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Supplementary Information

One-Pot Synthesis of 4*H*-Chromene and Dihydropyrano[3,2-*c*]chromene Derivatives in Hydroalcoholic Media

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Analytical data for selected compounds

2-Amino-3-cyano-4-(1,1-dicyanomethyl)-4H-chromene (Table 1, entry 1)

mp 147-148 ºC; IR (KBr) ν_{max}/cm^{-1}: 3486, 3386, 3181, 2201, 1643, 1600, 1568, 1408, 1236, 754, ^{1}H NMR (DMSO, 90 MHz), δ 4.82 (d, 1H, *J* 3.5 Hz, CH), 4.95 (d, 1H, *J* 3.60 Hz, CH), 6.69 (s, 2H, NH_2), 7.38 (m, 4H, aromatic).

2-Amino-8-methoxy-3-cyano-4-(1,1-dicyanomethyl)-4H-chromene (Table 1, entry 2)

mp 188-189 ºC; IR (KBr) ν_{max}/cm^{-1}: 3464, 3356, 2910, 2192, 1642, 1613, 1552, 1488, 1420, 1218, 750, ^{1}H NMR (DMSO, 90 MHz), δ 3.83 (s, 3H, CH_3), 4.53 (d, 1H, *J* 3.8 Hz, CH), 5.01 (d, 1H, *J* 3.90 Hz, CH), 7.07 (m, 3H, aromatic), 7.52 (s, 2H, NH_2).

2-Amino-6-methoxy-3-cyano-4-(1,1-dicyanomethyl)-4H-chromene (Table 1, entry 3)

mp 184-185 ºC; IR (KBr) ν_{max}/cm^{-1}: 3402, 3342, 3218, 2185, 1659, 1587, 1426, 1217, 1037, 820, ^{1}H NMR (DMSO, 90 MHz), δ 3.73 (s, 3H, CH_3), 4.54 (s, 1H, CH), 5.09 (s, 1H, CH), 7.02 (s, 3H, aromatic), 7.41 (s, 2H, NH_2). ^{13}C NMR [DMSO-d_6, 300 MHz]: δ 164.1, 156.3, 144.0, 120.0, 119.1, 118.4, 117.7, 116.3, 113.6, 113.4, 113.4, 56.0, 48.79, 38.0. Anal. Calc. C, 63.15; H, 3.79; N, 21.04%. Found: C, 62.90; H, 3.51; N, 20.65%. *m/z* 266.

2-Amino-6-nitro-3-cyano-4-(1,1-dicyanomethyl)-4H-chromene (Table 1, entry 4)

mp 180-181 ºC; IR (KBr) ν_{max}/cm^{-1}: 3408, 3319, 3074, 2199, 1659, 1608, 1526, 1352, 1262, 748, ^{1}H NMR (DMSO, 90 MHz), δ 4.76 (d, 2H, *J* 3.7 Hz, CH), 5.18 (d, 2H, *J* 3.7 Hz, CH), 7.32-7.42 (m, 1H, aromatic), 7.77 (s, 2H, NH_2), 8.23-8.50 (m, 2H, aromatic).

2-Amino-6-bromo-3-cyano-4-(1,1-dicyanomethyl)-4H-chromene (Table 1, entry 5)

mp 163-164 ºC; IR (KBr) ν_{max}/cm^{-1}: 3471, 3349, 2885, 2189, 1635, 1597, 1596, 1426, 1228, 817, ^{1}H NMR (DMSO, 90 MHz), δ 4.76 (d, 2H, *J* 3.5 Hz, CH), 5.19 (d, 2H, *J* 3.5 Hz, CH), 7.72-7.96 (m, 5H, aromatic and NH_2).

2-Amino-6, 8-dibromo-3-cyano-4-(1,1-dicyanomethyl)-4H-chromene (Table 1, entry 6)

mp 182-183 ºC; IR (KBr) ν_{max}/cm^{-1}: 3414, 3332, 2885, 2197, 1655, 1600, 1562, 1457, 1433, 871, ^{1}H NMR (DMSO, 90 MHz), δ 4.76 (d, 2H, *J* 3.6 Hz, CH), 5.17 (d, 2H, *J* 3.6 Hz, CH), 7.74-7.96 (m, 4H, aromatic and NH_2).

2-Amino-6-chloro-3-cyano-4-(1,1-dicyanomethyl)-4H-chromene (Table 1, entry 7)

mp 151-154 ºC; IR (KBr) ν_{max}/cm^{-1}: 3445, 3337, 2862, 2194, 1644, 1600, 1572, 1457, 1483, 819, ^{1}H NMR (DMSO, 90 MHz), δ 4.62 (d, 1H, *J* 3.8 Hz, CH), 5.14 (d, 1H, *J* 3.8 Hz, CH), 7.10-7.57 (m, 5H, aromatic and NH_2), ^{13}C NMR [DMSO-d6, 300 MHz]: δ 163.7, 149.0, 130.5, 129.0, 128.9, 120.3, 119.6, 119.2, 118.8, 113.4, 113.2, 48.9, 37.3. Anal. Calc. C, 57.69; H, 2.61; N, 20.07%. Found: C, 57.53; H, 2.36; N, 19.94%. *m/z* 270.

2-Amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 1)

mp 260-264 ºC; IR (KBr) ν_{max}/cm^{-1}: 3379, 3305, 2196, 1713, 1676, 1637, ^{1}H NMR (DMSO, 90 MHz), δ 4.45 (s, 1H, CH), 7.28-7.86 (m, 11H, aromatic and NH_2).

2-Amino-4-(4-chlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 2)

mp 265-267 ºC; IR (KBr) ν_{max}/cm^{-1}: 3380, 3291, 3189, 2191, 1713, 1676, ^{1}H NMR (DMSO, 90 MHz), δ 4.72 (s, 1H, CH), 7.40-8.13 (m, 10H, aromatic and NH_2).

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2-Amino-4-(4-methoxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 3)

mp 246-249 ºC; IR (KBr) ν_{max}/cm^{-1}: 3500, 3450, 3350, 2208, 1647,1174, ^{1}H NMR (DMSO, 90 MHz), δ 3.71 (s, 3H, CH_3), 4.39 (s, 1H, CH), 6.81-7.85 (m, 10H, aromatic and NH_2).

2-Amino-5-oxo-4-p-tolyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 4)

mp 252-254 ºC; IR (KBr) ν_{max}/cm^{-1}: 3388, 3311, 3189, 2194, 1713, 1676, 1637, ^{1}H NMR (DMSO, 90 MHz), δ 2.25 (s, 3H, CH_3), 4.40 (s, 1H, CH), 7.12-7.93 (m, 10H, aromatic and NH_2).

2-Amino-4-(4-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 5)

mp 255-258 ºC; IR (KBr) ν_{max}/cm^{-1}: 3482, 3370, 3071, 2196, 1718, 1673, 1606, 1505,1373, 1348, 766. ^{1}H NMR (DMSO, 90 MHz), δ 4.66 (s, 1H, CH), 7.47-8.21 (m, 10H, aromatic and NH_2).

2-Amino-4-(3-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 6)

mp 256-259 ºC; IR (KBr) ν_{max}/cm^{-1}: 3408, 3324, 3192, 2194, 1710, 1677, 1608, 1528,1380, 1347, 764. ^{1}H NMR (DMSO, 90 MHz), δ 4.72 (s, 1H, CH), 7.54-8.12 (m, 10H, aromatic and NH_2).

2-Amino-4-(4-bromophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 7)

mp 255-257 ºC; IR (KBr) ν_{max}/cm^{-1}: 3387, 3309, 3188, 2181, 1710, 1677, 1602, 1577,1062, 758. ^{1}H NMR (DMSO, 90 MHz), δ 4.46 (s, 1H, CH), 7.19-7.84 (m, 10H, aromatic and NH_2).

2-Amino-4-(2,4-dichlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 8)

mp 255-258 ºC; IR (KBr) ν_{max}/cm^{-1}: 3459, 3290, 3163, 2199, 1716, 1673, 1630, 1589,1061, 761. ^{1}H NMR (DMSO, 90 MHz), δ 4.94 (s, 1H, CH), 7.34-7.92 (m, 9H, aromatic and NH_2).

2-Amino-4-(2,3-dichlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 9)

mp 273-276 ºC; IR (KBr) ν_{max}/cm^{-1}: 3405, 3305, 3181, 2199, 1711, 1674, 1602, 1492,1062, 764. ^{1}H NMR (DMSO, 90 MHz), δ 5.07 (s, 1H, CH), 7.33-7.96 (m, 9H, aromatic and NH_2).

2-Amino-4-(2,6-dichlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 10)

mp 274-277 ºC; IR (KBr) ν_{max}/cm^{-1}: 3419, 3277, 3173, 2200, 1707, 1673, 1633, 1599,1379, 758. ^{1}H NMR (DMSO, 90 MHz), δ 5.51 (s, 1H, CH), 7.35-7.92 (m, 9H, aromatic and NH_2).

2-Amino-5-oxo-4-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 11)

mp 224-226 ºC; IR (KBr) ν_{max}/cm^{-1}: 3425, 3321, 2191, 1672, 1595, 1375, 1154, ^{1}H NMR (DMSO, 90 MHz), δ 3.63 (s, 3H, CH_3), 3.71 (s, 6H, CH_3), 4.43(s, 1H, H), 6.52 (s, 2H, NH_2), 7.36-7.93 (m, 6H, aromatic), ^{13}C NMR [DMSO-d6, 300 MHz]: δ 160.1, 158.5, 154.0, 153.3, 152.6, 139.4, 137.1, 133.3, 125.1, 123.0, 119.7, 117.0, 113.6, 105.4, 104.1, 60.4, 58., 56., 37.7. Anal. Calc. C, 65.02; H, 4.46; N, 6.89%. Found: C, 65.0; H, 4.27; N, 6.93%. *m/z* 404.

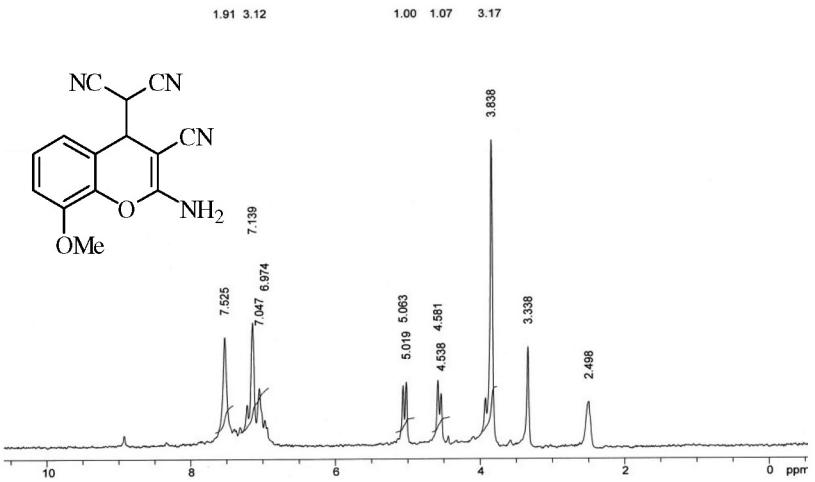

Figure S1. ^{1}H NMR (DMSO) 2-amino-8-methoxy-3-cyano-4-(1,1-dicyanomethyl)-4*H*-chromene (Table 1, entry 2).

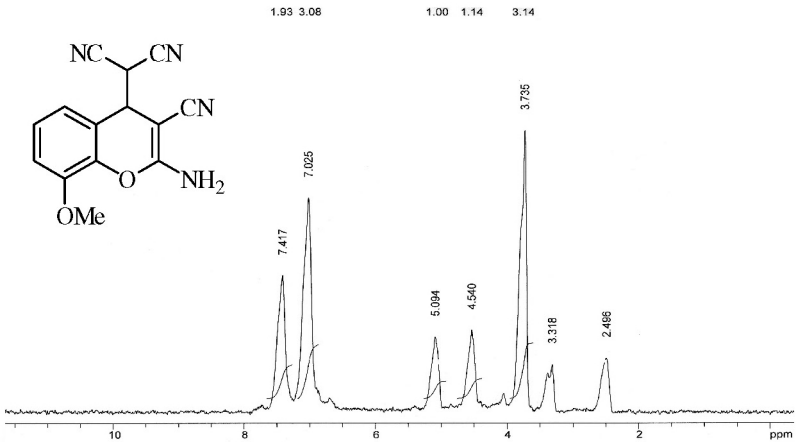

Figure S2. [1]H NMR (DMSO) 2-amino-6-methoxy-3-cyano-4-(1,1-dicyanomethyl)-4*H*-chromene (Table 1, entry 3).

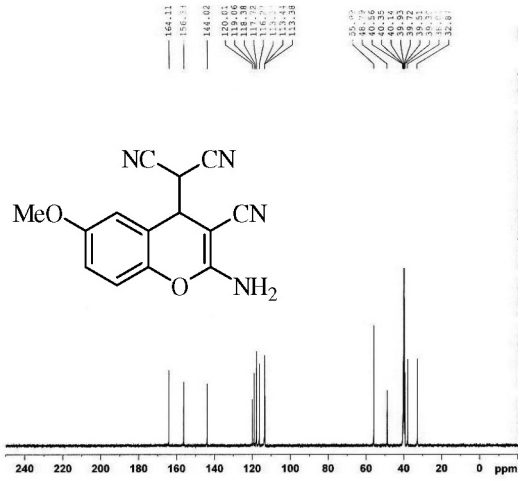

Figure S3. [13]C NMR (DMSO) 2-amino-6-methoxy-3-cyano-4-(1,1-dicyanomethyl)-4*H*-chromene (Table 1, entry 3).

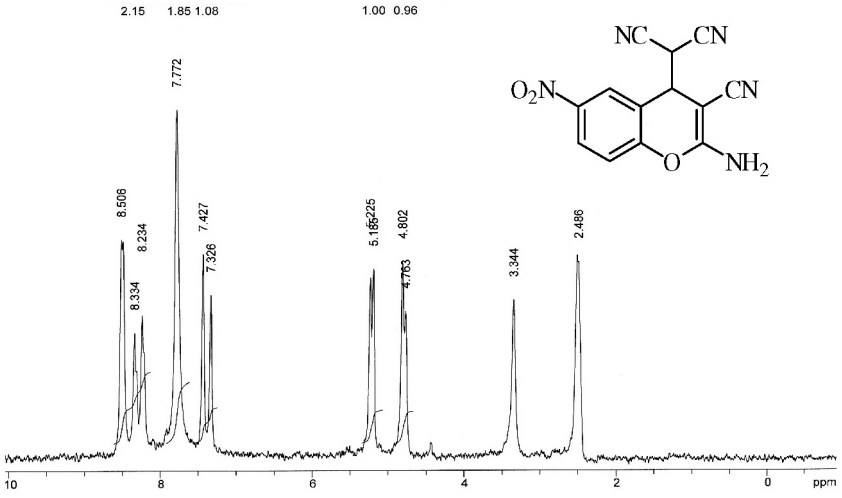

Figure S4. [1]H NMR (DMSO) 2-amino-6-nitro-3-cyano-4-(1,1-dicyanomethyl)-4*H*-chromene (Table 1, entry 4).

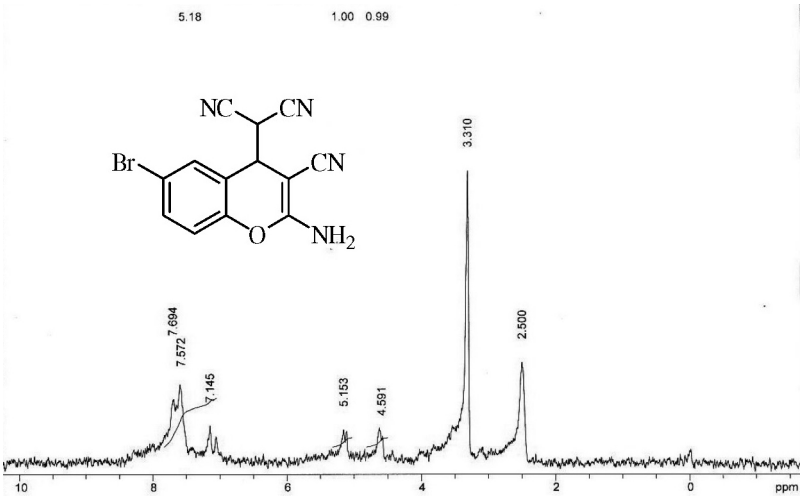

Figure S5. [1]H NMR (DMSO) 2-amino-6-bromo-3-cyano-4-(1,1-dicyanomethyl)-4*H*-chromene (Table 1, entry 5).

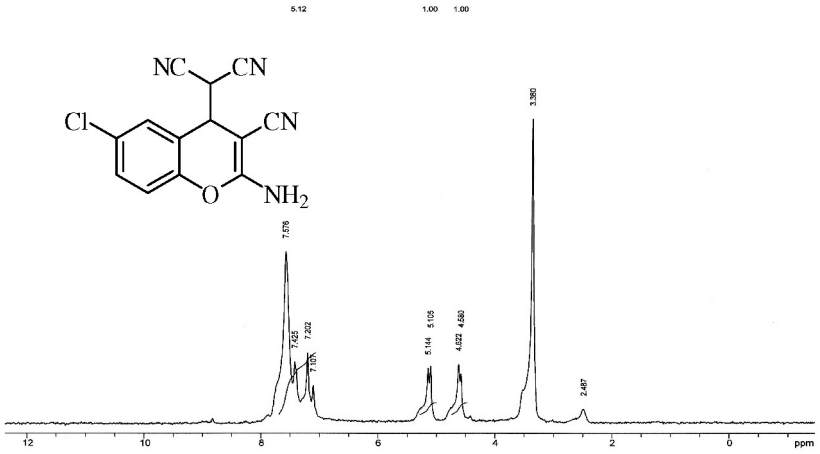

Figure S6. [1]H NMR (DMSO) 2-amino-6-chloro-3-cyano-4-(1,1-dicyanomethyl)-4*H*-chromene (Table 1, entry 7).

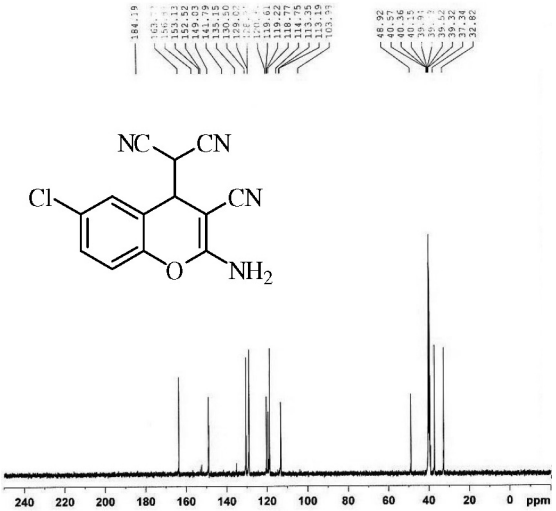

Figure S7. [13]C NMR (DMSO) 2-amino-6-chloro-3-cyano-4-(1,1-dicyanomethyl)-4*H*-chromene (Table 1, entry 7).

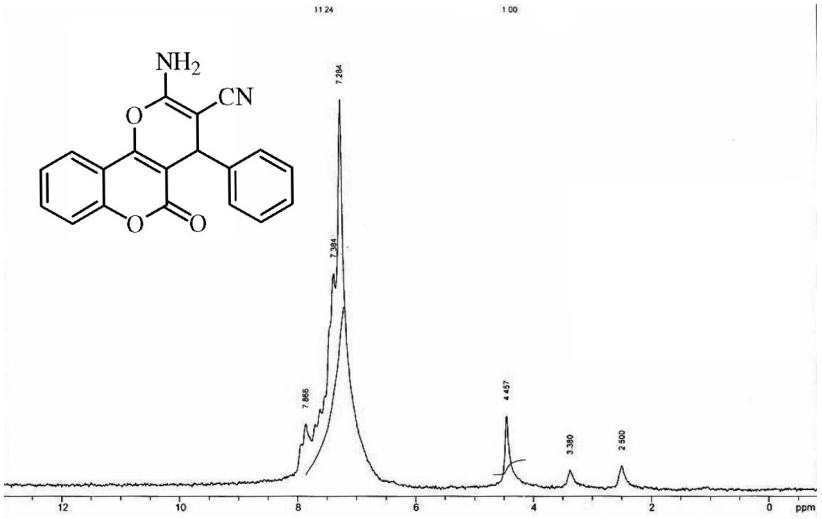

Figure S8. [1]H NMR (DMSO) 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 1).

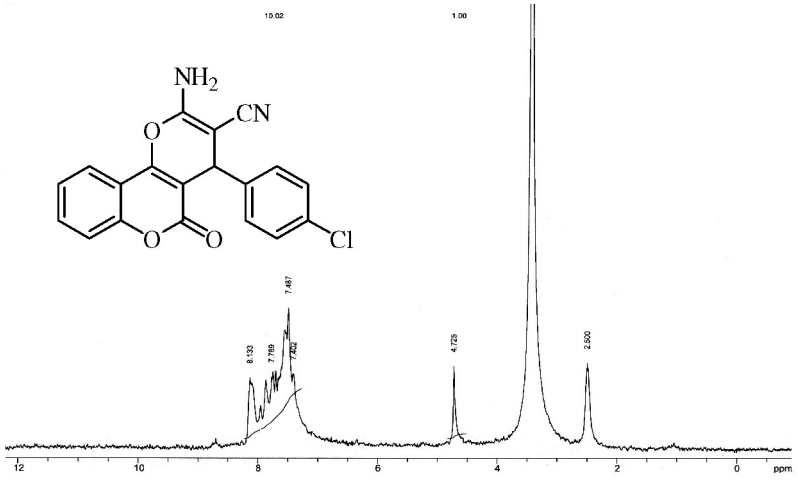

Figure S9. [1]H NMR (DMSO) 2-amino-4-(4-chlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 2).

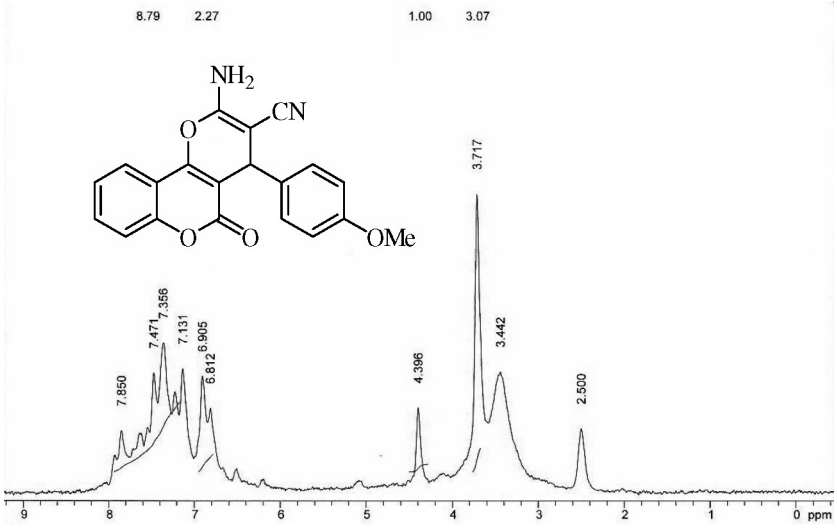

Figure S10. [1]H NMR (DMSO) 2-amino-4-(4-methoxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 3).

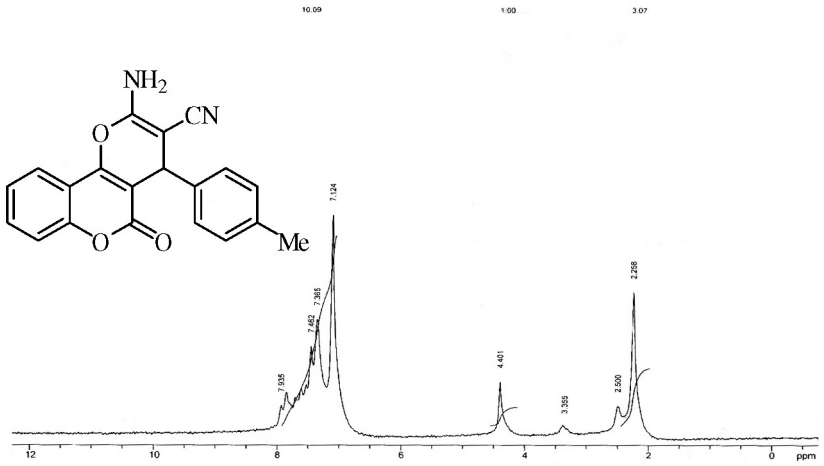

Figure S11. [1]H NMR (DMSO) 2-amino-5-oxo-4-p-tolyl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 4).

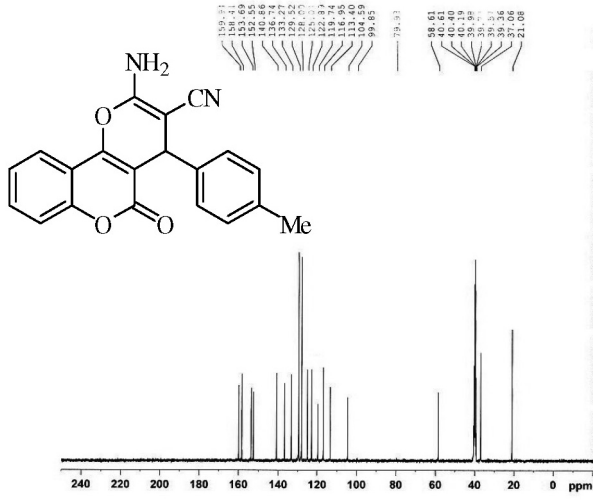

Figure S12. [13]C NMR (DMSO) 2-amino-5-oxo-4-p-tolyl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 4).

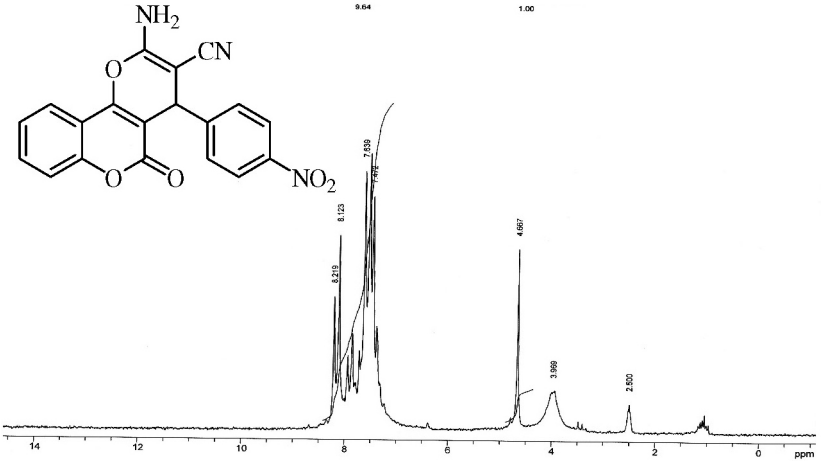

Figure S13. [1]H NMR (DMSO) 2-amino-4-(4-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 5).

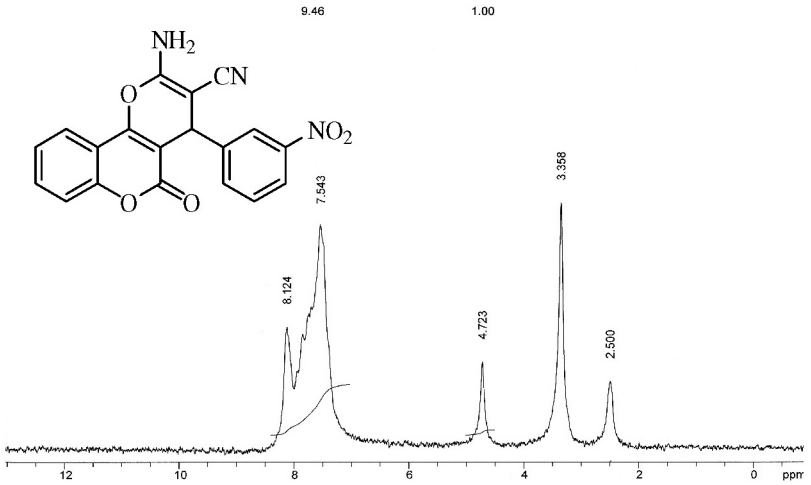

Figure S14. [1]H NMR (DMSO) 2-amino-4-(3-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 6).

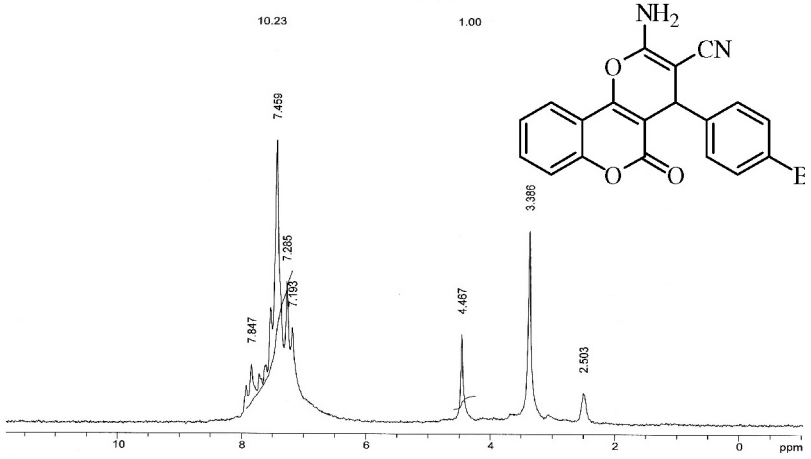

Figure S15. [1]H NMR (DMSO) 2-amino-4-(4-bromophenyl)-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 7).

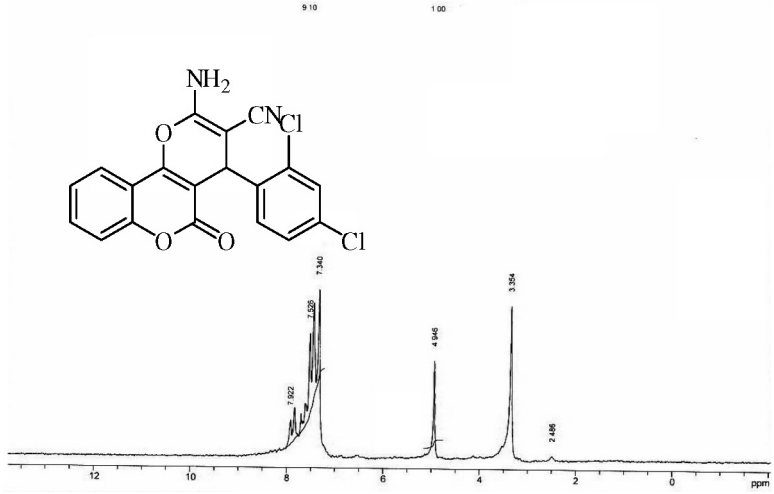

Figure S16. [1]H NMR (DMSO) 2-amino-4-(2,4-dichlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 8).

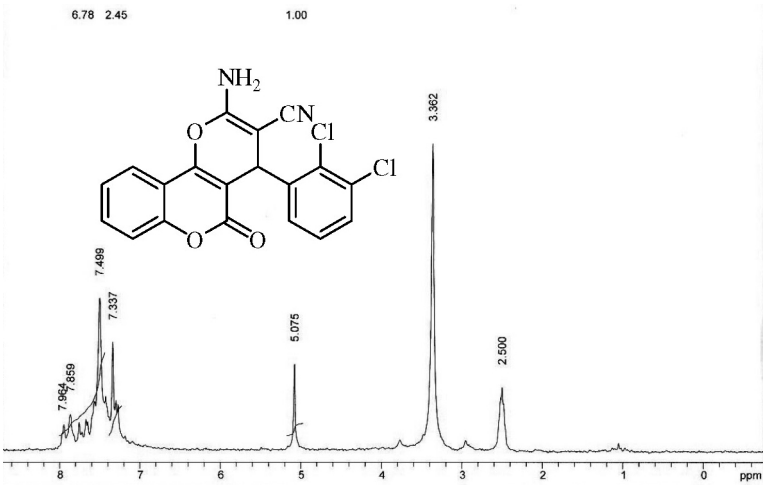

Figure S17. [1]H NMR (DMSO) 2-amino-4-(2,3-dichlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 9).

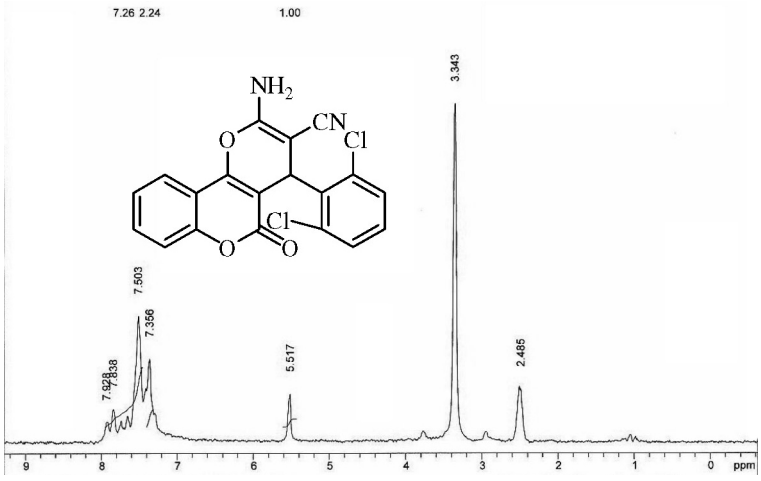

Figure S18. [1]H NMR (DMSO) 2-amino-4-(2,6-dichlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 10).

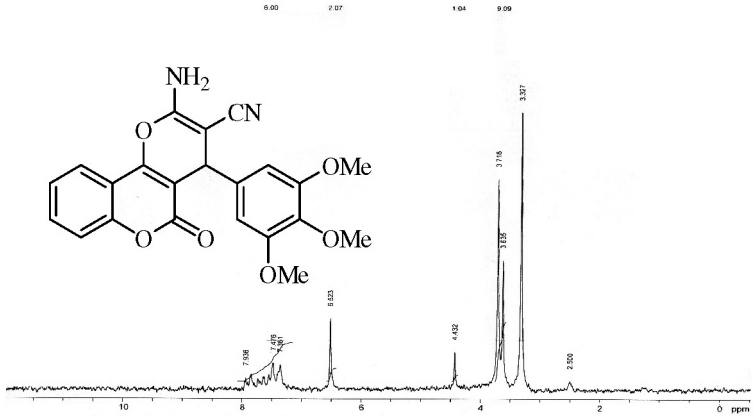

Figure S19. [1]H NMR (DMSO) 2-amino-5-oxo-4-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 11).

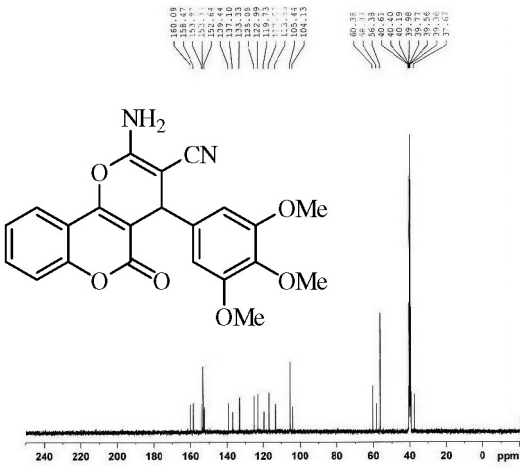

Figure S20. ^{13}C NMR (DMSO) 2-amino-5-oxo-4-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (Table 2, entry 11).