

SUPPLEMENTARY MATERIAL TO

Microwave-assisted synthesis of 2,8-di(alkyl/aryl)-4,6-dichloro-2H,8H-pyrano[3,2-g]chromene-3,7-dicarbaldehydes and their antimicrobial activity

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ANALYTICAL AND SPECTRAL DATA OF THE SYNTHESIZED COMPOUNDS

2,8-Di-tert-butyl-2,3,7,8-tetrahydro-4H,6H-pyrano[3,2-g]chromene-4,6-dione (4a). White solid; Anal. Calcd. for C₂₀H₂₆O₄: C, 72.70; H, 7.93 %. Found: C, 72.65; H, 7.88 %; IR (KBr, cm⁻¹): 2965 (Ar-H), 1740 (C=O), 1602, 1205; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.05 (12H, *s*, *tert*-butyl CH₃), 2.65 (2H, *br*, H_a), 2.67 (2H, *br*, H_b), 4.05–4.11 (2H, *m*, H_x), 6.56 (1H, *s*, Ar-H), 8.51 (1H, *d*, *J* = 3.0 Hz, Ar-H); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 25.35, 34.14, 34.17, 38.22, 38.25, 85.63, 85.79, 104.56, 104.72, 116.00, 116.05, 128.46, 128.70, 166.93, 167.03, 191.42 (C=O); LC-MS (*m/z*): 331.1 [M+H]⁺, 372.1 [M+H+CH₃CN]⁺.

2,8-Diisopropyl-2,3,7,8-tetrahydro-4H,6H-pyrano[3,2-g]chromene-4,6-dione (4b). White solid; Anal. Calcd. for C₁₈H₂₂O₄: C, 71.50; H 7.33 %. Found: C 74.41; H 5.54 %; IR (KBr, cm⁻¹): 2966 (Ar-H), 1700 (C=O), 1600, 1246; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.97–1.02 (12H, *m*, isopropyl CH₃), 1.96–2.00 (2H, *m*, isopropyl CH), 2.57 (2H, *dd*, *J*_{vicinal} = 7.3 Hz & *J*_{geminal} = 16.8 Hz, H_a), 2.73 (2H, *dd*, *J*_{vicinal} = 12.8 Hz & *J*_{geminal} = 16.8 Hz, H_b), 4.25–4.38 (2H, *m*, *J*_{vicinal} = 7.3 Hz & *J*_{vicinal} = 12.8 Hz, H_x), 6.50 (1H, *s*, Ar-H), 8.10 (1H, *s*, Ar-H); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 17.29, 17.46, 31.25, 82.42, 104.11, 104.27, 115.61, 126.38, 126.59, 166.03, 190.47 (C=O); LC-MS (*m/z*): 302.9 [M+H]⁺, 344.0 [M+H+CH₃CN]⁺.

2,8-Dicyclohexyl-2,3,7,8-tetrahydro-4H,6H-pyrano[3,2-g]chromene-4,6-dione (4c). White solid. Anal. calcd. for C₂₄H₃₀O₄: C, 75.36; H, 7.91 %. Found: C 74.30; H 5.56 %. IR (KBr, cm⁻¹): 2964 (Ar-H), 1742 (C=O); ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.09–1.29 (10H, *m*, cyclohexyl), 1.73–1.89 (10H, *m*, cyclohexyl), 1.94–1.98 (2H, *m*, cyclohexyl), 2.64–2.72 (4H, *m*, H_a & H_b), 4.18–4.28 (2H, *m*, H_x), 6.48 (1H, *d*, *J* = 4.5 Hz, Ar-H), 8.50 (1H, *s*, Ar-H); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 25.78, 25.84, 26.19, 26.49, 28.10, 28.18, 39.76,

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41.62, 82.48, 104.68, 114.19; 115.35, 132.32, 167.06, 188.46, 190.99 (C=O); LC-MS (m/z): 383 [M+H]⁺.

2,8-Diphenyl-2,3,7,8-tetrahydro-4H,6H-pyrano[3,2-g]chromene-4,6-dione (4d). White solid; Anal. Calcd. for C₂₄H₁₈O₄: C, 77.82; H, 4.90 %. Found: C, 77.76; H, 4.87 %; IR (KBr, cm⁻¹): 2964 (Ar-H), 1742 (C=O), 1602, 1244; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 2.93 (2H, *dd*, $J_{\text{vicinal}} = 7.3\text{ Hz}$, & $J_{\text{geminal}} = 17.1\text{ Hz}$, H_a), 3.09 (2H, *dd*, $J_{\text{vicinal}} = 12.8\text{ Hz}$ & $J_{\text{geminal}} = 17.1\text{ Hz}$, H_b), 5.53 (2H, *dd*, $J_{\text{vicinal}} = 7.3\text{ Hz}$ & $J_{\text{vicinal}} = 12.8\text{ Hz}$, H_x), 6.65 (1H, *d*, $J = 2.5\text{ Hz}$, Ar-H), 8.68 (1H, *s*, Ar-H); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 44.26, 44.40, 80.06, 80.08, 105.42, 105.53, 116.56, 126.20, 126.81, 128.87, 128.97, 129.06, 129.46, 138.02, 166.51, 166.54, 189.93 (C=O); LC-MS (m/z): 371.1 [M+H]⁺, 412.1 [M+H+CH₃CN]⁺.

2,8-Di-p-tolyl-2,3,7,8-tetrahydro-4H,6H-pyrano[3,2-g]chromene-4,6-dione (4e). White solid; Anal. Calcd. for C₂₆H₂₂O₄: C, 78.37; H, 5.57 %. Found: C, 78.31; H, 5.51 %; IR (KBr, cm⁻¹): 2962 (Ar-H), 1741 (C=O), 1366, 1215; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 2.38 (6H, *s*, *p*-tolyl-CH₃); 2.90 (2H, *dd*, $J_{\text{vicinal}} = 7.8\text{ Hz}$, & $J_{\text{geminal}} = 16.8\text{ Hz}$, H_a), 3.49 (2H, *dd*, $J_{\text{vicinal}} = 12.8\text{ Hz}$ & $J_{\text{geminal}} = 16.8\text{ Hz}$, H_b), 5.49 (2H, *dd*, $J_{\text{vicinal}} = 7.3\text{ Hz}$ & $J_{\text{vicinal}} = 12.8\text{ Hz}$, H_x), 6.62 (1H, *s*, Ar-H), 7.24–7.36 (8H, *m*, Ar-H), 8.60 (1H, *s*, Ar-H); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 21.23, 44.13, 44.27, 79.99, 105.38, 105.50, 116.51, 126.26, 128.84, 129.03, 129.60, 139.05, 139.07, 166.58, 190.11, 190.15; LC-MS (m/z): 399.0 [M+H]⁺, 440.1 [M+H+CH₃CN]⁺.

2,8-Di-tert-butyl-4,6-dichloro-2H,8H-pyrano[3,2-g]chromene-3,7-dicarbaldehyde (5a). Yellow solid; Anal. Calcd. for C₂₂H₂₄Cl₂O₄: C, 62.42; H, 5.71 %. Found: C, 62.36; H, 5.65 %; IR (KBr, cm⁻¹): 2963 (Ar-H), 1742 (CHO), 1669 (C=C), 1612, 1262; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.86 (18H, *s*, *tert*-butyl CH₃); 5.23 (2H, *s*, CH); 6.43 (1H, *d*, $J = 3.5\text{ Hz}$, Ar-H); 7.98 (1H, *d*, $J = 16.0\text{ Hz}$, Ar-H), 10.24–10.25 (1H, *d*, CHO); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 25.63, 40.02, 40.01, 82.00, 82.09, 102.67, 102.73, 114.65, 123.5, 125.42, 143.05, 162.43, 188.30, 188.38; LC-MS (m/z): 423 [M+H]⁺.

4,6-Dichloro-2,8-diisopropyl-2H,8H-pyrano[3,2-g]chromene-3,7-dicarbaldehyde (5b). Yellow solid; Anal. Calcd. for C₂₀H₂₀Cl₂O₄: C, 60.77; H, 5.10 %. Found: C, 60.70; H, 5.05 %; IR (KBr, cm⁻¹): 2968 (Ar-H), 1742 (CH=O), 1663 (C=C), 1609, 1229; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.92–0.94 (12H, *m*, isopropyl CH₃), 1.97–2.03 (2H, *m*, isopropyl CH); 5.16–5.19 (2H, *t*, CH); 6.45 (1H, *d*, $J = 10.8\text{ Hz}$, Ar-H), 8.00 (1H, *d*, $J = 12.8\text{ Hz}$, Ar-H), 10.19 (1H, *s*, CHO); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 17.43, 17.47, 18.26, 18.31, 33.27, 33.40, 80.27, 104.08, 104.31, 114.66, 125.22, 125.63, 125.76, 142.17, 142.21, 161.27, 161.28, 187.98; LC-MS (m/z): 395.0 [M+H]⁺, 397.0 [M+2+H]⁺.

4,6-Dichloro-2,8-dicyclohexyl-2H,8H-pyrano[3,2-g]chromene-3,7-dicarbaldehyde (5c). Yellow solid; Anal. calcd. for C₂₆H₂₈Cl₂O₄: C, 65.69; H, 5.94 %. Found: C, 65.64; H, 5.90 %; IR (KBr, cm⁻¹): 2970 (Ar-H), 1741 (CH=O), 1663 (C=C), 1220; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.93–1.13 (10H, *m*, cyclohexyl CH₂), 1.43–1.77 (12H, *m*, cyclohexyl CH₂), 5.12–5.13 (2H, *m*), 6.72 (1H, *d*, $J = 11.8\text{ Hz}$, Ar-H), 7.93 (1H, *d*, $J = 8.2\text{ Hz}$, Ar-H), 10.07 (1H, CHO); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 25.05, 25.25, 25.60, 25.67, 27.37, 27.96, 41.96, 41.15, 78.74, 78.90, 104.37, 114.39, 114.49, 124.65, 125.25, 140.56, 140.65, 160.40, 187.97; LC-MS (m/z): 475.3 [M+H]⁺, 477.6 [M+2+H]⁺.

4,6-Dichloro-2,8-diphenyl-2H,8H-pyrano[3,2-g]chromene-3,7-dicarbaldehyde (5d). Yellow solid; Anal. Calcd. for C₂₆H₁₆Cl₂O₄: C, 67.40; H, 3.48 %. Found: C, 67.36; H, 3.44 %; IR (KBr, cm⁻¹): 2923 (Ar-H), 1741 (CH=O), 1663 (C=C), 1596, 1239; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 6.40 (2H, *d*, *J* = 2.5 Hz), 6.41 (1H, *s*, Ar-H), 7.25–7.30 (10H, *m*, Ar-H), 8.11 (1H, *d*, *J* = 17.8 Hz, Ar-H), 10.23 (1H, *s*, CHO); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 76.34, 76.54, 105.61, 105.73, 114.38, 114.74, 125.58, 125.62, 125.64, 125.70, 126.75, 126.80, 128.68, 128.73, 129.09, 129.15, 137.75, 137.90, 142.19, 160.30, 160.39, 187.46; LC-MS (*m/z*): 462.9 [M+H]⁺, 464.9 [M+2+H]⁺.

4,6-Dichloro-2,8-di-p-tolyl-2H,8H-pyrano[3,2-g]chromene-3,7-dicarbaldehyde (5e). Yellow solid. Anal. Calcd. for C₂₈H₂₀Cl₂O₄: C, 68.44; H, 4.10 %. Found: C, 68.40; H, 4.06 %. IR (KBr, cm⁻¹): 2926 (Ar-H), 1740 (CHO), 1662 (C=C), 1592, 1237; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 2.29 (6H, *s*, Ar-CH₃), 6.36 (2H, *d*, *J* = 3.2 Hz, CH), 6.37 (1H, *s*, Ar-H), 7.05–7.18 (8H, *m*, Ar-H), 8.10 (1H, *d*, *J* = 19.3 Hz, Ar-H), 10.22 (2H, *s*, CH=O); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 21.14, 76.30, 105.60, 114.28, 125.54, 126.78, 126.87, 129.38, 134.91, 139.12, 142.10, 160.30, 187.50; LC-MS (*m/z*): 491.6 [M+H]⁺, 493.6 [M+2+H]⁺.

1,1'-(4,6-Dihydroxy-1,3-phenylene)bis[3-phenylprop-2-en-1-one] (3d). Pale yellow solid. Anal. Calcd. for C₂₄H₁₈O₄: C, 77.82; H, 4.90 %. Found, C, 76.68; H 4.80 %; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 6.54 (1H, *s*, Ar-H), 7.47–7.49 (6H, *m*, Ar-H), 7.56 (1H, *s*, olefinic H), 7.60 (1H, *s*, olefinic H), 7.68–7.71 (4H, *m*, Ar-H), 7.96 (1H, *s*, olefinic H), 8.02 (1H, *s*, olefinic H), 8.54 (1H, *s*, Ar-H), 13.62 (2H, *s*, Ar-OH); ¹³C-NMR (100 MHz, DMSO-*d*₆, δ / ppm): 103.83, 114.70, 121.94, 128.89, 129.27, 130.91, 134.42, 135.86, 144.69, 168.13, 191.98; LC-MS (*m/z*): 369.0 [M-H]⁻.

1,1'-(4,6-Dihydroxy-1,3-phenylene)bis[3-p-tolylprop-2-en-1-one] (3e). Pale yellow solid. Anal. Calcd. for C₂₆H₂₂O₄: C, 78.37; H, 5.57 %. Found: C, 77.52; H, 5.51 %; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 2.43 (6H, *s*, Ar-CH₃), 6.52 (1H, *s*, Ar-H), 7.27–7.29 (4H, *m*, Ar-H), 7.52 (1H, *s*, olefinic H), 7.56 (1H, *s*, olefinic H), 7.58–7.60 (4H, *m*, Ar-H), 7.94 (1H, *s*, olefinic H), 7.98 (1H, *s*, olefinic H), 8.52 (1H, *s*, Ar-H), 13.69 (2H, *s*, Ar-OH); ¹³C-NMR (100 MHz, DMSO-*d*₆, δ / ppm): 21.05, 103.98, 114.49, 120.88, 129.29, 129.50, 131.78, 135.73, 141.02, 144.49, 168.65, 191.79; LC-MS (*m/z*): 399.0 [M+H]⁺.