Electronic supplementary information

Nanozeolite clinoptilolite as a highly efficient heterogeneous catalyst for the synthesis of various 2-amino-4*H*-chromene derivatives in aqueous media

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2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6a, Table 2, entry 1). White solid, M.p. 213-214 °C (lit. [31a] 215-217); IR (KBr, υ, Cm^{-1}): 3458 and 3323 (NH_2), 2184 (CN), 1656 (C=O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 0.95 and 1.04 (2s, 6H, $2CH_3$), 2.11 and 2.25 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.54 (s, 2H), 4.20 (s, 1H, CH), 7.08 (s, 2H, NH_2), 7.17 and 7.35 (2d, *J* = 8.2 Hz, 4H, $CH_{arom.}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.8, 28.4, 32.1, 36.2, 50.4, 58.3, 112.5, 119.2, 128.4, 129.1, 133.2, 143.6, 158.1, 162.2, 196.1; Anal. Calcd. for $C_{18}H_{17}ClN_2O_2$: C, 65.75; H, 5.21; N, 8.52. Found: 65.82, H, 5.32; N, 8.72.

2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6b, Table 2, entry 2). White solid, M.p. 212-213 °C (lit. [31b] 214-215); IR (KBr, υ, Cm^{-1}): 3372 and 3253 (NH_2), 2188 (CN), 1673 (C=O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 0.92 and 1.03 (2s, 6H, $2CH_3$), 2.09 and 2.22 (2d, *J* = 16.1 Hz, 2H, CH_2), 2.52 (s, 2H), 4.32 (s, 1H, CH), 7.03 (s, 2H, NH_2), 7.12 and 7.37 (2d, *J* = 8.7 Hz, 4H, $CH_{arom.}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 27.4, 28.6, 32.3, 35.1, 50.2, 58.6, 113.5, 115.4, 115.8, 119.7, 129.5, 129.6, 140.6, 141.3, 158.8, 160.2, 162.4, 196.3; Anal. Calcd. for $C_{18}H_{17}ClN_2O_2$: C, 65.75; H, 5.21; N, 8.52. Found: 65.74, H, 5.17; N, 8.61.

2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6c, Table 2, entry 3). Yellow solid, M.p. 178-180 °C (lit. [31c] 178-180); IR (KBr, υ, Cm^{-1}): 3382 and 3334 (NH_2), 2192 (CN), 1703 (C=O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ =0.95 and 1.05 (2s, 6H, $2CH_3$), 2.10 and 2.25 (2d, *J* = 15.8 Hz, 2H, CH_2), 2.48 (s, 2H), 4.36 (s, 1H, CH), 7.18 (s, 2H, NH_2), 7.45 and 8.12 (2d, *J* = 8.1 Hz, 4H, $CH_{arom.}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 27.1, 28.3, 34.5, 35.7, 49.9, 57.1, 112.1, 119.3, 124.1, 128.5, 146.3, 152.3, 158.7, 162.9, 195.8; Anal. Calcd. for $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38. Found: 63.72, H, 5.06; N, 12.33.

2-Amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6d, Table 2, entry 4). Yellow solid, M.p. 178-180 °C (lit. [31a] 178-180); IR (KBr, υ, Cm^{-1}): 3432 and 3335 (NH_2), 2172 (CN), 1669 (C=O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ =1.05 and 1.2 (2s, 6H, $2CH_3$), 2.17 and 2.28 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.52 (s, 2H), 4.46 (s, 1H, CH), 6.42 (s, 2H, NH_2), 7.48-7.53 (m, 1H), 7.65-7.70 (m, 1H) and 8.06-8.08 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 27.1, 28.3, 33.1, 34.8, 40.2, 48.7, 59.5, 117.8, 119.3, 121.2, 125.6, 132.2, 136.4, 143.2, 151.1, 158.2, 163.2, 195.4; Anal. Calcd. for $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38. Found: 63.75, H, 5.07; N, 12.35.

Ethyl 2-amino-7,7-dimethyl-5-oxo-4-(4-methylphenyl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (6e, Table 2, entry 5). White solid, M.p. 152-153 °C (lit. [31e] 153-154); IR (KBr, υ, Cm^{-1}): 3412 and 3285 (NH_2), 2985(CH), 1685 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 and 1.06 (2s, 6H, CH_3), 1.12 (t, *J* = 7.2 Hz, 3H, CH_3), 2.11 and 2.24 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.54 (s, 2H), 3.95 (q, *J* = 7.2 Hz, 2H, OCH_2), 4.65 (s, 1H, CH), 7.05 and 7.19 (d, *J* = 8.0 Hz, 2H, $CH_{arom.}$), 7.56 (s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 27.6, 29.3, 32.5, 33.7, 40.8, 50.9, 59.8, 81.1, 117.1,

128.2, 130.1, 131.9, 144.8, 159.5, 162.7, 169.1, 197.3 ppm. Anal. Calcd for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94; found C, 70.92; H, 6.97; N, 3.89.

Ethyl 2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (6f, Table 2, entry 6). Yellow solid, M.p. 152-154 °C (lit. [31g] 154-156); IR (KBr, υ, Cm^{-1}): 3453 and 3326 (NH_2), 2964 (CH), 1695 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 and 1.13 (2s, 6H, $2CH_3$), 1.19 (t, *J* = 7.2 Hz, 3H, CH_3), 2.25 and 2.30 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.73 (s, 2H), 4.52 (q, *J* = 7.2 Hz, 2H, OCH_2), 6.74 (s, 2H, NH_2), 7.42 (t, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 27.5, 29.2, 32.5, 34.4, 41.1, 51.3, 60.5, 80.4, 115.6, 122.0, 123.3, 128.5, 135.2, 147.4, 159.3, 163.4, 169.2, 197.6 ppm. Anal. Calcd. for $C_{20}H_{22}N_2O_6$: C, 62.17; H, 5.74; N, 7.25; found C, 62.12; H, 5.69; N, 7.12.

2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6g, Table 2, entry 7). White solid, M.p. 233-235 °C (lit. [31d] 234-235); IR (KBr, υ, Cm^{-1}): 3389 and 3215 (NH_2), 2961(CH), 2289 (CN), 1683 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ =0.98 and 1.07 (2s, 6H, $2CH_3$), 2.12 and 2.26 (2d, *J* = 16.2 Hz, 2H, CH_2), 2.24 (s, 2H), 4.15 (s, 1H, CH), 6.97 (s, 2H, NH_2), 7.11-7.32 (m, 5H, $CH_{arom.}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 25.8, 28.2, 32.1, 35.5, 38.5, 50.1, 58.2, 112.3, 119.4, 126.4, 127.3, 128.3, 145.6, 158.2, 163.5, 195.5. Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.35; H, 6.23; N, 9.63%.

2-Amino-7,7-dimethyl-5-oxo-4-p-tolyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6h, Table 2, entry 8). White solid, M.p. 221-223 °C (lit. [31e] 220-222); IR (KBr, υ, Cm^{-1}): 3428 and 3315 (NH_2), 2982(CH), 2187 (CN), 1652 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 096 and 1.05 (2s, 6H, $2CH_3$), 2.10 and 2.25 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.47 (s, 2H), 4.13 (s, 1H, CH), 6.98 (s, 2H, NH_2), 7.09 and 7.15 (2d, *J* = 8.2 Hz, 4H, $CH_{arom.}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.4, 28.4, 30.3, 36.2, 37.5, 50.6, 57.3, 58.3, 112.5, 116.2, 124.3, 129.1, 132.2, 136.5, 140.4, 164.6, 196.1; Anal. Calcd. for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08. Found: C, 73.90; H, 6.42; N, 9.12.

2-Amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6i, Table 2, entry 9). Yellow solid, M.p. 223-225 °C (lit. [31d] 224-226); IR (KBr, υ, Cm^{-1}): 3468 and 3298 (NH_2), 2971 (CH), 2198 (CN), 1679 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.96 and 1.05 (2s, 6H, $2CH_3$), 2.07 and 2.23 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.53 (s, 2H), 4.05 (s, 1H, CH), 6.59 (s, 2H, NH_2), 6.68 and 7.18 (2d, *J* = 8.2 Hz, 4H, $CH_{arom.}$), 9.27 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 27.4, 29.2, 33.2, 35.3, 41.4, 50.6, 59.7, 114.2, 115.5, 122.2, 128.5, 135.7, 157.1, 158.9, 163.5, 196.2; Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.55; H, 5.52; N, 9.18.

2-Amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6j, Table 2, entry 10). Yellow solid, M.p. 198-202 °C (lit. [31d] 201-202); IR (KBr, υ, Cm^{-1}): 3417 and 3184 (NH_2), 2984 (CH), 2195 (CN), 1688 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.94 and 1.04 (2s, 6H, $2CH_3$), 2.06 and 2.24 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.56 (s, 2H), 3.72 (s, 3H, OCH_3), 4.15 (s, 1H, CH), 6.95 (s, 2H, NH_2), 6.83 and 7.04 (2d, *J* = 8.7 Hz, 4H, $CH_{arom.}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.5, 28.2, 31.9, 35.1, 50.1, 55.2, 58.9, 112.5, 113.9, 119.7, 129.1, 135.7, 158.3, 158.9, 162.1, 195.5; Anal. Calcd. for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.42; H, 6.10; N, 8.70.

2-Amino-4-(3,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6k, Table 2, entry 11). White solid, M.p. 216-217 °C (lit. [31f] 216-218); IR (KBr, υ, Cm^{-1}): 3389 and 3258 (NH_2), 2954(CH), 2163 (CN), 1667 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.98 and 1.05 (2s, 6H, $2CH_3$), 2.18 and 2.50 (2d, *J* = 16.3 Hz, 2H, CH_2), 2.68 (s, 2H), 3.72 and 3.74 (2s, 6H, OCH_3), 4.11 (s, 1H, CH), 6.65 and 6.69 (2 dd, *J* = 1.9, 7.9 Hz, $2H_{arom.}$), 6.86 (d, *J* = 7.9 Hz, $1H_{arom.}$), 6.95 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.4, 28.2, 31.9, 35.3, 50.2, 55.3, 56.3, 58.7, 59.3, 109.3, 110.6, 116.5, 119.1, 126.4, 130.1, 136.1, 148.9, 152.6, 162.2, 196.0; Anal. Calcd. for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.69; H, 6.22; N, 7.94.

2-Amino-4-(4-(dimethylamino)phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6l, Table 2, entry 12). Yellow solid, M.p. 210-213 °C (lit. [31g] 210-212); IR (KBr, υ, Cm^{-1}): 3232 and 3157 (NH_2), 2955 (CH), 2193 (CN), 1684 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.95 and 1.03 (2s, 6H, $2CH_3$), 2.07 and 2.25 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.47 (s, 2H), 2.93 (s, 6H, NCH_3), 4.12 (s, 1H, CH), 6.72 and 7.02 (2d, *J* = 8.7 Hz, 4H, $CH_{arom.}$), 6.90 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.2, 28.5, 32.1, 35.5, 39.4, 40.2, 50.1, 59.3, 112.3, 113.5, 120.4, 126.8, 132.5, 150.2, 158.3, 162.5, 195.8; Anal. Calcd. for $C_{20}H_{23}N_3O_2$: C, 71.19; H, 6.87; N, 12.45. Found: C, 69.82; H, 6.78; N, 12.34.

Ethyl 2-amino-7,7-dimethyl-5-oxo-4-(4-methylphenyl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (6m, Table 2, entry 13). White solid, M.p. 152-153 °C (lit. [31g] 151-152); IR (KBr, υ, Cm^{-1}): 3418 and 3286 (NH_2), 2978 (CH), 1688 and 1677 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.95 and 1.06 (s, 6H, $2CH_3$), 1.22 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 2.15 (s, 1H, CH_3), 2.13 and 2.38 (2d, *J* = 16.2 Hz, 2H, CH_2), 2.44 (s, 2H), 3.93 (q, *J* = 7.2 Hz, 2H, OCH_2), 4.76 (s, 1H, CH), 7.03 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.64 (s, 2H, NH_2),; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 14.1, 22.4, 28.3, 30.3, 32.5, 33.8, 41.2, 51.4, 59.5, 82.1, 118.1, 128.2, 128.6, 134.9, 143.7, 158.2, 160.9, 168.7, 196.6; Anal. Calcd. for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94; found C, 70.89; H, 7.01; N, 3.87.

(*E*)-2-amino-7,7-dimethyl-5-oxo-4-styryl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6n, Table 2, entry 14). Yellow solid, M.p. 183-185 °C (lit. [31h] 182-184); IR (KBr, υ, Cm^{-1}): 3355 and 3145 (NH_2), 2979 (CH), 2173 (CN), 1696 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.98 and 1.13 (2s, 6H, CH_3), 2.26 and 2.38 (2d, *J* = 16.2 Hz, 2H, CH_2), 2.46 (s, 2H), 4.27 (s, 1H, CH), 6.13 (m, 1H, CH), 6.55 (dd, *J* = 10.5, 15.9 Hz, 1H, CH), 7.20-7.38 (m, 5H, $CH_{arom.}$); ^{13}C NMR (100 MHz, DMSO-d_6): 27.9, 28.3, 30.3, 35.3, 44.3, 56.1, 59.6, 109.6, 117.6, 124.9, 126.5, 128.8, 127.6, 128.9, 132.5, 139.6, 163.6, 159.5; Anal. Calcd. for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.85; H, 6.35; N, 8.69.

2-Amino-4-(furan-2-yl)-7,7-dimethyl -5-oxo-5, 6, 7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6o, Table 2, entry 15). Black solid, M.p. 220-223 °C (lit. [31i] 220-223); IR (KBr, υ, Cm^{-1}): 3326 and 3123 (NH_2), 2987 (CH), 2184 (CN), 1677 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.98 and 1.06 (2s, 6H, CH_3), 2.15 and 2.32 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.45 (s, 2H), 4.35 (s, 1H, CH), 6.04 (d, *J* = 3.2 Hz, 1H, CH), 6.30 (q, *J* = 1.7 Hz, 1H, CH), 7.02 (s, 2H, NH_2), 7.52 (d, *J* = 1.2 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): 26.2, 28.5, 29.1, 31.9, 50.2, 55.7, 106.1, 110.5, 110.8, 119.4, 142.3, 155.6, 159.3, 163.4, 195.5; Anal. Calcd. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.43; H, 5.72; N, 9.72.

2-Amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-4*H*-chromene-3-carbonitrile (6p, Table 2, entry 16). Yellow solid, M.p. 223-225 °C (lit. [31j] 224-226); IR (KBr, υ, Cm^{-1}): 3379 and 3135 (NH_2), 2965 (CH), 2192 (CN), 1686 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.97 and 1.05 (2s, 6H, CH_3), 2.25 and 2.42 (2d, *J* = 16.0 Hz, 2H, CH_2), 2.49 (s, 2H), 4.56 (s, 1H, CH), 6.79 (d, *J* = 3.2 Hz, 1H, CH), 6.87 (dd, *J* = 3.2, 5.2 Hz, 1H, CH), 7.15 (s, 2H, NH_2), 7.42 (d, *J* = 5.2 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): 27.5, 29.5, 31.3, 32.7, 50.6, 58.5, 113.7, 120.9, 124.7, 125.6, 128.2, 150.4, 159.6, 163.4, 196.5; Anal. Calcd. for $C_{16}H_{16}N_2O_2S$: C, 63.98; H, 5.37; N, 9.33. Found: C, 64.15; H, 5.31; N, 9.43.

2-Amino-6-(hydroxymethyl)-8-oxo-4-phenyl-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (8a, Table 3, entry 1). Colorless solid, M.p. 221-224 °C (lit. [32] 220–222); IR (KBr, υ, Cm^{-1}): 3369 and 3289 (NH_2), 3352 (OH), 2225 (CN), 1665 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.12 (dd, 1H, ^2J=16.4, ^4J = 6.0 Hz, CH_{aliph}), 4.25 (dd, 1H, ^2J= 16.0, ^4J = 6.0 Hz, CH_{aliph}), 5.32 (t, 1H, ^4J = 6.0 Hz, OH), 5.65 (s, 1H, CH_{vinyl}), 6.32 (s, 1H, CH_{aiiph}), 7.08 (s, 2H, NH_2), 7.24-7.55 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 40.4, 55.7, 57.6, 111.5, 117.4, 118.7,128.7, 131.0, 132.1, 135.2, 136.5, 148.1, 159.2, 168.4, 169.7, 195.6; Anal. Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.92; H, 4.12; N, 9.44. Found: C, 64.90; H, 4.10; N, 9.47.

2-Amino-4-(4-chlorophenyl)-6-(hydroxymethyl)-8-oxo-4,8-dihydropyrano[3,2-b]pyran-3-carbonitrile (8b, Table 3, entry 2). Colorless solid, M.p. 198-203 °C; IR (KBr, υ, Cm^{-1}): 3853 and 3563 (NH_2), 3402 (OH), 2985 (CH), 2196 (CN), 1670 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.12 (dd, 1H, ^2J = 16.4 Hz, ^4J = 6.0 Hz, CH_{aliph}), 4.21 (dd, 1H, ^2J = 16.4 Hz, ^4J = 6.0 Hz, CH_{aliph}), 4.62 (s, 1H, CH_{vinyl}), 5.51 (t, 1H, *J* = 6.0 Hz, OH), 6.33 (s, 1H, CH_{aliph}), 6.75 (s, 2H, NH_2), 7.21 (d, 2H, *J* = 8.4 Hz, CH_{arom}), 7.29 (d, 2H, *J* = 8.8 Hz, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 40.5, 55.8, 59.7, 111.6, 119.2, 129.1, 129.5, 133.6, 136.8, 139.0, 148.4, 159.9, 168.6, 170.3; Anal. Calcd. for $C_{16}H_{11}ClN_2O_4$: C, 58.11; H, 3.35; N, 8.47. Found: C, 58.16, H, 3.42; N, 8.42.

2-Amino-4-(2-chlorophenyl)-6-(hydroxymethyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (8c, Table 3, entry 3). Colorless solid, M.p. 212-215 °C (lit. [32] 210–213); IR (KBr, υ, Cm^{-1}): 3586 and 3685 (NH_2), 3347 (OH), 2236 (CN), 1636 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.15 (dd, 1H, ^2J = 16.3, ^4J = 6.0 Hz, CH_{aliph}), 4.52 (dd, 1H, ^2J = 16.3, ^4J = 6.0 Hz, CH_{aliph}), 5.19 (t, 1H, ^4J= 6.0 Hz, OH), 5.75 (s, 1H, CH_{vinyl}), 6.38 (s, 1H, CH_{aliph}), 7.09 (s, 2H, NH_2), 7.24-7.56 (m, 4H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ =39.8, 54.8, 59.4,111.5, 118.9, 128.3,129.8, 130.1, 130.7, 131.9, 136.7, 137.5, 147.8, 159.6, 167.8, 169.2, 195.1; Anal. Calcd. for $C_{16}H_{11}C1N_2O_4$: C, 58.21; H, 3.40; N, 8.49. Found: C, 58.14; H, 3.38; N, 8.44.

2-Amino-4-(2,4-dichlorophenyl)-6-(hydroxymethyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (8d, Table 3, entry 4). Colorless solid; M.p. 240-241 °C (lit. [32] 240-242); IR (KBr, υ, Cm^{-1}): 3603 and 3675 (NH_2), 3455 (OH), 2245 (CN), 1629 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.12 (dd, 1H, ^2J = 16.0, ^4J = 6.0 Hz, CH_{aliph}), 4.28 (dd, 1H, ^2J= 16.0, ^{4}J = 6.0 Hz, CH_{aliph}), 5.47 (t, 1H, ^{4}J = 6.0 Hz, OH), 5.87 (s, 1H, CH_{vinyl}), 6.48 (s, 1H, CH_{aliph}), 7.43 (s, 2H, NH_2), 7.49 (d, 1H, ^3J = 7.9 Hz, CH_{arom}), 7.89 (d, 1H, ^4J = 2.4Hz, CH_{arom}), 7.94 (dd, 1H, ^3J = 7.9, ^4J = 2.5 Hz, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 39.5, 55.3, 59.4, 117.5, 119.1, 128.4, 129.4, 129.6, 130.4, 131.7, 136.5, 138.2, 149.1, 159.9, 169.1, 169.9, 194.8; Anal. Calcd. for $C_{16}H_{10}Cl_2N_2O_4$: C, 52.72; H, 2.80; N, 7.69. Found: C, 52.61; H, 2.83; N, 7.62.

2-Amino-4-(3-bromophenyl)-6-(hydroxymethyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (8e, Table 3, entry 5). Colorless solid; M.p. = 243-245 °C (lit. [32] 242-244); IR (KBr, υ, Cm^{-1}): 3425 and 3312 (NH_2), 3482 (OH), 2218 (CN), 1675 (C=O) cm^{-1}; ^{1}H NMR (400MHz, DMSO-d_6) δ =4.19 (dd, 1H, ^2J = 16.1, ^4J = 6.0 Hz, CH_{aliph}), 4.32 (dd, 1H, ^2J = 16.1, ^4J = 6.0 Hz, CH_{aliph}), 5.75 (t, 1H, ^4J = 6.0 Hz, OH), 5.89 (s, 1H, CH_{vinyl}), 6.74 (s, 1H, CH_{aliph}), 7.25 (s, 2H, NH_2), 7.46-7.79 (m, 4H, CH_{arom}); ^{13}CNMR(100 MHz, DMSO-d_6) δ = 38.7, 55.1, 59.5, 112.9, 119.4, 123.1, 127.1, 130.4, 130.7, 131.4, 137.1, 143.3, 143.9, 159.5, 168.3, 169.6, 195.7; Anal. Calcd. for $C_{16}H_{11}BrN_2O_4$: C, 51.33; H, 2.99; N, 7.48. Found: C, 51.27; H, 2.94; N, 7.52.

2-Amino-4-(4-fluorophenyl)-6-(hydroxymethyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (8f, Table 3, entry 6). Colorless solid; M.p. = 248–250 °C (lit. [32] 248-250); IR (KBr, υ, Cm^{-1}): 3523 and 3445 (NH_2), 3562 (OH), 2205 (CN), 1652 (C=0) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.19 (dd, 1H, ^2J= 16.3, ^4J= 6.0 Hz, CH_{aliph}), 4.33 (dd, 1H, ^2J= 16.3, ^4J = 6.0 Hz, CH_{aliph}), 4.78 (t, 1H, ^4J = 6.0 Hz, OH), 5.69 (s, 1H, CH_{vinyl}), 6.44 (s, 1H, CH_{aliph}), 7.20-7.27 (m, 2H, CH_{arom}), 7.30 (s, 2H, NH_2), 7.35-7.46 (m, 2H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 39.5, 56.5, 59.4, 112.4, 116.5 (d, ^2J = 25.0 Hz, C-F), 119.7, 129.5 (d, ^3J = 9.8 Hz, C-F), 136.5, 137.5 (d, ^4J = 3.8 Hz, C-F), 149.1, 160.2, 162.4 (d, ^1J = 295.2 Hz, C-F), 168.5, 169.7, 198.6; Anal. Calcd. for $C_{16}H_{11}FN_2O_4$: C, 61.26; H, 3.59; N, 8.93. Found: C, 61.19; H, 3.50; N, 8.89.

2-Amino-6-(hydroxymethyl)-8-oxo-4-*m*-tolyl-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (8g, Table 3, entry 7). Colorless solid; M.p. = 220-222 °C (lit. [32] 219-220); IR (KBr, υ, Cm^{-1}): 3372 and 3368 (NH_2), 3351 (OH), 2219 (CN), 1645 (C=O) cm^{-1}; ^{1}H NMR (400MHz, DMSO-d_6) δ = 2.38 (s, 3H, CH_3), 4.28 (dd, 1H, ^2J = 16.2, ^4J = 6.2 Hz, CH_{aliph}), 4.26 (dd, 1H, ^2J = 16.2, ^4J = 6.2 Hz, CH_{aliph}), 4.81 (t, 1H, ^4J = 6.2 Hz, OH), 5.72 (s, 1H, CH_{vinyl}), 6.38 (s, 1H, CH_{aliph}), 6.79 (d, 1H, ^3J = 8.0 Hz, CH_{arom}), 7.18 (d, 1H, ^3J = 8.0 Hz, CH_{arom}), 7.12 (s, 2H, NH_2), 7.32 (t, 1H, ^3J =8.0 Hz, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 32.9, 55.5, 59.2, 111.4, 119.6, 125.1, 128.1, 128.8, 137.3, 138.3, 141.1, 149.4, 159.2, 167.4, 169.5, 195.6; Anal. Calcd. for $C_{17}H_{14}N_2O_4$: C, 65.01; H, 4.16; N, 9.05. Found: C, 65.09; H, 4.35; N, 9.11.

2-Amino-4-(furan-2-yl)-6-(hydroxymethyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (8h, Table 3, entry 8). Colorless solid; M.p. = 221-223°C (lit. [32] 223-225); IR (KBr, υ, Cm^{-1}): 3427 and 3294 (NH_2), 3378 (OH), 2174 (CN), 1634 (C=0) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.18 (dd, 1H, ^2J=16.0, ^4J = 6.3 Hz, CH_{aliph}), 4.24 (dd, 1H, ^2J = 16.0, ^4J = 6.3 Hz, CH_{aliph}), 4.75 (t, 1H, ^4J= 6.3 Hz, OH), 5.22 (s, 1H, CH_{vinyl}), 6.48 (s, 1H, CH_{aliPh}), 7.19 (s, 2H, NH_2), 7.45 (d, 2H, ^3J = 4.5 Hz, CH_{arom}), 7.55-7.65 (m, 2H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 34.5, 55.6, 59.3, 107.6, 110.7, 111.8, 112.9, 118.5, 141.4, 142.2, 153.4, 159.5, 169.1, 196.7; Anal. Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.83; H, 3.57; N, 9.81. Found: C, 58.79; H, 3.50; N, 9.83.

2-Amino-6-(hydroxymethyl)-8-oxo-4-(thiophen-2-yl)-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (8i, Table 3, entry 9). Colorless solid; M.p. = 234-236 °C (lit. [32] 235-237); IR (KBr, υ, Cm^{-1}): 3589 and 3398 (NH_2), 3375 (OH), 2126 (CN), 1674 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.22 (dd, 1H, ^2J=16.2, ^4J = 6.2 Hz, CH_{aliph}), 4.29 (dd, 1H, ^2J = 16.2, ^4J =6.2 Hz, CH_{aliph}), 5.12 (t, 1H, ^4J = 6.2 Hz, OH), 5.35 (s, 1H, CH_{vinyl}), 6.35 (s, 1H, CH_{aliph}), 7.05 (s, 2H, NH_2), 7.42 (d, 2H, ^3J = 5.2, CH_{arom}), 7.50-7.65 (m, 2H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 37.2, 57.3, 59.1, 111.5, 112.7, 119.6, 124.6, 125.4, 127.5, 140.4, 142.6, 160.2, 169.3, 197.5; Anal. Calcd. for $C_{14}H_{10}N_2O_4S$: C, 55.70; H, 3.36; N, 9.29. Found: C, 55.69; H, 3.39; N, 9.22.

2-Amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile (10a, Table 4, entry 1): White solid, M.p. 255-258 °C; IR (KBr, υ, Cm^{-1}): 3643 and 3556 (NH_2), 2176 (CN), 1654 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.64 (s, 3H, CH_3), 4.65 (s, 1H, CH), 7.08 (s, 2H, NH_2), 7.22-7.46 (m, 6H, CH_{arom}), 7.58 (d, *J* = 8.0 Hz, 1H, CH_{arom}), 7.69-7.74 (m, 1H, CH_{arom}), 8.16 (d, *J* = 8.1 Hz, 1H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 28.3, 36.8, 58.4, 109.2, 112.7, 115.1, 118.6, 121.1, 121.6, 122.2, 125.8, 127.6, 129.9, 133.7, 140.7,146.2, 151.7, 158.6, 161.3; Anal. Calcd. for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.56; N, 12.76. Found: C, 73.02; H, 4.69; N, 12.91.

2-Amino-4-(4-chlorophenyl)-6-methyl-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile (10b, Table 4, entry 2). White solid, M.p. 280-282 °C; IR (KBr, υ, Cm^{-1}): 3723 and 3643 (NH_2), 2186 (CN), 1667 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): *δ* = 3.52 (s, 3H, CH_3), 4.52 (s, 1H, CH), 7.24 (s, 2H, NH_2), 7.33-7.99 (8H, m, $CH_{arom.}$); ^{13}C NMR (100 MHz, DMSO-d_6): *δ* = 29.7, 37.3, 57.8, 108.9, 113.0, 115.4, 120.1, 122.7, 128.7, 129.9, 131.7, 132.2, 139.1, 143.8, 150.6, 159.2, 160.2; Anal. Calcd. for $C_{20}H_{14}ClN_3O_2$: C, 66.03; H, 3.88; N, 11.55. Found: C, 66.16, H, 3.56; N, 11.58.

2-Amino-4-(3-chlorophenyl)-6-methyl-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile (10c, Table 4, entry 3): White solid, M.p. 285-286 °C; IR (KBr, υ, Cm^{-1}): 3683 and 3574 (NH_2), 2192 (CN), 1678 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.61 (s, 3H, CH_3); 4.63 (s, 1H, CH), 7.32 (s, 2H, NH_2), 7.26–7.54 (m, 8H, CH_{arom}), 7.71–7.75 (m, 1H, CH_{arom}), 8.09 (d, *J* = 8.4 Hz, 1H, CH_{arom}); ^{13}C NMR (DMSO-d_6): δ = 31.4, 38.5, 58.9, 110.3, 114.6, 121.4, 122.8, 123.3, 127.7, 128.5, 132.1, 135.1, 140.9, 148.8, 152.7, 158.2, 161.9; Anal. Calcd. for $C_{20}H_{14}ClN_3O_2$: C, 66.02; H, 3.85; N, 11.55. Found: C, 66.18; H, 3.98; N, 11.71.

2-Amino-4-(3-bromophenyl)-6-methyl-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile (10d, Table 4, entry 4): White solid, M.p. 260-262 °C; IR (KBr, υ, Cm^{-1}): 3655 and 3542 (NH_2), 2188 (CN), 1694 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.67 (s, 3H, CH_3), 4.64 (s, 1H, CH), 7.06 (s,1H), 7.28–7.59 (m, 7H), 7.70–7.76 (m, 1H), 8.12 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ =30.9, 39.0, 58.7, 107.1, 110.2, 115.5, 121.6, 123.4, 129.5, 132.7, 134.6, 140.1, 149.1, 152.7, 159.9, 161.5; Anal. Calcd. for $C_{20}H_{14}BrN_3O_2$: C, 58.82; H, 3.43; N, 10.29. Found: C, 58.97; H, 3.55; N, 10.38.

2-Amino-6-methyl-4-(3-nitrophenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile(10e, Table 4, entry 5): Yellow solid, M.p. 274-276 °C; IR (KBr, υ, Cm^{-1}): 3765 and 3647 (NH_2), 2194 (CN), 1697 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.60 (s, 3H, CH_3), 4.83 (s, 1H, CH), 7.04 (s, 2H), 7.39-7.44 (m, 1H), 7.78-7.60 (m, 4H), 8.07-8.11 (m, 3H); ^{13}C NMR (DMSO-d_6): δ =30.8, 34.2, 58.1, 109.6, 114.3, 116.8, 120.2, 122.1, 122.8, 125.3, 129.6, 132.5, 133.2, 134.7, 135.4, 141.1, 150.5, 152.1, 161.2, 163.5; Anal. Calcd. for $C_{20}H_{14}N_4O_4$: C, 64.17; H, 3.74; N, 14.97. Found: C, 64.30; H, 3.89; N, 15.12.

2-Amino-6-methyl-5-oxo-4-(3,4,5-trimethoxyphenyl)-5,6-dihy-dro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile (10f, Table 4, entry 6): White solid, M.p. 267-268 °C; IR (KBr, υ, Cm^{-1}): 3763 and 3652 (NH_2), 2174 (CN), 1685 (C=O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 3.68 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), and 3.79 (s, 6H, $2CH_3$), 4.60 (s, 1H, CH), 6.59 (s, 2H, NH_2), 7.21 (s, 2H), 7.38-7.44 (m, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.69-7.75 (m, 1H), 8.12 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ =31.2, 40.1, 57.6, 59.7, 62.6, 107.4, 111.2, 114.7, 116.6, 121.7, 123.1, 123.8, 133.1, 138.9, 140.5, 141.8, 152.3, 154.5, 160.9, 162.2; Anal. Calcd. for $C_{23}H_{21}N_3O_5$: C, 65.87; H, 5.01; N, 10.02. Found: C, 66.02; H, 5.18; N, 10.16.

2-Amino-4-(3-hydroxy-4-methoxyphenyl)-6-methyl-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile (10g, Table 4, entry 7): White solid, M.p. 262-263 °C; IR (KBr, υ, Cm^{-1}): 3754 and 3637 (NH_2), 2181 (CN), 1689 (C=O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 3.59 (s, 3H, CH_3), 3.75 (s, 3H, CH_3), 4.41(s, 1H, CH), 6.66 (s, 2H), 6.84 (d, *J* = 7.0 Hz, 1H), 7.29 (s, 2H, NH_2), 7.38-7.44 (m, 1H), 7.60 (d, *J*= 7.8 Hz, 1H), 7.69-7.75 (m, 1H), 8.10 (d, *J*= 8.2 Hz, 1H), 8.96 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ =30.5, 39.7, 57.4, 60.2, 111.3, 113.1, 113.9, 115.0, 116.5, 120.5, 122.1, 124.2, 133.4, 139.1, 140.8, 147.4, 148.2, 151.5, 159.9, 161.7; Anal. Calcd. for $C_{21}H_{17}N_3O_4$: C, 67.20; H, 4.53; N, 11.20. Found: C, 67.36; H, 4.69; N, 11.34.

2-Amino-4-(2-furyl)-6-methyl-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile(10h, Table 4, entry 8): Black solid, M.p. 282-283 °C; IR (KBr, υ, Cm^{-1}): 3762 and 3596 (NH_2), 2178 (CN), 1694 (C=O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 3.68 (s, 3H, CH_3), 4.77 (s, 1H, CH), 6.22 (d, *J* = 6.8 Hz, 1H), 6.40 (s, 1H), 6.98 (s, 2H, NH_2), 7.37-7.43 (m, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.70-7.75 (m, 1H), 8.11 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ = 30.8, 33.4, 58.2, 107.4, 109.2, 111.6, 114.1, 117.5, 120.9, 123.6, 124.7, 134.3, 140.5, 143.4, 144.6, 153.4, 157.3, 161.8; Anal. Calcd. for $C_{18}H_{13}N_3O_3$: C, 67.71; H, 4.07; N, 13.17. Found: C, 67.84; H, 4.18; N, 13.33.

2-Amino-6-methyl-5-oxo-4-(4-pyridinyl)-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile (10i, Table 4, entry 9): White solid, M.p. 287-289 °C; IR (KBr, υ, Cm^{-1}): 3696 and 3657 (NH_2), 2191 (CN), 1683 (C=O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ =3.57 (s, 3H, CH_3), 4.59 (s, 1H, CH), 7.26-7.47 (m, 5H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.68-7.74 (m, 1H), 8.11(d, *J* = 7.9 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ =30.9, 38.6, 59.2, 109.1, 114.3, 116.8, 120.8, 123.5, 124.6, 134.1, 140.7, 150.5, 151.7, 152.8, 154.4, 160.6, 161.2; Anal. Calcd. for $C_{19}H_{14}N_4O_2$: C, 69.09; H, 4.24; N, 16.97. Found: C, 69.24; H, 4.39; N, 17.15.

2-Amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (14a, Table 5, entry 1). Light yellow solid, M.p. = 233-235 °C (lit. [34a] 232-234); IR (KBr, υ, Cm^{-1}): 3435 (OH), 3222 (NH_2), 2195 (CN), 1654 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.68 (s, 1H, CH), 6.83 (s, 2H, NH_2), 6.55-7.28 (m, 8H, CH_{arom}), 9.72 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 41.9, 57.1, 102.2, 112.4, 113.8, 121.5, 126.4, 127.5, 128.4, 129.7, 145.2, 149.2, 156.1, 162.1; Anal. Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.68; H, 4.54; N, 10.65.

2-Amino-4-(4-chlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (14b, Table 5, entry 2). Light yellow solid, M.p. = 162-164 °C (lit. [34a] 162-163); IR (KBr, υ, Cm^{-1}): 3435 (OH), 3222 (NH_2), 2195 (CN), 1654 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.85 (s, 1H, CH), 6.55 (s, 2H, NH_2), 6.83 (d, *J* = 8.0 Hz, 1H, CH_{arom}), 7.05 (s, 2H, CH_{arom}), 7.62-7.68 (m, 2H, CH_{arom}); 8.03 (s, 1H, CH_{arom}); 8.10–8.14 (m, 1H, CH_{arom}); 9.78 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 35.1, 54.5, 103.2, 106.5, 110.6, 111.5, 113.4, 120.8, 130.2, 142.8, 149.5, 157.5, 157.8, 162.4; Anal. Calcd. for $C_{16}H_{11}ClN_2O_2$: C, 64.33; H, 3.71; N, 9.38. Found: C, 64.30; H, 3.68; N, 9.41.

2-Amino-4-(4-bromophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (14c, Table 5, entry 3). Yellow solid, M.p. = 227-230 °C (lit. [34a] 225-227); IR (KBr, υ, Cm^{-1}): 3446 (OH), 3342 (NH_2), 2185 (CN), 1644 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.68 (s, 1H, CH), 6.45 (d, 1H, *J* = 4.2 Hz, CH_{arom}), 6.52 (dd, 1H, *J* = 4.2, *J* = 8.2 Hz, CH_{arom}), 6.80 (d, 1H, *J* = 8.2 Hz, CH_{arom}), 6.97 (s, 2H, NH_2) 7.08-7.62 (m, 4H, CH_{arom}), 9.83 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6,): δ = 57.3, 102.7, 113.1, 113.5, 120.2, 121.3, 130.3, 130.5, 132.4, 145.2, 149.3, 158.1, 162.3; Anal. Calcd for $C_{16}H_{11}BrN_2O_2$: C, 56.00; H, 3.23; N, 8.16. Found: C, 55.87; H, 3.20; N, 8.18.

2-Amino-7-hydroxy-4-*p*-tolyl-4H-chromene-3-carbonitrile (14d, Table 5, entry 4). Yellow solid, M.p. = 186-188 °C (lit. [34a] 185-187); IR (KBr, υ, Cm^{-1}): 3424 (OH), 3322 (NH_2), 2193 (CN), 1647 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.32 (s, 3H, CH_3), 4.58 (s, 1H, CH), 6.85 (s, 2H, NH_2), 6.42-7.15 (m, 7H, CH_{arom}), 9.75 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.4, 43.4, 56.5, 102.7, 112.4, 114.1, 120.8, 128.1, 129.4, 129.7, 134.6, 144.6, 148.8, 157.3, 162.1; Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.30; H, 5.02; N, 10.10.

2-Amino-4-(furan-2-yl)-7-hydroxy-4*H*-chromene-3-carbonitrile (14e, Table 5, entry 5). Yellow solid, M.p. = 188-190 °C (lit. [34a] 189-191); IR (KBr, υ, Cm^{-1}): 3425 (OH), 3332 (NH_2), 2197 (CN), 1652 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.75 (s, 1H, CH), 6.92 (s, 2H, NH_2), 6.13-7.50 (m, 6H), 9.74 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 39.7, 52.2, 103.4, 104.9, 110.4, 111.6, 112.7, 121.1, 129.5, 142.4, 149.6, 157.1, 157.8, 160.7; Anal. Calcd. for $C_{14}H_{10}N_2O_3$: C, 66.14; H, 3.96; N, 11.02. Found: C, 66.20; H, 3.94; N, 11.05.

2-Amino-4-phenyl-4*H*-benzo[*h*]chromene-3-carbonitrile (15a, Table 5, entry 6). Yellow solid, M.p. = 177-179 °C (lit. [19] 178-180); IR (KBr, υ, Cm^{-1}): 3485 (NH_2), 2184 (CN), 1636 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.92 (1H, d, *J* = 8.2 Hz, CH_{arom}), 7.10-7.25 (5H, m, CH_{arom}), 7.45-7.55

(3H, m, CH_{arom}), 7.26 (1H, d, *J* = 8.2 Hz, CH_{arom}), 8.15 (1H, d, *J* = 8.2 Hz, CH_{arom}); ^{13}C NMR (400 MHz, DMSO-d_6): δ = 42.2, 59.1, 109.4, 117.2, 120.7, 123.2, 124.8, 125.9, 126.7, 126.9, 127.8, 129.5, 129.7, 133.7, 133.9, 142.9, 143.4, 159.1; Anal. Calcd. For $C_{20}H_{14}N_2O$: C, 80.52; H, 4.73; N, 9.39. Found: C, 80.45; H, 4.70; N, 9.34.

2-Amino-4-(4-chlorophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (15b, Table 5, entry 7). Yellow solid, M.p. = 230-233 °C (lit. [19] 230-232); IR (KBr, υ, Cm^{-1}): 3458 (NH_2), 2192 (CN), 1625 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 4.81 (s, 1H, CH), 7.05 (d, *J* = 8.0 Hz, 1H, CH_{arom}), 7.18 (s, 2H, NH_2), 7.27 (d, *J* = 8.0 Hz, 2H, CH_{arom}), 7.35 (d, *J* = 8.0 Hz, 2H, CH_{arom}), 7.58-7.72 (m, 3H, CH_{arom}), 7.92 (d, *J* = 8.0 Hz, 1H, CH_{arom}), 8.35 (d, *J* = 8.0 Hz, 1H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6): *δ* = 41.5, 57.2, 117.5, 120.4, 121.5, 123.4, 124.0, 126.2, 127.1, 127.5, 128.2, 129.1,129.9, 132.3, 133.4, 143.5, 145.2, 162.5; Anal. Calcd for $C_{20}H_{13}ClN_2O$: C, 72.18; H, 3.94; N, 8.42. Found C, 72.14; H, 3.89; N, 8.34.

2-Amino-4-(4-nitrophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (15c, Table 5, entry 8). Yellow solid, M.p. = 233-235 °C (lit. [35] 231-234); IR (KBr, υ, Cm^{-1}): 3462 (NH_2), 2182 (CN), 1634 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 5.2 (s, 1H, CH), 7.34 (s, 2H, NH_2), 7.12 (d, 1H, *J* = 8.2 Hz, CH_{arom}), 7.56-7.76 (m, 3H, CH_{arom}), 7.56 (d, 2H, *J* = 8.2 Hz, CH_{arom}), 7.94 (d, 1H, *J* = 8.2 Hz, CH_{arom}), 8.23 (d, 2H, CH_{arom}), 8.34 (d, 1H, *J* = 8.2 Hz, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6): *δ* = 40.1, 55.4, 116.6, 120.2, 120.7, 122.6, 124.0, 124.2, 125.8, 126.5, 127.1, 127.7, 128.9, 132.6, 142.8, 146.5, 152.8, 160.3; Anal. Calcd for $C_{20}H_{13}N_3O_3$: C, 69.96; H, 3.82; N, 12.24. Found: C, 69.92; H, 3.78; N, 12.28.

2-Amino-4-(4-hydroxyphenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (15d, Table 5, entry 9). Yellow solid, M.p. = 247-248 °C (lit. [35] 247-249); IR (KBr, υ, Cm^{-1}): 3454 (NH_2), 2215 (CN), 1629 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ =4.69 (s, 1H, CH), 6.82 (s, 2H, NH_2), 6.63 (d, 2H, *J* = 8.0 Hz, CH_{arom}), 6.93 (d, 1H, *J* = 8.0 Hz, CH_{arom}), 7.06 (d, 2H, *J* = 8.0 Hz, CH_{arom}), 7.55-7.64 (m, 3H, CH_{arom}), 8.10-8.19 (m, 2H, CH_{arom}), 9.25 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): *δ* = 41.4, 57.4, 115.9, 119.5, 120.8, 121.5, 123 .4, 124.7, 126.9, 127.4, 127.7, 128.6, 129.7, 134.4, 136.8, 143.5, 157.1, 160.9; Anal. Calcd for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.38; H, 4.42; N, 8.96.

2-Amino-4-*p*-tolyl-4*H*-benzo[*h*]chromene-3-carbonitrile (15e, Table 5, entry 10). Yellow solid, M.p. = 247-248 °C (lit. [35] 247-249); IR (KBr, υ, Cm^{-1}): 3412 (NH_2), 2204 (CN), 1665 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 2.32 (s, 3H, CH_3), 4.87 (s, 1H, CH), 7.14 (s, 2H, NH_2), 6.89-7.92 (m, 10H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6): *δ* = 27.5, 40.1, 55.3, 118.2, 120.4, 120.8, 122.7, 123.6,

126.3, 126.7, 126.9, 127.5, 128.4, 128.9, 132.6, 136.2, 137.9, 143.2, 159.8; Anal. Calcd for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.69; H, 5.19; N, 8.94.

3-Amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile (16a, Table 5, entry 11). Yellow solid, M.p. = 273-276 °C (lit. [36] 274–276); IR (KBr, υ, Cm^{-1}): 3422 (NH_2), 2195 (CN), 1624 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 5.35 (s, 1H, CH), 7.02 (s, 2H, NH_2), 7.15-7.30 (m, 5H, CH_{arom}), 7.37-7.52 (m, 3H, CH_{arom}), 7.89-7.97 (m, 3H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 39.3, 59.4, 116.2, 117.3, 120.9, 124.1, 125.4, 127.1, 127.5, 127.8, 128.9, 129.2, 129.9, 130.7, 131.3, 145.2, 147.3, 160.2; Anal. Calcd for $C_{20}H_{14}N_2O$: C, 80.52; H, 4.73; N, 9.39. Found: C, 80.60; H, 4.85; N, 9.41.

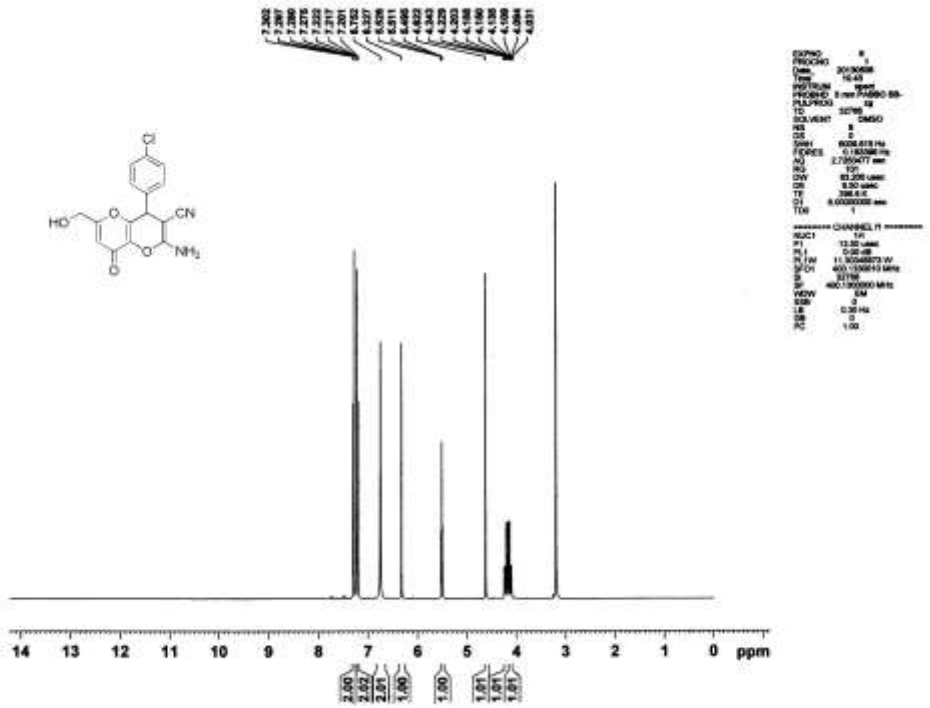
3-Amino-1-(4-chlorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (16b, Table 5, entry 12). Yellow solid, M.p. = 205-207 °C (lit. [36] 205–206); IR (KBr, υ, Cm^{-1}): 3452 (NH_2), 2205 (CN), 1632 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 5.32 (s, 1H, CH), 7.10 (s, 2H, NH_2), 7.24 (d, 2H, J = 8.2 Hz, CH_{arom}), 7.35-7.42 (m, 3H, CH_{arom}), 7.45-7.54 (m, 2H, CH_{arom}), 7.84 (d, 1H, J = 8.2 Hz, CH_{arom}), 7.95-8.03 (m, 2H, CH_{arom}). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 37.9, 58.2, 115.7, 117.3, 121.9, 124.3, 125.6, 127.6, 129.0, 129.4, 129.6, 130.2, 130.6, 131.3, 131.8, 132.6, 145.5, 147.3, 160.2; Anal. Calcd for $C_{20}H_{13}ClN_2O$: C, 72.18; H, 3.94; N, 8.42. Found: C, 72.15; H, 3.98; N, 8.39.

3-Amino-1-(2-chlorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (16c, Table 5, entry 13). Yellow solid, M.p. = 257-259 °C (lit. [36] 258–260); IR (KBr, υ, Cm^{-1}): 3468 (NH_2), 2186 (CN), 1598 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 5.51 (s, 1H, CH), 7.24 (s, 2H, NH_2), 7.05 (d, 2H, J = 8.2 Hz, CH_{arom}), 7.27-7.36 (m, 3H, CH_{arom}), 7.50 (d, 1H, J = 8.2 Hz, CH_{arom}), 7.57-7.82 (m, 3H, CH_{arom}), 7.92 (d, 1H, J = 8.2 Hz, CH_{arom}), 8.34 (d, 1H, J = 8.2 Hz, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 38.2, 59.2, 116.3, 118.9, 122.1, 123.2, 125.8, 126.3, 126.7, 127.3, 127.6, 128.3, 128.8, 129.3, 131.0, 133.5, 149.9, 151.8, 177.1; Anal. Calcd for $C_{20}H_{13}ClN_2O$: C, 72.18; H, 3.94; N, 8.42. Found: C, 72.22; H, 3.90; N, 8.47.

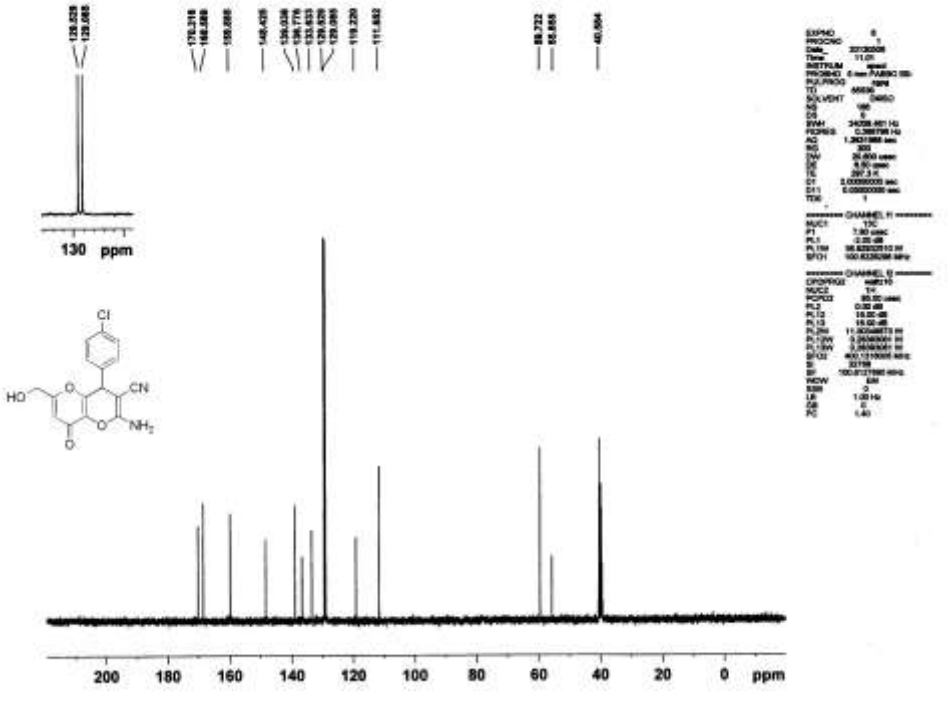
3-Amino-1-(4-nitrophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (16d, Table 5, entry 14). Yellow solid, M.p. = 185-188 °C (lit. [36] 186–187); IR (KBr, υ, Cm^{-1}): 3436 (NH_2), 2195 (CN), 1619 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 5.42 (s, 1H, CH), 7.26 (s, 2H, NH_2). 7.32-7.62 (m, 3H, CH_{arom}), 7.44 (d, 2H, J = 8.4 Hz, CH_{arom}), 7.72-8.05 (m, 2H, CH_{arom}), 7.82 (d, 1H, J = 8.4 Hz, CH_{arom}), 8.27 (d, 2H, J = 8.4 Hz, CH_{arom}). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 39.5, 60.3, 116.3, 117.6, 121.3, 124.5, 125.6, 127.4, 127.6, 129.1, 129.8, 129.9, 130.8, 131.5, 136.4, 143.4, 147.3, 160.4; Anal. Calcd for $C_{20}H_{13}N_3O_3$: C, 69.96; H, 3.82; N, 12.24. Found: C, 69.92; H, 3.78; N, 12.30.

3-Amino-1-(4-cyanophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (16e, Table 5, entry 15). Yellow solid, M.p. = 258-260 °C (lit. [36] 258–259); IR (KBr, υ, Cm^{-1}): 3465 (NH_2), 2194 (CN), 1655 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 5.41 (s, 1H, CH), 7.12 (s, 2H, NH_2), 7.26-7.52 (m, 3H, CH_{arom}), 7.62-7.88 (m, 2H, CH_{arom}), 7.92 (d, 1H, J = 8.2 Hz, CH_{arom}), 7.52 (d, 2H J = 8.2 Hz, CH_{arom}),

8.26 (d, 2H, *J* = 8.2 Hz, CH_{arom}). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 39.2, 60.1, 114.3, 116.6, 117.5, 121.3, 124.4, 125.6, 127.4, 127.8, 129.0, 129.7, 129.9, 130.8, 131.5, 136.3, 143.4, 148.6, 160.3; Anal. Calcd for C21H13N3O: C, 78.00; H, 4.05; N, 13.00. Found: C, 78.12; H, 4.10; N, 12.96.



^{1}H NMR for compound 8b



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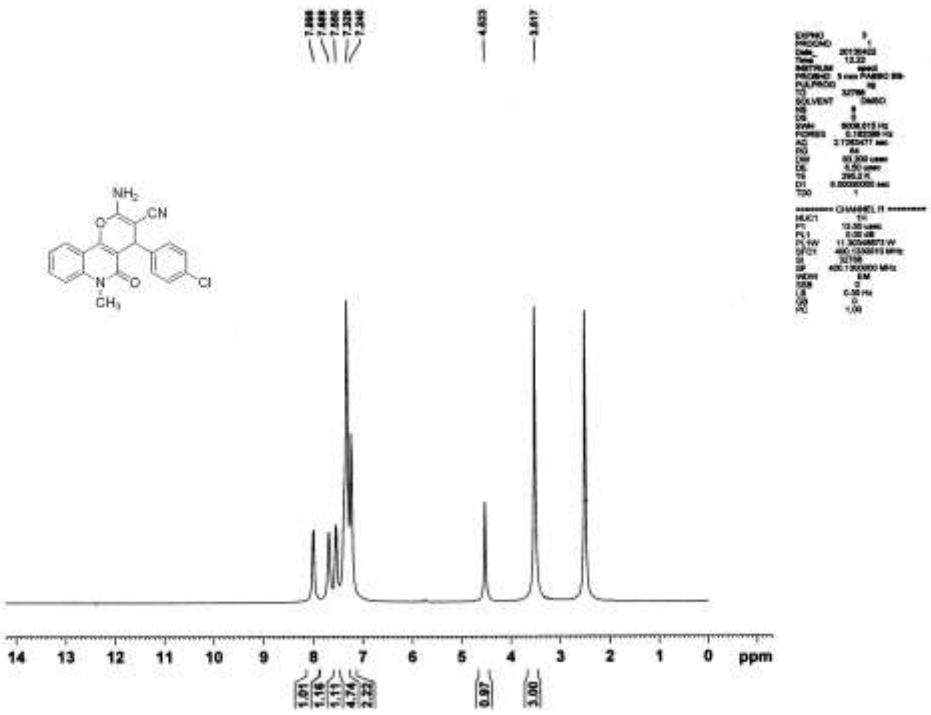
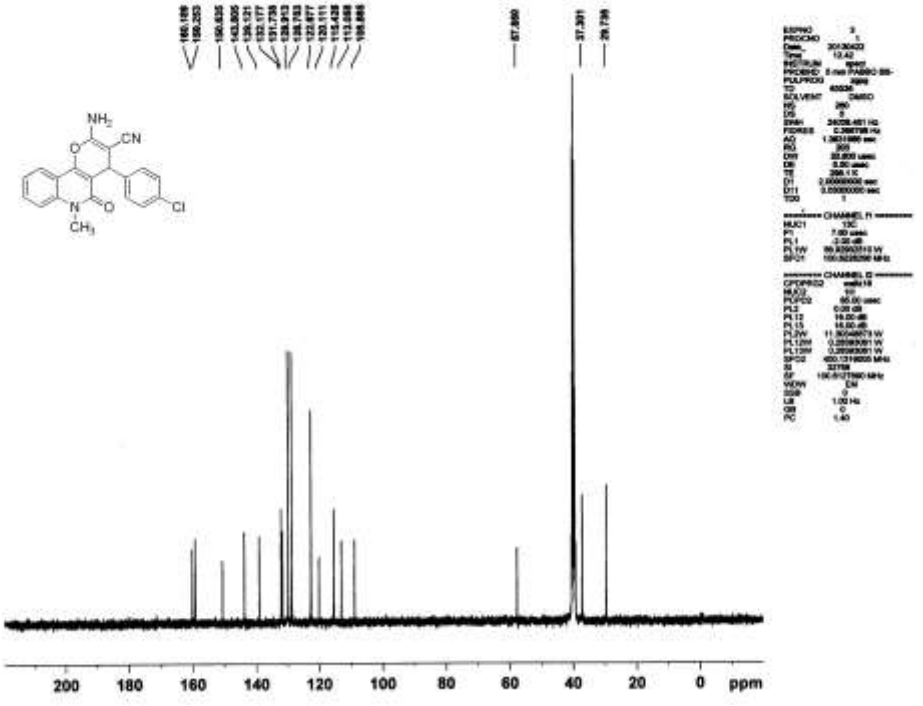


^{1}H NMR for compound 10b



^{13}C NMR for compound 10b