



SUPPLEMENTARY MATERIAL TO

**Synthesis and antimicrobial evaluation of some 1-(4-arylthiazol-2-yl)-1'-(aryl/heteroaryl)-3,3'-dimethyl-[4,5'-bi-1H-pyrazol]-5-ols**

SATBIR MOR<sup>1\*</sup>, RAJNI MOHIL<sup>1</sup>, SAVITA NAGORIA<sup>1</sup> and ASHWANI KUMAR<sup>2</sup>

<sup>1</sup>Department of Chemistry, Guru Jambheshwar University of Science & Technology, Hisar-125001, Haryana, India and Department of Pharmaceutical Sciences, Guru Jambheshwar University of Science & Technology, Hisar-125001, Haryana, India

J. Serb. Chem. Soc. 82 (2) (2017) 127–139

PHYSICAL AND SPECTRAL DATA OF THE SYNTHESIZED COMPOUNDS

*1-(4-(4-Methoxyphenyl)thiazol-2-yl)-3,3'-dimethyl-1'-phenyl-[4,5'-bi-1H-pyrazol]-5-ol (7a)*. The compound was obtained as white crystals (acetonitrile); Yield: 79 %; m.p.: 264–266 °C; Anal. Calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>5</sub>O<sub>2</sub>S (FW: 443.14): C, 64.99; H, 4.77; N, 15.79 %. Found: C, 65.12; H, 4.98; N, 16.11 %; IR (KBr, cm<sup>-1</sup>): 3099 (O–H, stretch), 1614, 1535, 1508, 1448, 1408, 1359, 1247, 1176, 1064, 1031, 950, 833, 750, 736; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 1.88 (3H, *s*, CH<sub>3</sub>-3), 2.41 (3H, *s*, CH<sub>3</sub>-3'), 3.86 (3H, *s*, OCH<sub>3</sub>-4'''), 6.29 (1H, *s*, H-4'), 6.96 (2H, *d*, *J* = 8.40 Hz, H-3''' & H-5'''), 7.02 (1H, *s*, H-5'''), 7.24–7.43 (5H, *m*, H-2'', H-3'', H-4'', H-5'', H-6''), 7.68 (2H, *d*, *J* = 8.40 Hz, H-2''' & H-6'''), 13.05 (1H, *brs*, OH-5, deuterium oxide exchangeable); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 13.6 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>), 55.4 (OCH<sub>3</sub>), 94.3, 108.9, 109.2, 114.3 (2C), 124.4 (2C), 126.4, 127.0, 127.4 (2C), 128.9 (2C), 135.2, 139.1, 147.6, 148.7, 152.3, 153.0, 159.8, 159.9; TOF MS ES<sup>+</sup> (*m/z* (relative abundance, %)): 466.1 (M<sup>+</sup>+Na, 15), 444.1 (M<sup>+</sup>+1, 100), 442.0 (61), 294.1 (3), 272.1 (32), 240.1 (3), 165.1 (6), 114.2 (2).

*3,3'-Dimethyl-1'-phenyl-1-(4-p-tolylthiazol-2-yl)-[4,5'-bi-1H-pyrazol]-5-ol (7b)*. The compound was obtained as white crystals (acetonitrile), Yield: 86 %; m.p.: 238–240 °C; Anal. Calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>5</sub>OS (FW: 427.15): C, 67.43; H, 4.95; N, 16.38 %. Found: C, 67.14; H, 5.27; N, 16.01 %; IR (KBr, cm<sup>-1</sup>): 3107 (O–H, stretch), 1614, 1525, 1508, 1452, 1398, 1384, 1357, 1276, 1246, 1174, 1091, 1062, 1026, 950, 893, 835, 761, 738, 709; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 1.87 (3H, *s*, CH<sub>3</sub>-3), 2.39 (3H, *s*, CH<sub>3</sub>-3'), 2.41 (3H, *s*, CH<sub>3</sub>-4'''), 6.29 (1H, *s*, H-4'), 7.11–7.43 (8H, *m*, H-2'', H-3'', H-4'', H-5'', H-6'', H-5''', H-3''',

\* Corresponding author. E-mail: satbir\_mor@yahoo.co.in

H-5'''), 7.64 (2H, *d*,  $J = 8.00$  Hz, H-2'''' & H-6'''), 13.05 (1H, *brs*, OH-5, deuterium oxide exchangeable);  $^{13}\text{C-NMR}$  (100 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 13.5 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 94.2, 109.1, 109.9, 124.5 (2C), 126.0 (2C), 127.8, 129.5 (2C), 129.6 (2C), 131.4, 134.9, 137.9, 139.8, 147.7, 148.3, 152.6, 153.3, 159.5; TOF MS ES<sup>+</sup> ( $m/z$  (relative abundance, %)): 428.5 (M<sup>+</sup>+1, 100), 412.0 (37), 386.1 (12), 338.1 (31), 272.1 (26), 256.2 (19), 240.1 (10), 239.2 (7), 228.7 (12), 165.1 (5), 157.2 (3).

*1-(4-(4-Chlorophenyl)thiazol-2-yl)-3,3'-dimethyl-1'-phenyl-[4,5'-bi-1H-pyrazol]-5-ol (7c)*. The compound was obtained as white crystals (acetonitrile), Yield: 83 %; m.p.: 258–260 °C; Anal. Calcd. for C<sub>23</sub>H<sub>18</sub>ClN<sub>5</sub>OS (FW: 447.09): C, 61.67; H, 4.05; N, 15.63 %. Found: C, 61.69; H, 3.79; N, 15.69 %; IR (KBr, cm<sup>-1</sup>): 3103 (O–H, stretch), 1637, 1618, 1523, 1506, 1446, 1402, 1382, 1357, 1273, 1193, 1122, 1091, 1062, 1033, 950, 835, 808, 763, 736, 705;  $^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 1.88 (3H, *s*, CH<sub>3</sub>-3), 2.43 (3H, *s*, CH<sub>3</sub>-3'), 6.30 (1H, *s*, H-4'), 7.17–7.52 (8H, *m*, H-2'', H-3'', H-4'', H-5'', H-6'', H-5''', H-3''', H-5'''), 7.68 (2H, *d*,  $J = 8.80$  Hz, H-2'''' & H-6'''), 13.06 (1H, *brs*, OH-5, deuterium oxide exchangeable);  $^{13}\text{C-NMR}$  (100 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 13.4 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>), 94.4, 109.3, 111.1, 124.1 (2C), 126.3, 127.1 (2C), 129.0 (2C), 129.2 (2C), 132.7, 133.6, 134.7, 138.9, 148.2, 148.5, 152.0, 153.1, 160.2; TOF MS ES<sup>+</sup> ( $m/z$  (relative abundance, %)): 448.2 (M<sup>+</sup>+1, 100), 372.0 (23), 338.1 (9), 295.1 (11), 275.9 (23), 272.1 (56), 240.1 (7), 165.1 (2), 157.1 (16), 114.2 (5).

*3,3'-Dimethyl-1'-phenyl-1-(4-phenylthiazol-2-yl)-[4,5'-bi-1H-pyrazol]-5-ol (7d)*. The compound was obtained as white crystals (acetonitrile), Yield: 78 %; m.p.: 270–272 °C (Lit.<sup>1</sup> m.p.: 272–274 °C); Anal. Calcd. for C<sub>23</sub>H<sub>19</sub>N<sub>5</sub>OS (FW: 413.13): C, 66.81; H, 4.63; N, 16.94 %. Found: C, 66.49; H, 4.97; N, 17.12 %; IR (KBr, cm<sup>-1</sup>): 3107 (O–H, stretch), 1622, 1535, 1502, 1450, 1390, 1361, 1280, 1246, 1178, 1029, 833;  $^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 1.88 (3H, *s*, CH<sub>3</sub>-3), 2.41 (3H, *s*, CH<sub>3</sub>-3'), 6.29 (1H, *s*, H-4'), 7.13–7.46 (9H, *m*, H-2'', H-3'', H-4'', H-5'', H-6'', H-5''', H-3''', H-4''', H-5'''), 7.75 (2H, *d*,  $J = 8.80$  Hz, H-2'''' & H-6'''), 13.16 (1H, *brs*, OH-5, deuterium oxide exchangeable);  $^{13}\text{C-NMR}$  (100 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 13.4 (CH<sub>3</sub>), 13.7 (CH<sub>3</sub>), 93.9, 109.7, 110.7, 124.7 (2C), 126.0, 126.4 (2C), 128.6, 128.9 (2C), 129.5 (2C), 132.8, 134.6, 138.6, 148.1, 149.0, 152.5, 153.2, 160.0; TOF MS ES<sup>+</sup> ( $m/z$  (relative abundance, %)): 414.1 (M<sup>+</sup>+1, 100), 412.2 (13), 398.4 (37), 338.1 (29), 253.1 (31), 272.1 (26), 241.7 (22), 240.1 (11), 159.2 (18), 157.1 (6), 114.2 (12).

*1'-(6-Chlorobenzothiazol-2-yl)-1-(4-(4-methoxyphenyl)thiazol-2-yl)-3,3'-dimethyl-[4,5'-bi-1H-pyrazol]-5-ol (7e)*. The compound was obtained as white crystals (acetonitrile), Yield: 84 %; m.p.: 302–304 °C; Anal. Calcd. for C<sub>25</sub>H<sub>19</sub>ClN<sub>6</sub>O<sub>2</sub>S<sub>2</sub> (FW: 534.13): C, 56.12; H, 3.58; N, 15.71 %. Found: C, 56.32; H, 3.93; N, 15.33 %; IR (KBr, cm<sup>-1</sup>): 3103 (O–H, stretch), 1625, 1531, 1508, 1440, 1361, 1249, 1184, 1112, 1028, 945, 823, 750;  $^1\text{H-NMR}$  (400 MHz,

DMSO- $d_6$ ,  $\delta$  / ppm): 2.26 (3H, *s*, CH<sub>3</sub>-3), 2.34 (3H, *s*, CH<sub>3</sub>-3'), 3.82 (3H, *s*, OCH<sub>3</sub>-4'''), 6.56 (1H, *s*, H-4'), 7.04 (2H, *d*,  $J = 8.80$  Hz, H-3'''' & H-5''''), 7.41–7.66 (3H, *m*, H-4'', H-5'' & H-5'''), 7.96 (2H, *d*,  $J = 8.80$  Hz, H-2'''' & H-6'''), 8.19 (1H, *d*,  $J = 1.60$  Hz, H-7''), 13.06 (1H, *brs*, OH-5, deuterium oxide exchangeable); <sup>13</sup>C-NMR (100 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 13.5 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>), 55.3 (OCH<sub>3</sub>), 93.8, 109.5, 109.9, 114.0 (2C), 121.5, 122.8, 126.0, 127.0, 127.5 (2C), 129.6, 135.0, 137.1, 147.7, 149.7, 151.0, 152.1, 153.2, 159.9, 160.0, 160.1; TOF MS ES<sup>+</sup> ( $m/z$  (relative abundance, %)): 556.9 (M<sup>++</sup>Na, 72), 535.0 (M<sup>++</sup>1, 78), 475.2 (10), 453.2 (10), 416.3 (3), 360.3 (32), 349.0 (11), 338.3 (100), 279.1 (21), 272.2 (9), 255.1 (45), 248.1 (13), 245.1 (8), 199.2 (2), 165.1 (11), 149.1 (5), 114.2 (4).

*1'-(6-Chlorobenzothiazol-2-yl)-3,3'-dimethyl-1-(4-p-tolylthiazol-2-yl)-[4,5'-bi-1H-pyrazol]-5-ol (7f)*. The compound was obtained as white crystals (acetonitrile), Yield: 77 %; m.p.: 276–278 °C; Anal. Calcd. for C<sub>25</sub>H<sub>19</sub>ClN<sub>6</sub>OS<sub>2</sub> (FW: 518.08): C, 57.85; H, 3.69; N, 16.19 %. Found: C, 58.19; H, 3.99; N, 16.38 %; IR (KBr, cm<sup>-1</sup>): 3103 (O–H, stretch), 1633, 1618, 1537, 1510, 1446, 1400, 1381, 1355, 1274, 1242, 1190, 1103, 945, 840, 815, 761, 731; <sup>1</sup>H-NMR (400 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 2.26 (3H, *s*, CH<sub>3</sub>-3), 2.34 (3H, *s*, CH<sub>3</sub>-3'), 2.35 (3H, *s*, CH<sub>3</sub>-4'''), 6.56 (1H, *s*, H-4'), 7.28 (2H, *d*,  $J = 7.60$  Hz, H-3'''' & H-5''''), 7.40–7.42 (1H, *s*, H-5''), 7.60–7.62 (1H, *m*, H-4''), 7.71 (1H, *s*, H-5'''), 7.93 (2H, *d*,  $J = 7.60$  Hz, H-2'''' & H-6'''), 8.19 (1H, *d*,  $J = 1.57$  Hz, H-7''), 13.09 (1H, *brs*, OH-5, deuterium oxide exchangeable); <sup>13</sup>C-NMR (100 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 13.5 (CH<sub>3</sub>), 13.7 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 93.7, 109.7, 110.0, 121.3, 123.1, 125.7 (2C), 125.9, 129.3 (2C), 130.0, 131.3, 134.6, 136.9, 138.6, 148.0, 149.9, 151.3, 152.5, 153.4, 159.3, 160.5; TOF MS ES<sup>+</sup> ( $m/z$  (relative abundance, %)): 540.9 (M<sup>++</sup>Na, 53), 518.9 (M<sup>++</sup>1, 100), 475.2 (29), 453.2 (12), 416.3 (2), 360.3 (31), 338.3 (92), 339.2 (26), 279.2 (21), 256.2 (27), 249.3 (1), 248.1 (15), 228.9 (19), 200.2 (3), 149.1 (5), 114.2 (4).

*1'-(6-Chlorobenzothiazol-2-yl)-1-(4-(4-chlorophenyl)thiazol-2-yl)-3,3'-dimethyl-[4,5'-bi-1H-pyrazol]-5-ol (7g)*. The compound was obtained as white crystals (acetonitrile), Yield: 69 %; m.p.: 312–314 °C; Anal. Calcd. for C<sub>24</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>6</sub>OS<sub>2</sub> (FW: 538.02): C, 53.43; H, 2.99; N, 15.58 %. Found: C, 53.59; H, 3.17; N, 15.87 %; IR (KBr, cm<sup>-1</sup>): 3097 (O–H, stretch), 1618, 1521, 1415, 1371, 1288, 1097, 939, 829, 775, 742; <sup>1</sup>H-NMR (400 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 2.26 (3H, *s*, CH<sub>3</sub>-3), 2.34 (3H, *s*, CH<sub>3</sub>-3'), 6.57 (1H, *s*, H-4'), 7.41–7.43 (1H, *m*, H-5''), 7.55–7.61 (3H, *m*, H-5''', H-2'''' & H-6'''), 7.86 (1H, *s*, H-4''), 8.06 (2H, *d*,  $J = 8.00$  Hz, H-3'''' & H-5''''), 8.19 (1H, *d*,  $J = 1.60$  Hz, H-7''), 13.17 (1H, *brs*, OH-5, deuterium oxide exchangeable); <sup>13</sup>C-NMR (100 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 13.6 (CH<sub>3</sub>), 13.7 (CH<sub>3</sub>), 94.0, 109.8, 111.0, 121.1, 123.2, 125.8, 127.3 (2C), 129.2 (2C), 129.8, 132.5, 132.8, 134.9, 136.3, 148.3, 149.8, 151.1, 152.8, 153.5, 159.4, 160.4; TOF MS ES<sup>+</sup> ( $m/z$  (relative abundance, %)): 560.8 (M<sup>++</sup>Na,

19), 540.7 ( $M^{+3}$ , 27), 538.7 ( $M^{+1}$ , 93), 462.0 (1), 419.1 (2), 338.3 (5), 294.0 (12), 276.1 (31), 273.2 (21), 272.1 (100), 247.9 (27), 240.1 (23), 201.2 (4), 165.2 (32), 148.9 (12), 136.4 (5), 121.2 (17).

*1'-(6-Chlorobenzothiazol-2-yl)-3,3'-dimethyl-1-(4-phenylthiazol-2-yl)-[4,5'-bi-1H-pyrazol]-5-ol (7h)*. The compound was obtained as white crystals (acetonitrile), Yield: 84 %; m.p.: 266–268 °C (Lit.<sup>1</sup> m.p.: 268–269 °C); Anal. Calcd. for  $C_{24}H_{17}ClN_6OS_2$  (FW: 504.06): C, 57.08; H, 3.39; N, 16.64 %. Found: C, 57.21; H, 3.17; N, 16.28 %; IR (KBr,  $cm^{-1}$ ): 3105 (O–H, stretch), 1631, 1614, 1529, 1506, 1444, 1394, 1379, 1359, 1282, 1213, 1182, 1066, 950, 839, 817, 729;  $^1H$ -NMR (400 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 2.24 (3H, s, CH<sub>3</sub>-3), 2.37 (3H, s, CH<sub>3</sub>-3'), 6.54 (1H, s, H-4'), 7.12–8.17 (9H, m, H-4'', H-5'', H-6'', H-7'', H-2''', H-3''', H-4''', H-5''' & H-6'''), 13.06 (1H, brs, OH-5, deuterium oxide exchangeable);  $^{13}C$ -NMR (100 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 13.6 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>), 93.8, 109.5, 110.8, 121.3, 122.9, 125.7, 126.5 (2C), 128.8 (2C), 128.9, 129.7, 132.7, 134.3, 136.5, 147.9, 150.1, 151.4, 152.7, 153.3, 159.6, 160.1; TOF MS ES<sup>+</sup> ( $m/z$  (relative abundance, %)): 505.13 ( $M^{+1}$ , 100), 475.2 (26), 448.2 (18), 360.3 (12), 322.0 (17), 338.3 (36), 256.2 (23), 248.1 (15), 245.1 (8), 241.9 (13), 165.2 (7), 149.1 (14).

*1'-(6-Methoxybenzothiazol-2-yl)-1-(4-(4-methoxyphenyl)thiazol-2-yl)-3,3'-dimethyl-[4,5'-bi-1H-pyrazol]-5-ol (7i)*. The compound was obtained as white crystals (acetonitrile), Yield: 91 %; m.p.: 320–322 °C; Anal. Calcd. for  $C_{26}H_{22}N_6O_3S_2$  (FW: 530.12): C, 58.85; H, 4.18; N, 15.84 %. Found: C, 58.59; H, 4.49; N, 16.12 %; IR (KBr,  $cm^{-1}$ ): 3105 (O–H, stretch), 1618, 1541, 1502, 1469, 1406, 1359, 1244, 1176, 1026, 945, 825, 754;  $^1H$ -NMR (400 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 2.24 (3H, s, CH<sub>3</sub>-3), 2.33 (3H, s, CH<sub>3</sub>-3'), 3.81 (3H, s, OCH<sub>3</sub>-4'''), 3.82 (3H, s, OCH<sub>3</sub>-6''), 6.52 (1H, s, H-4'), 6.97–7.63 (6H, m, H-4'', H-5'', H-7'', H-5''', H-3''', & H-5'''), 7.92–8.01 (2H, m, H-2''', & H-6'''), 13.11 (1H, brs, OH-5, deuterium oxide exchangeable);  $^{13}C$ -NMR (100 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 13.4 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>), 55.4 (OCH<sub>3</sub>), 55.8 (OCH<sub>3</sub>), 94.1, 105.1, 109.9, 110.0, 114.2 (2C), 114.3, 122.4, 126.9, 127.0 (2C), 134.9, 136.3, 143.8, 147.5, 151.5, 152.0, 153.3, 156.8, 159.9, 159.8, 160.5; TOF MS ES<sup>+</sup>, ( $m/z$  (relative abundance, %)): 531.1 ( $M^{+1}$ , 38), 502.0 (19), 499.1 (12), 338.3 (100), 273.2 (13), 272.1 (56), 255.1 (23), 245.1 (16), 240.1 (23), 201.2 (4), 165.2 (32), 149.2 (17), 136.6 (8).

*1'-(6-Methoxybenzothiazol-2-yl)-3,3'-dimethyl-1-(4-p-tolylthiazol-2-yl)-[4,5'-bi-1H-pyrazol]-5-ol (7j)*. The compound was obtained as white crystals (acetonitrile), Yield: 79 %; m.p.; 288–290 °C; Anal. Calcd. for  $C_{26}H_{22}N_6O_2S_2$  (FW: 514.12): C, 60.68; H, 4.31; N, 16.33 %. Found: C, 60.47; H, 4.53; N, 16.12 %; IR (KBr,  $cm^{-1}$ ): 3107 (O–H, stretch), 1629, 1604, 1543, 1506, 1469, 1460, 1355, 1265, 1226, 1062, 1024, 945, 813, 758, 734;  $^1H$ -NMR (400 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 2.24 (3H, s, CH<sub>3</sub>-3), 2.33 (3H, s, CH<sub>3</sub>-3'), 2.35 (3H, s, CH<sub>3</sub>-4'''),

3.81 (3H, *s*, OCH<sub>3</sub>-6''), 6.52 (1H, *s*, H-4'), 6.97–6.99 (1H, *m*, H-5''), 7.29 (2H, *d*, *J* = 8.00 Hz, H-3''' & H-5'''), 7.51–7.71 (3H, *m*, H-4'', H-7'' & H-5'''), 7.93 (2H, *d*, *J* = 8.00 Hz, H-2''' & H-6'''), 13.02 (1H, *brs*, OH-5, deuterium oxide exchangeable); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 13.4 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 55.7 (OCH<sub>3</sub>), 93.8, 104.8, 109.8, 110.2, 114.5, 122.3, 125.7 (2C), 129.5 (2C), 131.0, 134.1, 136.2, 138.5, 144.1, 148.1, 151.6, 152.1, 153.1, 156.5, 159.6, 160.3; TOF MS ES<sup>+</sup> (*m/z* (relative abundance, %)): 515.1 (M<sup>+</sup>+1, 100), 423.0 (5), 351.1 (29), 338.3 (36), 273.2 (63), 272.1 (19), 270.1 (23), 256.1 (18), 239.1 (26), 229.1 (17), 201.2 (7), 175.2 (52), 148.9 (9).

*1-(4-(4-Chlorophenyl)thiazol-2-yl)-1'-(6-methoxybenzothiazol-2-yl)-3,3'-dimethyl-[4,5'-bi-1H-pyrazol]-5-ol (7k)*. The compound was obtained as white crystals (acetonitrile), Yield: 76 %; m.p.: 316–318 °C; Anal. Calcd. for C<sub>25</sub>H<sub>19</sub>ClN<sub>6</sub>O<sub>2</sub>S<sub>2</sub> (FW: 534.07): C, 56.12; H, 3.58; N, 15.71 %. Found: C, 56.01; H, 3.44; N, 15.89 %; IR (KBr, cm<sup>-1</sup>): 3107 (O–H, stretch), 1625, 1608, 1546, 1506, 1467, 1402, 1355, 1265, 1228, 1199, 1124, 1087, 1062, 1029, 945, 837, 810, 763, 740, 711; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 2.24 (3H, *s*, CH<sub>3</sub>-3), 2.33 (3H, *s*, CH<sub>3</sub>-3'), 3.81 (3H, *s*, OCH<sub>3</sub>-6''), 6.52 (1H, *s*, H-4'), 6.99–7.05 (1H, *m*, H-5''), 7.54–7.86 (5H, *m*, H-4'', H-7'', H-5''', H-2''' & H-6'''), 8.06 (2H, *d*, *J* = 7.60 Hz, H-3''' & H-5'''), 13.12 (1H, *brs*, OH-5, deuterium oxide exchangeable); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 13.5 (CH<sub>3</sub>), 13.7 (CH<sub>3</sub>), 55.8 (OCH<sub>3</sub>), 94.2, 104.7, 110.0, 110.9, 114.1, 122.0, 127.4 (2C), 129.0 (2C), 132.4, 132.6, 134.5, 136.0, 144.0, 147.8, 151.2, 152.5, 153.4, 156.1, 159.9, 160.9; TOF MS ES<sup>+</sup> (*m/z* (relative abundance, %)): 556.8 (M<sup>+</sup>+Na, 12), 534.8 (M<sup>+</sup>+1, 41), 475.1 (28), 453.1 (32), 419.2 (2), 391.2 (4), 338.3 (15), 294.0 (2), 276.1 (21), 272.1 (100), 244.1 (15), 240.0 (22), 223.0 (2), 165.1 (17), 114.2 (14).

*1'-(6-Methoxybenzothiazol-2-yl)-3,3'-dimethyl-1-(4-phenylthiazol-2-yl)-[4,5'-bi-1H-pyrazol]-5-ol (7l)*. The compound was obtained as white crystals (acetonitrile), Yield: 92 %; m.p.: 250–252 °C (Lit.<sup>1</sup> m.p.: 252–253 °C); Anal. Calcd. for C<sub>25</sub>H<sub>20</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub> (FW: 500.11): C, 59.98; H, 4.03; N, 16.79 %. Found: C, 60.13; H, 3.76; N, 16.57 %; IR (KBr, cm<sup>-1</sup>): 3105 (O–H, stretch), 1631, 1614, 1529, 1504, 1475, 1402, 1379, 1359, 1327, 1284, 1247, 1195, 1087, 1066, 950, 833, 732; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 2.26 (3H, *s*, CH<sub>3</sub>-3), 2.33 (3H, *s*, CH<sub>3</sub>-3'), 3.81 (3H, *s*, OCH<sub>3</sub>-6''), 6.56 (1H, *s*, H-4'), 7.13–7.46 (9H, *m*, H-4'', H-5'', H-7'', H-5''', H-2''', H-3''', H-4''', H-5'' & H-6'''), 13.06 (1H, *brs*, OH-5, deuterium oxide exchangeable); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 13.6 (CH<sub>3</sub>), 13.7 (CH<sub>3</sub>), 55.6 (OCH<sub>3</sub>), 94.3, 105.0, 109.7, 110.7, 114.3, 122.2, 126.5 (2C), 128.5, 129.1 (2C), 132.6, 134.5, 136.1, 144.3, 148.0, 151.3, 152.3, 153.2, 156.3, 159.2, 160.7; TOF MS ES<sup>+</sup> (*m/z* (relative abundance, %)): 501.1 (M<sup>+</sup>+1, 27), 475.1 (68), 453.1 (12), 419.2 (8), 340.2 (42), 338.3 (100), 294.0 (2), 272.1 (66), 257.0 (12), 244.2 (39), 242.1 (19), 223.0 (2), 179.1 (27), 165.1 (6), 114.2 (4).



*1'-(Benzothiazol-2-yl)-1-(4-(4-methoxyphenyl)thiazol-2-yl)-3,3'-dimethyl-[4,5'-bi-1H-pyrazol]-5-ol (7m)*. The compound was obtained as white crystals (acetonitrile), Yield: 75 %; m.p.: 292–294 °C; Anal. Calcd. for C<sub>25</sub>H<sub>20</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub> (FW: 500.11): C, 59.98; H, 4.03; N, 16.79 %. Found: C, 60.21; H, 4.39; N, 16.43 %; IR (KBr, cm<sup>-1</sup>): 3101 (O–H, stretch), 1643, 1608, 1544, 1531, 1446, 1386, 1359, 1280, 1246, 1176, 1120, 1028, 943, 839, 804, 761; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 2.26 (3H, *s*, CH<sub>3</sub>-3), 2.39 (3H, *s*, CH<sub>3</sub>-3'), 3.82 (3H, *s*, OCH<sub>3</sub>-4'''), 6.55 (1H, *s*, H-4'), 7.03–7.05 (2H, *m*, H-3''' & H-5'''), 7.38–7.62 (4H, *m*, H-4'', H-5'', H-6'' & H-5'''), 7.96–8.04 (3H, *m*, H-7'', H-2''' & H-6'''), 13.07 (1H, *brs*, OH-5, deuterium oxide exchangeable); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 13.4 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>), 55.3 (OCH<sub>3</sub>), 94.1, 109.5, 110.1, 114.1 (2C), 121.4, 122.0, 124.4, 126.4, 126.8, 127.2 (2C), 133.0, 135.0, 147.6, 151.0, 151.2, 152.3, 153.1, 159.5, 159.9, 160.3; TOF MS ES<sup>+</sup> (*m/z* (relative abundance, %)): 501.1 (M<sup>+</sup>+1, 100), 470.1 (8), 423.1 (27), 419.2 (3), 391.2 (9), 338.3 (100), 309.0 (17), 272.2 (28), 256.1 (78), 244.9 (17), 240.0 (10), 223.0 (6), 214.1 (8), 165.1 (21).

*1'-(Benzothiazol-2-yl)-3,3'-dimethyl-1-(4-p-tolylthiazol-2-yl)-[4,5'-bi-1H-pyrazol]-5-ol (7n)*. The compound was obtained as white crystals (acetonitrile), Yield: 71 %; m.p.: 284–286 °C; Anal. calcd. for C<sub>25</sub>H<sub>20</sub>N<sub>6</sub>OS<sub>2</sub> (FW: 484.11): C, 61.96; H, 4.16; N, 17.34 %. Found: C, 61.59; H, 4.48; N, 17.71 %; IR (KBr, cm<sup>-1</sup>): 3055 (O–H, stretch), 1637, 1610, 1537, 1517, 1444, 1363, 1280, 1242, 1120, 1064, 1028, 941, 808, 759, 734; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 2.26 (3H, *s*, CH<sub>3</sub>-3), 2.34 (3H, *s*, CH<sub>3</sub>-3'), 2.36 (3H, *s*, CH<sub>3</sub>-4'''), 6.55 (1H, *s*, H-4'), 7.25 (2H, *d*, *J* = 7.60 Hz, H-3''' & H-5'''), 7.34–7.71 (4H, *m*, H-5'', H-6'', H-7'' & H-5'''), 7.93 (2H, *d*, *J* = 7.60 Hz, H-2''' & H-6'''), 8.02–8.04 (1H, *m*, H-4''), 13.12 (1H, *brs*, OH-5, deuterium oxide exchangeable); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 13.5 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 94.3, 109.3, 110.1, 121.5, 122.1, 124.5, 125.8 (2C), 126.4, 129.6 (2C), 131.4, 132.9, 134.3, 138.0, 147.9, 151.2, 151.4, 152.4, 153.0, 159.4, 160.2; TOF MS ES<sup>+</sup> (*m/z* (relative abundance, %)): 485.1 (M<sup>+</sup>+1, 100), 469.1 (42), 453.1 (12), 419.2 (25), 394.2 (7), 338.3 (65), 294.0 (12), 272.1 (68), 270.0 (21), 256.1 (36), 229.1 (25), 223.0 (6), 214.2 (9), 165.1 (13), 114.2 (4).

*1'-(Benzothiazol-2-yl)-1-(4-(4-chlorophenyl)thiazol-2-yl)-3,3'-dimethyl-[4,5'-bi-1H-pyrazol]-5-ol (7o)*. The compound was obtained as white crystals (acetonitrile), Yield: 69 %; m.p.: 308–310 °C; Anal. Calcd. for C<sub>24</sub>H<sub>17</sub>ClN<sub>6</sub>OS<sub>2</sub> (FW: 504.06): C, 57.08; H, 3.39; N, 16.64 %. Found: C, 56.78; H, 3.26; N, 16.43 %; IR (KBr, cm<sup>-1</sup>): 3064 (O–H, stretch), 1643, 1601, 1552, 1517, 1498, 1442, 1398, 1354, 1350, 1280, 1197, 1122, 1089, 943, 835, 763; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 2.26 (3H, *s*, CH<sub>3</sub>-3), 2.34 (3H, *s*, CH<sub>3</sub>-3'), 6.55 (1H, *s*, H-4'), 7.34–7.62 (5H, *m*, H-5'', H-6'', H-7'', H-2''' & H-6'''), 7.82 (1H, *s*, H-5'''), 8.02–8.07 (3H, *m*, H-4'', H-3''' & H-5'''), 13.14 (1H, *brs*, OH-5, deuterium oxide

exchangeable);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 13.6 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ), 94.0, 110.1, 111.0, 121.0, 121.8, 124.3, 126.3, 127.3 (2C), 129.3 (2C), 132.6, 132.7, 133.0, 134.3, 148.1, 151.4, 151.5, 152.1, 153.2, 159.6, 160.1; TOF MS  $\text{ES}^+$  ( $m/z$  (relative abundance, %)): 505.3 ( $\text{M}^++1$ , 71), 469.1 (11), 452.1 (19), 429.2 (17), 391.2 (31), 338.3 (41), 290.0 (13), 275.8 (23), 272.1 (100), 240.0 (8), 223.0 (11), 214.2 (14), 179.1 (7).

*1'-(Benzo[thiazol-2-yl]-3,3'-dimethyl-1-(4-phenylthiazol-2-yl)-[4,5'-bi-1H-pyrazol]-5-ol (7p)*. The compound was obtained as white needles (acetonitrile), Yield: 84 %; m.p.: 258–260 °C; Anal. Calcd. for  $\text{C}_{24}\text{H}_{18}\text{N}_6\text{OS}_2$  (FW: 470.10): C, 61.26; H, 3.86; N, 17.86 %. Found: C, 60.91; H, 4.16; N, 17.53 %; IR (KBr,  $\text{cm}^{-1}$ ): 3105 (O–H, stretch), 1620, 1525, 1512, 1446, 1371, 1290, 1246, 1182, 1026, 952, 819, 742, 725;  $^1\text{H}$ -NMR (400 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 2.26 (3H, *s*,  $\text{CH}_3$ -3), 2.34 (3H, *s*,  $\text{CH}_3$ -3'), 6.56 (1H, *s*, H-4'), 7.14–7.96 (10H, *m*, H-4'', H-5'', H-6'', H-7'', H-5''', H-2''', H-3''', H-4''', H-5''', & H-6'''), 13.06 (1H, *brs*, OH-5, deuterium oxide exchangeable);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 13.4 ( $\text{CH}_3$ ), 13.7 ( $\text{CH}_3$ ), 94.2, 109.8, 110.8, 121.4, 121.9, 124.6, 126.4 (2C), 126.5, 128.4 (2C), 128.9, 133.0, 133.1, 134.1, 147.8, 151.6, 151.7, 152.2, 153.3, 159.8, 160.0; TOF MS  $\text{ES}^+$  ( $m/z$  (relative abundance, %)): 471.3 ( $\text{M}^++1$ , 100), 455.1 (24), 452.1 (9), 429.2 (32), 387.2 (23), 338.3 (56), 310.0 (3), 272.1 (78), 256.0 (12), 241.8 (17), 215.0 (3), 179.1 (12), 165.1 (5).

## REFERENCES

1. S. P. Singh, L. S. Tarar, D. Kumar, *Indian J. Heterocycl. Chem.* **3** (1993) 5.