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RESEARCH ARTICLE

Reactions of hydrazonoyl halides 44 [1]: synthesis of some new 1,3,4-thiadiazolines, 1,3,4-selenadiazolines and triazolino[4,3-*a*]pyrimidines

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1,3,4-Thiadiazolines, 1,3,4-selenadiazolines and triazolino[4,3-*a*]pyrimidines have been synthesized from 3-aza-[2,4-dimethyl(1,3-thiazol-5-yl) -2-bromo-3-substituted-amino]prop-2-en-1-ones with potassium thiocyanate, potassium selenocyanate, alkyl carbodithioates and 6-methyl-2-methylthio-4-substituted 3,4-dihydropyrimidine-5-carboxylates. Structures of the newly synthesized compounds have been established by elemental analysis, spectral data and alternative synthesis whenever possible. Some of products have been tested towards bacteria.

Keywords: Thiazole; 1,3,4-Thiadiazolines; Hydrazonoyl halides; Triazolino [4,3-*a*]pyrimidines; 1,3-Dipolar cycloaddition

1. Introduction

Numerous patents have been issued on the synthesis and use of 1,3,4-thiadiazoles as fungicides, herbicides, insecticides, bactericides, dyes, lubricant additives and vulcanization accelerators [2]. Also, 1,2,4-triazolo[4,3-*a*]pyrimidines exhibit antiviral, antifungal, antimicrobial, herbicidal, plant regulator, antitumor, antihypertensive, cardiovascular and anxiolytic activities [3]. As an extension of our studies [4–11] and as a part of our program aimed at the synthesis of different 2,3-dihydro-1,3,4-thiadiazoles and 1,2,4-triazolino[4,3-a]pyrimidines we report here the synthesis and reactivity of 3-aza-1-[2,4-dimethyl(1,3-thiazol-5-yl)-2-bromo-3-(arylaminoamino)]prop-2-en-1-one.

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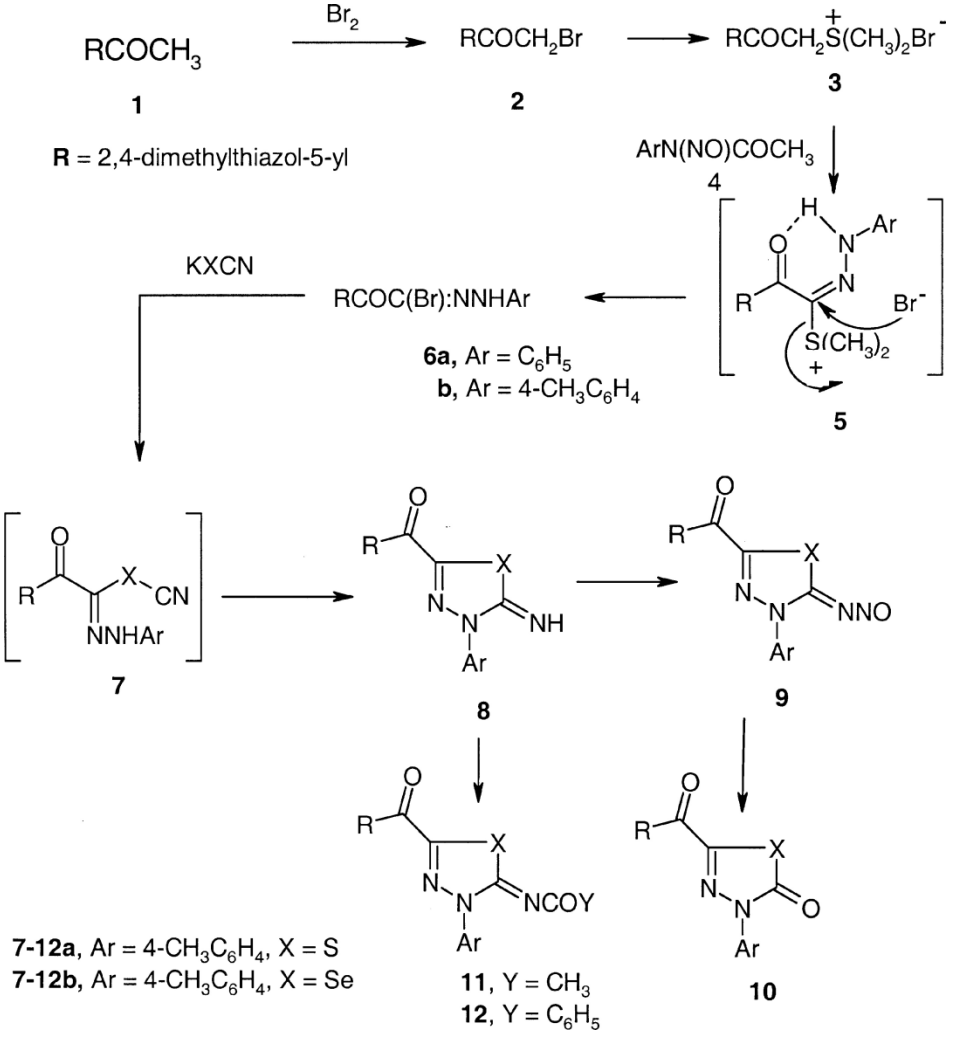
2. Results and discussion

Treatment of 1-[2,4-dimethyl(1,3-thiazol-5-yl)]-2-bromoethan-1-one (**2**) with dimethyl sulfide in boiling ethanol afforded salt **3**. The latter reacted with the appropriate *N*-nitrosoarylacetamide (**4**) [12] in ethanol at room temperature to give (2*Z*)-3-(arylamino)-3-aza-[2,4-dimethyl(1,3-thiazol-5-yl)-2-bromo]prop-2-en-1-one **6a** and **6b** (scheme 1). Spectral data, microanalytical analysis and chemical transformation confirmed the structure **6**.

Treatment of **6b** with potassium thiocyanate in ethanol at room temperature afforded a product that gave analytical and spectral data in accord with: 2,4-dimethyl(1,3-thiazol-5-yl)-2-imino-3-(4-methylphenyl-1,3,4-thiadiazolin-5-yl)ketone (**8a**). The IR spectrum of **8a** revealed the absence bands at 2156 (SCN) and showed bands at 3319 (NH), 3056 (CH) and 1657 (CO conjugated) cm^{-1}. Its ^1H NMR spectrum showed signals at $\delta = 2.32$ (s, 3H), 2.47 (s, 3H), 2.74 (s, 3H), 6.46–7.21 (m, 4H) and 15.17 (s, br, 1H) ppm. Upon shaking with D_2O, exchange was noted. Such results indicate that the reaction of **6b** with potassium thiocyanate proceeds through hydrazone intermediate **7a**, which cyclizes readily under the reaction conditions to give **8a** (scheme 1).



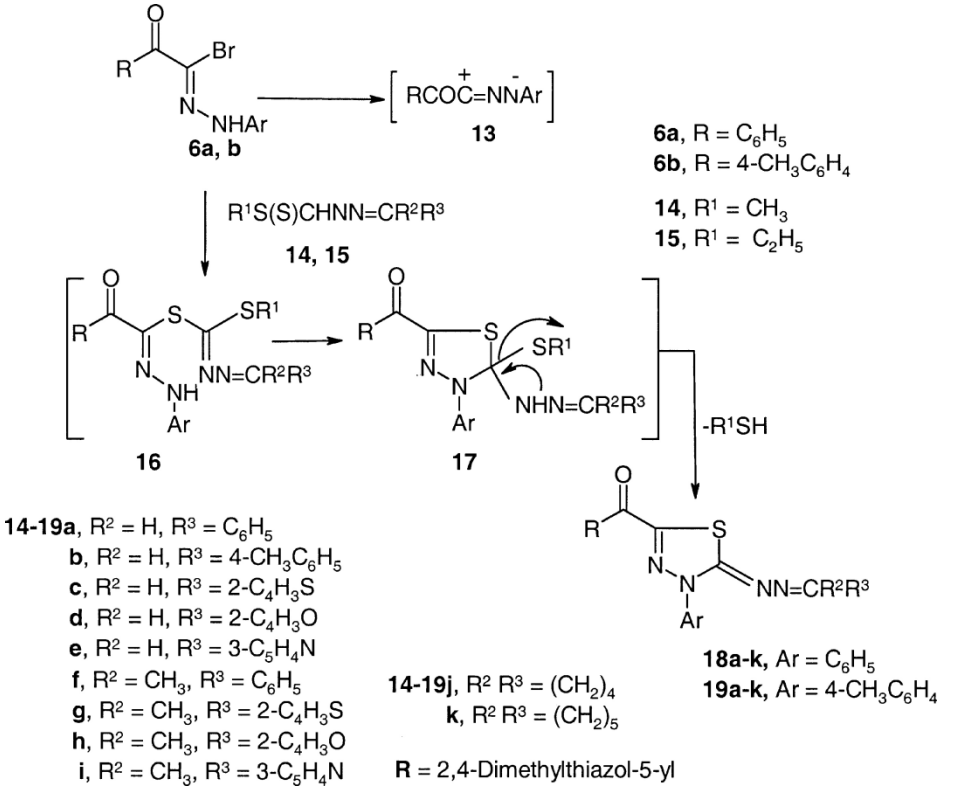
SCHEME 1

Nitrosation of **8a** with sodium nitrite in acetic acid solution gave heterocycle **9a**. The IR spectrum of **9a** showed no NH band between 3350 and 3150 cm^{-1}, but contained common bands at 3057 (CH), 1631 (CO), 1583 (C=C) and 1485 (NO) cm^{-1}. Compound **9a** decomposed to 5-[(2,4-dimethyl(1,3-thiazol-5-yl))carbonyl]-3-(4-methylphenyl)-1,3,4-thiadiazolin-2-one (**10a**) *via* boiling in xylene. Acylation of **8a** with acetic anhydride or benzoyl chloride in pyridine yielded N-acyl derivatives **11a** and **12a**, respectively. Both elemental analysis and spectral data were consistent with the assigned structure of products **11a** and **12a**.

Similarly, reaction of **6b** with potassium selenocyanate afforded 1,3,4-selenadiazoline **8b**. Also, compound **8b** was nitrosilated and acylated to afford 1,3,4-selenadiazolines **9b–12b** (scheme 1).

Treatment of **6a** with 1-aza-2-(phenylvinyl)aminomethylthiomethane-1-thione (**14a**) in ethanolic triethylamine solution gave one isolable product according tlc, and, upon elemental analysis, spectral data and an alternative synthesis route, the structure was formulated as 2-[(2*E*)-1,2-diaza-3-phenylprop-2-enylidene]-3-phenyl(1,3,4-thiadiazolin-5-yl)-2,4-dimethyl(1,3-thiazol-5-yl)ketone (**18a**) (scheme 2). **15a** reacted with **6a** in ethanolic triethylamine to give a product identical in all respects to **18a**.

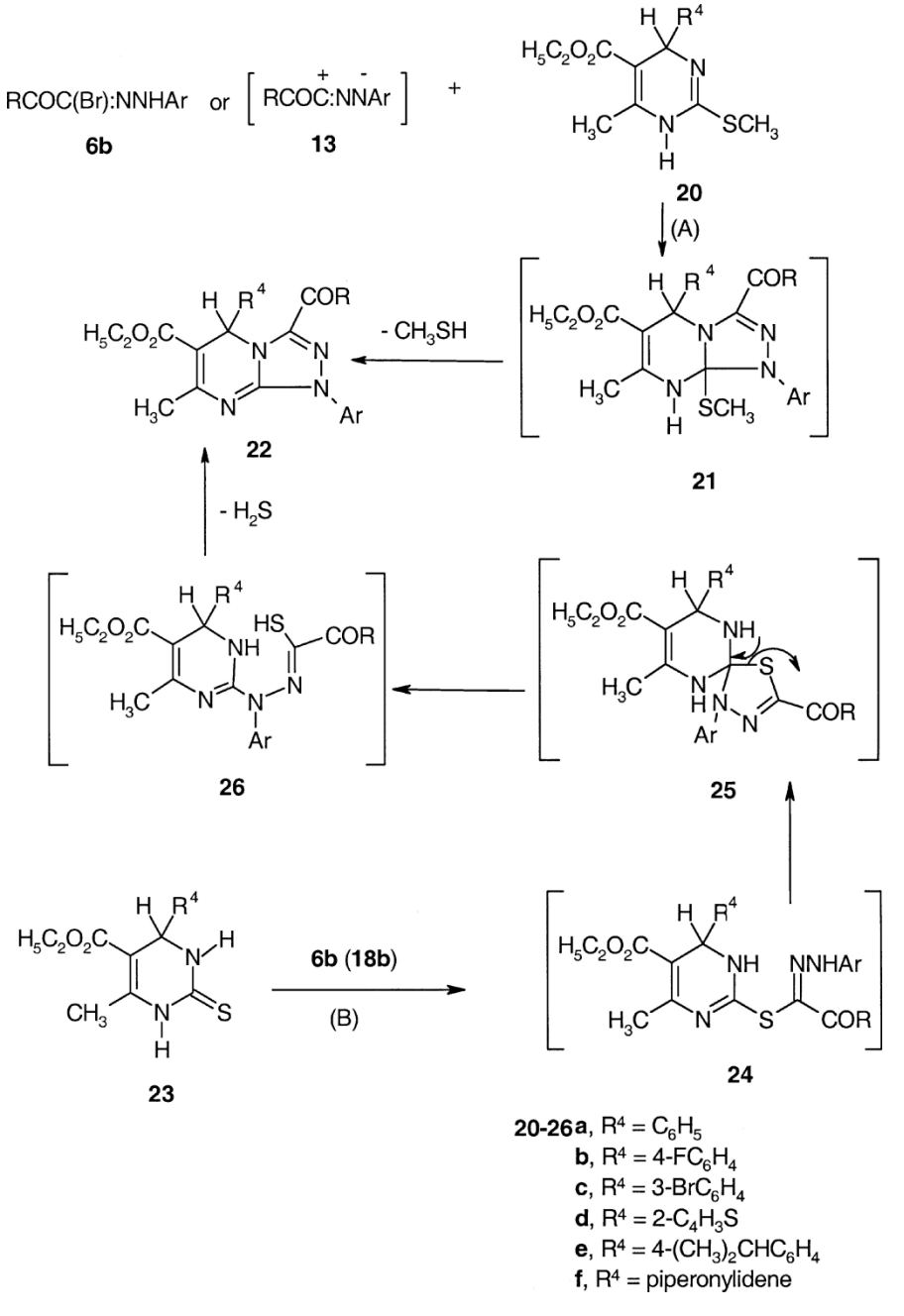
In view of the forgoing results, the mechanism outlined in scheme 2 seems to be the most plausible pathway for the formation of **18a** from the reaction of the **6a** with **14a** or **15a**. The reaction involves initial formation of thiohydrazonate **16a**, which undergoes intermolecular cyclization as soon as it is formed to yield the intermediate **17a** or *via* 1,3-dipolar cycloaddition of nitrilimine **13**, which was prepared *in situ* from **6a** with triethylamine, to the C=S double bond of **14a** (or **15a**). The latter was converted into the final product **18a** *via* elimination of the alkyl mercaptan. The formation of **16** and **17** are similar to the reaction



SCHEME 2

of hydrazonoyl chloride with 1-phenyl-1,4-dihydrotetrazole-5-thione [13] and 5-phenyl-1,3,4-thiadiazole-2(3*H*)-thione [14]. Each of **6a** and **6b** reacted with the appropriate alkyl carbodithioate **14b–k** (or **15b–k**) in ethanol containing triethylamine to afford thiadiazolines **18b–k** and **19b–k**, respectively (scheme 2).

Treatment **6b** with the appropriate ethyl 6-methyl-2-methylthio-4-substituted 3,4-dihydropyrimidine-5-carboxylates **20a–f** [15] in boiling ethanolic sodium ethoxide solution under reflux gave triazolino[4,3-*a*]pyrimidines **22a–f**, respectively, in good yields (scheme 3). The structure of **22** was elucidated on the basis of elemental analysis, spectral data and an



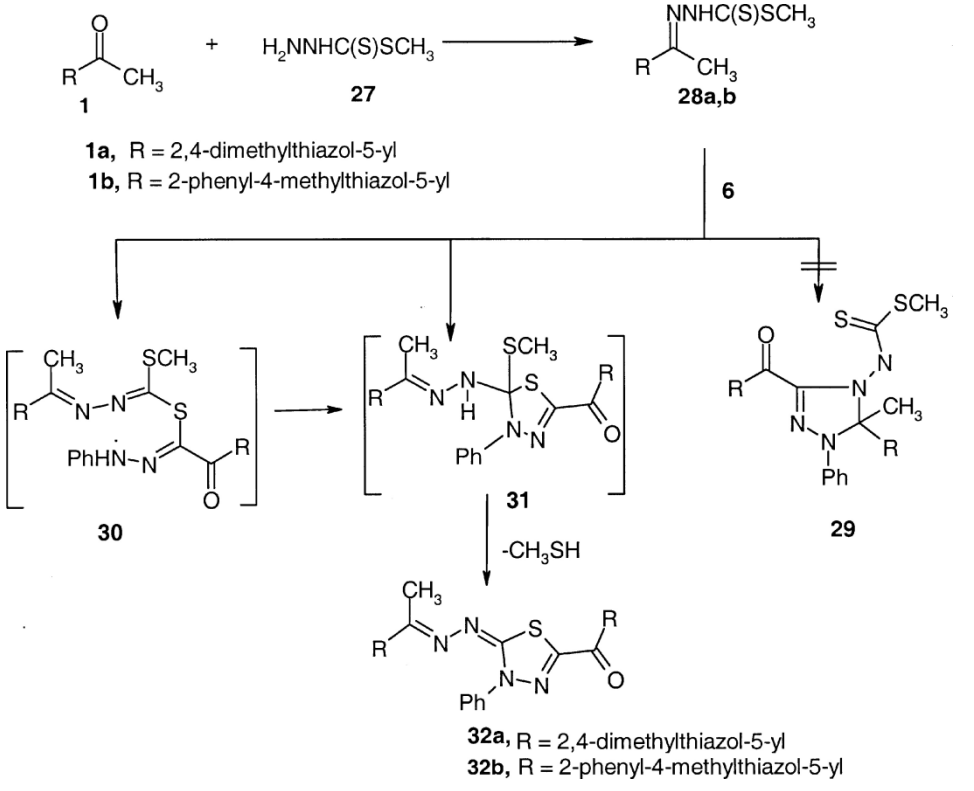
SCHEME 3

alternative synthesis route. Thus, treatment of **6b** with **23a** in boiling chloroform under reflux afforded a product identical in all respects to **22a**. Two possible pathways can account for the formation **22** *via* alkylation of NH or addition to C=N to give intermediate **21**, which readily loses methyl mercaptan to afford the final product **22** by either (a) 1,3-addition of the thiol tautomer of **23** to the nitrilimine **13** to give the thiohydrazonate ester **24**, which undergoes nucleophilic cyclization to yield spiro compounds **25**; or (b) 1,3-cycloaddition of nitrile imine **13** to the C=S double bond of **23** to give **25** directly. The latter intermediate ring opens to **26**, which cyclizes to yield **22** by loss hydrogen sulfide (scheme 3).

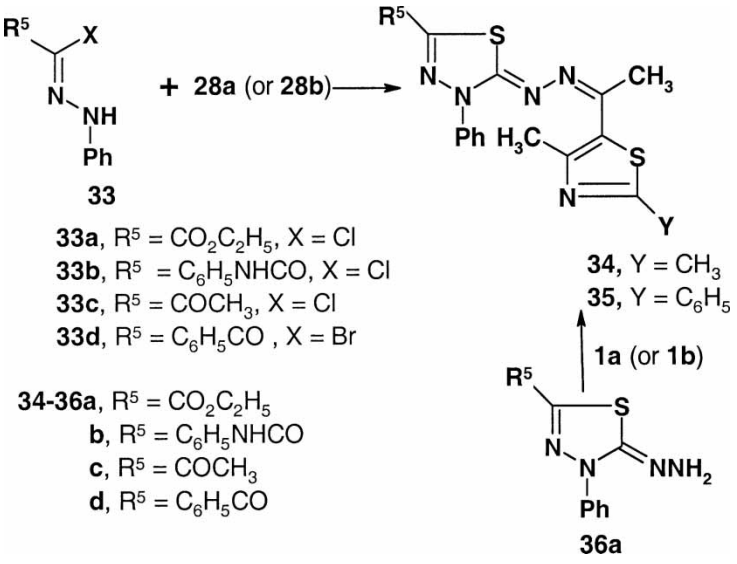
Conversely, treatment of **27** with each of **1a** and **1b** in 2-propanol afforded {(1*E*)-1-aza-2-[2,4-dimethyl(1,3-thiazol-5-yl)prop-1-enyl]amino}-methylthiomethane-1-thione (**28a**) and {[(1*E*)-1-aza-2-[4-methyl-2-phenyl(1,3-thiazol-5-yl)prop-1-enyl]amino}-methylthiomethane-1-thione (**28b**), respectively (scheme 4).

Structure **28** was elucidated by elemental analysis, spectral analysis and chemical transformation. Compound **28a** reacted with **6a** in ethanolic triethylamine at room temperature to give one isolated product, assigned as 2-[(2*E*)-1,2-diaza-3-(2,4-dimethyl(1,3-thiazol-5-yl)) but-2-enylidne]-3-phenyl(1,3,4-thiadiazolin-5-yl)-2,4-dimethyl(1,3-thiazol-5-yl)ketone (**32a**). Structure **32** was confirmed by elemental analysis, spectral data and alternative synthesis route. Similarly, treatment of **28b** with **6b** afforded thiadiazoline derivatives **32b** (scheme 4).

By analogy, the appropriate hydrazonoyl halides **33a–d** reacted with each of **28a** or **28b** in ethanolic triethylamine to afford thiadiazolines **34a–d** and **35a–d**, respectively (scheme 5). Structures **34** and **35** were elucidated by elemental analysis, spectral data and alternative synthesis. Thus, treatment of **36a** [7] with each of **1a** or **1b** in 2-propanol afforded products identical in all respects to **34a** or **35a**, respectively.



SCHEME 4



SCHEME 5

Table 1. Response of various microorganisms to some synthesized compounds in *in vitro* (culture).

Comp. no	Antibacterial activity (% inhibition)	Antifungal activity (% inhibition)
9b	49	0.0
19c	90	0.0
19d	90	0.0
19f	73	0.0
19g	70	0.0
19h	80	0.0
28b	25.5	0.0

2.1 *Antimicrobial activity*

The tested microorganism was Gram negative bacteria (*Bacillus cereus*). In addition, some fungal plant pathogens (*Fusarium, Oxysporum*) were tested. The sensitivity of the selected microorganisms to some synthesized compounds was determined in *in vitro* culture in chloroform. Tests were carried out using the filter paper and the hole plate method [16].

Studies of the biological activity of compounds **9b** and **28b** showed that these compounds have moderate–weak biological activity against the tested bacteria, whereas **19c,d,f–h** have strong activity (table 1). All the tested compounds showed negative antifungal activities.

3. Experimental

All melting points were determined on an Electrothermal melting point apparatus and are uncorrected. IR (cm^{-1}) spectra were recorded on KBr disk on a FT IR-8201 PC Schimadzu spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ or $(CD_3)_2SO$ on a Gemini 200 MHz spectrometer using TMS as internal reference and chemical shifts are expressed

as δ (ppm). Mass spectra were recorded on a GC-MS QP 1000 EX Schimadzu instrument. Elemental analyses were performed at the microanalytical center Cairo University. Hydrazonoyl halides [17–20] and alkyl carbodithioates [21–24] were prepared as previously reported.

3.1 *Synthesis of 1-(2,4-dimethyl(1,3-thiazol-5-yl))-2-bromoethan-1-one (2)*

Bromine [16 g (5 ml), 0.1 mmol] was added portion-wise to 5-acetyl-2,4-dimethylthiazole (15.5 ml, 0.1 mmol) in chloroform (25 ml) while stirring for 15 min. The reaction mixture was then heated under reflux for 15 min. and the chloroform was subsequently evaporated. The resultant oily residue was neutralized with sodium bicarbonate (200 ml, 10%) and extracted with methylene chloride (3 × 30 ml). the solvent was then dried and evaporated to give 1-[2,4-dimethyl(1,3-thiazol-5-yl)]-2-bromoethan-1-one (**2**) as an oil (56% yield) used without purification.

3.2 *Synthesis of 1-[2,4-dimethyl(1,3-thiazol-5-yl)]-2-oxodimethylsulfonium bromide (3)*

A mixture of **2** (23.4 g, 0.1 mol) and dimethyl sulfide (6.8 g, 0.11 mol) in ethanol (75 ml) was boiled under reflux for 30 min. the reaction mixture was then cooled and the solid collected by filtration from ethanol to give **3** (tables 2 and 3).

3.3 *Synthesis of (2Z)-3-aza-1-(2,4-dimethyl-1,3-thiazol-5-yl)-2-bromo-3-(phenylamino) prop-2-en-1-one(6a) and (2Z)-3-aza-1-(2,4-dimethyl-1,3-thiazol-5-yl)-2-bromo-3-[(4-methylphenyl)amino]prop-2-en-1-one (6b)*

A mixture of **3** (29.6 g, 0.1 mol) and the appropriate N-nitrosoarylacetamide (16 g, 0.11 mol) was stirred in ethanol (100 ml) for 3 h at room temperature. The resulting red solid was collected and crystallized to give **6a** and **6b** (tables 2 and 3).

Table 2. Characterization data of the newly synthesized compounds.

Comp. No.	Mp. (°C) Solvent	Color Yield %	Mol. formula (Mol. wt.)	Calcd./Found% C	H	N	S
3	142–44	Brown	$C_9H_{14}BrNOS_2$	36.49	4.76	4.73	21.56
	EtOH	66	296.25	36.42	4.81	4.70	21.58
6a	182–84	Pale red	$C_{13}H_{12}BrN_3OS$	46.16	3.58	12.42	9.48
	EtOH	60	338.22	46.20	3.56	12.39	9.51
6b	162–65	Pale red	$C_{14}H_{14}BrN_3OS$	47.74	4.01	11.93	9.10
	EtOH	65	352.25	47.77	3.99	11.97	9.15
8a	120–23	Red	$C_{15}H_{14}N_4OS_2$	54.52	4.27	16.96	19.41
	EtOH	70	330.43	54.48	4.31	17.01	19.45
8b	152–55	Red	$C_{15}H_{14}N_4OSSe$	47.75	3.74	14.85	8.50
	EtOH	70	377.32	47.72	3.77	14.89	8.47
9a	138–42	Orange	$C_{15}H_{13}N_5O_2S_2$	50.12	3.65	19.48	17.84
	EtOH	70	359.42	50.16	3.68	19.45	17.92
9b	162–65	Orange	$C_{15}H_{13}N_5O_2SSe$	44.34	3.22	17.24	7.89
	EtOH	70	406.32	44.37	3.19	17.26	7.92
10a	108–11	Pale red	$C_{15}H_{13}N_3O_2S_2$	54.36	3.95	12.68	19.35
	EtOH	70	331.41	54.39	4.00	12.64	19.38
10b	125–27	Pale red	$C_{15}H_{13}N_3O_2SSe$	47.62	3.46	11.11	8.48
	EtOH	70	378.30	47.66	3.50	11.08	8.51

(*continued*)

Table 2. Continued.

Comp. No.	Mp. (°C) Solvent	Color Yield %	Mol. formula (Mol. wt.)	Calcd./Found% C	H	N	S
11a	172–75	Pale red	$C_{17}H_{16}N_4O_2S_2$	54.82	4.33	15.04	17.22
	EtOH	70	372.46	54.85	4.29	15.10	17.25
11b	188–90	Pale red	$C_{17}H_{16}N_4O_2SSe$	48.69	3.85	13.36	7.65
	EtOH	70	419.36	48.72	3.81	13.40	7.68
12a	210–12	Pale red	$C_{22}H_{18}N_4O_2S_2$	60.81	4.18	12.89	14.76
	EtOH	70	434.53	60.85	4.22	12.93	14.73
12b	217–20	Pale red	$C_{22}H_{18}N_4O_2SSe$	54.89	3.77	11.64	6.66
	EtOH	70	481.43	54.86	3.79	11.68	6.62
18a	193–95	Pale red	$C_{21}H_{17}N_5OS_2$	60.12	4.08	16.69	15.29
	Dioxan	85	419.52	60.09	4.12	16.71	15.32
18b	205–07	Pale red	$C_{22}H_{19}N_5OS_2$	60.95	4.42	16.15	14.79
	Dioxan	80	433.55	60.91	4.39	16.17	14.82
18c	217–19	Pale red	$C_{19}H_{15}N_5OS_3$	53.63	3.55	16.46	22.61
	Dioxan	78	425.55	53.66	3.58	16.50	22.58
18d	225–7	Pale red	$C_{19}H_{15}N_5O_2S_2$	55.73	3.69	17.10	15.66
	Dioxan	82	409.48	55.78	3.72	17.08	15.68
18e	206–08	Pale red	$C_{20}H_{16}N_6OS_2$	57.12	3.84	19.99	15.25
	Dioxan	85	420.51	57.09	3.89	20.01	15.28
18f	165–67	Pale red	$C_{22}H_{19}N_5OS_2$	60.95	4.42	16.15	14.79
	Dioxan	80	433.55	60.98	4.45	16.12	14.82
18g	170–73	Pale red	$C_{20}H_{17}N_5OS_3$	54.65	3.90	15.93	21.88
	Dioxan	83	439.58	54.61	3.87	15.95	21.85
18h	220–2	Pale red	$C_{20}H_{17}N_5O_2S_2$	56.72	4.05	16.54	15.14
	Dioxan	79	423.51	56.69	4.10	16.58	15.11
18i	230–32	Pale red	$C_{21}H_{18}N_6OS_2$	58.04	4.18	19.34	14.76
	Dioxan	84	434.53	58.10	4.22	19.31	14.79
18j	200–203	Pale red	$C_{19}H_{19}N_5OS_2$	57.41	4.82	17.62	16.13
	Dioxan	85	397.51	57.38	4.85	17.66	16.10
18k	189–91	Pale red	$C_{20}H_{21}N_5OS_2$	58.37	5.14	17.02	15.58
	Dioxan	80	411.54	58.40	5.19	16.99	15.53
19a	218–20	Pale red	$C_{22}H_{19}N_5OS_2$	60.95	4.42	16.15	14.79
	Dioxan	88	433.55	60.99	4.39	16.19	14.78
19b	206–08	Pale red	$C_{23}H_{21}N_5OS_2$	61.72	4.73	15.65	14.33
	Dioxan	85	447.57	61.68	4.77	15.69	14.30
19c	208–10	Pale red	$C_{20}H_{17}N_5OS_3$	54.65	3.90	15.93	21.88
	Dioxan	85	439.58	54.68	3.94	15.90	21.91
19d	222–24	Pale red	$C_{20}H_{17}N_5O_2S_2$	56.72	4.05	16.54	15.14
	Dioxan	88	423.51	56.68	4.10	16.58	15.10
19e	225–27	Pale red	$C_{21}H_{18}N_6OS_2$	58.04	4.18	19.34	14.76
	Dioxan	78	434.53	57.99	4.15	19.39	14.78
19f	207–08	Pale red	$C_{23}H_{21}N_5OS_2$	61.72	4.73	15.65	14.33
	Dioxan	83	447.57	61.75	4.78	15.61	14.36
19g	175–78	Pale red	$C_{21}H_{19}N_5OS_3$	55.60	4.22	15.44	21.21
	Dioxan	85	453.60	55.57	4.19	15.49	21.17
19h	183–85	Pale red	$C_{21}H_{19}N_5O_2S_2$	57.65	4.38	16.01	14.66
	Dioxan	85	437.54	57.68	4.41	16.07	14.62

(*continued*)

Table 2. Continued.

Comp. No.	Mp. (°C) Solvent	Color Yield %	Mol. formula (Mol. wt.)	Calcd./Found% C	H	N	S
19i	238–40	Pale red	$C_{22}H_{20}N_6OS_2$	58.91	4.49	18.74	14.30
	Dioxan	88	448.56	58.87	4.52	18.71	14.33
19j	215–17	Pale red	$C_{20}H_{21}N_5OS_2$	58.37	5.14	17.02	15.58
	Dioxan	78	411.54	58.40	5.11	16.98	15.55
19k	173–75	Pale red	$C_{21}H_{23}N_5OS_2$	59.27	5.45	16.46	15.07
	Dioxan	80	425.57	59.31	5.49	16.41	15.01
22a	190–93	Brown	$C_{28}H_{27}N_5O_3S$	65.48	5.30	13.64	6.24
	EtOH	80	513.61	65.52	5.26	13.60	6.29
22b	156–58	Brown	$C_{28}H_{26}BrN_5O_3S$	56.76	4.42	11.82	5.41
	EtOH	75	592.50	56.72	4.46	11.79	5.39
22c	183–85	Brown	$C_{28}H_{26}FN_5O_3S$	63.26	4.93	13.17	6.03
	EtOH	85	531.60	63.30	4.97	13.14	5.99
22d	184–86	Brown	$C_{26}H_{25}N_5O_3S_2$	60.10	4.85	13.48	12.34
	EtOH	88	519.64	59.98	4.91	13.45	12.38
22e	147–49	Brown	$C_{31}H_{33}N_5O_3S$	67.00	5.99	12.60	5.77
	EtOH	85	555.69	67.05	6.01	12.56	5.72
22f	160–62	Brown	$C_{29}H_{27}N_5O_5S$	62.46	4.88	12.56	5.75
	EtOH	80	557.62	62.41	4.92	12.59	5.72
28a	188–190	Brown	$C_9H_{13}N_3S_3$	41.67	5.05	16.20	37.08
	EtOH	87	259.41	41.70	5.10	16.25	37.02
28b	182–84	Yellow	$C_{14}H_{15}N_3S_3$	52.30	4.70	13.07	29.92
	EtOH	90	321.48	52.27	4.66	12.99	29.99
32a	168–70	Yellow	$C_{21}H_{20}N_6OS_3$	53.82	4.30	17.93	20.53
	Dioxan	85	468.62	53.78	4.33	18.00	20.59
32b	198–200	Yellow	$C_{26}H_{22}N_6OS_3$	58.84	4.18	15.84	18.13
	Dioxan	90	530.69	58.89	4.13	15.88	18.19
34a	151–54	Yellow	$C_{18}H_{19}N_5O_2S_2$	53.85	4.77	17.44	15.97
	Dioxan	88	401.50	53.88	4.81	17.39	16.00
34b	224–26	Yellow	$C_{22}H_{20}N_6OS_2$	58.91	4.49	18.74	14.30
	Dioxan	86	448.56	58.87	4.52	18.78	14.33
34c	171–73	Yellow	$C_{17}H_{17}N_5OS_2$	54.96	4.61	18.85	17.26
	Dioxan	90	371.48	55.00	4.57	18.90	17.22
34d	217–18	Yellow	$C_{22}H_{19}N_5OS_2$	60.95	4.42	16.15	14.79
	Dioxan	80	433.55	60.99	4.45	16.20	14.83
35a	176–78	Yellow	$C_{23}H_{21}N_5O_2S_2$	59.59	4.57	15.11	13.83
	Dioxan	88	463.57	59.56	4.60	15.08	13.87
35b	197–200	Yellow	$C_{27}H_{22}N_6OS_2$	63.51	4.34	16.46	12.56
	Dioxan	90	510.63	63.55	4.30	16.49	12.51
35c	147–50	Yellow	$C_{22}H_{19}N_5OS_2$	60.95	4.42	16.15	14.79
	Dioxane	87	433.55	60.98	4.38	16.19	14.84
35d	215–17	Yellow	$C_{27}H_{21}N_5OS_2$	65.43	4.27	14.13	12.94
	Dioxan	84	495.62	65.39	4.30	14.09	13.00

Table 3. Spectra of some selected synthesized compounds.

Comp. No	Spectra
3	ν (cm^{-1}): 2989 (CH), 1675 (CO), 1632 (C=N) and 1582 (C=C)
6a	δ_H (ppm): 2.47 (s, 3H), 2.74 (s, 3H), 6.62–7.12 (m, 5H) and 8.24 (s, br, 1H) ν (cm^{-1}): 3241 (NH), 3049 (CH), 1665 (CO), 1642 (C=N) and 1582 (C=C)
6b	δ_H (ppm): 2.42 (s, 3H), 2.75 (s, 3H), 2.89 (s, 3H), 7.13–7.84 (m, 4H) and 8.72 (s, br, 1H) ν (cm^{-1}): 3245 (NH), 3050 (CH), 1657 (CO), 1645 (C=N) and 1590 (C=C)
8a	δ_H (ppm): 2.32 (s, 3H), 2.47 (s, 3H), 2.74 (s, 3H), 6.46–7.21 (m, 4H) and 15.17 (s, br, 1H) ν (cm^{-1}): 3319 (NH), 3056 (CH) and 1657 (CO conjugated)
8b	δ_H (ppm): 2.34 (s, 3H), 2.64 (s, 3H), 2.81 (s, 3H), 7.13–7.43 (m, 4H) and 15.16 (s, br, 1H) ν (cm^{-1}): 3384 (NH), 3030 (CH) and 1624 (CO) Mass m/z: 377 (1.9), 271 (6.1), 140 (100), 106 (18.8) and 71 (24.2)
9a	δ_H (ppm): 2.35 (s, 3H), 2.43 (s, 3H), 2.75 (s, 3H) and 7.28–7.75 (m, 4H) ν (cm^{-1}): 3057 (CH), 1631 (CO), 1583 (C=C) and 1485 (NO)
9b	δ_H (ppm): 2.35 (s, 3H), 2.43 (s, 3H), 2.75 (s, 3H) and 7.28–7.75 (m, 4H) ν (cm^{-1}): 3057, 2927 (CH), 1624 (CO), 1573 (C=C) and 1492 (NO)
10a	δ_H (ppm): 2.35 (s, 3H), 2.47 (s, 3H), 2.78 (s, 3H) and 6.64–7.21 (m, 4H) ν (cm^{-1}): 3061 (CH), 1691, 1633 (CO) and 1583 (C=C)
10b	δ_H (ppm): 2.33 (s, 3H), 2.51 (s, 3H), 2.82 (s, 3H) and 6.64–7.25 (m, 4H) ν (cm^{-1}): 3060, 2972 (CH), 1690, 1631 (CO) and 1587 (C=C)
11a	δ_H (ppm): 2.20 (s, 3H), 2.35 (s, 3H), 2.47 (s, 3H), 2.78 (s, 3H) and 6.64–7.21 (m, 4H) ν (cm^{-1}): 3060 (CH), 1631 (CO) and 1587 (C=C)
11b	δ_H (ppm): 2.38 (s, 3H), 2.45 (s, 3H), 2.74 (s, 3H), 2.86 (s, 3H) and 7.81–7.87 (m, 4H) ν (cm^{-1}): 3029 (CH), 1704 (CO) and 1624 (C=N)
12a	δ_H (ppm): 2.50 (s, 3H), 2.75 (s, 3H), 2.84 (s, 3H), and 7.42–8.27 (m, 9H) ν (cm^{-1}): 3030 (CH), 1647 (CO), 1628 (C=N) and 1590 (C=C)
12b	δ_H (ppm): 2.35 (s, 3H), 2.47 (s, 3H), 2.74 (s, 3H) and 6.34–7.81 (m, 9H) ν (cm^{-1}): 3030 (CH), 1647 (CO), 1628 (C=N) and 1590 (C=C)
18a	δ_H (ppm): 2.50 (s, 3H), 2.74 (s, 3H), 6.47–6.94 (m, 10H) and 7.53 (s, 1H) ν (cm^{-1}): 3056 (CH), 1737 (CO), 1620 (C=N) and 1587 (C=C)
18b	δ_H (ppm): 2.38 (s, 3H), 2.50 (s, 3H), 2.78 (s, 3H), 6.47–6.94 (m, 9H) and 7.53 (s, 1H) ν (cm^{-1}): 3056 (CH), 1737 (CO), 1620 (C=N) and 1587 (C=C)
18c	δ_H (ppm): 2.50 (s, 3H), 2.74 (s, 3H), 6.47–7.20 (m, 8H) and 8.21 (s, 1H) ν (cm^{-1}): 3056 (CH), 1737 (CO), 1620 (C=N) and 1587 (C=C)
18d	δ_H (ppm): 2.50 (s, 3H), 2.74 (s, 3H), 6.47–7.40 (m, 8H) and 8.20 (s, 1H) ν (cm^{-1}): 3056 (CH), 1737 (CO), 1620 (C=N) and 1587 (C=C)
18e	δ_H (ppm): 2.50 (s, 3H), 2.74 (s, 3H) and 7.01–9.23 (m, 10H) ν (cm^{-1}): 3056 (CH), 1737 (CO), 1620 (C=N) and 1587 (C=C)
18f	δ_H (ppm): 2.33 (s, 3H), 2.75 (s, 3H), 2.93 (s, 3H) and 7.32–8.15 (m, 10H) ν (cm^{-1}): 3061 (CH), 1704 (CO), 1645 (C=N) and 1597 (C=C)
18g	δ_H (ppm): 2.46 (s, 3H), 2.56 (s, 3H), 2.70 (s, 3H) and 7.04–7.45 (m, 8H) ν (cm^{-1}): 3109, 2920 (CH), 1630 (CO) and 1616 (C=C)
18h	δ_H (ppm): 2.40 (s, 3H), 2.77 (s, 3H), 2.83 (s, 3H) and 6.49–8.17 (m, 8H) ν (cm^{-1}): 3070 (CH), 1720 (CO), 1623 (C=N) and 1607 (C=C)
18i	δ_H (ppm): 2.10 (s, 3H), 2.47 (s, 3H), 2.74 (s, 3H) and 6.46–9.23 (m, 9H) ν (cm^{-1}): 2980 (CH), 1626 (CO) and 1570 (C=C)
18j	δ_H (ppm): 2.42 (s, 3H), 2.53 (quintet, 4H), 2.73 (s, 3H), 2.95 (t, 4H) and 7.27–7.45 (m, 5H) ν (cm^{-1}): 2920 (CH), 1616 (CO) and 1546 (C=C)

(*continued*)

Table 3. Continued.

Comp. No	Spectra
18k	δ_H (ppm): 1.59 (quintet, 2H), 2.17 (quintet, 4H), 2.45 (s, 3H), 2.73 (s, 3H), 2.82 (t, 4H) and 7.28–8.12 (m, 5H)
	ν (cm^{-1}): 3069 (CH), 1625 (CO) and 1574 (C=C)
19a	δ_H (ppm): 2.38 (s, 3H), 2.73 (s, 3H), 2.82 (s, 3H), 7.19–8.11 (m, 9H) and 8.83 (s, 1H)
	ν (cm^{-1}): 3027 (CH), 1641 (CO) and 1589 (C=C)
	Mass m/z: 433 (100), 316 (26.5), 140 (20.2) and 90 (14.8)
19b	δ_H (ppm): 2.35 (s, 6H), 2.47 (s, 3H), 2.85 (s, 3H), 6.45–7.52 (m, 8H) and 8.15 (s, 1H)
	ν (cm^{-1}): 3027 (CH), 1641 (CO) and 1589 (C=C)
19c	δ_H (ppm): 2.39 (s, 3H), 2.72 (s, 3H), 2.86 (s, 3H), 7.02–7.92 (m, 7H) and 8.47 (s, 1H)
	ν (cm^{-1}): 3027 (CH), 1648 (CO) 1598 (C=N) and 1583 (C=C)
19d	δ_H (ppm): 2.42 (s, 3H), 2.75 (s, 3H), 2.82 (s, 3H), 6.51–7.92 (m, 7H) and 8.25 (s, 1H)
	ν (cm^{-1}): 3030 (CH), 1618 (CO) and 1585 (C=C)
19e	δ_H (ppm): 2.35 (s, 3H), 2.75 (s, 3H), 2.78 (s, 3H) and 6.51–9.93 (m, 9H)
	ν (cm^{-1}): 3030 (CH), 1618 (CO) and 1585 (C=C)
19f	δ_H (ppm): 2.36 (s, 3H), 2.51 (s, 3H), 2.59 (s, 3H), 2.70 (s, 3H) and 7.30–7.92 (m, 9H)
	ν (cm^{-1}): 2920 (CH), 1620 (CO), 1620 (C=N) and 1600 (C=C)
	Mass m/z: 477 (37.3), 140 (83.7), 104 (81.4), 91 (19.8) and 77 (34.2)
19g	δ_H (ppm): 2.46 (s, 3H), 2.51 (s, 3H), 2.56 (s, 3H), 2.70 (s, 3H) and 7.04–7.44 (m, 7H)
	ν (cm^{-1}): 2920 (CH), 1620 (CO), 1620 (C=N) and 1600 (C=C)
19h	δ_H (ppm): 1.92 (s, 3H), 2.34 (s, 3H), 2.64 (s, 3H), 2.66 (s, 3H) and 6.61–7.91 (m, 7H)
	ν (cm^{-1}): 3027 (CH), 1641 (CO) and 1580 (C=C)
	Mass m/z: 437 (5.4), 380 (100), 350 (20.4), 245 (11.4), 209 (47.3), 167 (75.4) and 107 (44.3)
19i	δ_H (ppm): 2.28 (s, 3H), 2.39 (s, 3H), 2.69 (s, 3H), 2.74 (s, 3H) and 7.14–8.99 (m, 8H)
	ν (cm^{-1}): 3070, 2920 (CH), 1624 (CO) and 1577 (C=C)
19j	δ_H (ppm): 1.73 (s, 3H), 2.35 (quintet, 4H), 2.43 (s, 3H), 2.69 (s, 3H), 3.35 (t, 4H) and 7.30–7.92 (m, 4H)
	ν (cm^{-1}): 3032 (CH), 1643 (CO) and 1621 (C=N)
19k	ν (cm^{-1}): 3031 (CH), 1625 (CO) and 1582 (C=C)
	Mass m/z: 425 (12), 393 (1.3), 259 (2.8), 227 (4.0), 151 (27.4), 106 (100), 91 (45.6) and 77 (19.9)
22a	δ_H (ppm): 1.23 (t, 3H), 1.70 (s, 3H), 2.47 (s, 3H), 2.56 (s, 3H), 2.74 (s, 3H), 4.09 (q, 2H), 7.05 (s, 1H), 7.16–7.72 (m, 6H), 8.05 (s, 1H) and 8.24 (d, 2H)
	ν (cm^{-1}): 1702 (CO ester), 1650 (CO conjugated) and 1615 (C=N)
22b	δ_H (ppm): 1.23 (t, 3H), 1.27 (s, 3H), 2.37 (s, 3H), 2.45 (s, 3H), 2.77 (s, 3H), 4.08 (q, 2H), 5.36 (s, 1H) and 7.26–7.42 (m, 8H)
	ν (cm^{-1}): 1702 (CO ester), 1650 (CO conjugated) and 1615 (C=N)
22c	δ_H (ppm): 1.14 (t, 3H), 1.25 (s, 3H),2.30 (s, 3H), 2.41 (s, 3H), 2.76 (s, 3H), 4.08 (q, 2H), 5.38 (s, 1H) and 6.97–7.78 (m, 8H)
	ν (cm^{-1}): 1702 (CO ester), 1650 (CO conjugated) and 1615 (C=N)
22d	δ_H (ppm): 1.26 (t, 3H), 2.31 (s, 3H), 2.38 (s, 3H), 2.46 (s, 3H), 2.74 (s, 3H), 4.20 (q, 2H), 5.70 (s, 1H) and 7.25–7.82 (m, 7H)
	ν (cm^{-1}): 2975 (CH), 1705 (CO ester), 1631 (CO conjugated) and 1606 (C=N)
22e	δ_H (ppm): 1.09 (d, 6H), 1.22 (t, 3H), 1.71 (s, 3H), 2.38 (s, 3H), 2.41 (s, 3H), 2.66 (s, 3H), 3.18 (sept., 1H), 4.05 (q, 2H), 5.8 (s, 1H) and 7.11–8.2 (m, 8H)
	ν (cm^{-1}): 2975 (CH), 1705 (CO ester), 1631 (CO conjugated) and 1606 (C=N)

(*continued*)

Table 3. Continued.

Comp. No	Spectra
22f	δ_H (ppm): 1.20 (t, 3H), 1.25 (s, 3H), 2.31 (s, 3H), 2.44 (s, 3H), 2.76 (s, 3H), 4.08 (q, 2H), 5.27 (s, 1H), 5.87 (s, 2H) and 6.73-8.07 (m, 7H)
	ν (cm^{-1}): 2974 (CH), 1697 (CO ester), 1632 (CO conjugated) and 1608 (C=N)
28a	δ_H (ppm): 2.31 (s, 3H), 2.64 (s, 3H), 2.66 (s, 3H), 2.68 (s, 3H) and 9.94 (s, 1H)
	ν (cm^{-1}): 3170 (NH), 3029 (CH) and 1579 (C=C)
28b	δ_H (ppm): 2.38 (s, 3H), 2.67 (s, 3H), 2.78 (s, 3H), 7.44–7.98 (m, 5H) and 9.96 (s, 1H)
	ν (cm^{-1}): 3182 (NH), 3029 (CH) and 1581 (C=C)
32a	δ_H (ppm): 2.00 (s, 3H), 2.47 (s, 6H), 2.74 (s, 6H) and 6.62–7.26 (m, 5H)
	ν (cm^{-1}): 3057 (CH) 1635 (CO) and 1583 (C=C)
32b	δ_H (ppm): 2.00 (s, 3H), 2.47 (s, 3H), 2.74 (s, 6H) and 6.62-7.26 (m, 10H)
	ν (cm^{-1}): 3057 (CH) 1635 (CO) and 1583 (C=C)
34a	δ_H (ppm): 1.30 (t, 3H), 2.00 (s, 3H), 2.47 (s, 3H), 2.74 (s, 3H), 4.20 (q, 2H) and 7.01–7.42 (m, 5H)
	ν (cm^{-1}): 3066 (CH), 1739 (CO) and 1581 (C=C)
34b	δ_H (ppm): 2.45 (s, 3H), 2.65 (s, 3H), 2.67 (s, 3H), 7.81–8.04 (m, 10H) and 8.48 (s, 1H)
	ν (cm^{-1}): 3374 (NH), 3029 (CH), 1679 (CO) and 1581 (C=C)
35a	δ_H (ppm): 1.44 (t, 3H), 2.52 (s, 3H), 2.72 (s, 3H), 4.45 (q, 2H) and 7.32–8.09 (m, 10H)
	ν (cm^{-1}): 3061 (CH), 1740 (CO) and 1582 (C=C)
35b	δ_H (ppm): 2.51 (s, 3H), 2.77 (s, 3H), 7.51–8.06 (m, 15H) and 8.47 (s, 1H)
	ν (cm^{-1}): 3247 (NH), 3058 (CH), 1667 (CO) and 1583 (C=C)
35c	δ_H (ppm): 2.52 (s, 3H), 2.64 (s, 3H), 2.77 (s, 3H) and 7.35–8.09 (m, 10H)
	ν (cm^{-1}): 3061 (CH), 1685 (CO) and 1583 (C=C)
35d	δ_H (ppm): 2.54 (s, 3H), 2.79 (s, 3H) and 7.21–8.4 (m, 15H)
	ν (cm^{-1}): 3064 (CH), 1620 (CO) and 1580 (C=C)

3.4 *Synthesis of 2,4-dimethyl-(1,3-thiazol-5-yl)-2-imino-3-(4-methylphenyl-(1,3,4-thiadiazolin-5-yl)ketone (8a) and 2,4-dimethyl-(1,3-thiazol-5-yl)-2-imino-3-(4-methylphenyl)-1,3,4-selenadiazol-2-yl]methanone (8b)*

A mixture of **6b** (3.52 g, 0.01 mol) and the appropriate of KSCN or KSeCN (0.01 mol) in ethanol (20 ml) was boiled under reflux for 30 min. The resulting solid was filtered off and crystallized from ethanol to give pale red crystals of **8a** and **8b**, respectively (tables 2 and 3).

3.5 *Synthesis of 2-(azanitrosomethylene)-3-(4-methylphenyl)(1,3,4-thiadiazolin-5-yl)-2,4-dimethyl-(1,3-thiazol-5-yl)ketone (9a) and 2-(azanitrosomethylene)-3-(4-methylphenyl)(1,3,4-selenadiazolin-5-yl)-2,4-dimethyl-(1,3-thiazol-5-yl)ketone (9b)*

A saturated solution of sodium nitrite (10 ml) was added to the appropriate **8a** or **8b** (1 g) in glacial acetic acid (10 ml) while stirring at 0–5 °C. The resulting solid (pale red) was collected and crystallized from alcohol to give **9a** and **9b,** respectively (tables 2 and 3).

3.6 *Synthesis of 5-[(2,4-dimethyl-1,3-thiazol-5-yl)carbonyl]-3-(4-methylphenyl)-1,3,4-thiadiazol-2(3H)-one (10a) and 5-[(2,4-dimethyl-1,3-thiazol-5-yl)carbonyl]-3-(4-methylphenyl)-1,3,4-slenadiazol-2(3H)-one (10b)*

After **9a** or **9b** (1 g) was boiled under reflux in xylene (20 ml) for 15 min the reaction mixture was evaporated under reduced pressure and then triturated with light petroleum (40–60 °C). The resulting solid was collected and crystallized to give pale yellow crystals of **10a** and **10b**, respectively (tables 2 and 3).

3.7 *Synthesis of 1-aza-1-[5-(2,4-dimethyl(1,3-thiazol-5-yl))carbonyl]-3-(4-methylphenyl)-1,3,4-thiadiazolin-2-yliden]acetone (11a) and 1-aza-1-[5-(2,4-dimethyl(1,3-thiazol-5-yl))carbonyl]-3-(4-methylphenyl)-1,3,4-selenadiazolin-2-yliden]acetone (11a)*

A solution of **8a** or **8b** (1 g) was warmed in acetic anhydride (10 ml) for 5 min and then poured onto crushed ice (20 g) while stirring. The so-obtained solid was collected and crystallized to give **11a** and **11b**, respectively (tables 2 and 3).

3.8 *Synthesis of 2-aza-2-{5-([(2,4-dimethyl-1,3-thiazol-5-yl)carbonyl]-3-(4-methylphenyl)-1,3,4-thiadiazolin-2-ylidene)}-1-phenylethan-1-one (12a) and 2-aza-2-{5-([(2,4-dimethyl-1,3-thiazol-5-yl)carbonyl]-3-(4-methylphenyl)-1,3,4-thiadiazolin-2-ylidene)}-1-phenylethan-1-one (12b)*

An equimolar amount of **8a** or **8b** and benzoyl chloride (0.005 mol) in pyridine (10 ml) was boiled under reflux for 15 min and then poured onto on crushed ice (10 g) and acidified with hydrochloric acid (6 M). The resulting solid was collected, washed with hot water and crystallized to give **12a** and **12b**, respectively (tables 2 and 3).

3.9 *Synthesis of triazolino[4,3-a]pyrimidines derivatives 22a–f*

Method A: A mixture of the appropriate **20a–f**, **6a** (or **6b**) and sodium ethoxide (0.005 mol each) in ethanol (20 ml) was heated under reflux for 3 h. The resulting solid formed after cooling was collected and crystallized to give triazolino[4,3-*a*]pyrimidines **22a–f,** respectively (tables 2 and 3).

Method B: An equimolar amount of the appropriate **6a** (or **6b**), the appropriate pyrimidine-2-thione derivatives **23a–f** and triethylamine (0.005 mol) in chloroform (20 ml) was boiled under reflux for 10 h. Chloroform was then evaporated under reduced pressure and the residue was crystallized to give a product identical in all respects to that obtained from method A.

3.10 *Synthesis of {(1E)-1-aza-2-[2,4-dimethyl(1,3-thiazol-5-yl)prop-1-enyl]amino} methylthiomethane-1-thione (28a) and {[(1E)-1-aza-2-(4-methyl-2-phenyl(1, 3-thiazol-5-yl)prop-1-enyl]amino}methylthiomethane-1-thione (28b)*

An equimolar amount of the appropriate substituted acetylthiazole (**1a** or **1b**) and **27** (0.005 mol each) in ethanol (10 ml) were stirred for 2 h at room temperature. The resulting solids were collected and crystallized from ethanol to give yellow crystals of **28a** and **28b**, respectively (tables 2 and 3).

3.11 *Synthesis of 1,3,4-thiadiazolines 18a–k, 19a–k, 32a,b and 34, 35a–d*

An equimolar amount of the appropriate hydrazonoyl halides **6a**, **b**, **33a–d,** the appropriate alkyl carbodithioates **14a–k** (or **15a–k**) or **28a,b** and triethylamine (0.005 mol each) in ethanol (10 ml) were stirred for 2 h at room temperature. The resulting solids were collected and crystallized to give yellow crystals of **18a–k**, **19a–k**, **32a,b** and **34**, **35a–d** respectively (tables 2 and 3).

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