Experimental:

Melting points were determined in open capillaries and are uncorrected. IR spectra were run for KBr discs on a Perkin-Elmer 120-000A apparatus (υ_{max} in cm^{-1}) and ^{1}H-NMR & ^{13}C-NMR spectra were determined for solutions in $CDCl_3$ & DMSO-d_6 with TMS as internal standard on a Bruker DPX-400. CHN was recorded on 2400 series II CHN analyzer Perkin Elmer. HRMS and mass spectra were recorded on a Qtof Micro instrument. Silica gel (60-120 mesh) was used for chromatographic separation. Silica gel-G [E-Mark (India)] was used for TLC. Petroleum-ether refers to the fraction between 60 ^{o}C and 80 ^{o}C.

General Procedure for synthesis of thiopyrano derivatives 4: To a well-stirred suspension of the appropriate aromatic aldehyde **2** (1 equiv.) and malononitrile **3** (1 equiv) in water (5 mL) appropriate indolin-2-thione **1** (1 equiv) was added and the reaction mixture was heated at 100 ^{o}C for 30-40 minutes. As the reaction proceeds the reaction mixture gradually becomes deep brown colored. After completion of the reaction as monitored by TLC the reaction mixture was cooled and diluted with 20 mL of water and extracted with ethyl acetate (3x25 mL) and dried over anhydrous Na_2SO_4. The solvent was distilled off. The resulting crude product was purified by filtration through a pad of silica gel (60-120 mesh) using 4:1 petroleum ether-ethyl acetate mixture as eluent to give the pure compounds (**4**).

2-amino-4-(4-methoxyphenyl)-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4a**): Using the general procedure starting from 100 mg. (0.671 mmol) of indoline-2-thione **1a**, 91.3 mg. (0.671 mmol)of 4-methoxybenzaldehyde **2a**, 44.3 mg. (0.671 mmol) of malononitrile **3**, 219 mg. of title compound **4a** was isolated as grey colored solid, mp 178-180 ^{o}C, Yield = 98%, IR (KBr): 3390, 3381, 3252, 2186, 1624, 1572 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 3.69 (s, 3H), 5.05 (s, 1H), 6.78 (s, 2H), 6.84 (d, 2H, *J* = 8.4 Hz), 6.90 (t, 1H, *J* = 7.6 Hz), 7.03 (t, 1H, *J* = 8.0 Hz), 7.18-7.25 (m, 3H), 7.29 (t, 1H, *J* = 7.6 Hz), 11.45 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 157.9, 151.3, 137.2, 136.6, 128.3, 125.3, 121.2, 120.4, 120.0, 119.1, 117.3, 113.8, 110.7, 107.9, 74.5, 54.9. HRMS (ESI+): calcd. For $C_{19}H_{15}N_3OS$: [M+Na^+] 356.0834; found 356.0865.

2-amino-4-p-tolyl-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4b**): Using the general procedure starting from 100 mg. (0.671 mmol) of indoline-2-thione **1a**, 80.5 mg. (0.671 mmol) of 4-methylbenzaldehyde **2b**, 44.3 mg. (0.671 mmol) of malononitrile **3**, 204 mg. of title compound **4b** was isolated as grey colored solid, mp 184-186 ^{o}C, Yield = 96%, IR (KBr): 3394, 3284, 3200, 2188, 1624, 1573 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H = 2.22 (s, 3H), 5.04 (s, 1H), 6.77 (s, 2H), 6.89 (t, 1H, *J* = 7.2 Hz), 7.01 (t, 1H, *J* = 7.6 Hz), 7.07 (d, 2H, *J* = 7.6 Hz), 7.18-7.21 (m, 3H), 7.28 (d, 1H, *J* = 8.0 Hz), 11.43 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ_C = 151.5, 142.1, 136.5, 135.6, 129.0, 127.2, 125.3, 121.2, 120.5, 120.0, 119.1, 117.3, 110.7, 107.8, 74.3, 40.2, 20.6. MS: m/z = 339.9 [M+Na]$^{+}$. Anal. Calcd. For $C_{19}H_{15}N_3S$: C, 71.90; H, 4.76; N, 13.24 %. Found: C, 71.71; H, 4.90; N, 13.17 %.

2-amino-4-(4-bromophenyl)-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4c**): Using the general procedure starting from 100 mg. (0.671 mmol) of indoline-2-thione **1a**, 124.1 mg. (0.671 mmol) of 4-bromobenzaldehyde **2c**, 44.3 mg. (0.671 mmol) of malononitrile **3**, 248 mg. of title compound **4c** was isolated as grey colored solid, mp 192-194 ^{o}C, Yield = 97%, IR (KBr): 3374, 3273, 3191, 2191, 1627, 1582 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H = 5.13 (s, 1H), 6.88-6.92 (m, 3H), 7.03 (t, 1H, *J* = 7.6 Hz), 7.21 (d, 1H, *J* = 7.6 Hz), 7.29 (t, 3H, *J* = 7.2 Hz), 7.48 (d, 2H, *J* = 7.6 Hz), 11.50 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ_C = 151.9, 144.5, 136.6, 131.4, 129.5, 125.2, 121.3, 120.7, 119.8, 119.7, 119.3, 117.2, 110.8, 107.1, 73.4. MS: m/z = 381 [M^{+}], 383 [M^{+}+2]. Anal. Calcd. For $C_{18}H_{12}BrN_3S$: C, 56.55; H, 3.16; N, 10.99 %. Found: C, 56.68; H, 3.26; N, 11.04 %.

2-amino-4-(thiophen-2-yl)-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4d**): Using the general procedure starting from 100 mg. (0.671 mmol) of indoline-2-thione **1a**, 75.2 mg. (0.671 mmol) of thiophene-2-carbaldehyde **2d**, 44.3 mg. (0.671 mmol) of malononitrile **3**, 197 mg. of title compound **4d** was isolated as grey colored solid, mp 178-180 ^{o}C, yield = 95 %, IR (KBr): 3381, 3276, 3195, 2189, 1623, 1578 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H = 5.51 (s, 1H), 6.91 (s, 3H), 6.97 (t, 1H, *J* = 7.6 Hz), 7.05 (d, 2H, *J* = 7.6 Hz), 7.28 (d, 1H, *J* = 8.4 Hz), 7.32 (d, 1H, *J* = 8.0 Hz), 7.40 (d, 1H, *J* = 8.0 Hz), 11.49 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ_C = 152.4, 149.6, 136.5, 126.5, 125.2, 124.6, 123.7, 121.3, 120.7, 119.9, 119.3, 117.3, 110.8, 107.8, 73.9, 35.5. MS: m/z = 331.85

$[M+Na]^+$. Anal. Calcd. For $C_{16}H_{11}N_3S_2$: C, 62.11; H, 3.58; N, 13.58 %. Found: C, 62.33; H, 3.47; N, 13.61 %.

2-amino-9-methyl-4-phenyl-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4e**): Using the general procedure starting from 100 mg. (0.613 mmol) of 1-methylindoline-2-thione **1b**, 65 mg. (0.613 mmol) of benzaldehyde **2e**, 40.5 mg. (0.613 mmol) of malononitrile **3**, 188.6 mg. of title compound **4e** was isolated as grey colored glassy solid, mp 196-198 ^oC, yield = 97%, IR (KBr): 3428, 3314, 3213, 2188, 1634, 1575 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 3.71 (s, 3H), 4.57 (s, 2H), 5.19 (s, 1H), 7.01 (t, 1H, *J* = 7.6 Hz), 7.16-7.19 (m, 2H), 7.21 (s, 1H), 7.24 (d, 1H, *J* = 6.0 Hz), 7.29 (d, 2H, *J* = 8.8 Hz), 7.33 (d, 2H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 151.4, 144.9, 137.5, 128.5, 127.1, 126.6, 124.9, 123.0, 121.2, 119.9, 119.4, 117.4, 109.2, 107.5, 74.3, 40.8, 30.1. MS: m/z = 318.10 $[M+H]^+$. Anal. Calcd. For $C_{19}H_{15}N_3S$: C, 71.90; H, 4.76; N, 13.24 %. Found: C, 71.89; H, 4.63; N, 13.22 %.

2-amino-4-(4-chlorophenyl)-9-methyl-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4f**): Using the general procedure starting from 100 mg. (0.613 mmol) of 1-methylindoline-2-thione **1b**, 86 mg. (0.613 mmol) of 4-cholorobenzaldehyde **2f**, 40.5 mg. (0.613 mmol) of malononitrile **3**, 206.7 mg. of title compound **4f** was isolated as grey colored solid, mp 180-182 ^oC, Yield = 96%, IR (KBr): 3311, 3216, 2193, 1632, 1581 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 3.71 (s, 3H), 4.61 (s, 2H), 5.17 (s, 1H), 7.01-7.05 (m, 1H), 7.18 (td, 2H, *J* = 1.2 Hz, 6.8 Hz), 7.23-7.28 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 151.5, 143.9, 137.6, 131.2, 129.0, 128.5, 124.8, 123.1, 121.3, 119.7, 119.5, 117.4, 109.3, 106.9, 73.7, 30.1. MS: m/z = 374.07 $[M+Na]^+$. Anal. Calcd. For $C_{19}H_{14}ClN_3S$: C, 64.86; H, 4.01; N, 11.94 %. Found: C, 64.89; H, 3.97; N, 11.99 %.

2-amino-9-methyl-4-(3-nitrophenyl)-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4g**): Using the general procedure starting from 100 mg. (0.613 mmol) of 1-methylindoline-2-thione **1b**, 92.6 mg. (0.613 mmol) of 3-nitrobenzaldehyde **2g**, 40.5 mg. (0.613 mmol) of malononitrile **3**, 206.5 mg. of title compound **4g** was isolated as light yellow flupy solid, mp 182-184 ^oC, Yield = 93 %, IR (KBr): 3421, 3339, 3307, 2181, 1623, 1572 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 3.74 (s, 3H), 4.69

(s, 2H), 5.31 (s, 1H), 7.04 (d, 1H, *J* = 7.6 Hz), 7.19 (q, 2H, *J* = 8.0 Hz), 7.28 (d, 1H, *J* = 8.4 Hz), 7.49 (t, 1H, *J* = 8.0 Hz), 7.74 (d, 1H, *J* = 7.6 Hz), 8.08 (dd, 1H, *J* = 0.8 Hz, 8.0 Hz), 8.12 (d, 1H, *J* = 2.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 152.2, 147.9, 147.2, 137.6, 133.9, 130.2, 124.7, 123.4, 121.9, 121.5, 119.7, 119.6, 117.3, 109.4, 106.5, 73.1, 40.1, 30.2. MS: m/z = 384.83 $[M+Na]^+$. Anal. Calcd. For $C_{19}H_{14}N_4O_2S$: C, 62.97; H, 3.89; N, 15.46 %. Found: C, 62.96; H, 3.89; N, 15.39 %.

2-amino-4-(benzo[d][1,3]dioxol-5-yl)-9-methyl-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4h**): Using the general procedure starting from 100 mg. (0.613 mmol) of 1-methylindoline-2-thione **1b**, 92 mg. (0.613 mmol) of benzo[*d*][1,3]dioxole-5-carbaldehyde **2h**, 40.5 mg. (0.613 mmol) of malononitrile **3**, 210.4 mg. of title compound **4h** was isolated as light yellow flupy solid, mp 190-192 ^{o}C, Yield = 95%, IR (KBr): 3423, 3320, 3226, 2194, 1640, 1577 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 3.70 (s, 3H), 4.56 (s, 2H), 5.12 (s, 1H), 5.89 (dd, 2H, *J* = 1.2 Hz, 12.0 Hz), 6.72 (d, 2H, *J* = 8.4 Hz), 6.87 (dd, 1H, *J* = 2.0 Hz, 8.0 Hz), 7.03-7.05 (m, 1H), 7.17-7.19 (m, 1H), 7.22 (s, 1H), 7.25 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 151.1, 147.3, 145.9, 139.0, 137.5, 124.9, 122.9, 121.2, 120.1, 119.8, 119.4, 117.5, 109.2, 108.0, 107.5, 100.8, 79.1, 74.5, 40.4, 30.1. MS: m/z = 383.87 $[M+Na]^+$. Anal. Calcd. For $C_{20}H_{15}N_3O_2S$: C, 66.46; H, 4.18; N, 11.63 %. Found: C, 66.49; H, 4.17; N, 11.49 %.

2-amino-4-(2-bromophenyl)-9-methyl-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4i**): Using the general procedure starting from 100 mg. (0.613 mmol) of 1-methylindoline-2-thione **1b**, 113.4 mg. (0.613 mmol) of 2-bromobenzaldehyde **2i**, 40.5 mg. (0.613 mmol) of malononitrile **3**, 220.5 mg. of title compound **4i** was isolated as white solid, mp 208-210 ^{o}C, Yield = 91%, IR (KBr): 3424, 3314, 3219, 2185, 1636, 1571 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 3.71 (s, 3H), 4.58 (s, 2H), 5.87 (s, 1H), 7.00-7.06 (m, 2H), 7.14-7.17 (m, 2H), 7.23-7.28 (m, 3H), 7.57 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 150.9, 143.8, 137.5, 132.4, 130.8, 128.9, 128.5, 124.9, 123.3, 121.6, 121.4, 119.7, 119.0, 117.0, 109.3, 106.3, 73.1, 40.1, 30.1. MS: m/z = 395 $[M^+]$, 397 $[M^+ +2]$. Anal. Calcd. For $C_{19}H_{14}BrN_3S$: C, 57.58; H, 3.56; N, 10.60 %. Found: C, 57.51; H, 3.55; N, 10.48 %.

2-amino-4-(5-chloro-2-methoxyphenyl)-9-methyl-4,9-dihydrothiopyrano[2,3-b]indole-3-carbonitrile (**4j**): Using the general procedure starting from 100 mg. (0.613 mmol) of 1-methylindoline-2-thione **1b**, 104.5 mg. (0.613 mmol) of 5-chloro-2-methoxybenzaldehyde **2j**, 40.5 mg. (0.613 mmol) of malononitrile **3**, 212.7 mg. of title compound **4j** was isolated as grey colored solid, mp 188-190 ^{o}C, Yield = 91%, IR (KBr): 3424, 3316, 3216, 2189, 1634, 1571 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 3.71 (s, 3H), 3.97 (s, 3H), 4.57 (s, 2H), 5.75 (s, 1H), 6.84 (d, 1H, *J* = 8.8 Hz), 7.01 (t, 1H, *J* = 2.8 Hz), 7.04 (s, 1H), 7.09 (dd, 1H, *J* = 2.4 Hz, 8.8 Hz), 7.15-7.19 (m, 1H), 7.24-7.29 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 154.6, 152.2, 137.5, 134.8, 128.0, 127.7, 124.7, 124.4, 123.5, 121.4, 119.6, 117.1, 113.3, 109.3, 106.8, 73.2, 56.1, 33.4, 30.1. MS: m/z = 404.01 $[M+Na]^+$. Anal. Calcd. For $C_{20}H_{16}ClN_3OS$: C, 62.90; H, 4.22; N, 11.00 %. Found: C, 62.79; H, 4.12; N, 11.10 %.

2-amino-4-(3,4-dimethoxyphenyl)-9-methyl-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4k**): Using the general procedure starting from 100 mg. (0.613 mmol) of 1-methylindoline-2-thione **1b**, 101.8 mg. (0.613 mmol) of 3,4-dimethoxybenzaldehyde **2k**, 40.5 mg. (0.613 mmol) of malononitrile **3**, 217.4 mg. of title compound **4k** was isolated as colorless solid, mp 172-174 ^{o}C, Yield = 94%, IR (KBr): 3416, 3356, 3258, 2192, 1621, 1588 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 3.70 (s, 6H), 3.76 (s, 3H), 5.09 (s, 1H), 6.85 (s, 2H), 6.88 (s, 2H), 6.98 (s, 2H), 7.09 (t, 1H, *J* = 7.6 Hz), 7.34 (d, 1H, *J* = 7.6 Hz), 7.42 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 151.1, 148.5, 147.6, 137.5, 137.5, 124.9, 122.8, 121.2, 119.9, 119.4, 119.1, 117.6, 111.9, 111.2, 109.2, 107.8, 74.6, 55.4, 40.4, 30.1. MS: m/z = 416.11 $[M+K]^+$. Anal. Calcd. For $C_{21}H_{19}N_3O_2S$: C, 66.82; H, 5.07; N, 11.13 %. Found: C, 66.79; H, 5.06; N, 11.12 %.

2-amino-4-(4-methoxyphenyl)-9-methyl-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (**4l**): Using the general procedure starting from 100 mg. (0.613 mmol) of 1-methylindoline-2-thione **1b**, 83.4 mg. (0.613 mmol) of 4-methoxybenzaldehyde **2a**, 40.5 mg. (0.613 mmol) of malononitrile **3**, 198 mg. of title compound **4l** was isolated as grey colored solid, mp 184-186 ^{o}C, Yield = 93%, IR (KBr): 3392, 3386, 3252, 2181, 1622, 1573 cm^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 3.70 (s, 3H), 3.75 (s, 3H), 4.55 (s, 2H), 5.15 (s, 1H), 6.81 (d, 2H, *J* = 8.4 Hz), 7.01 (t, 1H, *J* = 7.2 Hz), 7.14-7.21 (m,

2H), 7.24 (d, 2H, *J* = 2.4 Hz), 7.25 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 158.0, 150.9, 137.5, 137.1, 128.2, 124.9, 122.8, 121.2, 119.9, 119.4, 117.5, 113.8, 109.2, 107.7, 74.7, 54.9, 30.1. MS: m/z = 347 [M^+]. Anal. Calcd. For $C_{20}H_{17}N_3OS$: C, 69.14; H, 4.93; N, 12.09 %. Found: C, 69.11; H, 4.92; N, 12.09 %.

2-amino-9-ethyl-4-p-tolyl-4,9-dihydrothiopyrano[2,3-*b*]indole-3-carbonitrile (4m): Using the general procedure starting from 100 mg. (0.565 mmol) of 1-ethylindoline-2-thione **1c**, 67.8 mg. (0.565 mmol) of 4-methylbenzaldehyde **2b**, 37.3 mg. (0.565 mmol) of malononitrile **3**, 185.2 mg. of title compound **4m** was isolated as colorless solid, mp 156-158 ^{o}C, yield = 95%, IR (KBr): 3426, 3320, 3219, 2177, 1629, 1567 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 1.28 (t, 3H, *J* = 8.8 Hz), 2.23 (s, 3H), 4.12-4.18 (m, 2H), 5.12 (s, 1H), 6.91 (s, 2H), 6.97 (t, 1H, *J* = 7.6 Hz), 7.08-7.13 (m, 3H), 7.23 (d, 2H, *J* = 8.0 Hz), 7.29 (d, 1H, *J* = 7.6 Hz), 7.45 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 150.9, 141.9, 136.5, 135.7, 129.0, 127.0, 125.2, 121.7, 121.2, 119.8, 119.4, 117.6, 109.1, 107.8, 74.6, 40.5, 30.6, 20.5, 15.0. HRMS (ESI+): calcd. For $C_{21}H_{19}N_3S$: [M+Na^+] 368.1198; found 368.1969.

General Procedure for synthesis of thiopyrano derivatives 6: To a well-stirred suspension of the appropriate aromatic aldehyde **2** (1 equiv) and malononitrile **3** (1 equiv) in water (5 mL) appropriate 4-hydroxy-2*H*-thiochromene-2-thione **5** (1 equiv) was added and the reaction mixture was heated at 100 ^{o}C for 40 minutes. As the reaction progressed the reaction mixture becomes partly water soluble and a deep yellow oily layer appeared in the upper portion of water layer. After completion of the reaction as monitored by TLC the reaction mixture was cooled and diluted with 20 mL of water and extracted with ethyl acetate (3x25 mL) and dried over anhydrous Na_2SO_4. The solvent was distilled off. The resulting crude product was purified by filtration through a pad of silica gel (60-120 mesh) using 4:1 petroleum ether-ethyl acetate mixture as eluent to give the pure compounds (**6**).

2-amino-4-(4-methoxyphenyl)-5-oxo-4,5-dihydrothiopyrano[2,3-*b*]thiochromene-3-carbonitrile (**6a**): Using the general procedure starting from 100 mg. (0.515 mmol) of 4-hydroxy-2*H*-thiochromene-2-thione **5a**, 70 mg. (0.515 mmol) of 4-methoxybenzaldehyde **2a**, 34 mg. (0.515 mmol) of malononitrile **3**, 173.4 mg. of title compound **6a** was isolated as grey colored solid, mp 224-226 ^{o}C,

Yield = 89%, IR (KBr): 3382, 3311, 3214, 2198, 1648, 1605, 1588 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ_H = 3.68 (s, 3H), 5.35 (s, 1H), 6.84 (d, 2H, *J* = 8.8 Hz), 7.17 (d, 2H, *J* = 8.4 Hz), 7.27 (s, 2H), 7.63 (t, 1H, *J* = 7.6 Hz), 7.75 (t, 1H, *J* = 7.2 Hz), 7.84 (d, 1H, *J* = 8.0 Hz), 8.34 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 175.0, 158.3, 152.4, 142.1, 135.2, 133.0, 132.4, 130.5, 129.6, 128.8, 128.4, 127.7, 126.2, 119.2, 114.0, 73.0, 55.0, 40.5. MS: m/z = 400.82 $[M+Na]^+$. Anal. Calcd. For $C_{20}H_{14}N_2O_2S_2$: C, 63.47; H, 3.73; N, 7.40 %. Found: C, 63.46; H, 3.71; N, 7.43 %.

2-amino-5-oxo-4-p-tolyl-4,5-dihydrothiopyrano[2,3-*b*]thiochromene-3-carbonitrile (**6b**): Using the general procedure starting from 100 mg. (0.515 mmol) of 4-hydroxy-2*H*-thiochromene-2-thione **5a**, 62 mg. (0.515 mmol) of 4-methylbenzaldehyde **2b**, 34 mg. (0.515 mmol) of malononitrile **3**, 164 mg. of title compound **6b** was isolated as grey colored solid, mp 258-260 ^oC, Yield = 88%, IR (KBr): 3370, 3309, 3205, 2201, 1643, 1610, 1585 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ_H = 2.22 (s, 3H), 5.38 (s, 1H), 7.09 (d, 4H, *J* = 11.6 Hz), 7.27 (s, 2H), 7.65 (d, 1H, *J* = 7.6 Hz), 7.77 (t, 1H, *J* = 6.8 Hz), 7.87 (d, 1H, *J* = 7.6 Hz), 8.34 (d, 1H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 175.0, 152.5, 142.4, 138.0, 136.3, 135.2, 132.4, 130.4, 129.6, 129.2, 128.8, 128.4, 126.5, 126.2, 119.2, 72.8, 40.9, 20.5. MS: m/z = 384.83 $[M+Na]^+$. Anal. Calcd. For $C_{20}H_{14}N_2OS_2$: C, 66.27; H, 3.89; N, 7.73 %. Found: C, 66.17; H, 3.91; N, 7.62 %.

2-amino-4-(2-bromophenyl)-5-oxo-4,5-dihydrothiopyrano[2,3-*b*]thiochromene-3-carbonitrile (**6c**): Using the general procedure starting from 100 mg. (0.515 mmol) of 4-hydroxy-2*H*-thiochromene-2-thione **5a**, 95.3 mg. (0.515 mmol) of 2-bromobenzaldehyde **2i**, 34 mg. (0.515 mmol) of malononitrile **3**, 182 mg. of title compound **6c** was isolated as grey colored solid, mp 226-228 ^oC, Yield = 83%, IR (KBr): 3425, 3349, 3185, 2212, 1663, 1621, 1571 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ_H = 5.77 (s, 1H), 7.14 (t, 1H, *J* = 7.6 Hz), 7.19 (s, 2H), 7.24 (t, 1H, *J* = 7.6 Hz), 7.34 (d, 1H, *J* = 7.6 Hz), 7.61 (t, 2H, *J* = 8.0 Hz), 7.77 (t, 1H, *J* = 8.0 Hz), 7.90 (d, 1H, *J* = 8.0 Hz), 8.25 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 160.6, 159.1, 142.0, 136.3, 133.1, 132.8, 131.4, 129.9, 129.0, 128.5, 128.1, 126.2, 123.0, 120.8, 115.7, 80.3, 72.4, 40.6. MS: m/z = 426 $[M^+]$, 428 $[M^+ +2]$. Anal. Calcd. For $C_{19}H_{11}BrN_2OS_2$: C, 53.40; H, 2.59; N, 6.56 %. Found: C, 53.39; H, 2.49; N, 6.71 %.

2-amino-8-chloro-4-(4-methoxyphenyl)-5-oxo-4,5-dihydrothiopyrano[2,3-b]thiochromene-3-carbonitrile (**6d**): Using the general procedure starting from 100 mg. (0.437 mmol) of 7-chloro-4-hydroxy-2H-thiochromene-2-thione **5b**, 59.5 mg. (0.437 mmol) of 4-methoxybenzaldehyde **2a**, 29 mg. (0.437 mmol) of malononitrile **3**, 151 mg. of title compound **6d** was isolated as grey colored solid, mp 210-212 ^{o}C, Yield = 84%, IR (KBr): 3389, 3305, 3211, 2199, 1651, 1604, 1581 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H = 3.69 (s, 3H), 5.33 (s, 1H), 6.85 (d, 2H, *J* = 8.8 Hz), 7.17 (d, 2H, *J* = 8.4 Hz), 7.29 (s, 2H), 7.68 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz), 8.14 (d, 1H, *J* = 2.0 Hz), 8.32 (d, 1H, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ_C = 174.4, 158.3, 152.2, 142.3, 137.5, 136.9, 132.8, 130.8, 130.6, 128.7, 128.4, 127.7, 125.5, 119.1, 114.0, 72.9, 55.0, 40.5. MS: m/z = 412 [M^{+}]. Anal. Calcd. For $C_{20}H_{13}ClN_2O_2S_2$: C, 58.18; H, 3.17; N, 6.78 %. Found: C, 58.19; H, 3.23; N, 6.88 %.

General Procedure for synthesis of thiopyrano derivatives 9: To a well-stirred suspension of the appropriate aromatic aldehyde **2** (1 equiv) and dimedone **8** (1 equiv) in water (5 mL) 4-hydroxy-2*H*-thiochromene-2-thione **5** (1 equiv) was added and the reaction mixture was heated at 100 ^{o}C for 45-60 minutes. As the reaction progressed the reaction mixture becomes partly water soluble and a deep yellow oily layer appeared in the upper portion of water layer. After completion of the reaction as monitored by TLC the reaction mixture was cooled and diluted with 20 mL of water and extracted with ethyl acetate (3x25 mL) and dried over anhydrous Na_2SO_4. The solvent was distilled off. The resulting crude product was purified by filtration through a pad of silica gel (60-120 mesh) using 9:1 petroleum ether-ethyl acetate mixture as eluent to give the pure compounds (**9**).

3,3-dimethyl-12-phenyl-3,4-dihydrothiochromeno[2,3-*b*]thiochromene-1,11(2*H*,12*H*)-dione (9a): Using the general procedure starting from 100 mg. (0.515 mmol) of 4-hydroxy-2*H*-thiochromene-2-thione **5a**, 54.6 mg. (0.515 mmol) of benzaldehyde **2e**, 72.2 mg. (0.515 mmol) of dimedone **8**, 195.7 mg. of title compound **9a** was isolated as red colored solid, mp 134-136 ^{o}C, yield = 94 %, IR (KBr): 1663, 1589 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.43 (d, 1H, *J* = 8.0 Hz), 7.52 (q, 1H, *J* = 7.2 Hz), 7.44 (t, 4H, *J* = 8.0 Hz), 7.19 (t, 2H, *J* = 7.6 Hz), 7.11 (t, 1H, *J* = 7.6 Hz), 6.25 (s, 1H), 2.66 (d, 1H, *J* = 17.6 Hz), 2.36-2.46 (m, 3H), 1.11 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 193.0, 176.1, 147.1, 142.4, 141.5, 135.5, 131.6, 131.1, 130.7, 129.9, 129.7, 128.4, 128.1, 128.0, 127.7, 126.9,

125.2, 51.5, 43.6, 37.0, 33.9, 29.5, 26.4. MS: m/z = 427.11 $[M+Na]^+$. Anal. Calcd. For $C_{24}H_{20}O_2S_2$: C, 71.25; H, 4.98 %. Found: C, 71.21; H, 5.05 %.

12-(benzo[*d*][1,3]dioxol-5-yl)-3,3-dimethyl-3,4-dihydrothiochromeno[2,3-*b*]thiochromene-1,11(2*H*,12*H*)-dione (9b): Using the general procedure starting from 100 mg. (0.515 mmol) of 4-hydroxy-2*H*-thiochromene-2-thione **5a**, 77.3 mg. (0.515 mmol) of benzo[*d*][1,3]dioxole-5-carbaldehyde **2h**, 72.2 mg. (0.515 mmol) of dimedone **8**, 205.5 mg. of title compound **9b** was isolated as red colored solid, mp 178-180 ^oC, yield = 89 %, IR : 1662, 1625, 1615, 1589 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.44 (d, 1H, *J* = 7.6 Hz), 7.44-7.56 (m, 3H), 6.98 (s, 1H), 6.94 (d, 1H, *J* = 8.0 Hz), 6.63 (d, 1H, *J* = 8.0 Hz), 6.14 (s, 1H), 5.83 (d, 2H, *J* = 2.4 Hz), 2.65 (d, 1H, *J* = 17.2 Hz), 2.40 (d, 3H, *J* = 18.4 Hz), 1.11 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 193.0, 176.0, 147.5, 146.7, 146.4, 142.3, 135.5, 131.6, 131.1, 130.7, 129.9, 129.7, 127.7, 125.2, 122.6, 121.3, 108.8, 108.1, 100.8, 51.5, 43.5, 36.6, 33.9, 29.5, 26.5. MS: m/z = 470.97 $[M+Na]^+$, 472.97 $[M+Na+2]^+$ Anal. Calcd. For $C_{25}H_{20}O_4S_2$: C, 66.94; H, 4.49 %. Found: 66.91; H, 4.54 %.

12-(2-bromophenyl)-3,3-dimethyl-3,4-dihydrothiochromeno[2,3-*b*]thiochromene-1,11(2*H*,12*H*)-dione (9c): Using the general procedure starting from 100 mg. (0.515 mmol) of 4-hydroxy-2*H*-thiochromene-2-thione **5a**, 95.3 mg. (0.515 mmol) of 2-bromobenzaldehyde **2i**, 72.2 mg. (0.515 mmol) of dimedone **8**, 216.2 mg. of title compound **9c** was isolated as red colored solid, mp 220-222 ^oC, yield = 87 %, IR: 1664, 1587 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.27 (d, 1H, *J* = 8.0 Hz), 7.69 (d, 1H, *J* = 7.6 Hz), 7.49-7.58 (m, 2H), 7.39 (t, 2H, *J* = 6.8 Hz), 7.21 (t, 1H, *J* = 7.6 Hz), 6.99 (t, 1H, *J* = 7.2 Hz), 5.84 (s, 1H), 2.68 (d, 2H, *J* = 8.0 Hz), 2.27 (d, 2H, *J* = 6.0 Hz), 1.16 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 204.4, 195.8, 161.5, 151.8, 141.1, 138.9, 136.7, 133.8, 130.5, 128.4, 127.4, 126.3, 126.1, 123.4, 123.3, 122.5, 113.1, 50.8, 40.6, 38.0, 32.3, 29.2, 27.6. MS: m/z = 505.08 $[M+Na]^+$. Anal. Calcd. For $C_{24}H_{19}BrO_2S_2$: C, 59.63; H, 3.96 %. Found: C, 59.64; H, 3.89 %.

12-(5-chloro-2-methoxyphenyl)-3,3-dimethyl-3,4-dihydrothiochromeno[2,3-*b*]thiochromene-1,11(2*H*,12*H*)-dione (9d): Using the general procedure starting from 100 mg. (0.515 mmol) of 4-hydroxy-2*H*-thiochromene-2-thione **5a**, 87.8 mg. (0.515 mmol) of 5-chloro-2-methoxybenzaldehyde **2j**, 72.2 mg. (0.515 mmol) of dimedone **8**, 207.5 mg. of title compound **9d** was isolated as red colored solid, mp 218-220 ^oC, yield = 86 %, IR (KBr): 1662, 1620, 1588 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$):

δ_H = 8.42 (d, 1H, *J* = 8.4 Hz), 7.44-7.56 (m, 4H), 7.06 (d, 1H, *J* = 8.4 Hz), 6.71 (d, 1H, *J* = 8.8 Hz), 6.18 (s, 1H), 3.77 (s, 3H), 2.59 (d, 1H, *J* = 17.2 Hz), 2.35 (d, 3H, *J* = 18.0 Hz), 1.10 (s, 3H), 0.95 (s, 3H). MS: m/z = 491.01 $[M+Na]^+$. Anal. Calcd. For $C_{25}H_{21}ClO_3S_2$: C, 64.02; H, 4.51 %. Found: C, 64.07; H, 4.50 %.

12-(3,4-dimethoxyphenyl)-3,3-dimethyl-3,4-dihydrothiochromeno[2,3-*b*]thiochromene-1,11(2*H*,12*H*)-dione (9e): Using the general procedure starting from 100 mg. (0.515 mmol) of 4-hydroxy-2*H*-thiochromene-2-thione **5a**, 85.5 mg. (0.515 mmol) of 3,4-dimethoxybenzaldehyde **2k**, 72.2 mg. (0.515 mmol) of dimedone **8**, 222.4 mg. of title compound **9e** was isolated as red colored solid, mp 140-142 ^oC, yield = 93 %, IR: 1660, 1615, 1589 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.45 (d, 1H, *J* = 7.6 Hz), 7.44-7.56 (m, 3H), 7.12 (s, 1H), 6.93 (d, 1H, *J* = 8.0 Hz), 6.67 (d, 1H, *J* = 8.0 Hz), 6.19 (s, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 2.67 (d, 1H, *J* = 17.6 Hz), 2.39 (d, 3H, *J* = 16.4 Hz), 1.12 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 193.1, 176.1, 148.7, 147.9, 146.8, 142.1, 135.5, 134.1, 131.6, 131.2, 130.8, 130.1, 129.7, 127.7, 125.2, 119.6, 111.8, 110.8, 55.8, 55.7, 51.5, 43.6, 36.5, 33.8, 29.6, 26.3. MS: m/z = 503.04 $[M+K]^+$. Anal. Calcd. For $C_{26}H_{24}O_4S_2$: C, 67.21; H, 5.21%. Found: C, 67.11; H, 5.22 %.

12-(4-fluorophenyl)-3,3-dimethyl-3,4-dihydrothiochromeno[2,3-*b*]thiochromene-1,11(2*H*,12*H*)-dione (9f): Using the general procedure starting from 100 mg. (0.515 mmol) of 4-hydroxy-2*H*-thiochromene-2-thione **5a**, 63.9 mg. (0.515 mmol) of 4-fluorobenzaldehyde **2l**, 72.2 mg. (0.515 mmol) of dimedone **8**, 198 mg. of title compound **9f** was isolated as red colored solid, mp 182-184 ^oC, yield = 91 %, IR: 1662, 1587 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.44 (d, 1H, *J* = 7.6 Hz), 7.44-7.57 (m, 5H), 6.87 (t, 2H, *J* = 8.0 Hz), 6.19 (s, 1H), 2.67 (d, 1H, *J* = 17.6 Hz), 2.40 (d, 3H, *J* = 17.6 Hz), 1.12 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 193.0, 176.0, 163.0, 160.6, 146.9, 142.5, 137.5, 135.5, 131.6, 131.0, 130.7, 129.8, 129.7, 129.6, 127.8, 125.2, 115.2, 115.0, 51.4, 43.6, 36.4, 33.9, 29.5, 26.3. MS: m/z = 461.03 $[M+K]^+$. Anal. Calcd. For $C_{24}H_{19}FO_2S_2$: C, 68.22; H, 4.53 %. Found: C, 68.26; H, 4.50 %.