Supporting Information

A mild and efficient route to 3-vinylchromones in aqueous micellar media

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GENERAL INFORMATION

The reagents were procured from commercial sources and were used without further purification. All solvents were obtained from local suppliers and were of research grade. All the chromones were purchased from Sigma–Aldrich and used without further purification. Other common reagents were procured either from SD Fine-Chem. Limited, Mumbai, India or from Merck, India.

^1H NMR and ^{13}C NMR spectra were recorded on BRUKER 300 MHz or BRUKER 400 MHz or JEOL 400 MHz NMR systems using tetramethylsilane as an internal standard. The chemical shifts are reported in parts per million (ppm) units relative to the solvent peak. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; m, multiplet; brs, broad singlet. Mass spectra were recorded on Waters Q-TOF micro mass spectrometer or Bruker Esquire 3000 mass spectrometer using ESI as the ion source. The IR spectra were recorded in KBr pellets with IR Affinity 1, Shimadzu. CHN data were recorded using Vario elemental CHNS analyzer. Melting points of the compounds were determined using Melting Point Apparatus, Bio Techniques, India. The reactions were monitored by thin layer chromatography (TLC) carried out on 0.25-mm silica gel on aluminium plates (60F-254) using UV light (254 or 365 nm) or naked eye for visualization. Column chromatography was performed on silica gel (60–120 mesh, Merck).

General experimental procedure for the synthesis of Knoevenagel condensation products (3):

To a solution of CTAB (0.05 mmol) in H_2O (2 mL) were added a 3-formylchromone (0.5 mmol), DABCO (0.05 mmol), and an active methylene compound (0.5 mmol) successively at room

temperature in a 10 mL round-bottom flask. The reaction mixture was sonicated for few min and then stirred at 40 °C for required time as listed in table 2. The reaction was monitored by TLC. The crude product was extracted with ethyl acetate, washed with brine, dried over anhydrous Na₂SO₄ and concentrated in vacuum. The crude product was purified by column chromatography (silica gel, 60-120 mesh) using a mixture of ethyl acetate and hexane as the eluent.

Diethyl 2-((4-oxo-4H-chromen-3-yl)methylene)malonate (3a).¹ Light yellow solid, mp. 109-110 °C (Lit. 111 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.29-1.37 (m, 6H), 4.28-4.38 (m, 4H), 7.43-7.49 (m, 2H), 7.68-7.74 (m, 1H), 7.78 (d, *J* = 0.6 Hz, 1H), 8.25 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.1 Hz, 1H), 8.32 (d, *J* = 0.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 14.0, 14.1, 61.7, 61.8, 118.2, 119.1, 123.8, 126.0, 126.4, 128.2, 133.1, 134.3, 155.9, 156.4, 163.9, 165.9, 175.1; IR (KBr): 3078, 1723, 1654 cm⁻¹; MS (ESI): *m/z* 339 (M + Na)⁺. *Anal.* Calcd. for C₁₇H₁₆O₆: C, 64.55; H, 5.10. Found: C, 64.72; H, 5.11.

(2E)-ethyl 3-oxo-2-((4-oxo-4H-chromen-3-yl)methylene)butanoate (3b).² Light yellow solid, mp. 119-121 °C (Lit. 122 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.36 (t, *J* = 7.5 Hz), 4.32 (q, *J* = 7.4 Hz, 2H), 7.30-8.07 (m, 4H), 8.21 (dd, *J*₁ = 1.5 Hz, *J*₂ = 7.5 Hz, 1H), 8.37 (s, 1H); IR (KBr): 3038, 1703, 1684, 1652 cm⁻¹. [This particular compound was characterized based on ¹H NMR, mp. and IR only, and matching them with the reported data].

(2Z)-Ethyl 2-cyano-3-(4-oxo-4H-chromen-3-yl)acrylate (3c).³ Light yellow solid, mp. 125-126 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.40 (t, *J* = 7.3 Hz, 3H), 4.40 (q, *J* = 7.4 Hz, 2H), 7.49-7.57 (m, 2H), 7.74-7.81 (m, 1H), 8.26 (d, *J* = 7.5 Hz, 1H), 8.65 (s, 1H), 9.15 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 14.1, 62.9, 103.6, 115.4, 117.7, 118.5, 123.5, 126.5, 126.6, 134.9, 145.7, 155.8, 158.3, 161.5, 174.5; IR (KBr): 3039, 2222, 1729, 1662 cm⁻¹; MS (ESI): *m/z* 292 (M + Na)⁺. *Anal.* Calcd. for C₁₅H₁₁NO₄: C, 66.91; H, 4.12; N, 5.20. Found: C, 67.07; H, 4.16; N, 5.24.

2-((4-Oxo-4H-chromen-3-yl)methylene)malononitrile (3d).³ Light yellow solid, mp. 184-185 °C (Lit. 186-187 °C); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.96 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.50-7.61 (m, 2H), 8.27 (d, *J* = 2.4 Hz, 1H), 8.73 (d, *J* = 2.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 114.1, 118.6, 118.9, 119.3, 127.1, 132.3, 137.2, 144.0, 152.7, 163.1, 165.6, 196.1; IR (neat): 3156, 2233, 1722 cm⁻¹; MS (ESI): *m/z* 245 (M + Na)⁺. *Anal.* Calcd. for C₁₃H₆N₂O₂: C, 70.27; H, 2.72; N, 12.61. Found: C, 70.10; H, 2.73; N, 12.58.

3-[(4-Oxo-4H-1-benzopyran-3-yl)methylene]pentan-2,4-dione (3e).² Light yellow solid, mp. 166-167°C (Lit. 168-170°C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 2.37 (s, 3H), 2.50 (s, 3H), 7.45-7.53 (m, 3H), 7.73 (dt, *J*₁ = 1.5 Hz, *J*₂ = 8.8 Hz, 1H), 8.25 (dd, *J*₁ = 1.5 Hz, *J*₂ = 7.8 Hz, 1H), 8.32 (d, *J* = 1.2 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 26.3, 31.3, 118.3, 118.7, 123.5, 126.1, 126.2, 130.6, 134.5, 144.3, 155.9, 156.8, 175.4, 197.3, 204.0; IR (KBr): 3050, 1709, 1651 cm⁻¹; MS (ESI): *m/z* 279 (M + Na)⁺. *Anal.* Calcd. for C₁₅H₁₂O₄: C, 70.31; H, 4.72. Found: C, 70.05; H, 4.73.

(2E)-3-(4-oxo-4H-chromen-3-yl) acrylic acid (3f).⁴ Light yellow color solid, mp. 252-253 °C (Lit. 253-254 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 7.13 (d, *J* = 16 Hz, 1H), 7.43 (d, *J* = 16 Hz, 1H), 7.53-7.57 (m, 1H), 7.72 (d, *J* = 8 Hz, 1H), 7.83-7.87 (m, 1H), 8.13-8.15 (m, 1H), 8.89 (s, 1H), 12.46 (s, 1H, exchangeable); ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm): 118.2, 118.6, 121.5, 123.5, 125.5, 126.1, 134.6, 135.8, 155.1, 159.8, 167.9, 175.4; IR (KBr): 2971, 1715, 1665 cm⁻¹; MS (ESI): *m/z* 239 (M + Na)⁺. *Anal.* Calcd. for C₁₂H₈O₄: C, 66.67; H, 3.73. Found: C, 66.58; H, 3.76.

(2E)-2-cyano-3-(4-oxo-4H-chromen-3-yl) acrylamide (3g).³ Light yellow color solid, mp. 182-183°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 7.57-7.61 (m, 1H), 7.78 (dd, *J*₁ = 0.6 Hz, *J*₂ = 8.4 Hz, 1H), 7.85 (brs, 1H), 7.89-7.93 (m, 1H), 8.05 (brs, 1H), 8.15 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.4 Hz, 1H), 8.17 (d, *J* = 1.0 Hz, 1H), 9.11 (d, *J* = 0.8 Hz, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 110.2, 117.0, 119.0, 120.0, 124.2, 126.7, 127.8, 136.4, 143.3, 156.7, 159.7, 163.1, 175.4; IR (KBr): 3430, 3373, 3157, 2362, 2219, 1705, 1660 cm⁻¹; MS (ESI): *m/z* 263 (M + Na)⁺. *Anal.* Calcd. for C₁₃H₈N₂O₃: C, 65.00; H, 3.36; N, 11.66. Found: C, 64.84; H, 3.37; N, 11.68.

Diethyl 2-((6-methyl-4-oxo-4H-chromen-3-yl)methylene)malonate (3h).¹ Pale yellow solid, mp. 119-120 °C (Lit. 120 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.24-1.36 (m, 6H), 2.47 (s, 3H), 4.27-4.38 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, *J*₁ = 1.8 Hz, *J*₂ = 8.0 Hz, 1H), 7.78 (s, 1H), 8.03 (d, *J* = 1.2 Hz, 1H), 8.29 (d, *J* = 0.6 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 14.0, 14.1, 20.9, 61.7, 117.9, 118.8, 123.4, 125.6, 127.9, 133.2, 135.4, 136.1, 154.1, 156.3, 163.9, 165.9, 175.1; IR (KBr): 3070, 1727, 1658 cm⁻¹; MS (ESI): *m/z* 331 (M + H)⁺. *Anal.* Calcd. for C₁₈H₁₈O₆: C, 65.45; H, 5.49. Found: C, 65.54; H, 5.52.

(2Z)-Ethyl 2-cyano-3-(6-methyl-4-oxo-4H-chromen-3-yl)acrylate (3i).³ Light yellow solid, mp. 118-119 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.40 (t, *J*₁ = 6.9 Hz, 3H), 2.49 (s, 3H), 4.39 (q, *J*₁ = 7.2 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.57 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.4 Hz, 1H), 8.06 (d, *J* = 1.4 Hz, 1H), 8.66 (d, *J* = 1.0 Hz, 1H), 9.13 (d, *J* = 0.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 14.2, 21.0, 62.8, 103.3, 115.5, 117.6, 118.3, 123.2, 125.9, 136.1, 136.9, 145.9, 154.1,

158.2, 161.6, 174.6; IR (KBr): 3055, 2234, 1710, 1662 cm^{-1} ; MS (ESI): m/z 306 ($M + \text{Na}$)⁺.

Anal. Calcd. for $\text{C}_{16}\text{H}_{13}\text{NO}_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 67.75; H, 4.66; N, 4.91.

2-((6-Methyl-4-oxo-4H-chromen-3-yl)methylene)malononitrile (3j).³ Light yellow solid, mp. 216-217 °C (Lit. 217-218 °C); ¹H NMR (300 MHz, CDCl_3) δ (ppm): 2.50 (s, 3H), 7.46 (d, J = 8.4 Hz, 1H), 7.60 (dd, J_1 = 1.5 Hz, J_2 = 8.4 Hz, 1H), 8.05 (s, 1H), 8.30 (s, 1H), 9.11 (s, 1H); ¹³C NMR (75 MHz, CDCl_3) δ (ppm): 21.1, 82.7, 112.6, 112.9, 117.5, 118.4, 123.0, 126.0, 136.6, 137.6, 151.4, 154.06, 158.6, 173.7; IR (KBr): 3031, 2234, 1698 cm^{-1} ; MS (ESI): m/z 237 ($M + \text{H}$)⁺. *Anal.* Calcd. for $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_2$: C, 71.18; H, 3.41; N, 11.86. Found: C, 71.39; H, 3.40; N, 11.90.

3-[(6-Methyl-4-oxo-4H-1-benzopyran-3-yl)-methylene]-pentan-2,4-dione (3k). Light yellow solid, mp. 138-139 °C; ¹H NMR (400 MHz, CDCl_3) δ (ppm): 2.34 (s, 3H), 2.45 (s, 3H), 2.46 (s, 3H), 7.36 (d, J = 8.5 Hz, 1H), 7.49-7.52 (m, 2H), 8.0 (s, 1H), 8.26 (s, 1H); ¹³C NMR (100 MHz, CDCl_3) δ (ppm): 21.1, 26.4, 31.4, 118.1, 118.6, 123.3, 125.6, 130.9,

135.8, 136.4, 144.3, 154.3, 156.8, 175.6, 197.4, 204.2; IR (KBr): 3066, 1702, 1650 cm^{-1} ; MS (ESI): m/z 271 ($M + H$)⁺. *Anal.* Calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_4$: C, 71.10; H, 5.22. Found: C, 71.24; H, 5.27.

(2E)-3-(6-methyl-4-oxo-4H-chromen-3-yl) acrylic acid (3l).⁴ Light yellow color solid, mp. 259-261 °C (Lit. 260 - 261 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 2.44 (s, 3H), 7.12 (d, J = 15.6 Hz), 7.42 (d, J = 15.7 Hz), 7.58-7.67 (m, 2H), 7.90 (d, J = 15.6 Hz, 1H), 8.85 (s, 1H), 12.50 (s, 1H, exchangeable); ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm): 20.5, 108.7, 117.5, 118.6, 122.7, 124.8, 136.2, 136.4, 142.2, 153.8, 158.3, 162.0, 174.1; IR (neat): 3064, 1724, 1661 cm^{-1} ; MS (ESI): m/z 253 ($M + \text{Na}$)⁺. *Anal.* Calcd. for $\text{C}_{13}\text{H}_{10}\text{O}_4$: C, 67.82; H, 4.38. Found: C, 67.63; H, 4.39.

(2Z)-2-cyano-3-(6-methyl-4-oxo-4H-chromen-3-yl)acrylamide (3m).³ Light yellow color solid, mp. 198 - 199 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 2.45 (s, 3H), 7.65-7.73 (m, 2H), 7.84 (brs, 1H), 7.93 (d, J = 4.0 Hz, 1H), 8.04 (brs, 1H), 8.17 (d, J = 1.0 Hz, 1H), 9.10 (d, J = 0.8

Hz, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ (ppm): 20.5, 96.0, 114.5, 118.3, 121.2, 122.5, 124.6, 124.7, 132.9, 135.5, 136.0, 157.4, 159.6; IR (KBr): 3390, 3292, 2231, 2362, 1660, 1617 cm^{-1} ; MS (ESI): m/z 277 ($\text{M} + \text{Na}$) $^+$. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_3$: C, 66.14; H, 3.96; N, 11.02. Found: C, 66.28; H, 3.95; N, 11.05.

Diethyl 2-((6-bromo-4-oxo-4H-chromen-3-yl)methylene)malonate (3n). Light yellow solid, mp. 67-68 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 1.25-1.34 (m, 6H), 4.26-4.34 (m, 4H), 7.35 (d, $J = 8.8$ Hz, 1H), 7.69 (s, 1H), 7.78 (dd, $J_1 = 2.4$ Hz, $J_2 = 8.8$ Hz, 1H), 8.30 (s, 1H), 8.34 (d, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 14.1, 14.2, 61.9, 119.3, 119.6, 120.2, 125.1, 128.8, 129.0, 132.6, 137.3, 154.7, 156.5, 163.8, 165.8, 173.9; IR (KBr): 3055, 1717, 1659 cm^{-1} ; MS (ESI): m/z 417 ($\text{M} + \text{Na}$) $^+$ for Br = 79, 419 ($\text{M} + \text{Na}$) $^+$ for Br = 81. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{15}\text{BrO}_6$: C, 51.67; H, 3.83. Found: C, 51.82; H, 3.88.

(2Z)-Ethyl-3-(6-bromo-4-oxo-4H-chromen-3-yl)-2-cyanoacrylate (3o). Pale yellow solid, mp. 185-186 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 1.38 (t, $J = 7.1$ Hz, 3H), 4.37 (q, $J = 7.2$ Hz, 2H), 7.44 (d, $J = 8.7$ Hz, 1H), 7.83 (dd, $J_1 = 2.3$ Hz, $J_2 = 8.7$ Hz, 1H), 8.37 (d, $J = 2.3$ Hz, 1H), 8.57 (d, $J = 0.7$ Hz, 1H), 9.10 (d, $J = 0.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 14.2, 63.1, 104.3, 115.4, 118.0, 120.3, 120.6, 124.9, 129.2, 138.0, 145.2, 154.7, 158.2, 161.4, 173.4; IR (KBr): 3093, 2214, 1729, 1650 cm^{-1} ; MS (ESI): m/z 370 ($\text{M} + \text{Na}$) $^+$ for Br = 79, 372 ($\text{M} + \text{Na}$) $^+$ for Br = 81. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{10}\text{BrNO}_4$: C, 51.75; H, 2.90; N, 4.02. Found: C, 51.62; H, 2.94; N, 4.05.

3-[(6-Bromo-4-oxo-4H-1-benzopyran-3-yl)-methylene]-pentan-2, 4-dione (3p). Light almond color solid, mp. 164-165 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 2.34 (s, 3H), 2.47 (s, 3H), 7.38 (d, $J = 8.7$ Hz, 1H), 7.44 (s, 1H), 7.78 (dd, $J_1 = 2.5$ Hz, $J_2 = 8.9$ Hz, 1H), 8.30 (s, 1H), 8.34 (d, $J = 2.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 26.4, 31.4, 119.0, 119.7, 120.4, 124.8, 128.9, 130.2, 137.6, 144.9, 154.8, 156.9, 174.3, 197.3, 203.9; IR (KBr): 3067, 1697, 1657 cm^{-1} ; MS (ESI): m/z 357 ($\text{M} + \text{Na}$) $^+$ for Br = 79, 359 ($\text{M} + \text{Na}$) $^+$ for Br = 81. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{11}\text{BrO}_4$: C, 53.76; H, 3.31. Found: C, 53.63; H, 3.39.

(2E)-3-(6-bromo-4-oxo-4H-chromen-3-yl) acrylic acid (3q).⁴ Light almond color solid, mp.

210-211 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 7.11 (d, *J* = 16 Hz, 1H), 7.41 (d, *J* = 16 Hz, 1H), 7.72 (d, *J* = 12 Hz, 1H), 7.99-8.02 (m, 1H), 8.19 (d, *J* = 3 Hz, 1H), 8.91 (s, 1H), 12.55 (brs, 1H, exchangeable); ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 118.6, 118.9, 121.4, 122.8, 124.2, 127.2, 136.0, 145.2, 156.7, 159.1, 164.5, 174.3; IR (KBr): 3071, 2928, 2851, 1738, 1672 cm⁻¹; MS (ESI): *m/z* 317 (M + Na)⁺ for Br = 79, 319 (M + Na)⁺ for Br = 81. *Anal.* Calcd. for C₁₂H₇BrO₄: C, 48.84; H, 2.39. Found: C, 49.03; H, 2.38.

Diethyl-2-((6-nitro-4-oxo-4H-chromen-3-yl)methylene)malonate (3r). Light yellow solid, mp. 65-66 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 1.25-1.36 (m, 6H), 4.27-4.39 (m, 4H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.68 (s, 1H), 8.37 (s, 1H), 8.54 (dd, *J*₁ = 2.8 Hz, *J*₂ = 8.9 Hz, 1H), 9.10 (d, *J* = 2.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 14.1, 14.2, 62.1, 119.9, 120.2, 123.2, 123.9, 128.6, 129.9, 131.7, 145.3, 156.5, 158.7, 163.6, 165.6,

173.8; IR (KBr): 3102, 1729, 1662 cm^{-1} ; MS (ESI): m/z 384 ($M + \text{Na}$)⁺. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{15}\text{NO}_8$: C, 56.51; H, 4.18; N, 3.88. Found: C, 56.65; H, 4.17; N, 3.97.

3-[(6-Nitro-4-oxo-4H-1-benzopyran-3-yl)-methylene]pentan-2,4-dione (3s). Light brown solid, mp. 107-108 °C; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm): 2.24 (s, 3H), 2.37 (s, 3H), 7.39 (s, 1H), 7.96 (d, $J = 9.3$ Hz, 1H), 8.60 (dd, $J_1 = 2.4$ Hz, $J_2 = 9.2$ Hz, 1H), 8.70 (d, $J = 2.4$ Hz, 1H), 8.75 (s, 1H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ (ppm): 26.9, 31.2, 119.5, 121.4, 121.9, 123.5, 129.4, 131.1, 139.8, 145.3, 158.7, 160.1, 173.6, 198.3, 202.5; IR (KBr): 3068, 1677, 1630 cm^{-1} ; MS (ESI): m/z 324 ($M + \text{Na}$)⁺. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{11}\text{NO}_6$: C, 59.80; H, 3.68; N, 4.65. Found: C, 59.68; H, 3.74; N, 4.69.

(2E)-3-(6-nitro-4-oxo-4H-chromen-3-yl) acrylic acid (3t).⁵ Light almond color solid, mp. 273-275°C (Lit. 274-278 °C); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm): 7.12 (d, $J = 15.8$ Hz, 1H), 7.43 (d, $J = 15.6$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 8.60 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.3$ Hz, 1H), 8.80 (d, $J = 2.8$ Hz, 1H), 8.98 (s, 1H), 12.53 (s, 1H, exchangeable); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ (ppm): 119.1, 121.5, 122.0, 122.9, 124.1, 129.1, 135.5, 145.2, 158.6, 160.7, 168.1, 175.0; IR

(KBr): 2950, 1697, 1672 cm^{-1} ; MS (ESI): m/z 284 ($M + \text{Na}$)⁺. *Anal.* Calcd. for $\text{C}_{12}\text{H}_7\text{NO}_6$: C, 55.18; H, 2.70; N, 5.36. Found: C, 55.10; H, 2.71; N, 5.38.

General experimental procedure for the synthesis of benzophenone derivative (4):

To a solution of CTAB (0.05 mmol) in H_2O (2 mL) were added a 3-formylchromone (0.5 mmol), DABCO (0.05 mmol), and an active methylene compound (1.1 mmol) successively at room temperature in a 10 mL round-bottom flask. The reaction mixture was sonicated for few min and then stirred at 40 °C for required time as listed in table 3. The crude product was extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was purified by column chromatography (silica gel, 60-120 mesh) using 8-10% ethyl acetate in hexane as the eluent.

Diethyl 5-(2-hydroxy benzoyl)-2-methyl-1,3-benzenedicarboxylate (4a).² Light yellow solid, mp. 53-55 °C (Lit. 55-57 °C); ^1H NMR (300 MHz, CDCl_3) δ (ppm): 1.40 (t, J = 5.4 Hz, 6H), 2.80 (s, 3H), 4.40 (q, J_1 = 5.4 Hz, 4H), 6.90-6.93 (dt, J_1 = 0.8 Hz, J_2 = 8.8 Hz, 1H), 7.10 (dd, J_1 = 0.8 Hz, J_2 = 6.6 Hz, 1H), 7.53-7.56 (m, 2H), 8.20 (s, 2H), 11.85 (s, 1H, exchangeable); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 14.2 (Ar- CH_3); 18.3, 61.7, 118.7, 118.8, 119.0, 132.9, 133.1, 133.4,

135.1, 136.8, 143.4, 163.3, 167.0, 199.4; IR (KBr): 2987, 1745, 1634 cm^{-1} ; MS (ESI): m/z 379 ($M + \text{Na}$)⁺. *Anal.* Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_6$: C, 67.41; H, 5.66. Found: C, 67.26; H, 5.68.

Diethyl-5-(2-hydroxy-5-methylbenzoyl)-2-methyl-1,3-benzenedicarboxylate (4b). Light yellow solid, mp. 75-77 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 1.42 (t, $J = 8.0$ Hz, 6H), 2.29 (s, 3H), 2.82 (s, 3H), 4.42 (q, $J = 8.0$ Hz, 4H), 7.02 (d, $J = 8$ Hz, 1H), 7.33 (d, $J = 2.5$ Hz, 1H), 7.38 (dd, $J_1 = 2.5$ Hz, $J_2 = 8.0$ Hz, 1H), 8.19 (s, 2H), 11.68 (s, 1H, exchangeable); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 14.2, 18.2, 20.5, 61.7, 118.4, 128.2, 132.8, 132.9, 133.3, 135.2, 137.9, 143.3, 161.2, 167.0, 199.3; IR (KBr): 2983, 1725, 1639 cm^{-1} ; MS (ESI): m/z 371 ($M + \text{H}$)⁺. *Anal.* Calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_6$: C, 68.10; H, 5.99. Found: C, 67.89; H, 6.00.

Diethyl-5-(5-bromo-2-hydroxybenzoyl)-2-methyl-1,3-benzenedicarboxylate (4c). Light yellow solid, mp. 59-60 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 1.44 (t, $J = 8.0$ Hz, 6H), 2.86 (s, 3H), 4.44 (q, $J = 8.0$ Hz, 4H), 7.02 (d, $J = 8.0$ Hz, 1H), 7.65 (dd, $J_1 = 1.5$ Hz,

$J_2 = 8.0$ Hz, 1H), 7.68 (d, $J = 1.5$ Hz, 1H), 8.19 (s, 2H), 11.76 (s, 1H, exchangeable); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 14.2, 18.3, 61.8, 110.6, 120.0, 120.7, 132.9, 133.6, 134.3, 135.0, 139.4, 144.1, 162.2, 166.7, 198.3; IR (KBr): 2979, 1725, 1634 cm^{-1} ; MS (ESI) m/z : 457 ($\text{M} + \text{Na}$) $^+$ for Br = 79, 459 ($\text{M} + \text{Na}$) $^+$ for Br = 81. *Anal.* Calcd. for $\text{C}_{20}\text{H}_{19}\text{BrO}_6$: C, 55.19; H, 4.40. Found: C, 55.30; H, 4.44.

Diethyl-5-(2-hydroxy-5-nitrobenzoyl)-2-methyl-1,3-benzenedicarboxylate (4d). Light yellow solid, mp. 75-76 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 1.42 (t, $J = 8.0$ Hz, 6H), 2.83 (s, 3H), 4.44 (q, $J = 8.0$ Hz, 4H), 7.24 (d, $J = 8.0$ Hz, 1H), 8.25 (s, 2H), 8.44 (dd, $J_1 = 1.5$ Hz, $J_2 = 8.0$ Hz, 1H), 8.59 (d, $J = 1.5$ Hz, 1H), 12.49 (s, 1H, exchangeable); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 14.2, 18.5, 61.9, 117.6, 119.8, 129.1, 131.3, 133.0, 133.5, 133.9, 139.6, 145.0, 166.5, 167.9, 198.4; IR (KBr): 2961, 1737, 1630 cm^{-1} ; MS (ESI): m/z 424 ($\text{M} + \text{Na}$) $^+$. *Anal.* Calcd. for $\text{C}_{20}\text{H}_{19}\text{NO}_8$: C, 59.85; H, 4.77; N, 3.49. Found: C, 60.03; H, 4.79; N, 3.45.

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VK 444.esp

VerticalScaleFactor = 1

38.79
38.51
38.23

38.96
40.06

40.35
38.68

175.34
167.88
159.76
155.12
135.80
134.57
126.09
125.47
123.53
121.54
118.55
118.20

VK446-13C-2.jdf
single pulse decoupled gated NOE