5.95%.

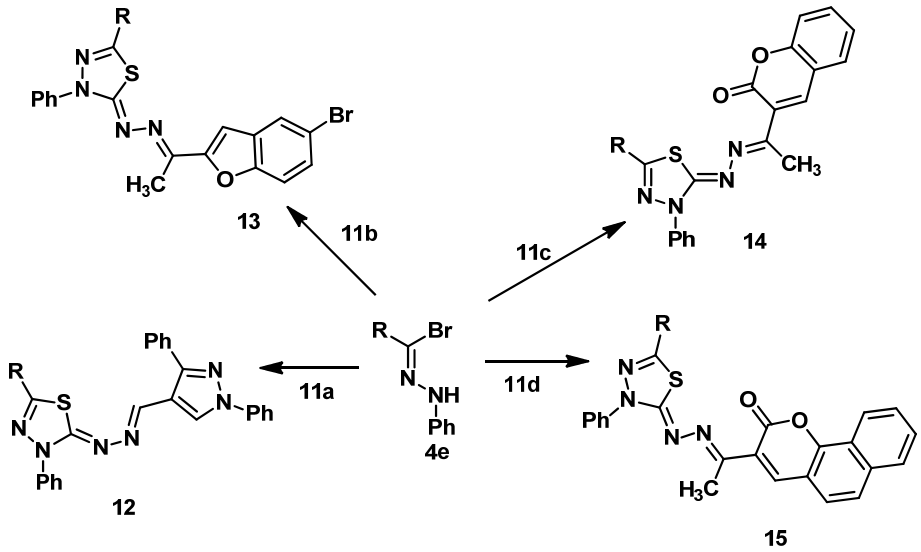
3-(1-{[5-(4-Cyano-5-phenyl-1-p-tolyl-2,3-dihydro-1H-pyrazole-3-carbonyl)-3-phenyl-3H-[1,3,4]thiadiazol-2-ylidene]-hydrazono}-ethyl)-5-phenyl-1-p-tolyl-1H-pyrazole-4-carbonitrile compound with ethane (**10e**): Brown: Yield: 78%. M.p.: 328-330 °C. IR (KBr, cm^{-1}): 3045 (CH, aromatic), 2922 (CH, aliphatic), 2227 (CN), 1675 (CO), 1609 (C=N), 1371 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.37 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 7.26-7.48 (m, 23 H, ArH's). MS (m/e, %): 762 (M+1, 0.5%), 584 (11%), 557 (3%), 284 (70%), 269 (38%), 256 (34%), 242 (29.6%), 229 (12.7%), 217 (22%), 194 (26.7%), 154 (24.5%), 140 (22%), 127 (25.7%), 114 (19.3%), 103 (33.14), 91 (100%), 77 (60%), 65 (52%). Anal. Calcd. for $C_{45}H_{32}N_{10}OS$ (760.87): C, 71.03; H, 4.24; N, 18.41; S, 4.21. Found: C, 67.02; H, 4.62; N, 18.72; S, 5.95%.

2.4. Synthesis of 1,3,4-thiadiazoline derivatives (12-15)

A mixture of the alkyl carbodithioate **11a-d** (5 mmol), the appropriate hydrazonoyl bromide **4e** (2.47 g, 5 mmol), and triethylamine (0.75 mL, 0.005 mol) in ethanol (20 mL) was stirred for 2 h at room temperature. The resulting solid was collected and recrystallized to give 2,3-dihydro-1,3,4-thiadiazoles **12**-**15**, respectively (Scheme 2).

3-{5-[(1,3-Diphenyl-1H-pyrazol-4-ylmethylene)-hydrazono]-4-phenyl-4,5-dihydro-[1,3,4]thiadiazole-2-carbonyl}-5-phenyl-1-p-tolyl-1H-pyrazole-4-carbonitrile (**12**): Red solid. Yield: 84%. M.p.: 269-271 °C. IR (KBr, cm^{-1}): 3056 (CH, aromatic), 2921 (CH, aliphatic), 2230 (CN), 1656 (CO), 1598 (C=C), 1300 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.36 (s, 3H, CH_3), 7.34-8.04 (m, 26 H, ArH's). MS (m/e, %): 709 (M+2, 25%), 708 (M+1, 40%), 706 (M-1, 44%), 479 (22%), 448 (25.9%), 399 (22%), 376 (29.6%), 312 (25.9%), 287 (25%), 286 (100%), 232 (48%), 231 (44%), 215 (25.9%), 193 (25.9%), 165 (25.9%), 164 (29.6%), 155 (40.7%), 135 (48%), 134 (29%), 129 (27%), 105 (44%(, 91 (48%), 90 (66%), 89 (40%), 77 (100%), 64 (44%). Anal. Calcd. for $C_{42}H_{29}N_9OS$, 707.8, C, 71.27; H, 4.13; N, 17.81; S, 4.53. Found: C, 71.62; H, 4.00; N, 17.62; S, 4.31%.

3-(5-{[1-(5-Bromo-benzofuran-2-yl)-ethylidene]-hydrazono}-4-phenyl-4,5-dihydro-[1,3,4]thiadiazole-2-carbonyl)-5-phenyl-1-p-tolyl-1H-pyrazole-4-carbonitrile (**13**): Brown solid. Yield: 81%. M.p.: 162-164 °C. IR (KBr, cm^{-1}): 3052 (CH, aromatic),



R = 5-phenyl-1-p-tolyl-1*H*-pyrazolyl-4-carbonitrile

11a = Methyl 2-[(1,3-diphenyl-1H-pyrazol-4-yl)methylene]hydrazinecarbodithioate

11b = Methyl 2-[1-(5-bromo-1-benzofuran-2-yl)ethylidene]hydrazinecarbodithioate

11c = Methyl (2-[1-(2-oxo-2H-chromen-3-yl)ethylidene]hydrazinecarbodithioate

11d = Methyl 2-[1-(3-oxo-3H-benzo[f]chromen-2-yl)ethylidene]hydrazinecarbodithioate

Scheme 2

2921 (CH, aliphatic), 2232 (CN), 1665 (CO), 1340 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.32 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 6.83-8.18 (m, 18 H, ArH's). MS (m/e, %): 699 (M+1, 29.8%), 697 (M-1, 30.6%), 412 (16%), 410 (15%), 286 (100%), 249 (19.2%), 274 (18%), 222 (12%), 220 (11.6%), 196 (38.5%), 194 (37.4%), 91 (57.7%), 90 (23.1%), 77 (15.4%), 65 (46.2%). Anal. Calcd. for $C_{36}H_{24}BrN_7O_2S$ (698.59) C, 61.89; H, 3.46; Br, 11.44; N, 14.03; S, 4.59. Found: C, 61.73; H, 3.67; Br, 11.23; N, 14.25; S, 4.70%.

3-(5-{[1-(2-Oxo-2H-chromen-3-yl)-ethylidene]-hydrazono}-4-phenyl-4,5-dihydro-[1,3,4]thiadiazole-2-carbonyl)-5-phenyl-1-p-tolyl-1H-pyrazole-4-carbonitrile (**14**): Brown solid. Yield: 78%. M.p.: 162-164 °C. IR (KBr, cm^{-1}): 3057 (CH, aromatic), 2926 (CH, aliphatic), 2230 (CN), 1715, 1665 (CO), 1342 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.37 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 6.83-8.18 (m, 19 H, ArH's). MS (m/e, %): 648 (M+1, 30.8%), 647 (M^+, 34.6%), 286 (100%), 225 (19.2%), 196 (38.5%), 145 (26.9%), 119 (38.5%), 91 (57.7%), 90 (23.1%), 77 (15.4%), 65 (46.2%). Anal. Calcd. for $C_{37}H_{25}N_7O_3S$ (647.7) C, 68.61; H, 3.89; N, 15.14; S, 4.95. Found: C, 68.45; H, 4.10; N, 15.00; S, 4.72%.

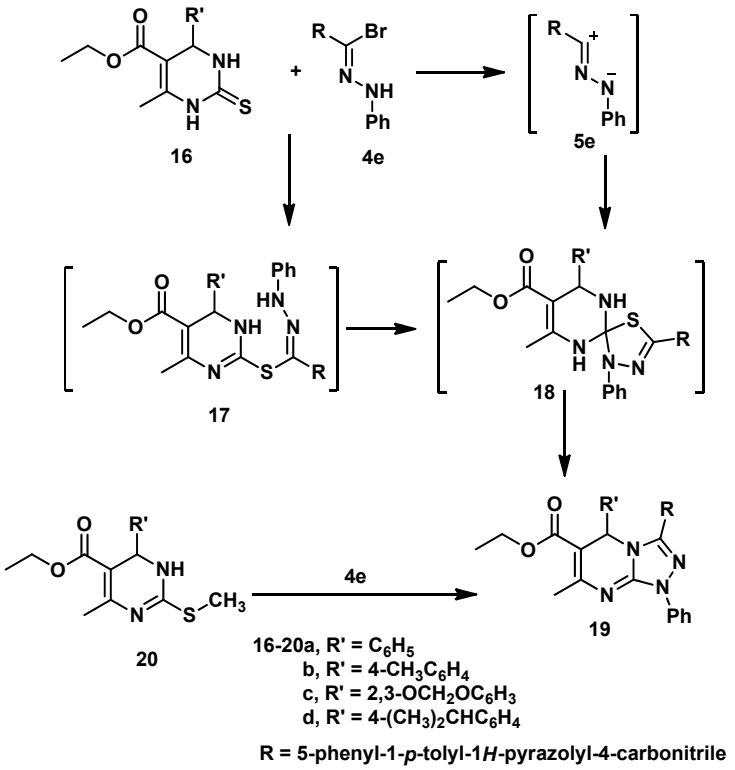
3-(5-{[1-(3-Oxo-3H-benzo[f]chromen-2-yl)-ethylidene]-hydrazono}-4-phenyl-4,5-dihydro-[1,3,4]thiadiazole-2-carbonyl)-5-phenyl-1-p-tolyl-1H-pyrazole-4-carbonitrile (**15**): Orange solid. Yield: 78%. M.p.: 258-260 °C. IR (KBr, cm^{-1}): 3051 (CH, aromatic), 2920 (CH, aliphatic), 2232 (CN), 1666 (CO), 1723, 1667 (CO), 1340 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.76 (s, 3H, CH_3), 2.91 (s, 3H, CH_3), 6.83-8.18 (m, 21 H, ArH's). MS (m/e, %): 698 (M+1, 30.8%), 679 (M^+, 34.6%), 286 (100%), 225 (19.2%), 194 (38.5%), 155 (26.9%), 139 (38.5%), 91 (57.7%), 90 (23.1%), 77 (15.4%), 65 (46.2%). Anal. Calcd. for $C_{41}H_{27}N_7O_3S$ (697.76) C, 70.57; H, 3.90; N, 14.05; S, 4.60. Found: C, 70.75; H, 3.73; N, 13.82; S, 4.75%.

2.5. Synthesis of ethyl 3-(4-Cyano-1,5-diphenyl-1H-pyrazole-3-carbonyl)-6-methyl-1-phenyl-4-substituted 3a,4-dihydro-1H-indazole-5-carboxylate (19a-e), [1,2,4]triazolo[3,4-b] quinazolin-5-one (21), 1H-benzo[4,5]imidazo[2,1-c][1,2,4] triazol-3-yl)-methanone (22) and 1,2,3a,10-tetraaza-cyclo-penta[b]fluoren-4-one (23)

Method A: A mixture of the hydrazonoyl bromide **4e** (2.47 g, 5 mmol) and the appropriate of pyrimidine-2-thione derivatives [26] **16a-e**, 2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one**,** 2-thioxo-2,3,5,6,7,8-hexahydro-1*H*-benzo[4,5]thieno[2,3-*d*]-pyrimidin-4-one, or 2-mercaptobenzimidazole (5 mmol) in chloroform (20 mL) containing triethylamine (0.5 g (0.75 mL), 5 mmol) was refluxed for 20 h. Chloroform was evaporated under reduced pressure and the remaining solid was crystallized from ethanol to give ethanol to give **19a-d**, and **21-23**, respectively (Scheme 3 and 4).

Method B: A mixture of the appropriate hydrazonoyl bromide **4e** (2.47 g, 5 mmol), the appropriate of **20a-e** (5 mmol), and sodium ethoxide (0.34 g, 5 mmol) in ethanol (20 mL) was refluxed for 3 hrs. The reaction mixture was cooled and the resulting solid was collected and crystallized from dioxane gave products identical in all aspects (m.p., mixed m.p., and spectra) with corresponding products obtained by Method A (Scheme 3 and 4).

Ethyl 3-(4-cyano-1,5-diphenyl-1H-pyrazole-3-carbonyl)-7-methyl-1,5-diphenyl-1,5-dihydro-[1,2,4]triazolo[4,3-a]pyrimidine-6-carboxylate (**19a**): Pale brown. Yield: 84%. M.p.: 178-180 °C. IR (KBr, cm^{-1}): 3050 (CH, aromatic), 2924 (CH, aliphatic), 2235 (CN), 1666 (CO), 1609 (C=C), 1372 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 1.13 (t, 3H, J = 7 Hz, CH_2CH_3), 2.29 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.03 (q, 2H, J = 7 Hz, CH_2CH_3), 6.53 (s, 1H), 7.23-8.18 (m, 19 H, ArH's).



Scheme 3

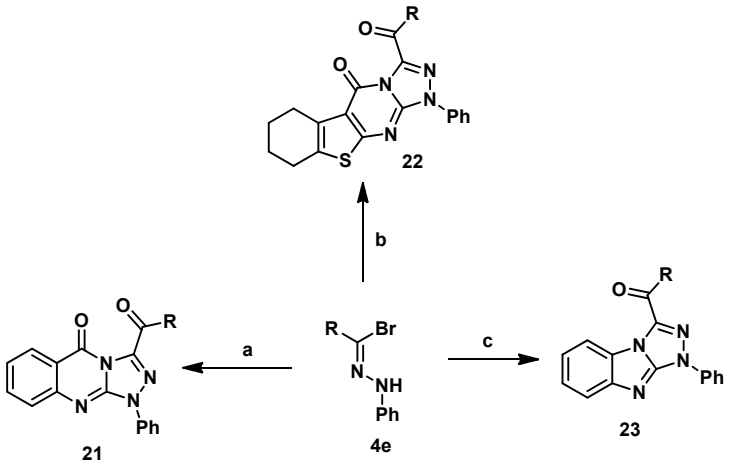
MS (m/e, %): 647 (M+2, 25%), 646 (M+1, 50%), 645 (M^+, 75%), 628 (65%), 569 (25%), 568 (75%), 567 (60%), 426 (40%), 334 (40%), 333 (50%), 332 (35%), 286 (45%), 285 (40%), 225 (45%), 223 (35%), 222 (60%), 169 (55%), 117 (30%), 116 (65%), 114 (45%), 101 (100%), 94 (25%), 93 (25%), 92 (30%), 91 (30%), 80 (50%), 79 (40%), 77 (100%), 65 (90%). Anal. Calcd. for $C_{39}H_{31}N_7O_3$ (645.71): C, 72.54; H, 4.84; N, 15.18. Found: C, 72.41; H, 4.68; N, 15.31%.

Ethyl 3-(4-cyano-1,5-diphenyl-1H-pyrazole-3-carbonyl)-7-methyl-1-phenyl-5-p-tolyl-1,5-dihydro-[1,2,4]triazolo[4,3-a] pyrimidine-6-carboxylate (**19b**): Brown solid. Yield: 85%. M.p.: 144-146 °C. IR (KBr, cm^{-1}): 3035 (CH, aromatic), 2924 (CH, aliphatic), 2233 (CN), 1670 (CO), 1600 (C=C), 1446 (CH_2), 1373 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 1.18 (t, 3H, *J* = 7 Hz, CH_2CH_3), 2.2.0 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.04 (q, 2H, *J* = 7 Hz, CH_2CH_3), 6.37 (s, 1H), 7.23-8.21 (m, 18 H, ArH's). MS (m/e, %): 660 (M+1, 0.68%), 644 (1.18%), 512 (8.69%), 484 (3.12%), 406 (4%), 297 (6.5%), 286 (33.6%), 270 (11.7%), 258 (29.8%), 242 (20.8%), 215 (11%), 194 (16.7%), 170 (11.2%), 155 (15.9%), 140 (21.8%), 114 (28.8%), 102 (43.5%), 77 (100%), 76 (73%). Anal. Calcd. for $C_{40}H_{33}N_7O_3$ (659.74): C, 72.82; H, 5.04; N, 14.86. Found: C, 73.01; H, 4.88; N, 14.68%.

Ethyl 5-benzo[1,3]dioxol-4-yl-3-(4-cyano-1,5-diphenyl-1H-pyrazole-3-carbonyl)-7-methyl-1-phenyl-1,5-dihydro-[1,2,4] triazolo[4,3-a]pyrimidine-6-carboxylate (**19c**): Brown solid. Yield: 86%. M.p.: 169-171 °C. IR (KBr, cm^{-1}): 3035 (CH, aromatic), 2921 (CH, aliphatic), 2235 (CN), 1671 (CO), 1607 (C=C), 1444 (CH_2), 1373 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 1.15 (t, 3H, *J* = 7 Hz, CH_2CH_3), 2.30 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.04 (q, 2H, *J* = 7 Hz, CH_2CH_3), 5.95 (s, 2H, OCH_2O), 6.15 (s, 1H), 7.23-8.21 (m, 17 H, ArH's). MS (m/e, %): 689 (M^+, 1.01%), 572 (1.29%), 556 (2.18%), 512 (1.52%), 445 (1.56%), 377 (1.17%), 357 (1.54%), 286 (5.28%), 244 (2.65%), 149 (14.8%), 104 (20.55%), 91 (65.2%), 77 (100%), 69 (31%). Anal. Calcd. for $C_{40}H_{31}N_7O_5$ (689.72): C, 69.66; H, 4.53; N, 14.22. Found: C, 69.85; H, 4.34; N, 14.10%.

Ethyl 3-(4-cyano-1,5-diphenyl-1H-pyrazole-3-carbonyl)-5-(1,3-diphenyl-1H-pyrazol-4-yl)-7-methyl-1-phenyl-1,5-dihydro-[1,2,4]triazolo[4,3-a]pyrimidine-6-carboxylate (**19d**): Pale brownsolid. Yield: 85%. M.p.: 202-204 °C (AcOH). IR (KBr, cm^{-1}): 3033 (CH, aromatic), 2963 (CH, aliphatic), 2234 (CN), 1662 (CO), 1605 (C=C), 1431 (CH_2), 1369, 1321 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 1.09 (d, 6H, *J* = 8 Hz, $CH(\underline{CH_3})_2$, 1.18 (t, 3H, *J* = 7 Hz, CH_2CH_3), 2.30 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.85 (sept, 1H, *J* = 8 Hz, $CH(CH_3)_2$), 4.10 (q, 2H, *J* = 7 Hz, CH_2CH_3), 6.15 (s, 1H), 7.23-8.21 (m, 18 H, ArH's). MS (m/e, %): 689 (M+2, 12.2%), 688 (M+1, 53.8%), 687 (M^+, 71%), 668 (17.3%), 614 (84.6%), 569 (33.3%), 541 (18.6%), 375 (100%), 287 (43.6%), 286 (87.8%), 243 (27.6%), 194 (16%), 155 (41.7%), 154 (24.4%), 141 (14.7%), 118 (19.9%), 105 (21.8%), 104 (19.2%), 103 (17.9%), 101 (16%), 91 (48.1%), 90 (19%), 78 (12.2%), 77 (53.2%), 66 (8.3%). Anal. Calcd. for $C_{42}H_{37}N_7O_3$ (687.79): C, 73.34; H, 5.42; N, 14.26. Found: C, 73.58; H, 5.71; N, 14.10%.

Ethyl 3-(4-cyano-5-phenyl-1-p-tolyl-1H-pyrazole-3-carbonyl)-5-(1,3-diphenyl-1H-pyrazol-4-yl)-7-methyl-1-phenyl-1,5-dihydro-[1,2,4]triazolo[4,3-a]pyrimidine-6-carboxylate (**19e**): Pale brown solid. Yield: 80%. M.p.: 142-144 °C. IR (KBr): 3033 (CH, aromatic), 2963 (CH, aliphatic), 2234 (CN), 1662 (CO), 1605 (C=C), 1431 (CH_2), 1369, 1321 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 1.18 (t, 3H, *J* = 7 Hz, CH_2CH_3), 2.30 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 4.10 (q, 2H, *J* = 7 Hz, CH_2CH_3), 6.15 (s, 1H), 7.23-8.21 (m, 25 H, ArH's). Anal. Calcd. for $C_{48}H_{37}N_9O3$ (787.87): C, 73.17; H, 4.73; N, 16.00. Found: C, 73.32; H, 4.52; N, 16.21%.



R =5-phenyl-1-*p*-tolyl-1*H*-pyrazolyl-4-carbonitrile
R = 4-cyano-5-phenyl-1-*p*-tolyl-1*H*-pyrazol-3-yl
a = 2-thioxo-2,3-dihydro-1H-quinazolin-4-one
b = 2-thioxo-2,3,5,6,7,8-hexahydro-1H-benzo[4,5]thieno[2,3-d]pyrimidin-4-one
c = 2-mercaptobenzimidazole

Scheme 4

3-(5-Oxo-1-p-tolyl-1,5-dihydro-[1,2,4]triazolo[3,4-b] quinazoline-3-carbonyl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole-4-carbonitrile (**21**): Pale brown solid. Yield: 80%. M.p.: 180-182 °C. IR (KBr): 3033 (CH, aromatic), 2963 (CH, aliphatic), 2233 (CN), 1675 (CO), 1605 (C=C), 1431 (CH_2), 1369, 1321 (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.36 (s, 3H, CH_3), 7.23-8.21 (m, 18 H, ArH's). Anal. Calcd. for $C_{33}H_{21}N_7O_2$ (547.57): C, 72.38; H, 3.87; N, 17.91. Found: C, 72.42; H, 4.05; N, 18.10%.

3-(4-Oxo-1-p-tolyl-1,4,5,6,7,8-hexahydro-9-thia-1,2,3a,10-tetraaza-cyclopenta[b]fluorene-3-carbonyl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole-4-carbonitrile (**22**): Yellow solid. Yield: 68%. M.p.: 136-138 °C. IR (KBr, cm^{-1}): 3045 (CH, aromatic), 2968 (CH, aliphatic), 2233 (CN), 1666 (CO), 1600 (C=C), 1435 (CH_2), 1370, (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 1.61-1.85 (m, 4H), 2.80-2.95 (m, 4H), 2.41 (s, 3H, CH_3), 7.23 (t, 1H, *J* = 8 Hz, ArH's), 7.41 (s, 1H, ArH), 7.42-7.52 (m, 2H, ArH,s), 7.89 (d, 1H, *J* = 8 Hz, ArH), 8.12 (d, 1H, *J* = 8 Hz, ArH), 8.19 (m, 7H, ArH's), 8.38 (s, 1H, ArH). MS (m/e, %): 6.7 (M^+, 4.79%), 510 (4.11%), 489 (7.53%), 462 (12.30%), 429 (5.73%), 312 (5.70%), 286 (100%), 243 (7.12%), 91 (78.12%), 77 (74.25%), 65 (56.57%). Calcd. for $C_{35}H_{25}N_7O_2S$ (607.68): C, 69.18; H, 4.15; N, 16.13; S, 5.28. Found: C, 69.12; H, 4.23; N, 16.11; S, 5.42%.

5-Phenyl-3-(1-phenyl-1H-benzo[4,5]imidazo[2,1-c][1,2,4] triazole-3-carbonyl)-1-p-tolyl-1H-pyrazole-4-carbonitrile (**23**): Pale brown. Yield: 72%. M.p.: 168-188 °C. IR (KBr, cm^{-1}): 3033 (CH, aromatic), 2963 (CH, aliphatic), 2233 (CN), 1716 (CO), 1616 (C=C), 1338, (CH_3) cm^{-1}. ^1H NMR (200 MHz, $(CH_3)_2SO$, δ, ppm): 2.31 (s, 3H, CH_3), 7.26-8.21 (m, 18 H, ArH's). MS (m/e, %): 519 (M^+, 0.27%), 312 (5.37%), 286 (6.19%), 251 (6.92%), 225 (21.48%), 187 (5.11%), 167 (6.28%), 149 (6.50%), 135 (10.31%), 108 (9.15%), 102 (26.51%), 91 (45.02%), 76 (100%), 65 (33.82%). Anal. Calcd. for $C_{32}H_{21}N_7O$ (519.56): C, 73.98; H, 4.07; N, 18.87. Found: C, 73.72; H, 3.88; N, 18.64%.

3. Results and discussion

Methyl 2-[1-(4-cyano-1,5-diphenyl-1*H*-pyrazol-3-yl)ethylidene]hydrazine-carbodithioate (**3a**) and benzyl 2-[1-(4-cyano-1,5-diphenyl-1*H*-pyrazol-3-yl)ethylidene]hydrazine carbodi thioate (**3b**) reacted with ethyl 2-chloro(phenylhydrazono) acetate (**4a**) to afford ethyl 5-{[1-(4-methyl-1,5-diphenyl-1H-pyrazol-3-yl)-ethylidene]-hydrazono}-4-phenyl-4,5-dihydro-[1,3,4]thiadiazole-2-carboxylate (**8a**) (Scheme 1). Structure **8a** was confirmed by elemental analysis, spectra and alternative synthetic route.

Thus, treatment of ethyl 2-hydrazino-3-phenyl-2,3-dihydro-1,3,4-thiadiazole-5-carboxylate (**9a**) with 3-acetyl-1,5-diphenyl-1*H*-pyrazole-4-carbonitrile (**1a**) gave a product identical in all aspects (m.p., mixed m.p. and spectra) with **8a**. The formation of **8a** is assumed to proceed via 1,3-addition of thiol tautomer of carbodithioate **3a** (or **3b**) to nitrilium imide **5a** (generated in situ by treatment of **4a** with triethylamine) can give **6a**, nucleophilic cyclization to yield **7a**. Alternatively, 1,3-cycloaddition of nitrilium imide **5a** to the C=S of carbodithioate **3a** (or **3b)** can give **7a** directly, and then afford **8a** by loss of alkyl mercaptan (Scheme 1). Analogously, treatment of the appropriate **4b**-**e** with the appropriate **3a**-**d** in ethanolic triethylamine gave thiadiazoline derivatives **8b**-**e** and **10b**-**e**, respectively.

Similarly, treatment of 2-(4-cyano-1,5-diphenyl-1*H*-pyrazol-3-yl)-2-oxo-*N*-phenylethanehydrazonoyl bromide (**4e**) with the appropriate **11a**-**e** gave {5-[(2,5-diphenyl-2*H*-pyrazol-3-ylmethylene)-hydrazono]-4-*p*-tolyl-4,5-dihydro-[1,3,4]-thiadiazol-2-yl}-(4-methyl-1,5-diphenyl-1*H*-pyrazol-3-yl)-methanone (**12**), {5-[(1-benzofuran-3-yl-ethylidene)-hydrazono]-4-*p*-tolyl-4,5-dihydro-[1,3,4]thiadiazol-2-yl}-(4-methyl-1,5-diphenyl-1*H*-pyrazol-3-yl)-methanone (**13**), 3-(1-{[5-(4-methyl-1,5-diphenyl-1*H*-pyrazole-3-carbonyl)-3-p-tolyl-3*H*-[1,3,4] thiadiazol-2-ylidene]-hydrazono}-ethyl)-chromen-2-one (**14**) and 2-(1-{[5-(4-methyl-1,5-diphenyl-*1H*-pyrazole-3-carbonyl)-3-p-tolyl-3*H*-[1,3,4]thiadiazol-2-ylidene]-hydrazono}-ethyl)-benzo[*f*]chromen-3-one (**15**), respectively (Scheme 2).

Also, treatment of **4e** with each of the pyrimidine-2-thione **16** and **21** in boiling chloroform gave triazolino[4,3-*a*]pyrimidines in a good yields **20**a-e, respectively (Scheme 3). Structure of **20** was elucidated by elemental analysis, spectral data and alternative synthetic route. Thus, ^1H NMR spectrum of **20a** showed signals at δ = 1.23 (t, 3H, CH_2CH_3), 2.24 (s, CH_3, 4-$CH_3C_6H_4$), 2.56 (s, 3H, CH_3), 4.09 (q, 2H, CH_2CH_3), 5.05 (s, 1H, pyrimidine H-4), 7.44-8.24 (m, 19H, ArH's). Its IR spectrum revealed bands at 1702 (CO ester), 1650 (CO conjugated) and 1615 (C=N).

Furthermore, compound **20a** was obtained from the reaction of ethyl 6-methy-2-methylthio-4-phenyl-3,4-dihydro-pyrimidine-5-carboxylate **21** with **11** in boiling sodium ethoxide solution. The mechanism outlined in Scheme 3 seems to be the most plausible pathway for the formation of **20** from the reaction of **11** with **16** or **21**. 1,3-Addition of the thiol tautomer **16** to the nitrilium imide **17** to give the thiohydrazonate ester **18** which undergoes nucleophilic cyclization to yield spiro compounds **19**. The latter ring open and cyclized to yield **20** by loss hydrogen sulfide; and 2)-1,3-cycloaddition of nitrilium imide **17** to C=S double bond of **16** to give directly **19** (Scheme 3). All attempts to isolate any intermediates were unsuccessful.

Analogously, reactions of 2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one [21]**,** 2-thioxo-2,3,5,6,7,8-hexahydro-1*H*-benzo[4,5]thieno[2,3-*d*]pyrimidin-4-one [22]**,** or 2-mercapto-benzimidazole with hydrazonoyl bromide **4e** were carried out in refluxing chloroform in presence of TEA gave [1,2,4]triazolo[3,4-*b*]quinazolin-5-one **21**, 1*H*-benzo[4,5] imidazo[2,1-*c*][1,2,4]triazol-3-yl)-methanone **22** and 1,2,3a,10-tetraaza-cyclopenta[*b*]fluoren-4-one **23**, respectively (Scheme 4).

4. Conclusion

The studies described above clearly demonstrate that the new 2,3-dihydro-1,3,4-thiadiazole, triazolino[4,3-*a*]pyrimidine, triazolo[3,4-*b*]quinazolin-5-one, 1*H*-benzo[4,5]imidazo[2,1-*c*] [1,2,4]triazol-3-yl)-methanone, and 1,2,3a,10-tetraaza-cyclo-penta[*b*]fluoren-4-one **23** derivatives containing pyrazole moiety can be synthesized in a good yield via hydrazonoyl halides.

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