

## Mg(ClO<sub>4</sub>)<sub>2</sub>-catalyzed one-pot synthesis of 2-amino-4H-chromenes and dihydropyrano[c]chromenes

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This report provides a description of an efficient and simple procedure for the synthesis of 2-amino-4H-chromenes and dihydropyrano[c]chromenes *via* one-pot three-component reaction of aldehydes, active methylene compounds and resorcinol or 4-hydroxycoumarin catalysed by magnesium perchlorate. The remarkable advantages are simplicity of the experimental procedure, high yields, short reaction times, and reusability of the catalyst.

**Keywords:** 2-Amino-4H-chromenes, Dihydropyrano[c]chromenes, Resorcinol, 4-Hydroxycoumarin, Magnesium perchlorate, One-pot

### INTRODUCTION

Coumarin derivatives like 2-amino-4H-chromenes and dihydropyrano[c]chromenes have received considerable attention because they possess several pharmacological properties [1]. These compounds can be prepared by one-pot three-component condensation of aldehydes, active methylene compounds and resorcinol or 4-hydroxycoumarin in the presence of a variety of acids or bases [2-11]. Some of these procedures suffer from the use of toxic, highly acidic and expensive catalysts and require organic solvents. Therefore, cleaning processes have been in permanent focus. Magnesium perchlorate as a solid acid is a moisture-stable, non-toxic, cheap, and commercially available material which can be handled easily and removed from the reaction mixtures. In continuation of our research on the applications of solid acids in organic synthesis [12,13], we have investigated the one-pot three-component synthesis of 2-amino-4H-chromenes and dihydropyrano[c]chromene derivatives in the presence of Mg(ClO<sub>4</sub>)<sub>2</sub>.

### RESULTS AND DISCUSSION

Initially, we explored the catalytic efficiency of Mg(ClO<sub>4</sub>)<sub>2</sub> and other salts with various cations and anions such as MgSO<sub>4</sub>, MgBr<sub>2</sub>, MgCl<sub>2</sub> and LiClO<sub>4</sub>. However, MgSO<sub>4</sub> and MgBr<sub>2</sub> did not exhibit any significant catalytic activity; only 60% and 70% yield was obtained in the presence of MgCl<sub>2</sub> and LiClO<sub>4</sub>, respectively, establishing that amongst the various salts used, Mg(ClO<sub>4</sub>)<sub>2</sub> was the most

effective catalyst for the synthesis of 2-amino-4H-chromenes and dihydropyrano[c]chromenes. For optimizing the experimental conditions, the reaction between malononitrile, benzaldehyde and 4-hydroxycoumarin in the presence of Mg(ClO<sub>4</sub>)<sub>2</sub> was considered as a model reaction. This condensation reaction was studied in various solvents at different temperatures and with different amounts of catalysts. The best conditions were found to be 0.035 g catalyst at 60 °C in H<sub>2</sub>O (Table 1).

After completion of the reaction, the mixture was filtered and the aqueous filtrate extracted by 5 mL of ethyl acetate to remove any starting materials. The aqueous phase containing magnesium perchlorate was separated and reused for three times although a gradual decline was observed in its activity (Table 1, entries 18, 19). Apparently, the reaction of various aldehydes, active methylene compounds and 4-hydroxycoumarin in the presence of an optimized amount of Mg(ClO<sub>4</sub>)<sub>2</sub> in H<sub>2</sub>O at 60 °C resulted in the formation of dihydropyrano[c]chromene derivatives (Table 2).

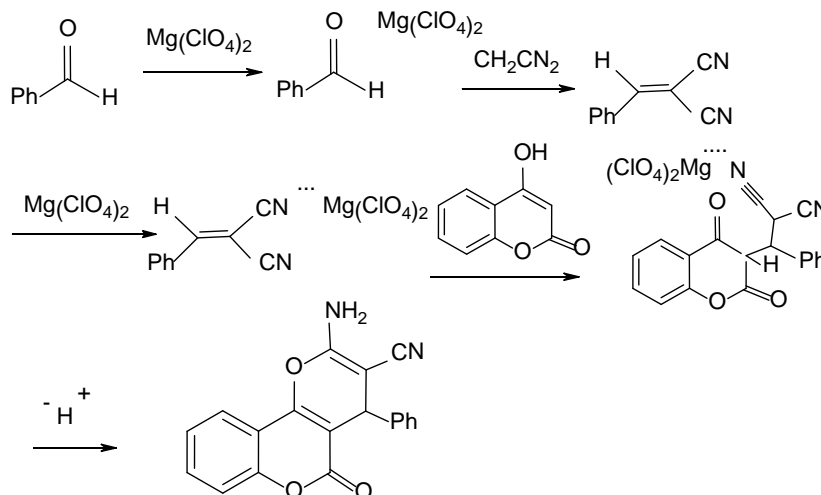
Aromatic aldehydes containing electron-withdrawing groups have reacted very well at a faster rate in a shorter time than aromatic aldehydes with electron-donating groups (Table 2, entries 2, 3). Also, in this reaction with ethyl cyanoacetate as a substrate instead of malononitrile, the corresponding products have been produced in high yields but in a longer reaction time (Table 2, entries 11,12). This may be due to the lower activity of ethyl cyanoacetate than malononitrile. Also, the reactions of active methylene compounds, pyridine carbaldehydes and 4-hydroxycoumarin were examined and the corresponding products were found to be yielded highly and within short times (Table 2, entries 13-16). Although the mechanism

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of the reaction has not yet been experimentally established, the formation of the product can be rationalized as outlined in the Scheme 1.

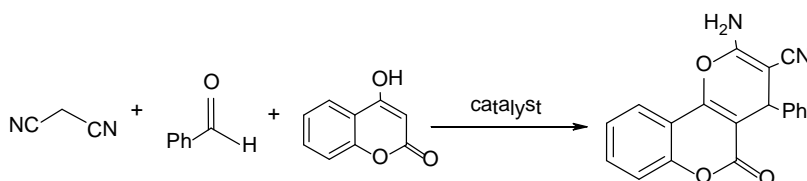
The reaction of malononitrile, resorcinol and aldehydes was carried out in the above-mentioned optimized reaction conditions and various 2-amino-4H-chromenes were obtained (Table 3). This

reaction produces 2-amino-7-hydroxy-4H-chromene derivatives instead of the expected 2-amino-5-hydroxy-4H-chromene derivatives, that is probably due to the steric hindrance between the two hydroxyl groups in resorcinol.



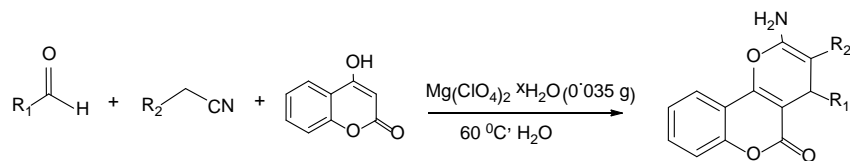
**Scheme 1.** A possible mechanism for the synthesis of dihydropyrano[c]chromenes

**Table 1.** Optimization of the reaction conditions for one-pot synthesis of dihydropyrano[c]chromenes<sup>a)</sup>



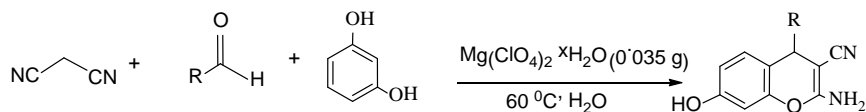
Entry	Catalyst (g)	Temp. (°C)	Solvent	Time (min)	Yield (%) <sup>b)</sup>
1	-	70	EtOH	120	30
2	MgCl <sub>2</sub> .xH <sub>2</sub> O (0.020)	70	EtOH	60	60
3	MgBr <sub>2</sub> (0.030)	70	EtOH	60	45
4	MgSO <sub>4</sub> (0.025)	70	EtOH	60	40
5	LiClO <sub>4</sub> (0.020)	70	EtOH	60	70
6	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.030)	70	EtOH	50	84
7	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.020)	70	EtOH	50	60
8	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	70	EtOH	50	90
9	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.045)	70	EtOH	50	87
10	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	70	EtOH/H <sub>2</sub> O	50	85
11	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	70	H <sub>2</sub> O	50	90
12	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	70	MeCN	50	50
13	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	70	CHCl <sub>3</sub>	50	-
14	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	r.t	H <sub>2</sub> O	50	60
15	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	40	H <sub>2</sub> O	50	72
16	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	50	H <sub>2</sub> O	50	83
17	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	60	H <sub>2</sub> O	50	90
18	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035) (2 <sup>th</sup> run)	60	H <sub>2</sub> O	50	82
19	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035) (3 <sup>th</sup> run)	60	H <sub>2</sub> O	50	75
20	Mg(ClO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O (0.035)	u.s. <sup>c)</sup>	H <sub>2</sub> O	15	50

<sup>a)</sup> Reaction conditions: malononitrile (1 mmol) benzaldehyde (1 mmol), 4-hydroxycoumarin (1 mmol). <sup>b)</sup> Isolated yields. <sup>c)</sup> Reaction under ultrasonic waves (60 W).

**Table 2.** Synthesis of dihydropyrano[c]chromenes in the presence of Mg(ClO<sub>4</sub>)<sub>2</sub><sup>a)</sup>

Entry	R <sub>1</sub>	R <sub>2</sub>	Time(min/h)	Yield (%) <sup>b)</sup>	M.p. (°C)		Ref.
					Observed	Reported	
1	C <sub>6</sub> H <sub>5</sub>	CN	50 min	89	256-258	256-258	[3]
2	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CN	45 min	95	260-261	256-259	[11]
3	3-OH-C <sub>6</sub> H <sub>4</sub>	CN	70 min	75	272-273	-	-
4	4-F-C <sub>6</sub> H <sub>4</sub>	CN	50 min	88	265-267	262-263	[3]
5	4-OMe-C <sub>6</sub> H <sub>4</sub>	CN	48 min	86	258-260	248-250	[3]
6	4-Me-C <sub>6</sub> H <sub>4</sub>	CN	55 min	88	254-256	253-255	[3]
7	2,6-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	CN	52 min	89	299-300	274-277	[11]
8	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	45 min	92	260-262	260-262	[3]
9	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	CN	60 min	74	190-192	187-188	[6]
10	2-furyl	CN	55 min	78	253-255	250-252	[4]
11	3-Br-C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	14 h	78	220-222	-	-
12	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	15 h	75	245-247	247-250	[12]
13	3-pyridiyl	CN	12 min	90	251-253	-	-
14	3-pyridiyl	CO <sub>2</sub> Et	20 min	85	227-229	-	-
15	4-pyridiyl	CN	10 min	94	186-188	182-184	[5]
16	4-pyridiyl	CO <sub>2</sub> Et	15 min	87	220-222	-	-

<sup>a)</sup> Reaction conditions: aldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol). <sup>b)</sup> Isolated yields

**Table 3.** Synthesis of 2-amino-4H-chromenes in the presence of Mg(ClO<sub>4</sub>)<sub>2</sub><sup>a)</sup>

Entry	R	Yield (%) <sup>b)</sup>	Time (min)	M. p. (°C)		Ref.
				Observed	Reported	
1	C <sub>6</sub> H <sub>5</sub>	83	80	237-238	235-236	[7]
2	4-Me-C <sub>6</sub> H <sub>4</sub>	82	85	190-191	182-184	[7]
3	4-F-C <sub>6</sub> H <sub>4</sub>	90	70	188-190	187-189	[7]
4	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	92	70	210-212	215-217	[13]
5	4-Cl-C <sub>6</sub> H <sub>4</sub>	88	75	165-167	163-164	[7]

<sup>a)</sup> Reaction conditions: malononitrile (1 mmol) aldehyde(1 mmol), resorcinol (1 mmol). <sup>b)</sup> Isolated yields

## EXPERIMENTAL

The products were characterized by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectra and by comparing their physical properties with those reported in the literature. IR spectra were run on a Bruker Equinox 55 spectrometer. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained using a Bruker Avance 500 MHz spectrometer (DRX). Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus. Purity determination of the substrates and reaction monitoring were accompanied by TLC using pre-coated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness.

### General procedure for the synthesis of dihydropyrano[c]chromenes and 2-amino-4H-chromenes

4-Hydroxycoumarin or resorcinol (1 mmol) was added to a stirred mixture of aldehyde (1 mmol), active methylene compound (1 mmol), Mg(ClO<sub>4</sub>)<sub>2</sub>.xH<sub>2</sub>O (0.035 g), and water (3 mL). The mixture was stirred at 60 °C for the appropriate period of time until the initial materials were no longer detectable (TLC). The mixture was filtered and recrystallized in ethanol to obtain pure products. The aqueous filtrate containing magnesium perchlorate was used to investigate the reusability of the catalyst.

*Selected spectra data*

**2-Amino-4-(3-hydroxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 3).** IR (KBr) ( $\bar{\nu}_{\max}$ ): 3314, 3186, 2209, 1707, 1668, 1604, 1587, 1484 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 4.35 (s, 1H), 6.62 (d, 1H, *J* = 7.1 Hz), 6.63 (s, 1H), 6.67 (d, 1H, *J* = 8.0 Hz), 7.10 (t, 1H, *J* = 7.5 Hz), 7.39 (brs, 2H), 7.47 (d, 1H, *J* = 8.5 Hz), 7.50 (t, 1H, *J* = 7.5 Hz), 7.72 (t, 1H, *J* = 8.1 Hz), 7.90 (dd, 1H, *J* = 7.9 Hz, *J* = 1.5 Hz), 9.36 (s, 1H). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 32.45, 60.45, 106.34, 114.64, 120.45, 124.89, 127.89, 129.35, 130.23, 133.23, 133.56, 134.23, 139.45, 142.12, 148.12, 155.46, 157.89, 164.12, 167.23. Anal. calc. for C<sub>19</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C 68.67, H 3.64, N 8.43. found: C 68.4, H 3.8, N 8.9.

**2-Amino-5-oxo-4-(2-phenylethyl)-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 9).** IR (KBr) ( $\bar{\nu}_{\max}$ ): 3368, 3167, 2202, 1703, 1639, 1612, 1601, 1376, 1171 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 1.80 (m, 1H), 2.10 (m, 1H), 2.50 (m, 1H), 2.54 (m, 1H), 3.54 (t, 1H, *J* = 4.0 Hz), 7.03 (t, 1H, *J* = 7.1 Hz), 7.12 (d, 2H, *J* = 7.4 Hz), 7.16 (t, 2H, *J* = 7.3 Hz), 7.36 (s, 2H), 7.45 (m, 2H), 7.69 (t, 1H, *J* = 7.8 Hz), 7.80 (d, 1H, *J* = 7.8 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 30.31, 30.75, 34.67, 54.60, 103.76, 112.92, 116.42, 119.60, 122.09, 124.47, 126.64, 128.14, 132.67, 141.30, 152.04, 154.04, 159.44, 159.91.

**2-Amino-4-(furan-2-yl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 10).** IR (KBr) ( $\bar{\nu}_{\max}$ ): 3364, 3164, 2201, 1702, 1670, 1639, 1604, 1374, 1257 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 84.63 (s, 1H), 6.27 (d, 1H, *J* = 3.1 Hz), 6.38 (dd, 1H, *J* = 3.0, 1.8 Hz), 7.47 (d, 1H, *J* = 3.3 Hz), 7.48 (s, 2H), 7.50 (t, 1H, *J* = 8.0 Hz), 7.53 (d, 1H, *J* = 6.0 Hz), 7.69 (t, 1H, *J* = 8.0 Hz), 7.79 (d, 1H, *J* = 7.0 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 29.23, 58.99, 105.23, 106.78, 111.88, 116.78, 117.67, 124.23, 125.67, 126.67, 141.67, 143.45, 152.56, 153.98, 159.47, 160.98, 161.90.

**Ethyl-2-amino-4-(3-bromophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (Table 2, entry 11).** IR (KBr) ( $\bar{\nu}_{\max}$ ): 3432, 3311, 1708, 1684, 1655, 1608, 1536, 1517, 1492, 1455 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 1.09 (t, 3H, *J* = 7.5 Hz), 3.99 (q, 2H, *J* = 7.0 Hz), 4.82 (s, 1H), 7.45 (d, 1H, *J* = 8.3 Hz), 7.51 (t, 1H, *J* = 7.4 Hz), 7.55 (t, 1H, *J* = 7.9 Hz), 7.7 (d, 1H, *J* = 8.4 Hz), 7.72 (t, 1H, *J* = 7.5 Hz), 7.96 (s, 2H), 8.00 (d, 1H, *J* = 8.0 Hz), 8.04 (d, 1H, *J* = 8.0 Hz), 8.06 (s, 1H). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 14.90,

36.36, 60.03, 106.32, 108.12, 113.91, 122.42, 123.49, 123.71, 125.53, 130.41, 133.77, 135.76, 148.02, 148.23, 153.12, 154.43, 159.36, 160.77, 168.12. Anal. calc. for C<sub>21</sub>H<sub>16</sub>BrNO<sub>5</sub>: C 57.03, H 3.65, N 3.17. found: C 57.3, H 3.4, N 2.9.

**2-Amino-5-oxo-4-(pyridin-3-yl)-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 13).** IR (KBr) ( $\bar{\nu}_{\max}$ ): 3376, 3190, 2194, 1713, 1674, 1639, 1603, 1506, 1460, 1377 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 4.56 (s, 1H), 7.35 (t, 1H, *J* = 7.2 Hz), 7.46-7.53 (m, 4H), 7.71-7.75 (m, 2H), 7.90 (d, 1H, *J* = 6.8 Hz), 7.46 (d, 1H, *J* = 4.0 Hz), 8.55 (s, 1H). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 34.45, 56.96, 102.92, 113.95, 116.57, 119.03, 122.54, 123.79, 124.66, 132.02, 135.45, 138.75, 148.23, 149.03, 152.21, 153.79, 158.02, 159.56. Anal. calc. for C<sub>18</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>: C 68.14, H 3.49, N 13.24. found: C 68.3, H 3.4, N 12.9.

**Ethyl-2-amino-5-oxo-4-(pyridin-3-yl)-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (Table 2, entry 14).** IR (KBr) ( $\bar{\nu}_{\max}$ ): 3376, 3190, 2194, 1713, 1674, 1639, 1603, 1506, 1460, 1377 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 1.07 (t, 3H, *J* = 7.2 Hz), 4.00 (d, 2H, *J* = 6.8 Hz), 4.73 (s, 1H), 7.38 (d, 1H, *J* = 8.0 Hz), 7.49-7.54 (m, 2H), 7.70 (t, 1H, *J* = 8.0 Hz), 7.78 (d, 1H, *J* = 8.0 Hz), 7.96-7.99 (m, 3H), 8.43 (d, 1H, *J* = 4.0 Hz), 8.58 (s, 1H). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 14.10, 33.35, 59.10, 62.55, 105.27, 113.05, 116.56, 122.60, 124.65, 132.88, 136.43, 137.38, 141.13, 146.10, 148.13, 152.24, 153.16, 158.49, 159.90, 167.20. Anal. calc. for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>: C 65.93, H 4.43, N 7.69. found: C 66.1, H 4.2, N 8.0.

**Ethyl-2-amino-5-oxo-4-(pyridin-4-yl)-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (Table 2 entry 16).** IR (KBr) ( $\bar{\nu}_{\max}$ ): 3358, 3182, 1715, 1688, 1658, 1594, 1549, 1492, 1373 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 1.10 (t, 3H, *J* = 7.2 Hz), 4.00 (d, 2H, *J* = 6.8 Hz), 4.74 (s, 1H), 7.42 (d, 2H, *J* = 6.2 Hz), 7.48 (d, 1H, *J* = 8.2 Hz), 7.51 (t, 1H, *J* = 8.0 Hz), 7.72 (t, 1H, *J* = 8.0 Hz), 7.76 (d, 1H, *J* = 8.0 Hz), 8.00 (s, 2H), 8.51 (d, 2H, *J* = 6.2 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 14.11, 35.34, 59.17, 62.13, 104.89, 112.98, 115.76, 116.58, 122.62, 124.15, 130.76, 133.02, 145.18, 147.66, 152.21, 155.59, 158.57, 159.86, 167.14. Anal. calc. for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>: C 65.93, H 4.43, N 7.69. found: C 65.9, H 4.4, N 7.8.

**2-Amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (Table 3, entry 1).** IR (KBr) ( $\bar{\nu}_{\max}$ ): 3500, 3428, 3331, 2193, 1650, 1619, 1588, 1506, 1453, 1403, 1325 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz,

DMSO-d<sub>6</sub>):  $\delta$  = 4.62 (s, 1H), 6.41 (d, 1H,  $J$  = 2.0 Hz), 6.48 (dd, 1H,  $J$  = 8.43, 2.0 Hz), 6.8 (d, 1H,  $J$  = 8.4 Hz), 6.84 (brs, 2H), 7.16 (d, 2H,  $J$  = 8.0 Hz), 7.20 (t, 1H,  $J$  = 7.0 Hz), 7.30 (t, 2H,  $J$  = 7.5 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 56.14, 102.11, 112.32, 113.70, 120.65, 126.60, 127.34, 128.55, 129.89, 146.35, 148.80, 157.02, 160.02.

**2-Amino-7-hydroxy-4-(p-tolyl)-4H-chromene-3-carbonitrile (Table 3, entry 2).** IR (KBr) ( $\bar{\nu}_{\max}$ ): 3441, 3339, 3207, 2190, 1643, 1588, 1508, 1464, 1406, 1155 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 2.25 (s, 3 H), 4.56 (s, 1H), 6.39 (d, 1H,  $J$  = 2.5 Hz), 6.47 (dd, 1H,  $J$  = 8.2, 2.3 Hz), 6.77 (d, 1H,  $J$  = 8.4 Hz), 6.81 (brs, 2H), 7.04 (d, 1H,  $J$  = 7.9 Hz), 7.10 (d, 1H,  $J$  = 7.9 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 15.87, 55.23, 104.21, 110.30, 117.87, 125.65, 126.32, 127.78, 128.54, 141.86, 143.56, 146.45, 159.10, 161.34.

In summary, this paper reports a facile and efficient method for the synthesis of 2-amino-4H-chromenes and dihydropyrano[c]chromenes in the presence of magnesium perchlorate. This method offers significant advantages such as high conversions, easy handling, clean and mild reaction profile, and a straightforward work-up which make it a useful and attractive process for the rapid synthesis of substituted 2-amino-4H-chromenes and dihydropyrano[c]chromenes.

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## ЕДНОСТАДИЙНА СИНТЕЗА НА 2-АМИНО-4Н-ХРОМЕНИ И ДИХИДРОПИРАНО [с] ХРОМЕНИ, КАТАЛИЗИРАНА ОТ Mg(ClO<sub>4</sub>)<sub>2</sub>

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(Резюме)

Тази статия дава описание на ефикасна и проста процедура за синтезата на 2-амино-4Н-хромени и дихидропирано [с] хромени чрез едностадийна три-компонентна реакция на алдехиди, активни метиленови съединения и резорцинол или 4-хидроксикумарин, катализирана от магнезиев перхлорат. Забележителни предимства са простотата на експерименталната процедура, високите добиви, кратките времена за реакцията и многократната употреба на катализатора.