



SUPPLEMENTARY MATERIAL TO  
**Synthesis of biscoumarin derivatives by the reaction of  
aldehydes and 4-hydroxycoumarin using ruthenium(III)  
chloride hydrate as a versatile homogeneous catalyst**

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SELECTED CHARACTERIZATION DATA OF THE NEWLY  
SYNTHESIZED COMPOUNDS

**3,3'-(2-Nitrocinnamylidene)bis(4-hydroxycoumarin) (2b).** Yellow solid; yield: 90 %; m.p. 190–192 °C; Anal. Calcd. for C<sub>27</sub>H<sub>17</sub>NO<sub>8</sub>: C, 67.08; H, 3.54; N, 2.90 %. Found: C, 67.02; H, 3.46; N, 2.99 %; IR (KBr, cm<sup>-1</sup>): 3400 (OH), 2950 (C–H stretching), 1700 (–C=O stretching of –COOR group), 1650, 1600 (–C=C stretching), 1550 (asymmetric stretching of NO<sub>2</sub>), 1390 (symmetric stretching of NO<sub>2</sub>), 760 (C–H out of plane bending); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ / ppm): 11.79 (1H, s, OH), 11.40 (1H, s, OH), 8.03–8.08 (2H, m, ArH), 7.98 (1H, dd, J = 1.1, 8.1 Hz, ArH), 7.74 (1H, d, J = 7.1 Hz, ArH), 7.67–7.42 (8H, m, ArH), 7.07 (1H, dd, J = 2.2, 15.9 Hz, –CH=CH), 6.71 (1H, dd, J = 4.1, 15.9 Hz, –CH=CH), 5.59 (1H, dd, J = 2.4, 4 Hz, –CH aliphatic); <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>, δ / ppm): 165.66 (C–OH), 164.80 (C=O), 153.04 (C=), 148.17 (C–NO<sub>2</sub>), 137.09 (CH=), 134.17 (C=C), 132.89 (C=), 132.67 (CH=), 129.09 (CH=), 128.85 (CH=), 125.03 (CH=), 124.67 (CH=), 124.55 (C=C), 123.31 (CH=), 118.75 (CH=), 116.79 (C=), 104.99 (C=), 35.97 (CH); MS (m/z, relative abundance, %): 483 (M<sup>+</sup>, 0.39), 481 (1.6), 393, 304, 274, 162, 121 (100), 92.

**3,3'-(2-Hydroxy-3-methoxybenzylidene)bis(4-hydroxycoumarin) (2c).** Yellow solid; yield: 84 %; m.p. 268–270 °C; Anal. Calcd. for C<sub>26</sub>H<sub>18</sub>O<sub>8</sub>: C, 68.12; H, 3.86 %. Found: C, 68.34; H, 3.66 %; IR (KBr, cm<sup>-1</sup>): 3100 (OH), 2800 (C–H stretching), 1710 (–C=O stretching of –COOR group), 1600 (C=C– stretching of olefin), 1550, 1500 (C=C– stretching of aromatic ring), 1200 (C–O–C, ester), 1100 (C–O ether), 750 (C–H out of plane bending); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ / ppm): 10.6 (1H, br, OH), 8.11 (1H, d, J = 7.7 Hz, ArH), 7.96 (1H, d, J = 7.1

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Hz, ArH), 7.39–7.53 (2H, *m*, ArH), 7.34 (1H, *t*,  $J = 7.8$  Hz, ArH), 7.28 (1H, *t*,  $J = 10.4$  Hz, ArH), 7.12–7.24 (2H, *m*, ArH), 6.95 (1H, *t*,  $J = 7.9$  Hz, ArH), 6.79 (1H, *d*,  $J = 10.4$  Hz, ArH), 6.73 (1H, *d*,  $J = 7.4$  Hz, ArH), 5.61 (1H, *s*, CH aliphatic), 3.91 (3H, *s*, OCH<sub>3</sub>); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 159.10 (C–OH), 158.35 (C=O), 146.89 (C–OCH<sub>3</sub>), 143.58 (C=), 143.41 (C–OH), 135.80 (CH=), 131.32 (CH=), 129.67 (CH=), 125.31 (C=), 124.05 (CH=), 121.25 (CH=), 119.82 (CH=), 119.48 (C=), 117.49 (CH=), 115.94 (C=), 56.67 (OCH<sub>3</sub>), 31.18 (CH aliphatic); MS (*m/z*, (relative abundance, %)): 458 (M<sup>+</sup>, 0.07), 440 (M–H<sub>2</sub>O, 35.9), 319, 279 (100), 236, 121.

*3,3'-(3,4-Difluorobenzylidene)bis(4-hydroxycoumarin)* (**2d**). White solid; yield: 90 %, m.p. 262–264 °C; Anal. Calcd. for C<sub>25</sub>H<sub>14</sub>F<sub>2</sub>O<sub>6</sub>: C, 66.97; H, 3.15 %. Found: C, 66.79; H, 3.11 %; IR (KBr, cm<sup>-1</sup>): 3500 (OH), 3080, 2850 (C–H stretching), 1640 (C=O stretching of –COOR group), 1610, 1500 (C=C– stretching of aromatic ring), 1360, 1300 (C–F), 1095 (C–O ether), 770 (C–H out of plane bending); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 11.63 (1H, *s*, OH), 11.35 (1H, *s*, OH), 8.12 (1H, *d*,  $J = 7.8$  Hz, ArH), 8.05 (1H, *d*,  $J = 7.7$  Hz, ArH), 7.69 (2H, *m*, ArH), 7.43–7.47 (4H, *m*, ArH), 7.15–6.98 (3H, *m*, ArH), 6.07 (1H, *s*, CH aliphatic); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 167.22 (C–OH), 165.10 (C=O), 152.87 (C=), 144.03 (C–F), 143.57 (C–F), 133.58 (C=), 125.46 (CH=), 124.88 (CH=), 122.93 (CH=), 117.86 (CH=), 117.72 (CH=), 117.17 (CH=), 116.40 (C=), 116.22 (CH=), 103.96 (C=), 36.08 (CH aliphatic); MS (*m/z*, (relative abundance, %)): 448 (M<sup>+</sup>, 39.1), 327, 285, 162, 120, 92 (100).

*3,3'-(2-Chloro-6-fluorobenzylidene)bis(4-hydroxycoumarin)* (**2e**). White solid; yield: 92 %, m.p. 288–290 °C; Anal. Calcd. for C<sub>25</sub>H<sub>14</sub>ClFO<sub>6</sub>: C, 64.60; H, 3.04 %. Found: C 64.71; H 3.10 %; IR (KBr, cm<sup>-1</sup>): 3100 (OH), 2700 (C–H stretching), 1660 (C=O stretching of –COOR group), 1600 (C=C– stretching of olefine), 1550, 1500 (C=C– stretching of aromatic ring), 1350, 1110 (C–F), 760 (C–H out of plane bending); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 10.6 (1H, *br*, OH), 8.06 (1H, *dd*,  $J = 1.5, 8.0$  Hz, ArH), 8.02 (1H, *dd*,  $J = 1.4, 7.9$  Hz, ArH), 7.45 (1H, *t*,  $J = 7.8$  Hz, ArH), 7.45 (1H, *t*,  $J = 7.8$  Hz, ArH), 7.38 (1H, *t*,  $J = 7.2$  Hz, ArH), 7.33 (1H, *t*,  $J = 8.2$  Hz, ArH), 7.12–7.27 (5H, *m*, ArH), 5.50 (1H, *s*, CH aliphatic); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 161.72 (C–F), 161.00 (C–OH), 153.21 (C=O), 152.84 (C=), 133.56 (C–Cl), 133.11 (CH=), 130.03 (CH=), 126.75 (CH=), 125.45 (CH=), 124.82 (C=), 123.58 (C=), 117.35 (CH=), 117 (C=), 116.20 (CH=), 114.33 (C=), 28.98 (CH aliphatic), MS (*m/z*, (relative abundance, %)): 463 (M<sup>+</sup>, 0.07), 444 (M–HF, 41.7), 409, 283 (100), 163, 121.

*3,3'-(3-Phenoxybenzylidene)bis(4-hydroxycoumarin)* (**2g**). White solid; yield: 90 %, m.p. 218–220 °C; Anal. Calcd. for C<sub>31</sub>H<sub>20</sub>O<sub>7</sub>: C, 73.80; H, 3.99 %. Found: C, 73.59; H, 3.84 %; IR (KBr, cm<sup>-1</sup>): 3100 (OH), 2750 (C–H stretching), 1660 (C=O stretching of –COOR group), 1600 (C=C– stretching of olefin), 1550, 1500 (C=C– stretching of aromatic ring), 1200 (C–O–C ester), 1110 (C–O

ether), 760 (C–H out of plane bending);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 11.66 (1H, *s*, OH), 11.33 (1H, *s*, OH), 8.10 (1H, *d*,  $J = 7.7$  Hz, ArH), 8.04 (1H, *d*,  $J = 7.7$  Hz, ArH), 7.65–7.68 (2H, *m*, ArH), 7.29–7.34 (3H, *m*, ArH), 6.92–7.07 (6H, *m*, ArH), 6.12 (1H, *s*, CH aliphatic);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm) 166.39 (C–OH), 165.14 (C=O), 157.24, 156.56, 152.75, 143.58, 143.46, 132.22, 130.25, 129.99, 124.45, 124.05, 123.37, 122.51, 118.87, 118.77, 118.41, 118.00, 116.33, 116.27, 104.23 (aromatic), 36.50 (CH aliphatic); MS (*m/z*, (relative abundance, %)): 504 ( $\text{M}^+$ , 15.3), 342, 274, 249, 162, 120, 92 (100), 63.

*3,3'-Propylidenebis(4-hydroxycoumarin)* (**2l**). Yellow solid; yield: 75 %; m.p. 144–146 °C; Anal. Calcd. for  $\text{C}_{21}\text{H}_{16}\text{O}_6$ : C, 69.23; H, 4.43 %. Found: C, 69.18; H, 4.39 %; IR (KBr,  $\text{cm}^{-1}$ ): 3100 (OH), 2900 (C–H stretching), 1650 (–C=O stretching of –COOR group), 1600, 1540, 1480 (C=C– stretching of aromatic ring), 1110 (C–O), 750 (C–H out of plane bending);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 12.03 (1H, *s*, OH), 11.22 (1H, *s*, OH), 8.04 (2H, *d*,  $J = 8.4$  Hz, ArH), 7.60–7.65 (2H, *m*, ArH), 7.38–7.42 (4H, *m*, ArH), 4.44 (1H, *t*, –CH–CH<sub>2</sub>,  $J = 8$  Hz), 2.41–2.51 (2H, *m*, CH–CH<sub>2</sub>–CH<sub>3</sub>), 1.01 (3H, *t*, –CH<sub>2</sub>–CH<sub>3</sub>,  $J = 7.4$  Hz);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 165.36 (C–OH), 164.69 (C=O), 152.50 (C=), 132.85 (CH=), 125.12 (CH=), 124.45 (CH=), 117.60 (CH=), 116.91 (C=), 106.02 (C=), 35.28 (CH), 22.13 (CH<sub>2</sub>), 13.60 (CH<sub>3</sub>); MS (*m/z*, (relative abundance, %)): 364 ( $\text{M}^+$ , 24.4), 335, 279, 241, 202, 176, 149, 121 (100), 92.

*3,3'-(4-Cyanobenzylidene)bis(4-hydroxycoumarin)* (**2m**). White solid; yield: 95 %; m.p. 240–242 °C; Anal. Calcd. for  $\text{C}_{26}\text{H}_{15}\text{NO}_6$ : C, 71.39; H, 3.45; N, 3.20 %. Found: C, 71.29; H, 3.32; N, 3.25 %; IR (KBr,  $\text{cm}^{-1}$ ): 3400 (OH), 3000 (C–H stretching), 2200 (–C≡N), 1660 (–C=O stretching of –COOR group), 1620 (C=C– stretching of olefin), 1560 (C=C– stretching of aromatic ring), 1340, 1080 (C–O ether), 780, 750, (C–H out of plane bending);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 11.57 (1H, *s*, OH), 11.39 (1H, *s*, OH), 8.13 (1H, *d*, ArH,  $J = 7.7$  Hz), 8.04 (1H, *d*, ArH,  $J = 7.7$  Hz), 7.67–7.72 (4H, *m*, ArH), 7.44–7.51 (4H, *m*, ArH), 7.40 (2H, *d*,  $J = 7.9$  Hz, ArH), 6.14 (1H, *s*, C–H aliphatic);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 167.50 (C–OH), 164.89 (C=O), 152.94 (C=), 148.71 (C=), 132.34 (CH=), 131.96 (CH=), 128.29 (CH=), 124.56 (CH=), 123.76 (CH=), 119.69 (CH=), 119.52 (C=), 116.20 (–C≡N), 108.39 (C=), 103.44 (C=), 37.14 (CH aliphatic); MS (*m/z*, (relative abundance, %)): 437 ( $\text{M}^+$ , 0.58), 342, 249, 165, 120, 92 (100).