

## Supporting Information

### **A design for convenient and greener route towards one pot multi-component synthesis of 7-aryl/heteroaryl substituted pyrano[3,2-c:5,6-c']dichromene-6,8-dione and 7-aryl/heteroaryl substituted chromeno[4,3-d]pyrido[1,2-a]pyrimidinone derivatives using sulphonated rice husk**

Sourav Dey, Puja Basak, Subhajit Sarkar and Pranab Ghosh\*

*Department of Chemistry, University of North Bengal, Dist-Darjeeling, West Bengal, India.*

*Tel.: +91 (0353) 2776381; fax: +91 (0353) 2699001*

*E-mail address: [pizy12@yahoo.com](mailto:pizy12@yahoo.com) (P.Ghosh)*

#### Table of contents

<b>1 Experimental</b>	<b>S1-S3</b>
<b>2 General Procedure for <sup>1</sup>H &amp; <sup>13</sup>C NMR</b>	<b>S3</b>
<b>3. Spectral data of compounds mentioned in scheme 1</b>	<b>S3-S6</b>
<b>4. Sanned copies of compounds mentioned in scheme 1</b>	<b>S6-S22</b>
<b>5. Spectral data of compounds mentioned scheme 2</b>	<b>S23-S25</b>
<b>6. Sanned copies of compounds mentioned scheme 2</b>	<b>S25-S34</b>
<b>7. EDX data of sulphonated rice husk and rice husk</b>	<b>S35-S36</b>
<b>8. References</b>	<b>S37</b>

## 1. Experimental

### Catalyst preparation

The heterogeneous catalyst (SRH) was prepared by direct sulphonation of rice husk (RH) following our previous synthetic method. The rice husk (RH) was collected from a nearby rice mill and was blended finely before use. It was first washed with dilute H<sub>2</sub>SO<sub>4</sub> for five times and next thoroughly washed with water followed by ethanol. After washing the solvent was fully evaporated through rotary evaporator. After that 5g of dry material was taken into 250 mL of a round bottom flask and 150 mL dichloromethane (DCM) was added to it. Then, 5 mL of pure Chlorosulphonic acid (98%) was added dropwise with continuous stirring until the whole suspension turned into brown. The suspension was then stirred for 18-20 h on a magnetic stirrer at room temperature. After stirring the solid catalyst was filtered off and washed with water and acetone repeatedly until the filtrate became light brown colour. Then the sample was dried in reduced pressure and later characterised by different spectroscopic techniques.[1]

### General procedure for synthesis of 7-aryl/heteroaryl-6*H*,7*H*,8*H*-pyrano[3,2-*c*:5,6-*c'*]dichromene-6,8-dione derivatives

A mixture of 4-hydroxycumarine (2 mmol), aromatic aldehyde (1.0 mmol), and SRH (80 mg) in a 25-mL round bottom flask was stirred at 60-80 °C temperature for 240 minutes. The progress of the reaction was monitored by thin-layer chromatography (TLC) (Scheme 1). After completion of the reaction, the product was extracted with ethyl acetate and the catalyst was removed by filtration. Then ethyl acetate extract was concentrated and white crude product was isolated by adding petroleum ether dropwise until white precipitation appears. Then white crude product was further purified by recrystallisation in petroleum ether/ethyl acetate (v/v ratio 80/20) mixture to

get the pure product. All the synthesized compounds were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and the spectral data were compared with the reported spectral data of corresponding compound.

### **General procedure for synthesis of 7-aryl/heteroaryl-6a,13a-dihydro-6*H*,7*H*-chromeno[4,3-*d*]pyrido[1,2-*a*]pyrimidin-6-one derivatives**

A mixture of 2-aminopyridine (1 mmol), 4-hydroxycumarine (1 mmol), aromatic aldehyde (1 mmol), and SRH (60 mg) in a 25-mL round bottom flask was stirred at 60-80 °C temperature for 210 minutes. The progress of the reaction was monitored by thin-layer chromatography (TLC) (Scheme 2). After completion of the reaction, the product was extracted with ethyl acetate and the catalyst was separated by simple filtration. Then ethyl acetate extract was concentrated and crude product was separated by simple precipitation by adding mixed solvent containing ethyl acetate and petroleum ether (1:10v/v) slowly dropwise. Finally the obtained solid was purified by slowly washing the crude with solvent containing ethyl acetate and petroleum ether (1:4v/v). After isolation, all the synthesized compounds were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and the spectral data were compared with the reported spectral data of corresponding compound.

### **2. General Procedure for $^1\text{H}$ & $^{13}\text{C}$ NMR**

NMR spectra of all the products were taken in DMSO- $d_6$  (TMS as an internal standard) using a Bruker 400MHz spectrometer (operating for  $^1\text{H}$  at 400 MHz and for  $^{13}\text{C}$  at 100 MHz) and Bruker Advance NEO 500MHz spectrometer (operating for  $^1\text{H}$  at 500 MHz and for  $^{13}\text{C}$  at 125 MHz).  $^1\text{H}$ -NMR spectroscopic data are represented as follows: chemical shift (ppm), multiplicity

(s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad), integration, coupling constants in Hertz (Hz). <sup>13</sup>C NMR spectroscopic data are reported in ppm.

### 3. Spectral data of the compounds mentioned in scheme 1

#### 7-(4-methoxyphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3a)

##### <sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)

3.65(s,3H),6.17(s,1H),6.70(d,3H),6.96(d,2H),7.18-7.24(m,4H),7.45-7.49(m,2H),7.78(dd,2H).

##### <sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)

35.90,55.43,104.26,113.68,116.00,120.40,123.42,124.62,128.16,131.43,134.50,153.02,157.36,165.08,167.96.

#### 7-phenyl-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3b)

##### <sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)

δ 6.24(s,1H),7.02-7.08(m,3H),7.11-7.15(m,2H),7.22-7.29(m,4H),7.45-7.50(m,2H),7.77(q,2H).

##### <sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)

δ36.68,103.95,116.00,120.50,123.41,124.67,125.34,127.20,128.23,131.44,142.93,153.06,165.12,168.25.

#### 7-(2-chlorophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3c)

##### <sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)

δ 6.12(s,1H),7.08-7.18(m,3H),7.21(d,4H),7.37(d,1H),7.44-7.77(m,2H),7.78(d,2H).

##### <sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)

δ36.66,103.32,115.99,120.46,123.44,124.59,126.52,127.57,129.88,130.91,131.37,133.24,140.95,152.96,164.41,168.24.

#### 7-(2-bromophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3d)

##### <sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)

δ 5.99(s,1H),7.02(t,1H),7.17-7.22(m,5H),7.38(dd,2H),7.46(t,2H),7.77(d,2H).

##### <sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)

δ38.89,103.46,116.00,120.47,123.43,124.57,127.06,127.88,131.11,131.34,133.32,152.97,164.35,168.17.

#### 7-(4-hydroxyphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3e)

**<sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 6.12(s,1H),6.52(d,2H),6.84(d,2H),7.17-7.22(m,4H),7.44-7.48(m,2H),7.77(dd,2H),8.90(s,1H).

**<sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 35.86,104.36,115.04,115.95,120.58,123.34,124.64,128.08,131.31,132.83,153.03,155.17,165.12,168.11.

**7-(4-fluorophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3f)**

**<sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 6.21(s,1H),7.02-7.08(m,3H),7.11-7.15(m,2H),7.22-7.29(m,4H),7.45-7.50(m,2H),7.77(q,2H).

**<sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 36.68,103.95,116.00,120.50,123.41,124.67,125.34,127.20,128.23,131.44,142.93,153.06,165.12,168.25.

**7-(2-methylphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3g)**

**<sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 1.96(s,3H),6.09(s,1H),6.97(s,3H),7.22-7.27(m,5H),7.47(d,2H),7.80(d,2H).

**<sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 21.63,36.55,105.20,116.14,120.03,123.66,124.64,126.31,127.78,128.31,131.68,137.06,142.16,152.96,165.26,168.96.

**7-(thiophen-2-yl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3h)**

**<sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 6.38(s,1H),6.57(t,1H),6.78(t,1H),7.12(d,1H),7.19-7.30(m,3H),7.40-7.52(m,2H),7.82(t,2H).

**<sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 33.47,104.27,116.06,120.42,123.21,123.52,123.56,124.77,126.66,131.66,148.61,153.03,164.67,168.48.

**7-(4-methylphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3i)**

**<sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 2.19(s,3H),6.19(s,1H),6.94(s,4H),7.20(q,4H),7.46-7.50(m,2H),7.78(d,2H).

**<sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)**

δ 21.06,36.30,104.09,115.99,120.50,123.42,124.64,127.11,128.84,131.42,134.04,139.73,153.03,165.16,168.21.

**7-(3-methylphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3j)**

**<sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)**

$\delta$  2.16(s,3H),6.24(s,1H),6.89(d,3H),7.04(t,1H),7.21-7.28(m,4H),7.48-7.53(m,2H),7.82(dd,2H).

**<sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)**

$\delta$ 21.83,104.20,116.14,120.03,123.66,124.44,124.64,126.31,127.78,128.21,131.69,137.06,  
142.36,152.96,165.25,167.74

**7-(furan-2-yl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3k)**

**<sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)**

$\delta$  6.36(s,1H),6.56(t,1H),6.77(t,1H),7.12(d,1H),7.18-7.31(m,3H),7.42-7.52(m,2H),  
7.80-7.85(m,2H).

**<sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)**

$\delta$ 32.47,105.26,116.06,120.42,123.21,123.52,123.56,124.77,126.66,131.66,148.61,153.03,164.67,  
168.48.

**7-(naphthalen-2-yl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3l)**

**<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)**

$\delta$  6.42(s,1H),7.22-7.30(m,5H),7.37-7.39(m,2H),7.51-7.54(m,3H),7.57-7.72(m,2H),  
7.78-7.83(m,3H).

**<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)**

$\delta$ 36.42,103.28,114.39,115.30,115.42,119.87,122.71,122.82,124.04,124.06,124.66,125.43,126.20,  
127.01,127.03,127.35,127.42,130.86,131.28,132.92,140.03,152.37,152.46,164.53,167.83.

**7-(naphthalen-1-yl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3m)**

**<sup>1</sup>H-NMR(400MHz,DMSO-d<sub>6</sub>)**

$\delta$  6.73(s,1H),7.18-7.26(m,3H),7.33-7.37(m,3H),7.45-7.50(m,3H),7.68(d,1H),  
7.76-7.83(m,3H),7.99(dd,1H).

**<sup>13</sup>C-NMR(400MHz,DMSO-d<sub>6</sub>)**

$\delta$ 35.46,104.80,116.07,120.27,123.59,124.60,124.73,125.42,125.54,125.94,126.27,126.69,129.05,  
131.53,132.19,134.22,138.67,152.84,164.78,168.64.

**7-(4-(trifluoromethyl)phenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3n)**

**<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)**

$\delta$  6.34(s,1H),7.23-7.34(m,6H),7.51-7.56(m,4H),7.83(q,2H).

**<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)**

$\delta$ 36.30,102.85,115.47,119.69,122.93,123.48,124.10,124.61,124.64,125.56,125.64,125.81,127.30,  
131.06,147.49,152.47,164.47,167.86.

**7-(4-nitrophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3o)**

**<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ 6.37(s,1H),7.23-7.30(m,4H),7.38(d,2H),7.51-7.55(m,2H),7.83(dd,2H),8.08(d,2H).

**<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ36.67,102.68,115.50,119.61,122.98,123.03,124.11,127.79,131.15,145.22,151.37,152.48,164.34,167.93

**7-(2-nitrophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3p)**

**<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)**

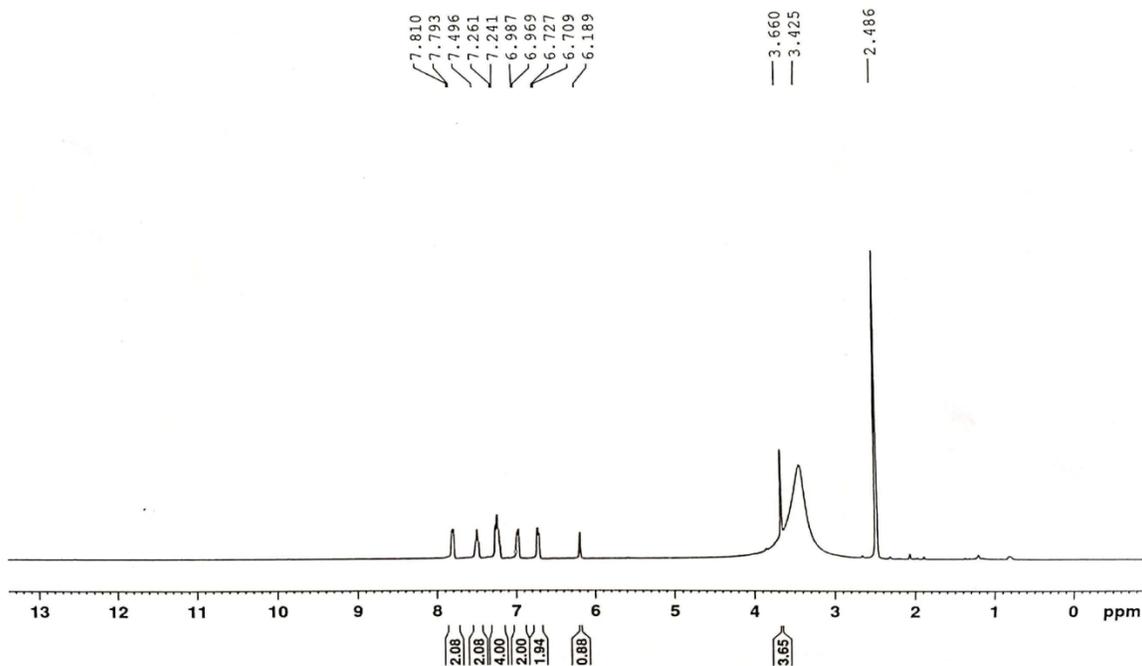
δ 6.50(s,1H),7.21-7.26(m,4H),7.34-7.38(m,2H),7.49-7.55(m,4H),7.78(d,2H).

**<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)**

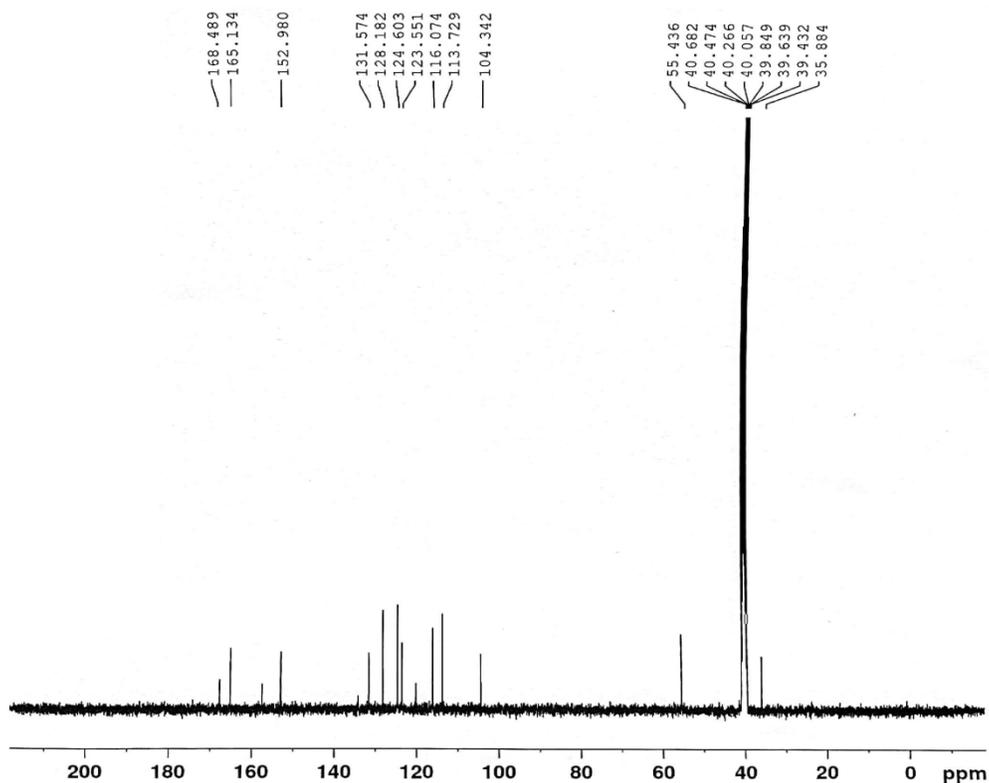
δ33.83,102.14,115.43,119.46,122.86,123.76,124.02,126.53,129.52,130.94,131.81,135.23,149.52,152.44,163.54,167.88.

**4.Sanned copies of compounds mentioned in scheme 1**

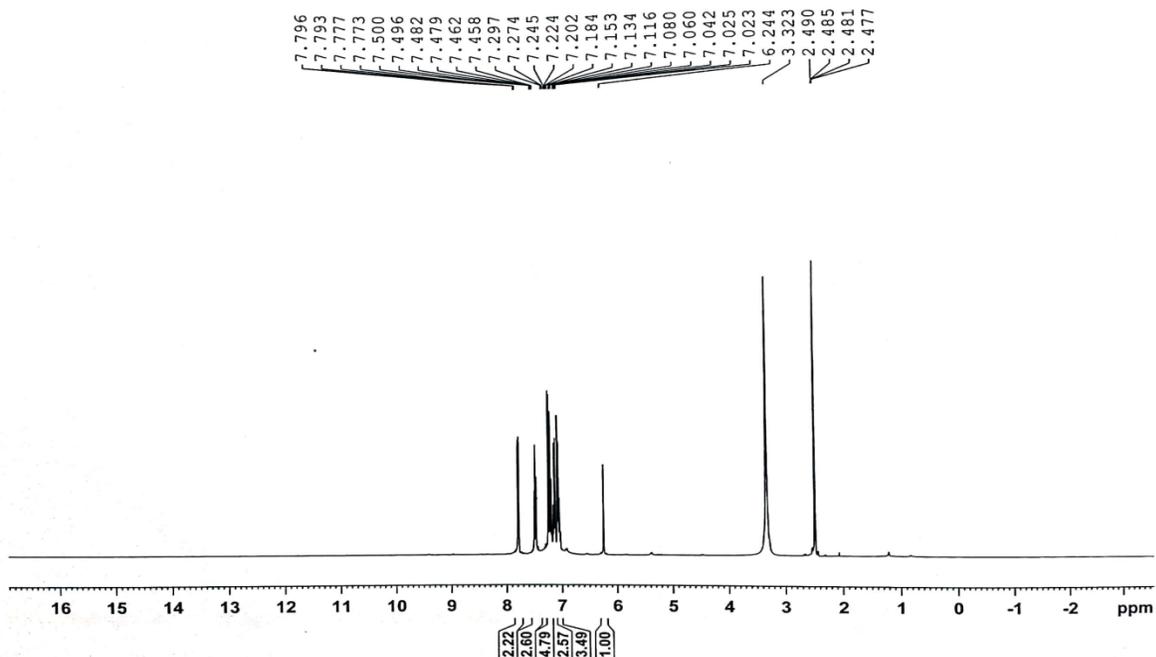
**7-(4-methoxyphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3a)**



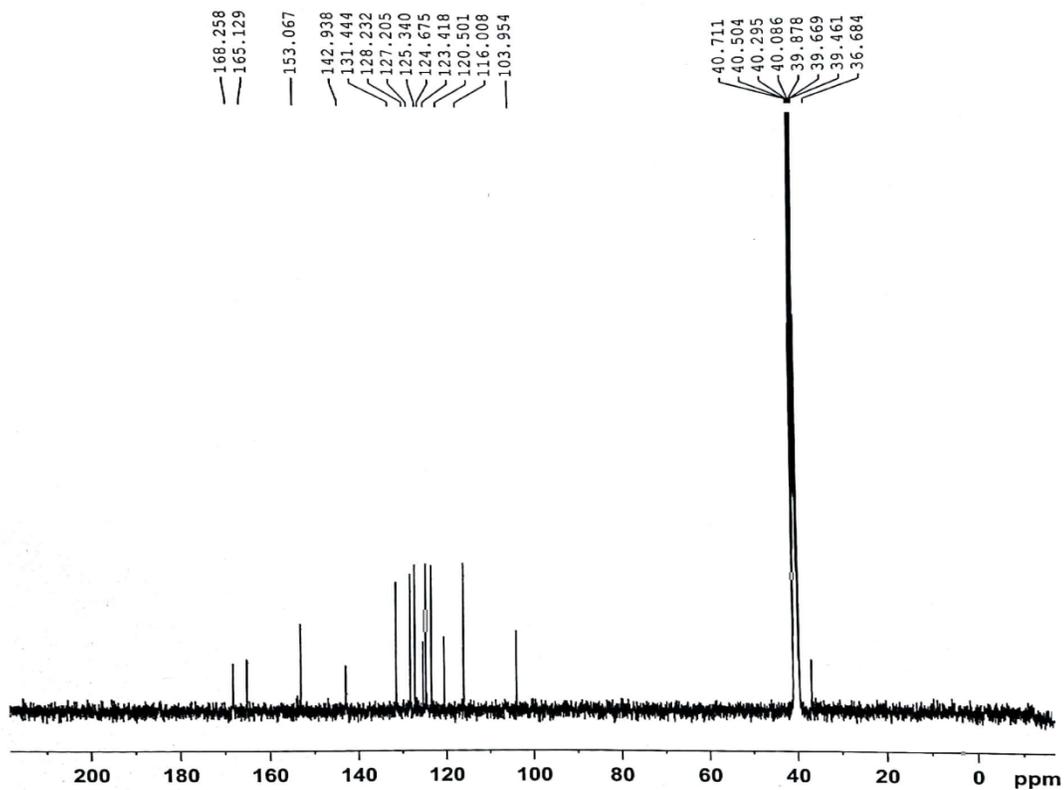
7-(4-methoxyphenyl)-6H,7H,8H-pyran o[3,2-c:5,6-c']dichromene-6,8-dione(3a)



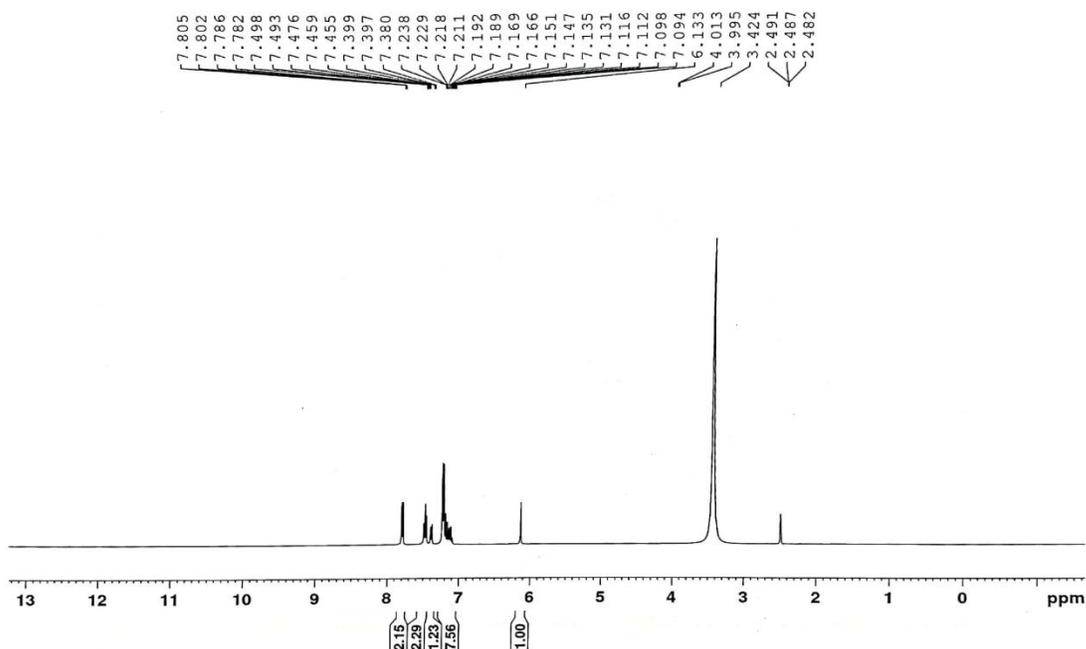
7-phenyl-6H,7H,8H-pyran o[3,2-c:5,6-c']dichromene-6,8-dione(3b)



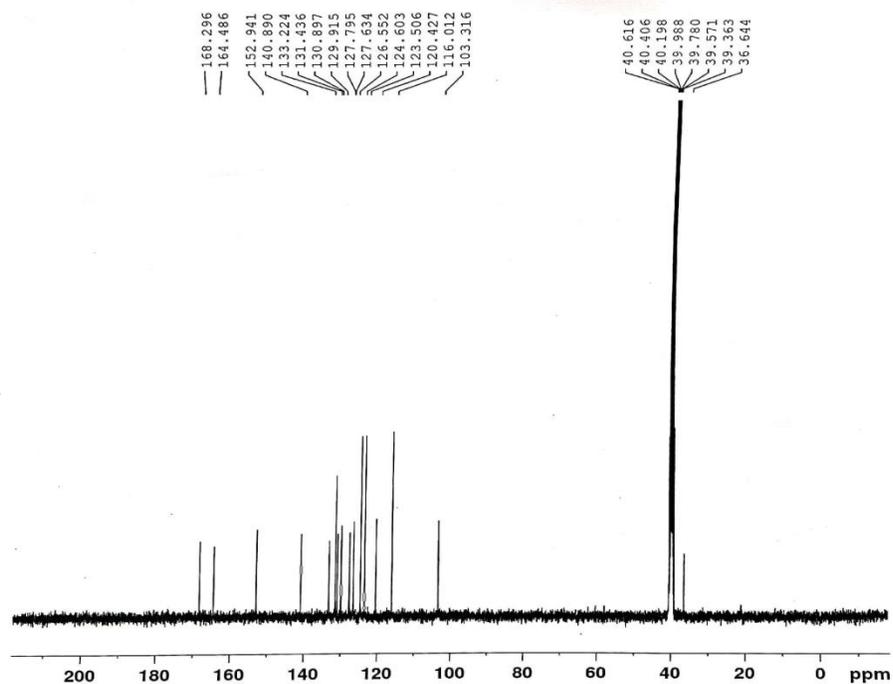
**7-phenyl-6H,7H,8H-pyran o[3,2-c:5,6-c']dichromene-6,8-dione(3b)**



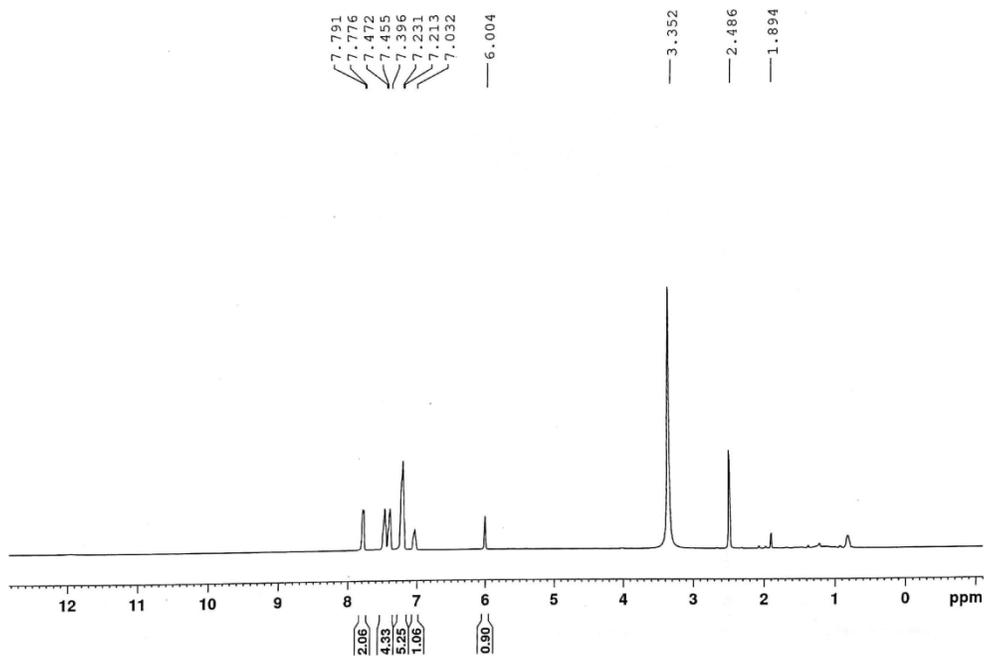
7-(2-chlorophenyl)-6H,7H,8H-pyran[3,2-c:5,6-c']dichromene-6,8-dione(3c)



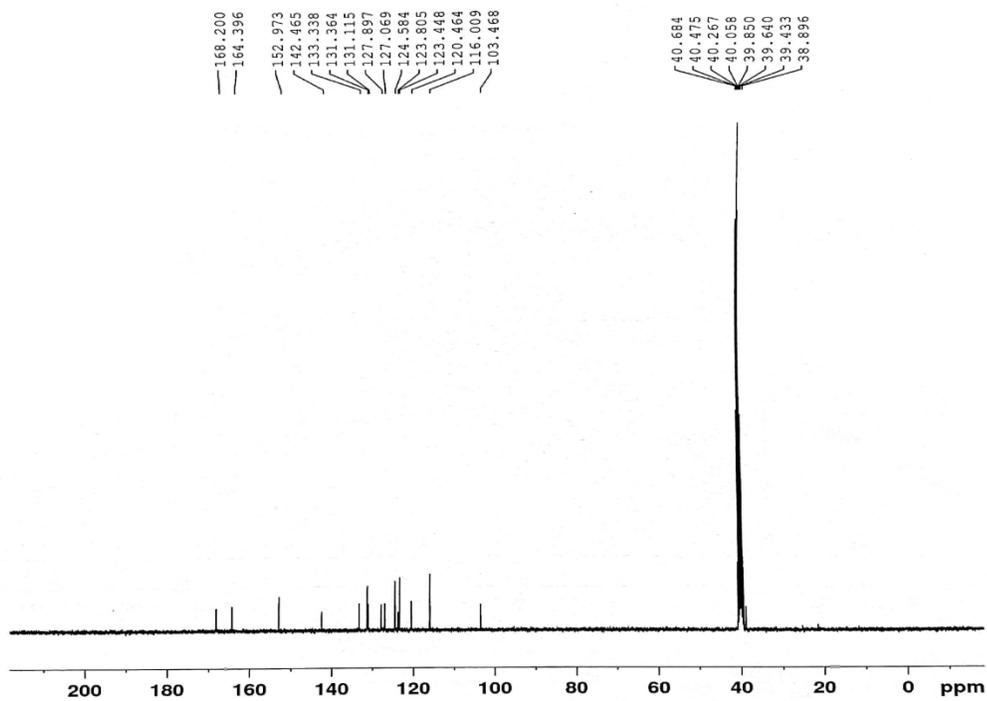
7-(2-chlorophenyl)-6H,7H,8H-pyran[3,2-c:5,6-c']dichromene-6,8-dione(3c)



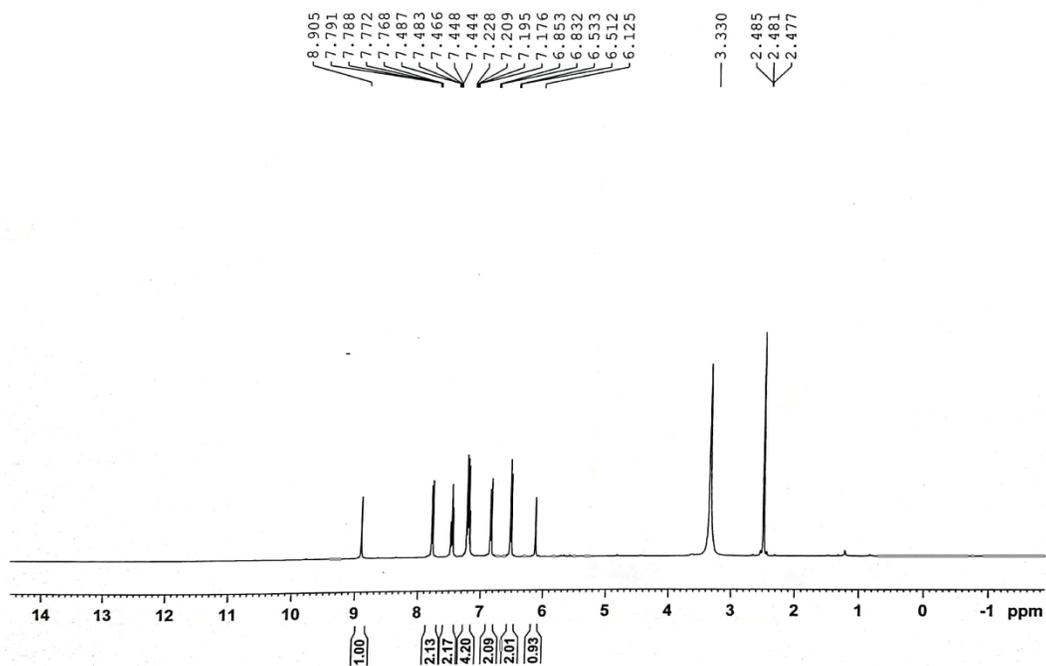
7-(2-bromophenyl)-6H,7H,8H-pyran[3,2-c:5,6-c']dichromene-6,8-dione(3d)



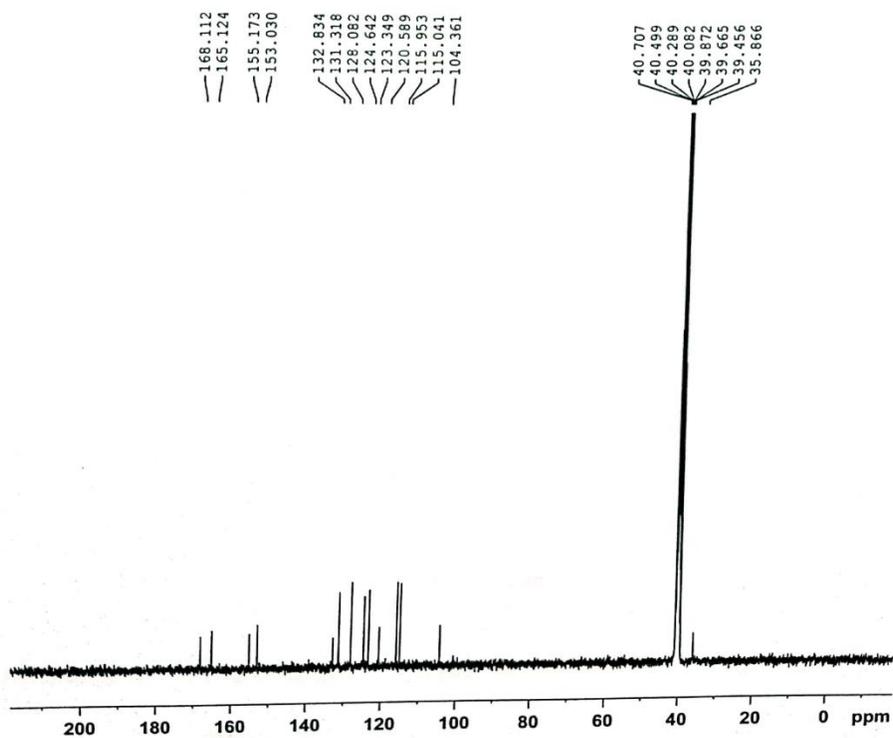
7-(2-bromophenyl)-6H,7H,8H-pyran[3,2-c:5,6-c']dichromene-6,8-dione(3d)



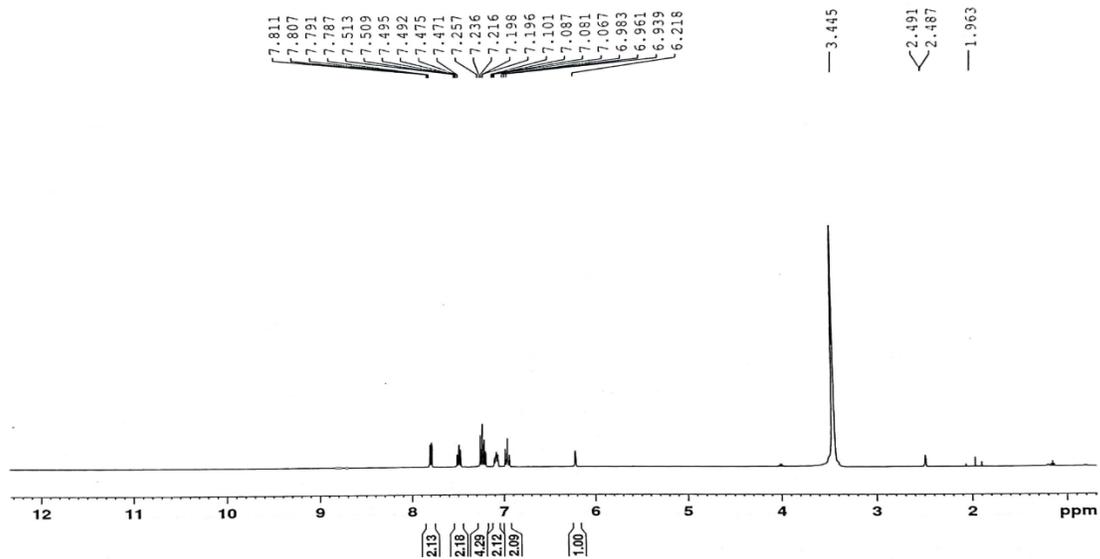
7-(4-hydroxyphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3e)



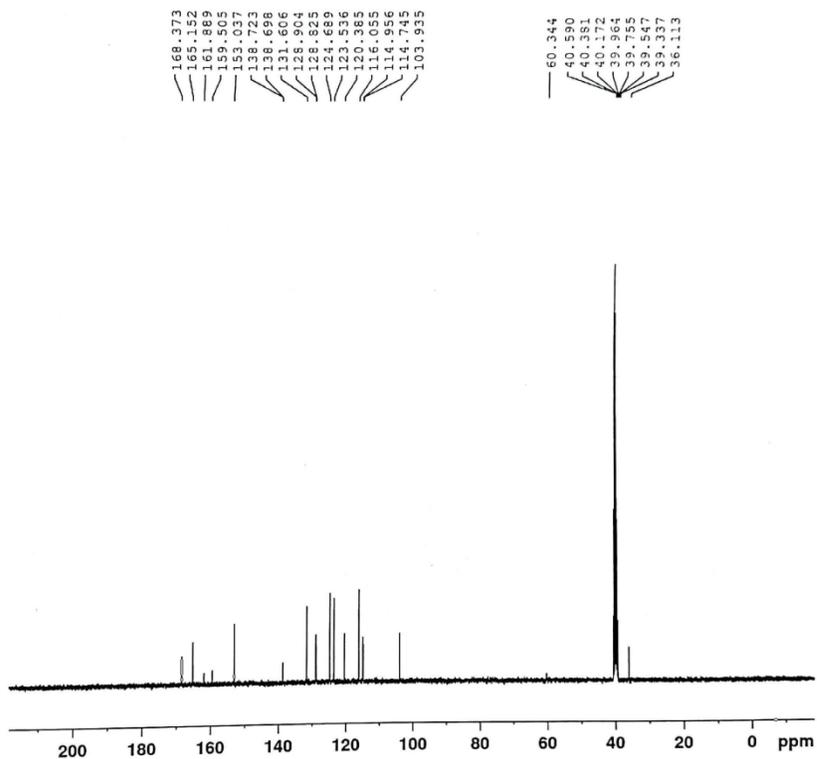
7-(4-hydroxyphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3e)



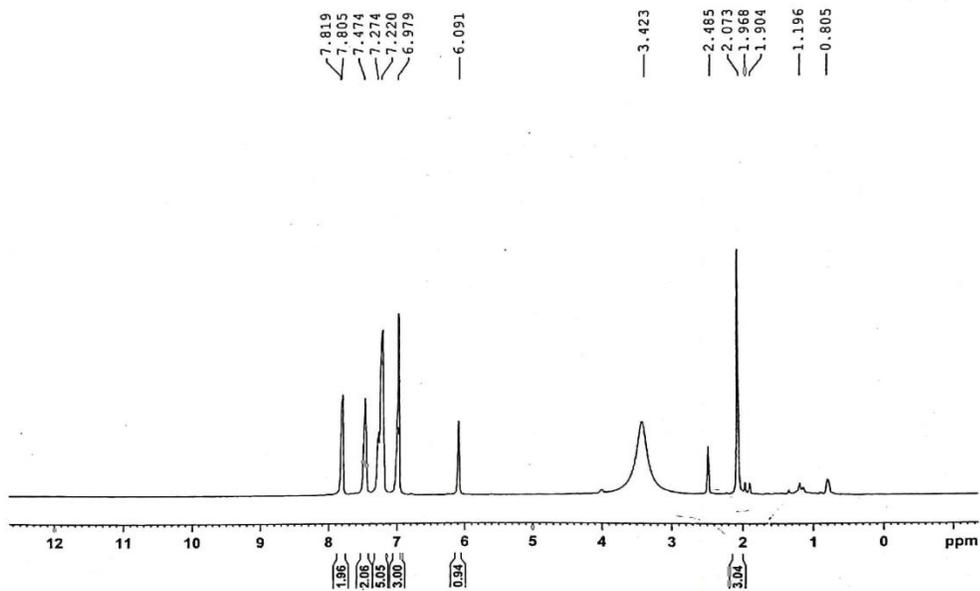
**7-(4-fluorophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3f)**



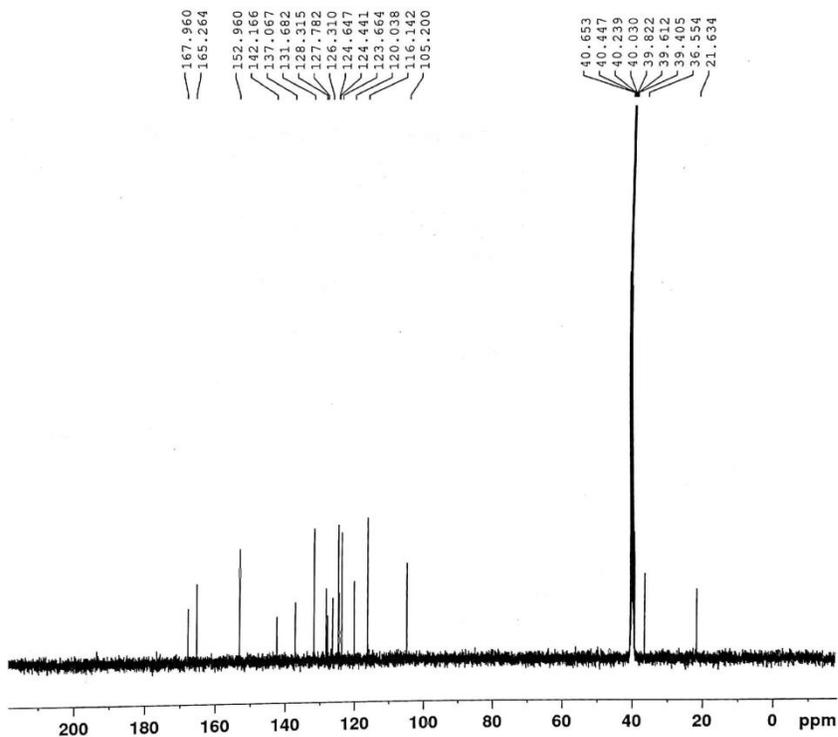
**7-(4-fluorophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3f)**



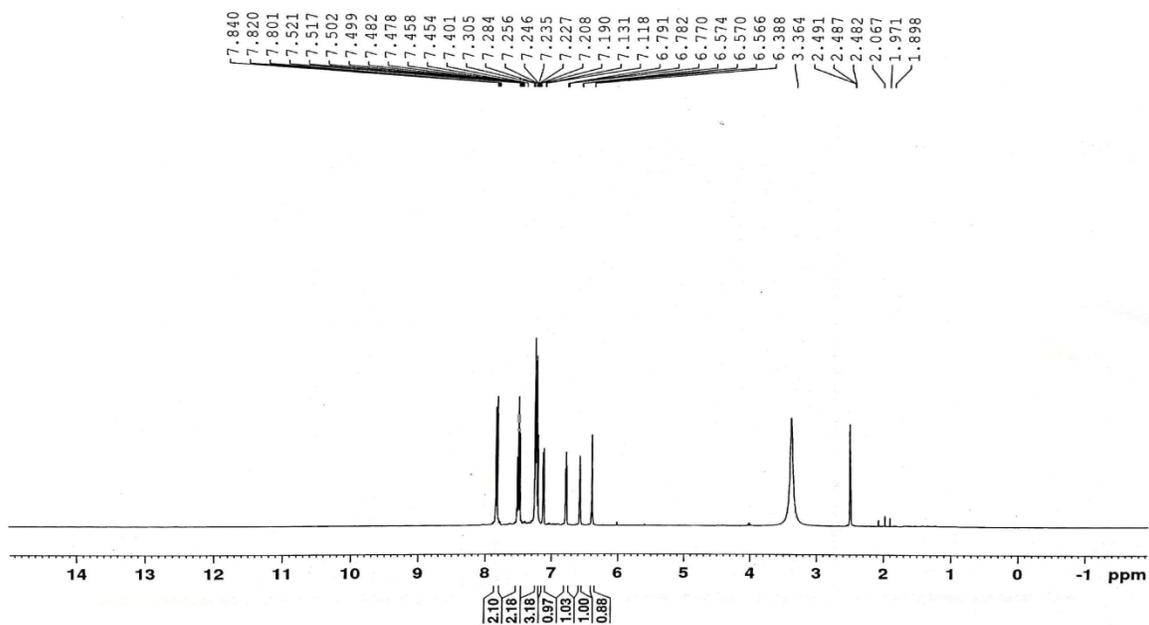
7-(2-methylphenyl)-6H,7H,8H-pyran o[3,2-c:5,6-c']dichromene-6,8-dione(3g)



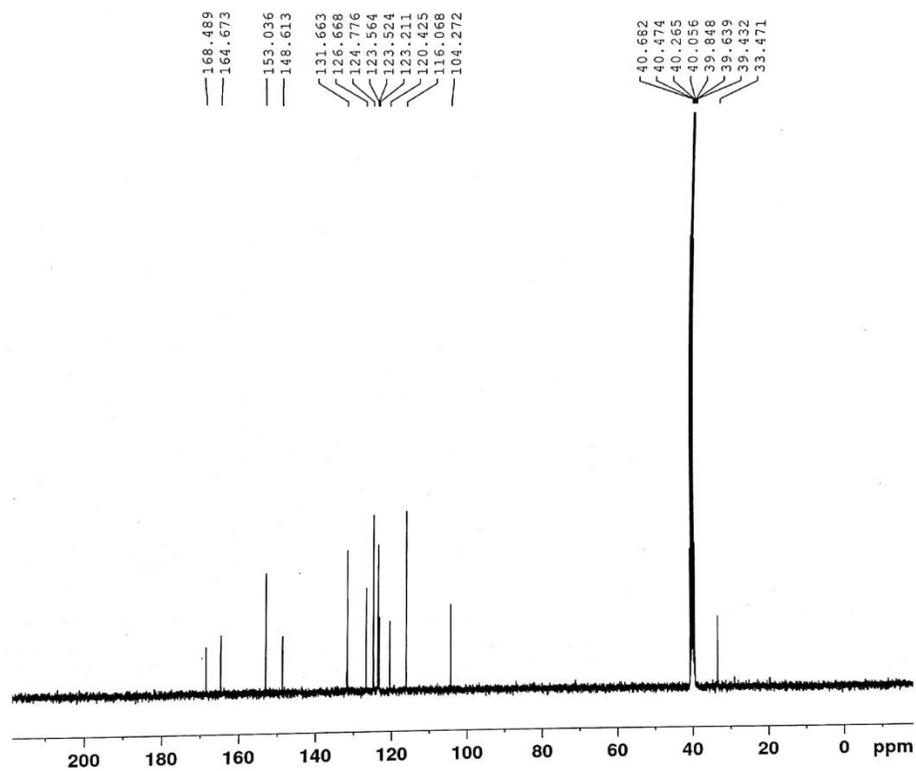
7-(2-methylphenyl)-6H,7H,8H-pyran o[3,2-c:5,6-c']dichromene-6,8-dione(3g)



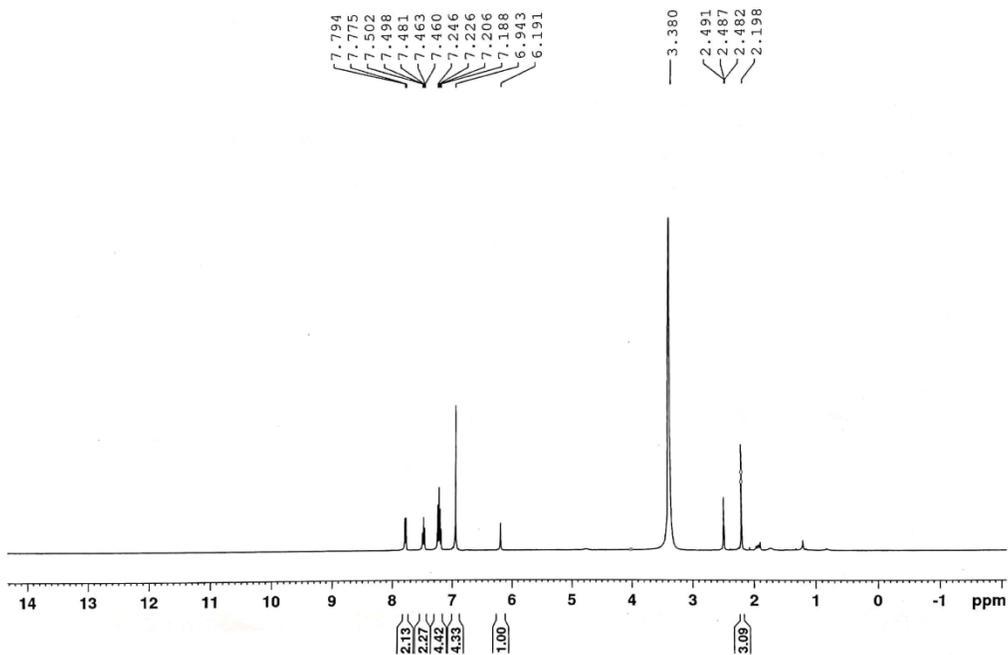
7-(thiophen-2-yl)-6H,7H,8H-pyran o[3,2-c:5,6-c']dichromene-6,8-dione(3h)



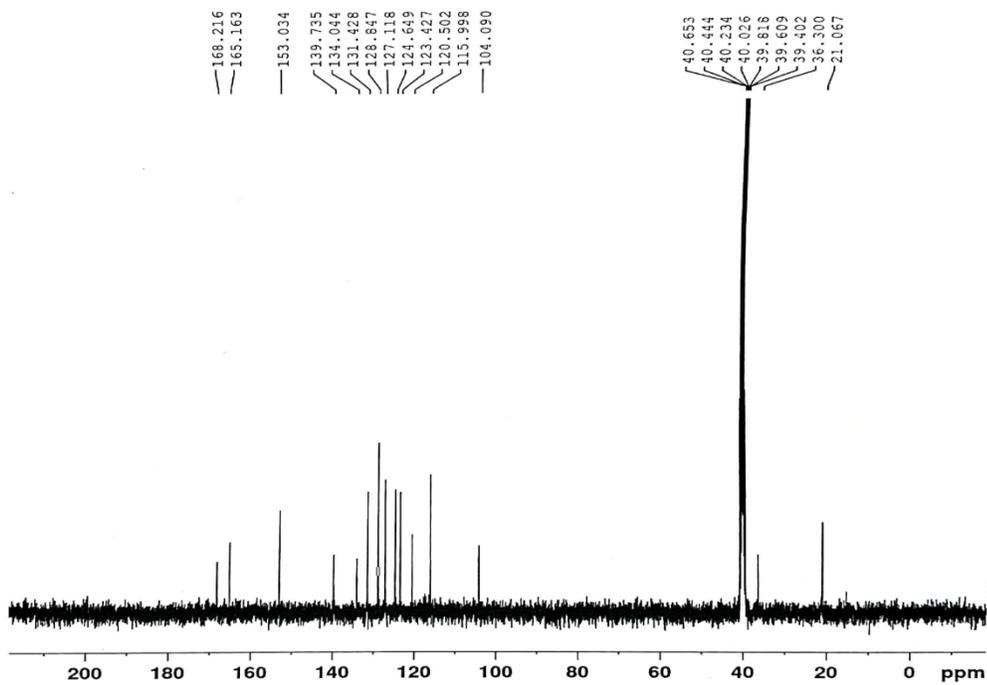
7-(thiophen-2-yl)-6H,7H,8H-pyran o[3,2-c:5,6-c']dichromene-6,8-dione(3h)



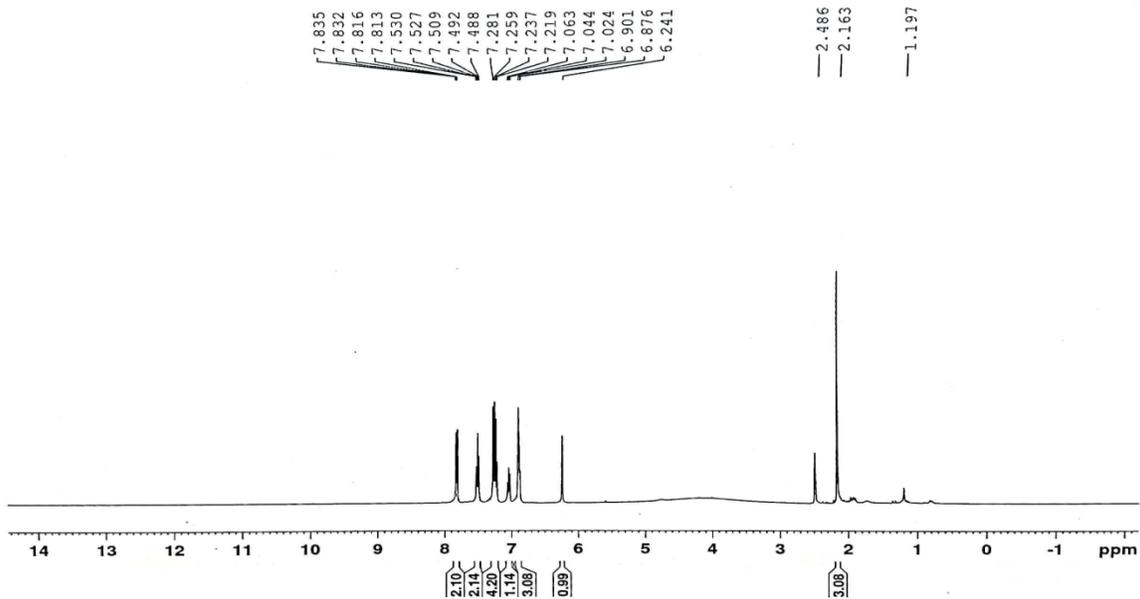
7-(4-methylphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3i)



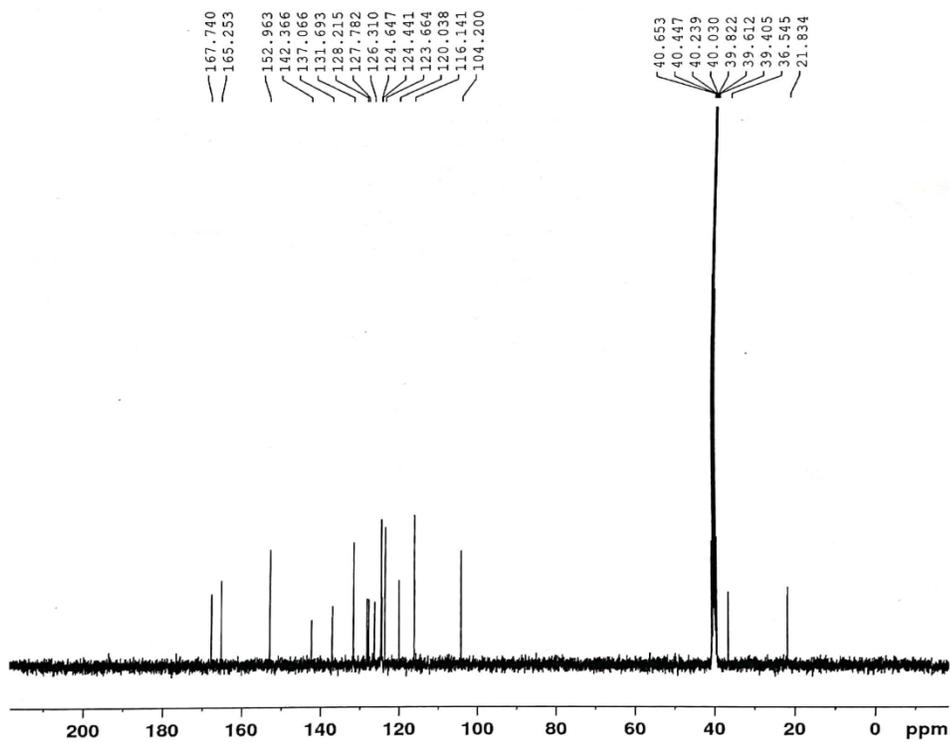
7-(4-methylphenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3i)



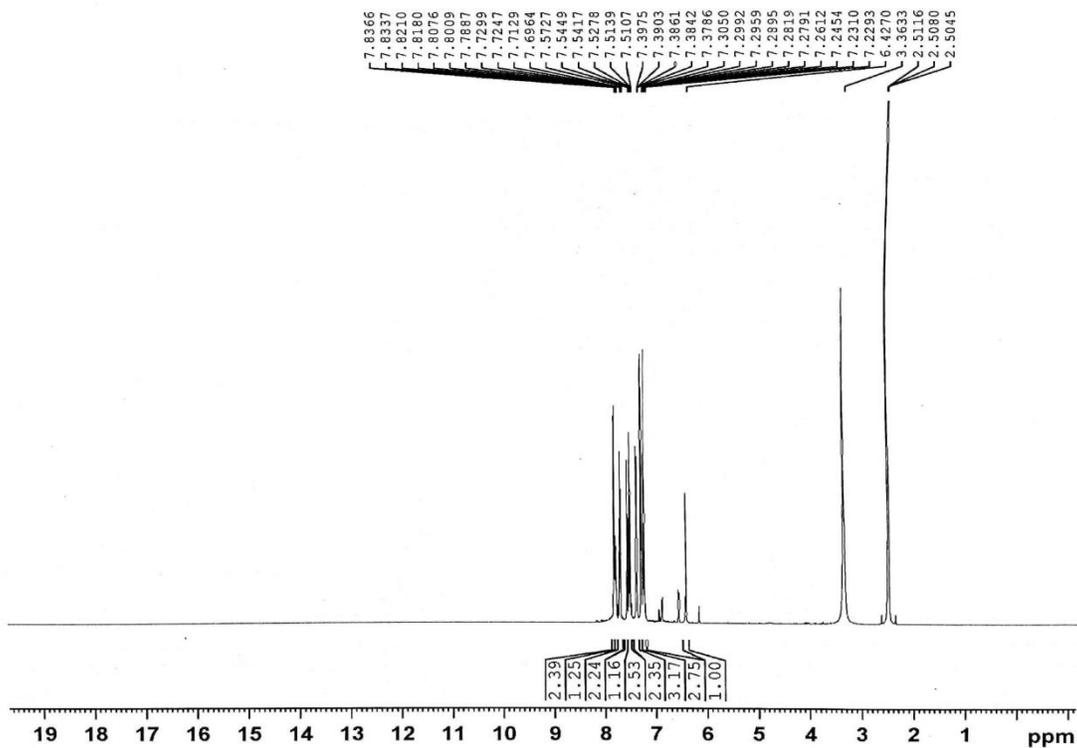
7-(3-methylphenyl)-6H,7H,8H-pyran[3,2-c:5,6-c']dichromene-6,8-dione(3j)



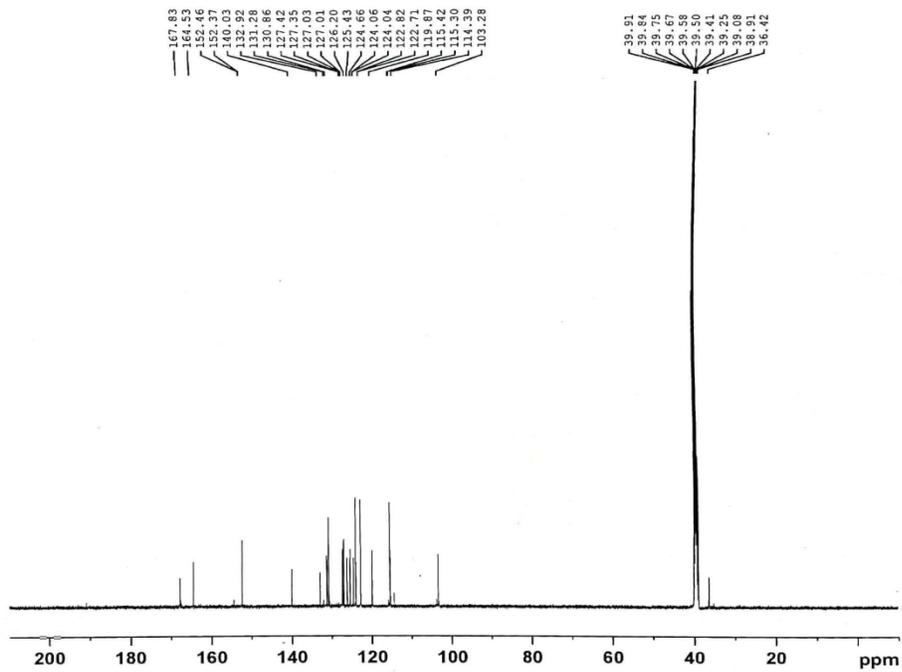
7-(3-methylphenyl)-6H,7H,8H-pyran[3,2-c:5,6-c']dichromene-6,8-dione(3j)



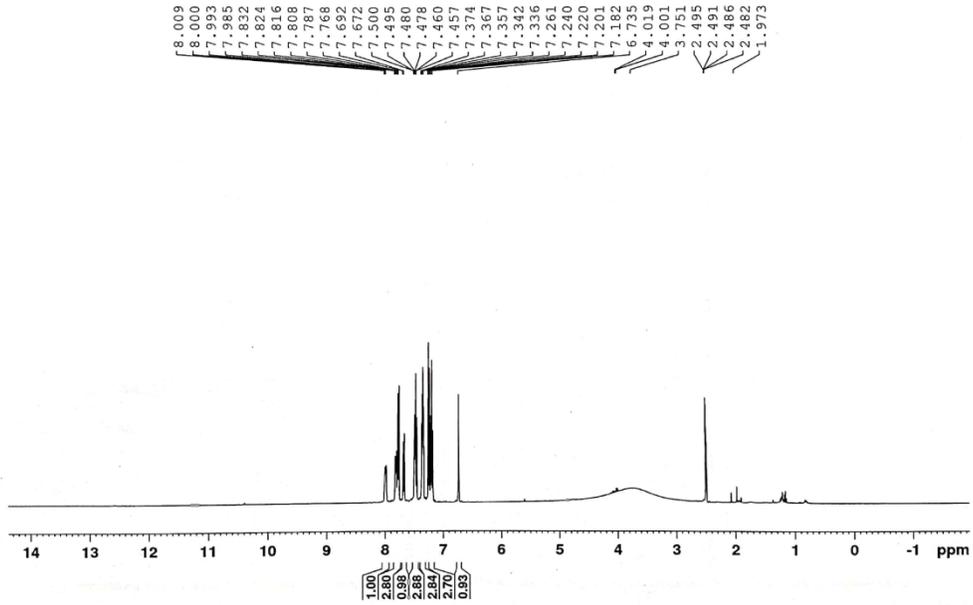
7-(naphthalen-2-yl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3I)



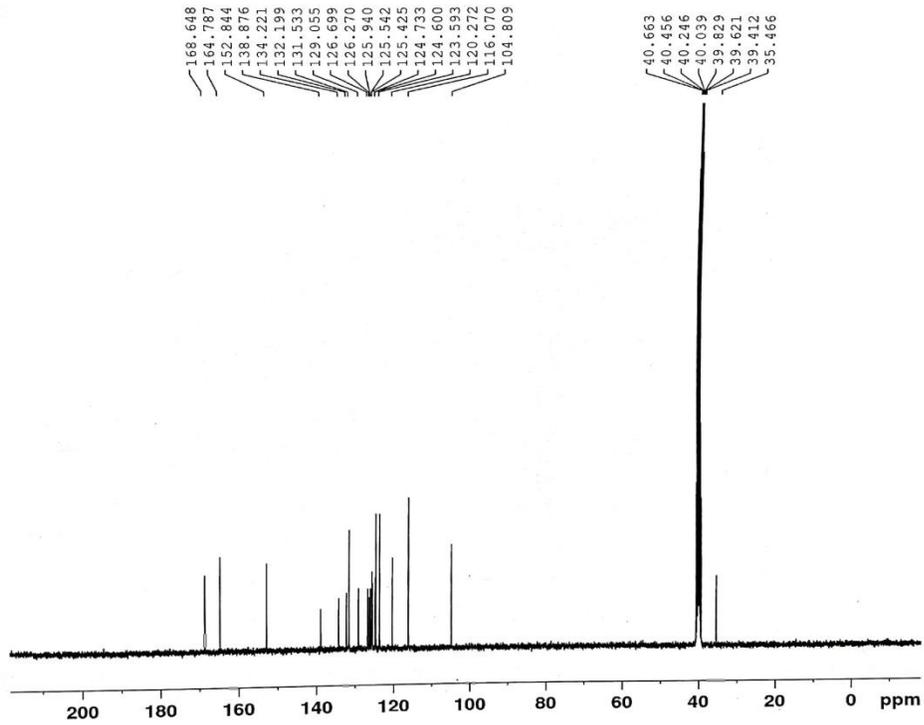
7-(naphthalen-2-yl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3I)



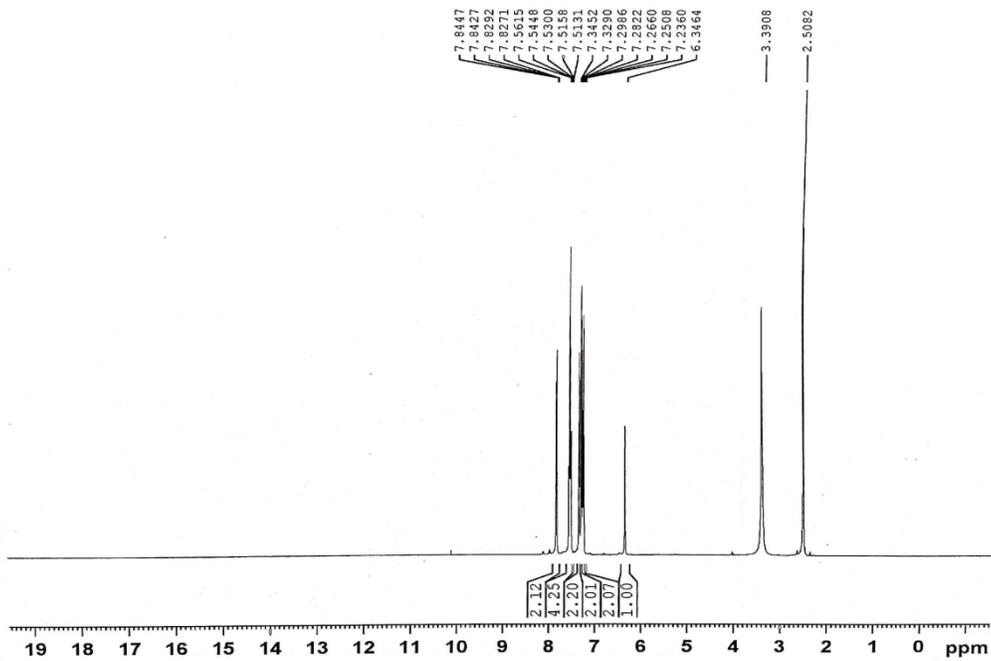
7-(naphthalen-1-yl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3m)



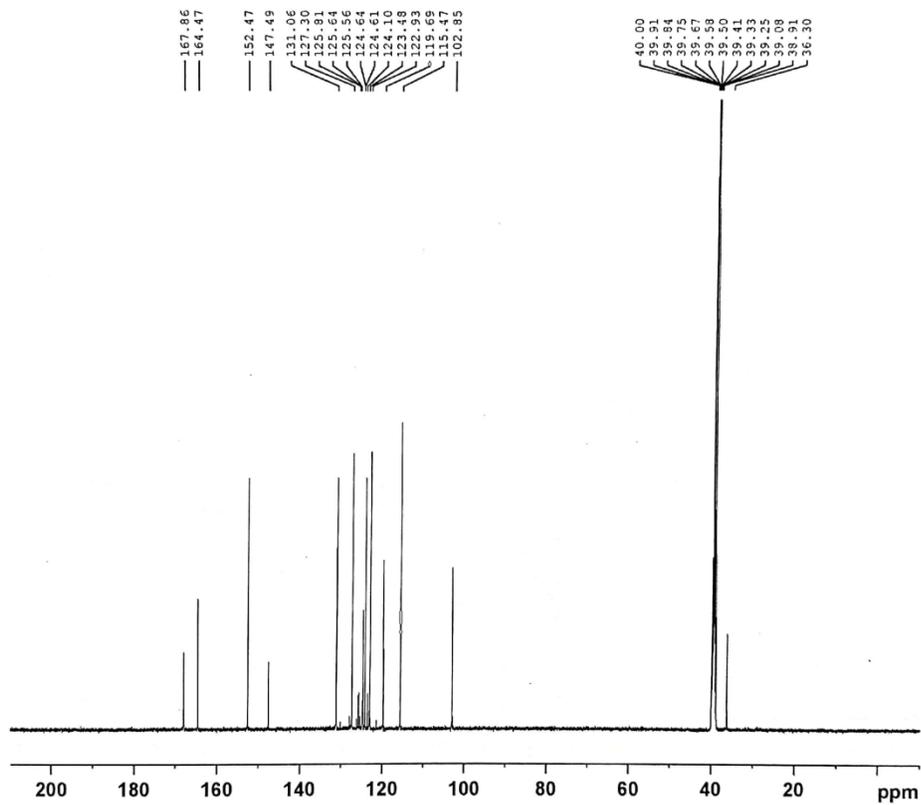
7-(naphthalen-1-yl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3m)



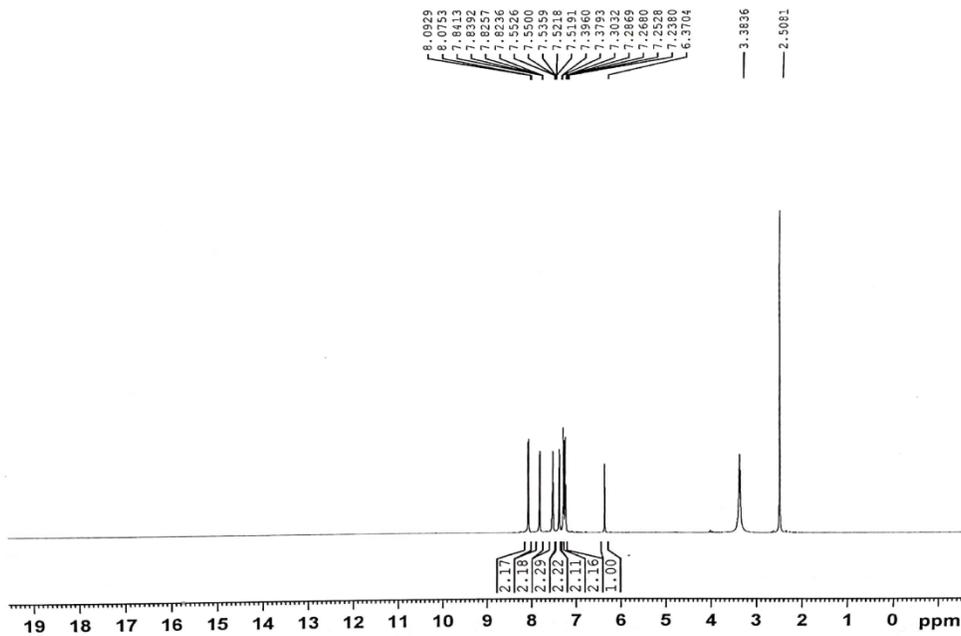
7-(4-(trifluoromethyl)phenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3n)



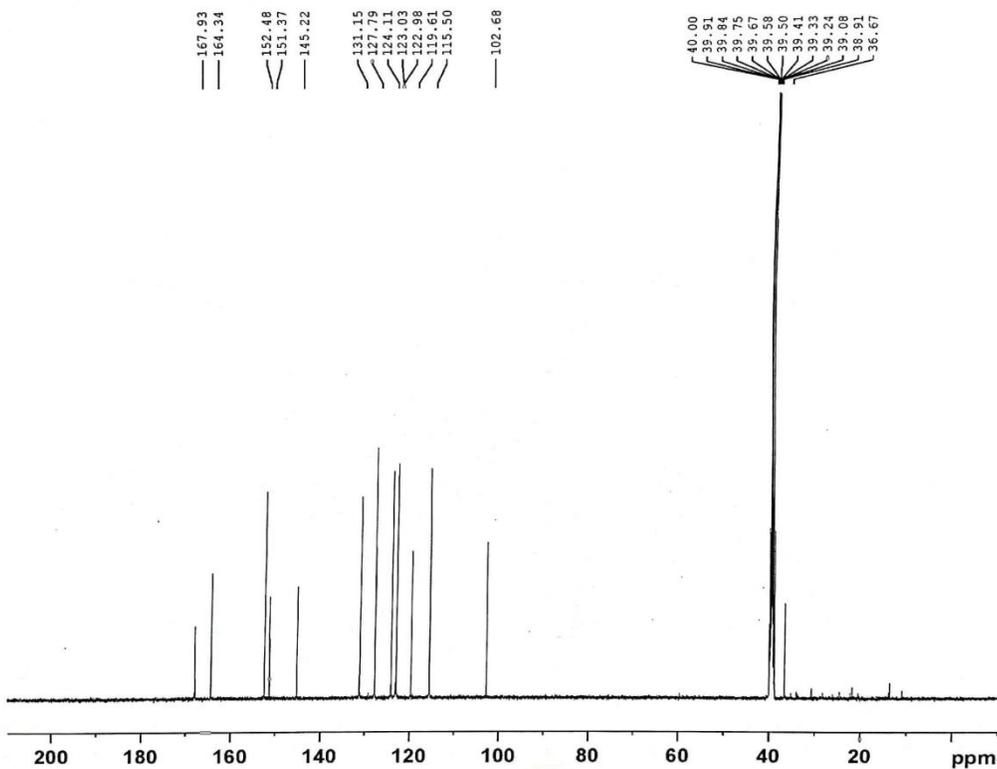
7-(4-(trifluoromethyl)phenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3n)



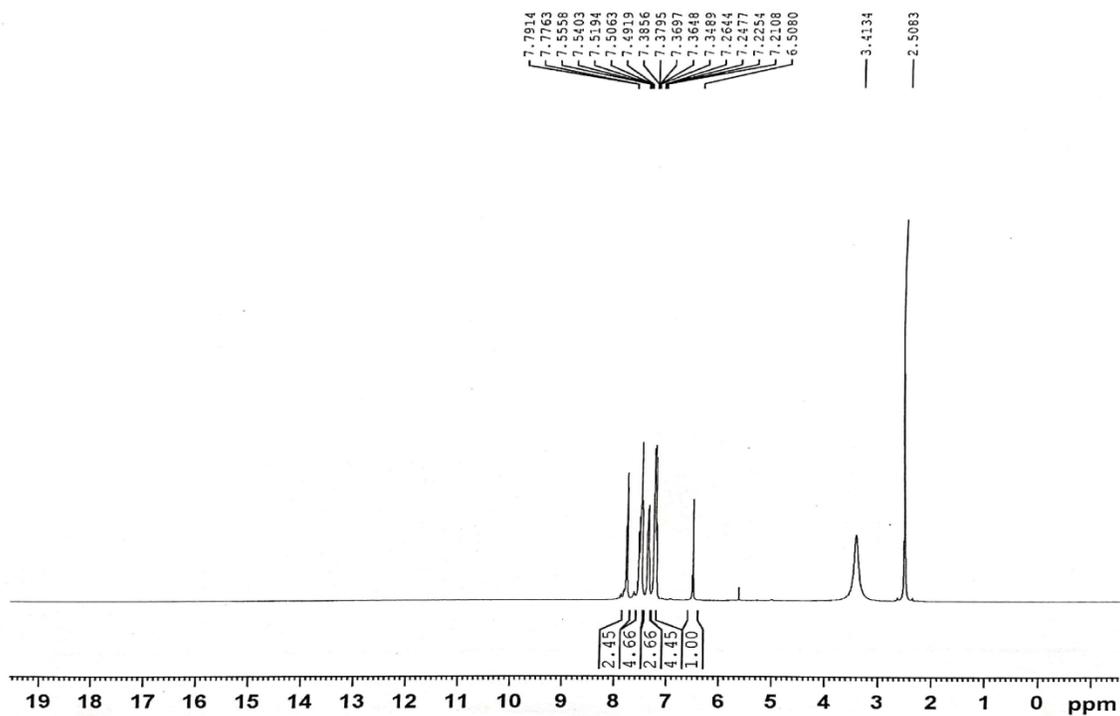
7-(4-nitrophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3o)



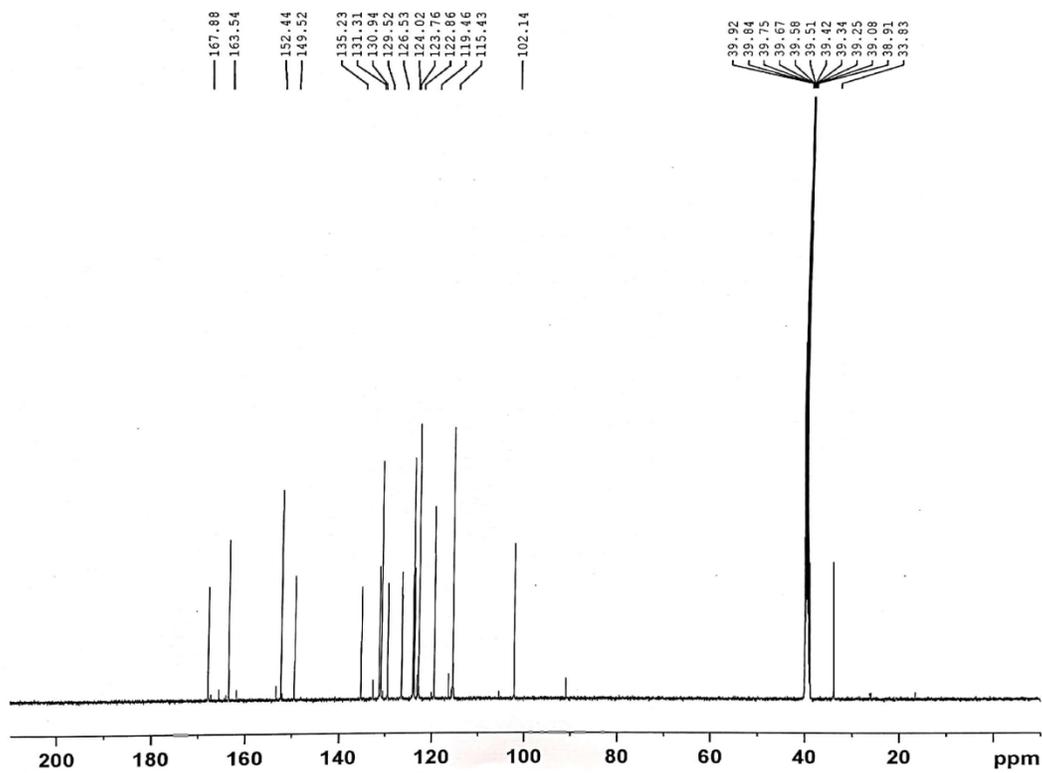
7-(4-nitrophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3o)



7-(2-nitrophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3p)



7-(2-nitrophenyl)-6H,7H,8H-pyrano[3,2-c:5,6-c']dichromene-6,8-dione(3p)



## 5. Spectral data of the compounds mentioned in scheme 2

### 7-phenyl-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4a)

#### <sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)

δ 6.31(s,1H),6.81-6.83(m,1H),6.94-7.08(m,1H),7.12-7.15(m,1H),7.17-7.27(m,4H),  
7.48-7.52(m,2H),7.83-7.92(m,4H).

#### <sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)

δ36.06,103.34,112.01,113.01,115.36,119.86,122.79,124.04,124.71,126.57,127.60,130.81,136.58,  
142.24,143.57,152.42,154.13,164.61,167.71.

### 7-(4-methoxyphenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4b)

#### <sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)

δ 3.68(s,3H),6.21(s,1H),6.74(d,2H),6.99(d,2H),7.20-7.26(m,3H),7.48-7.51(m,2H),  
7.80(d, 1H),7.82(d,2H).

#### <sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)

δ35.25,54.76,103.56,111.71,113.00,114.40,115.31,119.88,122.71,123.98,127.49,130.70,131.69,1  
34.00,139.40,141.85,152.38,155.53,156.67,164.45,167.51.

### 7-(2-chlorophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4c)

#### <sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)

δ 6.10(s,1H),6.82(m,1H),6.96(d,1H)7.11-7.25(m,5H),7.42(dd,1H),7.47-7.50(m,2H),  
7.81-7.92(m,3H).

#### <sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)

δ36.02,102.68,112.02,113.14,115.34,119.81,122.80,123.95,125.87,126.93,129.23,130.27,130.72,  
132.60,136.26,140.29,143.78,152.31,153.96,163.82,167.63.

### 7-(4-bromophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4d)

#### <sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)

δ 6.24(s,1H),6.80-6.83(m,1H),6.94(d,1H),7.05-7.07(dd,1H),7.21-7.27(m,3H),  
7.33-7.36(m,1H),7.49-7.52(m,1H),7.81-7.92(m,4H).

#### <sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)

δ35.76,102.98,111.99,112.94,115.39,117.70,119.73,122.83,124.03,128.92,130.43,130.92,136.70,  
141.85,143.50,152.42,154.18,164.39,167.69.

### 7-(4-fluorophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4e)

**<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ 6.27(s,1H),6.79-82(m,1H),6.92(d,1H),6.93-7.00(m,2H),7.11-7.14(m,1H),  
7.21-7.27(m,3H),7.49-7.52(m,1H),7.82-7.92(m,3H).

**<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ35.51,103.31,111.99,112.78,114.08,114.25,115.38,119.80,122.82,124.04,128.21,128.27,130.88,  
137.06,138.13,138.15,143.28,152.42,154.37,159.10,161.00,164.47,167.70.

**7-(4-hydroxy-3-methoxyphenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4f)**

**<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ 3.54(s,3H),6.19(s,1H),6.52-6.54(m,1H),6.58(d,1H),6.82(s,1H),6.94(d,1H),  
7.21-7.25(m,3H),7.47-7.51(m,1H),7.82-7.87(m,3H),8.53(broad s,1H).

**<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ35.56,55.59,103.72,111.68,112.04,112.98,114.81,115.33,119.20,119.93,122.76,124.00,130.70,1  
33.09,136.68,143.56,144.00,146.89,152.37,154.18,164.55,167.61.

**7-(3-nitrophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4g)**

**<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ 6.40(s,1H),6.81-6.83(m,1H),6.94(d,1H),7.23-7.30(m,2H),7.49-7.61(m,3H),  
7.59-7.61(m,1H),7.83-7.94(m,4H),7.99-8.01(m,1H).

**<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ36.19,102.57,111.99,113.02,115.52,119.59,120.25,121.00,123.00,124.11,129.28,131.17,133.74,  
136.55,143.58,145.05,147.68,152.48,154.12,164.37,167.94.

**7-(naphthalen-2-yl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4h)**

**<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ 6.46(s,1H),6.76-6.79(m,1H),6.90(d,1H),7.23-7.32(m,1H),7.29-7.32(m,2H),  
7.36-7.40(m,1H),7.51-7.54(m,2H),7.59(s,1H), 7.70-7.72(dd,2H),7.78-7.85(m,3H),7.90(d,1H).

**<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)**

36.46,103.31,111.97,112.54,115.44,119.89,122.85,124.09,124.67,125.45,126.22,127.03,127.06,1  
27.35,130.88,131.30,132.94,137.55,140.05,142.96,152.48,154.61,164.60,167.89.

**7-(thiophen-2-yl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4i)**

**<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)**

δ 6.44(s,1H),6.60-6.61(m,1H),6.79-6.84(m,1H),6.95(d,1H),7.13-7.14(m,1H),  
7.22-7.26(m,3H),7.49-7.52(m,1H),7.85-7.91(m,3H).

<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)

δ32.84,103.64,112.01,113.08,115.40,119.79,122.54,122.86,122.93,124.13,126.02,130.99,136.41,143.69,147.99,152.39,154.04,164.05,167.86.

**7-(p-tolyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4j)**

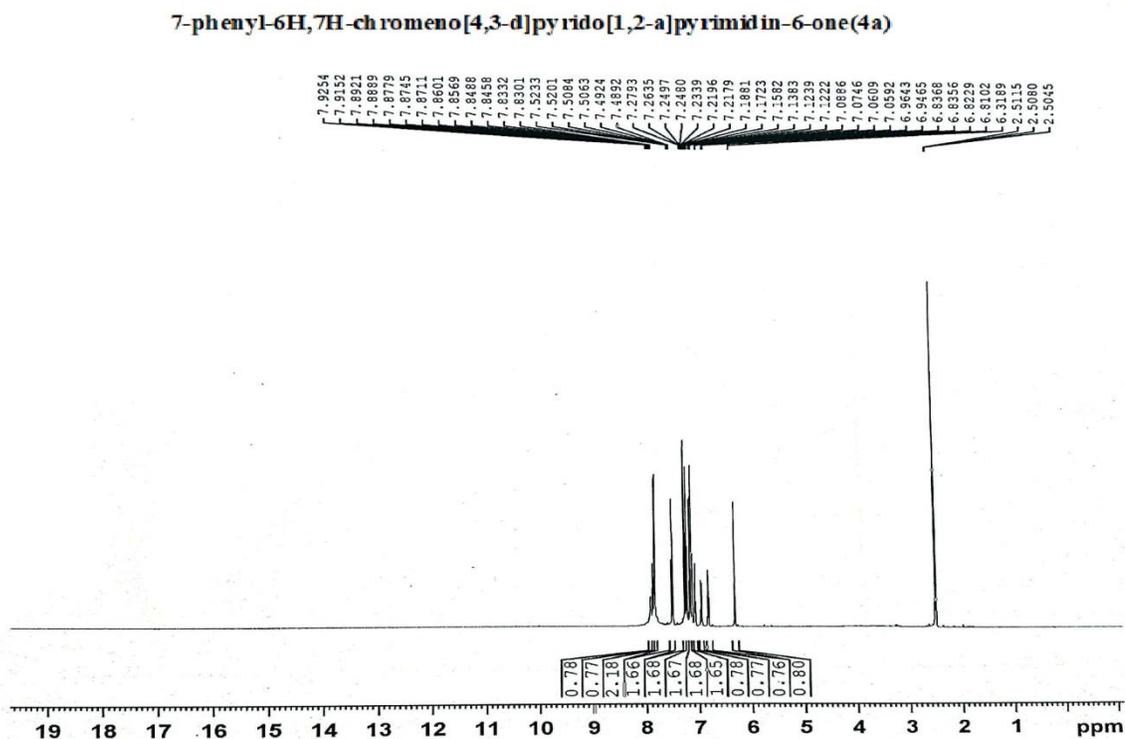
<sup>1</sup>H-NMR(500MHz,DMSO-d<sub>6</sub>)

δ 2.21(s,3H),6.21(s,1H),6.78-6.80(m,1H),6.88(d,1H),6.94-6.98(m,3H),7.20-7.25(m,3H),7.47-7.51(m,1H),7.79-7.84(m,2H),7.91-7.92(m,1H).

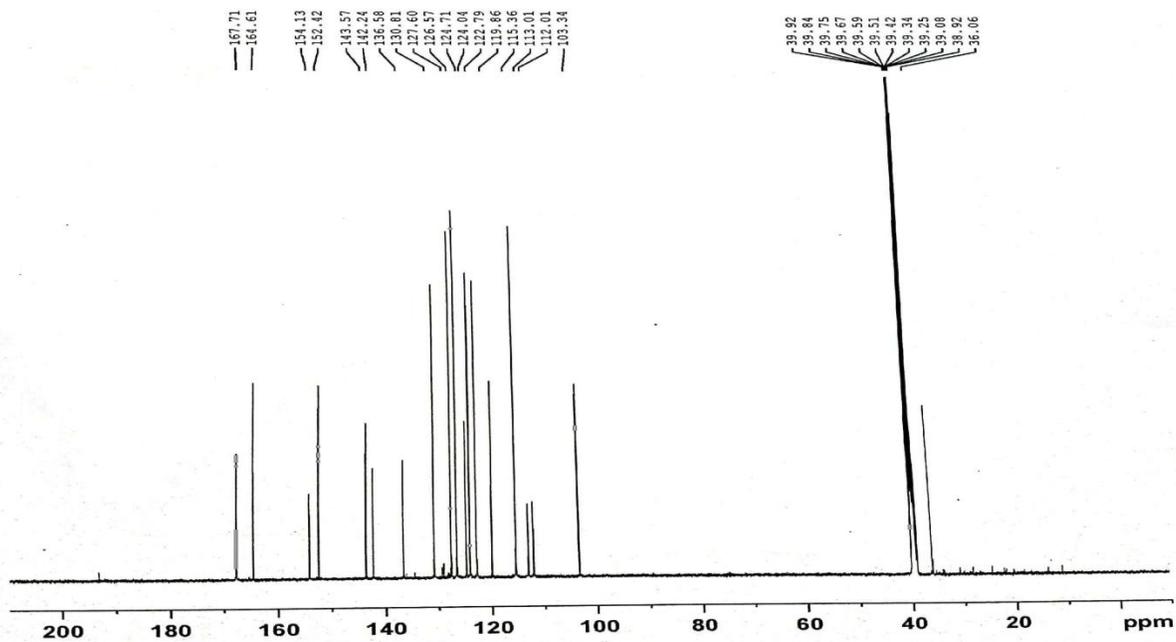
<sup>13</sup>C-NMR(500MHz,DMSO-d<sub>6</sub>)

δ20.39,35.65,103.42,111.96,112.34,115.30,119.87,122.70,123.98,126.46,128.15,130.70,133.32,137.97,139.14,142.76,152.38,154.80,164.42,167.50.

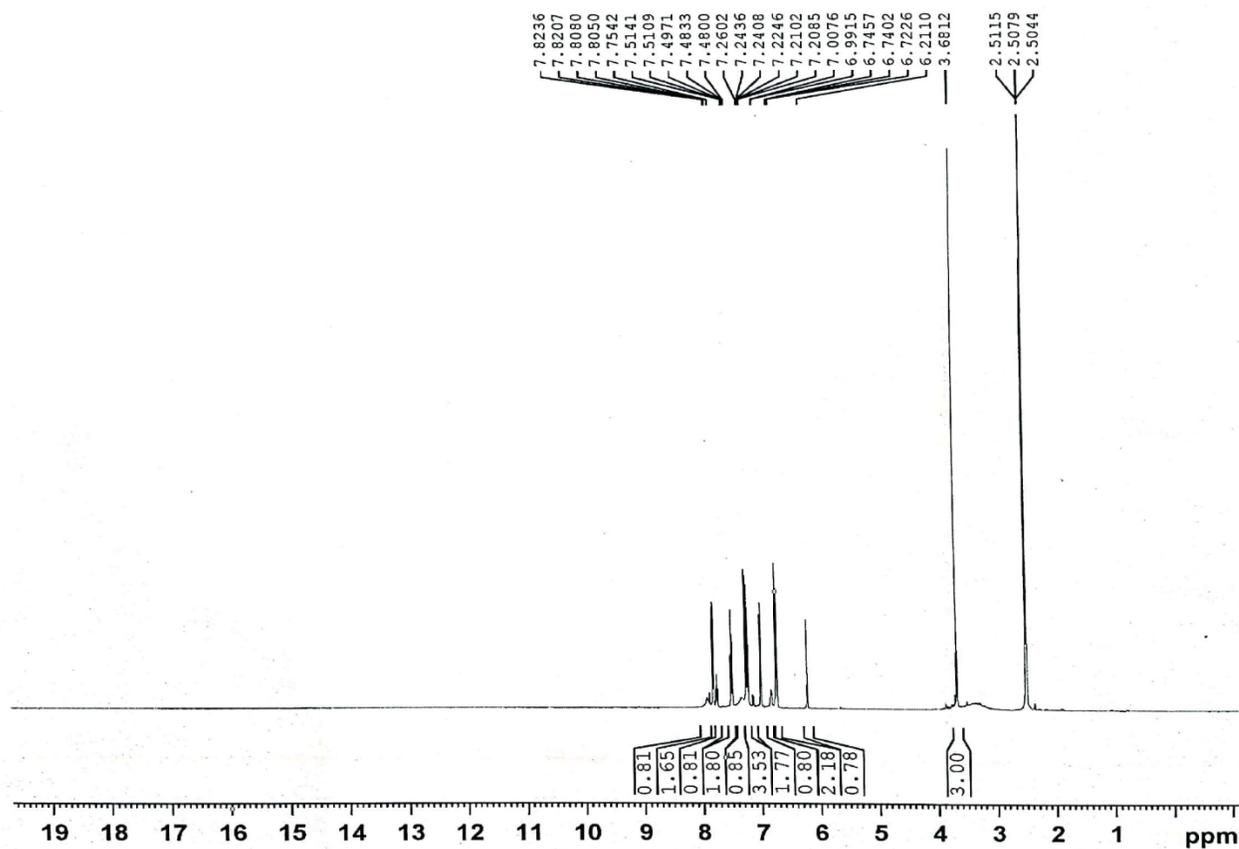
**6.Sanned copies of compounds mentioned in scheme 2**



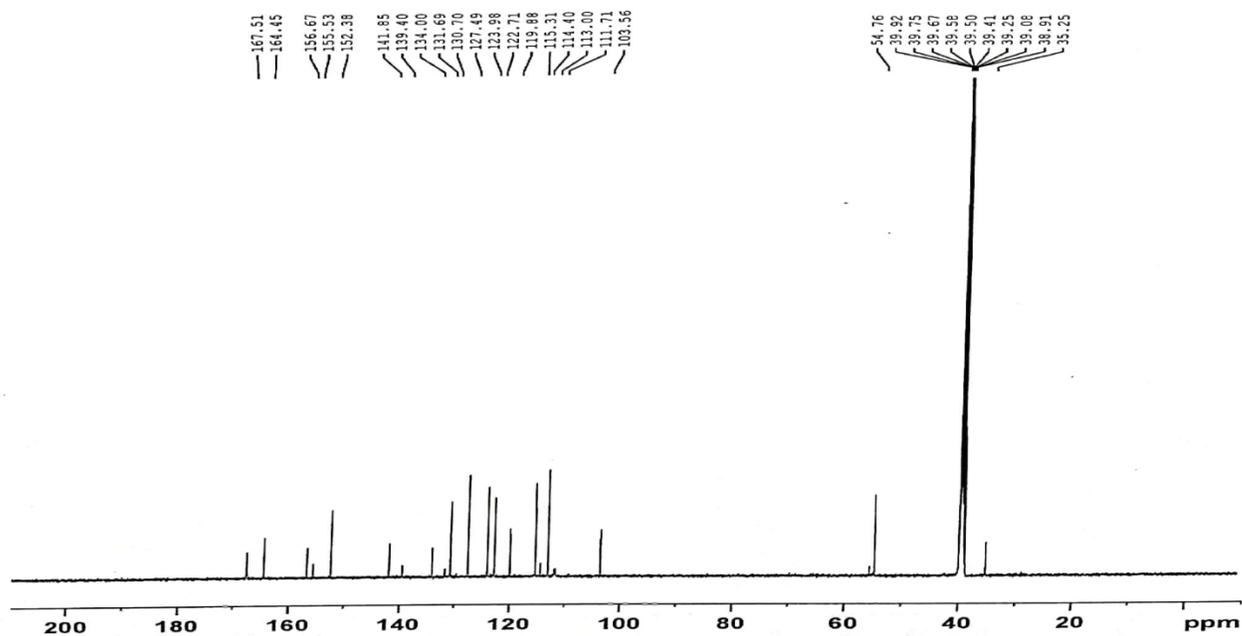
7-phenyl-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4a)



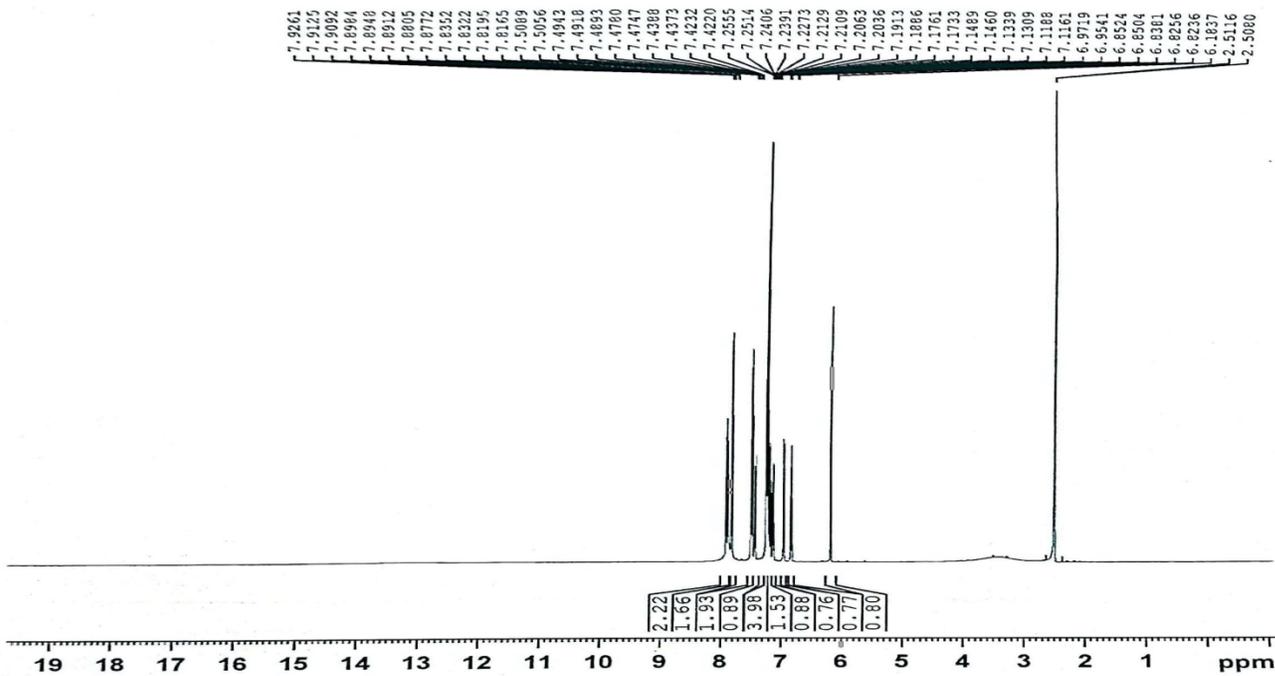
7-(4-methoxyphenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4b)



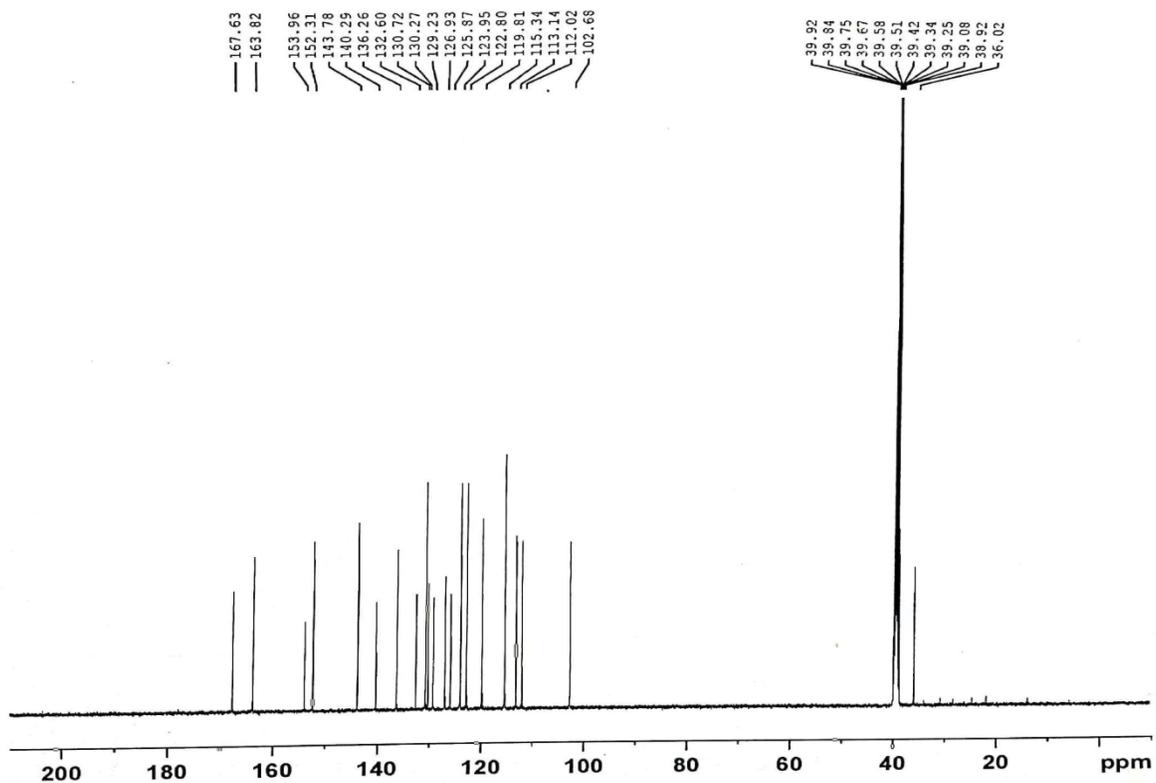
7-(4-methoxyphenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4b)



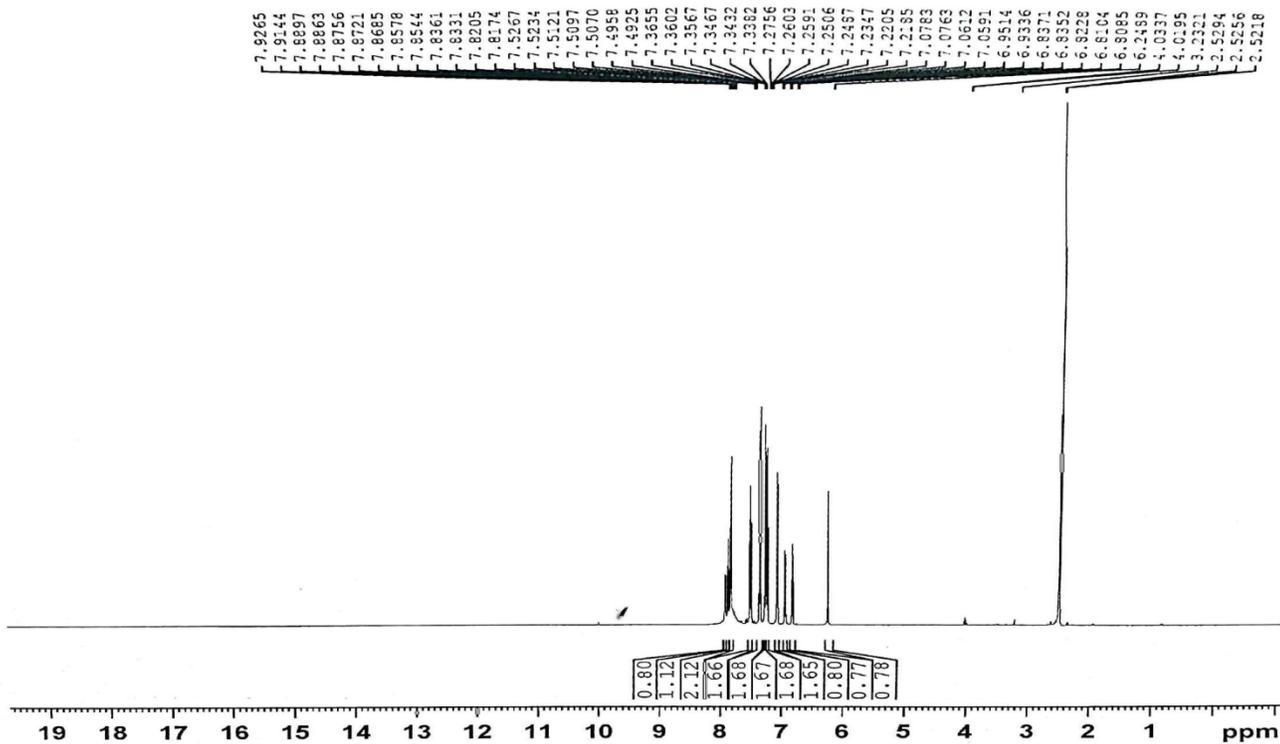
7-(2-chlorophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4c)



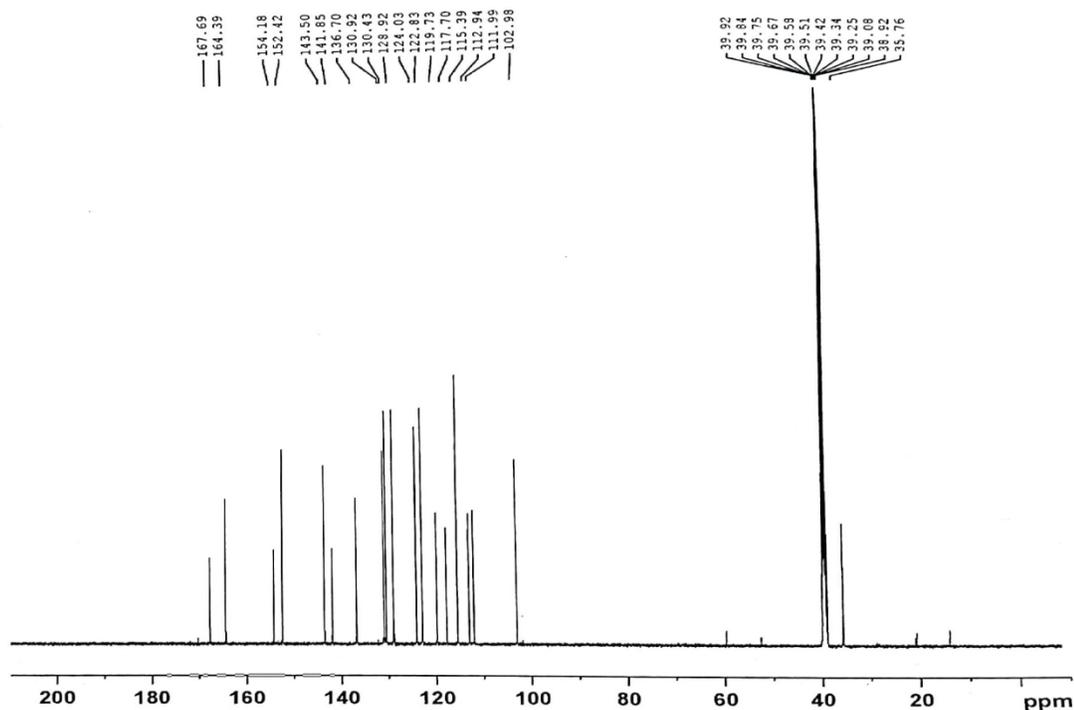
7-(2-chlorophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4c)



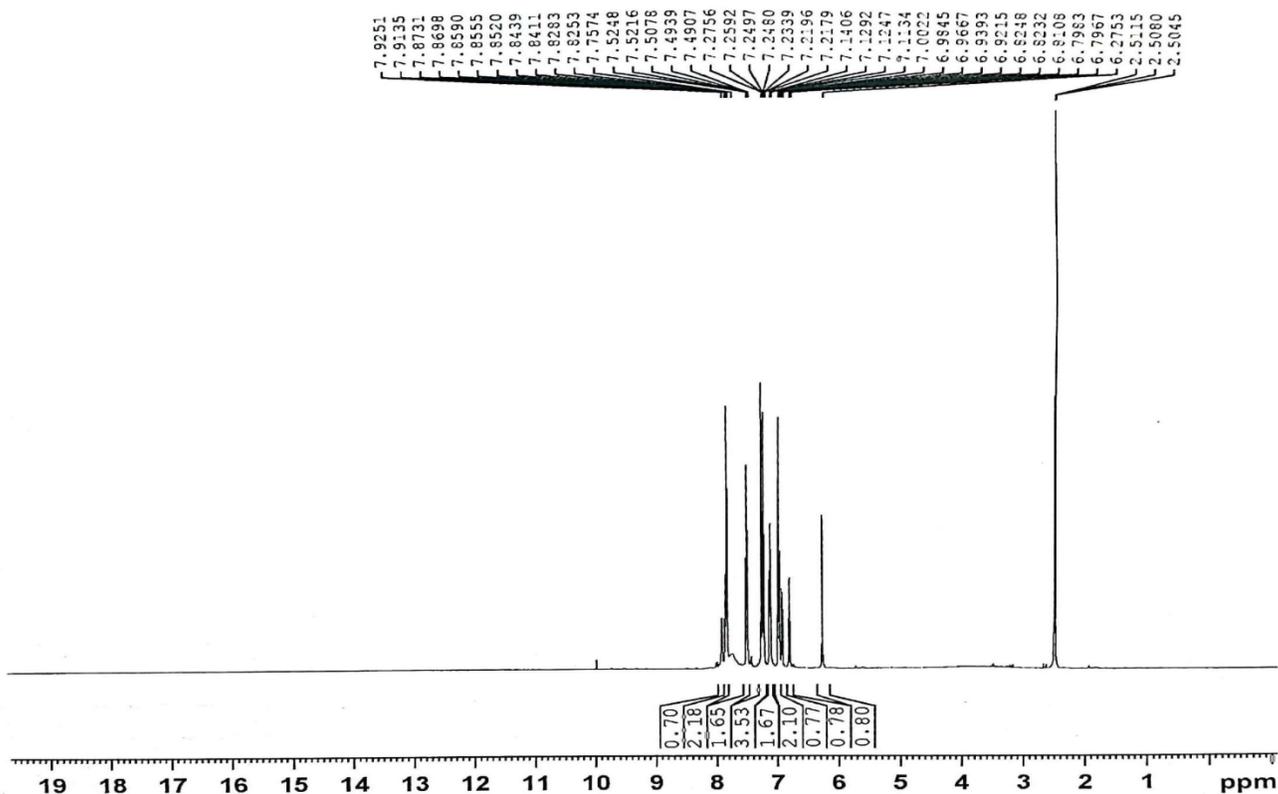
**7-(4-bromophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4d)**



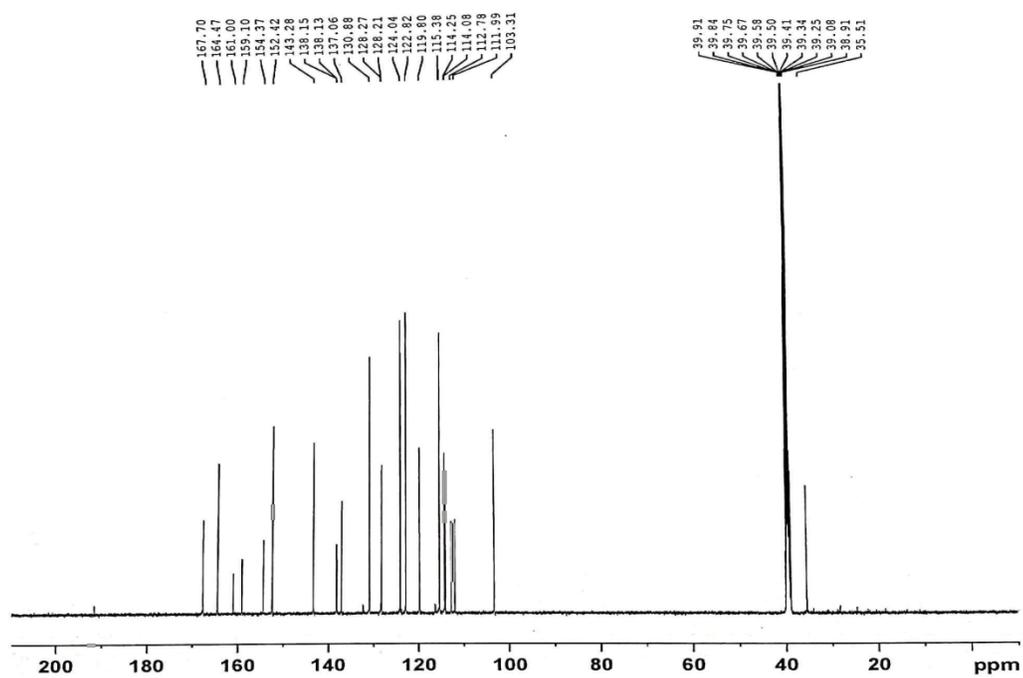
**7-(4-bromophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4d)**



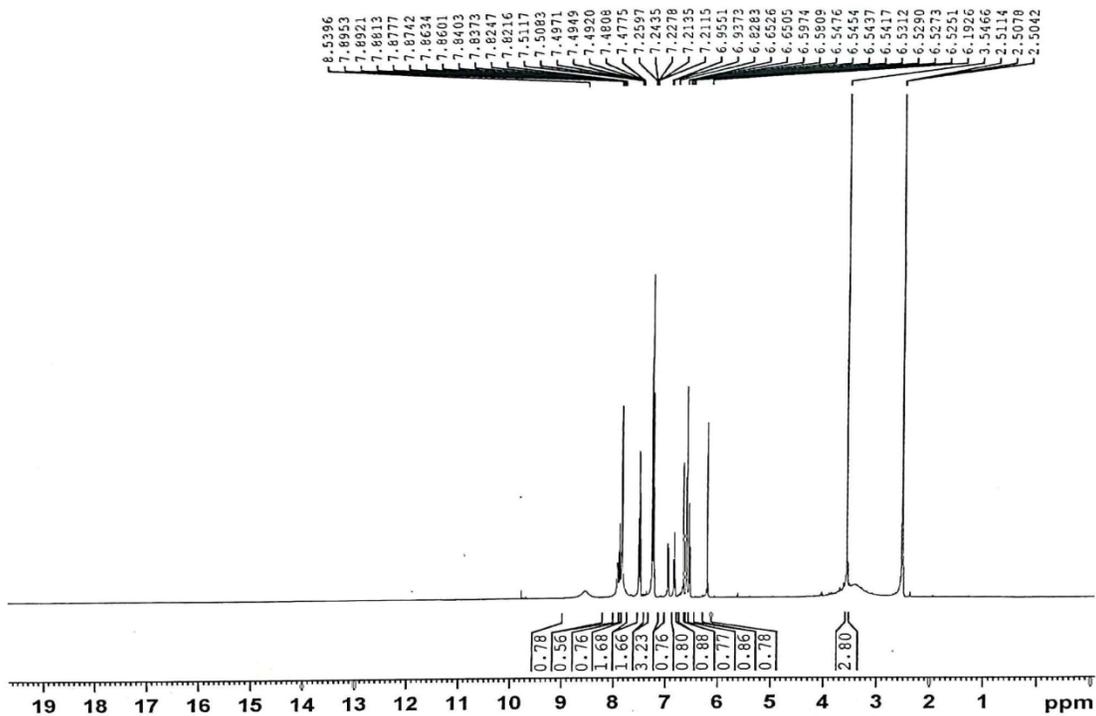
**7-(4-fluorophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4e)**



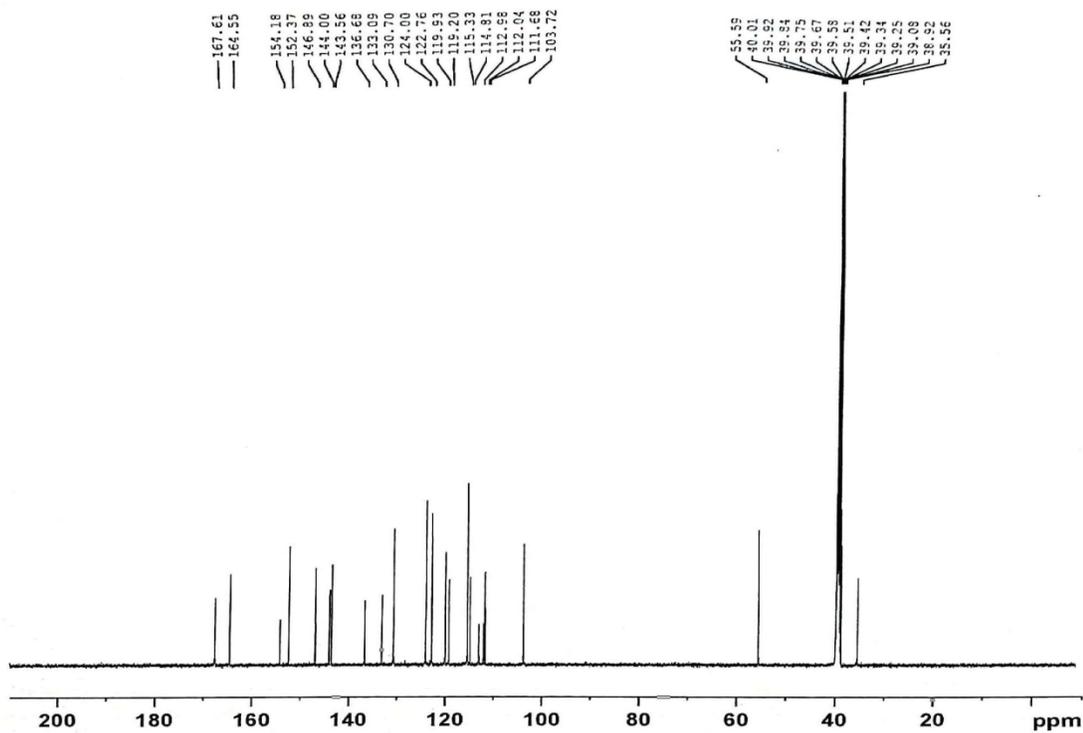
**7-(4-fluorophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4e)**



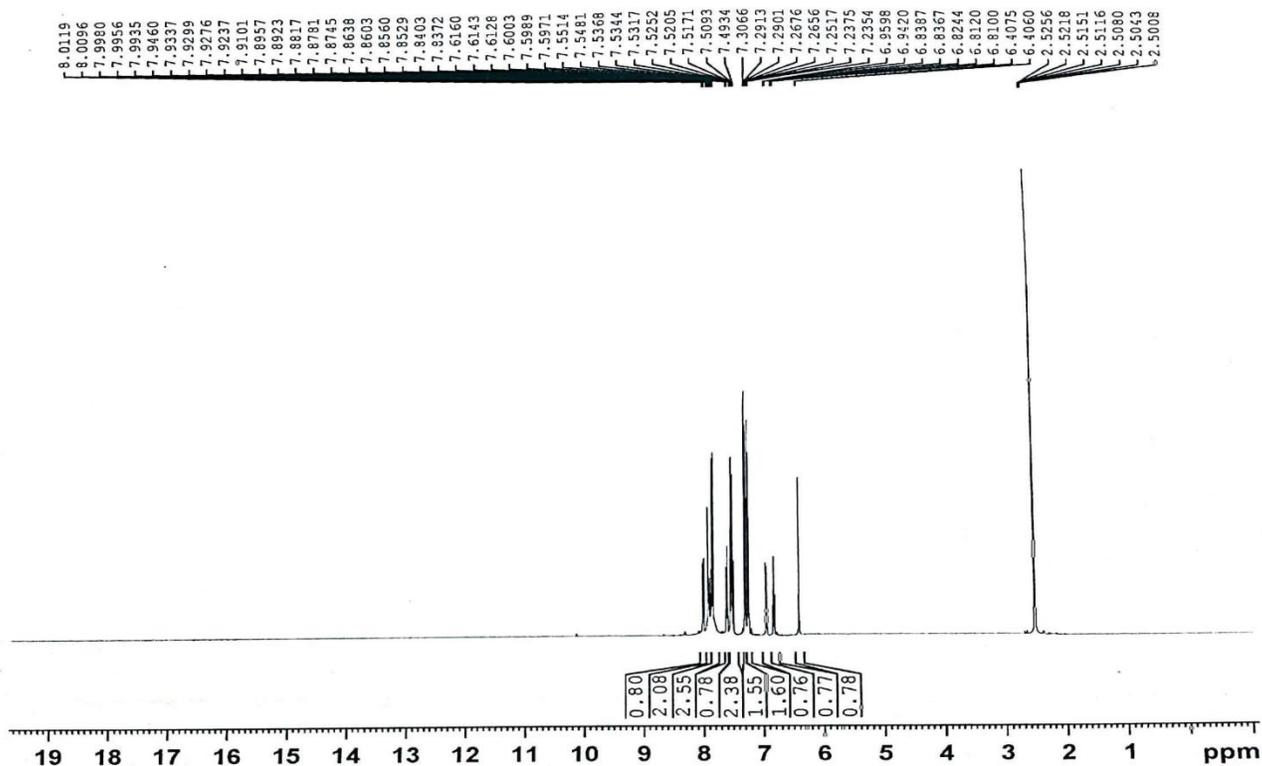
**7-(4-hydroxy-3-methoxyphenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one (4f)**



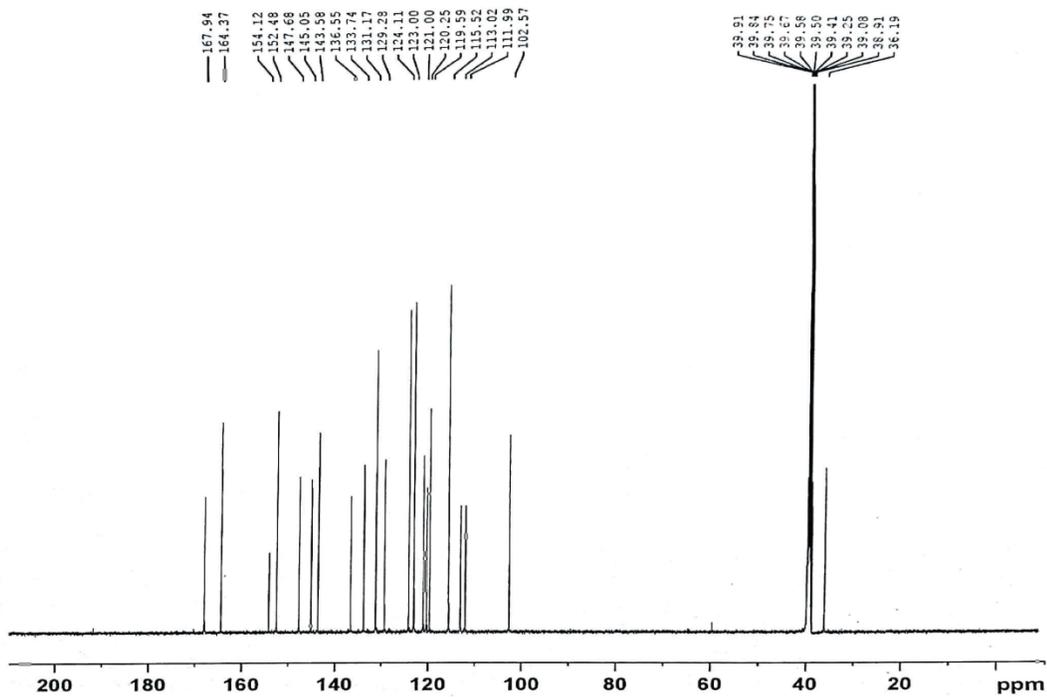
**7-(4-hydroxy-3-methoxyphenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one (4f)**



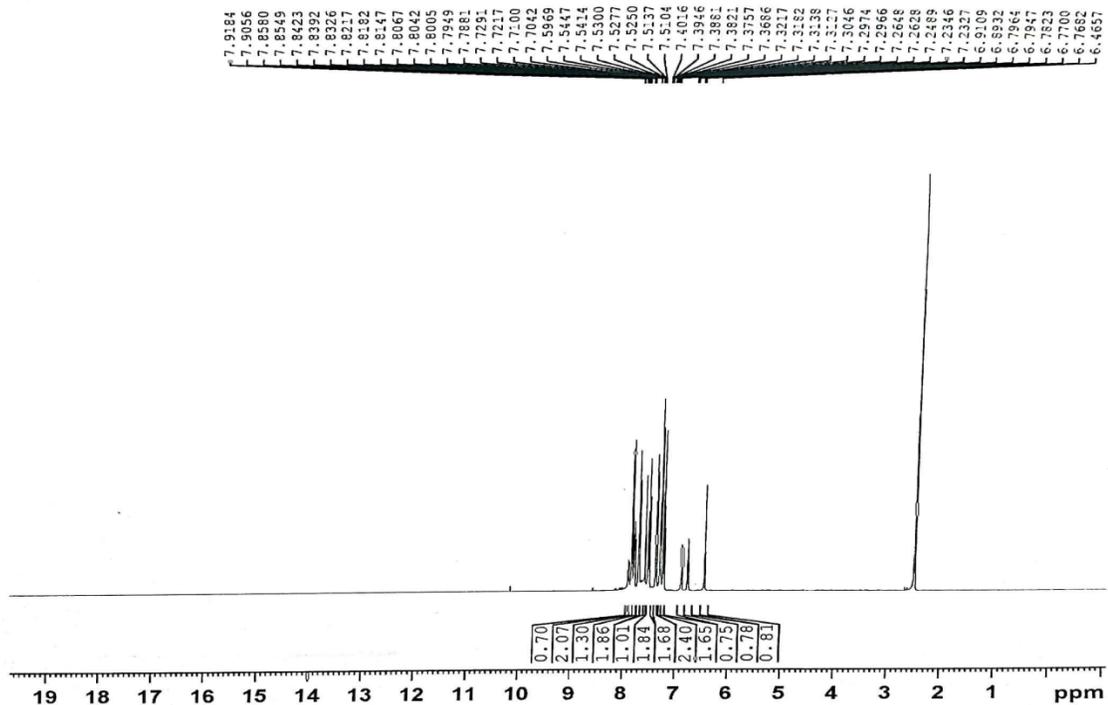
**7-(3-nitrophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4g)**



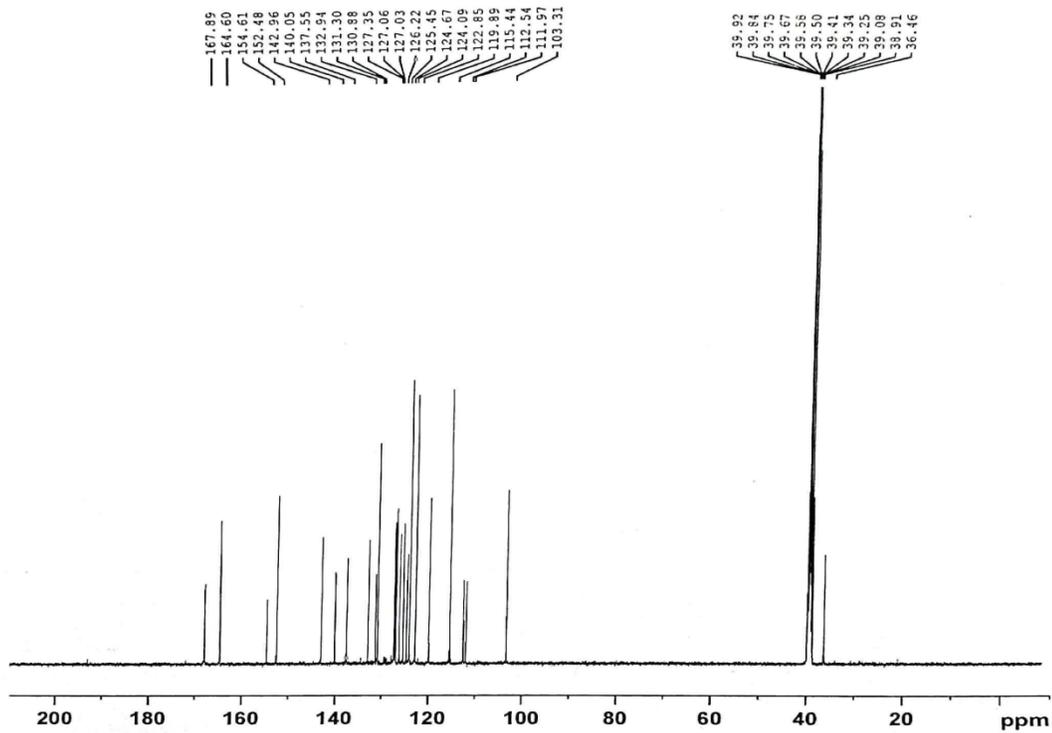
**7-(3-nitrophenyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4g)**



**7-(naphthalen-2-yl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4h)**

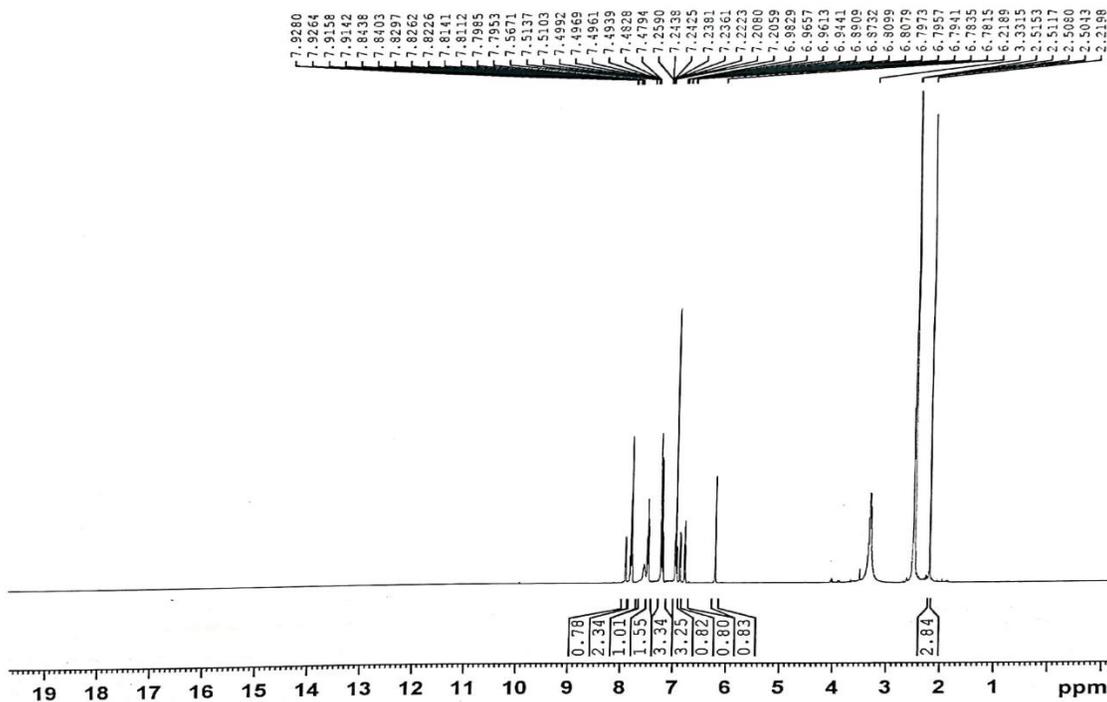


**7-(naphthalen-2-yl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4h)**

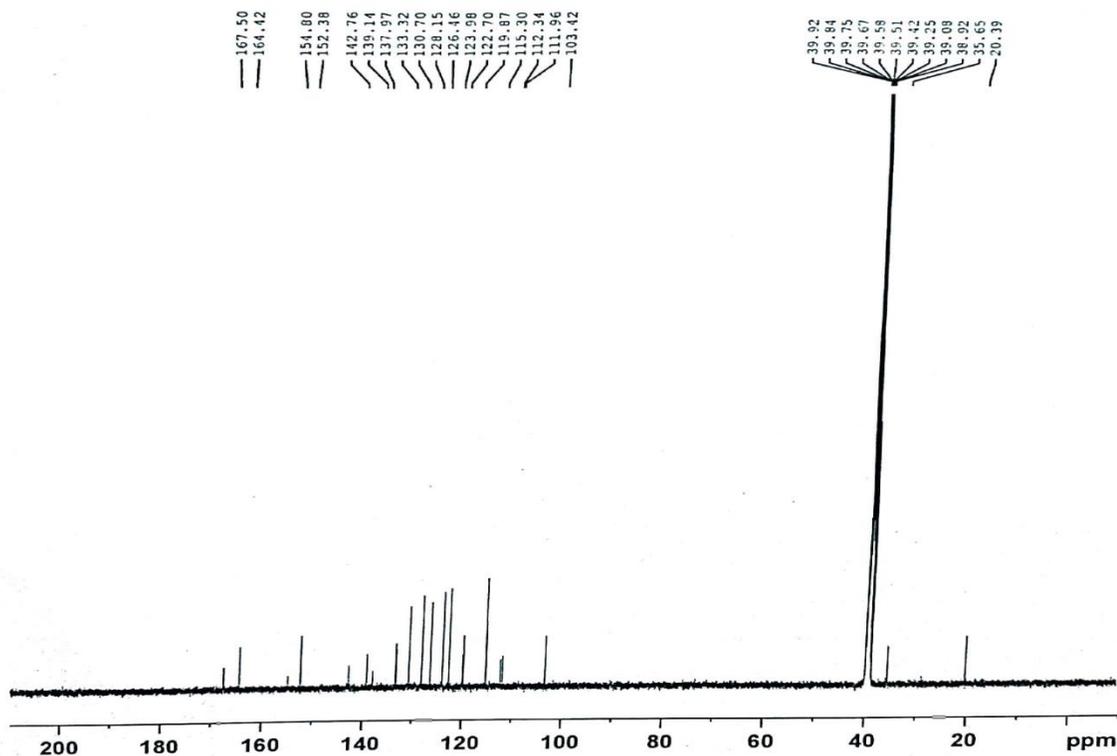




**7-(p-tolyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4j)**



**7-(p-tolyl)-6H,7H-chromeno[4,3-d]pyrido[1,2-a]pyrimidin-6-one(4j)**



## 7. EDX data of sulphonated rice husk and rice husk

### Project 1

1/21/2019 2:26:03 PM

Spectrum processing :

Peaks possibly omitted : 8.043, 8.626 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 6

Standard :

C CaCO<sub>3</sub> 1-Jun-1999 12:00 AM

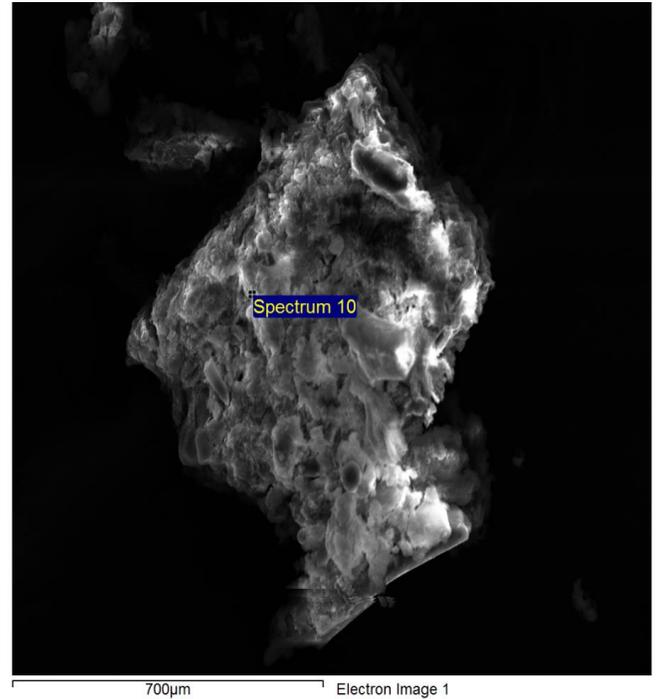
O SiO<sub>2</sub> 1-Jun-1999 12:00 AM

Si SiO<sub>2</sub> 1-Jun-1999 12:00 AM

S FeS<sub>2</sub> 1-Jun-1999 12:00 AM

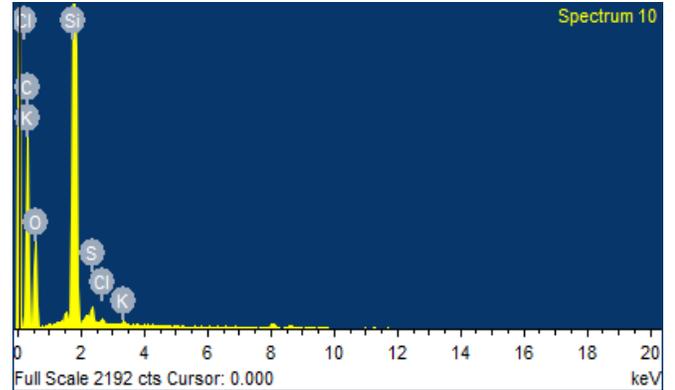
Cl KCl 1-Jun-1999 12:00 AM

K MAD-10 Feldspar 1-Jun-1999 12:00 AM



Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	71.39	0.4111	57.29	0.88	68.73
O K	24.20	0.3287	24.30	0.70	21.88
Si K	50.69	0.9435	17.73	0.37	9.09

Comment:sourav



OXFORD  
INSTRUMENTS  
The Business of Science®

S K	0.96	0.7957	0.40	0.04	0.18
Cl K	0.40	0.7250	0.18	0.03	0.07
K K	0.30	0.9905	0.10	0.03	0.04
Totals			100.00		

Spectrum processing :

Peaks possibly omitted : 8.036, 8.640, 8.905 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 5

Standard :

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

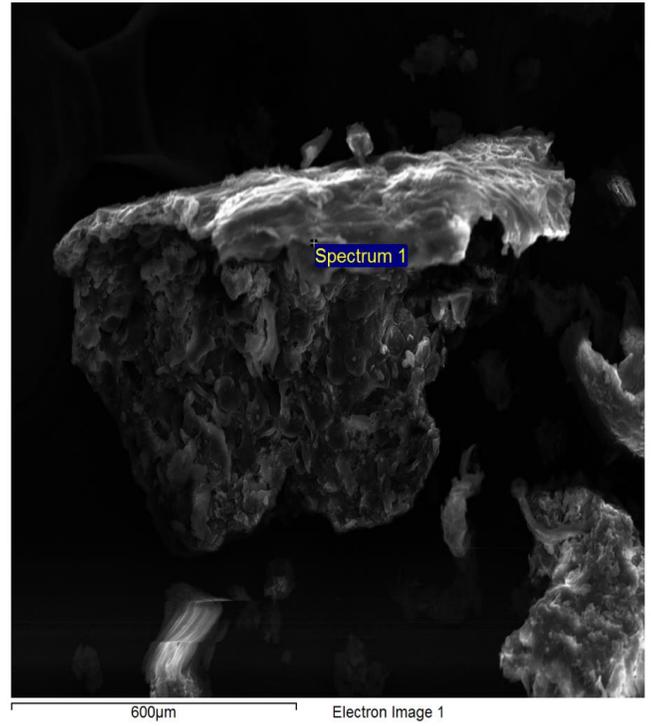
Mg MgO 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

P GaP 1-Jun-1999 12:00 AM

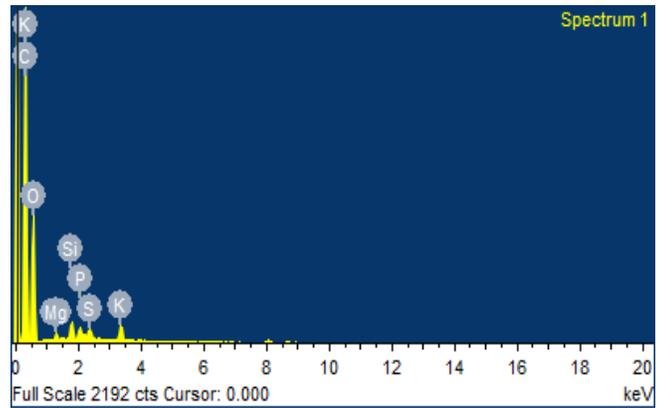
S FeS2 1-Jun-1999 12:00 AM

K MAD-10 Feldspar 1-Jun-1999 12:00 AM



Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	122.06	1.0292	55.96	0.82	63.40
O K	34.95	0.3931	41.95	0.81	35.68

Comment:sourav



Mg K	0.42	0.6145	0.32	0.05	0.18
Si K	0.87	0.8459	0.48	0.04	0.23
P K	0.92	1.2546	0.35	0.05	0.15
S K	0.69	0.9358	0.35	0.04	0.15
K K	1.32	1.0579	0.59	0.04	0.20

Totals	100.00
--------	--------

## 8. References

1. S. Dey, P. Basak, P. Ghosh. *ChemistrySelect*. **2020**,5,15209-15217.