

## Supplementary data

### **ZrP<sub>2</sub>O<sub>7</sub> nanoparticles as a robust and efficient catalyst for the synthesis of 2-aryl-5-methyl-2,3-dihydro-1*H*-3-pyrazolones under microwave irradiation**

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Spectral data

**4-[(2-Hydroxy-1-naphthyl)(phenyl)methyl]-5-methyl-2-phenyl-2,3-dihydro-1H-3-pyrazolone (5a):** Yield: 86%; White solid; m.p 204–206°C; (lit.<sup>23</sup> 205-206 °C), Rf value 0.35 (hexane/ethyl acetate, 8:2); FT-IR (KBr): 3417, 3162, 3083, 2911, 1612, 1593, 1492, 1412, 1279, 1212, 731, 695 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ (ppm) 2.12 (s, 3H, CH<sub>3</sub>), 6.21 (s, 1H,CH), 7.08 (m, 4H, ArH), 7.13 (m, 2H, ArH), 7.18 (m, 3H, ArH), 7.29 (m, 3H, ArH), 7.31 (s, 1H, NH), 7.71 (m, 3H, ArH), 8.23 (s, 1H, ArH), 10.83 (brs, 1H, OH); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ (ppm) 16.6, 40.9, 124.6, 125.3, 126.1, 127.4, 128.2, 130.5, 130.9, 131.6, 132.2, 133.0, 133.6, 133.8, 133.9, 134.2, 136.2, 138.9, 141.6, 146.8, 153.4, 159.1; Anal. Calcd. for C<sub>27</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 79.78; H, 5.46; N, 6.89; Found: C, 79.74; H, 5.51; N, 6.85.

**4-[(2-Hydroxy-1-naphthyl)(4-methoxyphenyl)methyl]-5-methyl-2-phenyl-2,3-dihydro-1H-3-pyrazolone (5b):** Yield: 82%; White solid; m.p180–181°C; (lit.<sup>23</sup> 180-181°C), Rf value 0.32 (hexane/ethyl acetate, 8:2); FT-IR (KBr): 3422, 3153, 3092, 2944, 1619, 1593, 1487, 1418, 1293, 815, 735, 685 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ (ppm) 2.13 (s, 3H, CH<sub>3</sub>), 3.59 (s, 3H, OCH<sub>3</sub>), 6.12 (s, 1H, CH), 6.77 (m, 2H, ArH), 6.95 (m, 2H, ArH), 7.08 (m, 1H, ArH), 7.23 (m, 2H, ArH),7.35 (s, 1H, NH), 7.46 (m, 3H, ArH), 7.68 (m, 3H, ArH), 7.79 (m, 1H, ArH), 8.19 (s, 1H, ArH), 10.86 (brs, 1H, OH); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ (ppm) 14.7, 34.4, 54.8, 106.6, 112.8, 119.1, 120.6, 121.8, 122.4, 124.9, 125.7, 128.2, 128.4, 128.5, 128.6, 132.6, 133.4, 133.6, 136.1, 147.5, 148.6, 153.2, 156.7; Anal. Calcd. for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>: C, 77.04; H, 5.54; N, 6.42; Found: C, 76.98; H, 5.48; N, 6.45.

***2-(4-chlorophenyl)-1,2-dihydro-4-((2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl)-5-methylpyrazol-3-one (5c)***: Yield: 86%; White solid; m.p 181–182°C; (lit.<sup>23</sup> 183-184°C), R<sub>f</sub> value 0.28 (hexane/ethyl acetate, 8:2); FT-IR (KBr): 3432, 3088, 2917, 1618, 1596, 1495, 1343, 814, 756, 734, 690, 597 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ (ppm) 2.19 (s, 3H, CH<sub>3</sub>), 6.31 (s, 1H, CH), 7.14 (m, 1H, ArH), 7.29 (s, 1H, NH), 7.33 (m, 3H, ArH), 7.46 (m, 1H, ArH), 7.56 (m, 2H, ArH), 7.71 (m, 5H, ArH), 8.14 (m, 1H, ArH), 8.26 (m, 1H, ArH), 10.73 (brs, 1H, OH); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ (ppm) 16.9, 40.8, 120.7, 121.4, 124.6, 125.9, 127.0, 127.2, 127.7, 128.3, 131.6, 133.5, 133.8, 134.2, 134.8, 138.2, 139.9, 149.6, 152.5, 153.7, 158.5, 159.2; 163.1; Anal. Calcd. for C<sub>27</sub>H<sub>20</sub>ClN<sub>3</sub>O<sub>4</sub>: C, 66.74; H, 4.15; N, 8.65; Found: C, 66.69; H, 4.10; N, 8.57.

***4-((4-bromophenyl)(2-hydroxynaphthalen-1-yl)methyl)-2-(4-chlorophenyl)-1,2-dihydro-5-methylpyrazol-3-one (5d)***: Yield: 83%; Yellowish solid; m.p 155–156°C; (lit.<sup>23</sup> 157-158°C); R<sub>f</sub> value 0.31 (hexane/ethyl acetate, 8:2); FT-IR (KBr): 3419, 3145, 3085, 2969, 1628, 1585, 1472, 1413, 1274, 816, 805, 736, 691 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ (ppm) 2.14 (s, 3H, CH<sub>3</sub>), 6.12 (s, 1H, CH), 7.05 (m, 5H, ArH), 7.08 (s, 1H, NH), 7.21 (m, 2H, ArH), 7.29 (m, 2H, ArH), 7.36 (t, 1H, ArH), 7.56 (t, 1H, ArH), 7.71 (d, 1H, ArH), 7.83 (d, 1H, ArH), 8.03 (d, 1H, ArH), 10.75 (brs, 1H, OH); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ (ppm) 14.7, 36.4, 106.4, 120.2, 121.5, 122.2, 123.4, 126.7, 127.2, 127.6, 128.4, 128.7, 128.9, 129.1, 129.2, 129.6, 131.4, 131.9, 133.5, 134.9, 138.6, 146.2, 153.9; Anal. Calcd. for C<sub>27</sub>H<sub>20</sub>BrClN<sub>2</sub>O<sub>2</sub>: C, 62.39; H, 3.88; N, 5.39; Found: C, 62.37; H, 3.75; N, 5.31.

***4-[(4-Chlorophenyl)(2-hydroxy-1-naphthyl)methyl]-5-methyl-2-phenyl-2,3-dihydro-***

***1H-3-pyrazolone (5e)***: Yield: 90%; Yellow solid; m.p 172-174°C; (lit.<sup>22</sup> 174-176°C); Rf value 0.29 (hexane/ethyl acetate, 8:2); FT-IR (KBr): 3402, 3085, 2913, 1615, 1594, 1492, 1341, 813, 754, 732, 691 cm<sup>-1</sup>; <sup>1</sup>H NMR(400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 2.20 (s, 3H, CH<sub>3</sub>), 6.21 (s, 1H, CH), 7.12-7.18 (m, 3H, ArH), 7.22 (s, 1H, NH), 7.27-7.34 (m, 4H, ArH), 7.48-7.54 (m, 3H, ArH), 7.75-7.83 (m, 3H, ArH), 7.89 (d, 1H, *J*= 8.3 Hz, ArH), 8.28 (d, 1H, *J*=8.3 Hz, ArH), 10.85 (bs, 1H, OH); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ (ppm): 12.1, 36.1, 106.2, 119.9, 120.7, 121.3, 122.9, 123.4, 125.7, 126.8, 128.1, 129.0, 129.1, 129.2, 129.4, 129.7, 130.4, 133.5, 133.8, 137.0, 141.2, 148.5, 154.0. Anal. Calcd for C<sub>27</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>2</sub>: C, 73.55; H, 4.80; N, 6.35; Found: C, 73.61; H, 4.85; N, 6.24.

***4-[(4-nitrophenyl)(2-hydroxy-1-naphthyl)methyl]-5-methyl-2-phenyl-2,3-dihydro-1H-3-pyrazolone (5f)***: Yield: 92%; Yellow solid; m.p 207-209°C; (lit.<sup>22</sup> 207-208°C); Rf value 0.30 (hexane/ethyl acetate, 8:2); FT-IR (KBr): 3432, 3088, 2917, 1618, 1596, 1552, 1495, 1353, 814, 756, 734, 692, 595 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 2.23 (s, 3H, CH<sub>3</sub>), 6.29 (s, 1H, CH), 7.12-7.16 (m, 1H, ArH), 7.20 (s, 1H, NH), 7.22-7.29 (m, 1H, ArH), 7.30-7.36 (m, 3H, ArH), 7.41-7.48 (m, 3H, ArH), 7.68-7.74 (m, 2H, ArH), 7.76-7.79 (m, 1H, ArH), 7.81-7.85 (m, 1H, ArH), 8.10-8.13 (m, 2H, ArH), 8.20-8.22 (m, 1H, ArH), 10.82 (bs, 1H, OH); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ (ppm): 12.0, 36.8, 105.3, 119.9, 120.3, 121.0, 123.0, 123.3, 123.4, 125.7, 126.9, 129.0, 129.1, 129.4, 129.5, 133.5, 133.7, 137.0, 138.2, 146.0, 148.5, 151.5, 153.9. Anal. Calcd for C<sub>27</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>: C, 71.83; H, 4.69; N, 9.31; Found: C, 71.75; H, 4.61; N, 9.25.

***4-[(2-Hydroxy-1-naphthyl)(4-methylphenyl)methyl]-5-methyl-2-phenyl-2,3-***

***1,2-dihydro-1H-3-pyrazolone (5g)***: Yield: 83%; White solid; m.p. 178-180°C; (lit.<sup>22</sup> 178-179°C); Rf value 0.33 (hexane/ethyl acetate, 8:2); FT-IR (KBr): 3422, 3082, 2914, 1615, 1594, 1491, 1341, 814, 753, 731, 692cm<sup>-1</sup>; <sup>1</sup>H NMR(400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 2.24 (s, 3H, CH<sub>3</sub>), 2.45 (s, 3H, CH<sub>3</sub>), 6.09 (s, 1H, CH), 7.02-7.09 (m, 4H, ArH), 7.15-7.21 (m, 2H, ArH), 7.30-7.37 (m, 3H, ArH), 7.39 (s, 1H, NH), 7.50 (m, 1H, ArH), 7.69-7.71 (m, 3H, ArH), 7.81 (m, 1H, ArH), 8.15 (d, 1H, *J*= 8.0 Hz, ArH), 10.81 (bs, 1H, OH); <sup>13</sup>C NMR (100 MHz DMSO-d<sub>6</sub>) δ (ppm): 11.9, 21.2, 35.9, 106.6, 120.2, 121.2, 121.6, 122.5, 125.6, 126.5, 127.4, 128.7, 128.8, 128.9, 129.0, 129.1, 129.8, 133.8, 134.7, 136.6, 138.3, 147.7, 154.1, 162.4. Anal. Calcd for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: C, 79.98; H, 5.75; N, 6.66; Found: C, 79.89; H, 5.81; N, 6.60.

***2-(4-Chlorophenyl)-4-[(4-chlorophenyl)(2-hydroxy-1-naphthyl)methyl]-5-methyl-2,3-dihydro-1H-3-pyrazolone (5h)***: Yield: 83%; Yellow solid; m.p. 152-154°C; (lit.<sup>22</sup> 152-153°C) Rf value 0.34 (hexane/ethyl acetate, 8:2); FT-IR (KBr): 3412, 3075, 2912, 1618, 1595, 1492, 1341, 812, 752, 733 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 2.26 (s, 3H, CH<sub>3</sub>), 6.09 (s, 1H, CH), 7.01-7.07 (m, 5H, ArH), 7.10 (s, 1H, NH), 7.19-7.24 (m, 2H, ArH), 7.26-7.30 (m, 2H, ArH), 7.36 (t, 1H, *J*=7.0 Hz, ArH), 7.55 (t, 1H, *J*=7.0 Hz, ArH), 7.68 (m, 1H, ArH), 7.82 (m, 1H, ArH), 8.06 (m, 1H, ArH), 10.71 (bs, 1H, OH); <sup>13</sup>C NMR (100 MHz DMSO-d<sub>6</sub>) δ (ppm): 12.9, 35.5, 106.1, 120.0, 121.3, 122.3, 123.1, 126.8, 127.0, 127.7, 128.3, 128.8, 128.9, 129.0, 129.2, 129.5, 131.2, 131.8, 133.4, 134.8, 139.0, 145.6, 153.5. Anal. Calcd for C<sub>27</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 68.22; H, 4.24; N, 5.89; Found: C, 68.28; H, 4.32; N, 5.81.

***1,2-dihydro-4-((2-hydroxynaphthalen-1-yl)(4-isopropylphenyl)methyl)-5-methyl-2-phenylpyrazol-3-one (5i)***: Yield: 82%; White solid; m.p.184-186 °C; Rf value 0.33

(hexane/ethyl acetate, 8:2); FT-IR (KBr): 3412, 3072, 2911, 1613, 1593, 1492, 1341, 815, 754, 692  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 1.13 (d,  $J=7$  Hz, 6H), 2.18 (s, 3H,  $\text{CH}_3$ ), 2.78 (m, 1H, CH), 5.75 (s, 1H, CH), 6.91 (m, 2H, ArH, NH), 7.19-7.32 (m, 11 H, ArH), 7.73 (m, 3H, ArH), 10.90 (bs, 1H, OH);  $^{13}\text{C}$  NMR (100 MHz  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 11.9, 23.7, 34.5, 35.1, 106.1, 119.6, 120.5, 121.3, 122.9, 123.4, 125.3, 126.4, 128.1, 128.8, 129.0, 129.1, 129.4, 129.7, 130.4, 132.5, 132.9, 137.2, 141.2, 147.3, 153.2. Anal. Calcd for  $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2$ : C, 80.33; H, 6.29; N, 6.25; Found: C, 80.44; H, 6.37; N, 6.14.