Anion-cation co-operative catalysis by artificial sweetener saccharine based ionic liquid for sustainable synthesis of 3,4-dihydropyrano[c]chromenes, 4,5-dihydropyrano[4,3-b]pyran and tetrahydrobenzo[b]pyrans in aqueous medium

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**Experimental General Remarks:** All chemicals were reagent grade and purchased from Aldrich, CDH, Spectrochem, and Fisher scientific and used without further purification. All reactions were monitored by TLC over silica gel plate. The spots on TLC plates were visualized under UV lamp or by iodine vapors. $^1$H and $^{13}$C NMR spectra were recorded on Jeol JNM ECX 500 MHz spectrometer in CDCl$_3$ and DMSO-d$_6$. Data expresses the chemical shift values in $\delta$ ppm from upfield to downfield in both $^1$H NMR and $^{13}$C NMR spectra. For all compounds, $^1$H NMR data is reported in the following order: Chemical shift (multiplicity, number of protons, J value, and nature of proton). IR spectra were recorded on a Bruker alpha FT-IR spectrometer. Melting points were determined by open glass capillary method and were uncorrected.

**Typical experimental procedure for the [Bmim]Sac (3):** Sodium Saccharinate (2) 27.0 g (0.112 mol) was added into a solution of 1-n-Butyl-3-methylimidazolium Bromide [Bmim]Br (1) 24.6 g (0.112 mol) in 100 mL acetone at rt. After stirring for 30h, the reaction mixture was filtered through a plug of Celite. The volatiles were removed under reduced pressure overnight and 31.0 g (96%) of viscous oil was obtained as pure product.

**General Experimental Procedure for 3,4-dihydropyrano [c] chromenes, tetrahydrobenzo [b] pyrans, 4,5-dihydropyrano[4,3-b]pyran (7a-j, 9a-k, 12a-g, and 11a-d):** A mixture of Aldehyde (1 mmol), (4) malononitrile (1.2 mmol), (5) 4-Hydroxy Coumarin (6)/4-hydroxy-6-methyl-2-pyrone (10) or 5,5-dimethyl-1,3cyclohexanedione/1,3-cyclohexanedione (1 mmol) (8)/ and [Bmim]Sac (3) (5 mol%) in water (2 mL) was heated at 80°C for an appropriate period of time as indicated in Table 2 and 3 respectively. During the procedure, the reaction was monitored by TLC. Upon completion, the product was separated by simple filtration. Then, the resulting solid product was recrystallized from ethanol to afford pure product in high yields without any purification.

**Reusability of the [Bmim] Sac:** After completion of reaction, ice water was added to the reaction mixtures. The solid product was filtered and the filtrate (Bmim-Sac in water) was dried under vacuum to remove water and the dried IL was found to be identical (spectral data) with an authentic sample of (unused ionic liquid) then the organic reaction mixture was added to the IL to start next run. It is interesting to note that recovered IL was reused for 5 successive batches of reactions to afford pure product after crystallisation.
$^1$H and $^{13}$C data of 3,4-Dihydropyrano[c]chromene, 4,5-Dihydropyrano[4,3-b]pyran and Tetrahydrobenzo[b]pyran

[Bmim]Sac (3):

Colorless oil; $^1$H NMR (DMSO-$d_6$, 300 MHz) $\delta = 0.90$ (t, 3H, $J = 7.3$ Hz, CH$_3$), 1.28 (m, 2H, CH$_2$), 1.80 (m, 2H, CH$_2$), 3.85 (s, 3H, CH$_3$), 4.18 (t, 2H, $J = 7.2$ Hz, NCH$_2$), 7.71 (s, 1H, ArH), 7.78 (d, $J = 2.0$ Hz, 4H, ArH), 7.89 (d, $J = 5.4$ Hz, 1H, ArH), 9.17 (s, 1H, ArH); $^{13}$C NMR (DMSO-$d_6$, 50 MHz) $\delta =$ 13.2, 18.7, 31.3, 35.7, 48.4, 120.0, 122.2, 123.5, 131.5, 133.0, 135.8, 142.5, 164.7, IR (neat, cm$^{-1}$): 766, 951, 1148, 1166, 1260, 1332, 1458, 1580, 1633, 2873, 2961, 3097, 3147;

2-Amino-4-(phenyl)-4, 5-dihydro-oxopyrano[3,2-c]chromene-3-carbonitrile (7a):

White solid, m. p. 262-263°C (reported m. p. 260-261); $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 4.46 (s, 1H, CH), 7.25 (d, 2H, $J = 7.80$ Hz, Ar-H), 7.28 (m, 1H, Ar-H), 7.33 (t, 2H, $J = 7.50$ Hz, Ar-H), 7.42 (br s, 2H, NH$_2$), 7.45 (d, 1H, $J = 8.40$ Hz, Ar-H), 7.49 (t, 1H, $J = 7.6$ Hz, Ar-H), 7.71 (t, 1H, $J = 7.50$ Hz, Ar-H), 7.91 (d, 1H, $J = 7.60$ Hz, Ar-H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 58.8, 104.9, 113.8, 117.4, 120.1, 123.3, 125.5, 128.0, 128.5, 129.4, 133.8, 144.2, 153.0, 154.3, 158.8, 160.4; IR (KBr, cm$^{-1}$): 1609, 1671, 1707, 2188, 3177, 3275, 3387.

2-Amino-4-(4-methoxyphenyl)-4, 5-dihydro-oxopyrano[3,2-c]chromene-3-carbonitrile (7b):

White solid, m. p. 262-263°C (reported m. p. 260-261); $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 4.46 (s, 1H, CH), 7.25 (d, 2H, $J = 7.80$ Hz, Ar-H), 7.28 (m, 1H, Ar-H), 7.33 (t, 2H, $J = 7.50$ Hz, Ar-H), 7.42 (br s, 2H, NH$_2$), 7.45 (d, 1H, $J = 8.40$ Hz, Ar-H), 7.49 (t, 1H, $J = 7.6$ Hz, Ar-H), 7.71 (t, 1H, $J = 7.50$ Hz, Ar-H), 7.91 (d, 1H, $J = 7.60$ Hz, Ar-H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 58.8, 104.9, 113.8, 117.4, 120.1, 123.3, 125.5, 128.0, 128.5, 129.4, 133.8, 144.2, 153.0, 154.3, 158.8, 160.4; IR (KBr, cm$^{-1}$): 1609, 1671, 1707, 2188, 3177, 3275, 3387.
White solid, m.p. 252-253 °C (reported m. p. 250-251);\(^1\) \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\): 3.72 (s, 3H, OCH\(_3\)), 4.40 (s, 1H, CH), 6.87 (d, 2H, J= 8.15 Hz, Ar-H), 7.18 (d, 2H, J= 8.15 Hz, Ar-H), 7.37 (br s, 2H, NH\(_2\)), 7.45 (d, 1H, J= 8.10 Hz, Ar-H), 7.49 (t, 1H, J= 7.85 Hz, Ar-H), 7.70 (t, 1H, J= 7.70 Hz, Ar-H), 7.89 (d, 1H, J= 7.7 Hz, Ar-H); \(^1\)^13\(^C\) NMR (DMSO-\(d_6\), 100 MHz,) \(\delta\): 55.9, 59.1, 105.1, 113.8, 114.7, 117.4, 120.2, 123.3, 125.5, 129.6, 133.66, 136.2, 152.9, 153.9, 158.8, 159.2, 160.4; IR (KBr, cm\(^{-1}\)): 1607, 1668, 1711, 2189, 3184, 3311, 3381.

\textit{2-Amino-4-(4-nitrophenyl)-5-oxo-4H, 5H-pyrano-[3,2-c]chromene-3-carbonitrile (7c)}\(^1\):

![Image of 2-Amino-4-(4-nitrophenyl)-5-oxo-4H, 5H-pyrano-[3,2-c]chromene-3-carbonitrile (7c)](image)

Pale yellow solid, m.p. 264-265 °C (reported m. p. 261-263); \(^1\)\(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\): 4.68 (s, 1H, CH), 7.47 (d, 1H, J= 8.00 Hz, Ar-H), 7.52 (t, 1H, J= 7.80 Hz, Ar-H), 7.57 (br s, 2H, NH\(_2\)), 7.60 (d, 2H, J= 8.00 Hz, Ar-H), 7.74 (t, 1H, J= 7.80 Hz, Ar-H), 7.91 (d, 1H, J= 7.80 Hz, Ar-H), 8.18 (d, 2H, J= 8.00 Hz, Ar-H); \(^1\)^13\(^C\) NMR (DMSO-\(d_6\),100 MHz,) \(\delta\): 57.6, 103.6, 113.7, 117.5, 119.8, 123.4, 124.6, 125.6, 130.0, 134.0, 147.4, 151.6, 153.1, 154.8, 158.9, 160.4; IR (KBr, cm\(^{-1}\)): 1292, 1379, 1518, 1609, 1666, 1711, 2190, 3323, 3369, 3422, 3477.

\textit{2-Amino-4-(4-hydroxyphenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile (7d)}\(^1\).

![Image of 2-Amino-4-(4-hydroxyphenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile (7d)](image)

White solid; m. p. 266-267 °C (reported m. p. 267-269); \(^1\)\(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\): 4.34 (1H, s, CH); 6.72 (2H, s, Ar-H); 7.07 (2H, s, NH\(_2\)); 7.34-7.43 (4H, m, Ar-H); 7.66 (1H, s Ar-H); 7.88 (1H, s Ar-H); 9.38 (1H, s, OH); \(^1\)\(^3\(^C\) NMR (DMSO-\(d_6\), 100 MHz,) \(\delta\): 36.13, 58.4, 104.4, 112.9, 115.1, 116.4, 119.3, 122.3, 124.5, 128.6, 132.7, 133.6, 152.0, 152.9, 156.4, 157.8, 159.4. IR (KBr, cm\(^{-1}\)): 1182, 1580, 1723, 2340, 3428.

\textit{2-Amino-4-(4-chlorophenyl)-5-oxo-4H, 5H-pyrano[3,2-c]chromene- 3-carbonitrile (7e)}\(^1\):

![Image of 2-Amino-4-(4-chlorophenyl)-5-oxo-4H, 5H-pyrano[3,2-c]chromene-3-carbonitrile (7e)](image)

White solid, m. p. 265-267 °C (reported m. p. 266-268); \(^1\)\(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\): 4.50 (s, 1H, CH), 7.31 (d, 2H, J= 8.00 Hz, Ar-H), 7.36 (br s, 2H, NH\(_2\)), 7.38 (br s, 2H, Ar-H), 7.44 (d, 1H, J= 8.00 Hz, Ar-H), 7.50 (d, 1H, J= 8.10 Hz, Ar-H), 7.54 (t, 1H, J= 7.85 Hz, Ar-H), 7.70 (t, 1H, J= 7.70 Hz, Ar-H), 7.89 (d, 1H, J= 7.7 Hz, Ar-H); \(^1\)\(^3\(^C\) NMR (DMSO-\(d_6\),100 MHz,) \(\delta\): 55.9, 59.1, 105.1, 113.8, 114.7, 117.4, 120.2, 123.3, 125.5, 129.6, 133.66, 136.2, 152.9, 153.9, 158.8, 159.2, 160.4; IR (KBr, cm\(^{-1}\)): 1607, 1668, 1711, 2189, 3184, 3311, 3381.
Hz, Ar-H), 7.49 (t, 1H, J= 7.6 Hz, Ar-H), 7.71 (t, 1H, J= 7.80 Hz, Ar-H), 7.92 (d, 1H, J= 7.80 Hz, Ar-H); \(^{13}\)C NMR (DMSO-d\(_6\), 100 MHz) \(\delta\): 36.4, 58.8, 104.4, 113.9, 117.3, 119.3, 123.3, 129.2, 130.4, 132.6, 133.8, 143.1, 153.0, 154.4, 158.9, 160.3; IR (KBr, cm\(^{-1}\)): 763, 1059, 1374, 1609, 1672, 1717, 2139, 3385.

2-Amino-4-(4-flourophenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (7f):

White solid, m.p. 257-258\(^\circ\)C (reported m. p. 258-259); \(^1\)H NMR (DMSO-d\(_6\), 400 MHz) \(\delta\): 4.44 (s,1H, CH), 7.09 (br.s, 2H, Ar-H), 7.28 (br.s, 2H, Ar-H), 7.41 (br s, 4H, Ar-H and NH\(_2\)), 7.65 (br.s, 1H, Ar-H), 7.95 (br.s, 1H, Ar-H); \(^{13}\)C NMR (DMSO-d\(_6\), 100 MHz) \(\delta\): 36.6, 58.2, 104.2, 113.4, 115.6, 117.0, 119.7, 122.8, 125.1, 130.1, 133.4, 140.0, 152.6, 153.9, 158.4, 160.0, 160.7, 162.7; IR (KBr, cm\(^{-1}\)): 1501, 1603, 1668, 1711, 2186, 3281, 3317, 3387.

2-Amino-4-(3-nitrophenyl)-5-oxo-4H,5H-pyrano-[3,2-c]chromene-3-carbonitrile (7g):

White solid, m.p. 255-256\(^\circ\)C (reported m. p. 250-251); \(^1\)H NMR (DMSO-d\(_6\), 400 MHz) \(\delta\): 4.74 (s, 1H, CH), 7.44 (d, 1H, J= 6.50 Hz, Ar-H), 7.51 (t, 1H, J= 7.50 Hz, Ar-H), 7.55 (br s, 2H, NH\(_2\)), 7.64 (t, 1H, J= 7.50 Hz, Ar-H), 7.73 (dt, 1H, J= 7.50 Hz, 1.25 Hz, Ar-H), 7.82 (d, 1H, J= 6.75 Hz, Ar-H), 7.92 (dd, 1H, J= 6.50 Hz, 1.25 Hz, Ar-H), 8.12 (dd, 1H, J= 8.50 Hz, 1.40 Hz, Ar-H), 8.14 (s, 1H, Ar-H); \(^{13}\)C NMR (DMSO-d\(_6\), 100 MHz) \(\delta\): 57.8, 103.7, 113.8, 117.4, 119.8, 123.1, 123.3, 123.5, 125.5, 130.9, 134.0, 135.6, 146.4, 148.7, 153.1, 154.7, 159.0, 160.5; IR (KBr, cm\(^{-1}\)): 1354, 1526, 1669, 1701, 2192, 3188, 3317, 3387.

2-Amino-4-(4-bromophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile (7h):

White solid, m.p. 257-258\(^\circ\)C (reported m. p. 255-258); \(^1\)H NMR (DMSO-d\(_6\), 400 MHz) \(\delta\): 4.48 (s,1H, CH), 7.25 (d, 2H, J= 8.00 Hz, Ar-H), 7.47-7.52 (m, 4H, Ar-H), 7.73 (t, 1H, J= 7.20 Hz, Ar-H), 7.91 (d, 1H, J= 7.40 Hz, Ar-H); \(^{13}\)C NMR (DMSO-d\(_6\), 100 MHz) \(\delta\): 57.8, 103.9, 113.4, 117.1, 119.5, 120.7,
123.0, 125.2, 130.5, 131.8, 133.5, 143.2, 152.6, 154.0, 158.3, 160.0; IR (KBr, cm\(^{-1}\)): 1057, 1371, 1612, 1670, 1705, 2166, 3371.

2-Amino-5-oxo-4-(thiophen-2-yl)-4,5-dihydropyrano-[3,2-c]chromene-3-carbonitrile (7i) \(^1\).

![Chemical Structure](image)

White Solid, m.p. 226-230°C (reported m.p. 228-230); \(^1\)H NMR (DMSO-\(d_6\), 400MHz) \(\delta\): 4.94 (s, 1H, CH), 6.54 (s, 2H, NH\(_2\)), 6.98 (m, 1H, thiophene ring), 7.20-7.22 (dd, 2H, J= 3.8Hz, 1.3Hz, thiophene ring), 7.65-7.67 (dd, 2H, J= 4.2Hz, 1.0Hz, ArH), 7.69-7.70 (dd, 2H, J = 2.6Hz, 1.1Hz, ArH); \(^13\)C NMR (DMSO-\(d_6\), 100MHz) \(\delta\): 31.94, 57.84, 103.97, 116.22, 118.94, 122.51, 124.27, 124.58, 124.67, 127.72, 132.52, 138.41, 140.90, 152.95, 153.84, 158.40, 159.49. IR (KBr, cm\(^{-1}\)): 1383, 1535, 1606, 1670, 1699, 2200, 3319, 3403.

2-amino-5-oxo-4-propyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (7j) \(^1\):

![Chemical Structure](image)

Light yellow colored solid; m.p. 195-200°C (reported m.p. 193-195); \(^1\)H NMR (DMSO-\(d_6\), 300MHz) \(\delta\): 0.73-0.91 (m, 3H, CH\(_3\)), 1.27-1.31 (m, 2H, CH\(_2\)), 1.44-1.53 (m, 1H, CH), 1.60-1.72 (m, 1H, CH), 3.36-3.39 (m, 1H, CH), 7.26 (s, 2H, NH\(_2\)), 7.33-7.44 (m, 2H, ArH), 7.65 (t, 1H, J = 7.2 Hz, ArH), 7.76 (d, 1H, J = 7.8 Hz, ArH); \(^13\)C NMR (DMSO-\(d_6\), 75MHz) \(\delta\): 14.3, 18.1, 31.3, 36.7, 55.7, 104.8, 113.4, 117.0, 120.1, 122.6, 125.1, 133.2, 152.5, 154.6, 159.9, 160.4; IR (KBr) cm\(^{-1}\): 473, 740, 813, 845, 955, 1169, 1214, 1277, 1403, 1460, 1509, 1591, 1629, 3051, 3246.

2-Amino-3-cyano-4-(phenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9a):

![Chemical Structure](image)

White solid, m.p. 238-240°C (reported m.p. 227-228); \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\): 0.94 (s, 3H, CH\(_3\)), 1.04 (s, 3H, CH\(_3\)), 2.08 (d, 1H, J= 16.10 Hz, CH\(_2\)), 2.23 (d, 1H, J= 16.10 Hz, CH\(_2\)), 2.50 (m, 2H, CH\(_2\)), 4.11 (s, 1H, CH), 7.06 (s, 2H, NH\(_2\)), 7.19 (m, 3H, Ar-H), 7.33 (m, 2H, Ar-H); \(^13\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\): 26.3, 27.6, 31.2, 35.1, 39.1, 50.0, 59.7, 113.1, 118.4, 125.8, 126.6, 127.5, 142.7, 158.5, 162.3, 194.2; IR (KBr, cm\(^{-1}\)): 1358, 1655, 1678, 2191, 2951, 3179, 3321, 3390.
2-Amino-3-cyano-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9b):

Pale yellow solid, m.p. 201-203°C (reported m. p. 194-196°C); $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 0.96 (s, 3H, CH$_3$), 1.04 (s, 3H, CH$_3$), 2.11 (d, 1H, J = 16.00 Hz, CH$_2$), 2.25 (d, 1H, J = 16.00 Hz, CH$_2$), 2.50 (s, 1H, J = 2.50 Hz, CH$_2$), 2.51 (s, 1H, J = 2.50 Hz, CH$_2$), 3.72 (s, 3H, OCH$_3$), 4.14 (s, 1H, CH), 6.85 (d, 2H, J = 8.60 Hz, Ar-H), 6.95 (s, 2H, NH$_2$), 7.07 (d, 2H, J = 8.60 Hz); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ: 27.6, 29.3, 32.6, 35.6, 50.9, 55.8, 59.5, 113.9, 114.5, 120.6, 129.1, 137.7, 158.8, 159.3, 163.0, 196.5; IR (KBr, cm$^{-1}$): 1209, 1606, 1657, 1679, 2191, 2960, 3321, 3371.

2-Amino-3-cyano-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9c):

Yellow solid, m. p. 179-181°C (reported m. p. 178-180°C); $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 0.97 (s, 3H, CH$_3$), 1.05 (s, 3H, CH$_3$), 2.12 (d, 1H, J = 16.00 Hz, CH$_2$), 2.27 (d, 1H, J = 16.00 Hz, CH$_2$), 2.54 (brs, 2H, CH$_2$), 4.38 (s, 1H, CH), 7.18 (s, 2H, NH$_2$), 7.46 (d, 2H, J = 8.60 Hz, Ar-H), 8.18 (d, 2H, J = 8.60 Hz, Ar-H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ: 27.8, 29.1, 32.7, 36.5, 50.7, 57.9, 112.6, 120.2, 124.5, 129.5, 147.1, 153.1, 159.5, 163.9, 196.5; IR (KBr, cm$^{-1}$): 1212, 1506, 1579, 1628, 1653, 1960, 2967, 3320, 3408.

2-Amino-3-cyano-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9d):


White solid, m. p. 269–270 °C (reported m. p. 265-266 °C); ¹H NMR (CDCl₃, 200 MHz) δ: 1.04 (s, 3H, CH₃), 1.25 (s, 3H, CH₃), 2.23 (s, 2H, CH₂), 2.44 (s, 2H, CH₂), 4.35 (s, 1H, CH), 4.49 (s, 2H, NH₂), 6.71-7.27 (m, 4H, Ar-H); IR (KBr, cm⁻¹): 1218, 1395, 1660, 2170, 2958, 3353.

2-Amino-3-cyano-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9e):

White solid, m.p. 212-213 °C (reported m. p. 207-209° C); ¹H NMR (DMSO-d₆, 400 MHz) δ: 0.96 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 2.12 (d, 1H, J= 16.00 Hz, CH₂), 2.26 (d, 1H, J= 16.00 Hz, CH₂), 2.51 (brs, 2H, CH₂), 4.22 (s, 1H, CH), 7.05 (s, 2H, NH₂), 7.19 (d, 2H, J= 8.40 Hz, Ar-H), 7.35 (d, 2H, J= 8.40 Hz, Ar-H); ¹³C NMR (DMSO-d₆,100 MHz) δ: 27.7, 29.2, 32.6, 36.0, 50.8, 58.7, 113.2, 120.4, 129.2, 123.0, 132.0, 144.6, 159.4, 163.4, 196.5; IR (KBr, cm⁻¹): 1215, 1363, 1493, 1638, 1676, 2189, 2960, 3184, 3381.

2-Amino-3-cyano-4-(4-flourophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9f):

White solid, m.p. 195-197 °C (reported m. p. 191-193° C); ¹H NMR (DMSO-d₆,400 MHz) δ: 0.90 (s, 3H, CH₃), 0.99 (s, 3H, CH₃), 2.08 (d, 1H, J=12.0 Hz, CH₂), 2.22 (d, 1H, J=12.0 Hz, CH₂), 2.51 (br,s, 2H, CH₂), 4.16 (s, 1H, CH), 7.01 (s, 2H, NH₂), 7.06-7.09 (m, 2H, Ar-H), 7.13-7.14 (m, 2H, Ar-H); ¹³C NMR (DMSO-d₆, 100 MHz, ) δ: 27.3, 28.8, 32.3, 35.4, 36.7, 50.4, 58.5, 112.9, 115.6, 120.2, 129.4, 141.4, 158.9, 160.4, 162.3, 163.0, 196.1; IR (KBr, cm⁻¹): 1212, 1601, 1653, 1671, 2195, 2959, 3341.

2-Amino-3-cyano-4-(3-nitrophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9g):
Yellow solid, m.p. 209-211 °C (reported m. p. 208-211 °C); \( ^1 \)H NMR (DMSO-d\(_6\), 400 MHz) \( \delta \): 1.03 (s, 3H, CH\(_3\)), 1.11 (s, 3H, CH\(_3\)), 2.16-2.17 (m, 2H, CH\(_2\)), 2.44-2.53 (m, 2H, CH\(_2\)), 4.51 (s, 1H, CH), 4.73 (s, 2H, NH\(_2\)), 7.46-7.49 (m, 1H, Ar-H), 7.67 (d, 1H, Ar-H), 8.03-8.09 (m, 2H, Ar-H); \( ^{13} \)C NMR (DMSO-d\(_6\), 100 MHz) \( \delta \): 27.6, 28.8, 32.2, 35.5, 40.5, 50.4, 61.9, 112.9, 118.1, 122.2, 122.3, 129.4, 134.4, 145.3, 148.5, 157.7, 162.3, 195.8; IR (KBr, cm\(^{-1}\)): 1375, 1529, 1678, 2186, 2958, 3337, 3430.

2-Amino-3-cyano-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9h):

White solid, m.p. 200-201 °C (reported m. p. 196-198 °C); \( ^1 \)H NMR (DMSO-d\(_6\), 300 Hz) \( \delta \): 0.94 (s, 3H, CH\(_3\)), 1.04 (s, 3H, CH\(_3\)), 2.09 (d, 1H, \( J = 16.0 \) Hz, CH\(_2\)), 2.26 (d, 1H, \( J = 16.0 \) Hz, CH\(_2\)), 2.50 (brs, 2H, CH\(_2\)), 4.17 (s, 1H, CH), 7.08 (brs, 2H, NH\(_2\)), 7.10 (d, 2H, \( J = 8.3 \) Hz, Ar-H), 7.48 (2H, d, J = 8.3 Hz, Ar-H); IR (KBr, cm\(^{-1}\)): 1676, 2188, 2958, 3182, 3322, 3389.

2-Amino-3-cyano-4-(thiophen-2-yl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9i):

Yellow solid, m.p. 226-228 °C (reported m. p. 230-231 °C); \( ^1 \)H NMR (DMSO-d\(_6\), 400 MHz) \( \delta \): 0.99 (s, 3H, CH\(_3\)), 1.05 (s, 3H, CH\(_3\)), 2.31 (m, 2H, CH\(_2\)), 2.49 (m, 2H, CH\(_2\)), 4.34 (s, 1H, CH), 6.33 (dd, 1H, \( J = 3.40 \) Hz, Ar-H), 6.15 (d, 1H, \( J = 3.40 \) Hz, Ar-H), 6.05 (d, 1H, \( J = 3.4 \) Hz, Ar-H), 7.08 (s, 2H, NH\(_2\)); \( ^{13} \)C NMR (DMSO-d\(_6\), 100 MHz) \( \delta \): 27.4, 29.6, 31.4, 32.7, 50.6, 58.4, 113.9, 121.1, 124.7, 125.7, 128.4, 151.5, 159.7, 163.4, 196.5; IR (KBr, cm\(^{-1}\)): 1201, 1664, 1686, 2202, 2973, 3211, 3401.

(E)-2-amino-7,7-dimethyl-5-oxo-4-styryl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (9k)
White solid, m.p. 200-202°C (reported m.p. 205-207°C); ¹H NMR (CDCl₃-d₆, 400 Hz) δ: 1.08 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.29 (s, 2H, CH₂), 2.38 (s, 2H, CH₂), 4.09 (d, 1H, J = 6.4 Hz, C-H), 4.59 (brs, 2H, NH₂), 6.11 (dd, 1H, J = 6.0, 12.0 Hz, =CH), 6.51 (d, 1H, J = 6.0 Hz, =CH), 7.18-7.21 (m, 1H, Ar-H) 7.26-7.29 (m, 2H, Ar-H) 7.33-7.35 (m, 2H, Ar-H); ¹³C NMR (CDCl₃-d₆, 100 MHz) δ: 27.4, 28.7, 29.6, 32.2, 32.3, 40.6, 50.7, 60.6, 113.3, 118.8, 126.5, 127.4, 128.3, 129.5, 131.0, 136.7, 158.2, 161.6, 196.1; IR (KBr, cm⁻¹): 1676, 2188, 2958, 3182, 3322, 3389

2-amino-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12a):

Yellow solid, m.p. 223-225°C (reported m.p. 224-226°C); ¹H NMR (400 MHz, DMSO-d₆+CDCl₃) δ: 1.83-1.96 (m, 2H, CH₂), 2.14-2.25 (m, 2H, CH₂), 2.42-2.54 (m, 2H, CH₂), 4.26 (s, 1H, CH), 4.42 (s, 2H, NH₂), 7.05 (d, J=12.0Hz, 2H, Ar-H), 7.12 (d, J=12.0Hz, Ar-H).

2-amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12b):

Yellow solid, m.p. 219-221°C (reported m.p. 220-222°C); ¹H NMR (400 MHz, CDCl₃) δ: 1.94-2.08 (m, 2H, CH₂), 2.28-2.38 (m, 2H, CH₂), 2.57-2.61 (m, 2H, CH₂), 4.42 (s, 1H, CH), 4.42 (brs, 2H, NH₂), 7.18-7.30 (m, 5H, Ar-H).

2-amino-4-(4-bromophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12c):
Yellow solid, m. p. 196-200 °C; 1H NMR (400 MHz, CDCl₃) δ: 1.95-2.03 (m, 2H, CH₂), 2.37-2.41 (m, 2H, CH₂), 2.56-2.66 (m, 2H, CH₂), 4.39 (s, 1H, CH), 4.54 (s, 2H, NH₂), 7.15 (d, J=16.0Hz, 2H, Ar-H), 7.44 (d, J=16.0Hz, Ar-H) ppm

**2-amino-4-(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12d):**

Yellow solid, m. p. 189-191 °C (reported m. p. 186-189°C); 1H NMR (400 MHz, CDCl₃) δ: 1.69-2.06 (m, 2H, CH₂), 2.28-2.40 (m, 2H, CH₂), 2.51-2.63 (m, 2H, CH₂), 3.76(s, 3H, OCH₃), 4.38 (s, 1H, CH), 4.49 (s, 2H, NH₂), 6.80 (d, J=12.0Hz, 2H, Ar-H), 7.12 (d, J=8.0Hz, 2H Ar-H)

**2-amino-5-oxo-4-(p-tolyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12e):**

Yellow solid, m. p. 228-230 °C; 1H NMR (400 MHz, CDCl₃) δ: 1.95-2.09 (m, 2H, CH₂), 2.29 (s, 3H, CH₃), 2.35-2.39 (m, 2H, CH₂), 2.54-2.64(m, 2H, CH₂), 4.38(s, 1H, CH), 4.48 (s, 2H, NH₂), 7.05-7.13 (m, 4H, Ar-H). **2-amino-5-oxo-4-propyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12f):**
Yellow solid, m. p. 200-205 °C; 1H NMR (400 MHz, CDCl₃) δ: 0.88 (t, 3H, CH₃), 0.95-1.07 (m, 2H, CH₂), 1.40-1.62 (m, 2H, CH₂), 1.93-2.06 (m, 1H, CHH), 2.31-2.53 (m, 3H, CH₂ CHH), 4.40 (t, 1H, CH), 4.48 (s, 2H, NH₂).

2-amino-4-(4-fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12g):

Yellow solid, m. p. 198-201 °C; 1H NMR (400 MHz, CDCl₃) δ: 1.94-2.07 (m, 2H, CH₂), 2.33-2.38 (m, 2H, CH₂), 2.51-2.63 (m, 2H, CH₂), 4.41 (s, 1H, CH), 4.57 (s, 2H, NH₂), 6.63-6.97 (m, 2H, Ar-H), 7.18-7.24 (m, 2H, Ar-H) ppm.

2-amino-4-(4-bromophenyl)-7-methyl-5-oxo-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile (11a):

Yellow solid, m. p. 239-242 °C (reported m. p. 240-242 °C); 1H NMR (CDCl₃, 400 MHz) δ: 2.23 (s, 3H, CH₃), 4.31 (s, 1H, CH), 4.57 (br.s, 2H, NH₂), 6.29 (s, 1H, =CH), 7.17 (d, 2H, J = 8.4 Hz, ArH), 7.51 (d, 2H, J = 8.4 Hz, ArH).
Yellow solid, m. p. 218-220°C (reported m. p. 220-222°C); 1H NMR (400 MHz, CDCl$_3$) δ: 0.91(t, 3H, CH$_3$), 1.09-1.20 (m, 1H, CH/H), 1.33-1.34 (m, 1H, CH/H), 1.61-1.66 (m, 1H, CH/H), 1.75-1.80 (m, 1H, CH/H), 2.24 (s, 3H, CH$_3$), 3.50(s, 1H, CH), 4.67 (br.s, 2H, NH$_2$), 5.82 (s, 1H, =CH).

2-amino-7-methyl-5-oxo-4,5-dihydropyran[4,3-b]pyran-3-carbonitrile (11c):

White solid, m. p. 236-238 (reported m. p. 237-239°C); 1H NMR (CDCl$_3$, 400 MHz) δ: 2.08(s, 3H, CH$_3$), 4.27(s, 1H, CH), 5.61 (br.s, 2H, NH$_2$), 5.79 (s, 1H, =CH), 7.05-7.15 (m, 5H, Ar-H).

2-amino-4-(4-methoxyphenyl)-7-methyl-5-oxo-4,5-dihydropyran[4,3-b]pyran-3-carbonitrile (11d):

Colourless crystals, m. p. 222-224°C (reported m. p. 223-225°C). 1H NMR (CDCl$_3$, 400 MHz) δ: 2.25(s, 3H, CH$_3$), 3.79 (s, 3H, OCH$_3$), 4.44 (s, 2H, CH), 5.91(s, 2H, NH$_2$), 5.79 (s, 1H, =CH), 6.83-6.87 (m, 2H, Ar-H), 7.01-7.28 (m, 2H, Ar-H).
Representative spectral data

Figure 1. $^1$H NMR of 3 in DMSO-$d_6$

Figure 2. $^{13}$C NMR of 3 in DMSO-$d_6$
Figure 3. $^1$H NMR of 7f in DMSO-$d_6$.

Figure 4. $^{13}$C NMR of 7f in DMSO-$d_6$. 
Figure 5. $^1$H NMR of 9a in DMSO-$d_6$.

Figure 6. $^1$H NMR of 9f in DMSO-$d_6$.
Figure 7. $^{13}$C NMR of 9f in DMSO-$d_6$

Figure 8. $^1$H NMR of 9g in DMSO-$d_6$
Figure 9. $^1$H NMR of 9k in DMSO-$d_6$

Figure 10. $^1$H NMR of 9k in DMSO-$d_6$
Figure 11. $^{13}$C NMR of 9k in DMSO-$d_6$

Figure 12 $^1$H NMR of 12a in CDCl$_3$
Figure 13 $^1$H NMR of 12b in CDCl$_3$

Figure 14 $^1$H NMR of 12c(a) in CDCl$_3$
**Figure 15** $^1$H NMR of 12c(b) in CDCl$_3$

**Figure 16.** $^1$H NMR of 12d in CDCl$_3$
Figure 17. $^1$H NMR of 12e in CDCl$_3$

Figure 18. $^1$H NMR of 12f in CDCl$_3$
Figure 19. $^1$H NMR of 12g in CDCl$_3$

Figure 20. $^1$H NMR of 11b in CDCl$_3$
Figure 21. $^1$H NMR of 11e in CDCl$_3$

References