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Ultrafine Pt Nanoparticles Supported on Dendrimer Containing Thiol groups: An Efficient Catalyst for Synthesis of Benzimidazoles and Benzothiazoles from Benzyl Alcohol derivatives in Water

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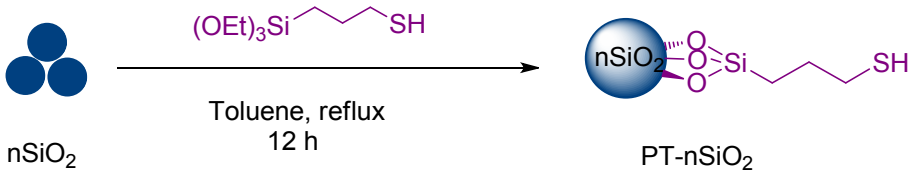
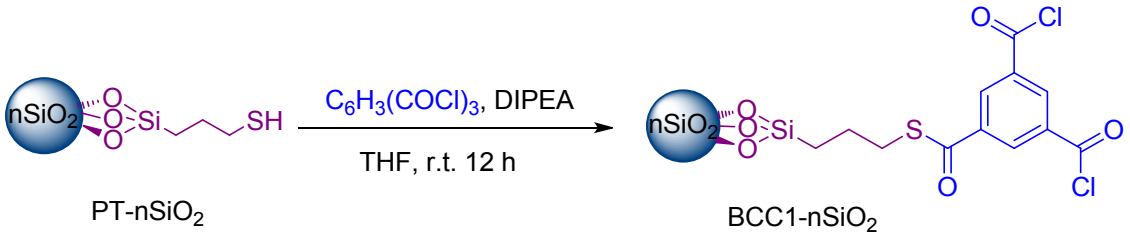
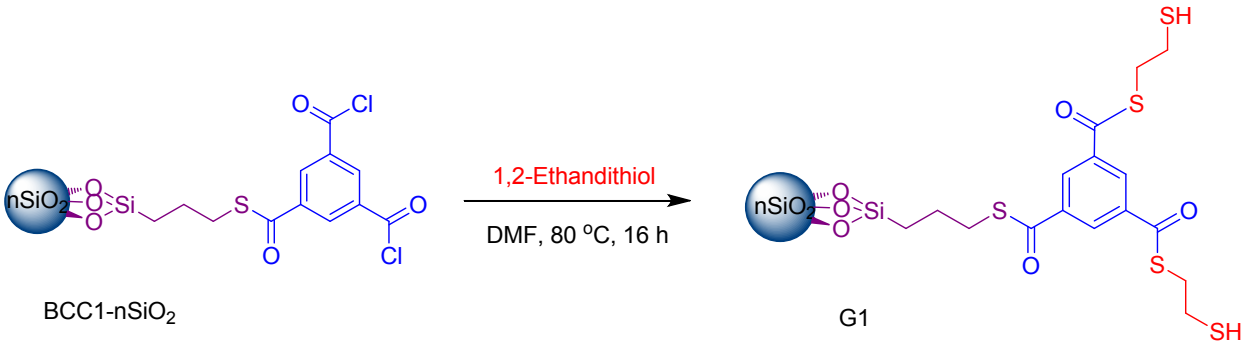


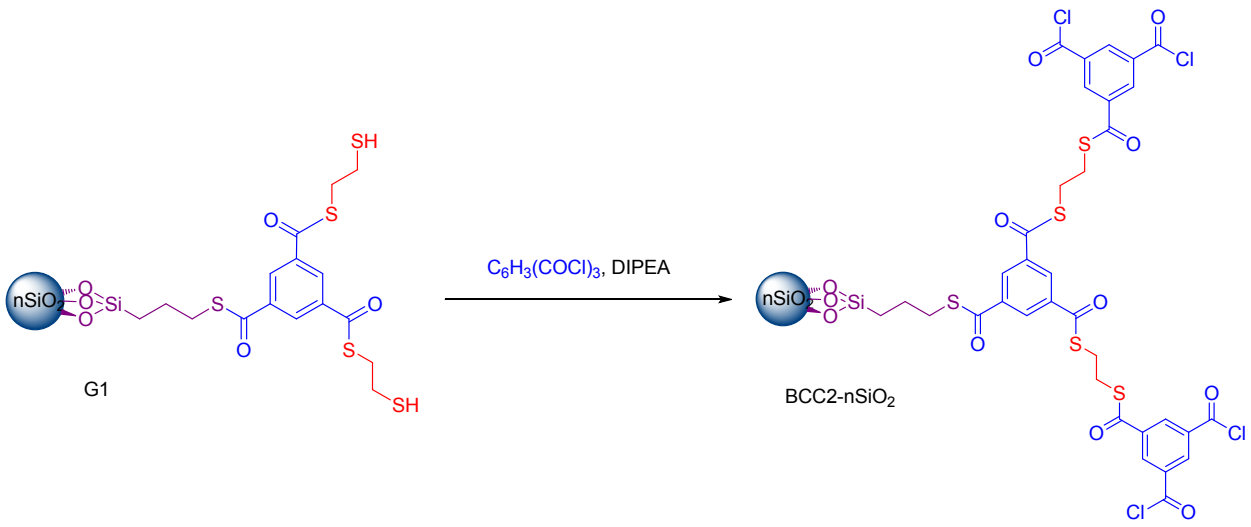
Scheme S1: Synthesis of Propylthiol–Functionalized Nano–Silica (PT–$nSiO_2$)



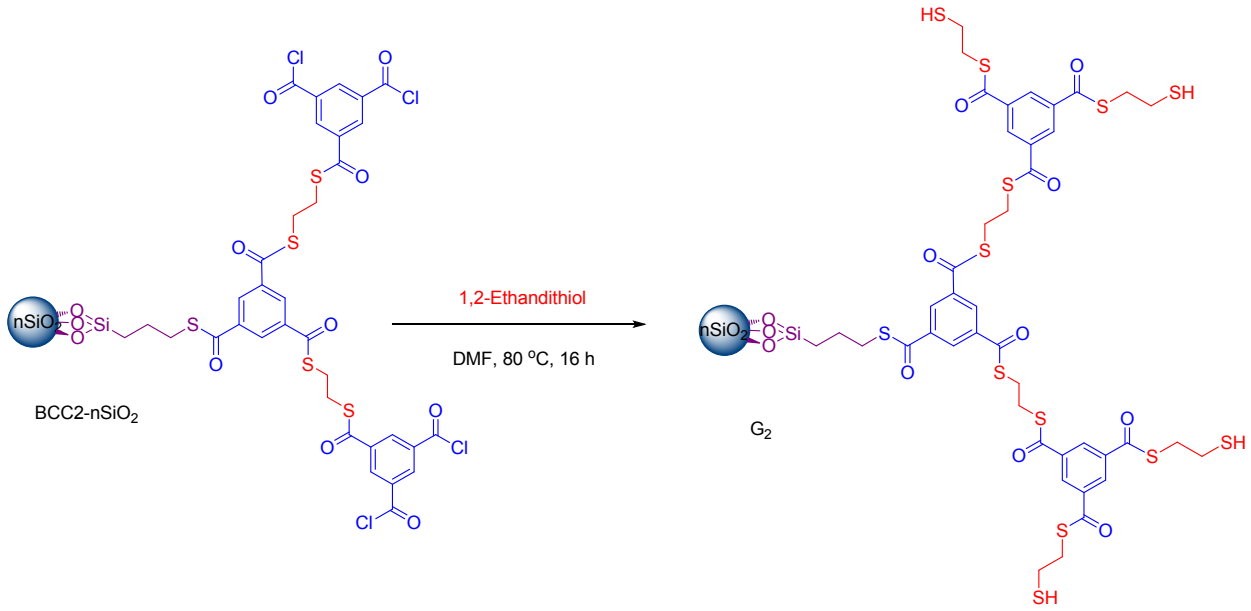
Scheme S2: Synthesis of BCC1–$nSiO_2$



Scheme S3: Synthesis Nano–Silica Supported Thiolated Dendritic Polymer (G1)



Scheme S4: Synthesis of BCC2−$nSiO_2$



Scheme S5: Synthesis of Nano−Silica Supported Thiolated Dendritic Polymer (G2 or nSTDP)

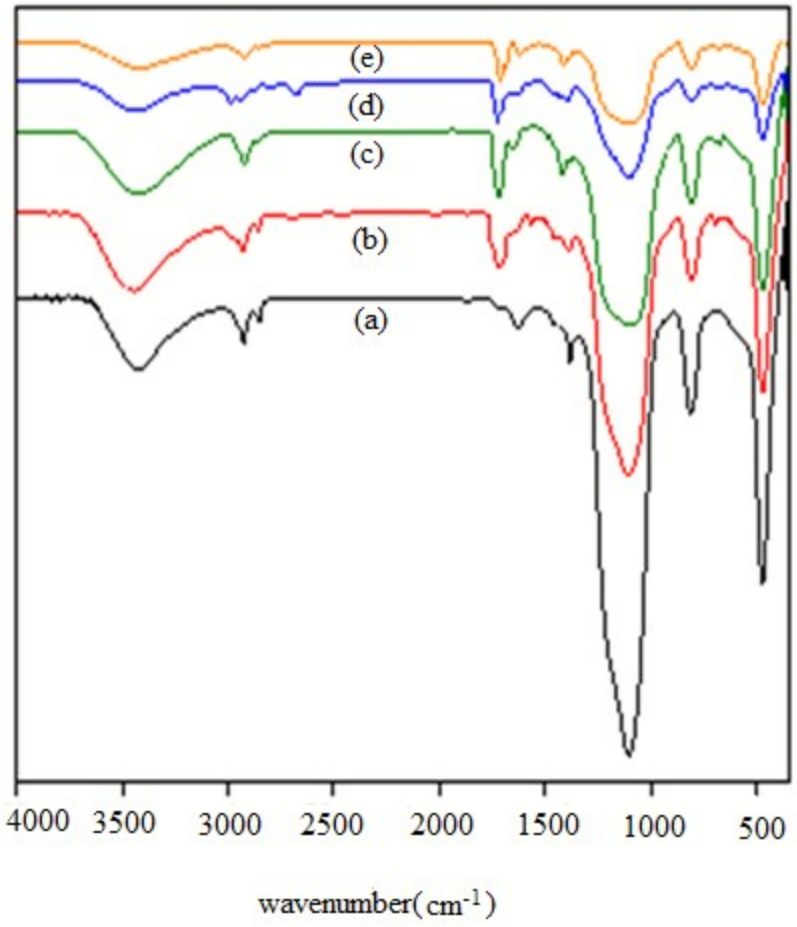


Figure S1. The FT−IR spectra of: a) PT−nSiO_2, b) BCC1− nSiO_2, c) G1, d) BCC2−nSiO_2, e) G2

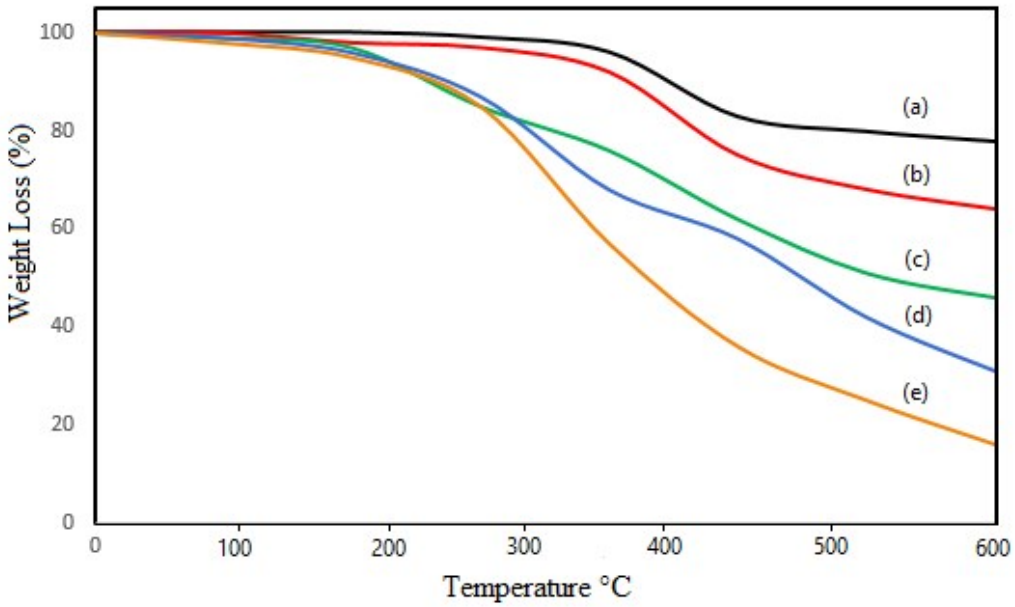


Figure S2. TGA spectra of: a) PT−$nSiO_2$; b) BCC1−$nSiO_2$; c) G1; d) BCC2−$nSiO_2$ and e) G2 (nSTDP)

1. Synthesis:

The general procedure for the preparation of thiol Dendritic Polymer Supported on Nano−Silica (nSTDP) was as follows.

1.1. Propylthiol−Functionalized Nano−Silica (PT−nSiO_2)

(3−mercaptopropyl)trimethoxysilane (8.5 mL) was added dropwise via a syringe to a stirred solution of activated nano−silica (3 g) in dried toluene (50 mL) under reflux conditions for 12 h. The reaction medium was cooled to room temperature and filtered. The solid was washed overnight with dried toluene by soxhlet extractor to remove the unreacted starting materials. The white solid was dried in a vacuum oven at 110 ˚C.

1.2. BCC1−nSiO_2

To a solution of 1,3,5−benzenetricarbonyl trichloride (2.65 g, 10 mmol) and diisopropylethylamine (DIPEA) (10 mmol, 1.7 mL) in anhydrous THF (10 mL) was slowly added the previously synthesized PT−nSiO_2 (2 g).The reaction mixture was cooled to 0 ˚C and stirred overnight. The solid material was filtered, washed overnight with hot tetrahydrofuran (THF) in a Soxhlet extractor. Then dried in a vacuum oven at 60 ˚C.

1.3. Nano−Silica Supported Thiolated Dendritic Polymer (G1)

BCC1−nSiO_2 (1 g) in dimethylformamide (DMF) (12 mL) was treated with 1,2−ethanedithiol (8.11 mmol, 0.7 mL) and DIPEA (8 mmol, 1.4 mL) at 80 ˚C for 16 h. The solid material was filtered and washed overnight with hot ethanol in a Soxhlet extractor and dried in a vacuum oven at 60 ˚C.

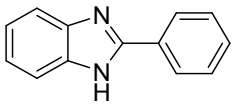
1.4. BCC2−nSiO_2

G1, (1 g) was added slowly to a solution of 1,3,5−benzenetricarbonyl trichloride (2.4 g, 9 mmol) and DIPEA (9 mmol, 1.55 mL) in THF (20 mL). The reaction mixture was cooled and stirred at 0 ˚C for 16 h. The reaction mixture was filtered and the solid was washed overnight with hot THF in a Soxhlet extractor. The BCC2−nSiO_2 was dried in a vacuum oven at 60 ˚C.

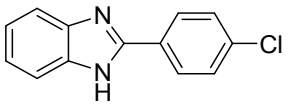
1.5. Nano−Silica Supported Thiolated Dendritic Polymer (G2 or nSTDP)

To a solution of BCC2−nSiO_2 (1 g) in DMF (20 mL), 1,2−ethanedithiol (9.5 mmol, 0.8 mL) and DIPEA (9.5 mmol, 1.65 mL) were added slowly and the reaction mixture was stirred at 80 ˚C for 16 h. The resulting nano−silica supported dendritic polymer (G2 or nSTDP) was filtered and washed with hot ethanol overnight in a Soxhlet extractor and dried in a vacuum oven at 60 ˚C.

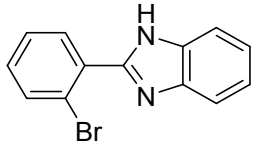
Spectroscopic data of products



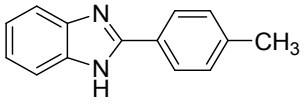
2-Phenyl-1H-benzimidazole: Mp 293-294 °C. IR (KBr): ν_{max} = 3046, 2921, 2674, 1590, 1541, 1461, 1443, 1275, 970, 742 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ = 12.92 (br s, 1H), 8.18 (d, *J* = 7.6 Hz, 2H), 7.61 (s, 2H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.23 (dd, ^1J = 7.6 Hz, ^2J = 1.2 Hz, 2H). MS: *m/z* (%): 194.25 ($[M]^+$, 75.69), 193.31 (100.00), 151.08 (69.80), 136.52 (65.88), 124.81 (99.00), 69.94 (77.65), 57.97 (21.45).



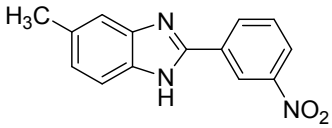
2-(4-Chlorophenyl)-1H-benzimidazole: Mp 298-300 °C. IR (KBr): ν_{max} = 3052, 2749, 1601, 1489, 1268, 1090, 744 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ = 13.07 (br s, 1H), 8.19 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 4H), 7.20 (dd, ^1J = 8.0 Hz, ^2J = 2.8 Hz, 2H). MS: *m/z* (%): 230.17 ($[M + 2]^+$, 4.01), 228 ($[M]^+$, 18.07), 192.31 (7.85), 136.60 (24.09), 110.91 (32.85), 96.69 (45.62), 83.00 (46.72), 69.04 (64.96), 57.08 (100.00).



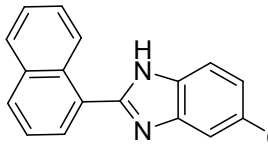
2-(2-Bromophenyl)-1H-benzimidazole: Mp 239-241 °C. IR (KBr): ν_{max} = 3053, 2917, 2671, 1588, 1536, 1440, 1270, 974, 874, 745 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ = 12.75 (br s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, ^1J = 7.6 Hz, ^2J = 1.6 Hz, 1H), 7.63 (s, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 77.45 (td, ^1J = 8.0, ^2J = 1.6 Hz, 1H), 7.25-7.20 (m, 2H). MS: *m/z* (%): 274.21 ($[M + 2]^+$, 2.27), 272.41 ($[M]^+$, 1.42), 148.84 (15.99), 110.94 (62.47), 96.98 (45.59), 83.01 (52.21), 69.04 (72.43), 57.07 (100.00).



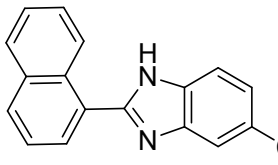
2-*p*-Tolyl-1H-benzimidazole: Mp 271-273 °C. IR (KBr): ν_{max} = 3056, 2856, 2755, 1619, 1588, 1501, 1429, 1370, 1274, 1120, 821, 745 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ = 12.65 (br s, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.57(s, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.18 (dd, ^1J = 8.0 Hz, ^2J = 2.8 Hz, 2H), 2.38 (s, 3H). MS: *m/z* (%): 208.24 ($[M]^+$, 8.52), 122.91 (15.75), 110.88 (30.82), 96.95 (52.05), 82.97 (60.97), 68.98 (84.25), 57.02 (100.00), 43.10 (82.88).



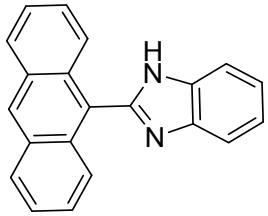
6-Methyl-2-(3-nitrophenyl)-1H-benzimidazole: Mp 202-204 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 13.15 (br s, 1H), 8.99 (s, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.60-7.36 (m, 2H), 7.16-7.09 (m, 1H), 2.45 (s, 3H). MS: *m/z* (%): 253.09 ([M]$^+$, 68.54), 222.00 (14.47), 206.33 (75.28), 191.72 (76.40), 179.32 (18.26), 151.19 (16.15), 124.93 (23.88), 110.94 (39.89), 102.95 (58.99), 83.01 (58.99), 77.00 (74.16), 69.04 (71.63), 57.08 (100.00).



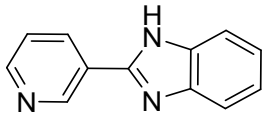
6-Methyl-2-(naphthalen-1-yl)-1H-benzimidazole: Mp 233-235 °C. IR (KBr): ν_{max} = 3045, 2987, 1609, 1590, 1540, 1465, 1374, 1125, 744 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.77 (br s, 1H), 9.09 (t, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.91-7.88 (dd, ^1J = 8.0 Hz and ^2J = 3.2 Hz, 1H), 7.70-7.61 (m, 4H), 7.06 (q, *J* = 7.2 Hz, 1H), 2.46 (s, 3H). ^{13}CNMR (100 MHz, DMSO-d_6) δ = 152.1, 140.8, 136.1, 131.5, 131.0, 129.4, 127.5, 126.6, 126.4, 123.8, 118.9, 111.3, 21.3. MS: *m/z* (%): 258.44 ([M]$^+$, 21.19), 256.77 (100.00), 242.15 (13.28), 228.16 (4.35), 178.43 (4.15), 153.03 (45.31), 140.83 (67.97), 127.61 (69.53), 114.88 (40.23), 83.01 (24.61), 77.00 (64.06), 57.08 (44.92). Anal. Calcd for $C_{18}H_{14}N_2$; C, 83.72; H, 5.43; N, 10.85%. Found: C, 83.70; H, 5.46; N 10.79%.



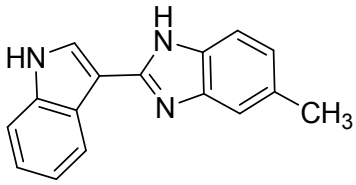
6-Chloro-2-(naphthalen-1-yl)-1H-benzimidazole: Mp 201-203 °C. IR (KBr): ν_{max} = 3416, 3051, 1582, 1504, 1435, 1397, 924, 775 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 13,15 (br s, 1H), 9.03 (dd, ^1J = 8.0 Hz and ^2J = 4 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.72-7.58 (m, 4H), 7.30 (dd, ^1J = 7.6 Hz and ^2J = 2.4 Hz, 1H). MS: *m/z* (%): 280.25 ([M + 2]$^+$, 2.49), 278.60 ([M]$^+$, 17.81), 276.76 (36.60), 242.30 (17.81), 214.12 (5.35), 153.08 (21.90), 121.00 (55.56), 97.01 (73.86), 69.04 (87.58), 57.07 (100.00).



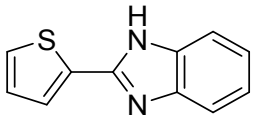
2-(Anthracen-9-yl)-1H-benzimidazole: Mp 263-265 ^{o}C. IR (KBr): ν_{max} = 3431, 3049, 2920, 1600, 1589, 1332, 736 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 13.11 (br s, 1H), 9.35(s, 1H), 8.68 (d, *J* = 2.8 Hz, 1H), 8.49 (dd, ^{1}J = 8.0 Hz ,^{2}J = 1.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.61-7.53 (m, 4H), 7.28-7.21 (m, 4H). MS: *m/z* (%): 294.32 ([M]$^{+}$, 1.37), 195.18 (60.55), 169.20 (35.51), 137.23 (33.86), 125.24 (55.63), 111.21 (78.02), 97.22 (94.14), 69.20 (96.68), 57.20 (100).



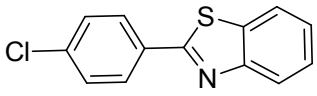
2-(Pyridin-3-yl)-1H-benzimidazole (Table 5, 1i): Mp 266-268 ^{o}C. IR (KBr): ν_{max} = 3404, 3045, 2922, 1576, 1538, 1487, 1446, 1316, 1277, 964, 813, 745, 740 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 13.14 (br s, 1H), 9.36 (s, 1H), 8.69 (s, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.32-7.27 (m, 2H).



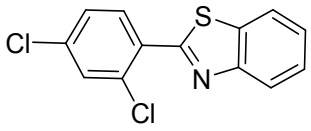
2-(1H-indol-3-yl)-1H-benzimidazole (Table 5, 1j): Mp 252-254 ^{o}C. IR (KBr): ν_{max} = 3393, 3055, 2990, 1624, 1576, 1453, 1322 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 12.25 (br s, 1H), 11.58(br s, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 6.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24-7.17 (m, 3H), 2.45 (s, 3H). ^{13}NMR (100 MHz, DMSO-d$_6$) δ: 148.5, 136.4, 131.0, 126.9, 124.7, 122.3, 121.0, 120.4, 118.7, 113.8, 112.0, 105.3, 21.3. Anal. Calcd for $C_{16}H_{13}N_3$; C: 77.71, H: 5.30, N: 16.99%. Found: C: 77.80, H: 5.29, N: 16.90%.



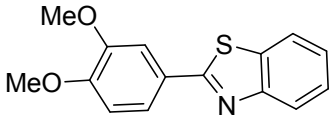
2-(Thiophen-2-yl)-1H-benzimidazole (Table 5, 1k): Mp 329-331^{o}C. IR (KBr): ν_{max} = 3063, 2672, 1620, 1569, 1450, 1425, 1313, 1234, 1096, 944, 861, 743, 705 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 2.94 (br s, 1H), 7.83 (d, *J* = 3.6 Hz, 1H), 7.72 (d, *J* = 5.4Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.24-7.17 (m, 3H). MS: *m/z* (%): 202.15 ([M + 2]$^{+}$, 5.06), 200.09 ([M]$^{+}$, 100.00), 199.16 (94.91), 155.25 (19.33), 108.85 (35.65), 96.98 (48.15), 68.98 (65.74), 57.04 (63.89).



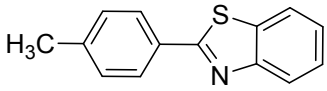
2-(4-Chlorophenyl)benzothiazole (Table 6, 2a): Mp 114-116 ^{o}C. IR (KBr): ν_{max} = 3060, 2961, 1588, 1508, 1476, 1307, 1260, 1070, 762 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.0 Hz, 1H), 8.10 (dd, ^{1}J = 7.6 Hz, ^{2}J = 2.0 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.56 (dd, ^{1}J = 8.0 Hz, ^{2}J = 1.2 Hz, 1H), 7.54-7.50 (m, 2H), 7.46 (dd, ^{1}J = 8.0 Hz, ^{2}J = 1.2 Hz, 1H). MS: *m/z* (%): 247.19 ([M + 2]$^{+}$, 6.16), 245.04 ([M]$^{+}$, 24.20), 210.17 (4.80), 164.17 (3.95), 138.84 (18.20), 122.60 (25.40), 107.79 (86.40), 81.95 (48.50), 68.98 (100), 57.08 (34.20).



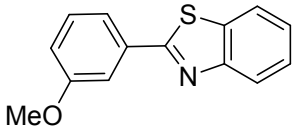
2-(2,4-Dichlorophenyl)benzothiazole (Table 6, 2b): Mp 146-147 ^{o}C. IR (KBr): ν_{max} = 3064, 1583, 1466, 1240, 1036, 832, 739 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.58 (td, ^{1}J = 7.6 Hz, ^{2}J = 1.2 Hz, 2H), 7.53-7.45 (m, 2H). MS: *m/z* (%): 282.98 ([M + 2]$^{+}$, 20.07), 280.99 ([M]$^{+}$, 73.89), 278.99 (80.79), 242.13 (72.91), 241.15 (100.00), 171.12 (29.93), 127.17 (23.03), 120.74 (74.38), 108.09 (94.09), 82.00 (86.70), 69.10 (96.06), 57.22 (46.31).



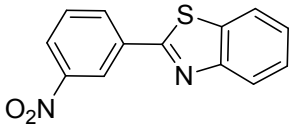
2-(3,4-Dimethoxyphenyl)benzothiazole (Table 6, 2c): Mp 129-131 ^{o}C. IR (KBr): ν_{max} = 3049, 2959, 2937, 1597, 1521, 1481, 1335, 1261, 1018, 872, 763 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, J = 8.4 Hz, 1H), 7.89 (dd, ^{1}J = 8.0 Hz, ^{2}J = 0.8 Hz, 1H), 7.82 (d, J = 1.2 Hz, 1H), 7.63 (dd, ^{1}J = 8.0 Hz, ^{2}J = 2.0 Hz, 1H), 7.50 (dd, ^{1}J = 8.0 Hz, ^{2}J = 2.0 Hz, 1H), 7.40 (dd, ^{1}J = 8.0 Hz, ^{2}J = 2.8 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 4.09 (s, 3H), 3.98 (s, 3H). MS: *m/z* (%): 273.30 ([M + 2]$^{+}$, 14.31), 271.31 ([M]$^{+}$, 50.20), 270.47 (100), 255.12 (62.35), 227.33 (83.53), 213.17 (24.12), 184.33 (55.29), 138.87 (23.33), 135.22 (47.06), 97.02 (60.39), 69.02 (69.03), 57.11 (57.25).



2-*p*-Tolylbenzothiazole (Table 6, 2d): Mp 84-86 ^{o}C. IR (KBr): ν_{max} = 3056, 2960, 1604, 1479, 1430, 1311, 1225, 967, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, J = 7.6 Hz, 1H), 8.06 (d, J = 7.6 Hz, 2H), 7.91 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 2H), 2.46 (s, 3H). MS: *m/z* (%): 227.14 ([M + 2]$^{+}$, 25.65), 225.15 ([M]$^{+}$, 100.00), 223.14 (39.90), 210.12 (9.72), 197.13 (8.00), 165.10 (5.67), 116.15 (64.77), 120.74 (74.38), 108.09 (94.09), 82.00 (86.70), 69.10 (96.06), 57.22 (46.31), 45.21 (68.91).

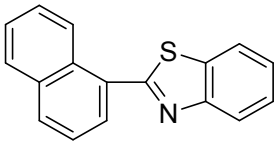


2-(3-Methoxyphenyl)benzothiazole (Table 6, 2e): Mp 82-84^{o}C. IR (KBr): ν_{max} = 3056, 2959, 2929, 1604, 1580, 1459, 1428, 1288, 993, 760 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.44 (t, J = 7.2 Hz , 1H), 7.38-7.32 (m, 2H), 7.00 (d, J = 7.6 Hz, 1H), 3.87 (s, 3H). MS: *m/z* (%): 241.11 ([M]$^{+}$, 13.73), 211.11 (9.57), 108.10 (22.84), 82.13 (29.32), 71.20 (35.80), 69.16 (91.36), 57.22 (76.23).

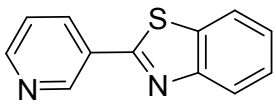


2-(3-Nitrophenyl)benzothiazole (Table 6, 2f): Mp 181-183 ^{o}C. IR (KBr): ν_{max} = 3085, 2923, 1574, 1529, 1458, 1345, 1269, 888,761, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.96 (s, 1H), 8.51 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz,

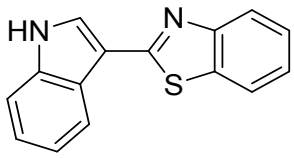
1H), 7.76-7.71 (m, 1H), 7.60-7.47 (m, 2H). MS: *m/z* (%): 257.34 ([M + 1]$^+$, 3.75), 256.04 ([M]$^+$, 22.55), 225.20 (6.45), 209.23 (25.00), 138.57 (9.85), 107.84 (23.37), 83.00 (48.84), 69.01 (100.00), 57.08 (94.57).



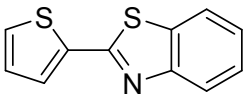
2-(Naphthalen-1-yl)benzothiazole (Table 6, 2g) Mp 80-82^{o}C. IR (KBr): ν_{max} = 3053, 2922, 1605, 1587, 1441, 1284, 1107, 889, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 8.4 Hz, 1H), 8.35-8.29 (m, 2H), 8.04-7.91 (m, 4H), 7.61 (s, 3H), 7.50 (s, 1H).



2-(Pyridin-3-yl)benzothiazole (Table 5, 2h): Mp 126-128 ^{o}C. IR (KBr): ν_{max} = 3051, 2923, 1613, 1573, 1426, 1228, 963, 760 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.32 (s, 1H), 8.74 (d, *J* = 4.0 Hz, 1H), 8.40 (dd ^1J = 8.0 Hz, ^2J = 1.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.53 (dd, ^1J = 8.0 Hz, ^1J = 1.2 Hz, 1H), 7.48-7.43 (m, 2H). MS: *m/z* (%): 212.14 ([M]$^+$, 1.12), 179.27 (1.23), 109.21 (15.44), 97.22 (31.88), 83.21 (41.95), 69.22 (73.15), 57.23 (97.32), 43.26 (100).



2-(1H-indol-3-yl)benzothiazole (Table 6, 2i): Mp 168-170 ^{o}C. IR (KBr): ν_{max} = 3118, 3056, 1592, 1551, 1440, 1348, 1243, 918, 750 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.59 (br s, 1H), 8.39 (t, *J* = 5.2 Hz, 1H), 8.27 (d, *J* = 5.2 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 5.2 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.26 (m, 2H). MS: *m/z* (%): 251.51 ([M + 1]$^+$, 15.53), 250.16 ([M]$^+$, 176.17), 248.91 (100), 222.16 (11.28), 14.80 (7.23), 111.28 (46.80), 97.02 (28.94), 68.99 (68.09), 57.08 (38.72).).



2-(Thiophen-2-yl)benzothiazole (Table 6, 2j): Mp 181-183 ^{o}C. IR (KBr): ν_{max} = 3095, 1581, 1542, 1464, 1311, 913, 826, 704 cm^{-1}. H NMR (400 MHz, $CDCl_3$) δ = 8.0 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.72 (dd, ^{1}J = 4.4 Hz, ^{1}J = 0.8, 1H), 7.46 (dd, ^{1}J = 8.0 Hz, ^{2}J = 1.2, 1H), 7.41 (td, ^{1}J = 8.0, ^{2}J =1.2 Hz, 1H), 7.30 (td, ^{1}J = 8.0, ^{2}J = 1.2 Hz, 1H, Ar), 7.08 (dd, ^{1}J = 8.0, ^{2}J =3.6 Hz, 1H, Ar). MS: *m/z* (%): 219.08 ([M + 2]$^{+}$, 4.02), 217.09 ([M]$^{+}$, 25.00), 122.14 (8.29), 109.11 (40.63), 82.12 (42.71), 69.14 (100.0), 57.19 (39.41).