

## Synthesis of functionalized chromenes using ketones and aldehyds

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**Abstract:** An efficient synthesis of 4-alkyl-4-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione or 4-aryl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-diones *via* reaction of 4-hydroxycoumarin with Meldrum's acid and ketones or aldehydes is described.

**Keywords:** Chromene; Meldrum's acid; Aqueous media; Meldrum's acid; 4-Hydroxycoumarin.

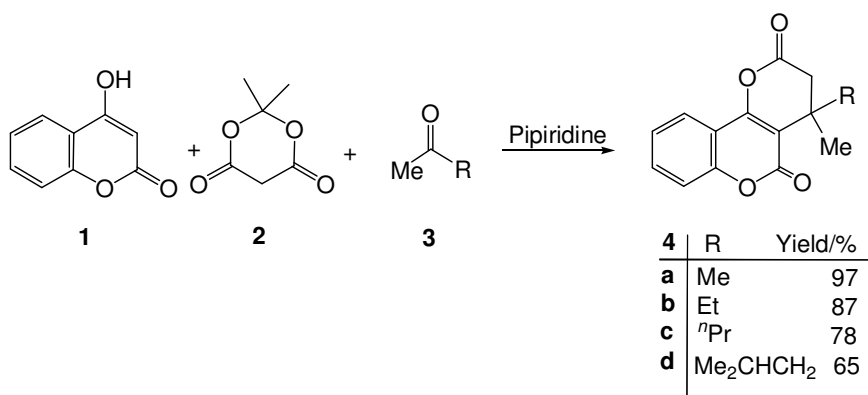
### Introduction

Natural products containing chromene structure represent an important class of compounds [1-4]. The bicyclic ring system of chromenes has inspired a number of different synthetic approaches [5,6]. Also, substituted 4*H*-chromenes are a new set of anticancer compounds [7]. For these reasons, their synthesis is very importance to organic chemists and many studies have been reported on the synthesis of the chromene ring system [8,9]. Consequently, a number of synthetic strategies for the construction of pyrano[3,2-*c*]chromene derivatives have been reported [10]. Some of the reported procedures require long reaction times, multi-step reactions and complex synthetic pathways, afford products with only modest yields [11-13].

Therefore, the development of more effective methods for their preparation is still necessary.

### Results and discussion

As part of our current studies [14-16] on the development of new routes to heterocyclic systems, we now report an efficient method to prepare functionalized chromenes. Thus the reaction of 4-hydroxycoumarin **1** with Meldrum's acid **2** and excess ketones **3** in the presence of piperidine at room temperature led to 4-alkyl-4-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione **4** in good yields (Scheme 1).

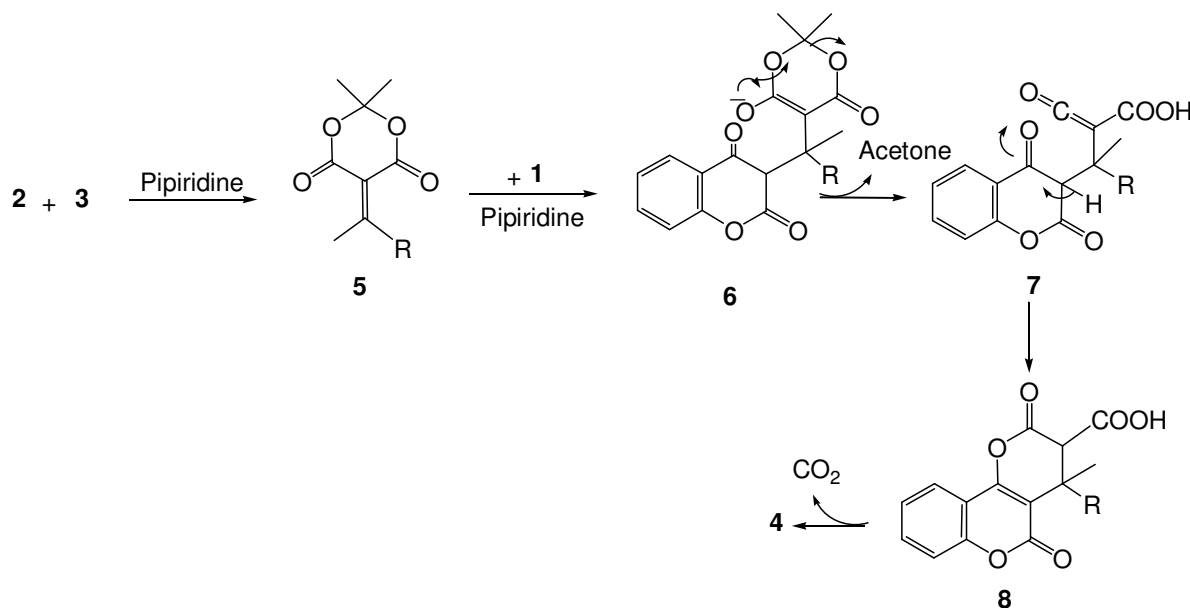


**Scheme 1.** Reaction of 4-hydroxycoumarin with Meldrum's acid and ketones in the presence of piperidine at rt.

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Structures of compounds **4a–4d** were assigned by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectral data. The  $^1\text{H}$  NMR spectrum of **4a** showed two singlets arising from methyl and methylene protons, along with the aromatic protons. The  $^1\text{H}$  NMR spectrum of **4b–4e** exhibited a characteristic AB system for the  $\text{CH}_2$  moiety. The carbonyl group resonances in the  $^{13}\text{C}$  NMR spectrum of **4a** appear at 159.5 and 164.8 ppm. The mass spectrum of **4a** displayed the molecular ion peak at  $m/z = 244$ .

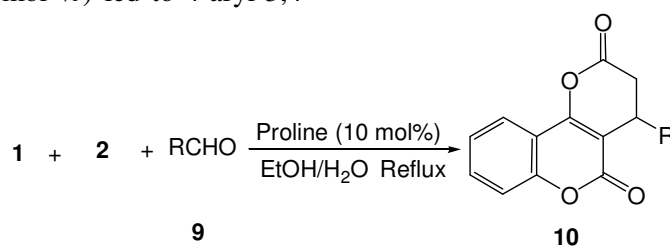
A tentative mechanism for this transformation is proposed in Scheme 2. It is conceivable that the initial event is the formation of **5** which undergoes Knoevenagel condensation with Meldrum's acid. This intermediate is subsequently attacked by 4-hydroxycoumarin to generate **6**. Intermediate **6** first loses acetone to give ketene **7**, which undergoes cyclization and decarboxylation to produce **4**.



**Scheme 2.** Proposed mechanism for the reaction of 4-hydroxycoumarin with Meldrum's acid and ketones in the presence of piperidine.

The reaction of 4-hydroxycoumarin **1** with Meldrum's acid **2** and benzaldehydes **9** in 50% aqueous EtOH in the presence of proline (10 mol %) led to 4-aryl-3,4-

dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-diones **10** in good yields (Scheme 3).



9, 10	R	Yield/% of 10
a	$\text{C}_6\text{H}_5$	94
b	3-Br- $\text{C}_6\text{H}_4$	92
c	4-Me- $\text{C}_6\text{H}_4$	85
d	4-MeO- $\text{C}_6\text{H}_4$	83

**Scheme 3.** The reaction of 4-hydroxycoumarin with Meldrum's acid and benzaldehydes in 50% aqueous EtOH in the presence of proline (10 mol %).

Structures of compounds **10a-d** were assigned by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectral data. For example, the  $^1\text{H}$  NMR spectrum of **10a** exhibited a characteristic ABM system for the  $\text{CH}_2\text{-CH}$  moiety. The resonances of the carbonyl groups in the  $^{13}\text{C}$  NMR spectrum of **10a** appear at 161.2 and 164.7 ppm. The mass spectrum of **10a** displayed the molecular ion peak at  $m/z = 292$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **10b-d** are similar to those of **10a** except for the benzene moieties, which show characteristic signals in the appropriate regions of the spectra.

## Conclusion

In conclusion, we have described a convenient route to 4-aryl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-diones or 4-alkyl-4-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione from 4-hydroxycoumarin, Meldrum's acid, and benzaldehydes or ketones. The functionalized chromenes reported in this work may be considered as potentially useful synthetic intermediates because they possess atoms with different oxidation states. The advantage of the present procedure is that the reaction is performed under neutral conditions by simple mixing of the starting materials. The simplicity of the present procedure makes it an interesting alternative to other approaches.

## Material and methods

Mp: *Electrothermal-9100* apparatus; uncorrected. IR Spectra: *Shimadzu IR-460* spectrometer.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra: Bruker DRX-500 AVANCE instrument; in  $\text{CDCl}_3$  at 500.1 and 125.7 MHz, resp.;  $\square$  in ppm,  $\square$  in Hz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer, in  $m/z$ . Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer. All chemicals were used as-received from the appropriate suppliers.

## General procedure

To a stirred solution of Meldrum's acid (0.29 g, 2 mmol) and methyl ketones as a solvent was added piperidine (0.84 g, 2 mmol). The reaction mixture was stirred for 4 hours. After completion of the reaction (monitored by TLC), was added 4-hydroxycoumarin (0.32 g, 2 mmol). The reaction mixture was stirred for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography ( $\text{SiO}_2$ ; hexane/AcOEt) to afford **4**.

## 4,4-Dimethyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**4a**)

White powder, yield: 0.47 g (97%), m.p. 128-131°C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1794, 1712, 1626, 1358  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 1.98 (s, 6 H, 2 Me), 3.23 (s, 2 H,  $\text{CH}_2$ ), 7.80 (t,  $^3J = 8.1$  Hz, 1 H, CH), 7.81 (d,  $^3J = 7.6$  Hz, 1 H, CH), 8.06 (td,  $^3J = 8.56$  Hz,  $^4J = 1.15$  Hz, 1 H, 1 CH), 7.81 (d,  $^3J = 7.8$  Hz, 1 H, CH).  $^{13}\text{C}$  NMR: 26.5 (2 Me), 33.8 (C), 44.3 ( $\text{CH}_2$ ), 111.1 (C), 114.0 (C), 116.4 (CH), 123.1 (CH), 124.4 (CH), 132.6 (CH), 152.7 (C), 156.0 (C), 159.5 (C=O), 164.8 (C=O). EI-MS: 245 ( $\text{M}^+ + 1$ , 95), 244 ( $\text{M}^+$ , 85), 229 (65), 216 (45), 201 (100), 121 (50), 92 (40). Anal. Calcd for  $\text{C}_{14}\text{H}_{12}\text{O}_4$  (244.24): C 68.85, H 4.95%. Found: C 68.10, H 5.01%.

## 4-Ethyl-4-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**4b**)

White powder, yield: 0.45 g (87%), m.p. 100-103 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1796, 1716, 1624, 1377  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 1.33 (t,  $^3J = 7.5$  Hz, 3 H, Me), 1.92 (s, 3 H, Me), 2.06 (dq,  $^2J = 6.7$  Hz,  $^3J = 7.4$  Hz, 1 H, CH), 2.56 (dq,  $^2J = 6.7$  Hz,  $^3J = 7.4$  Hz, 1 H, CH), 3.07 (d,  $^2J = 15.9$  Hz, 1 H, CH), 3.30 (d,  $^2J = 15.9$  Hz, 1 H, CH), 7.74-7.77 (m, 2 H, 2 CH), 8.02 (td,  $^3J = 7.35$  Hz,  $^4J = 1.55$  Hz, 1 H, 1 CH), 8.26 (dd,  $^3J = 8.1$  Hz,  $^4J = 1.45$  Hz, 1 H, CH).  $^{13}\text{C}$  NMR: 8.90 (Me), 25.3 (Me), 31.7 ( $\text{CH}_2$ ), 37.6 (C), 40.9 ( $\text{CH}_2$ ), 109.6 (C), 113.6 (C), 116.3 (CH), 122.9 (CH), 124.3 (CH), 132.6 (CH), 152.7 (C), 156.8 (C), 159.5 (C=O), 165.3 (C=O). EI-MS: 259 ( $\text{M}^+ + 1$ , 95), 258 ( $\text{M}^+$ , 85), 243 (74), 230 (42), 215 (100), 121 (44), 92 (42). Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_4$  (258.27): C 69.76, H 5.46%. Found: C 69.22, H 5.40%.

## 4-Methyl-4-propyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**4c**)

White powder, yield: 0.42 g (87%), m.p. 87-93 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1794, 1710, 1622, 1358  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 1.36 (t,  $^3J = 7.3$  Hz, 3 H, Me), 1.64-1.79 (m, 2 H,  $\text{CH}_2$ ), 1.95 (s, 3 H, Me), 2.01 (dt,  $^2J = 4.4$  Hz,  $^3J = 12.8$  Hz, 1 H, CH), 2.48 (dt,  $^2J = 4.4$  Hz,  $^3J = 12.8$  Hz, 1 H, CH), 3.09 (d,  $^2J = 15.9$  Hz, 1 H, CH), 3.31 (d,  $^2J = 15.9$  Hz, 1 H, CH), 7.75-7.78 (m, 2 H, 2 CH), 8.02 (td,  $^3J = 8.8$  Hz,  $^4J = 1.4$  Hz, 1 H, 1 CH), 8.27 (dd,  $^3J = 8.0$  Hz,  $^4J = 1.2$  Hz, 1 H, CH).  $^{13}\text{C}$  NMR: 14.3 (Me), 17.9 (Me), 25.7 ( $\text{CH}_2$ ), 37.4 (C), 41.4 ( $\text{CH}_2$ ), 41.5 ( $\text{CH}_2$ ), 109.9 (C), 113.6 (C), 116.4 (CH), 123.0 (CH), 124.3 (CH), 132.5 (CH), 152.7 (C), 156.6 (C), 159.5 (C=O), 165.2 (C=O). EI-MS: 273 ( $\text{M}^+ + 1$ , 95), 272 ( $\text{M}^+$ , 85), 257 (65), 244 (58), 229 (100), 121 (60), 92 (42). Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4$  (272.30): C 70.58, H 5.92%. Found: C 69.22, H 5.59%.

**4-Isobutyl-4-methyl-3,4-dihydro-2H,5H-pyrano[3,2-c]chromene-2,5-dione (4d)**

White powder, yield: 0.37 g (65%), m.p. 107-108°C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1797, 1710, 1620, 1359  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 0.93 (d,  $^3J = 6.6$  Hz, 3 H, Me), 0.97 (d,  $^3J = 6.6$  Hz, 3 H, Me), 1.56 (s, 3 H, Me), 1.59 (dd,  $^2J = 5.3$  Hz,  $^3J = 14.4$  Hz, 1 H, CH), 1.70-1.75 (m, 1 H, CH), 2.04 (dd,  $^2J = 5.3$  Hz,  $^3J = 14.4$  Hz, 1 H, CH), 2.69 (d,  $^2J = 15.9$  Hz, 1 H, CH), 2.96 (d,  $^2J = 15.8$  Hz, 1 H, CH), 7.35-7.38 (m, 2 H, 2 CH), 7.62 (td,  $^3J = 7.37$  Hz,  $^4J = 1.5$  Hz, 1 H, 1 CH), 7.89 (dd,  $^3J = 7.9$  Hz,  $^4J = 1.5$  Hz, 1 H, CH).  $^{13}\text{C}$  NMR: 24.7 (Me), 25.3 (CH), 25.6 (Me), 26.7 (Me), 37.9 (C), 42.4 ( $\text{CH}_2$ ), 47.7 ( $\text{CH}_2$ ), 111.2 (C), 114.0 (C), 116.9 (CH), 123.5 (CH), 124.7 (CH), 133.0 (CH), 153.1 (C), 156.7 (C), 160.1 (C=O), 165.7 (C=O). EI-MS: 287 ( $\text{M}^+ + 1$ , 80), 244 ( $\text{M}^+$ , 68), 272 (65), 259 (45), 244 (100), 121 (50), 92 (30). Anal. Calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_4$  (286.32): C 71.31, H 6.34%. Found: C 71.0, H 6.22%.

**Preparation of 4-aryl-3,4-dihydro-2H,5H-pyrano[3,2-c]chromene-2,5-diones (10):***General procedure*

To a stirred solution of benzaldehyde (0.21 g, 2 mmol) and Meldrum's acid (0.29 g, 2 mmol) in 50% aqueous EtOH (10 mL) was added 4-hydroxycoumarin (0.32 g, 2 mmol) and proline (11.5 mg, 10 mol%). The reaction mixture was stirred at reflux for 40 min. After completion of the reaction (monitored by TLC), the precipitate was collected by filtration and washed by cold 50% aqueous EtOH (5 mL) to afford **10**.

**4-Phenyl-3,4-dihydro-2H,5H-pyrano[3,2-c]chromene-2,5-dione (10a)**

White powder, yield: 0.55 g (94%), m.p. 69-171°C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1788, 1707, 1630, 1104  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 3.15 (dd,  $^2J = 16.2$  Hz,  $^3J = 1.7$  Hz, 1 H, CH), 3.21 (dd,  $^2J = 16.2$  Hz,  $^3J = 7.6$  Hz, 1 H, CH), 4.54 (dd,  $^3J = 7.6$  Hz,  $^3J = 1.7$  Hz, 1 H, CH), 7.26-7.29 (m, 3 H, 3 CH), 7.31 (d,  $^3J = 6.8$  Hz, 1 H, CH), 7.32 (d,  $^3J = 6.9$  Hz, 1 H, CH), 7.36-7.39 (m, 2 H, 2 CH), 7.62 (t,  $^3J = 7.3$  Hz, 1 H, CH), 7.92 (dd,  $^3J = 8.2$  Hz,  $^4J = 1.6$  Hz, 1 H, CH).  $^{13}\text{C}$  NMR: 36.3 ( $\text{CH}_2$ ), 36.4 (CH), 106.8 (C), 113.9 (C), 117.3 (CH), 123.2 (CH), 125.1 (CH), 127.1 (2 CH), 128.5 (CH), 129.7 (2 CH), 133.4 (CH), 139.8 (C), 153.6 (C), 157.7 (C), 161.2 (C=O), 164.7 (C=O). EI-MS: 292 ( $\text{M}^+$ , 8), 264 (5), 249 (5), 111 (18), 95 (18), 85 (30), 71 (58), 57 (100), 43 (94). Anal. Calcd for  $\text{C}_{18}\text{H}_{12}\text{O}_4$  (292.29): C 73.97, H 4.14%. Found: C 73.70, H 4.31.

**4-(3-Bromophenyl)-3,4-dihydro-2H,5H-pyrano[3,2-c]chromene-2,5-dione (10b)**

White powder, yield: 0.68 g (92%), m.p. 170-172°C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1736, 1692, 1449, 1109  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 3.13 (dd,  $^2J = 16.2$  Hz,  $^3J = 1.6$  Hz, 1 H, CH), 3.21 (dd,  $^2J = 16.2$  Hz,  $^3J = 7.7$  Hz, 1 H, CH), 4.54 (dd,  $^2J = 7.7$  Hz,  $^3J = 1.6$  Hz, 1 H, CH), 7.16-7.22 (m, 2 H, 2 CH), 7.38-7.42 (m, 4 H, 4 CH), 7.64 (t,  $^3J = 7.3$  Hz, 1 H, CH), 7.92 (dd,  $^3J = 8.0$  Hz,  $^4J = 1.3$  Hz, 1 H, CH).  $^{13}\text{C}$  NMR: 36.0 ( $\text{CH}_2$ ), 36.3 (CH), 105.9 (C), 113.9 (C), 117.4 (CH), 123.3 (CH), 123.8 (C), 125.2 (CH), 125.6 (CH), 130.3 (CH), 131.3 (CH), 131.7 (CH), 133.6 (CH), 142.0 (C), 153.7 (C), 158.0 (C), 161.0 (C=O), 164.1 (C=O). EI-MS: 371 ( $\text{M}^+$ , 11), 343 (16), 328 (18), 111 (17), 95 (16), 85 (35), 71 (55), 57 (100), 43 (100). Anal. Calcd for  $\text{C}_{18}\text{H}_{11}\text{BrO}_4$  (371.2): C 58.25, H 2.99%. Found: C 58.42, H 3.05%.

**4-(4-Methylphenyl)-3,4-dihydro-2H,5H-pyrano[3,2-c]chromene-2,5-dione (10c)**

White powder, yield: 0.52 g (85%), m.p. 68-170 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1785, 1701, 1658, 1097  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 2.29 (s, 3 H,  $\text{CH}_3$ ), 3.11 (dd,  $^2J = 16.1$  Hz,  $^3J = 1.8$  Hz, 1 H, CH), 3.18 (dd,  $^2J = 16.1$  Hz,  $^3J = 7.5$  Hz, 1 H, CH), 4.48 (dd,  $^3J = 7.5$  Hz,  $^3J = 1.8$  Hz, 1 H, CH), 7.08 (d,  $^3J = 6.0$  Hz, 2 H, 2 CH), 7.12 (d,  $^3J = 6.0$  Hz, 2 H, 2 CH), 7.34-7.40 (m, 2 H, 2 CH), 7.62 (t,  $^3J = 7.2$  Hz, 1 H, 1 CH), 7.90 (dd,  $^3J = 8.0$  Hz,  $^4J = 1.4$  Hz, 1 H, CH).  $^{13}\text{C}$  NMR: 21.0 ( $\text{CH}_3$ ), 35.6 ( $\text{CH}_2$ ), 36.1 (CH), 106.6 (C), 113.7 (C), 116.9 (CH), 122.8 (CH), 126.4 (CH), 126.5 (2 CH), 129.3 (CH), 129.9 (2 CH), 136.4 (C), 137.8 (C), 153.2 (C), 157.1 (C), 160.7 (C=O), 164.3 (C=O). EI-MS: 306 ( $\text{M}^+$ , 7), 278 (12), 263 (10), 111 (15), 95 (15), 85 (25), 71 (55), 57 (100), 43 (96). Anal. Calcd for  $\text{C}_{19}\text{H}_{14}\text{O}_4$  (306.32): C 74.50, H 4.61%. Found: C 74.32, H 4.49%.

**4-(4-Methoxyphenyl)-3,4-dihydro-2H,5H-pyrano[3,2-c]chromene-2,5-dione (10d)**

White powder, yield: 0.53 g (87%), m.p. 143-145°C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1777, 1699, 1659, 1660, 1098  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 3.08 (dd,  $^3J = 16.1$  Hz,  $^2J = 1.6$  Hz, 1H, CH), 3.17 (dd,  $^3J = 16.1$  Hz,  $^3J = 7.4$  Hz, 1 H, CH), 3.74 (s, 3 H,  $\text{OCH}_3$ ), 4.48 (dd,  $^3J = 7.4$  Hz,  $^2J = 1.8$  Hz, 1 H, CH), 6.82 (d,  $^3J = 8.6$  Hz, 2 H, 2 CH), 7.16 (d,  $^3J = 8.6$  Hz, 2 H, 2 CH), 7.34-7.39 (m, 2 H, 2 CH), 7.59 (t,  $^3J = 8.2$  Hz, 1 H, 1 CH), 7.90 (dd,  $^3J = 9.0$  Hz,  $^4J = 1.3$  Hz, 1 H, CH).  $^{13}\text{C}$  NMR: 35.2 ( $\text{CH}_2$ ), 36.2 (CH), 55.3 ( $\text{OCH}_3$ ), 106.7 (C), 114.7 (2 CH), 116.6 (C), 116.9 (CH), 127.6 (CH), 127.8 (2 CH), 132.7 (C), 132.8 (CH), 153.2 (C), 157.0 (C), 158.5 (C), 159.3 (C), 160.8 (C=O), 164.4 (C=O). EI-MS: 322

(M<sup>+</sup>, 9), 294 (14), 279 (12), 111 (16), 95 (15), 85 (22), 71 (55), 57 (100), 43 (92). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>O<sub>5</sub> (322.31): C 70.80, H 4.38%. Found: C 71.02, H 4.49%.

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