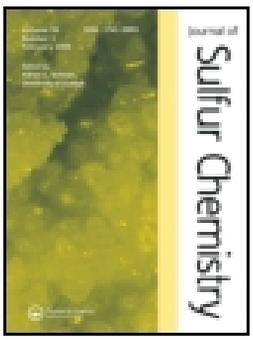

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Preparation of novel 2-(2-oxo-2*H*-chromen-4-yl)-3-arylthiazolidin-4-one derivatives using an efficient ionic liquid catalyst

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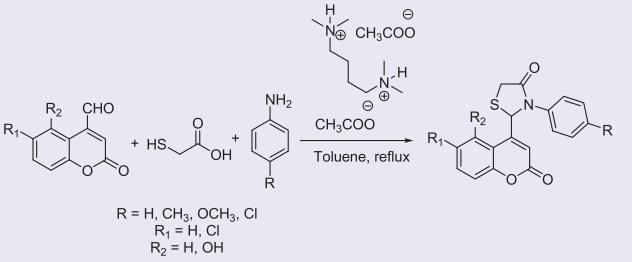
ABSTRACT

An eco-friendly procedure for synthesis of 2-(2-oxo-2*H*-chromen-4-yl)-3-arylthiazolidin-4-one derivatives by three-component reaction of 2-oxo-2*H*-chromene-4-carbaldehydes, aromatic amines and thioglycolic acid, with tetramethylbutane-1,4-diammonium acetate as a low-cost ionic liquid catalyst under reflux condition is described. The use of an ionic liquid as a catalyst has the advantages of high yields, short reaction time and environmentally friendly reaction media.



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1. Introduction

Heterocyclic compounds containing both nitrogen and sulfur atoms have attracted growing interest owing to their important medicinal activities. The chemistry of these compounds have been under extensive investigation for decades due to their wide applications in organic and medicinal chemistry.[1] Among the heterocycles of interest thiazolidin-4-ones are an important class since they closely resemble other important compounds with nitrogen and sulfur atoms. This nucleus is associated with diverse anticancer,[2] anti-HIV,[3,4,5] antimalarial,[6] tuberculostatic,[7] antihistaminic,[8] anticonvulsunt,[9,10] antibacterial,[11] and antiarrythmic[12] biological activity.

The cyclo-condensation reaction of aldehydes, amines and thioglycolic acid is the main synthetic route to thiazolidin-4-one derivatives. This condensation is commonly conducted using promoters such as *N*,*N*′-dicyclohexylcarbodiimide which involves a tedious

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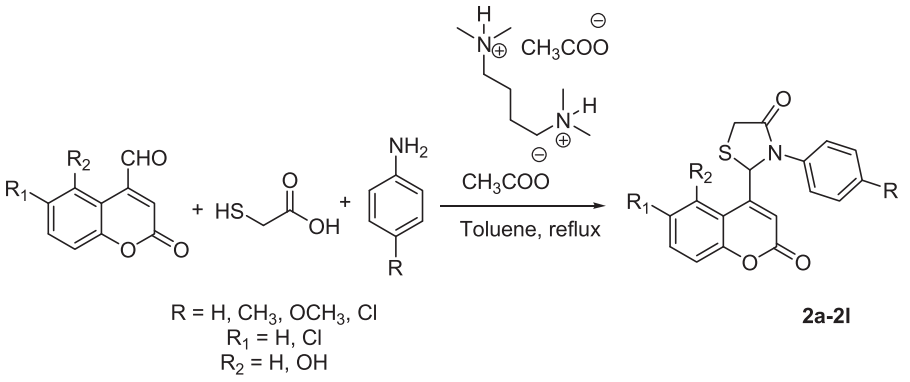


Scheme 1. Preparation of 2-(2-oxo-2*H*-chromen-4-yl)-3-arylthiazolidin-4-one derivatives.

work-up due to the formation of *N,N'*-dicyclohexyl urea as by-product,[13] and separation of ferrite,[14] $ZnCl_2$,[15] sodium sulfate,[16] [bmim][PF_6],[17,18] activated fly ash,[19] *Saccharomyces cerevisiae* [20] and $Bi(SCH_2COOH)_3$.[21] Some of these methods have certain limitations, such as harsh reaction conditions, prolonged heating and the need for inert and dry atmosphere. These procedures have advantages such as good to excellent yields; however, the discovery of new synthetic methodologies to facilitate the preparation of organic compounds is perhaps the most important aspect of this new reaction and is consequently a central research activity in modern organic chemistry.

In continuing our studies to explore the preparation of heterocyclic compounds,[22–27] herein, we report a cyclo-condensation reaction of 2-oxo-2*H*-chromene-4-carbaldehydes, aromatic amines and thioglycolic acid in the presence of tetramethylbutane-1,4-diammonium acetate as a catalyst to give a variety of thiazolidin-4-one derivatives (Scheme 1).

2. Results and discussion

The reaction of 2-oxo-2*H*-chromene-4-carbaldehyde, 4-methyl aniline and thioglycolic acid in the presence of tetramethylbutane-1,4-diammonium acetate under several conditions was selected as the model to optimize the reaction conditions (Table 1). Upon treatment of starting materials as well as a catalyst in nonpolar solvents and Et_2O the desired product **2b** was not obtained (Table 1, Entries 1–3). When the reaction was carried out in polar solvents the reaction has a yield from 31% to 64% (Table 1, Entries 4,5,7). No formation of **2b** was taking place in a solvent-free condition (Table 1, Entry 8). Employing toluene as the solvent resulted in higher yield of product (Table 1, Entry 6).

Next, to find the optimized amount of tetramethylbutane-1,4-diammonium acetate, the reaction was carried out by varying the amount of the catalyst (Table 1, Entries 9–12). Maximum yield was obtained when 0.5 mmol of catalyst was used (Table 1, Entry 10). A further increase in the amount of catalyst did not have any significant effect on the product yield. Under the standard conditions, no reaction was observed in the absence of a catalyst. This shows that the catalyst is essential for the product formation (Table 1, Entry 13).

Under the same reaction conditions a variety of Brønsted acid catalysts were employed to be compared with the results obtained by tetramethylbutane-1,4-diammonium acetate.

Table 1. Optimization of the reaction conditions in the synthesis of 2-(2-oxo-2*H*-chromen-4-yl)-3-*p*-tolylthiazolidin- 4-one.

Entry	Catalyst (mmol)	T (°C)	Solvent (5 mL)	Time (h)	Yield (%)[a]
1	A (0.25)	Reflux	*n*-Hexane	10	–
2	A (0.25)	Reflux	CH_2Cl_2	10	–
3	A (0.25)	Reflux	Et_2O	10	–
4	A (0.25)	Reflux	EtOAc	10	31
5	A (0.25)	Reflux	EtOH	10	45
6	A (0.25)	Reflux	Toluene	10	80
7	A (0.25)	Reflux	CH_3CN	10	64
8	A (0.25)	80	–	5	25
9	A (1)	Reflux	Toluene	6	82
10	A (0.5)	Reflux	Toluene	8	88
11	A (0.1)	Reflux	Toluene	15	63
12	A (0.05)	Reflux	Toluene	15	39
13	–	Reflux	Toluene	10	–
14	SiO_2-H_2SO_4 (0.25 mmol H^+)	Reflux	Toluene	10	48
15	SiO_2-$HClO_4$ (0.25 mmol H^+)	Reflux	Toluene	10	55
16	H_2SO_4 (0.25 mmol)	Reflux	Toluene	10	49
17	HCl (0.25)	Reflux	Toluene	10	32
18	CH_3COOH (0.25)	Reflux	Toluene	10	69

[a]Isolated Yields; **A**: tetramethylbutane-1,4-diammonium acetate; based on 2-oxo-2*H*-chromene-4-carbaldehyde (1 mmol), 4-methyl aniline (1 mmol) and thioglycolic acid (1 mmol).

The obtained results indicated that tetramethylbutane-1,4-diammonium acetate is more effective in comparison with other acid catalysts (Table 1, Entries 14–18).

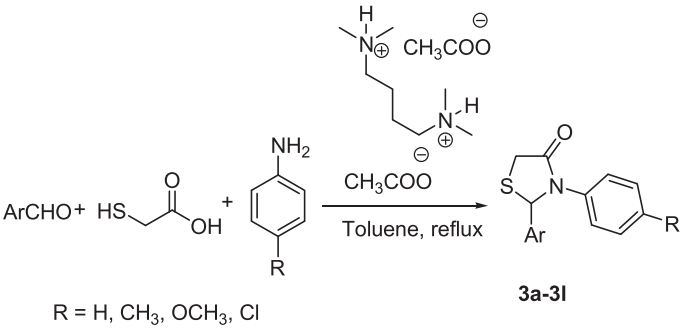
Having established the optimum reaction conditions, the scope and limitations of this study were investigated for the synthesis of 2-(2-oxo-2*H*-chromen-4-yl)-3-arylthiazolidin-4-one derivatives (Scheme 1, Table 2). As expected, this reaction proceeded smoothly and the desired products were obtained in good yields. In general, 2-oxo-2*H*-chromene-4-carbaldehydes and aromatic amines were well tolerated in this reaction system (Table 2, product **2a–2l**). However, this method is not applicable to aromatic amines containing electron-withdrawing groups (Table 2, Entry 13).

Encouraged by the above results, we next investigated the reaction of various aromatic aldehydes under the optimized reaction conditions established for 2-oxo-2*H*-chromene-4-carbaldehyde (Scheme 2), and the results are listed in Table 3. In general, the reaction

Table 2. Synthesis of 2-(2-oxo-2*H*-chromen-4-yl)-3-arylthiazolidin-4-one derivatives using tetramethylbutane-1,4-diammonium acetate as a catalyst (Scheme 1).

Entry	Aldehyde	Amine	Product	Time (h)	Yield (%)[a]
1	2-oxo-2H-chromene-4-carbaldehyde	Aniline	**2a**	8	85
2	2-oxo-2H-chromene-4-carbaldehyde	4-Methylaniline	**2b**	8	88
3	2-oxo-2H-chromene-4-carbaldehyde	4-Methoxyaniline	**2c**	8	90
4	2-oxo-2H-chromene-4-carbaldehyde	4-Chloroaniline	**2d**	10	78
5	6-chloro-2-oxo-2H-chromene-4-carbaldehyde	Aniline	**2e**	12	86
6	6-chloro-2-oxo-2H-chromene-4-carbaldehyde	4-Methylaniline	**2f**	12	92
7	6-chloro-2-oxo-2H-chromene-4-carbaldehyde	4-Methoxyaniline	**2g**	12	95
8	6-chloro-2-oxo-2H-chromene-4-carbaldehyde	4-Chloroaniline	**2h**	15	80
9	5-hydroxy-2-oxo-2H-chromene-4-carbaldehyde	Aniline	**2i**	8	85
10	5-hydroxy-2-oxo-2H-chromene-4-carbaldehyde	4-Methylaniline	**2j**	8	93
11	5-hydroxy-2-oxo-2H-chromene-4-carbaldehyde	4-Methoxyaniline	**2k**	8	91
12	5-hydroxy-2-oxo-2H-chromene-4-carbaldehyde	4-Chloroaniline	**2l**	10	77
13	5-hydroxy-2-oxo-2H-chromene-4-carbaldehyde	4-Nitroaniline	**2m**	10	–

[a]Isolated yields. All products were characterized by NMR spectra and CHN analysis.



Scheme 2. Preparation of 2,3-diarylthiazolidin-4-one derivatives.

Table 3. Synthesis of 2,3-diarylthiazolidin-4-one derivatives using tetramethylbutane-1,4-diammonium acetate as catalyst.

Entry	Aldehyde	Amine	Product	Time (h)	Yield (%)[a]
1	Benzaldehyde	Aniline	**3a**	4	85
2	4-Methylbenzaldehyde	Aniline	**3b**	3	89
3	4-Methoxybenzaldehyde	Aniline	**3c**	3	86
4	4-Chlorobenzaldehyde	Aniline	**3d**	4	80
5	Benzaldehyde	4-Methylaniline	**3e**	3	79
6	4-Methylbenzaldehyde	4-Methylaniline	**3f**	3	85
7	4-Methoxybenzaldehyde	4-Methylaniline	**3g**	3	88
8	4-Chlorobenzaldehyde	4-Methylaniline	**3h**	3.5	81
9	2-Methylbenzaldehyde	4-Methylaniline	**3i**	4	70
10	2-Chlorobenzaldehyde	4-Methylaniline	**3j**	4	73
11	3-Nitrobenzaldehyde	4-Methylaniline	**3k**	5	65
12	Butyraldehyde	4-Methylaniline	**3l**	5	–

[a]Isolated yields. All products were purified using plate chromatography (hexane/ethyl acetate 9/1) and characterized by ^{1}H-NMR spectra.

proceeded well with aromatic aldehydes having electron-withdrawing, electron-donating and halogen substituents (Table 3, Entries 1–11). It was observed that the scope of the reaction is limited to aromatic aldehydes and the reaction did not proceed when aliphatic aldehyde were used (Table 3, Entry 12). In the case of aryl aldehydes having electron-donating groups such as CH_3, OCH_3 (Table 3, Entries 2,3,6,7), the yield of the corresponding products is higher than that of electron-withdrawing groups (Table 3, Entry 11). Furthermore, electron-donating substituents on the aromatic ring both in aldehydes and amines increased the rate of the reaction (Table 3).

The work-up procedure is very clear-cut; that is, the products were isolated and purified by simple filtration and recrystallization from ethanol. All the synthesized compounds were confirmed by their ^{1}H and ^{13}C-NMR spectral data and elemental analysis.

In summary, an efficient protocol was described for the preparation of 2-(2-oxo-2*H*-chromen-4-yl)-3-arylthiazolidin-4-one derivatives. In the presence of tetramethylbutane-1,4-diammonium acetate the reactions were carried out in short reaction times with good yields of the corresponding products. This procedure was also successfully applied to the synthesis of 2,3-diarylthiazolidin-4-one derivatives in good yields. The present methodology has several advantages, including good yields, simple procedure, short reaction times and mild reaction conditions.

3. Experimental

3.1. Reagents and instrumentation

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. The NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument. The spectra were measured in $CDCl_3$ relative to TMS (0.00 ppm). Elemental analysis was performed on a Heraeus CHN-O-Rapid analyzer. TLC was performed on silica gel polygram SIL G/UV 254 plates. Tetramethylbutane-1,4-diammonium acetate can be easily prepared following the procedure reported by Alvarez et al.[28] The synthetic strategy prefparation of 2-oxo-2*H*-chromene-4-carbaldehyde derivatives is depicted in [29].

3.2. General procedure

To a mixture of aldehyde (1 mmol), aromatic amine (1 mmol) and thioglycolic acid (1 mmol) in toluene (10 mL) was added tetramethylbutane-1,4-diammonium acetate (0.5 mmol) and the mixture was stirred at reflux condition for the appropriate time (Tables 2 and 3). The progress of the reaction was monitored by TLC. Upon completion, the solvent was concentrated and the reaction mixture was recrystallized from ethanol to afford the pure product.

3.3. Selected data

2-(2-oxo-2H-chromen-4-yl)-3-phenylthiazolidin-4-one (*Table 2, Product* ***2a***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.72 (d, J = 12.4 Hz, 1H), 3.89 (d, J = 12.4 Hz, 1H), 5.90–5.93 (m, 2H), 7.18–7.42 (m, 8H), 7.73 (t, J = 8.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.6, 66.8, 115.9, 118.1, 118.9, 122.8, 123.2, 125.2, 126.6, 129.4, 129.7, 131.6, 145.6, 153.9, 160.5, 172.1 ppm; Found: C, 66.99; H, 4.23; N, 4.51 $C_{18}H_{13}NO_3S$; requires: C, 66.86; H, 4.05; N, 4.33%].

2-(2-oxo-2H-chromen-4-yl)-3-p-tolylthiazolidin-4-one (*Table 2, Product* ***2b***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.23 (s, 3H, CH_3), 3.71 (d, J = 12.4 Hz, 1H), 3.88 (d, J = 12.4 Hz, 1H), 5.92 (s, 1H), 5.97 (s, 1H, CH), 7.10 (d, J = 7.9 Hz, 1H), 7.39–7.43 (m, 5H), 7.74 (t, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 34.7, 66.9, 114.6, 115.8, 118.0, 119.3, 122.7, 126.5, 129.3, 130.1, 131.7, 132.8, 144.7, 153.9, 160.2, 172.3 ppm; Found: C, 67.77; H, 4.57; N, 4.27 $C_{19}H_{15}NO_3S$; requires: C, 67.64; H, 4.48; N, 4.15%].

3-(4-methoxyphenyl)-2-(2-oxo-2H-chromen-4-yl)thiazolidin-4-one (*Table 2, Product* ***2c***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.74–3.76 (m, 4H), 3.89 (d, J = 12.4 Hz, 1H), 5.93 (s, 1H), 6.07 (s, 1H, CH), 6.65 (d, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.39–7.43 (m, 3H), 7.73 (t, J = 8.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.6, 55.7, 66.5, 116.1, 116.8, 118.2, 119.6, 122.7, 123.9, 126.6, 129.4, 132.1, 144.7, 154.0, 157.4, 160.2, 172.1 ppm; Found: C, 64.81; H, 4.49; N, 4.15 $C_{19}H_{15}NO_4S$; requires: C, 64.58; H, 4.28; N, 3.96%].

3-(4-chlorophenyl)-2-(2-oxo-2H-chromen-4-yl)thiazolidin-4-one (*Table 2, Product* ***2d***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.75 (d, J = 12.4 Hz, 1H), 3.89 (d, J = 12.4 Hz, 1H), 5.93 (s, 1H), 6.17 (s, 1H, CH), 7.39–7.45 (m, 5H), 7.73 (t, J = 8.1 Hz, 1H) 7.85 (d, J = 7.9 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.7, 66.8, 116.2, 117.0, 118.3, 123.0, 125.9,

127.3, 129.4 (2C), 129.5, 131.7, 145.0, 153.9, 160.4, 172.5 ppm; Found: C, 60.56; H, 3.52; N, 4.12 $C_{18}H_{12}ClNO_3S$; requires: C, 60.42; H, 3.38; N, 3.91%].

2-(6-chloro-2-oxo-2H-chromen-4-yl)-3-phenylthiazolidin-4-one (*Table 2, Product* ***2e***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.75 (d, J = 12.4 Hz, 1H), 3.89 (d, J = 12.4 Hz, 1H), 5.93 (s, 1H), 6.17 (s, 1H, CH), 7.39–7.45 (m, 5H), 7.73 (t, J = 8.1 Hz, 1H), 7.85 (d, J = 7.9 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.7, 66.8, 116.2, 117.0, 118.3, 123.0, 125.9, 127.3, 129.4 (2C), 129.5, 131.7, 145.0, 153.9, 160.4, 172.5 ppm; Found: C, 60.59; H, 3.56; N, 4.11 $C_{18}H_{12}ClNO_3S$; requires: C, 60.42; H, 3.38; N, 3.91%].

2-(6-chloro-2-oxo-2H-chromen-4-yl)-3-p-tolylthiazolidin-4-one (*Table 2, Product* ***2f***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.23 (s, 3H, CH_3), 3.74 (d, J = 12.4 Hz, 1H), 3.88 (d, J = 12.4 Hz, 1H), 5.93 (s, 1H), 6.15 (s, 1H, CH), 7.10 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.40–7.44 (m, 3H), 7.95(s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 35.0, 66.9, 115.1, 116.3, 117.4, 118.1, 128.7, 129.3, 130.2, 130.6, 132.5, 132.7, 144.7, 153.8, 160.7, 172.1 ppm; Found: C, 61.49; H, 3.94; N, 3.95 $C_{19}H_{14}ClNO_3S$; requires: C, 61.37; H, 3.79; N, 3.77%].

2-(6-chloro-2-oxo-2H-chromen-4-yl)-3-(4-methoxyphenyl)thiazolidin-4-one (*Table 2, Product* ***2g***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.75–3.77 (m, 4H, CH_3), 3.90 (d, J = 12.4 Hz, 1H), 5.93 (s, 1H), 6.16 (s, 1H, CH), 6.67 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 8.1 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.94 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.2, 56.3, 66.7, 116.3, 116.9, 118.2, 119.3, 124.3, 128.7, 129.8, 130.9, 133.3, 144.7, 154.1, 157.4, 160.3, 172.1 ppm; Found: C, 58.97; H, 3.86; N, 3.84 $C_{19}H_{14}ClNO_4S$; requires: C, 58.84; H, 3.64; N, 3.61%].

2-(6-chloro-2-oxo-2H-chromen-4-yl)-3-(4-chlorophenyl)thiazolidin-4-one (*Table 2, Product* ***2h***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.75 (d, J = 12.4 Hz, 1H), 3.92 (d, J = 12.4 Hz, 1H), 5.93 (s, 1H), 6.21 (s, 1H, CH), 7.35 (d, J = 8.2 Hz, 1H), 7.42–7.44 (m, 3H), 7.84 (d, J = 7.9 Hz, 2H), 7.95 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.6, 67.0, 116.7, 118.1, 119.9, 125.7, 128.9, 129.2, 129.3, 129.5, 131.0, 132.8, 144.7, 154.1, 160.3, 172.3 ppm; Found: C, 55.27; H, 2.98; N, 3.76 $C_{18}H_{11}Cl_2NO_3S$; requires: C, 55.12; H, 2.83; N, 3.57%].

2-(5-hydroxy-2-oxo-2H-chromen-4-yl)-3-phenylthiazolidin-4-one (*Table 2, Product* ***2i***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.73 (d, J = 12.4 Hz, 1H), 3.89 (d, J = 12.4 Hz, 1H), 5.87 (s, 1H, CH), 5.89 (s, 1H), 6.53 (d, J = 8.0 Hz, 1H), 7.16–7.41 (m, 7H), 10.97 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.1, 67.0, 105.1, 114.9, 115.7, 122.3, 122.9, 125.2, 129.5, 130.1, 132.7, 145.2, 156.1, 159.6, 160.7, 171.5 ppm; Found: C, 63.90; H, 4.03; N, 4.37 $C_{18}H_{13}NO_4S$; requires: C, 63.71; H, 3.86; N, 4.13%].

2-(5-hydroxy-2-oxo-2H-chromen-4-yl)-3-p-tolylthiazolidin-4-one (*Table 2, Product* ***2j***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.22 (s, 3H, CH_3), 3.74 (d, J = 12.4 Hz, 1H), 3.91 (d, J = 12.4 Hz, 1H), 5.87 (s, 1H, CH), 5.89 (s, 1H), 6.53 (d, J = 8.0 Hz, 1H), 7.11 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 8.0 Hz, 1H), 7.40–7.43 (m, 3H), 11.25 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 33.8, 66.7, 104.9, 114.7, 115.3, 116.7, 122.2, 129.2, 130.1, 132.6, 133.0, 145.2, 155.9, 159.4, 160.1, 171.2 ppm; Found: C, 64.76; H, 4.50; N, 4.11 $C_{19}H_{15}NO_4S$; requires: C, 64.58; H, 4.28; N, 3.96%].

2-(5-hydroxy-2-oxo-2H-chromen-4-yl)-3-(4-methoxyphenyl)thiazolidin-4-one (*Table 2, Product* ***2k***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.81 (s, 3H, OCH_3), 3.75 (d, J = 12.4 Hz, 1H), 3.91 (d, J = 12.4 Hz, 1H), 5.92 (s, 1H, CH), 5.95 (s, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.69 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz,

1H), 11.05 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.6, 56.3, 66.7, 105.1, 114.7, 115.6, 115.8, 122.6, 123.9, 124.1, 129.2, 133.1, 144.7, 156.1, 157.3, 159.3, 160.1, 171.4 ppm; Found: C, 61.98; H, 4.36; N, 3.99 $C_{19}H_{15}NO_5S$; requires: C, 61.78; H, 4.09; N, 3.79%].

3-(4-chlorophenyl)-2-(5-hydroxy-2-oxo-2H-chromen-4-yl)thiazolidin-4-one (*Table 2, Product **2l***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.76 (d, J = 12.4 Hz, 1H), 3.93 (d, J = 12.4 Hz, 1H), 5.93–5.95 (m, 2H), 6.54 (d, J = 8.1 Hz, 1H), 7.26 (d, J = 8.1 Hz, 1H), 7.39–7.43 (m, 3H), 7.84 (d, J = 7.8 Hz, 2H), 11.31 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.1, 66.3, 104.4, 114.5, 115.7, 122.5, 125.7, 129.2, 129.3, 129.4, 132.9, 144.7, 156.2, 159.3, 160.1, 171.9 ppm; Found: C, 57.94; H, 3.43; N, 3.91 $C_{18}H_{12}ClNO_4S$; requires: C, 57.83; H, 3.24; N, 3.75%].

2,3-diphenylthiazolidin-4-one (*Table 3, Product **3a***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.82 (d, J = 14.1 Hz, 1H), 3.94 (d, J = 14.1 Hz, 1H), 6.02 (s, 1H), 7.16–7.37 (m, 10H).

3-phenyl-2-p-tolylthiazolidin-4-one (*Table 3, Product **3b***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.27 (s, 3H, CH_3), 3.85 (d, J = 14.2 Hz, 1H), 3.96 (d, J = 14.2 Hz, 1H), 6.07 (s, 1H), 7.08–7.30 (m, 9H).

2-(4-methoxyphenyl)-3-phenylthiazolidin-4-one (*Table 3, Product **3c***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.85 (d, J = 14.1 Hz, 1H), 3.76 (s, 3H, OCH_3), 3.96 (d, J = 14.1 Hz, 1H), 6.03 (s, 1H), 6.93 (d, J = 7.6 Hz, 2H), 7.08–7.29 (m, 7H).

2-(4-chlorophenyl)-3-phenylthiazolidin-4-one (*Table 3, Product **3d***): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.86 (d, J = 14.2 Hz, 1H), 3.98 (d, J = 14.2 Hz, 1H), 6.06 (s, 1H), 7.11–7.44 (m, 9H).

2-phenyl-3-p-tolylthiazolidin-4-one (*Table 3, Product **3e***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.22 (s, 3H, CH_3), 3.88 (d, J = 14.4 Hz, 1H), 3.99 (d, J = 14.4 Hz, 1H), 6.03 (s, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.15–7.36 (m, 7H).

2,3-dip-tolylthiazolidin-4-one (*Table 3, Product **3f***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.21 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.86 (d, J = 14.3 Hz, 1H), 3.97 (d, J = 14.3 Hz, 1H), 6.02 (s, 1H), 7.03–7.30 (m, 8H).

2-(4-methoxyphenyl)-3-p-tolylthiazolidin-4-one (*Table 3, Product **3g***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.22 (s, 3H, CH_3), 3.86 (d, J = 14.1 Hz, 1H), 3.74 (s, 3H, OCH_3), 3.98 (d, J = 14.1 Hz, 1H), 6.01 (s, 1H), 6.90 (d, J = 7.5 Hz, 2H),7.08–7.29 (m, 6H).

2-(4-chlorophenyl)-3-p-tolylthiazolidin-4-one (*Table 3, Product **3h***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.22 (s, 3H, CH_3), 3.85 (d, J = 14.2 Hz, 1H), 3.97 (d, J = 14.2 Hz, 1H), 6.11 (s, 1H), 7.08 (d, J = 7.5 Hz, 2H), 7.29–7.48 (m, 6H).

2-o-tolyl-3-p-tolylthiazolidin-4-one (*Table 3, Product **3i***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.22 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.85 (d, J = 14.1 Hz, 1H), 3.97 (d, J = 14.1 Hz, 1H), 6.02 (s, 1H), 7.08–7.30 (m, 8H).

2-(2-chlorophenyl)-3-p-tolylthiazolidin-4-one (*Table 3, Product **3j***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.22 (s, 3H, CH_3), 3.87 (d, J = 14.1 Hz, 1H), 3.98 (d, J = 14.1 Hz, 1H), 6.12 (s, 1H), 7.08 (d, J = 7.5 Hz, 2H), 7.25–7.44 (m, 6H).

2-(3-nitrophenyl)-3-p-tolylthiazolidin-4-one (*Table 3, Product **3k***): ^{1}H-NMR (400 MHz, $CDCl_3$): 2.22 (s, 3H, CH_3), 3.88 (d, J = 14.4 Hz, 1H), 4.02 (d, J = 14.4 Hz, 1H), 6.21 (s, 1H), 7.08 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.93 (d, J =7.6 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.21 (s, 1H).

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References

[1] Katritzky AR, Ramsden CA, Joule J, Zhdankin VV. Handbook of heterocyclic chemistry. 3rd ed. Oxford: Elsevier; 2010.
[2] Hongyu Z, Wu S, Zhai S, et al. Design, synthesis, cytoselective toxicity, structure–activity relationships, and pharmacophore of thiazolidinone derivatives targeting drug-resistant lung cancer cells. J Med Chem. 2008;51:1242–1251.
[3] Barreca ML, Balzsarini J, Chimirri A, et al. Design, synthesis, structure–activity relationships, and molecular modeling studies of 2,3-diaryl-1,3-thiazolidin-4-ones as potent anti-HIV agents. J Med Chem. 2002;45:5410–5413.
[4] Rao A, Balzarini J, Carbone A, et al. 2-(2,6-dihalophenyl)-3-(pyrimidin-2-yl)-1,3-thiazolidin-4-ones as non-nucleoside HIV-1 reverse transcriptase inhibitors. Antivir Res. 2004;63:79–84.
[5] Rawal RK, Tripathi R, Katti SB, Pannecouque C, De Clercq E. Synthesis and evaluation of 2-(2,6-dihalophenyl)-3-pyrimidinyl-1,3-thiazolidin-4-one analogues as anti-HIV-1 agents. Bioorg Med Chem. 2007;15:3134–3142.
[6] Solomon VR, Haq W, Srivastava K, Puri SK, Katti SB. Synthesis and antimalarial activity of side chain modified 4-aminoquinoline derivatives. J Med Chem. 2007;50:394–398.
[7] Kucukguzel GC, Shchullek JR, Kaocatepe A, De Clercq E, Sahinv F, Gulluce M. Synthesis and biological activity of 4-thiazolidinones, thiosemicarbazides derived from diflunisal hydrazide. Eur J Med Chem. 2006;41:353–359.
[8] Diurno MV, Mazzoni O, Calignano PE, Giorodano F, Bolognese A. Synthesis and antihistaminic activity of some thiazolidin-4-ones. J Med Chem. 1992;35:2910–2912.
[9] Archana Srivastava VK, Kumar A. Synthesis of newer thiadiazolyl and thiazolidinonyl quinazolin-4(3H)-ones as potential anticonvulsant agents. Eur J Med Chem. 2002;37:873–882
[10] Dwivedi C, Gupta SS, Parmar SS. Substituted thiazolidones as anticonvulsants. J Med Chem. 1972;15:553–554.
[11] Desai KG, Desai KR. A facile microwave enhanced synthesis of sulfur-containing 5-membered heterocycles derived from 2-mercaptobenzothiazole over $ZnCl_2$/DMF and antimicrobial activity evaluation. J Sulfur Chem. 2006;27:315–328.
[12] Jackson CM, Blass B, Coburn K, et al. Evolution of thiazolidine-based blockers of human Kv1.5 for the treatment of atrial arrhythmias. Bioorg Med Chem Lett. 2007;17:282–284.
[13] Srivastava T, Haq W, Katti SB. Carbodiimide mediated synthesis of 4-thiazolidinones by one-pot three-component condensation. Tetrahedron. 2002;58:7619–7624.
[14] Sadashiva CT, Narendr JN, Chandra S, et al. Synthesis and pharmacological evaluation of novel *N*-alkyl/aryl substituted thiazolidinone arecoline analogues as muscarinic receptor 1 agonist in Alzheimer's dementia models. Eur J Med Chem. 2009;44:4848–4854.
[15] Srivastava SK, Srivastava SL, Srivastava SD. Synthesis of 5-arylidene-2-aryl-3-(2-chlorophenothiazinoacetamidyl)-1,3- thiazolidin-4-ones as antifungal and anticonvulsant agents. J Ind Chem Soc. 2002;77:104–105.
[16] Kumar RC, Kumar D. Synthesis of some new thiazolidin-4-ones as possible antimicrobial agents. J Ind Chem Soc. 2002;77:492–493.
[17] Yadav AK, Kumar M, Yadav T, Jain R. An ionic liquid mediated one-pot synthesis of substituted thiazolidinones and benzimidazoles. Tetrahedron Lett. 2009;50:5031–5034
[18] Zhang X, Li X, Li D, et al. Ionic liquid mediated and promoted eco-friendly preparation of thiazolidinone and pyrimidine nucleoside–thiazolidinone hybrids and their antiparasitic activities. Bioorg Med Chem Lett. 2009;19:6280–6283.
[19] Kanagarajana V, Thanusua J, Gopalakrishnana M. Three component one-pot synthesis of novel pyrimidino thiazolidin-4-ones catalyzed by activated fly ash. Green Chem Lett Rev. 2009;2:161–167.

[20] Pratap UR, Jawale DV, Bhosle MR, Mane RA. *Saccharomyces cerevisiae* catalyzed one-pot three component synthesis of 2,3-diaryl-4-thiazolidinones. Tetrahedron Lett. 2011;52:1689–1691.
[21] Foroughifar N, Ebrahimi S. One-pot synthesis of 1,3-thiazolidin-4-one using $Bi(SCH_2COOH)_3$ as catalyst. Chin Chem Lett. 2013;24:389–391.
[22] Ghashang M. Preparation and application of barium sulfate nano-particles in the synthesis of 2,4,5-triaryl and *N*-aryl(alkyl)-2,4,5-triaryl imidazoles. Curr Org Synth. 2012;9:727–732.
[23] Ghashang M, Mansoor SS, Aswin K. Thiourea dioxide: an efficient and reusable organocatalyst for the rapid one-pot synthesis of pyrano[4,3-b]pyran derivatives in water. Chin J Catal. 2014;35:127–133.
[24] Mohammad Shafiee MR, Ghashang M, Fazlinia A. Preparation of 1,4-dihydropyridine derivatives using perchloric acid adsorbed on magnetic Fe_3O_4 nanoparticles coated with silica. Curr Nanosci. 2013;9:197–201.
[25] Ghashang M. 1-Butyl-1-methylpyrrolidinium hydrogen sulfate promoted preparation of 1,5-diaryl-3-(arylamino)-1H-pyrrol-2(5*H*)-one derivatives. Res Chem Intermed. 2013;39:2187–2195.
[26] Ghashang M. Aluminum hydrogen sulfate $[Al(HSO_4)_3]$ as an efficient catalyst for the preparation of thioacetals. Res Chem Intermed. 2013;39:2837–2842.
[27] Dehbashi M, Aliahmad M, Mohammad Shafiee MR, Ghashang M. Nickel doped SnO_2 nanoparticles: Preparation and evaluation of their catalytic activity in the synthesis of 1-amido alkyl-2-naphtholes. Synth React Inorg Met Org Chem. 2013;43:1301–1306.
[28] Alvarez VH, Mattedi S, Martin-Pastor M, Aznar M, Iglesias M. Thermophysical properties of binary mixtures of {ionic liquid 2-hydroxyethylammonium acetate + (water, methanol, or ethanol)}. J Chem Thermodyn. 2011;43:997–1010.
[29] ElAzab IH, Youssef MM, Amin MA. Microwave-assisted synthesis of novel 2*H*-chromene derivatives Bearing phenylthiazolidinones and their biological activity assessment. Molecules. 2014;19:19648–19664.