

## Supplementary Material

# Nanofibre Sepiolite Catalyzed Green and Rapid Synthesis of 2-Amino-4*H*-chromene Derivatives

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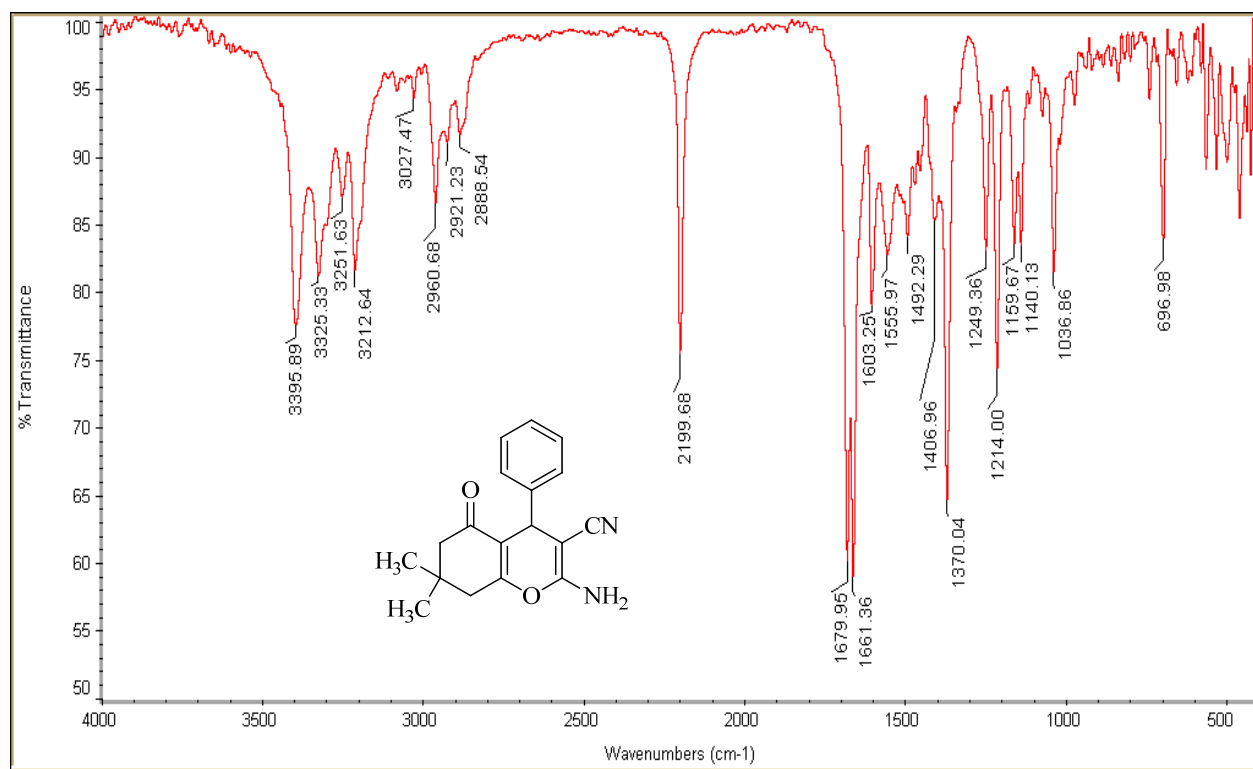
## Experimental

### General

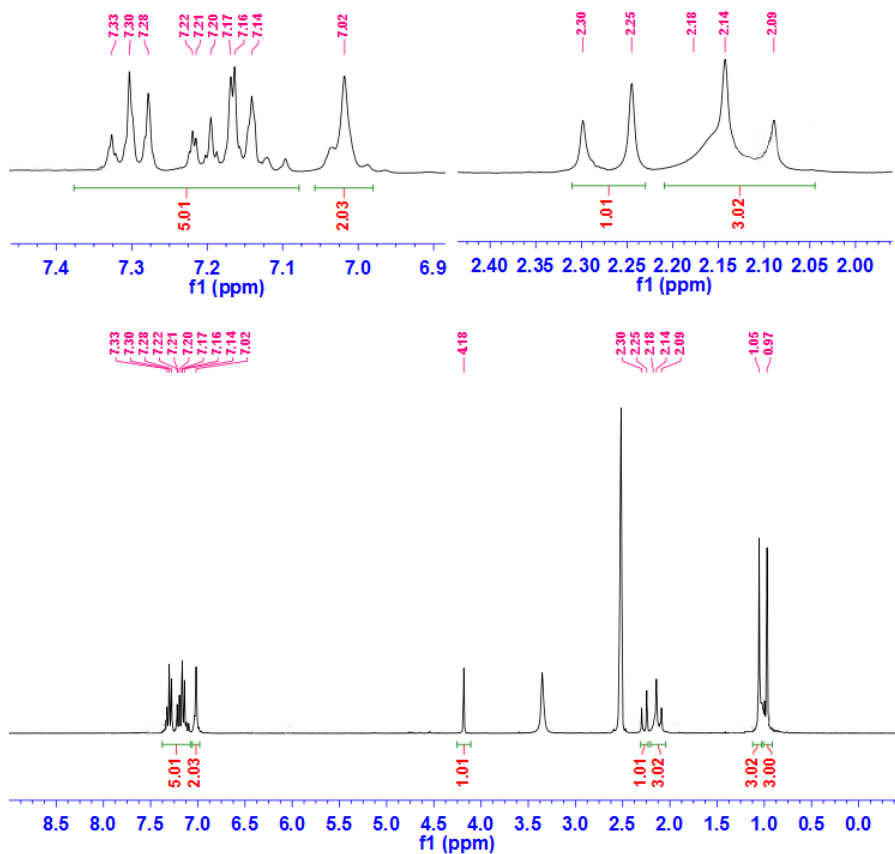
The purity determinations of the products and the progress of the reactions were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Thermo Nicolet spectrometer. The NMR spectra were provided on Bruker Avance 300 MHz instruments in DMSO. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in m/z (rel %). Transmission electron microscopy (TEM) was performed with a Leo 912 AB (120 kV) microscope (Zeiss,

Germany). X-ray powder diffraction (XRD) was performed on a X'Pert Pro MPD diffractometer with Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation. The chemical compositions of the sepiolite were specified with X-ray fluorescence spectroscopy (XRF), using PW 2404 Philips Holland spectrometer. All of the products have been isolated as solid and were initially characterized by comparison of their melting points with those reported in the literature. The molecular weights of all compounds were confirmed by mass spectrometry. Also, the structures of some selected compounds were deduced from their high-field  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and FT-IR spectral data. Sepiolite was obtained from Iran; Fariman resources. All yields refer to isolated products after purification by recrystallization.

**2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (a)** (0.279 g, 95%); white solid; mp 232-234 °C (from EtOH) (Lit.<sup>[1]</sup> 234-235 °C); FT-IR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3395, 3325 (NH<sub>2</sub>), 3212 (C-H, aromatic), 2960 (sp<sup>3</sup> C-H), 2199 (CN), 1679 (C=O), 1661 (C=C, vinyl nitrile), 1603, 1555 (C=C, aromatic), 1370 (C-O), 1214 (C-N);  $^1\text{H}$  NMR:  $\delta\text{H}$  (300 MHz; DMSO-*d*<sub>6</sub>) 7.33 – 7.14 (m, 5 H, Ar-H), 7.02 (s, 2 H, NH<sub>2</sub>), 4.18 (s, 1 H, C=CH), 2.19 (dd,  $J_1 = 48$  Hz,  $J_2 = 15$  Hz, 2 H, CH<sub>2</sub>), 2.18 (s, 2 H, CH<sub>2</sub>), 1.05 (s, 3 H, CH<sub>3</sub>), 0.97 (s, 3 H, CH<sub>3</sub>);  $^{13}\text{C}$  NMR:  $\delta\text{C}$  (76 MHz, DMSO- *d*<sub>6</sub>) 196.12, 162.96, 158.91, 145.21, 128.8, 127.61, 127.03, 120.19, 113.2, 58.76, 50.45, 36.04, 32.29, 31.65, 28.87, 27.28; MS,  $m/z$  294 (M<sup>+</sup>, 9%), 292 (M-2H, 85%), 235 (M-2H-C<sub>4</sub>H<sub>9</sub>, 46%), 209 (M-2H-C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>O, 65%), 215 (C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>, 100%), 160 (C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>, 71%), 132 (C<sub>9</sub>H<sub>8</sub>O, 63%), 77 (C<sub>6</sub>H<sub>5</sub>, 65%), 55 (C<sub>4</sub>H<sub>7</sub>, 65%), 28 (CO, 67%).



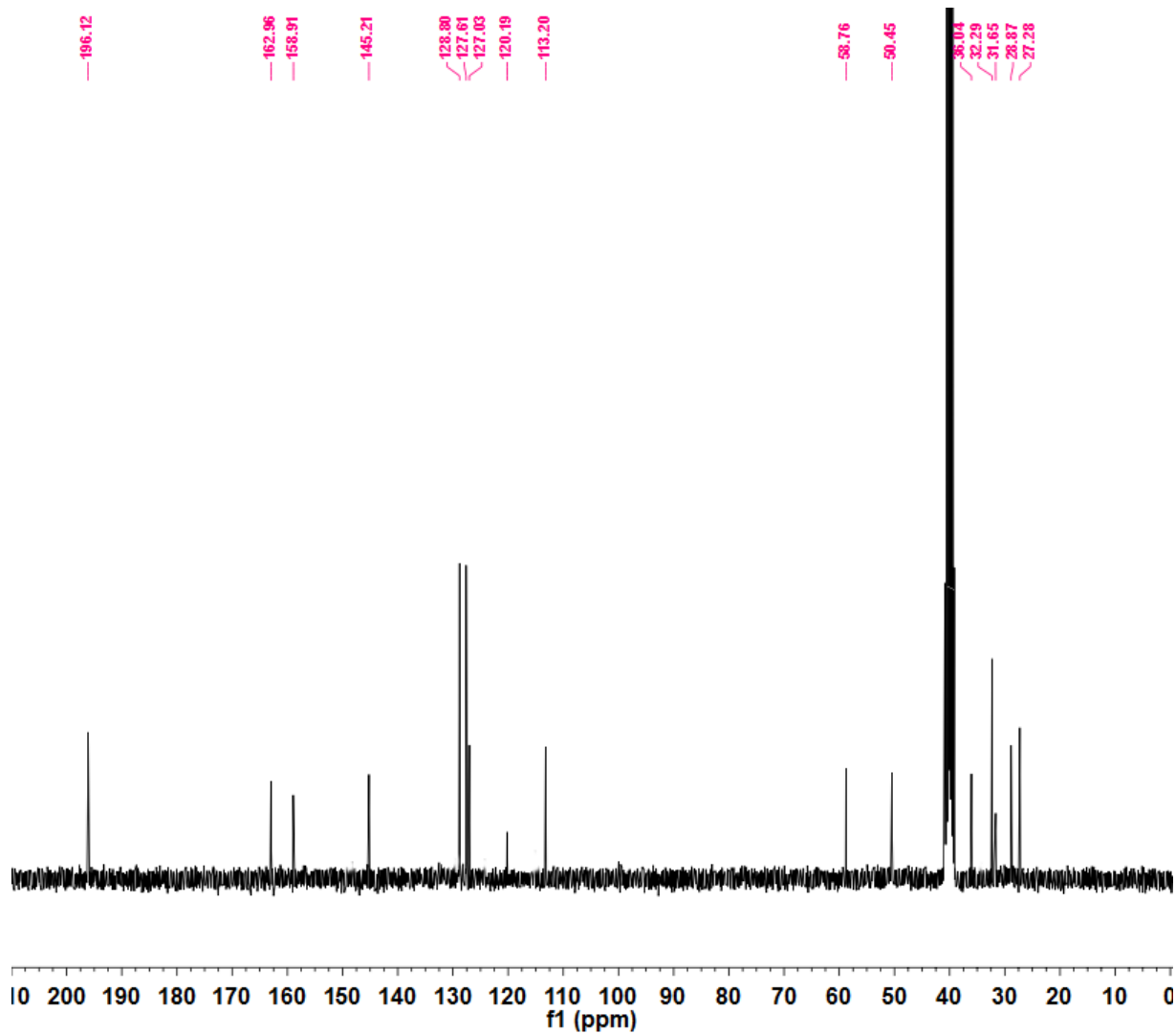
**Figure S1:** FT-IR (KBr) of 2-amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (a)



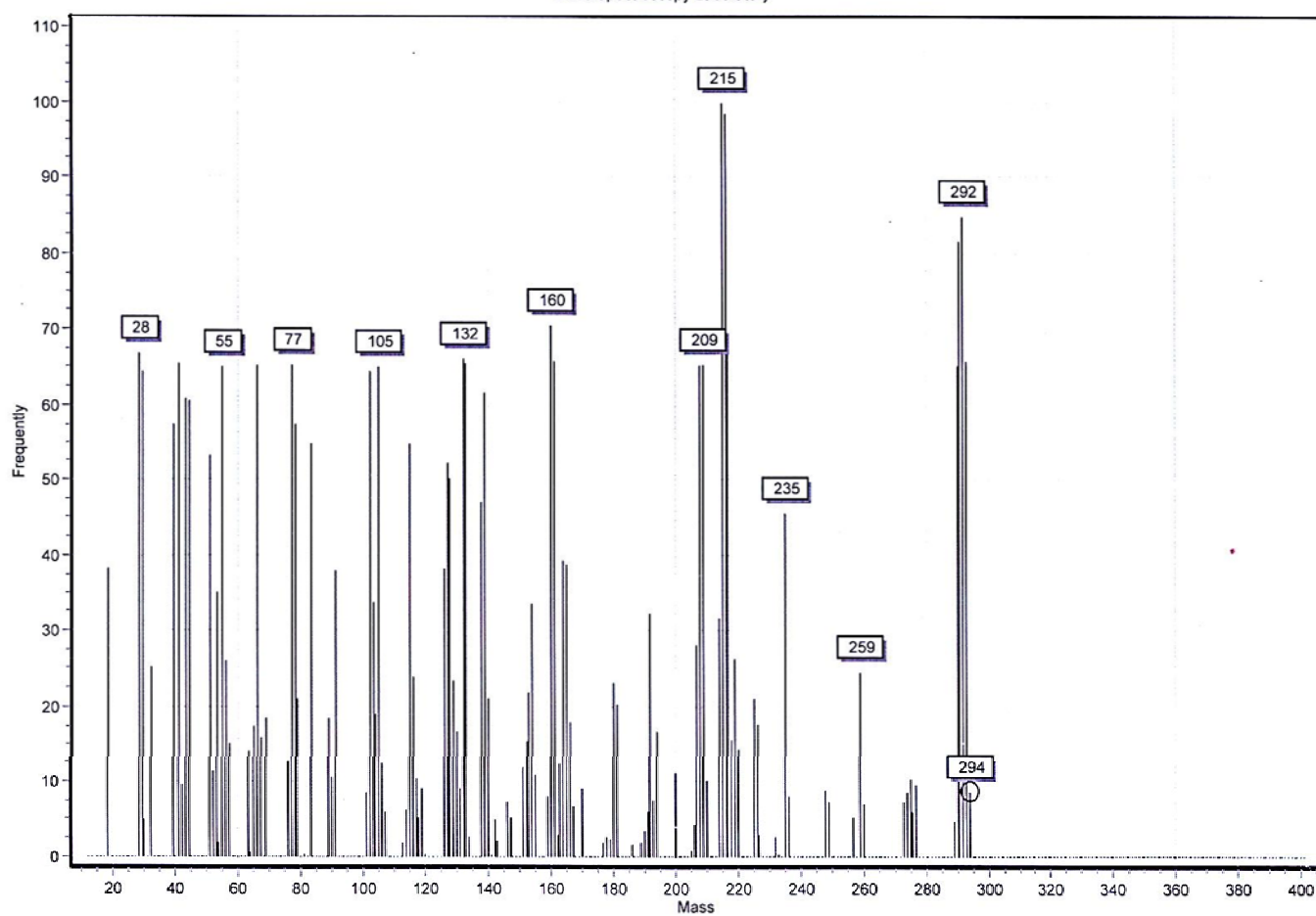
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Spectrometer	spect
Author	
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Pulse Sequence	zg30
Experiment	1D
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Receiver Gain	202
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
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Acquisition Date	2016-08-24T04:53:37
Modification Date	2016-08-24T16:23:38
Class	
Spectrometer Frequency	300.85
Spectral Width	6024.1
Lowest Frequency	-1153.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

**Figure S2:**  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (**a**)





**Figure S3:**  $^{13}\text{C}$  NMR (76 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (**a**)

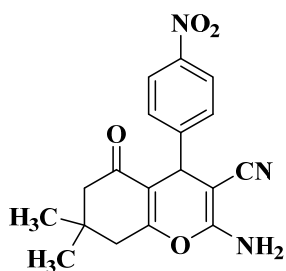


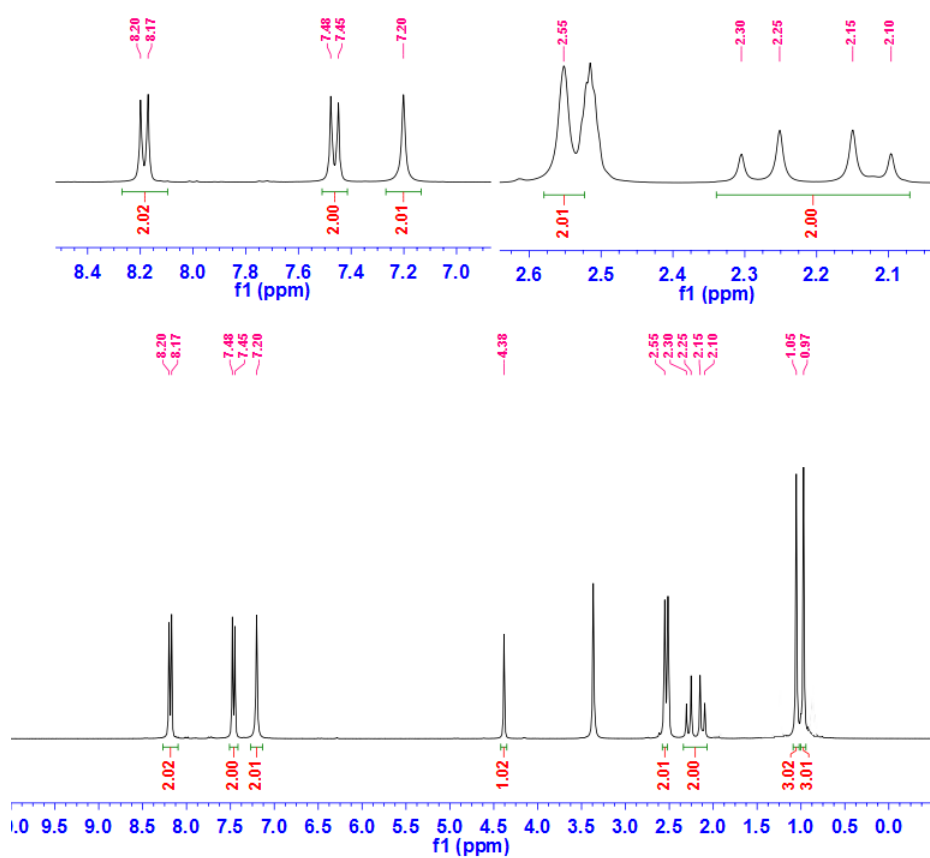
**Figure S4:** Mass spectrum of 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (**a**)

**2-amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-**

**carbonitrile (b)** (0.322 g, 95%); Yellow solid ; mp 178-179 °C (from EtOH) (Lit.<sup>[1]</sup> 179-180 °C);

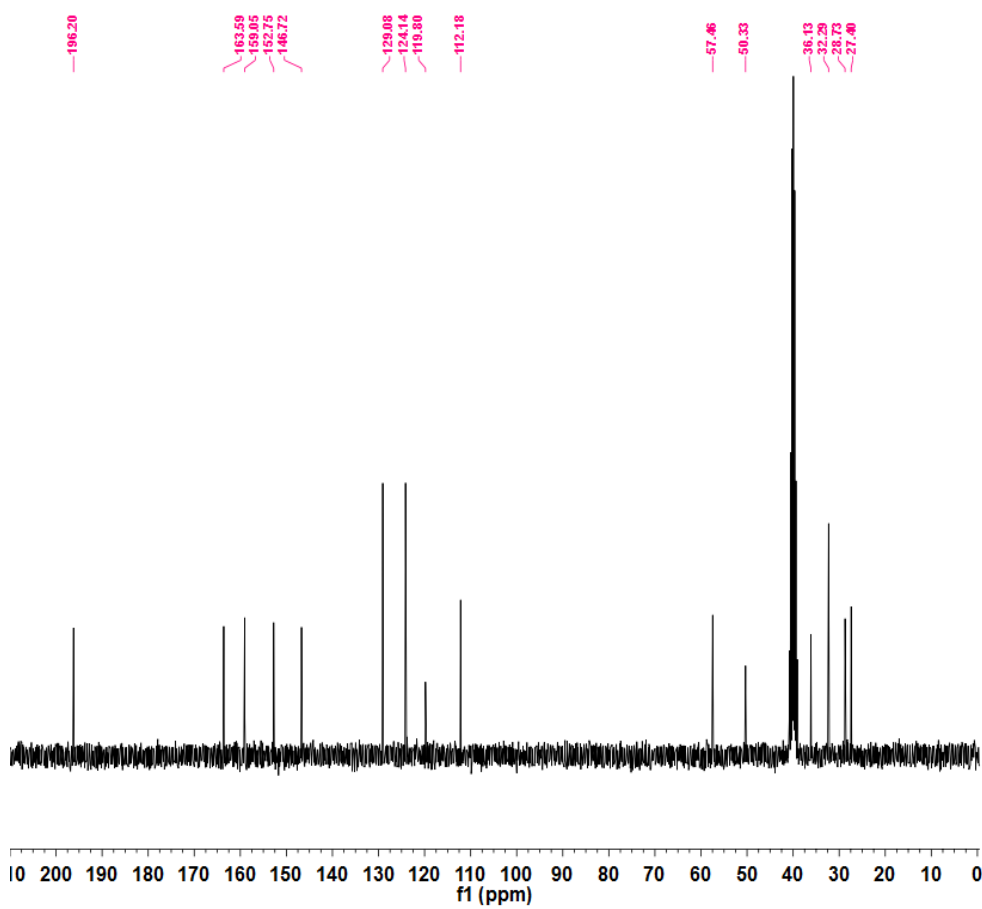
<sup>1</sup>H NMR: δH (300 MHz; DMSO-*d*<sub>6</sub>) 8.18 (d, *J*= 9 Hz, 2 H, Ar-H), 7.46 (d, *J*= 9 Hz, 2 H, Ar-H), 7.2 (s, 2 H, NH<sub>2</sub>), 4.38 (s, 1 H, CH), 2.55 (s, 2 H, CH<sub>2</sub>), 2.2 (dd, *J*<sub>1</sub>= 45 Hz, *J*<sub>2</sub>= 15 Hz, 2 H, CH<sub>2</sub>), 1.05 (s, 3 H, CH<sub>3</sub>), 0.97 (s, 3 H, CH<sub>3</sub>); <sup>13</sup>C NMR: δC (76 MHz, DMSO- *d*<sub>6</sub>) 196.2,163.59, 159.05, 152.75, 146.72, 129.08, 124.14, 119.8, 112.18, 57.46, 50.33, 36.13, 32.29, 28.73, 27.4; MS, *m/z* 339 (M<sup>+</sup>, 5 %), 336 (M-3H, 93%), 319 (M-3H-OH, 68%), 289 (M-3H-HNO<sub>2</sub>, 40%), 254 (M-3H-C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>O, 76%), 216 (C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>, 100%), 160 (C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>, 88%), 132 (C<sub>9</sub>H<sub>8</sub>O, 71%), 83 (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>O, 47%), 66 (C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 77%), 29 (HCO, 88%).





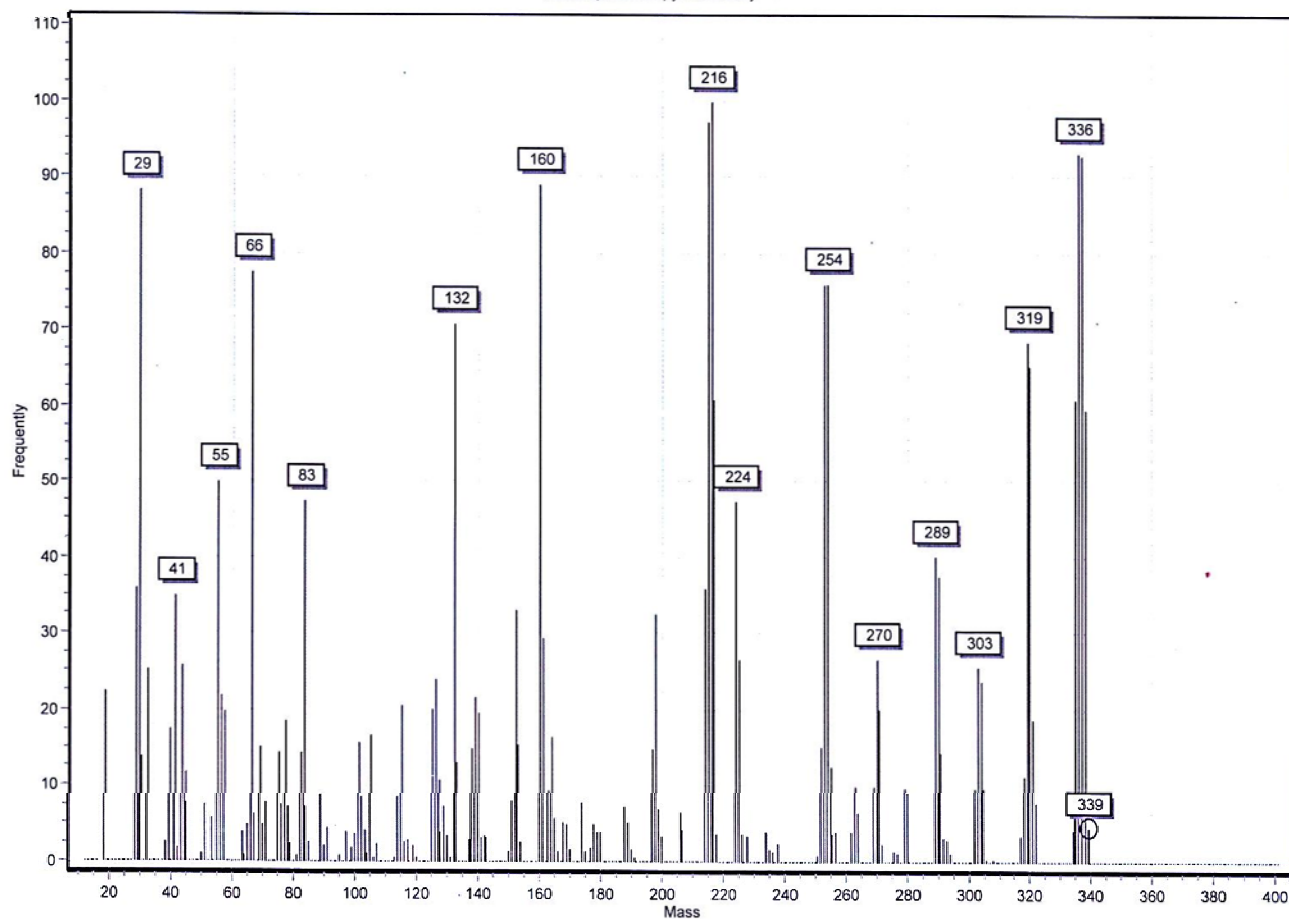
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Author	
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Number of Scans	16
Receiver Gain	113
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
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Modification Date	2016-08-13T15:59:06
Class	
Spectrometer Frequency	300.85
Spectral Width	6024.1
Lowest Frequency	-1153.8
Nucleus	<sup>1</sup> H
Acquired Size	32768
Spectral Size	65536

**Figure S5:** <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) of 2-amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**b**)



Parameter	Value
Origin	Bruker BioSpin GmbH
Owner	root
Site	
Spectrometer	spect
Author	
Solvent	DMSO
Temperature	308.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB-1H/ D Z-GRD Z104275/ 0252
Number of Scans	64
Receiver Gain	202
Relaxation Delay	2.0000
Pulse Width	10.0000
Presaturation	
Frequency	
Acquisition Time	1.8088
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Modification Date	2016-08-23T23:31:28
Class	
Spectrometer Frequency	75.66
Spectral Width	18115.9
Lowest Frequency	-1493.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

**Figure S6:**  $^{13}\text{C}$  NMR (76 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**b**)



**Figure S7:** Mass spectrum of 2-amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (b)

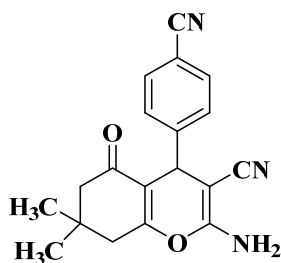
**2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-**

**carbonitrile (c)** (0.312 g, 98%); white solid; mp 224-226 °C (from EtOH) (Lit.<sup>[2]</sup> 227-230 °C);

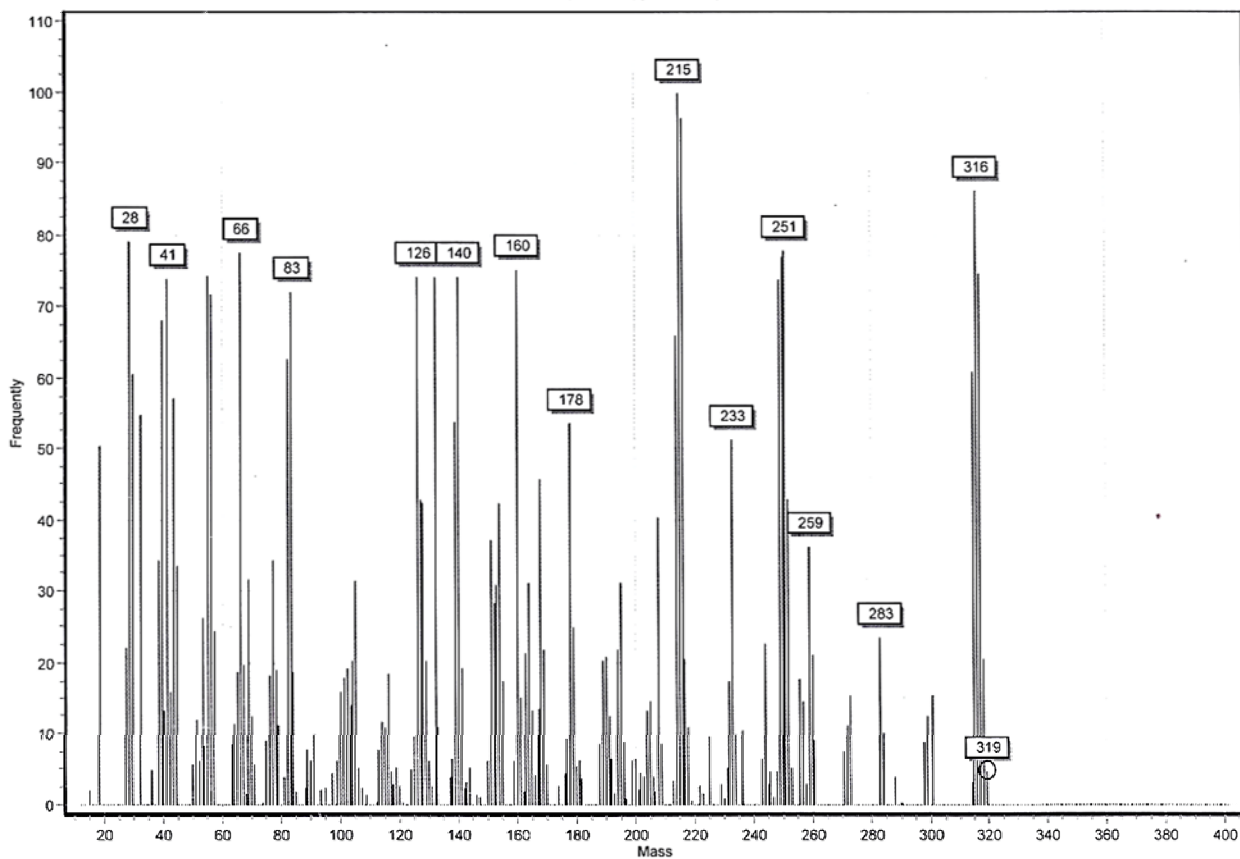
MS,  $m/z$  319 ( $M^+$ , 5%), 316 ( $M-3H$ , 86%), 251 ( $C_{16}H_{13}NO_2$ , 78%), 215 ( $C_{12}H_{11}N_2O_2$ , 100%),

160 ( $C_8H_4N_2O_2$ , 76%), 140 ( $C_8H_{12}O_2$ , 75%), 83 ( $C_3H_3N_2O$ , 72%), 66 ( $C_3H_2N_2$ , 78%), 41 ( $C_3H_5$ ,

74%), 28 ( $CO$ , 79%).

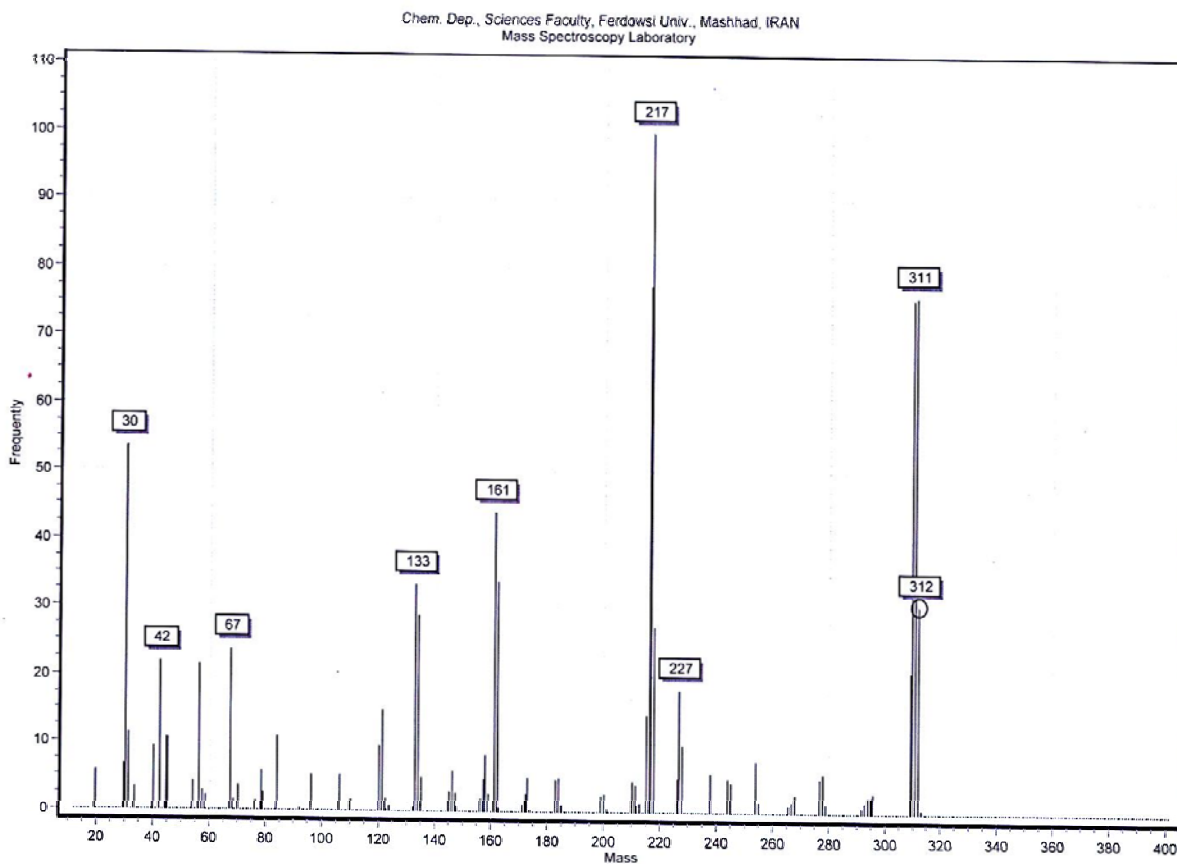
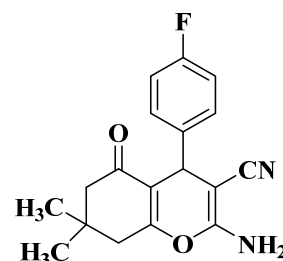


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**Figure S8:** Mass spectrum of 2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (c)

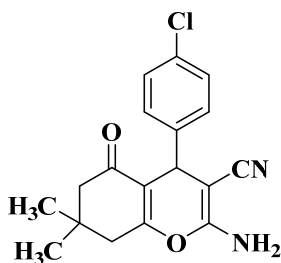
**2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (d)** (0.296 g, 95%); white solid ; mp 188-189 °C (from EtOH) (Lit.<sup>[3]</sup> 191 °C); MS, *m/z* (312, 31%), 311 (M-H, 76%), 227 (C<sub>15</sub>H<sub>12</sub>O<sub>f</sub>, 18%), 217 (C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>, 100%), 161 (C<sub>8</sub>H<sub>5</sub>N<sub>2</sub>O<sub>2</sub>, 44%), 133 (C<sub>9</sub>H<sub>9</sub>O, 34%), 67 (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>, 24%), 42 (C<sub>3</sub>H<sub>6</sub>, 22%), 30 (C<sub>2</sub>H<sub>6</sub>, 53%).

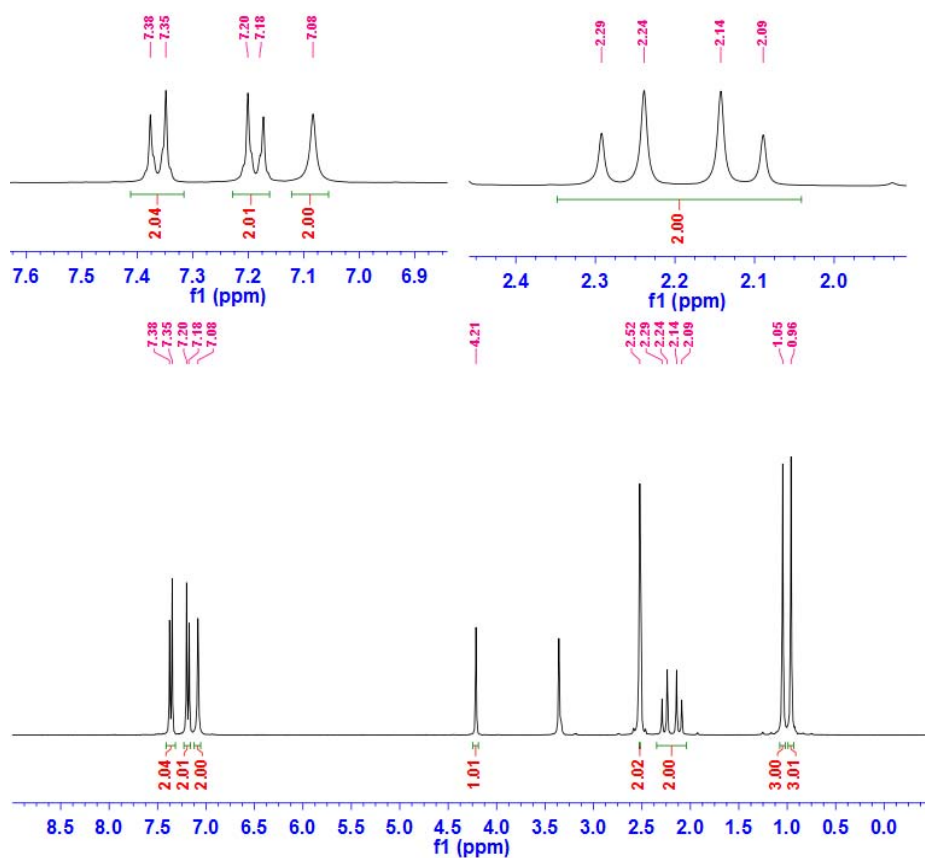




**Figure S9:** Mass spectrum of 2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**d**)

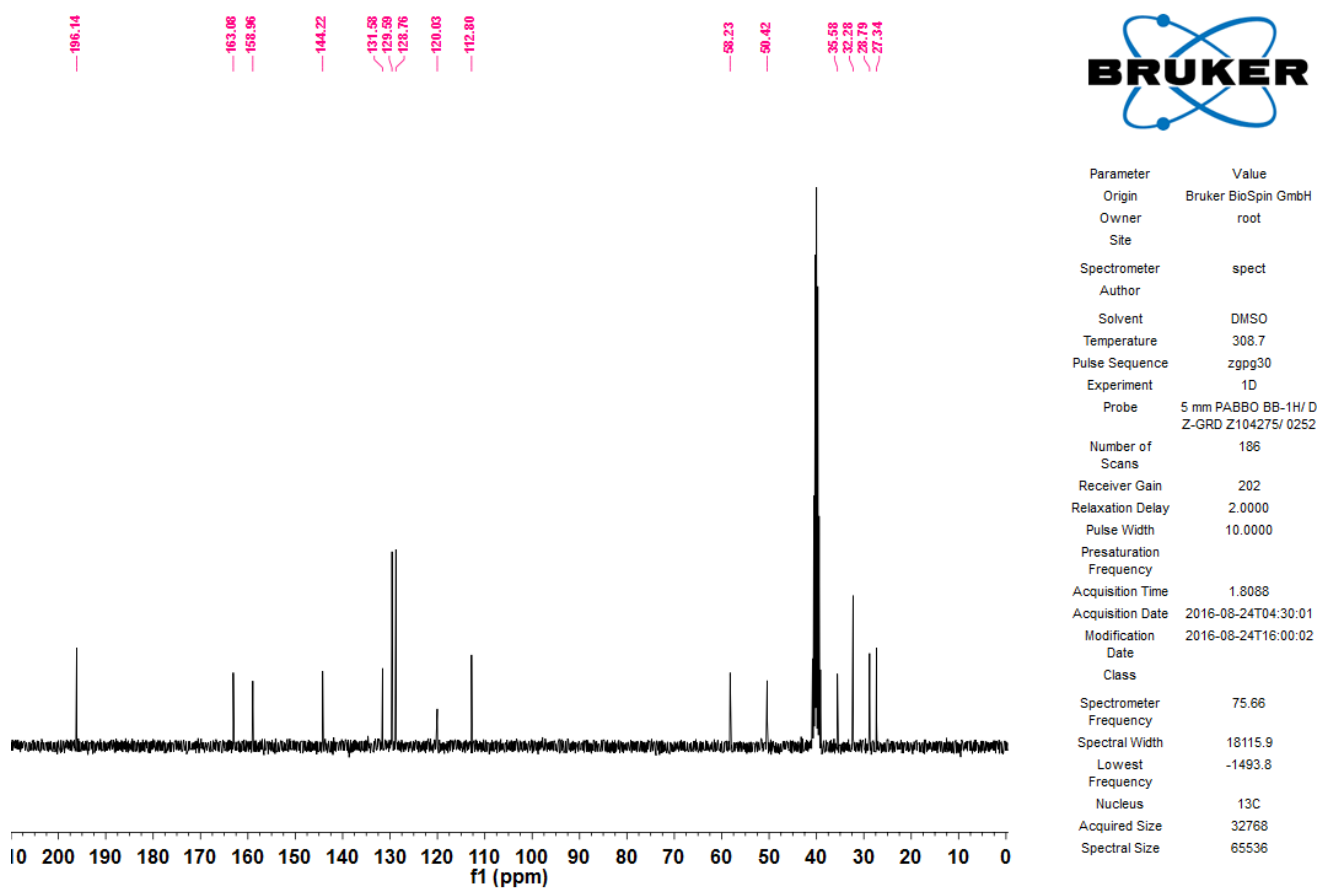
**2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (e)** (0.295 g, 90%); white solid ; mp 214-216 °C (from EtOH) (Lit.<sup>[1]</sup> 215-217 °C); <sup>1</sup>H NMR: δH (300 MHz; DMSO-*d*<sub>6</sub>) 7.36 (d, *J* = 9 Hz, 2 H, Ar-H), 7.19 (d, *J* = 6 Hz, 2 H, Ar-H), 7.08 (s, 2 H, NH<sub>2</sub>), 4.21 (s, 1 H, CH), 2.52 (s, 2 H, CH<sub>2</sub>), 2.19 (dd, *J*<sub>1</sub> = 45 Hz, *J*<sub>2</sub> = 15 Hz, 2 H, CH<sub>2</sub>), 1.05 (s, 3 H, CH<sub>3</sub>), 0.96 (s, 3 H, CH<sub>3</sub>) ; <sup>13</sup>C NMR: δC (76 MHz, DMSO- *d*<sub>6</sub>) 196.14, 163.08, 158.96, 144.22, 131.58, 129.59, 128.76, 120.03, 112.8, 58.23, 50.42, 35.58, 32.28, 28.79, 27.34; MS, *m/z* 328 (M<sup>+</sup>, 36 %), 325 (M-3H, 93%), 290 (M-3H-Cl, 53%), 242 (M-3H-C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>O, 17%), 215 (C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>, 100%), 160 (C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>, 83%), 132 (C<sub>9</sub>H<sub>8</sub>O, 56%), 83 (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>O, 30%), 66 (C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 66%), 41 (C<sub>3</sub>H<sub>5</sub>, 60%), 29 (HCO, 93%).



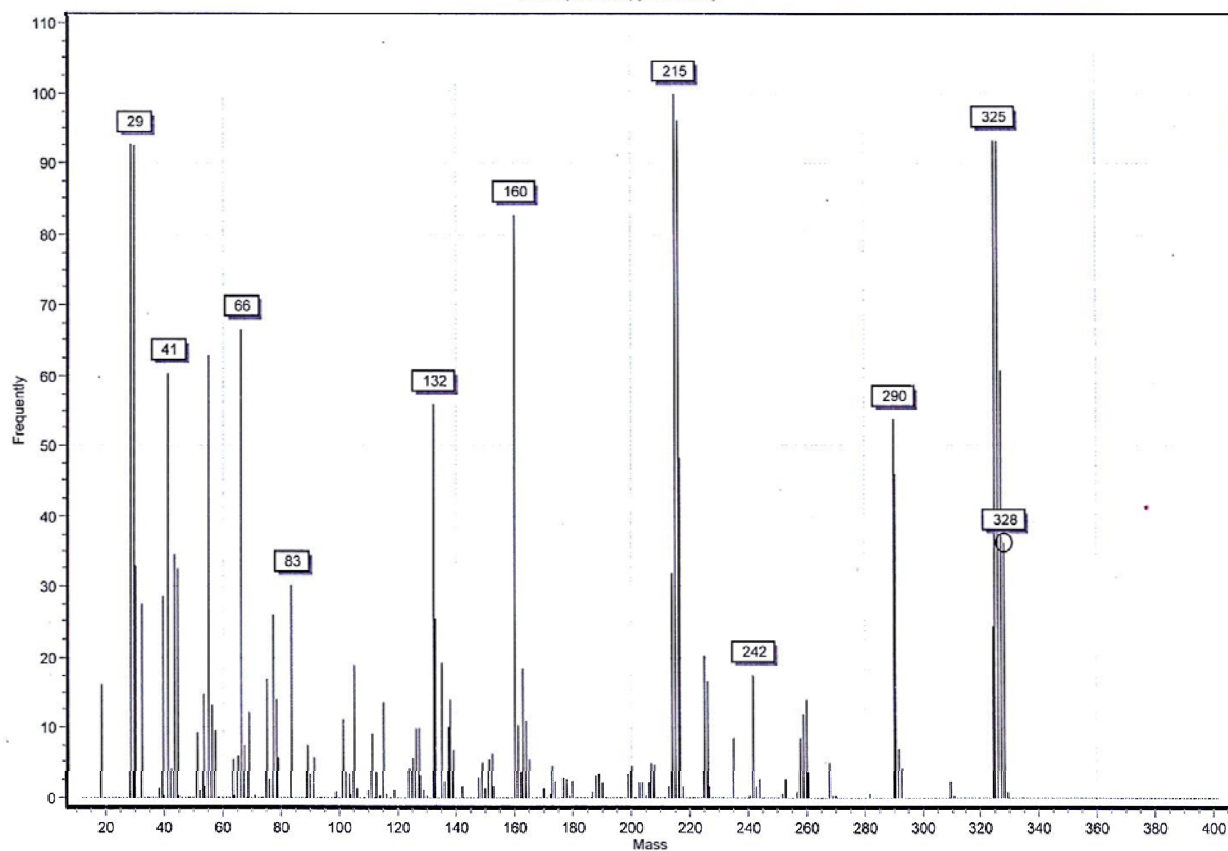


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Spectrometer	spect
Author	
Solvent	DMSO
Temperature	307.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB-1H/ D Z-GRD Z104275/ 0252
Number of Scans	16
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation	
Frequency	
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Class	
Spectrometer Frequency	300.85
Spectral Width	6024.1
Lowest Frequency	-1153.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

**Figure S10:**  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**e**)



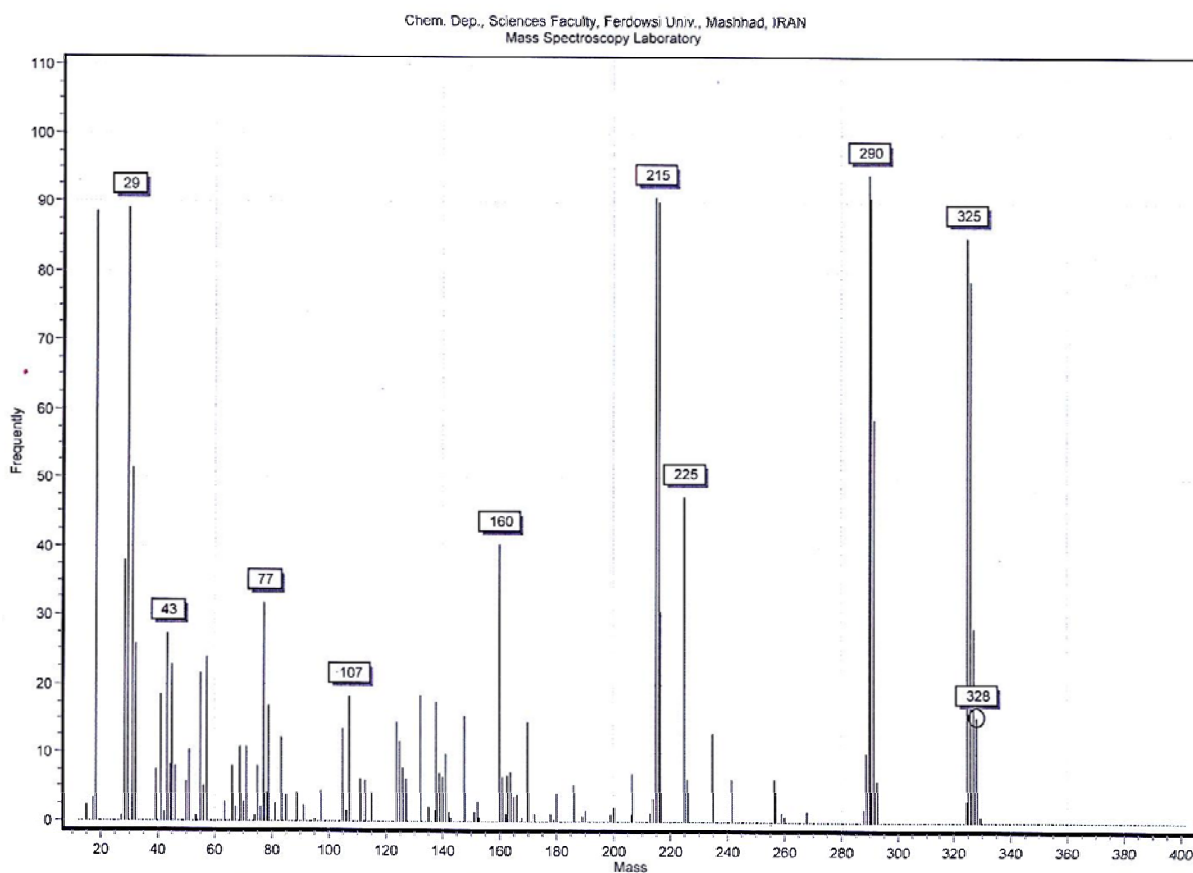
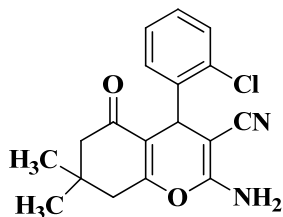
**Figure S11:**  $^{13}\text{C}$  NMR (76 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (e)



**Figure S12:** Mass spectrum of 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-

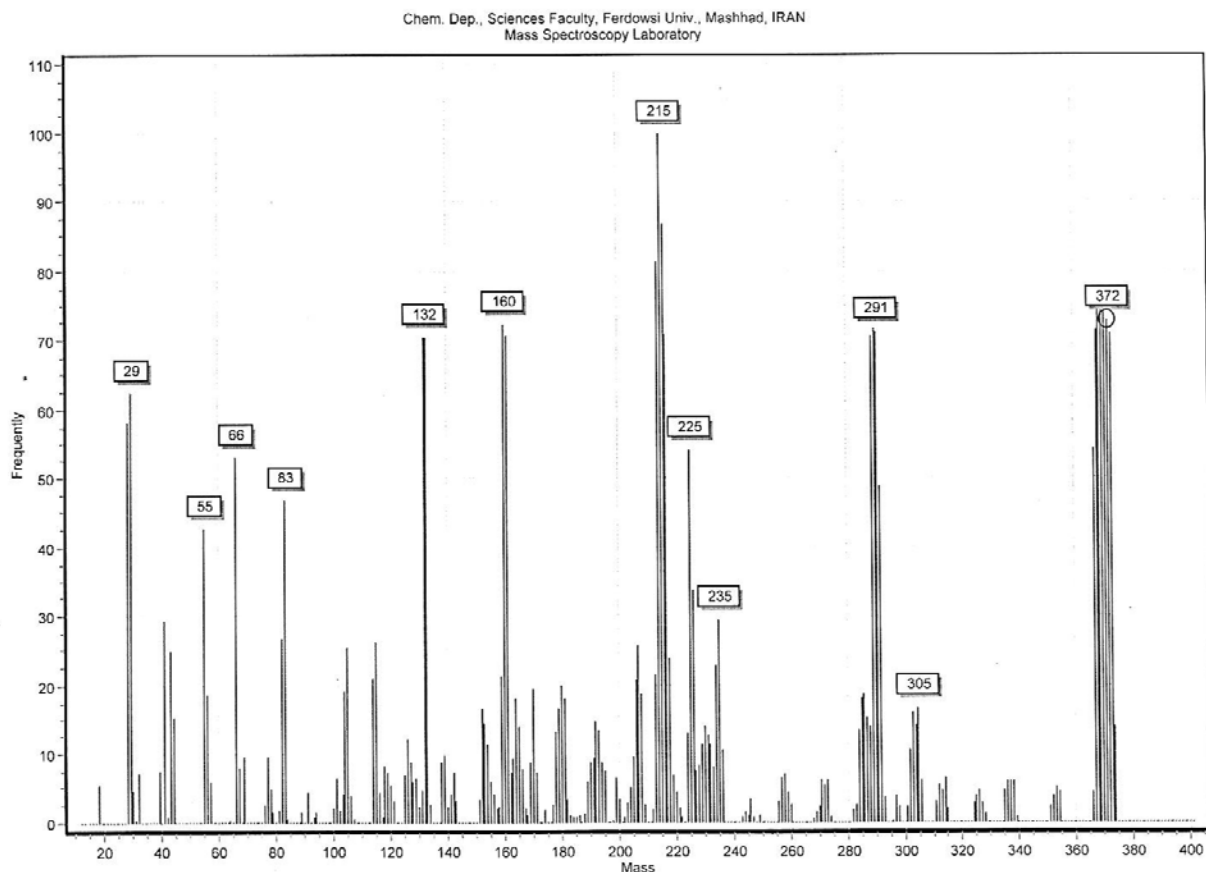
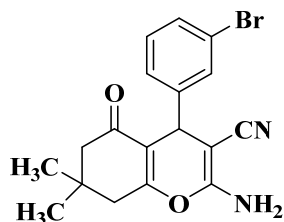
tetrahydro-4*H*-chromene-3-carbonitrile (e)

**2-amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (f)** (0.278 g, 85%); white solid ; mp 212-214 °C (from EtOH) (Lit.<sup>[1]</sup> 214-215 °C); MS,  $m/z$  328 ( $M^+$ , 16%), 325 (M-3H, 85%), 290 (M-3H-Cl, 94%), 225 (M-C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>Cl, 47%), 215 (C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>, 91%), 160 (C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>, 41%), 77 (C<sub>6</sub>H<sub>5</sub>, 32%), 43 (C<sub>3</sub>H<sub>7</sub>, 27%), 29 (HCO, 89%).



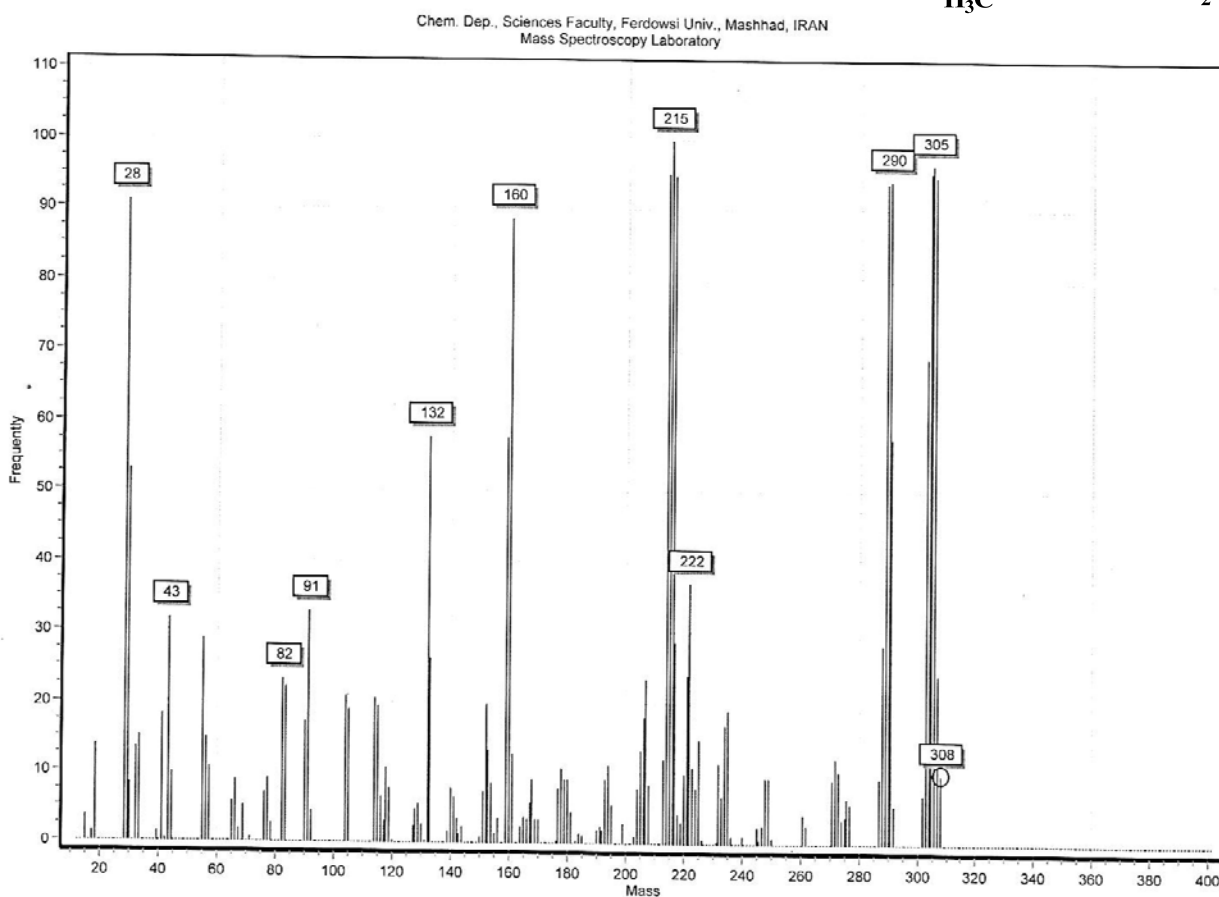
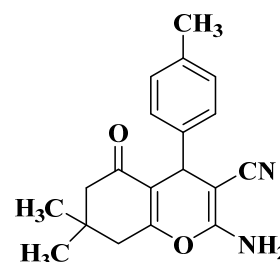
**Figure S13:** Mass spectrum of 2-amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (f)

**2-amino-4-(3-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (g)** (0.353 g, 95%); white solid; mp 225-227 °C (from EtOH) (Lit.<sup>[4]</sup> 228-230 °C); MS,  $m/z$  372 ( $M^+$ , 72%), 305 ( $M-C_3H_3N_2$ , 17%), 291 ( $M-Br$ , 72%), 215 ( $C_{12}H_{11}N_2O_2$ , 100%), 160 ( $C_8H_4N_2O_2$ , 73%), 132 ( $C_9H_8O$ , 71%), 83 ( $C_3H_3N_2O$ , 47%), 66 ( $C_3H_2N_2$ , 56%), 29 ( $HCO$ , 62%).



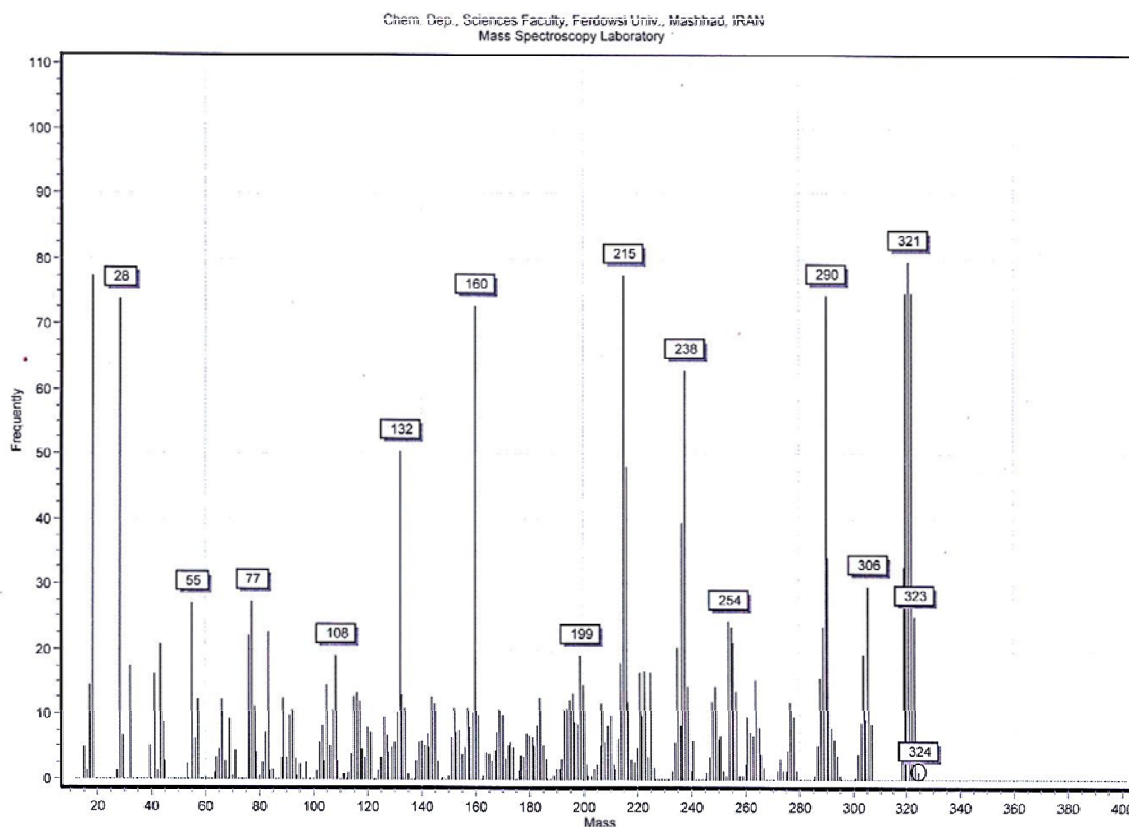
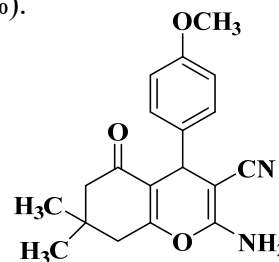
**Figure S14:** Mass spectrum of 2-amino-4-(3-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (g)

**2-amino-7,7-dimethyl-5-oxo-4-(p-tolyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (h)**  
(0.261 g, 85%); white solid ; mp 218-219 °C (from EtOH) (Lit.<sup>[1]</sup> 220-222 °C); MS,  $m/z$  308 ( $M^+$ , 9%), 305 ( $M-3H$ , 97%), 290 ( $M-3H-CH_3$ , 94%), 222 ( $C_{16}H_{14}O$ , 37%), 215 ( $C_{12}H_{11}N_2O_2$ , 100%), 160 ( $C_8H_4N_2O_2$ , 88%), 132 ( $C_9H_8O$ , 57%), 91 ( $C_7H_7$ , 33%), 82 ( $C_3H_2N_2O$ , 23%), 43 ( $C_3H_7$ , 31%), 28 ( $CO$ , 91%).



**Figure S15:** Mass spectrum of 2-amino-7,7-dimethyl-5-oxo-4-(p-tolyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (h)

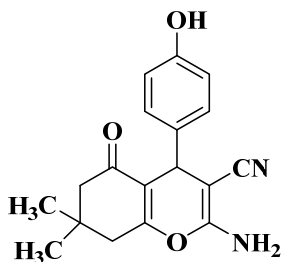
**2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (i)** (0.307 g, 95%); White solid; mp 199-201 °C (from EtOH) (Lit.<sup>[1]</sup> 201–202 °C); MS,  $m/z$  324 ( $M^+$ , 1%), 323 ( $M-H$ , 25%), 321 ( $M-3H$ , 79%), 306 ( $M-3H-CH_3$ , 29%), 290 ( $M-3H-OCH_3$ , 75%), 238 ( $M-3H-C_3H_3N_2O$ , 69%), 215 ( $C_{12}H_{11}N_2O_2$ , 77%), 160 ( $C_8H_4N_2O_2$ , 73%), 132 ( $C_9H_8O$ , 51%), 108 ( $C_7H_8O$ , 19%), 77 ( $C_6H_5$ , 27%), 28 ( $CO$ , 74%).

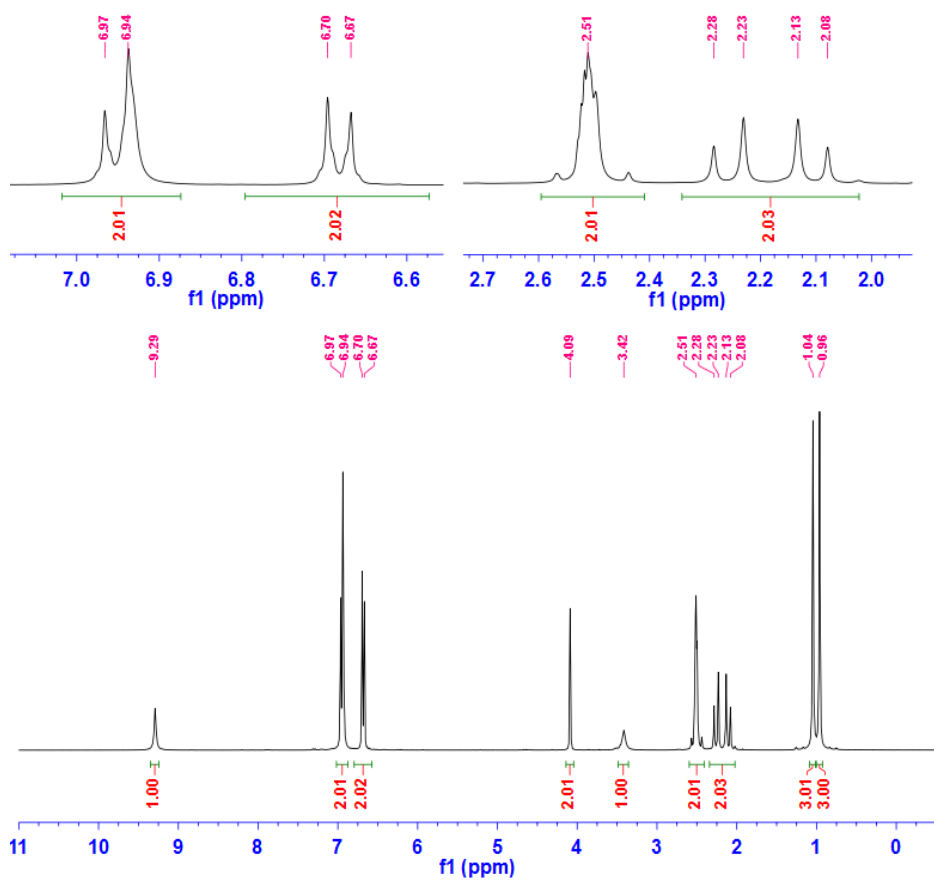


**Figure S16:** Mass spectrum of 2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (i)



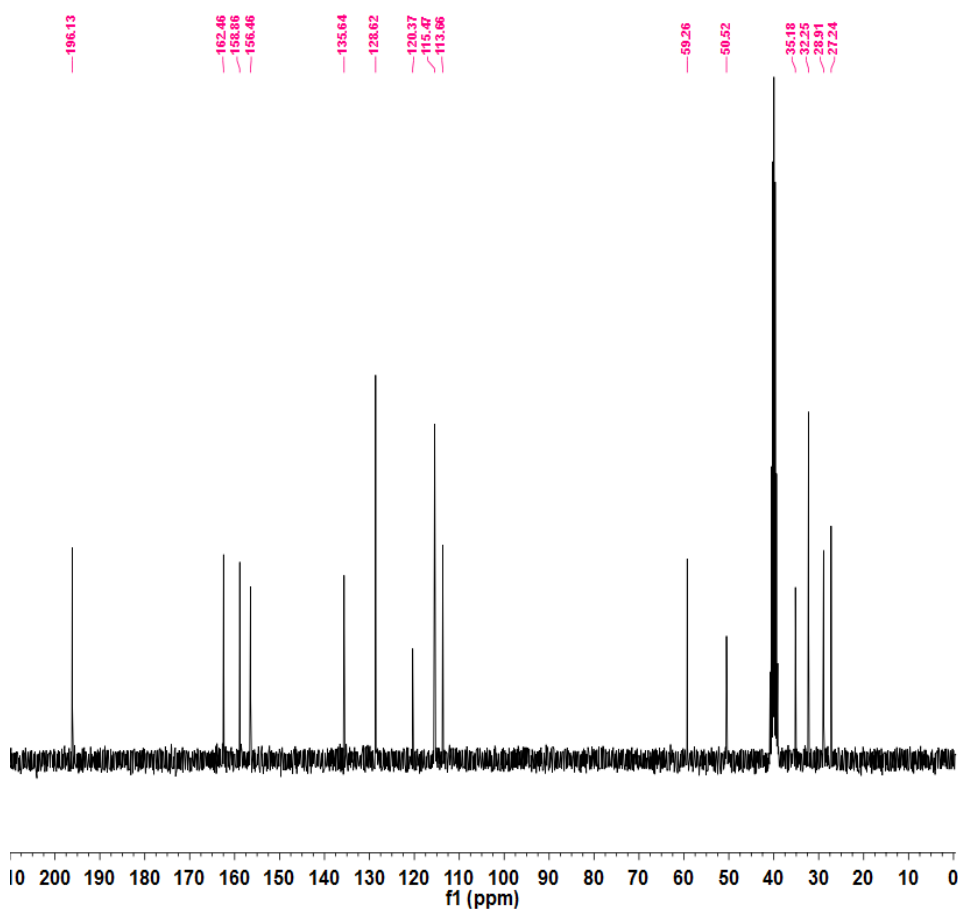
**2-amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (j)** (0.294 g, 95%); White solid ; mp 222-223 °C (from EtOH) (Lit.<sup>[1]</sup> 224–226 °C); <sup>1</sup>H NMR: δH (300 MHz; DMSO-*d*<sub>6</sub>) 9.29 (s, 1 H, OH), 6.95 (d, *J*= 9 Hz, 2 H, Ar-H), 6.68 (d, *J*= 9 Hz, 2 H, Ar-H), 4.09 (s, 2 H, NH<sub>2</sub>), 3.42 (s, 1 H, CH), 2.51 (s, 2 H, CH<sub>2</sub>), 2.18 (dd, *J*<sub>1</sub>= 45 Hz, *J*<sub>2</sub>= 15 Hz, 2 H, CH<sub>2</sub>), 1.04 (s, 3 H, CH<sub>3</sub>), 0.96 (s, 3 H, CH<sub>3</sub>) ; <sup>13</sup>C NMR: δC (76 MHz, DMSO-*d*<sub>6</sub>) 196.13, 162.46, 158.86, 156.46, 135.64, 128.62, 120.37, 115.47, 113.66, 59.26, 50.52, 35.18, 32.25, 28.91, 27.24; MS, *m/z* 310 (M<sup>+</sup>, 9%), 307 (M-3H, 100%), 290 (M-3H-OH, 42%), 242 (M-3H-C<sub>3</sub>HN<sub>2</sub>, 99%), 215 (C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>, 98%), 160 (C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>, 46%), 131 (C<sub>9</sub>H<sub>7</sub>O, 54%), 83 (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>O, 53%), 66 (C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 73%), 28 (CO, 56%).





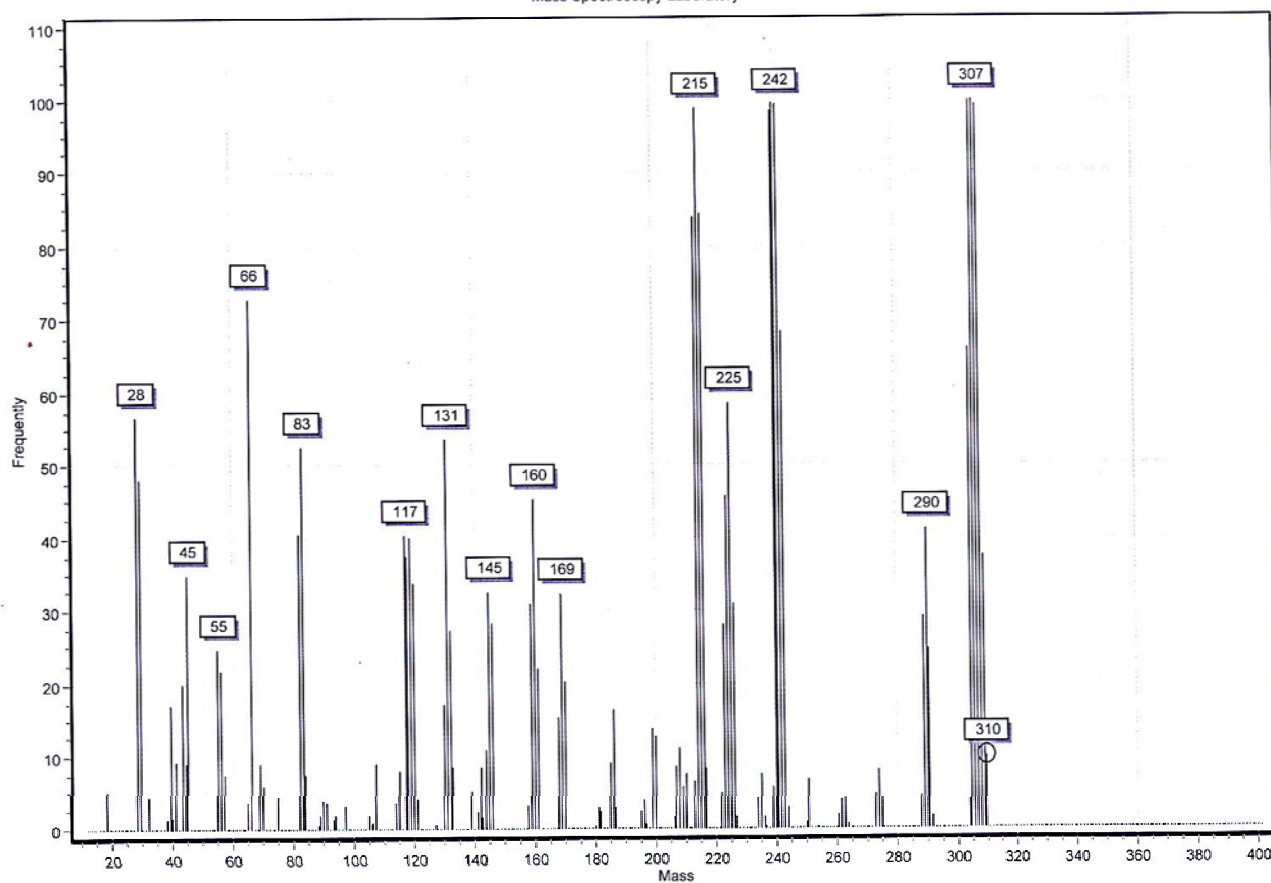
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Site	
Spectrometer	spect
Author	
Solvent	DMSO
Temperature	308.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB-1H/ D Z-GRD Z104275/ 0252
Number of Scans	16
Receiver Gain	79
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	5.4395
Acquisition Date	2016-08-24T04:44:22
Modification Date	2016-08-24T16:14:22
Class	
Spectrometer Frequency	300.85
Spectral Width	6024.1
Lowest Frequency	-1153.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

**Figure S17:**  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**j**)



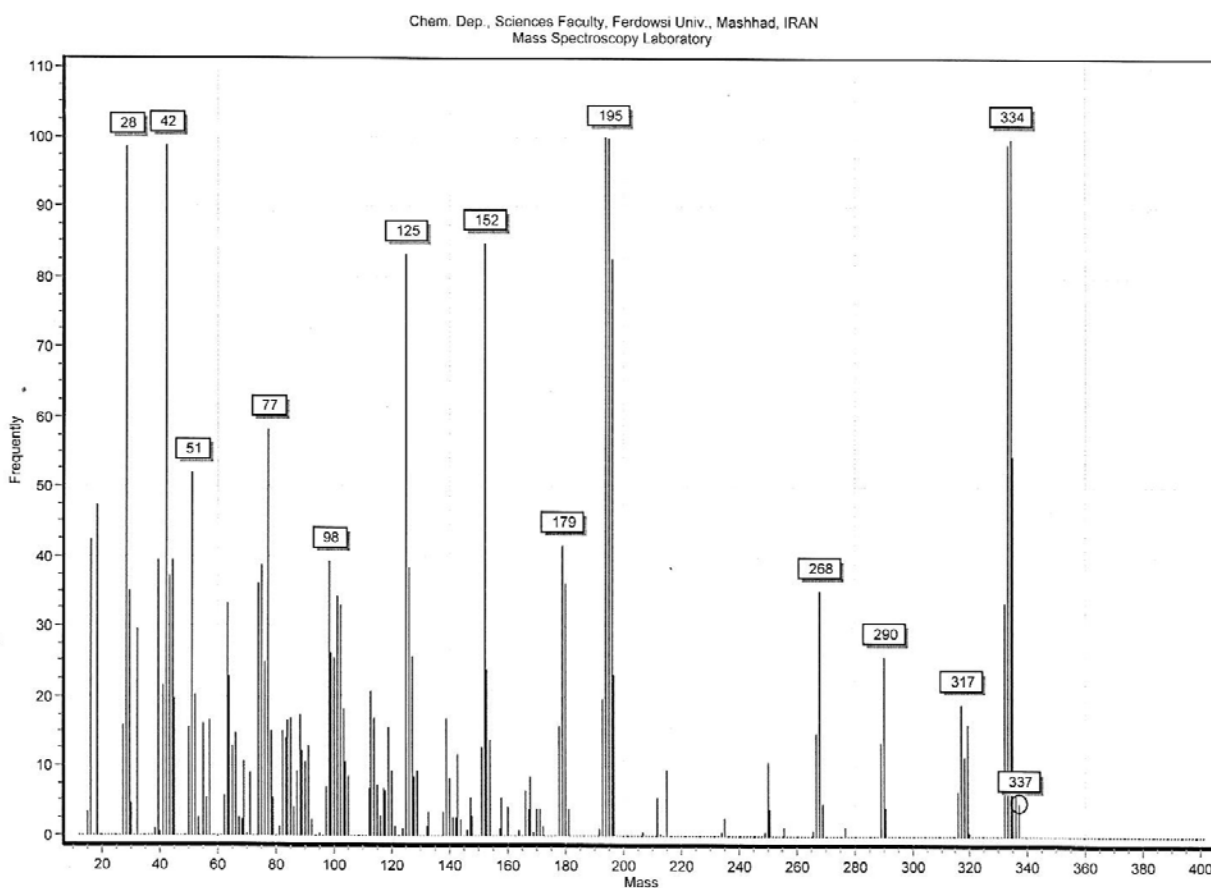
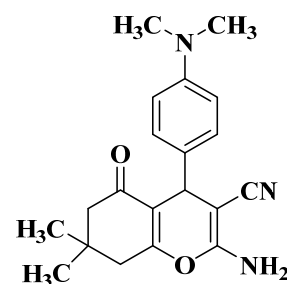
Parameter	Value
Origin	Bruker BioSpin GmbH
Owner	root
Site	
Spectrometer	spect
Author	
Solvent	DMSO
Temperature	308.6
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB-1H/ D Z-GRD Z104275/ 0252
Number of Scans	64
Receiver Gain	202
Relaxation Delay	2.0000
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	1.8088
Acquisition Date	2016-08-24T04:39:20
Modification Date	2016-08-24T16:09:20
Class	
Spectrometer Frequency	75.66
Spectral Width	18115.9
Lowest Frequency	-1493.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

**Figure S18:**  $^{13}\text{C}$  NMR (76 MHz, DMSO-  $d_6$ ) of 2-amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**j**)



**Figure S19:** Mass spectrum of 2-amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (j)

**2-amino-4-(4-(dimethylamino)phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (k)** (0.303 g, 90%); Yellow solid ; mp 210-211 °C (from EtOH) (Lit.<sup>[1]</sup> 210–212 °C); MS,  $m/z$  337 ( $M^+$ , 5%), 334 (M-3H, 100%), 290 (M-3H-C<sub>2</sub>H<sub>6</sub>N, 26%), 268 (M-3H-C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 36%), 195 (C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>, 100%), 152 (C<sub>10</sub>H<sub>4</sub>N<sub>2</sub>, 85%), 98 (C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>O, 39%), 77 (C<sub>6</sub>H<sub>5</sub>, 58%), 42 (C<sub>3</sub>H<sub>6</sub>, 99%), 28 (CO, 98%).

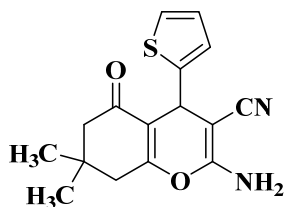


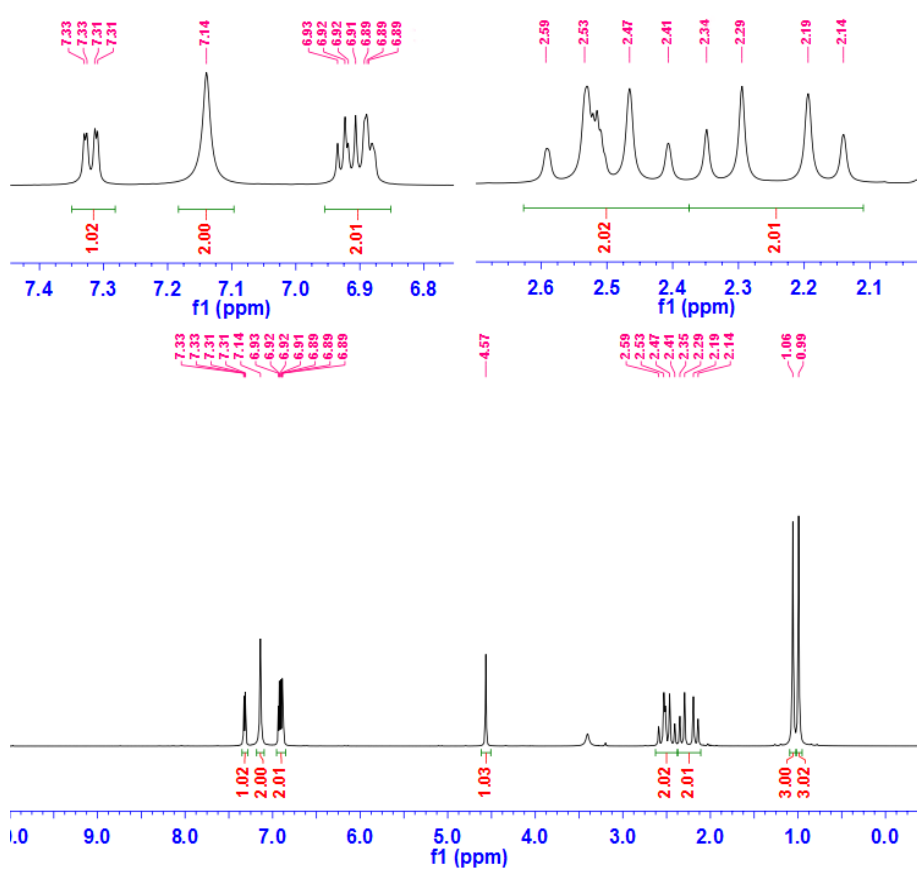
**Figure S20:** Mass spectrum of 2-amino-4-(4-(dimethylamino)phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (k)

**2-amino-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4H-chromene-3-**

**carbonitrile (I)** (0.27 g, 90%); Yellow solid ; mp 221-223 °C (from EtOH) (Lit.<sup>[1]</sup> 224–226 °C);

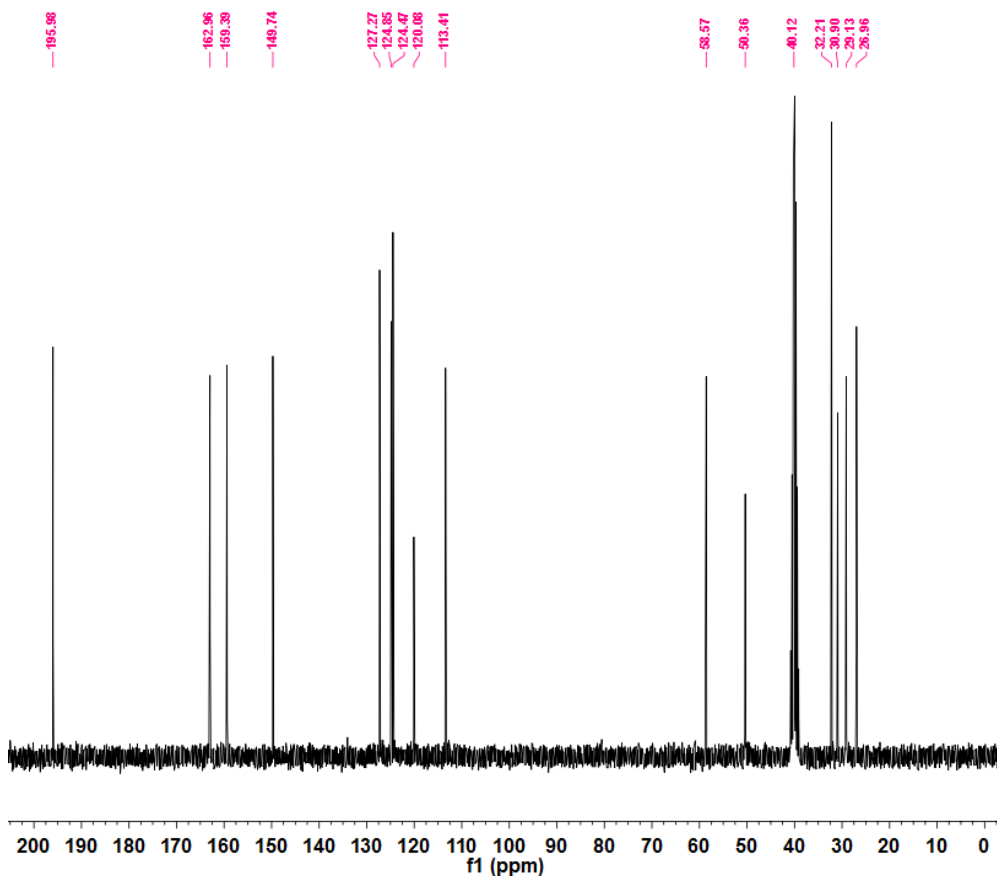
<sup>1</sup>H NMR: δH (300 MHz; DMSO-*d*<sub>6</sub>) 7.32 (d, *J* = 6 Hz, 1 H, Ar-H), 7.14 (s, 2 H, NH<sub>2</sub>), 6.93-6.89 (m, 2 H, Ar-H), 4.57 (s, 1 H, CH), 2.5 (dd, *J*<sub>1</sub> = 36 Hz, *J*<sub>2</sub> = 18 Hz, 2 H, CH<sub>2</sub>), 2.24 (dd, *J*<sub>1</sub> = 45 Hz, *J*<sub>2</sub> = 15 Hz, 2 H, CH<sub>2</sub>), 1.06 (s, 3 H, CH<sub>3</sub>), 0.99 (s, 3 H, CH<sub>3</sub>) ; <sup>13</sup>C NMR: δC (76 MHz, DMSO- *d*<sub>6</sub>) 195.98, 162.96, 159.39, 149.74, 127.27, 124.85, 124.47, 120.08, 113.41, 58.57, 50.36, 40.12, 32.21, 30.9, 29.13, 26.96; MS, *m/z* 300 (M<sup>+</sup>, 19%), 298 (M-2H, 100%), 265 (M-2H-HS, 25%), 232 (M-2H-C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 19%), 215 (C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>, 94%), 160 (C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>, 63%), 133 (C<sub>9</sub>H<sub>9</sub>O, 48%), 83 (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>O or C<sub>4</sub>H<sub>3</sub>S, 55%), 66 (C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 60%).





Parameter	Value
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Owner	root
Site	
Spectrometer	spect
Author	
Solvent	DMSO
Temperature	306.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB-1H/ D Z-GRD Z104275/ 0252
Number of Scans	16
Receiver Gain	52
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	5.4395
Acquisition Date	2016-08-13T04:02:17
Modification Date	2016-08-13T15:32:18
Class	
Spectrometer Frequency	300.85
Spectral Width	6024.1
Lowest Frequency	-1153.8
Nucleus	<sup>1</sup> H
Acquired Size	32768
Spectral Size	65536

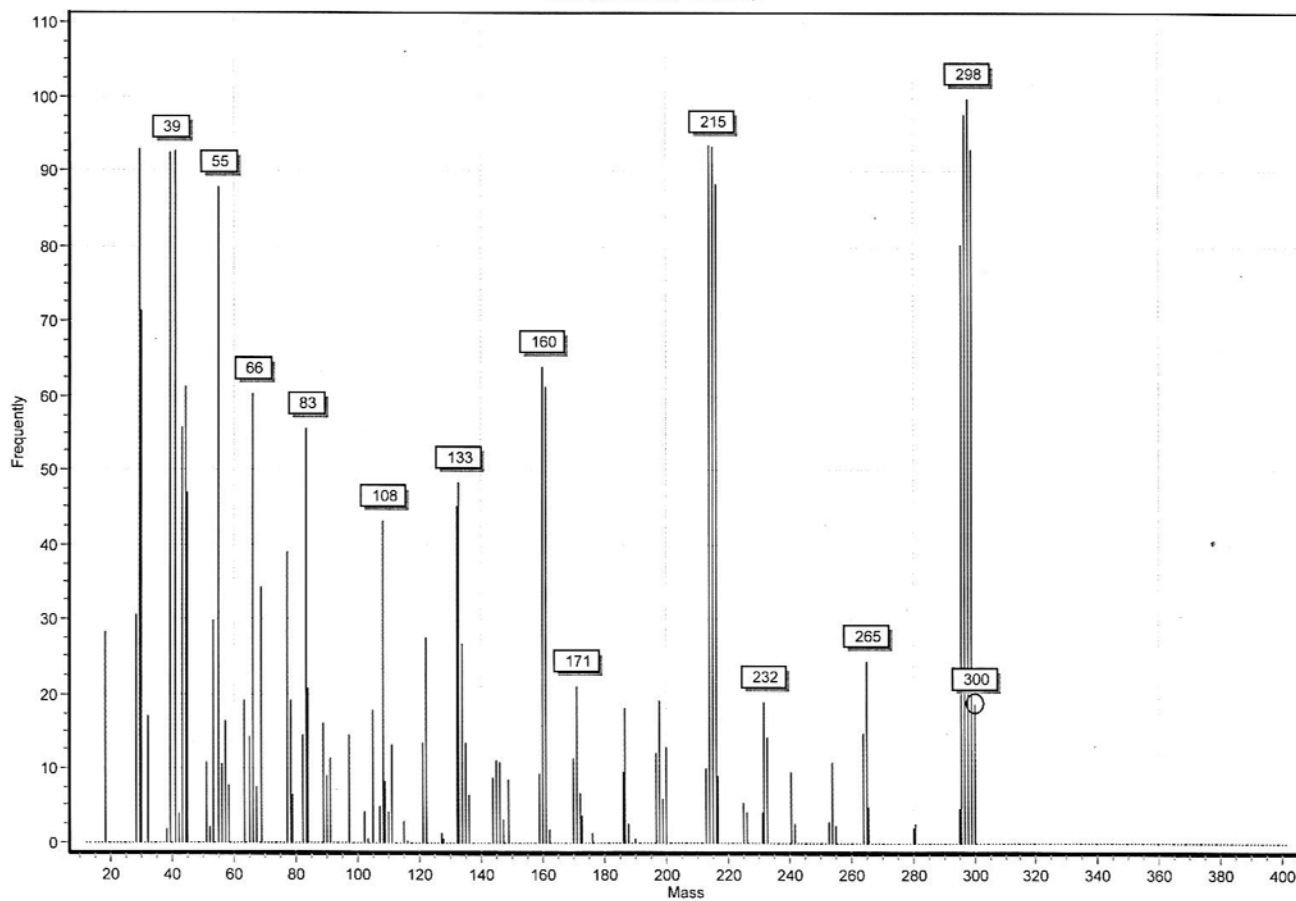
**Figure S21:** <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) of 2-amino-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**1**)



Parameter	Value
Origin	Bruker BioSpin GmbH
Owner	root
Site	
Spectrometer	spect
Author	
Solvent	DMSO
Temperature	308.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB-1H/ D Z-GRD Z104275/ 0252
Number of Scans	64
Receiver Gain	202
Relaxation Delay	2.0000
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	1.8088
Acquisition Date	2016-08-23T11:53:02
Modification Date	2016-08-23T23:23:02
Class	
Spectrometer Frequency	75.66
Spectral Width	18115.9
Lowest Frequency	-1493.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

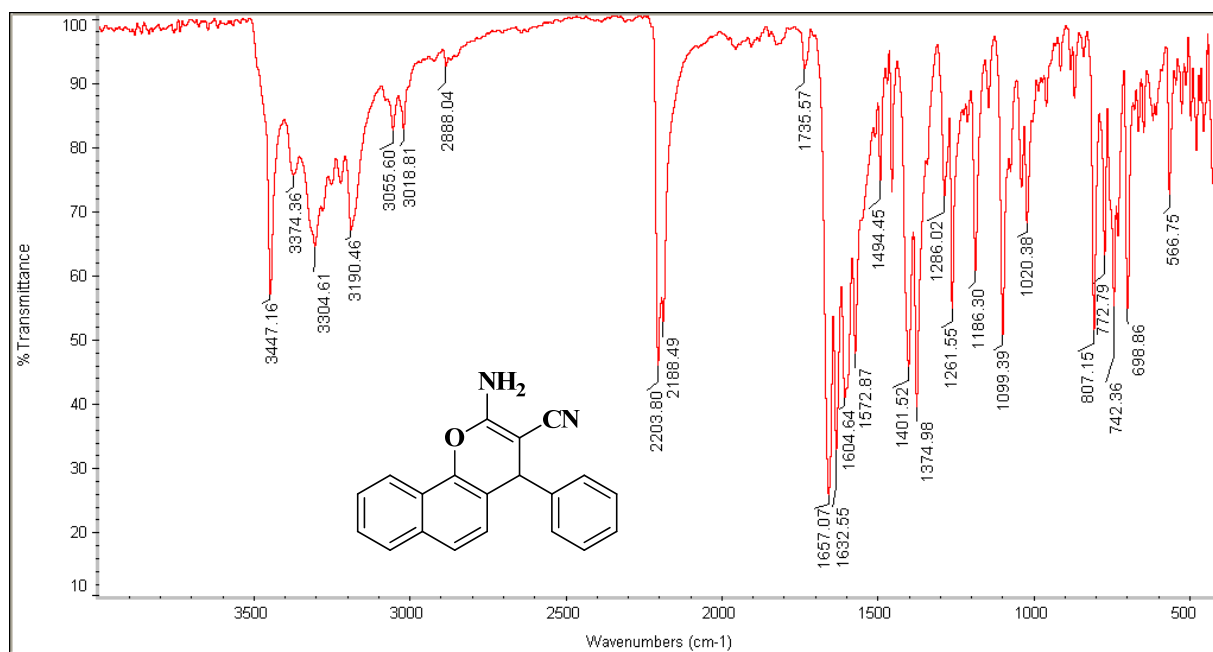
**Figure S22:**  $^{13}\text{C}$  NMR (76 MHz, DMSO-  $d_6$ ) of 2-amino-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1**)



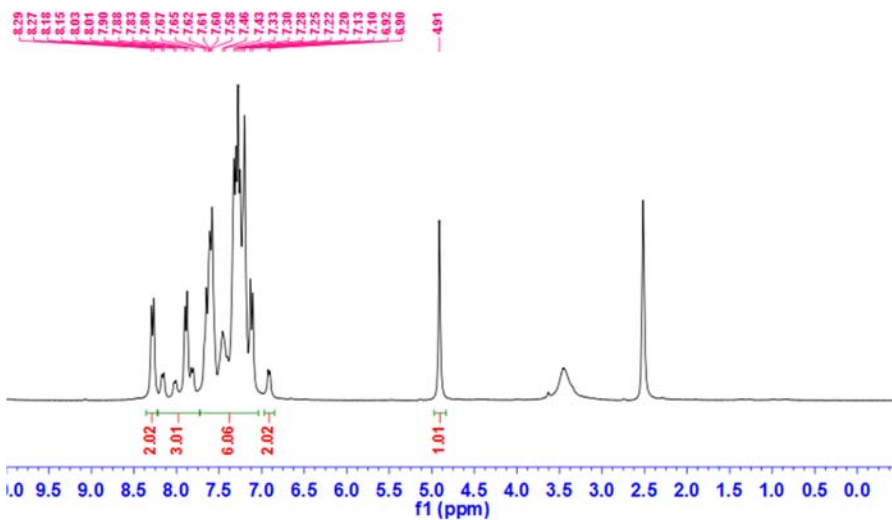
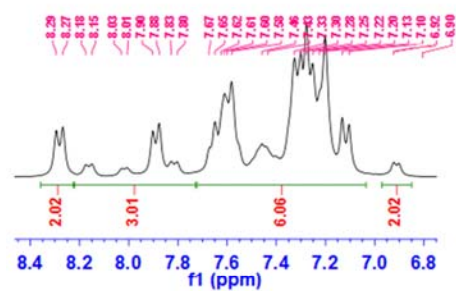


**Figure S23:** Mass spectrum of 2-amino-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**I**)

**2-amino-4-phenyl-4*H*-benzo[*h*]chromene-3-carbonitrile (m)** (0.283 g, 95%); Yellow solid ; mp 215-216 °C (from EtOH) (Lit.<sup>[5]</sup> 218–219 °C); FT-IR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3447.16, 3374 (NH<sub>2</sub>), 3190 (C-H, aromatic), 2888 (sp<sup>3</sup> C-H), 2203 (CN), 1657 (C=O), 1632 (C=C, vinyl nitrile), 1604, 1572 (C=C, aromatic), 1374 (C-O), 1261 (C-N); <sup>1</sup>H NMR:  $\delta$ H (300 MHz; DMSO-*d*<sub>6</sub>) 8.28 (d, *J*= 6 Hz, 2 H, Ar-H), 8.18-7.8 (m, 3 H, Ar-H), 7.67-7.1 (m, 4 H, Ar-H), 7.2 (s, 2 H, NH<sub>2</sub>), 6.91 (m, 2 H, Ar-H), 4.91 (s, 1 H, CH); <sup>13</sup>C NMR:  $\delta$ C (76 MHz, DMSO- *d*<sub>6</sub>) 160.64, 146.17, 143.21, 134.87, 133.16, 129.17, 128.14, 127.82, 127.39, 127.23, 127.14, 126.69, 124.98, 124.36, 123.23, 121.18, 118.4, 108.49, 56.74, 41.41; MS, *m/z* 298 (M<sup>+</sup>, 4%), 295 (M-3H, 57%), 266 (M-HCO, 6%), 219 (M-3H-C<sub>6</sub>H<sub>4</sub>, 81%), 170 (C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>O, 14%), 143 (C<sub>10</sub>H<sub>7</sub>O, 100%), 114 (C<sub>9</sub>H<sub>6</sub>, 98%), 89 (C<sub>7</sub>H<sub>5</sub>, 82%), 29 (HCO, 80%).



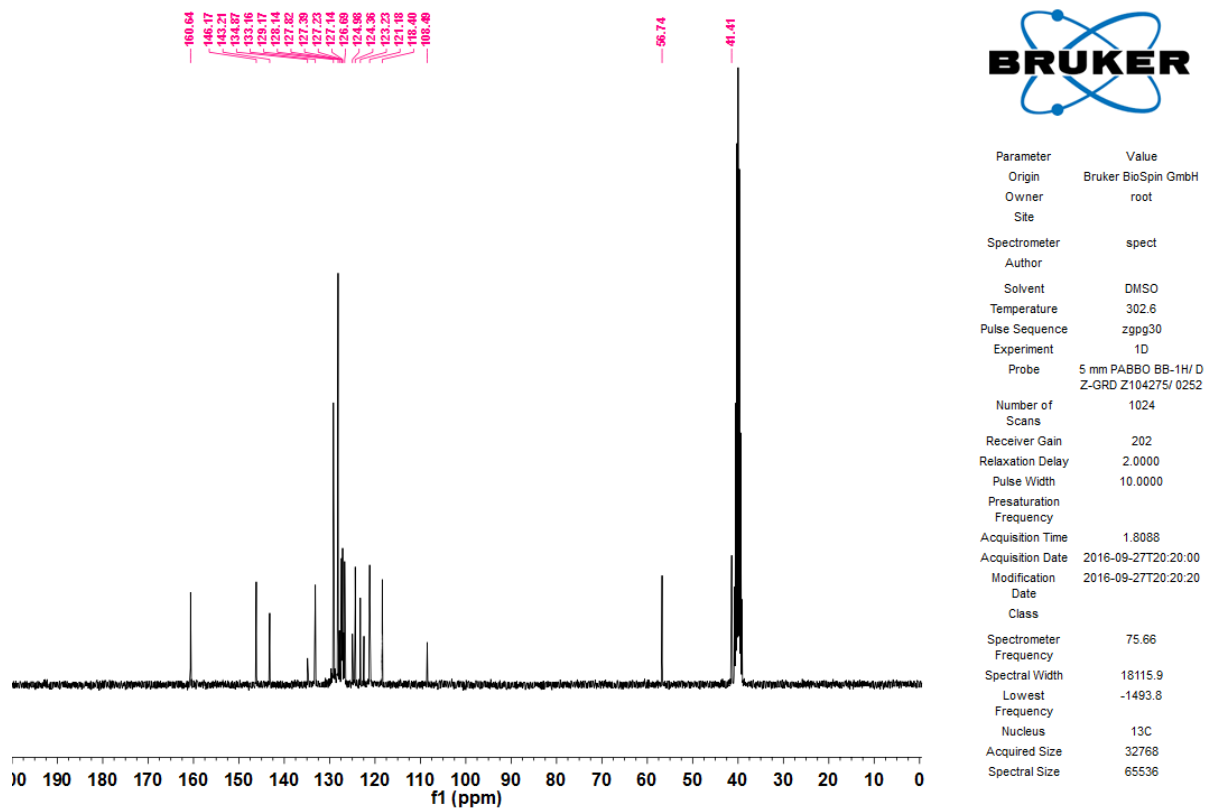
**Figure S24:** FT-IR (KBr) of 2-amino-4-phenyl-4*H*-benzo[*h*]chromene-3-carbonitrile (**m**).



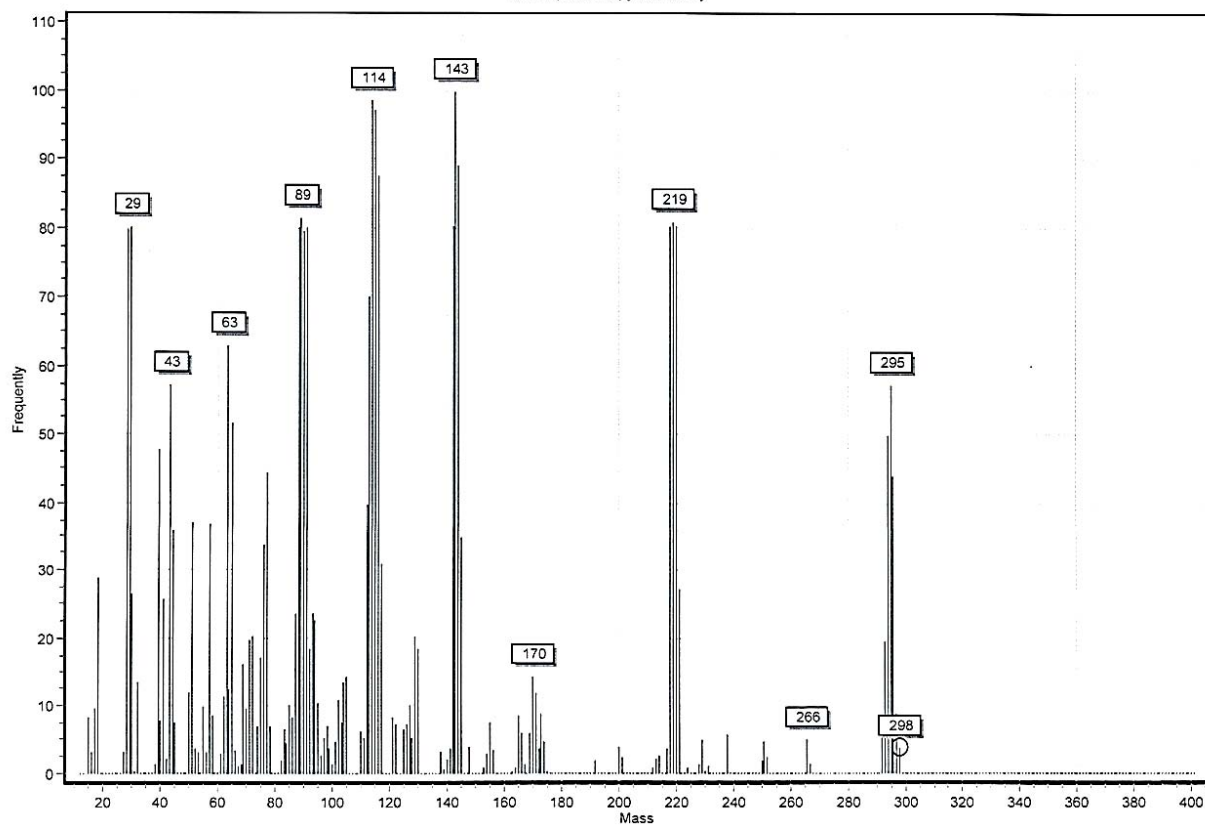
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Site	
Spectrometer	spect
Author	
Solvent	DMSO
Temperature	302.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB-1H/ D Z-GRD Z104275/ 0252
Number of Scans	16
Receiver Gain	127
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	5.4395
Acquisition Date	2016-09-27T20:22:00
Modification Date	2016-09-27T20:22:42
Class	
Spectrometer Frequency	300.85
Spectral Width	6024.1
Lowest Frequency	-1153.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

III

**Figure S25:**  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-4-phenyl-4*H*-benzo[*h*]chromene-3-carbonitrile (**m**).

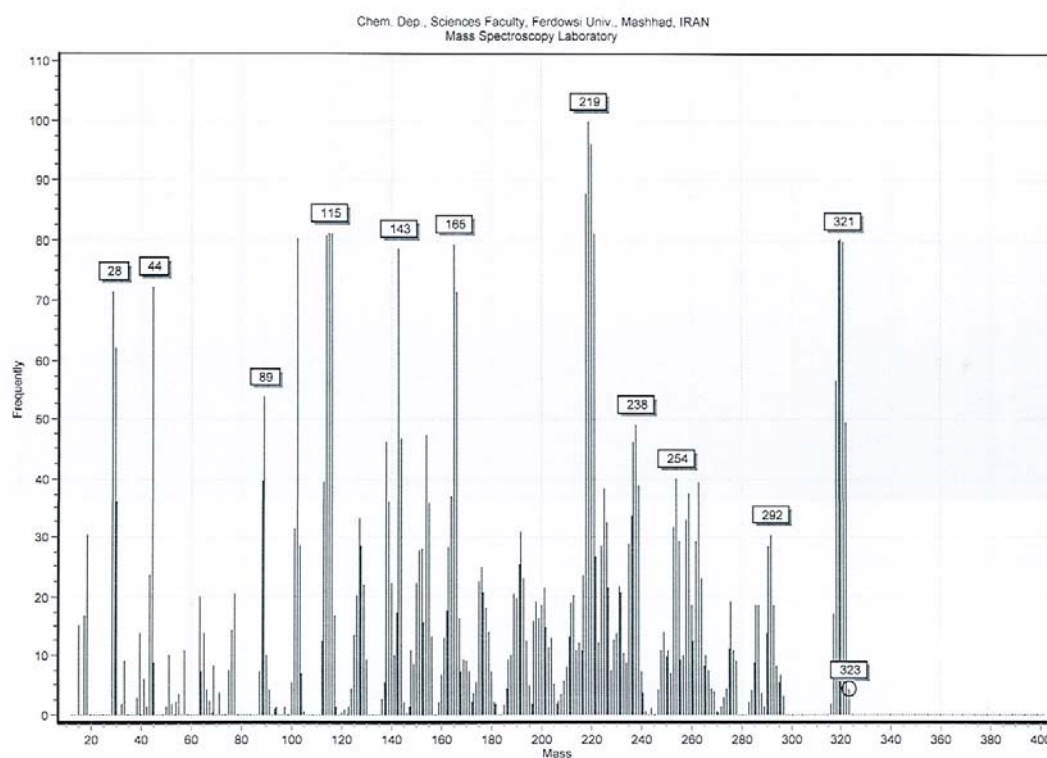
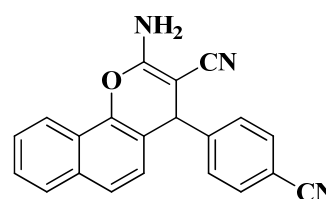


**Figure S26:**  $^{13}\text{C}$  NMR (76 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-4-phenyl-4*H*-benzo[*h*]chromene-3-carbonitrile (**m**).



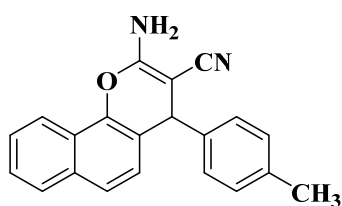
**Figure S27:** Mass spectrum of 2-amino-4-phenyl-4*H*-benzo[h]chromene-3-carbonitrile (**m**).

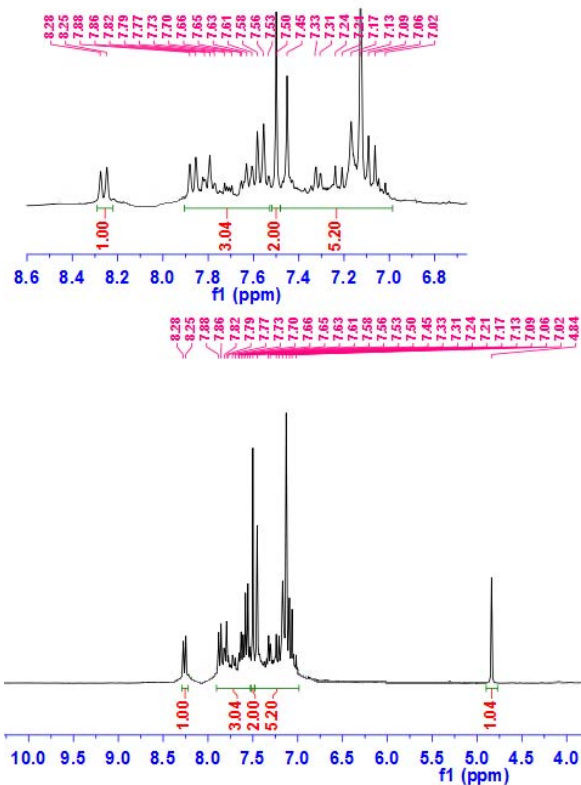
**2-amino-4-(4-cyanophenyl)-4H-benzo[h]chromene-3-carbonitrile (n)** (0.316 g, 98%); Yellow solid; mp 258-259 °C (from EtOH) (Lit.<sup>[5]</sup> 259–260 °C); MS,  $m/z$  323 ( $M^+$ , 4%), 321 (M-2H, 80%), 292 (M-2H-HCO, 31%), 254 (M-2H-C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>, 40%), 238 (M-2H-C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>O, 49%), 219 (C<sub>14</sub>H<sub>7</sub>N<sub>2</sub>O, 100%), 165 (M-2H-C<sub>11</sub>H<sub>10</sub>N, 79%), 143 (C<sub>10</sub>H<sub>7</sub>O, 78%), 115 (C<sub>9</sub>H<sub>7</sub>, 82%), 89 (C<sub>7</sub>H<sub>5</sub>, 54%), 28 (CO, 72%).



**Figure S28:** Mass spectrum of 2-amino-4-(4-cyanophenyl)-4H-benzo[h]chromene-3-carbonitrile (n).

**2-amino-4-(p-tolyl)-4H-benzo[h]chromene-3-carbonitrile (o)** (0.28 g, 90%); dark brown solid ; mp 202-203 °C (from EtOH) (Lit.<sup>[1]</sup> 205–206 °C); <sup>1</sup>H NMR: δH (300 MHz; DMSO-*d*<sub>6</sub>) 8.26 (d, *J*= 9 Hz, 2 H, Ar-H), 7.88-7.53 (m, 3 H, Ar-H), 7.65 (s, 2 H, NH<sub>2</sub>), 7.5-7.02 (m, 5 H, Ar-H), 4.84 (s, 1 H, CH), 2.25 (s, 3 H, CH<sub>3</sub>); <sup>13</sup>C NMR: δC (76 MHz, DMSO- *d*<sub>6</sub>) 160.53, 143.24, 143.11, 136.5, 133.1, 129.7, 128.11, 128.05, 127.17, 127.08, 126.71, 124.26, 123.22, 121.16, 121.02, 118.5, 56.86, 41.03, 21.07; MS, *m/z* 312 (M<sup>+</sup>, 3%), 309 (M-3H, 27%), 280 (M-3H-HCO, 6%), 219 (C<sub>14</sub>H<sub>7</sub>N<sub>2</sub>O, 38%), 143 (C<sub>10</sub>H<sub>7</sub>O, 100%), 115 (C<sub>9</sub>H<sub>7</sub>, 100%), 105 (C<sub>8</sub>H<sub>9</sub>, 57%), 89 (C<sub>7</sub>H<sub>5</sub>, 27%), 28 (CO, 74%).

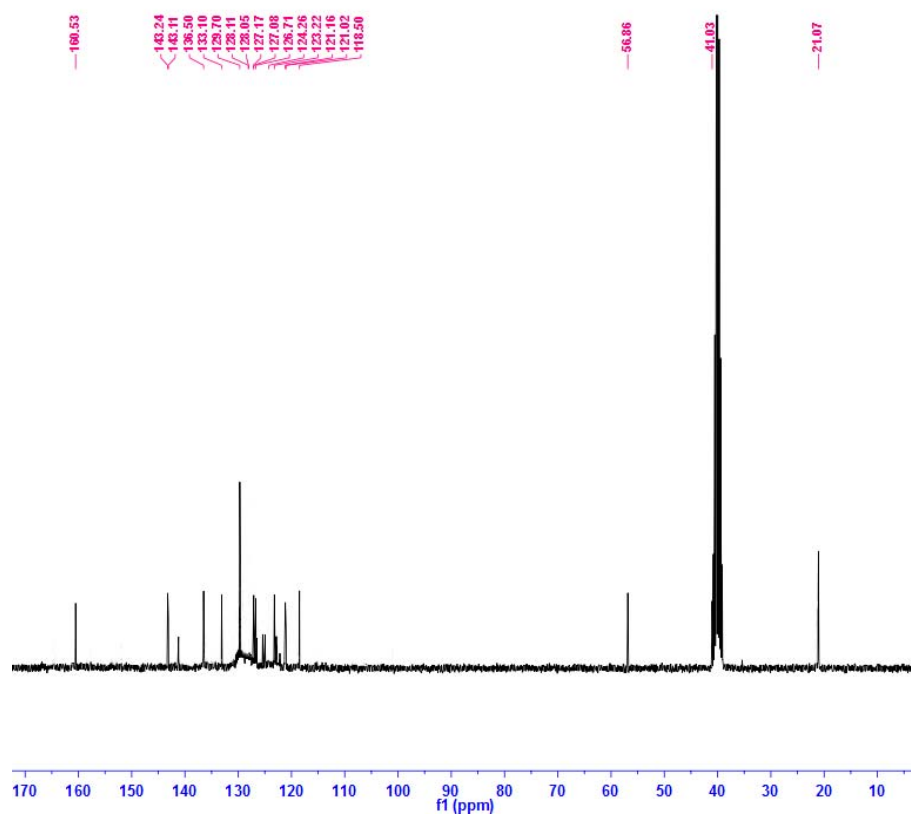




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Spectrometer	spect
Solvent	DMSO
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Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB-1H/D Z-GRD Z104275/ 0252
Number of Scans	16
Receiver Gain	89
Relaxation Delay	1.0000
Pulse Width	15.0000
Acquisition Time	5.4395
Acquisition Date	2016-09-28T12:50:00
Modification Date	2016-09-28T12:50:12
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Spectral Width	6024.1
Lowest Frequency	-1153.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

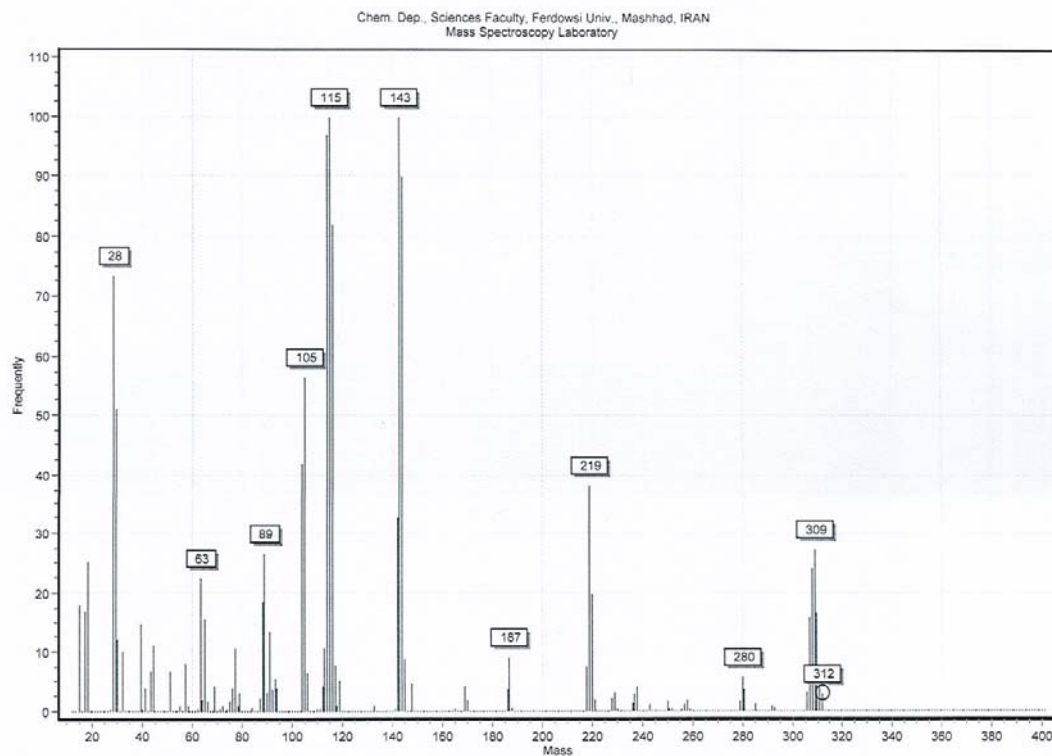
**Figure S29:**  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ) of 2-amino-4-(p-tolyl)-4H-benzo[h]chromene-3-carbonitrile (**o**).





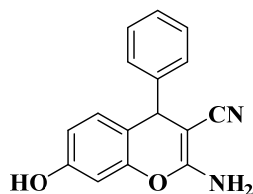
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Spectrometer	spect
Author	
Solvent	DMSO
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Number of Scans	1024
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Relaxation Delay	2.0000
Pulse Width	10.0000
Presaturation Frequency	
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Class	
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Lowest Frequency	-1493.8
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

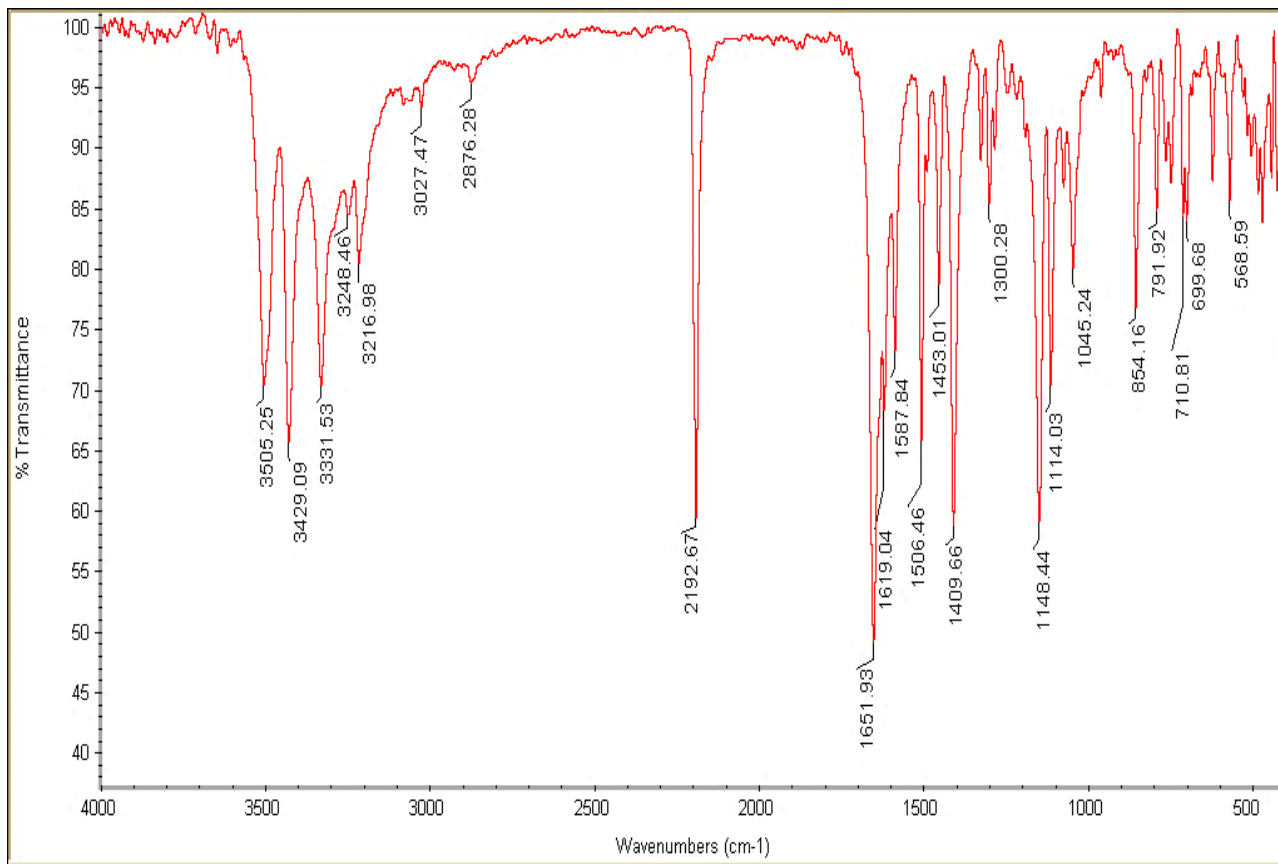
**Figure S30:** <sup>13</sup>C NMR (76 MHz, DMSO- *d*<sub>6</sub>) of 2-amino-4-(*p*-tolyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (**o**).



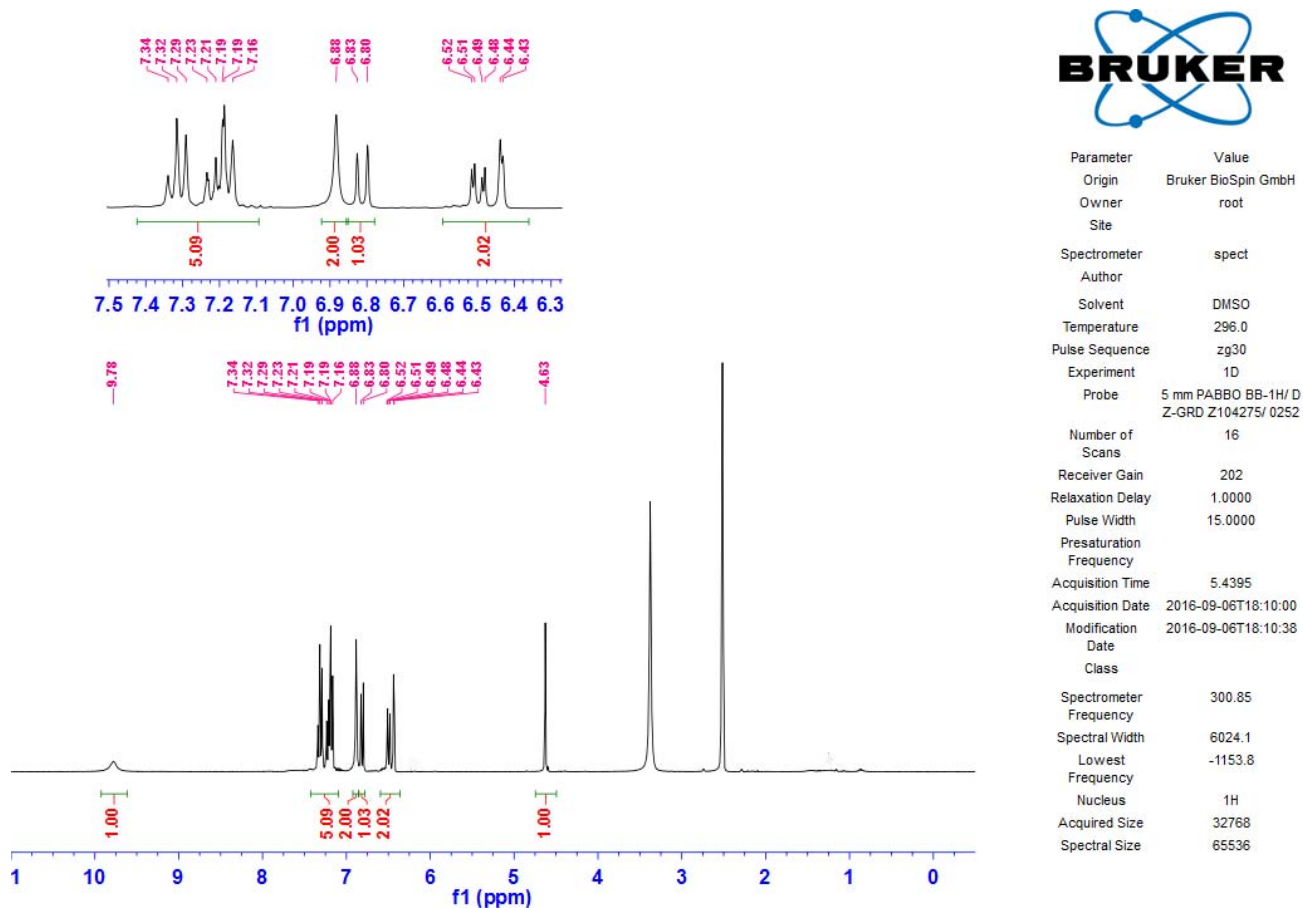
**Figure S31:** Mass spectrum of 2-amino-4-(p-tolyl)-4*H*-benzo[h]chromene-3-carbonitrile (**o**).

**2-amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (p)** (0.237 g, 90%); Light yellow solid; mp 231-234 °C (from EtOH) (Lit.<sup>[1]</sup> 232–234 °C); FT-IR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3505 (OH), 3429, 3331 (NH<sub>2</sub>), 3216 (C-H, aromatic), 2876 (sp<sup>3</sup> C-H), 2192 (CN), 1651 (C=C, vinyl nitrile), 1619, 1506 (C=C, aromatic), 1409 (C-O), 1148 (C-N) ; <sup>1</sup>H NMR:  $\delta$ H (300 MHz; DMSO-*d*<sub>6</sub>) 9.78 (s, 1 H, OH), 7.34-7.16 (m, 5 H, Ar-H), 6.88 (s, 2 H, NH<sub>2</sub>), 6.81 (d, *J*= 9 Hz, 1 H, Ar-H), 6.52-6.43 (m, 2 H, Ar-H), 4.63 (s, 1 H, CH); <sup>13</sup>C NMR:  $\delta$ C (76 MHz, DMSO- *d*<sub>6</sub>) 160.71, 157.55, 149.3, 146.84, 130.36, 129.04, 127.83, 127.09, 121.14, 114.18, 112.84, 102.63, 56.7; MS, *m/z* 264 (M<sup>+</sup>, 5%), 261 (M-3H, 74%), 234 (M-3H-HCN, 18%), 186 (C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>94%), 91 (C<sub>7</sub>H<sub>7</sub>, 54%), 77 (C<sub>6</sub>H<sub>5</sub>, 100%), 65 (C<sub>3</sub>HN<sub>2</sub>, 77%), 29 (HCO, 96%).

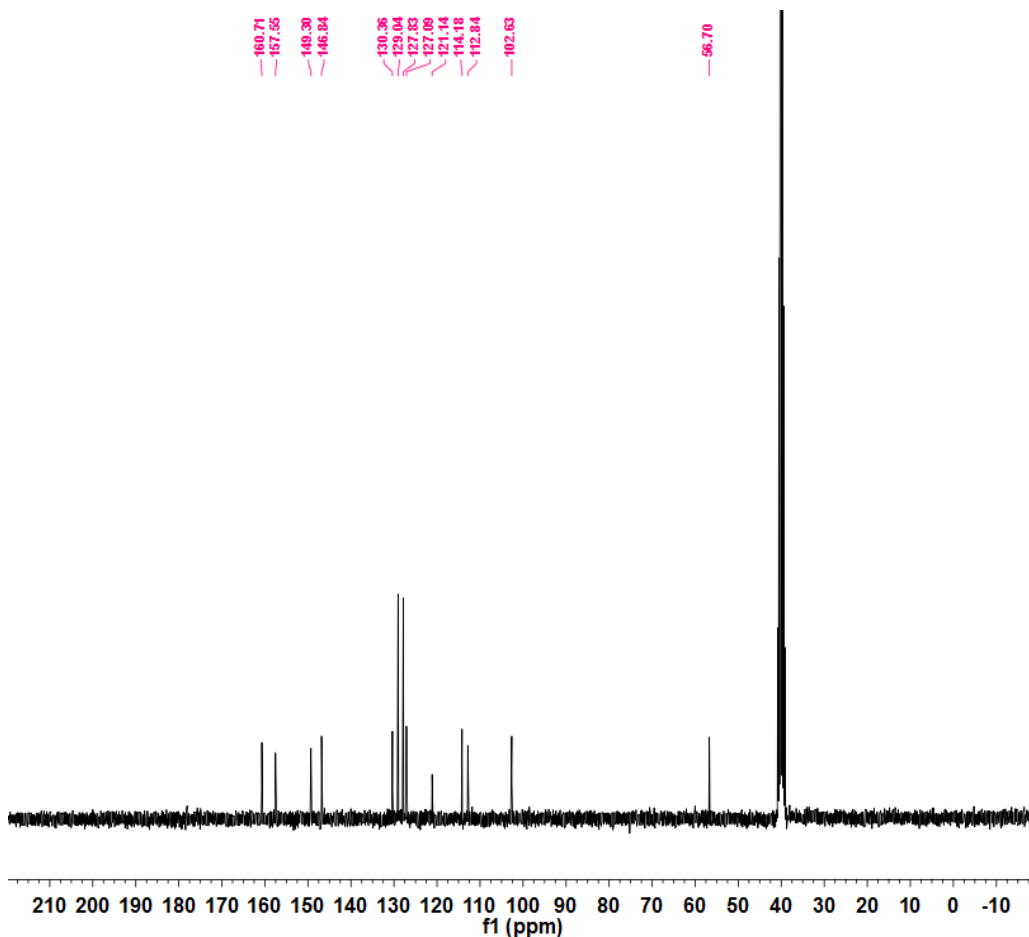




**Figure S32:** FT-IR (KBr) of 2-amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (**p**)

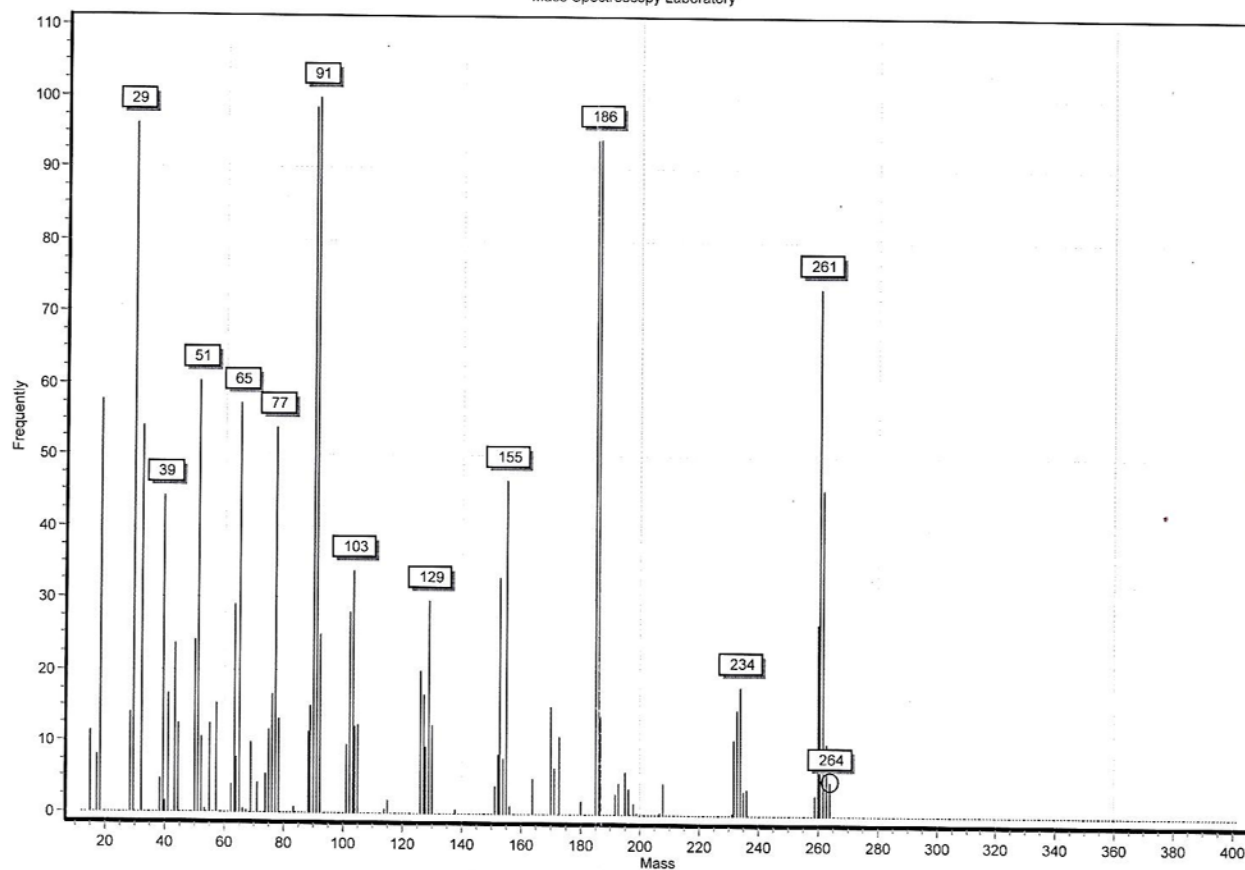


**Figure S33:**  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (**p**)



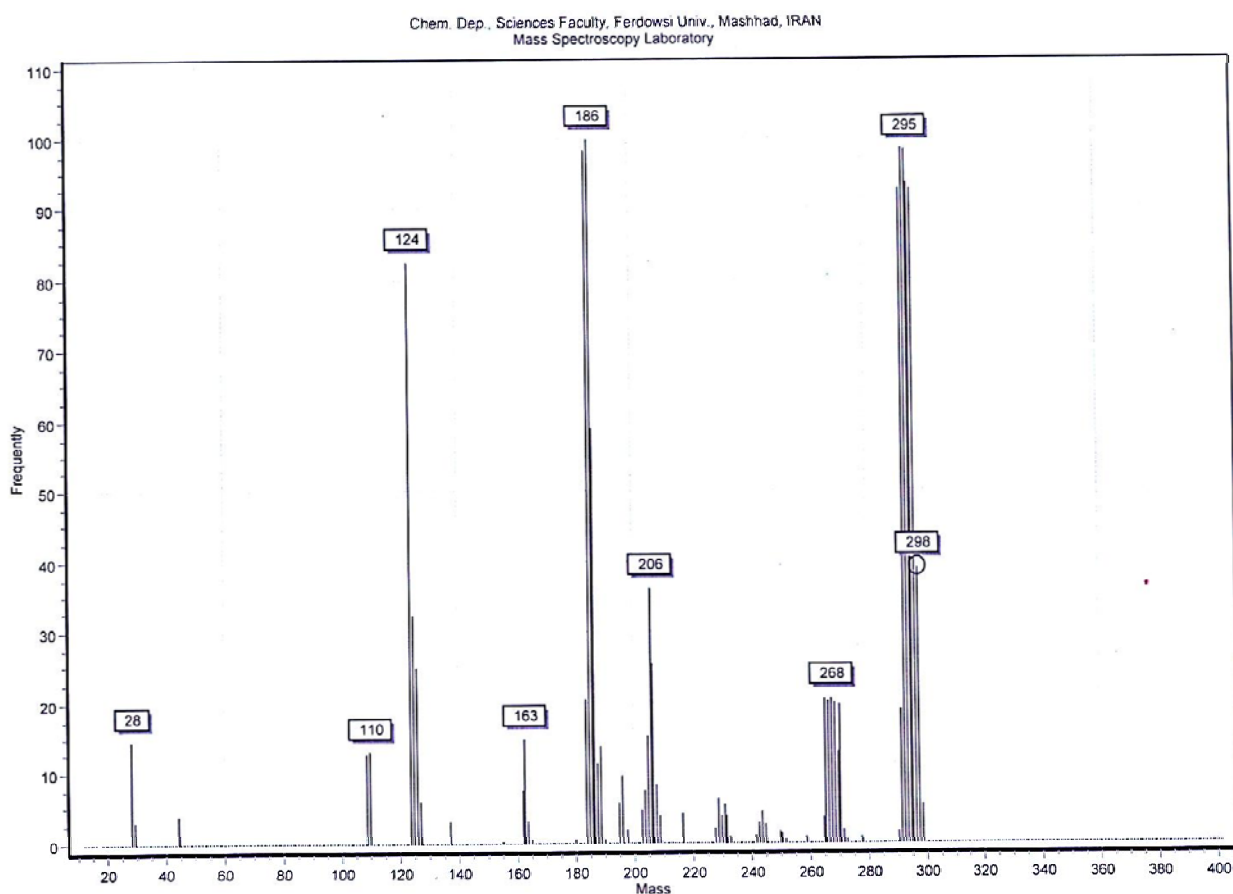
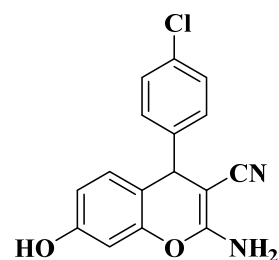
Parameter	Value
Origin	Bruker BioSpin GmbH
Owner	root
Site	
Spectrometer	spect
Author	
Solvent	DMSO
Temperature	296.7
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB-1H/D Z-GRD Z104275/ 0252
Number of Scans	480
Receiver Gain	202
Relaxation Delay	2.0000
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	1.8088
Acquisition Date	2016-09-06T18:42:00
Modification Date	2016-09-06T18:42:12
Class	
Spectrometer Frequency	75.66
Spectral Width	18115.9
Lowest Frequency	-1493.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

**Figure S34:**  $^{13}\text{C}$  NMR (76 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (**p**)



**Figure S35:** Mass spectrum of 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (p)

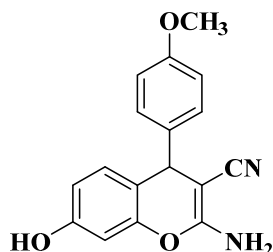
**2-amino-4-(4-chlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (q)** (0.274 g, 92%); Yellow solid; mp 157-159 °C (from EtOH) (Lit.<sup>[1]</sup> 163 °C); MS, *m/z* 298 (*M*<sup>+</sup>, 38%), 295 (*M*-3*H*, 98%), 268 (*M*-3*H*-HCN, 21%), 206 (*C*<sub>10</sub>*H*<sub>7</sub>*N*<sub>2</sub>*O**Cl*, 36%), 186 (*C*<sub>10</sub>*H*<sub>6</sub>*N*<sub>2</sub>*O*<sub>2</sub>, 100%), 163 (*C*<sub>9</sub>*H*<sub>6</sub>*NCl*, 15%), 124 (*C*<sub>7</sub>*H*<sub>5</sub>*Cl*, 83%), 110 (*C*<sub>6</sub>*H*<sub>6</sub>*O*<sub>2</sub>, 13%), 28 (*CO*, 15%).

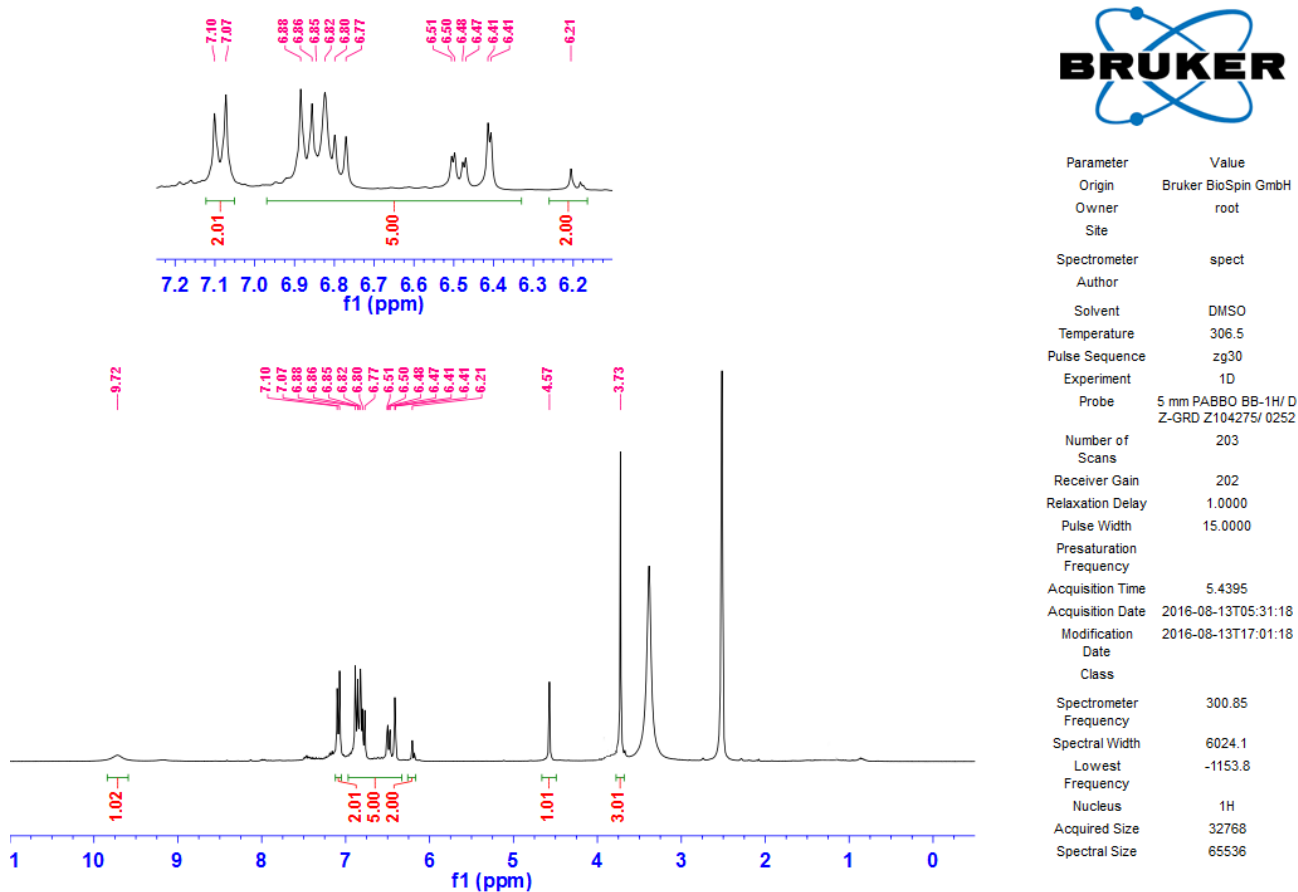


**Figure S36:** Mass spectrum of 2-amino-4-(4-chlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (q)

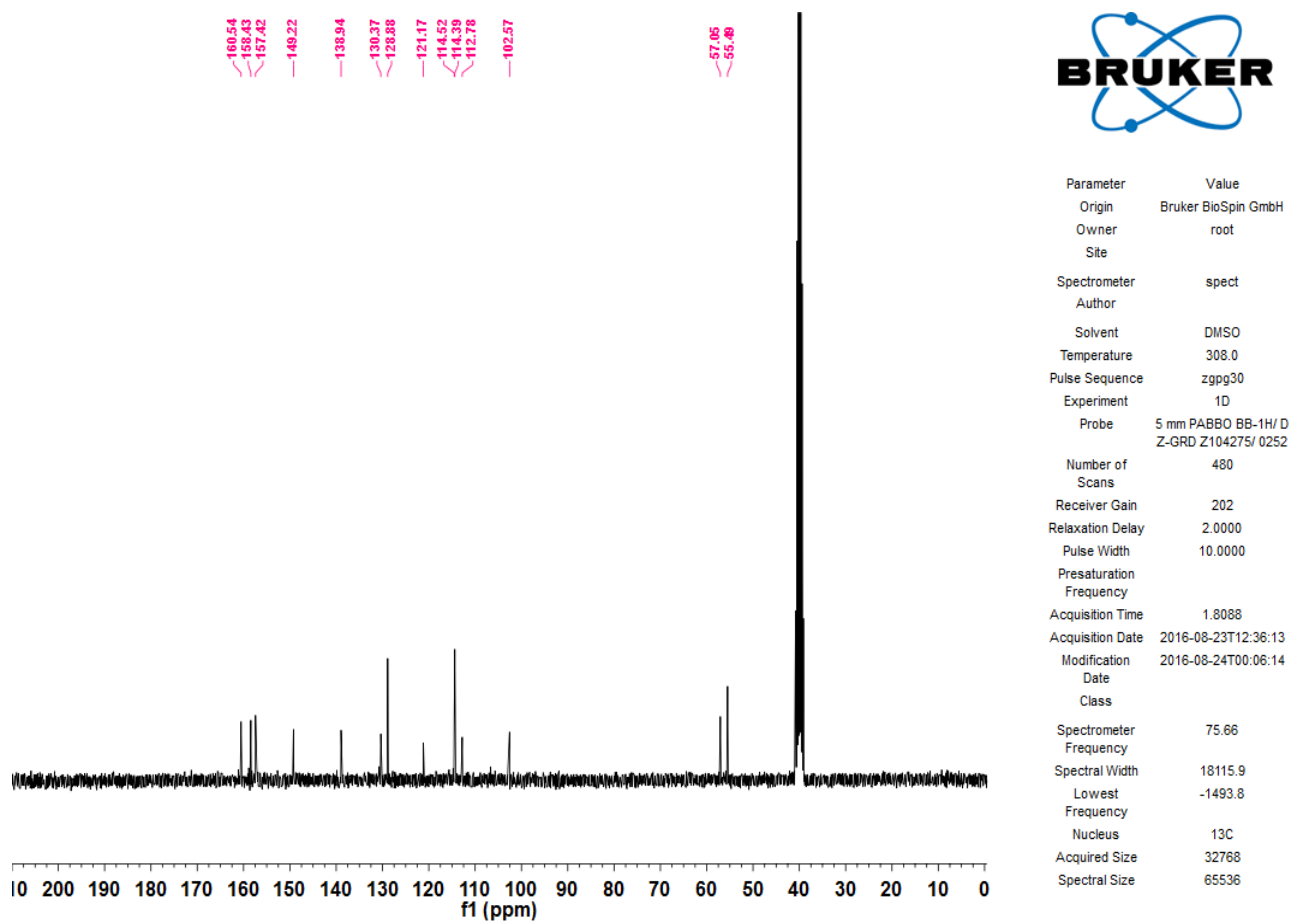


**2-amino-7-hydroxy-4-(4-methoxyphenyl)-4H-chromene-3-carbonitrile (r)** (0.249 g, 85%); Yellow solid (crystals); mp 108-110 °C (from EtOH) (Lit.<sup>[6]</sup> 110–112 °C; <sup>1</sup>H NMR: δH (300 MHz; DMSO-*d*<sub>6</sub>) 9.72 (s, 1 H, OH), 7.08 (d, *J* = 9 Hz, 2 H, Ar-H), 6.88-6.41 (m, 5 H, Ar-H), 6.21 (s, 2 H, NH<sub>2</sub>), 4.57 (s, 1 H, CH), 3.73 (s, 3 H, CH<sub>3</sub>); <sup>13</sup>C NMR: δC (76 MHz, DMSO- *d*<sub>6</sub>) 160.54, 158.43, 157.42, 149.22, 138.94, 130.37, 128.88, 121.17, 114.52, 114.39, 112.78, 102.57, 57.05, 55.49; MS, *m/z* 294 (M<sup>+</sup>, 9%), 292 (M-2H, 54%), 185 (C<sub>10</sub>H<sub>5</sub>N<sub>2</sub>O<sub>2</sub>, 9%), 183 (C<sub>10</sub>H<sub>3</sub>N<sub>2</sub>O<sub>2</sub> or C<sub>11</sub>H<sub>7</sub>N<sub>2</sub>O, 100%), 168 (C<sub>10</sub>H<sub>4</sub>N<sub>2</sub>O or M-2H-C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>, 44%), 140 (C<sub>9</sub>H<sub>4</sub>N<sub>2</sub>, 83%), 114 (C<sub>7</sub>H<sub>2</sub>N<sub>2</sub>, 82%), 109 (C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>,43%), 88 (C<sub>5</sub>N<sub>2</sub>,16%), 28 (CO, 45%).

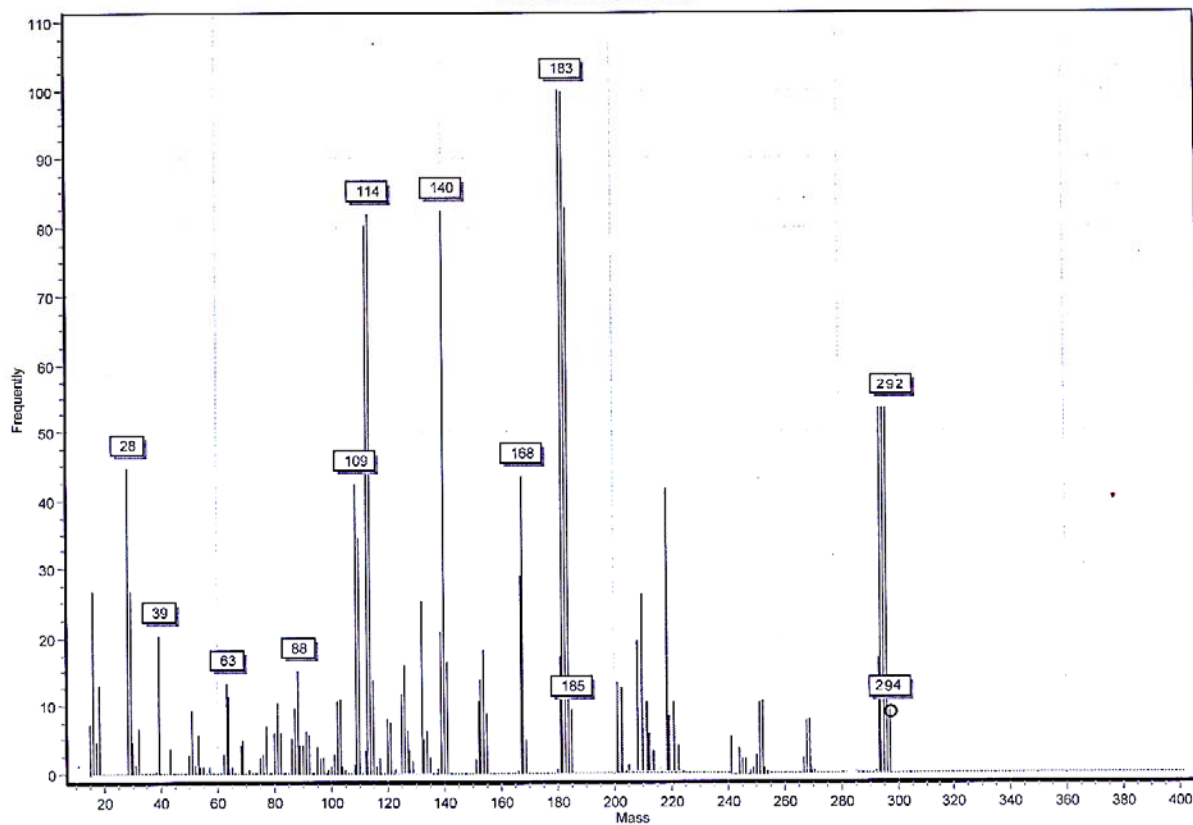




**Figure S37:**  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-7-hydroxy-4-(4-methoxyphenyl)-4H-chromene-3-carbonitrile (**r**)

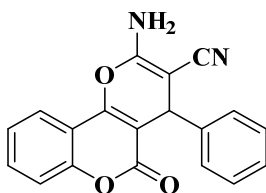


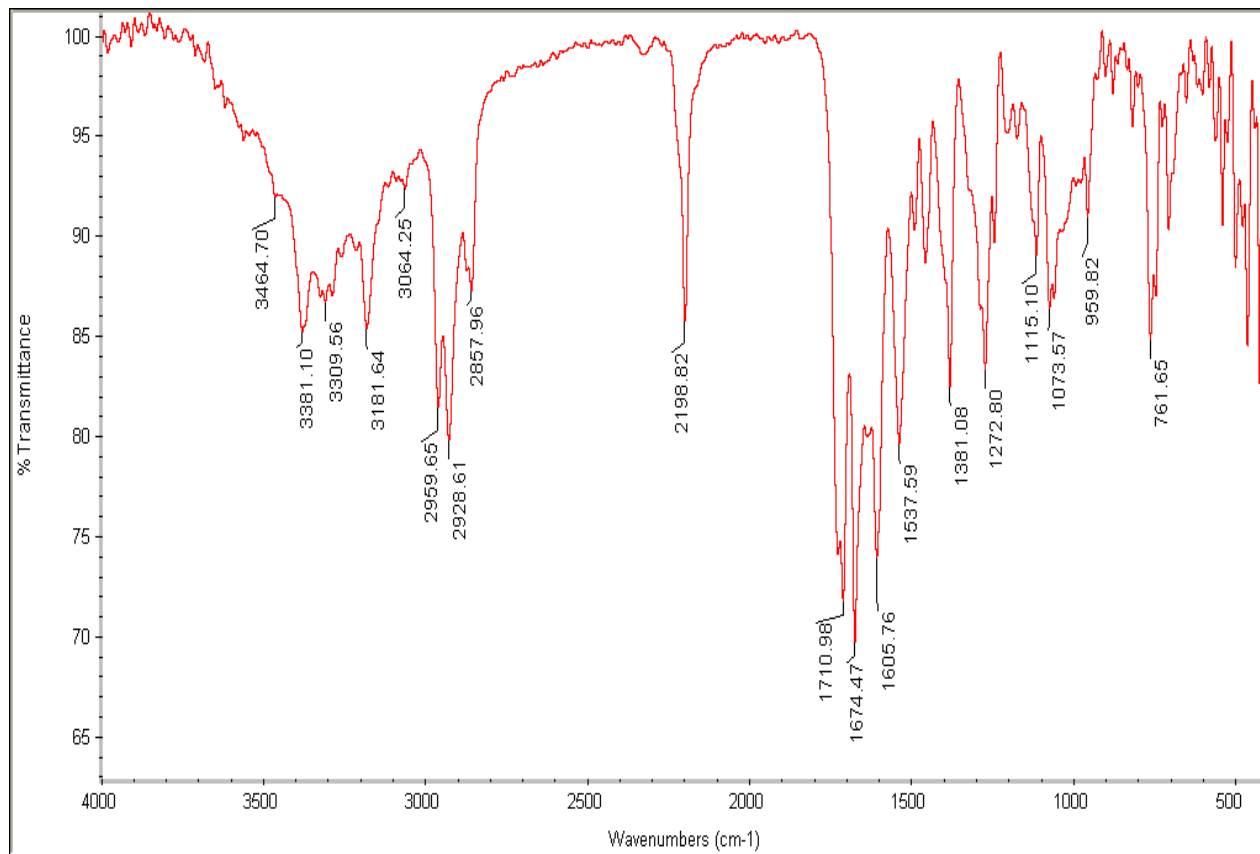
**Figure S38:**  $^{13}\text{C}$  NMR (76 MHz, DMSO-  $d_6$ ) of 2-amino-7-hydroxy-4-(4-methoxyphenyl)-4H-chromene-3-carbonitrile (**r**).



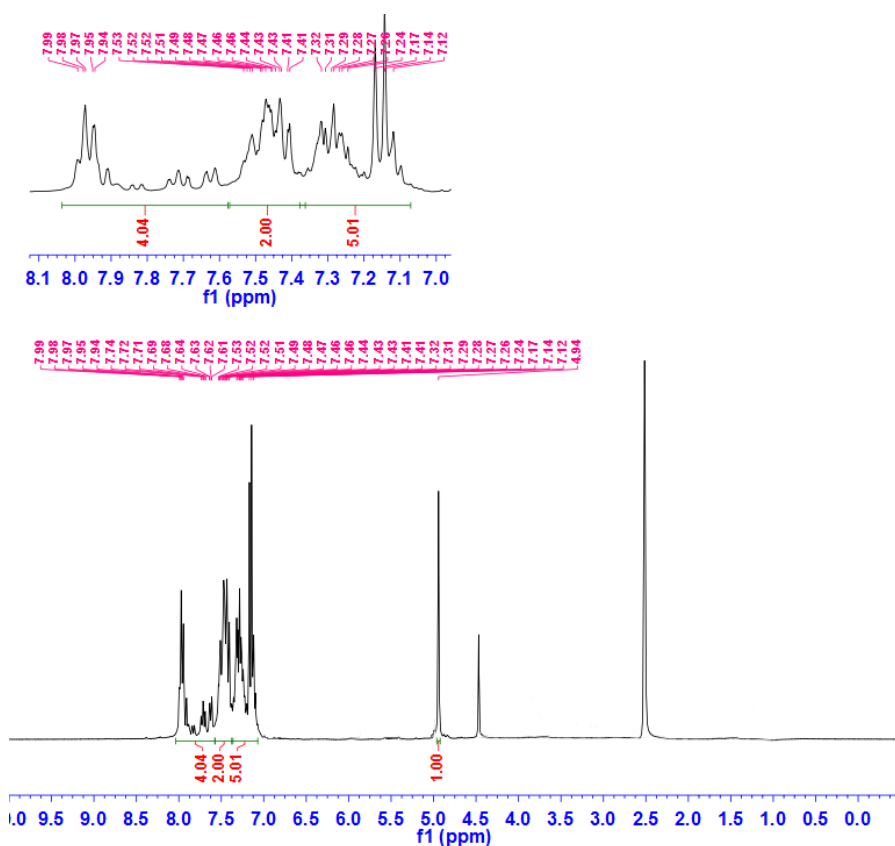
**Figure S39:** Mass spectrum of 2-amino-7-hydroxy-4-(4-methoxyphenyl)-4*H*-chromene-3-carbonitrile (**r**).

**2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (s)** (0.268 g, 85%); white solid; mp 257-259 °C (from EtOH) (Lit.<sup>[1]</sup> 260–262 °C); FT-IR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3464, 3381 (NH<sub>2</sub>), 3181 (C-H, aromatic), 2928 (sp<sup>3</sup> C-H), 2198 (CN), 1710 (C=O), 1674 (C=C, vinyl nitrile), 1605, 1537 (C=C, aromatic), 1381 (C-O), 1272 (C-N) ; <sup>1</sup>H NMR:  $\delta$ H (300 MHz; DMSO-*d*<sub>6</sub>) 7.99-7.61 (m, 2 H, Ar-H), 7.98 (s, 2 H, NH<sub>2</sub>), 7.53-7.43 (m, 2 H, Ar-H), 7.41-7.12 (m, 5 H, Ar-H), 4.94 (s, 1 H, CH); <sup>13</sup>C NMR:  $\delta$ C (76 MHz, DMSO-*d*<sub>6</sub>) 164.68, 164.15, 154.61, 153.96, 141.33, 128.48, 127.39, 125.5, 124.77, 122.95, 122.81, 121.62, 116.28, 116.03, 115.69, 95.78, 43.42; MS, *m/z* 316 (M<sup>+</sup>, 4%), 313 (M-3H, 77%), 269 (M-3H-CO<sub>2</sub>, 27%), 247 (M-3H-C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 73%), 237 (M-3H-C<sub>6</sub>H<sub>4</sub>, 100%), 91 (C<sub>7</sub>H<sub>7</sub>, 67%), 66 (C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 66%), 44 (CO<sub>2</sub>, 67%), 29 (HCO, 74%).



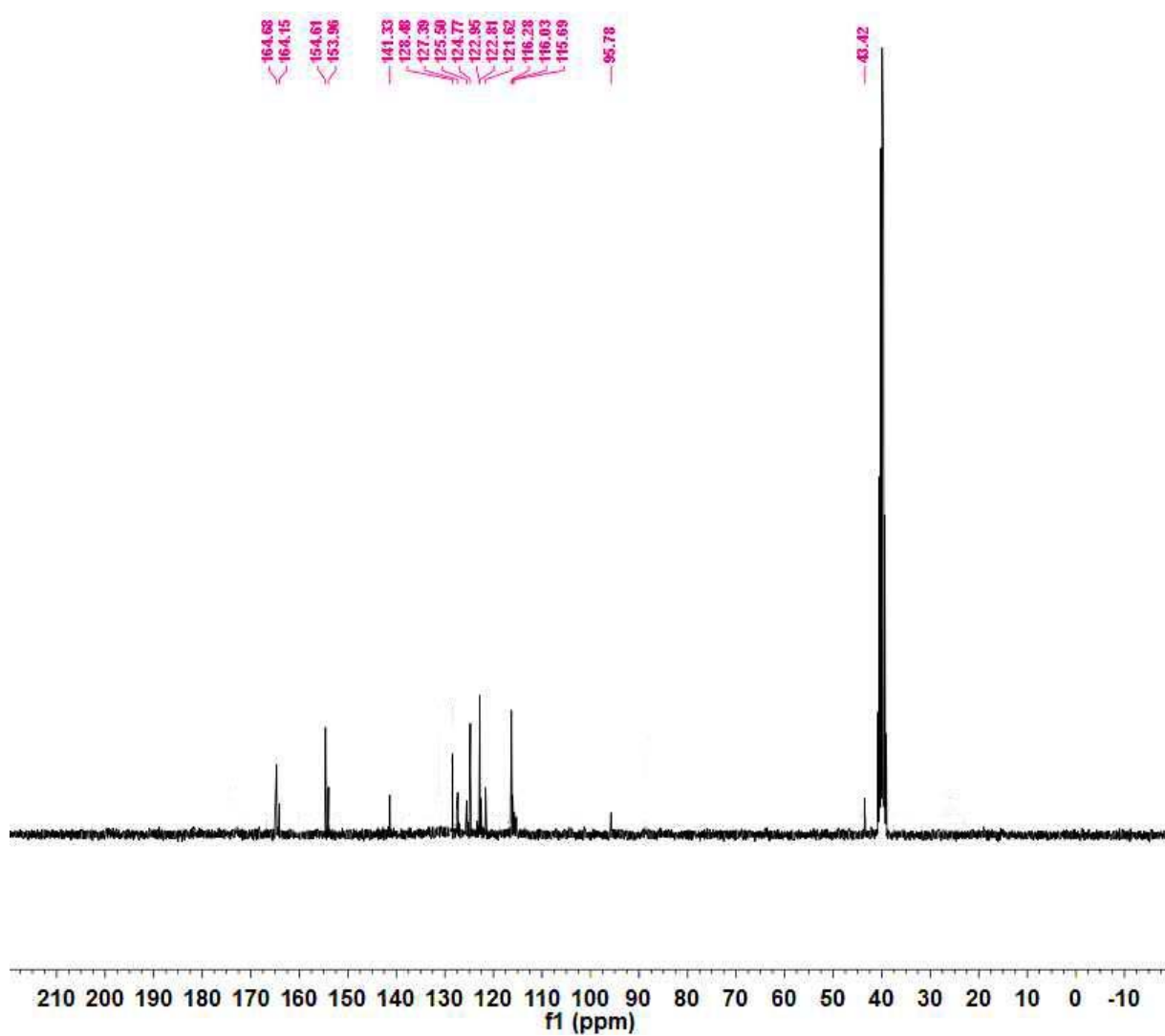


**Figure S40:** FT-IR (KBr) of 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (s).



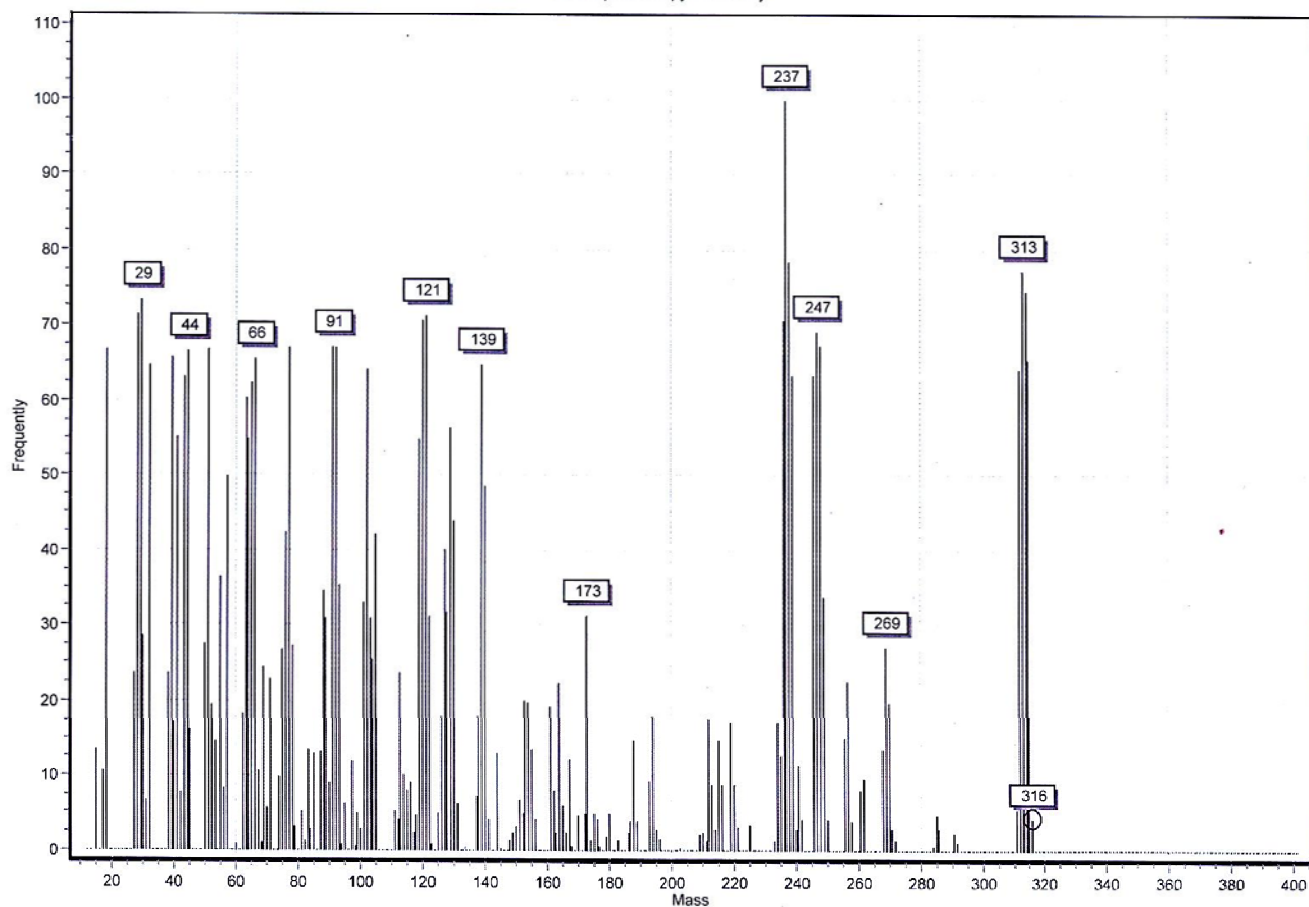
Parameter	Value
Origin	Bruker BioSpin GmbH
Owner	root
Site	
Spectrometer	spect
Author	
Solvent	DMSO
Temperature	296.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB-1H/ D Z-GRD Z104275/ 0252
Number of Scans	16
Receiver Gain	127
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	5.4395
Acquisition Date	2016-09-06T18:48:00
Modification Date	2016-09-06T18:48:14
Class	
Spectrometer Frequency	300.85
Spectral Width	6024.1
Lowest Frequency	-1153.8
Nucleus	<sup>1</sup> H
Acquired Size	32768
Spectral Size	65536

**Figure S41:** <sup>1</sup>H NMR (300 MHz, DMSO- *d*<sub>6</sub>) of 2-amino-5-oxo-4-phenyl-4,5-dihydroprano[3,2-*c*]chromene-3-carbonitrile (**s**).



**Figure S42:**  $^{13}\text{C}$  NMR (76 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**s**).

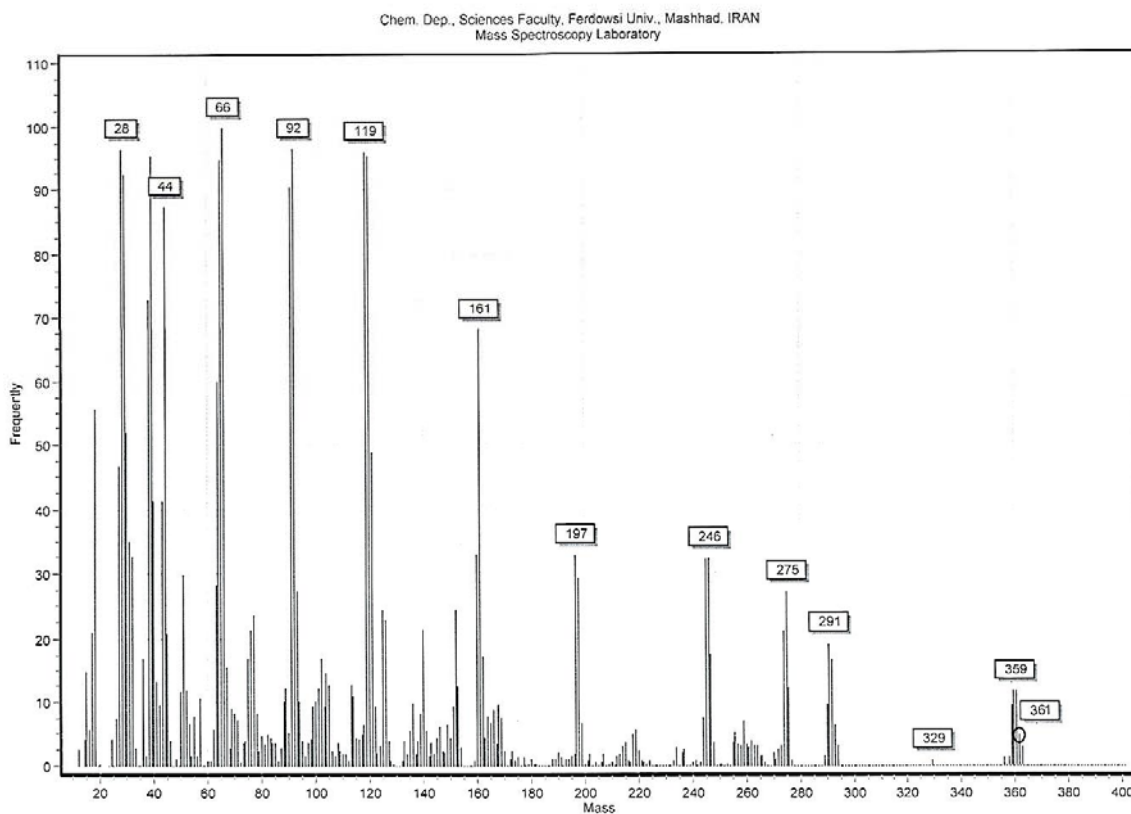
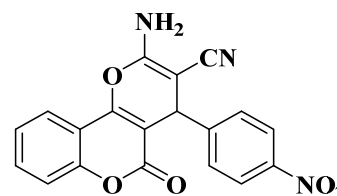




**Figure S43:** Mass spectrum of 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (s).

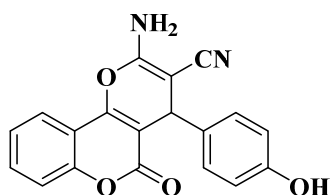
**2-amino-4-(4-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (t)**

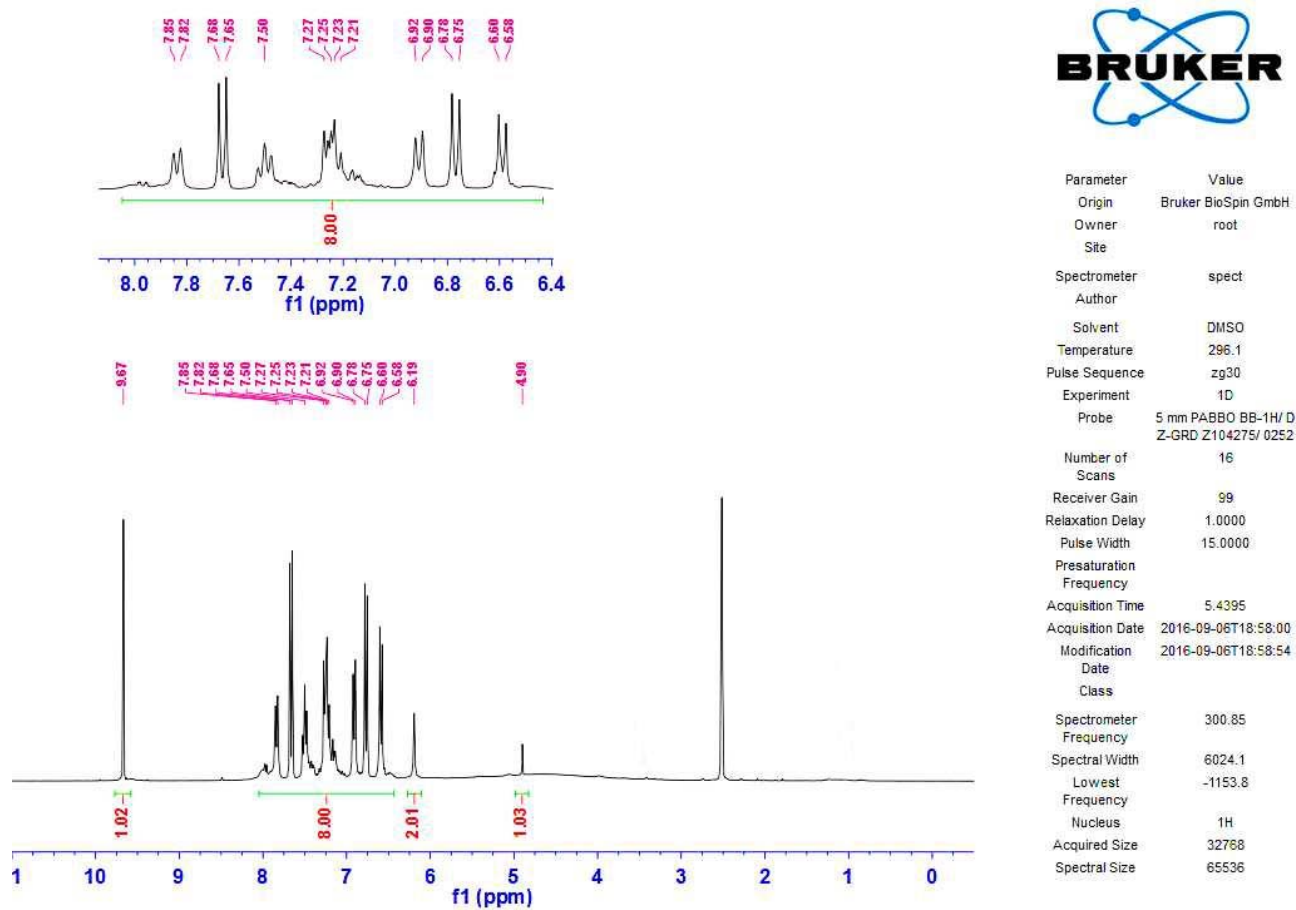
(0.324 g, 90%); white solid; mp 248-249 °C (from EtOH) (Lit.<sup>[1]</sup> 250–252 °C); MS,  $m/z$  361 ( $M^+$ , 5%), 359 ( $M-2H$ , 17%), 329 ( $M-2H-NO$ , 1%), 291 ( $M-C_3H_6N_2$ , 19%), 161 ( $C_9H_5O_3$ , 68%), 119 ( $C_8H_7O$ , 96%), 92 ( $C_6H_4O$ , 97%), 66 ( $C_3H_2N_2$ , 100%), 44 ( $CO_2$ , 87%), 28 ( $CO$ , 97%).



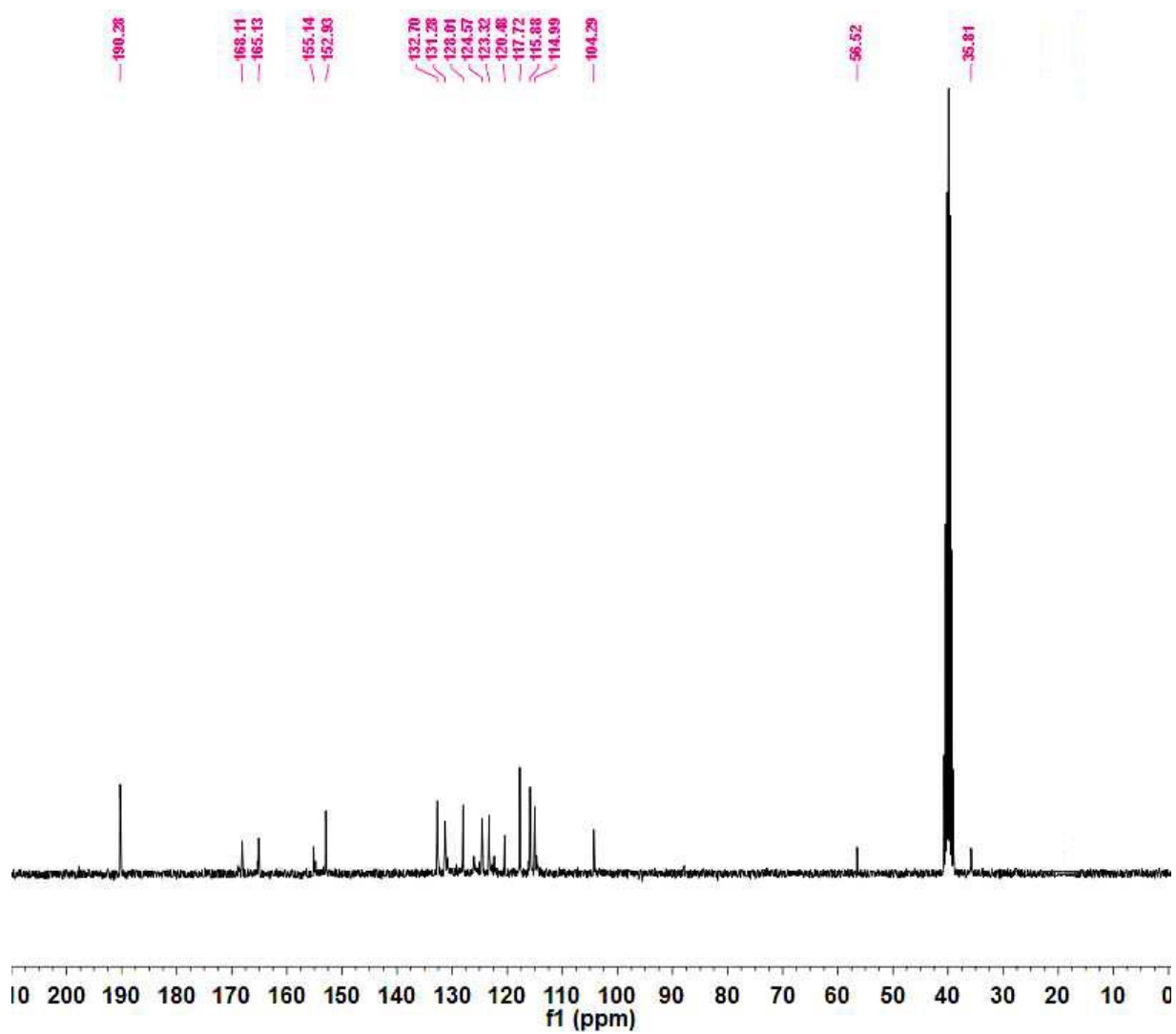
**Figure S44:** Mass spectrum of 2-amino-4-(4-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (t).

**2-amino-4-(4-hydroxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (u)**  
(0.282 g, 85%); white solid ; mp 258-259 °C (from EtOH) (Lit.<sup>[1]</sup> 259–260 °C); <sup>1</sup>H NMR: δH (300 MHz; DMSO-*d*<sub>6</sub>) 9.67 (s, 1 H, OH), 7.85-6.58 (m, 8 H, Ar-H), 6.19 (s, 2 H, NH<sub>2</sub>), 4.9 (s, 1 H, CH); <sup>13</sup>C NMR: δC (76 MHz, DMSO-*d*<sub>6</sub>) 190.28, 168.11, 165.13, 155.14, 152.93, 132.7, 131.28, 128.01, 124.57, 123.32, 120.48, 117.72, 115.88, 114.99, 104.29, 56.52, 35.81; MS, *m/z* 332 (M<sup>+</sup>, 5%), 330 (M-2H, 75%), 286 (M-2H-CO<sub>2</sub>, 29%), 161 (C<sub>9</sub>H<sub>5</sub>O<sub>3</sub>, 47%), 119 (C<sub>8</sub>H<sub>7</sub>O, 58%), 94 (C<sub>6</sub>H<sub>6</sub>O, 100%), 66 (C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 90%), 44, (CO<sub>2</sub>, 61%), 29 (HCO, 85%).

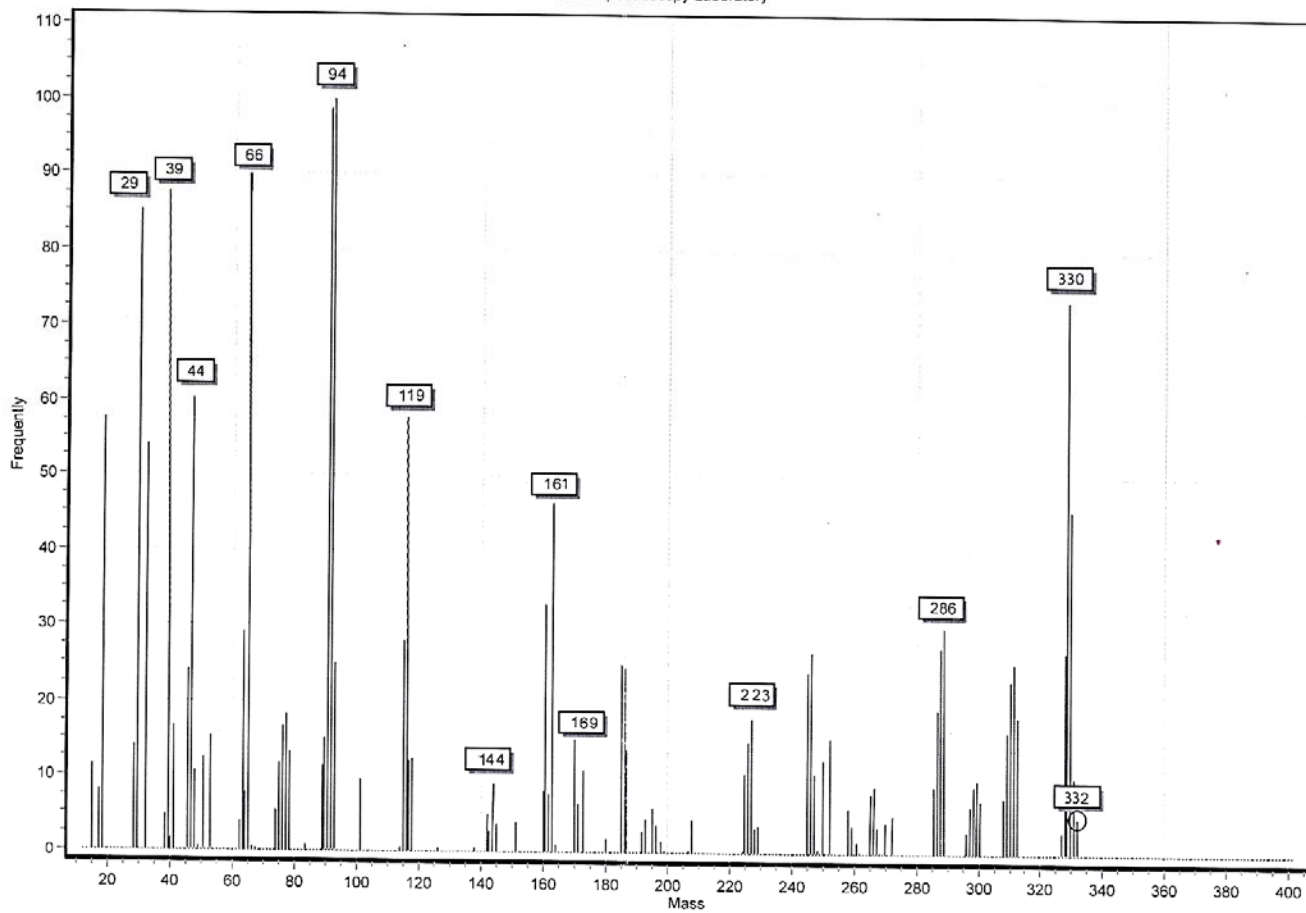




**Figure S45:** <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) of 2-amino-4-(4-hydroxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (**u**)



**Figure S46:**  $^{13}\text{C}$  NMR (76 MHz,  $\text{DMSO-}d_6$ ) of 2-amino-4-(4-hydroxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**u**)



**Figure S47:** Mass spectrum of 2-amino-4-(4-hydroxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (**u**)

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2. K. S. Pandit, P. V. Chavan, U. V. Desai, M. A. Kulkarni, P. P. Wadgaonkar, *New J. Chem.* **2015**, *39*, 4452.
3. P. L. Anandgaonker, S. Jadhav, S. T. Gaikwad, A. S. Rajbhoj, *J. Clust. Sci.* **2014**, *25*, 483.
4. M. Nasr-Esfahani, T. Abdizadeh, *J. Nanosci. Nanotechnol.* **2013**, *13*, 5004.
5. M. A. Zolfigol, M. Yarie, S. Baghery, *Synlett* **2016**, *27*, 1418.
6. G. T. Pawar, R. R. Magar, M. K. Lande, *Polycyclic Aromat. Compd.* **2016**, Doi: 10.1080/10406638.2016.1159584.