Synthesis of 2-amino-4-aryl-5-oxo-4,5-dihydropyrano[3,2-*c*] chromene derivatives catalysed by KF-montmorillonite

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A series of 2-amino-4-aryl-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene derivatives has been synthesised by the reaction of 4-hydroxycoumarin and substituted cinnamonitriles catalysed by KF-montmorillonite. The structures were characterised by IR and ^{1}H NMR spectroscopic data and confirmed by X-ray diffraction analysis.

Keywords: dihydropyrano[3,2-*c*]chromene, KF-montmorillonite, coumarin

Coumarin (1-benzopyran-2-one) and its derivatives are natural compounds and are important chemicals in perfume, cosmetic and pharmaceutical industrial production.[1] Some coumarin derivatives have been reported to exhibit biological properties.[2-10]2-amino-4-aryl-5-oxo-4,5-dihydropyrano[3,2-*c*] chromene derivatives are generally prepared by the reaction of 4-hydroxycoumarin and substituted cinnamonitriles in an organic solvent (*e.g.* ethanol) in the presence of an organic base like piperidine[11] or in aqueous media catalysed by triethylbenzylammonium chloride.[12]

Smectite clays, especially montmorillonite, have been used as heterogeneous catalyst in synthesis. Because of its stability and ease of separation, montmorillonite has found widespread use in a variety of heterogeneous reactions, such as rearrangement,[13-15] oxidation[16] and addition[17] reactions. In previous reports, montmorillonite clays were used as the acidic catalyst.[18-20] Recently, we have reported that montmorillonite coated with potassium fluoride (KF- montmorillonite) can be used as an alkaline catalyst for organic synthesis.[21-24] We now report the efficient synthesis of 2-amino-4-aryl-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene derivatives catalysed by KF-montmorillonite (Scheme 1).

To find the optimal solvent, the synthesis of **3a** by the reaction of 4-hydroxycoumarin (**1**) and 2-(4-bromobenzylidene) malononitrile (**2a**) was carried out at 90 °C catalysed by KF-montmorillonite using EtOH, acetone, DMF, THF and petroleum ether as solvents. The results are summarised in Table 1.

Table 1shows that the reaction with DMF as solvent resulted in a higher yield than those in other solvents. So DMF was chosen as the solvent of this reaction.

To optimise the catalyst loading, 0.10 g, 0.15 g, 0.20 g, 0.25 g, 0.30 g, 0.35 g and 0.40 g of KF- montmorillonite was tested. The results are summarised in Table 2 which shows that the reaction catalysed by about 0.25 g KF-montmorillonite results in the highest yield.

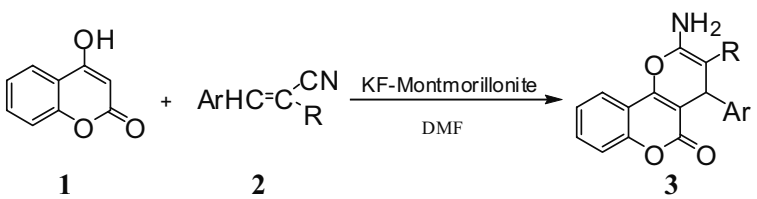
Under these optimised reaction conditions (15 ml DMF, 90 °C, 0.25 g KF-montmorillonite), a series of 2-amino-4-aryl-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene derivatives (**3**) were synthesised. The results are summarised in Table 3.

Structures of the products were established on the basis of spectroscopic data, particularly ^{1}H NMR analysis, and were further confirmed by the X-ray crystal structure analysis of the products **3e**[25] and **3s**[26] (Figs 1 and 2).

In summary, we have developed a simple, convenient and efficient synthetic protocol for the synthesis of 2-amino-4-aryl-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene derivatives in good to excellent yields catalysed by KF-montmorillonite. Compared to the standard methods,[11,12] this method has the advantages of good yields, mild reaction conditions, easy work-up and inexpensive reagents.

Experimental

IR spectra were recorded on a Tensor 27 spectrometer in KBr. ^{1}H NMR spectra were determined on a Bruker DPX-400 MHz spectrometer using DMSO-d_6 solutions. Chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane. Microanalyses were carried out on a Perkin-Elmer 2400 II elemental analyser.



1 **2** **3**

Scheme 1

Table 1 Solvent optimisation for the synthesis of **3a***

Entry	Solvent	Reaction temperature/°C	Isolated yield/%
1	Acetone	50	54
2	95% EtOH	80	75
3	Anhydrous EtOH	80	78
4	THF	70	85
5	DMF	90	94
6	Petroleum ether	60	26

*__1__ (2 mmol), **2a** (2 mmol) KF- montmorillonite (0.25 g), reaction time 6 h, in 15 ml solvent.

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Table 2 The effect of amounts of KF-montmorillonite for the synthesis of **3a***

Entry	Amounts of KF-montmorillonite/g	Isolated yield/%
1	0.10	42
2	0.15	47
3	0.20	86
4	0.25	94
5	0.30	94
6	0.35	86
7	0.40	86

*__1__ (2 mmol), **2a** (2 mmol) in 15 ml DMF, 90 °C, 6 h.

General procedure for the synthesis of 2-amino-4-aryl-4H,5H-pyrano[3,2-c][1]benzopyran-5-one derivatives (**4**): A mixture of 4-hydroxycoumarin **1** (2 mmol), substituted cinnamonitrile **2** (2 mmol) and KF-montmorillonite (0.25 g) in DMF (15 ml) was stirred for 6–14 h at 90 °C (monitored by TLC). Then the mixture was cooled to room temperature, the solid material was filtered off and was washed with DMF. The filtrate was poured into 200 ml water. The white solid was filtered off, and then washed with water. The crude solid was purified by recrystallisation from ethanol to give pure **3**.

2-Amino-4-(4-bromophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**3a**): M.p. 254–256 °C. IR: ν/cm^{-1} 3385, 3187, 2191, 1713, 1670, 1632, 1602, 1458, 1408, 1331, 1357, 1211, 1113, 1009, 956, 835, 774, 759. ^{1}H NMR (DMSO-d_6): δ 4.48 (1H, s, CH), 7.25 (2H, d, J = 8.4 Hz, ArH), 7.45 (2H, s, NH_2), 7.47–7.48 (1H, m, ArH), 7.49–7.52 (3H, m, ArH), 7.70–7.75 (1H, m, ArH), 7.91 (1H, d, J = 7.4 Hz, ArH). Found: C, 57.89; H, 2.77; N, 7.15% Calcd for $C_{19}H_{11}BrN_2O_3$: C, 57.74; H, 2.81; N, 7.09%.

2-Amino-4-(3,4-dichlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**3b**): M.p. 243–244 °C (Lit.[27] 242–244 °C). IR: ν/cm^{-1} 3382, 3176, 2192, 1715, 1682, 1615, 1493, 1469, 1375, 1273, 1208, 1178, 1098, 955, 894, 767. ^{1}H NMR (DMSO-d_6): δ 4.56 (1H, s, CH), 7.29–7.33 (1H, m, ArH), 7.46–7.51 (2H, m, ArH), 7.57–7.60 (2H, m, ArH), 7.71–7.76 (1H, m, ArH), 7.89–7.92 (1H, m, ArH), 7.96 (2H, s, NH_2).

2-Amino-4-(3-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**3c**): M.p. 253–255 °C (Lit.[12] 254–255 °C). IR: ν/cm^{-1} 3382, 3194, 2206, 1697, 1675, 1607, 1495, 1472, 1381, 1256, 1209, 959, 760. ^{1}H NMR (DMSO-d_6): δ 4.48 (1H, s, CH), 7.46–7.54 (4H, m, NH_2 + ArH), 7.61–7.65 (1H, m, ArH), 7.72–7.75 (1H, m, ArH), 7.81 (1H, d, J = 8.4 Hz), 7.91–7.95 (2H, m, ArH), 8.12 (1H, d, J = 8.4 Hz ArH).

2-Amino-4-(4-fluorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**3d**): M.p. 259–261 °C (Lit.[12] 260–262 °C). IR: ν/cm^{-1} 3394, 3328, 3198, 2960, 2874, 2199, 1682, 1603, 1469, 1414, 1368, 1330, 1251, 1214, 1159, 1141, 1037, 976, 750. ^{1}H NMR (DMSO-d_6): δ 4.49 (1H, s, CH), 7.11–7.15 (2H, m, ArH), 7.30–7.33 (2H, m, ArH), 7.41 (2H, s, NH_2), 7.45–7.52 (2H, m, ArH), 7.70–7.74 (1H, m, ArH), 7.90 (1H, d, J = 7.2 Hz, ArH).

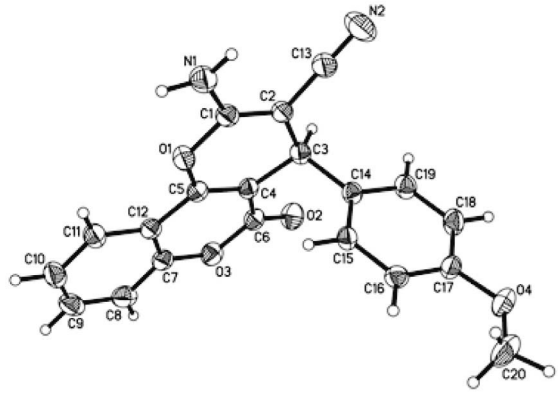

Fig. 1 The X-ray crystal structure of compound **3e**.

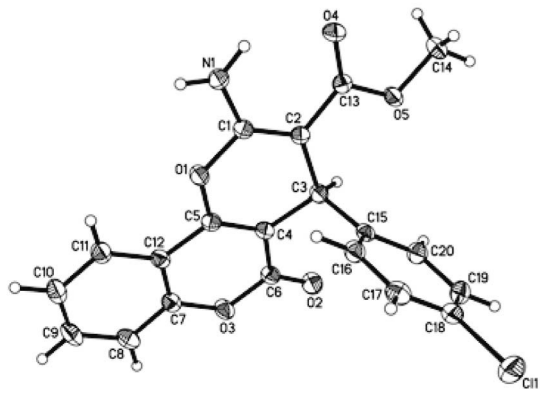

Fig. 2 The X-ray crystal structure of compound **3s**.

2-Amino-4-(4-methoxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**3e**): M.p. 229–230 °C (Lit.[11] 227 °C). IR: ν/cm^{-1} 3385, 3190, 3064, 2955, 2837, 2207, 1715, 1669, 1607, 1511, 1493, 1455, 1381, 1327, 1305, 1253, 1207, 1176, 1112, 1053, 1029, 957, 902, 837, 780, 752. ^{1}H NMR (DMSO-d_6): δ 3.72 (3H, s, CH_3O), 4.39 (1H, s, CH), 6.86 (2H, d, J = 8.8 Hz, ArH), 7.17 (2H, d, J = 8.8 Hz, ArH), 7.38 (2H, s, NH_2), 7.45–7.52 (2H, m, ArH), 7.69–7.73 (1H, m, ArH), 7.89 (1H, d, J = 7.6 Hz, ArH).

2-Amino-4-(3-chlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile(**3f**): M.p. 236–237 °C (Lit.[27] 235–236 °C). IR: ν/cm^{-1} 3384, 3311, 3195, 3056, 2890, 2206, 1705, 1669, 1607, 1495, 1472, 1458, 1431, 1414, 1384, 1316, 1256, 1208, 1177, 1114, 1059, 997, 959, 902, 760, 714. ^{1}H NMR (DMSO-d_6): δ 4.52 (1H, s, CH), 7.24–7.27 (1H, m, ArH), 7.30–7.38 (3H, m, ArH), 7.46 (2H, s, NH_2),

Table 3 The synthesis of **3**

Entry	Ar	R	Reaction times/h	Yield/%
3a	4-BrC_6H_4	CN	6	94
3b	3,4-$Cl_2C_6H_3$	CN	7	86
3c	3-$NO_2C_6H_4$	CN	11	91
3d	4-FC_6H_4	CN	8	93
3e	4-$CH_3OC_6H_4$	CN	8	86
3f	3-ClC_6H_4	CN	7	84
3g	3,4-$OCH_2OC_6H_3$	CN	12	90
3h	3,4-$(CH_3O)_2C_6H_3$	CN	10	84
3i	4-$CH_3C_6H_4$	CN	10	80
3j	3,4-$(CH_3)_2C_6H_3$	CN	11	80
3k	4-$CH_3OC_6H_4$	$COOC_2H_5$	9	85
3l	4-$CH_3C_6H_4$	$COOC_2H_5$	10	80
3m	4-FC_6H_4	$COOC_2H_5$	7	90
3n	C_6H_5	$COOC_2H_5$	8	85
3o	4-ClC_6H_4	$COOC_2H_5$	6	86
3p	3,4-$OCH_2OC_6H_3$	$COOC_2H_5$	14	84
3q	4-BrC_6H_4	$COOC_2H_5$	6	87
3r	2,4-$Cl_2C_6H_3$	$COOC_2H_5$	9	86
3s	4-ClC_6H_4	$COOCH_3$	7	80
3t	4-$CH_3C_6H_4$	$COOCH_3$	11	70

7.48–7.53 (2H, m, ArH), 7.71–7.75 (1H, m, ArH), 7.90–7.92 (1H, m, ArH).

2-Amino-4-(3,4-methylenedioxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**3g**): M.p. 245–247 °C (Lit.[12] 244–246 °C). IR: ν/cm^{-1} 3395, 3317, 3189, 3024, 2906, 2190, 1699, 1661, 1608, 1496, 1442, 1383, 1325, 1312, 1250, 1235, 1205, 1176, 1113, 1095, 1066, 1035, 959, 919, 905, 860, 826, 810, 767, 706. ^{1}H NMR (DMSO-d_6): δ 4.39 (1H, s, CH), 5.98 (2H, s, OCH_2O), 6.72–6.74 (1H, m, ArH), 6.82–6.84 (2H, m, ArH), 7.36 (2H, s, NH_2), 7.45–7.51 (2H, m, ArH), 7.69–7.73 (1H, m, ArH), 7.89 (1H, d, J = 8.4 Hz, ArH).

2-Amino-4-(3,4-dimethoxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**3h**): M.p. 233–235 °C (Lit.[12] 232–234 °C). IR: ν/cm^{-1} 3399, 3321, 3186, 2944, 2836, 2189, 1725, 1672, 1607, 1506, 1456, 1412, 1377, 1295, 1255, 1208, 1178, 1161, 1110, 1032, 954, 936, 830, 764. ^{1}H NMR (DMSO-d_6): δ 3.72 (6H, s, 2 × CH_3O), 4.41 (1H, s, CH), 6.74 (1H, d, J = 8.4 Hz, ArH), 6.85–6.89 (2H, m, ArH), 7.34 (2H, s, NH_2), 7.45–7.51 (2H, m, ArH), 7.69–7.73 (1H, m, ArH), 7.90 (1H, d, J = 7.2 Hz, ArH).

2-Amino-4-(4-methylphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**3i**): M.p. 252–254 °C (Lit.[11] 255 °C). IR: ν/cm^{-1} 3397, 3284, 3179, 2199, 1709, 1673, 1636, 1601, 1492, 1472, 1457, 1380, 1327, 1306, 1258, 1212, 1173, 1111, 1062, 957, 903, 755. ^{1}H NMR (DMSO-d_6): δ 2.26 (3H, s, CH_3), 4.40 (1H, s, CH), 7.12–7.15 (4H, m, ArH), 7.39 (2H, s, NH_2), 7.45–7.52 (2H, m, ArH), 7.70–7.73 (1H, m, ArH), 7.90 (1H, d, J = 8.8 Hz, ArH).

2-Amino-4-(3,4-dimethylphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**3j**): M.p. 231–232 °C (Lit.[27] 226–228 °C). IR: ν/cm^{-1} 3381, 3324, 3176, 3056, 2192, 1493, 1711, 1680, 1608, 1469, 1456, 1407, 1376, 1312, 1253, 1208, 1178, 1114, 1098, 1040, 1021, 956, 905, 767. ^{1}H NMR (DMSO-d_6): δ 2.17 (3H, s, CH_3), 2.18 (3H, s, CH_3), 4.37 (1H, s, CH), 6.95–6.97 (1H, m, ArH), 7.70–7.71 (1H, m, ArH), 7.06 (1H, d, J = 8.0 Hz, ArH), 7.35 (2H, s, NH_2), 7.45–7.52 (2H, m, ArH), 7.69–7.74 (1H, m, ArH), 7.90–7.92 (1H, m, ArH).

Ethyl 2-Amino-4-(4-methoxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (**3k**): M.p. 160–162 °C (Lit.[11] 160 °C). IR: ν/cm^{-1} 3403, 3289, 3048, 2984, 2944, 1713, 1670, 1611, 1532, 1485, 1456, 1426, 1397, 1378, 1290, 1235, 1196, 1080, 1053, 951, 903, 843, 785, 757. ^{1}H NMR (DMSO-d_6): δ 1.10 (3H, t, J = 7.2 Hz, CH_3), 3.67 (3H, s, CH_3O), 3.99 (2H, q, J = 7.2 Hz, CH_2O), 4.64 (1H, s, CH), 6.79 (2H, d, J = 8.4 Hz, ArH), 7.13 (2H, d, J = 8.4 Hz, ArH), 7.44–7.51 (2H, m, ArH), 7.68–7.72 (1H, m, ArH), 7.80 (2H, s, NH_2), 7.96 (1H, d, J = 8.8 Hz, ArH).

Ethyl 2-Amino-4-(4-methylphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (**3l**): M.p. 189–190 °C (Lit.[11] 190 °C). IR: ν/cm^{-1} 3407, 3293, 2980, 2889, 1692, 1683, 1622, 1522, 1471, 1402, 1366, 1288, 1226, 1198, 1158, 1140, 1081, 1033, 973, 846, 793. ^{1}H NMR (DMSO-d_6): δ 1.12 (3H, t, J = 7.2 Hz, CH_3), 2.21 (3H, s, CH_3), 3.99 (2H, q, J = 7.2 Hz, CH_2O), 4.66 (1H, s, CH), 7.03 (2H, d, J = 8.0 Hz, ArH), 7.11 (2H, d, J = 8.0 Hz, ArH), 7.43–7.51 (2H, m, ArH), 7.68–7.71 (1H, m, ArH), 7.80 (2H, s, NH_2), 7.97 (1H, d, J = 8.4 Hz, ArH).

Ethyl 2-Amino-4-(4-fluorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (**3m**): M.p. 223–225 °C (Lit.[12] 222–224 °C). IR: ν/cm^{-1} 3419, 3302, 2975, 2907, 1717, 1691, 1678, 1610, 1471, 1457, 1522, 1375, 1279, 1250, 1196, 1084, 1047, 953, 904, 860, 758, 744, 723. ^{1}H NMR (DMSO-d_6): δ 1.10 (3H, t, J = 7.2 Hz, CH_3), 3.99 (2H, q, J = 7.2 Hz, CH_2O), 4.69 (1H, s, CH), 7.03–7.08 (2H, m, ArH), 7.24–7.28 (2H, m, ArH), 7.44–7.52 (2H, m, ArH), 7.69–7.72 (1H, m, ArH), 7.86 (2H, s, NH_2), 7.97 (1H, d, J = 7.6 Hz, ArH).

Ethyl 2-Amino-4-phenyl-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (**3n**): M.p. 197–199 °C (Lit.[11] 196 °C). IR: ν/cm^{-1} 3416, 3309, 3083, 2975, 1711, 1685, 1610, 1544, 1493, 1477, 1456, 1376, 1278, 1250, 1192, 1112, 1084, 1023, 954, 913, 843, 822, 768, 739, 703. ^{1}H NMR (DMSO-d_6): δ 1.11 (3H, t, J = 7.2 Hz, CH_3), 3.99 (2H, q, J = 7.2 Hz, CH_2O), 4.70 (1H, s, CH), 7.13–7.16 (1H, m, ArH), 7.23–7.24 (4H, m, ArH), 7.44–7.51 (2H, m, ArH), 7.68–7.72 (1H, m, ArH), 7.82 (2H, s, NH_2), 7.98 (1H, d, J = 8.4 Hz, ArH).

Ethyl 2-Amino-4-(4-chlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (**3o**): M.p. 191–193 °C (Lit.[11] 192 °C). IR: ν/cm^{-1} 3412, 3303, 2958, 2837, 1690, 1675, 1621, 1584, 1527, 1508, 1467, 1445, 1367, 1288, 1250, 1233, 1200, 1162, 1142, 1085, 1035, 972, 825, 848, 795, 763. ^{1}H NMR (DMSO-d_6): δ 1.10 (3H, t, J = 7.2 Hz, CH_3), 3.99 (2H, q, J = 7.2 Hz, CH_2O), 4.68 (1H, s, CH), 7.24–7.31 (4H, m, ArH), 7.45–7.52 (2H, m, ArH), 7.69–7.73 (1H, m, ArH), 7.88 (2H, s, NH_2), 7.97 (1H, d, J = 8.8 Hz, ArH).

Ethyl 2-Amino-4-(3,4-methylenedioxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3- carboxylate (**3p**): 193–194 °C. IR: ν/cm^{-1} 3396, 3290, 3064, 2976, 2926, 1717, 1694, 1654, 1611, 1528, 1493, 1458, 1374, 1312, 1281, 1198, 1114, 1057, 1029, 951, 906, 896, 875, 820, 790, 759. ^{1}H NMR (DMSO-d_6): δ 1.13 (3H, t, J = 7.2 Hz, CH_3), 4.01 (2H, q, J = 7.2 Hz, CH_2O), 4.63 (1H, s, CH), 5.94 (1H, s, OCH_2O), 6.69 (1H, d, J = 8.4 Hz, ArH), 6.74–6.78 (2H, m, ArH), 7.44–7.51 (2H, m, ArH), 7.68–7.72 (1H, m, ArH), 7.80 (2H, s, NH_2), 7.96 (1H, d, J = 7.2 Hz, ArH). Found: C, 64.72; H, 4.19; N, 3.48. Calcd for $C_{22}H_{17}NO_7$: C 64.86, H 4.21, N 3.44%.

Ethyl 2-Amino-4-(4-bromophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (**3q**): M.p. 193–194 °C. IR: ν/cm^{-1} 3485, 3315, 3051, 2980, 1717, 1683, 1662, 1611, 1529, 1508, 1491, 1457, 1419, 1374, 1290, 1252, 1200, 1170, 1112, 1096, 1056, 954, 905, 844, 804, 785, 753, 726. ^{1}H NMR (DMSO-d_6): δ 1.10 (3H, t, J = 7.2 Hz, CH_3), 4.00 (2H, q, J = 7.2 Hz, CH_2O), 4.66 (1H, s, CH), 7.20 (2H, d, J = 8.0 Hz, ArH), 7.35–7.54 (4H, m, ArH), 7.67–7.71 (1H, m, ArH), 7.90 (2H, s, NH_2), 7.97 (1H, d, J = 7.6 Hz, ArH). Found: C, 57.15; H, 3.71; N, 3.06 Calcd for $C_{21}H_{16}BrNO_5$: C 57.03; H. 3.65; N. 3.17%.

Ethyl 2-Amino-4-(2,4-dichlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (**3r**): M.p. 200–201 °C (Lit.[12] 197–198 °C). IR: ν/cm^{-1} 3474, 3332, 2973, 2932, 2879, 1694, 1650, 1620, 1524, 1477, 1465, 1406, 1369, 1295, 1247, 1205, 1143, 1124, 1085, 1037, 971, 856, 839, 816. ^{1}H NMR (DMSO-d_6): δ 1.06 (3H, t, J = 7.2 Hz, CH_3), 3.96 (2H, q, J = 7.2 Hz, CH_2O), 5.06 (1H, s, CH), 7.29–7.34 (2H, m, ArH), 7.44–7.52 (3H, m, ArH), 7.69–7.73 (1H, m, ArH), 7.94–7.98 (3H, m, NH_2 + ArH).

Methyl 2-Amino-4-(4-chlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (**3s**): M.p. 227–229 °C (Lit.[12] 227–229 °C). IR: ν/cm^{-1} 3402, 3287, 3048, 2984, 2939, 1705, 1683, 1640, 1611, 1532, 1479, 1456, 1440, 1405, 1370, 1289, 1242, 1195, 1089, 1054, 1008, 951, 903, 843, 832, 785, 757. ^{1}H NMR (DMSO-d_6): δ 3.64 (3H, s, CH_3O), 4.90 (1H, s, CH), 6.48 (2H, s, NH_2), 7.21 (2H, d, J = 8.4 Hz, ArH), 7.27 (2H, d, J = 8.4 Hz, ArH), 7.31–7.35 (2H, m, ArH), 7.54–7.58 (1H, m, ArH), 7.82 (1H, dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, ArH).

Methyl 2-Amino-4-(4-methylphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (**3t**): M.p. 204–205 °C (Lit.[12] 204–206 °C). IR: ν/cm^{-1} 3393, 3285, 3084, 2984, 2951, 1705, 1689, 1613, 1532, 1485, 1455, 1400, 1378, 1323, 1289, 1239, 1196, 1110, 1076, 1054, 1008, 951, 904, 840, 786, 762. ^{1}H NMR (DMSO-d_6): δ 2.27 (3H, s, CH_3), 3.64 (3H, s, CH_3O), 4.91 (1H, s, CH), 6.42 (2H, s, NH_2), 7.05 (2H, d, J = 8.0 Hz, ArH), 7.25 (2H, d, J = 8.0 Hz, ArH), 7.29–7.34 (2H, m, ArH), 7.52~7.56 (1H, m, ArH), 7.82 (1H, dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, ArH).

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