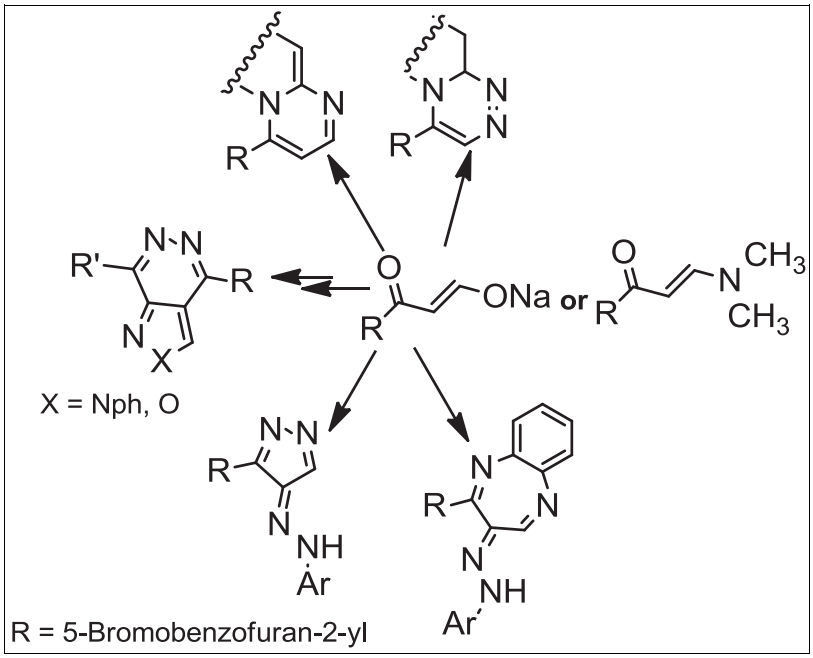
Useful Precursors for Synthesis of Some New Azolo[3,4-*d*]pyridiazines, Azolo[1,5-*a*]pyrimidines, Azolo[5,1-*c*]triazines, Pyrazoles, and Benzo[b][l,4]diazepine

Abdou O. Abdelhamid,* Abdelgawad A. Fahmi, and Basma S. Baaiu

Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt
*E-mail: Abdelhamid45@gmail.com

Received April 22, 2015
DOI 10.1002/jhet.2507
Published online 00 Month 2015 in Wiley Online Library (wileyonlinelibrary.com).



Pyrazolo[3,4-*d*]pyridazines, isoxazolo[3,4-*d*]pyridazines, azolo[1,5-*a*]pyrimidines, azolo[5,1-*c*]triazines, pyrazoles, and benzo[*b*][l,4]diazepine were synthesized from the appropriate hydrazonoyl halides, hydroximoyl halides, heterocyclic amines, diazotized heterocyclic amines, arenediazonium chlorides, and *o*-phenylenediamines with appropriate of sodium 3-(5-bromobenzofuran-2-yl)-3-oxoprop-1-en-1-olate or 1-(5-bromobenzofuran-2-yl)-3-(dimethylamino)prop-2-en-1-one. The newly synthesized compounds were elucidated by elemental analyses, spectral data, and alternative synthesis whenever possible.

J. Heterocyclic Chem., **00,** 00 (2015).

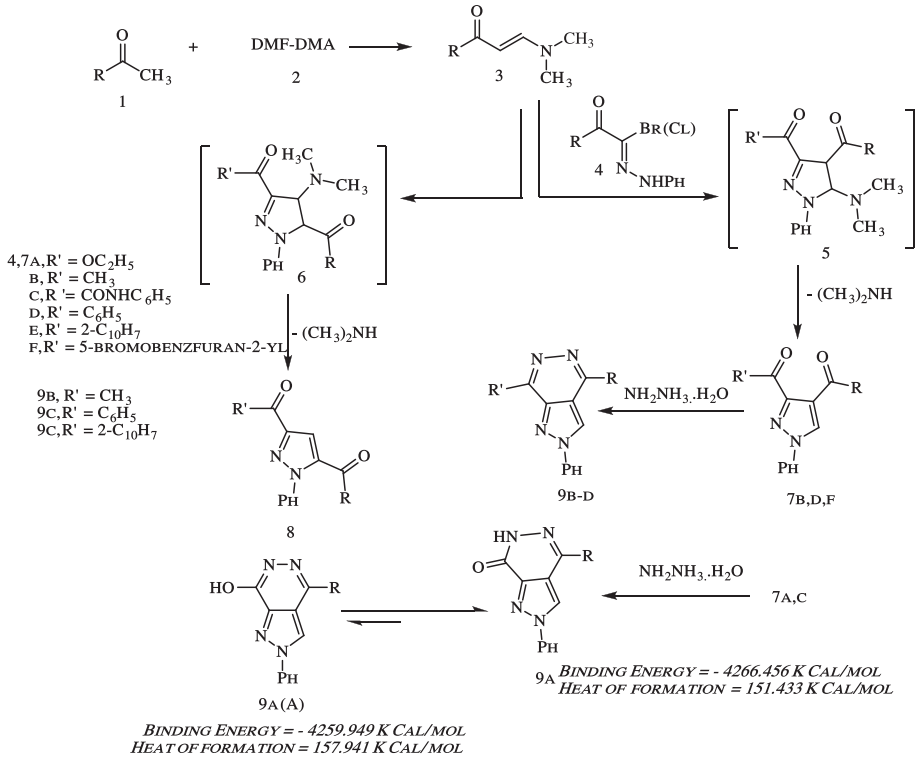
INTRODUCTION

Pyrazolo[l,5-*a*]pyrimidines, which are purine analogues proved to have wide varieties of useful pharmaceutical activities such as antitrypanisommal activity [1], antischistosomal activity [2], activity as HMG-CoA reductase inhibitors [3], COX-2 selective inhibitors [4], AMP phosphodiesterase inhibitors [5], KDR kinase inhibitors [6], selective peripheral benzodiazepine receptor ligands [7], and as antianxiety agents [8] and oncological agents [4,9], have been reported. Also, several pyrazolotriazines and triazolotriazines, as adenine analogues, were used as antagonists, antischistosomal, and antitumor agents [10–12]. Pyridazine compounds have been reported to possess varied biological agents such as antimicrobial [13], antihypertensive [14], anticancer [15], anti-inflammatory [16], and antifungal activities [17]. Also, pyrazole derivatives are important intermediates in organic synthesis and possess a range of interesting biological and antimicrobial properties [18–25]. Their fused pyrimidine derivatives are used as dyes [26–30]. In continuation of our work concerned with the synthesis of a variety of heterocyclic systems for biological evaluation [31–35], we report herein the synthesis of some new Azolo[3,4-*d*]pyridazines, Azolo[1,5-*a*]pyrimidines, Azolo[5,1-*c*]triazines, pyrazoles, and Benzo[*b*][l,4]diazepine an 5-bromobenzofuran moiety.

RESULTS AND DISCUSSION

Treatment of *C*-ethoxycarbonyl-*N*-phenylhydrazonoyl chloride (**4a**) with 1-(5-bromobenzofuran-2-yl)-3-(dimethylamino) prop-2-en-1-one (**3**), which prepared from 5-bromobenzofuran-2-ylethanone (**1**) and DMF–DMA in boiling xylene, containing triethylamine under refluxed afforded one isolable product according to *TLC*, formulated as ethyl 4-(5-bromobenzofuran-2-oyl)-1-phenyl-1*H*-pyrazole-3-carboxylate (**7a**) and not ethyl 5-(5-bromobenzofuran-2-oyl)-1-phenyl-1*H*-pyrazole-

Scheme 1. Synthesis of pyrazoles **7a–f** and pyrazolo[3,4-*d*]pyridazines **9a–d**.



3-carboxylate (**8a**) (Scheme 1). Structure **7a** was elucidated on elemental analysis, spectral data, and chemical transformation. ^{1}H NMR spectrum of **7a** showed signals at $\delta = 1.15$–1.19 and 4.17–4.21 ppm, a triplet and a quartet, are due to methyl and methylene of ethyl group, respectively; the signals at 7.27–7.31, 7.53–7.55, 7.77–7.88, 7.89–7.91, and 8.01–8.32 ppm correspond to the nine aromatic protons of phenyl and 5-bromobenzofuran-2-yl rings, while at 8.57 ppm, a singlet is due to H-5 of pyrazole.

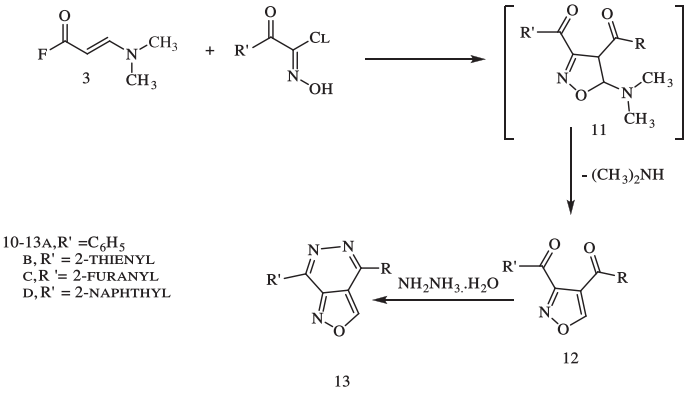
Thus, treatment of **7a** with hydrazine hydrate in boiling ethanol afforded 4-(5-bromobenzofuran-2-yl)-2-phenyl-2,6-dihydro-pyrazolo[3,4-*d*]-pyridazin-7-one (**9a**). Structure of **9a** was elucidated by elemental analysis, spectral data, and alternative synthesis. Structure **9a** may be two isomers A and B, but according to the result of molecular calculation using "Hyper Chem.," it is indicated that the isomer A is major. ^{1}H NMR spectrum of **9a** showed signals at $\delta = 7.33$–7.62 ppm are due to the nine aromatic protons of phenyl and 5-bromobenzofuran-2-yl rings; for the signals at 8.24 ppm, a singlet is due to H-5 pyrazole, while at 12.32 ppm, a singlet is due to NH group. Also, treatments of **7c** with hydrazine hydrate in boiling ethanol give a product identical in all aspects (mp, mixed mp, and spectra) with **9a**. Similarly, the appropriate hydrazonoyl halides **4b–f** were reacted with **3**, and gave 1-phenyl-3-substituted-4-(5-bromobenzofuran-2-carbonyl)pyrazoles **7b–f**. Pyrazolo[3,4-*d*]pyridazines **9b–d** were obtained from pyrazoles **7b**, **7d**, and **7e** with hydrazine hydrate in boiling ethanol (Scheme 1).

Analogously, treatment of the appropriate hydroximoyl chlorides **10a–d** with **3** and triethylamine in toluene at room temperature gave 3,4-diacylisoxazoles **12a–f**. Structures **12a–f** were elucidated by elemental analysis, spectral data, and chemical transformation. Compounds **12a–f** were converted to isoxazolo[3,4-*d*] pyridazines **13a–f** by boiling in hydrazine hydrate (Scheme 2).

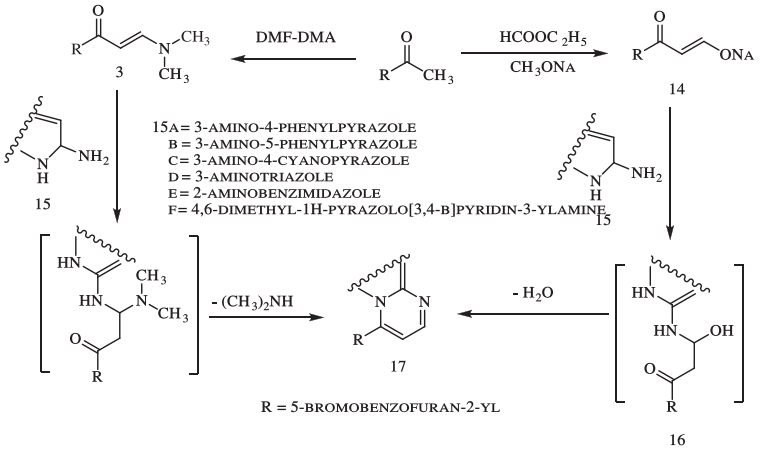
5-Bromobenzofuran-2-ylethanone (**1**) was reacted with ethyl formate in dried ether containing sodium methoxide and afforded sodium 3-(5-bromobenzofuran-2-yl)-3-oxoprop-1-en-1-olate (**14**). Structure **14** was confirmed by its reactions. Thus, treatment of **14** with 3-amino-4-phenyl-1*H*-pyrazole (**15a**) in acetic acid containing piperidine acetate afforded a product, namely 7-(5-bromobenzofuran-2-yl)-2-phenylpyrazolo[1,5-*a*]pyrimidine (**17a**) (Scheme 3).

Structure **17a** was elucidated by elemental analysis, spectral data, and an alternate synthetic route. The ^{1}H NMR spectrum of **17a** showed signals at $\delta = 6.92$, 7.34–7.81, 8.91–8.92 ppm corresponding to the 11 aromatic protons of phenyl and 5-bromobenzofuran-2-yl rings, while at 8.32 ppm, a singlet is due to H-5 pyrazole. Thus, treatment of 1-(5-bromobenzofuran-2-yl)-3-(dimethylamino)prop-2-en-1-one (**3**) with 3-amino-4-phenylpyrazole in acetic acid

Scheme 2. Synthesis of isoxazoles **11a–d** and isooxazolo[3,4-*d*]pyridazines **13a–d**.



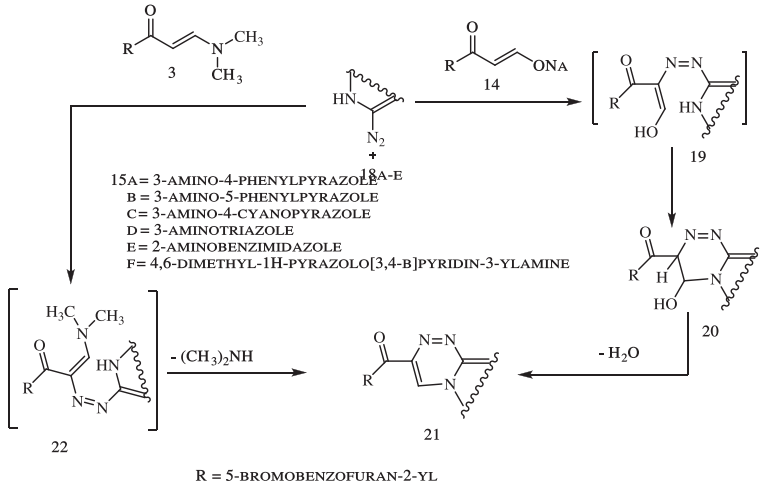
Scheme 3. Synthesis of pyrazolo[1,5-*a*]pyrimidines **17a–c**, triazolo[1,5-*a*]pyrimidine **17d**, imidazo[1,2-*a*]benzimidazole **17e**, and pyrido[2′,3′:3,4]pyrazolo [1,5-*a*]pyrimidine **17f**.



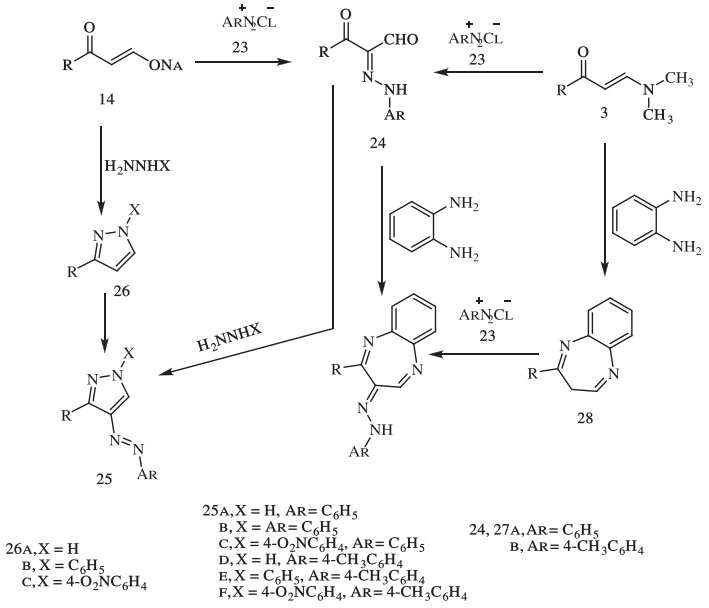
and ammonium acetate by heating under reflux gave a product identical in all aspects (mp, mixed mp, spectra) with **17a**. Analogously, compound **14** was reacted with the appropriate heterocyclic amines (3-amino-5-phenylpyrazole **15b**, 3-amino-4-cyanopyrazole **15c**, 3-amino-1,2,4-triazole **15d**, 2-aminobenzimidazole **15e**, or 4,6-dimethyl-1*H*-pyrazolo[3,4-*b*] pyridin-3-ylamine (**15f**) gave 7-(5-bromobenzofuran-2-yl)-2-phenylpyrazolo[1,5-*a*]pyrimidine **(17b),** 7-(5-bromobenzofuran-2-yl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**17c**), 5-(5-bromobenzofuran-2-yl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (**17d**), 4-(5-bromo-benzofuran-2-yl)-benzo[4,5]imidazo[1,2-*a*]pyrimidine (**17e**), and 8-(5-bromo-benzofuran-2-yl)-2,4-dimethyl-1,5,8a,9-tetraaza-fluorene (**17f**). Treatment of the diazotized 3-amino-4-phenylpyrazole (**18a**) with sodium 3-(5-bromobenzofuran-2-yl)-3-oxoprop-1-en-1-olate (**14**) in ethanolic sodium acetate solution gave (5-bromobenzofuran-2-yl)(7-phenylpyrazolo[5,1-*c*][1,2,4]triazin-3-yl)methanone (**21a**) in good yield. Structure **21a** was elucidated by elemental analysis, spectral data, and alternative synthetic route. The formation of **21a** accorded via coupling diazonium chloride of **18a** to **3** to form the intermediate **19**, which converted to **20**. The later afforded the final product **21** through elimination of one molecule of water. Meanwhile, treatment **3** with **18a** in ethanolic sodium acetate as buffer solution gave a product identical in all aspects (mp, mixed mp, and spectra) with **21a** (Scheme 3). Analogously, treatment of the appropriate diazonium salts **18b–e** with **3** or **14** in ethanolic sodium acetate afforded (5-bromobenzofuran-2-yl)(8-phenylpyrazolo[5,1-*c*][1,2,4] triazin-3-yl)methanone (**21b**), 3-(5-bromo-benzofuran-2-carbonyl)-pyrazolo[5,1-*c*][1,2,4]triazine-8-carbonitrile (**21c**), 5-bromo-benzofuran-2-yl)-[1,2,4]triazolo[5,1-*c*][1,2,4]triazin-6-yl-methanone (**21d**), benzo[4,5]imidazo[2,1-*c*][1,2,4]triazin-3-yl-(5-bromo-benzofuran-2-yl)-methanone (**21e**), and (5-bromo-benzofuran-2-yl)-(6,8-dimethyl-1,2,4a,5,9-pentaazafluoren-3-yl)-methanone (**21f**) (Scheme 4).

Moreover, treatment of **14** or **3** with each of benzenediazonium chloride and 4-methylbenzenediazonium chloride in ethanol containing sodium acetate as a buffer solution yielded 3-(5-bromobenzofuran-2-yl)-3-oxo-2-(2-phenylhydrazono)propanal **(24a)** and 3-(5-bromobenzofuran-

Scheme 4. Synthesis of pyrazolo[5,1-*c*]triazine **21a–c**, triazolo[5,1-*c*]triazine **21d**, imidazo[2,1-*c*]triazine **21e**, and pyrido[2′,3′:3,4]pyrazolo[5,1-*c*]triazine **21f**.



Scheme 5. Synthesis of pyrazoles **25a–f**, **26a–c**, and 3*H*-benzo[b][1,4]diazepines **28a**,**b**.



2-yl)-3-oxo-2-(2-(p-tolyl)hydrazono)propanal **(24b)**, respectively (Scheme 5). Structure **24** was confirmed by elemental analysis, spectral data, and chemical transformation. Thus, ^{1}H NMR spectrum of **24a** showed signal at $\delta = \delta = 6.66$ (s, 1H, $J = 6.0$ Hz, ArH), 7.19–7.85 (m, 8H, ArH's), 9.92 (s, 1H, CHO), and 14.85 (s, br., 1H, NH). Also, **24a** was reacted with each of hydrazine hydrate, phenylhydrazine, and 4-nitrophenylhydrazine in boiling ethanol under refluxed to give 3-(5-bromobenzofuran-2-yl)-4-(2-phenylhydrazono)-4*H*-pyrazole **(25a)**, 3-(5-bromobenzofuran-2-yl)-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazole **(25b)**, and 3-(5-bromobenzofuran-2-yl)-1-(4-nitrophenyl)-4-(phenyldiazenyl)-1*H*-pyrazole **(25c)**, respectively (Scheme 5). On the other hand, **14** was reacted with each of hydrazine hydrate, phenylhydrazine, or 4-nitrophenylhydrazine to afford 3-(5-bromobenzofuran-2-yl)-l*H*-pyrazole **(26a)**, 3-(5-bromobenzofuran-2-yl)-l-phenyl-l*H*-pyrazole **(26b)**, and 3-(5-bromobenzofuran-2-yl)-l-(4-nitrophenyl)-l*H*-pyrazole **(26c)**. Compound **26a** was reacted with benzenediazonium chloride in ethanolic sodium acetate solution and afforded a product identical in all respect (mp, mixed mp, and spectra) with **25a**. Compounds **25d** and **25c** were obtained by treatment of each **26b** and **26c** with benzenediazonium chloride in ethanolic sodium acetate at 0°C. Similarly, compounds **25d–f** were obtained by coupling 4-methylbenzenediazonium chloride with each **26a–c** in ethanolic sodium acetate solution at 0°C.

Finally, compounds **24a** and **24b** were reacted with *o*-phenylenediamine in boiling ethanol to afford 2-(5-bromobenzofuran-2-yl)-3*H*-benzo[*b*][l,4]diazepin-3-ylidene)-2-phenylhydrazine **(27a)** and 2-(5-bromobenzofuran-2-yl)-3*H*-benzo[*b*][l,4]diazepin-3-ylidene)-2-*p*-tolylhydrazine **(27b)**. Structures of **27a** and **27b** were confirmed by elemental analysis, spectral data, and alternative synthetic route. Thus, **3** or **14** was reacted with *o*-phenylenediamine and afforded 2-(5-bromobenzofuran-2-yl)-3*H*-benzo[*b*][l,4]-diazepine **(28)** in a good yield. The latter reacted with benzenediazonium chloride in ethanolic sodium acetate gave a product identical in all aspects (mp, mixed mp, and spectra) with **27a**.

CONCLUSION

In conclusion, 1-(5-bromobenzofuran-2-yl)-3-(dimethylamino) prop-2-en-1-one (**3**) or 3-(5-bromobenzofuran-2-yl)-1-substituted 4-(*p*-tolyldiazenyl)-1*H*-pyrazole (**14**) proved to be useful precursors for synthesis of various fused heterocycles via their reactions with hydrazonoyl halides, hydroximoyl chlorides, heterocyclic amines (4-aminopyrazole, 5-aminopyrazoles, 3-aminotriazole, 2-aminobenzoimidazole), diazotized heterocyclic amines, and *o*-phenylenediamine. The structures of the newly synthesized compounds were confirmed by spectral data, alternate synthesis, and elemental analyses.

EXPERIMENTAL

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 (Shimadzu, Tokyo, Japan). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ solutions on a Varian Mercury VX-300 NMR. ^{1}H NMR spectra were run at 300 MHz and ^{13}C spectra were run at 75.46 MHz spectrometer (Pullman, WA), 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 (Shimadzu), operating at 70 eV. Elemental analyses were carried out at Microanalytical Center of the University of Cairo, Giza, Egypt. Hydrazonoyl halide [36–41] and hydroximoyl halides [42–45] were prepared as previously reported.

l-(5-Bromobenzofuran-2-yl)-3-(dimethylamino)prop-2-en-l-one (3). A mixture of l-(5-bromobenzofuran-2-yl) ethanone (2.4 g, 10 mmol) and dimethylformamide–dimethylacetal (1.19 g, 10 mmol) in dry xylene (30 mL) was boiled under reflux for 3 h. Then, the solvent was evaporated and triturated with petroleum ether at 40–60°C. The resulting solid was collected and recrystallized from ethanol to give **3** (Tables 1 and 2).

Synthesis of pyrazoles 7a–d and isoxazoles 12a–d. Equimolar amounts of l-(5-bromobenzofuran-2-yl)-3-(dimethylamino) prop-2-en-l-one **(3)** (1.47 g, 5 mmol) and each of appropriate hydrazonoyl halides **4a–e** or hydroximoyl chlorides **10 a–d** (5 mmol) were refluxed in dry toluene (20 mL) containing triethylamine (0.75 mL) for 3 h. The hot solution was filtered off, and the filtrate was evaporated and triturated with petroleum ether (40–60°C). The resulting solid was collected and recrystallized from the proper solvent to give **7a–e** and **12a–d**, respectively (Tables 1 and 2).

Synthesis of pyrazolo[3,4-*d*]pyridazines 9a–d and isoxazolo [3,4-*d*]pyridazines 13a–d. Equimolar amount of each of the appropriate pyrazoles **7a–e** and appropriate isoxazoles **12a–d** (5 mmol) and hydrazine hydrate (1 mL, 99%) in ethanol (20 mL) was boiled under reflux for 2 h. The resulting solid was collected and crystallized from proper solvent to give pyrazolo[3,4-*d*]pyridazines **9a–d** and **13a–d** (Tables 1 and 2).

Synthesis of azolopyrimidines 17a–f. Method A: A mixture of 1-(5-bromobenzofuran-2-yl)-3-(dimethylamino)prop-2-en-1-one (**3**) (2.94 g, 10 mmol) and the appropriate heterocyclic amines **15a–f** (10 mmol) in acetic acid were stirred at room temperature for 2 h. The resulting solid was collected and recrystallized from the appropriate solvent to give **17a–f**, respectively.

Method B: A mixture of sodium salt **14** (2.87 g, 10 mmol) and the appropriate heterocyclic amines 1**5a–f** (10 mmol for each), in a solution of piperidenium acetate (piperidene (2.5 mL), water (5 mL), and acetic acid (2 mL)), were heated under refluxed for about 10 min; acetic acid (1.5 mL) was added to the reaction mixture while boiling; then the mixture was cooled, and the resulting solid was collected and recrystallized from the proper solvent to give **17a–f**, respectively (Tables 1 and 2).

Alternate synthetic routes of 17a. A mixture of 2-acetylfurane (**1**) (1.19 g, 5 mmol) and *N*,*N*-dimethyl-*N*′-(3-phenyl-1*H*-pyrazol-5-yl)formamidine (**13**) (1.06 g, 5 mmol) in ethanol (10 mL) was heated under reflux for 3 h. The resulting solid was collected and recrystallized from ethanol to give a product identical in all aspects (mp, mixed mp, and spectra) with **17a**.

Synthesis of azolotriazines 21a–f. ***General procedure.*** A solution of the appropriate diazonium salt of heterocyclic amine **19a–f** was added to a cold mixture of the appropriate **3** or **14** (5 mmol for each) and sodium acetate (0.41 g, 5 mmol) in ethanol (40 mL) at 0–5°C while stirring for 30 min. The reaction mixture was stirred for 3 h. The resulting solid was collected and recrystallized from the proper solvent to give **21a–d**, respectively (Tables 1 and 2).

3-(5-Bromobenzofuran-2-yl)-4-(2-phenylhydrazono)-4H-pyrazole (24a) 3-(5-bromobenzofuran-2-yl)-4-(2-(p-tolyl)hydrazono)-4H-pyrazole (24b). A solution of the appropriate arenediazonium chloride (5 mmol) was added to a cold solution of the appropriate of l-(5-bromobenzofuran-2-yl)-3-(dimethylamino)prop-2-en-l-one **(3)** or sodium

Table 1

Characterization data of the newly synthesized compounds.

Comp. no	Mp °C Solvent	Colour Yield %	Mol. formula Mol. Wt.	% Analysis Calcd / Found C	 H	 Br	 N
3	126-128	Yellow	$C_{13}H_{12}BrNO_2$	53.08	4.11	27.16	4.76
	EtOH	87	294.14	53.26	4.30	27.24	4.69
7a	88-91	Yellow	$C_{21}H_{15}BrN_2O_4$	57.42	3.44	18.19	6.38
	EtOH	65	439.26	57.39	3.32	18.00	6.51
7b	133.34	Pale yellow	$C_{20}H_{13}BrN_2O_3$	58.70	3.20	19.53	6.85
	AcOH	78	409.23	58.58	3.11	19.38	6.67
7c	133-35	Pale yellow	$C_{25}H_{16}BrN_3O_3$	61.74	3.32	16.34	8.64
	EtOH	78	486.32	61.81	3.14	16.34	8.75
7d	133-36	Pale yellow	$C_{25}H_{15}BrN_2O_3$	63.71	3.21	16.95	5.94
	AcOH	78	471.3	63.87	3.10	17.12	6.15
7e	147-150	Yellow	$C_{29}H_{17}BrN_2O_3$	66.81	3.29	15.33	5.37
	AcOH	86	521.37	66.65	3.02	15.45	5.18
7f	235-38	White	$C_{27}H_{14}Br_2N_2O_4$	54.94	2.39	27.08	4.75
	Dioxane	86	590.22	55.14	3.51	27.00	4.82
9a	>300	Pale yellow	$C_{19}H_{11}BrN_4O_2$	56.04	2.72	19.62	13.76
	Dioxane	84	407.22	56.12	2.65	19.71	13.67
9b	227-30	Pale yellow	$C_{20}H_{13}BrN_4O$	59.28	3.23	19.72	13.83
	AcOH	84	405.25	59.35	3.01	19.65	13.76
9c	240.42	Yellow	$C_{25}H_{15}BrN_4O$	64.25	3.24	17.10	11.99
	Dioxane	84	467.32	64.32	3.18	17.00	12.12
9d	255-58	Yellow	$C_{29}H_{17}BrN_4O$	67.32	3.31	15.44	10.83
	Dioxane	88	517.38	67.21	3.27	15.36	10.75
12a	148-50	Yellow	$C_{19}H_{10}BrNO_4$	57.60	2.54	20.17	3.54
	AcOH	81	396.19	57.69	2.45	20.00	3.42
12b	186-88	Brown	$C_{17}H_8BrNO_4S$	50.76	2.00	19.87	3.48
	Dioxane	82	402.22	50.65	2.11	19.75	3.34
12c	196-198	Green	$C_{17}H_8BrNO_5$	52.88	2.09	20.69	3.63
	AcOH	83	386.15	52.93	2.17	20.78	3.43
12d	166-68	Brown	$C_{23}H_{12}BrNO_4$	61.90	2.71	17.91	3.14
	AcOH	84	446.25	62.08	2.67	17.80	3.00
13a	184-186	Deep yellow	$C_{19}H_{10}BrN_3O_2$	58.18	2.57	20.37	10.71
	AcOH	89	392.21	58.00	2.71	20.21	10.80
13b	>300	Brown	$C_{17}H_8BrN_3O_2S$	51.27	2.02	20.06	10.55
	Dioxane	88	398.23	51.08	1.98	20.14	10.35
13c	240-42	Brown	$C_{17}H_8BrN_3O_3$	53.43	2.11	20.91	11.00
	Dioxane	84	382.17	53.34	2.08	20.78	10.92
13d	>300	Brown	$C_{23}H_{12}BrN_3O_2$	62.46	2.73	18.07	9.50
	DMF	88	442.26	62.32	2.55	17.82	9.72
17a	192-94	Orange	$C_{20}H_{12}BrN_3O$	61.56	3.10	20.48	10.77
	AcOH	89	390.23	61.48	3.18	20.54	10.68
17b	280-82	Yellow	$C_{20}H_{12}BrN_3O$	61.56	3.10	20.48	10.77
	DMF	90	390.23	61.58	3.17	20.62	10.47
17c	236-38	Yellow	$C_{15}H_7BrN_4O$	53.12	2.08	23.56	16.52
	DMF	81	339.15	53.19	2.13	23.64	16.67
17d	226-28	Yellow	$C_{13}H_7BrN_4O$	49.55	2.24	25.36	17.78
	AcOH	73	315.15	49.49	2.13	25.64	17.67
17e	>300	Yellow	$C_{18}H_{10}BrN_3O$	59.36	2.77	21.94	11.54
	DMF	72	364.2	59.41	2.70	22.14	11.59
17f	280-82	Yellow	$C_{19}H_{13}BrN_4O$	58.03	3.33	20.32	14.25
	DMF	82	393.24	58.11	3.38	20.41	14.34
21a	180-82	Yellow	$C_{20}H_{11}BrN_4O$	57.30	2.64	19.06	13.36
	DMF	90	419.23	57.27	2.60	18.87	13.29
21b	234-36	Orange	$C_{20}H_{11}BrN_4O_2$	57.30	2.64	19.06	13.36
	DMF/EtOH	71	419.23	57.38	2.69	19.22	13.47
21c	206-208	Yellow	$C_{15}H_6BrN_5O_2$	48.94	1.64	21.70	19.02
	EtOH	70	368.14	49.12	1.59	21.65	19.10
21d	223-225	White	$C_{13}H_6BrN_5O_2$	45.37	1.76	23.22	20.35
	EtOH	73	344.12	45.41	1.79	23.27	20.31
21e	134-136	Yellow	$C_{18}H_9BrN_4O_2$	54.98	2.31	20.32	14.25

(Continued)

Table 1

(*Continued*)

Comp. no	Mp °C Solvent	Colour Yield %	Mol. formula Mol. Wt.	% Analysis Calcd / Found C	H	Br	N
	EtOH	76	393.19	55.11	2.38	20.37	14.35
21f	280-82	Yellow	$C_{19}H_{12}BrN_5O_2$	54.05	2.68	18.92	16.59
	DMF	85	422.23	54.12	2.92	19.10	16.44
24a	164-66	Orange	$C_{17}H_{11}BrN_2O_3$	55.01	2.99	21.53	7.55
	AcOH	72	371.18	55.14	3.09	21.49	7.46
24b	180.82	Orange	$C_{18}H_{13}BrN_2O_3$	56.12	3.40	20.74	7.27
	AcOH	76	385.21	56.20	3.37	20.69	7.18
25a	198-200	Brown	$C_{17}H_{11}BrN_4O$	55.61	3.02	21.76	15.26
	EtOH	61	367.20	55.70	3.11	21.67	15.21
25b	246-248	Orange	$C_{23}H_{15}BrN_4O$	62.32	3.41	18.03	12.64
	DMF	72	443.30	62.39	3.34	17.90	12.68
25c	246-48	Red Bricks	$C_{23}H_{14}BrN_5O_3$	56.57	2.89	16.36	14.34
	DMF	72	488.29	56.50	3.00	16.45	14.41
25d	274-276	Orange	$C_{18}H_{13}BrN_4O$	56.71	3.44	20.96	14.70
	Dioxane	67	381.23	56.76	3.49	21.12	14.65
25e	238-40	Red	$C_{24}H_{17}BrN_4O$	63.03	3.75	14.47	12.25
	Dioxane	73	457.32	63.11	3.82	14.52	12.30
26a	182-84	White	$C_{11}H_7BrN_2O$	50.22	2.68	30.37	10.65
	EtOH	85	263.09	50.11	2.59	30.28	10.57
26b	128-130	Yellow	$C_{17}H_{11}BrN_2O$	60.20	3.27	23.56	8.26
	Benzene	70	339.19	60.14	3.11	23.65	8.26
26c	142-44	Red	$C_{17}H_{10}BrN_3O_3$	53.15	2.62	20.80	10.94
	EtOH	85	384.18	53.22	2.54	20.72	11.12
27a	210-12	Red	$C_{23}H_{15}BrN_4O$	62.32	3.41	18.03	12.64
	Dioxane	74	443.3	62.32	3.24	18.15	12.52
27b	194-196	Orange	$C_{24}H_{17}BrN_4O$	63.03	3.75	17.47	12.25
	Dioxane	81	457.32	63.11	3.82	17.40	12.22
28	168-70	Brown	$C_{17}H_{11}BrN_2O$	60.20	3.27	23.56	8.26
	EtOH	78	39.19	60.27	3.15	23.49	8.32

3-(5-bromobenzofuran-2-yl)-3-oxoprop-1-en-1-olate **(14)** (5 mmol), sodium acetate trihydrate (0.65 g, 5 mmol) in ethanol (25 mL) at 0–5°C while stirring. The reaction mixture was stirred for 3 h, and the solid formed was collected and crystallized to give **24a** and **24b**, respectively (Tables 1 and 2).

3-(5-Bromobenzofuran-2-yl)-1-substituted-4-(phenyldiazenyl)-1H-pyrazole 25a–c and 3-(5-bromobenzofuran-2-yl)-1-substituted-4-(p-tolyldiazenyl)-1H-pyrazole 25d–f. Method A: Equimolar amounts of the appropriate of 2-(2-phenylhydrazono)-3-(5-bromobenzofuran-2-yl)-3-oxopropanal **(24a)** 2-(2-(4)-tolylhydrazono)-3-(5-bromobenzofuran-2-yl)-3-oxopropanal **(24b)** and the appropriate hydrazine hydrate, phenylhydrazine, or 4-nitrophenylhydrazine (4 mmol for each) in ethanol (10 mL) were boiled under reflux for 2 h. The solid, so formed, after cooling was recrystallized from the proper solvent to give the corresponding **25a–f** (Tables 1 and 2).

Method B: Solution of the appropriate aryldiazonium chloride (5 mmol) was added dropwise with stirring to a cold stirred solution of the appropriate 3-(5-bromobenzofuran-2-yl)-l-substituted l*H*-pyrazole **26a–c** (5 mmol) in ethanolic solution (15 mL) at 0–5°C containing sodium acetate as a buffer solution. The reaction mixture was stirred for 3 h. The resulting solid was collected, washed with water, and recrystallized from the proper solvent to give products identical in all aspects (mp, mixed mp, and spectra) with **25a–f**, which were obtained in method A.

3-(5-Bromobenzofuran-2-yl)-lH-pyrazole (26a), 3-(5-bromobenzofuran-2-yl)-l-phenyl-lH-pyrazole (26b) and 3-(5-bromobenzofuran-2-yl)-1-(4-nitrophenyl)-1H-pyrazole (26c). A mixture of l-(5-bromobenzofuran-2-yl)-3-(dimethylamino) prop-2-en-l-one **(3)** (1.17 g, 4 mmol) and the appropriate hydrazine hydrate, phenylhydrazine, or 4-nitrophenylhydrazine (4 mmol) in ethanol (10 mL) were boiled under reflux for 2 h. The solid, so formed, after cooling was recrystallized from the proper solvent to give the corresponding **26a–c**, respectively (Tables 1 and 2).

2-(5-Bromobenzofuran-2-yl)-3H-benzo[b][l,4]diazepin-3-ylidene)-2-phenyl-hydrazine (27a) and 2-(5-bromobenzofuran-2-yl)-3H-benzo[b][l,4]diazepin-3-ylidene)-2-p-tolyl-hydrazine (27b). Method A: Equimolar amounts of the appropriate 2-(2-phenylhydrazono)-3-(5-bromobenzofuran-2-yl)-3-oxopropanal **(24a)** or 2-(2-*p*-tolylhydrazono)-3-(5-bromobenzofuran-2-yl)-3-oxopropanal **(24b)** (5 mmol) and *o*-phenylenediamine (0.54 g, 5 mmol) in ethanol (10 mL) were boiled under reflux for 2 h. The solid, so formed, after cooling was recrystallized from the proper solvent to give the corresponding **27a** and **27b**, respectively.

Table 2

Spectral data of the newly synthesized compounds.

Comp. no.	Spectral data
3	IR (KBr) cm^{-1}: 3064 (CH), 1665 (CO), 1604 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.18 (s, 6H, 2N(CH_3)$_2$), 5.79–5.83 (d, 1H, J = 12.0 Hz, COCH=CH), 7.48–7.62 (m, 3H, C9, C15, C16,), 7.79–7.33 (d, 1H, J = 12.0 Hz, CH=CHN(CH_3)$_2$), 7.93 (s, 1H, C14)
7a	IR (KBr) cm^{-1}: 3064 (CH), 1710 (CO), 1600 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.15 (t, 3H, J = 7.5 CH_2**CH_3**), 4.17 (q, 2H**,** J = 7.5**,** **CH_2**CH_3), 7.27 (t, 1H, C-4), 7.53 (d, 1H, C-22), 7.77 (m, 2H, C-17, C-18), 7.89 (d, 2H, ArH's), 8.01 (m, 2H, ArH's), 8.57 (s, 1H, pyrazole C-5) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.12 (CH_3), 59.89, 110.98, 114.17, 116.56, 120.30, 122.68, 125.34, 127.51, 128.22, 129.34, 129.52, 129.57, 140.70, 141.32, 154.00, 156.32, 162.16, 185.77.
7b	IR (KBr, cm^{-1}): 3064 (CH), 1685 (CO), 1602 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.87 (s, 3H, CH_3), 7.29–8.08 (m, 9H, ArH's), 8.59 (s, 1H, pyrazole H-5) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 27.70, 110.89, 114.17, 116.57, 120.30, 121.10, 125.34, 127.51, 129.34, 129.52, 129.57, 130.73, 141.32, 154.08, 156.36, 159.60, 158.77, 191.69.
7c	IR (KBr, cm^{-1}): 3429 (NH), 3064 (CH), 1687 (CO), 1602 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.29–8.08 (m, 15H, ArH's), 8.59 (s, 1H, pyrazole H-5), 8.90 (s, br., 1H, NH) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.98, 114.17, 116.57, 120.32, 123.53, 125.34, 127.51, 127.58, 128.54, 129.34, 129.52, 129.57, 136.94, 141.32, 143.57, 154.09, 156.35, 160.46, 158.77 MS, *m/z,* (%): 487 (M + 1, 20%), 485 (22%), 396 (19%), 393 (25%), 225 (33%), 224 (22%), 223 (31%), 167 (21%), 104 (25%), 87 (11%), 77 (100%), 64 (13%), 63 (11%)
7d	IR (KBr, cm^{-1}): 3064 (CH), 1645 (CO), 1600 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.29–8.08 (m, 14H, ArH's), 8.59 (s, 1H, pyrazole H-5). MS, *m/z,* (%): 472 (M + 1, 8.7%), 470 (M − 1, 9.2%), 182 (8%), 181 (6%), 105 (79%), 77 (100%), 76 (26%)
7e	IR (KBr, cm^{-1}): 3064 (CH), 1668 (CO), 1600 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.29–7.99 (m, 14H, ArH's), 8.64 (s, 1H, pyrazole H-5), 8.76–8.79 (d, 1H, J = 9.0H, ArH), 9.05 (s, 1H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.90, 114.17, 116.57, 118.29, 120.30,125.17, 125.34, 126.27, 127.01, 127.12, 128.12, 129.17, 129.43, 129.97, 130.09, 130.24, 131.37, 133.37, 134.46, 136.14, 141.29, 143.46, 154.09, 156.37, 184.64, 185.27
7f	IR (KBr, cm^{-1}): 3064(CH), 1655 (CO), 1600 (CN) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.29–7.99 (m, 11H, ArH's), 8.29–8.31 (d, 2H, J = 9.0H, ArH), 8.64 (s, 1H, pyrazole H-5)
3	IR (KBr) cm^{-1}: 3064 (CH), 1665 (CO), 1604 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.18 (s, 6H, 2N(CH_3)$_2$), 5.79–5.83 (d, 1H, J = 12.0 Hz, COCH=CH), 7.48–7.62 (m, 3H, C9, C15, C16,), 7.79–7.33 (d, 1H, J = 12.0 Hz, CH=CHN(CH_3)$_2$), 7.93 (s, 1H, C14)
7a	IR (KBr) cm^{-1}: 3064 (CH), 1710 (CO), 1600 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.15 (t, 3H, J = 7.5 CH_2**CH_3**), 4.17 (q, 2H**,** J = 7.5**,** **CH_2**CH_3), 7.27 (t, 1H, C-17), 7.53 (d, 1H, C-26), 7.77 (m, 2H, C-18, C-20), 7.89 (m, 3H, C-24, C-25, C-28), 8.01 (m, 2H, C-16,), 8.57 (s, 1H, pyrazole H-5) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.12 (CH_3), 59.89, 110.98, 114.17, 116.56, 120.30, 122.68, 125.34, 127.51, 128.22, 129.34, 129.52, 129.57, 140.70, 141.32, 154.00, 156.32, 162.16, 185.77.
7b	IR (KBr, cm^{-1}): 3064 (CH), 1685 (CO), 1602 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.87 (s, 3H, CH_3), 7.29–8.08 (m, 9H, C-16, C-17, C18, C-20, C-22, C-23, C-24, C-25, C-26), 8.59 (s, 1H, pyrazole H-5) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 27.70, 110.89, 114.17, 116.57, 120.30, 121.10, 125.34, 127.51, 129.34, 129.52, 129.57, 130.73, 141.32, 154.08, 156.36, 159.60, 158.77, 191.69.
7c	IR (KBr, cm^{-1}): 3429 (NH), 3064 (CH), 1687 (CO), 1602 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.29–8.08 (m, 14H, C-16, C-17, C-18, C-20, C-22, C-23, C-24, C-25, C-26, C-28, C-29, C-30, C-31, C-32), 8.59 (s, 1H, pyrazole H-5), 8.90 (s, br., 1H, NH) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.98, 114.17, 116.57, 120.32, 123.53, 125.34, 127.51, 127.58, 128.54, 129.34, 129.52, 129.57, 136.94, 141.32, 143.57, 154.09, 156.35, 160.46, 158.77 MS, *m/z,* (%): 487 (M + 1, 20%), 485 (22%), 396 (19%), 393 (25%), 225 (33%), 224 (22%), 223 (31%), 167 (21%), 104 (25%), 87 (11%), 77 (100%), 64 (13%), 63 (11%)
7d	IR (KBr, cm^{-1}): 3064 (CH), 1645 (CO), 1600 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.29–8.08 (m, 14H, C-16, C-17, C-18, C-20, C-22, C-23, C-24, C-25, C-26, C-27, C-28, C-29, C-30, C-31), 8.59 (s, 1H, pyrazole H-5). MS, *m/z,* (%): 472 (M + 1,8.7%), 470 (M − 1,9.2%), 182 (8%), 181 (6%), 105 (79%), 77 (100%), 76 (26%)
7e	IR (KBr, cm^{-1}): 3064 (CH), 1668 (CO), 1600 (C=C) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.29–7.99 (m, 14H, C-16, C-17, C-18, C-20, C-22, C-23, C-24, C-25, C-26, C-30, C-32, C-33, C-34. C-35), 8.64 (s, 1H, pyrazole H-5), 8.76–8.79 (d, 1H, J = 9.0H, C-31), 9.05 (s, 1H, C-27); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.90, 114.17, 116.57, 118.29, 120.30,125.17, 125.34, 126.27, 127.01, 127.12, 128.12, 129.17, 129.43, 129.97, 130.09, 130.24, 131.37, 133.37, 134.46, 136.14, 141.29, 143.46, 154.09, 156.37, 184.64, 185.27
7f	IR (KBr, cm^{-1}): 3064(CH), 1655 (CO), 1600 (CN) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.29–7.99 (m, 11H, C-16, C-17, C-18, C-20, C-23, C-24, C-25, C-27, C-31, C-33, C-34), 8.29–8.31 (d, 2H, J = 9.0H, C-22, C-26), 8.64 (s, 1H, pyrazole H-5).
9a	IR (KBr, cm^{-1}): 3429 (NH), 3051 (CH), 1670 (CO), 1608 (C=N), 1566 (C=C) **^{1}**H NMR (**300** MHz, DMSO-d_6): δ = 7.27–7.92 (m, 9H, C-16, C-17, C-18, C-20, C-22, C-23, C-24, C-25, C-26), 8.35 (s, 1H, pyrazole H-5), 12.25 (s, br., 1H, NH). **^{13}**C NMR (**75** MHz, DMSO-d_6): δ = 109.74, 114.18, 116.78, 120.30, 121.70, 121.75, 125.34, 127.51, 129.11, 129.34, 129.48, 129.58, 139.45, 139.87, 141.48, 154.44, 156.83; MS, *m/z* (%): 408 (M + 1, 45%), 406 (M − 1, 52%), 191 (12%), 189 (12%), 125 (7%), 112 (11%), 104 (34%), 82 (12%), 77 (100%), 64 (34%)
9b	IR (KBr, cm^{-1}): 3051 (CH), 1624 (C–N), 1601 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.56 (s, 3H, CH_3), 7.27–7.69 (m, 9H, C-16, C-17, C-18, C-20, C-22, C-23, C-24, C-25, C-26), 8.32 (s, 1H, pyrazole H-5). **^{13}**C NMR (**75** MHz, DMSO-d_6): δ = 19.17, 108.47, 114.15, 116.57, 120.30, 123.54, 124.30, 125.34, 127.51, 129.34, 129.57, 129.74, 138.61, 140.10, 141.34, 145.92, 151.34, 154.58.
9c	IR (KBr, cm^{-1}): 3429 (NH), 3051 (CH), 1670 (CO), 1608 (C=N), 1566 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.27–7.72 (m, 12H, C-16, C-17, C-18, C-20, C-22, C-23, C-24, C-25, C-26, C-28, C-29, C-30), 8.15 (s, 1H, pyrazole H-5), 8.21–8.23 (d, 2H, C-27, C-31) MS, *m/z,* (%): 468 (M + 1, 44%), 466 (M − 1, 39%), 394 (23%), 392 (26%), 227 (15%), 225 (21%), 104 (34%), 194 (13%), 180 (21%), 166 (13%), 140 (31%), 77 (100%), 63 (33%)
9d	IR (KBr, cm^{-1}): 3051 (CH), 1616 (C=N), 1588 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.27–7.99 (m, 12H, C-16, C-17, C-18, C-20, C-22, C-23, C-24, C-25, C-26, C-33, C-34, C-35), 8.05 (s, 1H, pyrazole H-5), 8.07 (s, 1H, C-32), 8.23–8.43 (m, 2H, C-30, C-31), 8.95 (s, 1H, C-27) **^{13}**C NMR (**75** MHz, DMSO-d_6): δ = 108.47, 114.17, 116.57, 120.30, 123.54, 124.78, 125.34, 126.24, 126.76, 127.41, 129.10, 129.34, 129.57, 129.81, 133.84, 134.42, 137.86, 141.31, 143.34, 151.10, 151.52, 154.12.

(Continued)

Table 2

(*Continued*)

Comp. no.	Spectral data
12a	IR (KBr, cm^{-1}): 3093 (CH), 1681 (CO), 1643 (C=N), 1555 (C=N) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.55–8.03 (m, 9H, C-12, C-13, C-14, C-15, C-16, C-20, C-21, C-22, C-24), 10.12 (s, 1H, isoxazole H-5) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.98, 114.12, 116.54, 116.82, 125.34, 128.45, 129.27, 129.57, 130.10, 132.42, 135.47, 154.10, 156.32, 157.82, 162.10, 181.62, 186.57.
12b	IR (KBr, cm^{-1}): 3089 (CH), 1674 (CO), 1643 (C=N), 1558 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.55–8.03 (m, 7H, C-15, C-16, C-17, C-19, C21, C-22, C-23), 10.12 (s, 1H, isoxazole H-5) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.98, 114.17, 116.56, 125.34, 128.10, 129.32, 129.57, 132.52, 137.24, 147.28, 151.42, 154.56, 156.32, 161.85, 170.67, 181.93 MS, *m/z,* (%): 403 (M + 1, 1.3%), 401 (M − 1, 1.0%), 112 (7%), 111 (100%), 110 (24%), 83 (6%)
12c	IR (KBr, cm^{-1}): 3093 (CH), 1658 (CO), 1555 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.62–6.63 (d, 1H, J = 4.0 Hz, C-22), 7.27–8.55 (m, 6H, C-15, C-16, C-17, C-19, C21, C-23), 10.12 (s, 1H, isoxazole H-5) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.45, 112.37, 114.70, 116.58, 116.75, 122.57, 125.36, 129.38, 129.64, 144.10, 146.95, 154.42, 154.67, 156.22, 161.85, 175.18, 181.98 MS, *m/z,* (%): 387 (M + 1, 1.1%), 385(M − 1, 1.0%), 96 (6%), 95 (100%), 94 (31%)
12d	IR (KBr, cm^{-1}): 3058 (CH), 1670 (CO), 1646 (C=N), 1555 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.65–8.29 (m, 10H, C-15, C-16, C-17, C-19, C-24, C-25, C-26, C-27, C-28, C-29), 10.12 (s, 1H, isoxazole H-5), 9.11 (s, 1H, C-21) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.98, 114.17, 116.57, 116.88, 125.34, 125.46, 126.10, 128.60, 129.34, 129.57, 130.14, 133.87, 136.74, 154.12, 156.44, 156.77, 162.48, 181.78, 184.89 MS, *m/z,* (%): 447 (M + 1, 0.9%), 445(M − 1, 2.0%), 172 (19%), 155 (100%), 127 (54%), 77 (8%)
13a	IR (KBr, cm^{-1}): 3047 (CH), 1627 (C=N), 1577 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.37–7.49 (m, 3H, C-15, C-16, C-23), 7.61-7.79 (m, 4H, C-17, C-19, C-22, C-24), 8.15–8.17 (d, 2H, J = 8.0 Hz, C-21, C-25), 8.87 (s, 1H, isoxazole H-5) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 108.47, 114.17, 116.57, 123.73, 125.34, 126.69, 129.34, 129.57, 129.68, 133.49, 135.79, 149.78, 150.48, 154.10, 158.57 MS, *m/z,* (%): 393 (M + 1, 59%), 391 (M − 1, 41%), 366 (26%), 363 (26%), 170 (22%), 169 (22%), 155 (41%), 115 (56%), 102 (22%), 97 (37%), 84 (37%), 77 (15%), 69 (100%), 66 (30%)
13b	IR (KBr, cm^{-1}): 3047 (CH), 1624 (C=N), 1569 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.30–7.76 (m, 6H, C-15, C-16, C-17, C-19, C-22, C-23), 8.57-8.58 (d, 1H, J = 4.0 Hz, thiophene H-3), 8.89 (s, 1H, isoxazole H-5) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 108.47, 114.17, 116.54, 125.34, 127.91, 128.95, 129.34, 129.57, 131.10, 139.71, 149.52, 150.81, 151.57, 154.15, 155.23. MS, *m/z,* (%): 400 (M + 2, 43%), 399 (M + 1, 100%), 398 (M^+, 86%), 397 (72%), 396 (55%), 318 (18%), 290 (35%), 288 (33%), 225 (71%), 223 (84%), 207 (24%), 205 (23%), 182 (14%), 180 (17%), 145 (21%), 119 (19%), 87 (59%), 77 (21%), 68 (28%)
13c	IR (KBr, cm^{-1}): 3047 (CH), 1639 (C=N), 1535 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.67–6.69 (d, 1H, J = 8.0 Hz, furan H-4), 7.36–7.41 (m, 2H, C-15, C-16), 7.61–7.70 (m, 4H, C-17, C-19, C-21, C-23), 8.87 (s, 1H, isoxazole H-5). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 108.47, 112.16, 114.17, 116.56, 117.97, 125.11, 125.43, 129.34, 129.57, 130.21, 143.61, 145.34, 149.25, 150.42, 151.43, 154.05, 157.58 MS, *m/z,* (%): 383 (M + 1, 26%), 382 (M^+, 100%), 381 (M − 1, 66%), 380 (17%), 225 (15%), 223 (15%), 190 (29%), 189 (31%), 188 (15%), 115 (20%), 114 (25%), 104 (25%), 94 (39%), 77 (39%), 63 (43%)
13d	IR (KBr, cm^{-1}): 3061 (H), 1582 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.37–8.31 (m, 10H, C-15, C-16, C-17, C19, C-24, C-25, C-26, C-27, C-28, C-29), 8.87 (s, 1H, isoxazole H-5), 8.88 (s, 1H, C-21) ^{13}C NMR (75 **MHz**, DMSO-d_6): δ = 108.47, 114.17, 116.34, 122.81, 125.34, 125.89, 127.54, 128.47, 129.00, 129.24, 129.57, 130.13, 133.34, 134.24, 136.81, 150.24, 150.89, 151.37, 154.10, 158.86 MS, *m/z,* (%): 444 (M + 2, 2.7%), 402 (M^+, 2.2%), 172 (29%), 171 (12%), 155 (100%), 127 (51%), 77 (13%), 62 (12%)
17a	IR (KBr, cm^{-1}): 3061 (CH), 1628 (C=N), 1595 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.92 (d, 2H, J = 8.0 Hz, C-12, C-16), 7.34–7.81 (m, 8H, C-3, C-13, C-14, C-15, C-17, C-21, C-22, C-24), 8.32 (s, 1H, pyrazole C-10), 8.91–8.92 (s, 1H, Pyrimidine C-4) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 105.52, 109.10, 109.82, 114.17, 116.57, 125.34, 127.75, 128.00, 128.35, 129.34, 130.10, 132.0, 144.31, 144.42, 144.85, 149.54, 154.12.
17b	IR (KBr, cm^{-1}): 3027 (CH), 1642 (C=N), 1607 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.27 (s, 1H, pyrazole C-7), 7.47–8.72 (m, 11H, C-3, C-4, C-11, C-15, C-17, C-18, C-21, C-22, C-23, C-24, C-25) ^{13}C NMR (400 MHz, DMSO-d_6): δ = 93.74, 105.51, 110.37, 114.17, 116.57, 125.34, 127.62, 128.25, 129.34, 129.57, 130.45, 133.44, 144.43, 145.85, 151.42, 151.78, 154.21.
17c	IR (KBr, cm^{-1}): 3027 (CH), 2232 (CN), 1640 (C=N), 1602 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.40–7.70 (m, 5H, C-3, C-11, C-15, C-17, C-18), 8.39 (s, 1H, pyrazole C-10), 9.17–9.19 (d, 1H, J = 8.0 Hz, pyrimidine C-4) ^{13}C NMR (400 MHz, DMSO-d_6): δ = 83.66, 105.52, 109.84, 112.80, 114.17, 116.34, 125.34, 129.37, 129.57, 130.21, 144.42, 147.00, 147.32, 151.71, 154.12. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 105.52, 107.10, 114.17, 116.34, 125.43, 129.34, 129.57, 136.71, 144.32, 154.27, 155.45, 157.57.
17d	IR (KBr, cm^{-1}): 3038 (CH), 1637 (C=N),1605 (C=C) ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 7.13–7.14 (d, 1H, J = 4.0 Hz, Pyrimidine C-3), 7.31–7.33 (d, 1H, J = 8.0 Hz, C-15), 7.61–7.64 (m, 1H, C-18), 8.18 (s, 1H, furan C-11), 8.25 (s, 1H, triazole C-10), 8.99–90 (d, 1H, J = 4.0 Hz, C-17), 9.29 (s, 1H, pyrimidine C-4) ^{13}C NMR (400 MHz, DMSO-d_6): δ = 105.52, 107.10, 114.17, 116.34, 125.43, 129.34, 129.57, 136.71, 144.32, 154.27, 155.45, 157.57.
17e	IR (KBr, cm^{-1}): 3038 (CH), 1624 (C=N), 1611 (C=C) ^{1}HNMR (400 MHz, DMSO-d_6)**:** δ = 7.24–7.65 (m, 8H, C-3, C15, C-17, C-18, C-20, C-21, C-22, C-23), 8.11 (s, 1H, furan C-11), 8.88–8.89 (d, 1H, J = 4Hz, pyrimidine C-4) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 102.11, 103.21, 114.17, 116.34, 120.54, 125.38, 126.11, 129.34, 129.57, 130.43, 134.86, 148.65, 149.33, 154.52, 155.37, 157.45
17f	IR (KBr, cm^{-1}): 3038 (CH), 1624 (C=N),1611 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.65 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 6.65 (s, 1H, C-1), 7.39–7.43 (m, 5H, C-13, C-20, C-21, C-22, C-24), 9.74–9.75 (d, 1H, J = 4.0 Hz, C-14) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 21.71, 23.821, 84.78, 105.52, 109.23, 114.17, 116.57, 120.61, 125.23, 126.31, 129.34, 129,357, 144.14, 144.34, 144.57, 148.74, 154.11, 160.32, 169.64
21a	IR (KBr, cm^{-1}): 3043 (CH), 1685 (CO), 1647 (C=N), 1566 (C=C) ^{1}H NMR (400 MHz, DMSO-4): δ = 7.42–7.86 (m, 9H, C-11, C-12, C-13, C-14, C-15, C-22, C-23, C-24, C-26), 9.04 (s, 1H, pyrazole C-4), 9.28 (s, 1H, C-6) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 99.96, 114.17, 115.58, 116.57, 125.34, 128.25, 128.62, 129.34, 129.57, 132.10, 138.32, 148.10, 151.25, 154.0, 155.36, 156.32, 180.10 MS, *m/z,* (%): 420 (M + 1, 68%), 418 (M − 1, 67%), 392 (73%), 390 (75%), 337 (10%), 335 (13%)
21b	IR (KBr, cm^{-1}): 3089 (CH), 1674 (CO), 1643 (C=N), 1558 (C=N) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.00–7.85 (m, 10H, C-3, C-16, C-17, C-18, C-20, C-23, C-24, C-25, C-26, C-27), 9.28 (s, 1H, C-6) ^{13}C NMR (400 MHz, DMSO-d_6): δ = 113.54, 114.17, 115.58, 116.57, 127.13, 128.38, 129.34, 129.57, 132.46, 136.00, 143.00, 145.89, 147.96, 154.10, 155.23, 180.00

(*Continued*)

Table 2
(*Continued*)

Comp. no.	Spectral data
21c	IR (KBr, cm^{-1}): 3033 (CH), 2228 (CN), 1685 (CO), 1636 (C=N), 1566 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.53–7.94 (m, 4H, C-16, C-17, C-18, C-20), 8.62 (s, 1H, pyrazole C-4), 10.35 (s, 1H, C-6) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 106.65, 113.58, 114.17, 115.34, 116.57, 125.34, 129.34, 129.57, 135.38, 138.64, 148.06, 149.92, 154.00, 155.32, 180.00
21d	IR (KBr, cm^{-1}): 3057 (CH), 1760 (CO), 1641 (C=N), 1560 (C=C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.53–7.78 (m, 4H, C-16, C-17, C-18, C-20), 8.45 (s, 1H, triazole C-5), 9.35 (s, 1H, C-6) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 114.17, 115.45, 116.57, 125.34, 129.34, 129.57, 130.62, 148.63, 154.00, 155.32, 156.23, 156.57, 180.00
21e	IR (KBr, cm^{-1}): 3030 (CH), 1680 (CO), 1640 (C=N), 1568 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.53–8.64 (m, 8H, C-16, C-17, C-18, C-20, C-22, C-23, C-24, C-25), 9.35 (s, 1H, C-6) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.78, 114.17, 115.56, 116.57, 118.24, 124.00, 125.24, 125.48, 129.34, 129.52, 129.57, 132.12, 141.10, 141.92, 154.12, 155.34, 180.00
21f	IR (KBr, cm^{-1}): 3030 (CH), 1690 (CO), 1637 (C=N), 1566 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.66 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 6.67 (s, 1H, C-1), 7.48–7.89 (m, 4H, C-16, C-17, C-18, C-20), 9.39 (s, 1H, C-13) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 21.72, 23.84, 100.87, 114.17, 115.54, 116.56, 121.00, 125.34, 129.34, 129.57, 136.10, 146.89, 147.42, 154.00, 155.34, 160.78, 163.85, 168.67, 180.00;
24a	IR (KBr, cm^{-1}): 3346 (NH), 3085 (CH), 1739 (CO), 1643 (C=N), 1566 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.66 (s, 1H, J = 6.0 Hz, C-10), 7.19–7.85 (m, 8H, C-8, C-9, C-11, C-12, C-13, C-17, C-19, C-20), 9.92 (s, 1H, C-22), 14.85 (s, br., 1H, NH) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 114.17, 114.57, 115.12, 116.56, 122.12, 125.34, 129.17, 129.34. 129.57, 140.71, 143.82, 154.00, 156.35, 183.89, 191.35 MS, *m/z*, (%): 372 (M + 1, 21%), 370 (M − 1, 21%), 341 (10%), 249 (33%), 225 (46%), 169 (27%), 167 (34%), 130 (10%), 102 (20%), 88 (55%), 77 (93%), 65 (100%)
24b	IR (KBr, cm^{-1}): 3350 (NH), 3066 (CH), 1739 (CO), 1635 (C=N), 1523 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.31 (s, 3H, $CH_3C_6H_4$), 7.28–8.16 (m, 8H, C-8, C-9, C-11, C-12, C-13, C-17, C-19, C-20), 9.94 (s, 1H, C-23), 14.45 (s, br., 1H, NH) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 20.81, 114.17, 115.11, 115.57, 116.56, 125.34, 129.14, 129.38, 130.00, 131.98, 140.16, 140.78, 154.00, 156.18, 183.89, 191.35 MS, *m/z* (%): 386 (M + 1, 0.2%), 384 (M − 1, 0.4%), 294 (15%), 105 (100%), 77 (44%)
25a	IR (KBr, cm^{-1}): 3286 (NH), 3066, 3920 (CH), 1635 (C=N), 1610 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.04–8.26 (m, 9H, C-10, C-14, C-16, C-17, C-19, C-20, C-21, C-22, C-23), 8.06 (s, 1H, C-2), 11.65 (s, br., 1H, NH) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 111.37, 114.74, 118.34, 116.57, 122.12, 125.34, 129.18,129.34, 129.57, 134.36, 137.45, 138.42, 143.82, 154.10, 155.34 MS, *m/z,* (%): 368(M + 1, 57%), 366 (M − 1, 18%), 353 (100%), 351 (34%), 321 (39%), 319 (26%), 307 (20%), 305 (16%), 274 (34%), 249 (10%),184 (10%), 171 (56%),141 (15%),128 (16%), 115 (16%), 77 (8%)
25b	IR (KBr, cm^{-1}): 3062 (CH), 1666 (C=N), 1604 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.17–7.67 (m, 13H, C-10, C-14, C-16, C-17, C-20, C-21, C-22, C-25, C-26, C-27, C-28, C-29, and pyrazole C-2), 8.03–8.06 (d, 2H, J = 9.0 Hz, C-19, C-23) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 20.81, 111.37, 114.17, 115.34, 116.56, 125.34, 129.34, 129.57, 130.00, 131.89, 134.38, 137.77, 138.64, 140.16, 154.00, 155.45
25c	IR (KBr, cm^{-1}): 3089 (CH), 1608 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.17–7.97 (m, 12H, C-10, C-14, C-16, C-17, C-19, C-20, C-21, C-22, C-23, C-25, C-29 and pyrazole C-2), 8.35–8.38 (d, 2H, C-26, C-28) ^{13}C NMR (75 MHz, DMSO-d_6): 111.58, 114.17, 116.56, 121.00, 123.25, 129.00, 129.11, 129.34,133.25, 139.11, 139.63, 148.92, 150.24, 151.37, 154.57, 158.37 MS, *m/z,* (%): 489 (M + 1, 3.4%), 487 (M − 1, 3.4%), 286 (21%), 268 (22%), 185 (98%), 183 (100%), 157 (14%), 155 (14%)
25d	IR (KBr, cm^{-1}): 3572 (NH), 3062, 2923 (CH), 1600(C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.36 (s, 3H, 4-$CH_3C_6H_4$), 7.17–7.97 (m, 8H, C-10, C-14, C-16, C-17, C-19, C-20, C-22, C-23), 8.67 (s, 1H, C-2), 11.45 (s, br, 1H, NH) MS, *m/z*, (%): 382 (M + 1, 54%), 381 (M^+, 30%), 291 (M − 1,47%), 289 (50%), 235 (29%), 233 (29%), 126 (19%), 104 (29%), 91 (100%), 77 (25%), 64 (10%)
25e	IR (KBr, cm^{-1}): 3051, 2920 (CH), 1608(C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.36 (s, 3H, 4-$CH_3C_6H_4$), 7.17–7.97 (m, 14H, C-10, C-14, C-16, C-17, C-19, C-20, C-22, C-23, C-26, C-27, C-28, C-29, C-30, pyrazole C-2) ^{13}C NMR (400 MHz, DMSO-d_6): δ = 20.93, 111.96, 114.17, 116.56, 122.20, 125.34, 129.34, 129.57, 129.77, 138.00, 138.20, 141.73, 147.56, 149.24, 150.00, 153.21 MS, *m/z*, (%): 458 (M + 1, 11%), 456 (M − 1, 11%), 379 (100%), 365 (10%), 363 (16%), 295 (20%), 213 (30%), 189 (15%), 165 (36%)
25f	IR (KBr, cm^{-1}): 3058, 2920 (CH), 1608(C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.36 (s, 3H, 4-$CH_3C_6H_4$), 7.17–7.97 (m, 11H, C-10, C-14, C-16, C-17, C-19, C-20, C-22, C-23, C-26, C-30, pyrazole C-2), 8.26–8.29 (d, 2H, J = 9 Hz, C-27, C-29) MS, *m/z*, (%): 503 (M + 1, 1.1%), 501 (M − 1, 1.1%), 255 (48%), 253 (100%), 251 (51%), 209 (31%), 208 (41%), 182 (12%), 180 (16%), 172
26a	IR (KBr, cm^{-1}): 3182 (NH), 3043, 2908 (CH), 1612 (C=N), 1574(C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.65 (d, 1H, J = 4.0 Hz, pyrazole H-4), 7.17–7.45 (m, 5H, C-1, C-2, C-7, C-11, C-13, C-14), 12.23 (s, 1H, NH) MS, m/z (%): 264 (M + 1, 4%), 262 (M − 1, 4.3%), 91 (100%), 65 (9%);
26b	IR (KBr, cm^{-1}): 2916 (CH), 1639 (C=N), 1569 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.65 (d. 1H. J = 4.0 Hz. pyrazole H-4), 7.17–7.45 (m, 8H, C-7, C-11, C-13, C-14, C-17, C-18, C-19, C-20, C-21, pyrazole H-5),
26c	IR (KBr, cm^{-1}): 1635 (C=N), 1577(C=C), 1519. 1419 (NO) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.65 (d. 1H. J = 4.0 Hz. pyrazole C-1), 7.17–7.45 (m, 8H, C-2, C-7, C-11, C-13, C-14, C-17, C-21, pyrazole H-5), 8.30 (d, 2H, C-18, C-20)
27a	IR (KBr, cm^{-1}): 3340 (NH), 3066 (CH), 1620 (C=N), 1539 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.83–6.86 (d, 1H, J = 9.0 Hz, C-15), 7.21–7.99 (m, 10H, ArH's, C-1, C-2, C-4, C-5, C-6, C-20, C-21, C-22, C-23, C-24, C-25, C-27, C-28), 11.23 (s, br., 1H, NH) MS, *m/z*, (%): 445 (M + 2, 11%), 443 (M^+, 11%), 431 (M − 1, 100%), 403 (13%), 401 (8%), 184 (23%), 152 (24%), 168 (32%), 140 (22%)
27b	IR (KBr, cm^{-1}): 3394 (NH), 3074 (CH), 1627 (C=N), 1569 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.36 (s, 3H, 4-$CH_3C_6H_4$), 6.83–6.86 (d, 1H, J = 9.0 *Hz*, C-15), 7.21–7.69 (m, 11H, C-1, C-2, C-3, C-4, C20, C-21, C-23, C-24, C-25, C-27, C-29), 6.97–7.99 (s, 1H, C-10), 11.23 (s, br., 1H, NH) MS, *m/z* (%): 458 (M + 1, 29%), 456 (M − 1, 15%), 254 (88%), 253 (100%), 252 (15%), 251 (13%), 237 (11%), 178 (97%), 151 (61%), 103 (16%), 77 (15%)
28	IR (KBr, cm^{-1}): 3074 (CH), 1624 (C=N), 1547 (C=C) ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.92 (m, 1H, C-9), 6.60 (d, 2H, CH_2), 7.21–7.88 (m, 7H, C-1, C-2, C-4, C-5, C-13, C-17, C-19, C-20,) MS, *m/z* (%): 339 (M + 1, 13%), 337 (M − 1, 12%), 266 (98%), 264 (100%), 249 (15%), 247 (12%), 225 (29%), 223 (27%), 213 (17%), 211 (18%), 184 (11%), 182 (12%), 157 (9%), 140 (18%), 114 (10%), 102 (16%), 75 (12%), 63 (8%)

Method B: Solution of the appropriate benzenediazonium chloride or 4-methylbenzenediazonium chloride (5 mmol for each) was added dropwise with stirring to a cold stirred solution of 2-(5-bromobenzofuran-2-yl)-3*H*-benzo[*b*]-[l,4]diazepine **(28)** (1.69 g, 5 mmol) in ethanolic solution (15 mL) at 0–5°C containing sodium acetate as a buffer solution. The reaction mixture was stirred for 3 h then was left on a refrigerator overnight. The resulting solid was collected, washed with water, and recrystallized from the proper solvent to give products identical in all aspects (mp, mixed mp, and spectra) with **27a** and **27b**, which were obtained in method A.

2-(5-Bromobenzofuran-2-yl)-3H-benzo[b][l,4]diazepine (28). Equimolar amounts of l-(5-bromobenzofuran-2-yl)-3-(dimethylamino)prop-2-en-l-one **(74)** (1.17 g, 4 mmol) and *o*-phenylenediamine (0.43 g, 4 mmol) in ethanol (10 mL) were boiled under reflux for 2 h. The solid, so formed, after cooling was recrystallized from ethanol to give **28** as brown crystals. Yield: 78%, mp: 168–70°C (ethanol). IR (KBr, cm^{-1}): 3074 (CH), 1624 (C=N) (Tables 1 and 2).

REFERENCES AND NOTES

[1] Novinson, T.; Bhooshan, B.; Okabe, T.; Revankar, T. G.; Robins, R. K.; Senga, K.; Wilson, R. H. J Med Chem 1976, 19, 512.

[2] Senga, K.; Novinson, T.; Wilson, R. H.; Robins, R. K. J Med Chem 1981, 24, 610.

[3] Suzuki, M.; Iwasaki, H.; Fujikawa, Y.; Sakashita, M.; Kitahara, M.; Sakoda, R. Bioorg Med Chem Lett 2001, 11, 1285.

[4] Almansa, C.; Cavalcanti, F. L.; Gómez, L. A.; Miralles, A.; Merlos, M.; García-Rafanell, J.; Forn, J. J Med Chem 2001, 44, 350.

[5] Fraley, M. E.; Hoffman, W. F.; Rubino, R. S.; Hungate, R. W.; Tebben, A. J.; Rutledge, R. Z.; McFall, R. C.; Huckle, W. R.; Kendall, R. L.; Coll, K. E.; Thomas, K. A. Bioorg Med Chem Lett 2002, 12, 2767.

[6] Novinson, T.; Hanson, R.; Dimmitt, M. K.; Simon, L. N.; Robins, R. K.; O'Brien, D. E. J Med Chem 1974, 17, 645.

[7] Selleri, S.; Bruni, F.; Costagli, C.; Costanzo, A.; Guerrini, G.; Costa, B.; Martini, C. Bioorg Med Chem 2001, 9, 2661.

[8] Kirkipatrick, W. E.; Okabe, T.; Hillyard, I. W.; Robins, R. K.; Dren, A. T.; Novinson, T. J Med Chem 1977, 20, 386.

[9] Kendall, R. L.; Rubino, R.; Rutledge, R.; Bilodeau, M. T.; Fraley, M. E.; Thomas, Jr. K. A.; Hungate, R. W. U.S. Patent 2001, 6235741; Chem Abstr 1999, 114, 033028w.

[10] Rao, D. R.; Raychaudhuri, S. P.; Verma, V. S. Int J Tropical Plant Dis 1994, 12, 177.

[11] Hinshaw, B. C.; Lconoudakis, O.; Townsend, L. B. Abstracts 112d National Meeting of the American Chemical Society, D. C. Washington. L. B. *Sept.* No MEDI-15, 1971.

[12] Ito, I. Japanese Patent. 1971, 7 030 101 1971; Chem Abstr 1971, 74, 22827.

[13] Asif, M. Curr Med Chem 2012, 19, 2984.

[14] Siddiqui, A. A.; Mishra, R.; Husain, A.; Rashid, M.; Pal, P. Bioorg Med Chem Lett 2011, 21, 1023.

[15] Rathish, I. G.; Kalim, J.; Shamim, A.; Sameena, B.; Alam, M. S.; Akhter, M.; Pillai, K. K.; Ovais, S.; Samim, M. Eur J Med Chem 2012, 49, 304.

[16] Al-Harbi, N. O.; Bahashwan, S. A.; Shadid, K. A. J Am Sci 2010, 6, 353.

[17] Yassin, F. A. Chem Heterocycl Comp 2009, 45, 997.

[18] Abdel-Ghany, Y. S. Alex J Pharm Sci 2008, 22, 31.

[19] Kaymakcioglu, B. K.; Rollas, S.; Korcegez, E.; Aricioglu, F. Eur J Pharm Sci 2005, 26, 97.

[20] Langer, P.; Wuckelt, J.; Doring, M.; Schreiner, P. R.; Gorls, H. Eur J Org Chem 2001, 12, 2257.

[21] Ho, Y. W.; Wang, I. J. Dye Pigment 1995, 29, 295.

[22] Jain, R.; Shukla, A. J Ind Chem Soc 1990, 67, 575.

[23] Henning, G. CODEN: GWXXBX DE 2616981 A1 19771027. 27 October 1977.

[24] Schmidt, P.; Druey, J. Helv Chim Acta 1956, 39, 986.

[25] Ho, Y. W. Dyes Pigments 2005, 64, 223.

[26] Tsai, P. C.; Wang, I. J. Dyes Pigments 2007, 74, 578.

[27] Tsai, P. C.; Wang, I. J. Dyes Pigments 2008, 76, 575.

[28] Tsai, P. C.; Wang, I. J. Dyes Pigments 2005, 64, 259.

[29] Karc, F.; Demirçal, A. Dyes Pigments 2007, 74, 288.

[30] El-Kholy, Y. M.; Abdel-Hafiz, S. A.; Ahmed, S. H. J Soc Dyers Colour 1998, 114, 45.

[31] Abdelhamid, A. O.; Abdelall, E. K. A.; Zaki, Y. H. J Heterocycl Chem 2010, 47, 477.

[32] Abdelhamid, A. O.; Abdelhalim, M. M.; Elmegeed, G. A. J Heterocycl Chem 2007, 44, 7.

[33] Abdelhamid, A. O.; Sayed, A. R.; Zaki, Y. H. Phosphorus Sulfur Silicon 2007, 182, 1447.

[34] Abdelhamid, A. O.; Abdelall, E. K. A.; Abdel-Riheem, N. A.; Ahmed, S. A. Phosphorus Sulfur Silicon 2010, 185, 709.

[35] Abdelhamid, A. O.; Fahmi, A. A.; Alsheflo, A. A. M. Int J Adv Res 2013, 1, 568.

[36] Shawali, A. S.; Abdelhamid, A. O. Tetrahedron 1971, 27, 2517.

[37] Shawali, A. S.; Abdelhamid, A. O. Bull Soc Japan 1976, 49, 321.

[38] Eweiss, N. F.; Osman, A. J Heterocycl Chem 1980, 17, 1713.

[39] Fravel, G. Bull Soc Chim Fr 1904, 31, 150.

[40] Hassaneen, H. M.; Shawali, A. S.; Elwan, N. M.; Abounada, N. M. Sulfur Lett 1992, 14, 41.

[41] Abdelhamid, A. O.; Fahmi, A. A.; Baeu, S. S. J Heterocycl Chem 2012, 49, 1098.

[42] Parkanyi, C.; Abdelhamid, A. O.; Cheng, J. C. S.; Shawali, A. S. J Heterocycl Chem 1948, 21, 1029.

[43] Abdelhamid, A. O.; Khalifa, F. A.; Ghabrial, S. S. Phosphorus Sulfur Silicon Relat Elem 1988, 40, 41.

[44] Abdelhamid, A. O.; Abdou, S. E.; Mahgoub, S. A. Arch Pharm Res 1992, 15, 317.

[45] Abdelhamid, A. O.; Al-Hamidi, A. A. J Chin Chem Soc 1995, 42, 83.