One-pot Synthesis of 2-Acylimino-3-aryl-1,3-thiazoline Derivatives in Aqueous Media

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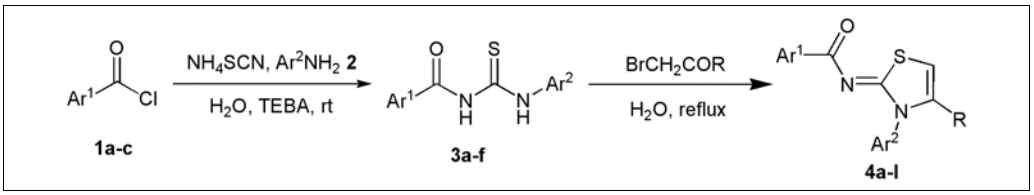

The one-pot two-step synthesis for acyliminothiazolines by treatment of N,N'-substituted thioureas with α-bromocarbonyl compounds under aqueous media was described. Compared to classical reaction in organic solvents, this method consistently has the advantages of short reaction time and being environmentally friendly.

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Introduction.

The use of water as a medium in organic reaction has received considerable attention due to its several advantages, for example, it is the cheapest solvent available on earth, non-hazardous to the environment, and isolation of the organic products can be performed simply by phase separation. To use water as reaction media is also beneficial to reaction rates and selectivity of important organic transformations, *e.g.* Diels-Alder reaction, aldol reaction and Michael addition [1-4].

Iminothiazoline derivatives have been reported to exhibit significant biological activities such as bactericidal, analgesicidal, fungicidal, and insecticidal [5-8]. Some thiazoline derivatives show interesting anti-HIV or anti-cancer activities and inhibition of cell division [9-11]. The classical synthesis of these compounds involves the Hantzsch condensation reaction of disymmetric thiourea and 2-chloroacetone in organic solvent or under microwave irradiation with the reagents supported on alumina under solvent free conditions [12,13]. All these methods, however, need the preparation and isolation of the intermediate isothiocyanate in toxic organic solvent such as dichloromethane and acetonitrile and need longer reaction time.

In continuation of our ongoing program to synthesize biologically active compounds and develop benign and rapid strategy for organic transformation [14], we have explored an expeditious one-pot route to the synthesis of 2-acylimino-3-aryl-1,3-thiazoline under aqueous media (Scheme 1).

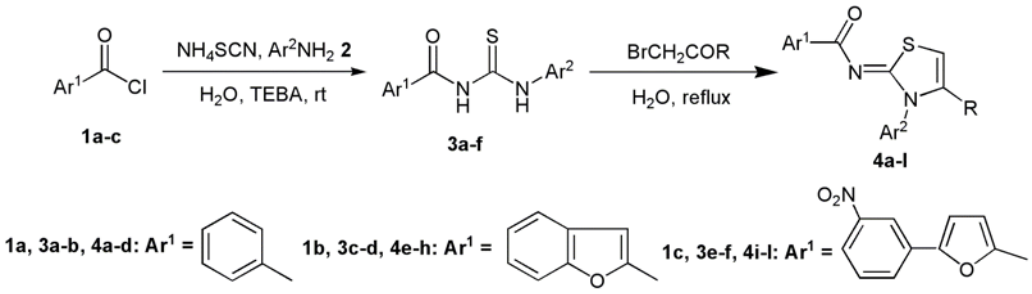
Results and Discussion.

As described in Scheme 1, treatment of benzoyl chloride **1a** with ammonium thiocyanate and arylamines **2** in the presence of benzyltriethylammonium chloride (TEBA) as catalyst in 3 mL H_2O at room temperature for 45 min afforded thioureas **3a-b**. Without isolation of the intermediate thioureas, one equimolar amount of α-bromoacetone was added to the reaction mixture and the mixture was stirred under refluxing for another 30 min afforded 2-benzoylimino-3-aryl-4-methyl-1,3-thiazolines **4a-b** in a total yields of 65-66%. 2-Benzoylimino-3-aryl-4-phenyl-1,3-thiazolines **4c-d** can also be obtained by above mentioned procedure using α-bromoacetophenone. However, these reactions need a longer time for 50 min in the second step reaction and only moderate total yields were obtained (Table 1, entries 3-4).

To further demonstrate the scope of the reaction, the preparation of 2-(2-benzofuroylimino)-3-aryl-1,3-thiazolines **4e-h** (Table 1, entries 5-8) and 2-[(5-aryl)-2-furoylimino]-3-aryl-1,3-thiazolines **4i-l** (Table 1, entries 9-12) were carried out as above mentioned procedure. 2-Benzofuroyl chloride **1b** and 5-(3-nitrophenyl)-2-furoyl chloride **1c** were treated in water with ammonium thiocyanate and arylamines in one-pot to afford corresponding *N*-aryl-*N*'-(2-benzofuroyl)thioureas **3c-d** and *N*-aryl-*N*'-[5-(3-nitrophenyl)-2-furoyl]thioureas **3e-f**, respectively. Subsequent condensation of thioureas **3c-f** with α-bromocarbonyl compounds in water gave corresponding 2-acylimino-1,3-thiazolines in acceptable total yields (Table 1).

All the product structures were characterized by IR, ^{1}H NMR, ^{13}C NMR, Mass and Elemental Analysis. The X-ray crystallography of **4e** identified the structure of the desired products (Figure 1) [15]. Crystal data, structure refinement of compound **4e**, atomic coordinates and equivalent isotropic displacement parameters of **4e** are listed in Tables 2 and 3. Selected bond distances and angles of **4e** are tabulated in Table 4 and 5. The X-ray

Scheme 1



crystal structure of compound **4e** clearly indicates that this reaction affords the *syn* product. So the formation of aroylimino-1,3-thiazolines could be explained by the mechanism described in Scheme 2. The reaction of aroyl chlorides **1** with ammonium thiocyanate, arylamines in the presence of a catalytic amount of benzyltriethyl-ammonium chloride (TEBA) give the intermediate thioureas **3**. Subsequently, compounds **3** reacted with α-bromocarbonyl compounds by the nucleophilic addition of the sulfur atom of thiourea to the α position of carbonyl carbon of α-bromocarbonyl compounds affording the *syn* products (**4**). The *syn* selectivity is likely due to the steric hindrance of the acyl group and the aryl group in the isothiourea intermediates (Scheme 2).

In order to compare this procedure with conventional method in organic solvent, we also carried out the reaction for **4a** by above mentioned materials in acetone. However, it did not give the desired product. The reason is that the reaction of acyl chloride with arylamine affording amide was dominant over those of acyl chlorides with ammonium thiocyanate.

EXPERIMENTAL

All reagents were obtained commercially and used without further purification. Thioureas **3a-b** were prepared according to the corresponding literature procedures [16] and m.p., IR, ^{1}H NMR, elemental analysis were compared with the literature [16]. Thioureas **3c-f** were prepared according to our previous work [17-18]. Melting points were determined on an XT-4 electrothermal micromelting point apparatus and uncorrected. IR spectra were recorded using KBr pellets on Nicolet AVATAR 36 FT-IR spectrophotometer. NMR spectra

Table 1

Synthesis of 2-acylimino-3-aryl-thiazolines **4a-l** in water.

Entry	Compd.	Ar^1	Ar^2	R	Yield (%) A [a]	B[b]
1	**4a**	**1a**	4-BrC_6H_4	CH_3	88	66
2	**4b**	**1a**	4-$CH_3C_6H_4$	CH_3	90	65
3	**4c**	**1a**	4-BrC_6H_4	C_6H_5	83	62
4	**4d**	**1a**	4-$CH_3C_6H_4$	C_6H_5	88	63
5	**4e**	**1b**	4-ClC_6H_4	CH_3	90	63
6	**4f**	**1b**	2-$NO_2C_6H_4$	CH_3	98	71
7	**4g**	**1b**	C_6H_5	C_6H_5	98	72
8	**4h**	**1b**	4-$CH_3C_6H_4$	C_6H_5	95	69
9	**4i**	**1c**	2-$CH_3C_6H_4$	CH_3	95	69
10	**4j**	**1c**	4-$CH_3C_6H_4$	CH_3	91	66
11	**4k**	**1c**	4-$CH_3OC_6H_4$	C_6H_5	97	73
12	**4l**	**1c**	4-$CH_3C_6H_4$	C_6H_5	97	72

[a] Overall isolated yield based on thiourea. [b] Overall isolated total yield based on aroyl chloride. [A] Preparation by thioureas with α-bromocarbonyl compounds in water under refluxing for 30-50 min. [B] Preparation by one-pot procedure in water.

Scheme 2

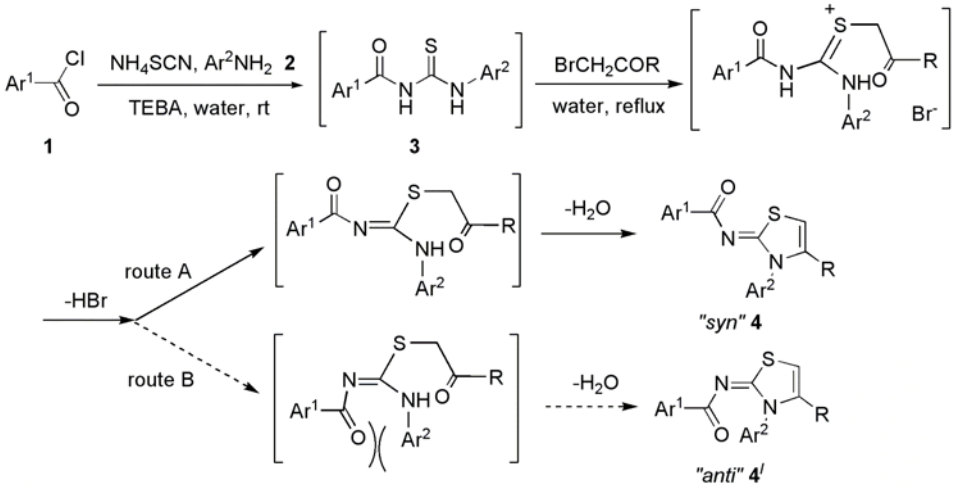


Table 2

Crystal and Refinement Parameters for Compound **4e**

Atom	X	Y	Z	U_{eq} (Å^2)
S(1)	878(1)	10504(1)	3893(1)	61(1)
Cl(1)	2891(1)	4658(1)	6016(1)	80(1)
N(1)	1122(2)	8584(1)	4239(1)	51(1)
N(2)	2720(2)	9581(1)	5193(1)	51(1)
O(1)	2769(2)	11372(1)	5080(1)	68(1)
O(2)	4649(2)	11515(1)	6544(1)	61(1)
C(1)	1711(2)	9513(2)	4525(1)	49(1)
C(2)	-202(3)	9619(2)	3278(2)	66(1)
C(3)	35(3)	8638(2)	3526(1)	57(1)
C(4)	-684(3)	7688(2)	3132(2)	81(1)
C(5)	1557(2)	7634(2)	4684(1)	49(1)
C(10)	3055(2)	7297(2)	4720(1)	58(1)
C(11)	3169(2)	10552(2)	5433(1)	52(1)
C(12)	4244(2)	10549(2)	6216(1)	51(1)
C(13)	4963(2)	9793(2)	6676(1)	55(1)
C(14)	5926(2)	10273(2)	7352(1)	54(1)
C(15)	6963(3)	9944(2)	8023(2)	69(1)
C(16)	7705(3)	10683(2)	8540(2)	78(1)
C(17)	7442(3)	11733(2)	8405(2)	80(1)
C(18)	6421(3)	12080(2)	7748(2)	74(1)
C(19)	5688(3)	11331(2)	7237(2)	58(1)
C(10)	3055(2)	7297(2)	4720(1)	58(1)

Table 3

Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [Å^2 x 10^3] for **4e.** U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Empirical formula	$C_{19}H_{13}ClN_2O_2S$	V, Å^3	1775.22(15)
Formula weight	368.82	Z	4
Temperature	293(2) K	ρ cacl. g cm^{-3}	1.380
Wavelength	0.71073 Å	Crystal size, mm	0.35 x 0.20 x 0.11
Crystal system	Monoclinic	θ range, deg	2.04 to 26.01°
Space group	P2 1/n	Absorption coefficient, mm^{-1}	0.347
a, Å	8.7622(4)	Reflections collected	9847
b, Å	12.9038(7)	Independent reflections	3470 (R_{int} = 0.0205)
c, Å	15.7760(8)	Data / restraints / parameters	3470 / 0 / 227
α, deg	90	Final R indices [I>2 σ (I)]	R1 = 0.0468, wR2 = 0.1237
β, deg	95.5980(10)	R indices (all data)	R1 = 0.0589, wR2 = 0.1329
γ, deg	90		

Table 4

Selected Bond Distances (Å) for **4e** [15]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S(1)	C(2)	1.720(3)	O(1)	C(11)	1.230(2)
S(1)	C(1)	1.738(2)	O(2)	C(19)	1.373(3)
N(1)	C(1)	1.364(3)	O(2)	C(12)	1.382(2)
N(1)	C(3)	1.403(3)	C(2)	C(3)	1.335(3)
N(1)	C(5)	1.444(2)	C(3)	C(4)	1.487(3)
N(2)	C(1)	1.311(3)	C(11)	C(12)	1.478(3)
N(2)	C(11)	1.357(3)	C(13)	C(14)	1.434(3)

Table 5

Selected Bond Angles (o) for **4e** [15]

Atoms	Bond Angles (o)	Atoms	Bond Angles (o)
C(2)-S(1)-C(1)	90.69(11)	C(19)-O(2)-C(12)	105.60(17)
C(1)-N(1)-C(3)	115.21(17)	N(2)-C(1)-N(1)	121.87(17)
C(1)-N(1)-C(5)	120.82(16)	N(2)-C(1)-S(1)	128.66(16)
C(3)-N(1)-C(5)	123.89(17)	N(1)-C(1)-S(1)	109.45(15)
C(1)-N(2)-C(11)	116.20(17)		

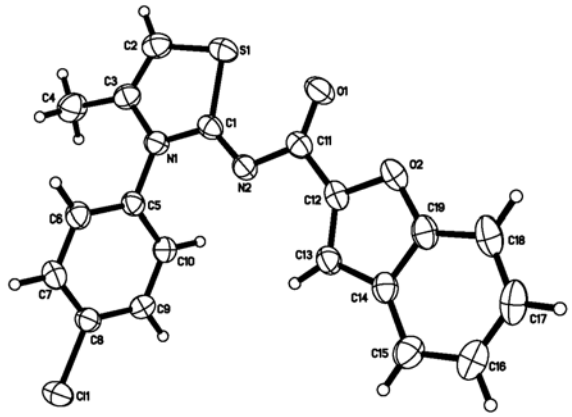


Figure 1. Molecular structure of compound **4e.**

were recorded at 400 (^{1}H) and 100 (^{13}C) MHz, respectively, on a Varian Mercury plus-400 instrument using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. Mass spectra were recorded on a ZAB-HS spectrometer. Elemental analyses were performed on a Carlo-Erba 1106 Elemental Analysis instrument.

General Procedure for Preparation of 2-Acylimino-3-phenyl-1,3-thiazolines (**4**).

Ammonium thiocyanate (1.5 mmol) and TEBA (0.1 mmol) were added into water (3 mL). At the same time, acyl chloride (1.0 mmol) and arylamine (1.0 mmol) were added. The suspension was stirred at room temperature for 45 min until the products were precipitated out fully. α-Bromoacetone/ α-bromoacetophenone (1.0 mmol) was then added to the suspension of thiourea and the mixture was refluxed for 30 min (50 min for α-bromoacetophenone). After the reaction was completed (monitored by TLC), crude product was obtained by filteration and recrystallization afforded pure product (Table 1).

2-Benzoylimino-3-(4-bromophenyl)-4-methyl-1,3-thiazoline (**4a**).

Mp 192-193 °C. (EtOH-H_2O) IR (KBr): 1597, 1563, 1494 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.09-7.23 (m, 9H, ArH), 6.40 (s, 1H, CH=C), 2.07 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 174.6, 170.6, 137.6, 136.6, 134.5, 133.4, 131.9, 130.1, 129.6, 128.8, 128.4, 123.9, 105.8, 15.5. MS (FAB): *m/z* =375, 373 (M^+ +H).

Anal. Calcd. for $C_{17}H_{13}BrN_2OS$: C, 54.69; H, 3.50; N, 7.50. Found: C, 54.78; H, 3.56; N, 7.54.

2-Benzoylimino-3-(4-methylphenyl)-4-methyl-1,3-thiazoline (**4b**).

Mp 217-218 °C. (EtOH-H_2O) IR (KBr): 1600, 1564, 1510 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.10-7.13 (m, 9H, ArH), 6.37 (s,

1H, CH=C), 2.48 (s, 3H, CH_3), 2.06 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 174.7, 170.6, 139.8, 137.6, 135.0, 134.9, 131.8, 130.6, 129.6, 128.6, 128.2, 104.8, 21.9, 15.5. MS (FAB): *m/z* = 309 (M^+ +H).

Anal. Calcd. for $C_{18}H_{16}N_2OS$: C, 70.09; H, 5.23; N, 9.08. Found: C, 70.01; H, 5.26; N, 9.12.

2-Benzoylimino-3-(4-bromophenyl)-4-phenyl-1,3-thiazoline (**4c**).

Mp 234-235 °C. (EtOH) IR (KBr): 1601, 1566, 1472 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.12-8.10 (m, 2H, ArH), 7.46-7.10 (m, 12H, ArH), 6.69 (s, 1H, CH=C). ^{13}C NMR ($CDCl_3$): δ = 174.5, 169.7, 138.9, 136.1, 136.0, 134.9, 132.2, 130.5, 130.2, 129.8, 129.3, 128.9, 128.3, 128.2, 125.1, 108.3. MS (FAB): *m/z* = 437, 435 (M^+ +H).

Anal. Calcd. for $C_{22}H_{15}BrN_2OS$: C, 60.70; H, 3.47; N, 6.43. Found: C, 60.59; H, 3.50; N, 6.47.

2-Benzoylimino-3-(4-methylphenyl)-4-phenyl-1,3-thiazoline (**4d**).

Mp 276-277 °C. (EtOH) IR (KBr): 1597, 1564, 1473 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.13-8.11 (m, 2H, ArH), 7.44-7.12 (m, 12H, ArH), 6.69 (s, 1H, CH=C), 2.39 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 174.5, 169.8, 139.2, 138.4, 136.8, 134.9, 131.4, 130.7, 129.4, 129.3, 128.9, 128.7, 128.4, 128.1, 127.9, 107.4, 21.3. MS (FAB): *m/z* = 371 (M^+ +H).

Anal. Calcd. for $C_{23}H_{18}N_2OS$: C, 74.57; H, 4.90; N, 7.56. Found: C, 74.51; H, 4.94; N, 7.52.

2-(2-Benzofuroylimino)-3-(4-chlorophenyl)-4-methyl-1,3-thiazoline (**4e**).

Mp 216-217 °C. (EtOH) IR (KBr): 3103, 1604, 1557, 1469, 1369, 1257, 1227 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.58-7.51 (m, 4H, ArH), 7.34-7.30 (m, 3H, ArH), 7.27-7.18 (m, 2H, ArH), 6.40 (s, 1H, C=CH), 2.05 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 169.6, 166.8, 155.8, 152.5, 138.3, 136.6, 135.8, 133.9, 130.0, 127.5, 126.9, 123.7, 122.9, 111.9, 111.2, 104.8, 15.1. MS (FAB): *m/z* = 371, 369 (M^+ +H).

Anal. Calcd. for $C_{19}H_{13}ClN_2O_2S$: C, 61.87; H, 3.55; N, 7.60. Found: C, 61.80; H, 3.61; N, 7.53.

2-(2-Benzofuroyl)-3-(2-nitrophenyl)-4-methyl-1,3-thiazoline (**4f**).

Mp 263-264 °C. (EtOH) IR (KBr): 3111, 1608, 1562, 1470, 1369, 1256, 1224 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.48-8.36 (m, 2H, ArH), 8.13-8.08 (m, 3H, ArH), 7.89-7.75 (m, 2H, ArH), 7.62-7.53 (m, 2H, ArH), 6.86 (d, 1H, *J* = 1.2 Hz, =CH), 2.07 (d, 3H, *J* = 0.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ = 175.5, 167.4, 154.9, 152.2, 151.1, 140.3, 138.5, 130.0, 129.5, 128.4, 127.5, 126.8, 124.5, 123.6, 122.9, 111.9, 111.2, 102.6, 12.6. MS (FAB): *m/z* = 380 (M^+ +H).

Anal. Calcd. for $C_{19}H_{13}N_3O_4S$: C, 60.15; H, 3.45; N, 11.08. Found: C, 60.20; H, 3.51; N, 11.01.

2-(2-Benzofuroylimino)-3-phenyl-4-phenyl-1,3-thiazoline (**4g**).

Mp 286-287 °C. (DMF-EtOH-H_2O) IR (KBr): 3094, 1605, 1557, 1467, 1446 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 7.71 (d, 1H, *J* = 7.2 Hz, ArH), 7.61 (t, 1H, *J* = 7.2 Hz, ArH), 7.46-7.37 (m, 6H, ArH), 7.36-7.17 (m, 7H, ArH), 7.16 (d, 1H, *J* = 1.2 Hz, C=CH). ^{13}C NMR (DMSO-d_6): δ = 169.5, 165.7, 154.0, 151.6, 138.7, 138.3, 134.8, 131.2, 129.7, 129.4, 129.3, 128.8, 128.6, 127.3, 126.9, 123.7, 122.4, 111.9, 111.1, 107.3. MS (FAB): *m/z* = 397 (M^+ +H).

Anal. Calcd. for $C_{24}H_{16}N_2O_2S$: C, 72.71; H, 4.07; N, 7.07. Found: C, 72.79; H, 4.04; N, 7.02.

2-(2-Benzofuroylimino)-3-(4-methylphenyl)-4-phenyl-1,3-thiazoline (**4h**).

Mp 240-241 °C. (DMF-EtOH-H_2O) IR (KBr): 3094, 1605, 1557, 1467, 1446 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 7.74 (dd, 1H, *J* = 8.0 Hz, *J* = 0.8 Hz, ArH), 7.64 (dd, 1H, *J* = 8.0 Hz, *J* = 0.8 Hz, ArH), 7.45-7.41 (m, 1H, ArH), 7.33-7.23 (m, 11H, ArH), 7.21 (d, 1H, *J* = 1.2 Hz, C=CH), 2.36 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ = 169.1, 165.6, 155.0, 152.5, 139.1, 138.3, 134.8, 130.3, 129.5, 129.2, 129.0, 128.5, 128.4, 127.3, 126.9, 123.7, 122.9, 111.9, 111.1, 108.3, 20.9. MS (FAB): *m/z* = 411 (M^+ +H).

Anal. Calcd. for $C_{25}H_{18}N_2O_2S$: C, 73.15; H, 4.42; N, 6.82. Found: C, 73.08; H, 4.46; N, 6.86.

2-[5-(3-Nitrophenyl)-2-furoylimino]-3-(2-methylphenyl)-4-methyl-1,3-thiazoline (**4i**).

Mp 223-224 °C. (DMF-EtOH-H_2O) IR (KBr): 3106, 1584, 1518, 1461, 1347, 1272 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.46 (s, 1H, ArH), 8.10-8.00 (m, 2H, ArH), 7.53-7.37 (m, 4H, ArH), 7.25-7.17 (m, 1H, ArH), 6.91-6.89 (m, 1H, FuH), 6.75-6.74 (m, 1H, FuH), 6.42 (d, 1H, *J* = 0.8 Hz, C=CH), 2.07 (s, 3H, CH_3), 1.98 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 168.7, 165.7, 153.1, 152.0, 148.6, 136.2, 136.0, 134.2, 131.7, 131.2, 129.9, 129.7, 129.6, 127.8, 127.1, 122.4, 119.1, 117.2, 108.8, 104.7, 17.5, 14.6. MS (FAB): *m/z* = 420 (M^+ +H).

Anal. Calcd. for $C_{22}H_{17}N_3O_4S$: C, 63.00; H, 4.09; N, 10.02. Found: C, 62.93; H, 4.13; N, 10.11.

2-[5-(3-Nitrophenyl)-2-furoylimino]-3-(4-methylphenyl)-4-methyl-1,3-thiazoline (**4j**).

Mp 246-247 °C. (DMF-EtOH-H_2O) IR (KBr): 3130, 1584, 1512, 1461, 1341, 1281 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.45 (s, 1H, ArH), 8.10-8.01 (m, 2H, ArH), 7.54-7.38 (m, 4H, ArH), 7.25-7.17 (m, 1H, ArH), 6.90-6.87 (m, 1H, FuH), 6.75-6.74 (m, 1H, FuH), 6.42 (d, 1H, *J* = 0.8 Hz, C=CH), 2.35 (s, 3H, CH_3), 2.03 (d, 3H, *J* = 0.8 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ = 168.9, 165.7, 153.1, 152.0, 148.6, 136.1, 134.3, 131.9, 131.7, 130.1, 129.7, 127.8, 127.1, 122.4, 119.1, 117.2, 110.0, 104.5, 20.1, 14.5. MS (FAB): *m/z* = 420 (M^+ +H).

Anal. Calcd. for $C_{22}H_{17}N_3O_4S$: C, 63.00; H, 4.09; N, 10.02. Found: C, 62.92; H, 4.12; N, 10.10.

2-[5-(3-Nitrophenyl)-2-furoylimino]-3-(4-methoxylphenyl)-4-phenyl-1,3-thiazoline (**4k**).

Mp 257-258 °C. (DMF-EtOH) IR (KBr): 3082, 1584, 1512, 1461, 1341 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.53 (s, 1H, ArH), 8.11-8.04 (m, 2H, ArH), 7.56-7.52 (m, 1H, ArH), 7.28-7.22 (m, 3H, ArH), 7.18-7.05 (m, 5H, ArH), 6.93-6.91 (m, 2H, FuH), 6.81-6.80 (m, 1H, FuH), 6.70 (s, 1H, C=CH), 3.84 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 169.5, 165.8, 159.4, 153.4, 152.0, 148.7, 139.5, 135.6, 131.8, 130.5, 129.9, 129.7, 129.5, 128.9, 128.8, 128.5, 122.5, 119.2, 117.7, 113.9, 108.9, 107.5, 55.5. MS (FAB): *m/z* = 498 (M^+ +H).

Anal. Calcd. for $C_{27}H_{19}N_3O_5S$: C, 65.18; H, 3.85; N, 8.45. Found: C, 65.12; H, 3.89; N, 8.38.

2-[5-(3-Nitrophenyl)-2-furoylimino]-3-(4-methylphenyl)-4-phenyl-1,3-thiazoline (**4l**).

Mp 238-239 °C. (DMF-EtOH) IR (KBr): 3100, 1584, 1521, 1461, 1338 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.53 (d, 1H, J = 2 Hz, ArH), 8.13-8.05 (m, 2H, ArH), 7.57-7.53 (m, 1H, ArH), 7.30-7.25 (m, 5H, ArH), 7.16-7.13 (m, 4H, ArH), 7.07 (d, 1H, J = 3.2 Hz, FuH), 6.81 (d, 1H, J = 3.2 Hz, FuH), 6.72 (d, 1H, J = 2.0 Hz, C=CH), 2.41 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 169.4, 165.7, 153.3, 152.0, 148.6, 139.4, 138.7, 134.6, 131.7, 130.4, 129.9, 129.7, 129.4, 128.9, 128.8, 128.4, 128.1, 122.4, 119.1, 117.6, 108.9, 107.6, 21.2. MS (FAB): m/z = 482 (M^+ +H).

Anal. Calcd. for $C_{27}H_{19}N_3O_4S$: C, 67.35; H, 3.98; N, 8.73. Found: C, 67.42; H, 3.95, N; 8.78.

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