**Supporting Information**

**Preparation of 7 from 5 (Step-wise synthesis)**

A mixture of **5** (10 mM) and aniline (10 mM) in methanol was stirred at RT for 10min. At the end of this period, a colourless solid separated out from reaction mixture which was collected by filtration. The isolated solid was washed with water (10mL) and dried.

**General procedure for preparation of 6a-p from 7**

A mixture of **7** (10mM), **2/4** (10mM) in methanol was stirred at RT for 10min. At the end of this period, a colourless solid separated out from reaction mixture which was collected by filtration. The isolated solid was washed with water (10mL) and dried. The product was recrystallized from a suitable solvent to obtain **6a-p**.

**General procedure for preparation of 6a-p from 5 by one-pot synthesis**

A mixture of **5** (10mM), aniline (10mM), **2/4** (10mM), and methanol (30mL) were stirred for 15min. At the end of this period, a colourless solid separated out from reaction mixture which was collected by filtration. The isolated solid was washed with water (10mL) and dried. The product was recrystallized from a suitable solvent to obtain **6a-p**.

**Characterization Data of the synthesized compounds**

***2-((1H-benzimidazol-2-yl)thio)-3-(4-nitrophenyl)acrylonitrile* (6b)**.m.p. 248-2500C; IR (KBr): 3400–2800 cm-1 (br, m, -NH-);  1H- NMR (400 MHz, DMSO-d6/ TMS): δ 8.16 (s, 1H), 8.02 (d, J=4.4 Hz, 2H), 7.62 -7.31 (m, J= 6.5 Hz, 2H), 7.61–7.44 (m, J= 6.5 Hz, 4H), 10.5 (s, 1H, -NH-), 13C NMR: δ 146.5 (Ar-C), 139.5 (**C**=N), 138.2 (2 Ar-**C**) , 134.2 (C=**C**H), 131.2 (C≡N), 128.3 (2 Ar-**C**), 126.7 (2 Ar-**C**), 124.2 (2 Ar-**C**), 113.2 (**C**=CH) ppm; MS (CI): m/z 323 [M.++1]; HRMS (C16H10N4SO): Calcd for [M.++H], 323.3581 found 323.3577.

***2-((1H-benzimidazol-2-yl)thio)-3-(3-nitrophenyl)acrylonitrile* (6c).** m.p. 229-2310C; IR (KBr): 3400–2800 cm-1 (br, m, -NH-);  1H- NMR (400 MHz, DMSO-d6/ TMS): δ 8.21 (s, 1H), 8.16 (d, J= 4.4 Hz, 2H), 7.98 -7.35 (m, J= 6.4 Hz, 2H), 7.60–7.43 (m, J= 6.5 Hz, 4H), 10.6 (s, 1H, -NH-), 13C NMR: δ 146.5 (Ar-C), 139.3 (**C**=N), 137.9 (2 Ar-**C**) , 133.1 (C=**C**H), 131.2 (C≡N), 128.2 (2 Ar-**C**), 126.5 (2 Ar-**C**), 124.0 (2 Ar-**C**), 112.8 (**C**=CH) ppm; MS (CI): m/z 323 [M.++1]; HRMS (C16H10N4SO): Calcd for [M.++H], 323.3581 found 323.3577.

***2-((1H-benzimidazol-2-yl)thio)-3-(o-tolyl)acrylonitrile* (6d)*.*** m.p. 240-2420C; IR (KBr): 3400–2800 cm-1 (br, m, -NH-);  1H-NMR (400 MHz, DMSO-d6/ TMS): δ 8.65 (s, 1H), 8.22 (d, J= 4.2 Hz, 2H), 7.85 -7.63 (m, J= 6.4 Hz, 2H), 7.62–7.45 (m, J= 6.3 Hz, 4H), 12.2 (s, 1H, -NH-), 3.96 (s, 3H), 13C NMR: δ 140.5 (Ar-C), 139.6 (**C**=N), 136.9 (2 Ar-**C**) , 133.4 (C=**C**H), 131.2 (C≡N), 127.4 (2 Ar-**C**), 126.5 (2 Ar-**C**), 124.0 (2 Ar-**C**), 112.8 (**C**=CH), 20.8 (**C**H3) ppm; MS (CI): m/z 292 [M.++1]; HRMS (C17H13N3S): Calcd for [M.++H], 292.5869 found 292.5873.

***2-((1H-benzimidazol-2-yl)thio)-3-(p-tolyl)acrylonitrile* (6e)**.m.p. 226-2280C; IR (KBr): 3400–2800 cm-1 (br, m, -NH-);  1H-NMR (400 MHz, DMSO-d6/ TMS): δ 8.63 (s, 1H), 8.25 (d, J= 4.1 Hz, 2H), 7.75 -7.53 (m, J= 6.3 Hz, 2H), 7.65–7.42 (m, J= 6.2 Hz, 4H), 12.4 (s, 1H, -NH-),3.72 (s, 3H), 13C NMR: δ 139.5 (Ar-C), 138.4 (**C**=N), 135.7 (2 Ar-**C**) , 133.4 (C=**C**H), 131.5 (C≡N), 127.6 (2 Ar-**C**), 125.5 (2 Ar-**C**), 124.4 (2 Ar-**C**), 112.9 (**C**=CH), 20.6 (**C**H3) ppm; MS (CI): m/z 292 [M.++1]; HRMS (C17H13N3S): Calcd for [M.++H], 292.5869 found 292.5873.

***2-((1H-benzimidazol-2-yl)thio)-3-(4-hydroxyphenyl)acrylonitrile* (6f)**.m.p. 238-2400C; IR (KBr): 3400–2800 cm-1 (br, m, -NH-);  1H-NMR (400 MHz, DMSO-d6/ TMS): δ 6.50 (s, 1H), 8.28 (d, J= 4.0 Hz, 2H), 7.78 -7.59 (m, J= 6.0 Hz, 2H), 7.60–7.48 (m, J= 6.0 Hz, 4H), 12.3 (s, 1H, -NH-, D2O exchangeable), 12.5 (s, 1H, -OH, D2O exchangeable); 13C NMR: δ 144.2 (Ar-C), 137.3 (**C**=N), 137.5 (2 Ar-**C**) , 133.6 (C=**C**H), 131.8 (C≡N), 127.2 (2 Ar-**C**), 125.5 (2 Ar-**C**), 124.5 (2 Ar-**C**), 111.6 (**C**=CH) ppm; MS (CI): m/z 294 [M.++1]; HRMS (C16H11N3SO): Calcd for [M.++H], 294.4969 found 294.4972.

***2-((1H-benzimidazol-2-yl)thio)-3-(2-hydroxyphenyl)acrylonitrile* (6g).** m.p. 256-2580C; IR (KBr): 3400–2800 cm-1 (br, m, -NH-);  1H-NMR (400 MHz, DMSO-d6/ TMS): δ 8.16 (s, 1H), 8.22 (d, J= 4.3 Hz, 2H), 7.72 -7.56 (m, J= 6.2 Hz, 3H), 7.58–7.28 (m, J= 6.0 Hz, 4H), 10.2 (s, 1H, -NH-, D2O exchangeable); 12.3 (s, 1H, -OH, D2O exchangeable); 13C NMR: δ 145.2 (Ar-C), 138.3 (**C**=N), 136.5 (2 Ar-**C**) , 134.6 (C=**C**H), 132.8 (C≡N), 128.2 (2 Ar-**C**), 125.5 (2 Ar-**C**), 124.7 (2 Ar-**C**), 111.8 (**C**=CH) ppm; MS (CI): m/z 294 [M.++1]; HRMS (C16H11N3SO): Calcd for [M.++H], 294.4969 found 294.4972.

***2-((1H-benzimidazol-2-yl)thio)-3-(3,4-dimethoxyphenyl)acrylonitrile* (6h).** m.p. 210-2120C; IR (KBr): 3400–2800 cm-1 (br, m, -NH-);  1H-NMR (400 MHz, DMSO-d6/ TMS): δ 8.52 (s, 1H), 7.78 (d, J= 4.1 Hz, 2H), 7.77 -6.92 (m, J= 6.2 Hz, 2H), 7.56–6.94 (m, J= 6.0 Hz, 4H), 12.2 (s, 1H, -NH-), 3.82 (s, 6H); 13C NMR: δ 137.2 (**C**=N), 135.3 (2 Ar-**C**) , 132.4 (C=**C**H), 131.7 (C≡N), 127.9 (2 Ar-**C**), 126.5 (2 Ar-**C**), 124.4 (2 Ar-**C**), 112.9 (**C**=CH), 48.4 (2 O**C**H3 ), 20.6 (**C**H3) ppm; MS (CI): m/z 338 [M.++1]; HRMS (C18H15N3O2S): Calcd for [M.++H], 338.2669 found 338.2666.

**6i**: m.p = 1720C. (lit 18 m.p. 1750C)

**6j**: m.p = 2380C. (lit 18 m.p. 2400C)

**6k**: m.p = 2160C. (lit 18 m.p. 2190C)

**6l**: m.p = 2760C. (lit 18  m.p. 2730C)

**6m**: m.p = 2480C. (lit 18 m.p. 2510C)

**6n**: m.p = 2110C. (lit 18 m.p. 2150C)

**6o**: m.p = 2780C. (lit 18 m.p. 2810C)

**6p**: m.p = 1980C. (lit 18  m.p. 1960C)