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Facile Synthesis of 3-Thioxo-3*H*-benzo[*f*]chromen-2-yl methanone and 3*H*-Benzo[*f*]chromene-3-one Under Solvent Free Condition

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A facile, convenient, efficient and high yielding synthesis of a combinatorial library of coumarins has been developed by the condensation of readily available *β*-oxodithioesters and *S*,*S*-acetal with 2-hydroxy-1-naphthaldehyde in the presence of catalytic amount of $CuCl_2$ under solvent free conditions.

Key Words: Coumarin, $CuCl_2$, Solvent free, *β*-Oxodithioesters, *S*,*S*-Acetal

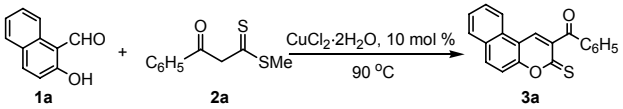
Introduction

Many classical routes have been available for the synthesis of coumarin. The Pechmann reaction for the synthesis of coumarin involves the condensation of phenols with *β*-ketonic esters in the presence of variety of acidic condensing agents such as sulfuric acid, hydrochloric acid and phosphoric acid, phosphorous pentoxide, trifluoroacetic acid and Lewis acids such as $ZnCl_2$, $AlCl_3$[1] and exchange resins[2], have been used. Recently there have been reports on the use of ionic liquid as a Lewis acid catalyst and solvent,[3] Zn/I_2,[4] *p*-TsOH[5] and $InCl_3$[6] as acid catalysts for the synthesis of coumarin. Knoevenagel condensation is reported recently to proceed with high selectivity and reactivity in the formation of coumarins over solid base catalysts.[7] Microwave irradiation accelerates these reactions several-fold with better yields of the products where the reactants, however, are taken in millimolar quantities.[8] There have been reports on the synthesis of dihydrocoumarins from *o*-hydroxycinnamaldehydes in a mild, atom-economic *N*-heterocyclic carbene-catalyzed redox lactonization.[9] Tellurium-triggered cyclizations[10] have also been reported synthesis of coumarins and 4-hydroxycoumarins.

In continuation of our works on the synthesis of bioactive heterocycles[11] and applications of cupric chloride as efficient catalyst in various organic transformations,[12-14] we report herein cupric chloride catalyzed facile synthesis of 3-thioxo-3*H*-benzo[*f*]chromen-2-ylmethanones and 3*H*-benzo[*f*]chromen-3-ones from *β*-oxodithio-esters and *α*-oxoketene dithioacetals respectively by the domino Knoevenagel cyclocondensations, under solvent free condition.

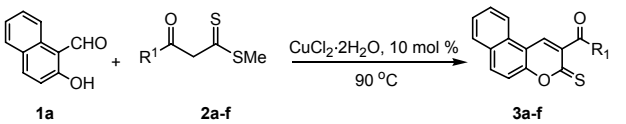
Result and Discussion

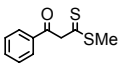
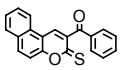
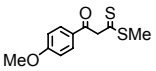
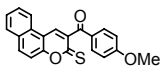
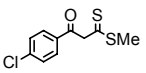
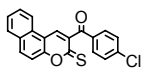
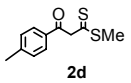
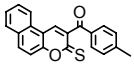
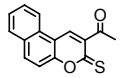
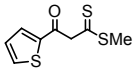
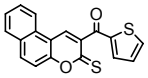
We first examined the reaction of 2-hydroxy-1-naphthaldehyde **1a** and *β*-oxodithioester **2a** by simply heating their molar equivalent mixture at 90 °C with 20 mol % cupric chloride as the catalyst (Scheme 1). After 5 min the whole reaction mixture melts, turned to a homogeneous liquid and then forms a paste.



Scheme 1. Synthesis of phenyl(2-thioxo-2*H*-benzochromen-3-yl)methanone **3a** under solvent free condition

Table 1. $CuCl_2·2H_2O$ catalysed synthesis of coumarins[a] **3a-f** under solvent free condition



Entry	Dithioester	Product	Yield (%)[b]
1	 **2a**	 **3a**	93
2	 **2b**	 **3b**	91
3	 **2c**	 **3c**	89
4	 **2d**	 **3d**	90
5	 **2e**	 **3e**	92
6	 **2f**	 **3f**	87

[a]Reaction conditions: **2** (2.5 mmol), **3** (2.5 mmol), $CuCl_2$ (10 mol %), 90 °C, 10 - 15 min. [b]Isolated yield.

Table 2. Evaluation of Different Catalytic Systems in Optimization of the Coumarin Synthesis[a]

Entry	Catalyst	Time (min)	Yield (%)[b]
1	$CuCl_2$	10	93
2	$ZnCl_2$	15	70
3	$FeCl_3$	20	75
4	$AlCl_3$	20	78
5	$SnCl_2$	15	80
6	$MgCl_2$	45	30
7	$BiCl_3$	60	25
8	$LaCl_3$	60	20

[a]2-Hydroxy-1-naphthaldehyde **1a** (5.0 mmol), catalyst (10 mol %), *β*-oxodithioester **2a** (5.0 mmol), [b]Isolated yield.

Then, the progress of the reaction was monitored by thin layer chromatography and complete transformation was observed in a short period of 10 min.

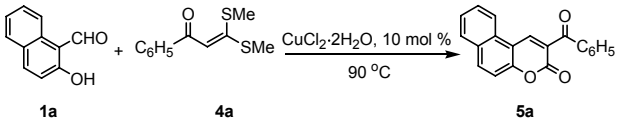
The reaction mixture was then poured into crushed ice and the solid product was separated, filtered and recrystallized from ethanol. The reaction went very smoothly and the corresponding coumarin **3a** was obtained in 93% yield (Table 1, entry 1).

The yield was still as high as 93% even when the amount of $CuCl_2$ was reduced from 20 mol % to 10 mol %. The same process was successfully extended to a wide range of *β*-oxodithioesters **2b-f** and 2-hydroxy-1-naphthaldehyde to afford the corresponding hitherto unreported coumarin **3b-f** in good to excellent yields (Table 1). The use of 5 mol % of catalyst caused a slight decrease in the yield.

To evaluate the scope of this catalytic system, the range of metal salts was extended to various metal halides guided by the template reaction of 2-hydroxy-1-naphthaldehyde **1a**, and β-oxodithioester **2a**. Among the different metal catalyst $CuCl_2$ was found to be the best catalyst, giving the highest yield of the product under a short duration of 10 min. It was also observed that $SnCl_2$, $ZnCl_2$, $AlCl_3$ and $FeCl_3$ gave good yields of the product with duration of 15 - 20 min, while $MgCl_2$, $BiCl_3$ and $LaCl_3$ gave poor yields of the desired products in a longer duration of 45 - 60 min (Table 2).

A control experiment in the absence of the catalyst provided no product. The reaction was also subjected in aqueous medium and provided no product. Moreover, it is noteworthy to mention that using different solvents such as DMSO, DMF, THF, EtOH and CH_3CN did not improve the yields and thus we have optimized the reaction condition at 90 °C for 10 min under solvent-free condition.

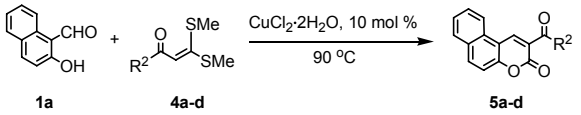
In our next plan, instead of *β*-oxodithioester, *S*,*S*-acetals **4a** were allowed to undergo cyclization with 2-hydroxy-1-naphthaldehyde **1a** under the same reaction condition (Scheme 2).



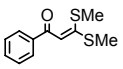
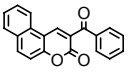
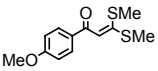
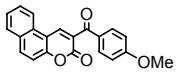
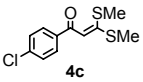
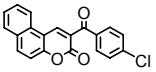
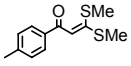
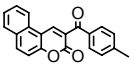
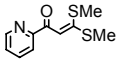
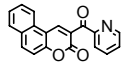
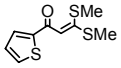
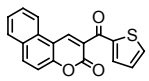
1a 4a 5a

Scheme 2. Synthesis of 2-Benzoyl-3*H*-benzo[*f*]chromen-3-one **5a** under solvent free condition

Table 3. $CuCl_2·2H_2O$ catalyzed synthesis of coumarins[a] **5a-d** under solvent free condition



1a 4a-d 5a-d

Entry	Dithioester	Product	Yield (%)[b]
1	 4a	 5a	91
2	 4b	 5b	95
3	 4c	 5c	90
4	 4d	 5d	95
5	 4e	 5e	80
6	 4f	 5f	85

[a]Reaction conditions: **4** (2.5 mmol), **5** (2.5 mmol), $CuCl_2$ (10 mol %), 90 °C, 1.0 - 2.0 h. [b]Isolated yield.

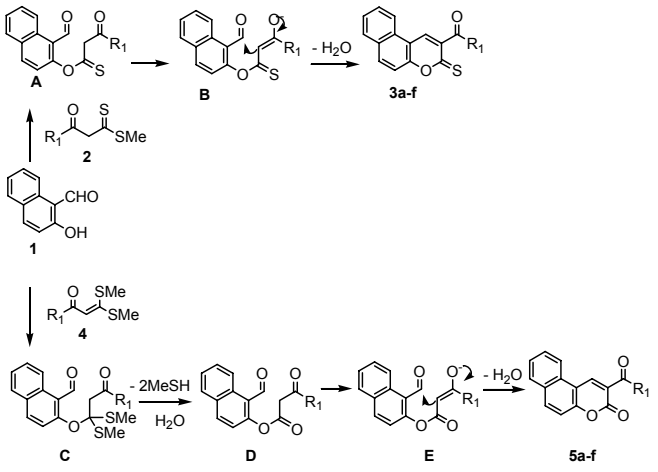
So in the presence of catalytic amount of $CuCl_2$, *S*,*S*-acetal **4a** was heated with 2-hydroxy-1-naphthaldehyde **1a** at 90 °C without any solvent. After 5 min the reaction mixture turns to a paste and the progress of the reaction was monitored by TLC and complete transformation was observed in 5 min. The reaction mixture was then poured into crushed ice and the solid product was separated, filtered and recrystallized from ethanol. The reaction went very smoothly and the yellow crystals of coumarin **5a** were obtained in 90% yield (Table 3, entry 1) which was confirmed by spectroscopy.

The reaction was also carried out in various organic solvents and can't improve the yield of the reaction. In the presence of aqueous solvent, no product was obtained. Further the reaction was also carried out in the presence of different metal catalyst without any solvent and it was observed that $CuCl_2$ gives the desired product in highest yield and thus the reaction condition was optimized at 90 °C in the presence of $CuCl_2$ under solvent free condition.

The reaction was extended to different *S*,*S*-acetals **4b-f** to afford coumarins **5b-f** in good to excellent yield.

A plausible reaction mechanism for these two domino Knovenagel cyclocondensation is proposed in Scheme 3.

The condensation product **A** of *o*-hydroxynaphthaldehyde **1** with *β*-oxodithioesters **2**, mediated by $CuCl_2$, generates enolate **B**, which participates in subsequent intramolecular aldol condensation to give **3**. On the other hand, *o*-hydroxynaphthalde-



Scheme 3. Plausible reaction mechanism

hyde **1** and α-oxoketenedithio acetals **4** condenses to give intermediate **C** which on subsequent hydrolysis followed by dethiomethylation catalysed by cupric chloride generates enolate **E**, which finally undergoes intramolecular aldol condensation to give **5**.

Experimental Section

The melting points were determined on a Mel-temp II laboratory device and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker FT-NMR-DRX300 (300 MHz) and chemical shifts are reported in parts per million (δ) and signals are quoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and dd (doublet of doublets). Analytical thin layer chromatographies (TLC) were carried out by pre-coated silica gel (E. Merck, Kiesegel 60F_{254} layer thickness 0.25 mm).

General Procedure for the Synthesis of 3a-f. A mixture of 2-hydroxy-1-naphthaldehyde (5 mmol), β-dithioester (5 mmol) and $CuCl_2$ (0.4 mmol, 20 mol %) was heated at 90 °C with stirring for 10 min. After 10 min the whole reaction mixture melts, turned to a homogeneous liquid and then forms a paste. The progress of the reaction was monitored by thin layer chromatography and complete transformation was observed in a short period of 10 min. The reaction mixture was then poured into crushed ice and the solid product was separated, filtered and recrystallized from ethanol. After cooling, the reaction mixture was poured into cold water. The solid was suction filtered, washed with cold water (20 mL), filtered and recrystallized from ethyl acetate or ethanol to afford pure product.

Phenyl(3-thioxo-3*H*-benzo[*f*]chromen-2-yl)methanone (3a): Yellow crystals. mp 200 - 201 °C .^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.50-7.56 (m, 3H), 7.61-7.69 (m, 2H), 7.73-7.78 (m, 1H), 7.94-8.02 (m, 3H), 8.13 (d, J = 9 Hz, 1H), 8.26-8.30 (m, 1H), 8.40 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 112.7, 116.5, 121.5, 125.4, 126.5, 128.7, 128.9, 129.4, 129.7, 129.9, 130.7, 134.8, 135.4, 138.9, 141.8, 157.8, 192.1, 192.7; IR (KBr) (ν_{max}, cm^{-1}) 1265, 1560, 1654, 3056 cm^{-1}; MS m/z 316 (M^+). Anal. Calcd for $C_{20}H_{12}O_2S$: C, 75.93; H, 3.82; S, 10.14. Found: C, 75.95; H, 3.85; S, 10.11.

(4-Methoxyphenyl)(3-thioxo-3*H*-benzo[*f*]chromen-2-yl) methanone (3b): Yellow crystals. mp 218 - 219 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 3.80 (s, 3H), 6.87 (d, J = 6.6 Hz, 2H), 7.54-7.65 (m, 3H), 7.87-7.89 (m, 3H), 8.03 (d, J = 6.9 Hz, 1H), 8.15 (d, J = 6.6 Hz, 1H), 8.27 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 113.91, 114.12, 115.26, 121.53, 127.06, 128.81, 128.91, 128.95, 129.22, 129.25, 129.35, 129.65, 130.68, 134.65, 139.16, 157.64, 164.34, 191.29, 192.73; MS m/z 346 (M^+). Anal. Calcd for $C_{21}H_{14}O_3S$: C, 72.81; H, 4.07; S, 9.26. Found: C, 72.79; H, 4.05; S, 9.29.

(4-Chlorophenyl)(3-thioxo-3*H*-benzo[*f*]chromen-2-yl)methanone (3c): Yellow crystals. mp 272 - 273 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.47 (d, J = 8.4 Hz, 2H), 7.66-7.69 (m, 2H), 7.74-7.79 (m, 1H), 7.92-8.01 (m, 3H), 8.15 (d, J = 9 Hz, 1H), 8.27 (d, J = 8.1 Hz, 1H), 8.42 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 115.2, 116.5, 121.7, 127.1, 128.9, 129.1, 129.2, 129.3, 130.4, 130.7, 131.0, 134.3, 135.0, 138.5, 140.4, 157.9, 191.6, 192.4; IR (KBr) (ν_{max}, cm^{-1}) 1259, 1558, 1666, 3083 cm^{-1}; MS m/z 350 (M^+). Anal. Calcd for $C_{20}H_{11}ClO_2S$: C, 68.47; H, 3.16; S, 9.14. Found: C, 68.49; H, 3.11; S, 9.19.

(3-Thioxo-3*H*-benzo[*f*]chromen-2-yl)(p-tolyl)methanone (3d): Yellow crystals. mp 240 - 241 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 2.34 (s, 3H), 7.19 (d, J = 6 Hz, 2H) 7.51-7.56 (m, 3H), 7.79-7.88 (m, 3H), 8.01 (d, J = 6.9 Hz,1H), 8.13 (d, J = 6.3 Hz, 1H), 8.27 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 21.9, 115.2, 116.5, 121.7, 126.6, 127.1, 128.9, 129.2, 129.3, 129.6, 130.0, 133.2, 133.9, 135.3, 139.0, 144.8, 157.7, 192.4, 192.7; MS m/z 330 (M^+). Anal. Calcd for $C_{21}H_{14}O_2S$: C, 76.34; H, 4.27; S, 9.70. Found: C, 76.37; H, 4.25; S, 9.69.

1-(3-Thioxo-3*H*-benzo[*f*]chromene-2-yl)ethanone (3e): Yellow crystals. mp 253 - 255 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 2.77 (s, 3H), 7.52-7.59 (m, 2H), 7.69 (t, 6.5Hz, 1H), 7.87 (d, J = 6.0 Hz, 1H), 8.03 (d, J = 6.9 Hz, 1H), 8.25 (d, J = 6.3 Hz, 1H), 8.53 (s, 1H);^{13}C NMR (75.5 MHz ,$CDCl_3$, δ) 30.2, 115.2, 116.3, 121.8, 127.2, 129.1, 129.2, 129.3, 130.6, 132.4, 135.7, 139.0, 158.2, 192.6, 199.5; MS m/z 254 (M^+). Anal. Calcd for $C_{15}H_{10}O_2S$: C, 70.84; H, 3.96; S, 12.61. Found: C, 70.87; H, 3.95; S, 12.59.

(Thiophen-2-yl)(3-thioxo-3*H*-benzo[*f*]chromen-2-yl)methanone (3f): Yellow crystals. mp 250 - 251 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.17-7.28 (m, 2H), 7,65-7.80 (m, 4H), 7.97 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 9 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 8.40 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 115.0, 116.5, 121.7, 127.1, 128.5, 128.9, 129.3, 129.4, 130.7, 134.9, 135,1, 135.6, 138.6, 142.9, 157.7, 174.4, 184.7, 192.3; IR (KBr) (ν_{max}, cm^{-1}) 1271, 1558, 1637, 3055 cm^{-1}; MS m/z 322 (M^+). Anal. Calcd for $C_{18}H_{10}O_2S_2$: C, 67.06; H, 3.13; S, 19.89. Found: C, 67.09; H, 3.15; S, 19.83.

General Procedure for the Synthesis of 5a-d. A mixture of 2-hydroxy-1-naphthaldehyde (5 mmol), *S*,*S*-acetal (5 mmol) and $CuCl_2$ (0.4 mmol, 20 mol %) was heated at 90 °C with stirring for 10 min. After 10 min the whole reaction mixture melts, turned to a homogeneous liquid and then forms a paste. The progress of the reaction was monitored by thin layer chromatography and complete transformation was observed in a short period of 10 mins. The reaction mixture was then poured into crushed ice and the solid product was separated, filtered and recrystallized from ethanol. After cooling, the reaction mixture was poured into cold water. The solid was suction filtered,

washed with cold water (20 mL), filtered and recrystallized from ethyl acetate or ethanol to afford pure product.

2-Benzoyl-3*H*-benzo[*f*]chromen-3-one (5a): Yellow crystals. mp 215 - 216 °C. ^{1}HNMR (300 MHz, $CDCl_3$, δ) 7.45-7.51 (m, 3H), 7.57-7.65 (m, 2H), 7.7 (t, *J* = 7.3 Hz, 1H), 7.89-7.94 (m, 3H), 8.08 (d, *J* = 9.3 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.89 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 112.6, 116.7, 121.5, 125.4, 126.5, 128.5, 128.9, 129.2, 129.4, 129.6, 130.3, 133.6, 135.3, 136.5, 141.7, 155.4, 158.5, 192.1; IR (KBr) (ν_{max}, cm^{-1}) 3102, 2959, 1700, 1654 cm^{-1}; MS *m*/*z* 300 (M^+). Anal. Calcd for $C_{20}H_{12}O_3$: C, 79.99; H, 4.03; O, 15.98. Found: C, 79.95; H, 4.02; O, 15.99.

2-(4-Methoxybenzoyl)-3*H*-benzo[*f*]chromen-3-one (5b): Yellow crystals. mp 231 - 232 °C. ^{1}HNMR (300 MHz, $CDCl_3$, δ) 3.82 (s, 3H), 6.89 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 9.3 Hz, 1H), 7.57 (br t, *J* = 7.8 Hz, 1H), 7.67 (br t, *J* = 7.3 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 9.3 Hz, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.79 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 55.6, 112.7, 113.9, 116.7, 121.5, 125.9, 126.5, 128.9, 129.1, 129.2, 129.3, 130.3, 132.2, 135.1, 141.2, 155.2, 158.8, 164.2, 190.5; IR (KBr) (ν_{max}, cm^{-1}) 3065, 2950, 1706, 1656 cm^{-1}; MS *m*/*z* 330 (M^+). Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27; O, 19.37. Found: C, 76.37; H, 4.26; O, 19.39.

2-(4-Chlorobenzoyl)-3*H*-benzo[*f*]chromen-3-one (5c): Yellow crystals. mp 231 - 232 °C. ^{1}HNMR (300 MHz, $CDCl_3$, δ) 7.47 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 9.3 Hz, 1H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.97 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 112.7, 116.7, 121.5, 124.7, 126.7, 128.9, 129.1, 129.3, 129.4, 130.3, 130.9, 134.8, 135.8, 140.2, 142.6, 155.6, 158.6, 191.0, IR (KBr) (ν_{max}, cm^{-1}) 3069, 2951, 1707, 1655 cm^{-1}; MS *m*/*z* 334 (M^+). Anal. Calcd for $C_{20}H_{11}ClO_3$: C, 71.76; H, 3.31; O, 14.34. Found: C, 71.77; H, 3.33; O, 14.33.

2-(4-Methylbenzoyl)-3*H*-benzo[*f*]chromen-3-one (5d): Yellow crystals. mp 191 - 192 °C. ^{1}HNMR (300 MHz, $CDCl_3$, δ) 2.45 (s, 3H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 9.3 Hz, 1H), 7.61 (br t, *J* = 7.8 Hz, 1H), 7.71 (br t, *J* = 7.3 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 9.3 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 8.90 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 21.8, 112.7, 116.7, 121.5, 125.6, 126.5, 128.9, 129.2, 129.3, 129.4, 129.8, 130.3, 133.8, 135.2, 141.4, 144.8, 155,3, 158.6, 191.7; IR (KBr) (ν_{max}, cm^{-1}) 3063, 2953, 1703, 1651 cm^{-1}; MS *m*/*z* 314 (M^+). Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49; O, 15.27. Found: C, 80.25; H, 4.48; O, 15.29.

2-Picolinoyl-3*H*-benzo[*f*]chromen-3-one (5e): Yellow crystals. mp 205 - 206 °C. ^{1}HNMR (300 MHz, $CDCl_3$, δ) 7.42 (d, *J* = 9.5 Hz, 1H), 7.45 (d, *J* = 9.5 Hz, 1H), 7.65-7.67 (m, 2H), 7.90-7.92 (m, 1H), 7.97-7.99 (m, 1H), 8.16-8.19 (m, 2H), 8.27 (d, *J* = 9.6 Hz, 1H), 8.44 (s, 1H), 8.85 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 115.5, 117.8, 120.5, 122.4, 123.6, 126.7, 128.7, 127.4, 128.3, 128.8, 130.5, 131.4, 137.2, 149.5, 150.5, 153.4, 159.2, 190.2; IR (KBr) (ν_{max}, cm^{-1}) 3110, 1705, 1650 cm^{-1}; MS *m*/*z* 301 (M^+). Anal. Calcd for $C_{19}H_{11}NO_3$: C, 75.74; H, 3.68; N, 4.65; O, 15.93. Found: C, 75.76; H, 3.66; N, 4.68; O, 15.96.

2-Thiophen-2-carbonyl)-3*H*-benzo[*f*]chromen-3-one (5f): Yellow crystals. mp 245 - 247 °C. ^{1}HNMR (300 MHz, $CDCl_3$, δ) 7.24 (m, 1H), 7.43 (d, *J* = 9.3 Hz, 1H), 7.46 (d, *J* = 9.3 Hz, 1H), 7.66-7.73 (m, 2H), 8.07 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 9.3 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.45 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 115.5, 117.5, 122.5, 123.7, 126.5, 127.7, 128.4, 128.9, 129.3, 130.4, 131.0, 132.4, 133.5, 138.3, 143.8, 153.8, 159.9, 180.7; IR (KBr) (ν_{max}, cm^{-1}) 1560, 1640, 3050 cm^{-1}; MS *m*/*z* 306 (M^+). Anal. Calcd for $C_{18}H_{10}O_3S$: C, 70.57; H, 3.29; S, 10.47. Found: C, 70.59; H, 3.31; S, 10.43.

Conclusion

We have successfully demonstrated the facile synthesis of two different coumarin derivatives by the reaction of 2-hydroxy-1-naphthaldehyde with easily accessible *β*-oxodithioester and *S*,*S*-acetal in the presence of catalytic amount of $CuCl_2$ under solvent free condition. This scheme offers a good scope for the synthesis of a wide variety of coumarins.

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