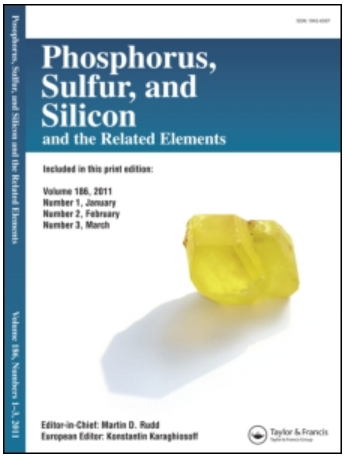

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Reactions of Hydrazonoyl Halides 54[1]: Synthesis and Reactivity of 3-aza-2-bromo-1-(3-oxo benzo[*f*]chromen-2-yl-3-(arylamino)prop-2-en-1-one

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Reactions of Hydrazonoyl Halides 54[1]: Synthesis and Reactivity of 3-aza-2-bromo-1-(3-oxobenzo[*f*]chromen-2-yl-3-(arylamino)prop-2-en-1-one

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2-(5-imino-4-aryl-4,5-dihydro-[1,3,4]-thiadiazole-2-(carbonyl)benzo[f]*chro-men-2-one, 2-(2-amino-5-arylazothiazol-4-yl)benzo[f]chromen-3-one and ethyl 6-methyl-3-oxo-benzo* [f]*chromen-2-yl)-1,4-dihydro-[1,2,4]triazolo[4,3-a]pyrimidine-5-carboxylate were synthesized from hydrazonoyl bromides. Structures of the newly synthesized compounds were established by elemental analysis, spectral data and alternative synthesis route whenever possible.*

Keywords 2,3-Dihydrothiadiazoles; 5-arylazothiazole; hydrazonoyl bromides; triazolino[4,3-*a*]pyrimidines

INTRODUCTION

1,3,4-Thiadiazoles have activities on many biological systems such as: antitumor,[2] hypoglycemic properties,[3] antihistamine,[4] and anticholinergic.[5] Also, 1,2,4-Triazolo[4,3-*a*]pyrimidines have been found to exhibit antiviral, antifungal, antimicrobial, herbicidal, plant regulator, antitumor, antihypertensive, cardiovascular, and anxiolytic activities.[6] Also, hydrazonoyl halides have been widely used for the synthesis of heterocyclic compounds.[7–11] We report, herein, the synthesis of some new 1,3,4-thiadiazoles, 5-arylazothiazoles, and triazolino[4,3-*a*]pyridazines.

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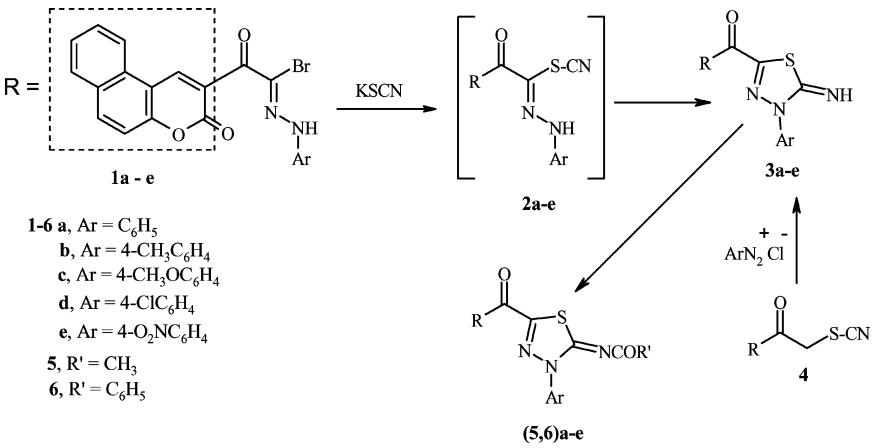
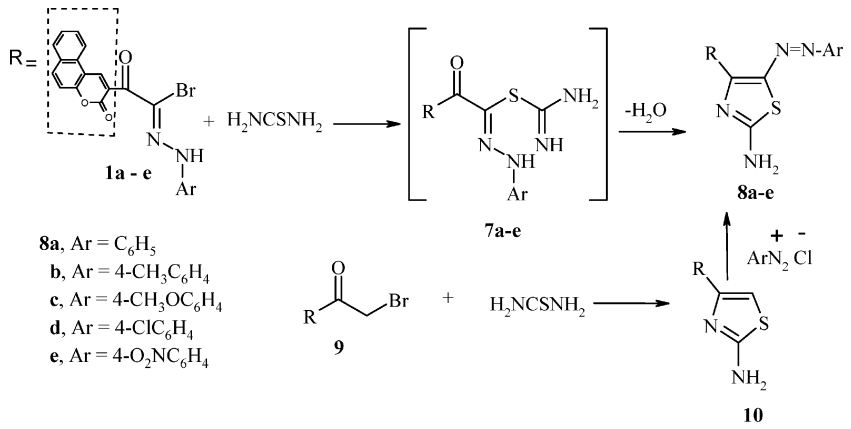


SCHEME 1

RESULTS AND DISCUSSION

Treatmentment of 3-aza-2-bromo-1-(3-oxobenzo[f]chromen-2-yl-3-(phenylamino)- prop-2-en-1-one[12] **(1a**) with potassium thiocyanate in ethanol gave analytical and spectral in accord with their formulation 2-(5-imino-4-phenyl-4,5-dihydro-[1,3,4]-thiadiazole-2-(carbonyl) benzo [*f*]-chromen-2-one (**3a)**. IR spectrum of **3a** revealed the absence bands at 2156 (SCN) and showed bands at 3185 (NH), 1736 and 1666 (CO's). Its ^{1}HNMR spectrum showed signals at $\delta = 7.27–9.38$ (m, 12H) and 12.44 (s, 1H) upon shaking with D_2O a new signal singlet appeared at $\delta = 4.55$ ppm assignable to DOH proton and multiplicity signals at $\delta =$ 7.27–9.38 ppm. Such results indicate that the reaction of **1** with potassium thiocyanate proceed through the hydrazone **2** which cyclized readily under the reaction condition to give **3a** (Scheme 1). Thus, benzenediazonium chloride reacted with 2-(2-thiocyanato)benzo[*f*]chromen-3-one **(4)** in ethanolic sodium acetate solution at 0–5°C, gave a product identical in all respects (mp. mixed mp. and spectra) with **3a**. Thus, acylation of **3a** with acetic anhydride or benzoyl chloride in pyridine yielded *N*-acetyl or *N*-benzoyl derivatives **5a** or **6a,** respectively. Both elemental analysis and spectral data were consistent with the assigned structures of **5a** and **6a**. IR spectrum of **5a** revealed bands at 1728, 1658 (CO's), and 1627 (C=N). Its ^{1}HNMR spectrum of **5a** showed signals at $\delta = 2.36$ (s, 3H, =NCOCH$_3$), 7.23–8.25 (m, 11H, ArH's), and 9.16 (s, 1H, C-4).

Similarly, treatment of the appropriate hydrazonoyl bromide **1b–e** with potassium thiocyanate, (or treatment of the appropriate



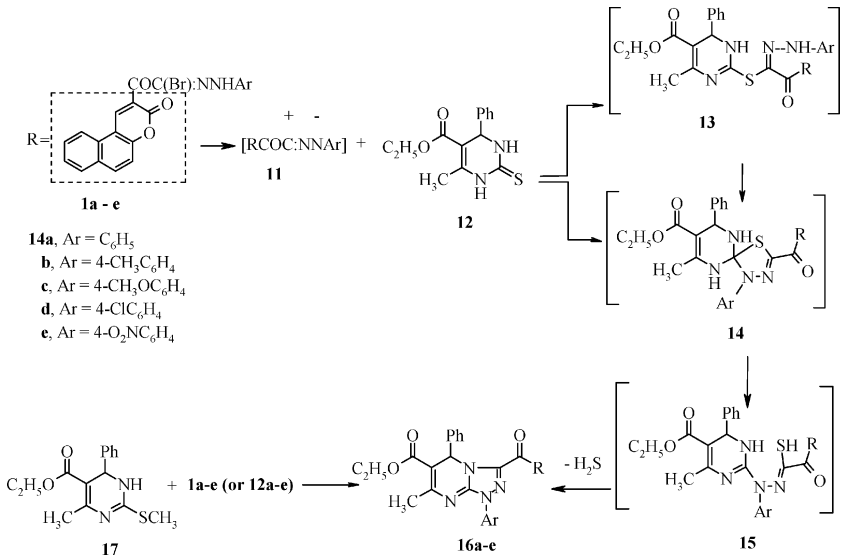
SCHEME 2

diazonium aromatic amine with **4** in ethanolic sodium acetate), to give the thiadiazoline **3b–e.** Also, acylation of **3b–e** with acetic anhydride and benzoyl chloride gave *N*-acetyl and *N*-benzoyl derivatives (**5**, **6**)**b–e**, respectively.

Treatment of the **1a** with thiourea in boiling ethanol gave 2-(2-amino-5-phenylazothiazol-4-yl)benzo[*f*]chromen-3-one **(8a)** (Scheme 2). The structure of the product was supported by its elemental analysis, spectral data, and alternative synthesis route. Thus, IR spectrum of **8a** reveled bands at 3321, 3139 (NH_2), 1708 (CO), and 1612 (C=N). Its ^{1}HNMR spectrum showed signals at δ = 5.02 (s, br, 2H, NH_2), 7.25–8.00 (m, 11H, ArH's), and 9.31 (s, 1H, C-4). Thus, 2-(2-aminothiazol-4-yl)benzo[*f*]chromen-3-one **(10)**, which prepared via reaction of 3-bromoacetylbenzo[*f*]chromen-2-one **(9)** with thiourea, reacted with benzenediazonium chloride in ethanol and sodium acetate as a buffer solution at 0°C gave product identical in all respects (m.p., mixed m.p., and spectra) with **8a**.

Similarly treatment of the appropriate **1b–e** with thiourea in boiling ethanol gave 2-(2-amino-5-arylazothiazol-4-yl)benzo[*f*]chromen-3-one derivatives **8b–e**, respectively.

On the other hand, treatment of **1a** with ethyl 6-methyl-3,4-dihydro-4-phenylpyrimidine-5-carboxylate[13] **(11)** in boiling chloroform containing triethylamine under reflux gave ethyl 6-methyl-3-oxo-benzo[*f*]chromen-2-yl)-1,4-dihydro-[1,2,4]triazolo[4,3-*a*]pyrimidine-5-carboxylate **(16a)** in good yield (Scheme 3). The structure of the product was supported by its elemental analysis, spectral data and alternative synthesis. ^{1}HNMR spectra of **16a** showed signals at δ = 1.25 (t, 3H, $\underline{CH_3}CH_2O$), 2.47 (s, 3H, CH_3), 4.28 (q, 2H, $CH_3\underline{CH_2}O$), 5.98



SCHEME 3

(s, 1H, pyrimidine C-4), 7.35–8.30 (m, 14H), 8.51 (s, 1H), 8.73 (d, 1H), 9.60 (s, 1H). Thus, treatment of **1a** with **17** in boiling ethanolic sodium methoxide under reflux afforded product identical in all respects (m.p., mixed m.p. and spectra) with **16a**.

Two possible pathways can account for the formation of **16a** via 1,3-addition of thiol toutomer of **11** to nitrilimine **12**, which prepared in situ by treatment of **1a** with triethylamine, can give the thiohydrazonate ester **13,** which undergoes neucleophilic cyclization to yield spiro compound **14**. Alternatively, 1,3-cyloaddition of nitrilimine **12** to CS double bond of **11** can give directly **14**. The intermediate **14** gave the final product **16a** through the intermediate **15** with elimination of hydrogen sulfide (Scheme 3).

Analogously, treatment of **1b–e** with pyrmidine-2-thione derivative **11** or **15** gave triazolino[4,3-*a*]pyrimidine **16b–e**, respectively.

EXPERIMENTAL

All melting points were determined on an electrothermal melting point Gallen-Kamp apparatus are uncorrected. IR (cm^{-1}) spectra were recorded on KBr disk on a FTIR-8201 PC Schimadzu spectrophotometer. ^{1}HNMR spectra were recorded in $CDCl_3$ or $(CD_3)_2SO$ on Gemini

200 MHz and varian 300 MHz spectrometer using TMS as internal reference and chemical shifts are express as δ ppm units. Mass spectroscopy was recorded in on a GC-MS QP 1000 EX Schimadzu. Elemental analysis was performed at the Microanalytical center in Cairo University.

Synthesis and Reactivity of *3-Aza-2-bromo-1-(3-oxo*benzo*[f]*chromen-2-yl-3-(arylamino)prop-2-en-1-one 1a–e

A solution of dimethyl[3-oxo-2-(3-oxo-6,10b-dihydro-3H-benzo[*f*]chromen-2-yl)ethyl]sulfonium bromide[12] (3.77g, 10 mmole) and the appropriate *N*-nitrosoarylacetamide (11 mmole) in ethanol (30 mL) was stirred at room temperature for 3 h, left overnight, and diluted with water. The resulting solid was collected and recrystallized from ethanol to give **1a–e,** respectively (Tables I and II).

2-(5-Imino-4-aryl-4,5-dihydro-[1,3,4]-thiadiazol-2-yl)carbonyl-3H-benzo*[f]*chromen-one 3a–e

Method (A)

A mixture of the appropriate **1a–e** (10 mmole) and potassium thiocyanate (1.24g, 12 mmole) in ethanol (20 mL) was refluxed for 30 min. The resulting solid was collected and recrystallized from dioxan to give **3a–e**, respectively (Tables I and II).

Method (B)

The appropriate diazotized aromatic amines (10 mmole) were added to a cold solution of **4** (2.95 g, 10 mmole) and sodium acetate (1.3 g, 10 mmole) in ethanol (30 mL) while stirring at 0–5°C. The reaction mixture was left in an ice-chest for 6 h. The resulting solid was collected, washed with water, and recrystallized from dioxan to give **3a–e**, respectively.

2-(2-Thiocyantoacetyl)benzo[f]chromen-3-one (4)

A mixture of 2-(2-bromoacetyl)-6,10b-dihydro-3H-benzo[*f*]chromen-3-one (**9**) (3.17 g, 10 mmole) in ethanol (20 mL) and potassium thiocyanate (0.97g, 10 mmole) in water (5 mL) was added while stirring for about 3 h. The solid product formed was filtered off and recrystallized from dioxan to give **4** (Tables I and II).

TABLE I Characterization Data of the Newly Synthesized Compounds

Comp. no	M.p.°C solvent	Color yield %	Mol. formula (mol. wt)	calcd./found %			
				C	H	N	S
1b	196–97	Yellow	$C_{22}H_{15}BrN_2O_3$	60.71	3.47	6.44	—
	Dioxan	79%	435.28	60.54	3.26	6.25	
1c	191–93	Yellow	$C_{22}H_{15}BrN_2O_4$	58.55	3.35	6.21	—
	Dioxan	70%	451.28	58.39	3.16	6.05	
1d	200–202	Yellow	$C_{21}H_{12}BrClN_2O_3$	55.35	2.65	6.15	—
	Dioxan	75%	455.70	55.24	2.47	5.98	
1e	184–85	Red	$C_{21}H_{13}BrN_3O_5$	54.10	2.59	9.01	—
	Dioxan	70%	466.25	53.95	2.47	8.85	
3a	213–15	Orange	$C_{22}H_{13}N_3O_3S$	66.15	3.28	10.52	8.03
	Dioxan-EtOH	85%	399.43	65.99	3.15	10.46	7.89
3b	233–35	Orange-red	$C_{23}H_{15}N_3O_3S$	66.81	3.66	10.16	7.76
	Dioxan-EtOH	80%	413.64	66.67	3.48	10.03	7.58
3c	228–30	Brown	$C_{23}H_{15}N3O_4S$	64.33	3.52	9.78	7.47
	Dioxan-EtOH	75%	429.46	64.17	3.42	9.57	7.38
3d	256–56	Red	$C_{22}H_{12}ClN_3O_3S$	60.90	2.79	9.69	7.39
	Dioxan	80%	433.88	60.75	2.65	9.48	7.18
3e	264–65	Brown	$C_{22}H_{12}N_4O_5S$	59.46	2.72	12.61	7.22
	Dioxan	78%	444.43	59.29	2.56	12.48	7.11
4	178–80	Yellow	$C_{16}H_9NO_3S$	65.07	3.07	4.74	10.86
	Dioxan	90%	295.32	64.87	2.98	4.62	10.79
5a	189–90	Brown	$C_{24}H_{15}N_3O_4S$	65.30	3.42	9.52	7.26
	EtOH	78%	441.47	65.12	3.37	9.43	7.09
5b	203–205	Brown	$C_{25}H_{17}N_3O_4S$	66.92	3.76	9.23	7.04
	EtOH	80%	455.50	66.78	3.58	9.07	6.89
5c	193–95	Brown	$C_{25}H_{17}N_3O_5S$	63.69	J3.63	J8.91	6.80
	EtOH	75%	471.50	63.45	3.57	8.76	6.66
5d	220–223	Brown	$C_{24}H_{14}ClN_3O_4S$	60.57	2.97	8.83	6.74
	EtOH	82%	475.91	60.41	2.84	8.76	6.63
5e	198–200	Brown	$C_{24}H_{14}N_5O_6S$	59.26	2.90	11.52	6.59
	EtOH	70%	486.47	59.08	2.75	11.42	6.38
6a	183–85	Brown	$C_{29}H_{17}N_3O_4S$	69.17	3.40	8.35	6.37
	EtOH	68%	503.54	69.05	3.12	8.19	6.21
6b	197–98	Red	$C_{30}H_{19}N_3O_4S$	69.62	3.70	8.12	6.20
	EtOH	65%	517.57	69.49	3.58	8.07	6.03
6c	180–81	Brown	$C_{30}H_{19}N_3O_5S$	67.53	3.59	7.88	6.01
	EtOH	69%	533.57	67.46	3.47	7.68	5.88
6d	195–96	Brown	$C_{29}H_{16}ClN_3O_4S$	64.74	3.00	7.81	5.96
	EtOH	75%	537.99	64.59	2.75	7.73	5.88
6e	208–10	Brown	$C_{29}H_{16}N_4O_6S$	63.50	2.94	10.21	5.85
	EtOH	70%	548.54	62.98	2.82	10.19	5.69
8a	228–30	Yellow	$C_{22}H_{14}N_4O_2S$	66.32	3.54	14.06	8.01
	EtOH	80%	398.45	66.27	3.42	13.98	7.99
8b	239–41	Yellow	$C_{23}H_{16}N_4O_2S$	66.97	3.91	13.85	7.77
	Dioxan	85%	412.47	66.87	3.85	13.76	7.58

TABLE I Characterization Data of the Newly Synthesized Compounds (*Continued*)

Comp. no	M.p.°C solvent	Color yield %	Mol. formula (mol. wt)	Calcd./Cound % C	H	N	S
8c	250–52	Yellow	$C_{23}H_{16}N_4O_3S$	64.47	3.76	13.08	7.48
	EtOH-H_2O	90%	428.47	64.38	3.68	13.00	7.37
8d	>300	Yellow	$C_{22}H_{13}ClN_4O_2S$	61.04	3.03	12.94	7.41
	EtOH-DMF	85%	432.89	60.96	3.29	12.76	7.34
8e	>300	Red	$C_{22}H_{13}N_5O_4S$	59.59	2.95	15.79	7.23
	DMF	80%	443.44	59.50	2.89	15.68	7.08
10	253–55	Yellow	$C_{16}H_{10}N_2O_2S$	65.29	3.42	9.52	10.89
	EtOH	90%	443.44	65.17	3.38	9.48	10.73
16a	233–35	Brown	$C_{35}H_{26}N_4O_5$	72.15	4.50	9.62	—
	EtOH	70%	582.62	72.07	4.38	9.57	
16b	297–99	Brown	$C_{36}H_{28}N_4O_5$	72.47	4.73	9.39	—
	EtOH	65%	596.65	72.38	4.61	9.24	
16c	285–87	Red	$C_{36}H_{28}N_4O_6$	70.58	4.61	9.15	—
	EtOH	65%	612.65	70.40	4.57	9.06	
16d	>300	Brown	$C_{35}H_{25}ClN_4O_5$	68.13	4.08	9.08	—
	EtOH	60%	617.07	68.04	4.00	8.97	
16e	>300	Orange	$C_{35}H_{25}N_5O_7$	66.98	4.02	11.16	—
	Dioxan-EtOH	62%	627.62	66.85	3.98	11.03	

3-Aryl-2-{[2-(1-aza-2-oxorylidene)-1,3,4-thiadiazolin-5-yl]carbonyl}benzo*[f]*-2H-chromen-3-one 5a–e and 3-Aryl-2-aza-2{-5-[(3-oxobenzo*[f]*-2H-chromen-2-yl)carbonyl}-1,3,4-thiadiazole-2-ylidene]-1-phenyl-1-one 6a–e

An appropriate of **3a–e** (5 mmole) and acetic anhydride (10 mL), or benzoyl chloride (0.7g, 5 mmole) in pyridine (10 mL), was heated under reflux for 15 min. The reaction mixture was cool and poured over crushed ice (50g), (acidified in case of benzoylation by hydrochloric acid); then, the crude solid was collected and recrystallized from ethanol to give **5a–e** and **6a–e,** respectively (Tables I and II).

2-(2-Amino-1,3-thiazol-4-yl) benzo*[f]*-2H- chromen-3-one (10)

A mixture of 2-(2-bromoacetyl))-6,10b-dihydrobenzo[*f*]-2H-chromen-3-one (**9**) (3.17 g, 0.01 mol) and thiourea (0.76 g, 10 mmole) in ethanol (20 mL) was refluxed for 1 h. The resulting solid was collected, washed with boiling water containing sodium acetate and, recrystallized from ethanol to give **10** (Tables I and II).

TABLE II IR Spectra, ^{1}HNMR Spectra, and Mass Spectra of the Newly Synthesis Compounds

Comp. No.	Spectral data
1b	IR: 3440 (NH); 1728, 1681 (CO). ^{1}HNMR [$(CD_3)_2SO$]: $\delta = 2.23$ (s, 3H, CH_3), 7.58–9.29 (m, 11H, ArH's) and 12.42 (s, 1H, NH).
	IR: 3417 (NH); 1728, 1681 (CO).
1c	^{1}HNMR [$(CD_3)_2SO$]: $\delta = 3.65$ (s, 3H, OCH_3), 7.61-9.34 (m, 11H, ArH's) and 12.44 (s, 1H, NH).
	IR: 3425 (NH); 1728, 1681 (CO).
1d	^{1}HNMR [$(CD_3)_2SO$]: $\delta = 7.60$- 9.32 (m, 11H, ArH's) and 12.43 (s, 1H, NH).
1e	IR: 3420 (NH); 1725, 1680 (CO's), 1519,1346 (NO_2). ^{1}HNMR [$(CD_3)_2SO$]: $\delta = 7.60$-9.32 (m, 11H, ArH's) and 12.43 (s, 1H, NH).
	IR: 3185 (NH); 1736, 1666 (CO's).
3a	^{1}HNMR ($CDCl_3$): $\delta = 7.27$-9.38 (m, 12H, ArH's) and 12.44 (s, 1H). Ms: [399] M^+
	IR: 3.143 (NH); 1732, 1650 (CO);
3b	^{1}HNMR ($CDCl_3$): 2.54 (s, 3H, CH_3); 7.02-9.51 (m, 12H, ArH's and NH) Ms: [413] M^+
	IR: 3.158 (NH); 1739, 1604 (CO).
3c	^{1}HNMR ($CDCl_3$): $\delta = 3.80$ (s, 3H, OCH_3); 6.93–9.10 ppm (m, 12H, ArH's and NH). Ms: [429] M^+
	IR: 3290 (NH); 1735, 1624(CO);
3d	^{1}HNMR ($CDCl_3$): $\delta = 7.26$-9.11 (m, ArH's and NH) Ms: [433] M^+
3e	IR: 3398 (NH); 1735, 1624 (CO) and 1558, 1338 (NO_2) ^{1}HNMR [$(CD_3)_2SO$]: $\delta = 7.36$-9.39 (m, ArH's and NH)
4	IR: 2152 (SCN); 1728, 1681 (CO). ^{1}HNMR ($CDCl_3$): $\delta = 4.72$ (s, 2H, CH_2) $\delta = 7.27 - 9.53$ (m, 7H, ArH's) Ms: [293] M^+
5a	IR: 1728, 1658 (CO). ^{1}HNMR ($CDCl_3$): $\delta = 2.36$ (s, 3H, N=$COCH_3$), 7.23-8.25 (m, 11H, ArH's) and 9.16 (s, 1H- C4).
5b	IR: 1728, 1658 (CO). ^{1}HNMR ($CDCl_3$): $\delta = 2.38$ (s, 3H, CH_3), 2.40 (s, 3H, N=$COCH_3$), 7.20- 9.17 (m, 11H, ArH's)
	IR: 1724, 1658 (CO).
5c	^{1}HNMR ($CDCl_3$): $\delta = 2.38$ (s, 3H, N=$COCH_3$), 3.70 (s, 3H, OCH_3); 7.20–9.16 (m, 11H, ArH's)
	IR: 1724, 1658 (C=O).
6c	^{1}HNMR ($CDCl_3$): $\delta = 3.70$; (s, 3H, OCH_3); 7.20-9.16 ppm (m, 16H, ArH's).
6e	IR: 1732, 1656, 1624 (CO) and 1519, 1346 (NO_2) ^{1}HNMR ($CDCl_3$): $\delta = 6.91$-9.16 (m, ArH's)
8a	IR: 3321, 3139 (NH_2), 1708 (CO). ^{1}HNMR ($CDCl_3$): $\delta = 5.02$ (s, br, 2H, NH_2), 7.25-8.00 (m, 11H, ArH's) and 9.31 (s, 1H, C-4).
	IR: 3321, 3129 (NH_2); 1708 (CO), 1624 (C=N).

TABLE II IR Spectra, ^{1}HNMR Spectra, and Mass Spectra of the Newly Synthesis Compounds (*Continued*)

Comp. No.	Spectral data
8b	^{1}HNMR ($CDCl_3$): $\delta = 2.35$ (s, 3H, CH_3), 5.38 (s, br, 2H, NH_2); 7.25–9.31 (m, 11H, ArH's)
	IR: 3363, 3159 (NH_2); 1677 (CO), 1630 (C=N)
8c	^{1}HNMR ($CDCl_3$): $\delta = 3.85$ (s, 3H, OCH_3) 5.15 (s, br, 2H, NH_2), 6.96-9.65 (m,11H, ArH's)
	IR: 3440, 3286 (NH_2); 1675 (CO).
8d	^{1}HNMR ($CDCl_3$): $\delta = 5.54$ (s, br, 2H, NH_2), 7.04-8.04 (m, 11H, ArH's)
8e	IR: 3325, 3286 (NH_2); 1675 (CO) and 1550, 1338 (NO_2) ^{1}HNMR [$(CD_3)_2SO$]: $\delta = 5.54$ (s, br, 2H, NH_2), 7.04-8.04 (m, 11H, ArH's)
10	IR: 3355, 3159 (NH_2), 1693 (CO).
	Ms: [294] M^+
16a	IR: 3363, 3159 (NH_2); 1677 (CO).
	^{1}HNMR [$(CD_3)_2SO$]: $\delta = 1.25$ (t, 3H, $\underline{CH_3}CH_2$); 2.47 (s, 3H, CH_3); 4.28 (q, 2H, $CH_3\underline{CH_2}$); 5.98 (s, 1H, CH); 7.35- 8.30 (m,14H, ArH's), 8.51 (s, 1H), 8.73 (d, 1H), 9.60 (s, 1H).
16b	IR: 1701 (CO).
	^{1}HNMR [$(CD_3)_2SO$]: $\delta = 1.28$ (t, 3H, $\underline{CH_3}CH_2$); 2.39(s, 3H, CH_3); 2.46 (s, H, CH_3); 4.18 (q, 2H, $CH_3\underline{CH_2}$); 5.79 (s, 1H, CH); 7.36- 9.60 (m,16H, ArH's)
16c	IR: 1701 (CO).
	^{1}HNMR [$(CD_3)_2SO$]: $\delta = 1.28$ (t, 3H, $\underline{CH_3}CH_2$); 2.48 (s, 3H, CH_3);); 3.79 (s, 3H, OCH_3); 4.33 (q, 2H, $CH_3\underline{CH_2}$); 5.98 (s, 1H, CH); 7.61- 9.86 (m,13H, ArH's), 8.51 (s, 1H) , 8.72 (d, 1H) and 9.60 (s, 1H)
16d	IR: 1701 (CO).
	^{1}HNMR [$(CD_3)_2SO$]: $\delta = 1.28$ (t, 3H, $\underline{CH_3}CH_2$); 2.48 (s, 3H, CH_3); 4.33 (q, 2H,$CH_3\underline{CH_2}$); 5.89 (s, 1H, CH); 7.61- 9.40 (m,16H, ArH's)
16e	IR: 1701 (CO).
	^{1}HNMR [$(CD_3)_2SO$]: $\delta = 1.05$ (t, 3H, $\underline{CH_3}CH_2$); 2.35 (s, 3H, CH_3);); 4.45 (q, 2H, $CH_3\underline{CH_2}$); 5.98 (s, 1H, CH); 7.60- 9.49 (m, 16H, ArH's)

2-{2-Amino-5-aryldiazenyl-1,3-thiazol-4-yl}benzo[f]-2H-chromen-3-one 8 a–e

Method (A)

A mixture of the appropriate hydrazonyl bromides **1a–e** (10 mmole) and thiourea (0.76 g, 10 mmole) in ethanol (20 mL) was heated under reflux for 2 h. The resulting solid was collected and recrystallized from the proper solvent to give **8a–e**, respectively (Tables I and II).

Method (B)

An appropriate of diazotized aromatic amines (0.01mol) was added dropwise to a solution of **10** (2.94 g, 10 mmole) and sodium acetate (1.3 g, 10 mmole) in ethanol (30 mL) at 0–5°C for 30 min while stirring. The reaction mixture was stirred for 6 h. The resulting solid was collected,

washed with water, and recrystallized from proper solvent to give **8a–e**, respectively (Tables I and II).

Ethyl 4-aryl-6-methyl—3-(3-oxobrnzo*[f]*-2H-chromen-2-yl)-4,7a-dihy-dro-7-phenyl-[1,2,4] triazolo[4,3-*a*] primidine-5-carboxylate 16 a–e

Method (A)

An equimolar amounts of hydrazonyl bromides **1a–e** (10 mmole) and pyrimidne-2-thione **11** (2.76 g, 10 mmole) and triethylamine (1 g, 10 mmole) in chloroform (20 mL) was refluxed for 10 h. The reaction mixture was evaporated under vacuum. The resulting solid was collected and recrystallized from ethanol to give **16a–e**, respectively (Tables I and II).

Method (B)

A mixture of the appropriate hydrazonyl bromides **1a–e** (10 mmole), **17** (3.01 g, 10 mmole) and sodium ethoxide (0.7 g, 10 mmole) in ethanol (20 mL) was refluxed for 3 h. The reaction mixture was cooled and the resulting solid was collected and recrystallized from ethanol to give **16a–e**, respectively (Tables I and II).

REFERENCES

[1] A.O. Abdelhamid, Z. H. Ismail, M. S. ElGendy, and M. M. Ghorab, Part 53: *Phosphorus, Sulfur, Silicon and Relat. Elemn*, **182(10)**, 2409–2418 (2007).
[2] A. Padwa, *Angew. Chem. Int. Ed. Engl.* **15,** 123 (1976).
[3] R. Huisgen, R. Sustmann, and G. Wallbillich, *Chem. Ber*., **100,** 1786 (1976).
[4] A. O. Abdelhamid and F. A. Attaby, *J. Heterocycl. Chem*., **28,** 41 (1991).
[5] D. I. Kornis, *Comprehensive Heterocyclic Chemistry,* A. R. Katritzky and C. W. Rees, Eds. (e.f.v. Scriven, Pergamon, 1996), Vol. 4.
[6] M. A. E. Shaban and A. A. Morgaan, *Advances in Heterocyclic Chemistry,* (Academic Press, 1999), Vol. 73, pp. 131.
[7] A.O. Abdelhamid, M. M. M. Sallam, and S. A. Amer, *Heteroatom Chem*, **12,** 468 (2001).
[8] A.O. Abdelhamid, H. F. Zohdi, and N. A. Ali, *Molecules*, **5,** 961 (2001).
[9] Y. H. Zaki, S. A. Ahmed, A. M. Hussein, and A.O. Abdelhamid. *Phosphorus and Sulfur,Silicon, Relat. Elemn.,* **181,** 825 (2006).
[10] A. O. Abdelhamid, M. M. Abdelhalim, and G. A. Elmegeed, *J. Heterocycl. Chem.*, **44,** 7 (2007).
[11] A. O. Abdelhamid, S. M. Abdelgawad, and S. F. El-Shrarnoby, *Phosphorus, Sulfur, Silicon and Relat. Elemn.*, **177,** 2699 (2002).
[12] C. Moustapha, N. A. Abdel-Riheem, and A.O. Abdelhamid, *Synthetic Communication*, **35,** 249 (2005).
[13] A. O. Abdelhamid and M. A. M. Alkhodshi, *Phosphorus, Sulfur, Silicon and Relat. Elem.*, **180,** 149 (2005).