Supporting Information for:

K₂CO₃-Promoted Domino Reactions for Synthesis of isocoumarins under Microwave Irradiation

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General: Analytical TLC was carried out on precoated silica gel plates. Column chromatography was conducted with 300–400 mesh silica gel. NMR spectra were recorded at 500 MHz for ¹H NMR using SiMe₄ as an internal standard in CDCl₃ and 125 MHz for ¹³C NMR. Infrared (IR) data were recorded using a Nicolet Av360 instrument. Microwave irradiation was performed by single mode microwave synthesis system (CEM Discover). Unless otherwise stated, all chemicals were purchased as the highest purity commercially available and were used without further purification.

Typical procedure: To a solution of 2-carboxybenzaldehyde (150 mg, 1 mmol) in DMF (5 mL) was added **2a** (299 mg, 1.5 mmol) and K₂CO₃ (278 mg, 2 mmol), the mixture was stirred under microwave irradiation at 70 °C until all starting material has been consumed. The solid was filtered, and the filtrate was diluted with ethyl acetate, then washed with water and brine. The organic layer was dried (Na₂SO₄), filtered and concentrated. The residue was purified by silica gel flash column chromatography to afford product **3a**.

3-benzoyl-1*H*-isochromen-1-one (**3a**),^[1] light yellow solid, m.p. 122-124 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.38 (d, *J*=8.0 Hz, 1H), 8.01 (d, *J*=7.5 Hz, 2H), 7.82 (t, *J*=7.5 Hz, 1H), 7.69 (t, *J*=7.5 Hz, 1H), 7.65~7.63 (m, 2H), 7.53 (t, *J*=7.5 Hz, 2H), 7.40 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 186.6, 160.6, 150.0, 135.5, 135.2, 135.1, 133.4, 130.9, 130.0, 129.9, 128.6, 128.0, 122.6, 113.0 ppm.

3-(4-methoxybenzoyl)-1*H*-isochromen-1-one (**3b**),^[2] white solid, m.p. 144-146 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.38 (d, *J*=8.0 Hz, 1H), 8.09 (d, *J*=9.0 Hz, 2H), 7.81 (t, *J*=8.0 Hz, 1H), 7.69~7.63 (m, 2H), 7.40 (s, 1H), 7.00 (d, *J*=8.5 Hz, 2H), 3.91 (s, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 184.7, 164.0, 160.8, 150.8, 135.4, 135.2, 132.6, 130.6, 130.0, 128.1, 127.8, 122.4, 113.9, 111.9, 55.6 ppm. .

3-(4-hydroxybenzoyl)-1*H*-isochromen-1-one (**3c**),^[2] white solid, m.p. 174-176 °C. ¹H NMR (500 MHz, CDCl₃) δ 10.59 (s, 1H), 8.22 (d, *J*=8.0 Hz, 1H), 7.95-8.87 (m, 3H), 7.78~7.73 (m, 2H), 7.52 (s, 1H), 6.92 (d, *J*=7.5 Hz, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 185.3, 163.1, 160.9, 149.9, 135.8, 133.0, 132.6, 130.9, 129.4, 127.0, 122.4, 121.8, 115.8, 113.0 ppm.

3-(4-fluorobenzoyl)-1*H*-isochromen-1-one (**3d**), light yellow solid, m.p. 243-245 °C. ¹H NMR

(500 MHz, CDCl₃) δ 8.38 (d, J =8.0 Hz, 1H), 8.10 (d, J =9.0 Hz, 2H), 7.81 (t, J =7.5 Hz, 1H), 7.69~7.63 (m, 2H), 7.40 (s, 1H), 7.00 (d, J =9.0 Hz, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 184.7, 164.0, 160.8, 150.7, 135.4, 135.2, 132.6, 130.6, 129.9, 128.1, 127.8, 122.4, 113.9, 111.9 ppm; IR (KBr, ν /cm⁻¹): 3423, 3080, 2924, 2853, 2026, 1734, 1685, 1663, 1604, 1576, 1421, 1310, 1262, 1176, 1027, 767, 616; HRMS (ESI) 291.0432 [M+Na]⁺ calculated for C₁₆H₉O₃FN⁺ 291.0433.

3-(4-chlorobenzoyl)-1H-isochromen-1-one (**3e**), light yellow solid, m.p. 158-160 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.37 (d, J =8.0 Hz, 1H), 7.99 (d, J =7.5 Hz, 2H), 7.82 (t, J =7.5 Hz, 1H), 7.71~7.64 (m, 2H), 7.49 (d, J =7.5 Hz, 2H), 7.43 (s, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 185.2, 160.4, 149.9, 140.0, 135.3, 135.1, 133.7, 131.4, 131.0, 130.1, 128.9, 128.1, 122.6, 112.8 ppm; IR (KBr, ν /cm⁻¹): 3084, 2025, 1720, 1655, 1590, 1454, 1327, 1209, 1182, 1160, 1093, 967, 762, 687; HRMS (ESI) 307.0140 [M+Na]⁺ calculated for C₁₆H₉O₃ClNa⁺ 307.0138.

3-(4-bromobenzoyl)-1H-isochromen-1-one (**3f**),^[2] light yellow solid, m.p. 112-114 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.38 (d, J =8.0 Hz, 1H), 7.91 (d, J =7.5 Hz, 2H), 7.83 (t, J =7.5 Hz, 1H), 7.71~7.65 (m, 2H), 7.43 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 185.4, 160.4, 149.9, 135.3, 135.1, 134.2, 131.9, 131.51, 131.0, 130.1, 128.8, 128.1, 122.6, 112.8 ppm.

3-(4-nitrobenzoyl)-1*H*-isochromen-1-one (**3g**), light yellow solid, m.p. 148-149 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.41~8.34 (m, 2H), 8.26~8.12 (m, 3H), 7.94~7.88 (m, 1H), 7.79 (s, 1H), 7.75 (d, *J*=7.5 Hz, 1H), 7.68~7.64 (m, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 186.3, 161.2, 150.5, 148.1, 141.6, 136.0, 132.1, 131.3, 129.4, 127.6, 126.4, 124.7, 124.1, 105.9 ppm. IR (KBr, ν/cm⁻¹): 3424, 3017, 2923, 2853, 2026, 1742, 1675, 1519, 1350, 1311, 1263, 1020, 776. HRMS (ESI) 318.0371 [M+Na]⁺ calculated for C₁₆H₉O₃ClNa⁺ 318.0378.

(*E*)-methyl 3-(1-oxo-1*H*-isochromen-3-yl)acrylate (**3f**), white solid, m.p. 97-99 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 15.6 Hz, 1H), 6.71 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 166.8, 161.2, 150.2, 136.3, 135.1, 135.0, 130.1, 129.7, 126.8, 122.0, 121.6, 111.2, 52.1 ppm. HRMS (ESI) 253.0472 [M+Na]⁺ calculated for C₁₃H₁₀O₄Na⁺ 253.0477.

Reference

- [1] Clerici, A.; Porta, O. *J. Org. Chem.* **1989**, *54*, 3872.
- [2] Koppula, P. K.; Purohit, N. *Journal of Chemical Sciences (Bangalore, India)*, **2013**, *125*, 1535.

Copies of ¹H and ¹³C NMR spectra for all new compounds