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Supporting Information

A simple and efficient mechanochemical route for the synthesis of 2-aryl benzothiazoles and substituted benzimidazoles

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Table of Contents

General Information

The reagents were purchased from commercial sources and were used without further purification. All solvents were obtained from local suppliers and were of research grade. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance (300 or 400 MHz, respectively) or Zeol 500 MHz with either tetramethylsilane (TMS) or solvent peak as internal standard. The chemical shifts are reported in parts per million (δ) units relative to the solvent peak. Mass spectra were recorded on Agilent Technologies 6220 Accurate-Mass TOF LC/MS using ESI as ion source. The IR spectra were recorded on IR Affinity 1, Shimadzu. KBr was used for solid samples and ATR probe was used for liquid samples. The reactions were monitored by thin layer chromatography (TLC) carried out on 0.25-mm silica gel on aluminium plates (60F-254) using UV light (254 or 365 nm) or naked eye for visualization. Column chromatography was performed on silica gel (60–120 mesh, Merck).

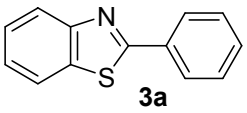
General procedure for the synthesis of 2-substituted benzimidazoles**:** *o*-Phenylenediamine (1 mmol) was dissolved in 0.5 mL of ethanol taken in a mortar (Agate made). The respective aromatic aldehyde was added in several small portions (0.2 mmol at a time) and the mixture was gently ground by a pestle for 2 min before addition of another portion. After addition was completed the grinding was continued for the time mentioned in Table 3. The progress of the reaction was monitored by TLC after each 5 min. The crude reaction mixture was purified by column chromatography (silica gel, 60-120 mesh) using EtOAc in petroleum ether.

Syntheses of 1,2-disubstituted benzimidazoles follow the same procedure for 2-aryl benzothiazoles as described in the main text.

Characterization:

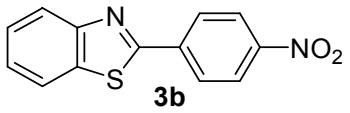
All the compounds are previously reported. The compounds synthesized by mechanochemical route were characterized by ^{1}H NMR, ^{13}C NMR and ESI-MS spectroscopy and matched with the literature data. The spectral data were forund in good agreement with the literature values in each case.

2-Phenylbenzo[*d*]thiazole[1] **(Table 2, entry 1):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42 (t, J = 7.2 Hz, 1H), 7.52-7.57 (m, 4H), 7.94 (d, J = 7.8 Hz, 1H), 8.08-8.12 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 121.5, 123.1, 125.0, 126.3, 127.5, 129.0, 130.8, 133.5, 134.9, 154.1, 167.8; ESI-MS (*m/z*): 211.9 $[M + H]^+$.



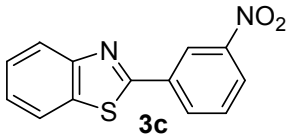
3a

2-(4-Nitrophenyl)benzo[*d*]thiazole[2] **(Table 2, entry 2):** ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 6.66 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 7.2 Hz, 1H), 7.98 (d, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 114.1, 120.6, 122.2, 122.3, 124.7, 126.6, 129.2, 134.2; 152.6, 154.4, 168.6; ESI-MS (*m/z*): 256.9 $[M + H]^+$.



3b

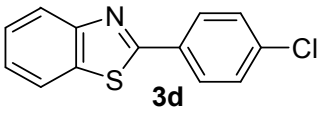
2-(3-Nitrophenyl)benzo[*d*]thiazole[1] **(Table 2, entry 3):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.44 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 7.6 Hz, 1H), 8.39 (d, J = 7.6 Hz, 1H), 8.90 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 121.8, 122.3,



3c

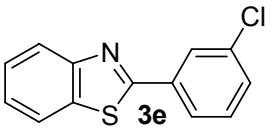
123.7, 125.1, 126.0, 126.8, 130.0, 132.9, 135.2, 135.3, 148.7, 153.9, 164.8; ESI-MS (*m/z*): 256.9 $[M + H]^+$.

2(4-Chloropnenyl)benzo[*d*]thiazole[1] **(Table 2, entry 4):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38-7.54 (m, 4H), 7.90 (d, *J* = 8.0 Hz, 1H), 8.01-8.10 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 121.7, 123.3, 125.4, 126.5, 128.7, 129.2, 132.1, 135.1, 137.0, 154.1, 166.6; ESI-MS (*m/z*): 245.9 $[M + H]^+$ (major peak, for ^{35}Cl), 247.9 $[M + H]^+$ (minor peak, for ^{37}Cl).



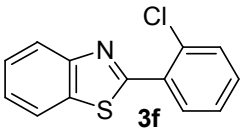
3d

2-(3-Chlorophenyl)benzo[*d*]thiazole[2] **(Table 2, entry 5):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38-7.54 (m, 4H), 7.91 (t like, *J* = 8.4 Hz, 2H), 8.01-8.11 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 121.7, 123.5, 125.5, 125.7, 126.5, 127.4, 129.3, 130.2, 130.8, 135.1, 135.3, 154.0, 166.2; ESI-MS (*m/z*): 245.9 $[M + H]^+$ (major peak, for ^{35}Cl), 247.9 $[M + H]^+$ (minor peak, for ^{37}Cl).



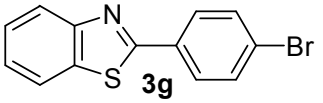
3e

2-(2-Chloropnenyl)benzo[*d*]thiazole[1] **(Table 2, entry 6):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40-7.45 (m, 3H), 7.51-7.56 (m, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.20-8.23 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 121.4, 123.5, 125.5, 126.2, 127.0, 130.6, 131.0, 131.7, 132.2, 132.6, 136.1, 152.5, 164.0; ESI-MS (*m/z*): 245245.9 $[M + H]^+$ (major peak, for ^{35}Cl), 247.9 $[M + H]^+$ (minor peak, for ^{37}Cl).



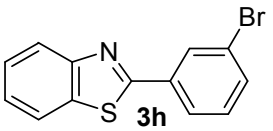
3f

2-(4-Bromophenyl) benzo[*d*]thiazole[3] **(Table 2, entry 7):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 120.6, 122.3, 124.4, 124.5, 125.3, 127.9, 131.2, 131.5, 134.0, 153.1, 165.5; ESI-MS (*m/z*): 289.8 $[M + H]^+$ (for ^{79}Br), 291.8 $[M + H]^+$ (for ^{81}Br).



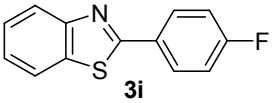
3g

2-(3-Bromophenyl) benzo[*d*]thiazole[4] **(Table 2, entry 8):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.33-7.54 (m, 3H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.8, 1H), 7.98 (d, *J* = 7.8, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 8.29 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 121.7, 123.2, 123.5, 125.5, 126.1, 126.5, 130.3, 130.4, 133.7, 135.1, 135.5, 154.0, 166.1; ESI-MS (*m/z*): 289.8 $[M + H]^+$ (for ^{79}Br), 291.8 $[M + H]^+$ (for ^{81}Br).



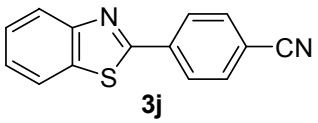
3h

2-(4-Fluorophenyl)benzo[*d*]thiazole[1] **(Table 2, entry 9):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.19 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 8.07-8.11 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 116.1 (d, *J* = 22.0 Hz), 121.6, 123.2, 125.2, 126.4, 129.5 (d, *J* = 8.5 Hz), 130.0 (d, *J* = 3.1 Hz), 135.1, 154.2, 164.5 (d, *J* = 250.3 Hz), 166.7; ESI-MS (*m/z*): 230.2 $[M + H]^+$.



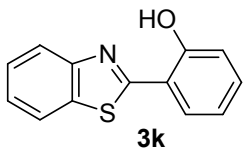
3i

4-(Benzo[*d*]thiazol-2-yl)benzonitrile[2] **(Table 2, entry 10):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.44 (t, *J* = 6.9 Hz, 1H), 7.54 (t, *J* = 6.9 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 2H).); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 114.1, 118.2, 121.8, 123.8, 126.1, 126.8, 127.9, 132.7, 135.3, 137.4, 154.0, 165.3; ESI-MS (*m/z*): 237.2 $[M + H]^+$.



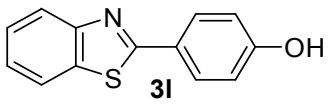
3j

(2-Hydroxypnenyl)benzo[*d*]thiazole[5] **(Table 2, entry 11):** ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.03 7.15 (m, 2H), 7.40-63 (m, 3H), 8.09-8.27 (m, 3H), 11.60 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 116.3, 117.4, 119.0, 121.1, 121.8, 125.2, 126.2, 127.9, 132.1, 132.3, 151.3, 157.5, 168.9; ESI-MS (*m/z*): 228.1 [M + H]$^+$.



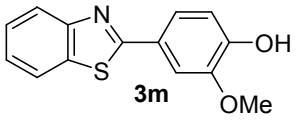
3k

4-(Benzo[*d*]thiazol-2-yl)phenol[6] **(Table 2, entry 12)**: ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 6.94 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.91-8.05 (m, 4H), 10.23 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 116.5, 122.5, 122.7, 124.5, 125.3, 126.8, 129.5, 134.6, 154.2, 161.0, 167.9; ESI-MS (*m/z*): 228.2 [M + H]$^+$.



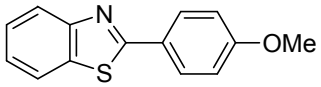
3l

4-(Benzo[*d*]thiazol-2-yl)-2-methoxyphenol[3] **(Table 2, entry 13):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.99 (s, 3H), 7.01 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.72 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 56.2, 110.0, 114.6, 121.4, 122.0, 122.7, 124.8, 126.2, 126.3, 134.7, 146.9, 148.6, 154.0, 168.1; ESI-MS (*m/z*): 258.1 [M + H]$^+$.



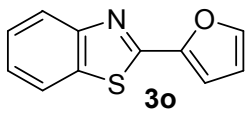
3m

2-(4-Methoxyphenyl)benzo[*d*]thiazole[1] **(Table 2, entry 14):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.87 (s, 3H), 6.98 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 55.4, 114.3, 121.5, 122.8, 124.8, 126.2, 126.5, 129.1, 134.9, 154.3, 161.9, 167.8; ESI-MS (*m/z*): 241.9 [M + H]$^+$.



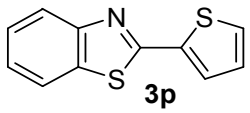
3n

2-(Furan-2-yl)benzo[*d*]thiazole[3] **(Table 2, entry 15):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.58 (s like, 1H), 7.19 (d, *J* = 3.3 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.59 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 111.4, 112.5, 121.5, 123.1, 125.2, 126.4, 134.3, 144.7, 148.8, 153.8, 157.5; ESI-MS (*m/z*): 202.3 [M + H]$^+$.



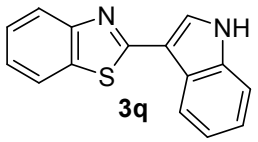
3o

2-(Thiophen-2-yl)benzo[*d*]thiazole[1] **(Table 2, entry 16):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.14 (s like, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.46-7.51 (m, 2H), 7.66 (d, *J* = 3.2 Hz), 7.84 (d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 121.4, 123.0, 125.2, 126.4, 128.0, 128.6, 129.3, 134.7, 137.4, 153.7, 161.4; ESI-MS (*m/z*): 218.1 [M + H]$^+$.



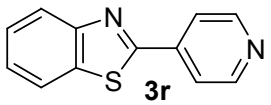
3p

2-(1*H*-Indol-3-yl)benzo[*d*]thiazole[2] **(Table 2, entry 17):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.34-7.51 (m, 5H), 7.90-7.95 (m, 2H), 8.06 (d, *J* = 7.5 Hz, 1H), 8.47 (d, *J* = 7.2 Hz, 1H), 8.96 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 111.7, 112.5, 121.1, 121.3, 121.8, 122.2, 123.5, 124.2, 125.0, 126.1, 126.3, 133.9, 136.5, 153.8, 163.0; ESI-MS (*m/z*): 251.2 [M + H]$^+$.



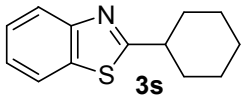
3q

2-(Pyridine-4-yl)benzo[*d*]thiazole[1] **(Table 2, entry 18):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.43 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.90-7.92 (m, 3H), 8.11 (d, *J* = 8.1 Hz, 1H), 8.74-8.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 121.1, 121.8, 123.9, 126.2, 126.8, 135.2, 140.4, 150.7, 154.0, 165.0; ESI-MS (*m/z*): 213.2 [M + H]$^+$.

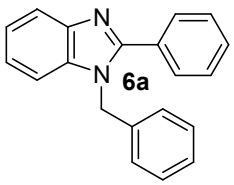


3r

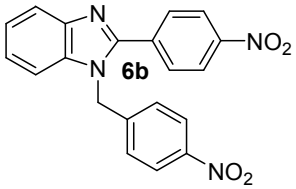
2-Cyclohexylbenzo[*d*]thiazole[7] **(Table 2, entry 19):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.30-1.50 (m, 3H), 1.61-1.89 (m, 4H), 1.92-1.94 (m, 2H), 2.20-2.25 (m, 2H), 3.12-3.16 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 25.7, 26.1, 33.4, 43.5, 121.5, 122.6, 124.5, 125.8, 134.6, 153.1; ESI-MS (*m/z*): 217.9 $[M + H]^+$.



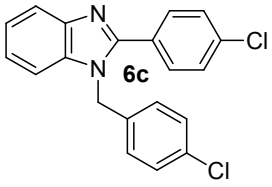
1-Benzyl-2-phenyl-1*H*-benzo[*d*]imidazole[8] **(Table 3, entry 1 & 2):** ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 5.53 (s, 2H), 7.02 (d, *J* = 7.0 Hz, 2H), 7.24-7.33 (m, 5H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.49-7.55 (m, 3H), 7.65-7.68 (m, 2H), 7.73 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 48.6, 112.2, 120.3, 123.3, 123.8, 127.2, 128.5, 130.0, 130.1, 130.9, 133.2, 137.0, 138.0, 143.7, 154.3; ESI-MS (*m/z*): 285.1 $[M + H]^+$.



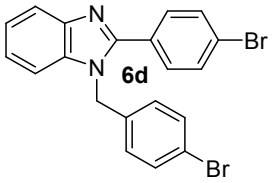
1-(4-Nitrobenzyl)-2-(4-nitrophenyl)-1*H*-benzo[*d*]imidazole[8] **(Table 3, entry 3 & 4):** ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 5.82 (s, 2H), 7.24-7.33 (m, 4H), 7.52-7.56 (m, 1H), 7.79-7.82 (m, 1H), 8.00 (d, *J* = 8.7 Hz, 2H), 8.15 (d, *J* = 8.7 Hz, 2H), 8.33 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 47.7, 111.7, 120.3, 123.4, 124.2, 124.4, 124.5, 127.9, 130.8, 136.4, 136.5, 143.1, 144.8, 147.4, 148.5, 151.5; ESI-MS (*m/z*): 374.9 $[M + H]^+$.



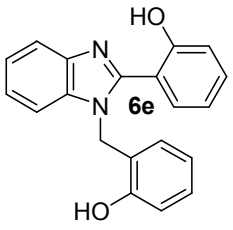
1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole[8] **(Table 3, entry 5 & 6)**: ^{1}H NMR (400 MHz, CD_3OD) : δ (ppm) 5.51 (s, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 7.29-7.35 (m, 4H), 7.40 (dd, J_1 = 4.4 Hz, J_2 = 6.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 48.3, 112.6, 120.8, 124.1, 124.6, 129.5, 130.0, 130.3, 130.5, 132.3, 133.6, 134.9, 136.4, 143.7, 153.6; ESI-MS (*m/z*): 352.9 $[M + H]^+$ (major peak, for ^{35}Cl).



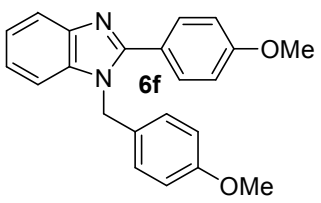
1-(4-Bromobenzyl)-2-(4-bromophenyl)-1H-benzo[d]imidazole[8] **(Table 3, entry 7 & 8)**: ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 5.56 (s, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 7.24-7.28 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 3H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 48.4, 112,7, 120.8, 122.2, 124.3, 124.8, 125.3, 129.8, 130.4, 132.6, 133.2, 133.5, 137.1, 137.5, 143.8, 153.7; ESI-MS (*m/z*): 440.9 $[M + H]^+$ (for ^{79}Br), 444.9 $[M + H]^+$ (for ^{81}Br).



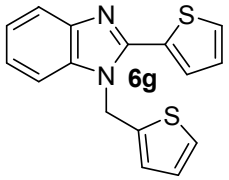
2-(1-(2-Hydroxybenzyl)-1*H*-benzo[*d*]imidazol-2-yl)phenol (Table 3, entry 9 & 10): ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 5.40 (s, 2H), 6.34 (d, *J* = 7.2 Hz, 1H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.88 (t, *J* = 7.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.20-7.22 (m, 2H), 7.32-7.42 (m, 3H), 7.71 (d, *J* = 6.8 Hz, 1H), 9.86 (brs, 1H), 11.15 (brs, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 43.7, 111.3, 115.5, 116.7, 116.9, 119.2, 119.5, 122.5, 123.0, 123.1, 127.2, 128.8, 130.7, 131.8, 135.8, 142.3, 154.9, 156.9; ESI-MS (*m/z*): 316.9 $[M + H]^+$.



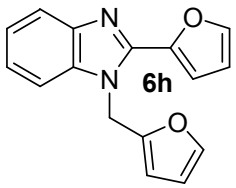
1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole[8] **(Table 3, entry 11 & 12):** ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.72 (s, 3H), 3.85 (s, 3H), 5.45 (s, 2H), 6.84 (d, J = 11.4 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 7.22-7.38 (m, 3H), 7.64 (d, J = 8.7 Hz, 2H), 7.70 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 48.0, 56.1, 56.4, 112.1, 115.2, 115.3, 120.1, 123.1, 123.4, 123.5, 128.4, 129.9, 131.6, 136.9, 143.7, 154.3, 159.6, 161.5; ESI-MS (*m/z*): 345.1 $[M + H]^+$.



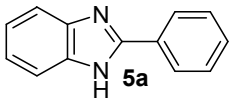
2-(Thiophen-2-yl)-1-((thiophen-2-yl)methyl)-1*H*-benzo[*d*]imidazole[8] **(Table 3, entry 13 & 14):** ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 5.93 (s, 2H), 6.95 (dd, J_1 = 3.3 Hz, J_2 = 4.9 Hz, 1H), 7.02 (s like, 1H), 7.23-7.28 (m, 3H), 7.39 (d, J = 5.1 Hz, 1H), 7.67-7.80 (m, 3H), 7.82 (d, J = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 43.53, 111.3, 119.4, 123.1, 123.4, 126.4, 126.5, 127.5, 128.4, 128.9, 130.1, 132.5, 136.3, 139.8, 142.9, 147.2; ESI-MS (*m/z*): 296.9 $[M + H]^+$.



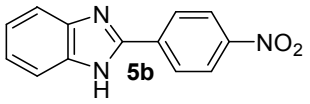
2-(Furan-2-yl)-1-((furan-2-yl)methyl)-1*H*-benzo[*d*]imidazole[8] **(Table 3, entry 15 & 16):** ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 5.77 (s, 2H), 6.38 (s, 1H), 6.47 (d, J = 2.7 Hz, 1H), 6.76 (t, J = 1.8 Hz, 1H), 7.22-7.32 (m, 3H), 7.54 (s, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 8.01 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 41.4, 109.2, 111.0, 111.4, 112.6, 113.4, 119.5, 123.0, 123.3, 135.8, 143.0, 143.6, 143.9, 145.2, 145.5, 150.2; ; ESI-MS (*m/z*): 264.9 $[M + H]^+$.



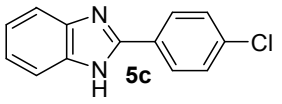
2-Phenyl-1*H*-benzo[*d*]imidazole[9] **(Table 3, entry 1 & 2):** ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 6.98 (s, 2H), 7.18-7.23 (m, 4H), 7.41-7.45 (m, 1H), 7.90-7.92 (m, 2H), 12.73 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 115.6, 120.9, 127.0, 127.8, 130.1, 131.4, 138.0, 150.6; ESI-MS (*m/z*): 195.1 $[M + H]^+$.



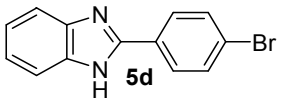
2-(4-Nitrophenyl)-1*H*-benzo[*d*]imidazole[9] **(Table 3, entry 3 & 4):** ^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 7.33-7.36 (m, 2H), 7.55-7.76 (m, 2H), 8.33 (d, J = 9.0 Hz, 2H), 8.43 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) 112.2, 119.8, 122.7, 124.0, 124.7, 127.7, 135.6, 136.4, 144.3, 148.1, 149.4; ESI-MS (*m/z*): 240.0 $[M + H]^+$.



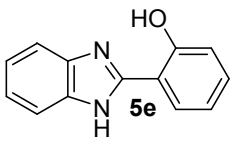
2-(4-Chlorophenyl)-1*H*-benzo[*d*]imidazole[9] **(Table 3, entry 5 & 6):** ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 7.24-7.29 (m, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.57-7.64 (m, 2H), 8.05 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 112.1, 119.5, 122.8, 123.9, 129.0, 129.8, 135.2, 135.9, 144.6, 151.0; ESI-MS (*m/z*): 229.0 $[M + H]^+$ (major peak, for ^{35}Cl), 231.0 $[M + H]^+$ (minor peak, for ^{37}Cl).



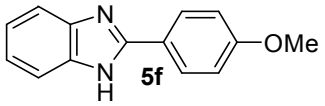
2-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole[10] **(Table 3, entry 7 & 8):** ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.18-7.22 (m, 2H), 7.50 (s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.2 Hz, 2H),), 8.10-8.14 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 111.3, 118.6, 121.7, 123.0, 128.3, 129.0, 131.7, 134.6, 143.4, 149.9; ESI-MS (*m/z*): 272.9 $[M + H]^+$ (for ^{79}Br), 274.9 $[M + H]^+$ (for ^{81}Br).



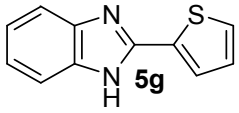
2-(2-Hydroxyphenyl)-1*H*-benzo[*d*]imidazole[9] **(Table 3, entry 9 & 10):** ^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 6.94-7.02 (m, 2H), 7.24-7.36 (m, 3H), 7.59-7.62 (m, 2H), 7.91 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) 113.0, 114.4, 116.8, 118.9, 122.5, 125.7, 131.2, 151.7, 158.1; ESI-MS (*m/z*): 211.1 $[M + H]^+$.



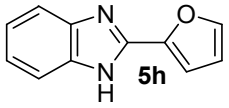
2-(4-Methoxyphenyl)-1*H*-benzo[*d*]imidazole[9] **(Table 3, entry 11 & 12):** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.84 (m, 3H), 6.64-6.76 (m, 3H), 6.83-6.88 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 112.3, 114.0, 116.6, 119.0, 120.7, 129.8, 131.4, 134.3, 137.6, 158.9; ESI-MS (*m/z*): 225.1 $[M + H]^+$.



2-(2-Thienyl)-1H-benzo[*d*]imidazole[10] **(Table 3, entry 13 & 14):** ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 7.12-7.20 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 4.8 Hz, 1H), 7.79 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 111.6, 119.1, 122.3, 123.1, 127.2, 128.8, 129.3, 134.2, 135.2, 144.1, 147.6; ESI-MS (*m/z*): 201.0 $[M + H]^+$.



2-(2-Furan-2-yl)-1H-benzo[*d*]imidazole[10] **(Table 3, entry 15 & 16):** ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 6.69 (s, 1H), 7.15-7.18 (m, 3H), 7.52 (s, 2H), 7.90 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 111.0, 112.8, 122.7, 144.1, 145.2, 146.1; ESI-MS (*m/z*): 185.0 $[M + H]^+$.



Infrared Spectroscopic studies:

Infrared spectroscopic studies were conducted to capture the progress of the reaction. The reaction between benzaldehyde and 2-aminothiophenol was monitored by taking IR spectra of the crude reaction mixture at different time interval. As the reaction was conducted by grinding in an Agate mortar in the presence of small amount of EtOH, each portion of the reaction mixture was quickly evaporated to dryness and vacuum dried before taking IR spectra. As shown in Fig. S1, the characteristic stretching bands of starting materials like carbonyl of aromatic aldehyde at 1691 cm^{-1} and amine N-H bands at 3452 cm^{-1} and 3357 cm^{-1} almost disappeared after grinding the reaction mixture for 5 min. In contrast, a sharp peak at 3388 cm^{-1} was appeared in the IR spectrum which is supposed to be the N-H stretching band of intermediate imine. As the reaction progressed further (see IR spectra after 10 min and 15 min) this peak significantly reduced indicating conversion of intermediate imine to 2-phenylbenzothiazole. The IR spectrum of the crude reaction mixture after 15 min revealed the completion of the reaction as the imine N-H stretching band is almost negligible; this spectrum also matched nicely with the IR spectrum of column purified 2-phenylbenzothiazole.

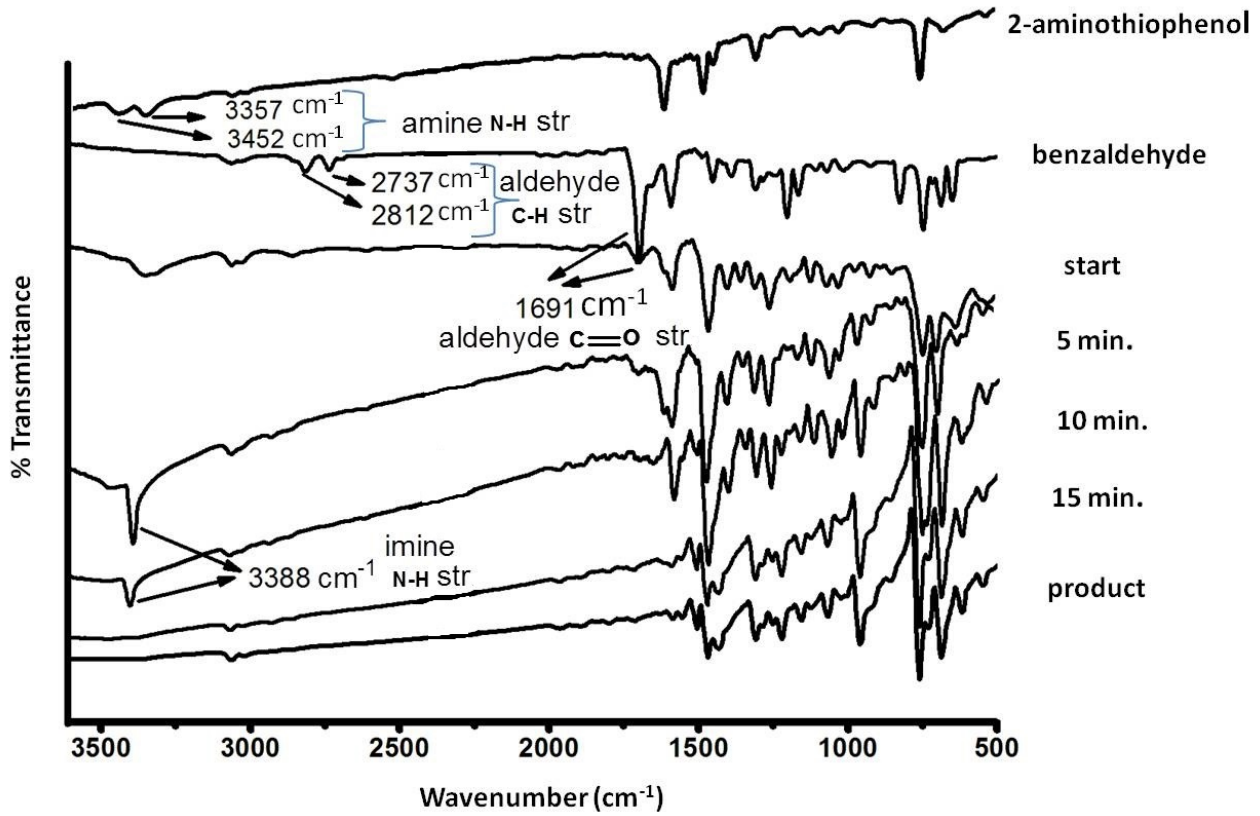


Fig. S1. IR studies to monitor the progress of the reaction between benzaldehyde and 2-aminothiophenol; "start" represents the IR spectrum taken just after few seconds of mixing the starting materials in a mortar and without adding EtOH; "str" is abbreviation "stretching".

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Some selected spectra