



SUPPLEMENTARY MATERIAL TO  
**A novel approach to bis(indolyl)methanes using nickel nanoparticles as a reusable catalyst under solvent-free conditions**

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J. Serb. Chem. Soc. 78 (4) (2013) 463–468

IR, <sup>1</sup>H- AND <sup>13</sup>C-NMR DATA FOR **3a–n**

*3,3'-(Phenylmethylene)bis-1H-indole (3a)*. IR (KBr, cm<sup>-1</sup>): 3416, 1630, 1460, 1371, 1090; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 5.68 (1H, *s*, methine-H), 6.67–7.22 (15H, *m*, Ar-H), 10.71 (2H, *s*, indole-NH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 40.58, 112.33, 118.91, 119.03, 119.94, 121.73, 124.39, 124.66, 126.64, 127.48, 128.89, 129.15, 137.44, 145.83.

*3,3'-(4-Nitrophenyl)methylene]bis-1H-indole (3b)*. IR (KBr, cm<sup>-1</sup>): 3425, 1590, 1456, 1340, 1229; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 5.89 (1H, *s*, methine-H), 6.72–8.01 (14H, *m*, Ar-H), 10.79 (2H, *s*, indole-NH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 40.35, 112.46, 117.55, 119.29, 119.78, 121.97, 124.28, 124.73, 127.24, 130.32, 137.47, 146.63, 154.00.

*3,3'-(3-Nitrophenyl)methylene]bis-1H-indole (3c)*. IR (KBr, cm<sup>-1</sup>): 3405, 1525, 1458, 1351, 1045; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 5.92 (1H, *s*, methine-H), 6.72–8.30 (14H, *m*, Ar-H), 10.77 (2H, *s*, indole-NH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 39.97, 112.46, 117.82, 119.29, 119.79, 121.92, 121.98, 123.47, 124.75, 127.23, 130.46, 135.97, 137.49, 148.27, 148.67.

*3,3'-(2-Nitrophenyl)methylene]bis-1H-indole (3d)*. IR (KBr, cm<sup>-1</sup>): 3415, 1574, 1461, 1350, 1227; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 6.41 (1H, *s*, methine-H), 6.77–7.87 (14H, *m*, Ar-H), 10.92 (2H, *s*, indole-NH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 34.93, 112.51, 116.83, 119.37, 119.43, 122.03, 124.80, 124.99, 127.19, 128.39, 131.41, 133.38, 137.47, 138.55, 150.39.

*3,3'-(2-Chlorophenyl)methylene]bis-1H-indole (3e)*. IR (KBr, cm<sup>-1</sup>): 3414, 1602, 1445, 1336, 1110; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 6.10 (1H, *s*, methine-H), 6.63–7.33 (14H, *m*, Ar-H), 10.74 (2H, *s*, indole-NH); <sup>13</sup>C-NMR

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(125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 37.02, 112.46, 117.39, 119.27, 119.55, 121.90, 124.88, 127.38, 127.84, 128.60, 130.10, 131.09, 133.57, 137.52, 142.73.

*3,3'*-(4-Chlorophenyl)methylene]bis-1H-indole (**3f**). IR (KBr, cm<sup>-1</sup>): 3412, 1610, 1487, 1455, 1012; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 5.84 (1H, *s*, methine-H), 6.82–7.36 (14H, *m*, Ar-H), 10.91 (2H, *s*, indole-NH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 22.94, 31.83, 112.38, 118.41, 119.11, 121.80, 124.49, 127.35, 128.85, 130.98, 131.14, 137.48, 144.89.

*3,3'*-(4-Bromophenyl)methylene]bis-1H-indole (**3g**). IR (KBr, cm<sup>-1</sup>): 3409, 1600, 1468, 1409, 1335, 1225, 1100; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 5.69 (1H, *s*, methine-H), 6.68–7.31 (14H, *m*, Ar-H), 10.8 (2H, *s*, indole-NH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 39.90, 112.39, 118.30, 119.10, 119.61, 119.87, 121.79, 124.50, 127.33, 131.41, 131.76, 137.47, 145.34.

*3,3'*-(4-Hydroxyphenyl)methylene]bis-1H-indole (**3h**). IR (KBr, cm<sup>-1</sup>): 3410, 1608, 1484, 1420, 1339, 1215, 1088; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 5.57 (1H, *s*, methine-H), 6.50–7.20 (14H, *m*, Ar-H), 8.99 (1H, *br*, OH), 10.61 (2H, *s*, indole-NH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 39.47, 112.25, 115.63, 115.79, 118.93, 119.55, 120.05, 121.64, 124.25, 127.54, 130.00, 130.12, 136.07, 137.47, 156.14.

*3,3'*-(4-Methylphenyl)methylene]bis-1H-indole (**3i**). IR (KBr, cm<sup>-1</sup>): 3403, 1600, 1457, 1218, 1090; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 2.10 (3H, *s*, CH<sub>3</sub>), 5.64 (1H, *s*, methine-H), 6.66–7.21 (14H, *m*, Ar-H), 10.64 (2H, *s*, indole-NH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 21.49, 40.58, 112.28, 118.97, 119.08, 120.00, 121.68, 124.34, 127.50, 129.05, 129.46, 135.42, 137.46, 142.82.

*3,3'*-(4-Chloro-3-nitrophenyl)methylene]bis-1H-indole (**3j**). Yellow solid; Anal. Calcd. for C<sub>23</sub>H<sub>16</sub>ClN<sub>3</sub>O<sub>2</sub>: C, 68.74; H, 3.98; N, 10.46 %. Found: C, 68.83; H, 3.90; N, 10.51 %; IR (KBr, cm<sup>-1</sup>): 3400, 1574, 1471, 1350, 1225; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 5.88 (1H, *s*, methine-H), 6.74–7.87 (13H, *m*, Ar-H), 10.80 (2H, *s*, indole-NH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 39.46, 112.49, 117.41, 119.36, 119.72, 122.03, 123.23, 124.82, 125.86, 127.13, 132.25, 134.57, 137.47, 147.25, 148.24.

*3,3'*-(2-Hydroxy-5-nitrophenyl)methylene]bis-1H-indole (**3k**). Yellow solid; Anal. Calcd. for C<sub>23</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>: C, 72.06; H, 4.43; N, 10.96. Found: C, 71.96; H, 4.52; N, 11.01 %; IR (KBr, cm<sup>-1</sup>): 3412, 1588, 1491, 1333, 1275, 1205; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 6.05 (1H, *s*, methine-H), 6.68–7.86 (13H, *m*, Ar-H), 10.74 (2H, *s*, indole-NH), 11.30 (1H, *br*, OH); <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 32.64, 112.46, 116.28, 117.57, 119.20, 119.51, 121.87, 124.47, 124.66, 125.78, 127.40, 133.21, 137.54, 140.24, 162.29; MS (*m/z*): 383 (M)<sup>+</sup>, 265, 139, 130, 118, 117, 89.

*3,3'*-(2-Bromo-5-hydroxyphenyl)methylene]bis-1H-indole (**3l**). Pink solid; Anal. Calcd. for C<sub>23</sub>H<sub>17</sub>BrN<sub>2</sub>O: C, 66.18; H, 4.07; N, 6.71 %. Found: C, 66.24; H, 4.00; N, 6.80 %; IR (KBr, cm<sup>-1</sup>): 3407, 1612, 1479, 1413, 1338, 1212, 1094;

$^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 6.14 (1H, *s*, methine-H), 6.76–7.35 (13H, *m*, Ar-H), 9.76 (1H, *s*, OH), 10.77 (2H, *s*, indole-NH);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 32.50, 110.74, 112.36, 118.10, 118.15, 119.08, 119.64, 121.78, 124.45, 127.53, 130.15, 132.30, 134.75, 137.45, 154.64; MS ( $m/z$ ): 418 ( $\text{M}+2$ )<sup>+</sup>, 416 ( $\text{M}$ )<sup>+</sup>, 300, 298, 245, 243, 220, 117, 97.

*3,3'-[(2-Chloro-6-fluorophenyl)methylene]bis-1H-indole (3m)*. Pink solid; Anal. Calcd. for  $\text{C}_{23}\text{H}_{16}\text{ClFN}_2$ : C, 73.69; H, 4.27; N, 7.47 %. Found: C, 73.53; H, 4.35; N, 7.40 %; IR (KBr,  $\text{cm}^{-1}$ ): 3410, 1608, 1452, 1343, 1100;  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 6.40 (1H, *s*, methine-H), 6.88–7.37 (13H, *m*, Ar-H), 10.89 (2H, *s*, indole-NH);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 36.45, 114.67, 117.58, 118.61, 118.79, 121.33, 121.52, 124.00, 126.82, 126.85, 128.87, 129.63, 131.92, 132.00, 133.14, 133.26, 136.52, 139.30; MS ( $m/z$ ): 376 ( $\text{M}+2$ )<sup>+</sup>, 374 ( $\text{M}$ )<sup>+</sup>, 337, 243, 222, 194, 117, 90, 89.

*3,3'-[[2-(Benzyloxy)phenyl]methylene]bis-1H-indole (3n)*. White solid; Anal. Calcd. for  $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}$ : C, 84.11; H, 5.60; N, 6.54 %. Found: C, 84.17; H, 5.65; N, 6.48 %; IR (KBr,  $\text{cm}^{-1}$ ): 3411, 1589, 1447, 1340, 1221, 1091;  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 5.14 (2H, *s*, O-CH<sub>2</sub>-), 6.34 (1H, *s*, methine-H), 6.79–7.38 (19H, *m*, Ar-H), 10.79 (2H, *s*, indole-NH);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 34.99, 72.40, 114.52, 115.45, 120.88, 121.22, 122.01, 123.40, 123.91, 126.79, 129.89, 130.03, 130.22, 130.59, 131.29, 132.23, 136.39, 139.70, 140.50, 158.38; MS ( $m/z$ ): 428 ( $\text{M}$ )<sup>+</sup>, 337, 243, 130, 117, 92, 91.