Tetrahedron 67 (2011) 584–589

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

An expedient route to highly functionalized 2*H*-chromene-2-thiones via ring annulation of β-oxodithioesters catalyzed by $InCl_3$ under solvent-free conditions

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ARTICLE INFO

Article history:
Received 23 September 2010
Received in revised form 9 November 2010
Accepted 16 November 2010
Available online 20 November 2010

Keywords:
3-Substituted-2*H*-chromene-2-thiones
Benzo[*f*]2*H*-chromene-2-thiones
β-Oxodithioesters
Indium trichloride
Solvent-free condition

ABSTRACT

A convenient and one-pot synthesis of 3-aroyl/heteroaroyl-2*H*-chromene-2-thiones and benzo[*f*]2*H*-chromene-2-thiones has been developed by the condensation of β-oxodithioesters and salicylaldehydes/α-hydroxynaphthaldehydes in the presence of indium trichloride under solvent-free conditions. The reaction is operationally facile, readily scalable, and offers rapid entry into differentially substituted chromene-2-thione scaffolds.

1. Introduction

Coumarins (2*H*-chromene-2-ones) are among the best known oxygen heterocycles and are present as a structural motif in numerous natural products including edible vegetables and fruits.[1] Thus, interest in their chemistry continues unabated because of the broad range of biological activity displayed by this class of compounds.[2] Because of the great relevance to both synthetic and medicinal chemists, and diverse pharmacological properties of coumarins, several elegant strategies[3] for their synthesis involving different types of catalysts have been developed.[4] However, the reports[5] on the synthesis of chromene-2-thiones are limited and suffer with many drawbacks, such as limitation of applicable β-ketoesters, expensive catalysts, harsh reaction conditions, multistep synthesis or low chemical yield, and lacking generality.

Recently, indium trichloride has emerged as a powerful Lewis acid catalyst imparting high regio- and chemo-selectivity in various chemical transformations,[6] due to its low toxicity, air and water compatibility, operational simplicity, and remarkable ability to suppress side reactions in acid sensitive substrates. In continuation of our interest in designing various heterocycles[7] by the development of new methodology, we report here remarkable catalytic activity of $InCl_3$ in the presence of urea under solvent-free conditions for the facile synthesis of highly functionalized 2*H*-chromene-2-thiones and benzo[*f*]2*H*-chromene-2-thiones via ring annulation of β-oxodithioesters.

2. Results and discussion

A careful survey of literature at this stage revealed that β-oxodithioesters **3** have been utilized as an unprecedented substrate for the synthesis of chromene-2-thiones by Singh et al.[5] We therefore became interested in devising more general synthetic strategy utilizing β-oxodithioesters **3** as the versatile templates for the construction of chromene-2-thiones **5** (Scheme 4). To further add diversity to coumarin motif, the β-oxodithioesters **3** were also subjected to ring annulation with 2-hydroxy-1-naphthaldehyde **7** to afford benzo[*f*]2*H*-chromene-2-thiones **8** in good yields (Scheme 4). The new methodology allows facile introduction of substituents at 3-position of chromene-2-thiones and flexibility for the construction of novel benzo[*f*]2*H*-chromene-2-thione frameworks. The desired β-oxodithioesters[8] **3** have been prepared in good yields (Table 1) by stirring ketones **1** with dimethyl trithiocarbonate **2** in the presence of sodium hydride in DMF/hexane (1:4) solvent mixture at room temperature (Scheme 1).

Our initial attempts to synthesize chromene-2-thione, involving the reaction of methyl-3-hydroxy-3-(*p*-methoxyphenyl)-prop-2-enedithioate **3a** and salicylaldehyde **4a** in the presence of $InCl_3$ (20 mol %) at 100 °C under solvent-free condition (Scheme 2) furnished the desired chromene-2-thione **5a** in very low yield, and surprisingly 3-substituted coumarin **6a** was formed as a major product (Table 2, entry 1). In order to confirm this observation, we carried out a series of

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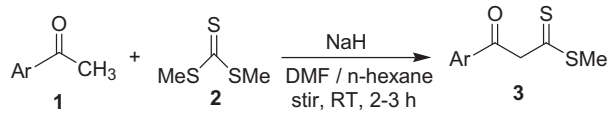
doi:10.1016/j.tet.2010.11.055

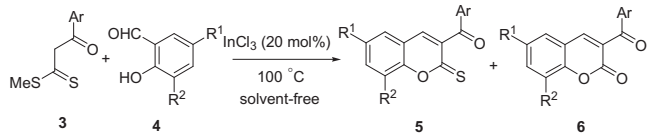
Table 1
Synthesis of β-oxodithioesters (**3a**–**g**)

Entry	Ar	Mp (°C)	Yield[a] (%)
3a	4-MeO·C_6H_4	74–75	73
3b	4-Me·C_6H_4	54–55	68
3c	2-Furyl	51–52	70
3d	2-Thienyl	49–50	80
3e	4-Cl·C_6H_4	72–73	75
3f	C_6H_5	57–58	72
3g	η^5-Ferrocenyl	103–104	45

[a] Yield of isolated pure product.



Scheme 1. Synthesis of β-oxodithioesters.



Scheme 2. Reaction of β-oxodithioesters (**3**) with salicylaldehydes (**4**) in the absence of urea.

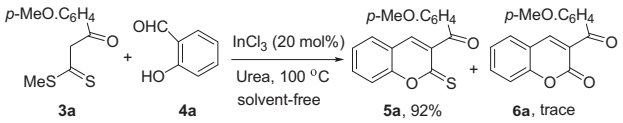
Table 2
Reaction of β-oxodithioesters (**3**) with salicylaldehydes (**4**)

Entry	Ar	R^1	R^2	Products **5**, **6** Yield[a] (%)	
1	4-MeO·C_6H_4	H	H	**5a** (15)	**6a** (70)
2	4-MeO·C_6H_4	H	OMe	**5b** (20)	**6b** (72)
3	4-MeO·C_6H_4	Br	H	**5c** (35)	**6c** (55)
4	4-Me·C_6H_4	H	H	**5e** (12)	**6e** (72)
5	4-Me·C_6H_4	NO_2	H	**5g** (10)	**6g** (68)
6	4-Cl·C_6H_4	H	H	**5m** (16)	**6m** (65)
7	C_6H_5	H	H	**5p** (10)	**6p** (75)

[a] Yield of isolated pure product.

reaction using different β-oxodithioesters **3** and various salicylaldehydes **4**, which provided corresponding chromene-2-ones **6** as the major products (65–75%) along with respective chromene-2-thiones **5** as the minor ones (10–20%) except in the case of 5-bromosalicylaldehyde, where both **5** and **6** were obtained in moderate yields (Table 2, entry 3). The results are summarized in Table 2. The chromene-2-ones **6** were characterized by comparing the physical, spectral, and analytical data with the previous reports.[9]

Then, we decided to perform the above reaction in the presence of urea as per previous reports.[5] Initially, the reaction of β-oxodithioester **3a** (1.0 mmol) and salicylaldehyde **4a** (1.2 mmol) as a model reaction was performed in the presence of both $InCl_3$ as well as urea (20 mol % each) at 100 °C under solvent-free condition yielding both chromene-2-thione **5a** (65%) and chromene-2-one **6a** (30%). The significant increase in the yield of **5a** in the presence of urea clearly indicates that somehow it prevents the formation of **6**. In order to further enhance the yield of chromene-2-thione **5a**, we carried out the above model reaction using equivalent amount of urea. To our delight, chromene-2-thione **5a** was formed as exclusive product with trace of chromene-2-one **6a** (Scheme 3). In order to check the real effect of urea in the above cyclocondensation reaction, a test reaction using β-oxodithioester **3a** and salicylaldehyde **4a** was performed in the absence of $InCl_3$ at 100 °C under solvent-free conditions utilizing urea in catalytic (20 mol %) as well as in equivalent amounts separately. It was found that no conversion to product was obtained under above both conditions even



Scheme 3. Synthesis of 2*H*-chromene-2-thiones in presence of urea.

after 6 h of heating. After prolonged heating (24 h) the β-oxodithioester decomposed extensively (monitored by TLC). Based on the above observations, it may be concluded that $InCl_3$ is acting as catalyst and urea as promoter. Thus, a more concise approach was exploited by carrying out the above model reaction in the presence of urea (1.2 equiv) under similar condition resulting **5** in excellent yields (Table 4). Though, the roles of urea in these transformations in not very clear, higher yields of chromene-2-thiones **5** were obtained in the presence of urea, which probably inhibits the hydrolysis of chromene-2-thione.

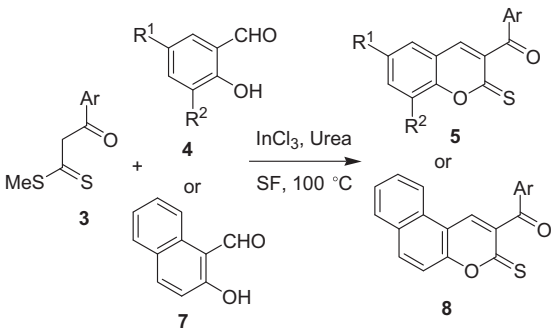
In order to evaluate the most appropriate catalyst and its loading, the above model reaction was performed utilizing different catalysts with varying loading percentages under different solvents and solvent-free conditions (Table 3). After optimization, 20 mol % of $InCl_3$ under solvent-free condition was found to be effective for the progress of the reaction (Table 3, entry 3). Higher percentage loading of the $InCl_3$ did not increase the yield but lowered the reaction time slightly (Table 3, entry 4). The effect of temperature was also studied and the optimum temperature of the reaction was found to be 100 °C, whereas lowering the temperature are detrimental to the reaction resulting in lower yields and long reaction time.

Table 3
Optimization of the catalyst on model reaction[a]

Entry	Catalyst	Loading (mol %)	Solvent	Time (h)	Yield[b] (%)
1	$InCl_3$	10	Solvent-free	4	65
2	$InCl_3$	15	Solvent-free	3	82
3	$InCl_3$	20	Solvent-free	2.5	92
4	$InCl_3$	25	Solvent-free	2.0	90
5	$InCl_3$	20	CH_3CN	24	55
6	$InCl_3$	20	EtOH	24	Trace
7	$InCl_3$	20	THF	24	Trace
8	$SbCl_3$	15	Solvent-free	3.5	58
9	$SbCl_3$	20	Solvent-free	2.5	65
10	$SbCl_3$	25	Solvent-free	2.0	68
11	$SbCl_3$	20	CH_3CN	24	Trace
12	PTA	5	CH_3CN	24	NR[c]
13	PTA	5	Solvent-free	6	35

[a] Reaction of methyl-3-hydroxy-3-(*p*-methoxyphenyl)-prop-2-enedithioate (1 mmol), salicylaldehyde (1.2 mmol), and urea (1.2 mmol) under solvent-free condition at 100 °C and in solvents at its reflux temperature.
[b] Isolated yields.
[c] No reaction.

To generate a small library of functionalized 3-substituted chromene-2-thiones **5** using the optimized reaction condition, we next utilized a variety of β-oxodithioesters **3** and salicylaldehydes **4** to explore the scope of this one-pot cyclocondensation reaction (Scheme 4). A number of functional groups, such as bromo, nitro, methoxy, and ethoxy in the salicylaldehyde component, and aryl, 2-thienyl, 2-furyl, and η^5-ferrocenyl at the β-position of the β-oxodithioester are tolerated well under the reaction conditions to provide structurally interesting chromene-2-thiones **5** in excellent yields (Table 4). To further demonstrate the scope, and to explore the limitations and generality of the reaction, the procedure was extended to 2-hydroxy-1-naphthaldehyde **7** as cyclocondensation partner. Compound **7** was reacted with various β-oxodithioesters **3** under similar reaction conditions to afford benzo[*f*]2*H*-chromene-2-thiones **8** in high yields (Scheme 4, Table 4), except in the case of methyl 3-(η^5-ferrocenyl)-3-hydroxyprop-2-enedithioate **3g**, which afforded **8g** in moderate yield (Table 4, entry 24).Given the range of



Scheme 4. Synthesis of chromene-2-thiones.

Table 4
Synthesis of chromene-2-thiones

Entry	Ar	R^1	R^2	Product	Yield[a] (%)
1	4-MeO·C_6H_4	H	H	**5a**	92
2	4-MeO·C_6H_4	H	OMe	**5b**	92
3	4-MeO·C_6H_4	Br	H	**5c**	90
4	4-MeO·C_6H_4	NO_2	H	**5d**	80
5	4-Me·C_6H_4	H	H	**5e**	90
6	4-Me·C_6H_4	H	OMe	**5f**	89
7	4-Me·C_6H_4	NO_2	H	**5g**	78
8	2-Furyl	H	H	**5h**	94
9	2-Furyl	H	OMe	**5i**	90
10	2-Furyl	Br	H	**5j**	95
11	2-Thienyl	Br	H	**5k**	85
12	2-Thienyl	H	OMe	**5l**	82
13	4-Cl·C_6H_4	H	H	**5m**	87
14	4-Cl·C_6H_4	H	OMe	**5n**	92
15	C_6H_5	H	OEt	**5o**	88
16	C_6H_5	H	H	**5p**	86
17	η^5-Ferrocenyl	H	H	**5q**	60
18	4-MeO·C_6H_4	2-Hydroxy-1-naphthaldehyde		**8a**	75
19	4-Me·C_6H_4	–do–		**8b**	72
20	2-Furyl	–do–		**8c**	80
21	2-Thienyl	–do–		**8d**	76
22	4-Cl·C_6H_4	–do–		**8e**	73
23	C_6H_5	–do–		**8f**	75
24	η^5-Ferrocenyl	–do–		**8g**	50

[a] Isolated pure yields in the presence of urea.

commercially available components for this protocol (β-oxodithioesters and salicylaldehydes), the method should prove valuable in the preparation of combinatorial libraries of functionalized coumarin motifs.

The structures were confirmed by spectral (IR, ^1H, ^{13}C, and mass) and analytical studies. The absence of nitrogen in the CHN analyses gave us a clue to the structural elucidation of the respective hitherto unknown coumarins. Importantly, the crystallinity of 3-(thien-2-oyl)-6-bromo-2*H*-chromene-2-thione **5k** allowed for its structural verification by X-ray crystallography[10] and thus, unambiguous regiochemical confirmation (Fig. 1).

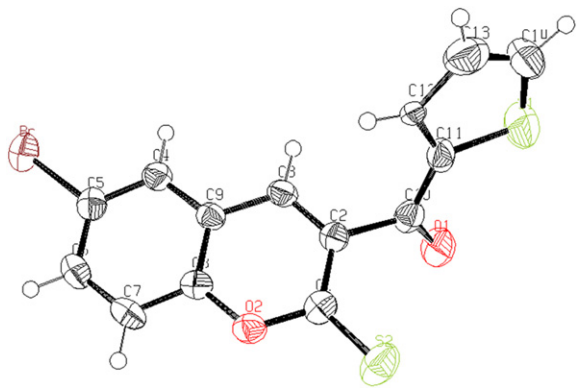


Fig. 1. Ortep diagram for 3-(thien-2-oyl)-6-bromo-2*H*-chromene-2-thione **5k**.

3. Conclusion

In conclusion, an efficient one-pot, ring annulation protocol for a variety of chromene-2-thiones has been devised involving β-oxodithioesters under solvent-free conditions. To the best of our knowledge, this is the first report of chromene-2-thione synthesis via ring annulation using β-oxodithioesters as a C-2 synthon utilizing $InCl_3$ as catalyst. The advantages of this strategy are short reaction time, high yields, mild reaction condition, easy purification, and economic availability of the catalyst. A particularly attractive feature of this approach is that depending on the structure of β-oxodithioesters, different substituents can be incorporated in the 3-position. This method is suitable to library production, diversity-oriented synthesis, and drug discovery. Further studies to extend the scope of β-oxodithioesters to diverse range of heterocyclic compounds are in progress in our laboratory.

4. Experimental

4.1. General

All the reagents were commercial and purchased from Merck, Aldrich and Fluka and were used as received. All ^1H and ^{13}C NMR spectra were recorded on JEOL AL 300 FT-NMR spectrometer. Chemical shifts are given as δ value with reference to tetramethylsilane (TMS) as the internal standard. The IR spectra were recorded on Varian 3100 FT-IR spectrophotometer. Mass spectra were recorded at 70 eV ionizing voltage on a JEOL-D300 MS instrument. The C and H analyses were performed from microanalytical laboratory with an Exeter Analytical Inc. 'Model CE-400 CHN Analyzer'. X-ray diffraction was measured on Xcalibur Oxford CCD Diffractometer. All the reactions were monitored by TLC using precoated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck $60F_{254}$) using UV light (254 nm/365 nm) for visualization. Melting points were determined with Büchi B-540 melting point apparatus and are uncorrected.

4.2. General procedure for the synthesis of β-oxodithioesters (3a–g)

Appropriate aryl/heteroaryl ketone **1** (10 mmol) was added to a suspension of NaH (60% suspension in mineral oil, 0.80 g, 20 mmol) in DMF/hexane solvent mixture (1:4, 30 mL). Dimethyl trithiocarbonate **2** (10 mmol) was slowly added to the reaction mixture and stirred well for 2 h (in the case of acetylferrocene, the reaction mixture was refluxed for 3 h to get the product). After completion of the reaction (monitored by TLC), the reaction mixture was washed with hexane to remove unreacted ketone and dimethyl trithiocarbonate. Reaction mixture was acidified with 1 N HCl (20 mL) to get the dithioesters precipitated. The precipitated dithioester was extracted with dichloromethane (2×30 mL) followed by washing with brine (2×25 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated under vacuum and the residue obtained was purified by column chromatography over silica gel using hexane as eluent to give the corresponding β-oxodithioester in high yield. The spectral and analytical data of the β-oxodithioesters **3a–g** are given below.

*4.2.1. Methyl 3-hydroxy-3-(p-methoxyphenyl)-prop-2-enedithioate (**3a**).* Yellow solid, mp 74–75 °C. IR (KBr): 3430, 1603, 1582, 1545, 1503, 1430, 1232, 1180, 1052 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$):

δ 15.16 (s, 1H, OH), 7.86 (d, *J*=8.7 Hz, 2H, ArH), 6.94 (d+s, *J*=8.7 Hz, 3H, ArH+H_{Olefin}), 3.87 (s, 3H, OCH_3), 2.65 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.5, 169.4, 162.7, 128.6, 126.1, 114.1, 107.0, 55.4, 16.9. FABMS (*m*/*z*): 241 (M^++1). Anal. Calcd for $C_{11}H_{12}O_2S_2$: C, 54.97%; H, 5.03%. Found: C, 54.88%; H, 4.91%.

*4.2.2. Methyl 3-hydroxy-3-(p-methylphenyl)-prop-2-enedithioate (**3b**).* Yellow solid, mp 54–55 °C. IR (KBr): 3382, 1654, 1584, 1560, 1529, 1502, 1456, 1421, 1236, 1184 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 15.09 (s, 1H, OH), 7.77 (d, *J*=8.1 Hz, 2H, ArH), 7.24 (d, *J*=8.1 Hz, 2H, ArH), 6.94 (s, 1H, H_{Olefin}), 2.65 (s, 3H, SCH_3), 2.40 (s, 3H, $ArCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 216.5, 169.6, 142.6, 131.5, 129.4, 126.7, 107.5, 21.7, 17.0. FABMS (*m*/*z*): 225 (M^++1). Anal. Calcd for $C_{11}H_{12}OS_2$: C, 58.89%; H, 5.39%. Found: C, 58.99%; H, 5.44%.

*4.2.3. Methyl 3-(furan-2-yl)-3-hydroxyprop-2-enedithioate (**3c**).* Yellow solid, mp 51–52 °C. IR (KBr): 3058, 3009, 1666, 1592, 1251 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 14.69 (s, 1H, OH), 7.57 (s, 1H, ArH), 7.13 (d, *J*=3.6 Hz, 1H, ArH), 6.92 (s, 1H, H_{Olefin}), 6.56 (s, 1H, ArH), 2.64 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 216.6, 159.1, 148.5, 145.6, 115.1, 112.7, 106.3, 17.0. FABMS (*m*/*z*): 201 (M^++1). Anal. Calcd for $C_8H_8O_2S_2$: C, 47.98%; H, 4.03%. Found: C, 47.92%; H, 4.10%.

*4.2.4. Methyl 3-hydroxy-3-(thiophen-2-yl)-prop-2-enedithioate (**3d**).* Yellow solid, mp 49–50 °C. IR (KBr): 3058, 3009, 1666, 1592, 1251 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 15.04 (s, 1H, OH), 7.73 (d, *J*=3.3 Hz, 1H, ArH), 7.56 (d, *J*=4.8 Hz, 1H, ArH), 7.12 (dd, *J*=4.5, 4.2 Hz, 1H, ArH), 6.86 (s, 1H, H_{Olefin}), 2.65 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.6, 164.0, 138.3, 130.9, 129.2, 128.3, 106.9, 16.9. FABMS (*m*/*z*): 217 (M^++1). Anal. Calcd for $C_8H_8OS_3$: C, 44.41%; H, 3.73%. Found: C, 44.52%; H, 3.61%.

*4.2.5. Methyl 3-(p-chlorophenyl)-3-hydroxyprop-2-enedithioate (**3e**).* Yellow solid, mp 72–73 °C. IR (KBr): 3429, 2922, 1591, 1555, 1485, 1415, 1229, 1092 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 15.04 (s, 1H, OH), 7.81 (d, *J*=8.7 Hz, 2H, ArH), 7.41 (d, *J*=8.7 Hz, 2H, ArH), 6.89 (s, 1H, H_{olefin}), 2.66 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 217.7, 167.6, 138.2, 132.9, 129.0, 128.1, 107.6, 17.3. FABMS (*m*/*z*): 245 (M^++1). Anal. Calcd for $C_{10}H_9ClOS_2$: C, 49.07%; H, 3.71%. Found: C, 49.14%; H, 3.59%.

*4.2.6. Methyl 3-hydroxy-3-phenyl-prop-2-enedithioate (**3f**).* Yellow solid, mp 55–56 °C. IR (KBr): 3731, 1585, 1559, 1489, 1451, 1392, 1298, 1236, 1055 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 15.08 (s, 1H, OH), 7.88 (d, *J*=6.9 Hz, 2H, ArH), 7.51–7.44 (m, 3H, ArH), 6.96 (s, 1H, H_{olefin}), 2.66 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 217.3, 169.4, 134.2, 132.0, 128.7, 126.8, 108.0, 17.2. FABMS (*m*/*z*): 211 (M^++1). Anal. Calcd for $C_{10}H_{10}OS_2$: C, 57.11%; H, 4.79%. Found: C, 57.14%; H, 4.69%.

*4.2.7. Methyl 3-(η^5-ferrocenyl)-3-hydroxyprop-2-enedithioate (**3g**).* Violet solid, mp 103–104 °C. IR (KBr): 2974, 1599, 1559, 1482, 1392, 1055, 761 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 15.05 (s, 1H, OH), 6.60 (s, 1H, H_{Olefin}), 4.81 (d, *J*=1.8 Hz, 2H, H_{Cp}), 4.54 (d, *J*=1.5 Hz, 2H, H_{Cp}), 4.22 (s, 5H, H_{Cp}), 2.62 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.2, 176.3, 107.4, 72.0, 70.4, 70.1, 68.0, 16.6. FABMS (*m*/*z*): 318 (M^++1). Anal. Calcd for $C_{14}H_{14}FeOS_2$: C, 52.84%; H, 4.43%. Found: C, 52.99%; H, 4.58%.

4.3. General procedure for the synthesis of 2*H*-chromene-2-thiones (5) and benzo[*f*]2*H*-chromene-2-thiones (8)

A mixture of β-oxodithioester **3** (1.0 mmol), substituted salicylaldehyde **4** (or 2-hydroxy-1-naphthaldehyde **7**) (1.2 mmol), and urea (1.2 mmol) was reacted in the presence of $InCl_3$ (20 mol %, 0.2 mmol, 0.044 g) with constant stirring at 100 °C. The heating was continued till the completion of the reaction (2–3 h, monitored by TLC). The reaction mixture was treated with water (20 mL) and extracted with ethyl acetate (2×20 mL). The organic layer was washed with brine (1×20 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum to give the product, which was purified either by recrystallization from ethyl acetate or by column chromatography over silica gel using increasing amount of ethyl acetate in hexane.

The spectral and analytical data for the compounds **5a**–**q** and **8a**–**g** are given below.

*4.3.1. 3-(4-Methoxybenzoyl)-2H-chromene-2-thione (**5a**).* Yellow solid, mp 188–190 °C. IR (KBr): 3058, 2928, 1657, 1600, 1559, 1257, 1170 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J*=8.7 Hz, 2H, ArH), 7.68–7.63 (m, 2H, ArH), 7.57 (s, 1H, ArH), 7.52 (d, *J*=8.4 Hz, 1H, ArH), 7.39–7.34 (m, 1H, ArH), 6.93 (d, *J*=8.7 Hz, 2H, ArH), 3.87 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.7, 190.8, 164.2, 156.9, 139.5, 133.1, 133.0, 132.1, 128.6, 128.4, 125.7, 119.9, 116.6, 114.0, 55.5. FABMS (*m*/*z*): 297 (M^++1). Anal. Calcd for $C_{17}H_{12}O_3S$: C, 68.90%; H, 4.08%. Found: C, 68.99%; H, 4.28%.

*4.3.2. 3-(4-Methoxybenzoyl)-8-methoxy-2H-chromene-2-thione (**5b**).* Yellow solid, mp 141–143 °C. IR (KBr): 3064, 2925, 1648, 1597, 1547, 1267, 1172 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J*=8.7 Hz, 2H, ArH), 7.54 (s, 1H, ArH), 7.27 (d, *J*=8.4 Hz, 1H, ArH), 7.17–7.10 (m, 2H, ArH), 6.92 (d, *J*=8.7 Hz, 2H, ArH), 4.01 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.9, 190.8, 164.2, 146.9, 146.7, 139.7, 133.2, 132.1, 128.5, 125.7, 120.7, 119.5, 114.4, 114.0, 56.2, 55.5. FABMS (*m*/*z*): 327 (M^++1). Anal. Calcd for $C_{18}H_{14}O_4S$: C, 66.24%; H, 4.32%. Found: C, 66.37%; H, 4.21%.

*4.3.3. 6-Bromo-3-(4-methoxybenzoyl)-2H-chromene-2-thione (**5c**).* Yellow solid, mp 207–208 °C. IR (KBr): 3050, 2921, 1659, 1601, 1553, 1261, 1234, 1174 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J*=9.0 Hz, 2H, ArH), 7.74–7.70 (m, 2H, ArH), 7.46 (s, 1H, ArH), 7.40 (d, *J*=8.7 Hz, 1H, ArH), 6.94 (d, *J*=9.0, 2H, ArH), 3.88 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.0, 190.3, 164.5, 155.7, 140.4, 135.7, 132.2, 131.3, 130.5, 128.3, 121.5, 118.5, 118.3, 114.2, 55.6. FABMS (*m*/*z*): 377 (M^++2). Anal. Calcd for $C_{17}H_{11}BrO_3S$: C, 54.41%; H, 2.95%. Found: C, 54.53%; H, 3.09%.

*4.3.4. 3-(4-Methoxybenzoyl)-6-nitro-2H-chromene-2-thione (**5d**).* Orange solid, mp 208–209 °C. IR (KBr): 3752, 3066, 2926, 1654, 1601, 1535, 1240, 1151 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.48 (s, 1H, ArH), 8.46 (s, 1H, ArH), 7.89 (d, *J*=8.7 Hz, 2H, ArH), 7.63–7.58 (m, 2H, ArH), 6.95 (d, *J*=8.7 Hz, 2H, ArH), 3.89 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.2, 189.6, 164.6, 159.3, 145.1, 144.6, 141.3, 132.1, 130.7, 127.9, 127.3, 123.9, 120.1, 117.6, 114.2, 55.6. FABMS (*m*/*z*): 342 (M^++1). HRMS (ESI^+) Calcd for $C_{17}H_{11}NO_5S$: 341.0357. Found: 341.0346.

*4.3.5. 3-(4-Methylbenzoyl)-2H-chromene-2-thione (**5e**).* Yellow solid, mp 171–172 °C. IR (KBr): 3041, 2922, 1660, 1604, 1556, 1239, 1164 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, *J*=8.1 Hz, 2H, ArH), 7.68–7.51 (m, 4H, ArH), 7.39–7.37 (m, 1H, ArH), 7.26 (d, *J*=8.1 Hz, 2H, ArH), 2.42 (s, 3H, $ArCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.7, 192.0, 157.1, 145.2, 139.3, 133.0, 129.9, 129.4, 128.5, 125.9, 125.6, 120.0, 116.5, 21.8. FABMS (*m*/*z*): 281 (M^++1). Anal. Calcd for $C_{17}H_{12}O_2S$: C, 72.83%; H, 4.31%. Found: C, 72.91%; H, 4.29%.

*4.3.6. 3-(4-Methylbenzoyl)-8-methoxy-2H-chromene-2-thione (**5f**).* Yellow solid, mp 164–165 °C. IR (KBr): 3054, 2961, 2922, 1658, 1604, 1564, 1241, 1158 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J*=8.1 Hz, 2H, ArH), 7.55 (s, 1H, ArH), 7.18–7.11 (m, 5H, ArH), 4.01 (s, 3H, OCH_3), 2.41 (s, 3H, $ArCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.0, 192.1, 146.9, 145.0, 139.9, 133.5, 133.1, 129.8, 129.6, 126.0, 120.9, 119.3, 114.5, 56.4, 21.9. FABMS (*m*/*z*): 311 (M^++1). Anal. Calcd for $C_{18}H_{14}O_3S$: C, 69.66%; H, 4.55%. Found: C, 69.81%; H, 4.25%.

*4.3.7. 3-(4-Methylbenzoyl)-6-nitro-2H-chromene-2-thione (**5g**).* Yellow solid, mp 233–234 °C. IR (KBr): 3722, 1662, 1606, 1547,

1290, 1151 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.49–8.47 (m, 2H, ArH), 7.82 (d, J=8.1 Hz, 2H, ArH), 7.63–7.59 (m, 2H, ArH), 7.29–7.25 (m, 2H, ArH), 2.43 (s, 3H, $ArCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.1, 190.7, 159.3, 145.7, 144.6, 141.2, 132.5, 130.9, 129.8, 129.6, 127.4, 123.9, 120.1, 117.6, 21.8. FABMS (m/z): 326 (M^++1). Anal. Calcd for $C_{17}H_{11}NO_4S$: C, 62.76%; H, 3.41%; N, 4.31%. Found: C, 62.55%; H, 3.25%; N, 4.45%.

*4.3.8. 3-(Furan-2-oyl)-2H-chromene-2-thione (**5h**).* Orange crystals, mp 164–165 °C. IR (KBr): 3118, 2923, 1657, 1604, 1557, 1465, 1252, 1173 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.67–7.50 (m, 5H, ArH), 7.39–7.26 (m, 2H, ArH), 6.59 (dd, J=1.2, 2.1 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.2, 179.5, 157.0, 151.7, 147.5, 138.0, 133.6, 133.3, 128.6, 125.8, 120.1, 119.7, 116.6, 112.8. FABMS (m/z): 257 (M^++1). Anal. Calcd for $C_{14}H_8O_3S$: C, 65.61%; H, 3.15%. Found: C, 65.55%; H, 3.35%.

*4.3.9. 3-(Furan-2-oyl)-8-methoxy-2H-chromene-2-thione (**5i**).* Orange crystals, mp 169–170 °C. IR (KBr): 2928, 1657, 1600, 1559, 1257, 1170 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J=6.3 Hz, 1H, ArH), 7.59 (s, 1H, ArH), 7.29–7.11 (m, 4H, ArH), 6.57 (dd, J=1.5, 1.8 Hz, 1H, ArH), 4.01 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 179.6, 151.7, 147.5, 146.7, 138.3, 133.7, 125.7, 120.4, 120.1, 119.6, 114.7, 112.8, 56.3. FABMS (m/z): 287 (M^++1). Anal. Calcd for $C_{15}H_{10}O_4S$: C, 62.93%; H, 3.52%. Found: C, 62.69%; H, 3.31%.

*4.3.10. 3-(Furan-2-oyl)-6-bromo-2H-chromene-2-thione (**5j**).* Yellow crystals, mp 198–199 °C. IR (KBr): 3119, 1639, 1552, 1460, 1363, 1240, 1174 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.75–7.70 (m, 2H, ArH), 7.63 (s, 1H, ArH), 7.51 (s, 1H, ArH), 7.38 (d, J=8.7 Hz, 1H, ArH), 7.28 (d, J=3.3 Hz, 1H, ArH), 6.60–6.59 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.4, 179.0, 155.7, 151.5, 147.6, 138.8, 135.9, 131.7, 130.6, 121.2, 120.2, 118.4, 118.2, 112.9. FABMS (m/z): 337 (M^++2). HRMS (ESI^+) Calcd for $C_{14}H_7BrO_3S$: 333.9299. Found 333.9210.

*4.3.11. 3-(Thien-2-oyl)-6-bromo-2H-chromene-2-thione (**5k**).* Yellow crystal, mp 202–203 °C. IR (KBr): 3054, 2923, 1639, 1601, 1549, 1236, 1162 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.77–7.69 (m, 3H, ArH), 7.64 (d, J=3.3 Hz, 1H, ArH), 7.50 (s, 1H, ArH), 7.39 (d, J=8.7 Hz, 1H, ArH), 7.13 (t, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.4, 183.7, 155.7, 142.5, 139.6, 135.9, 135.1, 131.2, 131.1, 130.6, 128.4, 121.2, 118.5, 118.2. FABMS (m/z): 353 (M^++2). Anal. Calcd for $C_{14}H_7BrO_2S_2$: C, 47.87%; H, 2.01%. Found: C, 47.63%; H, 2.32%.

*4.3.12. 3-(Thien-2-oyl)-8-methoxy-2H-chromene-2-thione (**5l**).* Yellow solid, mp 167–168 °C. IR (KBr): 3025, 1632, 1602, 1549, 1405, 1234, 1158 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, J=4.5 Hz, 1H, ArH), 7.65 (d, J=3.3 Hz, 1H, ArH), 7.57 (s, 1H, ArH), 7.31–7.25 (m, 1H, ArH), 7.18–7.10 (m, 3H, ArH), 4.01 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.6, 184.9, 146.2, 144.2, 143.1, 138.5, 135.6, 134.9, 127.9, 125.0, 121.2, 120.1, 119.7, 111.5, 56.1. FABMS (m/z): 303 (M^++1). HRMS (ESI^+) Calcd for $C_{15}H_{10}O_3S_2$: 302.0071. Found 302.0054.

*4.3.13. 3-(4-Chlorobenzoyl)-2H-chromene-2-thione (**5m**).* Yellow crystals, mp 184–186 °C. IR (KBr): 3093, 3045, 1663, 1611, 1233 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J=8.7 Hz, 2H, ArH), 7.72–7.60 (m, 3H, ArH), 7.54–7.51 (m, 1H, ArH), 7.42 (d, J=8.4 Hz, 2H, ArH), 7.39–7.37 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.5, 191.0, 157.2, 140.3, 138.8, 134.0, 133.5, 131.0, 129.2, 128.6, 126.1, 119.7, 116.6. FABMS (m/z): 301 (M^++1). Anal. Calcd for $C_{16}H_9ClO_2S$: C, 63.90%; H, 3.02%. Found: C, 63.85%; H, 3.11%.

*4.3.14. 3-(4-Chlorobenzoyl)-8-methoxy-2H-chromene-2-thione (**5n**).* Yellow solid, mp 176–177 °C. IR (KBr): 2966, 2932, 1674, 1568, 1468, 1376, 1236, 1169 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J=8.1 Hz, 2H, ArH), 7.59 (s, 1H, ArH), 7.42 (d, J=8.1 Hz, 2H, ArH), 7.30–7.25 (m, 1H, ArH), 7.20–7.15 (m, 2H, ArH), 4.02 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.7, 191.3, 147.1, 146.5, 140.3, 138.9, 134.2, 134.1, 131.0, 129.2, 126.0, 120.7, 119.9, 114.5, 56.3. FABMS (m/z): 331 (M^++1). Anal. Calcd for $C_{17}H_{11}ClO_3S$: C, 61.73%; H, 3.35%. Found: C, 61.61%; H, 3.39%.

*4.3.15. 3-Benzoyl-8-ethoxy-2H-chromene-2-thione (**5o**).* Orange solid, mp 164–165 °C. IR (KBr): 2924, 2855, 1661, 1564, 1459, 1235, 1166 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, J=7.2 Hz, 2H, ArH), 7.57 (s, 2H, ArH), 7.45 (t, 2H, ArH), 7.26 (d, J=6.3 Hz, 1H, ArH), 7.18–7.10 (m, 2H, ArH), 4.25 (q, 2H, OCH_2), 1.53 (t, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.9, 192.3, 147.2, 146.1, 139.4, 135.7, 133.8, 133.7, 129.5, 128.6, 125.7, 120.7, 119.5, 115.8, 65.1, 14.6. FABMS (m/z): 311 (M^++1). Anal. Calcd for $C_{18}H_{14}O_3S$: C, 69.66%; H, 4.55%. Found: C, 69.75%; H, 4.51%.

*4.3.16. 3-Benzoyl-2H-chromene-2-thione (**5p**).* Yellow solid, mp 171–172 °C. IR (KBr): 3060, 2924, 1663, 1602, 1555, 1243, 1166 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.95–7.92 (m, 2H, ArH), 7.67–7.25 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6, 192.3, 157.0, 139.0, 135.6, 133.9, 133.7, 133.2, 129.6, 128.7, 128.5, 125.9, 120.0, 116.7. FABMS (m/z): 267 (M^++1). Anal. Calcd for $C_{16}H_{10}O_2S$: C, 72.16%; H, 3.78%. Found: C, 72.29%; H, 3.59%.

*4.3.17. 3-η^5-Ferrocenoyl-2H-chromene-2-thione (**5q**).* Violet solid, mp 250–252 °C (decomp.). IR (KBr): 3090, 2927, 1727, 1635, 1447, 1363, 1264, 1170 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.96 (s, 1H, ArH), 7.63–7.57 (m, 2H, ArH), 7.41–7.25 (m, 2H, ArH), 4.86 (br s, 2H, H_{cp}), 4.64 (br s, 2H, H_{cp}), 4.29 (s, 5H, H_{cp}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.8, 192.3, 141.7, 135.6, 133.9, 133.7, 129.6, 128.7, 125.9, 116.7, 82.3, 73.4, 70.9, 70.4. FABMS (m/z): 375 (M^++1). Anal. Calcd for $C_{20}H_{14}FeO_2S$: C, 64.19%; H, 3.77%. Found: C, 64.35%; H, 3.51%.

*4.3.18. 3-(4-Methoxybenzoyl)-benzo[f]2H-chromene-2-thione (**8a**).* Yellow solid, mp 246–247 °C. IR (KBr): 1662, 1596, 1547, 1259, 1203 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.34 (s, 1H, ArH), 8.23 (d, J=8.1 Hz, 1H, ArH), 8.11 (d, J=9.0 Hz, 1H, ArH), 7.96 (d, J=8.4 Hz, 3H, ArH), 7.74–7.63 (m, 3H, ArH), 6.95 (d, J=8.7 Hz, 2H, ArH), 3.88 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.6, 191.2, 164.3, 157.6, 141.0, 139.1, 135.0, 134.5, 132.2, 130.6, 129.5, 129.2, 128.9, 128.6, 127.0, 121.6, 116.4, 115.2, 114.0, 113.8, 55.5. FABMS (m/z): 347 (M^++1). Anal. Calcd for $C_{21}H_{14}O_3S$: C, 72.81%; H, 4.07%. Found: C, 72.59%; H, 3.92%.

*4.3.19. 3-(4-Methylbenzoyl)-benzo[f]2H-chromene-2-thione (**8b**).* Yellow solid, mp 264–265 °C. IR (KBr): 2925, 1654, 1603, 1395, 1201, 790 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1H, ArH), 8.24 (d, J=8.1 Hz, 1H, ArH), 8.11 (d, J=9.3 Hz, 1H, ArH), 7.96 (d, J=8.1 Hz, 1H, ArH), 7.89 (d, J=8.1 Hz, 2H, ArH), 7.75–7.61 (m, 3H, ArH), 7.27 (d, J=10.8 Hz, 2H, ArH), 2.43 (s, 3H, $ArCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.6, 192.3, 157.0, 145.1, 139.1, 134.6, 133.2, 130.6, 129.9, 129.7, 129.5, 129.2, 128.9, 128.8, 127.0, 121.6, 116.5, 115.2, 21.8. FABMS (m/z): 331 (M^++1). HRMS (ESI^+) Calcd for $C_{21}H_{14}O_2S$: 330.0714. Found 330.0735.

*4.3.20. 3-(Furan-2-oyl)-benzo[f]2H-chromene-2-thione (**8c**).* Yellow solid, mp 252–253 °C. IR (KBr): 1641, 1558, 1462, 1284, 1170 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.39 (s, 1H, ArH), 8.25 (d, J=8.1 Hz, 1H, ArH), 8.11 (d, J=9.0 Hz, 1H, ArH), 7.96 (d, J=7.8 Hz, 1H, ArH), 7.76–7.62 (m, 4H, ArH), 7.33 (d, J=3.6 Hz, 1H, ArH), 6.61–6.59 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.3, 179.9, 157.7, 151.8, 147.5, 137.7, 134.9, 130.6, 130.0, 129.2, 129.0, 128.8, 127.0, 121.6, 120.1, 116.4, 115.0, 112.8. FABMS (m/z): 307 (M^++1). Anal. Calcd for $C_{18}H_{10}O_3S$: C, 70.57%; H, 3.29%. Found: C, 70.69%; H, 3.41%.

*4.3.21. 3-(Thien-2-oyl)-benzo[f]2H-chromene-2-thione (**8d**).* Yellow solid, mp 267–268 °C. IR (KBr): 3058, 1634, 1554, 1407, 1352, 1198

cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (s, 1H, ArH), 8.23 (d, J=8.4 Hz, 1H, ArH), 8.12 (d, J=9.0 Hz, 1H, ArH), 7.96 (d, J=7.5 Hz, 1H, ArH), 7.78–7.63 (m, 5H, ArH), 7.15–7.12 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.2, 184.6, 176.7, 157.7, 151.3, 147.4, 135.6, 135.1, 134.9, 129.3, 129.2, 129.0, 128.4, 127.0, 121.6, 116.5, 112.8. FABMS (m/z): 323 (M^++1). Anal. Calcd for $C_{18}H_{10}O_2S_2$: C, 67.06%; H, 3.13%. Found: C, 66.91%; H, 3.26%.

*4.3.22. 3-(4-Chlorobenzoyl)-benzo[f]2H-chromene-2-thione (**8e**).* Yellow solid, mp 254–255 °C. IR (KBr): 3066, 2933, 1660, 1561, 1387, 1204, 1169 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (s, 1H, ArH), 8.25 (d, J=8.4 Hz, 1H, ArH), 8.13 (d, J=9.3 Hz, 1H, ArH), 7.98–7.90 (m, 3H, ArH), 7.74–7.64 (m, 3H, ArH), 7.44 (d, J=8.4 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 192.7, 191.7, 164.0, 158.6, 141.2, 139.0, 135.1, 134.5, 133.5, 130.3, 130.2, 129.6, 128.5, 128.4, 128.1, 126.5, 121.3, 115.5, 114.1. FABMS (m/z): 351 (M^++1). Anal. Calcd for $C_{20}H_{11}ClO_2S$: C, 68.47%; H, 3.16%. Found: C, 68.26%; H, 3.09%.

*4.3.23. 3-Benzoyl-benzo[f]2H-chromene-2-thione (**8f**).* Yellow solid, mp 241–242 °C. IR (KBr): 3047, 2925, 1657, 1553, 1394, 1202, 1155 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (s, 1H, ArH), 8.25 (d, J=8.1 Hz, 1H, ArH), 8.12 (d, J=9.0 Hz, 1H, ArH), 7.99–7.95 (m, 3H, ArH), 7.75–7.59 (m, 4H, ArH), 7.50–7.45 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.7, 192.5, 160.6, 157.7, 141.1, 138.8, 135.7, 134.8, 133.9, 130.0, 129.7, 129.2, 129.0, 128.7, 127.0, 123.7, 121.7, 116.5, 115.2. FABMS (m/z): 317 (M^++1). Anal. Calcd for $C_{20}H_{12}O_2S$: C, 75.93%; H, 3.82%. Found: C, 75.82%; H, 3.91%.

*4.3.24. 3-η^5-Ferrocenoyl-benzo[f]2H-chromene-2-thione (**8g**).* Dark violet solid, mp 242–243 °C (decomp.). IR (KBr): 3051, 1635, 1549, 1413, 1348, 1191 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (s, 1H, ArH), 8.27 (d, J=8.4 Hz, 1H, ArH), 8.11 (d, J=9.0 Hz, 1H, ArH), 7.97 (d, J=7.8 Hz, 1H, ArH), 7.77–7.72 (m, 1H, ArH), 7.67–7.63 (m, 2H, ArH), 4.86 (s, 2H, H_{cp}), 4.64 (s, 2H, H_{cp}), 4.35 (s, 5H, H_{cp}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.4, 192.2, 157.5, 139.0, 134.6, 130.6, 129.3, 129.0, 128.8, 128.4, 127.0, 121.4, 116.5, 114.9, 77.9, 73.2, 70.9, 70.4. FABMS (m/z): 425 (M^++1). Anal. Calcd for $C_{24}H_{16}FeO_2S$: C, 67.94%; H, 3.80%. Found: C, 67.67%; H, 3.91%.

Acknowledgements

This work was carried out under financial support from Council of Scientific and Industrial Research (Grant 01(2260)/08/EMR-II) and Department of Science and Technology (Grant SR/S1/OC-66/2009), New Delhi. R.K.V. is grateful to Council of Scientific and Industrial Research (CSIR), New Delhi for senior research fellowship and G. K.V. is thankful to University Grants Commission (UGC), New Delhi for junior research fellowship.

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10. Crystal data for **5k**: $C_{14}H_7BrO_2S_2$, yellow, M=351.24, monoclinic, space group P 21/n, a=9.3601(3), b=10.4053(3), c=13.5327(4) Å, V=1314.91 Å^3, μ=3.436 cm^{-1}, Z=4, T=293 K, F_{000}=996, R=0.0394, wR^2=0.0948. The CCDC deposition number: CCDC 783653.