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Sonochemistry as a General Procedure for the Synthesis of Coumarins, Including Multigram Synthesis

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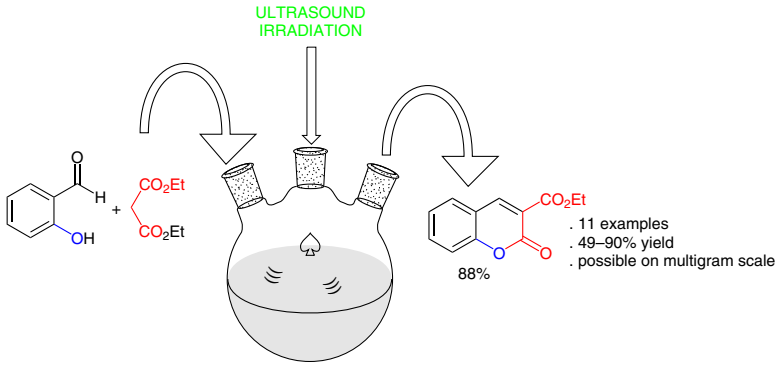

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Abstract This study describes a general procedure for the synthesis of different coumarins via sonochemistry using active methylene compounds and 2-hydroxybenzaldehydes or resorcinol. The application of sonochemistry for the synthesis of these compounds was also very effective on a multigram scale with a higher yield, higher amount of crystalline compound, and shorter reaction time compared with the compounds obtained using the classical procedures.

Key words coumarins, sonochemistry, synthesis, multigram scale, smaller scale

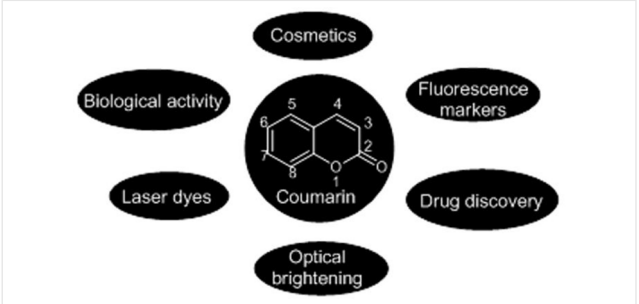


Figure 1 Applications of coumarin nucleus

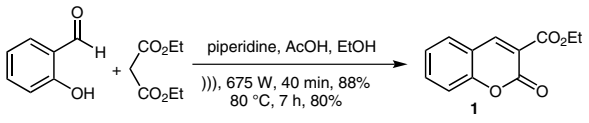
Coumarins are a class of natural products that are found in many plant species belonging to the benzopyrone family. This class and its derivatives are important compounds in the drug development and natural product fields because they possess a wide range of pharmacological activities, including anti-HIV, antibacterial, antifungal, anti-inflammatory, antileishmanial, antimalarial, antitumor, and antidepressant activities.[1,2] Coumarins also have applications in cosmetics an can be used as optical brightening agents, laser dyes, and fluorescence markers (Figure 1).[3–6] The synthesis of the coumarin nucleus was first described in 1868 by the great English chemist Willian Henry Perkin using salicylaldehyde, acetic anhydride, and sodium acetate.[7] Other synthetic methods such as Pechmann[8] and Knoevenagel[9] condensations are also effective for the preparation of this nucleus, and owing to the recent increase in its importance, new synthetic methodologies are still being developed.[10,11]

Ultrasound also has a wide range of applications and is used in sonochemistry, which is a field that studies the effect of ultrasonic waves in chemical reactions because of acoustic cavitation (defined as the formation, growth of vapor cavities, and implosive collapse of bubbles in a liquid).[12,13] It is important to note that there are previously reported examples of using ultrasound in synthesizing other coumarin analogues.[14–16] In some cases, compared with the classical procedures, sonochemistry has several advantages such as higher yields,[17] greater amount of crystalline compounds,[18] and a reduced reaction time.[17] Considering these advantages, this study describes sonochemistry as a general procedure for the synthesis of different coumarins using active methylene compounds and 2-hydroxybenzaldehydes or resorcinol. The application of sonochemistry for the synthesis of these compounds was also very effective on a multigram scale and produced a higher yield and a crystalline compound with a shorter reaction time compared with the compounds obtained using classical procedures.

Multigram Synthesis

The multigram synthesis of 3-ethoxycarbonylcoumarin (**1**) by Knoevenagel condensation involved a procedure that used ultrasonic irradiation and reflux with vigorous magnetic stirring in absolute ethanol (Scheme 1). The workup procedure for both the ultrasonic and reflux reactions involved washing the solid with a mixture of ethanol and wa-

ter. The advantage of using the ultrasonic procedure over the reflux temperature method is a significantly reduced reaction time (40 min compared with 7 h) and an increased yield (88% compared with 80%). Moreover, it produces more crystalline coumarin **1**. These advantages are useful for industrial applications (Figure 2).

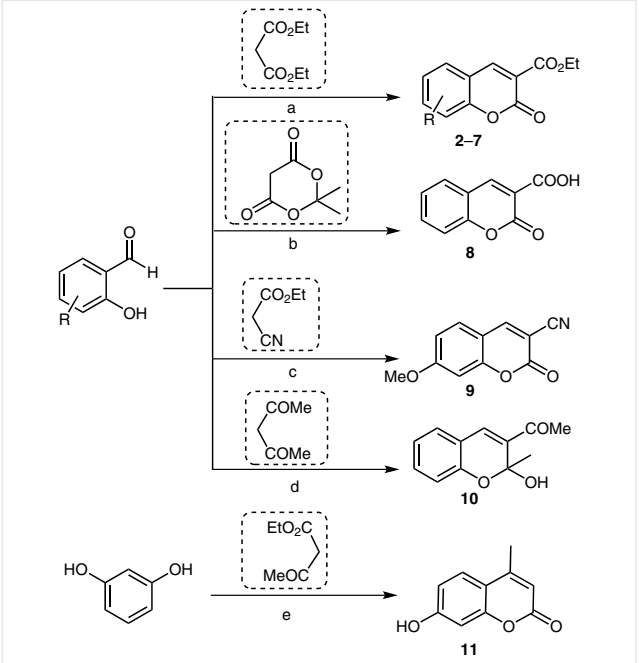


Scheme 1 Reagents and conditions for synthesis of coumarins and comparison of the ultrasonic and reflux procedure

Figure 2 Coumarin **1** furnished by 1) ultrasonic irradiation and 2) reflux with vigorous magnetic stirring

General Procedure for Coumarins by Using Ultrasonic Irradiation

A variety of coumarins were also prepared using ultrasonic irradiation (at a frequency of 20 kHz with 90% of the maximum power output without pulsing) (Scheme 2). Comparisons of the yields and reaction times for the two processes are listed in Table 1. Compounds **2–7** were obtained with reaction times between 5–30 minutes and yields of 60–88%. Comparable yields using the reflux method were obtained only after 240–1440 minutes of the reaction because of the ultrasonic cavitation effects. The advantage in the preparation of compound **8** using the ultrasonic method was the reduced reaction time, that is, 30 minutes compared to 120 minutes. Compound **9** was obtained with a comparable reaction time and yield for both the ultrasonic and reflux procedures. The chromene **10** was obtained in a significantly reduced reaction time (5 min compared to 360 min) and an increased yield (90% compared to 66%). Compound **11** was obtained with a 2-minute reaction time and an 87% yield. A comparable yield using the reflux method was only obtained after 60 minutes of the reaction.

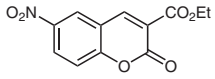
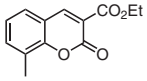
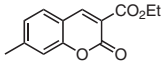
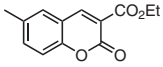
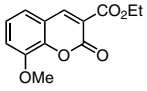
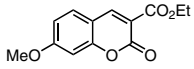
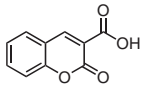
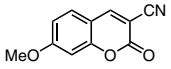
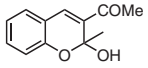
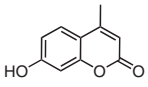


Scheme 2 *Reagents and conditions*: ultrasound and reflux; a) piperidine, AcOH, EtOH; b) H_2O; c) piperidine, EtOH; d) piperidine, AcOH, EtOH; e) H_2SO_4 (70%).

Characterization of the compounds synthesized in this study was achieved using IR and NMR spectra and HRMS data. For compounds **2–7**, the general spectral findings are as follows: (i) the chemical shifts of the =CH, CH_2, and CH_3 protons in the ^{1}H NMR spectra occurred in the ranges of 8.94–8.67, 4.29–4.33, and 1.31–1.33 ppm, respectively, and (ii) the C=O (ester) and C=O (lactone) stretching vibrations in the IR spectra occurred in the ranges of 1737–1756 and 1687–1710 cm^{-1}, respectively. For compound **8**, (i) the chemical shifts of the OH and =CH protons in the ^{1}H NMR spectra were at 13.26 and 8.75 ppm, respectively, and (ii) the C=O (carboxylic acid) and C=O (lactone) stretching vibrations in the IR spectrum occurred at 1737 and 1671 cm^{-1}, respectively. For compound **9**, (i) the chemical shift of the =CH proton in the ^{1}H NMR spectra occurred at 8.84 ppm, and (ii) C≡N and C=O (lactone) stretching vibrations in the IR spectra occurred at 2229 and 1712 cm^{-1}, respectively. For compound **10**, (i) the chemical shifts of the =CH, $COCH_3$, and CH_3 protons in the ^{1}H NMR spectra occurred at 7.71, 2.40, and 1.83 ppm, respectively, and (ii) the O–H and C=O (ester) stretching vibrations in the IR spectra occurred at 3430 and 1648 cm^{-1}, respectively. For compound **11** (i) the chemical shifts of the =CH and CH_3 protons in the ^{1}H NMR spectra occurred at 6.81 and 2.37 ppm, respectively, and (ii) the C=O (lactone) stretching vibrations in the IR spectra occurred at 1666 cm^{-1}.

In this study, the use of ultrasound in combination with organic synthesis proves that sonochemistry is effective as a tool for preparing coumarin nucleus and its derivatives on

Table 1 Comparisons of Heating and Ultrasound Methods for Coumarins

Product	Structure	Heating method		Ultrasound method	
		Time (min)	Yield (%)	Time (min)	Yield (%)
2		1080[19]	64[19]	30	60
3		300	82	5	78
4		240	48	5	82
5		360[20]	82[20]	5	88
6		960[21]	85	5	80
7		1440	84	5	83
8		120[22]	95[22]	30	80
9		30	50	20	49
10		360	66	5	90
11		60[23]	89[23]	2	87

a multigram scale. Coumarins are an important class of natural products with a wide range of applications in different fields. In drug discovery, for example, this class plays a critical role against a wide range of diseases, which will be explored by our medicinal chemistry group in the future.

Chemical reagents and solvents were obtained from Merck and Aldrich and used without further purification. A multiwave Eco-sonics QR750 ultrasonic generator (20 kHz, 750 W) equipped with a converter/transducer and titanium oscillator (horn, diameter = 4 mm and 13 mm) was used for the ultrasonic irradiation. Melting points were determined using a MQAPF-302 Micro Química apparatus and are uncorrected. IR spectra were recorded using a Thermo Nicolet Nexus 670 spectrometer as KBr discs. HRMS was performed using a Bruker Compact QTOF mass spectrometer system. Solution NMR spectra were recorded in DMSO-d_6 using a Bruker Avance 500 spectrometer operating at 400 and 500 MHz (^{1}H) and 100 and 125 MHz (^{13}C) at r.t.

3-Ethoxycarbonylcoumarin (1); Ultrasonic Procedure

A 2-L flask was charged with salicylaldehyde (200 g, 1.6 mol), diethyl malonate (288 g, 1.8 mol), and absolute EtOH (500 mL). To this mixture were added piperidine (21 mL, 0.2 mol) and glacial AcOH (2.1 mL, 0.04 mol) and ultrasonic irradiation was performed for 40 min (frequency = 20 kHz, amplitude = 90% of the maximum power output) without a pulse. Then, hot H_2O (60 °C) (500 mL) was added to the flask, and after cooling at r.t., the mixture was stored overnight in a refrigerator. The product was collected by filtration and washed with a solution of EtOH (200 mL) and distilled H_2O (300 mL). After washing with distilled H_2O (1 L), the coumarin **1** was obtained as a white solid; yield: 313 g (1.4 mol, 88%); mp 87.5–88.9 °C (Lit.[24] mp 91–93 °C).

IR (KBr): 3065 (C–H arom), 2979, 2930, 2865 (C–H aliphatic), 1780 (C=O ester), 1763 (C=O lactone), 1607 cm^{-1} (C=C).

^{1}H NMR (400 MHz, DMSO-d_6/TMS): δ = 8.76 (1 H, s, H-4), 7.93 (1 H, dd J = 7.7, 1.6 Hz, H-5), 7.77–7.73 (1 H, m, H-7), 7.46–7.40 (2 H, m, H-6, 8), 4.30 (2 H, q, J = 7.1 Hz, CH_2), 1.32 (3 H, t, J = 7.1 Hz, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.5, 155.9, 154.4, 148.6, 134.4, 130.2, 124.8, 117.7, 117.6, 116.1, 61.1, 14.0.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{10}O_4Na$: 241.0579; found: 241.0474

3-Ethoxycarbonylcoumarin (1); Thermal Procedure

A 2-L flask was charged with salicylaldehyde (200 g, 1.6 mol), diethyl malonate (288 g, 1.8 mol), and absolute EtOH (500 mL). To this mixture, piperidine (21 mL, 0.2 mol) and glacial AcOH (2.1 mL, 0.04 mol) were added, and the solution was heated under reflux for 7 h. After this period of time, hot H_2O (60 °C) (500 mL) was added. After cooling the reaction mixture at r.t., it was stored overnight in a refrigerator. The product was collected by filtration and washed with a solution of EtOH (200 mL) and distilled H_2O (300 mL). After washing with distilled H_2O (1 L), the coumarin **1** was obtained as a yellow solid; yield: 286 g (1.3 mol, 80%); mp 89.4–90.7 °C (Lit.[24] mp 91–93 °C).

The spectral data were identical with the sample prepared above by ultrasonic procedure.

Ultrasound Irradiation for the Synthesis of Coumarin Derivatives 2–9, 11, and Chromene Derivative 10; General Procedures

3-Ethoxycarbonylcoumarins 2–7; General Ultrasonic Procedure

The 3-ethoxycarbonylcoumarin derivatives were prepared from a 1:1.1 mol ratio of the appropriate salicylaldehyde (500 mg, 4.1 mmol) and diethyl malonate (722 mg, 4.51 mmol) in absolute EtOH (2 mL). To this mixture, piperidine (34.5 mg, 0.4 mmol) and a catalytic amount of glacial AcOH were added. Ultrasonic irradiation was performed (frequency = 20 kHz, amplitude = 90% of the maximum power output) without a pulse for 5–30 min. After this period of time, hot H_2O (60 °C) (3 mL) was added, and after cooling the mixture at r.t., it was stored overnight in a refrigerator. The product was collected by filtration and washed with a solution of EtOH (1 mL) and distilled H_2O (2 mL). Finally, the product was washed with distilled H_2O (20 mL).

3-Ethoxycarbonyl-6-nitrocoumarin (2)

Yield: 477 mg (1.8 mmol, 60%); white solid; mp 190.4–190.5 °C (Lit.[19] mp 195.5–196.5 °C).

IR (KBr): 3090, 3057 (C–H arom), 1756 (C=O ester), 1687 (C=O lactone), 1615 (C=C), 1524, 1343 cm^{-1} (NO_2).

^{1}H NMR (400 MHz, DMSO-d_6/TMS): δ = 8.94–8.93 (2 H, m, H-4, H-5), 8.51 (1 H, dd, *J* = 9.2, 2.8 Hz, H-7), 7.66 (1 H, d, *J* = 9.2 Hz, H-8), 4.33 (2 H, q, *J* = 7.1 Hz, CH_2), 1.33 (3 H, t, *J* = 7.1 Hz, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.0, 158.0, 155.0, 147.6, 143.6, 128.4, 126.0, 119.4, 118.1, 117.6, 61.4, 14.0.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_9NO_6Na$: 286.0430; found: 286.0331.

3-Ethoxycarbonyl-8-methylcoumarin (3)

Yield: 665 mg (2.9 mmol, 78%); white solid; mp 79.4–80.7 °C.

IR (KBr): 3052 (C–H arom), 2984 (CH_3), 1741 (C=O ester), 1700 (C=O lactone), 1602, 1574, 1461 cm^{-1} (C=C).

^{1}H NMR (400 MHz, DMSO-d_6/TMS): δ = 8.72 (1 H, s, H-4), 7.74 (1 H, dd, *J* = 7.6, 0.8 Hz, H-5 or H-7), 7.61 (1 H, dd, *J* = 7.6, 0.8 Hz, H-7 or H-5), 7.30 (1 H, t, *J* = 7.6 Hz, H-6), 4.31 (2 H, q, *J* = 7.1 Hz, CH_2), 2.37 (1 H, s, ArCH_3), 1.32 (3 H, t, *J* = 7.1 Hz, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.5, 156.0, 152.7, 148.9, 135.4, 127.9, 125.0, 124.3, 117.4, 117.2, 61.1, 14.7, 14.0.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}O_4$: 233.0736; found: 233.0814.

3-Ethoxycarbonyl-7-methylcoumarin (4)

Yield: 699 mg (3.0 mmol, 82%); white solid; mp 97.6–98.3 °C.

IR (KBr): 3041 (C–H arom), 2985 (CH_3), 1745 (C=O ester), 1710 (C=O lactone), 1611, 1557, 1481 cm^{-1} (C=C).

^{1}H NMR (400 MHz, DMSO-d_6/TMS): δ = 8.72 (1 H, s, H-4), 7.80 (1 H, d, *J* = 7.9 Hz, H-5), 7.27–7.23 (2 H, m, H-6, H-8), 4.29 (2 H, q, *J* = 7.1 Hz, CH_2), 2.44 (1 H, s, ArCH_3), 1.31 (3 H, t, *J* = 7.1 Hz, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.6, 156.0, 154.6, 148.7, 145.9, 129.9, 125.9, 116.2, 116.0, 115.4, 61.0, 21.4, 14.0.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{12}O_4Na$: 255.0736; found: 255.0638.

3-Ethoxycarbonyl-6-methylcoumarin (5)

Yield: 751 mg (3.2 mmol, 88%); white solid; mp 99.0–100.1 °C (Lit.[20] mp 105 °C).

IR (KBr): 3055 (C–H arom), 2989 (CH_3), 1756 (C=O ester), 1705 (C=O lactone), 1619, 1574, 1493 cm^{-1} (C=C).

^{1}H NMR (400 MHz, DMSO-d_6/TMS): δ = 8.67 (1 H, s, H-4), 7.69 (1 H, d, *J* = 1.7 Hz, H-5), 7.56 (1 H, dd, *J* = 8.5, 1.7 Hz, H-7), 7.34 (1 H, d, *J* = 8.5 Hz, H-8), 4.30 (2 H, q, *J* = 7.1 Hz, CH_2), 2.37 (1 H, s, ArCH_3), 1.32 (3 H, t, *J* = 7.1 Hz, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.6, 156.0, 152.6, 148.4, 135.3, 134.0, 130.0, 117.5, 117.4, 115.8, 61.1, 20.1, 14.0.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{12}O_4Na$: 255.0736; found: 255.0639.

3-Ethoxycarbonyl-8-methoxycoumarin (6)

Yield: 653 mg (2.6 mmol, 80%); white solid; mp 91.9–92.2 °C (Lit.[25] mp 88–90 °C).

IR (KBr): 3086, 3041 (C–H arom), 2983 (OCH_3), 1737 (C=O ester), 1702 (C=O lactone), 1610, 1577, 1479 (C=C), 1242 cm^{-1} (Ar–O–CH_3).

^{1}H NMR (400 MHz, DMSO-d_6/TMS): δ = 8.73 (1 H, s, H-4), 7.47–7.41 (2 H, m, H-5, H-6), 7.36–7.32 (1 H, m, H-7), 4.30 (2 H, q, *J* = 7.1 Hz, CH_2), 3.92 (1 H, s, OCH_3), 1.32 (3 H, t, *J* = 7.1 Hz, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.5, 155.6, 148.8, 146.1, 143.8, 124.7, 121.1, 118.2, 117.7, 116.3, 61.2, 56.1, 14.0.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}O_5$: 249.0685; found: 249.0757.

3-Ethoxycarbonyl-7-methoxycoumarin (7)

Yield: 677 mg (2.7 mmol, 83%); white solid; mp 127.7–130.2 °C (Lit.[26] mp 135–137 °C).

IR (KBr): 3054 (C–H arom), 2983 (OCH_3), 1745 (C=O ester), 1694 (C=O lactone), 1606, 1563, 1508 (C=C), 1212 cm^{-1} (Ar–O–CH_3).

^{1}H NMR (400 MHz, DMSO-d_6/TMS): δ = 8.72 (1 H, s, H-4), 7.84 (1 H, d, *J* = 8.6 Hz, H-5), 7.04–6.99 (1 H, m, H-6, H-8), 4.28 (2 H, q, *J* = 7.1 Hz, CH_2), 3.90 (1 H, s, OCH_3), 1.31 (3 H, t, *J* = 7.1 Hz, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.6, 162.7, 156.9, 156.1, 149.1, 131.5, 113.2, 111.3, 100.2, 60.8, 56.2, 14.0.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}O_5$: 249.0685; found: 249.0765.

Coumarin-3-carboxylic Acid (8); Ultrasonic Procedure

A 10 mL round-bottomed flask was charged with H_2O (2 mL), salicylaldehyde (93.2 mg, 7.6 mol), and Meldrum's acid (100 mg, 6.9 mol). Ultrasonic irradiation was applied for 30 min (frequency = 20 kHz, amplitude = 90% of the maximum power output) without a pulse. The

product was collected by filtration and washed with distilled H_2O to afford **8** as a white solid; yield: 105.6 mg (0.5 mmol, 80%); mp 181.2–182.5 °C (Lit.[22] mp 188.0–188.8 °C).

IR (KBr): 3058 (C–H arom), 2819 (CH_3), 1737 (C=O carboxylic acid), 1671 (C=O lactone), 1607, 1567 cm^{-1} (C=C).

^1H NMR (400 MHz, DMSO-d_6/TMS): δ = 13.26 (1 H, s, OH), 8.75 (1 H, s, H-4), 7.92 (1 H, dd, *J* = 7.7, 1.6 Hz, H-5), 7.76–7.72 (1 H, m, H-7), 7.46–7.39 (2 H, m, H-6, H-8).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.9, 156.5, 154.4, 148.3, 134.2, 130.1, 124.7, 118.3, 117.9, 116.0.

HRMS: *m*/*z* [M – H]$^-$ calcd for $C_{10}H_5O_4$: 189.0266; found: 189.0195.

3-Cyano-7-methoxycoumarin (9); Ultrasonic Procedure

A mixture of 4-methoxysalicylaldehyde (500 mg, 3.3 mmol) and ethyl cyanoacetate (373 mg, 3.3 mmol) in absolute EtOH (2 mL) and piperidine (34.5 mg, 0.4 mmol) was irradiated with ultrasound for 20 min (frequency = 20 kHz, amplitude = 90% of the maximum power output) without a pulse. After cooling the reaction mixture, the resulting precipitate was recrystallized from EtOH to furnish **9** as a yellow solid; yield: 324 mg (1.6 mmol, 49%); mp 214.7–216.1 °C (Lit.[27] mp 217–218 °C).

IR (KBr): 3084 (C–H arom), 2955 (OCH_3), 2229 (C≡N), 1712 (C=O lactone), 1617, 1599 (C=C), 1254 cm^{-1} (Ar–O–CH_3).

^1H NMR (400 MHz, DMSO-d_6/TMS): δ = 8.84 (1 H, s, H-4), 7.73 (1 H, d, *J* = 8.8 Hz, H-5), 7.12 (1 H, d, *J* = 2.4 Hz, H-8), 7.07 (1 H, dd, *J* = 8.8, 2.4 Hz, H-6), 3.91 (1 H, s, OCH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.3, 157.3, 156.4, 153.1, 131.2, 115.0, 113.8, 111.2, 100.9, 97.4, 56.4.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_7NO_3Na$: 224.0426; found: 224.0320.

1-(2-Hydroxy-2-methyl-2*H*-chromen-3-yl)ethanone (10); Ultrasonic Procedure

A mixture of salicylaldehyde (500 mg, 4.1 mmol), pentane-2,4-dione (451 mg, 4.5 mmol), absolute EtOH (2 mL), piperidine (34.5 mg, 0.4 mmol), and a catalytic amount of glacial AcOH was irradiated with ultrasound (frequency = 20 kHz, amplitude = 90% of the maximum power output) without a pulse for 5 min. After solvent removal, the residue was purified by column chromatography over a silica gel column (eluent: hexane/EtOAc 85:15) to afford **10** as a yellow solid; yield: 754 mg (3.7 mmol, 90%); mp 83.5–84.8 °C (Lit.[28] mp 135–136 °C).

IR (KBr): 3430 (OH), 3065, 3038 (C–H arom), 2994 (CH_3), 1648 (C=O ester), 1624, 1603, 1567 cm^{-1} (C=C).

^1H NMR (400 MHz, DMSO-d_6/TMS): δ = 7.71 (1 H, s, H-4), 7.43 (1 H, dd, *J* = 7.5, 1.4 Hz, H-5), 7.36–7.32 (1 H, m, H-7), 7.00 (1 H, td, *J* = 7.5, 1.4 Hz, H-6), 6.94 (1 H, s, OH), 6.91 (1 H, d, *J* = 7.5 Hz, H-8), 2.40 (1 H, s, $COCH_3$), 1.83 (1 H, s, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 196.2, 152.8, 134.2, 133.8, 132.0, 128.8, 121.0, 119.5, 116.1, 97.6, 27.2, 27.0.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{12}O_3Na$: 227.0786; found: 227.0681.

7-Hydroxy-4-methylcoumarin (11); Ultrasonic Procedure

H_2SO_4 (70%, 4.5 mL) was added dropwise over 3 min to a stirred mixture of resorcinol (500 mg, 4.5 mmol) and ethyl acetoacetate (582 mg, 4.5 mmol) in an ice bath. Ultrasonic irradiation was applied (frequency = 20 kHz, amplitude = 90% of the maximum power output) without a pulse for 2 min. The reaction mixture was poured over ice water, the separated solid was collected by filtration, and purified via recrystallization from MeOH; yield: 493 mg (2.8 mmol, 87%); white solid; mp 182.1–184.4 °C (Lit.[23] mp 184–186 °C).

IR (KBr): 3481, 3437 (OH), 3123 (C–H arom), 2819 (CH_3), 1666 (C=O lactone), 1602, 1565 cm^{-1} (C=C).

^1H NMR (500 MHz, DMSO-d_6/TMS): δ = 10.53 (1 H, s, OH), 7.59 (1 H, d, *J* = 8.5 Hz, H-5), 6.81 (1 H, dd, *J* = 8.5, 2.5 Hz, H-6), 6.71 (1 H, d, *J* = 2.5 Hz, H-8), 6.13 (1 H, s, H-3), 2.37 (1 H, s, CH_3).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 161.2, 160.3, 154.8, 153.5, 126.6, 112.8, 112.0, 110.2, 102.2, 18.1.

HRMS: *m*/*z* [M – H]$^-$ calcd for $C_{10}H_7O_3$: 176.0473; found: 175.0403.

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