

## Supporting information

### Multi-walled carbon nanotubes supported Fe<sub>3</sub>O<sub>4</sub>NPs: an efficient and reusable catalyst for the one-pot synthesis of 4H-pyran derivatives

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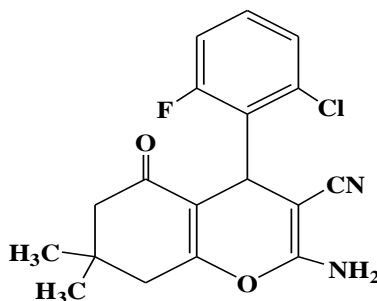
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#### Experimental:

Fe<sub>3</sub>O<sub>4</sub> NPs/MWCNTs (5 mg) was added to a mixture of aldehyde (1.0 mmol), malononitrile (1.0 mmol), and cyclic 1,3-diketone or ethyl acetoacetate (1.0 mmol) in ethanol (5 mL). The reaction mixture stirred magnetically at refluxing condition for the appropriate time. In the case of the microwave, the mixture was irradiated at 800 W at 40 °C for a few minutes depending on the reactants. After completion of the reaction as indicated by TLC, the catalyst was collected by magnetic separation using an external magnet and washed repeatedly with warm ethanol. The aqueous phase was filtrated and cooled to room temperature. Then the solid product was collected and washed with warm ethanol to afford the pure product. For further purification, the products were recrystallized from ethanol.

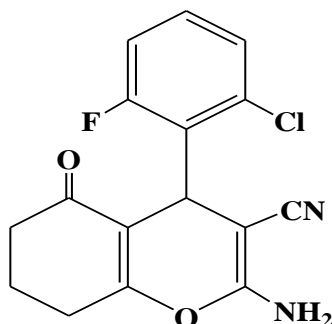
Except for some compounds (Table 2, entries 4, 11 and Table 3, entry 2), all products are known compounds. The spectral (IR, <sup>1</sup>H and <sup>13</sup>C NMR) data of new compounds are presented below:

**2-amino-4-(2-chloro-6-fluorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4a):** white solid, m.p. 202-204°C; IR (KBr):  $\nu_{\max}$  3410, 3331, 3214, 3070, 2964, 2931, 2198, 1684, 1600, 1540, 1452, 1369, 1215, 1159, 1037, 898, 781, 682, 562 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  0.95 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>), 2.07 (d, 1H, *J* = 16.4 Hz, -CH<sub>2</sub>), 2.28 (d, 1H, *J* = 16 Hz, -CH<sub>2</sub>), 2.37 (d, 1H, *J* = 17.6 Hz, -CH<sub>2</sub>), 2.56 (d, 1H, *J* = 18 Hz, -CH<sub>2</sub>), 4.89 (s, 1H, CH), 7.116 (s, 2H, NH<sub>2</sub>), 7.13 (br, 1H, ArH), 7.26-7.29 (m, 2H, ArH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  195.68, 163.55, 159.31, 154.44, 133.64, 129.17, 129.07, 125.52, 119.21, 115.11, 115.04, 55.99, 49.84, 49.82, 31.67, 26.31, 26.23, 18.53 ppm; Anal. Calc for C<sub>18</sub>H<sub>16</sub>ClFN<sub>2</sub>O<sub>2</sub>: C, 62.34; H, 4.65; N, 8.08. Found: C, 62.54; H, 4.71; N, 8.16.



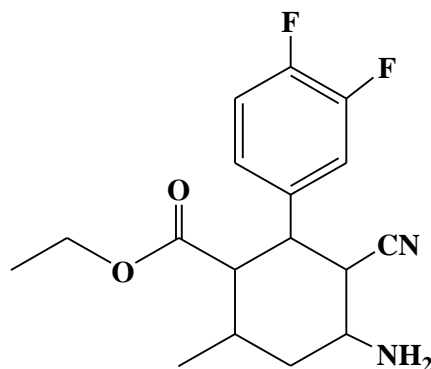
**2-amino-4-(2-chloro-6-fluorophenyl)-5,6,7,8-tetrahydro-5-oxo-4H-chromene-3-carbonitrile (2b) :**

white solid, m.p. 228-230°C; IR (KBr):  $\nu_{\max}$  3506, 3376, 3175, 2190, 1681, 1648, 1600, 1509, 1454, 1363, 1243, 1211, 1168, 1067, 1003, 898, 780, 703, 590  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  1.88-1.94 (m, 1H, -CH $_2$ ), 1.99-2.05 (m, 1H, -CH $_2$ ), 2.24-2.40 (m, 2H, -CH $_2$ ), 2.59-2.65 (m, 2H, -CH $_2$ ), 4.94 (s, 1H, CH), 7.16 (s, 2H, NH $_2$ ), 7.21 (d, 1H,  $J$  = 9.2 Hz, ArH), 7.29-7.33 (m, 1H, ArH), 7.36 (d, 1H,  $J$  = 8 Hz, ArH) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  195.81, 165.36, 159.24, 159.16, 133.65, 128.99, 126.20, 125.64, 119.21, 115.01, 114.76, 53.95, 36.19, 30.67, 26.40, 19.88 ppm; Anal. Calc for C $_{16}$ H $_{12}$ ClFN $_2$ O $_2$ : C, 60.29; H, 3.79; N, 8.79. Found: C, 60.34; H, 3.85; N, 8.71.

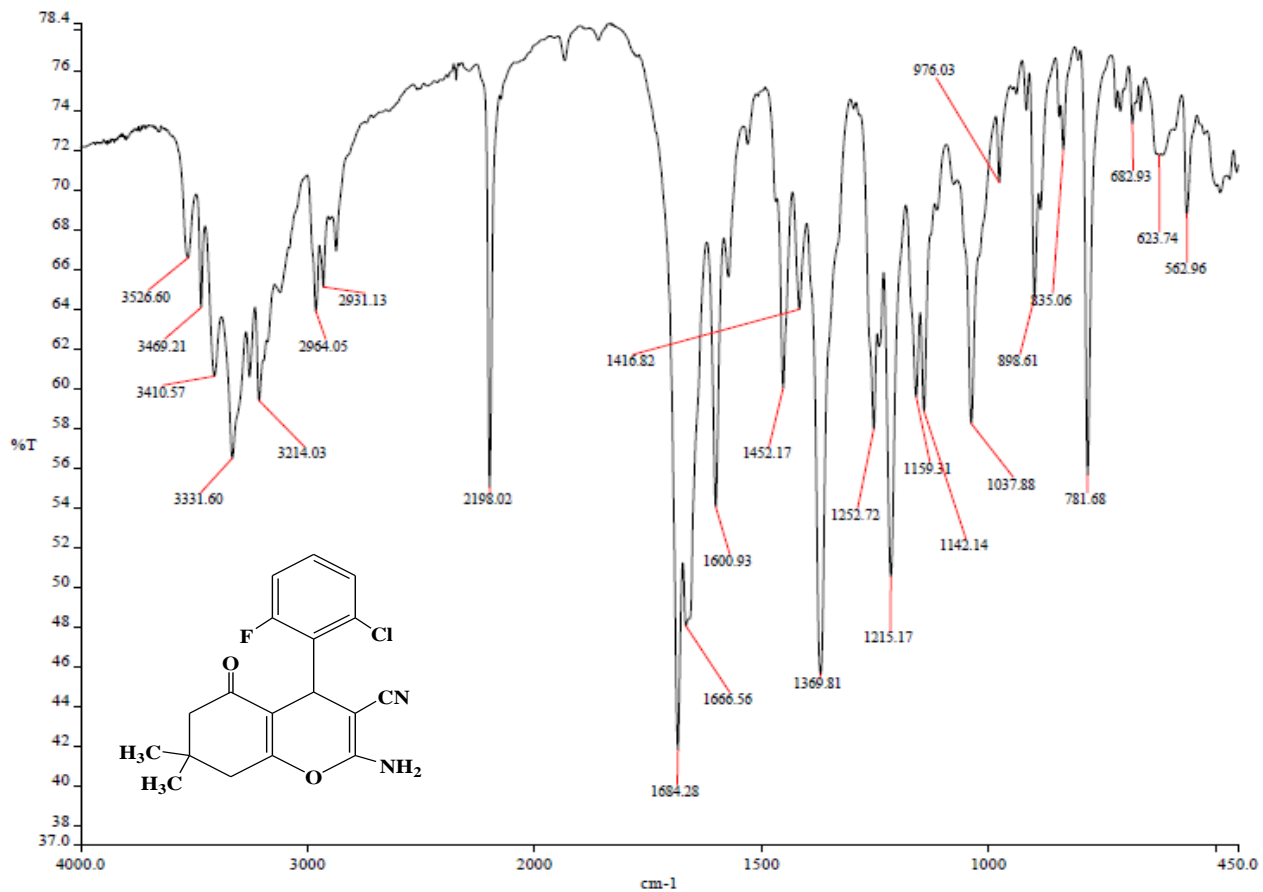


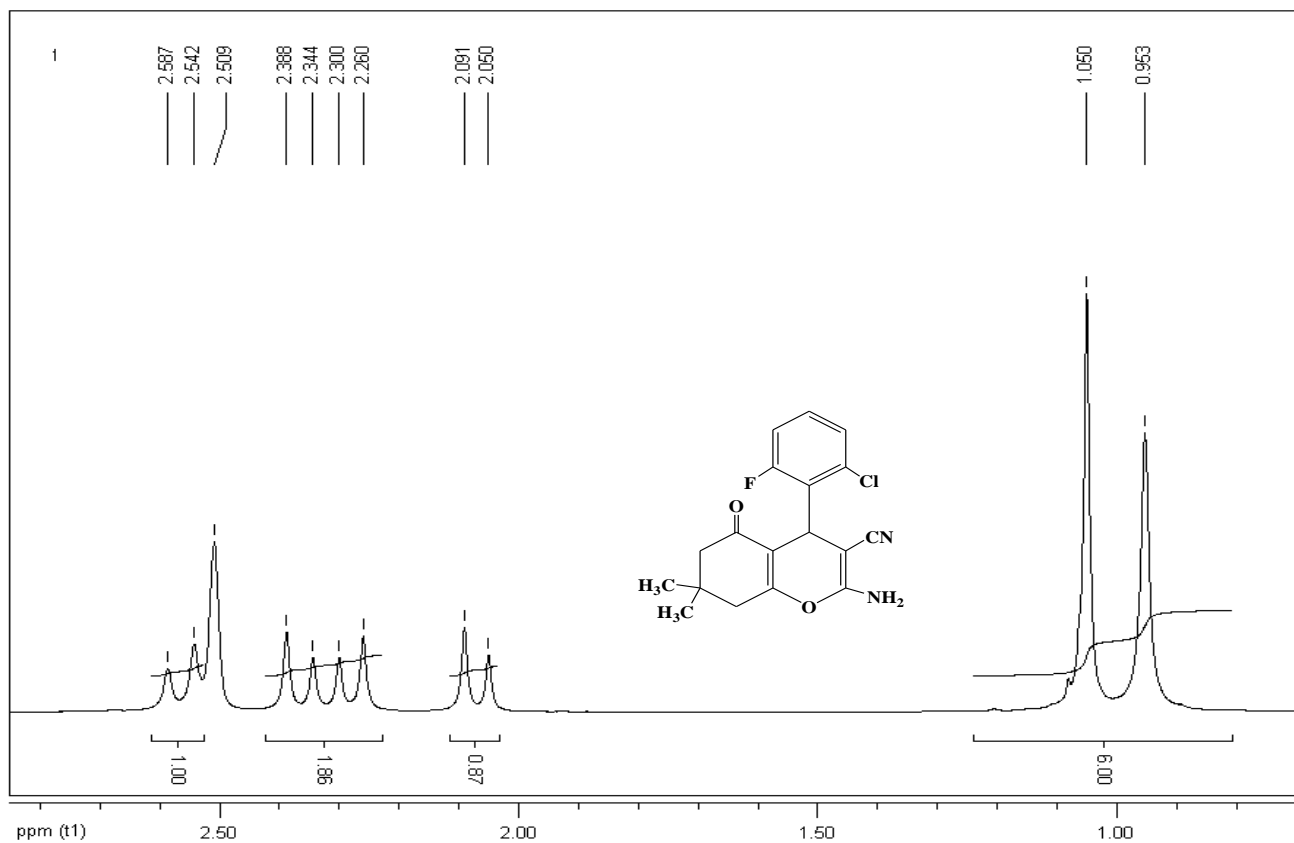
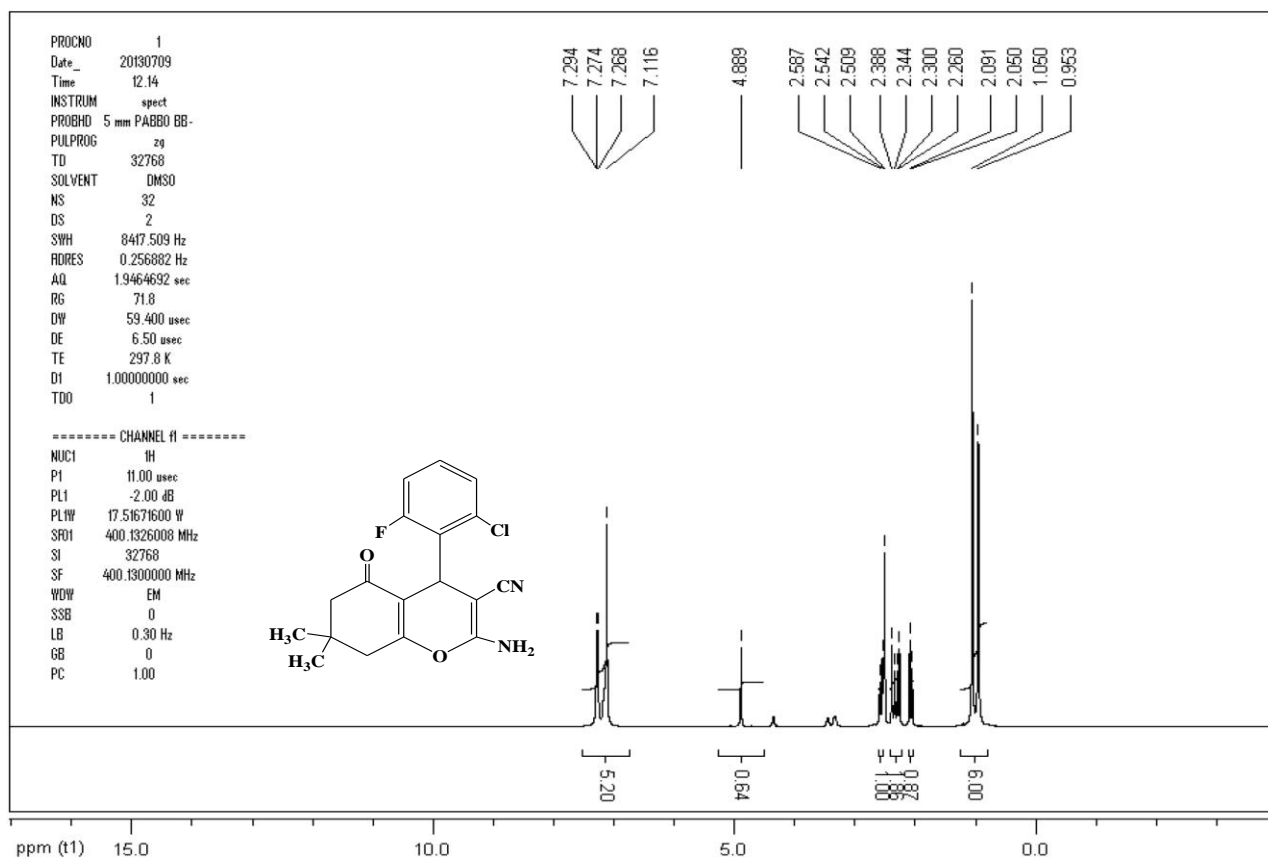
**6-amino-5-cyano-2-methyl-4-(3,4-difluorophenyl)-4H-pyran-3-carboxylic acid ethyl ester (2c) :**

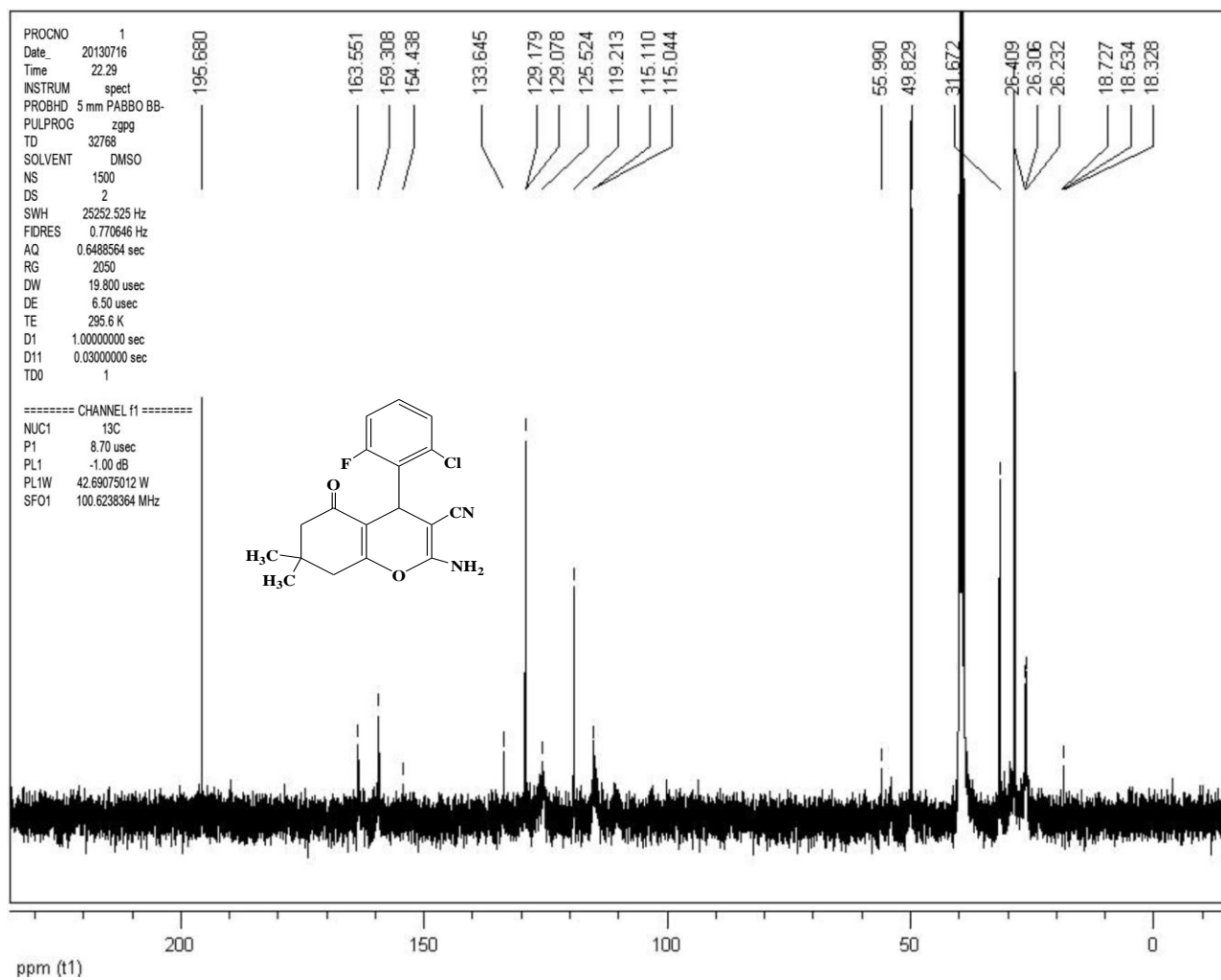
white solid, m.p. 166-168 °C; IR (KBr):  $\nu_{\max}$  3406, 3333, 3205, 2989, 2193, 1692, 1649, 1518, 1466, 1341, 1270, 1210, 1174, 1060, 957, 865, 814, 751, 650  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  1.03 (t, 3H, CH $_3$ ), 2.32 (s, 3H, CH $_3$ ), 3.98 (q, 2H, CH $_2$ ), 4.35 (s, 1H, CH), 7.00 (s, 2H, NH $_2$ ), 7.01 (br, 1H, ArH), 7.17-7.22 (m, 1H, ArH), 7.34-7.41 (m, 1H, ArH) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  165.19, 158.39, 157.32, 149.39, 146.96, 142.84, 123.94, 119.45, 117.51, 116.22, 106.31, 60.19, 59.55, 38.05, 18.21, 13.67 ppm; Anal. Calc for C $_{16}$ H $_{14}$ F $_2$ N $_2$ O $_3$ : C, 60.00; H, 4.41; N, 8.75. Found: C, 60.14; H, 4.50; N, 8.70.



**2-amino-4-(2-chloro-6-fluorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4a) :**

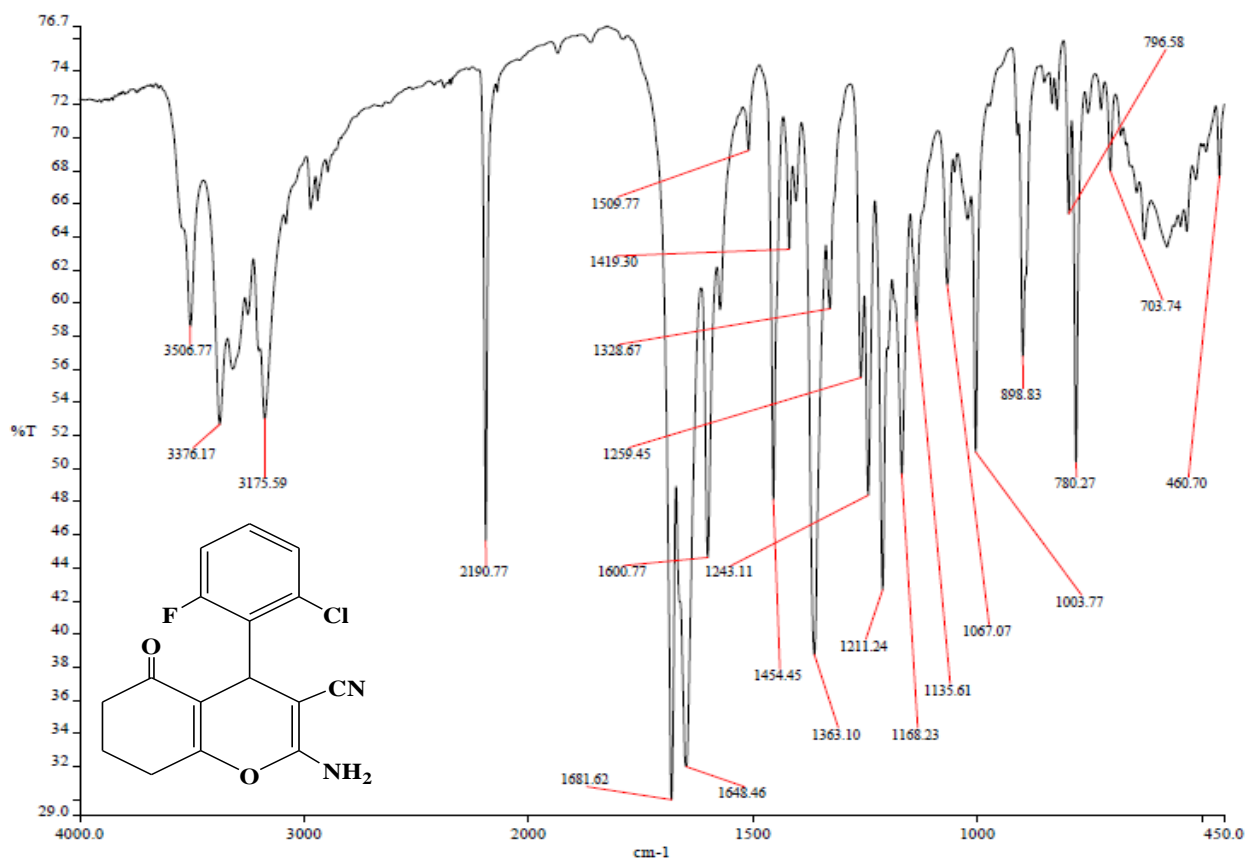


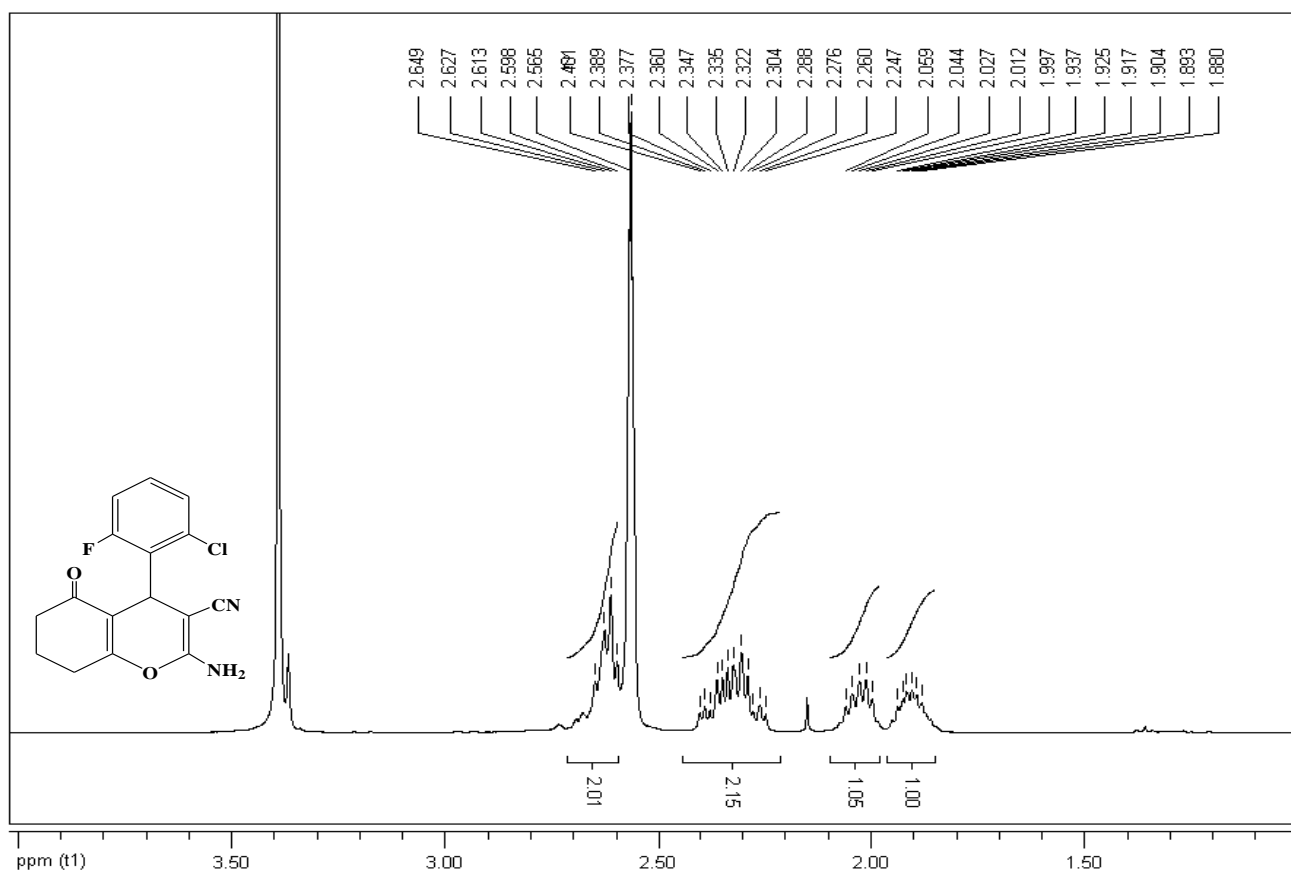
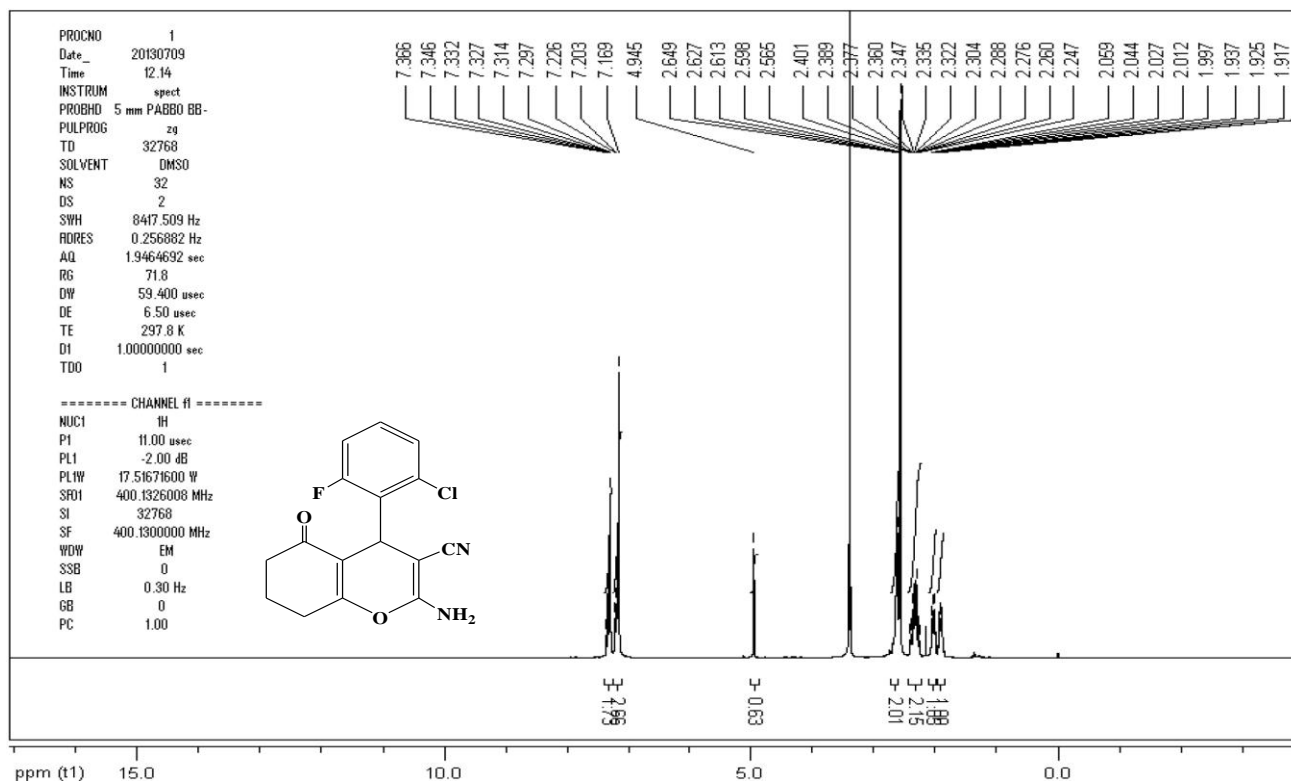


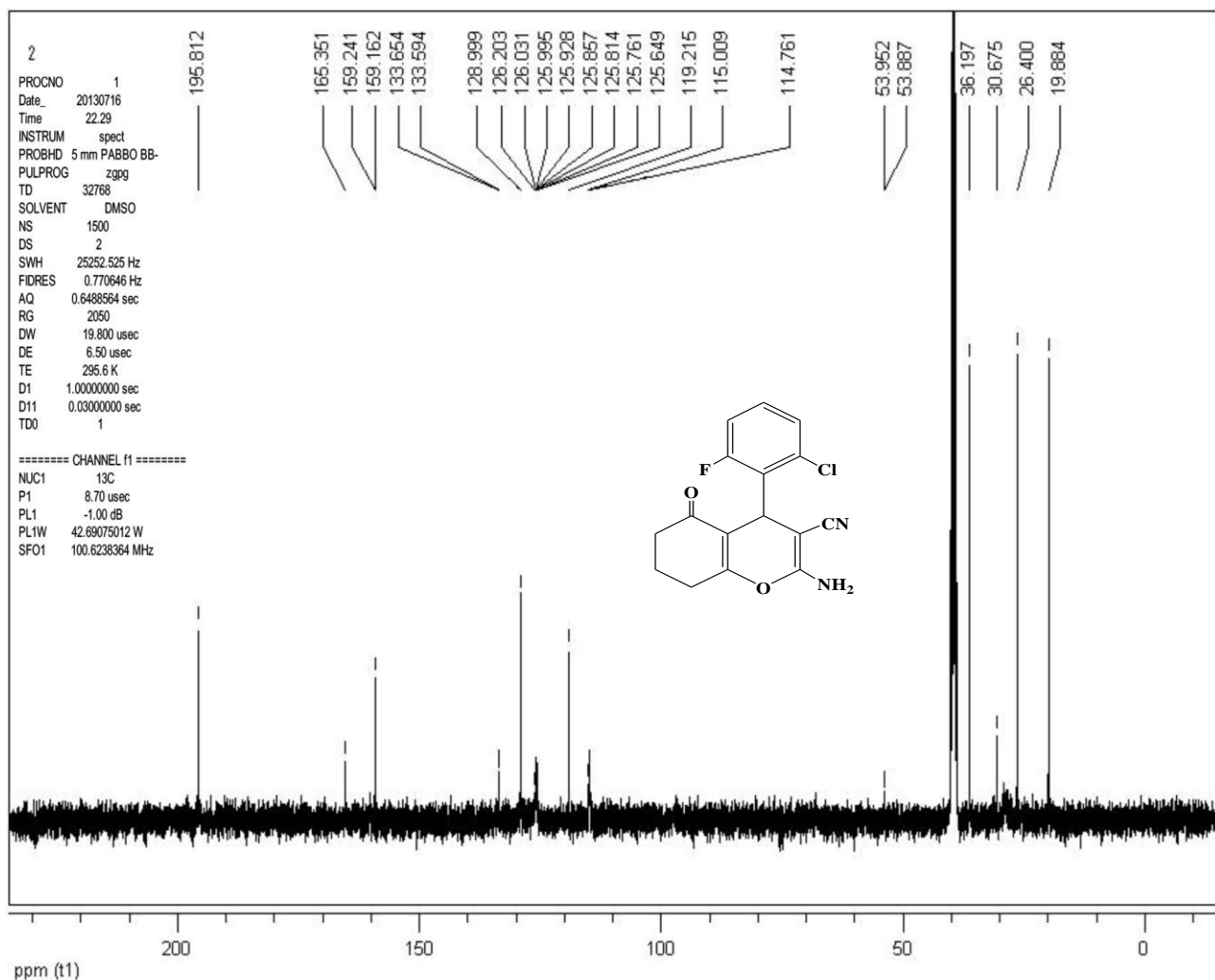


## 2-amino-4-(2-chloro-6-fluorophenyl)-5,6,7,8-tetrahydro-5-oxo-4H-chromene-3-carbonitrile

(2b) :









**6-amino-5-cyano-2-methyl-4-(3,4-difluorophenyl)-4H-pyran-3-carboxylic acid ethyl ester  
(2c) :**

