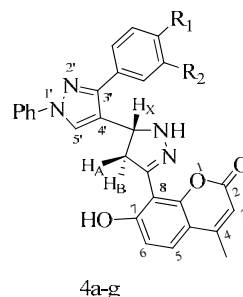
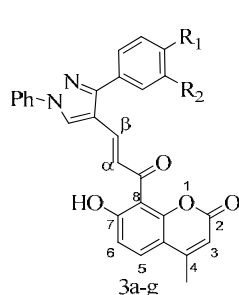


SUPPLEMENTARY MATERIAL TO  
**Microwave-assisted synthesis of some new coumarin–pyrazoline hybrids and their antimicrobial activity**

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*J. Serb. Chem. Soc.* 80 (3) (2015) 305–313



General structures of the synthesized compounds with atomic numbering.

ANALYTICAL AND SPECTRAL DATA FOR COMPOUNDS **3a–g** AND **4a–g**

(*E*)-8-[3-(1,3-Diphenyl-1*H*-pyrazol-4-yl)-1-oxo-2-propen-1-yl]-7-hydroxy-4-methyl-2*H*-1-benzopyran-2-one (**3a**). Anal. Calcd. for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: C, 74.94; H, 4.46; N, 6.21 %. Found: C, 74.99; H, 4.50; N, 6.25 %; IR (KBr, cm<sup>-1</sup>): 3440 (OH), 1636 (C=N); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ / ppm): 2.45 (3H, *d*, *J* = 1.004 Hz, CH<sub>3</sub>), 6.20 (1H, *d*, *J* = 1.0 Hz, H<sub>3</sub>), 6.96 (1H, *d*, *J* = 9.0 Hz, H<sub>6</sub>), 7.33–7.37 (1H, *m*, Ar-H), 7.46–7.54 (5H, *m*, Ar-H), 7.68 (1H, *d*, *J* = 9.0 Hz, H<sub>5</sub>), 7.73–7.75 (2H, *m*, Ar-H), 7.85–7.87 (2H, *m*, Ar-H), 8.04 (1H, *d*, *J* = 15.5 Hz, H<sub>α</sub>), 8.18 (1H, *d*, *J* = 15.5 Hz, H<sub>β</sub>), 8.62 (1H, *s*, pyrazole H), 13.94 (1H, *s*, OH); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ / ppm): 19.3, 109.7, 110.9, 115.3, 118.6, 119.4, 122.8, 125.6, 126.3, 127.3, 128.7, 128.8, 129.5, 130.8, 134.2, 137.2, 137.5, 153.4, 154.8, 156.3, 153.5, 159.6, 163.6, 193.0; MS (*m/z*): 449 ([M+H]<sup>+</sup>, 100 %).

(*E*)-7-Hydroxy-8-[3-[3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl]-1-oxo-2-propen-1-yl]-4-methyl-2*H*-1-benzopyran-2-one (**3b**). Anal. Calcd. for C<sub>29</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub>: C, 72.79; H, 4.63; N, 5.85 %. Found: C, 72.81; H, 4.65; N, 5.87 %;

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IR (KBr,  $\text{cm}^{-1}$ ): 3444 (OH), 1635 (C=N);  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.45 (3H, *d*,  $\text{CH}_3$ ,  $J = 1.0$  Hz), 3.89 (3H, *s*,  $\text{OCH}_3$ ), 6.20 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.96 (1H, *d*,  $J = 8.7$  Hz,  $\text{H}_6$ ), 7.05 (2H, *d*,  $J = 9.0$  Hz, Ar-H), 7.33–7.37 (1H, *m*, Ar-H), 7.48–7.52 (2H, *m*, Ar-H), 7.67 (1H, *d*,  $J = 8.7$  Hz,  $\text{H}_5$ ), 7.69 (2H, *d*,  $J = 9.0$  Hz, Ar-H), 7.84–7.86 (2H, *m*, Ar-H), 8.03 (1H, *d*,  $J = 15.3$  Hz,  $\text{H}_\alpha$ ), 8.16 (1H, *d*,  $J = 15.3$  Hz,  $\text{H}_\beta$ ), 8.60 (1H, *s*, pyrazole H), 13.97 (1H, *s*, OH);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.3, 55.4, 110.9, 112.0, 114.3, 115.3, 118.4, 119.4, 120.3, 123.8, 124.1, 124.6, 125.3, 127.2, 129.5, 130.0, 130.8, 136.9, 139.4, 156.3, 156.6, 159.7, 160.1, 167.4, 196.1; MS ( $m/z$ ): 479 ( $[\text{M}+\text{H}]^+$ , 100 %).

(E)-8-{3-[3-(3,4-Dimethoxyphenyl)-1-phenyl-1H-pyrazol-4-yl]-1-oxo-2-propen-1-yl}-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**3c**). Anal. Calcd. for  $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_6$ : C, 70.86; H, 4.76; N, 5.51 %. Found: C, 70.90; H, 4.78; N, 5.49 %; IR (KBr,  $\text{cm}^{-1}$ ): 3447 (OH), 1633 (C=N);  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.45 (3H, *d*,  $J = 1.0$  Hz,  $\text{CH}_3$ ), 3.87 (3H, *s*,  $\text{OCH}_3$ ), 3.89 (3H, *s*,  $\text{OCH}_3$ ), 6.20 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.97 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_6$ ), 7.33–7.37 (1H, *m*, Ar-H), 7.46–7.54 (3H, *m*, Ar-H), 7.68 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_5$ ), 7.76–7.78 (2H, *m*, Ar-H), 7.86–7.88 (2H, *m*, Ar-H), 8.05 (1H, *d*,  $J = 15.5$  Hz,  $\text{H}_\alpha$ ), 8.18 (1H, *d*,  $J = 15.5$  Hz,  $\text{H}_\beta$ ), 8.64 (1H, *s*, pyrazole H), 13.97 (1H, *s*, OH);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.3, 55.2, 55.4, 110.8, 114.8, 118.6, 119.6, 121.8, 124.3, 125.4, 126.8, 127.1, 127.7, 128.1, 128.5, 129.5, 131.8, 132.5, 134.8, 137.2, 137.5, 153.4, 154.8, 156.3, 153.5, 159.6, 163.7, 193.0; MS ( $m/z$ ): 509 ( $[\text{M}+\text{H}]^+$ , 100 %).

(E)-7-Hydroxy-4-methyl-8-[3-(1-phenyl-3-p-tolyl-1H-pyrazol-4-yl)-1-oxo-2-propen-1-yl]-2H-1-benzopyran-2-one (**3d**). Anal. Calcd. for  $\text{C}_{29}\text{H}_{22}\text{N}_2\text{O}_4$ : C, 75.31; H, 4.79; N, 6.06 %. Found: C, 75.34; H, 4.82; N, 6.04 %; IR (KBr,  $\text{cm}^{-1}$ ): 3436 (OH), 1637 (C=N);  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.43 (3H, *s*,  $\text{CH}_3$ ), 2.45 (3H, *d*,  $J = 1.0$  Hz,  $\text{CH}_3$ ), 6.20 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.95 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_6$ ), 7.31–7.36 (3H, *m*, Ar-H), 7.48–7.52 (2H, *m*, Ar-H), 7.63 (2H, *d*,  $J = 8.0$  Hz, Ar-H), 7.68 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_5$ ), 7.85 (2H, *d*,  $J = 8.0$  Hz, Ar-H), 8.04 (1H, *d*,  $J = 15.5$  Hz,  $\text{H}_\alpha$ ), 8.16 (1H, *d*,  $J = 15.5$  Hz,  $\text{H}_\beta$ ), 8.60 (1H, *s*, pyrazole H), 13.95 (1H, *s*, OH);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.3, 21.37, 109.6, 110.9, 112.0, 115.3, 118.5, 119.4, 125.4, 126.6, 127.2, 129.2, 129.5, 129.5, 129.6, 130.8, 138.6, 139.4, 153.4, 154.3, 154.8, 159.6, 167.4, 192.9; MS ( $m/z$ ): 463 ( $[\text{M}+\text{H}]^+$ , 100 %).

(E)-8-[3-[3-(4-Fluorophenyl)-1-phenyl-1H-pyrazol-4-yl]-1-oxo-2-propen-1-yl]-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**3e**). Anal. Calcd. for  $\text{C}_{28}\text{H}_{19}\text{FN}_2\text{O}_4$ : C, 72.10; H, 4.11; N, 6.01 %. Found: C, 72.12; H, 4.14; N, 6.06 %; IR (KBr,  $\text{cm}^{-1}$ ): 3448 (OH), 1636 (C=N);  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.45 (3H, *d*,  $J = 1.0$  Hz,  $\text{CH}_3$ ), 6.20 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.95 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_6$ ), 7.05 (2H, *d*,  $J = 8.5$  Hz, Ar-H), 7.35–7.36 (1H, *m*, Ar-H), 7.40–7.53 (2H, *m*, Ar-H), 7.69 (2H, *d*,  $J = 8.5$  Hz, Ar-H), 7.71 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_5$ ), 7.84–7.86 (2H, *m*, Ar-H), 8.04 (1H, *d*,  $J = 15.3$  Hz,  $\text{H}_\alpha$ ), 8.15 (1H, *d*,  $J =$

= 15.3 Hz,  $H_{\beta}$ ), 8.60 (1H, *s*, pyrazole H), 13.95 (1H, *s*, OH);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.3, 110.7, 111.5, 114.4, 115.3, 118.4, 119.4, 120.3, 123.8, 124.1, 124.6, 125.2, 127.2, 129.5, 130.0, 130.8, 131.2, 135.6, 136.9, 139.4, 158.3, 159.6, 160.7, 164.1, 167.4, 196.1; MS ( $m/z$ ): 467 ( $[\text{M}+\text{H}]^+$ , 100%).

(*E*)-8-[3-[3-(4-Chlorophenyl)-1-phenyl-1H-pyrazol-4-yl]-1-oxo-2-propen-1-yl]-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**3f**). Anal. Calcd. for  $\text{C}_{28}\text{H}_{19}\text{ClN}_2\text{O}_4$ : C, 69.64; H, 3.97; N, 5.80 %. Found: C, 69.68; H, 4.01; N, 5.84 %; IR (KBr,  $\text{cm}^{-1}$ ): 3445 (OH), 1636 (C=N);  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.46 (3H, *d*,  $J = 1.0$  Hz,  $\text{CH}_3$ ), 6.20 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.97 (1H, *d*,  $J = 8.7$  Hz,  $\text{H}_6$ ), 7.34–7.37 (3H, *m*, Ar-H), 7.49–7.51 (2H, *m*, Ar-H), 7.63 (2H, *d*,  $J = 8.5$  Hz, Ar-H), 7.68 (1H, *d*,  $J = 8.7$  Hz,  $\text{H}_5$ ), 7.85 (2H, *d*,  $J = 8.0$  Hz, Ar-H), 8.04 (1H, *d*,  $J = 15.5$  Hz,  $\text{H}_a$ ), 8.16 (1H, *d*,  $J = 15.5$  Hz,  $\text{H}_{\beta}$ ), 8.60 (1H, *s*, pyrazole H), 13.95 (1H, *s*, OH);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.3, 110.9, 112.1, 115.4, 118.7, 119.2, 125.1, 125.7, 126.4, 127.4, 129.2, 129.5, 129.5, 129.6, 130.8, 138.6, 139.4, 142.8, 153.4, 154.3, 154.8, 159.6, 167.4, 192.9; MS ( $m/z$ ): 483 ( $[\text{M}+\text{H}]^+$ , 100 %).

(*E*)-8-[3-[3-(4-Bromophenyl)-1-phenyl-1H-pyrazol-4-yl]-1-oxo-2-propen-1-yl]-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**3g**). Anal. Calcd. for  $\text{C}_{28}\text{H}_{19}\text{BrN}_2\text{O}_4$ : C, 63.77; H, 3.63; N, 5.31 %. Found: C, 63.80; H, 3.67; N, 5.35 %; IR (KBr,  $\text{cm}^{-1}$ ): 3441 (OH), 1654 (C=N);  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.45 (3H, *d*,  $J = 1.0$  Hz,  $\text{CH}_3$ ), 6.20 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.96 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_6$ ), 7.36–7.44 (5H, *m*, Ar-H), 7.68 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_5$ ), 7.73–7.75 (2H, *m*, Ar-H), 7.85–7.87 (2H, *m*, Ar-H), 8.04 (1H, *d*,  $J = 15.5$  Hz,  $\text{H}_a$ ), 8.18 (1H, *d*,  $J = 15.5$  Hz,  $\text{H}_{\beta}$ ), 8.62 (1H, *s*, pyrazole H), 13.94 (1H, *s*, OH);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.2, 109.62, 114.3, 115.2, 120.8, 123.2, 124.6, 126.8, 127.3, 127.7, 128.9, 129.5, 130.4, 134.3, 137.4, 137.3, 153.2, 154.6, 156.1, 153.5, 157.6, 162.8, 192.4; MS ( $m/z$ ): 527 ( $[\text{M}+\text{H}]^+$ , 100 %).

8-(4',5'-Dihydro-1,3-diphenyl[4,5'-bi-1H-pyrazol]-3'-yl)-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**4a**). Anal. Calcd. for  $\text{C}_{28}\text{H}_{22}\text{N}_4\text{O}_4$ : C, 72.71; H, 4.79; N, 12.11 %. Found: C, 72.75; H, 4.82; N, 12.14 %; IR (KBr,  $\text{cm}^{-1}$ ): 3333 (OH), 1597 (C=N);  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.41 (3H, *d*,  $J = 1.0$  Hz,  $\text{CH}_3$ ), 3.78 (1H, *dd*,  $J = 17.8$  Hz,  $J = 9.0$  Hz,  $\text{H}_A$ ), 4.09 (1H, *dd*,  $J = 17.8$  Hz,  $J = 10.5$  Hz,  $\text{H}_B$ ), 5.14 (1H, *dd*,  $J = 9.0$  Hz,  $J = 10.5$  Hz,  $\text{H}_X$ ), 5.97 (1H, *brs*, N-H,  $\text{D}_2\text{O}$  exchangeable), 6.12 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.97 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_6$ ), 7.29–7.31 (1H, *m*, Ar-H), 7.39–7.50 (6H, *m*, Ar-H), 7.69–7.74 (4H, *m*, Ar-H,  $\text{H}_5$ ), 8.05 (1H, *s*, pyrazole H), 12.54 (1H, *s*, OH);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.1, 44.2, 54.3, 105.4, 110.9, 112.3, 113.9, 119.2, 122.0, 125.9, 126.6, 128.2, 128.3, 128.8, 129.4, 132.8, 139.8, 151.5, 153.2, 155.5, 160.3, 161.8; MS ( $m/z$ ): 463 ( $[\text{M}+\text{H}]^+$ , 100 %).

8-[4',5'-Dihydro-3-(4-methoxyphenyl)-1-phenyl[4,5'-bi-1H-pyrazol]-3'-yl]-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**4b**). Anal. Calcd. for  $\text{C}_{29}\text{H}_{24}\text{N}_4\text{O}_4$ :

C, 70.72; H, 4.91; N, 11.38 %. Found: C, 70.75; H, 4.94; N, 11.42 %; IR (KBr,  $\text{cm}^{-1}$ ): 3335 (OH), 1599 (C=N);  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.42 (3H, *d*,  $J = 1.0$  Hz,  $\text{CH}_3$ ), 3.78 (1H, *dd*,  $J = 17.8$  Hz,  $J = 9.0$  Hz,  $\text{H}_A$ ), 3.84 (3H, *s*,  $\text{OCH}_3$ ), 4.10 (1H, *dd*,  $J = 17.8$  Hz,  $J = 10.5$  Hz,  $\text{H}_B$ ), 5.13 (1H, *dd*,  $J = 9.0$  Hz,  $J = 10.5$  Hz,  $\text{H}_X$ ), 5.83 (1H, *brs*, N-H,  $\text{D}_2\text{O}$  exchangeable), 6.13 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.97 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_6$ ), 6.99 (2H, *d*,  $J = 8.7$  Hz, Ar-H), 7.42–7.54 (4H, *m*, Ar-H,  $\text{H}_5$ ), 7.62 (2H, *d*,  $J = 8.7$  Hz, Ar-H), 7.69–7.73 (2H, *m*, Ar-H), 8.04 (1H, *s*, pyrazole H), 13.92 (1H, *s*, OH);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.3, 43.2, 53.7, 55.6, 109.7, 110.9, 115.3, 118.6, 119.4, 122.8, 125.6, 126.3, 127.3, 128.7, 128.8, 129.5, 130.8, 134.2, 137.2, 137.5, 153.4, 154.8, 156.3, 153.5, 159.6, 162.8; MS ( $m/z$ ): 493 ( $[\text{M}+\text{H}]^+$ , 100 %).

8-[3-(3,4-Dimethoxyphenyl)-4',5'-dihydro-1-phenyl[4,5'-bi-1H-pyrazol]-3'-yl]-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**4c**). Anal. Calcd. for  $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_5$ : C, 68.95; H, 5.02; N, 10.72 %. Found: C, 70.01; H, 5.06; N, 10.76 %; IR (KBr,  $\text{cm}^{-1}$ ): 3340 (OH), 1596 (C=N);  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.41 (3H, *d*,  $J = 1.0$  Hz,  $\text{CH}_3$ ), 3.77 (1H, *dd*,  $J = 17.8$  Hz,  $J = 9.0$  Hz,  $\text{H}_A$ ), 3.84 (3H, *s*,  $\text{OCH}_3$ ), 3.87 (3H, *s*,  $\text{OCH}_3$ ), 4.08 (1H, *dd*,  $J = 17.8$  Hz,  $J = 10.5$  Hz,  $\text{H}_B$ ), 5.14 (1H, *dd*,  $J = 9.0$  Hz,  $J = 10.5$  Hz,  $\text{H}_X$ ), 5.95 (1H, *brs*, N-H,  $\text{D}_2\text{O}$  exchangeable), 6.12 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.96 (1H, *d*,  $J = 9.0$  Hz,  $\text{H}_6$ ), 7.27–7.30 (1H, *m*, Ar-H), 7.39–7.50 (4H, *m*, Ar-H), 7.69–7.74 (4H, *m*, Ar-H,  $\text{H}_5$ ), 8.06 (1H, *s*, pyrazole H), 12.55 (1H, *s*, OH);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.0, 44.1, 52.3, 55.1, 55.4, 109.7, 110.9, 114.2, 114.4, 115.2, 116.3, 124.3, 112.3, 127.8, 130.5, 130.6, 131.4, 131.8, 132.7, 153.3, 158.5, 159.3, 160.4. MS ( $m/z$ ): 523 ( $[\text{M}+\text{H}]^+$ , 100 %).

8-[4',5'-Dihydro-1-phenyl-3-*p*-tolyl-[4,5'-bi-1H-pyrazol]-3'-yl]-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**4d**). Anal. Calcd. for  $\text{C}_{29}\text{H}_{24}\text{N}_4\text{O}_4$ : C, 73.09; H, 5.08; N, 11.76 %. Found: C, 73.11; H, 5.11; N, 11.79 %; IR (KBr,  $\text{cm}^{-1}$ ): 3336 (OH), 1599 (C=N);  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 2.41 (3H, *d*,  $J = 1.0$  Hz,  $\text{CH}_3$ ), 2.43 (3H, *s*,  $\text{CH}_3$ ), 3.77 (1H, *dd*,  $J = 17.8$  Hz,  $J = 9.0$  Hz,  $\text{H}_A$ ), 4.09 (1H, *dd*,  $J = 17.8$  Hz,  $J = 10.5$  Hz,  $\text{H}_B$ ), 5.14 (1H, *dd*,  $J = 9.0$  Hz,  $J = 10.5$  Hz,  $\text{H}_X$ ), 5.30 (1H, *brs*, N-H,  $\text{D}_2\text{O}$  exchangeable), 6.12 (1H, *d*,  $J = 1.0$  Hz,  $\text{H}_3$ ), 6.95 (2H, *d*,  $J = 8.5$  Hz, Ar-H), 6.99 (1H, *d*,  $J = 8.7$  Hz,  $\text{H}_6$ ), 7.42–7.54 (4H, *m*, Ar-H,  $\text{H}_5$ ), 7.62 (2H, *d*,  $J = 8.5$  Hz, Ar-H), 7.69–7.73 (2H, *m*, Ar-H), 8.04 (1H, *s*, pyrazole H), 13.92 (1H, *s*, OH);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 19.2, 21.3, 44.8, 54.6, 108.4, 112.4, 113.2, 115.5, 121.2, 122.4, 125.3, 125.8, 126.2, 127.3, 129.71, 130.4, 131.3, 133.2, 151.0, 153.2, 159, 162.5; MS ( $m/z$ ): 477 ( $[\text{M}+\text{H}]^+$ , 100 %).

8-[3-(4-Fluorophenyl)-4',5'-dihydro-1-phenyl[4,5'-bi-1H-pyrazol]-3'-yl]-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**4e**). Anal. Calcd. for  $\text{C}_{28}\text{H}_{21}\text{FN}_4\text{O}_3$ : C, 69.99; H, 4.41; F, 3.95; N, 11.66. Found: C, 70.02, H, 4.45, N, 11.69; IR (KBr,  $\text{cm}^{-1}$ ): 3334 (OH), 1597 (C=N);  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm):

2.41 (3H, *d*,  $J = 1.0$  Hz, CH<sub>3</sub>), 3.77 (1H, *dd*,  $J = 17.8$  Hz,  $J = 9.0$  Hz, H<sub>A</sub>), 4.08 (1H, *dd*,  $J = 17.8$  Hz,  $J = 10.5$  Hz, H<sub>B</sub>), 5.13 (1H, *dd*,  $J = 9.0$  Hz,  $J = 10.5$  Hz, H<sub>X</sub>), 4.97 (1H, *brs*, N–H, D<sub>2</sub>O exchangeable), 6.11 (1H, *d*,  $J = 1.0$  Hz, H<sub>3</sub>), 6.95 (1H, *d*,  $J = 9.0$  Hz, H<sub>6</sub>), 6.97 (2H, *d*,  $J = 8.3$  Hz, Ar-H), 7.40–7.48 (4H, *m*, Ar-H, H<sub>5</sub>), 7.64 (2H, *d*,  $J = 8.3$  Hz, Ar-H), 7.69–7.74 (2H, *m*, Ar-H), 8.03 (1H, *s*, pyrazole H), 12.53 (1H, *s*, OH); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 19.4, 44.2, 54.8, 109.7, 111.9, 115.3, 118.6, 119.4, 122.8, 125.6, 126.3, 127.3, 128.7, 128.8, 129.5, 130.8, 134.2, 137.2, 137.5, 153.4, 154.8, 156.3, 153.5, 159.6, 163.6; MS (*m/z*): 481 ([M+H]<sup>+</sup>, 100 %).

8-[3-(4-Chlorophenyl)-4',5'-dihydro-1-phenyl[4,5'-bi-1H-pyrazol]-3'-yl]-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**4f**). Anal. Calcd. for C<sub>28</sub>H<sub>21</sub>ClN<sub>4</sub>O<sub>3</sub>: C, 67.67; H, 4.26; N, 11.27 %. Found: C, 67.70; H, 4.30; N, 11.30 %; IR (KBr, cm<sup>-1</sup>): 3332 (OH), 1595 (C=N); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 2.42 (3H, *d*,  $J = 1.0$  Hz, CH<sub>3</sub>), 3.75 (1H, *dd*,  $J = 17.8$  Hz,  $J = 9.0$  Hz, H<sub>A</sub>), 4.06 (1H, *dd*,  $J = 17.8$  Hz,  $J = 10.5$  Hz, H<sub>B</sub>), 5.14 (1H, *dd*,  $J = 9.0$  Hz,  $J = 10.5$  Hz, H<sub>X</sub>), 5.63 (1H, *brs*, N–H, D<sub>2</sub>O exchangeable), 6.12 (1H, *d*,  $J = 1.0$  Hz, H<sub>3</sub>), 6.98 (1H, *d*,  $J = 9.0$  Hz, H<sub>6</sub>), 7.18 (2H, *d*,  $J = 8.4$  Hz, Ar-H), 7.37–7.42 (4H, *m*, Ar-H, H<sub>5</sub>), 7.48 (2H, *d*,  $J = 8.4$  Hz, Ar-H), 7.71–7.74 (2H, *m*, Ar-H), 8.02 (1H, *s*, pyrazole H), 12.58 (1H, *s*, OH); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 19.2, 43.2, 54.8, 111.6, 116.3, 118.1, 119.8, 121.8, 125.8, 126.3, 127.3, 128.7, 128.9, 129.5, 130.8, 134.2, 137.2, 137.5, 153.4, 154.7, 156.3, 153.5, 157.6, 162.6; MS (*m/z*): 497 ([M+H]<sup>+</sup>, 100 %).

8-[3-(4-Bromophenyl)-4',5'-dihydro-1-phenyl[4,5'-bi-1H-pyrazol]-3'-yl]-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (**4g**). Anal. Calcd. for C<sub>28</sub>H<sub>21</sub>BrN<sub>4</sub>O<sub>3</sub>: C, 62.12; H, 3.91; N, 10.35 %. Found: C, 62.15; H, 3.94; N, 10.38 %; IR (KBr, cm<sup>-1</sup>): 3330 (OH), 1596 (C=N); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 2.43 (3H, *d*,  $J = 1.0$  Hz, CH<sub>3</sub>), 3.80 (1H, *dd*,  $J = 17.8$  Hz,  $J = 9.0$  Hz, H<sub>A</sub>), 4.08 (1H, *dd*,  $J = 17.8$  Hz,  $J = 10.5$  Hz, H<sub>B</sub>), 5.16 (1H, *dd*,  $J = 9.0$  Hz,  $J = 10.5$  Hz, H<sub>X</sub>), 5.42 (1H, *brs*, N–H, D<sub>2</sub>O exchangeable), 6.14 (1H, *d*,  $J = 1.0$  Hz, H<sub>3</sub>), 6.92 (1H, *d*,  $J = 9.0$  Hz, H<sub>6</sub>), 7.18 (2H, *d*,  $J = 8.3$  Hz, Ar-H), 7.37–7.42 (4H, *m*, Ar-H, H<sub>5</sub>), 7.51 (2H, *d*,  $J = 8.3$  Hz, Ar-H), 7.68–7.72 (2H, *m*, Ar-H), 8.02 (1H, *s*, pyrazole H), 12.58 (1H, *s*, OH); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 19.3, 43.5, 54.3, 11.7, 110.0, 114.3, 119.0, 119.4, 122.4, 123.6, 125.3, 127.1, 128.4, 128.8, 129.1, 130.4, 134.1, 137.2, 137.5, 153.4, 154.6, 154.9, 155.5, 157.6, 164.6; MS (*m/z*): 541 ([M+H]<sup>+</sup>, 100 %).