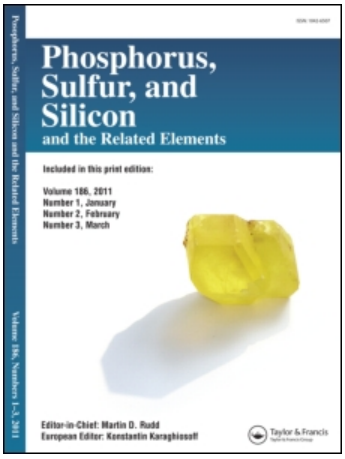

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SYNTHESIS AND SOME REACTIONS OF 2-MERCAITO-4-HYDROXYPYRIMIDINE [3,4-b]COUMARIN

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SYNTHESIS AND SOME REACTIONS OF 2-MERCAPTO-4-HYDROXYPYRIMIDINE [3,4-b]COUMARIN

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2-Mercapto-4-hydroxypyrimidine[3,4-b]coumarin (**3**) was prepared by the condensation of 3-ethoxycarbonylcoumarin (**1**) with thiourea. Alkylation of **3** with alkyl halides (namely, methyl iodide, ethyl iodide, benzyl chloride and ethyl chloroacetate) yielded the corresponding 2-alkylthio-4-hydroxypyrimidine[3,4-b]coumarin **4a-d**. Hydrolysis of **4d** with 2 N NaOH gave acid derivative **6**, and condensation of **4d** with hydrazine hydrate gave hydrazone 7. 1,3,4-Oxadiazol derivatives **9** and **11** were obtained by the reaction of **7** with aromatic aldehydes to give aryldene derivatives **8a,b**. Cyclization of **8** followed with bromine in acetic acid and treatment of **7** with ethyl chloroformate in pyridine and sodium acetate led to **11**.

Keywords: Pyrimidines; Coumarin; Alkylation

In continuation of our previous papers[1–5] towards the synthesis of fused O-, N-heterocycle compounds, we report an efficient synthesis of 2-thioxo-2H-4-hydroxypyrimidine[3,4-b]coumarin starting from salicylaldehyde. Such compounds are expected to show some pharmacological activities.[6–7]

Condensation of salicylaldehyde with diethyl malonate in presence of piperidine afforded the corresponding 3-ethoxycarbonylcoumarin (**1**). The reaction of **1** with thiourea in the presence of anhydrous potassium carbonate in methanol under reflux produced the potassium salt of 2-thioxo-4-hydroxypyrimidine[3,4-b]coumarin (**2**). Dissolving **2** in water and acidifying with 2 N hydrochloric acid led to the formation of 2-thioxo-4-hydroxypyrimidine[3,4-b]coumarin (**3**, Scheme 1)

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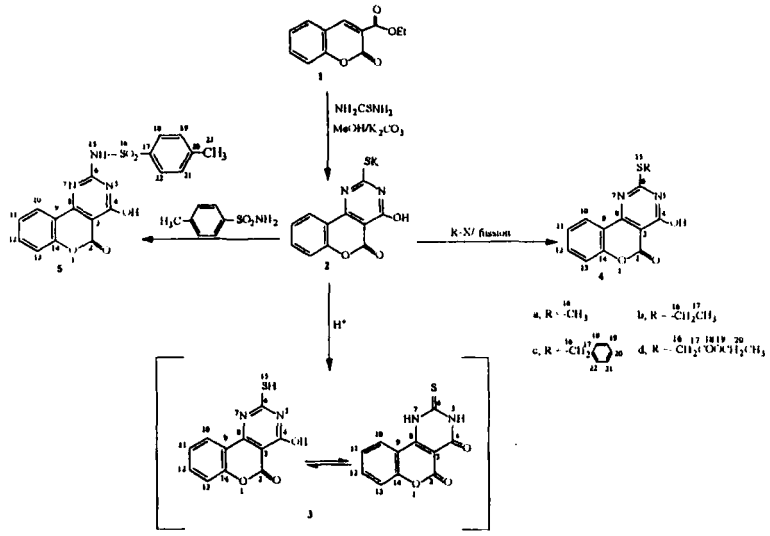
Heating the potassium salt of 2-mercapto-4-hydroxypyrimidine[3,4-b]coumarin (**2**) with alkyl halides (such as methyl iodide, ethyl iodide, benzyl chloride and ethyl chloroacetate) under fusion conditions gave the corresponding 2-alkylthio-4-hydroxypyrimidine[3,4-b]coumarin (**4a-d**). The structure **4** was also established by treatment of compound **3** with alkyl halides (namely, methyl iodide, ethyl iodide, benzyl chloride and ethyl chloroacetate) in the presence of fused sodium acetate in ethanol. Subsequently, the potassium salt of 2-mercapto-4-hydroxypyrimidine[3,4-b]coumarin (**2**) was transformed to 2-(p-tolylsulphonamido)-4-hydroxypyrimidine[3,4-b]coumarin (**5**, Scheme 1) via fusion with p-tolylsulphonamide.

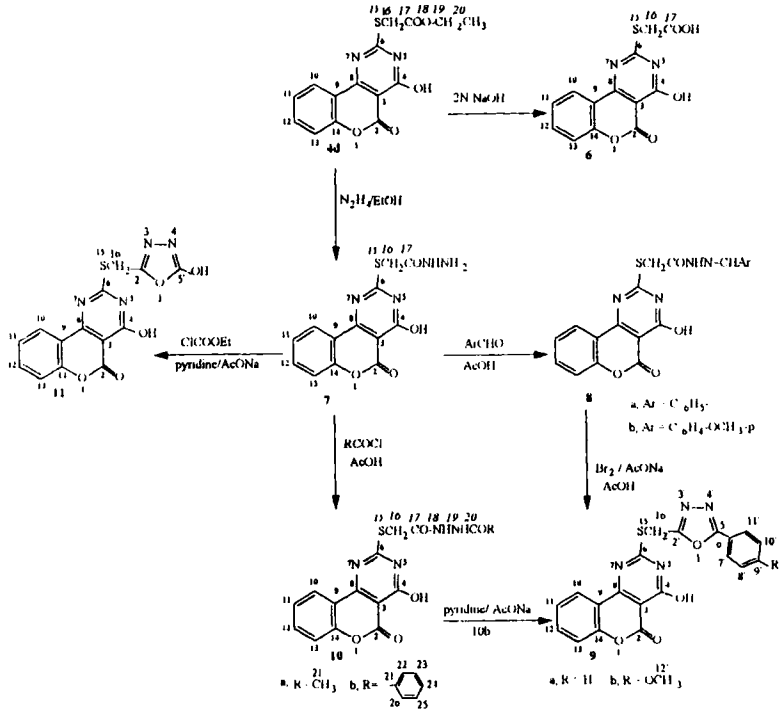


SCHEME I

2-(Ethoxycarbonylmethylthio)-4-hydroxyprimidine[3,4-b]coumarin (**4d**) was hydrolyzed with sodium hydroxide to cleave only the ethyl ester and led to 2-(hydroxycarbonylmethylthio)-4-hydroxypyrimidine[3,4-b]coumarin (**6**, scheme 2). On the other hand, the reaction of **4d** with hydrazine hydrate under reflux yielded the corresponding 2-(hydrazinylcarbonylmethylthio)-4-hydroxypyrimidine[3,4-b]coumarin (**7**, Scheme 2). Treatment of **7** with aromatic aldehydes (namely, benzalde-

hyde, and anizaldehyde) in acetic acid gave the corresponding 2-(aryldenehydrazinylcarbonylethylthio)-4-hydroxypyrimidine[3,4-b]coumarin (**8a,b**; Scheme 2).

2-(5′-Aryl-1′,3′,4′-oxadiazol-2′-methylthio)-4-hydroxypyrimidine [3,4-b]coumarin (**9a,b**; Scheme 2) was obtained by treatment of **8** with bromine in presence of fused sodium acetate in acetic acid. The structure of **9a** was also established via reaction of compound **7** with benzoyl chloride in acetic acid to give 2-(benzoylhydrazinylcarbonylmethylthio)-4-hydroxypyrimidine[3,4-b]coumarin (**10b**), followed by boiling in pyridine in presence of fused sodium acetate which gave **9b**.



SCHEME 2

Subsequent, treatment of compound **7** with acetyl chloride in acetic acid gave 2-(acetylhdrazinylcarbnylmethylthio)-4-hydroxypyrimidine [3,4-b] coumarin (**10a**). Compound **7** was transformed into 2-(5′-hydroxy-

1′,3′,4′-oxadiazol-2′-methylthio)-4-hydroxypyrimidine[3,4-b]coumarin (**11**) by refluxing with ethyl chloroformate in presence of fused sodium acetate in pyridine.

EXPERIMENTAL

Melting points were determined on a Boetius micro hostage apparatus and are uncorrected. An elemental analyzer, Hereaus CHN-OS-Rapid, was used for microanalyses. The IR spectra were recorded on a perkin-Elmer FTIR 1725 spectrometer. The mass spectra were taken on a VG12–250 instrument (70 ev EI ionzation, source temperature 200 °C). The ^{1}H-NMR and ^{13}C-NMR spectra were recoreded on a Varian unity 400 spectrometer at 399.952 and 200 MHz, respectively, with TMS as the internal standard.

Potassium salt of 2-mercapto-4-hydroxypyrimidine[3,4-b]coumarin (2)

A mixture of **1** (0.01 mol), thiourea (0.01 mol), and anhydrous potassium carbonate (0.03 mol) was heated under reflux with stirring in methanol (70 ml) for 2 h. The solid formed was filtered off and dried to give **2** as pale yellow powder, yield 53%.

2-Mercapto-4-hydroxypyrimidine[3,4-b]coumarin (3)

A potassium salt of **2** (0.01 mol) was dissolve in hot water (50 mL), then cooled and acidified with 2 N hydrochloric acid. The solid obtained was filtered off, washed with water, dried, and purified by recrytallization (dimethyl formamide) to give **3** as orange crystals, yield 87%, mp: 360°C. ν_{max} (KBr): 3430–2253 (br. OH), 3173 (NH), 1747 (C=O), 1632 (C=N), 1109, 1056 (C-O) cm^{-1}. δ_H (DMSO-d_6): 7.31–7.38 (dd, 2 H, Ar-H), 7.73–7.78 (dt, 2 H, Ar-H), 8.83 (s, 1H, OH), 8.88 (s, 1 H, SH) ppm. δ_c (DMSO-d_6): 156.40 (C-2), 117.04 (C-3), 154.86 (C-4), 176.75 (C-6), 151.72 (C-8), 110.75 (C-9). 125.30 (C-10), 124.26 (C-11), 135.40 (C-12), 98.08 (C-13), 153.83 (C-14) ppm. MS: m/z = 248 [(M^++ 2), 11.70], 247 [(M^++1), 77.10], 246 [M^+, 100]. Anal. $C_{11}H_6N_2O_3S$ for Calcd: C, 53.66; H, 2.44; N, 11.38; S, 13.00. Found: C, 53. 52; H, 2.36; N, 11.35; S, 13.03.

2-Alkylthio-4-hydroxypyrimidine[3,4-b]coumarin (4a-d)

Method A

A mixture of **2** (0.0 mol) and alkyl halides (namely, methyl iodide, ethyl iodide, benzyl chloride and ethyl chloroacetate) (0.01 mol) was fused in an oil bath at 150 °C for 2 h and then was cooled and poured into water. The solid obtained was filtered off, washed with water, dried and purified by recrystallization (ethanol) to give **4**.

Method B

A mixture of **3** (0.01 mol), alkyl halides (such as methyl iodide, ethyl iodide, benzyl chloride and ethyl chloroacetate) (0.01 mol) and fused sodium acetate (0.03 mol) in ethanol (70 mL) was heated under reflux for 12 h. The reaction mixture was cooled, and poured into water. The product formed was collected by filtration, washed with water, dried, and purified by recrystallization (ethanol) to give **4**.

Compound **4a** as colourless crystals, yield 63%, mp: 275 °C. ν_{max}(KBr): 3410–2451 (br. OH), 1743 (C=O). 1625 (C=N). 1110, 1083 (C-O) cm^{-1}. δ_H (DMSO-d_6): 2.35 (s, 3 H, CH_3), 7.32–7.39 (dd, 2 H, Ar-H), 7.73–7.7 (dt, 2 H, Ar-H), 8.82 (s, 1 H, OH) ppm. δ_c(DMSO-d_6): 156.23 (C-2), 117.10 (C-3), 161.35 (C-4), 158.20 (C-6), 150.89 (C-8), 110.71 (C-9), 125.66 (C-10), 124.17 (C-11), 134.11 (C-12), 101.21 (C-13), 153.63 (C-14), 13.25 (C-16) ppm. MS: m/z = 261 [(M^++1), 15.30], 260 [M^+, 45.37], 244 [100]. Anal. $C_{12}H_8N_2O_3S$ for Calcd: C, 55.38; H, 3.08; N, 10.76; S, 12.31. Found: C, 55.34; H, 3.02; N, 10.58; S, 12.26.

Compound **4b** as colourless crystals, yield 66%, mp: 260°C. ν_{max}(KBr): 3401–2358 (br. OH), 1734 (C=O), 1630 (C=N), 1095, 1053 (C-O) cm^{-1}. δ_H (DMSO- d_6): 1.20 (t, 3 H, CH_3), 2.83 (q, 2 H, CH_2), 7.31–7.38 (dd, 2 H, Ar-H), 7.71–7.78 (dt, 2 H, Ar-H), 8.83 (s, 1 H, OH) ppm. δ_c (DMSO-d_6): 156.25 (C-2), 117.13 (C-3), 161.32 (C-4), 158.27 (C-6), 150.85 (C-8), 110.73 (C-9), 125.64 (C-10), 124.18 (C-11), 134.03 (C-12), 101.23 (C-13), 153.8 (C-14), 20.11 (C-16), 12.57 (C-17) ppm. MS: m/z = 275 [(M^++1), 12.03], 274 [M^+, 37.25], 244 [100]. Anal. $C_{13}H_{10}N_2O_3S$ for Calcd: C, 56.93; H, 3.65; N, 10.22; S, 11.68. Found: C, 56.86; H, 3.48; N, 10.08; S, 11.54.

Compound **4c** as colourless crystals, yield 68% mp: 220 °C. ν_{max}(KBr): 3381–2251 (br. OH), 2931, 1753 (C=O), 1627 (C=N), 1058, 1032 (C-O) cm^{-1}. δ_H (DMSO-d_6): 3.52 (s, 2 H, CH_2), 7.21–7.98 (m, 9 H, Ar-H), 8.82 (s, 1 H, OH) ppm. δ_c (DMSO-d_6): 156.24 (C-2), 117.12 (C-3), 161.30

(C-4), 158.26 (C-6), 150.84 (C-8), 110.74 (C-9), 125.62 (C-10), 124.20 (C-11), 134.10 (C-12), 101.11 (C-13), 153.56 (C-14), 40.62 (C-16), 141.21 (C-17), 126.20 (C-18, C-22), 129.10 (C-19, C-21), 128.07 (C-20) ppm. MS: m/z = 337 [(M^++1), 9.11], 336 [M^+, 23.31], 244 [100]. Anal. $C_{18}H_{12}N_2O_3S$ for Calcd: C, 64.28; H, 3.57; N, 8.33; S, 9.52. Found : C, 64.08; H, 3.52; N, 8.07; S, 9.42.

Compound **4d** as colourless crystals, yield 69%, mp: 230°C. ν_{max}(KBr): 3410–2751 (br. OH), 1764 (C=O of ester), 1731 (C=O), 1632 (C=N), 1161, 1101, 1014 (C-O) cm^{-1}. δ_H (DMSO-d_6): 1.23 (t, 3 H, CH_3), 3.51 (s, 2 H, SCH_2), 4.10 (q, 2 H, CH_2), 7.32–7.39 (dd, 2 H, Ar-H), 7.73–7.79 (dt, 2 H, Ar-H), 8.82 (s, 1 H, OH) ppm. δ_c (DMSO-d_6): 156.23 (C-2), 117.15 (C-3), 161.25 (C-4), 158.24 (C-6), 150.68 (C-8), 110.72 (C-9), 125.63 (C-10), 124.22 (C-11), 134.11 (C-12), 101.01 (C-13), 153.47 (C-14), 38.71 (C-16), 167.81 (C-17), 61.29 (C-19), 14.20 (C-20) ppm. MS: m/z = 333 [(M^++1), 18.23], 332 [M^+, 25.41], 295 [100]. Anal. $C_{15}H_{12}N_2O_5S$ for Calcd: C, 54.21; H, 3.61; N, 8.43; S, 9.64. Found: C, 54.03; H, 3.47; N, 8.22; S, 9.43.

2-(p-Tolylsulphonamido)-4-hydroxypyrimidine[3,4-b]coumarin(5)

A mixture of 2 (0.01 mol) and *p*-tolylsulphonamide (0.01 mol) was fused in oil-bath at 150–160 °C for 2 h, then cooled and poured into water. The crude product was isolated by filtration and purified by crystallization (acetic acid) to give **5** as colourless crystals, yield 58%, mp: 235°C. ν_{max} (KBr): 3126 (NH), 3413–2360 (br. OH), 1724 (C=O), 1622 (C=N), 1095, 1008 (C-O)cm^{-1}. δ_H (DMSO-d_6): 2.31 (s, 3 H, CH_3), 7.31–7.98 (m, 8 H, Ar-H), 8.83 (s, 1 H, OH), 10.31 (s, 1 H, NH) ppm. δ_c (DMSO-d_6): 156.34 (C-2), 117.08 (C-3), 160.21 (C-4), 145.31 (C-6), 150.42 (C-8), 110.47 (C-9), 125.30 (C-10), 124.24 (C-11), 134.31 (C-12), 100.41 (C-13), 153.53 (C-14), 142.61 (C-17), 125.73 (C-18, C-22), 129.41 (C-19, C-21), 139.41 (C-20), 21.11 (C-23) ppm. MS: m/z = 384 [(M^++1), 11.52], 383 [M^+, 38.13], 214 [100]. Anal. $C_{18}H_{13}N_3O_5S$ for Calcd : C, 56.40; H, 3.39; N, 10.96; S, 8.35. Found : C, 56.31; H, 3.22; N, 10.78 S, 8.17.

2-(Hydroxycabonylmethylthio)-4-hydroxypyrimidine[3,4-b]coumarin (6)

A mixture of **4d** (0.01 mol) and 20 mL of 2 N sodium hydroxide was heated under reflux for 4 h. The hot reaction mixture was acidified to pH 2

with concentrated hydrochloric acid. The resulting solid was recrystallized (dimethyl formamide) to give **6** as yellow crystals, yield 61%, mp: > 400 °C. ν_{max} (KBr): 3450–2341 (br. OH), 1740–1705 (C=O), 1621 (C=N), 1101, 1037, 1006 (C-O) cm^{-1}. δ_H (DMSO-d_6): 3.40 (s, 2 H, CH_2), 7.30–7.37 (dd, 2 H, Ar-H), 7.63–7.69 (dt, 2 H, Ar-H), 8.81 (s, 1H, OH), 10.30 (br.s, 1 H, OH) ppm. δ_c (DMSO-d_6): 156.32 (C-2), 117.13 (C-3), 159.61 (C-4), 157.32 (C-6), 150.45 (C-8), 110.70 (C-9), 125.56 (C-10), 124.24 (C-11), 134.1 (C-12), 101.20 (C-13), 153.96 (C-14), 33.14 (C-16), 17253 (C-17) ppm. MS: m/z = 305 [(M^+ + 1), 13.21], 304 [M^+, 21.31], 272 [100]. Anal. $C_{13}H_8N_2O_5S$ for Calcd: C, 51.32 H, 2.63; N, 9.21; S, 10.53. Found: C, 51.01; H; 2.46; N, 9.05; S, 10.33.

2-(Hydrazinylcarbonylmethythio)-4-hydroxypyrimidine[3,4-b] coumarin (7)

A solution of **4d** (0.01 mol) and hydrazine hydrate (0.01 mol) in ethanol (70 mL) was heated under reflux for 6 h. The solid obtained after cooling was filtered off, washed with ethanol, dried and recrystallized (ethanol) to give **7** as pale orange crystals, yield 64%, mp: 293 °C. ν_{max} (KBr): 3354, 3186 (NH_2), 3271 (NH), 1723 (C=O), 1627 (C=N), 1074, 1008 cm^{-1}. δ_H (DMSO-d_6): 3.45 (s, 2 H, CH_2), 7.37 (dd, 2 H, Ar-H), 7.72–7.77 (dt, 2 H, Ar-H), 8.84 (s, 1 H, OH) ppm. δ_c (DMSO-d_6): 156.35 (C-2), 116.29 (C-3), 159.35 (C-4), 156.35 (C-6), 150.32 (C-8), 112.32 (C-9), 124.91 (C-10), 123.50 (C-11), 132.33 (C-12), 116.02 (C-13), 153.46 (C-14), 32.34 (C-16), 16.90 (C-17) ppm. MS: m/z = 319 [(M^++1), 16.21], 318 [M^+, 34.37], 259 [100]. Anal. $C_{13}H_{10}N_4O_4S$ for Calcd: C, 49.05; H, 3.14; N, 17.61; S, 10.06. Found: C, 48.89; H, 3.01; N, 17.43; S, 9.79.

2-(Aryldenehydrazinylcarbonylmethylthio)-4-hydroxypyrimidine [3,4-b]coumarin (8a,b)

A mixture of **7** (0.01 mol) and aromatic aldehydes (namely, benzaldehyde and anisaldehyde) (0.01 mol) in acetic acid (60 mL) was heated under reflux for 6 h. The solid obtained after cooling was filtered, dried and recrystallized (acetic acid) to give **8**.

Compound **8a** as yellow crystals, yield 63%, mp: 230 °C. ν_{max}(KBr): 3210 (NH), 3413–2651 (br. OH), 1734, 1695, 1631, 1100, 1006 cm^{-1}. δ_H(DMSO-d_6): 3.43 (s, 2 H, CH_2), 6.63 (s, 1 H, CH), 7.23–7.86 (m, 9 H,

Ar-H), 8.83 (s, 1 H, OH), 9.82 (s, 1H, NH) ppm. MS: M/z = 407 [(M^++1), 17.35], 406 [M^+, 34.61], 259 [100]. Anal. $C_{20}H_{14}N_4O_4S$ for Calcd: C, 59.11; H, 3.45; N, 13.79; S, 7.88. Found: 59.01; H, 3.27; N, 13.53; S, 7.66.

Compound **8b** as yellow crystals, yield 67%, mp: 343 °C. ν_{max}(KBr): 3217 (NH), 3384–2281 (br. OH) 1735, 1689, 1625, 1126, 1091, 1062 cm^{-1}. δ_H (DMSO-$\underline{d}_6$): 3.48 (s, 2 H, CH_2), 3.86 (s, 3 H, OCH_3), 6.51 (s, 1H, CH=), 7.27–7.89 (m, 8 H, Ar-H), 8.84 (s, 1 H, OH), 9.84 (s, 1 H, NH) ppm. MS: m/z = 437 [(M^++1), 13.21], 436 [M^+, 23.21], 259 [100]. Anal. $C_{21}H_{16}N_4O_5S$ for Calcd: C, 57.79; H, 3.67; N, 12.84; S, 7.34. Found: C, 57.58; H, 3.48; N, 12.59; S, 7.18.

2-(5′-Aryl-1′,3′,4′-oxadiazol-2′-methythio)-4-hydroxypyrimidine-[3,4-b]coumarin (9a, b)

A mixture of **8** (0.01 mol), bromine (0.01 mol) and fused sodium acetate (0.03 mol) was heated under reflux with stirring in acetic acid (50 mL) for 2 h. The reaction mixture was cooled and poured into water. The deposited solid was filtered, washed with water, dried and recrystallized (acetic acid) to give **9**.

Compound **9a** as pale yellow crystals, yield 59%, mp: 360°C. ν_{max}(KBr): 3420–2528 (br. OH), 1732, 1632, 1610, 1172, 1122, 1051 cm^{-1}. δ_H (DMSO-$\underline{d}_6$): 3.49 (s, 2 H, CH_2), 7.31–7.96 (m, 9 H, Ar-H), 8.82 (s, 1 H, OH) ppm. δ_c (DMSO-$\underline{d}_6$): 156.31 (C-2), 117.32 (C-3), 161.12 (C-4), 158.31 (C-6), 149.89 (C-8), 111.02 (C-9), 125.48 (C-10), 124.30 (C-11), 133.91 (C-12), 103.01 (C-13), 154.21 (C-14), 32.51 (C-16), 164.83 (C-2′), 171.67 (C-5′), 142.31 (C-6′), 129.41 (C-7′, C-11′), 129.91 (C-8′, C-10′), 134.30 (C-9′) ppm. MS: m/z = 405 [(M^++1), 13.01], 404 [M^+, 27.61], 244 [100]. Anal. $C_{20}H_{12}N_4O_4S$ for Calcd: C, 59.40; H, 2.97; N, 13.86; S, 7.92. Found: C, 59.23; H, 2.68; N, 13.64; S, 7.73.

Compound **9b** as pale yellow crystals, yield 61%, mp: 370°C. ν_{max}(KBr): 3340–2518 (br. OH), 1736, 1625, 1612, 1162, 1010, 1028 cm^{-1}. δ_H (DMSO-$\underline{d}_6$): 3.49 (s, 2 H, SCH_2), 3.86 (s, 3 H, OCH_3), 7.21–7.87 (m, 8 H, Ar-H), 8.84 (s, 1 H, OH) ppm. δ_c (DMSO-$\underline{d}_6$): 156.23 (C-2), 117.31 (C-3), 161.07 (C-4), 158.35 (C-6), 150.10 (C-8), 110.92 (C-9), 125.56 (C-10), 124.27 (C-11), 133.89 (C-12), 105.27 (C-13), 154.01 (C-14), 32.62 (C-16), 165.32 (C-2′), 171.82 (C-5′), 146.98 (C-6′), 129.73 (C-7′, C-11′), 113.93 (C-8′, C-10′), 160.21 (C-9′), 55.02 (C-12′) ppm. MS: m/z = 435 [(M^++ 1), 17.21], 434 [M^+, 35.41], 259 [100]. Anal.

$C_{21}H_{14}N_4O_5S$ for Calcd C; 58.06; H, 3.23; N, 12.90; S, 7.37. Found: C, 57.87; H, 3.06; N, 12.67; S, 7.26.

2-(Aroylhydrazinocarbonylmethylthio)-4-hydroxypyrimidine[3,4-b] coumarin (10a, b)

A mixture of **7** (0.01 mol) and acid chlorides (such as acetyl chloride and benzoyl chloride) (0.01 mol) in acetic acid (30 mL) was heated under reflux for 2 h. The solid obtained after cooling was filtered off, and dried, and recrystallized (acetic acid) to give **10**.

Compound **10a** as pale yellow crystals, yield 72%, mp: 261 °C. ν_{max} (KBr): 3178 (NH), 3391–2341 (br. OH), 1732, 1683, 1632, 1601, 1062, 1039 cm^{-1}. δ_H (DMSO-d_6): 2.01 (s, 3 H, CH_3), 3.51 (s, 2 H, SCH_2), 7.31–7.38 (dd, 2 H, Ar-H), 7.72–7.79 (dt, 2 H, Ar-H), 8.82 (s, 1 H, OH), 10.27 (s, 1 H, NH), 10.41 (s, 1 H, NH) ppm. δ_c (DMSO-d_6): 156.28 (C-2), 117.01 (C-3), 160.31 (C-4), 158.10 (C-6), 150.03 (C-8), 111.26 (C-9), 125.27 (C-10), 123.82 (C-11), 133.98 (C-12), 102.87 (C-13), 154.06 (C-14), 31.62 (C-16), 164.31 (C-17), 162.13 (C-20), 20.89 (C-21) ppm. MS: m/z = 361 [(M^++ 1), 2.32], 360 [M^+, 42.31], 244 [100]. Anal. $C_{15}H_{12}N_4O_5S$ for Calcd: C, 50.00; H, 3.33; N, 15.55; S, 8.88. Found: C, 49.79; H, 3.02; N, 15.27; S, 8.66.

Compound **10b** as pale yellow crystals, yield 76%, mp: 230 °C. ν_{max}(KBr): 3181 (NH), 3395–2240 (br. OH), 1747, 1685, 1631, 1174, 1039 cm^{-1}. δ_H (DMSO-d_6): 3.51 (s, 2 H, SCH_2), 7.30–7.94 (m, 9 H, Ar-H), 8.84 (s, 1 H, OH), 10.04 (s, 1 H, NH), 10.24 (s, 1 H, NH) ppm. δ_c (DMSO-d_6): 156.30 (C-2), 117.38 (C-3), 160.28 (C-4), 158.0 1 (C-6), 150.11 (C-8), 111.2 (C-9), 125.24 (C-10), 123.50 (C-11), 133.83 (C-12), 102.83 (C-13), 154.02 (C-14), 31.52 (C-16), 164.28 (C-17), 169.75 (C-20), 136.41 (C-21), 129.52 (C-22, C-26), 129.01 (C-23, C-25), 13.21 (C-24) ppm. MS: m/z = 423 [(M^+ + 1), 18.52], 422 [M^+, 36.12], 244 [100] Anal. $C_{20}H_{14}N_4O_5S$ for Calcd: C, 56.87; H, 3.32, N, 13.27; S, 7.58. Found: C, 56.63; H, 3.18; N, 13.09; S, 7.45.

2-(5′-Hydroxy-1′,3′,4′-oxadiazol-2′-methylthio)-4-hydroxypyrimidine [3,4-b]coumarin (11)

A mixture of **7** (0.01 mol), ethyl chloroformate (0.01 mol) and fused sodium acetate (0.03 mol) in pyridine (50 mL) was heated under reflux for

12 h. The reation mixture was cooled, poured onto crushed ice-HCl. The product formed was collected by filtration, washed with ice-water, dried and crystallized (ethanol) to give **11** as yellow crystals, yield 57%, mp: 360 °C. ν_{max} (KBr): 3430–2210 (br. OH), 1743, 1625, 1105, 1089, 1060 cm^{-1}. δ_H (DMSO-d_6): 3.51 (s, 2 H, SCH_2), 7.31–7.37 (dd, 2 H, Ar-H), 7.72–7.79 (dt, 2 H, Ar-H), 8.83 (s, 1 H, OH), 9.37 (s, 1 H, OH) ppm. δ_c (DMSO-d_6): 156.31 (C-2), 117.30 (C-3), 160.8 (C-4), 158.23 (C-6), 150.01 (C-8), 111.31 (C-9), 125.45 (C-10), 124.31 (C-11), 134.01 (C-12), 102.71 (C-13), 154.20 (C-14), 32.37 (C-16), 165.12 (C-2′) 179.83 (C-5′) ppm. MS: m/z = 344 [M^+, 8.37], 342 [(M^+-2), 3.24], 244 [100]. Anal. $C_{14}H_8N_4O_5S$ for Calcd: C, 48.84; H, 2.32; N, 16.28; S, 9.30. Found: C, 48.59; H, 2.20; N, 16.06; S, 9.17.

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