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### An Efficient, Uncatalyzed, and Rapid Synthesis of Thiazoles and Aminothiazoles Under Microwave Irradiation and Investigation of Their Biological Activity

Sudhakar A. Gaikwad<sup>a</sup>; Amol A. Patil<sup>a</sup>; Madhukar B. Deshmukh<sup>a</sup>

<sup>a</sup> Department of Chemistry, Shivaji University, Vidyanagar, Kolhapur, India

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## COMMUNICATION

### AN EFFICIENT, UNCATALYZED, AND RAPID SYNTHESIS OF THIAZOLES AND AMINOTHAZOLES UNDER MICROWAVE IRRADIATION AND INVESTIGATION OF THEIR BIOLOGICAL ACTIVITY

**Sudhakar A. Gaikwad, Amol A. Patil,  
and Madhukar B. Deshmukh**

*Department of Chemistry, Shivaji University, Vidyanagar, Kolhapur, India*

*A convenient method for the synthesis of thiazoles by treatment of  $\alpha$ -bromoketones with thioamides (Hantzsch synthesis) in the absence of catalysts under microwave irradiation has been developed. The products were formed rapidly in excellent yields. An efficiency comparison of time, yield, and effort clearly proved the microwave technique to be superior. The structures of the newly synthesized compounds were characterized by spectroscopic data and elemental analyses. The synthesized compounds were tested for their biological activity. Depending on the substituents, some of the thiazoles exhibit very good antibacterial or antifungal activity.*

**Keywords** Aminothiazole; biological activity; microwave irradiation; thiazole; thiourea

## INTRODUCTION

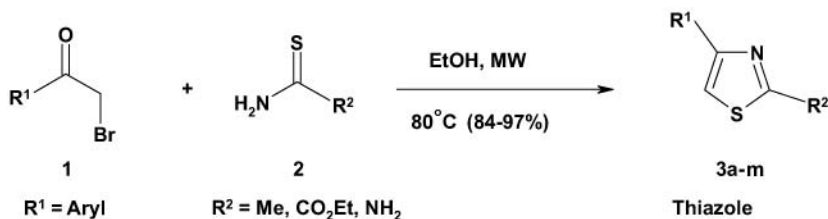
The thiazole ring system is a common structural moiety found in numerous biologically active molecules.<sup>1</sup> This heterocyclic moiety has been employed in the preparation of different important drugs required for the treatment of hypertension.<sup>2</sup> Some of the thiazole analogues are used as fungicides, inhibiting the in vivo growth of *Xanthomonas*, and as ingredient of herbicides or schistosomicidal and anthelmintic drugs.<sup>3</sup> Recently they have been utilized for the treatment of pain,<sup>4</sup> as fibrinogen receptor antagonists with antithrombotic activity,<sup>5</sup> and as inhibitors of bacterial DNA gyrase B.<sup>6</sup>

The application of microwave (MW) irradiation as a nonconventional energy source for the activation of reactions has now become a very popular and useful technology in organic chemistry. MW irradiation has led to enhanced reaction rates, higher yields of pure products, easier workup, and, sometimes, to selective conversions with several advantages of the ecofriendly approach in the framework of green chemistry. However, in spite of their potential utility, many of the reported methods suffer from drawbacks such as harsh

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Address correspondence to Madhukar B. Deshmukh, Department of Chemistry, Shivaji University, Vidyanagar, Kolhapur M.S. 416 004, India. E-mail: sudhakar.gaikwad@yahoo.com



Scheme 1

reaction conditions, unsatisfactory yields, prolonged reaction time, cumbersome product isolation procedures, and use of hazardous organic solvents and often expensive catalysts. Here, we report the use of MW irradiation to enhance the condensation reaction between  $\alpha$ -bromoketones with thioamides, i.e., the Hantzsch synthesis (Tables I–III).

## RESULTS AND DISCUSSION

### Syntheses

All the reactions shown in Scheme 1 were carried out at 80°C, and the products were formed within 20 min. No catalysts were used. A variety of  $\alpha$ -bromoketones and thioamides or thiourea was applied (Table III). The yields of thiazoles and aminothiazoles were excellent. The structures of the products were confirmed from their spectroscopic data (IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and MS) and elemental analyses. The methodical optimization was carried out at different temperatures (Table I). To optimize the reaction conditions for the MW-assisted Hantzsch cyclization, the reaction of **1** ( $\text{R}^1 = \text{C}_6\text{H}_3\text{Cl}_2$ ) with thiourea **2** ( $\text{R}^2 = \text{NH}_2$ ) was selected (Table I). Using an automated Emrys Optimizer single mode MW reactor, the thiazole **3b** was formed in 20 min at 80°C (Table III, Entry 2) with an isolated yield of 97%. As a standard procedure, the  $\alpha$ -bromoketone **1** and the thioamide derivative **2** were dissolved in ethanol (3 mL). At higher temperature, the reaction mixture became darker and the yield dropped slightly. Therefore it was decided to perform the microwave

**Table I** Optimization of the reaction conditions for 3b with MW Irradiation<sup>a</sup>

No.	Temp (°C)	Initial power (W)	Time (min) <sup>b</sup>	Isolated yield (%) <sup>c,d</sup>
<b>1</b>	50	100	40	90
<b>2</b>	60	110	30	85
<b>3</b>	70	125	30	90
<b>4</b>	80	150	20	96
<b>5</b>	100	200	20	89
<b>6</b>	130	250	20	79
<b>7</b>	150	250	30	90
<b>8</b>	175	300	20	55

<sup>a</sup>Emrys Optimizer microwave from Biotage using Emrys process vials (5 mL),  $\alpha$ -bromoketone (1.5 mmol),  $(\text{NH}_2)_2\text{CS}$  (1 mmol), ethanol (3 mL).

<sup>b</sup>Reaction monitored by TLC.

<sup>c</sup>After chromatographic purification.

<sup>d</sup>For exact procedures see the Experimental section.

**Table II** Variation of solvent for **3b** under microwave irradiation (80°C) and conventional heating (80°C)

Entry	Solvent	MW Irradiation		Conventional Heating	
		Time (min)	Yield (%)	Time (h)	Yield (%)
1	EtOH	20	96	1.5	93
2	MeOH	20	85	1.0	90
3	CH <sub>3</sub> CN	35	78	2.5	82
4	H <sub>2</sub> O	40	70	3.0	89

reactions at 80°C. The corresponding thermal reactions were carried out using identical reaction conditions (solvent volume, concentration, temperature; Table II). As shown in Table II, different results were obtained in the presence of different solvents.

### Antimicrobial Activities

The antimicrobial activities of the synthesized thiazoles were determined using the cup plate method.<sup>7</sup> This method depends on the diffusion of an antibiotic through a cavity into the solidified agar layer in a Petri dish. About 15–20 mL of molten nutrient agar was poured into each of the sterile plates. With the help of a sterile cork borer, the cups were punched and scooped out of the solidified agar. The agar plates so prepared were divided into different sets, and each set of the plates was inoculated with the suspension of a particular organism by the spread plate technique.

The cups of inoculated plates were then filled with 0.1 mL of the test solution, and the plates were allowed to stay in their upright position for 2 h. Then the plates were incubated at 37°C and kept overnight. The zone of inhibition developed was measured for the test organism for the particular compound. The in vitro antibacterial activity was carried out

**Table III** Synthesis of thiazoles under MW irradiation

$\alpha$ -Bromoketone <b>1</b> Ar-CO-CH <sub>2</sub> -Br Ar	Thioamide <b>2</b> R-CS-NH <sub>2</sub> R	Thiazole <b>3</b> <sup>a</sup>	Time <sup>b</sup> (min)	Yield <sup>c</sup> (%)	Mp (°C)
3,4-Dichlorophenyl	NH <sub>2</sub>	<b>3a</b>	15	90	193–194
2,5-Dichlorophenyl	NH <sub>2</sub>	<b>3b</b>	20	97	152–155
4-Iodophenyl	NH <sub>2</sub>	<b>3c</b>	10	90	126–128
3-Bromophenyl	NH <sub>2</sub>	<b>3d</b>	15	93	130–133
3,4-Dimethoxyphenyl	NH <sub>2</sub>	<b>3e</b>	25	86	198–200
4-Methoxyphenyl	NH <sub>2</sub>	<b>3f</b>	20	87	203–204
2-Methoxyphenyl	NH <sub>2</sub>	<b>3g</b>	20	89	Oil
3,4-Dichlorophenyl	Me	<b>3h</b>	10	94	126–128
3-Bromophenyl	Me	<b>3i</b>	15	91	Oil
2-Chlorophenyl	Me	<b>3j</b>	20	88	Oil
4-Nitrophenyl	CO-OEt	<b>3k</b>	10	93	Oil
Phenyl	CO-OEt	<b>3l</b>	15	84	Oil
3,4-Dichlorophenyl	CO-OEt	<b>3m</b>	10	90	Oil

<sup>a</sup>All products were identified by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MS data, and elemental analyses (C, H, and N).

<sup>b</sup>Reaction monitored by TLC.

<sup>c</sup>Isolated yields.

**Table IV** Antimicrobial activity of the thiazoles

Compound	Antibacterial activity zone of inhibition (mm)			Antifungal activity zone of inhibition (mm)		
	<i>E. coli</i>	<i>M. luteus</i>	<i>S. aureus</i>	<i>A. flavus</i>	<i>A. niger</i>	<i>C. lunata</i>
<b>3</b>	25	32	21	15	—	11
<b>3b</b>	22	26	16	22	16	15
<b>3c</b>	—	—	—	—	—	—
<b>3d</b>	24	29	20	15	12	10
<b>3e</b>	18	15	16	24	17	13
<b>3f</b>	—	—	—	—	—	—
<b>3g</b>	26	30	19	22	18	15
<b>3h</b>	12	18	17	16	13	12
<b>3i</b>	14	—	12	12	14	10
<b>3j</b>	23	26	19	18	11	13
<b>3k</b>	—	—	—	—	—	—
<b>3l</b>	19	26	14	20	10	—
<b>3m</b>	26	30	20	25	14	14
<b>Standard<sup>a</sup></b>	27	32	22	25	18	16
<b>DMF<sup>b</sup></b>	+ve	+ve	+ve	+ve	+ve	+ve

<sup>a</sup>Standard for antibacterial activity: Chloramphenicol (0.001 mol/mL). Standard for antifungal activity: Fluconazole (0.001 mol/mL).

<sup>b</sup>Control: DMF (0.01% solution in distilled water), +ve indicates growth of microbes.

against 24 old cultures of *Escherichia coli*, *Micrococcus luteus*, and *Staphylococcus aureus*. The fungi used were *Aspergillus flavus*, *Aspergillus niger*, and *Curvularia lunata*. The compounds were tested at concentrations of 0.001 mol/mL in DMF using Chloramphenicol and Fluconazole as standards for the antibacterial and antifungal activities, respectively. All the microbial strains were used as non-invasive species of their genera and thus were applicable for work. *E. coli* and *S. aureus* are common bacteria causing food poisoning; therefore we have selected these two bacteria for the antimicrobial screening.

The investigation of the antibacterial screening data revealed that the tested compounds exhibit moderate to good bacterial inhibitions. Compounds **3a**, **3d**, **3g**, and **3m** showed very good inhibition against *E. coli*, *M. luteus*, and *S. aureus* at 0.001 mol/mL. The thiazoles **3c**, **3f**, and **3k** were biologically inactive (antimicrobial study) as compared with the standard drug. The results are presented in Table IV. The newly prepared compounds were screened for their antifungal activity against *A. flavus*, *A. niger*, and *C. lunata* in DMSO by the cup plate method. The inhibition zones were measured and compared with the controls. The fungal activity of each compound was compared with Fluconazole as the standard drug. Compounds **3b**, **3e**, **3g**, and **3m** showed very good antifungal activity. The fungal zones of inhibition values are given in Table IV.

## CONCLUSION

In conclusion, we have found out a very simple, efficient, and eco-friendly synthesis of thiazoles under microwave irradiation. In addition, the biological activity results indicated that several of the obtained compounds exhibit good or excellent antimicrobial activities.

## EXPERIMENTAL

### General

All solvents and chemicals were of research grade and were used as obtained from Sigma-Aldrich, Alfa Aesar, and Acros Organics. Melting points were determined on an Electrothermal 9100 apparatus, and are not corrected. Thin layer chromatography (TLC) on commercial aluminum-blackened plates of silica gel 60<sub>PF254</sub> was used to monitor the progress of the reactions. The spots were visualized by heat staining with anisaldehyde in ethanol/sulfuric acid. Column chromatography was performed with Merck silica gel 60 (0.063–0.200 mm). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX-400 instrument at 400 and 100 MHz, respectively. The chemical shifts  $\delta$  were recorded in ppm using TMS as an internal standard. IR spectra were recorded as KBr pellets or neat on a Perkin Elmer Paragon 1000 spectrometer. Elemental analyses were obtained using a flash EA 1112 Thermo Finnigan instrument. The mass spectra were recorded on a VG-S-70 micro mass spectrometer operating at 70 eV.

### General Procedure for the Synthesis of Thiazole (3a–m)

A MW vial (5 mL) was charged with the  $\alpha$ -bromoketone **1** (1.5 mmol) and the thioamide or thiourea **2** (1mmol) and ethanol (3 mL). The vial was sealed and heated at 80°C (IR temperature detection) for 10 to 20 min under MW irradiation using an Emrys optimizer (an automated multiuser microwave synthesizer). If the reaction was performed under conventional heating, the MW vial was immersed into a preheated oil bath. In both cases, the reaction mixture was monitored by TLC. The MW vial was opened, and the ethanol was evaporated in a Radleys GreenHouse Blow-down Evaporator. The resulting product was directly charged on a silica gel column and eluted with 10% ethyl acetate/cyclohexane to afford the pure 2,4-disubstituted thiazoles **3a–m**.

### Spectroscopic Data of the Thiazoles (3a–m)

**2-Amino-4-(3,4-dichlorophenyl)-1,3-thiazole (3a).** Faint green solid, mp 193–194°C, IR: 3456, 3204, 1648, 1549, 1411, 1025 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>)  $\delta$  2.07 (s, 2H, NH<sub>2</sub>), 7.17 (s, 1H, thiazole), 7.60–7.88 (m, 3H, ArH); <sup>13</sup>C NMR (acetone-d<sub>6</sub>)  $\delta$  109.1, 118.2, 128.8, 130.23, 130.43, 130.95, 137.12, 147.25, 168.16. M<sup>+</sup>: 245. Anal. Calcd. for C<sub>9</sub>H<sub>6</sub>Cl<sub>2</sub>N<sub>2</sub>S: C, 44.12; H, 2.48; N, 11.45; Found: C, 44.05; H, 2.43; N, 11.32.

**2-Amino-4-(2,5-dichlorophenyl)-1,3-thiazole (3b).** Brown solid, mp 152–155°C, IR: 3446, 3210, 1630, 1542, 1413, 1035 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>)  $\delta$  2.08 (s, 2H, NH<sub>2</sub>), 7.10 (s, 1H, thiazole), 7.30–7.54 (m, 3H, ArH); <sup>13</sup>C NMR (acetone-d<sub>6</sub>)  $\delta$  106.9, 118.25, 129.11, 130.26, 130.39, 131.33, 136.7, 147.70, 169.51. M<sup>+</sup>: 245. Anal. Calcd. for C<sub>9</sub>H<sub>6</sub>Cl<sub>2</sub>N<sub>2</sub>S: C, 44.10; H, 2.46; N, 11.42; Found: C, 44.12; H, 2.49; N, 11.50.

**2-Amino-4-(4-iodophenyl)-1,3-thiazole (3c).** Pale yellow colored solid, mp 126–128°C, IR: 3324, 3291, 1518, 1457, 1052 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  3.64 (s, 2H, NH<sub>2</sub>), 6.95 (s, 1H, thiazole), 7.26 (d, 2H, ArH), 7.31 (d, 2H, ArH); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>)  $\delta$  103.5, 115.7, 122.4, 127.4, 129.6, 131.3, 140.6, 155.8, 169.3. M<sup>+</sup>: 304. Anal. Calcd. for C<sub>9</sub>H<sub>7</sub>IN<sub>2</sub>S: C, 35.78; H, 2.35; N, 9.26; Found: C, 35.71; H, 2.41; N, 9.33.

**2-Amino-4-(3-bromophenyl)-1,3-thiazole (3d).** Dark green solid, mp 130–133°C, IR: 3325, 3204, 1518, 1464, 1047 cm<sup>-1</sup>. <sup>1</sup>H NMR (MeOH-d<sub>4</sub>)  $\delta$  4.86 (s,

2H, NH<sub>2</sub>), 6.99 (s, 1H, thiazole), 7.30–7.61 (m, 4H, ArH); <sup>13</sup>C NMR (MeOH-d<sub>4</sub>) δ 103.25, 116.95, 117.3, 129.7, 130.2, 134.5, 138.8, 154.1, 170.0. M<sup>+</sup>: 255. Anal. Calcd. for C<sub>9</sub>H<sub>7</sub>BrN<sub>2</sub>S: C, 42.37; H, 2.77; N, 10.98; Found: C, 42.31; H, 2.81; N, 11.05.

**2-Amino-4-(3,4-dimethoxyphenyl)-1,3-thiazole (3e).** Pale yellow colored solid, mp 198–200°C, IR: 3316, 3273, 1503, 1458, 1049 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 3.01 (s, 2H, NH<sub>2</sub>), 3.64 (s, 6H, OCH<sub>3</sub>), 6.90 (s, 1H, thiazole), 7.09–7.14 (s, 3H, ArH); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) δ 56.3, 56.1, 100.9, 111.9, 116.4, 120.9, 128.5, 149.3, 149.5, 151.4, 170.2. M<sup>+</sup>: 237. Anal. Calcd. for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S: C, 55.91; H, 5.12; N, 11.86; Found: C, 55.90; H, 5.14; N, 11.89.

**2-Amino-4-(4-methoxyphenyl)-1,3-thiazole (3f).** Yellow colored solid, mp 203–204°C, IR: 3313, 3270, 1519, 1461, 1055 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 3.04 (s, 2H, NH<sub>2</sub>), 3.68 (s, 3H, OCH<sub>3</sub>), 6.85 (s, 1H, thiazole), 7.3 (d, 2H, ArH); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) δ 56.35, 56.4, 100.1, 112.0, 116.1, 122.1, 128.7, 149.9, 151.0, 152.1, 170.5. M<sup>+</sup>: 207. Anal. Calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>OS: C, 58.23; H, 4.89; N, 13.58; Found: C, 58.25; H, 4.93; N, 13.63.

**2-Amino-4-(2-methoxyphenyl)-1,3-thiazole (3g).** Yellow oil, IR: 3335, 3263, 1530, 1472, 910 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 2.10 (s, 2H, NH<sub>2</sub>), 3.70 (s, 3H, OCH<sub>3</sub>), 6.96 (s, 1H, thiazole), 7.15–7.55 (m, 4H, ArH); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) δ 56.75, 100.3, 112.1, 116.3, 122.4, 128.65, 149.96, 151.25, 152.5, 170.75. M<sup>+</sup>: 207. Anal. Calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>OS: C, 58.23; H, 4.89; N, 13.58; Found: C, 58.30; H, 4.92; N, 13.61.

**4-(3,4-Dichlorophenyl)-2-methyl-1,3-thiazole (3h).** Pale yellow solid, mp 126–128°C, IR: 2935, 1655, 1602, 1530, 1419, 1039, 1020 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 2.7 (s, 3H, CH<sub>3</sub>), 7.22 (s, 1H, thiazole), 7.66–7.95 (m, 4H, ArH); <sup>13</sup>C NMR (acetone-d<sub>6</sub>) δ 34.1, 109.6, 118.26, 128.91, 130.2, 130.45, 131.1, 137.2, 147.28, 168.16. M<sup>+</sup>: 244. Anal. Calcd. for C<sub>10</sub>H<sub>7</sub>Cl<sub>2</sub>NS: C, 49.20; H, 2.89; N, 5.74; Found: C, 49.25; H, 2.95; N, 5.80.

**4-(3-Bromophenyl)-2-methyl-1,3-thiazole (3i).** Pale yellow oil, IR: 2950, 1600, 1512, 1449, 1033 cm<sup>-1</sup>. <sup>1</sup>H NMR (MeOH-d<sub>4</sub>) δ 2.65 (s, 3H, CH<sub>3</sub>), 7.00 (s, 1H, thiazole), 7.35–7.67 (m, 4H, ArH); <sup>13</sup>C NMR (MeOH-d<sub>4</sub>) δ 34.3, 103.25, 116.95, 117.3, 129.7, 130.2, 134.5, 138.8, 154.1, 170.0. M<sup>+</sup>: 255. Anal. Calcd. for C<sub>10</sub>H<sub>8</sub>BrNS: C, 47.26; H, 3.17; N, 5.51; Found: C, 47.21; H, 3.10; N, 5.45.

**4-(2-Chlorophenyl)-2-methyl-1,3-thiazole (3j).** Brown oil, IR (neat): 2933, 1622, 1518, 1444, 1026 cm<sup>-1</sup>. <sup>1</sup>H NMR (MeOH-d<sub>4</sub>) δ 2.64 (s, 3H, CH<sub>3</sub>), 7.02 (s, 1H, thiazole), 7.30–7.64 (m, 4H, ArH); <sup>13</sup>C NMR (MeOH-d<sub>4</sub>) δ 34.1, 103.3, 117.2, 118.25, 130.1, 130.6, 135.2, 138.9, 155.6, 170.1. M<sup>+</sup>: 210. Anal. Calcd. for C<sub>10</sub>H<sub>8</sub>ClNS: C, 57.28; H, 3.85; N, 6.68; Found: C, 57.33; H, 3.91; N, 6.63.

**Ethyl 4-(4-Nitrophenyl)-1,3-thiazole-2-carboxylate (3k).** Yellow solid, mp 214°C, IR: 1660, 1550, 1532, 1340, 1310, 1166, 834 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 1.24 (t, CH<sub>3</sub>), 4.18 (q, CH<sub>2</sub>), 7.20 (s, 1H, thiazole), 7.57 (d, 2 H, ArH), 8.10 (d, 2 H, ArH); <sup>13</sup>C NMR (acetone-d<sub>6</sub>) δ 16.2, 62.7, 110.0, 121.1, 128.5, 133.3, 134.2, 135.0, 137.8, 151.2, 169.2. M<sup>+</sup>: 280. Anal. Calcd. for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>S: C, 51.79; H, 3.62; N, 10.07. Found: C, 51.80; H, 3.59; N, 10.10.

**Ethyl 4-Phenyl-1,3-thiazole-2-carboxylate (3l).** Yellow colored oil, IR (neat): 1651, 1600, 1523, 1325, 1175, 1088 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 1.27 (t, CH<sub>3</sub>), 4.20 (q, CH<sub>2</sub>), 7.18 (s, 1H, thiazole), 7.33–7.43 (m, 3 H, ArH), 7.58–7.68 (m, 2 H, ArH); <sup>13</sup>C NMR (acetone-d<sub>6</sub>) δ 15.1, 60.5, 109.0, 120.0, 129.9, 132.0, 133.2, 133.5, 138.1, 150.1, 169.2. M<sup>+</sup>: 234. Anal. Calcd. for C<sub>12</sub>H<sub>11</sub>NO<sub>2</sub>S: C, 61.79; H, 4.75; N, 6.00. Found: C, 61.81; H, 4.79; N, 6.10.

**Ethyl 4-(3,4-Dichlorophenyl)-1,3-thiazole-2-carboxylate (3m).** Pale yellow colored oil, IR (neat): 2850, 1657, 1611, 1516, 1500, 1301, 1168, 890  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  1.25 (t,  $\text{CH}_3$ ), 4.18 (q,  $\text{CH}_2$ ), 7.16 (s, 1H, thiazole), 7.58–7.86 (m, 3H, 3H, ArH);  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  14.7, 60.3, 108.9, 117.5, 128.7, 130.19, 130.4, 130.8, 137.2, 147.5, 168.4.  $\text{M}^+$ : 303. Anal. Calcd. for  $\text{C}_{12}\text{H}_9\text{Cl}_2\text{NO}_2\text{S}$ : C, 47.70; H, 3.00; N, 4.64. Found: C, 47.85; H, 2.94; N, 4.06.

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