European Journal of Chemistry 3 (3) (2012) 322-331

European Journal of Chemistry

Journal homepage: www.eurjchem.com

Synthesis of 5-arylazothiazoles, pyridines and thieno[2,3-*b*]pyridines derivatives containing 1,2,3-triazole moiety

Abdou Osman Abdelhamid*, Nadia Abdelhamid Abdel-Riheem, Tamer Tawhid El-Idreesy and Huda Refat Mahmoud Rashdan

Department of Chemistry, Faculty of Science, Cairo University, Giza, 12613, Egypt

**Corresponding author at: Department of Chemistry, Faculty of Science, Cairo University, Giza, 12613, Egypt. Tel.: +20.2.1005205750; fax: +20.2.35676573. E-mail address: abdelhamid45@gmail.com (A.O. Abdelhamid).*

ARTICLE INFORMATION

Received: 04 May 2012
Received in revised form: 25 June 2012
Accepted: 25 June 2012
Online: 30 September 2012

KEYWORDS

Urea
Pyridines
Quinazoline
Carbamates
5-Arylthiazoles
Thieno[2,3-*b*]pyridines

ABSTRACT

1-(2-(4,5-Dihydro-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-5-phenylpyrazol-1-yl)-4-substituted-thiazol-5-yl)-2-phenyldiazene (**4**) and substituted pyridines (**5-12**) were synthesized *via* reaction of 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-phenylprop-2-en-1-one with hydrazonoyl halides and active methylene compounds. Also, thieno[2,3-*b*]pyridines (**14a-e**) were prepared through reactions of 2-mercapto-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenyl-pyridine-3-carbonitrile with halo ester and halo ketones, respectively. The newly synthesized derivetived were elucidated by elemental analysis, spectral data and alternative synthetic routes wherever possobile.

1. Introduction

The pharmaceutical importance of pyrazolines lies in the fact that they can be effectively utilized as antibacterial, antifungal, antiviral, antiparasitic, antitubercular and insecticidal agents [1-6]. Some of these compounds have also anti-inflammatory, antidiabetic, anaesthetic and analgesic properties [7-9]. In addition, pyrazolines have played a crucial part in the development of theory in heterocyclic chemistry and also been used extensively in organic synthesis [10-14]. On the other hand, thienopyrimidine derivatives are characterized by a very broad spectrum of biological activities such as antiallergic [15], antiatherosclerotic [16], antibacterial [17-19], anticancer [20], antiviral [21,22], antihypertensive [23,24], antidepressant [25], antihistaminic [26], antimicrobial [27-31] and neurotropic [32] activities. As an extension of our study [33-41] and as a part of our program aiming at the synthesis of different heterocyclic derivatives, we report herein the convenient synthesis of 5-arylazothiazoles, synthesis of pyridines and thienopyridine derivatives containing 1,2,3-triazole moiety

2. Experimental

2.1. Instrumentation

All melting points were determined on an electrothermal 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 300 MHz and JNM-LA 400 FT-NMR system spectrometer and chemical shifts are expressed in δ ppm units using TMS as an internal reference. Mass spectra were recorded on a GC-MS QP1000 EX Shimadzu. Elemental analyses were carried out at the Microanalytical Center of Cairo University. Hydrazonoyl halides [42,43] and 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone [44] were prepared as previously reported.

2.2. Synthesis

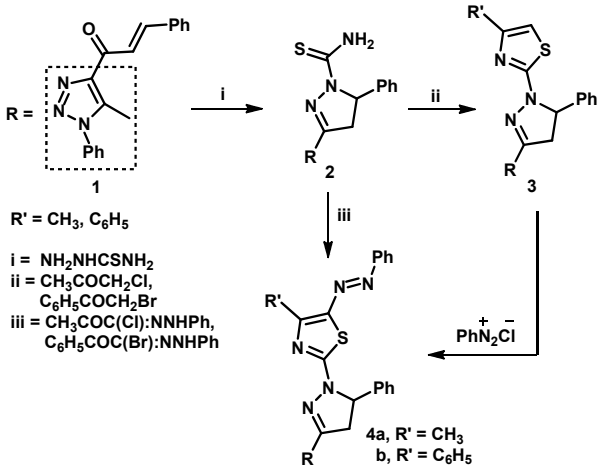
2.2.1. 1-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-3-phenylprop-2-en-1-one (1)

Sodium hydroxide (10 mL, 10%) was added dropwise to a mixture of 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl) ethanone (2 g, 10 mmol) and benzaldehyde (1 g, 10 mmol) in ethanol (20 mL) while stirring at 0-5 °C**.** The reaction mixture was left for 2 h then the resulting solid was collected and recrystallized from ethanol to give **1** (Scheme 1). Color: White. Yield: 87%. M.p.: 126-128 °C (M.p.: 123-125 °C [45]). FT-IR (KBr, ν, cm^{-1}): 3064 (CH), 1665 (CO), 1604 (C=N), 1574 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.60 (s, 3H, CH_3), 7.42-7.44 (m, 3H, ArH's), 7.47-7.50 (m, 2H, ArH's), 7.75-7.60 (m, 3H, ArH's), 7.72-7.75 (m, 2H, ArH's), 7.90-7.96 (d, 1H, *J* = 16 Hz, CH=C), 8.10-8.15 (d, 1H, *J* = 16 Hz, CH=C). MS (EI, *m/z* (%)): 289 (M^+, 3), 233 (60), 217 (11), 180 (25), 140 (6), 130 (53), 118 (66), 115 (25), 103 (50), 77 (100), 51 (70). Anal calcd. for $C_{18}H_{15}N_3O$: (289.33) C, 74.72; H, 5.23; N, 14.52.. Found: C, 74.79; H, 5.18; N, 14.61%.

2.2.2. 3-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-5-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (2)

A mixture of 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-phenylprop-2-en-1-one (**1**) (1.45 g, 5 mmol), thiosemicarbazide

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
DOI:10.5155/eurjchem.3.3.322-331.629



Scheme 1

(0.46 g, 5 mmol) and sodium hydroxide (0.5 g, 10 mmol) in ethanol (20 mL) was refluxed for 3 h. The resulting solid was collected and recrystallized from ethanol to give **2** (Scheme 1). Color: White. Yield: 82%. M.p.: 184-186 °C. FT-IR (KBr, ν, cm^{-1}): 3475, 3355(NH_2), 3035 (CH), 1600 (C=N), 1562 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.54 (s, 3H, CH_3), 3.66 (dd, 1H, *J* = 18.1, 5.8 Hz, CH_2 (pyraz)), 4.01 (dd, 1H, *J* = 18.1, 12 Hz, CH_2 (pyraz)), 5.33 (dd, 1H, *J* = 12.2, 5.8 Hz , CH (pyraz)), 7.25-7.72 (m, 10H, ArH's), 9.11 (s. br., 2H, NH_2). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 7.90 (CH_3), 39.52 (CH_2), 60.12 (CH), 118.35, 127.22, 127.41, 127.80, 129.31, 129.67, 131.47, 138.36, 139.45, 142.67, 144.44, 178.24. MS (EI, *m/z* (%))**:** 359 (M-3, 0.1), 358 (M-4, 0.2), 93 (4.4), 91 (100), 60 (59), 59 (27), 58 (8). Anal. calcd. for $C_{19}H_{18}N_6S$: C, 62.96; H, 5.01; N, 23.19; S, 8.85. Found: C, 63.10; H, 4.88; N, 23.00; S, 8.78%.

2.2.3. 4-(4,5-Dihydro-1-(4-substituted thiazol-2-yl)-5-phenyl-1H-pyrazol-3-yl)-5-methyl-1-phenyl-1H-1,2,3-triazole (3a, b)

A mixture of 4,5-dihydro-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-5-phenyl-pyazole-1-carbothioamide (**2**) (1.81 g, 5 mmol), the appropriate of chloroacetone or ω-bromo acetophenone (5 mmol) in ethanol (20 mL) refluxes for 3 h. The resulting solid, after cooling was collected and recrystallized to give **3a** and **3b**, respectively (Scheme 1).

4-(4,5-Dihydro-1-(4-methylthiazol-2-yl)-5-phenyl-1H-pyrazol-3-yl)-5-methyl-1-phenyl-1H-1,2,3-triazole (**3a**): Color: Grey crystals from acetic acid. Yield: 81%. M.p.: 198-200 °C. FT-IR (KBr, ν, cm^{-1}): 3058 (CH), 1595 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.10 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 3.66 (dd, 1H, *J* = 18.1, 5.8 Hz, CH_2(pyraz)), 4.01 (dd, 1H, *J* = 18.1, 12.0 Hz, CH_2(pyraz)), 5.33 (dd, 1H, *J* = 12.2, 5.8 Hz , CH(pyraz)), 6.10 (s, 1H, thiazole H-5), 7.25-7.66 (m, 10H, ArH's). MS (EI, *m/z* (%)): 400 (M^+, 19), 399 (19), 389 (16), 385 (22), 374 (21), 362 (26), 341 (24), 322 (18), 302 (26), 279 (25), 256 (23), 244 (21), 222 (28), 212 (48), 206 (18), 167 (27), 149 (91), 139 (19), 125 (42), 110 (63), 95 (58). Anal. calcd. for $C_{22}H_{20}N_6S$: C, 65.98; H, 5.03; N, 20.98; S, 8.01. Found: C, 66.12; H, 4.97; N, 21.20; S, 7.89%.

4-(4,5-Dihydro-5-phenyl-1-(4-phenylthiazol-2-yl)-1H-pyrazol-3-yl)-5-methyl-1-phenyl-1H-1,2,3-triazole (**3b**): Color: Yellow crystals from dioxane. Yield: 79%. M.p.: 250-252 °C. FT-IR (KBr, ν, cm^{-1}): 3058 (CH), 1597 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.54 (s, 3H, CH_3), 3.66 (dd, 1H, *J* = 18.1, 5.8 Hz, CH_2(pyraz)), 4.01 (dd, 1H, *J* = 18.1, 12 Hz, CH_2(pyraz)), 5.33 (dd, 1H, *J* = 12.2, 5.8 Hz , CH(pyraz)), 6.58 (s, 1H, thiazole H-5), 7.21-7.69 (m, 15H, ArH's). MS (EI, *m/z* (%)): 462 (M^+, 0.06), 400 (46), 242 (6), 240 (8), 156 (14), 130 (26), 113 (15), 103 (20), 91 (15), 77 (100), 67 (11). Anal. calcd. for $C_{27}H_{22}N_6S$: C, 70.11; H, 4.79; N, 18.17; S, 6.93. Found: C, 70.23; H, 4.92; N, 17.88; S, 7.13%.

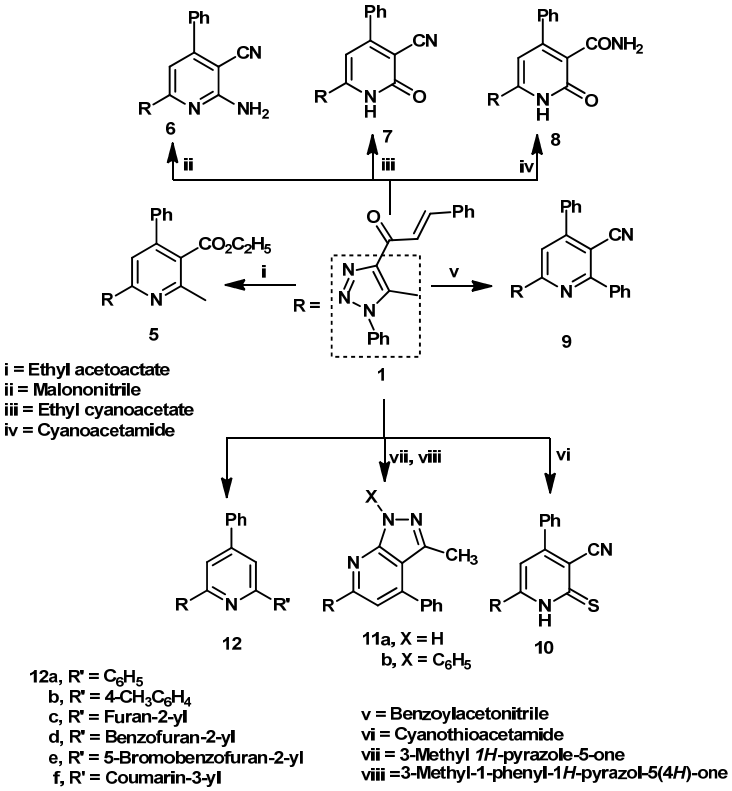
2.2.4. 1-(2-(4,5-Dihydro-3-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-5-phenylpyrazol-1-yl)-4-substituted thiazol-5-yl)-2-phenyldiazene (4a, b)

Method A: A mixture of 4,5-dihydro-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-5-phenyl-pyazole-1-carbothioamide (**2**) (1.81 g, 5 mmol), the appropriate of hydrazonoyl halides (5 mmol) and triethylamine (0.75 mL, 0.5 g, 5 mmol) in ethanol (20 mL) refluxes 4 h. The resulting solid was collected and recrystallized to give **4a** and **4b**, respectively (Scheme 1).

Method B: Benzenediazonium chloride (5 mmol), which prepared from aniline (0.45 mL, 5 mmol), hydrochloric acid (6 N, 6 mL), and sodium nitrite (0.35 g, 5 mmol), was added dropwise with stirring to a cold solution (0-5 °C) of a mixture of the appropriate **3a** or **3b** (5 mmol) and sodium acetate trihydrate (1.3 g, 10 mmol) in ethanol (50 ml). The resulting solid was collected and recrystallized to afford products identical with **4a** and **4b**.

1-(2-(4,5-Dihydro-3-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-5-phenylpyrazol-1-yl)-4-methylthiazol-5-yl)-2-phenyldiazene (**4a**): Color: Orange crystals from acetic acid. Yield: 82%. M.p.: 218-220 °C. FT-IR (KBr, ν, cm^{-1}): 3023 (CH), 1597 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.44 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 3.61 (dd, 1H, *J* = 18.1, 5.8 Hz, CH_2(pyraz)), 4.01 (dd, 1H, *J* = 18.1, 12 Hz, CH_2(pyraz)), 5.32 (dd, 1H, *J* = 12.2, 5.8 Hz , CH(pyraz)), 7.21-7.89 (m, 15H, ArH's). MS (EI, *m/z* (%)): 505 (M+1, 2.8), 504 (M^+, 15), 169 (5), 155 (9), 143 (6), 130 (21), 112 (14), 104 (15), 91 (13), 77 (100), 66 (11). Anal. calcd. for $C_{28}H_{24}N_8S$: C, 66.65; H, 4.79; N, 22.21; S, 6.35. Found: C, 66.55; H, 4.87; N, 22.00; S, 6.51%.

1-(2-(4,5-Dihydro-3-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-5-phenylpyrazol-1-yl)-4-phenylthiazol-5-yl)-2-phenyldiazene (**4b**): Color: Red crystals from acetic acid. Yield: 81%. M.p.: 246-248 °C. FT-IR (KBr, ν, cm^{-1}): 3062 (CH), 1601 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.56 (s, 3H, CH_3), 3.61 (dd, 1H, *J* = 18.1, 5.8 Hz, CH_2(pyraz)), 4.01 (dd, 1H, *J* = 18.1, 12 Hz, CH_2(pyraz)), 5.32 (dd, 1H, *J* = 12.2, 5.8 Hz , CH(pyraz)), 7.09-8.19 (m, 20H, ArH's). MS (EI, *m/z* (%)): 566 (M^+, 0.4), 174 (31), 102 (38), 80 (100), 74 (38), 73 (13). Anal. calcd. for $C_{33}H_{26}N_8S$ (566.68) C, 69.94; H, 4.62; N, 19.77; S, 5.66. Found: C, 70.12; H, 4.75; N, 19.62; S, 5.81%.



Scheme 2

2.2.5. 6-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenyl pyridine derivatives (5-10) and pyrazolo[3,4-b]pyridine **(11a, b)**

Method A: A mixture of 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-phenylprop-2-en-1-one (**1**) (1.45 g, 5 mmol), the appropriate ethyl acetoacetate, malononitrile, ethylcyano-acetate, cyanoacetamide, benzoylacetonitrile, cyanothio-acetamide, 3-methyl-1*H*-pyrazol-5(4*H*)-one or 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (5 mmol) and ammonium acetate (0.38 g, 5 mmol), was heated in acetic acid (10 mL) under reflux for 3 h. on cooling, the separated solid was filtered, washed with water and crystallized from the proper solvent to afford **5**-**11a** and **11b** (Scheme 2).

Method B: A mixture of 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone (1 g, 5 mmol), benzaldehyde (0.51 g, (5 mmol)) and the appropriate ethyl acetoacetate, malononitrile, ethyl cyanoacetate, cyanoacetamide, benzoylacetonitrile, cyanothioacetamide, 3-methyl-1*H*-pyrazol-5(4*H*)-one or 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (5 mmol) and ammonium acetate (4.0 g), was heated in *n*-butanol (10 mL) under reflux for 4 h. on cooling, the separated yellow solid was filtered, washed with water and recrystallized from the proper solvent to give corresponding products which obtained in method A.

Ethyl 2-methyl-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridine-3-carboxylate (**5**): Color: Yellow. Crystals from ethanol. Yield: 69%. M.p.: 188-190 °C. FT-IR (KBr, ν, cm^{-1}): 2923, 2854 (CH), 1681 (CO), 1612 (C=N), 1570 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.03 (t, 3H, *J* = 7, 12 Hz, CH_2CH_3), 2.22 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.57 (q, 2H, *J* = 7 Hz, CH_2CH_3), 7.11-7.60 (m, 10H, ArH's), 8.35 (s, 1H, pyridine H-5). MS (EI, *m/z* (%)): 398 M^+, (4)), 343 (13), 295 (14), 267 (98), 164 (11), 130 (24), 118 (19), 115 914), 77 (100), 65 (11). Anal. calcd. for $C_{24}H_{22}N_4O_2$: C, 72.34; H, 5.57; N, 14.06. Found: C, 72.41; H, 5.70; N, 13.8%.

2-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridine-3-carbonitrile (**6**): Color: Yellow crystals from ethanol. Yield: 73%. M.p.: 224-226 °C [45]. FT-IR (KBr, ν, cm^{-1}): 3465, 3502 (NH_2), 2202 (CN), 1589 ν(C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.49 (s, 3H, CH_3), 7.02 (s. br., 2H, NH_2), 7.41-7.61 (m, 11H, ArH's). MS (EI, *m/z* (%)): 353 (M+1, 3.3), 351 (M^+, 29), 324 (93), 281 (11), 247 (13), 220 (48), 194 (11), 17614), 149 (13), 130 (85), 77 (92), 51 (63). Anal. calcd. for $C_{21}H_{16}N_6$: C, 71.58; H, 4.58; N, 23.85. Found: C, 71.62; H, 4.74; N, 23.69%.

1,2-Dihydro-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-2-oxo-4-phenylpyridine-3-carbonitrile (**7**): Color: White crystals from acetic acid. Yield: 87%. M.p.: 250-252 °C. FT-IR (KBr, ν, cm^{-1}): 3344 (NH), 3062 (CH), 2218 (CN), 1701 (CO), 1616 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.45 (s, 3H, CH_3), 7.02 -7.61 (m, 11H, ArH's and pyridine H-5), 11.65 (s. br., 1H, NH). MS (EI, *m/z* (%)): 353 (M^+, 27.8), 352 (M-1, 32), 327 (91), 269 (12), 254 (16), 221 (37), 194 (10), 176 (15), 152 (15), 130 (69), 77 (100), 51 (55). Anal. calcd. for $C_{21}H_{15}N_5O$: C, 71.38; H, 4.28; N, 19.82. Found: C, 71.41; H, 4.15; N, 20.00%.

1,2-Dihydro-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-2-oxo-4-phenylpyridine-3-carboxamide (**8**): Color: White crystals from ethanol. Yield: 72%. M.p.: 230-232 °C. FT-IR (KBr, ν, cm^{-1}): 3440, 3394 (NH_2), 3062 (CH), 1693 (CO), 1601 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.48 (s, 3H, CH_3), 7.10-7.62 (m, 13H, ArH's and pyridine H-5), 14.86 (s. br., 1H, NH). MS (EI, *m/z* (%)): 373 (M^+, 1.6), 233 (3.3), 188 (1.7), 130 (29), 117 (52), 103 (7), 77 (100), 51 (50). Anal. calcd. for $C_{21}H_{17}N_5O_2$: C, 67.91; H, 4.61; N, 18.86. Found: C, 68.11; H, 4.52; N, 18.79%.

6-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-2,4-diphenyl-pyridine-3-carbonitrile (**9**): Color: White crystals from acetic acid. Yield: 87%. M.p.: 244-246 °C. FT-IR (KBr, ν, cm^{-1}): 3062

(CH), 2218 (CN), 1589 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.55 (s, 3H, CH_3), 7.17-8.42 (m, 16H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 414 (M+1, 8), 413 (M^+, 27), 385 (100), 308 (15), 281 (39), 191 (17), 171 (14), 130 (45), 77 (80), 51 (56). Anal. calcd. for $C_{27}H_{19}N_5$: C, 78.43; H, 4.63; N, 16.94. Found: C, 78.43; H, 4.63; N, 16.94%.

1,2-Dihydro-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenyl-2-thioxopyridine-3-carbonitrile (**10**): Color: Orange crystals from dioxane. Yield: 87%. M.p.: 244-246 °C. FT-IR (KBr, ν, cm^{-1}): 3310 (NH), 3066 (CH), 2218 (CN), 1616 (C=N), 1589 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.45 (s, 3H, CH_3), 7.10-7.69 (m, 11H, ArH's and pyridine H-5), 15.45 (s. br., 1H, NH). MS (EI, *m/z* (%)): 371 (M+2, 2.6), 370 (M+1, 6), 369 (M^+, 22), 341 (95), 340 (82), 339 (12), 307 (12), 237 (34), 130 (56), 77 (100), 51 (79). Anal. calcd. for $C_{21}H_{15}N_5S$: C, 68.27; H, 4.09; N, 18.96; S, 8.68. Found: C, 68.34; H, 4.21; N, 18.82; S, 8.54%.

3-Methyl-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenyl-1H-pyrazolo[3,4-b]pyridine (**11a**): Color: Brown crystals from benzene. Yield: 91%. M.p.: 168-170 °C. FT-IR (KBr, ν, cm^{-1}): 3379 (NH), 3062 (CH), 1635 (C=N), 1596 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.56 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 7.10-7.75 (m, 11H, ArH's and pyridine H-5), 11.23 (s. br., 1H, NH). MS (EI, *m/z* (%)): 366 (M^+, 100), 365 (M-1, 48), 250 (11), 234 (13), 221 (20), 220 (14), 219 (14), 206 (15), 145 (14), 130 (19), 118 (13),103 (15), 77 (24). Anal. calcd. for $C_{22}H_{18}N_6$: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.24; H, 5.11; N, 22.76%.

3-Methyl-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (**11b**): Color: Brown crystals from ethanol. Yield: 89%. M.p.: 118-120 °C. FT-IR (KBr, ν, cm^{-1}): 3476 (NH), 3070 (CH), 1632 (C=N), 1603 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.65 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 7.00-7.82 (m, 16H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 443 (M+1, 29), 442 (M^+, 100), 413 (15), 346 (16), 345 (41), 316 (10), 264 (24), 248 (10), 228 (58), 214 (45), 200 (12), 196 (17),148 (16), 174 (14), 158 (14), 146 (18), 144 (18), 131 (20), 115 (11), 77 (6), 54 (14). Anal. calcd. for $C_{28}H_{22}N_6$: C, 76.00; H, 5.01; N, 18.99. Found: C, 76.12; H, 5.14; N, 18.78%.

2.2.6. 2-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenyl-6-substituted pyridine (12a-f)

A mixture of 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-phenylprop-2-en-1-one (**1**) (1.45 g, 5 mmol), the appropriate 1-(2-oxo-2-substituted ethyl)-pyridinium bromides (5 mmol) and ammonium acetate (0.38 g, 5 mmol) in acetic acid (10 mL) refluxes for 4 h. The resulting solid, which formed after cooling, was filtered, washed with water and crystallized from the proper solvent to give **12a-f** (Scheme 2).

2-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4,6-diphenyl-pyridine (**12a**): Color: White crystals from acetic acid. Yield: 84%. M.p.: 186-188 °C. FT-IR (KBr, ν, cm^{-1}): 3058 (CH), 2931 (CH), 1602 (C=N), 1550 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.76 (s, 3H, CH_3), 7.30-8.12 (m, 17H, ArH's and pyridine H-3 & H-5). MS (EI, *m/z* (%)): 388 (M^+, 33), 387 (M-1, 33), 361 (33), 373 (47), 360 (88), 359 (100), 256 (47), 227 (17), 158 (17), 130 (50), 129 (67), 85 (133), 77 (33), 69 (33), 61 (36). Anal. calcd. for $C_{26}H_{20}N_4$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.39; H, 5.19; N, 14.42%.

2-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenyl-6-p-tolylpyridine (**12b**): Color: White crystals from acetic acid. Yield: 87%. M.p.: 170-172 °C. FT-IR (KBr, ν, cm^{-1}): 3026 (CH), 2914 (CH), 1601 (C=N), 1549 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.34 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 7.30-8.28 (m, 16H, ArH's and pyridine H-3 & H-5). MS (EI, *m/z* (%)): 403 (M+1, 9), 402 (M^+, 26), 401 (M-1, 25), 375 (24), 374 (89), 373 (100), 270 (30), 130 (22), 91(11), 77 (60), 51 (39). Anal. calcd. for $C_{27}H_{22}N_4$: C, 80.57; H, 5.51; N, 13.92. Found: C, 80.71; H, 5.36; N, 14.00%.

2-(Furan-2-yl)-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridine (**12c**): Color: White crystals from acetic acid. Yield: 87%. M.p.: 170-172 °C. FT-IR (KBr, ν, cm^{-1}): 3026 (CH), 2914 (CH), 1601 (C=N), 1549 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.64 (s, 3H, CH_3), 7.32-8.22 (m, 15H, ArH's and pyridine H-3, H-5, furan H-3, H-4, H-5). MS (EI, *m/z* (%)): 378 (M^+, 0.02), 360 (100), 289 (5), 283 (15), 256 (34), 179 (15), 202 (8), 180 (15), 130 (25), 118 (23), 103 (16), 77 (69), 64 (6). Anal. calcd. for $C_{24}H_{18}N_4O$: C, 76.17; H, 4.79; N, 14.81. Found: C, 76.24; H, 4.61; N, 14.97%.

2-(Benzofuran-2-yl)-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridine (**12d**): Color: Brown crystals from acetic acid. Yield: 87%. M.p.: 208-210 °C. FT-IR (KBr, ν, cm^{-1}): 3082 (CH), 2920 (CH), 1604 (C=N), 1562 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.62 (s, 3H, CH_3), 7.21-7.59 (m,17H, ArH's and pyridine H-3, H-5, furan H-3)).
MS (EI, *m/z* (%)): 428 (M^+, 5), 426 (M-2, 9), 394 (7), 382 (6), 361 (6), 334 (9), 306 (7), 279 (8), 262 (6), 233 (9), 212 (16), 190 (12), 185 (11), 181 (14), 175 (9), 167 (6), 155 (16), 149 (10), 123 (13), 111 (10), 105 (9), 95 (16), 93 (21), 81 (34), 75 (16), 71 (74), 69 (43), 67 (25). Anal. calcd. for $C_{28}H_{20}N_4O$: C, 78.49; H, 4.70; N, 13.08. Found: C, 78.53; H, 4.64; N, 13.16%.

2-(5-Bromobenzofuran-2-yl)-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridine (**12e**): Color: White crystals from acetic acid. Yield: 87%. M.p.: 196-198 °C. FT-IR (KBr, ν, cm^{-1}): 3060 (CH), 2915 (CH), 1610 (C=N), 1576 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.67 (s, 3H, CH_3), 7.12-7.89 (m, 16H, ArH's and pyridine H-3, H-5 and furan H-3). MS (EI, *m/z* (%)): 509 (M^+, 20), 507 (M^+, 22), 480 (87), 479 (100), 375 (19), 373 (26), 293 (13), 212 (11), 200 (29), 199 (22), 164 (13), 130 (63), 77 (63), 51 (48). Anal. calcd. for $C_{28}H_{19}BrN_4O$: C, 66.28; H, 3.77; Br, 15.75; N, 11.04. Found: C, 66.35; H, 3.65; Br, 15.56; N, 11.13%.

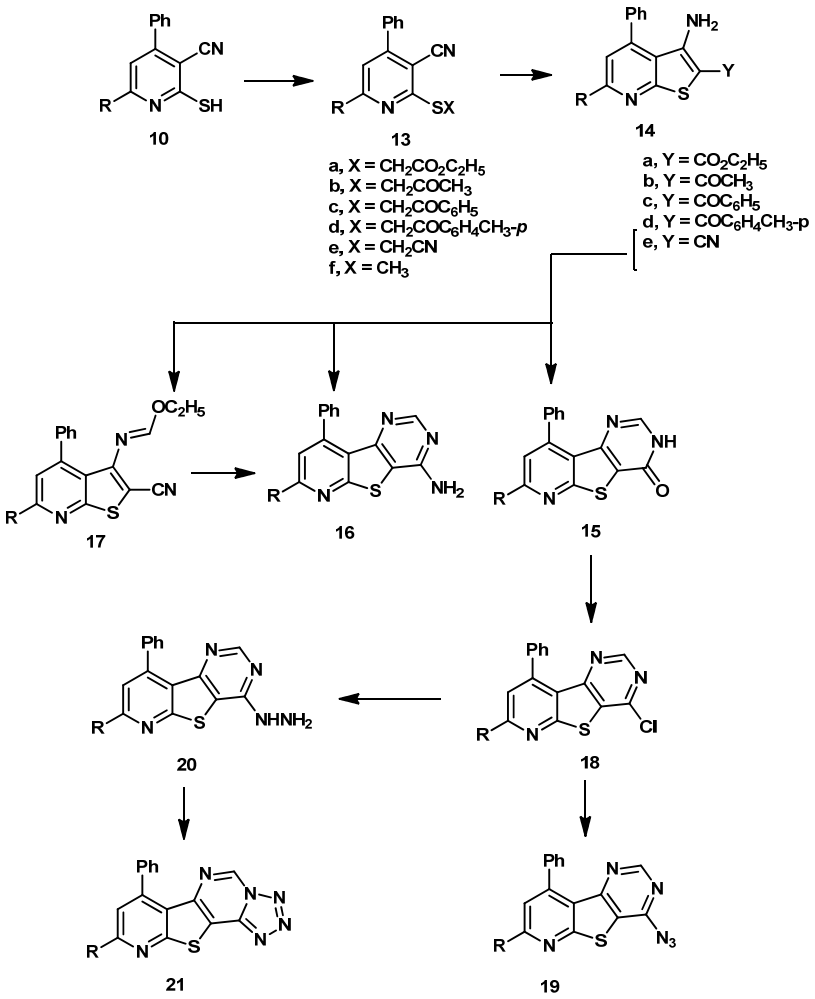
3-(6-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridin-2-yl)-2H-chromen-2-one (**12f**): Color: Beige crystals from dioxane. Yield: 72%. M.p.: 264-266 °C. FT-IR (KBr, ν, cm^{-1}): 3055 (CH), 2920 (CH), 1602 (C=N), 1700 (CO), 1550 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.63 (s, 3H, CH_3), 7.12-7.82 (m, 15H, ArH's and pyridine H-3), 7.95 (s, 1H, pyridine H-5), 8.78 (s, 1H, pyrane H-4). MS (EI, *m/z* (%)): 456 (M-2, 30), 428 (58), 267 (20), 164 (18), 125 (15), 119 (15), 103 (22), 82 (27), 67 (22). Anal. calcd. for $C_{29}H_{20}N_4O_2$: C, 76.30; H, 4.42; N, 12.27. Found: C, 76.42; H, 4.34; N, 12.10%.

2.2.7. 2-(Substituted thio)-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridine-3-carbonitrile (13a-f)

A mixture of 1,2-dihydro-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenyl-2-thioxopyridine-3-carbonitrile (**10**) (1.84 g, 5 mmol), potassium hydroxide (0.28 g, 5 mmol) in *N,N*-dimethylformamide (10 mL) was stirred for 2h at room temperature. The appropriate of ethyl chloroacetate, chloroacetone, 2-bromo-1-phenylethanone, 2-bromo-1-*p*-tolylethanone, chloroacetonitrile or iodomethane (5 mmol) was added while stirring. Stirred was continued for 2h. The resulting solid was collected and crystallized to afford **13a-f**, respectively, (Scheme 3).

Ethyl 2-(3-cyano-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridin-2-ylthio)acetate (**13a**): Color: Brown crystals from ethanol. Yield: 77%. M.p.: 138-140 °C. FT-IR (KBr, ν, cm^{-1}): 3065 (CH), 2977, 2929 (CH), 2114 (CN), 1742 (CO), 1587 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.09 (t, 3H, CH_2CH_3), 2.62 (s, 3H, CH_3), 4.05 (q, 2H, CH_2CH_3), 4.29 (s, 2H, SCH_2), 7.59-7.97 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 456 (M+1, 5), 455 (M^+, 18), 426 (11), 352 (33), 351 (23), 339 (10), 250 (10), 130 (13), 77 (100), 51 (58). Anal. calcd. for $C_{25}H_{21}N_5O_2S$: C, 65.92; H, 4.65; N, 15.37; S, 7.04. Found: C, 66.12; H, 4.54; N, 15.52; S, 7.17%.

2-(2-Oxopropylthio)-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridine-3-carbonitrile (**13b**): Color: Brown crystals from ethanol. Yield: 87%. M.p.: 154-156 °C.



Scheme 3

FT-IR (KBr, ν, cm^{-1}): 3058 (CH), 2916 (CH), 2211 (CN), 1720 (CO), 1581 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.32 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 4.42 (s, 2H, SCH_2), 7.27-7.95 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 426 (M+1, 5), 425 (M$^+$, 25), 424 (20), 396 (14), 382 (19), 353 (49), 251 (10), 129 (19), 77 (100), 51 (69). Anal. calcd. for $C_{24}H_{19}N_5OS$: C, 67.74; H, 4.50; N, 16.46; S, 7.54. Found: C, 67.91; H, 4.48; N, 16.64; S, 7.41%.

6-(5-Methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-2-(2-oxo-2-phenyl-ethylsulfanyl)-4-phenyl-nicotinonitrile (**13c**): Color: White crystals from acetic acid. Yield: 88%. M.p.: 158-160 °C. FT-IR (KBr, ν, cm^{-1}): 3061 (CH), 2908 (CH), 2213 (CN), 1679 (CO), 1585 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.62 (s, 3H, CH_3), 4.52 (s, 2H, SCH_2), 7.27-7.82 (m, 16H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 489 (M+1, 2), 488 (M$^+$, 8), 487 (19), 457 (28), 353 (17), 130 (12.4), 77 (100), 76 (13), 51 (29). Anal. calcd. for $C_{29}H_{21}N_5OS$: C, 71.44; H, 4.34; N, 14.36; S, 6.58. Found: C, 71.23; H, 4.45; N, 14.61; S, 6.72%.

6-(5-Methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-2-(2-oxo-2-p-tolyl-ethylsulfanyl)-4-phenyl-nicotinonitrile (**13d**): Color: White crystals from acetic acid. Yield: 88%. M.p.: 208-210 °C. FT-IR (KBr, ν, cm^{-1}): 3050 (CH), 2914 (CH), 2210 (CN), 1678 (CO), 1588 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.37 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 4.62 (s, 2H, SCH_2), 7.27-7.95 (m, 15H, ArH's and pyridine H-5). Anal. calcd. for $C_{30}H_{23}N_5OS$: C, 71.83; H, 4.62; N, 13.96; S, 6.39. Found: C, 71.95; H, 4.57; N, 14.15; S, 6.28%.

2-(Cyanomethylthio)-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylpyridine-3-carbonitrile (**13e**): Color: Gray crystals from ethanol. Yield: 78%. M.p.: 198-200 °C. FT-IR (KBr, ν, cm^{-1}): 3062 (CH), 2970, 2924 (CH), 2214 (CN), 1647(C=N), 1585 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.72 (s, 3H, CH_3), 4.42 (s, 2H, SCH_2), 7.58-8.06 (m, 11H, ArH's and pyridine H-5). Anal. calcd. for $C_{23}H_{16}N_6S$: C, 67.63; H, 3.95; N, 20.57; S, 7.85. Found: C, 67.81; H, 4.11; N, 20.68; S, 7.98%.

6-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-2-(methylthio)-4-phenylpyridine-3-carbonitrile (**13f**): Color: White crystals from acetic acid. Yield: 78%. M.p.: 210-212 °C. FT-IR (KBr, ν, cm^{-1}): 3062 (CH), 2923, 2854 (CH), 2210 (CN), 1627(C=N), 1595 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.62 (s, 6H, $2CH_3$), 7.24-7.89 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 384 (M+1, 23), 383 (M-1, 100), 171 (14), 170 (100), 168 (20), 154 (15), 149 (18), 127 (10). Anal. calcd. for $C_{22}H_{17}N_5S$: C, 68.91; H, 4.47; N, 18.26; S, 8.36. Found: C, 69.10; H, 4.54; N, 18.43; S, 8.18%.

2.2.8. 3-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenyl-2-substituted thieno[2,3-b]pyridine derivatives **(14a-e)**

A mixture of the appropriate **13a-e** (5 mmol) and catalytic amount of piperidine (5 drops) in ethanol (20 mL) refluxes for 1h. The resulting solid was collected and recrystallized from acetic acid to give thieno[2,3-*b*]pyridines **14a-e**, respectively, (Scheme 3).

Ethyl 3-amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridine-2-carboxylate (**14a**): Color: Yellow. Yield: 92%. M.p.: 214-216 °C. FT-IR (KBr, ν, cm^{-1}): 3474, 3355 (NH_2), 3060 (CH), 2972, 2917 (CH), 1672 (CO), 1600 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.04 (t, 3H, CH_2CH_3), 2.71 (s, 3H, CH_3), 4.22 (q, 2H, CH_2CH_3), 5.81 (s. br., 2H, NH_2), 7.59-7.89 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 455 (M^+, 16), 454 (M-1, 63), 380 (27), 379 (31), 353 (18), 317 (14), 258 (12), 148 (14), 139 (28), 107 (20), 76 (100), 57 (18), 51 (65). Anal. calcd. for $C_{25}H_{21}N_5O_2S$: C, 65.92; H, 4.65; N, 15.37; S, 7.04. Found: C, 66.12; H, 4.56; N, 15.42; S, 7.17%.

1-(3-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)ethanone (**14b**): Color: Orange. Yield: 71%. M.p.: 226-228 °C. FT-IR (KBr, ν, cm^{-1}): 3476, 3314 (NH_2), 3056 (CH), 2918, 2885 (CH), 1720 (CO), 1590 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.35 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 5.80 (s. br., 2H, NH_2), 7.39-7.69 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 452 (M^+, 100), 424 (M-1, 95), 395 (47), 391 (47), 353 (30), 292 (23), 248 (11), 198 (29), 196 (13), 177 (16), 130 (64), 77 (92), 51 (67). Anal. calcd. for $C_{24}H_{19}N_5OS$: C, 67.74; H, 4.50; N, 16.46; S, 7.54. Found: C, 67.64; H, 4.36; N, 16.54; S, 7.35%.

(3-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)(phenyl)methanone (**14c**): Color: Yellow. Yield: 86%. M.p.: 260-262 °C. FT-IR (KBr, ν, cm^{-1}): 3471, 3275 (NH_2), 3052 (CH), 2919, 2851 (CH), 1712 (CO), 1591 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.64 (s, 3H, CH_3), 6.22 (s. br., 2H, NH_2), 7.21-7.79 (m, 16H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 487 (M^+, 55), 486 (M-1, 49), 458 (92), 229 (20), 130 (19), 77 (100), 51 (27). Anal. calcd. for $C_{29}H_{21}N_5OS$: C, 71.44; H, 4.34; N, 14.36; S, 6.58. Found: C, 71.52; H, 4.41; N, 14.54; S, 6.66%.

(3-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)(4-methylphenyl)methanone (**14d**): Color: Yellow. Yield: 80%. M.p.: 262-264 °C. FT-IR (KBr, ν, cm^{-1}): 3478, 3292 (NH_2), 3031 (CH), 2918, 2852 (CH), 1709 (CO), 1590 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.26 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 5.09 (s. br., 2H, NH_2), 7.31-7.94 (m, 15H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 501 (M^+, 52), 500 (M-1, 41), 472 (100), 235 (17), 190 (11), 130 (14), 77 (35), 65 (19), 51 (14). Anal. calcd. for $C_{30}H_{23}N_5OS$ (501.6) C, 71.83; H, 4.62; N, 13.96; S, 6.39. Found: C, 71.92; H, 4.51; N, 14.15; S, 6.52%.

3-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridine-2-carbonitrile (**14e**): Color: Yellow. Yield: 87%. M.p.: 246-248 °C. FT-IR (KBr, ν, cm^{-1}): 3467, 3328 (NH_2), 2923, 2854 (CH), 2191 (CN), 1631 (C=N), 1585 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.65 (s, 3H, CH_3), 5.60 (s. br., 2H, NH_2), 7.51-7.90 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 409 (M+1, 13), 408 (M^+, 54), 407 (45), 380 (91), 379 (100), 277 (13), 190 (16), 169 (14), 130 (83), 77 (77), 51 (65). Anal. calcd. for $C_{23}H_{16}N_6S$: C, 67.63; H, 3.95; N, 20.57; S, 7.85. Found: C, 67.75; H, 4.12; N, 20.42; S, 7.96%.

2.2.9. 2-(5-Methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-9-thia-1,5,7-triaza-fluorene derivatives (15 and 16)

A mixture of **14e** (2 g, 5 mmol) and the appropriate of formic acid (99%) or formamide (5 mL) in *N,N*,-dimethylformamide refluxes for 7 h. The reaction mixture was poured onto ice (50 g). The resulting solid was collected and recrystallized from from the proper solvent to give **15** and **16**, respectively, (Scheme 3).

2-(5-Methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-7H-9-thia-1,5,7-triaza-fluoren-8-one (**15**): Color: White crystals from *N,N*-dimethylformamide. Yield: 90%. M.p.: >300 °C. FT-IR (KBr, ν, cm^{-1}): 3452 (NH), 3047 (CH), 2920, 2850 (CH), 1686 (CO), 1577 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.67 (s, 3H, CH_3), 7.51-8.35 (m, 12H, ArH's), 12.85 (s. br., 1H, NH). MS (EI, *m/z* (%)): 436 (M^+, 18), 355 (10), 318 (15), 317 (64), 265 (11), 264 (55), 257 (25), 235 (10), 222 (14), 221 (61), 209 (12), 194 (54), 193 (100), 153 (14), 98 (19), 83 (16), 67 (15), 55 (34). Anal. calcd. for $C_{24}H_{16}N_6OS$: C, 66.04; H, 3.69; N, 19.25; S, 7.35. Found: C, 66.15; H, 3.75; N, 19.37; S, 7.22%.

2-(5-Methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-9-thia-1,5,7-triaza-fluoren-8-ylamine (**16**): Color: Brown crystals from dioxane. Yield: 92%. M.p.: >300 °C. FT-IR (KBr, ν, cm^{-1}): 3309, 3120 (NH_2), 3062 (CH), 2923, 2854 (CH), 1647 (C=N), 1570 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.63 (s, 3H, CH_3), 6.68 (s. br., 2H, NH_2), 7.51-8.11 (m, 12H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 435 (M^+, 3), 285 (9), 241 (11), 240 (38), 151 (40), 150 (13), 91 (100), 65 (6). Anal. calcd. for $C_{24}H_{17}N_7S$: C, 66.19; H, 3.93; N, 22.51; S, 7.36. Found: C, 66.25; H, 4.12; N, 22.37; S, 7.43%.

2.2.10. Ethyl N-[2-cyano-6-(5-methyl-1-phenyl-1H-[1,2,3] triazol-4-yl)-4-phenyl-thieno[2,3-b]pyridin-3-yl]-formimidate (17)

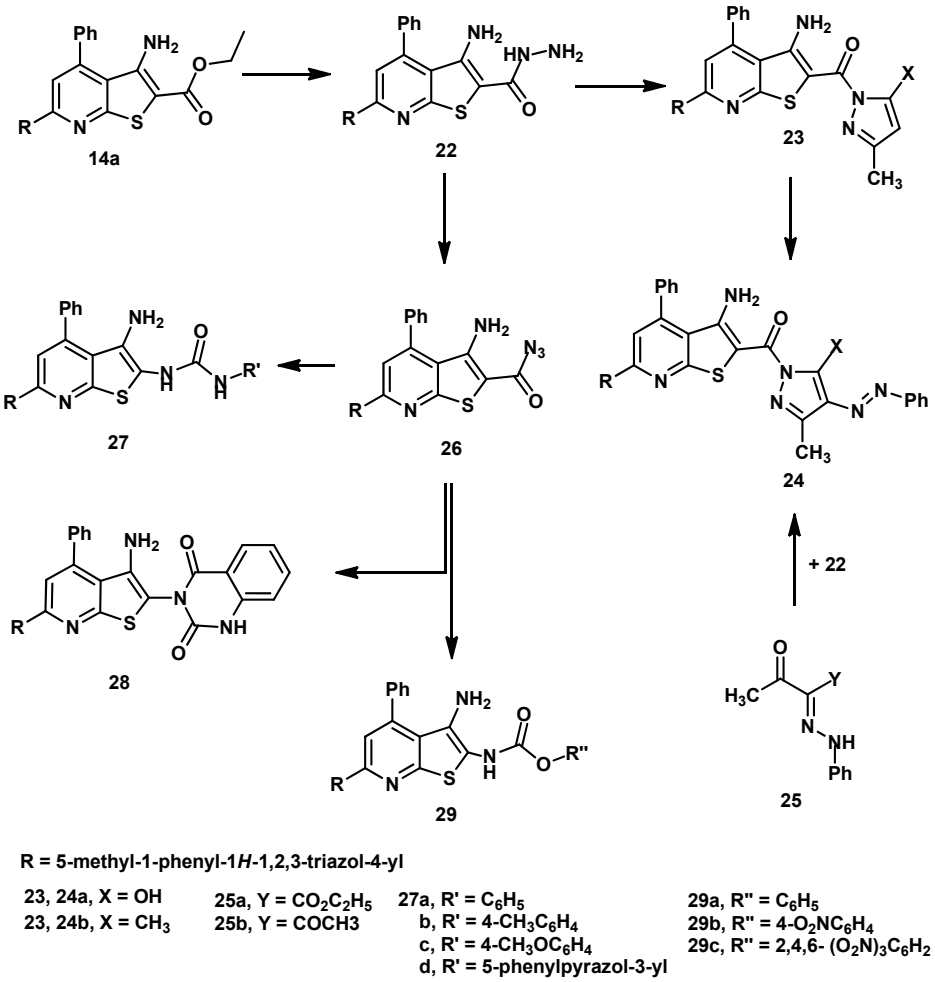
A mixture of **14e** (2 g, 5 mmol) and triethyl ortho-formate (1.48 g, 10 mmol) in acetic anhydride (20 mL) refluxes for 6 h. The reaction mixture was poured onto ice (30 g). The resulting solid was collected and recrystallized from ethanol to give **17** (Scheme 3). Color: Brown. Yield: 88%. M.p.: 180-182 °C. FT-IR (KBr, ν, cm^{-1}): 3062 (CH), 2854 (CH), 2206 (CN), 1639 (C=N), 1582 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.37 (t, 3H, CH_2CH_3), 2.58 (s, 3H, CH_3), 4.21 (q, 2H, CH_2CH_3), 7.15-7.48 (m, 11H, ArH's and pyridine H-5), 8.15 (s, 1H, CH=N). MS (EI, *m/z* (%)): 464 (M^+, 0.3), 297 (10), 256 (8), 150 (100), 130 (7), 120 (6), 105 (13), 104 (15), 76 (6). Anal. calcd. for $C_{26}H_{20}N_6OS$: C, 67.22; H, 4.34; N, 18.09; S, 6.90. Found: C, 67.41; H, 4.43; N, 17.79; S, 6.82%.

2.2.11. 8-Chloro-2-(5-methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-9-thia-1,5,7-triaza-fluorene (18)

A mixture of **15** (2.18 g, 5 mmol) and phosphorus oxychloride (20 mL) refluxes for 5 h. The reaction mixture was cooled and poured onto ice (50 g). The resulting solid was collected and recrystallized from acetic acid to afford **18** (Scheme 3). Color: Yellow. Yield: 96%. M.p.: 240-242 °C. FT-IR (KBr, ν, cm^{-1}): 3056 (CH), 2920, 2850 (CH), 1647 (C=N), 1585 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.62 (s, 3H, CH_3), 7.15-7.77 (m, 11H, ArH's and pyridine H-5), 8.68 (s, 1H, pyrimidine H-2). MS (EI, *m/z* (%)): 456 (M+2, 0.03), 454 (M^+, 0.1), 370 (10), 369 (36), 354 (100), 353 (54), 263 (31), 262 (8), 248 (11), 247 (7.6), 236 (27), 233 (23), 221 (13), 177 (11), 118 (21), 106 (12), 77 (31), 51 (5). Anal. calcd. for $C_{24}H_{15}ClN_6S$: C, 63.36; H, 3.32; Cl, 7.79; N, 18.47; S, 7.05. Found: C, 63.12; H, 3.23; Cl, 7.87; N, 18.37; S, 7.11%.

2.2.12. 8-Azido-2-(5-methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-9-thia-1,5,7-triaza-fluorene (19)

A mixture of **18** (2.77 g, 5 mmol) and sodium azide (0.65 g, 19 mmol) in *N,N*-dimethylformamide was stirred at room temperature for 2h. Then, poured onto ice-cold water (50 mL). The resulting solid was collected and recrystallized from ethanol to give **19** (Scheme 3). Color: Brown. Yield: 96%. M.p.: >300 °C. FT-IR (KBr, ν, cm^{-1}): 3055 (CH), 2920, 2854 (CH), 2044 (N_3) [46], 1658 (C=N), 1543 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.62 (s, 3H, CH_3), 7.15-7.82 (m, 11H, ArH's and pyridine H-5), 8.68 (s, 1H, pyrimidine H-2). Anal. calcd. for $C_{24}H_{15}ClN_6S$: C, 62.46; H, 3.28; N, 27.32; S, 6.95. Found: C, 62.52; H, 3.31; N, 27.46; S, 7.17%.



Scheme 4

2.2.13. [2-(5-Methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-9-thia-1,5,7-triaza-fluoren-8-yl]-hydrazine (20)

A mixture of **18** (2.18 g, 5 mmol) and hydrazine hydrate (1 g, 20 mmol) in ethanol (20 mL) refluxes for 3 h. The resulting solid was collected and recrystallized from acetic acid to give **20** (Scheme 3). Color: Yellow. Yield: 96%. M.p.: 240-242 °C. FT-IR (KBr, ν, cm^{-1}): 3388, 3337, 3217 (NH, NH_2), 3062 (CH), 2920, 2851 (CH), 1645 (C=N), 1551 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.62 (s, 3H, CH_3), 6.25 (s. br., 3H, NH, NH_2), 7.15-7.77 (m, 11H, ArH's and pyridine H-5), 8.68 (s, 1H, pyrimidine H-2). MS (EI, *m/z* (%)): 450 (M^+, 4), 332 (20), 331 (100), 238 (54), 174 (12), 160 (64), 155 (62), 94 (12), 93 (35), 91 (54), 84 (17), 65 (8), 56 (9). Anal. calcd. for $C_{24}H_{18}N_8S$: C, 63.98; H, 4.03; N, 24.87; S, 7.12. Found: C, 64.12; H, 4.11; N, 24.94; S, 7.23%.

2.2.14. 8-(5-Methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-6-phenyl-10-thia-1,2,3,3a,5,9-hexaaza-cyclopenta[a]fluorene (21)

Saturated solution of sodium nitrite (10 mL) was added while stirring to a cold solution at 0 °C of **20** (2.25 g, 5 mmol) in acetic acid (30 mL). The reaction was stirred for 1h. The resulting solution was collected and recrystallized from acetic acid gave **21** (Scheme 3). Color: Brown. Yield: 89%. M.p.: >300 °C. FT-IR (KBr, ν, cm^{-1}): 3070 (CH), 2920, 2850 (CH), 1625 (C=N), 1585 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.64 (s, 3H, CH_3), 7.15-7.68 (m, 11H, ArH's and pyridine H-5), 8.48 (s, 1H, pyrimidine H-2). MS (EI, *m/z* (%)): 461 (M^+, 6), 360 (100), 289 (23), 260 (39), 248 (23), 232 (81), 220 (15), 202 (20), 189 (75), 178 (10), 174 (55), 155 (29), 148 (45), 136 (51), 97 (12), 91 (77), 43 (19). Anal. calcd. for $C_{24}H_{15}N_9S$: C, 62.46; H, 3.28; N, 27.32; S, 6.95. Found: C, 62.61; H, 3.37; N, 27.28; S, 7.11%.

2.2.15. 3-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridine-2-carbohydrazide (22)

A mixture of ethyl 3-amino-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-*b*]pyridine-2-carboxylate (**14a**) (2.27 g, 5 mmol) and hydrazine hydrate (1g, 1 mL, 10 mmol) in ethanol (20 mL) refluxes for 1h. The solid formed was collected and recrystallized from ethanol afforded **22** (Scheme 4). Color: Yellow. Yield: 82%. M.p.: 230-232 °C. FT-IR (KBr, ν, cm^{-1}): 3483, 3359, 3267 (NH, NH_2), 3062(CH), 2920, 2854 (CH), 1659 (CO), 1593 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.56 (s, 3H, CH_3), 5.88 (s. br., 5H, NH, $2NH_2$), 7.10-7.60 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 441 (M^+, 49), 426 (24), 289 (23), 260 (39), 248 (23), 232 (81), 220 (15), 202 (20), 189 (75), 178 (10), 174 (55), 155 (29), 148 (45), 380 (29), 353 (36), 312 (24), 249 (22), 191 (38), 149 (76), 77 (100), 51 (76). Anal. calcd. for $C_{23}H_{19}N_7OS$: C, 62.57; H, 4.34; N, 22.21; S, 7.26. Found: C, 62.75; H, 4.24; N, 22.141; S, 7.356%.

2.2.16. (3-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)(5-substituted 3-methyl-1H-pyrazol-1-yl)methanone dervatives (23a and b)

A mixture of 3-amino-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-*b*]pyridine-2-carbohydrazide (**22**) (2.2 g, 5 mmol), ethyl acetoacetate or acetylacetone in ethanol (20 mL) and acetic acid (5 drops) refluxes for 3 h. on cooling, the separated yellow solid was filtered, washed with water and crystallized from acetic acid to afford **23a** and **23b** (Scheme 4).

2-[3-Amino-6-(5-methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-thieno[2,3-b]pyridine-2-carbonyl]-5-methyl-2,4-dihydro-pyrazol-3-one (**23a**): Color: Brown. Yield: 89%. M.p.: 180-182 °C. FT-IR (KBr, ν, cm^{-1}): 3479, 3325 (NH_2), 3062 (CH), 2924, 2855 (CH), 1724, 1674 (CO), 1593 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.12 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 4.31 (dd, 1H, CH_2, , pyrazolole), 3.56 (dd, 1H, CH_2, pyrazole), 6.77 (s. br., 2H, NH_2), 7.12-7.74 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 507 (M^+, 10), 450 (18), 449 (28), 448 (100), 390 (13), 274 (16). Anal. calcd. for $C_{27}H_{21}N_7O_2S$: C, 63.89; H, 4.17; N, 19.32; S, 6.32. Found: C, 64.00; H, 4.05; N, 19.45; S, 6.48%.

3-Amino-6-(5-methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-thieno[2,3-b]pyridin-2-yl]-(3,5-dimethyl-pyrazol-1-yl)-methanone (**23b**): Color: Brown. Yield: 89%. M.p.: 218-220 °C. FT-IR (KBr, ν, cm^{-1}): 3479, 3325 (NH_2), 3062 (CH), 2923, 2855 (CH), 1670 (CO), 1627 (C=N), 1593 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.28 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 5.52 (s, 1H, pyrazole H-4), 6.55 (s. br., 2H, NH_2), 7.12-7.79 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 505 (M^+, 3.6), 503 (14), 465 (9), 448 (41), 406 (21), 331 (39), 220 (7), 206 (10), 178 (27), 169 (78), 136 (23), 135 (23), 127 (14), 109 (24), 43 (100). Anal. calcd. for $C_{28}H_{23}N_7OS$: C, 66.52; H, 4.59; N, 19.39; S, 6.34. Found: C, 66.45; H, 4.48; N, 19.28; S, 6.52%.

2.2.17. 2-[3-Amino-6-(5-methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-thieno[2,3-b]pyridine-2-carbonyl]-5-methyl-4-(phenyl-hydrazono)-2,4-dihydro-pyrazol-3-one (24a) *and [3-Amino-6-(5-methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-thieno[2,3-b]pyridin-2-yl]-(3,5-dimethyl-4phenylazo-pyrazol-1-yl)-methanone* (24b)

Method A: Benzenediazonium chloride (5 mmol), which was prepared *via* reaction of aniline (0.46 g. 5 mmol), hydrochloric acid (3 mL, 6 M) and sodium nitrite (0.37 gm, 5 mmole) at 0-5 °C, was added to a mixture of the appropriate **23a** or **32b** (5 mmole) and sodium acetate (0.41 g, 5 mmole) in ethanol (30 mL) at 0-5 °C, while stirring. The reaction mixture was stirred for 3 h. The resulting solid, was collected, washed with water and recrystallized from acetic acid to give **24a** and **24b**, respectively, (Scheme 4).

Method B: A mixture of **22a** (2.2 g, 5 mmol) and the appropriate of ethyl 2-(2-phenylhydrazono)-3-oxobutanoate or 3-(2-phenyl-hydrazono)pentane-2,4-dione (5 mmol) in ethanol (20 mL) and catalytic amount of acetic acid (2 drops) was refluxed for 2 h. The resulting solid, so formed, was collected and recrystallized from acetic acid to give products identical in all aspects to those obtained from method A.

2-[3-Amino-6-(5-methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-thieno[2,3-b]pyridine-2-carbonyl]-5-methyl-4-(phenyl-hydrazono)-2,4-dihydro-pyrazol-3-one (**24a**): Color: Brown. Yield: 92%. M.p.: 208-210 °C. FT-IR (KBr, ν, cm^{-1}): 3479, 3359, 3325 (NH, NH_2), 3066 (CH), 2920 (CH), 1678, 1647 (CO), 1605 (C=N), 1550 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.10 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 6.89-7.72 (m, 16H, ArH's and pyridine H-5), 9.42 (s. br., 3H, NH, NH_2). MS (EI, *m/z* (%)): 611 (M^+, 0.2), 373 (6), 355 (100), 313 (9), 256 (10), 240 (17), 239 (96), 227 (12), 171 (47), 159 (14), 158 (23), 117 (26), 112 (14), 98 (34), 95 (13), 83 (24), 73 (13), 69 (26)57 (55), 43 (57). Anal. calcd. for $C_{33}H_{25}N_9O_2S$: C, 64.80; H, 4.12; N, 20.61; S, 5.24. Found: C, 64.92; H, 4.00; N, 20.75; S, 5.35%.

(3-amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)(3,5-dimethyl-4-(phenyldiazen-yl)-1H-pyrazol-1-yl)methanone (**24b**): Color: Brown. Yield: 88%. M.p.: 240-242 °C. FT-IR (KBr, ν, cm^{-1}): 3614, 3568 (NH_2), 3058 (CH), 2916, 2850 (CH), 1693 (CO), 1608 (C=N), 1550 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.18 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 6.78 (s. br., 2H, NH_2), 7.12-7.99 (m, 16H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 609 (M^+, 35), 608 (100), 607 (45), 593 (11), 397 (29), 396 (29), 381 (25), 365 (12), 214 (11), 212 (20), 195 (20). Anal. calcd. for $C_{34}H_{27}N_9OS$: C, 66.98; H, 4.46; N, 20.68; S, 5.26. Found: C, 67.11; H, 4.34; N, 20.88; S, 5.14%.

2.2.18. (3-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)azidomethanone (26)

A stirred solution of **22** (2.2 g, 5 mmol) in hydrochloric acid (15 mL, 6 M) at 0-5 °C, sodium nitrite was added portionwise tell effervescence ended. The reaction mixture was stirred for 1 h. The resulting solid, was collected, filtered, washed with water and recrystallized from acetic acid to give **26** (Scheme 4). Color: Beige. Yield: 88%. M.p.: 190-192 °C. FT-IR (KBr, ν, cm^{-1}): 3479, 3325 (NH_2), 3031 (CH), 2920 (CH), 2124 (Azide), 1678 (CO), 1596 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.61 (s, 3H, CH_3), 6.65 (s. br., 2H, NH_2), 7.12-7.85 (m, 11H, ArH's and pyridine H-5). MS (EI, *m/z* (%)): 455 (M+1, 18), 454 (16), 440 (41), 380 (38), 354 (22), 324 (19), 286 (19), 265 (45), 239 (25), 220 (41), 205 (38), 189 (31), 161 (34), 134 (44), 128 (47), 98 (53), 91 (16), 82 (100), 77 (41), 64 (25), 51 (28). Anal. calcd. for $C_{23}H_{16}N_8OS$: C, 61.05; H, 3.56; N, 24.76; S, 7.09. Found: C, 61.12; H, 3.42; N, 24.61; S, 7.00%.

2.2.19. Urea derivatives (27a-d)

A mixture of appropriate aniline, *p*-toluidine, *p*-anisidine or 3-amino-5-phenylpyrazole (5 mmol) and azido compound **26** (2.26 g, 5 mmol) in dry dioxane (20 mL) refluxes for 4 h. The resulting solid, so formed, was collected and recrystallized to give **27a-d**, respectively, (Scheme 4).

1-(3-amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)-3-phenylurea (**27a**): Color: Brown crystals from ethanol. Yield: 78%. M.p.: 240-242 °C. FT-IR (KBr, ν, cm^{-1}): 3614, 3568 (NH_2), 3031 (CH), 2920(CH), 1678 (CO), 1596 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.54 (s, 3H, CH_3), 7.12-7.66 (m, 20H, ArH's, pyridine H-5, 2NH, NH_2). MS (EI, *m/z* (%)): 517 (M^+, 0.2), 309 (100), 280 (18), 231 (7), 208 (18), 204 (14), 206 (24), 128 (15), 105 (41), 77 (19). Anal. calcd. for $C_{29}H_{23}N_7OS$: C, 67.29; H, 4.48; N, 18.94; S, 6.19. Found: C, 67.29; H, 4.48; N, 18.94; S, 6.19%.

1-(3-amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)-3-p-tolylurea (**27b**): Color: Brown crystals from ethanol. Yield: 87%. M.p.: 208-210 °C. FT-IR (KBr, ν, cm^{-1}): 3429, 3568 (NH_2), 3066 (CH), 2924, 2823 (CH), 1685 (CO), 1604 (C=N), 1551 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.25 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 7.12-7.99 (m, 19H, ArH's and pyridine H-5, 2H, NH_2). MS (EI, *m/z* (%)): 531 (M^+, 38), 530 (100), 516 (18), 515 (49), 219 (31), 203 (12), 189 (10), 147 (15), 67 (13), 83 (15), 71 (12), 69 (18), 57 (57), 43 (22). Anal. calcd. for $C_{30}H_{25}N_7OS$: C, 67.78; H, 4.74; N, 18.44; S, 6.03. Found: C, 67.87; H, 4.7456; N, 18.22; S, 6. 14%.

1-(3-amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)-3-(4-methoxyphenyl)urea (**27c**): Color: Beige crystals from acetic acid. Yield: 89%. M.p.: 140-142 °C. FT-IR (KBr, ν, cm^{-1}): 3614, 3568 (NH_2), 2923, 2854 (CH), 1653 (CO), 1600 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.61 (s, 3H, CH_3), 3.65 (s, 3H, OCH_3), 7.12-7.99 (m, 19H, ArH's and pyridine H-5), NH_2, 2NH). MS (EI, *m/z* (%)): 547 (M^+, 2.7), 305 (5), 304 (33), 303 (100), 273 (6), 195 (6), 117 (9), 81

(6). Anal. calcd. for $C_{30}H_{25}N_7O_2S$: C, 65.80; H, 4.60; N, 17.90; S, 5.86. Found: C, 65.98; H, 4.51; N, 18.12; S, 5.64%.

1-(3-amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)-3-(3-phenyl-1H-pyrazol-5-yl)urea (**27d**): Color: Brown crystals from acetic acid. Yield: 88%. M.p.: 240-242 °C. FT-IR (KBr, ν, cm^{-1}): 3433, 3394 (NH_2), 2974, 2939 (CH), 1647 (CO), 1550 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.61 (s, 3H, CH_3), 5.23 (s, 1H, pyrazole H-4), 7.12-7.99 (m, 16H, ArH's and pyridine H-5), 9.26 (s. br., 5H, 3NH, NH_2). MS (EI, *m/z* (%)): 583 (M^+, 65), 300 (34), 299 (100), 288 (12), 287 (17), 286 (78), 241 (11), 239 (15.19), 211 (18), 197 (7), 106 (6), 79 (4), 44 (31). Anal. calcd. for $C_{32}H_{25}N_9OS$: C, 65.85; H, 4.32; N, 21.60; S, 5.49. Found: C, 65.99; H, 4.16; N, 21.72; S, 5.55%.

2.2.20. 3-(3-Amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-yl)quinazoline-2,4(1H,3H)-dione (28)

A mixture of appropriate methyl anthranilate or anthranilic acid (5 mmol) and azido compound **26** (2.26 g, 5 mmol) in dry dioxane (20 mL) refluxes for 4 h. The resulting solid, so formed, was collected and recrystallized from ethanol to give **28** (Scheme 4). Color: Brown. Yield: 93.6%. M.p.: >300 °C. FT-IR (KBr, ν, cm^{-1}): 3433, 3394, 3179 (NH, NH_2), 3062 (CH), 2923 (CH), 1681 (CO), 1600 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.62 (s, 3H, CH_3), 926 (s. br., 2H, NH_2), 7.14-7.99 (m, 15H, ArH's and pyridine H-5), 10.55 (s. br., 1H, NH). MS (EI, *m/z* (%)): 544 (M^+, 2.7), 305 (5), 303 (100), 227 (8), 126 (9), 117 (9), 81 (6). Anal. calcd. for $C_{30}H_{21}N_7O_2S$: C, 66.28; H, 3.89; N, 18.04; S, 5.90. Found: C, 66.12; H, 3.979; N, 1800; S, 6.10%.

2.2.21. Aryl carbamates (29a-c)

A mixture of **26** (2.26 g, 5 mmol) and the appropriate phenol, 4-nitrophenol or picric acid (5 mmol) in dry benzene (20 mL) refluxes for 4 h. The resulting solid, so formed, was collected and recrystallized from ethanol to give **29a-c**, respectively, (Scheme 4).

Phenyl 3-amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-ylcarbamate (**29a**): Color: Brown. Yield: 73%. M.p.: 226-228 °C. FT-IR (KBr, ν, cm^{-1}): 3271, 3190 (NH_2), 3062 (CH), 2974, 2939 (CH), 1700 (CO), 1627 (C=N), 1593 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.62 (s, 3H, CH_3), 5.23 (s, 1H, pyrazole H-4), 6.88-7.89 (m, 18H, ArH's, pyridine H-5, NH, NH_2). MS (EI, *m/z* (%)): 518 (M^+, 0.1), 310 (31), 308 (100), 280 (18), 265 (5), 208 (18), 204 (14), 203 (24), 202 (20), 154 (9), 128 (15), 105 (41), 77 (18). Anal. calcd. for $C_{29}H_{22}N_6O_2S$: C, 67.17; H, 4.28; N, 16.21; S, 6.18. Found: C, 67.17; H, 4.28; N, 16.21; S, 6.18%.

4-Nitrophenyl 3-amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-ylcarbamate (**29b**): Color: Yellow. Yield: 79%. M.p.: >300 °C. FT-IR (KBr, ν, cm^{-1}): 3352 (NH), 3059 (NH_2), 2922, 2854 (CH), 1667 (CO), 1594 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.63 (s, 3H, CH_3), 7.15-7.66 (m, 16H, ArH's, pyridine H-5, NH, NH_2), 8.30-8.32 (d, 2H, *J* = 8 Hz, ArH's). MS (EI, *m/z* (%)): 564 (M+1, 7), 551 (16), 548 (6), 533 (9), 494 (7), 478 (10), 463 (10), 419 (7), 400 (5), 382 (7), 363 (11), 323 (12), 273 (12), 239 (13), 218 (10), 197 (10), 179 (11), 155 (13), 138 (20), 123 (22), 113 (19), 111 (38), 97 (15), 93 (31), 86 (14), 62 (33). Anal. calcd. for $C_{29}H_{21}N_7O_4S$: C, 61.80; H, 3.76; N, 17.40; S, 5.69. Found: C, 61.80; H, 3.76; N, 17.40; S, 5.69%.

2,4,6-Trinitrophenyl 3-amino-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-b]pyridin-2-ylcarbamate (**29c**): Color: Yellow. Yield: 74%. M.p.: >300 °C. FT-IR (KBr, ν, cm^{-1}): 3352 (NH), 3059 (NH_2), 2922, 2854 (CH), 1667 (CO), 1594 (C=C). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.62 (s, 3H, CH_3), 7.15-7.89 (m, 14H, ArH's, pyridine H-5, NH, NH_2), 9.14 (s, 2H, ArH's). MS (EI, *m/z* (%)): 653 (M^+, 0.1), 460 (10), 445 (13), 255 (9), 216 (5), 122 (7), 105 (100), 77 (24). Anal. calcd. for $C_{29}H_{19}N_9O_8S$: C, 53.29; H, 2.93; N, 19.29; S, 4.91. Found: C, 53.42; H, 3.12; N, 19.419; S, 5.00%.

3. Results and discussion

Treatment of 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-phenyl-prop-2-en-1-one (**1**) with thiosemicarbazide in boiling ethanolic sodium hydroxide gave 4,5-dihydro-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-5-phenyl-pyazole-1-carbothioamide (**2**). Compound **2** reacted with the appropriate hydrazonoyl halides in boiling ethanol containing catalytic amount of triethylamine gave 1-(2-(4,5-dihydro-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-5-phenylpyrazol-1-yl)-4-methyl-thiazol-5-yl)-2-phenyldiazene (**4a**) and 1-(2-(4,5-dihydro-3-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-5-phenylpyrazol-1-yl)-4-phenylthiazol-5-yl)-2-phenyldiazene (**4b**), respectively (Scheme 1).

Structures **4a** and 4**b** were confirmed by elemental analyses, spectral data, and alternative synthetic routes. Thus, benzenediazonium chloride reacted with each of 4-(4,5-dihydro-1-(4-methylthiazol-2-yl)-5-phenyl-1*H*-pyrazol-3-yl)-5-methyl-1-phenyl-1*H*-1,2,3-triazole (**3a**) and 4-(4,5-dihydro-5-phenyl-1-(4-phenylthiazol-2-yl)-1*H*-pyrazol-3-yl)-5-methyl-1-phenyl-1*H*-1,2,3-triazole (**3b**), which prepared via reaction of **2** with the appropriate chloroacetone or ω-bromoacetophenone, in pyridine to give a product identical in all aspects (m.p., mixed m.p., and spectra) with **4a** and **4b**, respectively (Scheme 1).

Condensation of compound **1** with ethyl acetoacetate in presence of ammonium acetate in acetic acid afforded the corresponding ethyl 2-methyl-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenylpyridine-3-carboxylate (**5**) (Scheme 2). Similarly, the reaction of compound **1** with malononitrile, ethyl cyanoacetate, cyanoacetamide, benzoylacetonitrile, 2-cyanothioacetamide, 3-methyl-1*H*-pyrazol-4-one or 1-phenyl-3-methyl-1*H*-pyrazol-4-one yielded the corresponding pyridine derivatives **6-10,** 3-methyl-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (**11a**) and 3-methyl-6-(5-methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-1,4-di-phenyl-1*H*-pyrazolo-[3,4-*b*]pyridine (**11b**) in good yields, respectively (Scheme 2). The structures of the synthesized compounds were confirmed on the basis of their elemental analysis and alternative synthetic route. Thus, one pot reaction of 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone, benzaldehyde, appropriate ethyl acetoacetate, malononitrile, ethyl cyanoacetate, cyanoacetamide, benzoylacetonitrile, cyano-thioacetamide, 3-methyl-1*H*-pyrazol-4-one or 1-phenyl-3-methyl-1*H*-pyrazol-4-one and excess ammonium acetate in n-butanol gave identical product in all aspects (mp., mixed mp. and spectra) with corresponding compounds **5**-**11** (Scheme 2). 2-(5-Methyl-1-phenyl-1H-1,2,3-triazol-4-yl)-4-phenyl-6-substituted pyridine **12a-f** were also prepared in good yield by Krohnke reaction *via* tratment of **1** with 1-(2-oxo-2-substituted ethyl)-pyridinium bromides in glacial acetic acid.

2-Mercapto-6-(5-methyl-1-phenyl-*1*H-1,2,3-triazol-4-yl)-4-phenyl-pyridine-3-carbonitrile (**10**) was reacted with each of ethyl chloroacetate, chloroacetone, ω-bromoacetophenone, chloroacetonitrile or iodomethane gave corresponding S-alkylated derivatives **13a-f**, respectively. Structures **13a-f** were elucidated by elemental analysis, spectral data and chemical transformation. Thus, boiling pyridine derivatives in ethanol in presence of catalytic amount of piperidine afforded 2-substituted 6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-*b*]pyridin-3-amine derivatives **14a-c**, respectively (Scheme 3).

Structures **14e** was converted to 2-(5-methyl-1-phenyl-1*H*-[1,2,3]triazol-4-yl)-4-phenyl-7*H*-9-thia-1,5,7-triaza-fluoren-8-one (**15**) and 2-(5-methyl-1-phenyl-1*H*-[1,2,3]triazol-4-yl)-4-phenyl-9-thia-1,5,7-triaza-fluoren-8-ylamine (**16**) by its boiling in formic acid and formamide, respectively. Also, compound **14e** reacted with triethyl orthoformate in acetic anhydride

gave ethyl *N*-[2-cyano-6-(5-methyl-1-phenyl-1*H*-[1,2,3]triazol-4-yl)-4-phenyl-thieno[2,3-*b*]pyridin-3-yl]-formimidate (**17**), which was converted to **16** with ammonia (Scheme 3).

Also, compound **15** was converted to 8-chloro-2-(5-methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-9-thia-1,5,7-triaza-fluorene (**18**) by reaction with phosphrous oxychloride. The chloro derivative **18** was reacted with sodium azide and hydrazine hydrate gave 8-azido-2-(5-methyl-1-phenyl-1H-[1,2,3]triazol-4-yl)-4-phenyl-9-thia-1,5,7-triazafluorene (**19**) and [2-(5-methyl-1-phenyl-1*H*-[1,2,3]triazol-4-yl)-4-phenyl-9-thia-1,5,7-triaza-fluoren-8-yl]-hydrazine (**20**) in a good yield. The later was converted to 8-(5-methyl-1-phenyl-1*H*-[1,2,3]triazol-4-yl)-6-phenyl-10-thia-1,2,3,3a,5,9-hexaaza-cyclopenta[a]fluorene (**21**) by reaction with nitrous acid at 0 ^{o}C.

On the other hand, treatment of **14a** with hydrazine hydrate gave 3-amino-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenylthieno-[2,3-*b*]pyridine-2-carbohydrazide (**22**). Structure of **22** was confirmed by elemental analysis, spectral data and chemical transformation. Thus, **22** was reacted with each of ethyl acetoacetate, acetylacetone or nitrous acid afforded 2-[3-amino-6-(5-methyl-1-phenyl-1*H*-[1,2,3]triazol-4-yl)-4-phenylthieno[2,3-*b*]pyridine-2-carbonyl]-5-methyl-2,4-dihydro-pyrazol-3-one (**23a**), [3-amino-6-(5-methyl-1-phenyl-1*H*-[1,2,3]triazol-4-yl)-4-phenyl-thieno[2,3-*b*]-pyridin-2-yl]-(3,5-dimethyl-pyrazol-1-yl)-methanone (**23b**) and (3-amino-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenylthieno[2,3-*b*]-pyridin-2-yl)azidomethanone (**26**), respectively (Scheme 4). Structures **23** were elucidated by elemental analysis, spectral data and chemical transformation. Thus, benzenediazonium chloride was reacted with **23a** and **23b** in ethanolic sodium acetate solution at 0 ^{o}C afforded 2-[3-amino-6-(5-methyl-1-phenyl-1*H*-[1,2,3]triazol-4-yl)-4-phenylthieno[2,3-*b*]pyridine-2-carbonyl]-5-methyl-4-(phenyl-hydrazono)-2,4-dihydro-pyrazol-3-one (**24a**) and [3-amino-6-(5-methyl-1-phenyl-1*H*-[1,2,3]triazol-4-yl)-4-phenyl-thieno[2,3-*b*]pyridin-2-yl]-(3,5-dimethyl-4-phenylazoyrazol-1-yl)-methanone (**24b**), respect-tively. Also, compounds **24a**,**b** were obtained by reaction of **22** with the appropriate of ethyl 2-(2-phenylhydrazono)-3-oxobutanoate (**25a**) and 3-(2-phenylhydrazono)pentane-2,4-dione (**25b**), respectively.

Compound **26** was reacted with the appropriate aniline, 4-toluidine, 4-anisidine, 3-amino-5-phenylpyrazole, anthranilc acid, phenol, 4-nitrophenol or picric acid afforded urea derivatives **27a-d**, 3-(3-amino-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenylthieno-[2,3-*b*]pyridin-2-yl)quinazoline-2,4(1*H*,3*H*)-dione (**28**) and aryl 3-amino-6-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-phenylthieno-[2,3-*b*]pyridin-2-ylcarbamate **29a-c**, respectively.

4. Conclusion

The present work describes the synthesis of 5-arylazothiazole, pyridine and thieno[2,3-*b*]pyridine derivatives contaninig 1,2,3-triazole moiety in a good yields by reaction of 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-phenylprop-2-en-1-one and different reagents.

References

[1]. Grosscurt, A. C.; Hes, R. V.; Wellinga, K. *J. Agric. Food Chem.* **1979**, *27*, 406-409.
[2]. Keats, G. H. *Brit. Pat.* 1, *209*, *631*, (1970); *Chem. Abstr.* 1971, 74, 141787b.
[3]. Kedar, R. M.; Vidhale, N. N.; Chincholkar, M. M. *Orient. J. Chem.* **1997**, *13*, 143-148.
[4]. Singh, A.; Rathod, S.; Berad, B. N.; Patil, S. D.; Dosh, A. G. *Orient. J. Chem.* **2000**, *16*, 315-317.
[5]. Khalil, Z. H.; Yanni, A. S. *J. Indian Chem. Soc.* **1981**, *58*, 168-170.
[6]. Das, N. B.; Mittra, A. S. *Indian J. Chem.* **1978**, *16B*, 638-640.
[7]. Regaila, H. A.; El-Bayouki, A. K.; Hammad, M. *Egypt J. Chem.* **1977**, *20*, 157-166.
[8]. Raman, K.; Pandey, B. R.; Barthwal, J. P.; Parmar, S. S. *Eur. J. Med. Chem. Ther.* **1980**, *15*, 567-569.
[9]. Husain, M. I.; Shukla, S. *Indian J. Chem.* **1985**, *24B*, 761-764.
[10]. Tomilovi, Y. V.; Okonnishnikova, G. P.; Shulishov, E. V.; Nefedov, O. M. *Russ. Chem. Bull.* **1995**, *44*, 2114-2117.
[11]. Klimova, E. I.; Garcia; M. M.; Berestneva, T. K.; Toledano, C. A.; Toskano, R. A.; Ramierz, L. R. *J. Organomet. Chem.* **1999**, *585*, 106-114.
[12]. Azarifar, D.; Ghasemnejad, H. *Molecules* **2003**, *8*, 642-648.
[13]. Padmavathi, V.; Sumathi, R. P.; Babu, N. C.; Bhaskar, D. *J. Chem. Res.* **1999**, *10*, 610-611.
[14]. Reddy, D. B.; Babu, N. C.; Padmavathi, V.; Sumathi, R. P. *Synthesis* **1998**, *3*, 491-494.
[15]. Gillespie, E.; Dungan, K. W.; Gomol, A. W.; Seidehamel, R. *Int. J. Immunopharmacol.* **1985**, *7*, 655-660.
[16]. Bol'but, A. V.; Vovk, M. V. Abstracts of International Confeerence on the Chemistry of Nitrogen Containing Heterocycles, CNH-2003, Kharkiv (Ukraine), 2003, pp. 68.
[17]. Allan, J. D.; Eliopoulos, G. M.; Reiszner, E.; Moellering, R. C. *Antimicrob Agents Chemoth.* **1987**, *31*, 1997-2001.
[18]. Khalil, Z. H.; Geies, A. A. *Phosphorus, Sulfur, Silicon and Relat. Elem.* **1991**, *60*, 223-231.
[19]. Hozien, Z. A.; Abdel-Wahab, A. A.; Hassan, K. M.; Atta, F. M.; Ahmed, S. A. *Pharmazie* **1997**, *52*, 753-758.
[20]. Munchhof, M. J.; Sobolov-Jaynes, S. B.; Marx, A. M. (Pfizer Inc., USA) U. S. Pat. 6, 492, 83 (Cl. 514-301; A61K31/44); *Chem. Abstr.* 2003, 138, 24721e.
[21]. Kharizomenova, I. A.; Grinev, A. N.; Samsonova, N. V.; Panisheva, E. K.; Kaplina, N. V.; Nikolaeva, I. S.; Pushkina, T. V.; Pershin, G. N. *Khim. Farm. Zh.* **1981**, *15(9)*, 40-44.
[22]. Kaplina, N. V.; Grinev, A. N.; Bogdanova, G. A.; Alekseeva, L. N.; Pushkina, T. V.; Fomina, A. N. *Khim. Farm. Zh.* **1987**, *21(2)*, 197-200.
[23]. Pathak, U. S.; Alagarsamy, V. *Acta Pharm. Turc.* **1999**, *41*, 37-41.
[24]. Ismail, M. A. -H.; Aboul-Einein, M. N. Y.; Abouzid, K. A. M.; Kandil, S. B. A. *Alexandria J. Pharm. Sci.* **2002**, *16*, 143-151.
[25]. Ninomya, K.; Nitsuta, K.; Tobe, A.; Egawa, M.; Kikumoto, R. (Mitsubishi Chem Ind) Jpn. Kokai Tokkyo Koho Jp 06 16, 55794 16, 557; *Chem. Abstr.* 1994, 120, 290120.
[26]. Shishoo, C. J.; Shirsath, V. S.; Rathod, I. S.; Yande, V. D. *Eur. J. Med. Chem.* **2000**, *35*, 351-358.
[27]. Moneer, A. A. *Bull. Fac. Pharm. (Cairo Univ.)* **2001**, *39*, 27-34.
[28]. Ammar, Y. A.; Ismail, M. M.; El-Gaby, M. S. A.; Zahran, M. A. *Indian J. Chem.* **2002**, *41B*, 1486-1491.
[29]. Chambhare, R. V.; Bobade, A. S.; Khadse, B. G. *Indian J. Heterocycl. Chem.* **2002**, *12*, 67-68.
[30]. Sayed, A. Z. *Adv. Colour Sci. Techn.* **2002**, *5*, 24-30.
[31]. Shah, M.; Patel, P.; Parekh, H. *Orient. J. Chem.* **2002**, *18*, 159-161.
[32]. Oganisyan, A. Kh.; Noravyan, A. S.; Dzhagatspanyan, I. A.; Melikyan, G. G. *Pharm. Chem. J.* **2003**, *37*, 13-14.
[33]. Abdelhamid, A. O.; Afifi, M. A. M. *Phosphorus, Sulfur, Silicon and Rela. Elem.* **2008**, *183*, 2703-2713.
[34]. Abdelhamid, A. O.; Afifi, M. A. *Synth. Commun.* **2010**, *40*, 1539-1550.
[35]. Abdelhamid, A. O.; Abdelall, E. K. A.; Zaki, Y. H. *J. Heterocycl Chem.* **2010**, *47*, 477- 482.
[36]. Abdelhamid, A. O. *J. Heterocycl. Chem.* **2009**, *46*, 680-686.
[37]. Abdelhamid, A. O.; Abdelall, E. K. A.; Abdel-Riheem, N. A.; Ahmed, S. A. *Phosphorus, Sulfur, Silicon and Relat. Elem.* **2010**, *185*, 709-718.
[38]. Abdelhamid, A. O.; Afifi, M. A. *J. Adv. Res.* **2010**, *1*, 137-144.
[39]. Abdelhamid, A. O.; Fahmi, A. A.; Halim, K. M. N. *Eur. J. Chem.* **2011**, *2(3)*, 317-323.
[40]. Abdelhamid, A. O.; Fahmi, A. A.; Ali, A. B. *Eur. J. Chem.* **2011**, *2(4)*, 544-551.
[41]. Abdelhamid, A. O.; Shokry, S. A.; Tawfiek, S. M. *J. Heterocycl. Chem.* **2012**, *49*, 116-124.
[42]. Shawali, A. S.; Abdelhamid, A. O. *Bull. Soc. Japan* **1976**, *49*, 321-332.
[43]. Eweiss, N. F.; Osman, A. *J. Heterocycl. Chem.* **1980**, *17*, 1713-1717.
[44]. Wang, H. C.; Li, R. S.; Dong, H. R.; Dong, H. S. *Indian J. Chem.* **2010**, *49B*, 521-525.
[45]. Dong, H. S.; Wang, H. C.; Gao, Z. L.; Li, R. S.; Cui, F. H. *J. Heterocycl. Chem.* **2010**, *47*, 389-395.
[46]. Bellamy, L. J. The infrared Spectra of Complex Molecules, 3th edition, Published by Chapman and Hall Ltd. London EC4p 4EE, 1975, pp. 305.