



SUPPLEMENTARY MATERIAL TO  
**Synthesis and characterization of novel benzimidazole  
embedded 1,3,5-trisubstituted pyrazolines as antimicrobial  
agents**

GOPAL K. PADHY<sup>1,2</sup>, JAGADEESH PANDA<sup>3</sup> and AJAYA K. BEHERA<sup>1\*</sup>

<sup>1</sup>Organic Synthesis Laboratory, School of Chemistry, Sambalpur University, Jyoti Vihar, Burla 768019, India, <sup>2</sup>Maharajah's College of Pharmacy, Phool Baugh, Vizianagaram 535002, India and <sup>3</sup>Raghu College of Pharmacy, Dakamarri, Visakhapatnam 531162, India

J. Serb. Chem. Soc. 82 (9) (2017) 985–993

ANALYTICAL AND SPECTRAL DATA FOR SYNTHESISED COMPOUNDS

*1-(1-Benzyl-1H-benzimidazol-2-yl)-3-phenylprop-2-en-1-one (8)*.<sup>1</sup> Yield: 80 %; off-white solid; m.p.: 112–114 °C; Anal. Calcd. for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O: C, 81.63; H, 5.36; N, 8.28 %. Found: C, 81.70; H, 5.28; N, 8.16 %; IR (KBr, cm<sup>-1</sup>): 1661 (C=O), 1597 (C=N); <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 8.25 (1H, *d*, *J* = 20 Hz, H<sub>β</sub>), 7.94 (1H, *d*, *J* = 10 Hz, Ar-H), 7.89–7.84 (3H, *m*, H<sub>α</sub> & Ar-H), 7.75 (1H, *d*, *J* = 10 Hz, Ar-H), 7.50–7.39 (5H, *m*, Ar-H), 7.32–7.29 (2H, *m*, Ar-H), 7.26–7.23 (1H, *m*, Ar-H), 7.19 (2H, *d*, *J* = 5 Hz, Ar-H), 6.01 (2H, *s*, CH<sub>2</sub>); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 182.52 (C=O), 146.88, 144.59, 141.80, 137.75, 136.98, 134.74, 131.57, 129.62, 129.39, 129.11, 127.92, 127.22, 126.66, 124.38, 123.40, 121.96, 112.46, 48.47 (CH<sub>2</sub>); ESI-MS (*m/z*): 339.2 [M+H].

*1-(1-Benzyl-1H-benzimidazol-2-yl)-3-p-tolylprop-2-en-1-one (9)*. Yield: 78 %; pale yellow solid; m.p.: 179–182 °C; Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O: C, 81.79; H, 5.72; N, 7.95 %. Found: C, 81.67; H, 5.80; N, 7.85 %; IR (KBr, cm<sup>-1</sup>): 1651 (C=O), 1588 (C=N); <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 8.19 (1H, *d*, *J* = 17.5 Hz, H<sub>β</sub>), 7.92 (1H, *d*, *J* = 10 Hz, Ar-H), 7.83 (1H, *d*, *J* = 17.5 Hz, H<sub>α</sub>), 7.74 (3H, *d*, *J* = 10 Hz, Ar-H), 7.47–7.44 (1H, *m*, Ar-H), 7.41–7.38 (1H, *m*, Ar-H), 7.31–7.28 (4H, *m*, Ar-H), 7.25–7.22 (1H, *m*, Ar-H), 7.18 (2H, *d*, *J* = 10 Hz, Ar-H), 5.99 (2H, *s*, CH<sub>2</sub>), 2.36 (3H, *s*, CH<sub>3</sub>); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 182.53 (C=O), 146.95, 144.70, 141.83, 141.78, 137.76, 136.95, 132.04, 130.28, 129.45, 129.11, 127.92, 127.20, 126.60, 124.35, 122.37, 121.91, 112.44, 48.44 (CH<sub>2</sub>), 21.61 (CH<sub>3</sub>); ESI-MS (*m/z*): 353.2 [M+H].

\*Corresponding author. E-mail: [ajay.behera1962@gmail.com](mailto:ajay.behera1962@gmail.com)

*1-(1-Benzyl-1H-benzimidazol-2-yl)-3-(4-chlorophenyl)prop-2-en-1-one (10)*.<sup>1</sup> Yield: 74 %; off-white solid; m.p.: 156–158 °C; Anal. Calcd. for C<sub>23</sub>H<sub>17</sub>ClN<sub>2</sub>O: C, 74.09; H, 4.60; N, 7.51 %. Found: C, 73.87; H, 4.51; N, 7.70 %; IR (KBr, cm<sup>-1</sup>): 1652 (C=O) 1587 (C=N); <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 8.24 (1H, *d*, *J* = 20 Hz, H<sub>β</sub>), 7.93–7.83 (4H, *m*, H<sub>α</sub> & Ar-H), 7.75 (1H, *d*, *J* = 10.0 Hz, Ar-H), 7.54 (2H, *d*, *J* = 7.5, Ar-H), 7.48–7.39 (2H, *m*, Ar-H), 7.31–7.18 (5H, *m*, Ar-H), 5.99 (2H, *s*, CH<sub>2</sub>); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 182.40 (C=O), 146.79, 143.10, 141.78, 137.71, 136.99, 136.03, 133.70, 131.10, 129.66, 129.11, 127.94, 127.21, 126.74, 124.43, 124.09, 121.96, 112.48, 48.46 (CH<sub>2</sub>); ESI-MS (*m/z*): 373.1 [M+H].

*1-(1-Benzyl-1H-benzimidazol-2-yl)-3-(4-bromophenyl)prop-2-en-1-one (11)*. Yield: 78 %; pale yellow solid; m.p.: 198–200 °C; Anal. Calcd. for C<sub>23</sub>H<sub>17</sub>BrN<sub>2</sub>O: C, 66.20; H, 4.11; N, 6.71 %. Found: C, 66.16; H, 4.04; N, 6.58 %; IR (KBr, cm<sup>-1</sup>): 1652 (C=O), 1594 (C=N), 1581; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 8.26 (1H, *d*, *J* = 15 Hz, H<sub>β</sub>), 7.93 (1H, *d*, *J* = 7.5 Hz, Ar-H) 7.86–7.82 (3H, *m*, H<sub>α</sub> & Ar-H), 7.76 (1H, *d*, *J* = 10 Hz, Ar-H), 7.69 (2H, *d*, *J* = 5 Hz, Ar-H), 7.49–7.46 (1H, *m*, Ar-H), 7.43–7.40 (1H, *m*, Ar-H), 7.32–7.29 (2H, *m*, Ar-H), 7.26–7.23 (1H, *m*, Ar-H), 7.19 (2H, *d*, *J* = 5 Hz, Ar-H), 6.00 (2H, *s*, CH<sub>2</sub>); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 182.41 (C=O), 146.80, 143.19, 141.79, 137.72, 137.00, 134.03, 132.60, 131.28, 129.11, 127.93, 127.21, 126.74, 124.94, 124.42, 124.14, 121.97, 112.49, 48.47 (CH<sub>2</sub>); ESI-MS (*m/z*): 417.1 [M+H], 419.0 [M+2].

*1-(1-Benzyl-1H-benzimidazol-2-yl)-3-(4-fluorophenyl)prop-2-en-1-one (12)*. Yield: 83 %; white solid; m.p.: 160–162 °C; Anal. Calcd. for C<sub>23</sub>H<sub>17</sub>FN<sub>2</sub>O: C, 77.51; H, 4.81; N, 7.86 %. Found: 77.04; H, 4.96; N, 8.02 %; IR (KBr, cm<sup>-1</sup>): 1662 (C=O), 1590 (C=N); <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 8.19 (1H, *d*, *J* = 16 Hz, H<sub>β</sub>), 7.95–7.92 (3H, *m*, Ar-H) 7.87 (1H, *d*, *J* = 16 Hz, H<sub>α</sub>), 7.75 (1H, *d*, *J* = 8.0 Hz, Ar-H), 7.48–7.45 (1H, *m*, Ar-H), 7.42–7.39 (1H, *m*, Ar-H), 7.34–7.29 (4H, *m*, Ar-H), 7.26–7.24 (1H, *m*, Ar-H), 7.20–7.18 (2H, *m*, Ar-H), 6.00 (2H, *s*, CH<sub>2</sub>); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 182.47 (C=O), 165.12, 163.13, 146.84, 143.38, 141.79, 137.74, 136.97, 131.87, 131.80, 131.45, 131.43, 129.10, 127.92, 127.21, 126.65, 124.37, 123.30, 121.93, 116.74, 116.57, 112.46, 48.46 (CH<sub>2</sub>); ESI-MS (*m/z*): 357.1 [M+H].

*1-Benzyl-2-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzimidazole (13)*. Yield: 70 %; white solid; m.p.: 208–210 °C; Anal. Calcd. for C<sub>29</sub>H<sub>24</sub>N<sub>4</sub>: C, 81.28; H, 5.65; N, 13.07 %. Found: C, 81.45; H, 5.46; N, 12.78 %; IR (KBr, cm<sup>-1</sup>): 1595 (C=N), 1543, 1503, 1495, 1463, 1456, 1408, 1392, 1325 (C–N), 1306, 1164; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ / ppm): 7.85 (1H, *d*, *J* = 10 Hz, Ar-H), 7.52–7.49 (2H, *m*, Ar-H) 7.36–7.31 (4H, *m*, Ar-H) 7.28–7.23 (2H, *m*, Ar-H), 7.20–7.15 (4H, *m*, Ar-H), 7.07–7.04 (1H, *m*, Ar-H), 6.99–6.96 (2H, *m*, Ar-H), 6.83–6.80 (3H, *m*, Ar-H), 5.75 (1H, *dd*, *J*<sub>AX</sub> = 10 Hz, *J*<sub>BX</sub> = 15 Hz, H<sub>X</sub>),

5.39 (1H, *d*,  $J_{DC} = 20$  Hz,  $H_D$ ), 5.34 (1H, *d*,  $J_{CD} = 20$  Hz,  $H_C$ ), 3.71 (1H, *dd*,  $J_{BX} = 15$  Hz,  $J_{AB} = 20$  Hz,  $H_B$ ), 3.06 (1H, *dd*,  $J_{AX} = 10.0$  Hz,  $J_{AB} = 20.0$  Hz,  $H_A$ );  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 153.04 (C3 pyrazoline), 147.80, 145.14, 142.12, 136.81, 135.67, 131.83, 129.14, 129.01, 128.85, 128.60, 128.47, 127.49, 126.10, 125.86, 123.44, 122.65, 120.14, 120.00, 113.55, 110.14, 60.36 (C5 pyrazoline), 47.35 ( $\text{CH}_2$  benzyl), 40.03 (C4 pyrazoline); ESI-MS ( $m/z$ ): 429.0 [ $\text{M}+\text{H}$ ].

*1-Benzyl-2-(1-phenyl-5-p-tolyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzimidazole (14)*. Yield: 71 %; white solid; m.p.: 206–208 °C; Anal. Calcd. for  $\text{C}_{30}\text{H}_{26}\text{N}_4$ : C, 81.42; H, 5.92; N, 12.66 %. Found: C, 81.32; H, 5.70; N, 12.46 %; IR (KBr,  $\text{cm}^{-1}$ ): 1596 (C=N), 1576, 1498, 1462, 1455, 1409, 1379, 1318 (C–N), 1307, 1159, 1118;  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 7.85 (1H, *d*,  $J = 10$  Hz, Ar-H), 7.41 (2H, *d*, Ar-H), 7.33–7.30 (1H, *m*, Ar-H), 7.27–7.21 (3H, *m*, Ar-H), 7.18–7.14, (5H, *m*, Ar-H), 7.06 (1H, *t*,  $J = 7.5$  Hz, Ar-H), 7.0–6.96 (2H, *m*, Ar-H), 6.82–6.78 (3H, *m*, Ar-H), 5.72 (1H, *dd*,  $J_{AX} = 10$  Hz &  $J_{BX} = 15$  Hz,  $H_X$ ), 5.38 (1H, *d*,  $J_{DC} = 17.5$  Hz,  $H_D$ ), 5.33 (1H, *d*,  $J_{CD} = 17.5$  Hz,  $H_C$ ), 3.70 (1H, *dd*,  $J_{BX} = 15$  Hz &  $J_{AB} = 20$  Hz,  $H_B$ ), 3.05 (1H, *dd*,  $J_{AX} = 10$  Hz &  $J_{AB} = 20$  Hz,  $H_A$ ), 2.37 (3H, *s*,  $\text{CH}_3$ );  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 153.19 (C3 pyrazoline), 147.97, 145.34, 142.11, 139.18, 136.76, 135.68, 129.60, 129.45, 129.20, 129.11, 129.08, 128.84, 128.61, 127.48, 126.14, 125.87, 123.55, 123.41, 122.63, 120.00, 119.97, 113.53, 110.20, 60.34 (C5 pyrazoline), 47.39 ( $\text{CH}_2$  benzyl), 40.16 (C4 pyrazoline), 21.45 ( $\text{CH}_3$ ); ESI-MS ( $m/z$ ): 443.1 [ $\text{M}+\text{H}$ ].

*1-Benzyl-2-(5-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzimidazole (15)*. Yield: 60 %; off-white solid; m.p.: 207–209 °C; Anal. Calcd. for  $\text{C}_{29}\text{H}_{23}\text{ClN}_4$ : C, 75.23; H, 5.01; N, 12.10 %. Found: C, 75.12; H, 4.90; N, 11.92 %; IR (KBr,  $\text{cm}^{-1}$ ): 1596 (C=N), 1571, 1505, 1492, 1453, 1410, 1392, 1328 (C–N), 1088;  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 7.84 (1H, *d*,  $J = 8$  Hz, Ar-H), 7.42–7.39 (2H, *m*, Ar-H), 7.34–7.25 (5H, *m*, Ar-H), 7.19–7.14 (4H, *m*, Ar-H), 7.06 (1H, *t*,  $J = 7.5$  Hz, Ar-H), 7.01–6.98 (2H, *m*, Ar-H), 6.84–6.80 (3H, *m*, Ar-H), 5.75 (1H, *dd*,  $J_{AX} = 9.2$  Hz &  $J_{BX} = 13.7$  Hz,  $H_X$ ), 5.37 (1H, *d*,  $J_{DC} = 17.0$  Hz,  $H_D$ ), 5.33 (1H, *d*,  $J_{CD} = 17.0$  Hz,  $H_C$ ), 3.65 (1H, *dd*,  $J_{BX} = 13.5$  Hz &  $J_{AB} = 17.5$  Hz,  $H_B$ ), 2.99 (1H, *dd*,  $J_{AX} = 9.2$  Hz,  $J_{AB} = 17.7$  Hz,  $H_A$ );  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  / ppm): 153.74 (C3 pyrazoline), 146.68, 144.49, 142.52, 136.98, 136.24, 133.69, 131.30, 130.32, 129.35, 129.19, 129.16, 128.08, 127.76, 127.12, 123.15, 122.47, 119.72, 119.55, 113.26, 111.29, 57.54 (C5 pyrazoline), 47.01 ( $\text{CH}_2$  benzyl); ESI-MS ( $m/z$ ): 463.1 [ $\text{M}+\text{H}$ ].

*1-Benzyl-2-(5-(4-bromophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzimidazole (16)*. Yield: 72 %; white solid; m.p.: 198–200 °C; Anal. Calcd. for  $\text{C}_{29}\text{H}_{23}\text{BrN}_4$ : C, 68.64; H, 4.57; N, 11.04 %. Found: C, 68.50; H, 4.49; N, 10.86 %; IR (KBr,  $\text{cm}^{-1}$ ): 1597 (C=N), 1571, 1503, 1488, 1351, 1304 (C–N), 1044;  $^1\text{H}$ -NMR (500 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  / ppm): 7.64–7.55 (5H, *m*, Ar-H), 7.52–

-7.50 (1H, *m*, Ar-H), 7.29–7.26 (4H, *m*, Ar-H), 7.24–7.18 (2H, *m*, Ar-H), 7.11–7.07 (3H, *m*, Ar-H), 6.86 (2H, *d*,  $J = 10$  Hz, Ar-H), 6.71 (1H, *t*,  $J = 7.5$  Hz, Ar-H), 5.88 (1H, *dd*,  $J_{AX} = 5$  Hz &  $J_{BX} = 15$  Hz, H<sub>X</sub>), 5.69 (1H, *d*,  $J_{DC} = 17.5$  Hz, H<sub>D</sub>), 5.56 (1H, *d*,  $J_{CD} = 17.5$  Hz, H<sub>C</sub>), 3.85 (1H, *dd*,  $J_{BX} = 15$  Hz &  $J_{AB} = 20$  Hz, H<sub>B</sub>), 3.25 (1H, *dd*,  $J_{AX} = 5$  Hz &  $J_{AB} = 20$  Hz, H<sub>A</sub>); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 152.74 (C3 pyrazoline), 146.68, 144.78, 141.97, 136.78, 135.67, 131.63, 130.82, 129.21, 128.66, 127.59, 127.23, 126.04, 123.57, 122.98, 122.76, 120.37, 120.01, 113.56, 110.08, 60.34 (C5 pyrazoline), 47.27 (CH<sub>2</sub> benzyl), 39.77 (C4 pyrazoline); ESI-MS (*m/z*): 506.9 [M+H], 508.7 [M+2].

*1-Benzyl-2-(5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzimidazole (17)*. Yield: 62 %; white solid; m.p.: 188–190 °C; Anal. Calcd. for C<sub>29</sub>H<sub>23</sub>N<sub>4</sub>: C, 78.01; H, 5.19; N, 12.55 %. Found: C, 78.21; H, 5.12; N, 12.31 %; IR (KBr, cm<sup>-1</sup>): 1597 (C=N), 1531, 1497, 1330 (C–N), 1223; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 7.72–7.69 (2H, *m*, Ar-H), 7.59 (1H, *dd*,  $J = 5$  & 10 Hz, Ar-H), 7.50 (1H, *d*,  $J = 10$  Hz, Ar-H), 7.29–7.25 (5H, *m*, Ar-H), 7.24–7.18 (2H, *m*, Ar-H), 7.10–7.07 (4H, *m*, Ar-H), 6.87 (2H, *d*,  $J = 10$  Hz, Ar-H), 6.71 (1H, *t*,  $J = 7.5$  Hz, Ar-H), 5.85 (1H, *dd*,  $J_{AX} = 7.5$  Hz &  $J_{BX} = 12.5$  Hz, H<sub>X</sub>), 5.68 (1H, *d*,  $J_{DC} = 17.5$  Hz, H<sub>D</sub>), 5.56 (1H, *d*,  $J_{CD} = 17.5$  Hz, H<sub>C</sub>), 3.86 (1H, *dd*,  $J_{BX} = 12.5$  Hz &  $J_{AB} = 17.5$  Hz, H<sub>B</sub>), 3.26 (1H, *dd*,  $J_{AX} = 7.5$  Hz &  $J_{AB} = 17.5$  Hz, H<sub>A</sub>); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 163.85, 161.89, 153.83 (C3 pyrazoline), 146.95, 144.74, 142.52, 136.99, 136.26, 129.34, 129.14, 129.02, 129.00, 128.31, 128.25, 128.06, 127.11, 123.14, 122.46, 119.72, 119.39, 116.25, 116.08, 113.19, 111.29, 57.60 (C5 pyrazoline), 47.01 (CH<sub>2</sub> benzyl); ESI-MS (*m/z*): 446.8 [M+H].

*3-(1-Benzyl-1H-benzimidazol-2-yl)-5-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (18)*. Yield: 76 %; pale yellow solid; m.p.: 232–234 °C; Anal. Calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>5</sub>S: C, 70.05; H, 5.14; N, 17.02 %. Found: C, 70.25; H, 5.04; N, 16.80 %; IR (KBr, cm<sup>-1</sup>): 3406 & 3238 (NH<sub>2</sub>), 1595 (C=N), 1506, 1446, 1369, 1292 (C–N); <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 8.30 (1H, *brs*, NH), 7.85 (1H, *brs*, NH), 7.76–7.72 (2H, *m*, Ar-H), 7.36 (1H, *t*,  $J = 8.5$  Hz, Ar-H), 7.30–7.27 (4H, *m*, Ar-H), 7.23–7.17 (3H, *m*, Ar-H), 7.12 (2H, *d*,  $J = 6.5$  Hz, Ar-H), 6.94 (2H, *d*,  $J = 6.5$  Hz, Ar-H), 6.17 (1H, *d*,  $J_{DC} = 16.5$  Hz, H<sub>D</sub>), 6.07 (1H, *d*,  $J_{CD} = 16.5$  Hz, H<sub>C</sub>), 5.92 (1H, *dd*,  $J_{AX} = 2.7$  Hz &  $J_{BX} = 10.2$  Hz, H<sub>X</sub>), 4.10 (1H, *dd*,  $J_{BX} = 12.2$  Hz &  $J_{AB} = 17.5$  Hz, H<sub>B</sub>), 3.12 (1H, *dd*,  $J_{AX} = 3$  Hz &  $J_{AB} = 18.5$  Hz, H<sub>A</sub>); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 176.88 (C=S), 148.67 (C3 pyrazoline), 144.33, 142.89, 142.79, 138.26, 137.21, 129.07, 128.96, 127.76, 127.49, 127.11, 125.53, 125.09, 123.39, 120.40, 111.66, 62.62 (C5 pyrazoline), 48.18 (CH<sub>2</sub> benzyl), 44.45 (C4 pyrazoline); ESI-MS (*m/z*): 412.1 [M+H].

*3-(1-Benzyl-1H-benzimidazol-2-yl)-5-p-tolyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (19)*. Yield: 60 %; pale yellow solid; m.p.: 240–242 °C; Anal.

Calcd. for  $C_{25}H_{23}N_5S$ : C, 70.56; H, 5.45; N, 16.46 %. Found: C, 70.32; H, 5.38; N, 16.18 %; IR (KBr,  $cm^{-1}$ ): 3410 & 3244 ( $NH_2$ ), 1595 ( $C=N$ ), 1509, 1443, 1366, 1296 ( $C-N$ );  $^1H$ -NMR (500 MHz,  $DMSO-d_6$ ,  $\delta$  / ppm): 8.26 (1H, *brs*, NH), 7.81 (1H, *brs*, NH), 7.77–7.72 (2H, *m*, Ar-H), 7.38–7.35 (1H, *m*, Ar-H), 7.33–7.30 (4H, *m*, Ar-H), 7.13–7.12 (2H, *m*, Ar-H), 7.03 (2H, *d*,  $J = 5$  Hz, Ar-H), 6.83 (2H, *d*,  $J = 5$  Hz, Ar-H), 6.17 (1H, *d*,  $J_{DC} = 20$  Hz,  $H_D$ ), 6.07 (1H, *d*,  $J_{CD} = 20$  Hz,  $H_C$ ), 5.87 (1H, *dd*,  $J_{AX} = 5$  Hz &  $J_{BX} = 15$  Hz,  $H_X$ ), 4.08 (1H, *dd*,  $J_{BX} = 15$  Hz &  $J_{AB} = 20$  Hz,  $H_B$ ), 3.10 (1H, *dd*,  $J_{AX} = 5$  Hz &  $J_{AB} = 20$  Hz,  $H_A$ ), 2.24 (3H, *s*,  $CH_3$ );  $^{13}C$ -NMR (125 MHz,  $DMSO-d_6$ ,  $\delta$  / ppm): 176.81 ( $C=S$ ), 148.68 (C3 pyrazoline), 144.35, 142.88, 139.87, 138.26, 137.20, 136.61, 129.48, 129.07, 127.76, 127.11, 125.53, 125.07, 123.38, 120.39, 111.67, 62.40 (C5 pyrazoline), 48.15 ( $CH_2$  benzyl), 44.43 (C4 pyrazoline), 21.10 ( $CH_3$ ); ESI-MS ( $m/z$ ): 426.0 [ $M+H$ ].

3-(1-Benzyl-1H-benzimidazol-2-yl)-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (**20**). Yield: 72 %; pale yellow solid; m.p.: 242–244 °C; Anal. Calcd. for  $C_{24}H_{20}ClN_5S$ : C, 64.64; H, 4.52; N, 15.70 %. Found: C, 64.28; H, 4.71; N, 15.48 %; IR (KBr,  $cm^{-1}$ ): 3406 & 3241 ( $NH_2$ ), 1595 ( $C=N$ ), 1501, 1446, 1369, 1294 ( $C-N$ );  $^1H$ -NMR (500 MHz,  $DMSO-d_6$ ,  $\delta$  / ppm): 8.34 (1H, *brs*, NH), 7.86 (1H, *brs*, NH), 7.77–7.73 (2H, *m*, Ar-H), 7.38–7.35 (1H, *m*, Ar-H), 7.33–7.27 (6H, *m*, Ar-H), 7.13–7.11 (2H, *m*, Ar-H), 6.96 (2H, *d*,  $J = 10$  Hz, Ar-H), 6.15 (1H, *d*,  $J_{DC} = 17.5$  Hz,  $H_D$ ), 6.08 (1H, *d*,  $J_{CD} = 17.5$  Hz,  $H_C$ ), 5.90 (1H, *dd*,  $J_{AX} = 5$  Hz &  $J_{BX} = 10$  Hz,  $H_X$ ), 4.11 (1H, *dd*,  $J_{BX} = 10$  Hz &  $J_{AB} = 20$  Hz,  $H_B$ ), 3.13 (1H, *dd*,  $J_{AX} = 5.0$  Hz &  $J_{AB} = 20$  Hz,  $H_A$ );  $^{13}C$ -NMR (125 MHz,  $DMSO-d_6$ ,  $\delta$  / ppm): 176.85 ( $C=S$ ), 148.63 (C3 pyrazoline), 144.25, 142.90, 141.82, 138.29, 137.23, 132.01, 129.09, 128.90, 127.75, 127.63, 127.12, 125.09, 123.39, 120.42, 111.67, 62.06 (C5 pyrazoline), 48.18 ( $CH_2$  benzyl), 44.22 (C4 pyrazoline); ESI-MS ( $m/z$ ): 446.1 [ $M+H$ ].

3-(1-Benzyl-1H-benzimidazol-2-yl)-5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (**21**). Yield: 75 %; pale yellow solid; m.p.: 245–247 °C; Anal. Calcd. for  $C_{24}H_{20}BrN_5S$ : C, 58.78; H, 4.11; N, 14.28 %. Found: C, 59.05; H, 4.11; N, 13.91 %; IR (KBr,  $cm^{-1}$ ): 3408 & 3244 ( $NH_2$ ), 1594 ( $C=N$ ), 1507, 1490, 1451, 1436, 1370, 1298 ( $C-N$ ), 1073, 1031;  $^1H$ -NMR (500 MHz,  $DMSO-d_6$ ,  $\delta$  / ppm): 8.38 (1H, *brs*, NH), 7.89 (1H, *brs*, NH), 7.75 (2H, *t*,  $J = 7.5$  Hz, Ar-H), 7.42 (2H, *d*,  $J = 10$  Hz, Ar-H), 7.38–7.34 (1H, *m*, Ar-H), 7.33–7.26 (4H, *m*, Ar-H), 7.12 (2H, *d*,  $J = 5$  Hz, Ar-H), 6.90 (2H, *d*,  $J = 10$  Hz, Ar-H), 6.16 (1H, *d*,  $J_{DC} = 17.5$  Hz,  $H_D$ ), 6.08 (1H, *d*,  $J_{CD} = 17.5$  Hz,  $H_C$ ), 5.90 (1H, *dd*,  $J_{AX} = 5$  Hz &  $J_{BX} = 10$  Hz,  $H_X$ ), 4.11 (1H, *dd*,  $J_{BX} = 10$  Hz &  $J_{AB} = 20$  Hz,  $H_B$ ), 3.13 (1H, *dd*,  $J_{AX} = 5$  Hz &  $J_{AB} = 20$  Hz,  $H_A$ );  $^{13}C$ -NMR (125 MHz,  $DMSO-d_6$ ,  $\delta$  / ppm): 176.79 ( $C=S$ ), 148.63 (C3 pyrazoline), 144.22, 142.89, 142.25, 138.30, 137.23, 131.82, 129.09, 127.98, 127.76, 127.14, 127.11, 125.11, 123.41, 120.52,

120.42, 111.68, 62.12 (C5 pyrazoline), 48.17 (CH<sub>2</sub> benzyl), 44.17 (C4 pyrazoline); ESI-MS (*m/z*): 491.8 [M+H].

*3-(1-Benzyl-1H-benzimidazol-2-yl)-5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (22)*. Yield: 70 %; pale yellow solid; m.p.: 241–243 °C; Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>FN<sub>5</sub>S: C, 67.11; H, 4.69; N, 16.31 %. Found: C, 66.90; H, 4.59; N, 16.20 %; IR (KBr, cm<sup>-1</sup>): 3413 & 3237 (NH<sub>2</sub>), 1595 (C=N), 1509, 1453, 1436, 1371, 1283 (C–N); <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 8.33 (1H, *brs*, NH), 7.86 (1H, *brs*, NH), 7.75 (2H, *t*, *J* = 10 Hz, Ar-H), 7.37 (1H, *t*, *J* = 7.5 Hz, Ar-H), 7.33–7.28 (4H, *m*, Ar-H), 7.13–7.11 (2H, *m*, Ar-H), 7.07–7.04 (2H, *m*, Ar-H), 6.99–6.96 (2H, *m*, Ar-H), 6.16 (1H, *d*, *J*<sub>DC</sub> = 17.5 Hz, H<sub>D</sub>), 6.08 (1H, *d*, *J*<sub>CD</sub> = 17.5 Hz, H<sub>C</sub>), 5.92 (1H, *dd*, *J*<sub>AX</sub> = 5 Hz & *J*<sub>BX</sub> = 15 Hz, H<sub>X</sub>), 4.10 (1H, *dd*, *J*<sub>BX</sub> = 15 Hz & *J*<sub>AB</sub> = 20 Hz, H<sub>B</sub>), 3.13 (1H, *dd*, *J*<sub>AX</sub> = 5 Hz & *J*<sub>AB</sub> = 20 Hz, H<sub>A</sub>); <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, δ / ppm): 176.82 (C=S), 162.54, 160.61, 148.64 (C3 pyrazoline), 144.29, 142.89, 139.02, 139.00, 138.31, 137.24, 129.09, 127.77, 127.69, 127.11, 125.09, 123.39, 120.41, 115.75, 115.58, 111.68, 61.98 (C5 pyrazoline), 48.16 (CH<sub>2</sub> benzyl), 44.33 (C4 pyrazoline); ESI-MS (*m/z*): 430.0 [M+H].

#### REFERENCES

1. P. K. Dubey, C. R. Kumar, B. Babu, *Indian J. Chem., B* **42** (2003) 3128.