

## Supplementary Data

All NMR analysis was performed on a 300 MHz Bruker machine using deuterated DMSO as the solvent. Melting points were determined using a Gallenkamp instrument.

Benzimidazole (**3a**): m.p. 171–174 (170);<sup>1</sup> <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 7.17 – 7.20 (2H, m, Ar H), 7.58 – 7.59 (2H, m, Ar H), 8.21 (1H, s, H-2) ppm;<sup>2</sup> <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 108.8, 120.7, 122.0, 142.3 ppm.

2-Methylbenzimidazole (**3b**): m.p. 177-178 (176);<sup>1</sup> <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 2.51 (s, 3H, CH<sub>3</sub>), 7.11 – 7.14 (2H, m, Ar H), 7.46 – 7.49 (2H, m, Ar H) ppm;<sup>2</sup> <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 15.0, 24.6, 114.5, 121.3, 139.4, 151.6 ppm.<sup>3</sup>

2-Isopropylbenzimidazole (**3c**): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 1.33 (6H, d, *J* = 6.9, CH<sub>3</sub>), 3.13 (1H, sept., *J* = 6.8, CH), 7.08 – 7.11 (2H, m, Ar H), 7.42 – 7.49 (2H, m, Ar H) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 21.7, 28.7, 111.1, 118.5, 121.1, 121.7, 128.7, 134.7, 143.4, 160.1 ppm.

2-*t*-Butylbenzimidazole (**3d**): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 1.40 (9H, s, CH<sub>3</sub>), 7.09 – 7.13 (2H, m, Ar H), 7.39 – 7.55 (2H, m, Ar H) ppm;<sup>4</sup> <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 29.6, 33.5, 111.1, 118.6, 121.0, 121.7, 128.7, 135.0, 143.1, 162.5 ppm.

2-Benzylbenzimidazole (**3e**): m.p. 189 – 190 (191);<sup>5</sup> <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 4.18 (2H, s, CH<sub>2</sub>), 7.11 – 7.53 (9H, m, Ar H) ppm;<sup>6</sup> <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 35.3, 111.3, 118.6, 121.3, 121.9, 126.9, 128.8, 129.1, 134.8, 138.0, 143.7, 153.9 ppm.

2-Phenylbenzimidazole (**3f**): m.p. 299 – 300 (295);<sup>7</sup> <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 7.22 – 7.25 (2H, m, Ar H), 7.48 – 7.60 (5H, m, Ar H), 8.21 – 8.24 (2H, m, Ar H) ppm;<sup>2</sup> <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 111.7, 119.2, 112.2, 112.7, 126.8, 129.3, 130.2, 130.5, 135.4, 144.1, 151.6 ppm.<sup>2</sup>

2,2'-Bi-1H-benzimidazole (**5g**): Poorly soluble therefore NMR not run. C:H:N Microanalysis for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>·½H<sub>2</sub>O: Calculated C 69.11, H 4.57, N 23.03; Actual C 68.71, H 4.16, N 22.93.<sup>8</sup>

2,2'-(1,2-ethanediyl)bis-1H-benzimidazole (**5h**): Poorly soluble therefore NMR not run. C:H:N Microanalysis for C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>: Calculated C 73.26, H 5.38, N 21.36; Actual C 73.15, H 5.43, N 21.31.<sup>9</sup>

2,2'-(1,4-phenylene)bis-1H-benzimidazole (**5i**): Poorly soluble therefore NMR not run. C:H:N Microanalysis for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>·¼H<sub>2</sub>O: Calculated C 76.29, H 4.64, N 17.79; Actual C 76.78, H 4.55, N 17.84.

2,2'-(1,2-phenylene)bis-1H-benzimidazole (**5j**): Poorly soluble therefore NMR not run. C:H:N Microanalysis for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>·¼H<sub>2</sub>O: Calculated C 76.29, H 4.64, N 17.79; Actual C 76.71, H 4.64, N 17.82.

---

<sup>1</sup> M. A. Phillips, *J. Chem. Soc.*, 1928, 2393.

<sup>2</sup> I. H. Lee, E. H. Jeung and C. K. Lee, *J. Heterocyclic Chem.*, 1996, **33**, 1711.

<sup>3</sup> A. R. Katritzky, G. W. Rewcastle and W. Fan, *J. Org. Chem.* 1988, **53**, 5685.

<sup>4</sup> J. J. Vanden Eynde, A. Mayence, A. Maquestiau and E. Anders, *B. Soc. Chim. Belg.*, 1993, **102**, 357.

<sup>5</sup> F. E. King and R. M. Acheson, *J. Chem. Soc.*, 1949, 1396.

<sup>6</sup> J. V. Hay, D. E. Portlock and J. F. Wolfe, *J. Org. Chem.*, 1973, **38**, 4379.

<sup>7</sup> V. I. Cohen, *J. Heterocyclic Chem.*, 1979, **16**, 13.

<sup>8</sup> B. F. Fieselmann, D. N. Hendrickson and G. D. Stucky, *Inorg. Chem.*, 1978, **17**, 2078.

<sup>9</sup> P. C. Vyas, C. K. Oza and A. K. Goyal, *Chemistry and Industry*, 1980, **7**, 287.