

An Efficient and Rapid Access to the Synthesis of Tetrahydrochromeno[4,3-*b*]chromene-6,8-dione Derivatives by Magnesium Perchlorate

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ABSTRACT

A rapid and green procedure has been introduced for the preparation of tetrahydrochromeno[4,3-*b*]chromene-6,8-dione derivatives in the presence of magnesium perchlorate. This solvent-free procedure offers some advantages such as short reaction times, high yields, an easy-to-handle catalyst, and avoidance of organic solvents. In this work four new compounds are reported.

KEYWORDS

Tetrahydrochromeno[4,3-*b*]chromene-6,8-dione, solvent-free, magnesium perchlorate, three-component reactions.

1. Introduction

Multi-component reactions (MCRs), involving three or more reactants in one pot, have been used to synthesize structurally diverse bioactive heterocyclic compounds.¹ A number of tetrahydrochromeno[4,3-*b*]chromene-6,8-dione derivatives have been synthesized utilizing one-pot three-component reactions.^{2–6} There are a few reports on coupling of 4-hydroxycoumarin, aldehydes, and cyclic 1,3-diketone compounds.^{7–10} However, these methods for preparing tetrahydrochromeno[4,3-*b*]chromene-6,8-dione derivatives have not been entirely satisfactory and involve some disadvantages such as long reaction times and use of organic solvents. Magnesium perchlorate [Mg(ClO₄)₂] is a non-toxic, cheap, commercially available, moisture stable white crystal. In continuation of our research on the applications of solid acids in organic synthesis,¹¹ it was found interesting to develop a green and more general protocol for the efficient one-pot three-component synthesis of tetrahydrochromeno[4,3-*b*]chromene-6,8-dione derivatives in the presence of Mg(ClO₄)₂.

2. Results and Discussion

The 10,10-dimethyl-7-phenyl-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione was synthesized by the condensation of 4-hydroxycoumarin, 5,5-dimethyl-1,3-cyclohexanedione (dimedone) and benzaldehyde in the presence of Mg(ClO₄)₂ as a catalyst. Initially, we explored the catalytic efficiency of Mg(ClO₄)₂ and the other Lewis acids such as MgSO₄, MgBr₂, MgCl₂, and LiClO₄. However, MgSO₄, MgBr₂, and LiClO₄ did not exhibit any significant catalytic activity, and only a 70% yield was obtained in the presence of MgCl₂. This establishes the fact that amongst the various salts used, Mg(ClO₄)₂ was the most effective catalyst for the synthesis of 10,10-dimethyl-7-phenyl-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione. To optimize the reaction conditions, dimedone **1** (1 mmol), 4-hydroxycoumarin **2** (1 mmol) and benzaldehyde **3** (1 mmol) were used in the presence of Mg(ClO₄)₂ under different conditions. We found that using a 0.04 g (0.18 mmol) catalyst at 90 °C in solvent-free conditions gave optimum results (Table 1, Entries 7, 10–14). We also observed that, besides **4a**, a trace of **4b** was formed in the above optimized conditions. This is due to the

high reactivity of the 3-position of 4-hydroxycoumarins. When the reaction was carried out in the presence of a solvent, **4b** was obtained in a higher yield in comparison to the amount obtained in solvent-free conditions. To examine the reusability of Mg(ClO₄)₂ under solvent-free conditions, after each run, the catalyst residue was washed with hot CH₂Cl₂ and reused. The catalyst was reusable although a gradual decline was observed in its activity (Table 1, Entry 12).

We investigated the generality of this reaction by using, dimedone **1**, 4-hydroxycoumarin **2**, and various aromatic aldehydes under the optimized conditions (Table 2).

Aromatic aldehydes containing electron-withdrawing groups reacted very well with higher yields in a shorter time than aromatic aldehydes with electron-donating groups (Table 2, Entry 3, 12). Also, α,β -unsaturated aldehydes such as cinnamaldehyde were easily converted to the desired product under the same experimental conditions, but in lower yields (Table 2, Entry 14). Entries 4, 10, 12 and 14 in Table 2 are new compounds.

Finally, in order to assess the efficiency and generality of this methodology, we compared this method with some reported results in the literature. From comparison with the results depicted in Table 3, it was found that Mg(ClO₄)₂ is the most efficient catalyst with respect to reaction time, temperature and yield of the product (Table 3).

It is clear from the results that our method compare better than the best methods currently available in literature. Although the mechanism of the reaction has not yet been established experimentally, the formation of the product can be rationalized as outlined in Scheme 1.

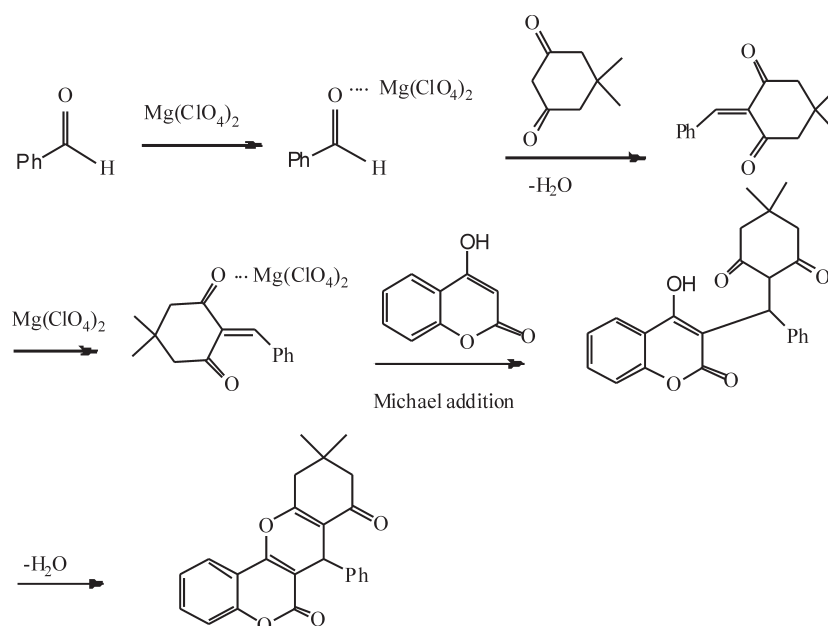
In summary, this paper reports a quick and efficient procedure for the synthesis of tetrahydrochromeno[4,3-*b*]chromene-6,8-dione derivatives *via* a one-pot three-component reaction. The short reaction time, high yield, and availability of Mg(ClO₄)₂ as a catalyst are the prominent features of this transformation. Moreover, the experimental procedure for this reaction is remarkably simple and without the use of hazardous or expensive organic solvents.

3. Experimental

3.1. Materials and Instruments

The products were characterized by IR, ¹H-, and ¹³C-NMR and

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Scheme 1

The proposed mechanism of synthesizing 7-phenyl-tetrahydrochromeno[4,3-*b*]chromene-6,8-dione catalyzed by $\text{Mg}(\text{ClO}_4)_2$.

by comparison of their physical properties with those reported in the literature. IR spectra were recorded on a Bruker, Etnox 55 spectrometer. ^1H - and ^{13}C -NMR spectra were obtained using a Bruker Avance 400- and 500-MHz spectrometer (DRX). The melting points were determined with a Buchi melting point B-540 B.V.CHI apparatus.

3.2. General Procedure for the Synthesis of 10,11-Dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione Derivatives

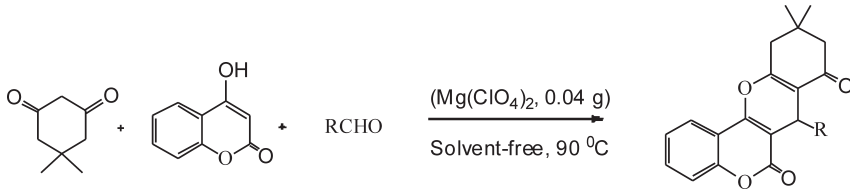
A mixture of dimedone (1 mmol, 0.14 g), 4-hydroxycoumarin (1 mmol, 0.16 g), aldehyde (1 mmol) and $\text{Mg}(\text{ClO}_4)_2$ (0.18 mmol, 0.04 g) was heated under solvent-free conditions at 90 °C for an appropriate time. After completion of the reaction, for isolation

Table 1 Reaction of dimedone, 4-hydroxycoumarin and benzaldehyde under different conditions.^a

Entry	Catalyst/g	Temp/°C	Solvent	Time/min	Yield/%	
1	–	70	–	50	–	
2	LiClO_4 (0.01)	70	–	30	45	
3	MgBr_2 (0.03)	70	–	35	30	
4	MgCl_2 (0.02)	70	–	25	70	
5	MgSO_4 (0.02)	70	–	40	25	
6	$\text{Mg}(\text{ClO}_4)_2$ (0.03)	70	–	25	70	
7	$\text{Mg}(\text{ClO}_4)_2$ (0.03)	90	–	25	83	
8	MgCl_2 (0.02)	90	–	25	72	
9	$\text{Mg}(\text{ClO}_4)_2$ (0.03)	110	–	25	85	
10	$\text{Mg}(\text{ClO}_4)_2$ (0.01)	90	–	25	60	
11	$\text{Mg}(\text{ClO}_4)_2$ (0.02)	90	–	25	75	
12 ^b	$\text{Mg}(\text{ClO}_4)_2$ (0.04)	90	–	25	93, 89, 85	
13	$\text{Mg}(\text{ClO}_4)_2$ (0.05)	90	–	25	92	
14	$\text{Mg}(\text{ClO}_4)_2$ (0.06)	90	–	25	93	
15	$\text{Mg}(\text{ClO}_4)_2$ (0.04)	Reflux	n-Hexane	60	–	
16	$\text{Mg}(\text{ClO}_4)_2$ (0.04)	Reflux	THF	60	20	
17	$\text{Mg}(\text{ClO}_4)_2$ (0.04)	Reflux	MeC	60	30	
18	$\text{Mg}(\text{ClO}_4)_2$ (0.04)	Reflux	EtOAc	60	40	
19	$\text{Mg}(\text{ClO}_4)_2$ (0.04)	Reflux	CHCl_3	60	50	
20	$\text{Mg}(\text{ClO}_4)_2$ (0.04)	Reflux	H_2O	60	55	
21	$\text{Mg}(\text{ClO}_4)_2$ (0.04)	Reflux	EtOH	60	80	

^a Reaction conditions: dimedone (1 mmol), 4-hydroxycoumarin (1 mmol), benzaldehyde (1 mmol).

^b Catalyst was recycled three times.

Table 2 Preparation of tetrahydrochromeno[4,3-*b*]chromene-6,8-diones under optimized conditions.^a


Entry	R	Time/min	Yield/%	Ref.
1	C ₆ H ₅	27	93	7
2	3-NO ₂ C ₆ H ₄	22	90	9
3	4-NO ₂ C ₆ H ₄	20	92	9
4	3-FC ₆ H ₄	25	93	–
5	4-FC ₆ H ₄	23	91	8
6	4-ClC ₆ H ₄	23	89	9
7	4-MeC ₆ H ₄	27	87	8
8	3-BrC ₆ H ₄	25	90	10
9	4-OMeC ₆ H ₄	30	88	7
10	3,4-(OMe) ₂ C ₆ H ₃	32	87	–
11	3-OHC ₆ H ₄	37	85	7
12	4-OHC ₆ H ₄	35	83	–
13	4-OH-3-OMeC ₆ H ₃	32	85	7
14	C ₆ H ₅ CH=CH	40	78	–
15	2,4-Cl ₂ C ₆ H ₃	30	90	7

^a Reaction conditions: dimedone (1 mmol), 4-hydroxycoumarin (1 mmol), aldehyde (1 mmol).**Table 3** Comparison of the efficiency of Mg(ClO₄)₂ with that of the reported catalysts for the synthesis of tetrahydrochromeno[4,3-*b*]chromene-6,8-diones.

Entry	Catalyst/mol%	Solvent	Temp/°C	Time/min	Yield/%	Ref.
1	[DMDBSI] ₂ HSO ₄ ^a /20 mol%	H ₂ O	Reflux	240	93	7
2	Fe(DS) ₃ ^b /10 mol%	H ₂ O	70	120	87	8
3	<i>p</i> -TSA/5 mol%	–	120	300	76	9
4	Mg(ClO ₄) ₂ ^c /18 mol%	–	90	25	93	–

^a Acid-functionalized ionic liquids [1,3-dimethyl-2-oxo-1,3-bis(4-sulfobutyl)imidazolidine-1,3-dium hydrogen sulfate].^b FeCl₃/Sodium dodecyl sulfate.^c Reaction conditions: dimedone (1 mmol), 4-hydroxycoumarin (1 mmol), aldehyde (1 mmol).

of catalyst the mixture was dissolved in hot CH₂Cl₂ and filtered. The solvent of resulted filtrate was evaporated and the pure product was obtained by recrystallization from ethanol. In Table 2, entries **4**, **10**, **12** and **14** are new tetrahydrochromeno[4,3-*b*]chromene-6,8-dione derivatives. The IR and NMR spectra of the new compounds are provided as supplementary material.

3.3. Spectroscopic Data

10,10-Dimethyl-7-phenyl-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7H,9H)-dione (Table 2, Entry **1**): M.p. 220–222 °C [7], IR: 2960, 1711, 1664, 1604, 1490, 1452, 1364, 1324, 1288, 1182, 1164, 1051, 1031, 892, 764. ¹H-NMR (500 MHz, CDCl₃): 1.09 (s, 3 H); 1.11 (s, 3 H); 2.22 (d, *J* = 16.4 Hz, 2 H); 2.64 (d, *J* = 16.4 Hz, 2 H); 4.96 (s, 1 H); 7.17 (t, *J* = 7.4 Hz, 1 H); 7.25 (t, *J* = 7.4 Hz, 2 H); 7.29 (d, *J* = 7.6 Hz, 2 H); 7.37–7.44 (m, 2 H); 7.62 (t, *J* = 8.0 Hz, 1 H); 7.85 (dd, *J* = 8.0 Hz, *J* = 1.8 Hz, 1 H). ¹³C-NMR (125 MHz, CDCl₃): 27.2, 28.9, 32.0, 33.2, 40.3, 50.9, 105.0, 114.2, 115.3, 115.9, 120.1, 123.2, 125.3, 127.6, 128.5, 131.2, 140.3, 153.3, 153.7, 161.9, 196.2.

10,10-Dimethyl-7-(3-nitrophenyl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7H,9H)-dione (Table 2, Entry **2**): M.p. 230–232 °C [9], IR: 2973, 1719, 1657, 1609, 1526, 1351, 1181, 1142, 1093, 1034, 1031, 818, 764. ¹H-NMR (500 MHz, CDCl₃): 1.10 (s, 3 H); 1.13 (s, 3 H);

2.24 (d, *J* = 16.0 Hz, 2 H); 2.41 (d, *J* = 16.4 Hz, 2 H); 4.99 (s, 1 H); 7.22 (t, *J* = 7.5 Hz, 1 H); 7.29 (d, *J* = 7.5 Hz, 1 H); 7.40 (d, *J* = 7.6 Hz, 2 H); 7.61–7.68 (m, 2 H); 7.88 (t, *J* = 7.8 Hz, 1 H); 8.05 (d, *J* = 7.8 Hz, 1 H). ¹³C-NMR (125 MHz, CDCl₃): 28.3, 29.2, 30.5, 34.8, 39.4, 51.2, 107.0, 113.4, 114.0, 115.6, 122.6, 124.0, 127.0, 128.2, 128.9, 130.9, 132.8, 136.4, 138.4, 149.5, 155.0, 163.2, 196.0.

10,10-Dimethyl-7-(4-nitrophenyl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7H,9H)-dione (Table 2, Entry **3**): M.p. 208–210 °C [9], IR: 2930, 1719, 1651, 1605, 1528, 1458, 1342, 1178, 1098, 1033, 863, 760. ¹H-NMR (400 MHz, CDCl₃): 1.10 (s, 3 H); 1.12 (s, 3 H); 2.18 (d, *J* = 16.4 Hz, 1 H); 2.26 (d, *J* = 16.4 Hz, 1 H); 2.67 (d, *J* = 18.1 Hz, 1 H); 2.73 (d, *J* = 18.1 Hz, 1 H); 4.95 (s, 1 H); 6.90 (d, *J* = 8.8 Hz, 2 H); 7.04 (d, *J* = 8.8 Hz, 2 H); 7.34–7.40 (m, 2 H); 7.59 (t, *J* = 8.2 Hz, 1 H); 7.89 (dd, *J* = 8.2 Hz, *J* = 1.6 Hz, 1 H). ¹³C-NMR (100 MHz, CDCl₃): 27.3, 29.3, 31.2, 32.8, 40.8, 50.7, 114.8, 115.0, 115.1, 115.3, 115.5, 117.0, 122.5, 124.4, 129.8, 129.9, 130.2, 130.3, 132.4, 162.0, 162.3, 163.0, 196.5.

10,10-Dimethyl-7-(3-fluorophenyl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7H,9H)-dione (Table 2, Entry **4**): M.p. 247–249 °C, IR: 2957, 1720, 1664, 1607, 1362, 1260, 1175, 1054, 1030, 889, 766. ¹H-NMR (500 MHz, CDCl₃): 1.14 (s, 3 H); 1.21 (s, 3 H); 2.32 (d, *J* =

16.5 Hz, 1 H); 2.37 (d, J = 16.5 Hz, 1 H); 2.70 (d, J = 16.5 Hz, 1 H); 2.77 (d, J = 18.5 Hz, 1 H); 5.01 (s, 1 H); 6.87–6.91 (m, 1 H); 7.08 (d, J = 10.0 Hz, 1 H); 7.24–7.28 (m, 2 H); 7.37 (d, J = 8.5 Hz, 1 H); 7.42 (t, J = 8.0 Hz, 1 H); 7.62 (t, J = 7.5 Hz, 1 H); 7.91 (dd, J = 8.0 Hz, J = 1.5 Hz, 2 H). ^{13}C -NMR (100 MHz, CDCl_3): 27.5, 29.8, 31.8, 32.6, 39.3, 50.9, 105.3, 115.2, 115.4, 123.3, 123.6, 123.7, 128.1, 128.2, 131.0, 132.0, 143.3, 147.2, 147.9, 159.8, 161.3, 164.0, 196.4. Anal. calc. for $\text{C}_{24}\text{H}_{19}\text{FO}_4$ (390.40): C 73.84, H 4.91; found C 73.5, H 4.8.

10,10-Dimethyl-7-(4-chlorophenyl)-10,11-dihydrochromeno[4,3-b]chromene-6,8(7H,9H)-dione (Table 2, Entry 6): M.p. 248–250 °C [9], IR: 2983, 1718, 1662, 1607, 1490, 1360, 1189, 1092, 1013, 895, 762. ^1H -NMR (500 MHz, CDCl_3): 1.02 (s, 3 H); 1.10 (s, 3 H); 2.20 (d, J = 16.0 Hz, 1 H); 2.33 (d, J = 15.5 Hz, 1 H); 2.73–2.82 (m, 2 H); 4.66 (s, 1 H); 7.01 (d, J = 8.0 Hz, 2 H); 7.12 (d, J = 8.0 Hz, 2 H); 7.46 (m, 2 H); 7.70 (t, J = 7.5 Hz, 1 H); 7.95 (d, J = 7.5 Hz, 1 H). ^{13}C -NMR (125 MHz, CDCl_3): 27.5, 28.2, 30.7, 34.7, 39.5, 57.0, 105.9, 113.0, 116.6, 119.0, 122.5, 123.8, 124.7, 133.0, 135.5, 138.8, 148.2, 149.0, 152.2, 153.8, 158.0, 162.9, 196.2.

10,10-Dimethyl-7-(4-methylphenyl)-10,11-dihydrochromeno[4,3-b]chromene-6,8(7H,9H)-dione (Table 2, Entry 7): M.p. 208–210 °C [8], IR: 2957, 1714, 1666, 1605, 1562, 1453, 1353, 1307, 1265, 1192, 1034, 952, 762. ^1H -NMR (500 MHz, CDCl_3): 1.00 (s, 3 H); 1.09 (s, 3 H); 2.27 (d, J = 16.6 Hz, 2 H); 2.46 (d, J = 16.6 Hz, 2 H); 4.74 (s, 1 H); 7.31 (d, J = 8.0 Hz, 2 H); 7.40 (d, J = 8.0 Hz, 2 H); 7.52 (m, 2 H); 7.75 (t, J = 8.0 Hz, 1 H); 7.91 (dd, J = 8.1 Hz, J = 1.5 Hz, 1 H). ^{13}C -NMR (125 MHz, CDCl_3): 28.2, 28.4, 29.7, 33.0, 38.9, 52.2, 105.1, 111.2, 114.9, 116.6, 124.2, 125.8, 126.2, 130.8, 136.9, 137.1, 141.2, 148.5, 152.4, 155.1, 157.3, 161.9, 196.1.

10,10-Dimethyl-7-(3-bromophenyl)-10,11-dihydrochromeno[4,3-b]chromene-6,8(7H,9H)-dione (Table 2, Entry 8): M.p. 258–260 °C [10], IR: 2970, 1719, 1664, 1607, 1568, 1454, 1360, 1185, 1140, 1054, 1050, 1034, 755. ^1H -NMR (500 MHz, CDCl_3): 1.30 (s, 3 H), 1.19 (s, 3 H), 2.29 (d, J = 16.8 Hz, 1 H); 2.35 (d, J = 16.4 Hz, 1 H); 2.67 (d, J = 17.1 Hz, 1 H); 2.76 (d, J = 17.1 Hz, 1 H); 4.94 (s, 1 H); 7.16 (t, J = 8.0 Hz, 1 H); 7.28–7.43 (m, 5 H); 7.61 (t, J = 7.6 Hz, 1 H); 7.90 (dd, J = 8.0 Hz, J = 1.2 Hz, 1 H). ^{13}C -NMR (125 MHz, CDCl_3): 27.6, 29.1, 32.4, 33.3, 40.8, 50.7, 106.1, 113.7, 114.7, 117.0, 122.4, 128.0, 129.8, 130.3, 131.3, 132.5, 144.7, 150.0, 154.1, 160.6, 162.3, 195.9.

10,10-Dimethyl-7-(4-methoxyphenyl)-10,11-dihydrochromeno[4,3-b]chromene-6,8(7H,9H)-dione (Table 2, Entry 9): M.p. 187–189 °C [7], IR: 2957, 1725, 1660, 1606, 1509, 1456, 1359, 1302, 1250, 1183, 1167, 1140, 1033, 893, 764. ^1H -NMR (500 MHz, CDCl_3): 1.14 (s, 3 H); 1.17 (s, 3 H); 2.21 (m, 2 H); 2.39 (m, 2 H); 4.85 (s, 1 H); 7.24 (d, J = 7.5 Hz, 2 H); 7.43 (d, J = 7.5 Hz, 2 H); 7.55 (m, 2 H); 7.79 (t, J = 8.0 Hz, 1 H); 7.98 (d, J = 8.0 Hz, 1 H). ^{13}C -NMR (125 MHz, CDCl_3): 27.0, 27.2, 28.4, 30.1, 37.0, 54.5, 106.3, 114.0, 114.1, 115.2, 123.0, 123.8, 128.3, 135.9, 136.2, 138.2, 143.9, 150.8, 153.1, 156.8, 158.1, 161.0, 195.9.

10,10-Dimethyl-7-(3,4-dimethoxyphenyl)-10,11-dihydrochromeno[4,3-b]chromene-6,8(7H,9H)-dione (Table 2, Entry 10): M.p. 184–185 °C, IR: 2921, 1721, 1660, 1620, 1513, 1455, 1361, 1262, 1139, 896, 742. ^1H -NMR (400 MHz, CDCl_3): 1.13 (s, 3 H); 1.19 (s, 3 H); 2.30 (d, J = 16.0 Hz, 1 H); 2.35 (d, J = 16.0 Hz, 1 H); 2.68 (d, J = 17.6 Hz, 1 H); 2.74 (d, J = 17.6 Hz, 1 H); 3.81 (s, 3 H); 3.89 (s, 3 H); 4.93 (s, 1 H); 6.74 (d, J = 8.1 Hz, 1 H); 6.82 (dd, J = 8.0 Hz, J = 1.6 Hz, 1 H); 7.05 (s, 1 H); 7.33–7.39 (m, 2 H); 7.58 (t, J = 8.0 Hz, 1 H); 7.88 (d, J = 8.0 Hz, 1 H). ^{13}C -NMR (100 MHz, CDCl_3): 27.5, 29.3, 32.4, 32.8, 40.9, 50.7, 106.9, 110.9, 112.7, 113.7, 115.2, 116.9, 120.2, 122.4, 124.3, 132.2, 135.4, 148.0, 148.6, 152.6, 153.7, 160.7, 161.9, 196.2. Anal. calc. for $\text{C}_{26}\text{H}_{24}\text{O}_6$ (432.47): C 72.21, H 5.59; found C 72.0, H 5.8.

10,10-Dimethyl-7-(3-hydroxyphenyl)-10,11-dihydrochromeno[4,3-b]

chromene-6,8(7H,9H)-dione (Table 2, Entry 11): M.p. 267–269 °C [7], IR: 3400, 2983, 1697, 1665, 1607, 1488, 1364, 1175, 1137, 1058, 897, 767. ^1H -NMR (500 MHz, $\text{DMSO}-d_6$): 1.00 (s, 3 H); 1.10 (s, 3 H); 2.75 (sbr, 2 H); 2.37 (d, J = 16.5 Hz, 1 H); 4.62 (s, 1 H); 6.55 (dd, J = 7.5 Hz, J = 2.1 Hz, 1 H); 6.66 (d, J = 7.0 Hz, 1 H); 6.71 (s, 1 H); 7.03 (t, J = 8.0 Hz, 1 H); 7.44 (d, J = 8.5 Hz, 1 H); 7.46 (t, J = 7.0 Hz, 1 H); 7.69 (t, J = 7.5 Hz, 1 H); 7.93 (dd, J = 7.5 Hz, J = 1.5 Hz, 1 H); 9.29 (s, 1 H). ^{13}C -NMR (125 MHz, $\text{DMSO}-d_6$): 27.6, 29.4, 32.9, 33.6, 50.9, 106.8, 114.0, 114.7, 114.8, 116.4, 117.4, 119.7, 123.4, 125.6, 129.9, 133.7, 145.0, 152.8, 154.5, 158.0, 163.4, 196.7.

10,10-Dimethyl-7-(4-hydroxyphenyl)-10,11-dihydrochromeno[4,3-b]chromene-6,8(7H,9H)-dione (Table 2, Entry 12): M.p. 267–268 °C, IR: 3431, 1697, 1665, 1607, 1585, 1488, 1364, 1176, 897, 767. ^1H -NMR (400 MHz, $\text{DMSO}-d_6$): 1.03 (s, 3 H); 1.09 (s, 3 H); 2.18 (d, J = 16.6 Hz, 2 H); 2.33 (d, J = 16.6 Hz, 2 H); 4.60 (s, 1 H); 6.62 (d, J = 8.6 Hz, 2 H); 7.05 (d, J = 8.6 Hz, 2 H); 7.46 (m, 2 H); 7.70 (t, J = 7.6 Hz, 1 H); 7.94 (t, J = 7.6 Hz, 1 H); 9.29 (s, 1 H). ^{13}C -NMR (100 MHz, $\text{DMSO}-d_6$): 26.7, 28.5, 31.9, 32.0, 39.5, 50.0, 106.2, 113.2, 114.1, 114.8, 116.5, 122.5, 124.7, 129.3, 132.7, 133.3, 151.9, 153.3, 156.1, 159.9, 162.3, 195.9. Anal. calc. for $\text{C}_{24}\text{H}_{20}\text{O}_5$ (388.41): C 74.21, H 5.19; found C 73.9, H 5.0.

10,10-Dimethyl-7-(4-hydroxy-3-methoxyphenyl)-10,11-dihydrochromeno[4,3-b]chromene-6,8(7H,9H)-dione (Table 2, Entry 13): M.p. 271–273 °C [7], IR: 3434, 2993, 1713, 1662, 1608, 1514, 1361, 1272, 1181, 1033, 863, 779. ^1H -NMR (400 MHz, $\text{DMSO}-d_6$): 1.02 (s, 3 H); 1.10 (s, 3 H); 2.20 (d, J = 16.0 Hz, 1 H); 2.34 (d, J = 16.0 Hz, 1 H); 2.76 (s, 2H), 3.70 (s, 3H); 4.61 (s, 1H); 6.61 (d, J = 8.0 Hz, 1 H); 6.64 (d, J = 8.0 Hz, 1 H); 6.81 (d, J = 1.6 Hz, 1 H); 7.43–7.48 (m, 2 H); 7.69 (t, J = 7.8 Hz, 1 H); 7.92 (d, J = 8.0 Hz, 1 H); 8.88 (s, 1 H). ^{13}C -NMR (100 MHz, $\text{DMSO}-d_6$): 26.5, 28.6, 31.9, 32.2, 39.6, 50.0, 55.6, 106.1, 112.8, 113.2, 114.0, 115.1, 116.5, 120.5, 122.5, 124.7, 132.6, 133.8, 145.5, 147.0, 151.8, 153.3, 160.0, 162.4, 196.0.

10,10-Dimethyl-7-styryl-10,11-dihydrochromeno[4,3-b]chromene-6,8(7H,9H)-dione (Table 2, Entry 14): M.p. 132–134 °C, IR: 2956, 1713, 1661, 1609, 1453, 1361, 1239, 1173, 1138, 1032, 970, 762, 696. ^1H -NMR (400 MHz, CDCl_3): 1.10 (s, 3 H); 1.12 (s, 3 H); 2.36 (s, 2 H); 2.53 (d, J = 16.8 Hz, 1 H); 2.62 (d, J = 16.8 Hz, 1 H); 4.56 (br s, 1 H); 6.22 (dd, J = 16.0 Hz, J = 6.4, 1 H); 6.32 (d, J = 16.0 Hz, 1 H); 7.09 (t, J = 7.2 Hz, 1 H); 7.14–7.23 (m, 4 H); 7.26–7.31 (m, 2 H); 7.51 (t, J = 8.0 Hz, 1 H); 7.76 (d, J = 7.2 Hz, 1 H). ^{13}C -NMR (100 MHz, CDCl_3): 27.6, 29.0, 32.2, 33.5, 40.9, 50.8, 107.1, 116.9, 122.4, 124.3, 126.4, 126.5, 127.5, 128.3, 128.4, 129.5, 131.8, 132.3, 147.6, 162.1, 165.0, 166.9, 196.6. Anal. calc. for $\text{C}_{32}\text{H}_{26}\text{O}_4$ (474.55): C 80.99, H 5.52; found C 81.3, H 5.8.

10,10-Dimethyl-7(2,4-dichlorophenyl)-10,11-dihydrochromeno[4,3-b]chromene-6,8(7H,9H)-dione (Table 2, Entry 15): M.p. 250–252 °C [7], IR: 2956, 1716, 1664, 1611, 1583, 1470, 1360, 1265, 1173, 1061, 1052, 832, 753. ^1H -NMR (400 MHz, CDCl_3): 1.08 (s, 3 H), 1.12 (s, 3 H); 2.22 (d, J = 16.0 Hz, 1 H); 2.28 (d, J = 16.0 Hz, 1 H); 2.69 (s, 2 H); 4.92 (s, 1 H); 7.01 (d, J = 8.0 Hz, 1 H); 7.13 (d, J = 8.0 Hz, 1 H); 7.30 (s, 1 H); 7.39–7.49 (m, 2 H); 7.69 (t, J = 7.6 Hz, 1 H); 7.98 (d, J = 7.8 Hz, 1 H). ^{13}C -NMR (100 MHz, CDCl_3): 28.0, 28.9, 31.9, 33.1, 40.9, 52.3, 107.2, 112.2, 114.8, 115.1, 116.0, 118.2, 123.9, 124.1, 124.3, 135.4, 137.9, 144.2, 150.0, 151.0, 156.9, 158.3, 160.9, 195.0.

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Supplementary Material

The IR and NMR spectra of the four new compounds reported herein are provided as supplementary material.

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