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ORIGINAL PAPER

# Carbon-based leaving group capability of Meldrum's acid in substitution reactions: a new strategy toward the synthesis of 4-phenyl-3, 4-dihydro-2H-benzo[g]chromene-2, 5, 10-triones

**Milad Pedarpour Vajargahy**[1] · **Minoo Dabiri**[1] · **Ayoob Bazgir**[1]

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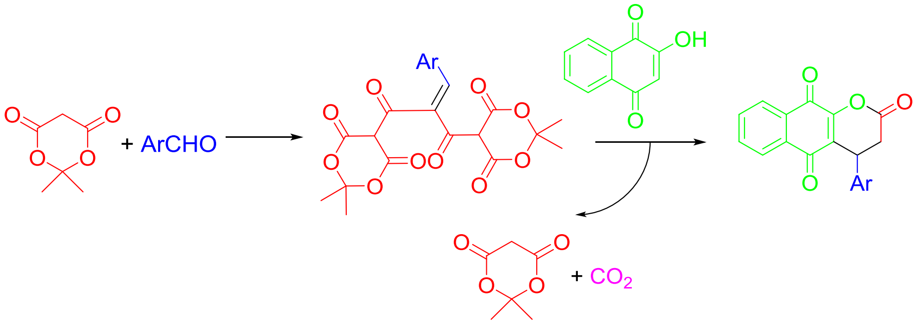
**Abstract** An efficient and straightforward method for the synthesis of new 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) derivatives by the reaction of Meldrum's acid and aldehydes under mild reaction conditions is reported. Furthermore, the leaving group potency of Meldrum's acid molecules toward the synthesis of 3,4-dihydro-2H-benzo[g]chromene-2,5,10-triones is investigated.

## Graphical Abstract



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✉ Minoo Dabiri
m_dabiri@sbu.ac.ir

✉ Ayoob Bazgir
a_bazgir@sbu.ac.ir

[1] Department of Chemistry, Shahid Beheshti University, General Campus, Tehran 1983963113, Iran

**Keywords** 3,4-Dihydro-2H-benzo[g]chromene-2,5,10-triones · Meldrum's acid arylidene Meldrum's acid · Benzo[g]chromene-triones · Meldrum's acid · Arylidene Meldrum's acid · 2-Hydroxynaphthalene-1,4-dione

## Introduction

The use of environmentally friendly methods and reagents to deplete undesirable products, harsh work-up procedures, and evaluation of toxic gases is important in synthetic chemistry and the chemical industry. Within the recent years, the development of sustainable, eco-friendly routes for the construction of medicinally important compounds has become a significant area in the field of synthesis [1]. Reactions that can be performed in the presence of benign solvent such as water, ethanol, or in the absence of solvents are a worthwhile aspect of green chemistry [2, 3].

Meldrum's acid and its derivatives have garnered a great deal of interest regarding their value as reagents for chemical synthesis and due to their unusually high acidities [4–10], serving as powerful acylating agents in C–C [11–17], C–O, and C–N bond forming reactions [18, 19] and as building blocks in the synthesis of numerous natural products. Due to its great acidity (pKa 7.5) [20] and tendency to regenerate acetone, Meldrum's acid appears to be an exceptional reagent in organic synthesis [21, 22].

Although Knoevenagel condensation of aldehydes and Meldrum's acid for the synthesis of arylidene Meldrum's acids or 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) has been reported in various conditions [23–26], to the best of our knowledge, employing aldehydes and Meldrum's acid for the synthesis of 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) has not been reported yet. Herein, for the first time, the preparation of novel Meldrum's acid derivatives, 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) derivatives, by the reaction of aldehydes and Meldrum's acid is reported.

## Experimental

All starting materials were obtained from Merck or Acros and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a FT-IR 102 MB BOMEM apparatus. $^1$H and $^{13}$C NMR spectra were recorded on a BRUKERDRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz, respectively. $^1$H and $^{13}$CNMR spectra were obtained in DMSO-$d_6$ using TMS as internal standard.

### X-ray crystallography

The X-ray diffraction measurements were taken with a STOE IPDS-II diffractometer with graphite-monochromated MoKa radiation. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 4998 unique reflections for **6a**. Data were collected at a temperature of 298(2) K to a maximum 2*q* value of 51.988 and in a series of w scans in 18 oscillations and integrated using the Stoe X-AREA [27] software package. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods and refined on F2 by full-matrix least-squares procedure. All hydrogen atoms were added at ideal positions and constrained to ride on their parent atoms, with Uiso(H) = 1.2 Ueq. All refinements were performed by using the X-STEP32 crystallographic software package [28]. Complete crystallographic data for compound **6a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-1455796. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

*Typical procedure for the preparation of 5,5′-(2-(2-Nitrobenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3a)** A mixture of 2-nitrobenzaldehyde (1 mmol), Meldrum's acid (3 mmol), and $Et_3N$ (10 mol %) in EtOH (5 mL) was stirred at room temperature for 24 h. After completion of the reaction, the reaction mixture was filtered and the precipitate was purified using flash chromatography to afford the pure product **3a**: Yield 85%. white powder; m.p. 174–175 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3001, 2930, 2869, 1784, 1744, 1529, 1314. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$1.71 (s, 6H, 2Me), 1.78 (s, 6H, 2Me), 4.03 (s, 2 CH), 7.61 (d, $^3J = 7.5$ Hz, 1H arom), 7.74 (t, $^3J = 8$ Hz, 1H arom), 7.85 (t, $^3J = 8$ Hz, 1H arom), 8.27 (d, $^3J = 7.5$ Hz, 1H arom), 8.85 (1H, s). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.3, 27.4, 27.6, 31.1, 105.8, 106.2, 117.9, 124.8, 130.7, 130.8, 131.4, 134.7, 146.8, 156.6, 159.5, 161.7, 164.6, 168.8. MS, m/z: 489 ($M^+$). Anal. Calcd. for $C_{22}H_{19}NO_{12}$: C, 53.99; H, 3.91; N, 2.86. Found: C, 53.91; H, 3.83; N, 2.94%.

*5,5′-(2-Benzylidenemalonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3b)** Yield 80%. White powder; m.p. 164–165 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3001, 2950, 2904, 2860, 1775, 1737. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.72 (s, 6H, 2Me), 1.77 (s, 6H, 2Me), 4.03 (s, 2 CH), 7.49 (m, 2H arom), 7.60 (m, 1H arom), 8.00 (d, $^3J = 7.5$ Hz, 2H arom), 8.38 (1H, s). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.4, 27.5, 31.1, 105.1, 106.2, 116.2, 128.9, 129.3, 132.3, 133.3, 133.5, 157.0, 160.0, 163.0, 168.8. MS, m/z: ↱444 (M$^+$). Anal. Calcd. for $C_{22}H_{20}O_{10}$: C, 59.46; H, 4.54. Found: C, 59.38; H, 4.44%.

*5,5′-(2-(2-bromobenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3c)** Yield 83%. White powder; m.p. 173–174 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 2999, 2925, 2860, 1784, 1742. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.71 (s, 6H, 2Me), 1.79 (s, 6H, 2Me), 4.03 (s, 2 CH), 7.44–7.46 (m, 2H, arom), 7.63 (m, 1H arom), 7.75 (d, $^3J = 7$ Hz, 1H arom), 8.41 (s, 1H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.4, 27.7, 31.2, 105.7, 106.3, 119.2, 123.7, 127.8, 129.2, 131.9, 132.9, 133.1, 133.6, 155.0, 159.2, 162.0, 164.6. MS, m/z: ↱522 (M$^+$). Anal. Calcd. for $C_{22}H_{19}BrO_{10}$: C, 50.50; H, 3.66. Found: C, 50.39; H, 3.57%.

*5,5′-(2-(3-Bromobenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3d)** Yield 81%. White powder; m.p. 165–166 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3079, 2907, 2811, 1791, 1648. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.71 (s, 6H, 2Me), 1.77 (s, 6H, 2Me), 4.03 (s, 2 CH), 7.46 (t, $^3J = 7.5$ Hz, 1H arom), 7.75 (d, $^3J = 7.5$ Hz, 1H arom), 7.91 (d, $^3J = 7.5$ Hz, 1H arom), 8.22 (s, 1H arom), 8.35 (s, 1H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.4, 27.5, 36.4, 104.8, 105.5, 106.2, 116.2, 122.4, 130.1, 131.7, 133.4, 135.1, 135.9, 155.8, 159.3, 162.6, 163.2. MS, m/z: ↱522 (M$^+$). Anal. Calcd. for $C_{22}H_{19}BrO_{10}$: C, 50.50; H, 3.66. Found: C, 50.61; H, 3.78%.

*5,5′-(2-(4-Methylbenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3e)** Yield 87%. White powder; m.p. 195–196 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3001, 2948, 2915, 2865, 1774, 1736. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.71 (s, 6H, 2Me), 1.75 (s, 6H, 2Me), 2.39 (s, 3H, Me), 4.03 (s, 2H, CH), 7.32 (d, $^3J = 9$ Hz, 2H arom), 7.98 (d, $^3J = 9$ Hz, 2H arom), 8.33 (s, 1H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 21.9, 27.4, 37.1, 104.9, 106.2, 114.7, 129.2, 129.6, 129.7, 134.0, 144.9, 157.2, 160.2, 163.2, 164.6. MS, m/z: 458 (M$^+$). Anal. Calcd. for $C_{23}H_{22}O_{10}$: C, 60.26; H, 4.84. Found: C, 60.17; H, 4.73%.

*5,5′-(2-(3-Nitrobenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3f)** Yield 83%. White powder; m.p. 156–157 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3003, 2922, 2860, 1773, 1737, 1537, 1319. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.70 (s, 6H, 2Me), 1.78 (s, 6H, 2Me), 4.02 (s, 2H, CH), 7.78 (d, $^3J = 7.5$, 1H arom), 8.29 (d, $^3J = 7.5$ Hz, 1H arom), 8.37 (d, $^3J = 7.5$ Hz, 1H arom), 8.52 (s, 1H arom), 8.87 (1H, s). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.4, 27.6, 31.1, 102.8, 106.1, 118.1, 122.8, 123.4, 124.7, 130.2, 133.9, 147.9, 148.4, 154.4, 159.5, 162.6, 168.6. MS, m/z: ↱489 (M$^+$). Anal. Calcd. for $C_{25}H_{19}NO_{12}$: C, 53.99; H, 3.91; N, 2.86. Found: C, 54.12; H, 4.02; N, 2.77%.

*5,5′-(2-(4-Nitrobenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3g)** Yield 79%. White powder; m.p. 186–187 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3006, 2917, 2862, 1772, 1734, 1527, 1317. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.72 (s, 6H, 2Me), 1.76 (s, 6H, 2Me), 4.03 (s, 2H, CH), 8.06 (d, $^3J = 9.0$ Hz, 2H arom), 8.28 (d, $^3J = 9.0$ Hz, 2H arom), 8.51 (s, 1H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.7, 31.1, 102.8, 105.6, 119.6, 123.6, 124.7, 133.0, 139.0, 149.1, 154.3, 159.5, 162.1, 162.6. MS, m/z: 489 (M$^+$). Anal. Calcd. for $C_{25}H_{19}NO_{12}$: C, 53.99; H, 3.91; N, 2.86. Found: C, 53.88; H, 4.00; N, 2.77%.

*5,5′-(2-(3-Hydroxybenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3h)** Yield 87%. White powder; m.p. 126–127 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3483, 3004, 2910, 2852, 1778, 1738. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.71 (s, 6H, 2Me), 1.75 (s, 6H, 2Me), 4.03 (s, 2H, CH), 6.98 (d, $^3J = 7.5$ Hz, 1H arom), 7.31(t, $^3J = 7.5$ Hz, 1H arom), 7.38 (d, $^3J = 7.5$ Hz, 1H arom), 7.47 (s, 1H arom), 8.25 (1H, s), 9.83 (1H, s, OH). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.4, 31.1, 105.0, 106.2, 116.0, 119.0, 120.9, 125.0, 130.0, 133.3, 157.1, 157.5, 159.9, 163.1, 164.6, 168.8. MS, m/z: 460 (M$^+$). Anal. Calcd. for $C_{22}H_{20}O_{11}$: C, 57.40; H, 4.38. Found: C, 57.50; H, 4.47%.

*5,5′-(2-(2-Fluorobenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3i)** Yield 75%. White powder; m.p. 173–174 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3001, 2909, 2948, 2910, 2864, 1779, 1737. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.71 (s, 6H, 2Me), 1.78 (s, 6H, 2Me), 4.02 (s, 2 CH), 7.29–7.36 (m, 2H arom), 7.57–7.61(m, 1H arom), 7.84 (t, $^3J = 7.5$ Hz, 1H arom), 8.34 (s, 1H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.5, 27.8, 31.2, 105.4, 106.0, 106.2, 116.1, 116.4, 119.5, 121.2, 124.6, 124.9, 132.6, 134.6, 148.4, 159.7, 162.1, 164.6. MS, m/z: 462 (M$^+$). Anal. Calcd. for $C_{22}H_{19}FO_{10}$: C, 57.15; H, 4.14. Found: C, 57.03; H, 4.04%.

*5,5′-(2-(3-Fluorobenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3j)** Yield 73%. White powder; m.p. 168–169 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3001, 2950, 2916, 2862, 1776, 1739. $^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.72 (s, 6H, 2Me), 1.78 (s, 6H, 2Me), 4.03 (s, 2H, CH), 7.44 (t, $^{3}J = 9.0$ Hz, 1H arom), 7.53–7.60(m, 1H arom), 7.77 (d, $^{3}J = 7.5$ Hz, 1H arom), 7.90 (d, $^{3}J = 10.5$ Hz, 1H arom), 8.38 (s, 1H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.4, 27.6, 31.1, 104.0, 105.3, 106.2, 117.5, 118.7, 119.8, 129.6, 130.8, 134.4, 155.3, 159.8, 162.7, 164.6, 168.8. MS, m/z: 462 (M$^+$). Anal. Calcd. for $C_{22}H_{19}FO_{10}$: C, 57.15; H, 4.14. Found: C, 57.07; H, 4.23%.

*5,5′-(2-(4-Chlorobenzylidene)malonyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione)* **(3k)** Yield 77%. White powder; m.p. 193–194 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3005, 2950, 2909, 2863, 1780, 1740. $^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 1.71 (s, 6H, 2Me), 1.76 (s, 6H, 2Me), 4.03 (s, 2 CH), 7.57 (d, $^{3}J = 8.0$ Hz, 2H arom), 8.02 (d, $^{3}J = 8.0$ Hz, 2H arom), 8.37 (s, 1H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 27.4, 27.5, 31.1, 105.2, 106.2, 116.6, 129.0, 131.2, 131.4, 135.0, 138.1, 155.6, 159.9, 162.8, 164.6. MS, m/z: 478 (M$^+$). Anal. Calcd. for $C_{22}H_{19}ClO_{10}$: C, 55.18; H, 4.00. Found: C, 55.26; H, 4.09%.

*Typical procedure for the preparation of 4-Phenyl-3,4-dihydro-2H-benzo[g]chromene-2,5,10-trione* **(6a)** A mixture of 2-hydroxynaphthalene-1,4-dione (**5**) (1 mmol), 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) **(3b)** (1 mmol), and Et$_3$N (10 mol %) in EtOH (5 mL) was stirred at room temperature for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was filtered and the precipitate was recrystallized from chloroform/ethanol to afford the pure product **(6a)** [29]: Yield 86%. Yellow powder; m.p. 207–208 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3095, 3083, 3006, 2901, 1790, 1679, 1660, 1642, 1592. $^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 2.89 (bd, 1H, CH), 3.38 (dd, $^{1}J = 16.0$ Hz, $^{2}J = 7.0$ Hz CH), 4.60 (d, $^{3}J = 7.5$ Hz, CH), 7.27–7.32 (m, 4H, arom), 7.89–7.91 (m, 2H arom), 7.99–8.02 (m, 1H arom), 8.10–8.13 (m, 1H arom). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 35.0, 36.3, 125.4, 126.5, 126.7, 127.4, 128.1, 129.6, 131.5, 134.8, 135.1, 140.1, 152.6, 166.0, 177.6, 183.2. MS, m/z: 304 (M$^+$). Anal. Calcd. for $C_{19}H_{12}O_4$: C, 74.99; H, 3.98. Found: C, 75.11; H, 4.08%.

## X-ray data for 6a

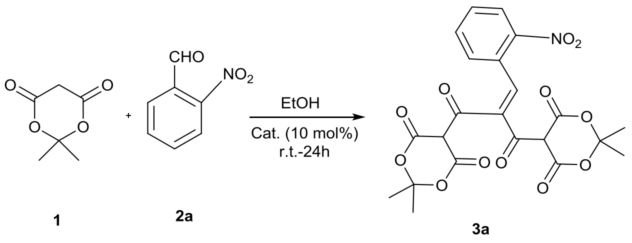
$C_{19}H_{12}O_4$, $M = 304.29$ g/mol, monoclinic system, space group P21/n, $a = 5.4870(13)$, $b = 10.4386(18)$, $c = 25.056(6)$ Å, $\alpha = 90^{\circ}$, $\beta = 91.50(2)^{\circ}$, $\gamma = 90^{\circ}$, $V = 1434.6(5)$ Å$^3$, $Z = 4$, $Dc = 1.409$ g.cm$^{-3}$, μ(Mo-Kα) = 0.099 mm$^{-1}$, crystal dimension of 0.50 × 0.49 × 0.35 mm. The structure was solved by using SHELXS. The structure refinement and data reduction were carried out with SHELXL of the X-Step32 suite of programs. The non-hydrogen atoms were refined anisotropically by full-matrix least squares on F$^2$ values to final $R_1 = 0.0608$, $wR_2 = 0.1113$, and $S = 1.021$ with 208 parameters using 3865 independent reflection ($\theta$ range = 2.54–29.18). Hydrogen atoms were located from expected geometry and were not refined.

*4-(P-tolyl)-3,4-dihydro-2H-benzo[g]chromene-2,5,10-trione* **(6b)** Yield 90%. Yellow powder; m.p. 187–188 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3024, 2919, 2854, 1793, 1680, 1656, 1634, 1594. $^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 2.27 (s, 3H, Me), 2.89 (bd, 1H, CH), 3.35 (dd, $^{1}J = 16.5$ Hz, $^{2}J = 7.0$ Hz CH), 4.56 (d, $^{3}J = 7.5$ Hz, CH), 7.12–7.18 (m, 4H arom), 7.87–7.90 (m, 2H arom), 8.00 (m, 1H arom), 8.11 (m, 1H arom). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 21.0, 34.6, 36.3, 125.6, 126.5, 126.6, 127.2, 130.0, 131.4, 131.5, 134.8, 135.1, 136.9, 137.3, 152.5, 166.0, 177.6, 183.1. MS, m/z: 318 (M$^+$). Anal. Calcd. For $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.35; H, 4.52%.

*4-(3-Bromophenyl)-3,4-dihydro-2H-benzo[g]chromene-2,5,10-trione* **(6c)** Yield 81%. Yellow powder; m.p. 214–215 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3075, 3046, 2905, 1791, 1681, 1657, 1637, 1590. $^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 2.90 (bd, 1H, CH), 3.38 (dd, $^{1}J = 16.0$ Hz, $^{2}J = 7.0$ Hz CH), 4.60 (d, $^{3}J = 7.5$ Hz, CH), 7.26–7.36 (m, 2H arom), 7.47 (d, $^{3}J = 7.5$ Hz, 1H arom), 7.61 (s, 1H arom), 7.89–7.91 (m, 2H arom), 7.99–8.01 (m, 1H arom), 8.10–8.13 (m, 1H arom). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 34.7, 36.2, 122.8, 124.3, 126.4, 126.6, 130.3, 131.0, 131.5, 131.6, 134.8, 135.0, 142.8, 153.0, 165.8, 177.5, 183.2. MS, m/z: 381 (M$^+$). Anal. Calcd. for $C_{19}H_{11}BrO_4$: C, 59.55; H, 2.89. Found: C, 59.46; H, 2.78%.

*4-(2-Nitrophenyl)-3,4-dihydro-2H-benzo[g]chromene-2,5,10-trione* **(6d)** Yield 89%. Yellow powder; m.p. 221–222 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3073, 2929, 2854, 1798, 1683, 1650, 1592, 1523, 1344. $^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 2.94 (bd, 1H, CH), 3.56 (dd, $^{1}J = 16.2$ Hz, $^{2}J = 8.7$ Hz CH),, 4.95 (d, $^{3}J = 7.5$ Hz, CH), 7.51–7.64 (m, 3H arom),, 7.90–7.92 (m, 3H arom), 8.07–8.14 (m, 2H arom). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 31.6, 35.2, 123.6, 125.9, 126.4, 126.7, 129.3, 129.8, 131.3, 131.5, 134.1, 134.8, 134.9, 135.1, 148.6, 153.4, 165.2, 177.4, 183.0. MS, m/z: 349 (M$^+$). Anal. Calcd. for $C_{19}H_{11}NO_6$:

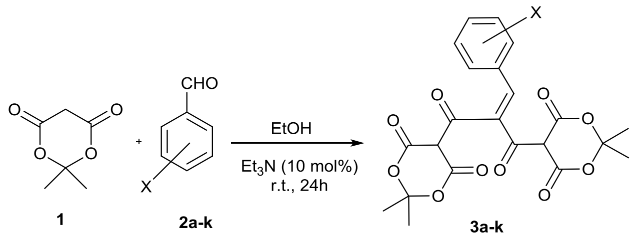
**Table 1** Optimization of the reaction conditions



| Entry | Solvent | Catalyst | Yield (%) |
|---|---|---|---|
| 1 | Toluene | $Et_3N$ | 31 |
| 2 | $CH_2Cl_2$ | $Et_3N$ | 38 |
| 3 | MeCN | $Et_3N$ | 62 |
| 4 | $H_2O$ | $Et_3N$ | Trace |
| 5 | MeOH | $Et_3N$ | 57 |
| 6 | EtOH | $Et_3N$ | 85 |
| 7 | EtOH | *p*-TSA | 52 |
| 8 | EtOH | $H_2SO_4$ | 56 |
| 9 | EtOH | Catalyst free | 49 |

2-nitro benzaldehyde (1 mmol), Meldrum's acid (3 mmol), cat. (10% mol), room temperature, reaction time = 24 h

**Table 2** Synthesis of products **3a–k**



| Product 3 | X | Yield (%) |
|---|---|---|
| **a** | 2-$NO_2$ | 85 |
| **b** | H | 80 |
| **c** | 2-Br | 83 |
| **d** | 3-Br | 81 |
| **e** | 4-Me | 87 |
| **f** | 3-$NO_2$ | 83 |
| **g** | 4-$NO_2$ | 79 |
| **h** | 3-OH | 87 |
| **i** | 2-F | 75 |
| **j** | 3-F | 73 |
| **k** | 4-Cl | 77 |

C, 65.33; H, 3.17; N, 4.01 Found: C, 65.42; H, 3.28; N, 3.92%.

*4-(3-Nitrophenyl)-3,4-dihydro-2H-benzo[g]chromene-2,5,10-trione* **(6e)** Yield 85%. Yellow powder; m.p. 235–236 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3085, 3035, 2930, 2852, 1800, 1685, 1659, 1637, 1532, 1346. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 2.99 (bd, 1H, CH), 3.43 (dd, $^1J$ = 16.2 Hz, $^2J$ = 7.8 Hz CH), 4.80 (d, $^3J$ = 7.5 Hz, CH), 7.62 (t, $^3J$ = 7.5 Hz, 1H arom), 7.79 (d, $^3J$ = 7.5 Hz, 1H arom), 7.86–7.91 (m, 2H arom), 7.98–8.00 (m, 1H arom), 8.10–8.15 (m, 2H arom), 8.27 (s, 1H arom). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 31.1, 34.7, 122.8, 123.1, 124.1, 126.5, 126.6, 131.0, 131.5, 134.1, 134.8, 135.0, 142.3, 148.7, 153.0, 165.7, 177.5, 183.2. MS, m/z: 349 (M$^+$). Anal. Calcd. for $C_{19}H_{11}NO_6$: C, 65.33; H, 3.17; N, 4.01. Found: C, 65.24; H, 3.25; N, 4.11%.

*4-(4-Nitrophenyl)-3,4-dihydro-2H-benzo[g]chromene-2,5,10-trione* **(6f)** Yield 86%. Yellow powder; m.p. 216–217 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3075, 2999, 2937, 2858, 1782, 1731, 1678, 1640, 1520, 1347. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 2.95 (bd, 1H, CH), 3.47 (bd, 1H, CH Overlapped with solvent), 4.77 (d, $^3J$ = 7.5 Hz, CH), 7.65–7.68 (d, $^3J$ = 7.5 Hz, 2H arom), 7.82–7.99 (m, 4H arom), 8.16–8.19 (d, $^3J$ = 7.5 Hz, 2H arom). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 31.2, 34.9, 124.1, 124.6, 126.2, 126.5, 126.6, 129.0, 131.5, 134.9, 135.1, 147.4, 147.7, 153.0, 165.5, 177.5, 183.1. MS, m/z: 349 (M$^+$). Anal. Calcd. for $C_{19}H_{11}NO_6$: C, 65.33; H, 3.17; N, 4.01. Found: C, 65.45; H, 3.30; N, 3.88%.

*4-(3-Hydroxyphenyl)-3,4-dihydro-2H-benzo[g]chromene-2,5,10-trione* **(6g)** Yield 93%. Yellow powder; m.p. 243–244 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3391, 3051, 3019, 2919, 1784, 1670, 1660, 1640, 1594. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 2.85 (bd, 1H, CH), 3.41 (d, 1H, CH Overlapped with solvent), 4.49 (d, $^3J$ = 7.5 Hz, CH), 6.65–6.72 (m, 3H arom), 7.12 (t, $^3J$ = 7.5 Hz, CH), 7.92 (bs, 2H arom), 8.01 (bs, 1H arom), 8.11 (bs, 1H arom), 9.49 (s, 1H, OH). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 34.8, 36.1, 114.1, 114.9, 117.8, 125.6, 126.5, 126.7, 130.6, 131.3, 131.4, 134.9, 135.2, 141.3, 152.3, 158.1, 166.0, 177.6, 183.1. MS, m/z: 320 (M$^+$). Anal. Calcd. for $C_{19}H_{12}O_5$: C, 71.25; H, 3.78. Found: C, 71.14; H, 3.66%.

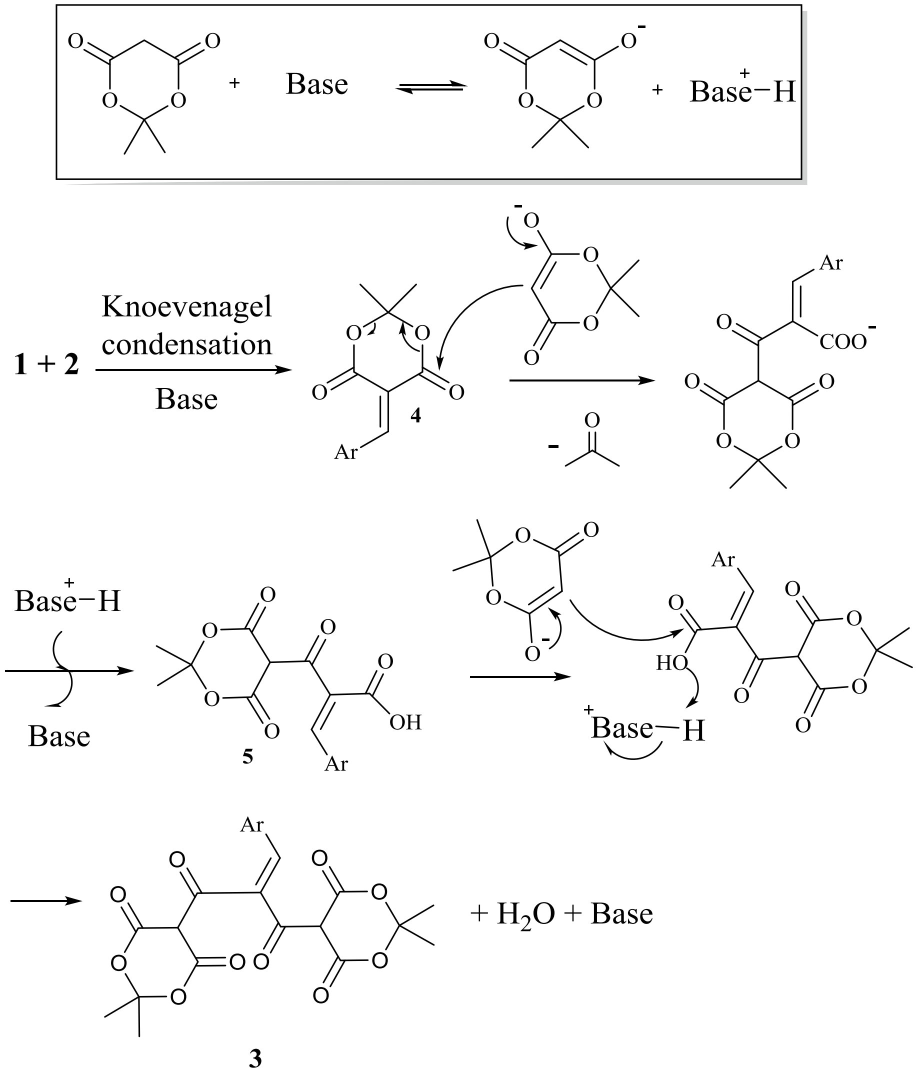
*4-(2-Fluorophenyl)-3,4-dihydro-2H-benzo[g]chromene-2,5,10-trione* **(6h)** Yield 86%. Yellow powder; m.p. 227–228 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3064, 3010, 2923, 1796, 1682, 1658, 1640, 1594. $^1$H NMR

(300 MHz, DMSO-$d_6$): $\delta_H$ 2.81 (bd, 1H, CH), 3.42 (dd, 1 $J = 15.9$ Hz, $^2J = 8.1$ Hz CH), 4.75 (d, $^3J = 7.5$ Hz, CH), 7.10 (t, $^3J = 6$ Hz, 1H arom), 7.22–7.35 (m, 3H arom), 7.88 (bs, 2H arom), 7.96 (s, 1H arom), 8.09 (s, 1H arom). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 29.6, 34.8, 116.3 (d, $^2J = 21.7$ Hz), 123.6, 125.3, 126.4, 126.6, 126.8, 129.4, 130.3 (d, $^3J = 7.8$ Hz), 131.4, 134.8, 135.1, 153.0, 160.2 (d, $^1J = 243.8$ Hz), 165.3, 177.4, 183.0. MS, m/z: 322 (M$^+$). Anal. Calcd. for $C_{19}H_{11}FO_4$: C, 70.81; H, 3.44. Found: C, 70.73; H, 3.53%.

*4-(4-Chlorophenyl)-3,4-dihydro-2H-benzo[g] chromene-2,5,10-trione* **(6i)** Yield 82%. Yellow powder; m.p. 214–215 °C. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3102, 3019, 2936, 1792, 1680, 1656, 1637, 1593. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H$ 2.89 (bd, 1H, CH), 3.37 (dd, $^1J = 16.2$ Hz, $^2J = 7.5$ Hz CH), 4.61 (d, $^3J = 7.5$ Hz, 1H), 7.38 (s, 4H arom), 7.89–7.90 (m, 2H arom), 7.98–7.99 (m, 1H arom), 8.09–8.10 (m, 1H arom). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C$ 34.4, 36.1, 124.8, 126.5, 126.6, 129.4, 129.5, 131.4, 131.5, 132.7, 134.8, 135.0, 139.0, 152.7, 165.8, 177.5, 183.1. MS, m/z: 338 (M$^+$). Anal. Calcd. for $C_{19}H_{11}ClO_4$: C, 67.37; H, 3.27. Found: C, 67.46; H, 3.17%.

## Results and discussion

Initially, the reaction of 2-nitro benzaldehyde **2a** (1 mmol) and Meldrum's acid **1** (3 mmol) in the presence of various catalysts and solvents was investigated (Table 1). As shown in Table 1, the use of ethanol as a green solvent at room temperature in the presence of $Et_3N$ (10 mol %) as base catalyst allowed the formation of 5,5′-(2-(2-nitrobenzylidene)malonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) **(3a)** in 85% yield (Table 1, entry 6).



**Scheme 1** Proposed mechanism for the synthesis of products **3**

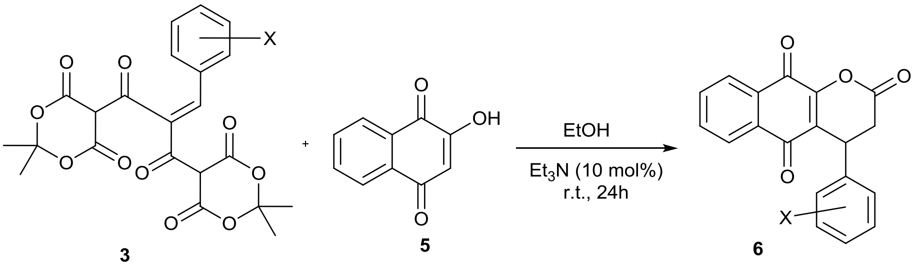
According to the optimized conditions, various aldehydes **2a–k** were selected to react with Meldrum's acid **1** under optimal conditions to give 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) **3a–k** in good yields (Table 2).

All the products were characterized by IR, mass, NMR spectra, and elemental analysis. The mass spectrum of **3a** shows the molecular ion peak at m/z 489. The IR spectrum of **3a** exhibits distinct absorption bands due to carbonyl groups at 1784 and 1744 $cm^{-1}$. The $^1$H-NMR spectrum of **3a** consisted of two sharp singlet for the methyl groups of Meldrum's acid ($\delta_H$ 1.71, 1.78 ppm), one sharp singlet ($\delta_H$ 4.03 ppm) for two methine groups of two Meldrum's acid. Four aromatic hydrogens were observed as two doublets ($\delta_H$ 7.61 and 8.27 ppm, $J$ = 8.0 Hz) and two triplet ($\delta_H$ 7.74 and 7.85 ppm, $J$ = 8.0 Hz), and finally, the alkylidene hydrogen was appeared as a sharp singlet (δH 8.85 ppm). The $^1$H-decoupled $^{13}$C-NMR spectrum of **3a** shows 18 distinct signals, in agreement with the proposed structure.

As of yet, in spite of great deal of research around the interesting properties related to Meldrum's acid, there has not been any reports in the literature which indicates that Meldrum's acid could react with aldehyde with 3:1 molar ratio. Surprisingly, and in continuation of the studies around the unique characteristics of the Meldrum's acid, we observed for the first time that one molecule of arylidene Meldrum's acid **4** (formed in situ by the reaction of Meldrum's acid **1** and aldehyde **2**) was decomposed to acetone and $H_2O$ by the reaction with second molecule of Meldrum's acid to afford intermediate **5**. The intermediate **5** reacts with the other molecule of Meldrum's acid **1** and after elimination of water [30] affords 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) derivatives **3** (Scheme 1).

Fillion et al. for the first time reported the leaving group ability of Meldrum's acid in hydrogenolysis of unstrained carbon–carbon σ-bonds. They have described substitution reactions employing Meldrum's acid and 5-methyl Meldrum's acid as carbon-based leaving groups which transform unstrained quaternary and tertiary benzylic $Csp^3$–$Csp^3$ bonds into $Csp^3$–X bonds (X=C, H, N) [31, 32]. So, we investigated the leaving group ability of Meldrum's acid in the reaction of 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) derivatives **3** with 2-hydroxynaphthalene-1,4-dione **5** and obtained 4-phenyl-3,4-dihydro-2*H*-benzo[g]chromene-2,5,10-trione derivatives **6a–j** in good isolated yields (Table 3). Up to now, the synthesis of benzo[g]chromene-2,5,10-trione has reported via a three-component reaction of aldehyde, Meldrum's acid, and 2-hydroxynaphthalene-1,4-dione [33–35]. Fortunately, herein for the first time, we report the leaving group capability of Meldrum's acid in an organic reaction which includes functionalization of $Csp^2$–$Csp^3$ bond into $Csp^2$–X bond (X=O). This observation brings about the fact that Meldrum's acid is not only capable of

**Table 3** Synthesis of benzo[g]chromene-2,5,10-trione **6**



| Product 6 | X | Yield (%) |
|---|---|---|
| **a** | H | 86 |
| **b** | 4-Me | 90 |
| **c** | 3-Br | 81 |
| **d** | 2-$NO_2$ | 89 |
| **e** | 3-$NO_2$ | 85 |
| **f** | 4-$NO_2$ | 86 |
| **g** | 3-OH | 93 |
| **h** | 2-F | 86 |
| **i** | 4-Cl | 82 |

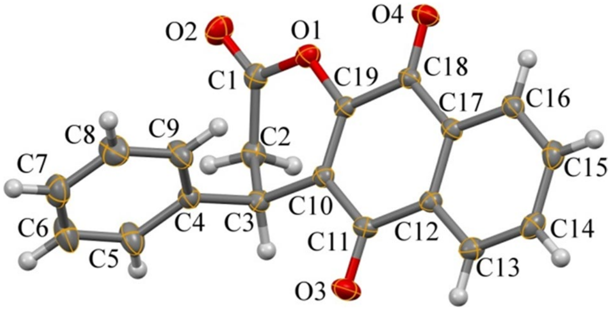


**Fig. 1** ORTEP diagram of product **6a**

decomposing to acetone and $CO_2$ [36], but can also serve as a potential leaving group in organic synthesis.

The structures of products **6** were established by IR, $^1$H NMR, and $^{13}$CNMR spectroscopy. The structure of **6a** was confirmed by a single-crystal X-ray analysis (Fig. 1).

A possible mechanism for the formation of **6** is proposed in Scheme 2. Michael-type addition reaction of the 2-hydroxynaphthalene-1,4-dione **5** and the 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) 3 followed by cyclization and losing one molecule of Meldrum's acid leads to intermediate **8**. The nucleophilic attack of $H_2O$ on the carbonyl group of intermediate **8** followed by the extrusion of the second Meldrum's acid's molecule produces intermediate **9**. Finally, the decarboxylation reaction of **9** creates product **6** (Scheme 2).

## Conclusion

In summary, we have described a facile method for the synthesis of novel 5,5′-(2-benzylidenemalonyl)*bis*(2,2-dimethyl-1,3-dioxane-4,6-dione) derivatives with superb leaving group ability of Meldrum's acid molecules for the synthesis of benzo[g]chromene-triones. The reactions in both categories are easy to perform in good yields by using inexpensive starting materials. The operational simplicity, combined with environmental friendly aspect, makes this new heterocycle synthetic strategy highly attractive and promising for the development of compounds of potential synthetic interest. Finally, the arylidene framework presented here is likely to be inserted to organic structures regarding their potential bidentate leaving group capability.

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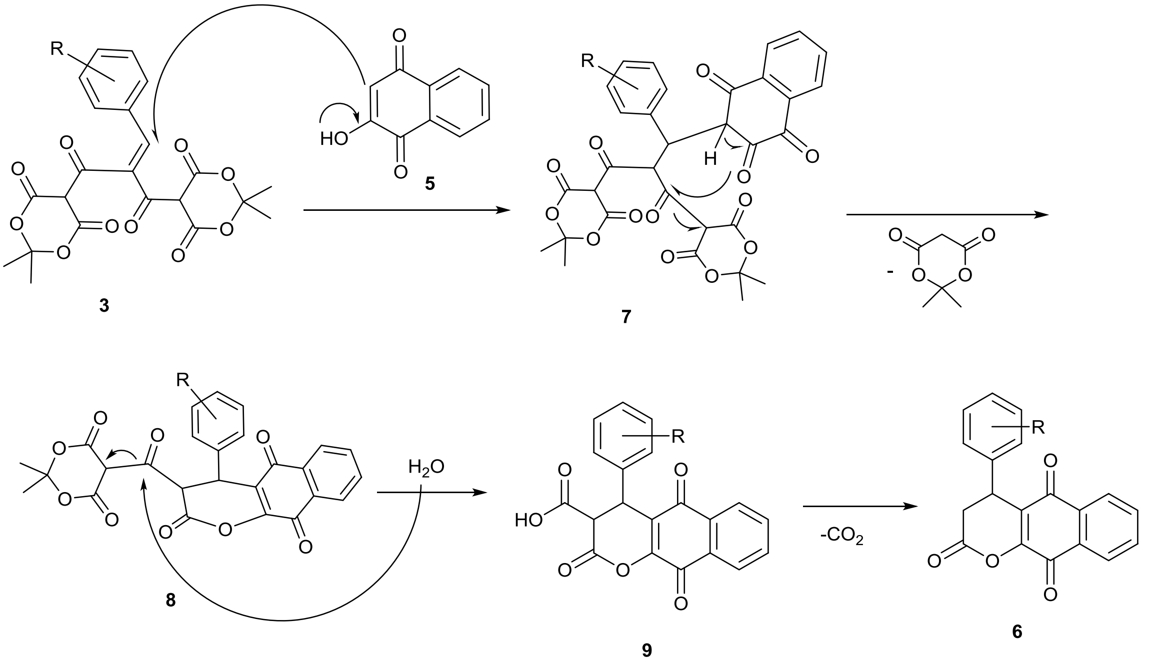

**Scheme 2** Proposed mechanism for the synthesis of products **6**

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