

## Original article

## Sodium fluoride as an efficient catalyst for the synthesis of 2,4-disubstituted-1,3-thiazoles and selenazoles at ambient temperature

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## ABSTRACT

Sodium fluoride was found to be a simple, mild and efficient catalyst for the synthesis of 2,4-disubstituted 1,3-thiazoles and selenazoles utilizing phenacyl bromides/3-(2-bromoacetyl)-2H-chromen-2-one and thiourea/phenylthiourea/selenourea in aqueous methanol at ambient temperature. Analytically pure products are formed within 1–3 min in excellent yields.

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## 1. Introduction

Thiazole is a core structural motif present in a variety of natural products, such as vitamin B<sub>1</sub> (thiamine) and penicillin. Thiazole derivatives also exhibit a broad spectrum of medicinal and biological properties, such as antibacterial, antifungal [1], anti-inflammatory [2], antiviral [3], antimalarial [4] and anti-HIV activities [5]. Thiazole analogs have also been reported as ligands at estrogen receptors [6], neuropeptide Y5 [7], adenosine receptors [8], and act as inhibitors of human platelet aggregation factor [9], urokinase [10] and poly (ADP-Ribose) polymerase-1 [11]. Selenazoles have been reported to possess antibacterial [12], and superoxide anion scavenging activity [13], and exhibit cytotoxicity and DNA fragmentation effects in human HT-1080 fibrosarcoma cells [14]. The structures of sulfathiazole, meloxicam, and selenazofurin and their pharmacological activities are given in Fig. 1.

In view of the importance of thiazole and selenazole derivatives in medicinal chemistry, several methods for their synthesis have been reported utilizing various catalytic systems, such as ammonium-12-molybdophosphate [15],  $\beta$ -cyclodextrin [16],

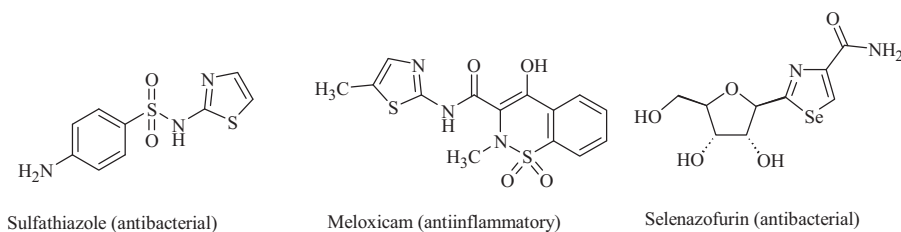
CuPy<sub>2</sub>Cl<sub>2</sub> [17], HMCM-41 [9], and also under different solvent systems, such as ionic liquid/water [18], PEG-400 [19], glycerin [20] and water [21]. However, most of these reported methods suffer from drawbacks, such as harsh reaction conditions, unsatisfactory yields, longer reaction times and critical isolation procedures, and use of hazardous and expensive catalysts. Therefore, to overcome the above limitations we have developed a simple, mild and highly efficient protocol for the synthesis of thiazoles and selenazoles utilizing sodium fluoride (NaF) as a catalyst in aqueous methanol.

## 2. Experimental

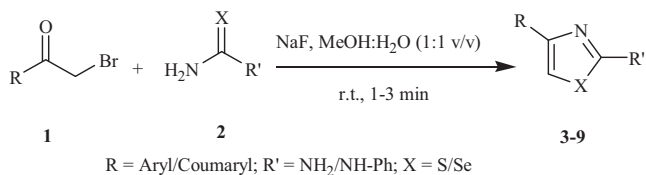
Melting points were recorded on Stuart SMP30 apparatus and are uncorrected. Analytical thin layer chromatography was performed on F<sub>254</sub> silica-gel pre-coated sheets using hexane/ethyl acetate (8:2) as eluent, and visualized with UV light and iodine vapor. Products were characterized by comparison with authentic samples, and by spectral data (IR, <sup>1</sup>H NMR and mass spectrometry). IR spectra were recorded on a Perkin-Elmer 100S spectrophotometer using a KBr disk. <sup>1</sup>H NMR spectra were recorded on a Bruker 400 MHz spectrometer using DMSO-*d*<sub>6</sub> as solvent and TMS as internal standard. Elemental analyses were performed on a Carlo Erba modal EA1108 unit, and the values obtained are within  $\pm 0.4\%$  of the theoretical values. Mass spectra were recorded on a Jeol JMSD-300 spectrometer.

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**Fig. 1.** Biologically active thiazole and selenazole derivatives.



**Scheme 1.** Synthesis of 1,3-thiazoles and 1,3-selenazoles.

### 2.1. General procedure for the synthesis of 1,3-thiazoles and selenazoles (3–9):

The appropriate phenacylbromide or 3-(2-bromoacetyl)-2H-chromen-2-one (1 mmol) and either thiourea, phenylthiourea or selenourea (1 mmol) were dissolved in 2 mL of methanol, water (2 mL) containing 0.02 g of NaF added and the mixture stirred at room temperature for the appropriate time. After completion of

**Table 1**

Comparison of the catalytic activity of NaF with other catalysts in the synthesis of 4-(4-chlorophenyl)thiazol-2-amine (4a).

Entry <sup>a</sup>	Catalyst (0.02 g)	Time (min)	Yield <sup>b</sup> (%)
1	NaF	1	99
2	KF	5	94
3	CuCl <sub>2</sub>	5	90
4	AlCl <sub>3</sub>	5	88
5	SnCl <sub>2</sub>	10	86
6	BaCl <sub>2</sub>	10	85
7	PCl <sub>5</sub>	5	82
8	CuPy <sub>2</sub> Cl <sub>2</sub>	5	88
9	CoPy <sub>2</sub> Cl <sub>2</sub>	5	87

CuPy<sub>2</sub>Cl<sub>2</sub>, Dipyridine copper chloride; CoPy<sub>2</sub>Cl<sub>2</sub>, Dipyridine cobalt chloride.

<sup>a</sup> Reaction conditions: 4-chlorophenacyl bromide (1 mmol), thiourea (1 mmol), catalyst (0.02 g), methanol:water (1:1 v/v), stirring at ambient temperature.

<sup>b</sup> Isolated yields.

**Table 2**

NaF-catalyzed synthesis of substituted 1,3-thiazoles and 1,3-selenazoles.

Entry <sup>a</sup>	Product	X	R'	Time (min)	Yield <sup>b</sup> (%)	Melting point (°C)		
						Found	Lit. [Ref.]	
1		<b>3a</b>	S	NH <sub>2</sub>	1	98	150–152	150–151 [21]
		<b>3b</b>	S	NH-Ph	1	98	134–136	135–136 [21]
		<b>3c</b>	Se	NH <sub>2</sub>	2	97	132–134	132 [16]
2		<b>4a</b>	S	NH <sub>2</sub>	1	99	166–168	167–168 [19]
		<b>4b</b>	S	NH-Ph	1	98	145–146	144–146 [19]
		<b>4c</b>	Se	NH <sub>2</sub>	1	97	154–156	157 [16]
3		<b>5a</b>	S	NH <sub>2</sub>	1	96	182–184	176–177 [23]
		<b>5b</b>	S	NH-Ph	1	98	230–232	–
		<b>5c</b>	Se	NH <sub>2</sub>	1	98	177–178	132 [16]
4		<b>6a</b>	S	NH <sub>2</sub>	3	93	204–206	206–207 [21]
		<b>6b</b>	S	NH-Ph	2	95	137–138	138–139 [21]
		<b>6c</b>	Se	NH <sub>2</sub>	3	94	194–195	173 [16]
5		<b>7a</b>	S	NH <sub>2</sub>	2	97	135–136	–
		<b>7b</b>	S	NH-Ph	1	98	102–103	–
		<b>7c</b>	Se	NH <sub>2</sub>	2	98	166–168	167 [16]
6		<b>8a</b>	S	NH <sub>2</sub>	2	97	284–286	–
		<b>8b</b>	S	NH-Ph	1	97	206–207	–
		<b>8c</b>	Se	NH <sub>2</sub>	2	98	269–271	250 [16]
7		<b>9a</b>	S	NH <sub>2</sub>	1	99	228–229	–
		<b>9b</b>	S	NH-Ph	1	98	188–190	–
		<b>9c</b>	Se	NH <sub>2</sub>	1	98	217–218	280 [17]

<sup>a</sup> Reaction conditions: phenacyl bromide/3-(2-bromoacetyl)-2H-chromen-2-one (1 mmol), thiourea/phenylthiourea/selenourea (1 mmol), methanol:water (1:1 v/v), stirring at ambient temperature.

<sup>b</sup> Isolated yields.

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