

A green one-pot three-component synthesis of tetrahydrobenzo [b]pyran and 3,4-dihydropyrano[c]chromene derivatives using $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -imid-PMAⁿ magnetic nanocatalyst under ultrasonic irradiation and reflux conditions

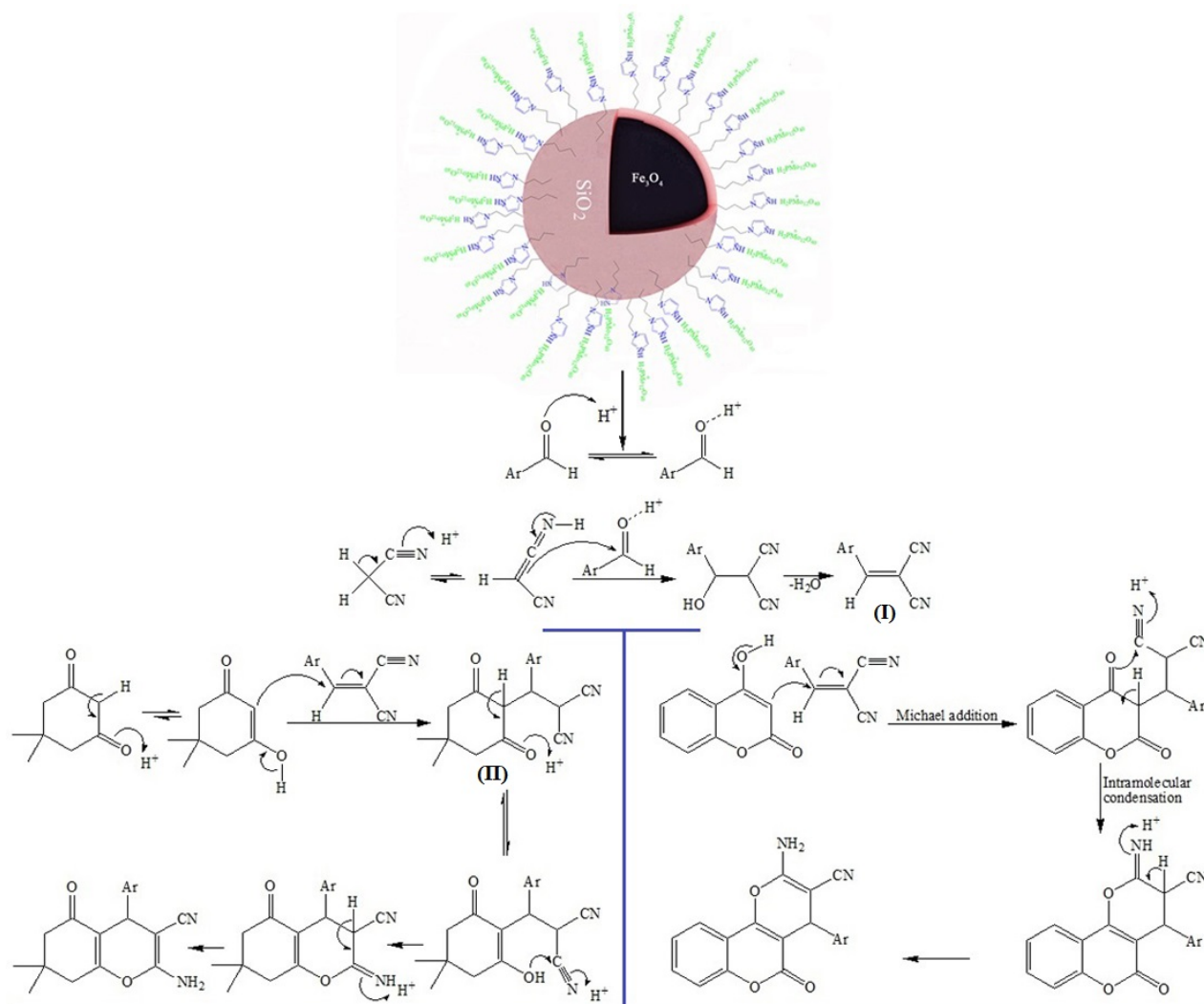
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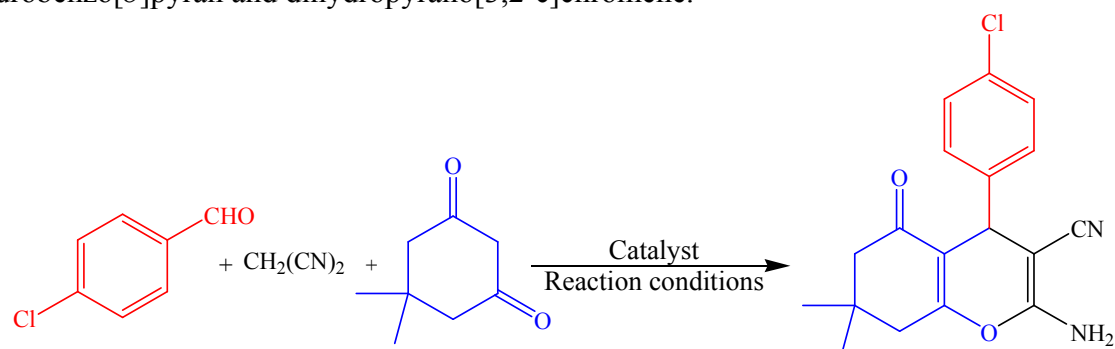
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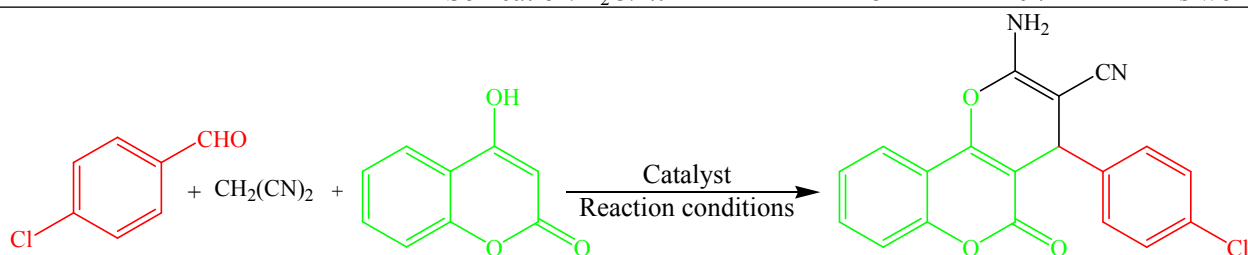


S1: Plausible mechanism for the synthesis of tetrahydrobenzo [b]pyrans and dihydropyrano [3,2-c]chromenes catalyzed by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -imid-PMAⁿ nanoparticles

S2: Comparison between different catalysts/reagents with Fe₃O₄@SiO₂-imid-PMAⁿ in synthesis of tetrahydrobenzo[*b*]pyran and dihydropyrano[3,2-*c*]chromene.



Entry	Catalyst	Condition	Time (min)	Yield (%)	Ref.
1	SO ₄ ²⁻ /MCM-41	EtOH/Reflux	60	80	[47]
2	Fe ₃ O ₄ @SiO ₂ @NH-NH ₂ -PW	H ₂ O/Reflux	25	92	[48]
3	NH ₄ H ₂ PO ₄ /Al ₂ O ₃	Solvent free/80°C	30	88	[26]
4	Sodium selenate	EtOH/H ₂ O/Reflux	180	90	[49]
5	Phenylboronic acid	EtOH/H ₂ O/Reflux	30	84	[50]
6	Molecular iodine	DMSO/120°C	210	88	[51]
7	NH ₄ Al(SO ₄) ₂ ·12H ₂ O	EtOH/Reflux	120	94	[52]
8	CaCl ₂	Ultrasonic/EtOH/r.t	8	96	[53]
9	La _{0.7} Sr _{0.3} MnO ₃	Ultrasonic/EtOH/r.t	9	97	[54]
10	KF/Al ₂ O ₃	Ultrasonic/EtOH/r.t	30	96	[55]
11	n-TiO ₂ /H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	Ultrasonic/EtOH/40°C	15	94	[20]
12	Nano titania sulfuric acid	Ultrasonic/EtOH/40°C	15	94	[56]
13	TBAB	H ₂ O/Reflux	30	95	[57]
14	KF-Al ₂ O ₃	DMF/Reflux	180	81	[12b]
15	NaBr	solvent free/MW/70°C	10	90	[13]
16	Fe ₃ O ₄ NPs/MWCNTs	MW/40°C	25	98	[23]
17	H ₃ PMO ₁₂ O ₄₀ (PMA ^b)	H ₂ O/Reflux	25	76	This work
		Sonication/H ₂ O/r.t	8	80	This work
18	Nano H ₃ PMO ₁₂ O ₄₀ (PMA ⁿ)	H ₂ O/Reflux	15	88	This work
		Sonication/H ₂ O/r.t	5	95	This work
19	Fe ₃ O ₄ @SiO ₂ -Imid- PMA ⁿ	H ₂ O/Reflux	10	95	This work
		Sonication/H ₂ O/r.t	5	97	This work



20	Silicotungstic acid	EtOH /Reflux	60	38	[17]
21	<i>p</i> -Toluenesulfonic acid	EtOH /Reflux	60	35	[58]
22	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	EtOH/H ₂ O	90	74	[59]
23	H ₆ P ₂ W ₁₈ O ₆₂ ·18H ₂ O	EtOH/H ₂ O/Reflux	45	80	[59]
24	Sulfamic acid	H ₂ O/Reflux	600	45	[60]
25	SiO ₂ -Pr-SO ₃ H	EtOH/H ₂ O	30	100	[61]
26	PBBS	EtOH/H ₂ O/Reflux	180	90	[62]
27	TBBDA	EtOH/H ₂ O/Reflux	195	89	[62]
28	Nano zinc oxide	EtOH /Reflux	90	49	[58]

29	Nano aluminum oxide	EtOH /Reflux	120	71	[58]
30	Nano aluminum hydroxide	EtOH /Reflux	120	48	[58]
31	DMAP	EtOH /Reflux	5	94	[63]
32	HMTA	EtOH /Reflux	40	95	[58]
33	TBAB	H ₂ O/Reflux	45	93	[63]
34	S-proline	EtOH/H ₂ O/100°C	180	78	[64]
35	H ₃ PMO ₁₂ O ₄₀ (PMA ^b)	H ₂ O/Reflux	35	82	This work
		Sonication/H ₂ O/r.t	10	90	This work
36	Nano H ₃ PMO ₁₂ O ₄₀ (PMA ⁿ)	H ₂ O/Reflux	15	97	This work
		Sonication/H ₂ O/r.t	6	96	This work
37	Fe ₃ O ₄ @SiO ₂ -Imid- PMA ⁿ	H ₂ O/Reflux	12	95	This work
		Sonication/H ₂ O/r.t	5	96	This work

S3: Selected spectral data

2-Amino-3-cyano-4-(phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4a**): White solid, mp. 238-240 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 0.94 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 2.08 (d, 1H, *J* = 16.10 Hz), 2.23 (d, 1H, *J* = 16.10 Hz), 2.50 (m, 2H, CH₂), 4.11 (s, 1H, CH), 7.06 (s, 2H, NH₂), 7.19 (m, 3H, Ar-H), 7.33 (m, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃) δ: 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): 3390, 3321, 3179, 2951, 2191, 1678, 1655, 1358; Anal. Calcd. for C₁₈H₁₈N₂O₂ (%): C, 73.45; H, 6.16; N, 9.52%; Found: C, 73.37; H, 6.21; N, 9.59.

2-Amino-3-cyano-4-(4-methylphenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4b**): White solid, mp. 212-214 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 0.96 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 2.10 (d, 1H, *J* = 16.00 Hz), 2.25 (d, 1H, *J* = 16.00 Hz), 2.26 (s, 3H, CH₃), 2.52 (s, 2H, CH₂), 4.14 (s, 1H, CH), 6.96 (s, 2H, NH₂), 7.03 (d, 2H, *J* = 8.20 Hz), 7.54 (d, 2H, *J* = 8.20 Hz); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 21.46, 27.65, 29.29, 32.66, 36.06, 50.88, 59.36, 113.77, 120.61, 127.95, 129.74, 136.48, 142.69, 159.31, 163.14, 196.47; IR (KBr, cm⁻¹): 3391, 3207, 2193, 1682, 1638, 1597, 1484, 1412; Anal. Calcd. for C₁₉H₂₀N₂O₂ (%): C, 74.03; H, 6.49; N, 9.09; Found: C, 74.14; H, 6.37; N, 9.14.

2-Amino-3-cyano-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4d**): Pale yellow solid, mp. 201-203 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 0.96 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 2.11 (d, 1H, *J* = 16.00 Hz), 2.25 (d, 1H, *J* = 16.00 Hz), 2.50 (s, 1H, *J* = 2.50 Hz), 2.51 (s, 1H, *J* = 2.50 Hz), 3.72 (s, 3H, OCH₃), 4.14 (s, 1H, CH), 6.85 (d, 2H, *J* = 8.60 Hz), 6.95 (s, 2H, NH₂), 7.07 (d, 2H, *J* = 8.60 Hz); ¹³C NMR (100 MHz, DMSO-*d*₆) 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): 3371, 3321, 2960, 2191, 1679, 1657, 1606, 1209; Anal. Calcd. for C₁₉H₂₀N₂O₃ (%): C, 70.37; H, 6.17; N, 8.64. Found: C, 70.29; H, 6.28; N, 8.55.

2-Amino-3-cyano-4-(3-methoxyphenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4e**): Yellow solid, mp. 200–201 °C; ¹H NMR (400 MHz, CDCl₃) δ: 1.08 (s, 3H, CH₃), 1.14 (s, 3H, CH₃), 2.26 (d, 2H, *J* = 18.00 Hz, CH₂), 2.47 (d, 2H, *J* = 19.4 Hz, CH₂), 3.81 (m, 3H, OCH₃), 4.40 (s, 1H, CH), 4.57 (s, 2H, NH₂), 7.30-6.76 (m, 4H, Ar-H); ¹³C NMR (100 MHz, CDCl₃) δ: 27.7, 28.8, 32.2, 35.4, 40.6, 50.6, 55.2, 63.5, 112.3, 113.5, 113.9, 118.6, 119.9, 129.6, 144.8, 157.4, 159.7, 161.6, 195.8; IR (KBr, cm⁻¹): 3394, 3290, 2295, 1679, 1385.

2-Amino-3-cyano-4-(4'-N,N-dimethylaminophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4f**): Yellow solid, mp. 207-209 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 0.95 (s, 3H, CH₃), 1.06 (s, 3H, CH₃), 2.09 (d, 1H), 2.25 (d, 1H), 2.53 (s, 2H, CH₂), 2.84 (s, 6H, (CH₃)₂), 4.04 (s, 1H, CH), 6.88 (s, 2H, NH₂), 6.62-6.64 (d, 2H, Ar-H), 6.93-6.95 (d, 2H, Ar-H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 27.2, 28.9, 32.2, 39.9, 128.1, 40.6, 50.5, 59.4, 112.8, 120.4, 132.9, 149.7, 158.8,

162.3, 196.1; IR (KBr, cm^{-1}): 2960, 2189, 1687, 1654, 1607, 13381; Anal. Calcd. for $\text{C}_{20}\text{H}_{23}\text{N}_3\text{O}_2$ (%): C, 71.22; H, 6.82; N, 8.31, Found: C, 71.10; H, 6.92; N, 8.39.

2-Amino-3-cyano-4-(3,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4g**): Pale yellow solid, mp. 229- 231 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 0.97 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.12 (d, 1H), 2.24 (d, 1H), 2.50 (s, 2H), 3.71 (d, 6H, $(\text{OCH}_3)_2$), 4.13 (s, 1H, CH), 6.64-6.67 (dd, 1H, Ar-H), 6.69-6.70 (d, 1H, Ar-H), 6.86-6.88 (d, 1H, Ar-H), 6.95 (s, 2H, NH_2); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 27.1, 28.9, 32.2, 39.9, 40.5, 50.4, 55.92, 55.96, 59.0, 112.2, 113.3, 119.5, 137.7, 148.9, 158.8, 162.7, 196.1; IR (KBr, cm^{-1}): 3391, 2957, 2192, 1680, 1659, 1601; Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_4$ (%): C, 67.81; H, 6.48; N, 7.89, Found: C, 67.69; H, 6.56; N, 7.84.

2-Amino-3-cyano-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4k**): White solid, mp. 212–213 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 0.96 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.12 (d, 1H, $J = 16.00$ Hz), 2.26 (d, 1H, $J = 16.00$ Hz), 2.51 (brs, 2H), 4.22 (s, 1H, CH), 7.05 (s, 2H, NH_2), 7.19 (d, 2H, $J = 8.40$ Hz), 7.35 (d, 2H, $J = 8.40$ Hz); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) 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}): 3381, 3184, 2960, 2189, 1676, 1638, 1493, 1363, 1215 ; Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{ClN}_2\text{O}_2$ (%): C, 65.85; H, 5.18; N, 8.54, Found: C, 65.72; H, 5.09; N, 8.61.

2-Amino-3-cyano-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4l**): Pale yellow solid, mp. 213-214 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 0.98 (s, 3H, CH_3), 1.07 (s, 3H CH_3), 2.09 (d, 1H), 2.27 (d, 1H), 2.53(s, 2H), 4.70 (s, 1H), 7.03 (s, 2H, NH_2), 7.17-7.22 (m, 2H, Ar-H), 7.26-7.30 (m, 1H, Ar-H), 7.36-7.38 (dd, 1H, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 27.3, 28.8, 32.3, 39.4, 40.5, 50.4, 57.3, 112.2, 119.7, 128.6, 129.9, 130.4, 142.0, 159.1, 163.6, 196.0; IR (KBr, cm^{-1}): 3393, 3331, 2955, 2200, 1680, 1642, 1485, 1367, 1213; Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{ClN}_2\text{O}_2$: C, 65.85; H, 5.18; N, 8.54, Found: C, 65.70; H, 5.27; N, 8.57.

2-Amino-3-cyano-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4m**): Yellow solid, mp. 179-181 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 0.97 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.12 (d, 1H, $J = 16.00$ Hz), 2.27 (d, 1H, $J = 16.00$ Hz), 2.54 (brs, 2H), 4.38 (s, 1H), 7.18 (s, 2H, NH_2), 7.46 (d, 2H, $J = 8.60$ Hz), 8.18 (d, 2H, $J = 8.60$ Hz); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) 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}): 3408, 3320, 2967, 2189, 1653, 1628, 1591, 1518, 1212; Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_4$ (%): C, 63.72; H, 5.01; N, 8.26, Found: C, 63.59; H, 4.92; N, 8.33.

2-Amino-3-cyano-4-(3-nitrophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4n**): Yellow solid, mp. 209-211 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 0.97 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.13 (d, 1H, $J = 16.00$ Hz), 2.27 (d, 1H, $J = 16.0$ Hz), 2.56 (s, 2H, CH_2), 7.18 (s, 2H, NH_2), 7.62 (t, 1H, $J = 7.9$ Hz, Ar-H), 7.68 (d, 1H, $J = 7.8$ Hz, Ar-H), 7.99 (s, 1H, Ar-H), 8.09 (d, 1H, $J = 8.1$ Hz, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 27.6, 29.2, 32.7, 36.3, 50.7, 58.1, 112.7, 120.2, 122.5, 122.6, 130.8, 135.0, 147.9, 148.7, 159.5, 164.0, 196.6; IR (KBr, cm^{-1}): 3429, 3319, 2951, 2183, 1666, 1603, 1527, 1373, 1347, 1249, 1209, 1135, 1040; Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_4$ (%): C, 63.72; H, 5.01; N, 8.26, Found: C, 63.61; H, 5.08; N, 8.36.

2-Amino-3-cyano-4-(2-nitrophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4o**): Yellow solid, mp. 237-238 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 0.88 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 2.03 (d, 1H), 2.22 (d, 1H), 2.55 (s, 2H, CH_2), 4.94 (s, 1H, CH), 7.19 (s, 2H, NH_2), 7.35-7.38 (dd, 1H, Ar-H), 7.42-7.44 (m, 1H, Ar-H), 7.64-7.68 (m, 1H, Ar-H), 7.80-7.83 (dd, 1H, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 27.1, 28.7, 32.3, 39.4, 40.5, 50.0, 56.8, 112.7, 119.5, 124.1, 128.3, 130.7, 149.4, 159.6, 163.2, 196.3; IR (KBr, cm^{-1}): 3471, 3315, 3076, 2194, 1688, 1665, 1597, 1526, 1216; Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_4$ (%): C, 63.72; H, 5.01; N, 8.26, Found: C, 63.84; H, 4.92; N, 8.35.

2-Amino-3-cyano-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (**4q**): White solid, mp. 227-228 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 0.96 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.13 (d, 1H, $J = 16.00$ Hz), 2.26 (d, 1H, $J = 16.00$ Hz), 2.53 (s, 2H, CH_2), 4.31 (s, 1H, CH), 7.16 (s, 2H,

NH₂), 7.37 (d, 2H, *J* = 8.10 Hz, Ar-H), 7.77 (d, 2H, *J* = 8.10 Hz, Ar-H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 27.8, 29.1, 32.7, 36.7, 50.7, 58.0, 110.3, 112.6, 119.6, 120.2, 129.2, 133.3, 151.1, 159.5, 163.9, 196.5; IR (KBr, cm⁻¹): 3348, 3187, 2225, 2189, 1685, 1593, 1215.

2-Amino-3-cyano-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (**4r**): White solid, mp. 188–189 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 0.94 (s, 3H, CH₃), 1.03 (s, 3H, CH₃), 2.12 (d, 1H), 2.26 (d, 1H), 2.51 (s, 2H), 4.20 (s, 1H), 7.03 (s, 2H, NH₂), 7.09–7.13 (m, 2H, Ar-H), 7.17–7.20 (m, 2H, Ar-H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 27.3, 28.7, 32.2, 39.4, 40.4, 50.4, 58.5, 113.0, 115, 120.1, 129.5, 141.1, 158.9, 196.1; IR (KBr, cm⁻¹): 3341, 2959, 2195, 1671, 1653, 1601 1212;

Anal. Calcd. for C₁₈H₁₇FN₂O₂(%): C, 69.23; H, 5.45; N, 8.97, Found: C, 69.15; H, 5.56; N, 8.91.

2-Amino-3-cyano-4-(thiophen-2-yl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (**4w**): Yellow solid, mp. 221–222 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 0.99 (s, 3H, CH₃), 1.05 (s, 3H, CH₃), 2.31 (m, 2H, CH₂), 2.49 (m, 2H, CH₂), 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, NH₂); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 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): 3401, 3211, 2973, 2202, 1686, 1664, 1201; Anal. Calcd. for C₁₆H₁₆N₂O₂S (%): C, 64.14; H, 5.33; N, 9.41, Found: C, 64.20; H, 5.25; N, 9.39.

2-Amino-3-cyano-4-(furan-2-yl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (**4x**): white solid, mp. 219–221 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 0.99 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 2.18 (m, 2H, CH₂), 2.47 (m, 2H, CH₂), 4.32 (s, 1H, CH), 6.06 (d, 1H, *J* = 3.90 Hz, Ar-H), 6.32 (dd, 1H, *J* = 3.90, 1.80 Hz, Ar-H), 7.08 (s, 2H, NH₂), 7.48 (d, 1H, *J* = 3.9 Hz, Ar-H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 27.4, 29.5, 31.3, 32.7, 50.8, 59.0, 113.9, 120.5, 124.8, 125.3, 127.8, 150.2, 159.7, 163.5, 196.5; IR (KBr, cm⁻¹): 3393, 3201, 2966, 2203, 1680, 1661, 1602, 1195; Anal. Calcd. for C₁₆H₁₆N₂O₃ (%): C, 67.59; H, 5.67; N, 9.85, Found: C, 67.68; H, 5.58; N, 9.79.

2-Amino-4-(phenyl)-4,5-dihydro-5-oxopyrano[3,2-*c*]chromene-3-carbonitrile (**6a**): White solid, mp. 260–261 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 4.46 (1H, s, CH), 7.25 (2H, d, *J* = 7.80 Hz, Ar-H), 7.28 (1H, m, Ar-H), 7.33 (2H, t, *J* = 7.50 Hz, Ar-H), 7.42 (2H, br s, NH₂), 7.45 (1H, d, *J* = 8.40 Hz, Ar-H), 7.49 (1H, t, *J* = 7.6 Hz, Ar-H), 7.71 (1H, t, *J* = 7.50 Hz, Ar-H), 7.91 (1H, d, *J* = 7.60 Hz, Ar-H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 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): 3387, 3275, 3177, 2188, 1707, 1671, 1609; Anal. Calcd for C₁₉H₁₂N₂O₃ (%): C, 72.15; H, 3.79; N, 8.86, Found: C, 72.26; H, 3.68; N, 8.80.

2-Amino-4-(4-methoxyphenyl)-4,5-dihydro-5-oxopyrano[3,2-*c*]chromene-3-carbonitrile (**6b**): White solid, mp. 244–246 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 3.72 (3H, s, OCH₃), 4.40 (1H, s, CH), 6.87 (2H, d, *J* = 8.15 Hz, Ar-H), 7.18 (2H, d, *J* = 8.15 Hz, Ar-H), 7.37 (2H, br s, NH₂), 7.45 (1H, d, *J* = 8.10 Hz, Ar-H), 7.49 (1H, t, *J* = 7.85 Hz, Ar-H), 7.70 (1H, t, *J* = 7.70 Hz, Ar-H), 7.89 (1H, d, *J* = 7.7 Hz, Ar-H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 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): 3381, 3311, 3184, 2189, 1711, 1668, 1607; Anal. Calcd for C₂₀H₁₄N₂O₄ (%): C, 69.36; H, 4.05; N, 8.09, Found: C, 69.27; H, 4.11; N, 8.03.

2-Amino-4-(4-hydroxyphenyl)-4,5-dihydro-5-oxopyrano[3,2-*c*]chromene-3-carbonitrile (**6d**): Yellow solid, mp. 261–263 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 4.33 (1H, s, CH), 6.71 (2H, d, *J* = 8.60 Hz, Ar-H), 7.06 (2H, d, *J* = 8.80 Hz, Ar-H), 7.36 (2H, s, NH₂), 7.43–7.49 (2H, m, Ar-H), 7.69 (1H, dt, *J*₁ = 7.60 Hz, *J*₂ = 1.80 Hz, Ar-H), 7.89 (1H, dd, *J*₁ = 7.60 Hz, *J*₂ = 1.60 Hz, Ar-H), 9.41 (1H, s, O-H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 58.8, 104.9, 113.4, 115.6, 116.9, 119.9, 122.9, 125.1, 129.2, 133.2, 134.2, 152.5, 153.4, 156.8, 158.3, 160.0; IR (KBr, cm⁻¹): 3390, 3283, 3172, 2185, 1703, 1666, 1605.

2-Amino-4-(3,4,5-trimethoxyphenyl)-4,5-dihydro-5-oxopyrano[3,2-*c*]chromene-3-carbonitrile (**6i**): Yellow solid, mp. 234–236 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 3.63 (3H, s, CH₃), 3.71 (6H, s, CH₃), 4.43 (1H, s, CH), 6.52 (2H, s, NH₂), 7.37–7.93 (6H, m, Ar-H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 37.8, 56.1, 58.2, 60.4, 104.1, 105.4, 113.6, 117.0, 119.7, 123.0, 125.1, 133.3, 137.1, 139.4, 152.6,

153.3, 154.0, 158.5, 160.1; IR (KBr, cm^{-1}): 3413, 3309, 2187, 1668, 1601, 1373, 1151; Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_6$ (%): C, 65.02; H, 4.46; N, 6.89, Found: C, 64.90; H, 4.32; N, 6.96.

2-Amino-4-(4-bromophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile (**6j**): Yellow solid, mp. 250-251°C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 4.48 (1H, s, CH), 7.25 (2H, d, J = 8.00 Hz, Ar-H), 7.47-7.52 (4H, m), 7.73 (1H, t, J = 7.20 Hz, Ar-H), 7.91 (1H, d, J = 7.40 Hz, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 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}): 3371, 2166, 1705, 1670, 1612, 1371, 1057.

2-amino-4-(4-chlorophenyl)-5-oxo-4H, 5H-pyrano[3,2-c]chromene- 3-carbonitrile (**6k**): White solid, mp. 265-267 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 4.50 (1H, s, CH), 7.31 (2H, d, J = 8.00 Hz, Ar-H), 7.36 (2H, br s, NH_2), 7.38 (2H, br s, Ar-H), 7.44 (1H, d, J = 8.00 Hz, Ar-H), 7.49 (1H, t, J = 7.6 Hz, Ar-H), 7.71 (1H, t, J = 7.80 Hz, Ar-H), 7.92 (1H, d, J = 7.80 Hz, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 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}): 3385, 2139, 1717, 1672, 1609, 1374, 1059, 763; Anal. Calcd for $\text{C}_{19}\text{H}_{11}\text{N}_2\text{O}_3\text{Cl}$ (%): C, 65.05; H, 3.14; N, 7.99, Found: C, 64.93; H, 3.08; N, 8.13.

2-amino-4-(2,4-dichlorophenyl)-5-oxo-4H, 5H-pyrano[3,2-c]chromene- 3-carbonitrile (**6m**): White solid, mp = 260–261 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 4.99 (1H, s, CH), 7.36 (1H, dd, J_1 = 8.25 Hz, J_2 = 1.90 Hz, Ar-H), 7.40 (1H, d, J = 8.25 Hz, Ar-H), 7.41 (2H, br s, NH_2), 7.46 (1H, d, J = 8.25 Hz, Ar-H), 7.51 (1H, t, J = 7.80 Hz, Ar-H), 7.56 (1H, d, J = 2.10 Hz, Ar-H), 7.73 (1H, t, J = 8.25 Hz, Ar-H), 7.92 (1H, d, J = 8.70 Hz, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 57.1, 103.4, 113.7, 117.5, 119.4, 123.4, 125.6, 128.7, 129.7, 132.9, 133.3, 133.9, 134.3, 140.3, 153.1, 155.1, 159.0, 160.2; IR (KBr, cm^{-1}): 3451, 3284, 3152, 3067, 2191, 1712, 1667, 1594; Anal. Calcd. for $\text{C}_{19}\text{H}_{10}\text{N}_2\text{O}_3\text{Cl}_2$ (%): C, 59.22; H, 2.60; N, 7.27, Found: C, 59.15; H, 2.51; N, 7.38.

2-amino-4-(4-fluorophenyl)-5-oxo-4H, 5H-pyrano[3,2-c]chromene- 3-carbonitrile (**6n**): White solid, mp. 260 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 4.47 (1H, s, CH), 7.07 (2H, dd, J_1 = 8.20 Hz, J_2 = 8.00 Hz, Ar-H), 7.31 (2H, dd, J_1 = 8.20 Hz, J_2 = 7.80 Hz, Ar-H), 7.38 (2H, br s, NH_2), 7.41 (1H, d, J = 8.25 Hz, Ar-H), 7.46 (1H, t, J = 7.60 Hz, Ar-H), 7.67 (1H, t, J = 7.5 Hz, Ar-H), 7.88 (1H, d, J = 7.50 Hz, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 36.3, 57.9, 103.8, 112.9, 115.1, 116.5, 119.0, 123.5, 129.6, 132.8, 139.4, 152.1, 153.4, 157.9, 159.4, 160.2, 162.2; IR (KBr, cm^{-1}): 3386, 3281, 2186, 1711, 1668, 1603, 1501.

2-Amino-4-(4-cyanophenyl)-5-oxo-4H,5H-pyrano- [3,2-c]chromene-3-carbonitrile (**6o**): Light yellow solid, mp. 281-283 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 4.60 (1H, s, CH), 7.46-7.52 (6H, m, Ar-H, NH_2), 7.73 (1H, t, J = 7.00 Hz, Ar-H), 7.78 (2H, t, J = 8.00 Hz, Ar-H), 7.91 (1H, d, J = 8.00 Hz, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 37.0, 56.9, 102.8, 109.9, 112.9, 116.6, 118.8, 118.8, 122.6, 124.7, 128.9, 132.5, 133.1, 148.7, 152.2, 153.9, 158.0, 159.5; IR (KBr, cm^{-1}): 3439, 3317, 2231, 2193, 1721, 1674, 1605, 1467, 1378, 1261, 1158.

2-Amino-4-(4-nitrophenyl)-5-oxo-4H,5H-pyrano- [3,2-c]chromene-3-carbonitrile (**6p**): Pale yellow solid, mp. 252-254 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 4.68 (1H, s, CH), 7.47 (1H, d, J = 8.00 Hz, Ar-H), 7.52 (1H, t, J = 7.80 Hz, Ar-H), 7.57 (2H, br s, NH_2), 7.60 (2H, d, J = 8.00 Hz, Ar-H), 7.74 (1H, t, J = 7.80 Hz, Ar-H), 7.91 (1H, d, J = 7.80 Hz, Ar-H), 8.18 (2H, d, J = 8.00 Hz, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 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}): 3477, 3422, 3369, 3323, 2190, 1711, 1666, 1609, 1518, 1379, 1292; Anal. Calcd for $\text{C}_{19}\text{H}_{11}\text{N}_3\text{O}_5$ (%): C, 63.16; H, 3.05; N, 11.63, Found: C, 63.04; H, 3.17; N, 11.71.

2-Amino-4-(3-nitrophenyl)-5-oxo-4H,5H-pyrano- [3,2-c]chromene-3-carbonitrile (**6q**): White solid, mp. 266-267 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 4.74 (1H, s, CH), 7.44 (1H, d, J = 6.50 Hz, Ar-H), 7.51 (1H, t, J = 7.50 Hz, Ar-H), 7.55 (2H, br s, NH_2), 7.64 (1H, t, J = 7.50 Hz, Ar-H), 7.73 (1H, dt, J_1 = 7.50 Hz, J_2 = 1.25 Hz, Ar-H), 7.82 (1H, d, J = 6.75 Hz, Ar-H), 7.92 (1H, dd, J_1 = 6.50 Hz, J_2 = 1.25 Hz, Ar-H), 8.12 (1H, dd, J_1 = 8.50 Hz, J_2 = 1.40 Hz, Ar-H), 8.14 (1H, s, Ar-H); ^{13}C NMR (100 MHz,

DMSO-*d*₆) δ : 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): 3387, 3317, 3188, 2192, 1701, 1669, 1526, 1354; Anal. Calcd for C₁₉H₁₁N₃O₅ (%): C, 63.16; H, 3.05; N, 11.63, Found C, 63.19; H, 2.96; N, 11.55.

2-Amino-4-(cyclohexyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (**6w**): White solid, mp. 283-285 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 0.95-1.19 (4H, m, CH₂), 1.31-1.39 (2H, m, CH₂), 1.58-1.75 (5H, m, CH₂, CH), 3.28 (1H, d, *J* = 7.50 Hz, CH), 7.32 (2H, br s, NH₂), 7.45-7.48 (2H, m, Ar-H), 7.70 (1H, t, *J* = 7.50 Hz, Ar-H), 7.82 (1H, d, *J* = 7.50 Hz, Ar-H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 26.0, 26.4, 26.6, 27.5, 30.7, 37.2, 43.7, 53.1, 105.1, 113.5, 117.1, 121.0, 122.6, 125.1, 133.2, 152.5, 155.2, 160.5, 161.1; IR (KBr, cm⁻¹): 3431, 3165, 2182, 1718, 1666, 1627, 1591, 1462, 1383, 1309, 1261.

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