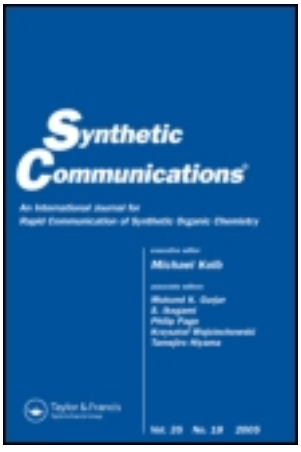

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One-Pot Synthesis of 2-Acylimino-3-aryl-thiazoline Derivatives in Aqueous Media

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One-Pot Synthesis of 2-Acylimino-3-aryl-thiazoline Derivatives in Aqueous Media

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Abstract: A one-pot, two-step synthesis for acyliminothiazolines by treated N,N′-substituted thioureas with α-bromocarbonyl compounds under aqueous media was described. Compared to the classical reaction in organic solvents, this method consistently has the advantage of short reaction times, convenient procedures, and mild reaction conditions.

Keywords: Aqueous media, 2-iminothiazolines, one-pot procedure, thioureas

INTRODUCTION

The use of water as a medium in organic reactions has received considerable attention because of its advantages: it is inexpensive, not hazardous to the environment, and nontoxic, and isolation of the organic products can be performed by simple phase separation. Also, there are beneficial effects of aqueous solvents on rates and selectivity of important organic transformations, for example, Diels–Alder reaction, aldol reaction, and Michael addition.[1–3]

Iminothiazoline derivatives have been reported to exhibit significant biological activities such as bactericidal, analgesicidal, fungicidal, and insecticidal activities.[4–6] Some thiazoline derivatives show interesting anti-HIV or anticancer activities and can inhibit cell division.[7–9] The classical

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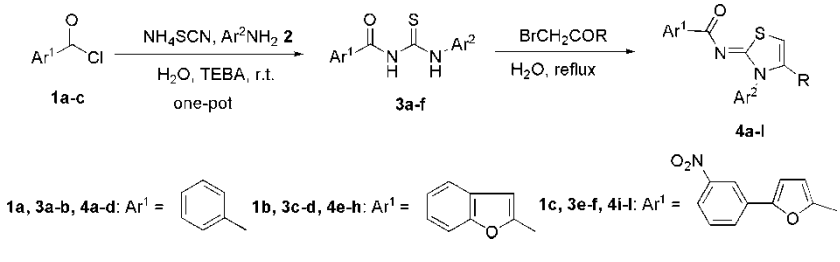
synthesis of these compounds involve the Hantzsch condensation reactions of disymmetric thioureas and chloroacetone in organic solvent or under microwave irradiation supported by alumina in solvent-free conditions.[10,11] More recently, one-pot, three-component condensation of aroylthiourea, primary amine, and α-halocarnony derivatives for the synthesis for the 2-acyliminothiazoline derivatives in alcohol has been reported.[12] However, all these methods need the preparation and isolation of the intermediates isothiocyanate in a toxic organic solvent such as dichloromethane or acetonitrile and longer reaction times.

In continuation of our ongoing program to synthesize biologically active compounds and develop benign and rapid strategy for organic transformation,[13] we have explored an expeditious one-pot route for the synthesis of 2-acylimino-3-phenyl-1,3-thiazoline under aqueous media (Scheme 1).

As described in Scheme 1, treatment of equimolar proportions of benzoyl chloride **1a** with ammonium thiocyanate and arylamines **2** in the presence of triethylbenzylammonium chloride (TEBA) as catalyst in H_2O at room temperature for 30 min afforded thioureas **3a**–**b**. Without isolation of the intermediate thiourea, one equimolar amount of bromoacetone was added to the reaction mixture, and the mixture was stirred under refluxing for another 45 min, affording 2-benzoylimino-3-aryl-4-methyl-1,3-thiazolines **4a, b** in 73 and 71% yield, respectively (Table 1, entries 1 and 2). 2-Benzoylimino-3-aryl-4-phenyl-1,3-thiazolines **4c, d**, can also be obtained by extending bromoacetone to phenacyl bromide by this procedure; however, these reactions need a longer time (50 min) with moderate total yields (Table 1, entries 3 and 4).

To further demonstrate the scope of the reaction, this reaction was extended to 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). The preparation of compounds **4e**–**h** and **4i**–**l** were carried out as previously described. 2-Benzofuroyl chloride **1b** and 5-(3-nitrophenyl)-2-furoyl chloride **1c** were treated in water with ammonium thiocyanate and arylamines **2** in one pot to afford the corresponding N-aryl-N′-(2-benzofuroyl)thioureas **3c**–**d** and N-aryl-N′-[5-(3-nitrophenyl)-2-furoyl]thioureas **3e**–**f**, respectively. Subsequent condensation with



Scheme 1.

Table 1. Synthesis of 2-acylimino-3-aryl-thiazolines **4a–l**

Entry	Compound	Ar_1	Ar_2	R	Yield (%)[a]
1	**4a**	**1a**	C_6H_5	CH_3	73
2	**4b**	**1a**	4-ClC_6H_4	CH_3	71
3	**4c**	**1a**	C_6H_5	C_6H_5	60
4	**4d**	**1a**	4-ClC_6H_4	C_6H_5	61
5	**4e**	**1b**	C_6H_5	CH_3	63
6	**4f**	**1b**	3-BrC_6H_4	CH_3	67
7	**4g**	**1b**	4-ClC_6H_4	C_6H_5	68
8	**4h**	**1b**	4-BrC_6H_4	C_6H_5	59
9	**4i**	**1c**	C_6H_5	CH_3	71
10	**4j**	**1c**	4-ClC_6H_4	CH_3	71
11	**4k**	**1c**	C_6H_5	C_6H_5	62
12	**4l**	**1c**	4-ClC_6H_4	C_6H_5	69

[a]Overall isolated total yield based on benzoyl chloride.

α-bromocarbonyl compounds in water gave the corresponding 2-acylimino-1,3-thiazolines **4c–l** in acceptable total yields (59–71%).

All the product structures were characterized by IR, ^{1}H NMR, ^{13}C NMR, and element analysis. The X-ray crystallography of **4a** identified the structure of the desired products (Figure 1).[12]

In order to compare this procedure with the conventional method in organic solvent, we carried out the reaction for **4a** with the previously

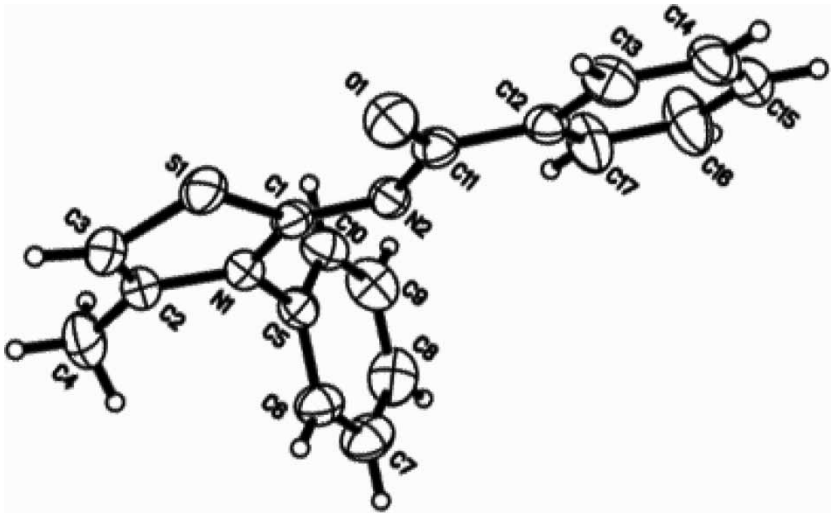


Figure 1. X-ray structure of compound **4a**.

mentioned materials in acetone; however, it did not give the desired. The reason is that the reaction of acyl chloride with arylamine affording amide was dominant over those of acyl chlorides with ammonium thiocyanate.

In summary, this approach constitutes a novel and efficient synthesis of 2-aroylimino-3-substituted-4-methyl (or phenyl)-1,3-thiazolines using a one-pot, two-step reaction by thioureas, which derived simultaneously from aroyl chloride, ammonium thiocyanate, and arylamines, with bromoacetone/phenacyl bromide in aqueous media under mild reaction conditions. Finally, this reaction sequence could conveniently be performed in water in one pot without isolation of the intermediates, allowing the development of a straightfoward, simple, green chemical, and efficient procedure for the generation of libraries of 2-imino-1,3-thiazolines.

EXPERIMENTAL

All reagents were obtained commercially and used without further purification. Melting points were determined on an XT-4 electrothermal micromelting-point apparatus and are uncorrected. IR spectra were recorded using KBr pellets on Nicolet Avatar 36 FT-IR spectrophotometer. NMR spectra 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 triethylbenzylammonium chloride (TEBA) (0.1 mmol) were added to water (3 mL). At the same time, acyl chloride (1.0 mmol) and arylamine (1.0 mmol) were added. The suspension was stirred at rt for 45 min until the products were fully precipitated. Then bromoacetone/phenacyl bromide (1.0 mmol) was added to the suspension of thiourea, and the mixture was heated under refluxing for 30 min (50 min for phenacyl bromide). After the reaction was completed (monitored by TLC), crude product was obtained by filtering and recrystallization from EtOH-H_2O (4 : 1), affording pure product (Table 1).

Data

2-Benzoylimino-3-phenyl-4-methyl-1,3-thiazoline 4a: Mp 156–157 °C. IR (KBr): 1597, 1564, 1492 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 8.10–7.20$ (m, 10H, ArH), 6.38 (s, 1H, CH═C), 2.05 (s, 3H, CH_3). ^{13}C NMR

($CDCl_3$): $\delta = 170.5$, 174.7, 137.8, 137.3, 134.8, 131.7, 129.9, 129.6, 128.5, 128.3, 104.9, 15.5. Anal. calcd. for $C_{17}H_{14}N_2OS$: C, 69.35; H, 4.79; N, 9.51. Found: C, 69.55; H, 4.74; N, 9.54.

Crystal structure of **4a:** $C_{17}H_{14}N_2OS$, space group P-1, T = 293 (2) K, a = 9.635(3) Å, b = 9.962(3) Å, c = 16.258(4) Å, $\alpha = 97.177(4)^\circ$, $\beta = 92.595(4)^\circ$, $\gamma = 97.864(4)^\circ$, V = 1530.7(7) $Å^3$, Z = 4, $D_c = 1.277\,Mg/m^3$. Crystal size: 0.47 × 0.34 × 0.11 mm; θ range for data collection 2.08 to 26.03°. Limiting indices $-5 < h < 11$, $-12 < k < 12$, $-20 < I < 19$. Reflections collected: 8491; independent reflections: 5845 ($R_{int} = 0.0135$); refinement method: Full-matrix least-squares on F^2; goodness-of-fit on F^2: 0.981; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0490$, $wR_2 = 0.1404$; R indices (all data): $R_1 = 0.0603$, $wR_2 = 0.1539$. Largest diff. peak and hole: 0.615 and −0.275 e $Å^{-3}$. Selected bond lengths (Å) and angles (0): S(1)-C(3): 1.734(3), S(1)-C(1): 1.7452(19), O(1)-C(11): 1.234(2), N(1)-C(1): 1.358(3), N(1)-C(2): 1.405(3), N(1)-C(5): 1.448(3), N(2)-C(1): 1.310(2), N(2)-C(11): 1.366(3), C(2)-C(3): 1.329(4), C(2)-C(4): 1.491(4), C(5)-C(10): 1.368(3), C(5)-C(6): 1.373(3), C(6)-C(7): 1.377(3), C(7)-C(8): 1.369(4), C(8)-C(9): 1.377(4), C(9)-C(10): 1.381(4), C(11)-C(12): 1.491(3), C(12)-C(17): 1.373(3), C(12)-C(13): 1.388(3), C(13)-C(14): 1.378(3), C(14)-C(15): 1.353(4), C(15)-C(16): 1.365(4), C(16)-C(17): 1.382(3), C(3)-S(1)-C(1): 90.53(11), C(1)-N(1)-C(2): 114.87(18), C(1)-N(1)-C(5): 121.45(16), C(2)-N(1)-C(5): 123.39(18), C(1)-N(2)-C(11): 116.60(16), N(2)-C(1)-N(1): 121.43(17), N(2)-C(1)-S(1): 128.87(16), N(1)-C(1)-S(1): 109.70(14), C(3)-C(2)-N(1): 111.9(2), C(3)-C(2)-C(4): 128.5(2), N(1)-C(2)-C(4): 119.6(2), C(2)-C(3)-S(1): 112.99(18), O(1)-C(11)-N(2): 124.89(19), O(1)-C(11)-C(12): 120.56(18), N(2)-C(11)-C(12): 114.55(16). (Crystallographic data for the structure analysis have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication, CCDC no. 281801, for **4a**. Copies of this information can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (44) 01223 336033 or e-mail: deposit@ccdc.cam.ac.uk.)

2-Benzoylimino-3-(4-chlorophenyl)-4-methyl-1,3-thiazoline 4b: Mp 210–211 °C. IR (KBr): 1597, 1565, 1492 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.05$–7.26 (m, 9H, ArH), 6.40 (s, 1H, CH═C), 2.07 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 174.6$, 170.2, 136.6, 135.7, 133.8, 131.9, 129.6, 129.5, 127.8, 104.8, 15.1. Anal. calcd. for $C_{17}H_{13}ClN_2OS$: C, 62.09; H, 3.98; N, 8.52. Found: C, 62.15; H, 4.04; N, 8.54.

2-Benzoylimino-3-phenyl-4-phenyl-1,3-thiazoline 4c: Mp 209–210 °C. IR (KBr): 1598, 1565, 1472 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.10$–8.06 (m, 2H, ArH), 7.43–7.20 (m, 13H, ArH), 6.66 (s, 1H, CH═C). ^{13}C NMR ($CDCl_3$): $\delta = 174.5$, 169.7, 137.3, 136.8, 136.4, 134.4, 131.3, 130.1, 129.6, 129.4, 129.3, 128.8, 128.4, 128.3, 106.9. Anal. calcd. for $C_{22}H_{16}N_2OS$: C, 74.13; H, 4.52; N, 7.86. Found: C, 74.20; H, 4.56; N, 7.80.

2-Benzoylimino-3-(4-methylphenyl)-4-phenyl-1,3-thiazoline 4d: Mp 276–277 °C. IR (KBr): 1597, 1564, 1473 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.13–8.11$ (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. 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-phenyl-4-methyl-1,3-thiazoline 4e: Mp 190–191 °C. IR (KBr): 3093, 1605, 1557, 1469, 1369, 1257, 1227 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 7.56–7.48$ (m, 2H, ArH), 7.44–7.31 (m, 4H, ArH), 7.30–7.21 (m, 4H, ArH), 6.41 (d, 1H, $J = 1.2$ Hz, C═CH), 2.06 (d, 3H, $J = 0.8$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 169.6$, 167.4, 154.9, 152.2, 137.3, 134.8, 130.0, 129.9, 129.6, 127.5, 126.9, 123.6, 122.9, 111.9, 111.2, 104.9, 15.5. Anal. calcd. for $C_{19}H_{14}N_2O_2S$: C, 68.25; H, 4.22; N, 8.38. Found: C, 68.34; H, 4.13; N, 8.33.

2-(2-Benzofuroylimino)-3-(3-bromophenyl)-4-methyl-1,3-thiazoline 4f: Mp 230–231 °C. IR (KBr): 3104, 1605, 1557, 1469, 1369, 1256, 1227 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 7.73$ (d, 1H, $J = 1.6$ Hz, ArH), 7.71–7.48 (m, 4H, ArH), 7.35–7.20 (m, 4H, ArH), 6.42 (d, 1H, $J = 1.2$ Hz, C═CH), 2.08 (d, 3H, $J = 1.2$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 169.6$, 166.7, 155.7, 152.5, 138.0, 133.9, 132.5, 131.2, 130.7, 127.0, 126.4, 123.1, 122.7, 123.4, 112.3, 111.3, 105.1, 15.0. Anal. calcd. for $C_{19}H_{13}BrN_2O_2S$: C, 55.22; H, 3.17; N, 6.78. Found: C, 55.15; H, 3.23; N, 6.73.

2-(2-Benzofuroylimino)-3-(4-chlorophenyl)-4-phenyl-1,3-thiazoline 4 g: Mp 250–251°C. IR (KBr): 3098, 1600, 1557, 1467, 1442 cm^{-1}. ^1H NMR (DMSO-d_6): δ =7.74–7.72 (m, 1H, ArH), 7.65–7.63 (m, 1H, ArH), 7.45–7.41 (m, 1H, ArH), 7.38–7.25 (m, 11H, ArH), 7.15 (s, 1H, C═CH). ^{13}C NMR (DMSO-d_6): δ =169.3, 165.7, 155.2, 152.5, 140.5, 138.4, 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. Anal. calcd. for $C_{24}H_{15}ClN_2O_2S$: C, 66.90; H, 3.51; N, 6.50. Found: C, 66.81; H, 3.55; N, 6.46.

2-(2-Benzofuroylimino)-3-(4-bromophenyl)-4-phenyl-1,3-thiazoline 4 h: Mp 252–253 °C. IR (KBr): 3100, 1601, 1557, 1461, 1446 cm^{-1}. ^1H NMR (DMSO-d_6): $\delta = 7.76–7.73$ (dd, 1H, $J = 8.0$ and 0.8 Hz, ArH), 7.67–7.64 (dd, 1H, $J = 8.0$ and 0.8 Hz, ArH), 7.46–7.40 (m, 1H, ArH), 7.38–7.22 (m, 11H, ArH), 7.20 (d, 1H, $J = 1.2$ Hz, C═CH). ^{13}C NMR (DMSO-d_6): δ =169.4, 165.6, 155.0, 152.5, 141.1, 138.4, 134.5, 131.0, 129.9, 129.4, 129.1, 128.8, 128.6, 127.5, 126.7, 123.7, 123.2, 120.1, 111.3, 108.4. Anal. calcd. for $C_{24}H_{15}BrN_2O_2S$: C, 60.64; H, 3.18; N, 5.89. Found: C, 60.69; H, 3.15; N, 5.84.

2-[5-(3-Nitrophenyl)-2-furoylimino]-3-phenyl-4-methyl-1,3-thiazoline 4i: Mp 235–236 °C. IR (KBr): 3106, 1611, 1512, 1476, 1344, 1272, 1221 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.45$ (d, 2H, $J = 2.0$ Hz, ArH), 8.09–8.06 (m, 1H, ArH), 8.00–7.98 (m, 1H, ArH), 7.62–7.48 (m, 6H, ArH), 6.94–6.93 (m, 1H, FuH), 6.76–6.75 (m, 1H, FuH), 6.40 (s, 1H, C═CH), 2.07 (d, 3H, $J = 0.8$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 169.6$, 165.5, 153.1, 151.9, 148.6, 136.9, 134.5, 131.7, 129.9, 129.6, 129.5, 129.4, 127.9, 122.3, 119.1, 117.3, 108.8, 104.8, 15.0. Anal. calcd. for $C_{21}H_{15}N_3O_4S$: C, 62.21; H, 3.73; N, 10.36. Found: C, 62.29; H, 3.70; N, 10.41.

2-[5-(3-Nitrophenyl)-2-furoylimino]-3-(4-chlorophenyl)-4-methyl-1,3-thia-zoline 4j: Mp 217–218 °C. IR (KBr): 3106, 1620, 1533, 1461, 1353, 1260 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.46$ (s, 1H, ArH), 8.10–8.00 (m, 2H, ArH), 7.55–7.38 (m, 4H, ArH), 7.30–7.24 (m, 1H, ArH), 6.92–6.88 (m, 1H, FuH), 6.77–6.74 (m, 1H, FuH), 6.40 (d, 1H, $J = 0.8$ Hz, C═CH), 2.07 (d, 3H, $J = 0.8$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 169.3$, 165.6, 153.1, 151.8, 148.6, 136.9, 136.7, 134.5, 131.7, 131.4, 129.6, 129.5, 129.4, 127.9, 127.4, 122.3, 119.3, 117.3, 109.1, 104.9, 15.0. Anal. calcd. for $C_{21}H_{14}ClN_3O_4S$: C, 57.34; H, 3.21; N, 9.55. Found: C, 57.40; H, 3.16; N, 10.01.

2-[5-(3-Nitrophenyl)-2-furoylimino]-3-phenyl-4-phenyl-1,3-thiazoline 4k: The previous described method for the reaction of 2-benzofuroyl chloride (**1b**) with ammonium thiocyanate (1.5 mmol), aniline (1.0 mmol), and phenacyl bromide (1.0 mmol) was used to prepare the product. It was purified by recrystallization from DMF-EtOH. Mp 194–195 °C. IR (KBr): 3088, 1599, 1521, 1452, 1344 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.53$ (d, 1H, $J = 2.0$ Hz, ArH), 8.13–8.05 (m, 2H, ArH), 7.57–7.53 (m, 1H, ArH), 7.33–7.24 (m, 10H, ArH), 7.07 (d, 1H, $J = 3.6$ Hz, FuH), 6.80 (d, 1H, $J = 3.2$ Hz, FuH), 6.70 (d, 1H, $J = 2.0$ Hz, C═CH). ^{13}C NMR ($CDCl_3$): $\delta = 169.6$, 165.6, 153.2, 151.9, 148.6, 137.4, 136.8, 134.6, 131.7, 130.1, 129.8, 129.6, 129.5, 128.8, 128.6, 128.3, 128.1, 122.4, 119.0, 117.4, 108.8, 107.6. Anal. calcd. for $C_{26}H_{17}N_3O_4S$: C, 66.80; H, 3.67; N, 8.99. Found: C, 66.72; H, 3.73; N, 8.93.

2-[5-(3-Nitrophenyl)-2-furoylimino]-3-(4-chlorophenyl)-4-phenyl-1,3-thi-azoline 4l: Mp 236–237°C. IR (KBr): 3100, 1584, 1521, 1461, 1338 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.53$ (d, 1H, $J = 2.0$ Hz, ArH), 8.16–8.07 (m, 2H, ArH), 7.59–7.54 (m, 1H, ArH), 7.32–7.19 (m, 9H, ArH), 6.95 (d, 1H, $J = 3.6$ Hz, FuH), 6.81 (d, 1H, $J = 3.2$ Hz, FuH), 6.72 (d, 1H, $J = 2.0$ Hz, C═CH). ^{13}C NMR ($CDCl_3$): $\delta = 169.4$, 165.7, 153.3, 152.0, 148.5, 139.2, 138.8, 134.9, 131.5, 130.4, 129.7, 129.4, 128.7, 128.5, 128.2, 122.5, 120.2, 117.8, 109.2, 108.1. Anal. calcd. for $C_{26}H_{16}ClN_3O_4S$: C, 62.21; H, 3.21; N, 8.37. Found: C, 62.14; H, 3.19; N, 8.34.

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