

## One-pot synthesis of pyrano[3,2-*c*]pyran derivatives catalyzed by KF/Al<sub>2</sub>O<sub>3</sub>

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### Abstract

A series of pyrano[3,2-*c*]pyran derivatives have been synthesized by the reaction of aromatic aldehyde, malononitrile or cyanoacetate and 4-hydroxy-5-methylpyran-2-one in EtOH at room temperature catalyzed by KF/Al<sub>2</sub>O<sub>3</sub>. The structures of the products were characterized by IR, <sup>1</sup>H NMR and elemental analysis, and 4a was further confirmed by X-ray diffraction analysis.

**Keywords:** Pyrano[3,2-*c*]pyran, KF/Al<sub>2</sub>O<sub>3</sub>, synthesis

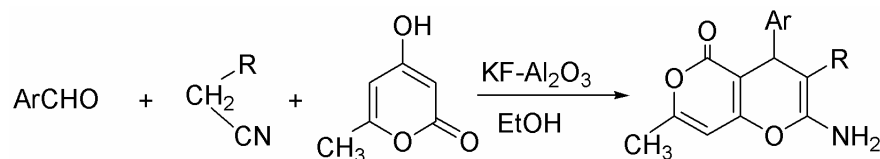
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### Introduction

It is known that many pyran derivatives exhibit a wide spectrum of pharmacological activities and biological activities at melanocortin receptors being used in the design of peptidomimetics relating to a tripeptide structure,<sup>1</sup> such as fungicidal, insecticidal and acaricidal activity,<sup>2</sup> antiviral activity,<sup>3</sup> miticidal activity,<sup>4</sup> stimulant activity,<sup>5</sup> and anticonvulsant activity.<sup>6</sup> These promoted us to synthesis these compounds via a new way. Particularly, we focused our attention on the use of KF-alumina as catalyst, because the utility of fluoride salts as potential base in a variety of synthetic reactions has been recognized in recent years,<sup>7</sup> resulting in their higher selectivity, milder reaction conditions and easier work-up. Especially alumina coated with potassium fluoride (KF-alumina) has been a versatile solid-supported reagent developed by Ando *et al.* for alkylation.<sup>8</sup> Over the years the reagent has been found application in a large number of organic reactions.<sup>9</sup> In order to further enlarge the application of the reagent of KF-alumina, in this paper, we would like to report one pot synthesis these potential active pyrano[3,2-*c*]pyran derivatives by the reaction of aromatic aldehyde, malononitrile or cyanoacetate and 4-hydroxy-6-methylpyran-2-one catalyzed by KF-alumina at room temperature.

## Results and Discussion

When aromatic aldehyde (**1**), malononitrile, or cyanoacetate (**2**) and 4-hydroxy-6-methylpyran-2-one (**3**) were treated with KF-Al<sub>2</sub>O<sub>3</sub> in ethyl alcohol at room temperature, 2-amino-4-aryl-4*H*, 5*H*-pyrano[3,2-*c*]pyran-5-one derivatives (**4**) were obtained in slightly high yields (75-98%) (Scheme 1).



**Scheme 1**

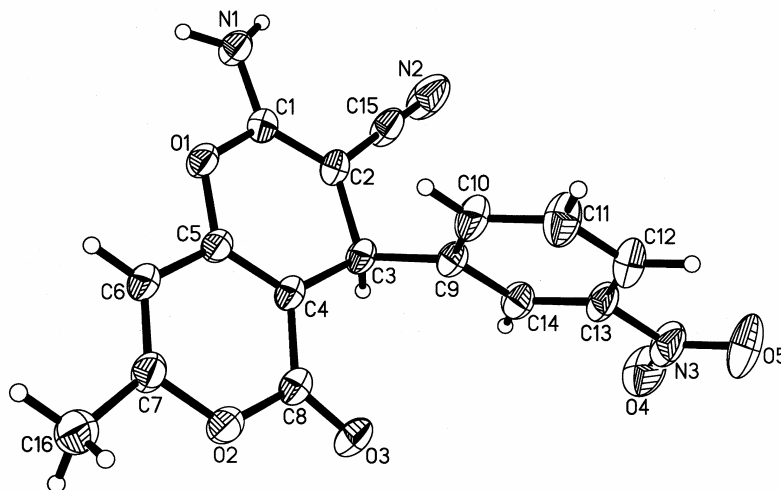
**Table 1.** The reaction time and the yields of the products **4**

Entry	Ar	R	Time(h)	Yields (%)
<b>4a</b>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	CN	6	75
<b>4b</b>	4-BrC <sub>6</sub> H <sub>4</sub>	CN	8	94
<b>4c</b>	2-ClC <sub>6</sub> H <sub>4</sub>	CN	8	98
<b>4d</b>	4-ClC <sub>6</sub> H <sub>4</sub>	CN	8	76
<b>4e</b>	4-Cl-2-NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CN	5	84
<b>4f</b>	3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CN	5	83
<b>4g</b>	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CN	5	86
<b>4h</b>	3-ClC <sub>6</sub> H <sub>4</sub>	CN	8	94
<b>4i</b>	3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CO <sub>2</sub> Et	8	93
<b>4j</b>	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CO <sub>2</sub> Et	8	87
<b>4k</b>	3-ClC <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	10	82
<b>4l</b>	2-ClC <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	10	81
<b>4m</b>	4-ClC <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	10	94
<b>4n</b>	3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CO <sub>2</sub> Me	8	88

In order to demonstrate the efficiency and the applicability of the present method, we performed the reaction of a variety of aromatic aldehyde with malononitrile or cyanoacetate and **3** in EtOH at room temperature and in the presence of KF-Al<sub>2</sub>O<sub>3</sub>. As shown in Table 1, we can see a series of **1** reacted with **2** and **3** to give the corresponding products **4** in good yields under same reaction conditions.

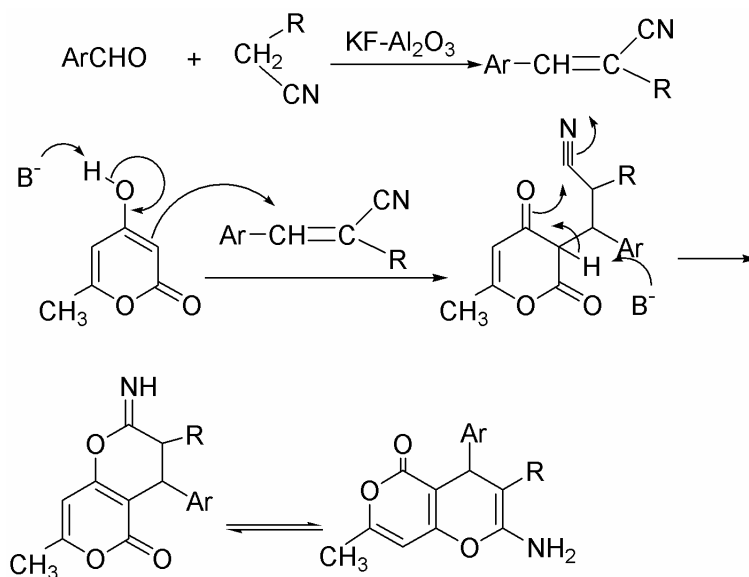
The isolated pyrano[3,2-*c*]pyran derivatives **4** were completely characterized by IR, <sup>1</sup>H NMR and elemental analyses. The analyses were in agreement with their structures. The melting

points of known compounds were conformed to those of the references reported. The IR spectra for **4a** exhibited sharp bands at  $3400$ ,  $3327\text{ cm}^{-1}$  ( $\text{NH}_2$ ),  $2199\text{ cm}^{-1}$  ( $\text{CN}$ ),  $1716\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ). The  $^1\text{H}$  NMR spectrum of **4a** exhibited a singlet identified as methyl ( $2.24$ ), two singlets exhibited at  $4.57$  and  $6.32$  ppm identified as two methines ( $\text{CH}$  and  $\text{CH}=\text{}$ ), respectively, and along with multiplets ( $7.64\text{--}8.14$ ) for aromatic protons. The  $\text{NH}$  proton resonance at  $7.35$  disappeared after addition of  $\text{D}_2\text{O}$  to the  $\text{DMSO-}d_6$  solution of **4a**. In order to further confirm the structure of the product, the X-ray analysis<sup>10</sup> of **4a** was carried out. The crystal structure of **4a** was shown in Figure 1.



**Figure 1.** The crystal structure of **4a**.

Although the detailed mechanism of the above reaction has not been clarified yet, the formation of **4** can be explained by the possible mechanism presented in Scheme 2.



**Scheme 2**

In conclusion, we find a novel one-pot method available for the synthesis of pyrano[3,2-*c*]pyran derivatives. Meanwhile, the new method also further expands the application of the catalyst of KF-Al<sub>2</sub>O<sub>3</sub> in organic synthesis. Compared with other methods,<sup>11</sup> this method has the advantage of one-step, easy work-up, milder reaction conditions and good yields in synthesis these potential active compounds.

## Experimental Section

**General Procedures.** Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr. <sup>1</sup>H NMR spectra were obtained for solutions in DMSO-*d*<sub>6</sub> with Me<sub>4</sub>Si as internal standard using a Bruker-400 spectrometer. Elemental analyses were carried out using Carlo Erba 1110 analyzer. X-ray diffraction was measured on a Siemens P4 diffractometer.

**General procedure for pyrano[3,2-*c*]pyran derivatives (4).** A dry 50 mL flask was charged with aromatic aldehyde **1** (2 mmol), malononitrile or cyanoacetate **2** (2.5 mmol) and 4-hydroxy-6-methylpyran-2-one **3** (2 mmol), KF-Al<sub>2</sub>O<sub>3</sub> (100 mg) and ethyl alcohol (10 mL), the mixture was stirred at room temperature for 5-10 h. The mixture was poured into 200 mL water, the solid filtered off, and washed with water. The crude product was purified by recrystallization from DMF and water to give **4**.

**2-Amino-3-cyano-4-(3-nitrophenyl)-4*H*,5*H*-pyrano[3,2-*c*]pyran-5-one (4a).** Pale yellow crystals; m.p. 238-240 °C (lit.<sup>11</sup> 234-235 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ, ppm) δ: 2.24 (s, 3H, CH<sub>3</sub>), 4.57 (s, 1H, CH), 6.32 (s, 1H, =CH), 7.35 (s, 2H, NH<sub>2</sub>), 7.64 (t, *J* = 8.0 Hz, 1H, ArH), 7.73 (tt, *J* = 8.0 Hz, *J'* = 1.2 Hz, 1H, ArH), 8.05 (t, *J* = 2.0 Hz, 1H, ArH), 8.13 (dd, dd, *J* = 8.0 Hz, *J'* = 2.0 Hz, *J''* = 1.2 Hz, 1H, ArH). IR (KBr, cm<sup>-1</sup>): 3400, 3327, 2199, 1716, 1615, 1526, 1448, 1383, 1263, 1200, 1143, 1024, 977, 817, 759, 733 cm<sup>-1</sup>.

**2-Amino-3-cyano-4-(4-bromophenyl)-4*H*,5*H*-pyrano[3,2-*c*]pyran-5-one (4b).** Pale yellow crystals; m.p. 223-225 °C (lit.<sup>11</sup> 223-224 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ, ppm): 2.23 (s, 3H, CH<sub>3</sub>), 4.31 (s, 1H, CH), 6.29 (s, 1H, =CH), 7.17 (d, 2H, *J* = 8.4 Hz, ArH), 7.26 (s, 2H, NH<sub>2</sub>), 7.51 (d, 2H, *J* = 8.4 Hz, ArH). IR (KBr, cm<sup>-1</sup>): 3388, 3324, 2201, 1707, 1644, 1589, 1486, 1445, 1408, 1314, 1261, 1196, 1176, 1142, 1012, 982, 854, 829, 776.

**2-Amino-3-cyano-4-(2-chlorophenyl)-4*H*,5*H*-pyrano[3,2-*c*]pyran-5-one (4c).** Pale yellow crystals; m.p. 270-271 °C (lit.<sup>11</sup> 267-268 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ, ppm): 2.24 (s, 3H, CH<sub>3</sub>), 4.79 (s, 1H, CH), 6.29 (s, 1H, =CH), 7.21-7.32 (m, 5H, ArH + NH<sub>2</sub>), 7.39 (dd, 1H, *J* = 7.6 Hz, *J'* = 1.2 Hz, ArH). IR (KBr, cm<sup>-1</sup>): 3471, 3344, 3104, 2192, 1700, 1638, 1579, 1473, 1443, 1377, 1263, 1197, 1180, 1139, 1043, 964, 820, 762.

**2-Amino-3-cyano-4-(4-chlorophenyl)-4*H*,5*H*-pyrano[3,2-*c*]pyran-5-one (4d).** Pale yellow crystals; m.p. 231-232 °C (lit.<sup>11</sup> 230-231 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ, ppm): 2.23 (s, 3H, CH<sub>3</sub>), 4.32 (s, 1H, CH), 6.29 (s, 1H, =CH), 7.23 (d, 2H, *J* = 8.4 Hz, ArH), 7.26 (s, 2H, NH<sub>2</sub>), 7.37 (d,

2H,  $J = 8.4$  Hz, ArH). IR (KBr,  $\text{cm}^{-1}$ ): 3382, 3324, 2202, 1711, 1645, 1590, 1488, 1445, 1414, 1385, 1314, 1261, 1196, 1092, 1015, 981, 854, 830, 807, 777.

**2-Amino-3-cyano-4-(4-chloro-2-nitrophenyl)-4H,5H-pyrano[3,2-c]pyran-5-one (4e).** Pale yellow crystals; m.p. 247-249 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 2.09 (s, 3H,  $\text{CH}_3$ ), 5.08 (s, 1H, CH), 6.30 (s, 1H, =CH), 7.44 (s, 2H,  $\text{NH}_2$ ), 7.54 (d, 1H,  $J = 2.0$  Hz, ArH), 7.59 (dd, 1H,  $J = 8.8$  Hz,  $J' = 2.0$  Hz, ArH), 7.93 (d, 1H,  $J = 8.8$  Hz, ArH). IR (KBr,  $\text{cm}^{-1}$ ): 3419, 3332, 2195, 1703, 1644, 1588, 1522, 1449, 1382, 1338, 1260, 1198, 1145, 1040, 977, 900, 849, 199, 774. Anal. calcd for  $\text{C}_{16}\text{H}_{10}\text{ClN}_3\text{O}_5$ : C 53.42, H 2.80, N 11.68. Found: C 53.29, H 2.91, N 11.52.

**2-Amino-3-cyano-4-(3,4-dichlorophenyl)-4H,5H-pyrano[3,2-c]pyran-5-one (4f).** Pale yellow crystals; m.p. 239-241 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 2.23 (s, 3H,  $\text{CH}_3$ ), 4.39 (s, 1H, CH), 6.29 (s, 1H, =CH), 7.22 (dd, 1H,  $J = 8.0$  Hz,  $J' = 2.0$  Hz, ArH), 7.32 (s, 2H,  $\text{NH}_2$ ), 7.49 (d, 1H,  $J = 2.0$  Hz, ArH), 7.58 (d, 1H,  $J = 8.0$  Hz, ArH). IR (KBr,  $\text{cm}^{-1}$ ): 3391, 3326, 2200, 1715, 1645, 1590, 1465, 1445, 1381, 1298, 1261, 1185, 1141, 1031, 983, 969, 898, 810, 786, 770. Anal. calcd for  $\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_3$ : C 55.04, H 2.89, N 8.02. Found: C 54.90, H 2.99, N 8.00.

**2-Amino-3-cyano-4-(2,4-dichlorophenyl)-4H,5H-pyrano[3,2-c]pyran-5-one (4g).** Pale yellow crystals; m.p. 234-235 °C (lit.  $^{11}$  230-231 °C).  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 2.24 (s, 3H,  $\text{CH}_3$ ), 4.79 (s, 1H, CH), 6.30 (s, 1H, =CH), 7.29 (d, 1H,  $J = 8.0$  Hz, ArH), 7.30 (s, 2H,  $\text{NH}_2$ ), 7.38 (dd, 1H,  $J = 8.0$  Hz,  $J' = 2.0$  Hz, ArH), 7.57 (d, 1H,  $J = 2.0$  Hz, ArH). IR (KBr,  $\text{cm}^{-1}$ ): 3408, 3348, 2196, 1706, 1642, 1583, 1472, 1444, 1376, 1265, 1198, 1137, 1105, 1047, 966, 857, 828, 738.

**2-Amino-3-cyano-4-(3-chlorophenyl)-4H,5H-pyrano[3,2-c]pyran-5-one (4h).** Pale yellow crystals; m.p. 255-257 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 2.24 (s, 3H,  $\text{CH}_3$ ), 4.35 (s, 1H, CH), 6.29 (s, 1H, =CH), 7.17 (d, 1H,  $J = 7.6$  Hz, ArH), 7.25-7.38 (m, 5H, ArH +  $\text{NH}_2$ ). IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3396, 3323, 2198, 1707, 1644, 1590, 1473, 1442, 1430, 1383, 1303, 1259, 1179, 1140, 1041, 980, 833, 803, 770. Anal. calcd for  $\text{C}_{16}\text{H}_{11}\text{ClN}_2\text{O}_3$ : C 61.06, H 3.52, N 8.90. Found: C 61.04, H 3.70, N 8.77.

**Ethyl 2-amino-3-cyano-4-(3,4-dichlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]pyran-3-carboxylate (4i).** Pale yellow crystals; m.p. 179-181 °C. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3447, 3320, 1983, 1717, 1690, 1622, 1513, 1468, 1448, 1378, 1286, 1257, 1211, 1174, 1138, 1086, 1030, 976, 814, 787;  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 1.08 (t, 3H,  $J = 6.8$  Hz,  $\text{CH}_3$ ), 2.10 (s, 3H,  $\text{CH}_3$ ), 3.97 (q, 2H,  $J = 6.8$  Hz,  $\text{CH}_2$ ), 4.52 (s, 1H, CH), 6.32 (s, 1H, =CH), 7.15 (dd, 1H,  $J = 8.8$  Hz,  $J' = 2.0$  Hz, ArH), 7.38 (d, 1H,  $J = 2.0$  Hz, ArH), 7.52 (d, 1H,  $J = 8.8$  Hz, ArH) 7.82 (s, 2H,  $\text{NH}_2$ ). Anal. calcd for  $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{NO}_5$ : C 54.56, H 3.82, N 3.54. Found: C 54.48, H 3.93, N 3.50.

**Ethyl 2-amino-3-cyano-4-(2,4-dichlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]pyran-3-carboxylate (4j).** Pale yellow crystals; m.p. 206-208 °C (lit.  $^{11}$  204-205 °C).  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 1.04 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 2.10 (s, 3H,  $\text{CH}_3$ ), 3.92 (q, 2H,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 4.88 (s, 1H, CH), 6.29 (s, 1H, =CH), 7.26 (d, 1H,  $J = 8.4$  Hz, ArH), 7.32 (dd, 1H,  $J = 8.4$  Hz,  $J' = 2.4$  Hz, ArH), 7.43 (d, 1H,  $J = 2.4$  Hz, ArH), 7.85 (s, 2H,  $\text{NH}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3435, 3298, 2957, 1712, 1689, 1615, 1584, 1505, 1471, 1380, 1290, 1250, 1174, 1139, 1080, 1046, 957, 849, 817.

**Ethyl 2-amino-3-cyano-4-(3-chlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]pyran-3-carboxylate (4k).** Pale yellow crystals; m.p. 180-182 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 1.08 (t, 3H,  $J = 6.8$

Hz, CH<sub>3</sub>), 2.10 (s, 3H, CH<sub>3</sub>), 3.96 (q, 2H,  $J = 6.8$  Hz, CH<sub>3</sub>), 4.52 (s, 1H, CH), 6.32 (s, 1H, =CH), 7.17 (d, 1H,  $J = 7.6$  Hz, ArH), 7.11-7.31 (m, 4H, ArH), 7.79 (s, 2H, NH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3426, 3294, 2979, 1710, 1687, 1619, 1506, 1475, 1442, 1378, 1286, 1252, 1212, 1174, 1140, 1073, 1041, 958, 816, 782, 750. Anal. calcd for C<sub>18</sub>H<sub>16</sub>ClNO<sub>5</sub>: C 59.76, H 4.46, N 3.87. Found: C 59.76, H 4.57, N 3.72.

**Ethyl 2-amino-3-cyano-4-(2-chlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]pyran-3-carboxylate (4l).** Pale yellow crystals; m.p. 203-204 °C (lit.<sup>11</sup> 203-205 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 1.03 (t, 3H,  $J = 7.2$  Hz, CH<sub>3</sub>), 2.22 (s, 3H, CH<sub>3</sub>), 3.92 (q, 2H,  $J = 7.2$  Hz, CH<sub>3</sub>), 4.90 (s, 1H, CH), 6.29 (s, 1H, =CH), 7.14-7.24 (m, 3H, ArH), 7.29 (d, 1H,  $J = 8.0$  Hz, ArH), 7.81 (s, 2H, NH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3421, 3295, 2988, 1715, 1688, 1621, 1509, 1440, 1379, 1287, 1176, 1077, 980, 956, 815, 773, 756.

**Ethyl 2-amino-3-cyano-4-(4-chlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]pyran-3-carboxylate (4m).** Pale yellow crystals; m.p. 160-161 °C (lit.<sup>11</sup> 156-157 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 1.07 (t, 3H,  $J = 6.8$  Hz, CH<sub>3</sub>), 2.22 (s, 3H, CH<sub>3</sub>), 3.95 (q, 2H,  $J = 6.8$  Hz, CH<sub>3</sub>), 4.52 (s, 1H, CH), 6.31 (s, 1H, =CH), 7.19 (d, 2H,  $J = 8.4$  Hz, ArH), 7.30 (d, 2H,  $J = 8.4$  Hz, ArH), 7.77 (s, 2H, NH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3431, 3306, 2980, 1715, 1678, 1618, 1490, 1443, 1378, 1291, 1215, 1172, 1140, 1076, 1014, 981, 955, 841, 818.

**Methyl 2-amino-3-cyano-4-(3,4-dichlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]pyran-3-carboxylate (4n).** Pale yellow crystals; m.p. 193-197 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 2.10 (s, 3H, CH<sub>3</sub>), 3.52 (s, 3H, CH<sub>3</sub>O), 4.53 (s, 1H, CH), 6.32 (s, 1H, =CH), 7.17 (dd, 1H,  $J = 8.4$  Hz,  $J = 2.0$  Hz, ArH), 7.36 (d, 1H,  $J = 2.0$  Hz, ArH), 7.52 (d, 1H,  $J = 8.4$  Hz, ArH), 7.83 (s, 2H, NH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3426, 3304, 2955, 1712, 1687, 1619, 1514, 1468, 1439, 1380, 1296, 1254, 1219, 1176, 1141, 1085, 1033, 973, 941, 810, 774, 746. Anal. calcd for C<sub>17</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>5</sub>: C 53.42, H 3.43, N 3.66. Found: C 53.29, H 3.50, N 3.51.

## Supplementary Information Available

Crystallographic data for the structure **4a** reported in this paper has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication with No. CCDC-605772. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0) 1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## Acknowledgements

We are grateful to the Natural Science Foundation (04KJB150139) of the Education Committee of Jiangsu Province for financial support.

## References and Footnotes

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10. X-ray crystallography for **4a**: Empirical formula  $C_{16}H_{11}N_3O_5$ ,  $F_w = 325.28$ ,  $T = 289(2)$  K, Monoclinic, space group  $P2(1)/c$ ,  $a = 5.709(1)$  Å,  $b = 14.616(2)$  Å,  $c = 18.228(3)$  Å,  $\beta = 94.219(2)^\circ$ ,  $V = 1516.8(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.424$  Mg/m<sup>3</sup>,  $\lambda(MoK\alpha) = 0.71073$  Å,  $\mu = 0.109$  mm<sup>-1</sup>,  $F(000) = 672$ .  $1.79^\circ < \theta < 25.49^\circ$ ,  $R = 0.0423$ ,  $wR = 0.0961$ .  $S = 0.952$ , Largest diff. Peak and hole: 0.153 and  $-0.181$  e<sup>-</sup>Å<sup>-3</sup>
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