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One-pot solvent-free synthesis of naphtho[1,2-*e*][1,3]oxazin-3-one/thione derivatives using a snail shell as a green and efficient catalyst

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Abstract

A facile synthetic route for 1,2-dihydro-1-arylnaphtho[1,2-e] [1,3]oxazine-3-one/thione derivatives by one-pot three-component condensation reaction of 2-naphthol, aromatic aldehydes, and urea or thiourea in presence of snail shell as a novel, efficient, green and nontoxic catalyst, under solvent free conditions has been described. The method is associated with some attractive characteristics such as short reaction time, high yield of products, and recyclability of recovered catalyst from the reaction mixture.

1. Introduction

Oxazinone, benzoxazinone and their derivatives are a significant class of heterocyclic compounds, because many of these derivatives display biological activities, such as HIV-1 reverse transcriptase inhibitors [1] and antibacterial properties [2], including anti inflammatory, antiulcer, antipyretic, antihypertensive and antifungal activities [3]. Some of these compounds also exhibit several important biological activities such as DP receptor antagonism [4], integrin antagonism [5], platelet fibrinogen receptor antagonism [6], calmodulin antagonism [7], and inhibition of the transforming growth factor β (TGF-β) signaling pathway [8], soybean lipoxygenase [9] and other protein kinase [10]. In addition, naphthalene-condensed 1,3-oxazin-3-ones have also been used in the preparation of chiral amino phosphine ligands for asymmetric catalysis [11]. Recently, a few methods for the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones have been reported.

Recently, the preparation of naphtha-oxazine derivatives has been achieved in the presence of various catalyst such as *P*-TSA [12], [bmim]Br [13], TMSCl/NaI [14], $HClO_4$/ SiO_2 [15], phosphomolybdic acid [16], silica gel [17], ZnONPs [18], CuNPs [19], Thiamine hydrochloride [20], TMSCl [21], $FeCl_3/SiO_2$NPs [22], Wet TCT [23], $RuCl_2(PPh_3)_3$ [24], Pyridinium-based [25], Nano-Fe_2O_3 [26].

The snail shell has been utilized as natural source of calcium carbonate, as a coagulant very effective in the treatment of waste water [27] and also as a source of calcium for the preparing nanocrystalline hydroxyapatite [28]. However, the use of snail shell, abundant in Morocco, as a catalyst in the synthesis of organic compounds has not been reported.

In continuation of our work and considering the importance of solid catalytic systems [29-30], we report a green, one-pot, efficient synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones derivatives catalyzed by snail shell under solvent-free conditions.

2. Experimental

2.1. Materials

All chemicals products were purchased from Merck, Fluka, and Aldrich. All materials were of commercial reagent grade.

2.2. Apparatus

All the synthesized are known, and were identified by comparison of spectral and physical data with the literature. Melting points were taken on a KOFLER hot stage apparatus and are uncorrected. 1H NMR and 13C NMR spectra were recorded on a Brucker 300-MHz spectrometer in DMSO-d6. The crystalline properties of the particles were investigated using an X-ray diffractometer (Shimadzu XRD-6000 powder diffractometer using CuKα (λ = 1.540562 Å) at 40 kV and 30 mA). All reactions were monitored by TLC on silica gel plates (Fluka Kieselgel 60 F254).

2.3. Preparation of snail shell catalyst

The waste of snail shells were collected, cleaned and dried in an oven at 100 °C during 24h. The shells obtained, without calcinations, are transformed by crushing into white soft powder.

2.4. Typical experimental procedure

In a general procedure, a mixture of an aldehyde (1 mmol), a β-naphthol (1 mmol), urea or thiourea (3 mmol) and snail shell (12.9 mol % is equiv to 0.1 g) was heated at reflux with constant stirring till the reaction was complete. After completion of the reaction (monitored by thin-layer chromatography), the catalyst was removed by filtration, and the filtrate was cooled into ice water. The resulting solid precipitate was filtered and recrystallized from ethanol to give pure 1,2-dihydro-1-arylnaphtho[1,2-e] [1,3]oxazine-3-one or thione **4a-i** in high yields . Products were identified by comparison of their ^{1}H and ^{13}C NMR spectra and melting points with those of authentic samples [22-24, 26]. Spectroscopic data for synthesized products are listed as follows:

1,2-dihydro-1-phenyl-naphtho[1,2-e][1,3]oxazin-3(2H)-one (**4a**). White solid, Mp = 214-216 °C (Lit. [22] 214-216 °C). ^{1}H NMR (DMSO-d_6) δ ppm : 8.86 (s, 1H, NH), 7.20-7.97 (m, 11H, ArH), 6.18 (d, 1H, J = 3.0 Hz, CH). ^{13}C NMR (DMSO-d_6) δ ppm : 149.8, 147.9, 143.3, 130.9, 130.7, 129.4, 129.3, 129.1, 128.5, 127.8, 127.4, 125.6, 123.5, 117.3, 114.5, 54.2.

1-(4-chlorophenyl)- 1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3(2H)-one (**4b**). White solid, Mp = 213-215 °C (Lit. [23] 213-215 °C). ^{1}H NMR (DMSO-d_6) δ ppm : 8.64 (s, 1H, NH), 7.16-7.99 (m, 10H, ArH), 6.72 (d, 1H, J = 2.8 Hz, CH). ^{13}C NMR (DMSO-d_6) δ ppm : 153.9, 142.6, 138.2, 136.5, 133.6, 131.3, 130.4, 129.6, 129.5, 129.2, 128.9, 127.2, 126.4, 123.7, 119.5, 117.3, 114.6, 52.7.

1-(2-chlorophenyl)- 1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3(2H)-one (**4c**). White solid, Mp = 249-251 °C (Lit. [23] 249-251 °C). ^{1}H NMR (DMSO-d_6) δ ppm : 8.87 (s, 1H, NH), 7.13-8.00 (m, 10H, ArH), 6.49 (d, 1H, J = 2.7 Hz, CH). ^{13}C NMR (DMSO-d_6) δ ppm : 153.5, 149.2, 148.2, 140.3, 136.2, 133.8, 132.1, 131.1, 130.5, 129.7, 129.6, 129.3, 128.4, 127.4, 125.6, 123.8, 122.7, 119.4, 117.3, 113.9, 52.2.

1,2-dihydro-1-(4-nitrophenyl)-naphtho[1,2-e][1,3]oxazin-3-one (**4d**). Yellow solid, Mp = 206-208 °C (Lit. [23] 206-207 °C). ^{1}H NMR (DMSO-d_6) δ ppm : 8.54 (s, 1H, NH), 7.06-7.89 (m, 10H, ArH), 6.62 (d, 1H, J = 2.7 Hz, CH). ^{13}C NMR (DMSO-d_6) δ ppm : 153.8, 142.6, 138.2, 134.7, 133.5, 132.1, 131.3, 130.3, 129.6, 129.4, 129.2, 128.8, 127.2, 126.4, 123.1, 119.5, 117.3, 114.6, 52.6.

1,2-dihydro-1-(p-tolyl)-naphtho[1,2-e][1,3]oxazin-3(2H)-one (**4e**). White solid, Mp = 171-173 °C (Lit. [23] 171-173 °C). ^{1}H NMR (DMSO-d_6) δ ppm : 8.82 (s, 1H, NH), 7.06-8.81 (m, 10H, ArH), 6.12 (d, 1H, J = 2.6 Hz, CH), 2.17 (s, 3H, CH3). ^{13}C NMR (DMSO-d_6) δ ppm : 155.7, 149.8, 147.8, 140.4, 137.8, 135.0, 130.6, 130.6, 129.9, 129.3, 129.1, 128.2, 127.8, 127.3, 126.6, 125.5, 123.5, 119.0, 117.3, 114.5, 109.1, 54.0, 21.0.

1-(2,4-dichlorophenyl)-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3(2H)-one (**4f**). White solid, Mp = 212-214 °C (Lit. [26] 212-215 °C). ^{1}H NMR (DMSO-d_6) δ ppm : 8.20 (s, 1H, NH), 7.11-7.83 (m, 9H, ArH), 6.47 (d, 1H, J = 2.4 Hz, CH). ^{13}C NMR (DMSO-d_6) δ ppm : 153.4, 148.9, 139.3, 135.4, 134.5, 133.4, 132.3, 131.6, 130.9, 129.7, 129.2, 128.9, 127.9, 127.4, 125.6, 122.6, 119.4, 117.2, 112.5, 51.9.

1,2-dihydro-1-(4-nitrophenyl)-naphtho[1,2-e][1,3]oxazine-3(2H)-thione (**4g**). Yellow solid, Mp = 137-139 °C (Lit. [24] 135-138 °C). ^{1}H NMR (DMSO-d_6) δ ppm : 8.54 (s, 1H, NH), 7.06-7.89 (m, 10H, ArH), 6.62 (d, 1H, J = 2.7 Hz, CH). ^{13}C NMR (DMSO-d_6) δ ppm : 152.7, 142.6, 138.2, 136.5, 134.7, 133.5, 132.1, 131.6, 130.3, 129.5, 129.2, 128.9, 127.9, 126.4, 123.7, 122.9, 119.5, 117.3, 114.6, 52.7.

1-phenyl-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3-thione (**4h**). White solid, Mp = 207-209 °C (Lit. [24] 208-210 °C). ^{1}H NMR (DMSO-d_6) δ ppm : 8.39 (s, 1H, NH), 7.19-7.87 (m, 10H, ArH), 5.99 (d, 1H, J = 2.8 Hz, CH). ^{13}C NMR (DMSO-d_6) δ ppm : 161.4, 146.5, 140.2, 131.4, 130.9, 129.5, 129.1, 129.0, 128.9, 127.7, 127.3, 125.7, 122.7, 116.6, 56.3.

1-(4-methoxyphenyl)-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3-thione (**4i**). White solid, Mp = 191-193 °C (Lit. -[24] 190-192 °C). ^{1}H NMR (DMSO-d_6) δ ppm : 8.21 (s, 1H, NH), 7.10-7.80 (m, 10H, ArH), 5.95 (d, 1H, J = 2.8 Hz), 3.69 (s, 3H). ^{13}C NMR (DMSO-d_6) δ ppm : 159.9, 146.4, 132.5, 131.4, 130.8, 129.0, 128.9, 128.6, 127.6, 125.6, 122.8, 116.5, 114.8, 111.9, 55.8, 55.3

3. Results and discussion

3.1. General information for the catalyst

The waste of snail shells were collected, cleaned and dried in an oven at 100°C during 24h. The shells obtained, without calcinations, are transformed by crushing into white soft powder. The latter has been characterized by X-ray diffraction, by scanning electron microscope and by measuring the specific surface.

The Analysis of the X-ray powder diffraction (Figure 1) showed a well-crystallized phase. The presence of aragonite was confirmed by the characteristic 111, 221, and 202 reflections at 26.26°, 45.90° and 48.48° (2θ) (Joint Committee on Powder Diffraction International Centre for Diffraction Data (JCPDS : 76-0606). Further, it notes the absence of the characteristic reflections of calcium carbonate in the different allotropes calcite (JCPDS : 86-2334) and vaterite (JCPDS: 74-1867) [31]. The analysis by scanning electron microscopy (Figure 2) shows that it crystallizes as irregular needles. The snail shell (aragonite) powder has an average specific surface of 3.15 m^2/g by measurements were carried out by the BET (Brunauer Emmett and Teller). The infrared spectrum shows well-defined bands that can be easily identified from their wave number (Figure 3). The peaks present in the spectrum reflect the natural abundance of aragonite polymorphs in the snail shell.

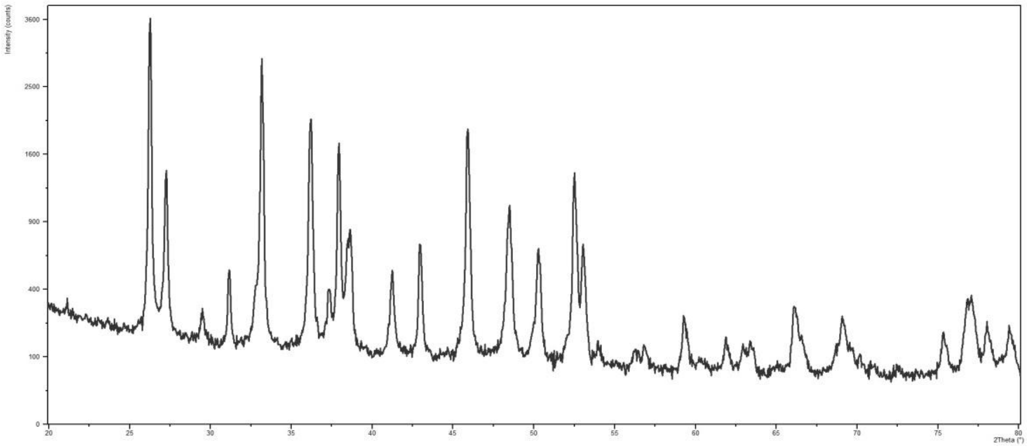


Figure 1: XRD patterns of obtained powder of aragonite

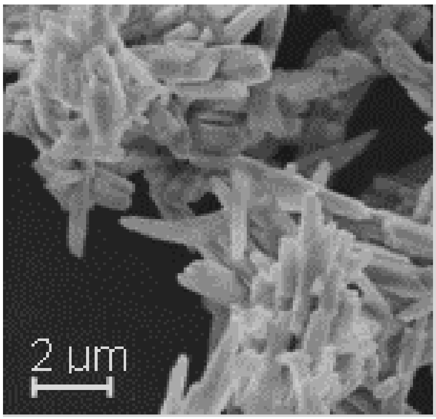


Figure 2: Scanning electron microscopy of powder of snail shell (aragonite)

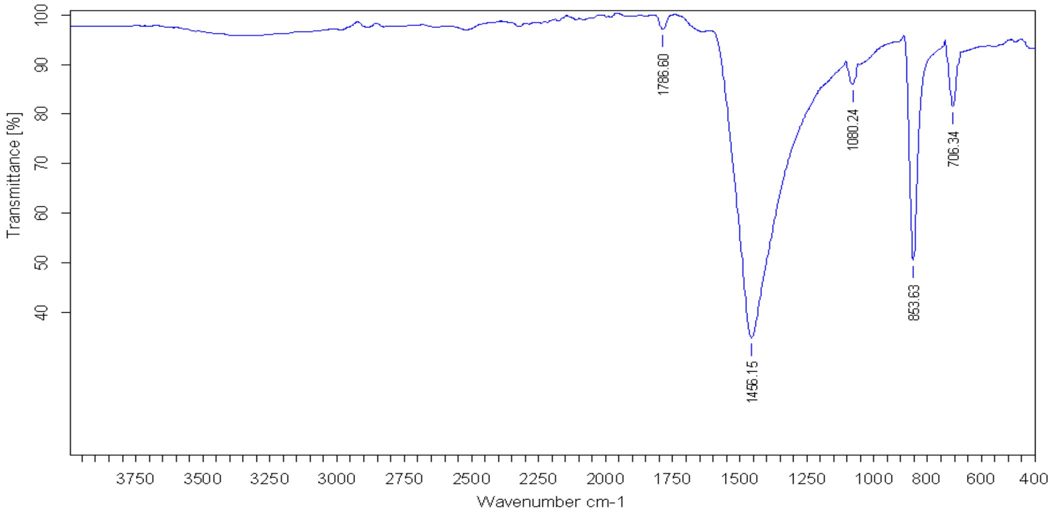
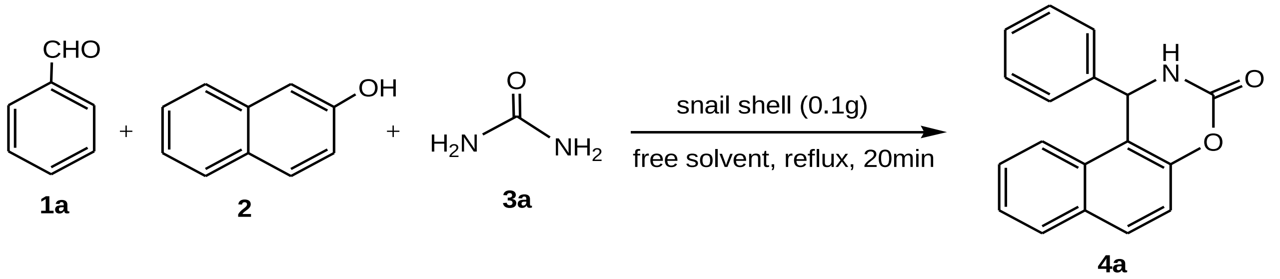


Figure 3: FT-IR spectra of obtained powder of snail shell

3.2. The catalytic activity of snail shell in synthesis of naphtho[1,2-e][1,3]oxazine-3-ones

In an initial study and in order to examine the catalytic activity of the catalyst, we examined in this condensation reaction of benzaldehyde and β-naphthol and urea was selected as model (Scheme 1). It showed that nearly no product could be detected when a mixture of benzaldehyde (1 mmol) with 2-naphthol (1 mmol) and urea (1 mmol) was heated at 120°C for 100 min in absence of snail shell (Table 1, entry 1),which indicated that the catalyst should be absolutely necessary for this transformation. We found that the best result was obtained when the reaction was carried out solvent-free at reflux in the presence of 0.15 g of snail shell (Table 1, entry 4).



Scheme-1: Model reaction for the synthesis of naphtho[1,2-e][1,3]oxazine-3-ones.

Table 1: Catalytic performance in the model reaction of 2-naphthol, benzaldehyde and urea

Entry	Catalyst	Reaction Conditions	Time (min)	Yield (%)
1	-	120 °C	100	Trace
2	snail shell	EtOH/reflux	120	80
3	snail shell	H_2O/reflux	120	15
4	snail shell	free solvent/reflux	20	90[a]
5	snail shell	EtOH/RT	120	54
6	snail shell	MeOH/reflux	120	75

[a] 2-naphthol (1 mmol), benzaldehyde (1 mmol), urea (1 mmol), snail shell (19,35 mol% is equiv to 0.15 g) in solvent-free condition at reflux.

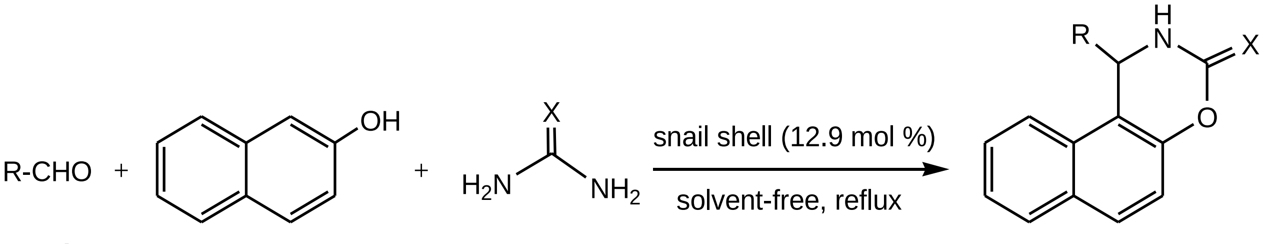
To determine the optimum quantity of snail shell in reaction of benzaldehayde, 2-naphthol and urea under thermal and solvent free conditions, we used different amounts including 3.22, 6.45, 12.9, 19.35, 25.8 and 32.25 mol% of snail shell. The best amount of corresponding catalyst was obtained 12.9 mol% (is equiv. to 0.1g) in 15 min (Table 2, entry 3). After the best reaction conditions were achieved, the generality of these conditions to other substrates was studied, employing snail shell as catalyst. Using this method, different kinds of aromatic compounds were reacted with 2-naphthol to produce the corresponding 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-one/thione derivatives **4** at reflux under solvent-free conditions. The results are summarized in

Table 3. The structures of compounds **4a-i** were confirmed by the comparison of melting points and spectral data with those reported in the literature [22-24, 26].

Table 2: Screening the amount of snail shell on the model reaction[a]

Entry	Catalytic amounts (g)	Catalytic amounts (mol %)	Time (min)	Isolated Yield (%)
1	0.025	3.22	40	81
2	0.05	6.45	30	86
3	0.10	12.90	15	94
4	0.15	19.35	20	90
5	0.20	25.80	20	90
6	0.25	32.25	20	87

[a] 2-naphthol (1 mmol), benzaldehyde (1 mmol), urea (1 mmol), snail shell (12,9 mol%, 0.1 g) in solvent-free condition at reflux.



1a-i **2** **3** **4a-i**

Scheme 2: Green synthesis of naphthoxazin-2-ones and thiones **4** on snail shell under solvent free conditions.

Table 3: Preparation of naphthoxazine-3-one and thione derivatives **4a-i**

Product	R	X	Time (min)	Yield (%)[a]
4a	C_6H_5	O	15	94
4b	$4\text{-}ClC_6H_4$	O	7	96
4c	$2\text{-}ClC_6H_4$	O	8	99
4d	$4\text{-}NO_2C_6H_4$	O	5	99
4e	$4\text{-}MeC_6H_4$	O	12	97
4f	$2,4\text{-}Cl_2C_6H_3$	O	15	98
4g	$4\text{-}NO_2C_6H_4$	S	25	95
4h	C_6H_5	S	15	96
4i	$4\text{-}MeOC_6H_4$	S	7	94

[a] Isolated yields

To evaluate the stability of the catalytic activity and the potential for recycling, we completed several catalytic cycles. In each cycle, snail shell was washed with ethanol and dried under vacuum to remove the residual solvent. The catalyst could be reused for eight times with a minimal loss of activity (Table 4).

Table 4: Effect of reusability of snail shell catalyst on the synthesis of 1,2-dihydro-1-phenyl naphtho[1,2-e][1,3]oxazine-3-one **4a**.

Run	Time (min)	Yield (%)[a]
1	15	94
2	15	94
3	15	93
4	15	92
5	15	92
6	15	91
7	15	91
8	15	91

[a] Isolated yields.

To show the merit of the present work in comparison with the previously reported, we compared results of snail shell with other catalysts in the synthesis of 1,2-dihydro-1-aryl naphtho[1,2-e][1,3]oxazine-3-ones. As shown in Table-5, snail shell can act as effective catalyst with respect to reaction times, yields and the obtained products.

Table 5: Comparison of the obtained results using the snail shell with the results of other catalysts[a].

Catalyst	Reaction conditions	Yield (%)	Litt.
PTSA	Solvent-free, 160°C, 1.5h, catalyst (0.3 mmol)	63	[12]
TMSCl/NaI	CH_3CN/DMF, 140°C, 2.6h, catalyst (1.5 equiv)	86	[14]
$HClO_4/SiO_2$	Solvent-free, 150°C, 60 min, catalyst (2 mol%)	88	[15]
Phosphomolybdic acid	DMF, 100°C, 3h, catalyst (0.001 mmol)	89	[16]
Silica gel	Solvent-free, 160°C, 1.8h, catalyst (2 mol%)	78	[17]
ZnO NPs	Solvent-free, 150°C, 60 min, catalyst (0.3 equiv)	90	[18]
Cu NPS	PEG-400, RT, 60 min, catalyst (0.001 g)	89	[19]
Thiamine hydrochloride	150°C, 30 min, catalyst (0.5 mmol)	85	[20]
TMSCl	DMF, 140°C, 12h, catalyst (10 mg)	83	[21]
$FeCl_3$/nano-SiO_2	Solvent-free, 150°C, 7 min, catalyst (0.4 mol%)	95	[22]
Snail shell	Solvent-free, reflux, 7 min, catalyst (12.9 mol%)	96	This work

[a] based on 4-chlorobenzaldehyde (0.01 mol), 2-naphtol (0.01 mol) and urea (0.01 mol).

Conclusion

In conclusion, we have demonstrated that snail shell is a novel, efficient, green and non toxic catalyst for the synthesis of naphthoxazine-3-one/thione derivatives and thought it would be an excellent fit at green chemistry, sustainability and environmental safety. The one-pot three-component condensation of aryl aldehydes, 2-naphthol and urea or thiourea in the presence of snail shell afforded naphthoxazinones under solvent-free conditions. Easy work-up, low cost, ready availability, effective recovery and reusability of the catalyst, abundant in Morocco, make the procedure an attractive alternative to the existing methods for the synthesis of naphthoxazine-3-one/thione derivatives.

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