

## Supplementary information

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### General:

Melting points of all the synthesized compounds were taken in a Riechert Thermovar instrument and are uncorrected. The IR spectra were recorded on Perkin Elmer RXI spectrometer using KBr pellets. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX-400 spectrometer using tetramethylsilane (TMS) as an internal standard and DMSO-*d*<sub>6</sub>/ CDCl<sub>3</sub> as solvent. Mass spectra were recorded on Micromass Quattro II (ESI) spectrometer. Elemental analyses (C, H and N) were conducted using the Elemental vario EL III elemental analyser and the results were found to be in agreement with the calculated values. X-ray diffractograms (XRD) of the catalyst were recorded in the 2θ range of 5-80° with scan rate of 4°/ min on a Rigaku Minifax X-ray diffractometer with Ni-filtered Cu Kα radiation at a wavelength of 1.54060Å. EDX characterization of the catalyst was performed on QUANTA 200 FEG from FEI Netherlands. TEM analysis was performed on JEM-2100 F Model (ACC. Voltage: 200kV) electron microscope. All other reagents were purchased from Merck and Aldrich and were used without further purification. The purity of compounds was checked by thin layer chromatography (TLC) on glass plates coated with silica gel G254 (E. Merck) using S2 chloroform-methanol (3:1) mixture as mobile phase and visualised by iodine vapours and alcoholic ferric chloride.

Table 1S. Effect of SO<sub>3</sub>H content on thermal stability and activity of catalyst.

Entry	SO <sub>3</sub> H Content	Thermal stability	Catalyst activity on model reaction	
			Time (min)	Yield (%)
1	0.40 ml/g	593°C	40	91
2	0.45ml/g	556°C	34	93
3	0.55 ml/g	510°C	28	96

### Spectral data of compounds:

- 1. (Z)-3-(5-methylthiophen-2-yl)-2-(4-nitrophenyl)acrylonitrile(3a);** Yellowish crystals. Yield:96%, m.p.191-192°C; Rf Value: 0.42 (10% methanol in chloroform); IR (KBr,  $\text{cm}^{-1}$ ): 2928, 2208, 1640,1580, 1510, 1340, 1248,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.51 (s, 3H,  $\text{CH}_3$ ),  $\delta$  7.63(s,  $1\text{H}_{\text{olefinic}}$ ), 6.83-8.14 (m, 6H, ArH) ppm.  $^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ ):15.079, 107.079, 111.925, 116.911, 124.718, 127.190, 130.309, 131.367, 132.241, 134.053, 134.630, 137.715, 140.079, 143.925 ppm. Anal. Found ( $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ ) C, 62.21; H, 3.73; N, 10.36. ESI-MS m/z : 270 ( $\text{M}++1$ ).
- 2. (Z)-2-(4-nitrophenyl)-3-(thiophen-2-yl)acrylonitrile (3b) ;** Reddish crystals. Yield:96%, m.p.191-192°C; Rf Value: 0.40 (10% methanol in chloroform); IR (KBr,  $\text{cm}^{-1}$ ): 3177, 2210, 1640, 1564, 1511, 1333, 1255.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.83(s,  $1\text{H}_{\text{olefinic}}$ ), 7.14-8.14 (m, 7H, ArH) ppm.  $^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ ):107.295, 116.101, 120.079, 123.675, 126.427, 127.111, 128.863, 129.836, 130.694, 134.184, 140.079, 143.531, 153.321 ppm. Anal. Found ( $\text{C}_{13}\text{H}_8\text{N}_2\text{O}_2\text{S}$ ) C, 60.93; H, 3.15; N, 10.93. ESI-MS m/z : 256 ( $\text{M}++1$ ).
- 3. (Z)-2-(4-nitrophenyl)-3-(4-oxo-4H-chromen-3-yl)acrylonitrile (3c);** Yellowish crystals. Yield:96%, m.p.190-191 °C; Rf Value: 0.44 (10% methanol in chloroform); IR (KBr,  $\text{cm}^{-1}$ ): 3177, 2211, 1638, 1562, 1517, 1340, 1240.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01(s,  $1\text{H}_{\text{olefinic}}$ ),  $\delta$  7.93(s 1H), 7.55-9.11 (m, 8H, ArH) ppm.  $^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ ):110.866, 112.360, 117.533, 119.226, 121.153, 123.014, 124.030, 125.070, 127.172, 128.679, 135.929, 136.911, 141.420, 146.198, 151.903, 152.204, 156.760, 165.921 ppm. Anal. Found ( $\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}_4$ ) C, 67.93; H, 3.17; N, 8.80. ESI-MS m/z : 318 ( $\text{M}++1$ ).
- 4. (2Z,4E)-2-(4-nitrophenyl)-5-phenylpenta-2,4-dienenitrile (3d);** Yellowish crystals. Yield:96%, m.p.190-192 °C; Rf Value: 0.44 (10% methanol in chloroform); IR (KBr,  $\text{cm}^{-1}$ ): 3178, 2214, 1638, 1562, 1514, 1341, 1287.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.92(dd,1H, $\text{H}_A$ ),  $\delta$  7.27(d,1H, $\text{H}_B$ ),  $\delta$  8.01(d,1H $_{\text{olefinic}}$ ,  $\text{H}_C$ ),  $\delta$  7.27-8.45 (m, 9H, ArH) ppm.  $^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ ):124.050, 124.398, 124.558, 124.806, 126.386, 127.067, 127.969, 128.142, 128.569, 129.070, 129.136, 129.255, 129.290, 130.175, 130.602, 144.601, 145.232.ppm. Anal. Found ( $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_2$ ) C, 73.90; H, 4.38; N, 10.90. ESI-MS m/z : 276 ( $\text{M}++1$ ).

5. **(Z)-3-(3-formylphenyl)-2-(4-nitrophenyl)acrylonitrile (3e);** Yellowish crystals. Yield: 96%, m.p. 190-192 °C; Rf Value: 0.40 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3175, 2216, 1640, 1562, 1516, 1344, 1240. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.01(s, 1H<sub>olefinic</sub>), δ 10.10(s, 1H, CHO) 7.23-8.35 (m, 8H, ArH) ppm. <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): 109.079, 110.079, 111.925, 116.911, 124.053, 24.718, 127.190, 130.309, 131.367, 132.241, 134.053, 134.630, 137.295, 140.079, 143.925, 191.384 ppm. Anal. Found (C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>) C, 69.06; H, 3.62; N, 10.07. ESI-MS m/z : 278 (M++1).
6. **(Z)-3-(5-chloro-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-2-(4-nitrophenyl)acrylonitrile (3f);** Orange crystals. Yield: 96%, m.p. 190-192 °C; Rf Value: 0.40 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3176, 2219, 1638, 1561, 1414, 1343, 1250. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.51 (s, 3H, CH<sub>3</sub>), δ 7.57(s, 1H<sub>olefinic</sub>), 7.23-8.33 (m, 9H, ArH) ppm. <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): 15.760, 110.300, 112.300, 116.760, 124.120, 124.650, 127.117, 129.121, 134.760, 135.154, 139.907, 141.711, 148.154, 148.425, 151.903, 152.204, 156.760, 160.760. ppm. Anal. Found (C<sub>19</sub>H<sub>15</sub>ClN<sub>4</sub>O<sub>2</sub>) C, 62.22; H, 4.12; N, 15.27. ESI-MS m/z : 366 (M++1).
7. **(Z)-2-(4-nitrophenyl)-3-(pyridin-3-yl)acrylonitrile (3g);** White crystals. Yield: 96%, m.p. 190-192 °C; Rf Value: 0.40 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3177, 2212, 1638, 1562, 1517, 1340, 1240. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.53(s, 1H<sub>olefinic</sub>), 7.23-8.89 (m, 8H, ArH) ppm. <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): 110.300, 112.300, 116.760, 124.120, 124.650, 127.113, 129.131, 135.114, 139.207, 141.711, 148.425, 151.903, 152.204, 156.760 ppm. Anal. Found (C<sub>14</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>) C, 66.93; H, 3.61; N, 16.73. ESI-MS m/z : 251 (M++1).
8. **(Z)-2-(4-nitrophenyl)-4-phenylbut-2-enenitrile (3h);** Yellowish crystals. Yield: 96%, m.p. 190-192 °C; Rf Value: 0.40 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3177, 2211, 1640, 1562, 1517, 1342, 1242. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.33(d, 1H, H<sub>A</sub>), δ 7.37(s, 1H<sub>olefinic</sub>, H<sub>B</sub>), 7.03-8.34 (m, 8H, ArH) ppm. <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): 110.174, 113.925, 114.503, 116.016, 123.675, 126.427, 127.111, 128.863, 129.836, 130.644, 134.184, 137.295, 139.392, 140.079, 143.531, 157.321. ppm. Anal. Found (C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>) C, 72.72; H, 4.58; N, 10.60. ESI-MS m/z : 264 (M++1).

9. **(Z)-2,3-bis(4-nitrophenyl)acrylonitrile (3i)**; Deep yellowish crystals. Yield: 96%, m.p. 192-194 °C; Rf Value: 0.44 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3178, 2222, 1639, 1563, 1517, 1343, 1286. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.74(s, 1H<sub>olefinic</sub>), 7.83-8.36 (m, 8H, ArH) ppm <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 110.079, 111.925, 116.911, 124.053, 124.554, 124.753, 17.402, 130.281, 130.549, 134.053, 134.630, 137.295, 140.079, 143.925, 142.454 ppm. Anal. Found (C<sub>15</sub>H<sub>9</sub>N<sub>3</sub>O<sub>4</sub>) C, 72.72; H, 4.58; N, 10.60. ESI-MS m/z : 295 (M++1).
10. **(Z)-3-(4-hydroxyphenyl)-2-(4-nitrophenyl)acrylonitrile (3j)**; Yellowish crystals. Yield: 96%, m.p. 191-193 °C; Rf Value: 0.42 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3437, 3177, 2208, 1640, 1560, 1518, 1340, 1213. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.83(s, 1H<sub>olefinic</sub>), 7.03-8.89 (m, 8H, ArH) ppm <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 110.866, 112.360, 117.533, 119.226, 121.199, 123.014, 124.030, 125.670, 127.172, 128.679, 135.921, 136.911, 141.420, 146.198, 147.533 ppm. Anal. Found (C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>) C, 67.67; H, 3.79; N, 10.52. ESI-MS m/z : 266 (M++1).
11. **(Z)-3-(4-chlorophenyl)-2-(4-nitrophenyl)acrylonitrile (3k)**; Yellowish crystals. Yield: 96%, m.p. 190-192 °C; Rf Value: 0.42 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3176, 2217, 1639, 1585, 1511, 1342, 1207. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.93(s, 1H<sub>olefinic</sub>), 7.73-8.79 (m, 8H, ArH) ppm <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 101.652, 111.112, 112.115, 117.543, 118.226, 123.054, 124.031, 124.982, 126.172, 127.172, 128.925, 136.922, 137.444, 142.520, 147.544, 148.625 ppm. Anal. Found (C<sub>15</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>2</sub>) C, 63.28; H, 3.19; N, 9.84. ESI-MS m/z : 284 (M++1).
12. **(Z)-3-(4-fluorophenyl)-2-(4-nitrophenyl)acrylonitrile (3l)**; Yellowish crystals. Yield: 96%, m.p. 190-192 °C; Rf Value: 0.42 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3174, 2216, 1638, 1561, 1514, 1344, 1246. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.83(s, 1H<sub>olefinic</sub>), 7.13-8.32 (m, 8H, ArH) ppm <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 109.423, 116.643, 117.299, 124.620, 126.925, 129.393, 129.427, 132.182, 132.269, 140.605, 144.299, 148.559, 163.324, 165.899 ppm. Anal. Found (C<sub>15</sub>H<sub>9</sub>FN<sub>2</sub>O<sub>2</sub>) C, 67.16; H, 3.38; N, 10.44. ESI-MS m/z : 268 (M++1).
13. **(Z)-3-(3-chlorophenyl)-2-(4-nitrophenyl)acrylonitrile (3m)**; Reddish crystals. Yield: 96%, m.p. 190-192 °C; Rf Value: 0.42 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3113, 2212, 1639, 1560, 1514, 1350, 1248. <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>):  $\delta$  7.63(s,1H<sub>olefinic</sub>), 7.23-8.34(m, 8H, ArH) ppm 13C NMR (400MHz, CDCl<sub>3</sub>):110.174, 113.925, 116.101, 123.675, 126.423, 127.111, 128.863, 129.836, 130.640, 134.184, 137.295, 139.392, 140.079, 143.531, 147.321.ppm. Anal. Found (C<sub>15</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>2</sub>) C, 63.28; H, 3.19; N, 9.84. ESI-MS m/z : 284 (M++1).

14. **(Z)-3-(3-bromophenyl)-2-(4-nitrophenyl)acrylonitrile (3n)**; Yellowish crystals.Yield:96%, m.p.191-193 °C; Rf Value: 0.44 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3177, 2216, 1639, 1562, 1513, 1346, 1209. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.40(s,1H<sub>olefinic</sub>), 7.22-8.33 (m, 8H, ArH) ppm 13C NMR (400MHz, CDCl<sub>3</sub>): 110.174, 112.111, 117.124, 124.056, 124.999, 127.625, 130.042, 132.111, 132.799, 137.656, 141.201, 143.554, 147.656, 148.525. ppm. Anal. Found (C<sub>15</sub>H<sub>9</sub>BrN<sub>2</sub>O<sub>2</sub>) C, 54.74; H, 2.76; N, 8.51. ESI-MS m/z : 327 (M++1).
15. **(Z)-3-(3-nitrophenyl)-2-(4-nitrophenyl)acrylonitrile (3o)**; Light Yellowish crystals.Yield:96%, m.p.191-193 °C; Rf Value: 0.44 (10% methanol in chloroform); IR (KBr, cm<sup>-1</sup>): 3177, 2211, 1638, 1562, 1517, 1340, 1240. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.79(s,1H<sub>olefinic</sub>), 7.26-8.36 (m, 8H, ArH) ppm 13C NMR (400MHz, CDCl<sub>3</sub>):111.925, 114.503, 116.016, 124.016, 14.691, 125.738, 127.523, 129.626, 131.099, 131.635, 134.731, 139.256, 142.883, 147.519, 148.658.ppm. Anal. Found (C<sub>15</sub>H<sub>9</sub>N<sub>3</sub>O<sub>4</sub>) C, 61.02; H, 3.07; N, 14.23. ESI-MS m/z : 295 (M++1).