Electronic Supplementary Information (ESI†)

Nano Zirconia Catalysed One Pot Synthesis of Some Novel Substituted Imidazoles under Solvent Free Conditions

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1. General remarks

All chemicals were procured from Aldrich, USA, and E. Merck, Germany and used as such. N-substituted isatins were prepared by earlier reported procedures. TLC was carried out on SiO₂ gel (HF254, 200 mesh). The solvent system employed was ethyl acetate: n-hexane (1: 1) and the spots were identified by placing the plate in Iodine chamber. IR spectra were recorded on a PerkinElmer FT/IR version10.03.05 spectrometer. NMR spectra were run on a JEOL AL300 FTNMR spectrometer; chemical shifts are given in δ ppm, relative to TMS as internal standard. Elemental microanalysis was performed on Exeter Analytical Inc Model CE-440 CHN Analyzer. Melting points were measured in open capillaries and are uncorrected. An XRD spectrum was recorded on a Scifert X-Ray Diffraction System. TEM image was taken from TECNAI G2, FEI. SEM image was recorded from Scanning Electron Microscope, QUANTA 200 F. BET surface area analysis was carried by Smart Sorb-93 manufactured by Smart Instruments Pvt. Ltd.

2. Typical procedure for the synthesis of ZrO₂ NPs

0.075 M solution of ZrOCl₂·8H₂O was prepared and then precipitated with NH₄OH (25%) with continuous stirring on a magnetic stirrer till the PH raises in the range of 10 to 10.5. This resulted in the formation of precipitate of zirconium hydroxide. The precipitate was filtered and washed with double distilled water until traces of chloride ion were completely removed from the filtrate. Complete removal of chloride ion from filtrate was checked by titrating it with AgNO₃ solution using potassium chromate as indicator. Now, the precipitate was dried in oven at 80 – 90 °C for 24 h. and calcinated at 600 °C for 3 h in order to formation of white nano zirconia powder.
3. IR spectra of ZrO$_2$ NPs

Figure A: FT-IR spectrum of ZrO$_2$ NPs
4. SEM image of ZrO$_2$ NPs

Figure B: SEM image of ZrO$_2$ NPs
5. BET surface area analysis data of ZrO$_2$ NPs

**Table:**

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**Remarks:** SHAM

**Graph:**

![Graph for Sample 1](image)

**Figure C:** BET surface area of ZrO$_2$ NPs
6. SEM image of bulk ZrO$_2$

Figure D: SEM image of bulk ZrO$_2$
7. BET surface area analysis data of bulk ZrO₂

**Figure E: BET surface area of bulk ZrO₂**
8. General procedure for the synthesis of substituted imidazoles 4a-s

To a mixture of isatin derivatives 1a-g (1 mmol), ammonium acetate 2 (5 mmol), substituted aromatic aldehydes 3a-f (1 mmol), 15 mol% of ZrO₂ NPs was added [Scheme 1]. The mixture was heated and stirred at 110 °C for 30 min. The progress of the reaction was monitored by thin layered chromatography (n-hexane: ethyl acetate, 1:1). After completion, 20 ml acetone was added to the reaction mixture; the catalyst was removed by filtration and washed with xylene and acetone. Then, 50 ml of double distilled water is added to the liquid portion. This resulted in the formation of precipitate of products 4a-s. The precipitate was filtered, dried and recrystallized with ethanol.
9. Characterization data and $^1$H & $^{13}$C spectra of substituted imidazoles 4a-s

9.1. 2-phenyl-3,4-dihydroimidazo[4,5-b]indole (4a)

Brown solid, IR (KBr) $\nu$: 3400, 3209, 3019, 2964, 1660, 1614, 1567, 1484, 1316, 1210, 1171, 1010, 877, 742, 653, 580 cm$^{-1}$. $^1$H NMR (300 MHz, DMSO) $\delta$: 7.80- 8.86 (m, 9H, aromatic protons), 9.15 (s, 1H, NH), 9.66 (s, 1H, NH) ppm. $^{13}$C NMR (75.45 MHz, DMSO) $\delta$: 124.0, 126.7, 127.5, 130.2, 130.7, 132.0, 133.7, 135.5, 139.1, 148.2, 160.9 ppm. Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{N}_3$: C, 77.24; H, 4.74; N, 18.01 Found C, 77.20; H, 4.76; N, 18.03.
9.2. 7-chloro-2-phenyl-3,4-dihydroimidazo[4,5-b]indole (4b)

Brown solid, IR (KBr) ν: 3364, 3190, 2981, 2964, 1648, 1609, 1559, 1447, 1311, 1199, 1143, 1019, 872, 744, 651, 566 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ: 7.51-8.59 (m, 8H, aromatic protons), 9.14 (s, 1H, NH), 9.45 (s, 1H, NH) ppm. ¹³C NMR (75.45 MHz, CDCl₃) δ: 123.9,
125.7, 128.5, 128.6, 130.3, 130.8, 132.7, 135.0, 137.5, 149.2, 159.4 ppm. Anal. Calcd for C_{15}H_{10}ClN_{3}: C, 67.28; H, 3.78; N, 15.72. Found C, 67.32; H, 3.76; N, 15.70
9.3. 2-(2-nitrophenyl)-3,4-dihydroimidazo[4,5-b]indole (4c)

Brown solid, IR (KBr) $\nu$: 3332, 3201, 2995, 2917, 1658, 1623, 1549, 1485, 1348, 1280, 1176, 1068, 864, 708, 667, 544 cm$^{-1}$. $^1$H NMR (300 MHz, DMSO) $\delta$: 7.61- 8.69 (m, 8H, aromatic protons), 9.67 (s, 1H, NH), 9.94 (s, 1H, NH) ppm. $^{13}$C NMR (75.45 MHz, DMSO) $\delta$: 123.8, 126.7, 128.8, 130.1, 131.8, 135.4, 135.8, 135.9, 148.3, 160.7 ppm. Anal. Calcd for C$_{15}$H$_{10}$N$_4$O$_2$: C, 64.74; H, 3.62; N, 20.13 Found C, 64.69; H, 3.65; N, 20.14.
9.4. 7-chloro-2-(2-nitrophenyl)-3,4-dihydropyrimidazo[4,5-b]indole (4d)

Brown solid, IR (KBr) ν: 3399, 3229, 2916, 2885, 1645, 1600, 1539, 1457, 1329, 1253, 1162, 1027, 885, 703, 647, 553 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.66-8.36 (m, 7H, aromatic protons), 8.96 (s, 1H, NH), 9.50 (s, 1H, NH) ppm. $^{13}$C NMR (75.45 MHz, CDCl$_3$) δ: 123.4, 123.8, 124.8, 127.1, 128.0, 128.6, 129.4, 133.9, 134.1, 134.4, 139.7, 148.7, 150.4, 160.6 ppm.

Anal. Calcd for C$_{15}$H$_9$ClN$_4$O$_2$: C, 57.60; H, 2.91; N, 17.91 Found C, 57.51; H, 3.0; N, 17.94.
9.5. 2-(3-nitrophenyl)-3,4-dihydroimidazo[4,5-b]indole (4e)

Brown solid, IR (KBr) ν: 3315, 3194, 3066, 2978, 1662, 1623, 1572, 1482, 1353, 1286, 1135, 1025, 832, 797, 661, 542 cm⁻¹. ¹H NMR (300 MHz, DMSO) δ: 7.58- 8.55 (m, 8H, aromatic protons), 8.97 (s, 1H, NH), 9.67 (s, 1H, NH) ppm. ¹³C NMR (75.45 MHz, DMSO) δ: 122.3, 123.6, 125.2, 127.9, 128.4, 129.7, 130.4, 134.4, 134.5, 135.2, 139.0, 147.6, 161.7 ppm. Anal. Calcd for C₁₅H₁₀N₄O₂: C, 64.70; H, 3.63; N, 20.16 Found C, 64.51; H, 3.72; N, 20.23.
9.6. 7-chloro-2-(3-nitrophenyl)-3,4-dihydroimidazo[4,5-b]indole (4f)

Brown solid, IR (KBr) \(\nu:\) 3385, 3211, 3003, 2959, 1646, 1603, 1538, 1458, 1367, 1248, 1122, 1022, 831, 741, 635, 564 cm\(^{-1}\). \(^1\)H NMR (300 MHz, DMSO) \(\delta:\) 7.77-8.83 (m, 7H, aromatic protons), 9.13 (s, 1H, NH), 9.62 (s, 1H, NH) ppm. \(^{13}\)C NMR (75.45 MHz, DMSO) \(\delta:\) 124.0, 126.6, 127.5, 127.6, 130.2, 130.7, 132.0, 133.6, 135.4, 139.1, 148.2, 160.8, 160.9 ppm. Anal. Calcd for C\(_{15}\)H\(_9\)ClN\(_4\)O\(_2\): C, 57.61; H, 2.90; N, 17.92. Found C, 57.67; H, 2.90; N, 17.90.
9.7. 2-(3-chlorophenyl)-3,4-dihydroimidazo[4,5-b]indole (4g)

Brown solid, IR (KBr) ν: 3405, 3217, 2948, 2909, 1671, 1617, 1568, 1454, 1371, 1283, 1134, 1018, 892, 754, 641, 577 cm$^{-1}$. $^1$H NMR (300 MHz, DMSO) δ: 7.60- 8.56 (m, 9H, aromatic protons and 1H, NH), 9.69 (s, 1H, NH) ppm. $^{13}$C NMR (75.45 MHz, DMSO) δ: 123.8, 126.6, 128.8, 128.7, 130.1, 131.0, 131.6, 135.2, 137.0, 148.4, 160.6 ppm. Anal. Calcd for C$_{15}$H$_{10}$ClN$_3$: C, 67.30; H, 3.77; N, 15.70 Found C, 67.29; H, 3.75; N, 15.70.
9.8.  7-chloro-2-(3-chlorophenyl)-3,4-dihydroimidazo[4,5-b]indole (4h)

Brown solid, IR (KBr) υ: 3398, 3227, 2977, 2893, 1664, 1605, 1551, 1477, 1358, 1242, 1163, 1011, 844, 743, 650, 567 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.62-8.31 (m, 7H, aromatic protons), 8.90 (s, 1H, NH), 9.42 (s, 1H, NH) ppm. $^{13}$C NMR (75.45 MHz, CDCl$_3$) δ: 124.1, 125.8, 126.6, 128.6, 129.8, 130.3, 130.7, 133.2, 134.8, 135.2, 139.3, 149.0, 160.5 ppm. Anal. Calcd for C$_{15}$H$_9$Cl$_2$N$_3$: C, 59.62; H, 3.00; N, 13.91 Found C, 59.52; H, 3.05; N, 13.89.
9.9. 2-(4-chlorophenyl)-3,4-dihydroimidazo[4,5-b]indole (4i)

Brown solid, IR (KBr) \(\nu: 3362, 3255, 3015, 2882, 1669, 1620, 1565, 1482, 1375, 1235, 1140, 1026, 890, 777, 663, 526 \text{ cm}^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta: 7.48-8.58 \text{ (m, 8H, aromatic protons), 9.45 (s, 1H, NH), 10.16 (s, 1H, NH)} \text{ ppm.} \)

\(^{13}\)C NMR (75.45 MHz, CDCl\(_3\)) \(\delta: 123.3, 127.8, 127.9, 128.7, 129.7, 134.9, 135.6, 136.2, 149.7, 161.3 \text{ ppm.}\)

Anal. Calcd for C\(_{15}\)H\(_{10}\)ClN\(_3\): C, 67.30; H, 3.77; N, 15.70 Found C, 67.31; H, 3.75; N, 15.73.
9.10. 7-chloro-2-(4-chlorophenyl)-3,4-dihydroimidazo[4,5-b]indole (4j)

Brown solid, IR (KBr) ν: 3386, 3233, 3047, 2960, 1657, 1612, 1558, 1435, 1348, 1282, 1153, 1019, 871, 742, 654, 552 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ: 7.46-8.54 (m, 7H, aromatic protons), 8.99 (s, 1H, NH), 9.35 (s, 1H, NH) ppm. \(^1^3\)C NMR (75.45 MHz, CDCl\(_3\)) δ: 123.9, 125.8, 128.8, 129.8, 130.3, 133.0, 135.2, 136.0, 137.1, 149.1, 159.5 ppm. Anal. Calcd for C\(_{15}\)H\(_9\)Cl\(_2\)N\(_3\): C, 59.62; H, 3.00; N, 13.91 Found C, 59.55; H, 3.10; N, 13.90.
9.11. 2-(4-methoxyphenyl)-3,4-dihydroimidazo[4,5-b]indole (4k)

Brown solid, IR (KBr) \( \nu: \) 3351, 3138, 3001, 2944, 2881, 1667, 1619, 1575, 1450, 1371, 1284, 1157, 1021, 863, 743, 654, 534 cm\(^{-1}\). \(^1\)H NMR (300 MHz, DMSO) \( \delta: \) 4.00 (s, 3H, CH\(_3\)), 7.26-8.69 (m, 9H, aromatic protons and 1H, NH), 9.72 (s, 1H, NH) ppm. \(^{13}\)C NMR (75.45 MHz, DMSO) \( \delta: \) 56.9, 122.2, 123.2, 125.9, 127.7, 127.4, 127.9, 128.7, 129.0, 129.6, 130.7, 131.2, 131.4, 131.5, 138.5, 139.7, 140.1, 143.9, 145.8, 154.6 ppm. Anal. Calcd for C\(_{16}\)H\(_{13}\)N\(_3\)O: C, 72.99; H, 4.98; N, 15.96 Found C, 72.91; H, 5.04; N, 15.95.
9.12. 7-chloro-2-(4-methoxyphenyl)-3,4-dihydroimidazo[4,5-b]indole (4l)

Brown solid, IR (KBr) ν: 3370, 3259, 2991, 2911, 1675, 1614, 1558, 1480, 1436, 1377, 1291, 1186, 1049, 869, 745, 651, 522 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ: 3.61 (s, 3H, CH\(_3\)), 7.44-8.47 (m, 8H, aromatic protons), 8.58 (s, 1H, NH), 9.36 (s, 1H, NH) ppm. \(^{13}\)C NMR (75.45 MHz,
CDCl$_3$ $\delta$: 61.8, 122.16, 122.29, 124.0, 125.3, 126.6, 130.1, 130.4, 132.3, 133.9, 135.5, 138.5, 148.1, 148.2, 157.8 ppm. Anal. Calcd for C$_{10}$H$_{12}$ClN$_3$O: C, 64.54; H, 4.06; N, 14.11 Found C, 64.70; H, 4.00; N, 14.10.
9.13. 1-(2-(3-nitrophenyl)imidazo[4,5-b]indol-4(3H)-yl)ethanone (4m)

Brown solid, IR (KBr) \(\nu:\) 3389, 3266, 2978, 2935, 1694, 1616, 1571, 1467, 1346, 1224, 1133, 1021, 823, 744, 572 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta:\) 1.91 (s, 3H, CH\(_3\)), 7.22-8.51 (m, 8H, aromatic protons), 9.40 (s, 1H, NH) ppm. \(^{13}\)C NMR (75.45 MHz, CDCl\(_3\)) \(\delta:\) 23.7,
122.1, 122.4, 123.2, 123.5, 124.8, 127.2, 127.4, 127.6, 128.2, 129.7, 130.1, 130.9, 133.0, 134.1, 134.4, 135.6, 138.0, 141.0, 148.7, 150.4, 160.3, 172.2 ppm. Anal. Calcd for C$_{17}$H$_{12}$N$_{4}$O$_3$: C, 63.75; H, 3.78; N, 17.49 Found C, 63.68; H, 3.88; N, 17.52.
9.14. 1-(2-(3-chlorophenyl)imidazo[4,5-b]indol-4(3H)-yl)ethanone (4n)

Brown solid, IR (KBr) \( \nu: 3367, 3215, 2947, 2923, 1692, 1662, 1607, 1580, 1477, 1359, 1272, 1144, 1042, 807, 735, 653, 546 \text{ cm}^{-1} \). \(^{1}\text{H} \text{NMR (300 MHz, CDCl}_{3}\text{)} \delta: 1.25 \text{ (s, 3H, CH}_{3}\text{)}, 7.34-8.11 \text{ (m, 8H, aromatic protons), 9.36 \text{ (s, 1H, NH) ppm.}^{13}\text{C NMR (75.45 MHz, CDCl}_{3}\text{)} \delta: 23.6, 122.5, 124.1, 125.3, 126.6, 130.1, 130.4, 130.7, 132.3, 133.9, 134.6, 135.5, 138.5, 148.1, 148.2, \]
157.8, 160.9, 166.2 ppm. Anal. Calcd for C$_{17}$H$_{12}$ClN$_3$O: C, 65.92; H, 3.90; N, 13.57 Found C, 66.01; H, 3.95; N, 13.47.
9.15. 1-(2-(4-chlorophenyl)imidazo[4,5-b]indol-4(3H)-yl)ethanone (4o)

Brown solid, IR (KBr) \( \nu: 3350, 3285, 3011, 2935, 1685, 1654, 1611, 1572, 1485, 1455, 1343, 1284, 1132, 1062, 899, 783, 659, 531 \text{ cm}^{-1} \). \(^1^H\) NMR (300 MHz, CDCl\(_3\)) \( \delta: 1.66 \) (s, 3H, CH\(_3\)), 7.35-8.12 (m, 8H, aromatic protons), 9.37 (s, 1H, NH) ppm. \(^{13}C\) NMR (75.45 MHz, CDCl\(_3\)) \( \delta: 23.5, 123.3, 125.6, 127.2, 128.1, 128.4, 128.7, 129.0, 129.2, 129.5, 133.1, 134.3, 134.6, 134.7, \)
9.16.  4-ethyl-2-(2-nitrophenyl)-3,4-dihydroimidazo[4,5-b]indole (4p)

Brown solid, IR (KBr) $\nu$: 3416, 3199, 3012, 2999, 2942, 2872, 1654, 1607, 1561, 1441, 1453, 1351, 1283, 1192, 1021, 861, 741, 657, 526 cm$^{-1}$. $^1$H NMR (300 MHz, DMSO) $\delta$: 1.41-1.45 (t, $J=6.6$, 3H, CH$_3$), 4.38-4.45 (q, $J=6.9$, 2H, CH$_2$), 7.53-8.63 (m, 8H, aromatic protons), 9.63 (s, 1H, NH) ppm. $^{13}$C NMR (75.45 MHz, DMSO) $\delta$: 12.5, 24.9, 122.1, 122.8, 123.1, 124.6, 127.5, 127.8, 130.2, 130.4, 130.7, 133.5, 134.4, 137.7, 135.4, 136.4, 137.5, 140.7, 148.3, 149.7, 159.9.
Brown solid, IR (KBr) ν: 3400, 3301, 3221, 3135, 2951, 2912, 2865, 1664, 1616, 1571, 1478, 1422, 1371, 1271, 1181, 1037, 873, 739, 649, 536 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ: 1.05-1.10 (t, $J$ = 6.9, 3H, CH$_3$), 1.70-1.82 (m, 2H, CH$_2$), 3.19-3.24 (t, $J$=6.6, 2H, CH$_2$), 7.47- 8.41 (m, 8H, aromatic protons), 8.94 (s, 1H, NH) ppm. $^{13}$C NMR (75.45 MHz, CDCl$_3$) δ: 10.1, 21.3,
44.0, 121.5, 124.2, 125.2, 125.5, 125.6, 129.3, 136.1, 136.7, 140.5, 150.9, 159.3 ppm. Anal.
Calcd for \( \text{C}_{18}\text{H}_{16}\text{N}_{4}\text{O}_{2} \) C, 67.49; H, 5.03; N, 17.49 Found C, 67.44; H, 5.10; N, 17.52.
9.18. Ethyl 2-(2-(2-nitrophenyl)imidazo[4,5-b]indol-4(3H)-yl)acetate (4r)

Brown solid, IR (KBr) ν: 3389, 3255, 3129, 3116, 3027, 2969, 2913, 2847, 1735, 1657, 1618, 1569, 1435, 1353, 1264, 1158, 1049, 854, 751, 651, 546 cm⁻¹. ¹H NMR (300 MHz, DMSO) δ: 1.22-1.27 (t, J= 7.2, 3H, CH₃), 4.19-4.26 (q, J=6.9, 2H, CH₂), 5.32 (s, 2H, CH₂), 7.37-8.28 (m, 8H, aromatic protons), 9.63 (s, 1H, NH) ppm. ¹³C NMR (75.45 MHz, DMSO) δ: 15.0, 52.6, 65.1, 122.3, 123.6, 125.2, 127.9, 128.4, 130.5, 134.0, 135.2, 139.0, 148.3, 149.6, 161.7, 171.0
ppm. Anal. Calcd for C\textsubscript{19}H\textsubscript{16}N\textsubscript{4}O\textsubscript{4}: C, 62.63; H, 4.43; N, 15.38 Found C, 62.71; H, 4.51; N, 15.30.
9.19. **7-methyl-2-phenyl-3,4-dihydroimidazo[4,5-b]indole (4s)**

Brownish white solid, IR (KBr) $\nu$: 3398, 3242, 2963, 2931, 1648, 1607, 1559, 1451, 1311, 1232, 1142, 1027, 813, 741, 655, 534 cm$^{-1}$. $^1$H NMR (300 MHz, DMSO) $\delta$: 2.22 (s, 3H, CH$_3$), 7.55-8.57 (m, 8H, aromatic protons), 9.69 (s, 1H, NH), 10.10 (s, 1H, NH) ppm. $^{13}$C NMR (75.45 MHz, DMSO) $\delta$: 23.9, 122.9, 123.1, 127.7, 128.5, 129.6, 130.2, 130.7, 131.3, 133.3, 136.8, 146.3, 154.1, 161.2, ppm. Anal. Calcd for C$_{16}$H$_{13}$N$_3$: C, 77.71; H, 5.30; N, 16.99 Found C, 77.64; H, 5.34; N, 17.02.