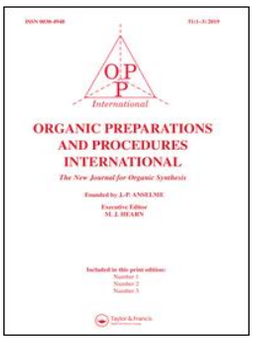

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Novel Route for the Synthesis of 5-(4-Hydroxy-2-oxo-2*H*-chromen-3-yl)-1,3-dimethyl-1*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-diones

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A scaffold that incorporates chromene and a bioactive moiety such as coumarin might integrate valuable properties of both, and the potential synergy of the heterocyclic units within a single molecule could lead to significant new products.[1] A literature survey revealed that there are scanty reports in which chromene is associated with 4-hydroxycoumarin.[2–6] Furthermore, some previous methods suffer from drawbacks such as the use of hazardous solvents, long reaction times, unsatisfactory yields or difficulties in the isolation of product. As a continuation of our interest in eco-benign synthesis of bioactive and photoluminescent heterocycles,[7–9] we have developed a novel method for the synthesis of chromenochromenepyrimidinediones (CCP) by the multicomponent reaction of substituted salicylaldehydes, 6-amino-1,3-dimethyluracil and 4-hydroxycoumarin in ethanol at 80 °C employing sulfamic acid as an inexpensive, easily available and cost effective reagent (*Scheme 1*).

Initially, screening of reagents was carried out for the model reaction of salicylaldehyde **(1)**, 6-amino-1,3-dimethyluracil **(2)** and 4-hydroxycoumarin **(3)**. Our focus was on the achievement of good yields within a practical timeframe, as well as convenience. Reagents, like $AlCl_3$, *p*-TSA, EPZ-10, EPZ–G, $[EAHEPiPY]^+$ $[AlCl_4]^-$, $[BMim]^+$ $[HSO_4]^-$ and sulfamic acid, were employed for the model reaction (*Table 1*, entries 1–7). Sulfamic acid was found to be the reagent of choice for the transformation (*Table 1*, entry 7). The effect of the amount of sulfamic acid on the model reaction was studied with 10, 20, 30 and 40 mol % of sulfamic acid (*Table 1*, entries 7–10). Results summarized in *Table 1* revealed that 30 mol % of sulfamic acid was enough to give the

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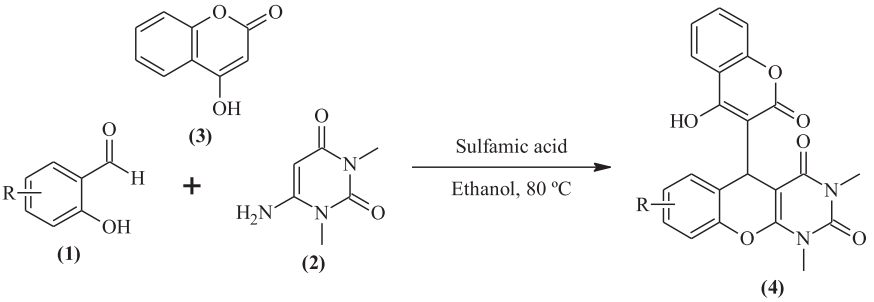
Table 1
Screening of Reagents for Synthesis of **4**[a]

Entry	Reagents	mol %	Time (h)	Yield (%)
1	$AlCl_3$	30	3.45	71
2	*p*-TSA	30	3.45	75
3	EPZ-10	30	3.30	79
4	EPZ – G	30	3.20	78
5	$[EAHEPiPY]^+ [AlCl_4]^-$	30	3.30	77
6	[BMim] $[HSO_4]$	30	5.00	65
7	**Sulfamic acid**	**30**	**2.00**	**85**
8	Sulfamic acid	10	2.30	76
9	Sulfamic acid	20	2.30	77
10	Sulfamic acid	40	2.00	84

[a]Reaction conditions: salicylaldehyde (1 mmol), 6-amino-1,3-dimethyluracil (1 mmol), 4-hydroxycoumarin (1 mmol), temp.: 80 °C, solvent: 5 mL ethanol.

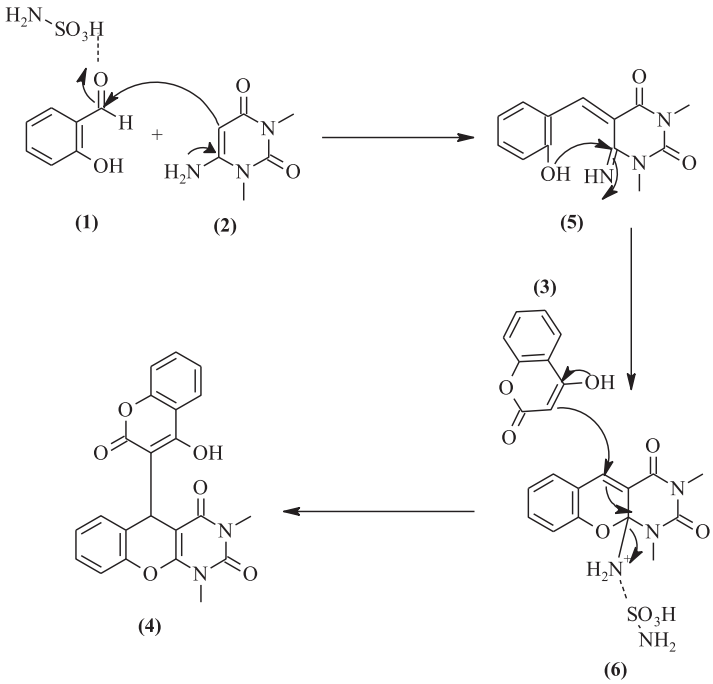


Scheme 1. Synthesis of chromenochromenepyrimidinediones (4).

chromenochromenepyrimidinediones (**4**) in good yield (*Table 1*, entry 7). However, a further increase in the amount of sulfamic acid (40 mol %) did not induce any significant change in yield of product and reaction time (*Table 1*, entry 10). When the catalyst amount was lowered to 10 and 20 mol %, more time was required for completion of reaction, accompanying a decrease in the yield of final product (*Table 1*, entries 8 and 9).

Based on our earlier experience with mixed solvent systems[3,4] we summarised that ethanol:water system might be effective (*Table 2*). Hence the model reaction was carried out in the presence of a mixed solvent system with different proportions of ethanol and water (*Table 2*, entries 2-11). The presence of water negatively alters the transformation with respect to yield and time (*Table 2*, entries 1-10). Thus our investigation revealed the optimized reaction conditions as 30 mol % of sulfamic acid in 95% ethanol at 80 °C.

A plausible mechanism for the formation of product **4a** is depicted in *Scheme 2*. Initially, the sulfamic acid promoted Knoevenagel condensation of salicylaldehyde (**1**) and 6-amino-1,3-dimethyl uracil (**2**), with subsequent ring closure, leads to the formation of an intermediate (**6**). Then, Michael attack of 4-hydroxycoumarin (**3**) on (**6**) followed by loss of ammonia, furnishes the final product (**4**).



Scheme 2. Plausible mechanism for the formation of **4**.

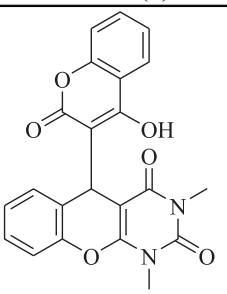
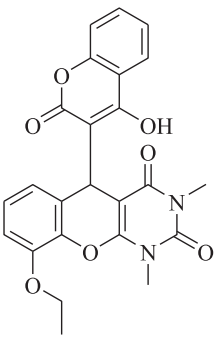
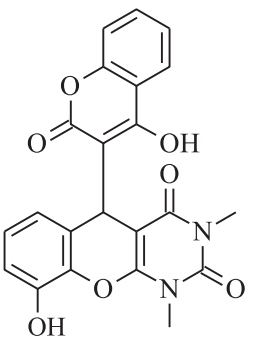
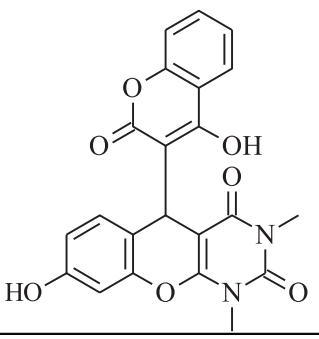
Table 2
Screening of Solvents for the Synthesis of **4**

Entry	Solvent	Time (h)	Yield[a] (%)
1	Water	10	–
2	Ethanol: Water (1:9)	9	12
3	Ethanol: Water (2:8)	8	12
4	Ethanol: Water (3:7)	9	21
5	Ethanol: Water (4:6)	9	33
6	Ethanol: Water (5:5)	8	43
7	Ethanol: Water (6:4)	7	60
8	Ethanol: Water (7:3)	6	62
9	Ethanol: Water (8:2)	5	71
10	Ethanol: Water (9:1)	3	74
11	**Ethanol: Water (9.5:0.5)**	**2**	**85**
12	Ethanol	2	82

[a]Reaction conditions: salicylaldehyde (1 mmol), 6-amino-1,3-dimethyluracil (1 mmol), 4-hydroxycoumarin (1 mmol), reagent: sulfamic acid (30 mmol %), temp.: 80 °C, solvent: 5 mL.

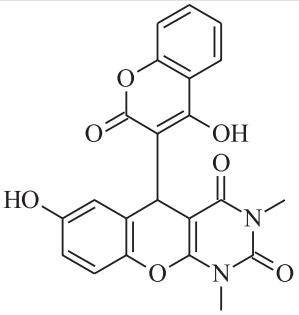
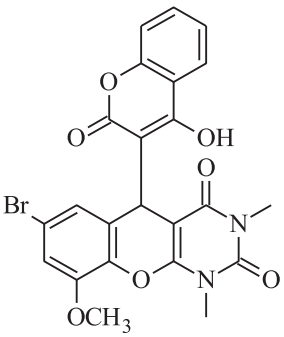
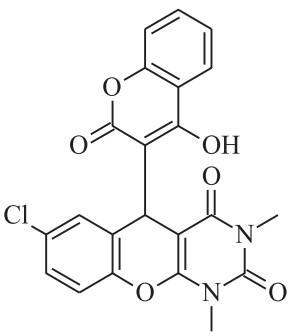
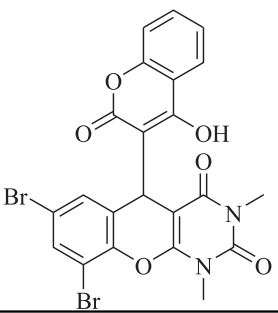
With the optimized reaction conditions in hand, we explored the generality of the method employing a variety of substituted salicylaldehydes (*Table 3*). The reaction proceeds smoothly to furnish the expected products with very good yields. The completion of reaction was monitored by thin layer chromatography. The identity of product was confirmed by several techniques (IR, ^{1}H, ^{13}C NMR, GCMS, HRMS and elemental

Table 3
Synthesis of Library of Substituted Chromenochromenepyrimidinediones

Entry	Product (4)	Compound	Time (h)	Yield[a] (%)
1		**4a**	2.00	85
2		**4b**	2.15	88
3		**4c**	2.00	85
4		**4d**	2.00	86

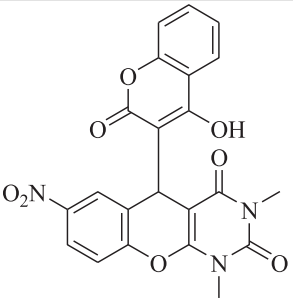
(*Continued*)

Table 3
(*Continued*)

Entry	Product (4)	Compound	Time (h)	Yield[a] (%)
5		**4e**	2.00	85
6		**4f**	2.00	84
7		**4g**	2.00	86
8		**4h**	1.45	85

(*Continued*)

Table 3
(*Continued*)

Entry	Product (4)	Compound	Time (h)	Yield[a] (%)
9		**4i**	2.00	87

[a]Reaction conditions: salicylaldehyde (1 mmol), 6-amino-1,3-dimethyluracil (1 mmol), 4-hydroxycoumarin (1 mmol), temp.: 80 °C, solent: 5 mL ethanol, sulfamic acid (30 mol %).

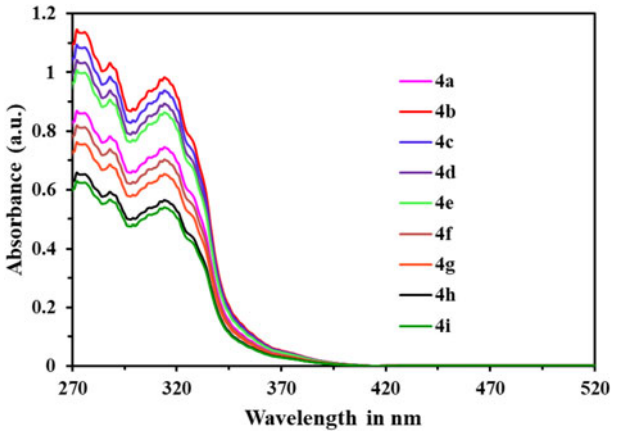


Figure 1. Absorption spectra of synthesized compounds **4a** to **4i** in DMSO (Concentration of each solution: 1×10^{-6} M).

analysis). The method was found to be suitable for both electron donating and withdrawing groups present on the salicylaldehydes (*Table 3*, entries 1-9).

In the last few decades, coumarin and salicylaldehyde based organic compounds exhibiting fluorescence properties have attracted much more attention in the field of chemosensors.[10,11] Multi-functional organic compounds possessing conjugated π-systems exhibit excellent fluorescence properties for potential applications in the field of sensing.[12–15] We thus analyzed the new compounds for their photophysical properties.

Because of the good solubility of compounds **4a**-**4i** (CCP) in DMSO, it was used to prepare solutions of known concentration to examine their absorption and fluorescence emission properties. Choice of other solvents was ruled out due to poor solubility.

Absorption Study

Figure. 1 shows absorption spectra of CCP (**4a**) and its derivatives (**4b to 4i)** in DMSO. The change in absorbance value for the compounds correlates with the

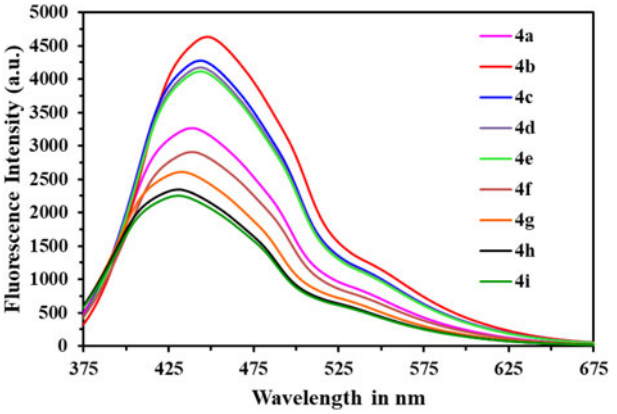


Figure 2. Fluorescence spectra of synthesized compounds 4a to 4i in DMSO (Concentration of each solution: 1×10^{-6} M).

substituent on the aromatic ring. From *Figure 1*, it is clear that the absorption spectra of CCP and its derivatives exhibited sharp structured bands at 295 and 318 nm due to the $S_0 \longrightarrow S_1$ and $S_0 \longrightarrow S_2$ absorption transitions, respectively. The absorption transition $S_0 \longrightarrow S_1$ was ascribed to $\pi \longrightarrow \pi^*$ whereas $S_0 \longrightarrow S_2$ corresponds to $n \longrightarrow \pi^*$. The values of molar extinction coefficients were estimated from absorption data.[16,17]

Fluorescence Study

Figure 2 represents the fluorescence emission spectra of CCP (**4a**) and its derivatives (**4b to 4i**). The DMSO solution of the compound **4a** displays a strong fluorescence emission band at 439 nm attributed to the most probable $\pi^* \rightarrow \pi$ transition when excited at wavelength 325 nm. The less probable $\pi^* \rightarrow$ n transition exhibits a minor band of fluorescence emission at 530 nm. Compounds **4b to 4e** are derivatives of compound **4a** bearing electron donating substituents on the aromatic ring. Such compounds have significant fluorescence intensity enhancement with a spectral shift in wavelength maxima of about 10-12 nm as compared to compound **4a.**[9,18] The electron donating groups are capable of extended π-conjugation in the molecule and may responsible for smaller HOMO–LUMO gaps, thus resulting in a bathochromic shift in wavelength maxima.[19] On the other hand, compounds bearing electron withdrawing groups in their structure (**4f to 4i**) have decreased fluorescence intensity with a slight hypsochromic shift with respect to compound **4a**.[20] The fluorescence quantum yield (ϕ_f) for each compound **4a to 4i** was calculated using quinine sulfate as reference and the values are listed in *Table 4*.

The photophysical properties of all synthesized compounds **4a to 4i** are summarized in *Table 4*. Compounds having an electron donating group in the structure have larger Stokes shift.

In conclusion we have investigated a novel route for the synthesis of new chromenochromenepyrimidinediones **4** by a multicomponent reaction of substituted salicylaldehydes, 6-amino-1,3-dimethyluracil and 4-hydroxycoumarin with sulfamic acid (30 mol %) in ethanol at 80 °C. The attractive features of this method are operational simplicity, short reaction time, general applicability, isolation of product by mere filtration, very good isolated yields of products and the avoidance of hazardous organic solvents and toxic catalysts. Thus, the method fulfills a number of principles of green chemistry.

Table 4
Photophysical Data of Compounds **4a to 4i** in DMSO[a]

Entry	Compound	Absorbance Maxima (λ_{abs}) in nm	Molar Extinction Coefficient (ε, × 10^5) in M^{-1} cm^{-1}	Fluorescence Maxima (λ_f) in nm	Stokes Shift (v) in cm^{-1}	Fluorescence Quantum yield (ϕ_f)
1	**4a**	295, 318	7.446	439	7990.18	0.47
2	**4b**	295, 318	9.829	448	8447.80	0.35
3	**4c**	295, 318	9.382	444	8246.70	0.37
4	**4d**	295, 318	8.935	444	8246.70	0.39
5	**4e**	295, 318	8.637	444	8246.70	0.40
6	**4f**	295, 318	7.024	439	7990.18	0.44
7	**4g**	295, 318	6.531	433	7674.54	0.46
8	**4h**	295, 318	5.641	430	7513.41	0.47
9	**4i**	295, 318	5.395	429	7459.20	0.49

[a]Fluorescence spectra of synthesized compounds monitored at the excitation wavelength (λ_{ex} = 325 nm).

Significant aspects in the absorption spectra and fluorescence emission of compounds **4a** to **4i** explained on the basis of electron donating and withdrawing groups.

Experimental Section

All reagents were obtained from Sigma Aldrich and used without further purification. Melting points were measured in open capillary using a Thiele tube and are corrected. IR spectra were recorded on Agilent Cary 630 spectrophotometer. NMR spectra were recorded on a Bruker AC-(300 MHz spectrometer for ^{1}H NMR and 75 MHz for ^{13}C NMR) in DMSO-d_6 using TMS as an internal standard; δ values are expressed in ppm. Mass spectra were recorded on a Shimadzu QP2010 GCMS.High resolution mass spectra (HRMS) were performed on Thermo Scientific Q – Exactive, Accela 1250 pump, instrument. Elemental analyses were obtained by using FLASH EA 1112 series from SAIF, IIT Bombay, Powai, Mumbai, Maharashtra, India. Fluorescence spectra were recorded using a JASCO (FP-8300) Spectrofluorimeter. The concentration of each sample was maintained in the range of~10^{-6} M for the absorption and fluorescence studies.

Typical Procedure for Synthesis of Chromenochromenepyrimidinediones

In a 25 mL round bottom flask, a mixture of a salicylaldehyde (1 mmol), 6-amino-1,3-dimethyluracil (1 mmol) and 30 mol % of sulfamic acid in 5 mL ethanol was stirred until formation of the Knoevenagel adduct, confirmed by using TLC. 4-Hydroxycoumarin (1 mmol) was added and the resultant reaction mixture was stirred at 80 °C in a thermostatted oil bath until completion of the reaction for the period shown in *Table 3*. The progress of reaction was monitored by TLC. After completion of the reaction, the mixture was poured into ice cold water, filtered and washed with ethanol to furnish the corresponding pure chromenochromenepyrimidinediones. The products were characterized by IR, NMR, GCMS, HRMS and elemental analysis.

5-(4Hydroxy-2-oxo-2H-chromen-3-yl)-1,3-dimethyl-1H-chromeno[2,3-d]pyrimidine-2,4(3H,5H)-dione (4a)

White powder; mp 268-270 °C; IR: 3262, 1715, 1688, 1625, 1580, 1483, 1450, 1393, 1300, 1272, 1239, 1215, 1210, 1170, 1111, 1063, 977, 943, 898, 873, 750, 691, 628 cm^{-1}; ^{1}H-NMR(300 MHz, DMSO-d_6): δ 3.40 (s, 3H), 3.64 (s, 3H), 5.31 (s, 1H), 7.12-8.05 (m, 8ArH & 1 -OH), ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ 29.4, 29.5, 30.0, 87.1, 108.9, 115.9, 116.2, 121.9, 123.4, 123.7, 124.3, 125.7, 128.4, 128.4, 128.7, 131.7, 131.9, 150.9, 153.0, 161.9, 165.4 ppm; MS (EI): 404 (M^+), 289, 243, 186, 115 m/z; HRMS: mass calculated for [$C_{22}H_{16}N_2O_6$]: 427.0897 $[M+Na]^+$; Obs. Mass: 427.0901 $[M+Na]^+$.

Anal. Calcd for $C_{22}H_{16}N_2O_6$: C, 65.34; H, 3.99; N, 6.93. Found: C, 65.42; H, 3.79; N, 6.83.

9-Ethoxy-5-(4-hydroxy-2-oxo-2H-chromen-3-yl)-1,3-dimethyl-1H-chromeno[2,3-d]pyrimidine-2,4(3H,5H)-dione (4b)

White powder; mp 269–271 ^{0}C; IR: 2968, 1702, 1654, 1618, 1580, 1471, 1399, 1335, 1257, 1220, 1080, 1037, 966, 901, 871, 837, 800, 773, 761, 732, 670, 635 cm^{-1}; ^{1}H-

NMR (300 MHz, DMSO-d_6): δ 1.39 (m, 3H), 3.11 (s, 3H), 3.45 (s, 3H), 4.09 – 4.11 (m, 2H), 5.60 (s, 1H), 6.69 – 6.72 (d, 1ArH, $J = 7.5$ Hz), 6.94 – 7.06 (m, 2ArH), 7.28 – 7.37 (m, 2ArH), 7.55 – 7.61 (m, 1ArH), 7.99 (s, 1H, -OH) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ 15.1, 28.0, 29.2, 64.7, 112.5, 116.5, 116.6, 119.9, 123.7, 124.4, 125.6, 132.5, 146.7, 150.6, 152.5, 153.8, 161.7 ppm; MS (EI): 449 $[M + 1]^+$, 419, 327, 289, 265, 242, 230, 202, 186, 173, 159, 145, 121, 105, 92, 77 m/z; HRMS: mass calculated for $[C_{24}H_{20}N_2O_7]$: 449.1341 $[M + H]^+$and 471.1160 $[M + Na]^+$; Obs. Mass: 449.1343 $[M + H]^+$and 471.1163 $[M + Na]^+$.

Anal. Calcd for $C_{24}H_{20}N_2O_7$: C, 64.28; H, 4.50; N, 6.25. Found: C, 64.19; H, 4.25; N, 6.34.

9-Hydroxy-5-(4-hydroxy-2-oxo-2H-chromen-3-yl)-1,3-dimethyl-1,5-dihydro-2H-chromeno[2,3-d]pyrimidine-2,4(3H)-dione (4c)

White powder; mp > 300 °C; IR: 3162, 1716, 1667, 1625, 1573, 1493, 1392, 1346, 1289, 1244, 1205, 1148, 1063, 1026, 968, 944, 903, 880, 795, 772, 745, 626, 581 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 3.11 (s, 6H), 5.60 (s, 1H), 6.58 (d, 1H, $J = 7.5$ Hz), 6.78 (s, 1H), 6.93 (s, 1H), 7.30 (m, 3H), 7.55 (m, 1H), 7.99 (s, 1H), 9.91 (s, 1H) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ 28.0, 29.4, 115.6, 116.5, 116.7, 118.6, 124.0, 124.3, 125.5, 132.4, 138.8, 145.3, 150.6, 152.5, 153.9, 160.5, 161.7 ppm; MS (EI): 421 $[M+1]^+$, 391, 258, 199, 169, 146, 111, 106, 102 m/z; HRMS: mass calculated for $[C_{22}H_{16}N_2O_7]$: 421.1025 $[M + H]^+$ and 443.0845 $[M + Na]^+$; Obs. Mass: 421.1030 $[M + H]^+$ and 443.0850 $[M + Na]^+$.

Anal. Calcd for $C_{22}H_{16}N_2O_7$: C, 62.86; H, 3.84; N, 6.66. Found: C, 62. 78; H, 3.78; N, 6.44.

8-Hydroxy-5-(4-hydroxy-2-oxo-2H-chromen-3-yl)-1,3-dimethyl-1,5-dihydro-2H-chromeno[2,3-d]pyrimidine-2,4(3H)-dione (4d)

Light brown powder; mp 279-281 °C; IR: 3289, 1714, 1674, 1627, 1493, 1450, 1396, 1354, 1302, 1267, 1217, 1149, 1100, 972, 942, 891, 846, 785, 750, 678, 624 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 3.15 (s, 6H), 5.44 (s, 1H), 6.48 (s, 2H), 6.90 (d, 1H, $J = 7.5$ Hz), 7.14 (s, 1H), 7.23 (s, 1H), 7.45 (s, 1H), 7.94 (s, 1H), 9.55 (s, 1H) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ 28.0, 28.2, 29.1, 102.9, 112.8, 113.2, 116.1, 116.9, 123.7, 124.1, 129.1, 131.6, 150.4, 152.6, 154.1, 157.4, 160.6 ppm; MS (EI): 421 $[M+1]^+$, 391, 258, 199, 169, 146, 111, 106, 102 m/z; HRMS: mass calculated for $[C_{22}H_{16}N_2O_7]$: 421.1027 $[M + H]^+$ and 443.0846 $[M + Na]^+$; Obs. Mass: 421.1030 $[M + H]^+$ and 443.0850 $[M + Na]^+$.

Anal. Calcd for $C_{22}H_{16}N_2O_7$: C, 62.86; H, 3.84; N, 6.66. Found: C, 62. 68; H, 3.68; N, 6.87.

7-Hydroxy-5-(4-hydroxy-2-oxo-2H-chromen-3-yl)-1,3-dimethyl-1,5-dihydro-2H-chromeno[2,3-d]pyrimidine-2,4(3H)-dione (4e)

Buff colored powder; mp 297-299 °C; IR: 3403, 1712, 1644, 1586, 1486, 1442, 1335, 1314, 1219, 1035, 904, 893, 819, 797, 758, 662 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 3.15 (s, 6H), 5.46 (s, 1H), 6.53 – 6.62 (m, 1H), 6.6.89 – 6.92 (d, 1H, $J = 8.7$ Hz),

7.14 (s, 1H), 7.23 (s, 1H), 7.45 (s, 1H), 7.94 (s, 1H), 9.20 (s, 1H) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ 32.7, 32.8, 58.9, 119.1, 119.9, 120.9, 121.4, 121.6, 128.5, 128.9, 136.5, 155.2, 157.4, 159.5 ppm; 421 $[M+1]^+$, 391, 259, 145, 111, 102 m/z; HRMS: mass calculated for $[C_{22}H_{16}N_2O_7]$: 421.1027 $[M+H]^+$ and 443.0847 $[M+Na]^+$; Obs. Mass: 421.1030 $[M+H]^+$ and 443.0850 $[M+Na]^+$.

Anal. Calcd for $C_{22}H_{16}N_2O_7$: C, 62.86; H, 3.84; N, 6.66. Found: C, 62. 84; H, 3.75; N, 6.61.

7-Bromo-5-(4-hydroxy-2-oxo-2H-chromen-3-yl)-9-methoxy-1,3-dimethyl-1,5-dihydro-2H-chromeno[2,3-d]pyrimidine-2,4(3H)-dione (4f)

White powder; mp 284-286 °C; IR: 3466, 3385, 1699, 1625, 1576, 1472, 1325, 1265, 1216, 1189, 1092, 987, 867, 789, 755, 721, 681, 637, 597 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ2.96 (s, 3H), 3.17 (s, 3H), 3.82 (s, 3H), 4.91(s, 1H), 6.75 – 7.24 (m, 4H & 1 -OH), 7.91 (s, 1H), 5.97 (d, 1H) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ 27.4, 27.9, 29.1, 30.1, 56.4, 87.4, 113.4, 116.5, 122.3, 147.8, 150.4, 151.3, 152.4 ppm; MS (EI)**:**514 $[M+1]^+$, 413, 391, 212, 199, 169, 152, 111, 106 m/z; HRMS: mass calculated for $[C_{23}H_{17}N_2O_7Br]$: 535.0113 $[M+Na]^+$; Obs. Mass: 535.0111 $[M+Na]^+$.

Anal. Calcd for $C_{23}H_{17}N_2O_7Br$: C, 53.82; H, 3.34; N, 5.46. Found: C, 53.70; H, 3.46; N, 5.37.

7-Chloro-5-(4-hydroxy-2-oxo-2H-chromen-3-yl)-1,3-dimethyl-1,5-dihydro-2H-chromeno[2,3-d]pyrimidine-2,4(3H)-dione (4g)

Cream powder; mp 239-241 °C; IR: 1702, 1657, 1616, 1571, 1476, 1446, 1413, 1241, 1189, 1047, 976, 903, 812, 756, 675, 645 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 3.16 (s, 3H), 3.19 (s, 3H), 5.58 (s, 1H), 6.21 – 8.00 (m, 7ArH & 1 -OH), ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ 28.8, 29.2, 30.6, 33.2, 115.5, 116.2, 116.6, 116.8, 117.6, 123.8, 124.1, 124.3, 124.5, 126.8, 128.0, 128.3, 129.8, 131.8, 148.7, 150.3, 150.4, 152.1, 152.7, 153.9, 154.8, 164.6 ppm; MS (EI)**:**439 $[M+1]^+$, 391, 258, 276, 111, 106, 102 m/z; HRMS: mass calculated for $[C_{22}H_{15}ClN_2O_6]$: 461.0507 $[M+Na]^+$; Obs. Mass: 461.0511 $[M+Na]^+$.

Anal. Calcd for $C_{22}H_{15}ClN_2O_6$: C, 60.22; H, 3.45; N, 6.38. Found: C, 60.10; H, 3.36; N, 6.47.

7,9-Dibromo-5-(4-hydroxy-2-oxo-2H-chromen-3-yl)-1,3-dimethyl-1H-chromeno[2,3-d]pyrimidine-2,4(3H,5H)-dione (4h)

White powder; mp 151-153 °C; IR: 3078, 1700, 1654, 1615, 1562, 1494, 1338, 1314, 1250, 1228, 1171, 1102, 1054, 982, 907, 858, 797, 754, 715, 676, 617 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 3.16 (s, 3H), 3.53 (s, 3H), 5.62 (s, 1H), 7.10 – 8.00 (m, 6ArH & 1 -OH), ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ 28.0, 29.3, 29.4, 58.9, 110.8, 116.2, 116.6, 117.4, 123.8, 130.6, 132.0, 133.7, 150.2, 152.7, 161.8 ppm; HRMS: mass calculated for $[C_{22}H_{14}N_2O_6Br_2]$: 562.9270 $[M+H]^+$ and 584.9089 $[M+Na]^+$; Obs. Mass: 562.9271 $[M+H]^+$ and 584.9090 $[M+Na]^+$.

Anal. Calcd for $C_{22}H_{14}N_2O_6Br_2$: C, 47.00; H, 2.51; N, 4.98. Found: C, 47.15; H, 2.35; N, 4.76.

5-(4-Hydroxy-2-oxo-2H-chromen-3-yl)-1,3-dimethyl-7-nitro-1,5-dihydro-2H-chromeno[2,3-d]pyrimidine-2,4(3H)-dione (4i)

Cream powder; mp 209-211^{0}C; IR: 3374, 3225, 1683, 1610, 1519, 1495, 1438, 1334, 1292, 1249, 1209, 1107, 1092, 997, 903, 829, 770, 751, 676, 637 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d$_6$): δ 3.18 (s, 3H), 3.39 (s, 3H), 5.62 (s, 1H), 6.84 – 6.86 (d, 1ArH, $J = 8.7$Hz), 6.27 – 7.34 (m, 3ArH), 7.55 – 7.58 (d, 1ArH, $J = 7.5$ Hz), 7.84 – 7.97 (m, 3ArH), 11.02 (s, 1H, -OH) ppm; ^{13}C-NMR (75 MHz, DMSO-d$_6$) δ 28.5, 30.8, 33.2, 115.4, 116.2, 117.3, 124.1, 124.4, 124.9, 139.7, 150.4, 152.1, 155.0, 162.2, 164.5 ppm; MS (EI): 449 $[M + 1]^+$, 419, 327, 289, 145, 121, 105, 92, 77 m/z; HRMS: mass calculated for $[C_{22}H_{15}N_3O_8]$: 472.0748 $[M + Na]^+$; Obs. Mass: 472.0751 $[M + Na]^+$.

Anal. Calcd for $C_{22}H_{15}N_3O_8$: C, 58.80; H, 3.36; N, 9.36. Found: C, 58.71; H, 3.35; N, 9.57.

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