

## **4-Dialkylaminopyridine Modified Magnetic Nanoparticles: As an Efficient Nano-organocatalyst for one-pot Synthesis of 2-Amino-4H-chromene-3-carbonitrile Derivatives in Water**

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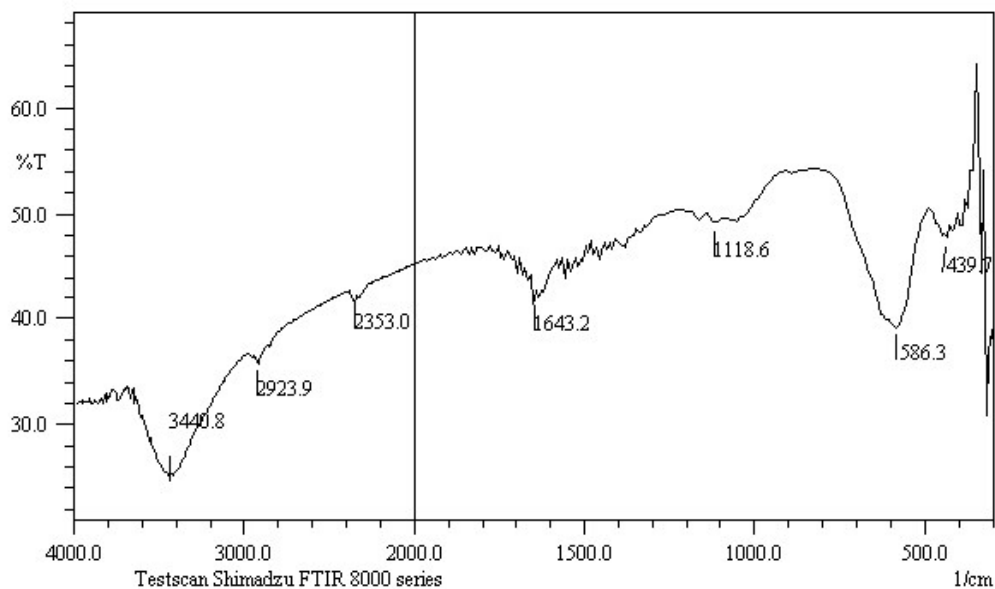
<sup>b</sup> Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Iran.

\*khalafi@susc.ac.ir; fpanahi@aut.ac.ir

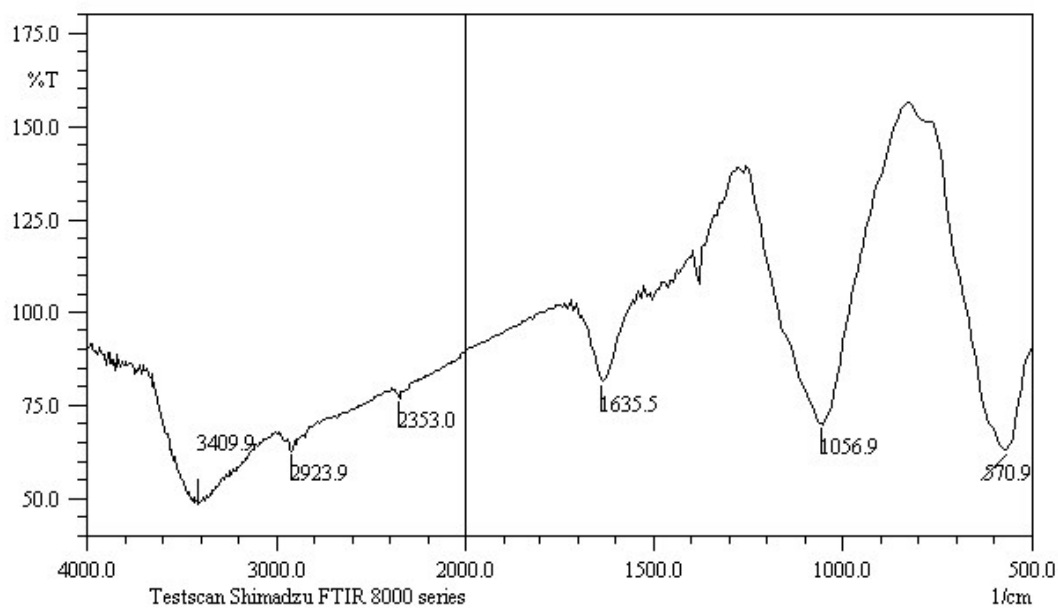
# 1. Catalyst characterization

## 1.1. FT-IR study

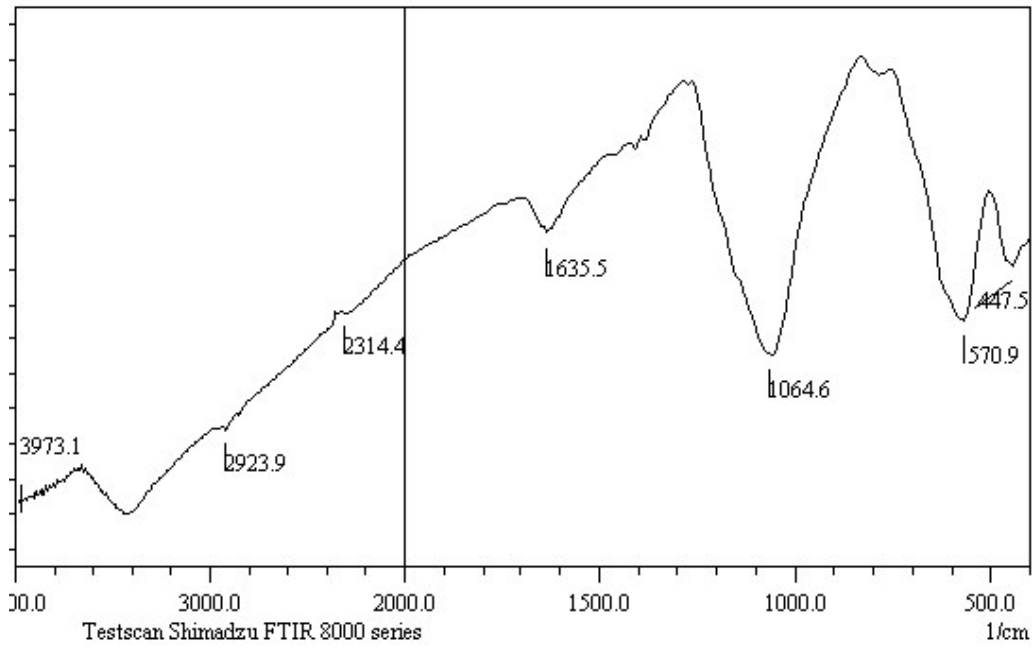
### FT-IR of $\text{Fe}_3\text{O}_4$



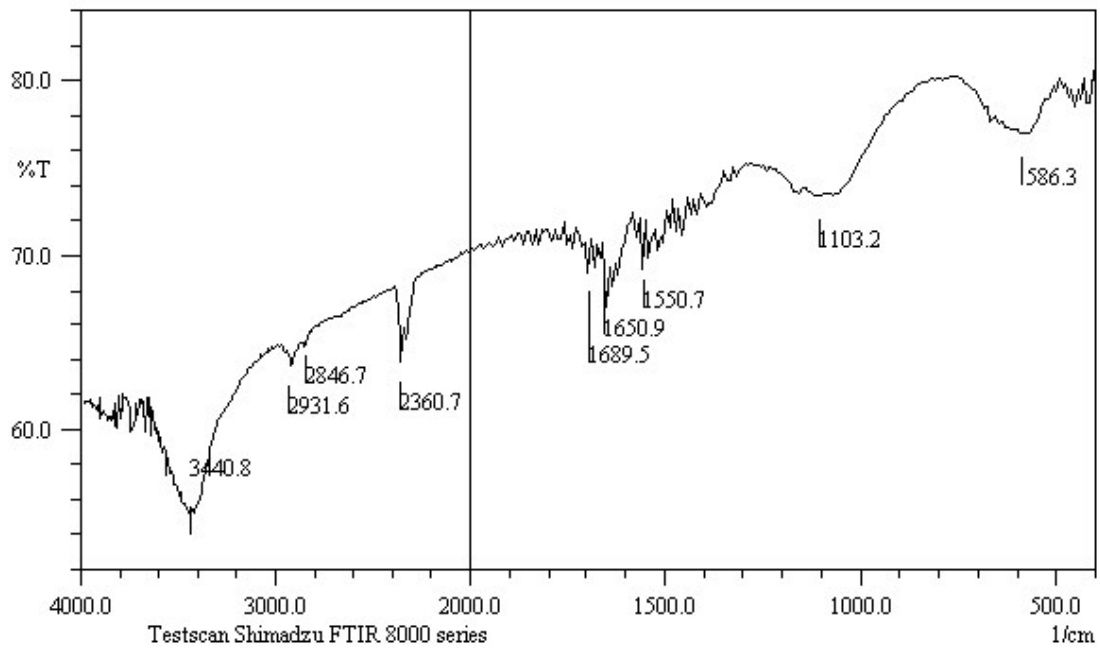
### FT-IR of $\text{Fe}_3\text{O}_4@\text{SiO}_2$



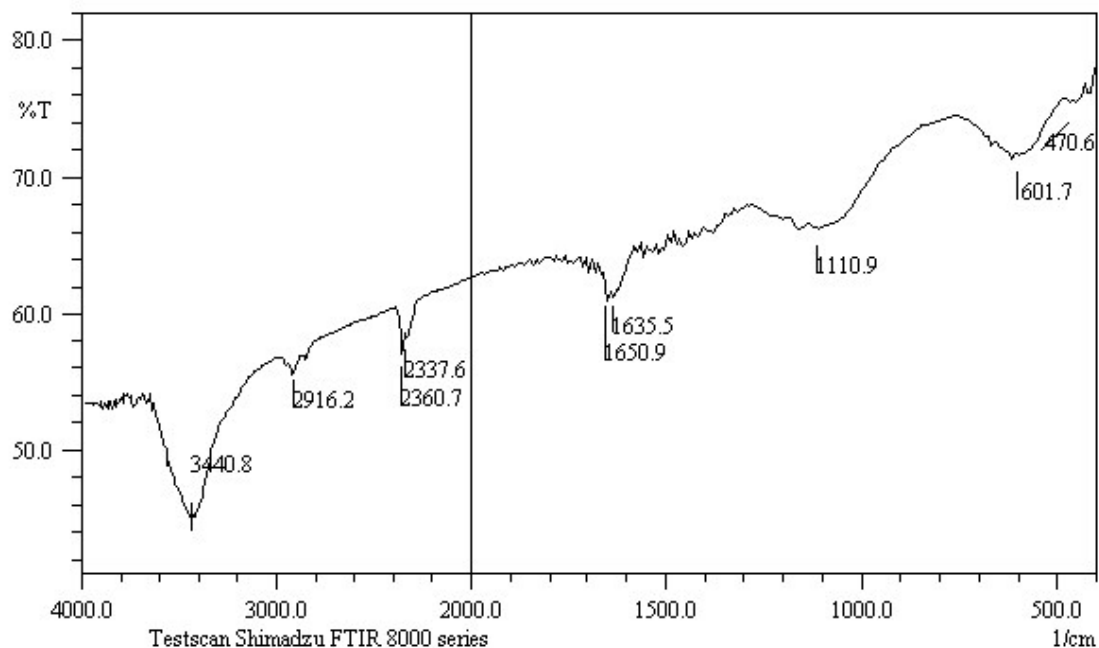
### FT-IR of VMNP



FT-IR of MNPO



## FT-IR of MNP-DMAP

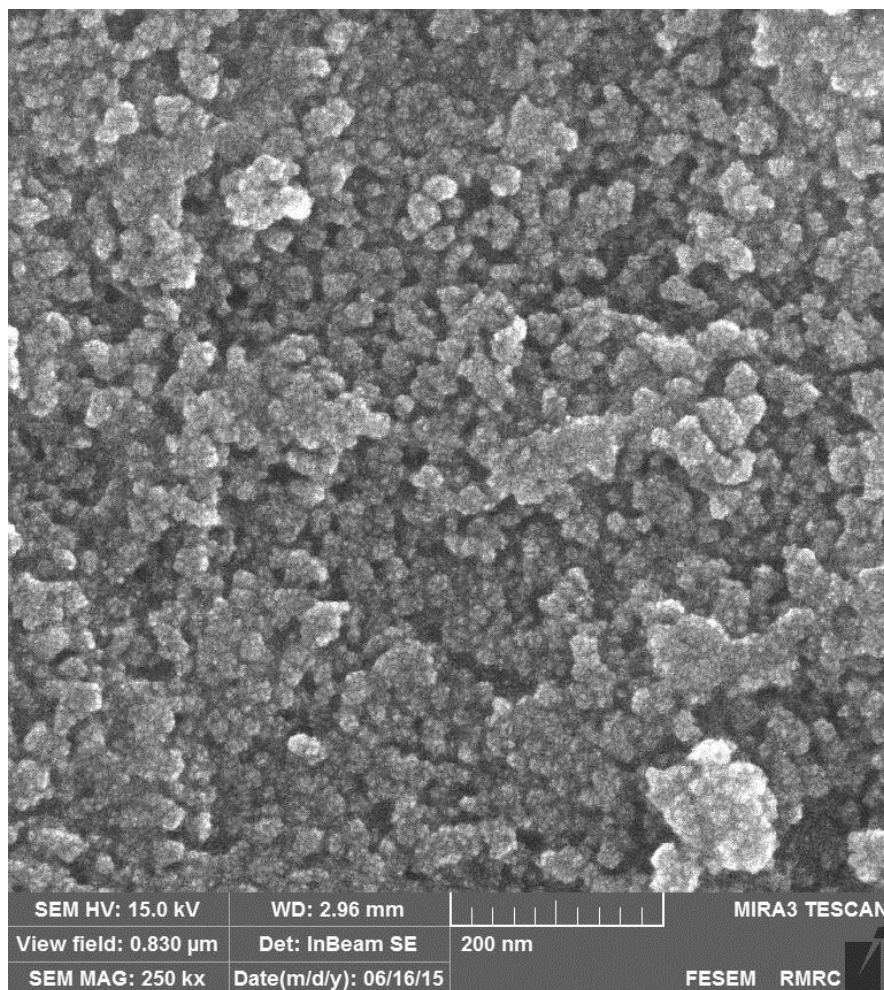


The peaks positioned at 586  $\text{cm}^{-1}$  is related to the formation of  $\text{Fe}_3\text{O}_4$  nanoparticles which is attributed to the Fe-O bonds. The FT-IR spectrum for the  $\text{Fe}_3\text{O}_4$  nanoparticles also shows a peak at 3441  $\text{cm}^{-1}$  which incorporates the contributions from both symmetrical and asymmetrical modes of the O-H bonds which are exist on the surface MNPs. The presence of an adsorbed water layer is confirmed by observation of peak at 1639  $\text{cm}^{-1}$ .

The  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles have stretches at 571, 1057, 1635 and 3410  $\text{cm}^{-1}$  which are refer to the Fe-O, Si-O-Si, and water stretches, respectively.

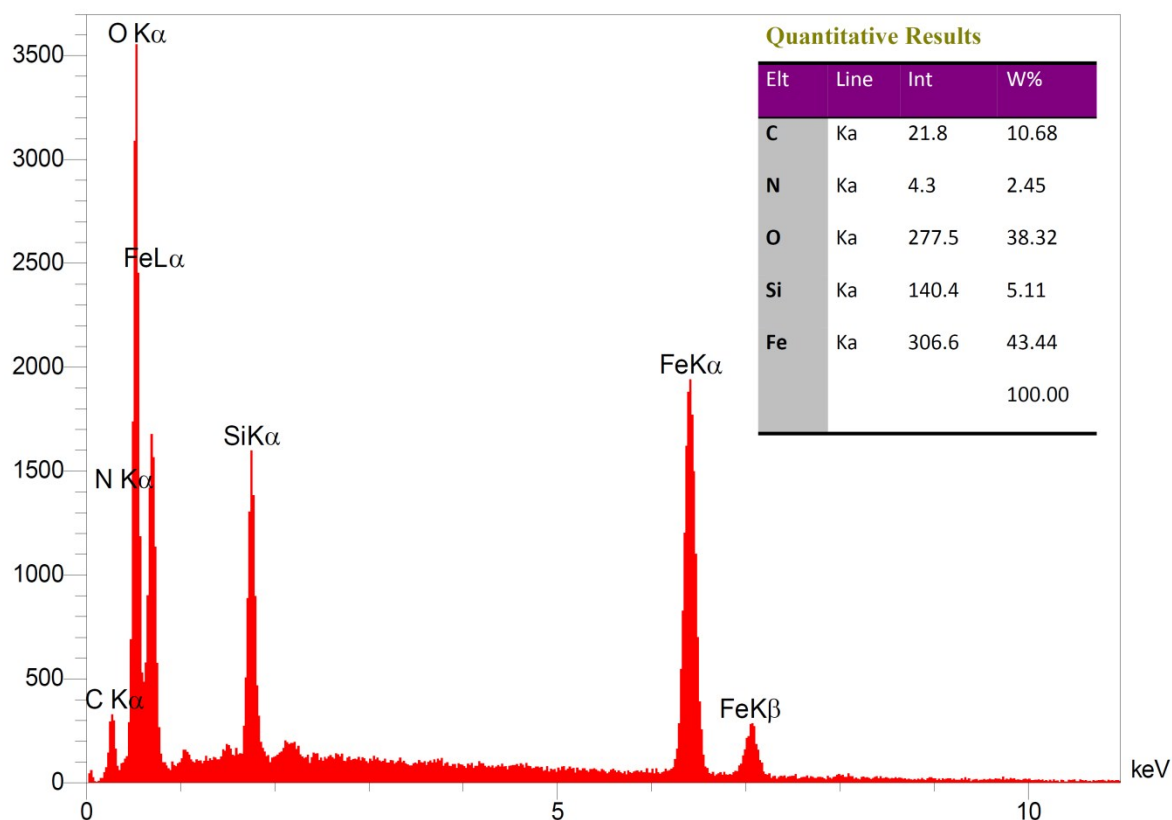
In the spectrum for the MNP-DMAP catalyst, in addition to assigned peaks some stretches are attributed to the presence of the DMAP on the surface of catalyst. Alkyl C-H stretches are found at 2916 and 2901  $\text{cm}^{-1}$ , while aromatic C-C stretches are observed between 1300 and 1500  $\text{cm}^{-1}$ .

## 2. SEM image from the surface of catalyst



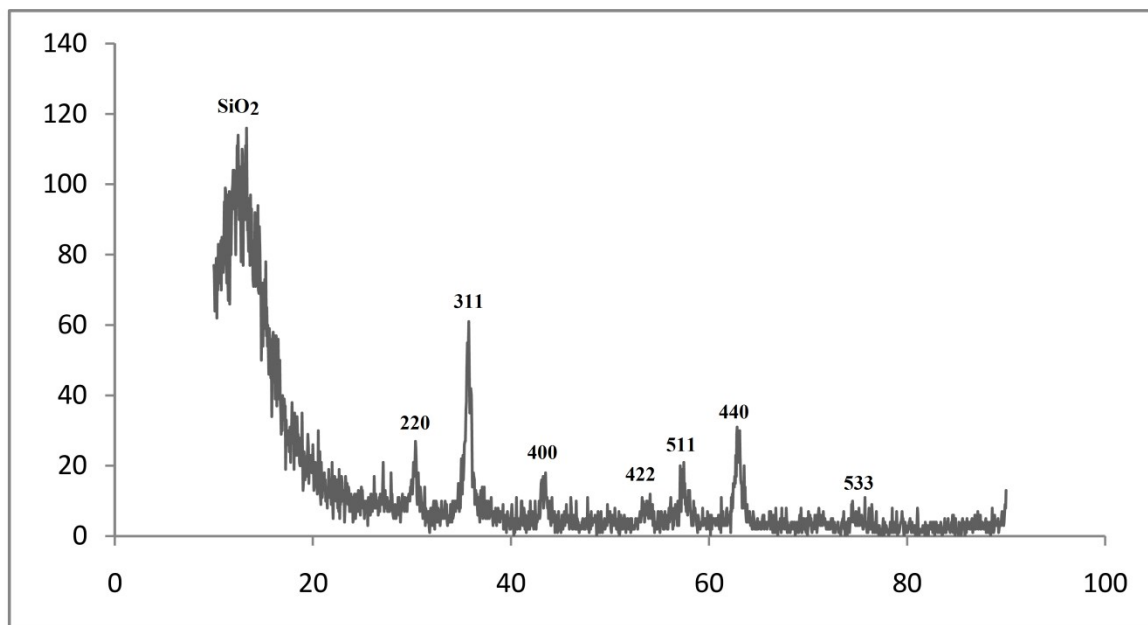
The surface morphology of the MNP-DMAP catalyst was investigated by scanning electron microscopy (SEM) and is shown in above.

### 3. EDX analysis



The energy-dispersive X-ray (EDX) spectra of the MNP-DMAP material (Fig. 4) show the elements C, N, O, Si, and Fe with wt% of 10.68, 2.45, 38.32, 5.11, and 43.44, respectively. According to the amount of 2.45% for N, it is possible to calculate the amount of the grafted DMAP on the surface of magnetic nanoparticles which is equal to 1.75 mmol per gram of the catalyst. Also the elemental analysis of the MNP-DMAP catalyst shows the presence of C, H and N atoms, which confirms the presence of DMAP on the magnetic nanoparticle surface. Also, based on the data obtained from elemental analysis, it can be concluded that there are about 1.81 mmol of DMAP per gram of material.

#### 4. XRD pattern of MNP-DMAP catalyst

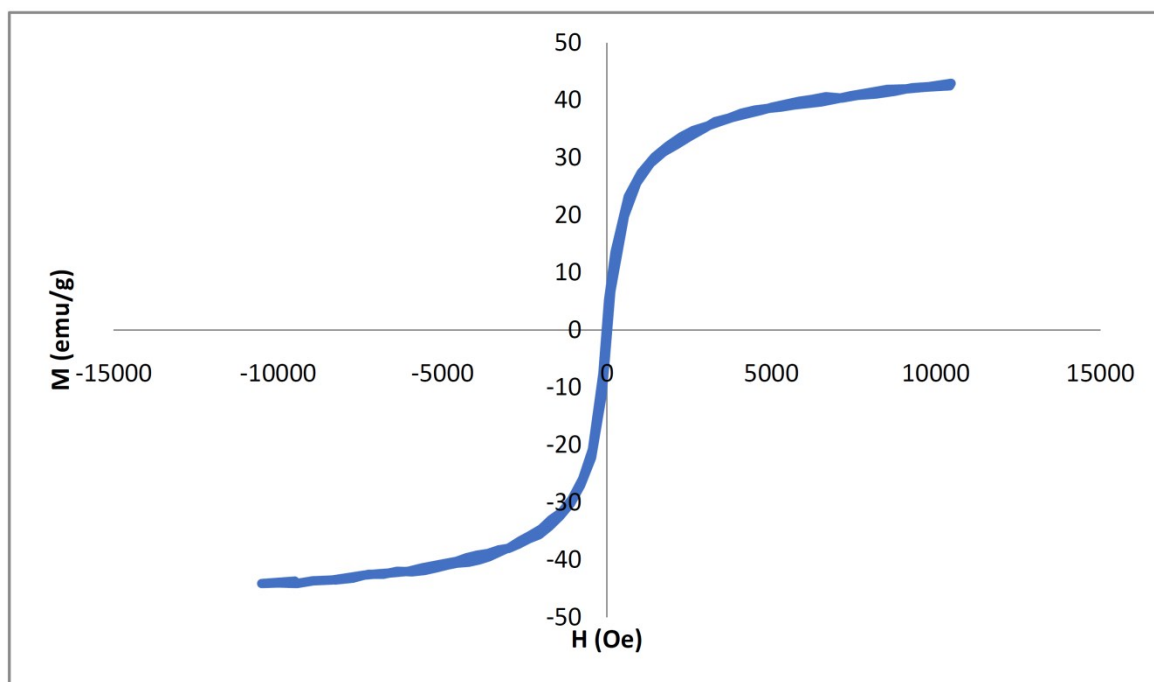


The XRD pattern of the MNP-DMAP catalyst also shows the presence of magnetic nanoparticles (Fig. 5). The peaks are indexed as the (220), (311), (400), (422), (511), (440) and (533) planes of the  $\text{Fe}_3\text{O}_4$  nanoparticles (JCPDS no. 19-0629).<sup>1</sup> The strongest peak of the XRD pattern match to  $\text{SiO}_2$ , representing the core-shell structure of the catalyst.

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<sup>1</sup> - A. Khalafi-Nezhad, M. Nourisefat and F. Panahi, *Org. Biomol. Chem.* 2015, **13**, 7772–7779;

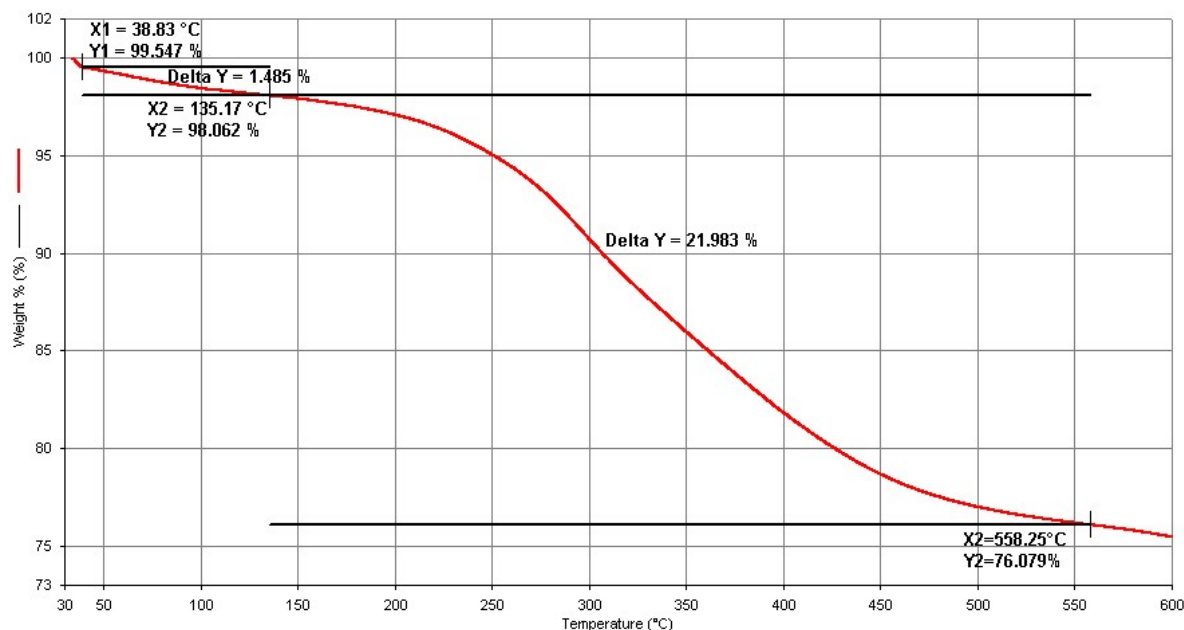
## 5. VSM analysis



The magnetic properties of the catalyst were explored at room temperature using a vibrating sample magnetometer (VSM). Based on the magnetization curve, the magnetization is saturated up to 44 emu g<sup>-1</sup> at an applied field of 10500 Oe, with an almost unimportant coercivity.



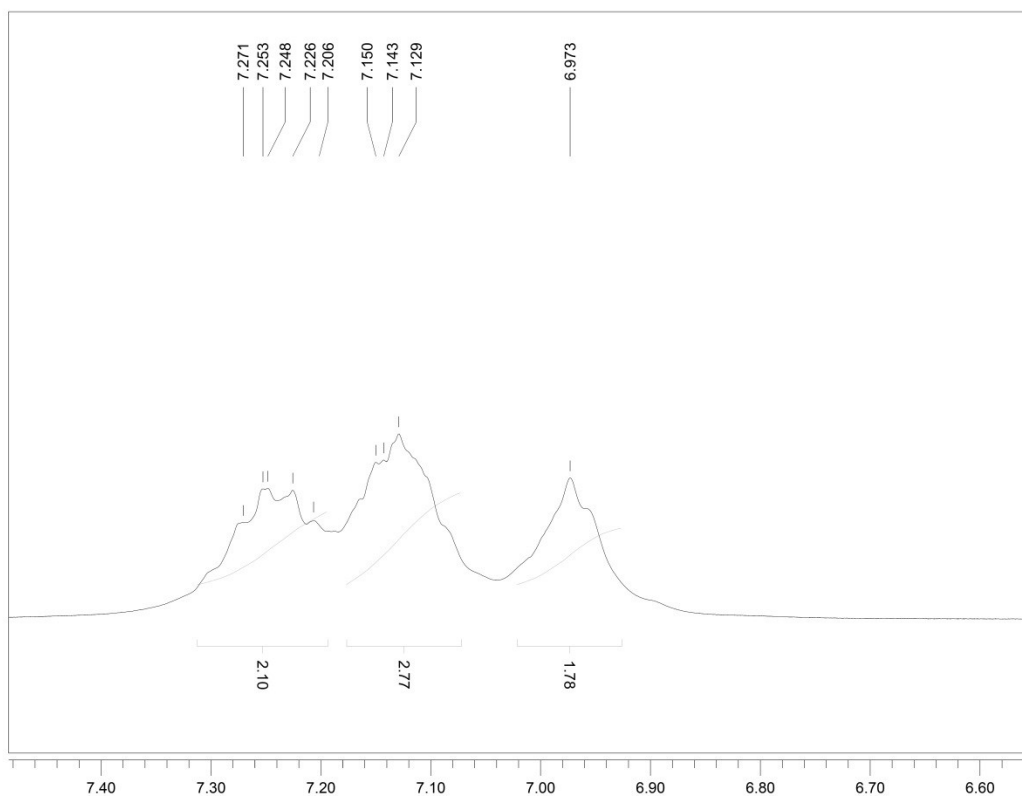
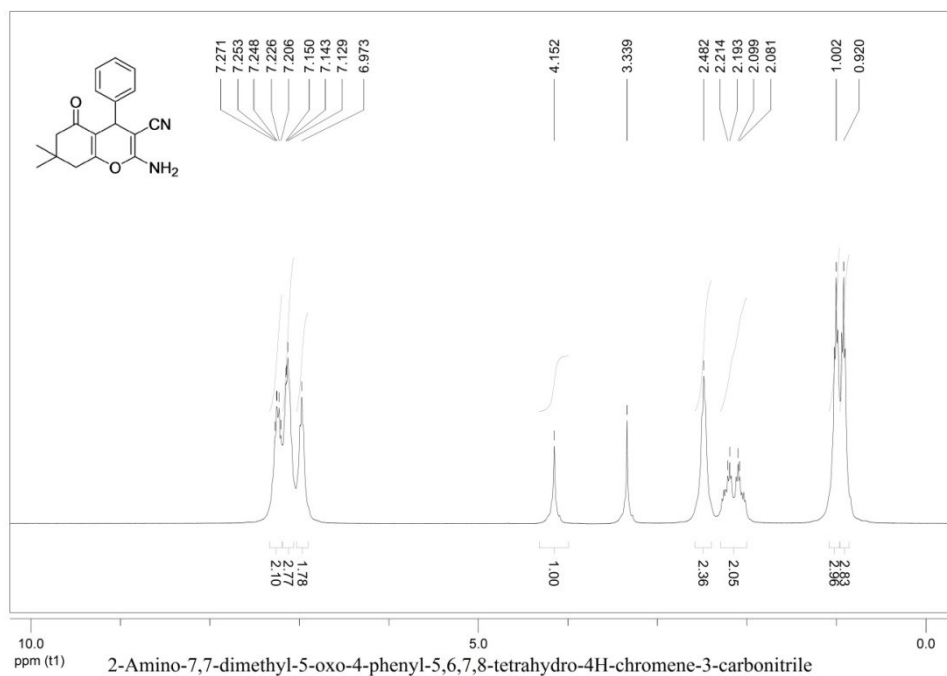
## 6. TGA analysis

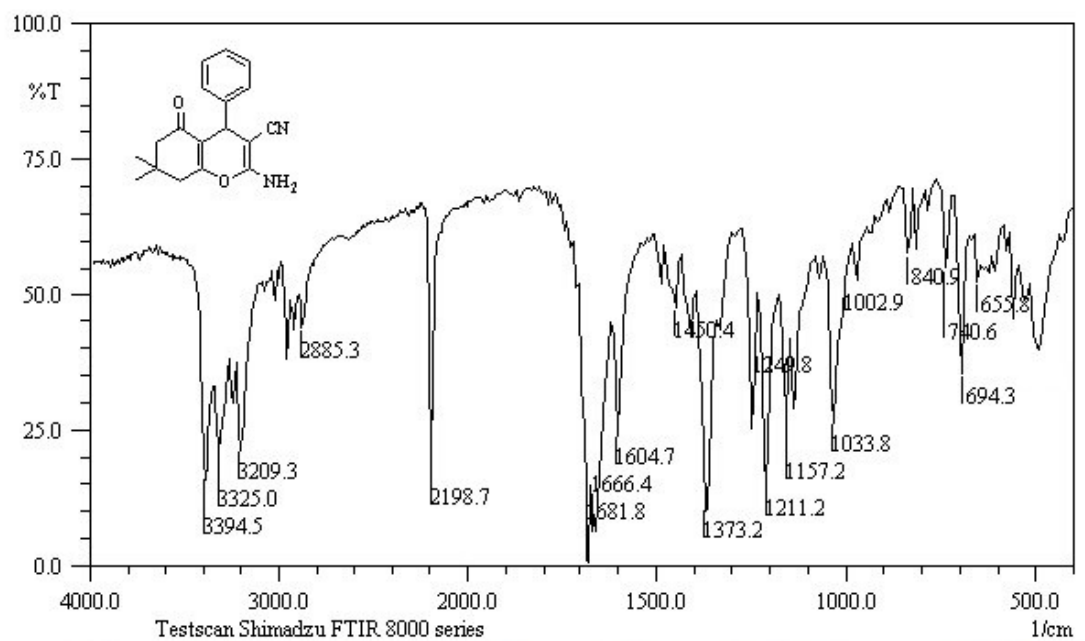
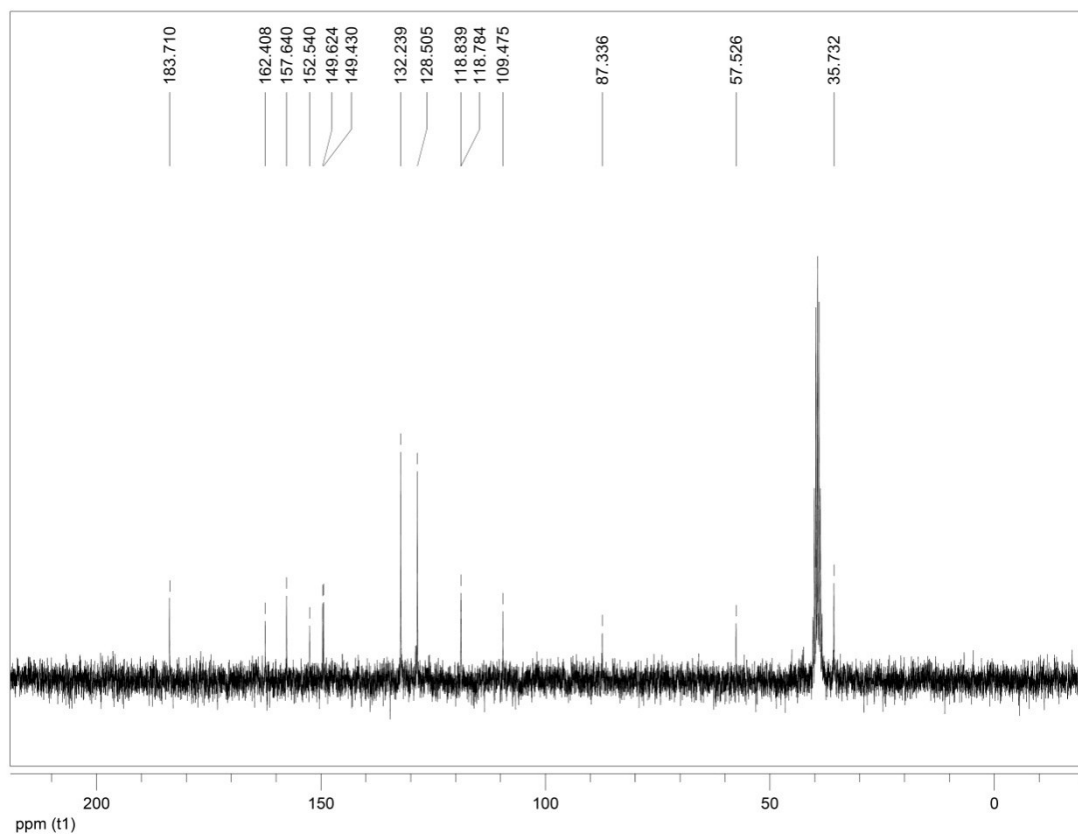


The thermal gravimetric analysis (TGA) curve of the MNP-DMAP substrates show a ~22% weight loss (150-308 °C) which this is due to the loss of the grafted organic layer. Considering the molecular weight of grafted organic moiety to magnetic nanoparticles (~151.2 g/mol) it is possible to calculate the amount of grafted DMAP on magnetic nanoparticle surface. This result is also in good agreement with the amount of grafted DMAP on the magnetic nanoparticle surface according to the EDX analysis.

# Copy of <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR of synthesized compounds

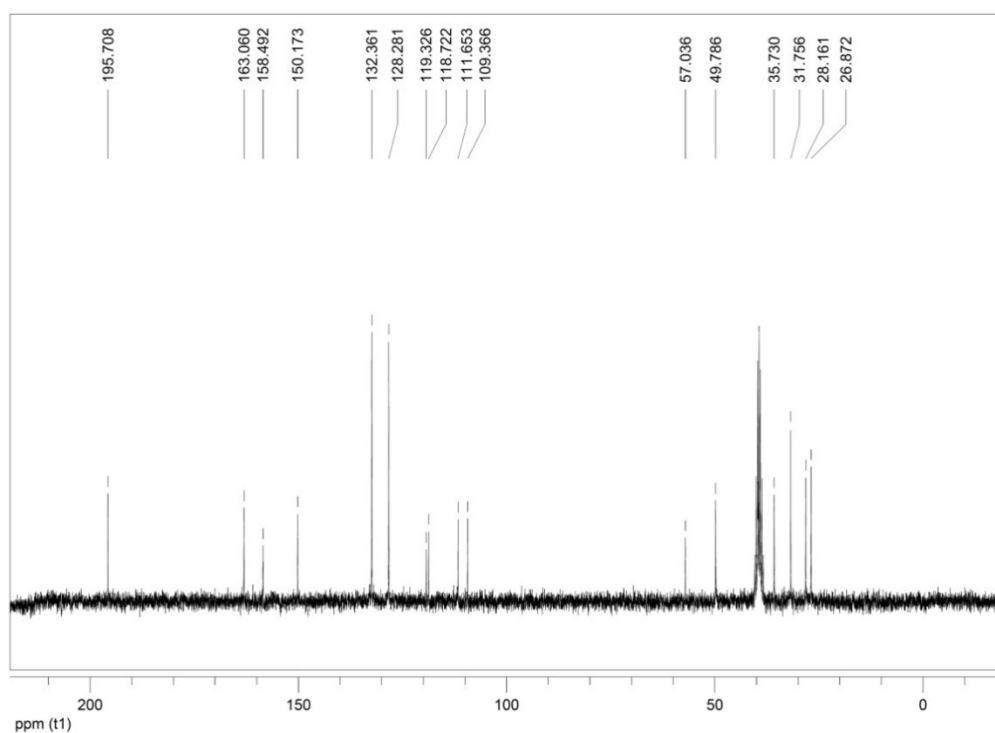
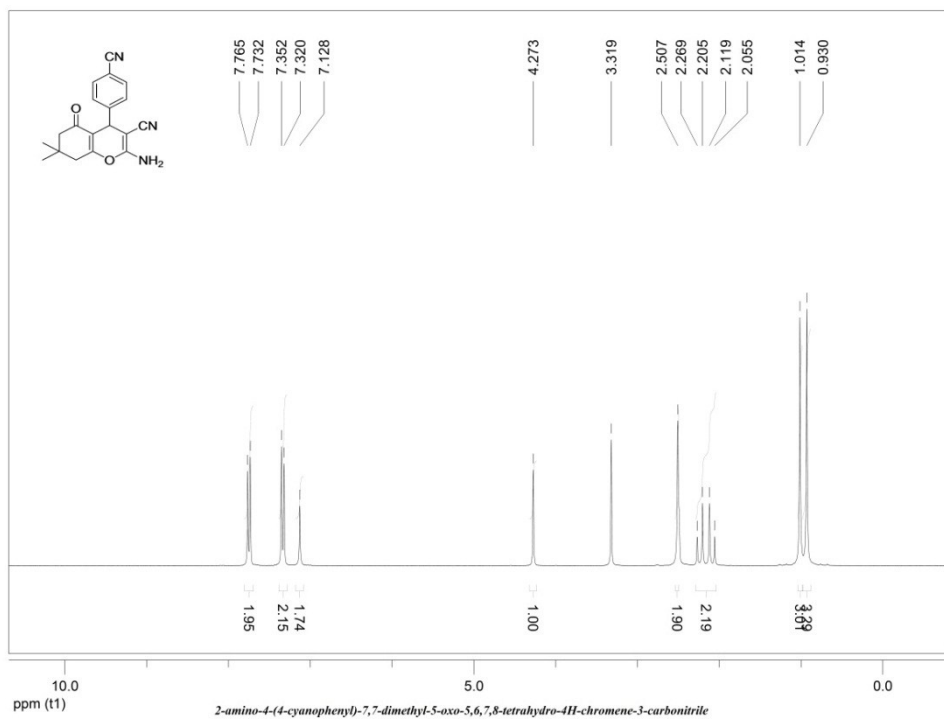
## 1. 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4a)

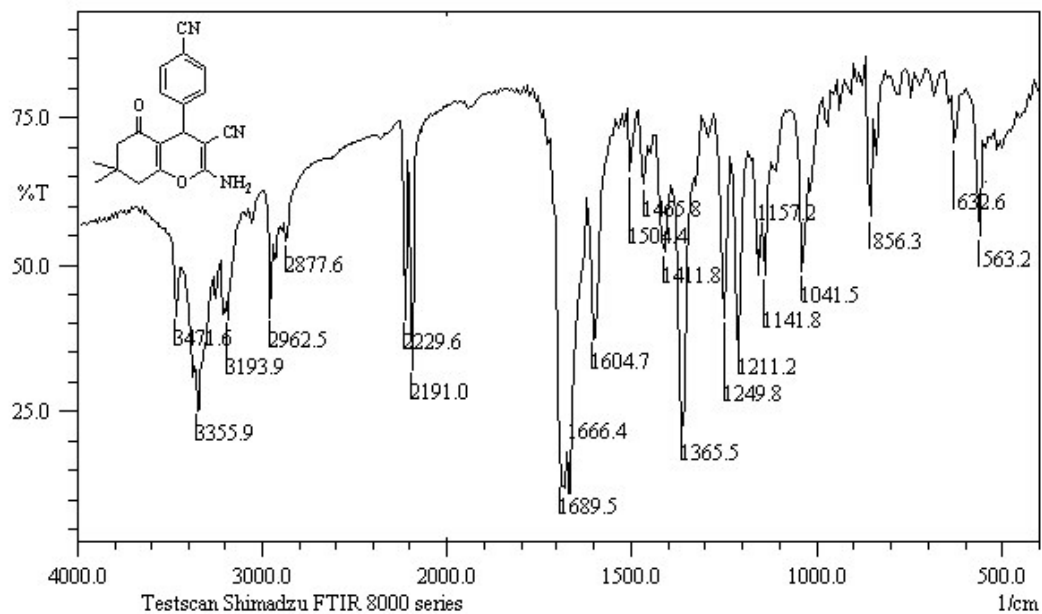




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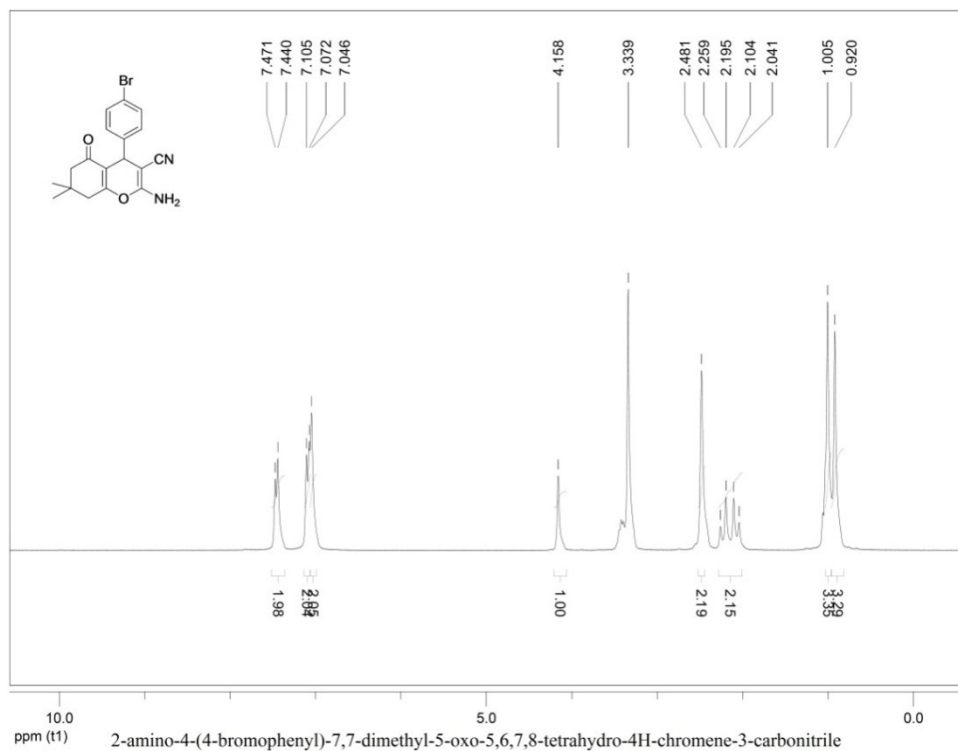
**2. 2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4b)**

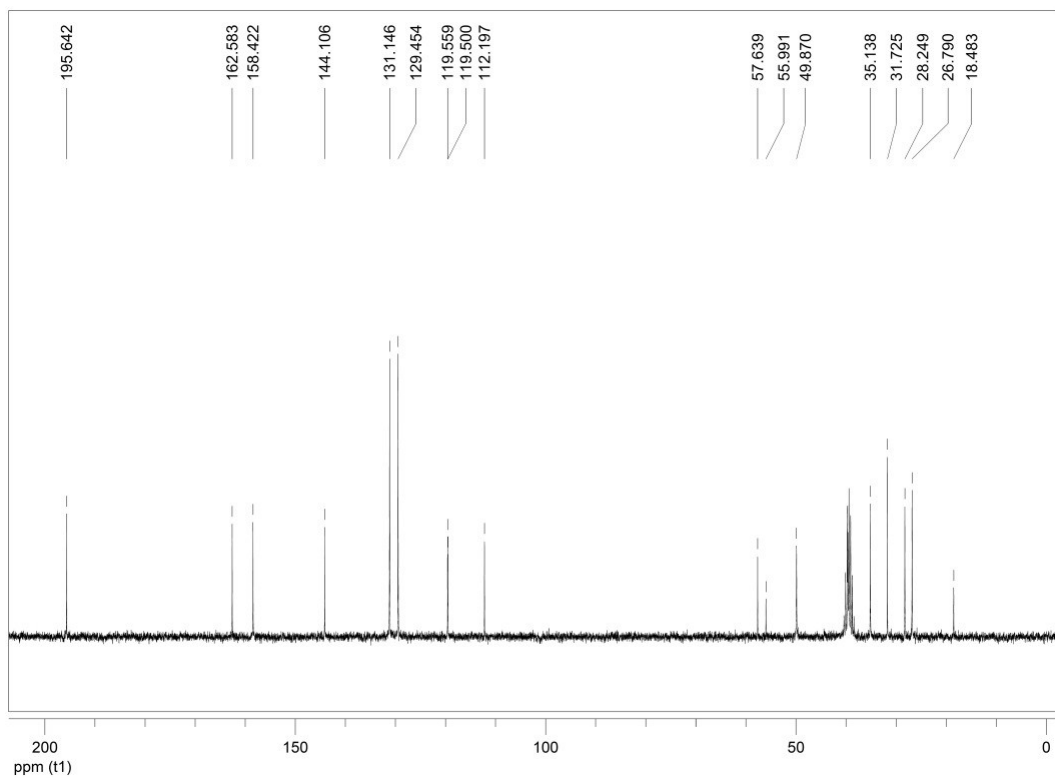
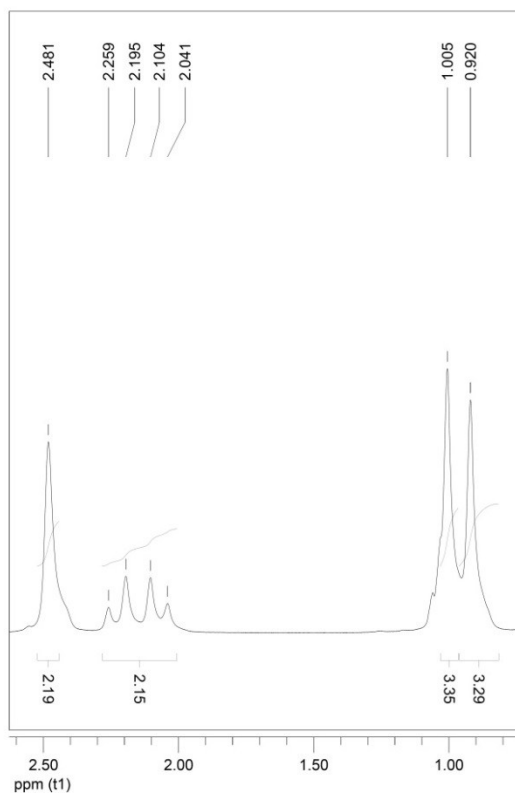
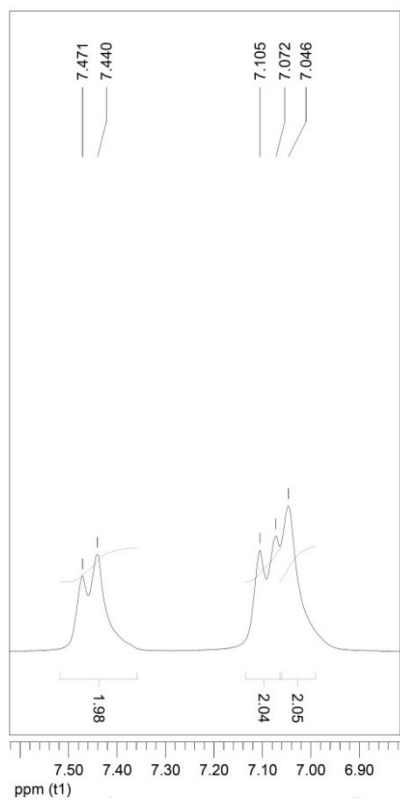


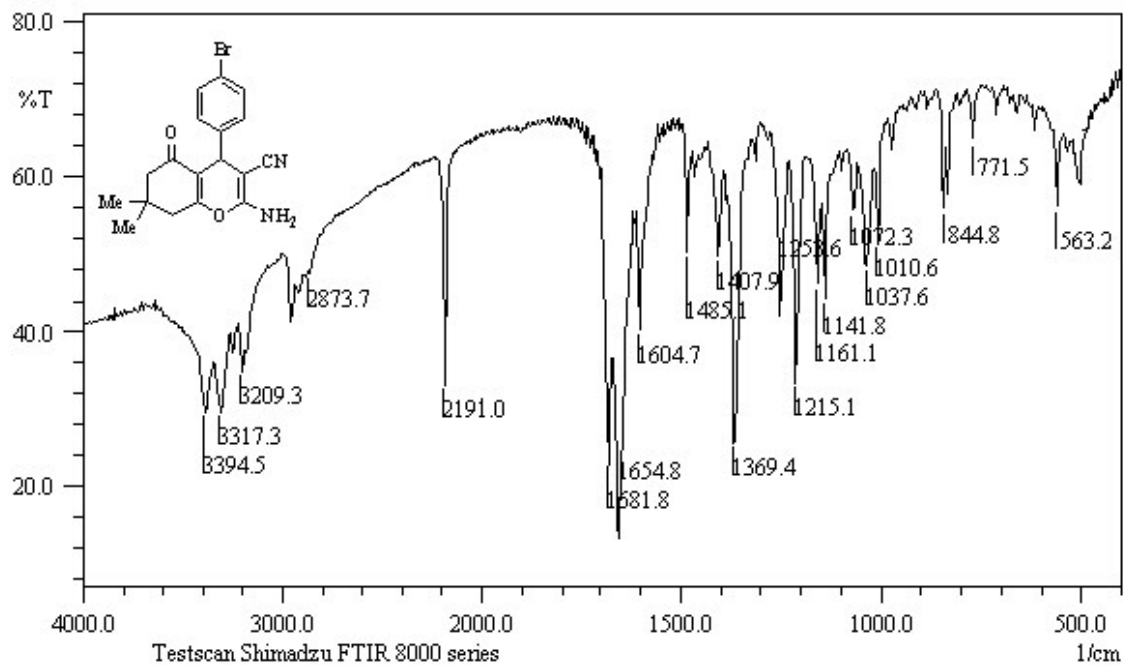


2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

### 3. 2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4c)

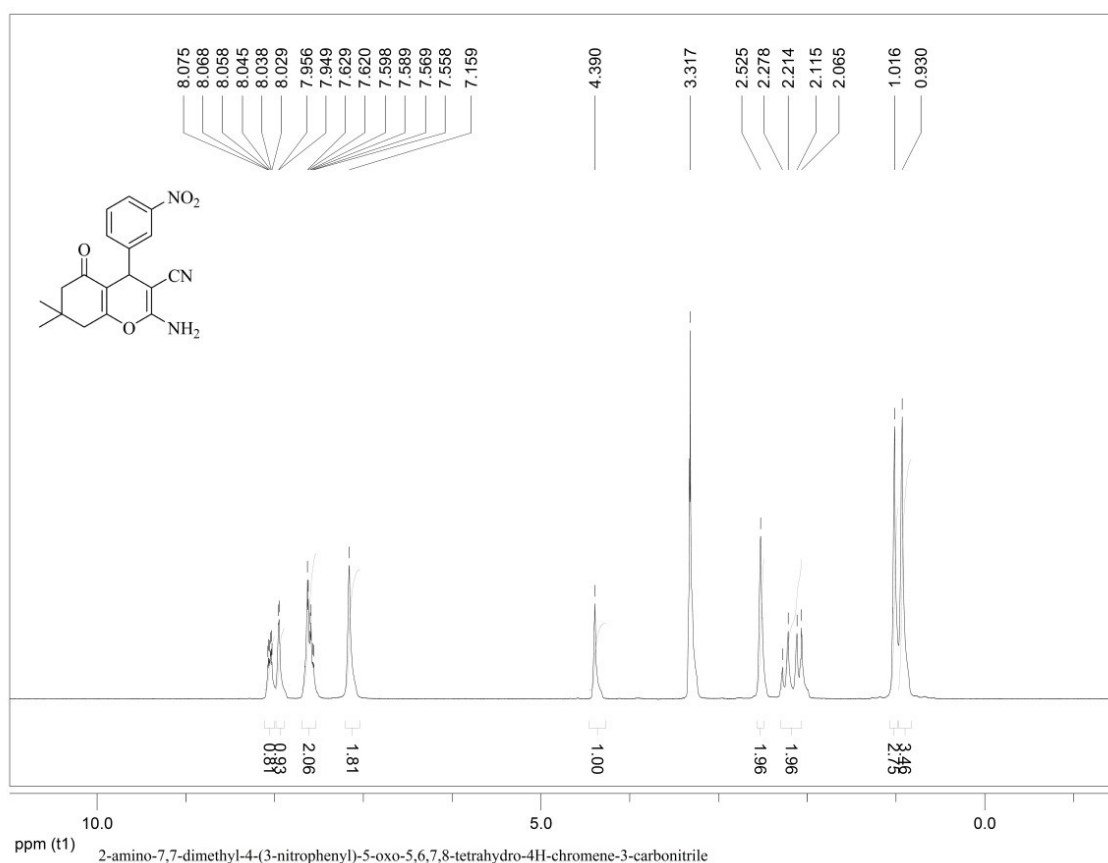


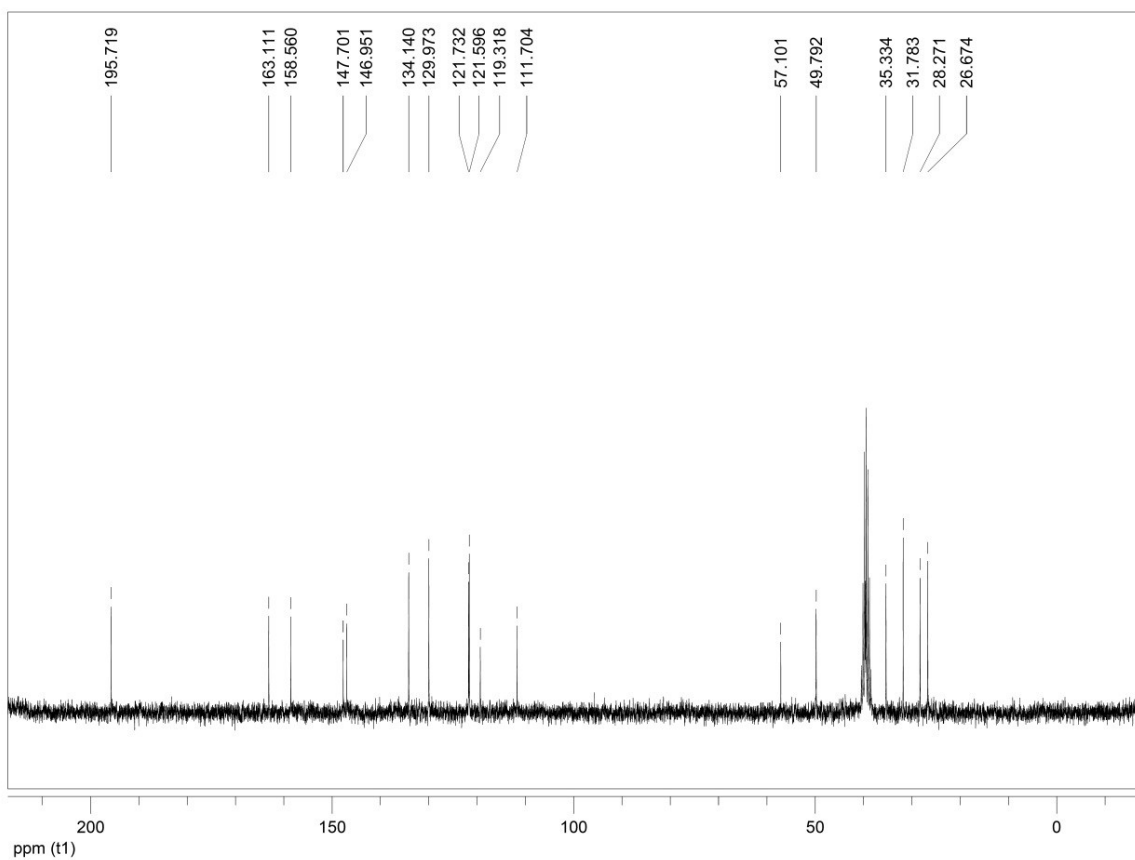
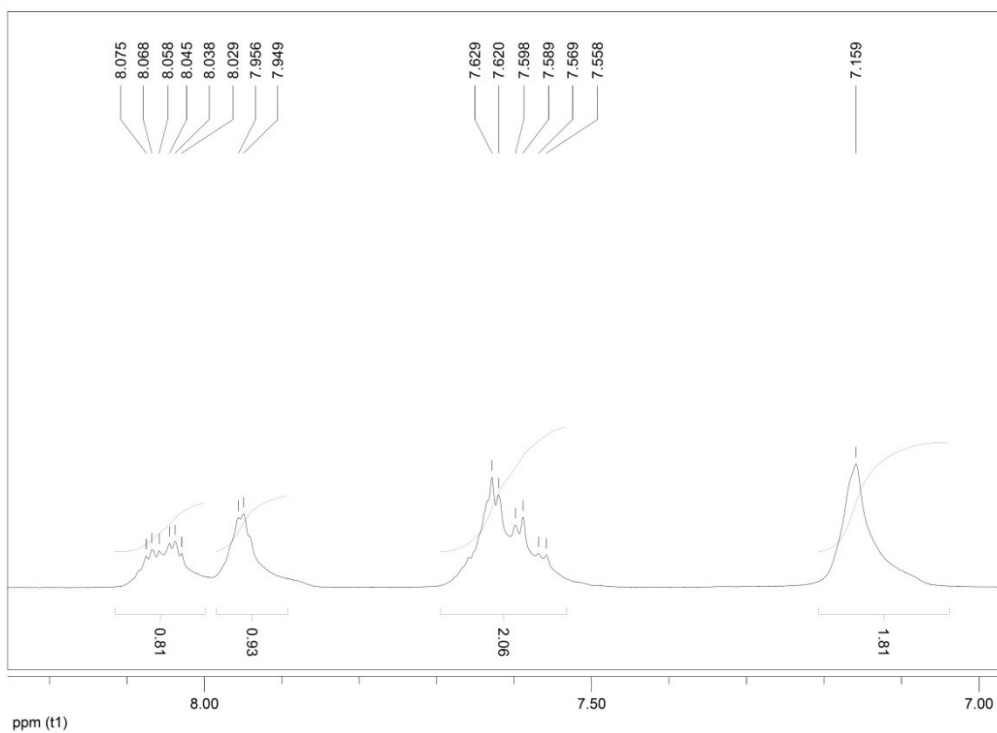




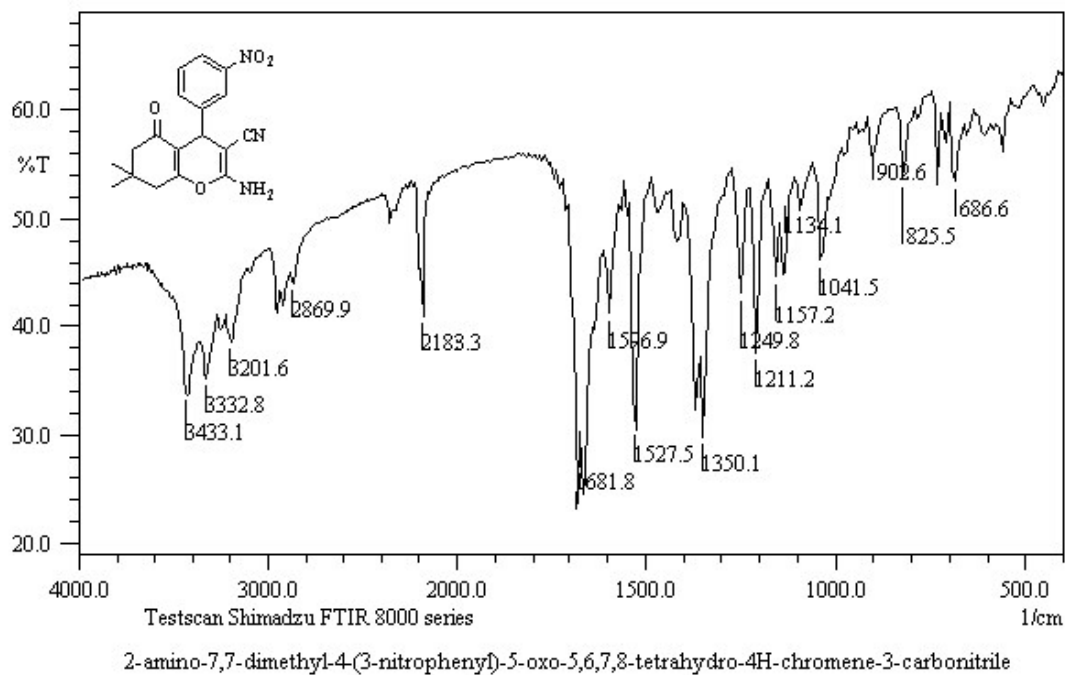
2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

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

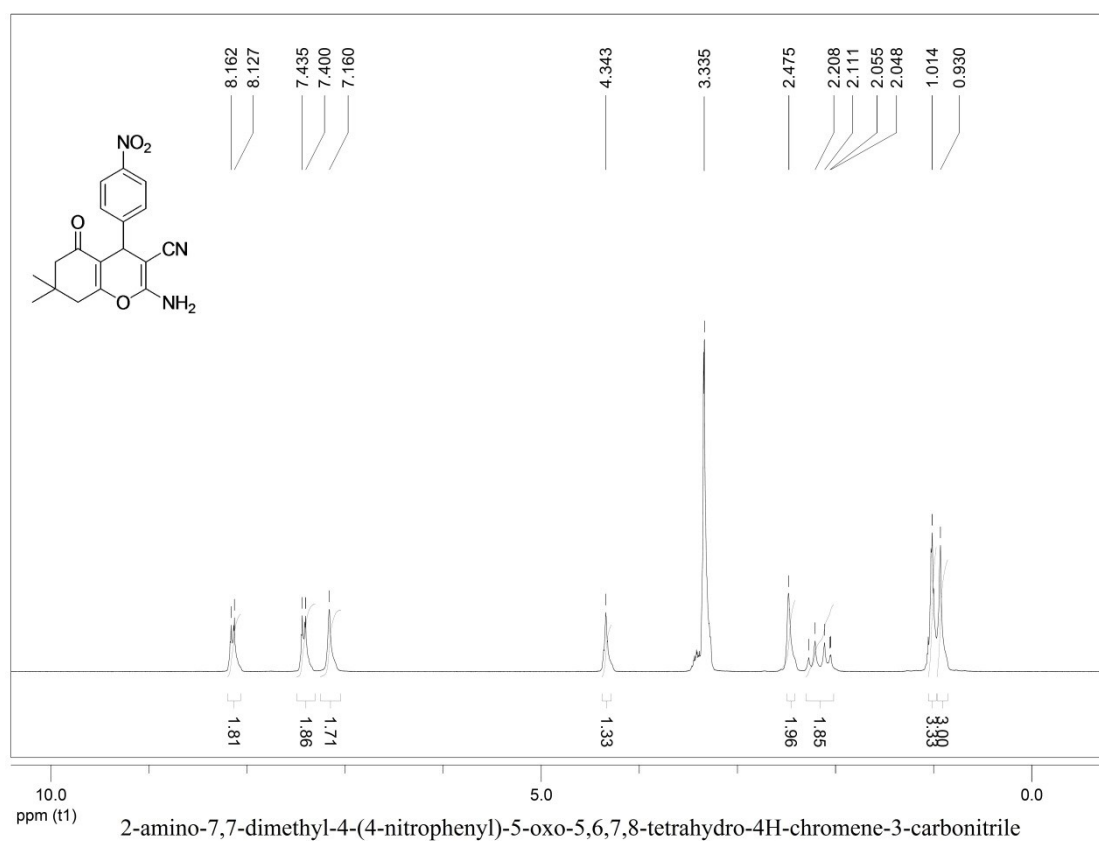


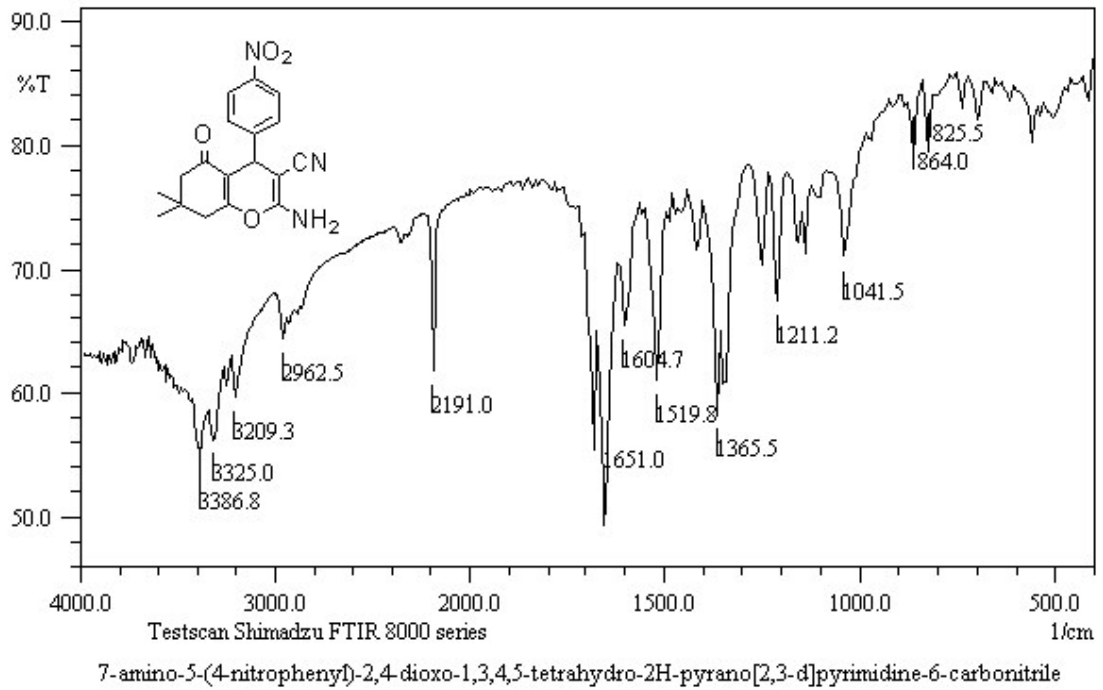
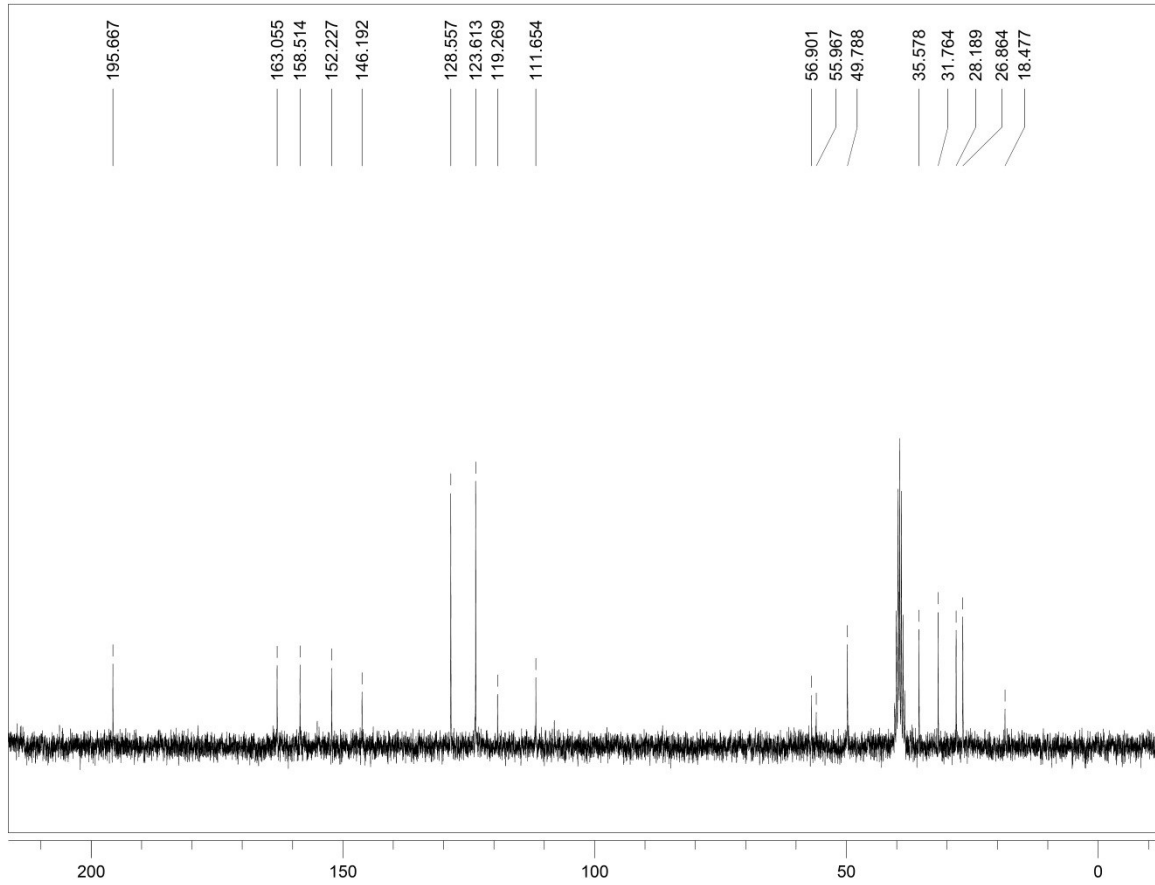




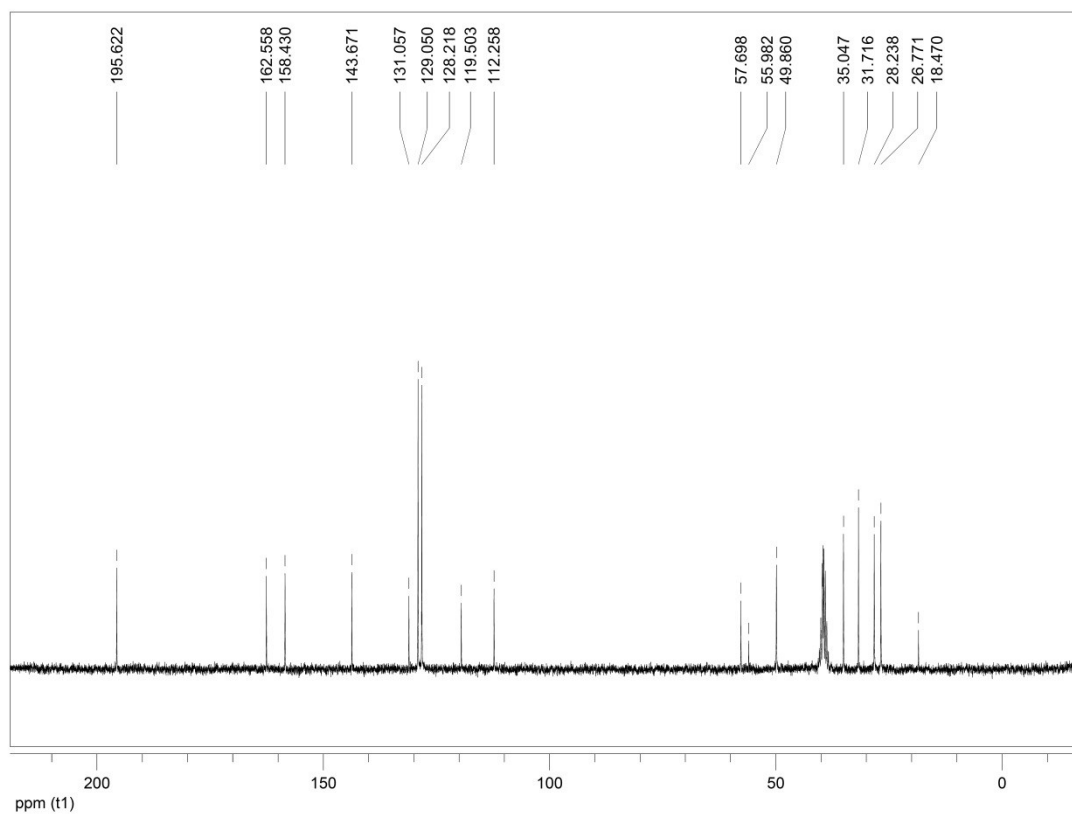
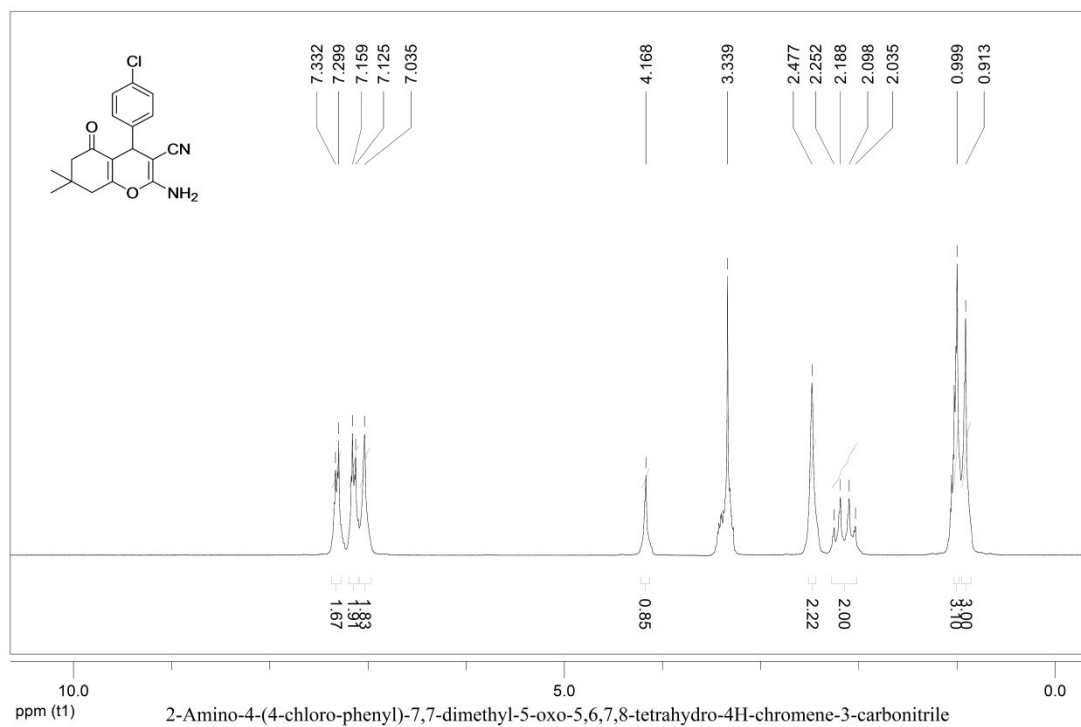


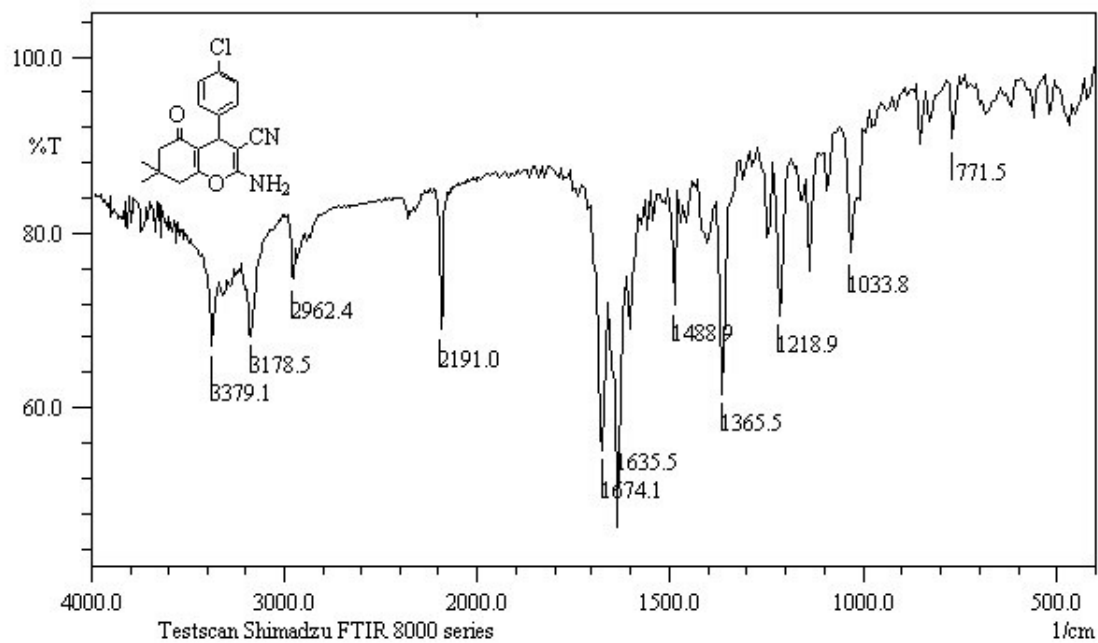
**5. 2-amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4e)**





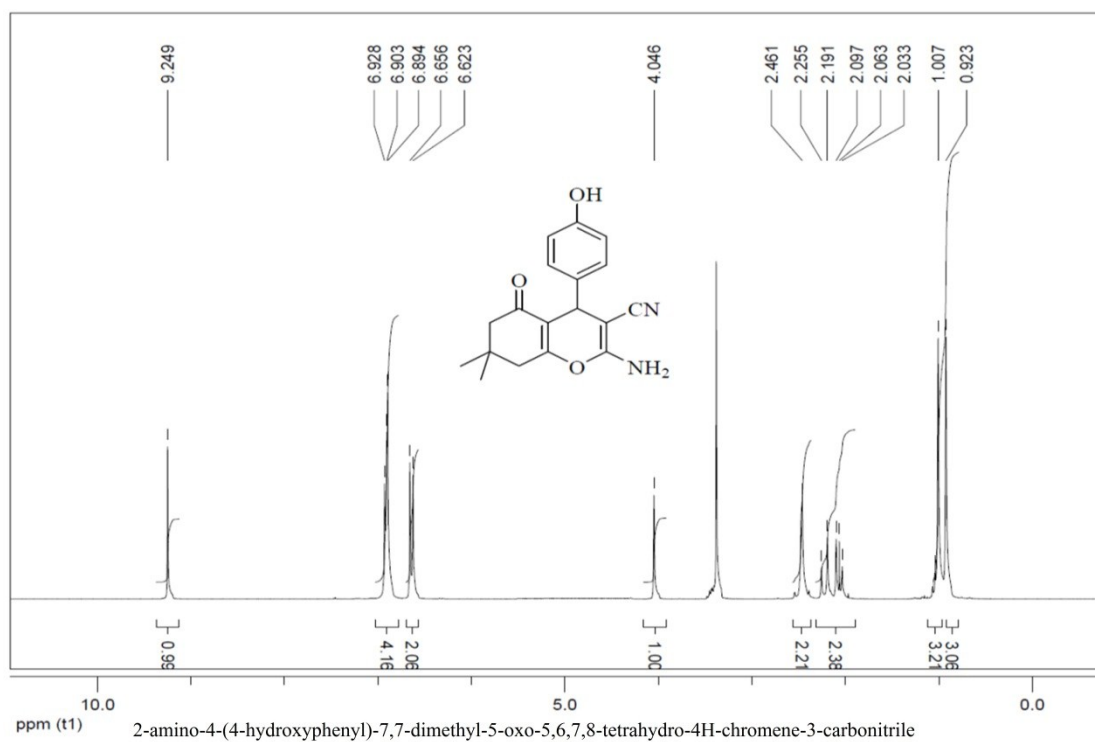
## 6. 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4f)

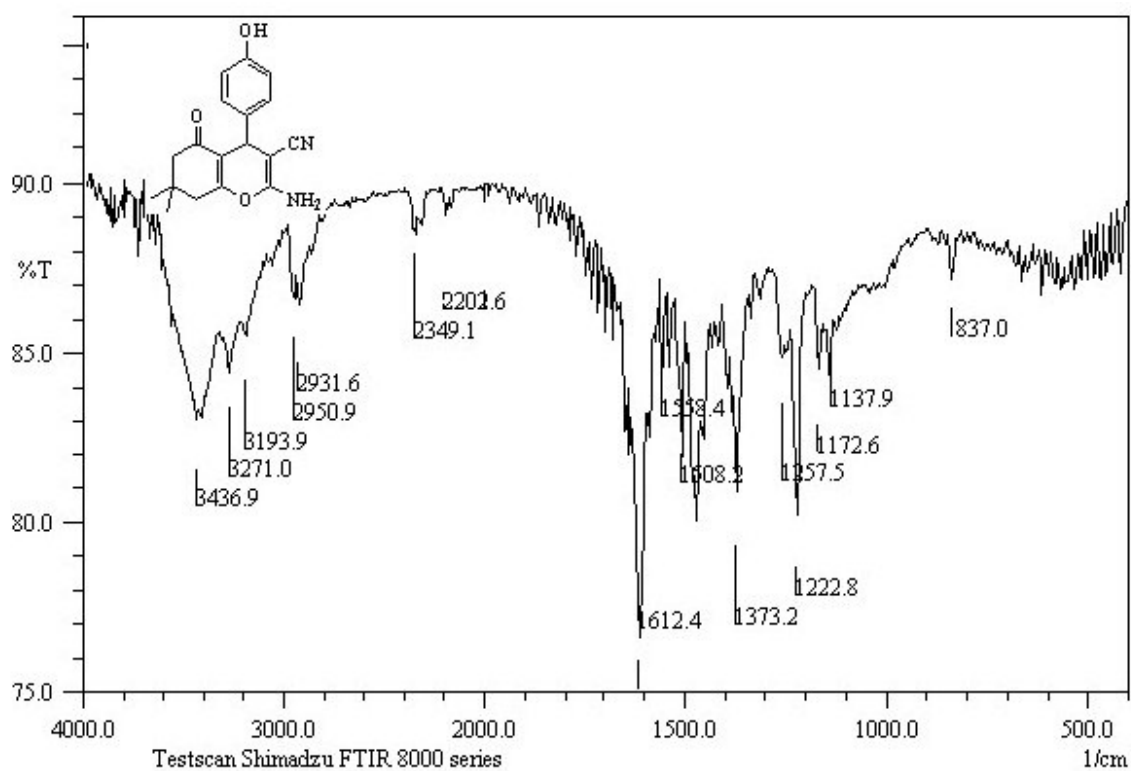
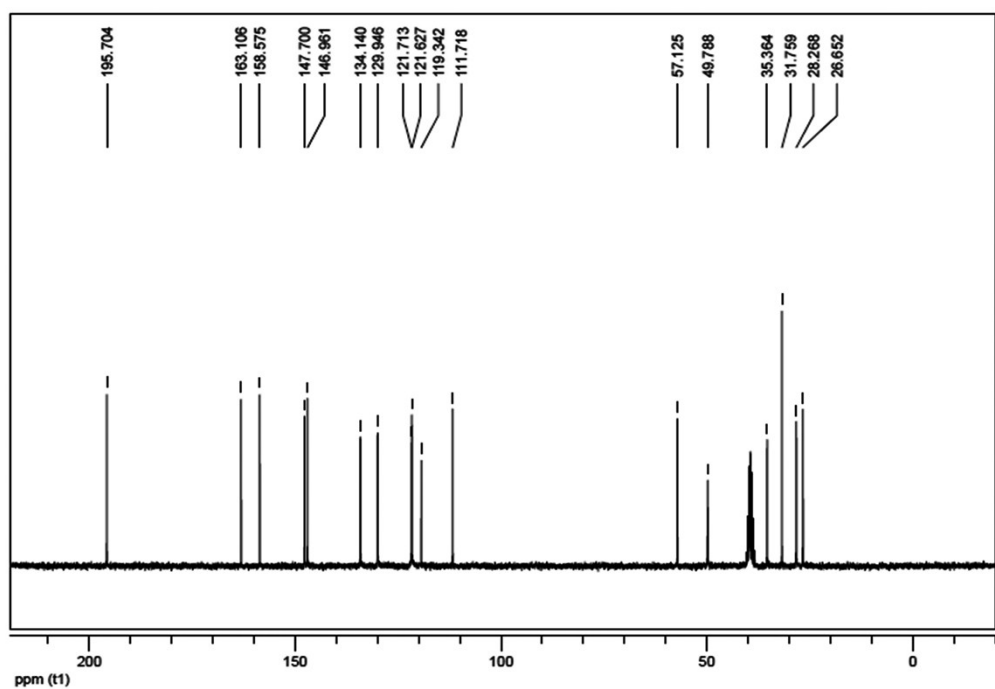




2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

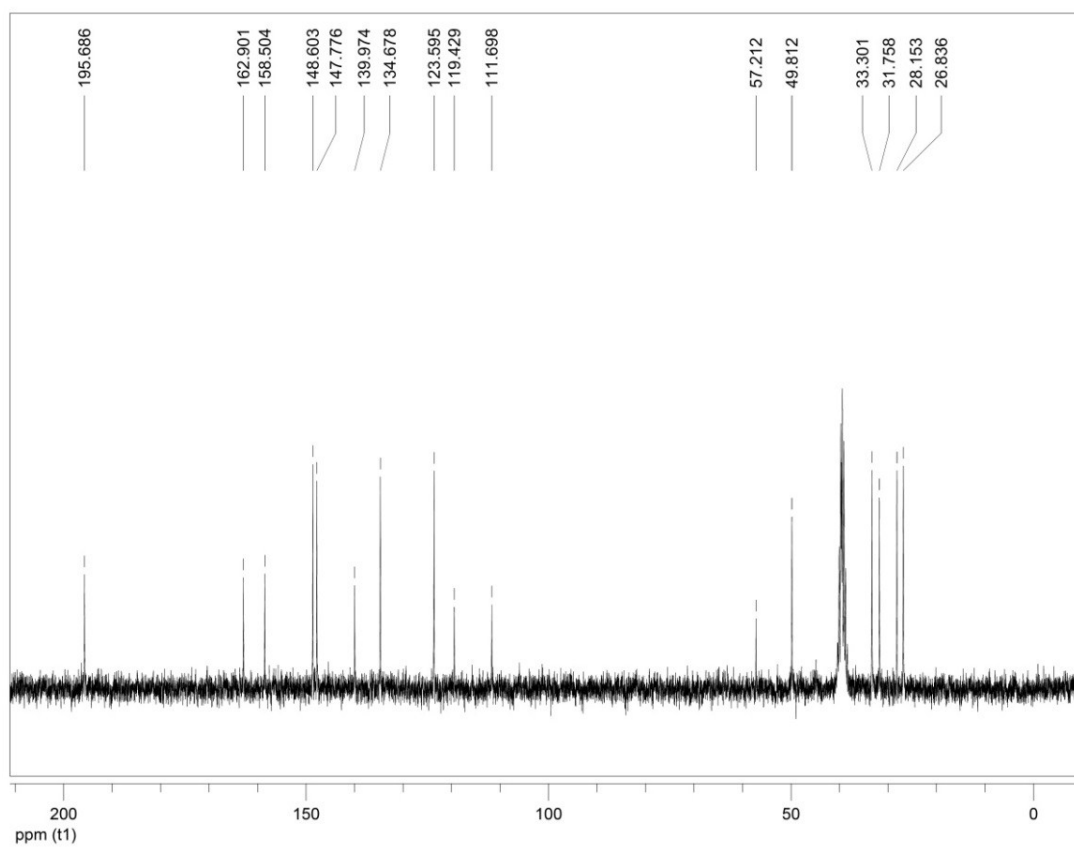
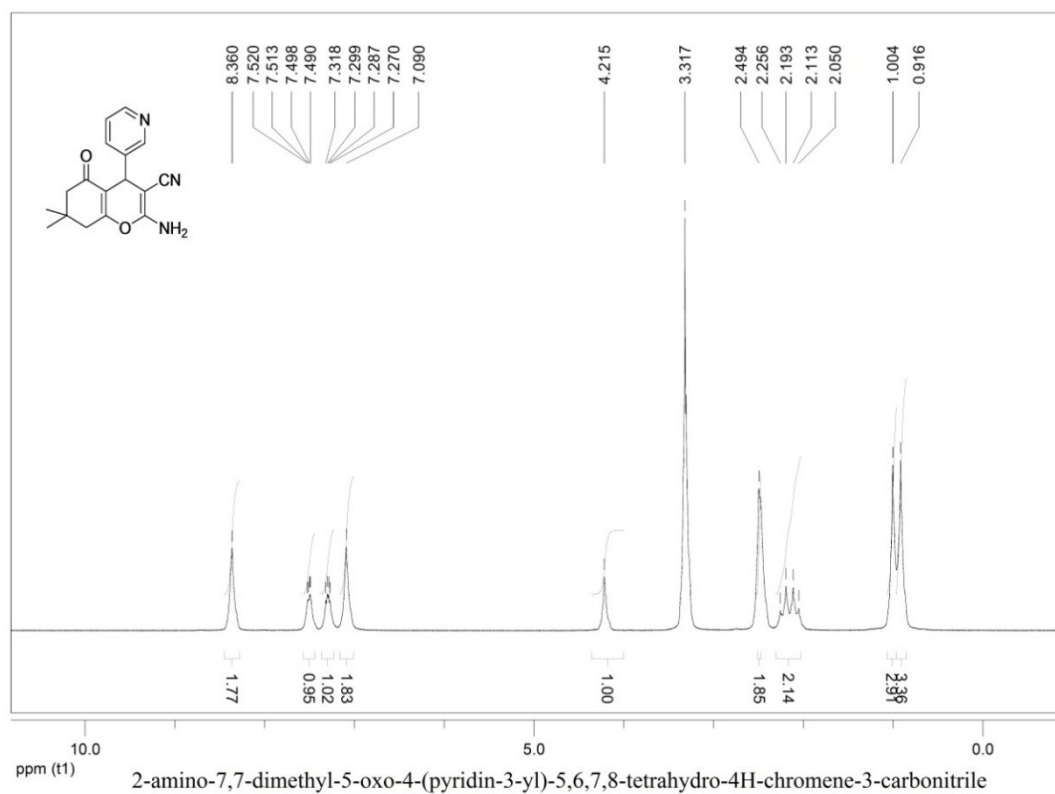
**7. 2-Amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4g)**

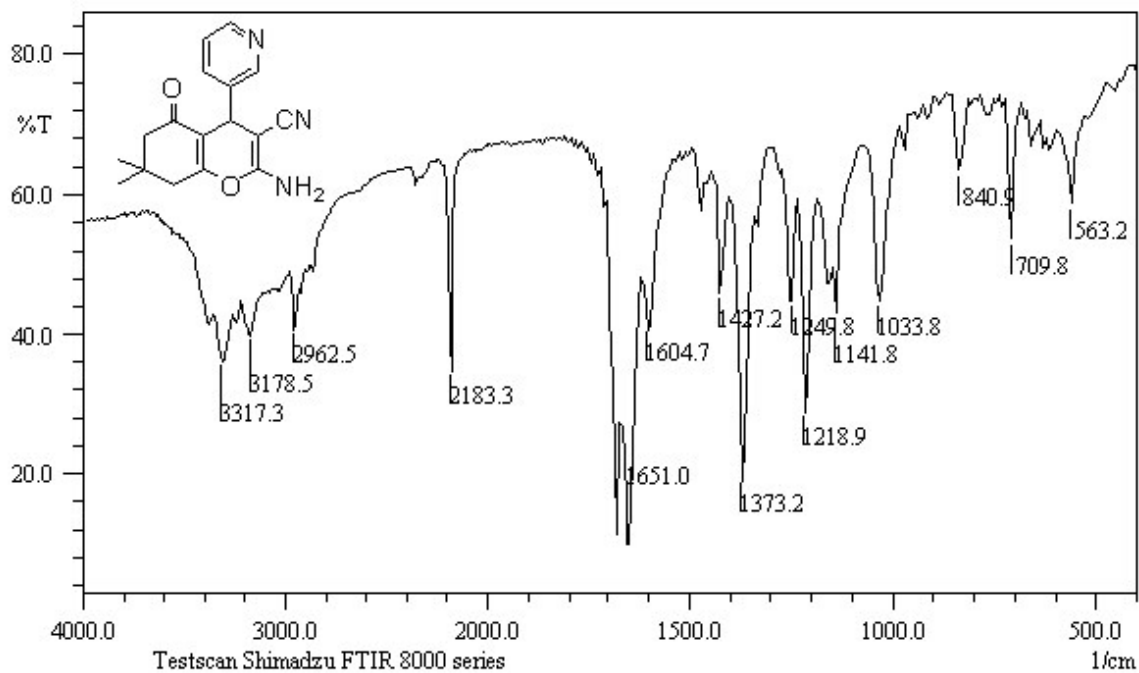




2-amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

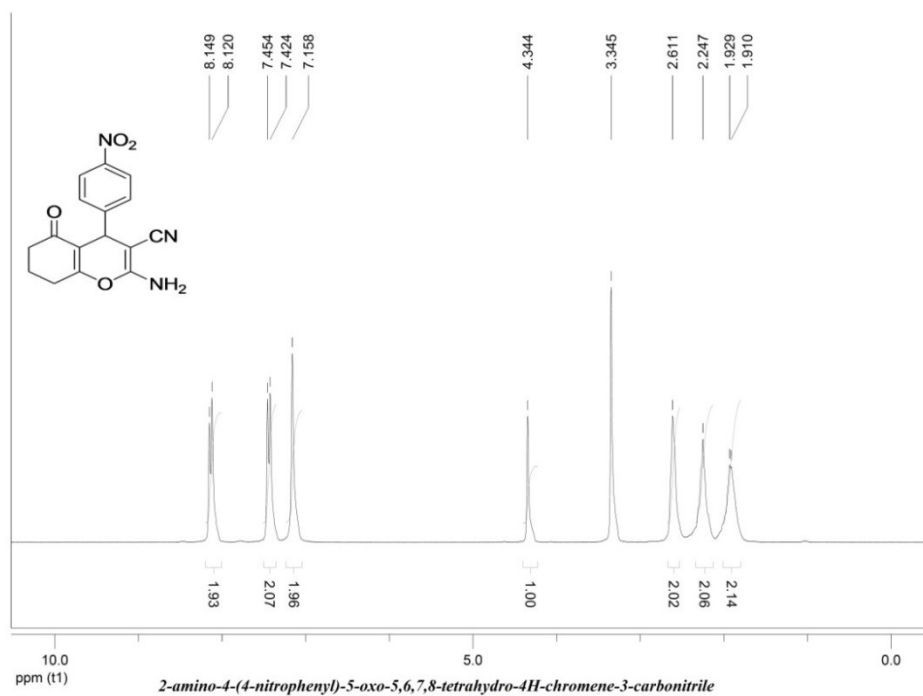
**8. 2-amino-7,7-dimethyl-5-oxo-4-(pyridin-3-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4h)**

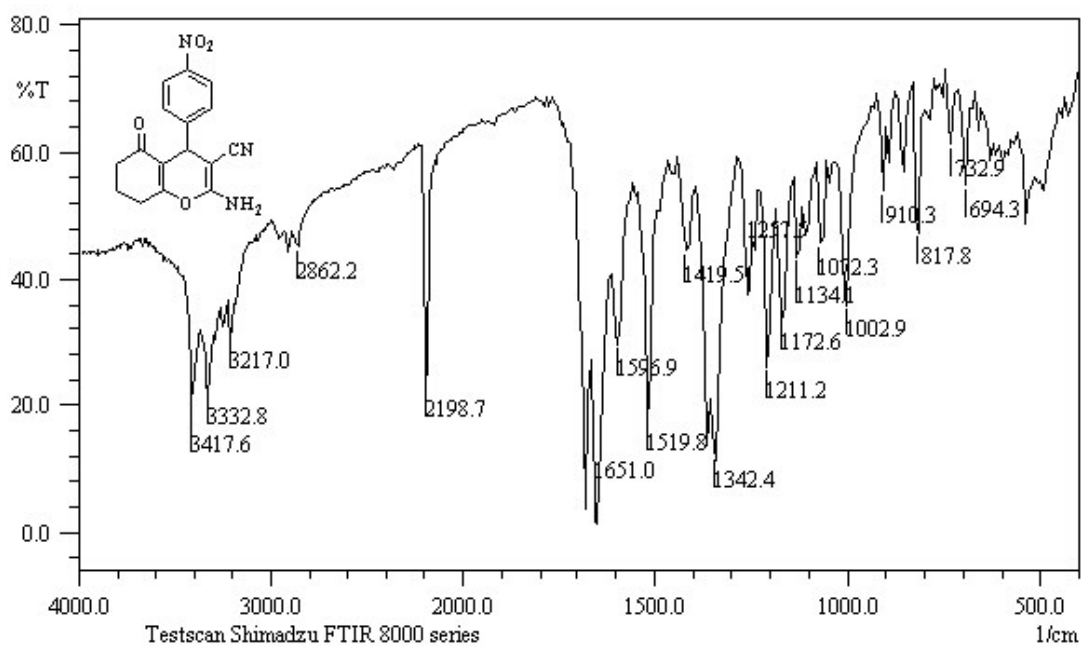
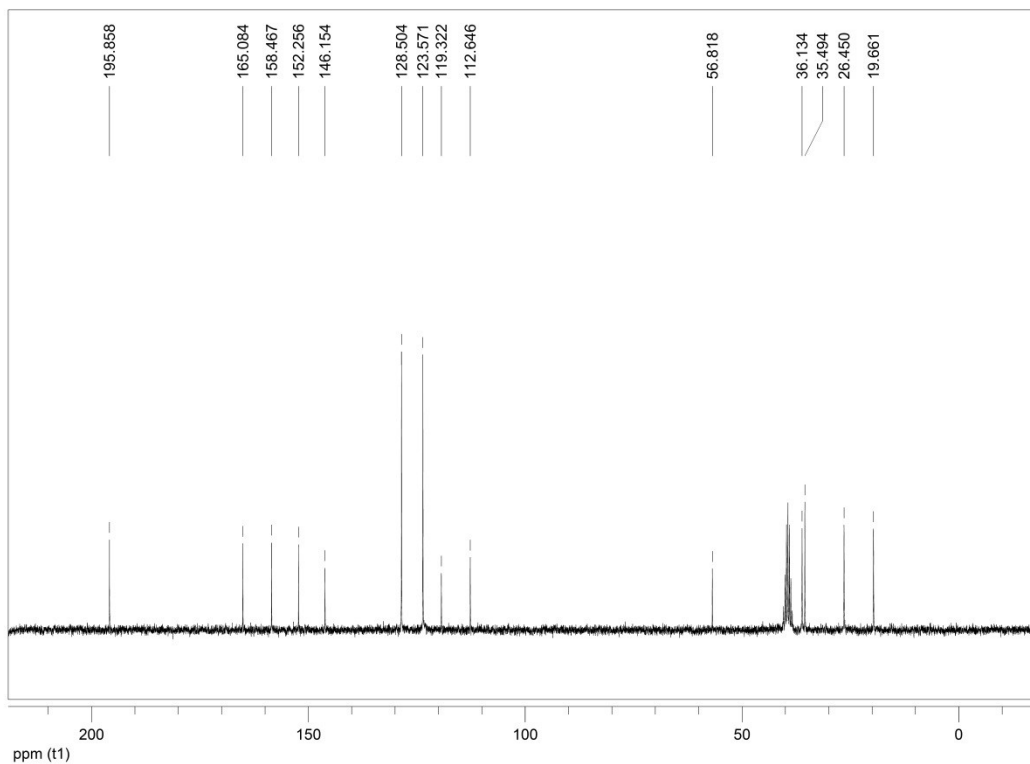




7-amino-2,4-dioxo-5-(pyridin-3-yl)-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile

### 9. 2-amino-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4i)



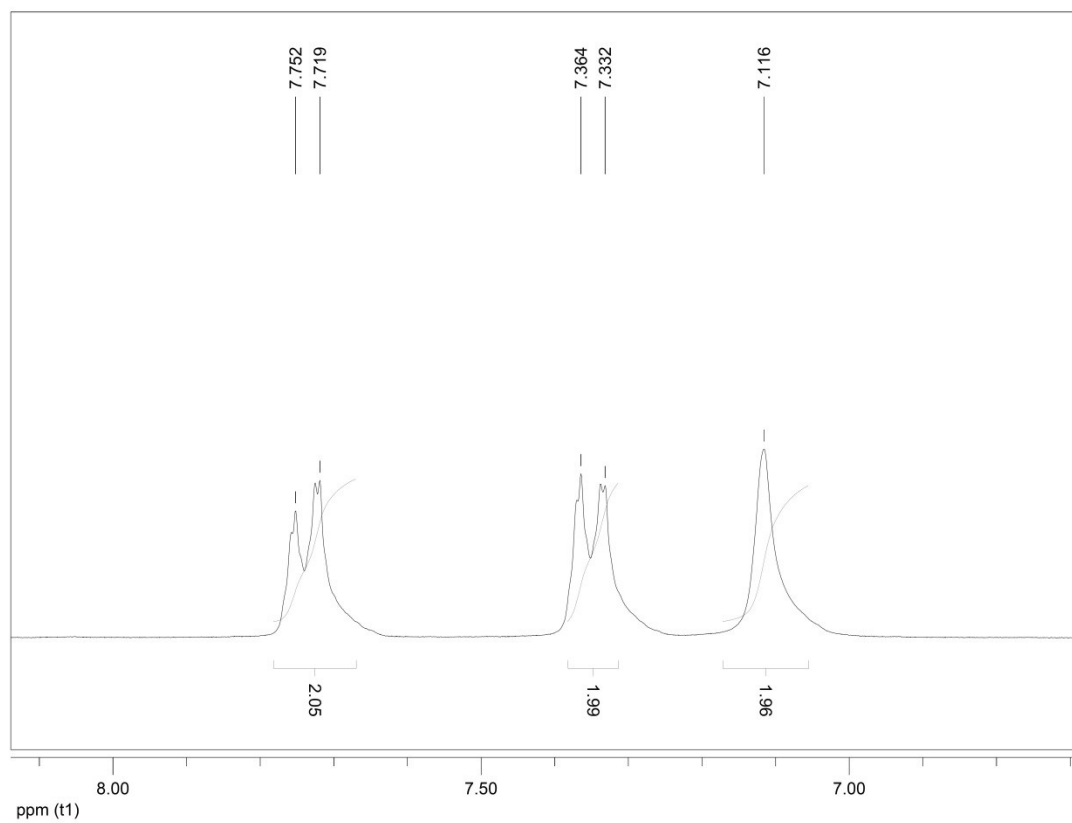
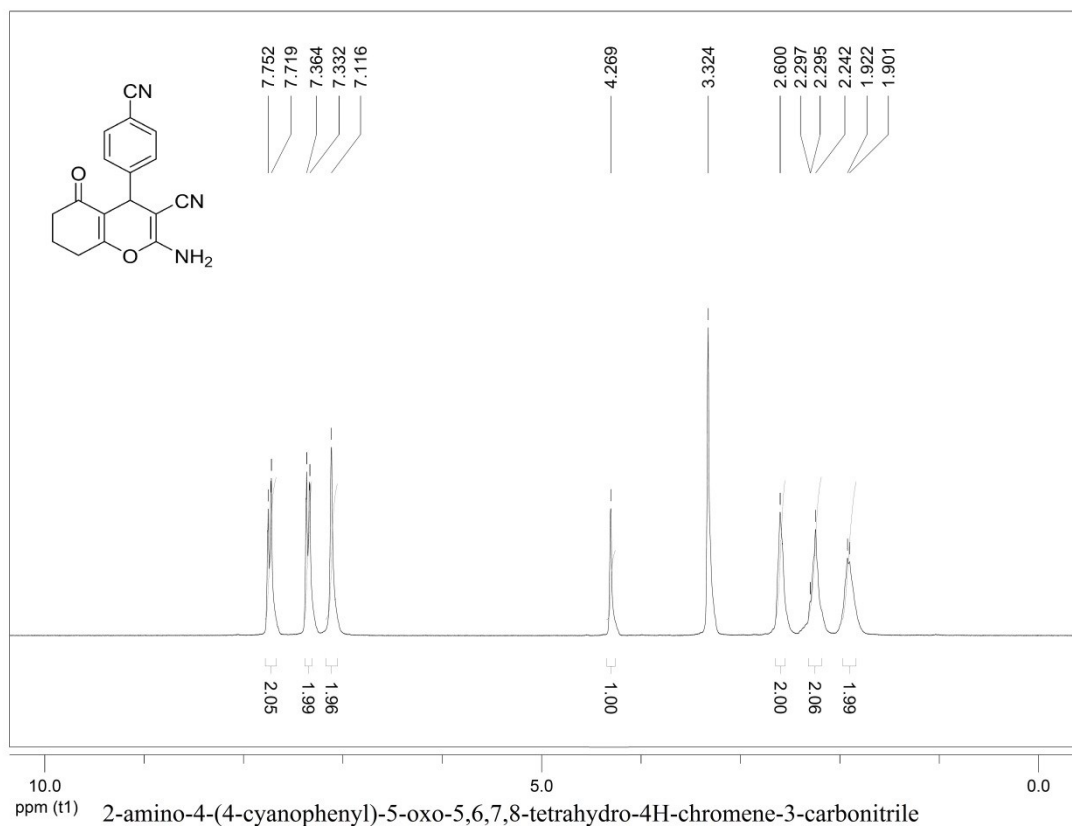


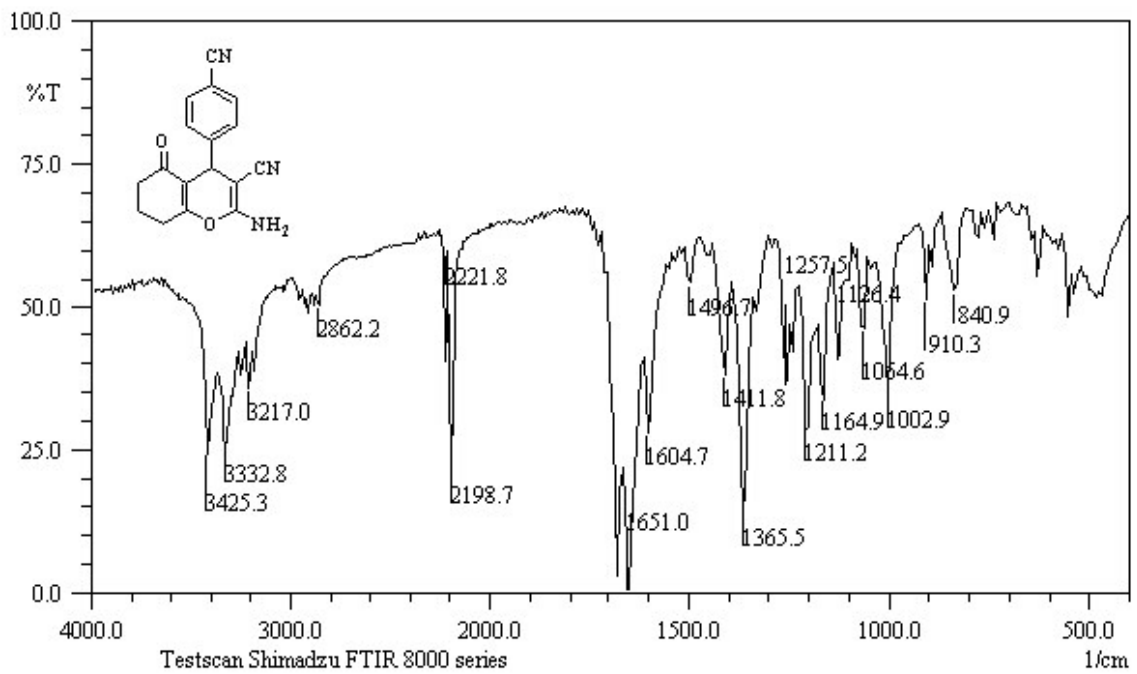
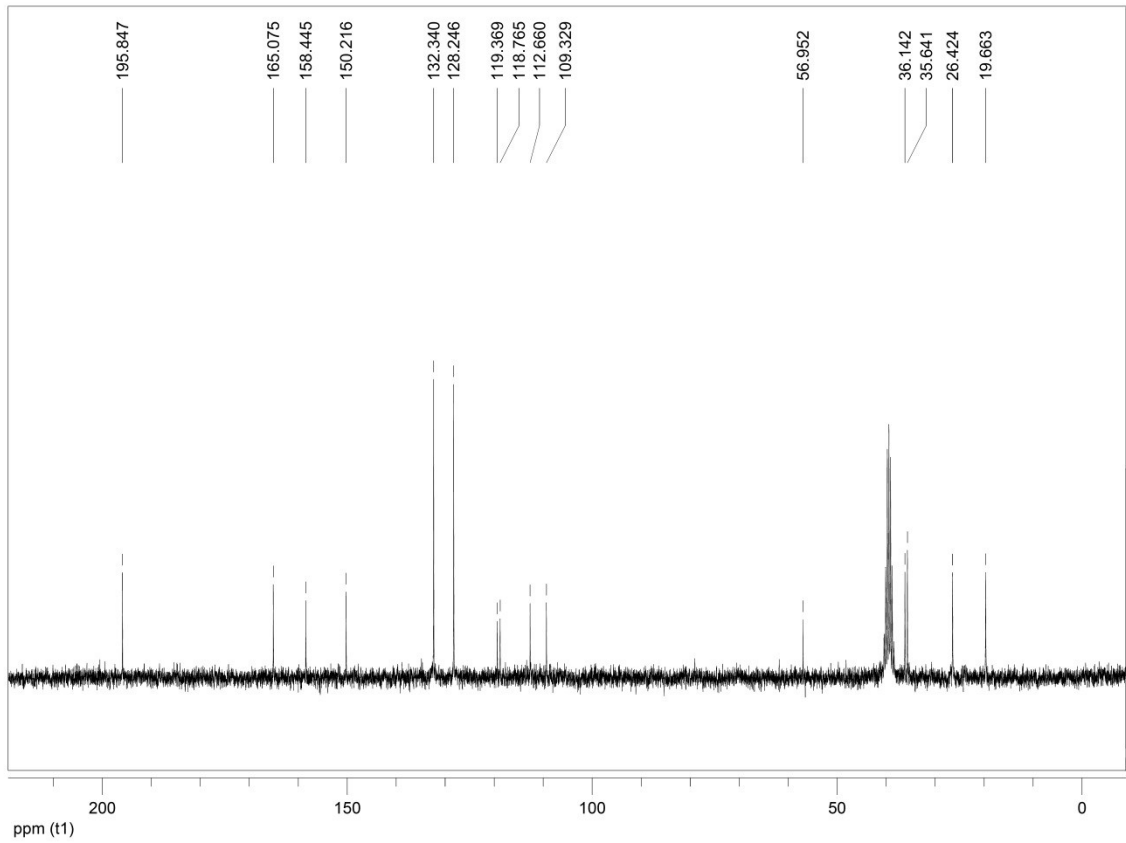
2-amino-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile



10. 2-amino-4-(4-cyanophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

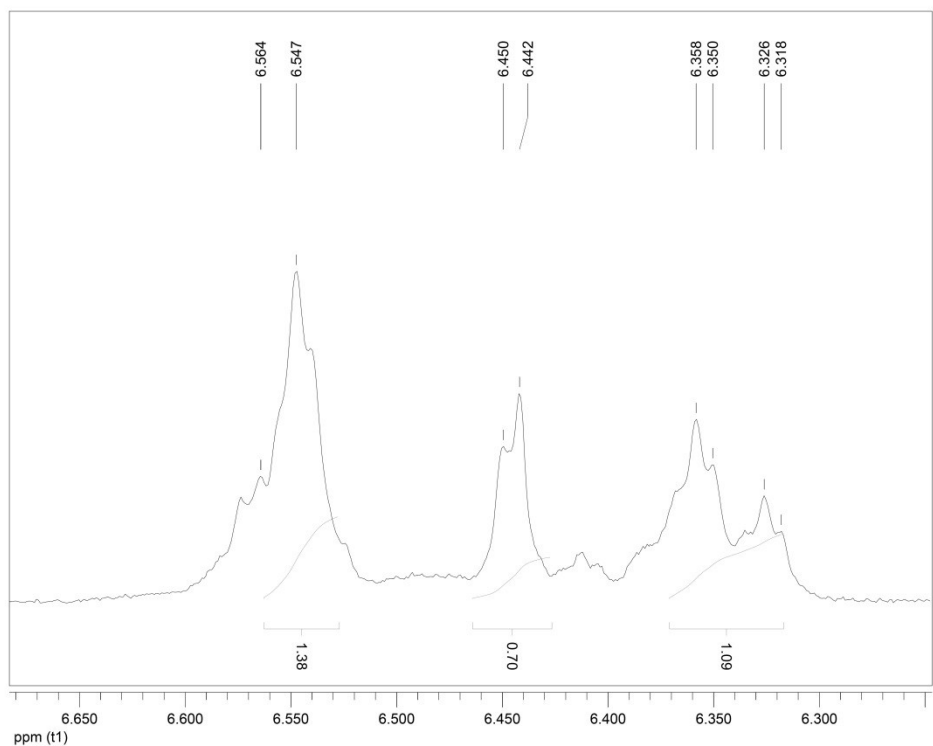
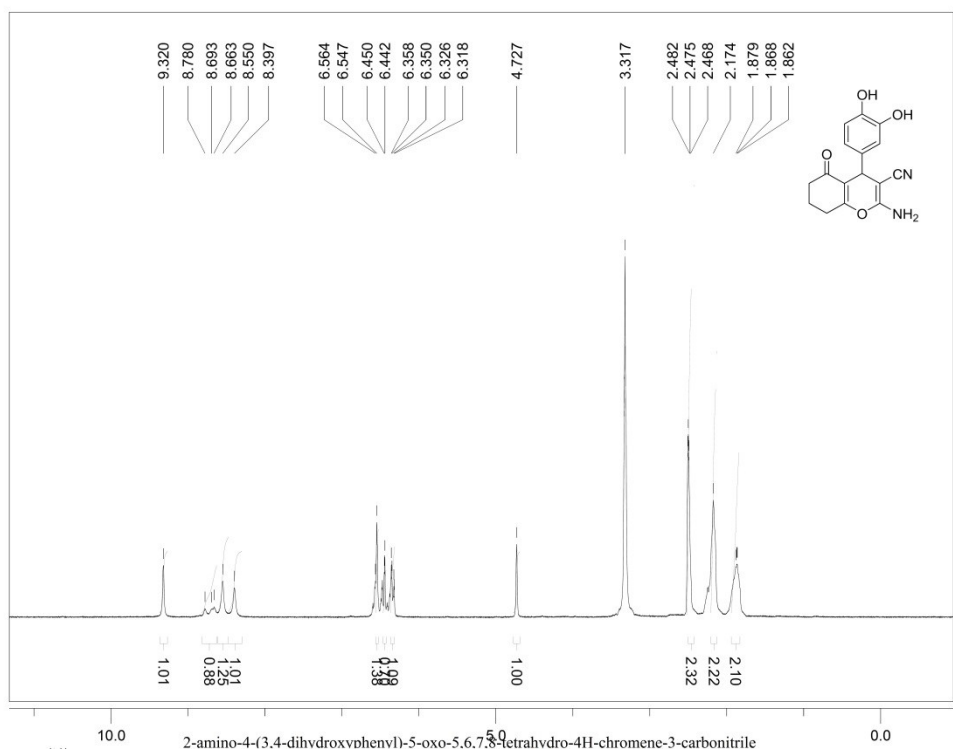
(4j)

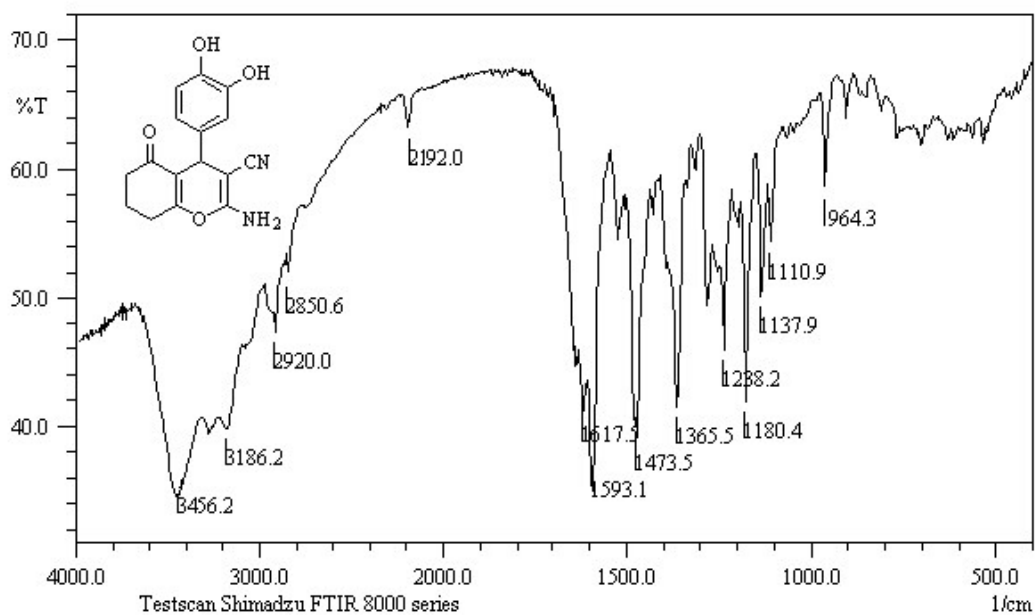
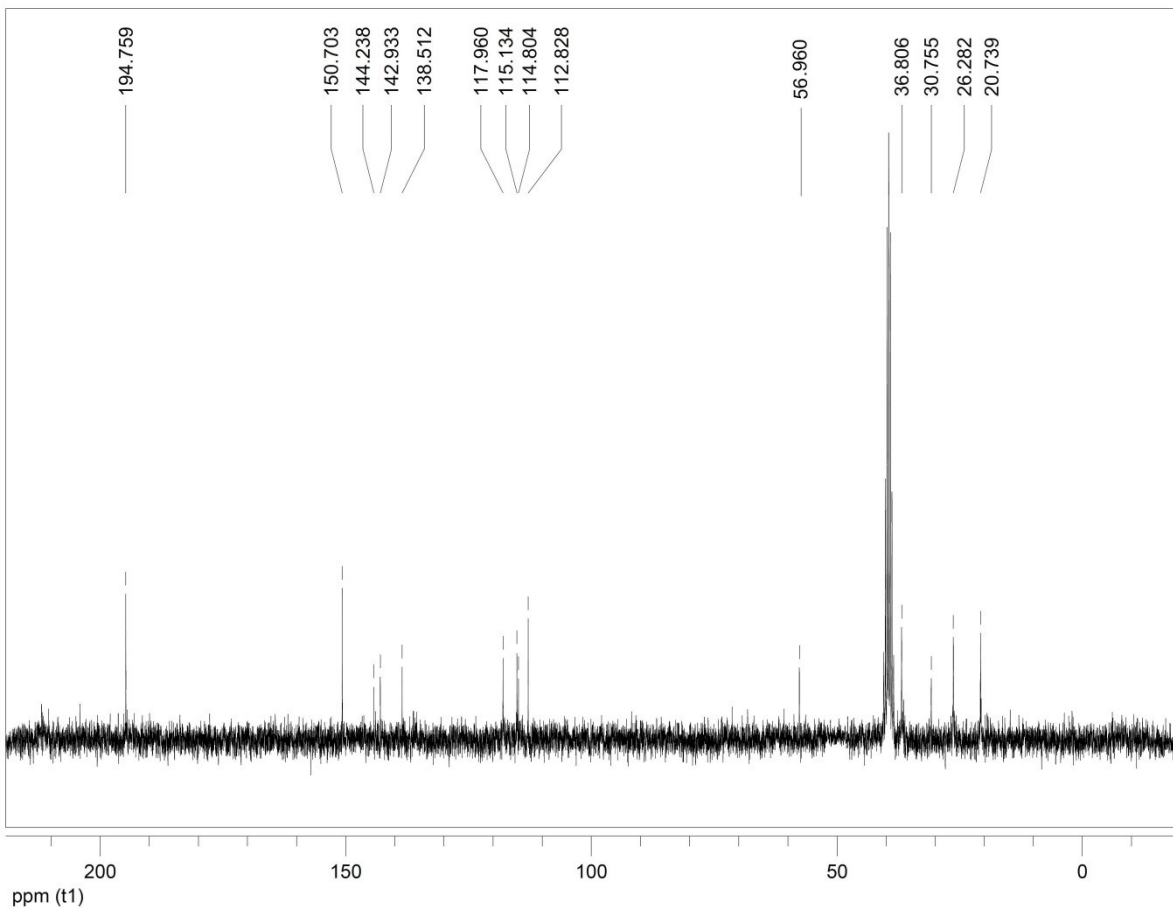




2-amino-4-(4-cyanophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

# 11. 2-amino-4-(3,4-dihydroxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4k)

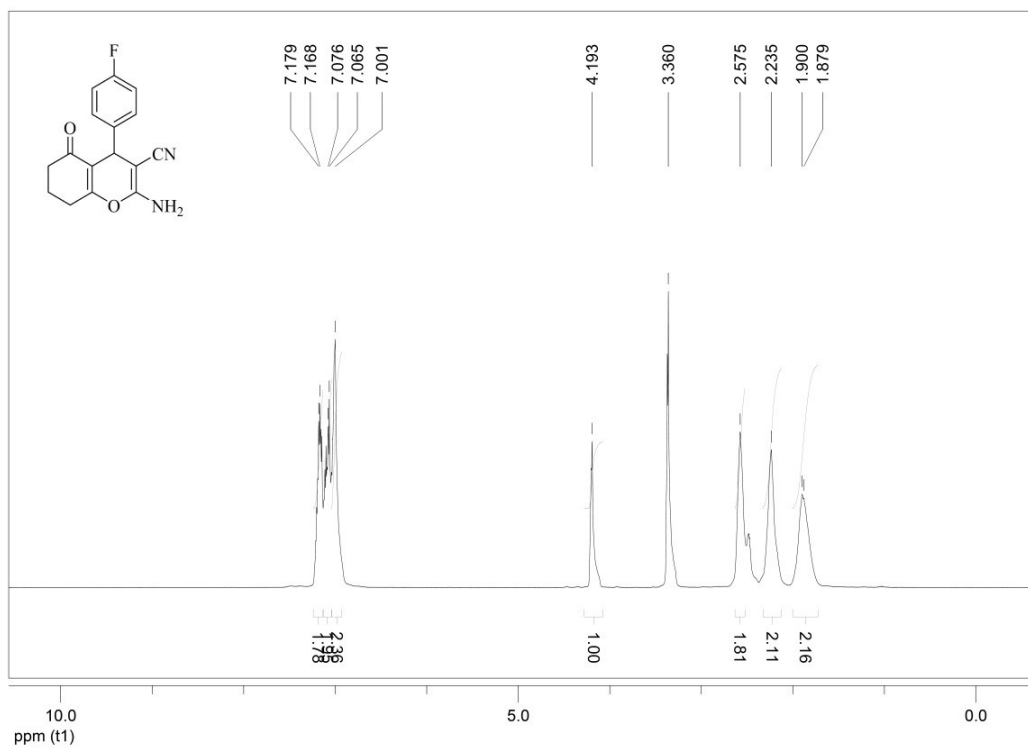




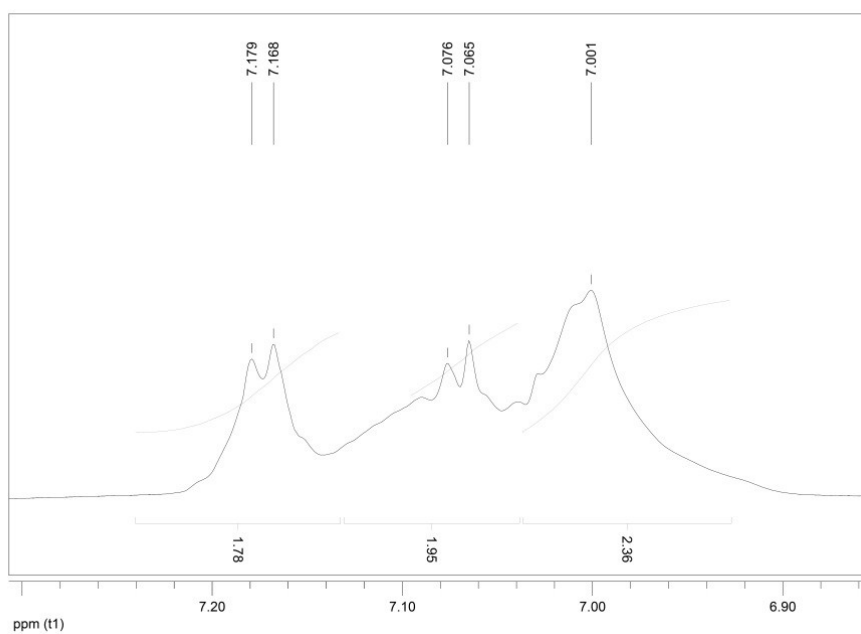
2-amino-4-(3,4-dihydroxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

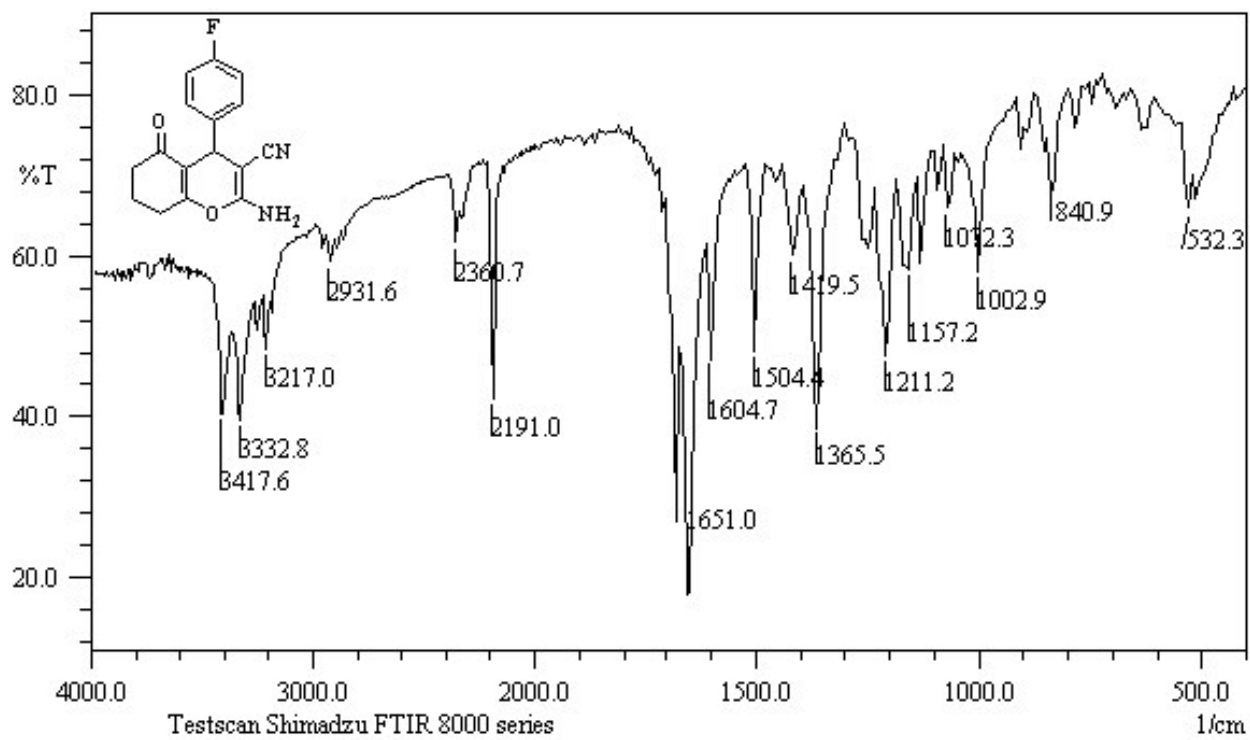
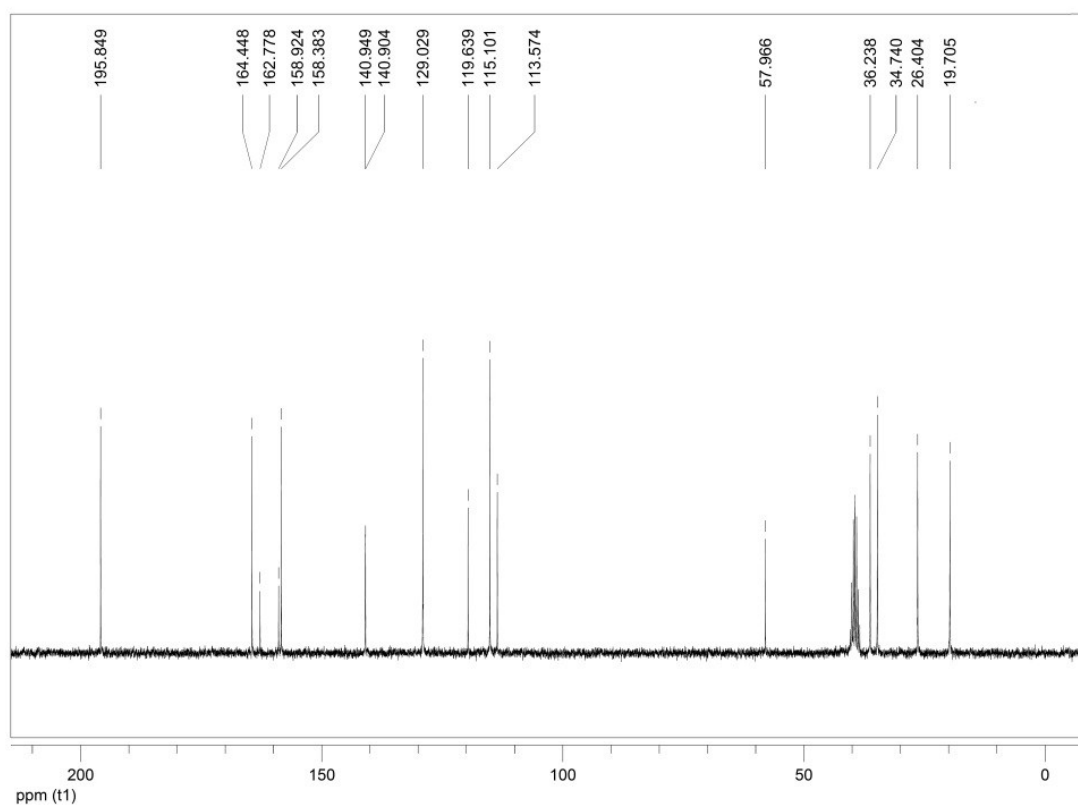
## 12. 2-amino-4-(4-fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

(41)



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

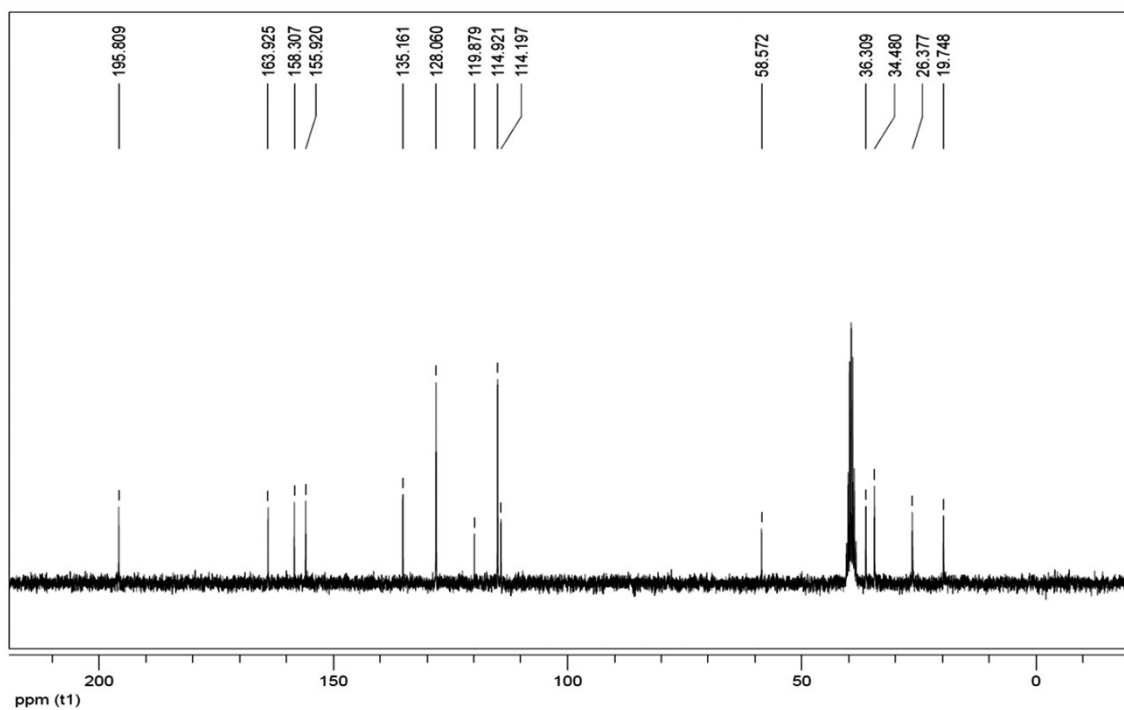
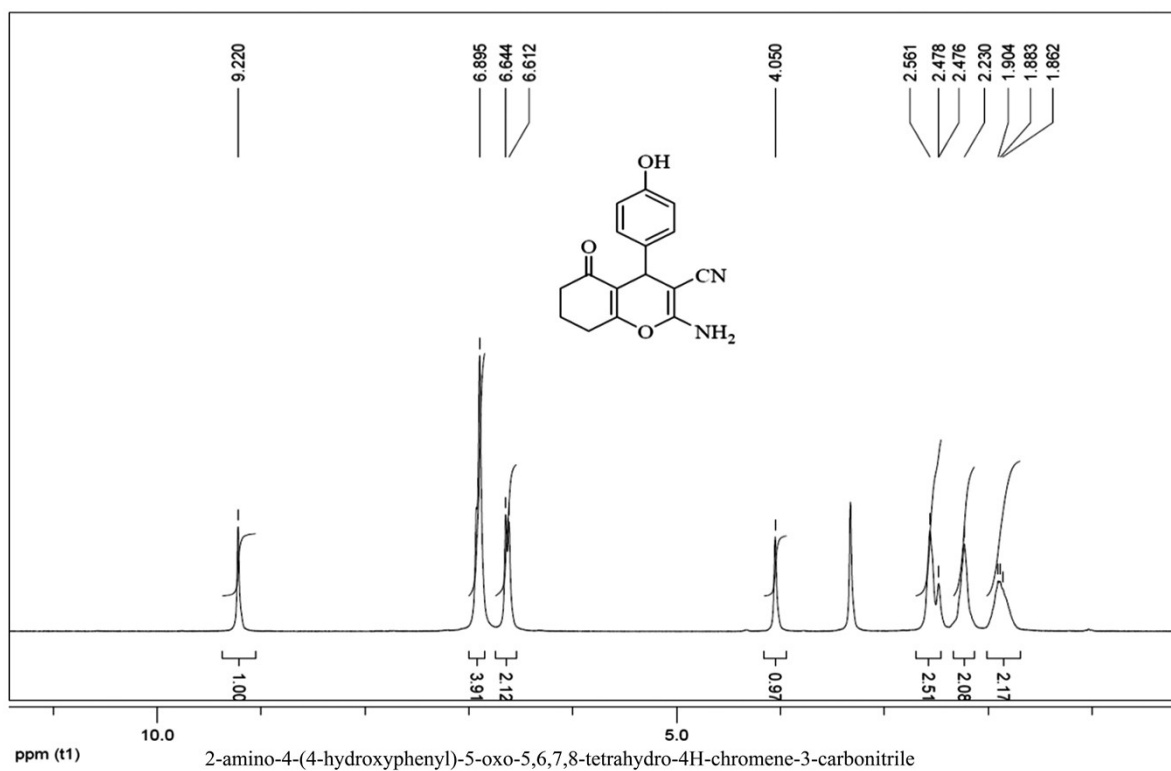


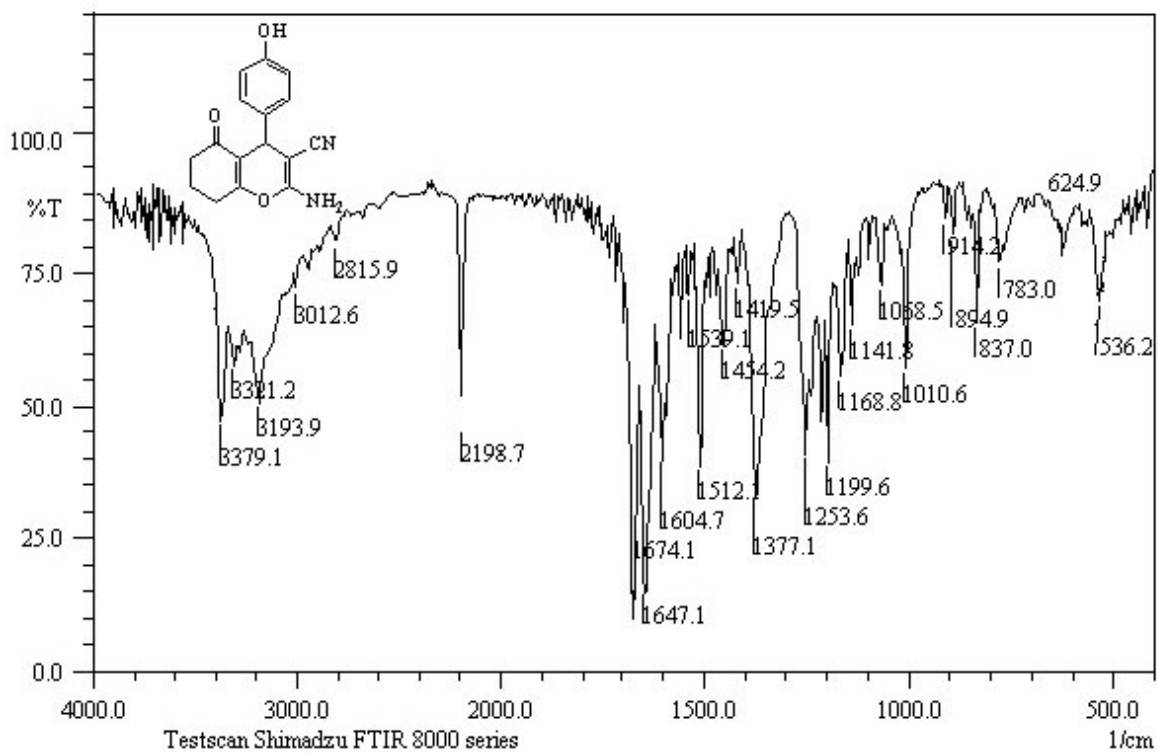


2-amino-4-(4-fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

### 13. 2-amino-4-(4-hydroxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

(4m)

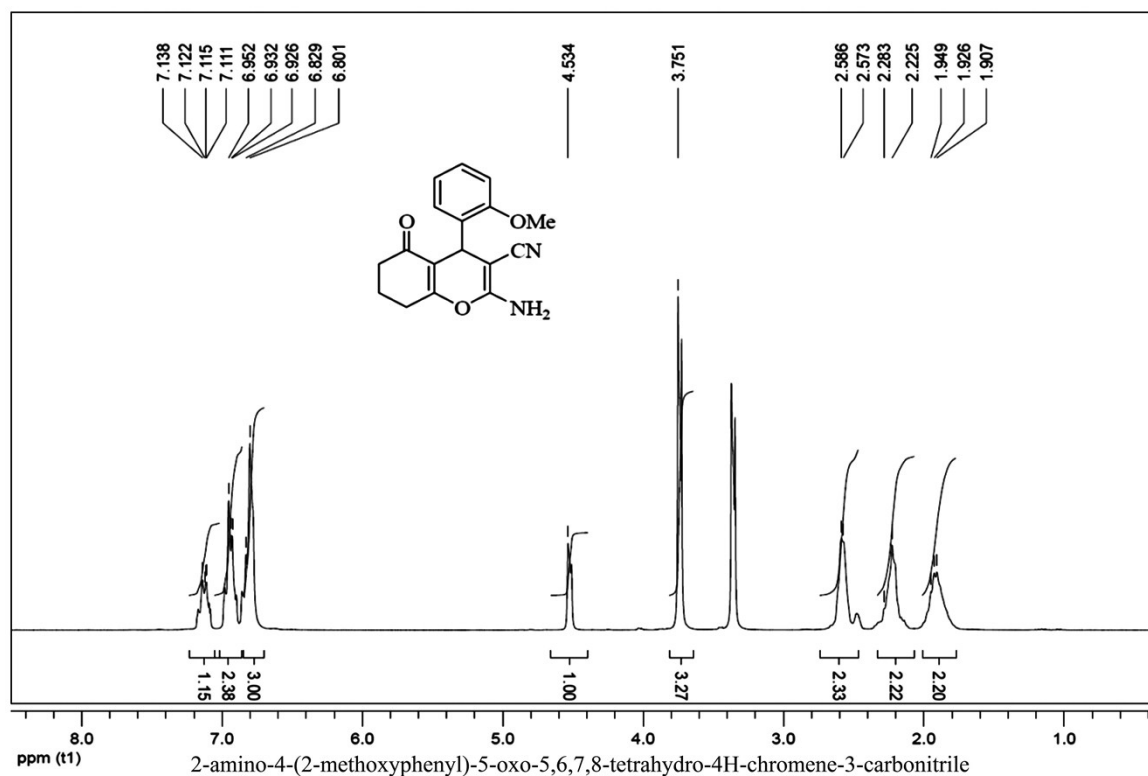




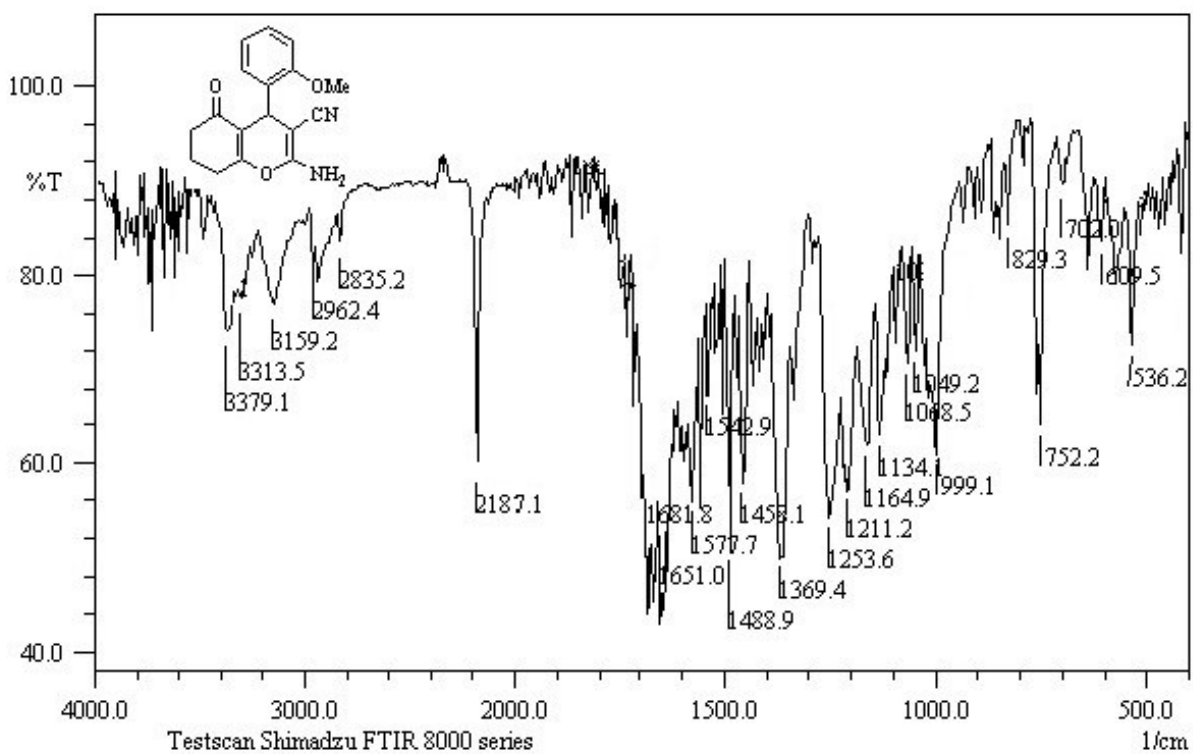
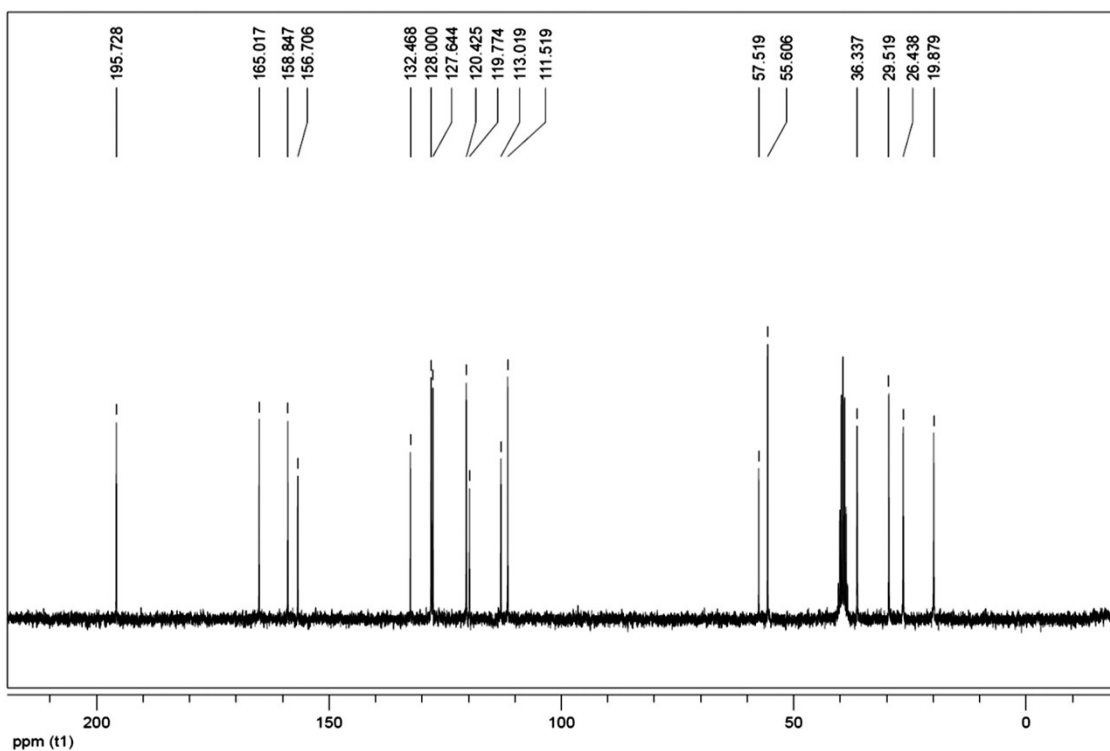
2-amino-4-(4-hydroxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

**14.2-amino-4-(2-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile**

**(4n)**



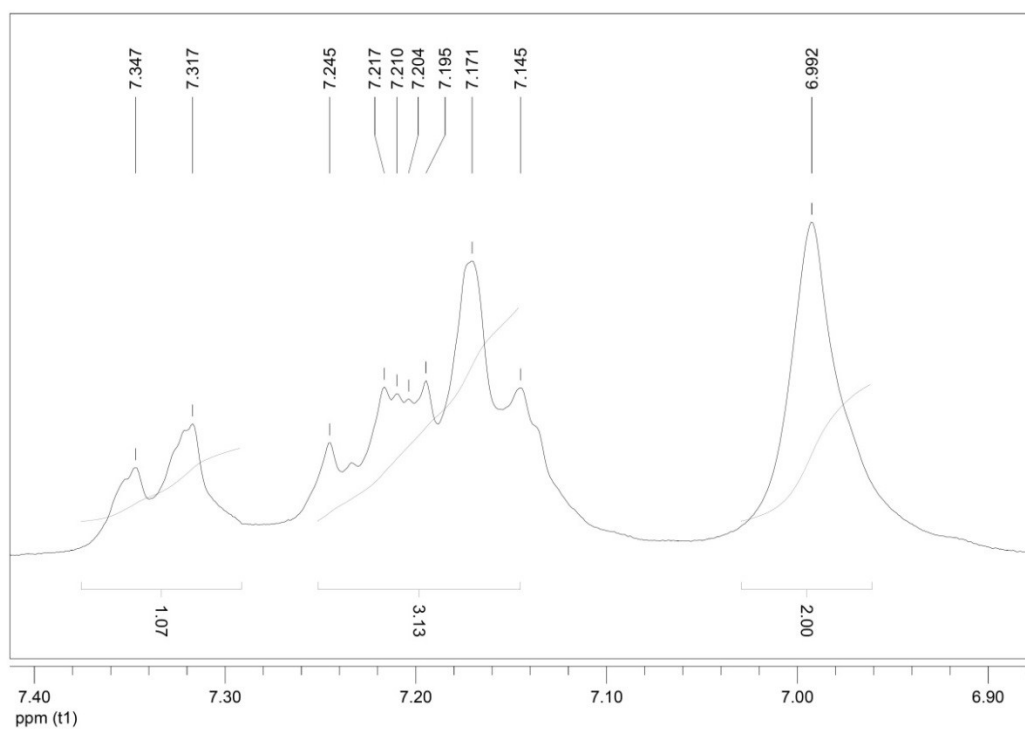
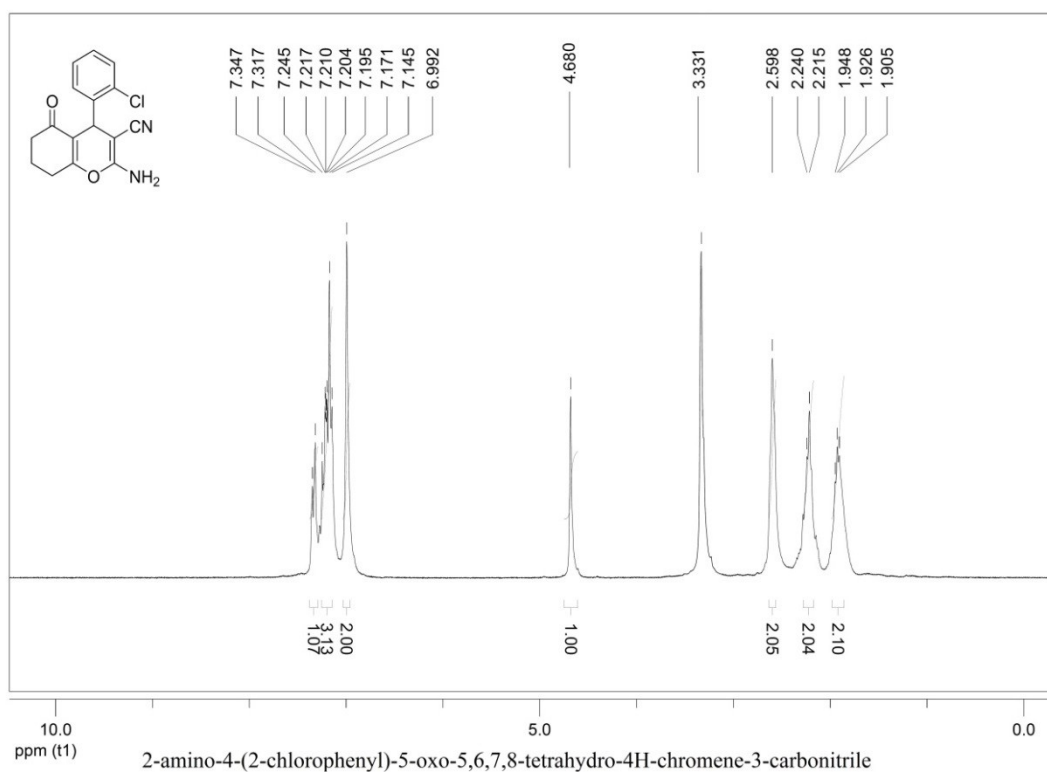


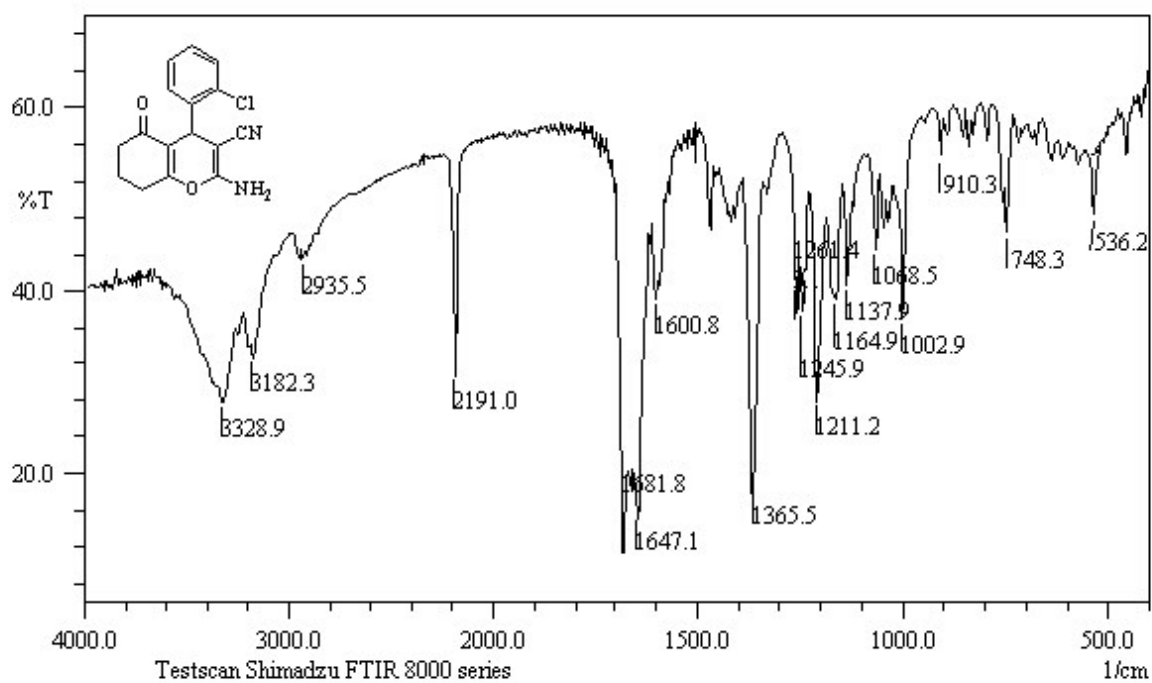
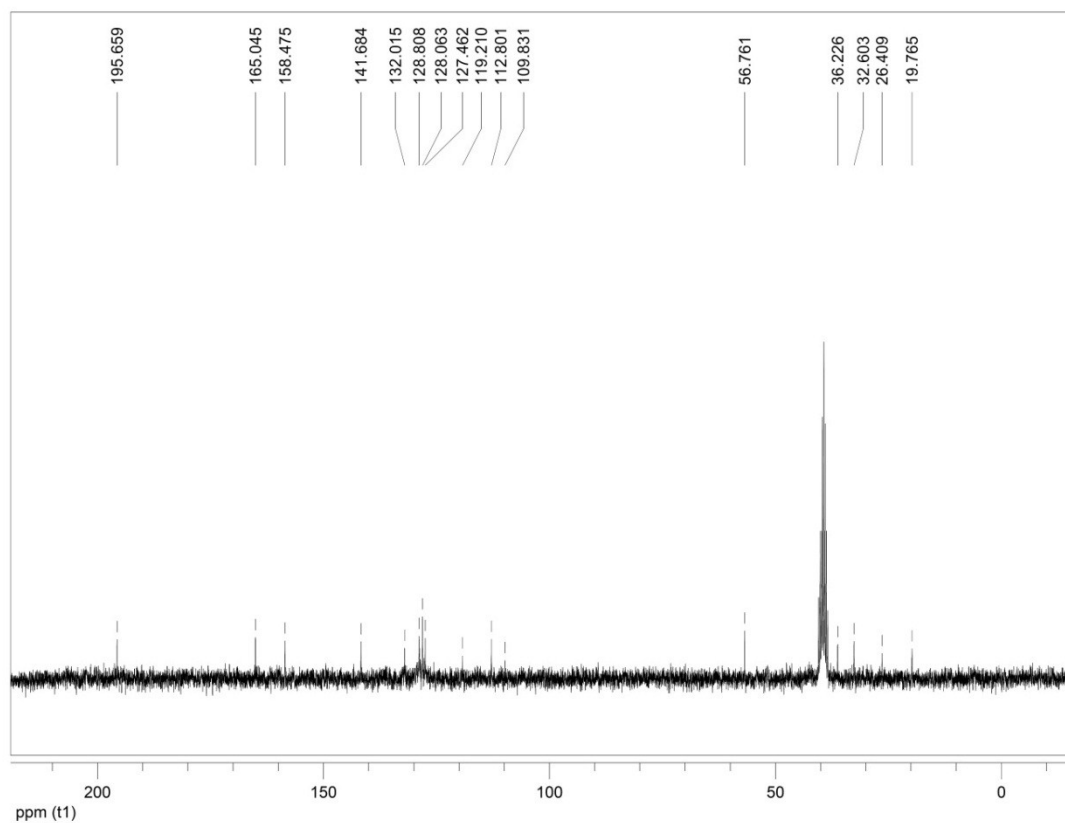


2-amino-4-(2-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

15.2-amino-4-(2-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

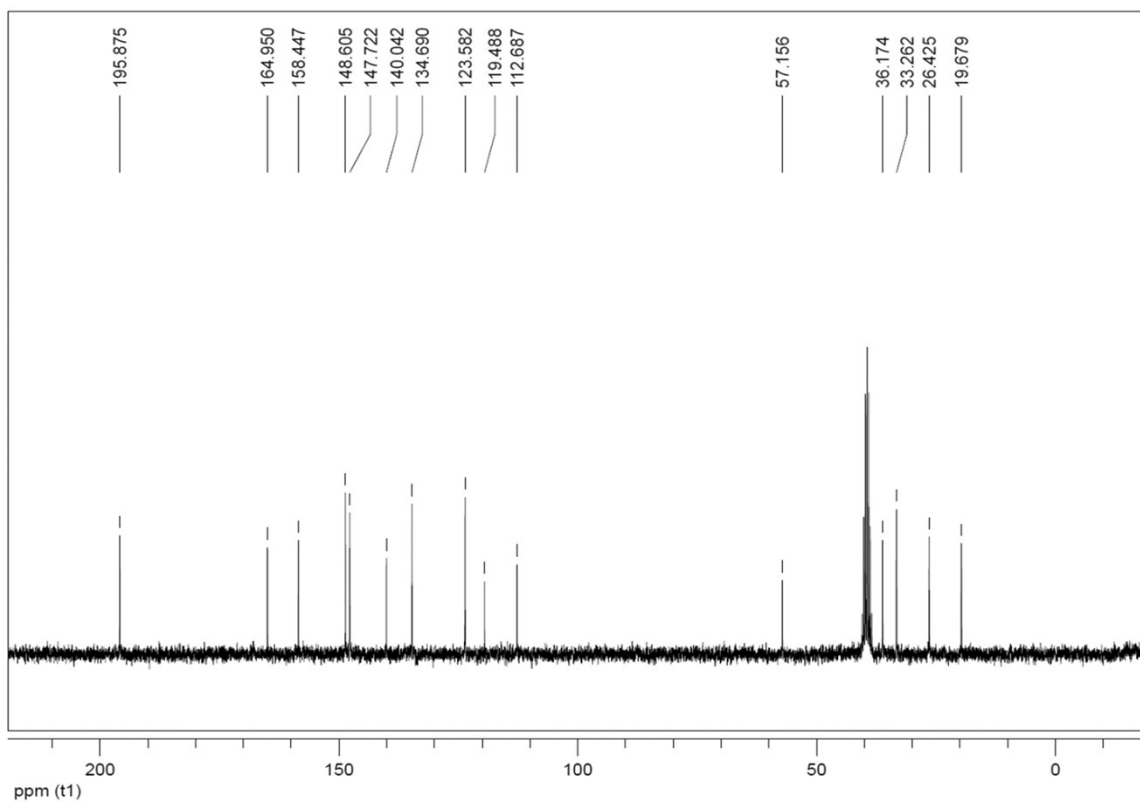
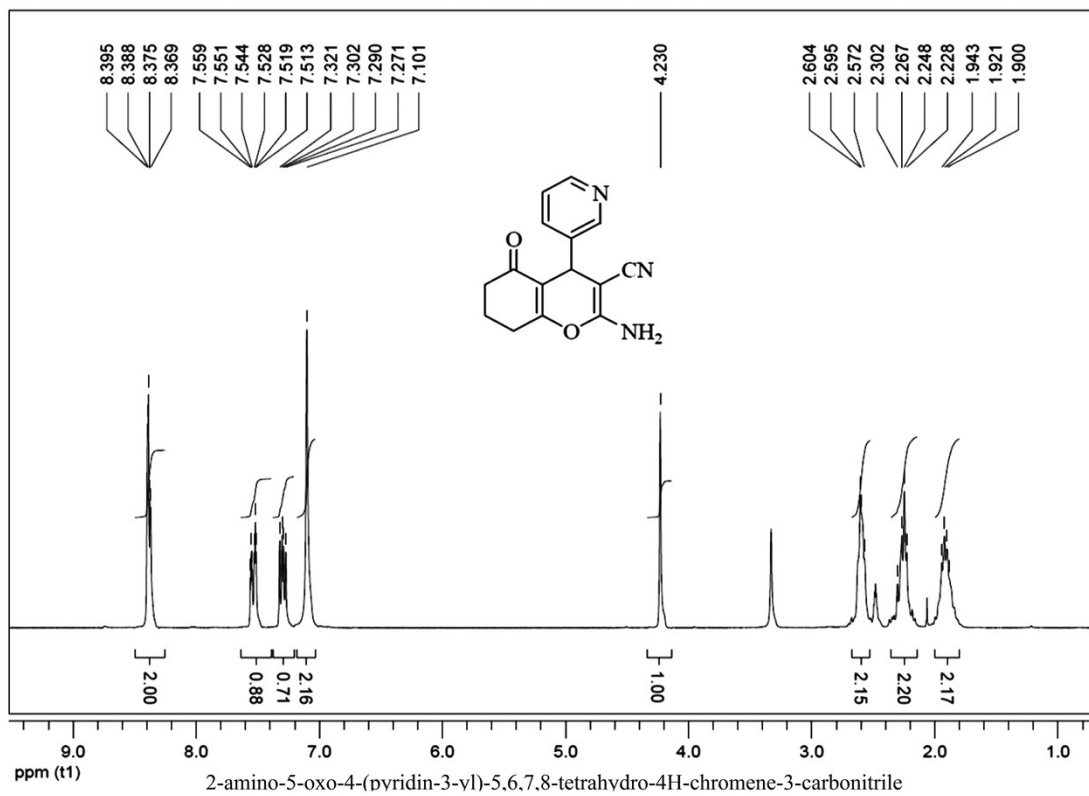
(40)

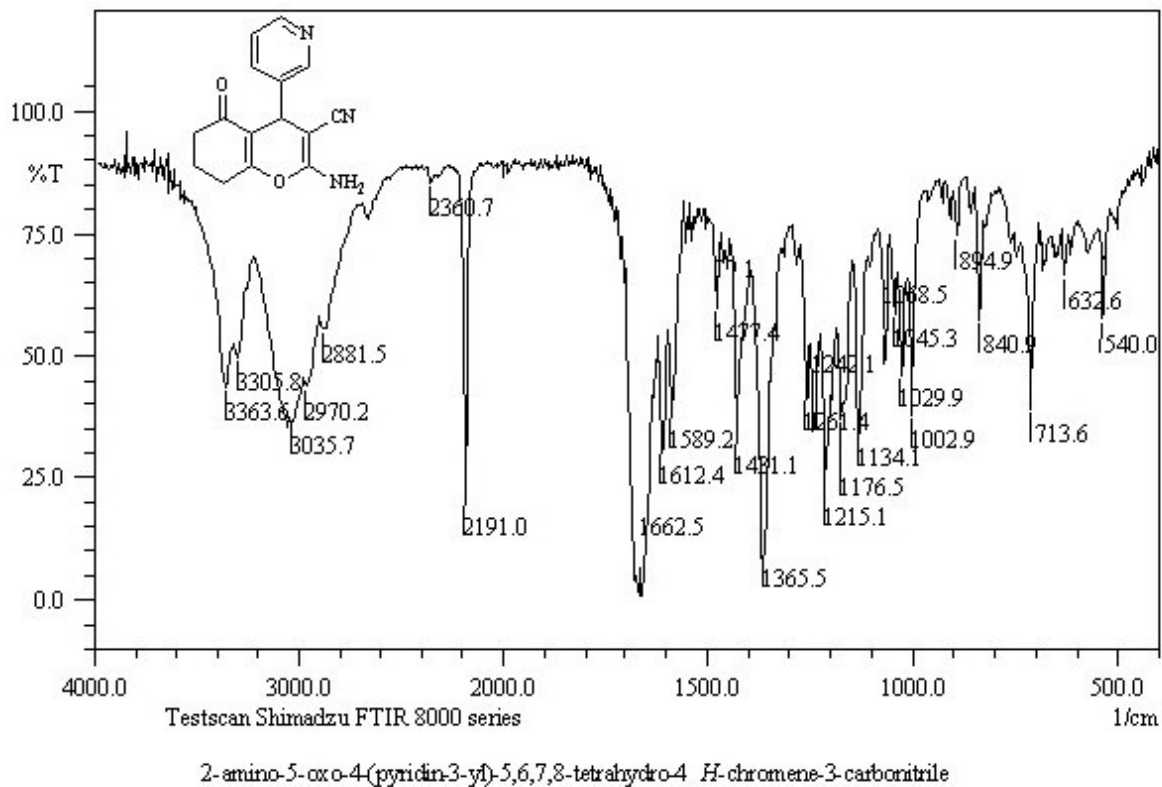




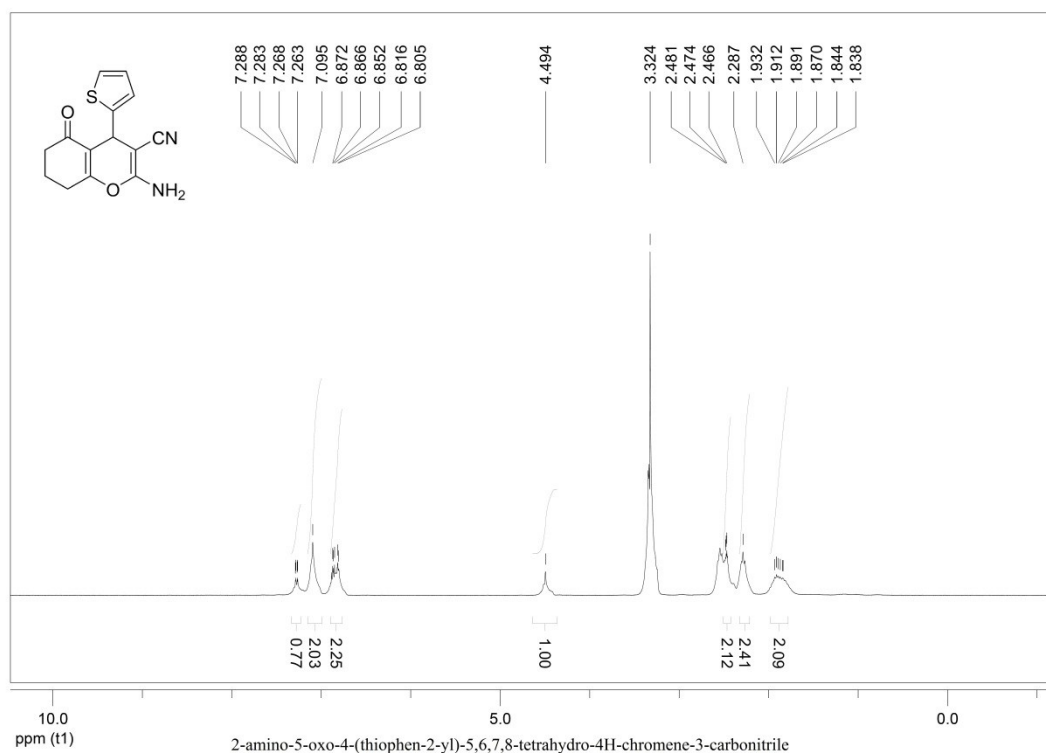
2-amino-4-(2-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

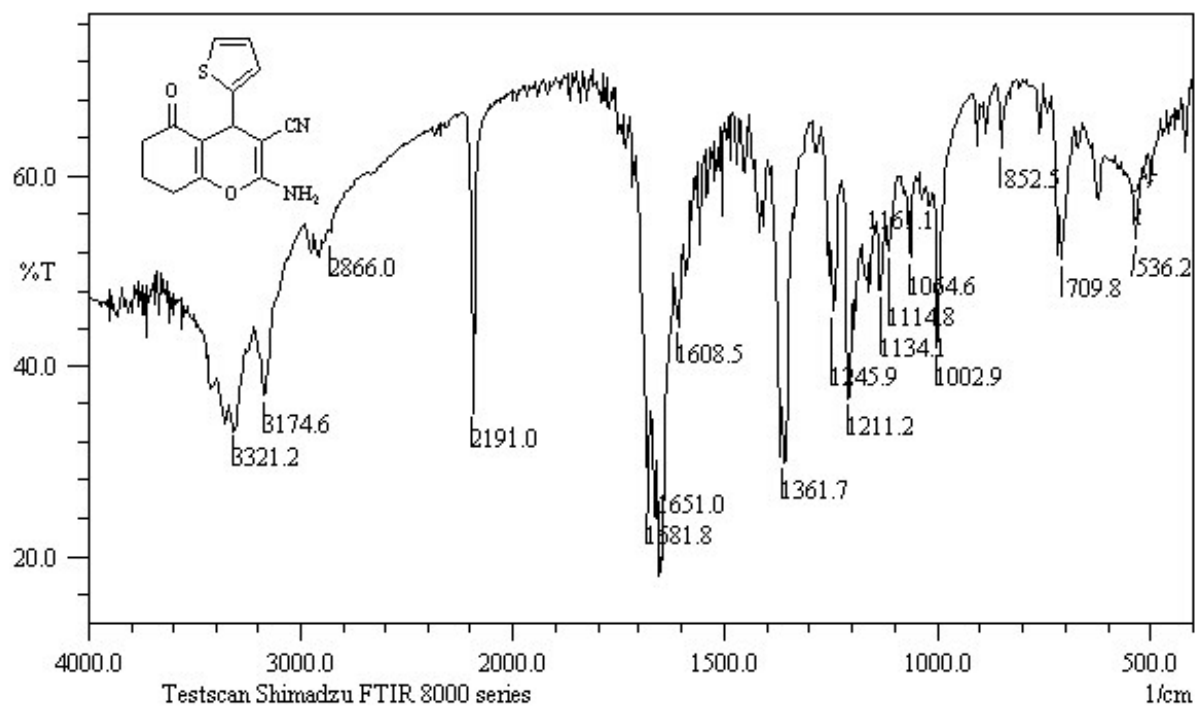
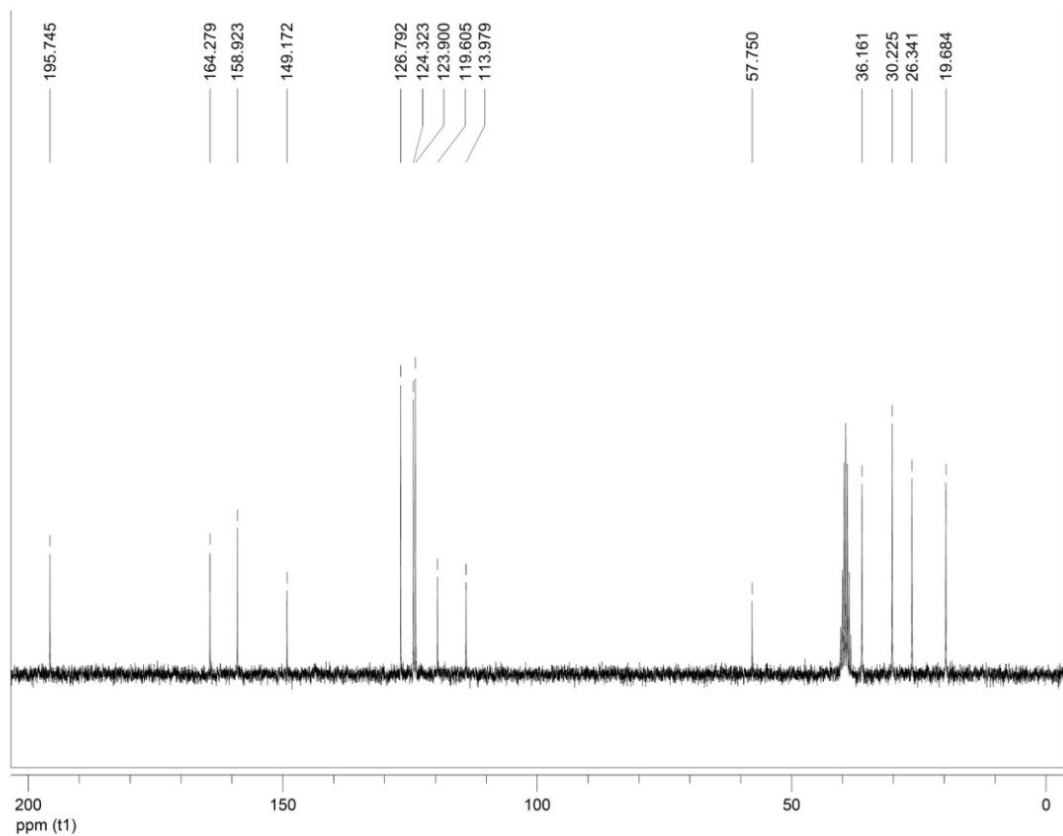
16. 2-amino-5-oxo-4-(pyridin-3-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4p)





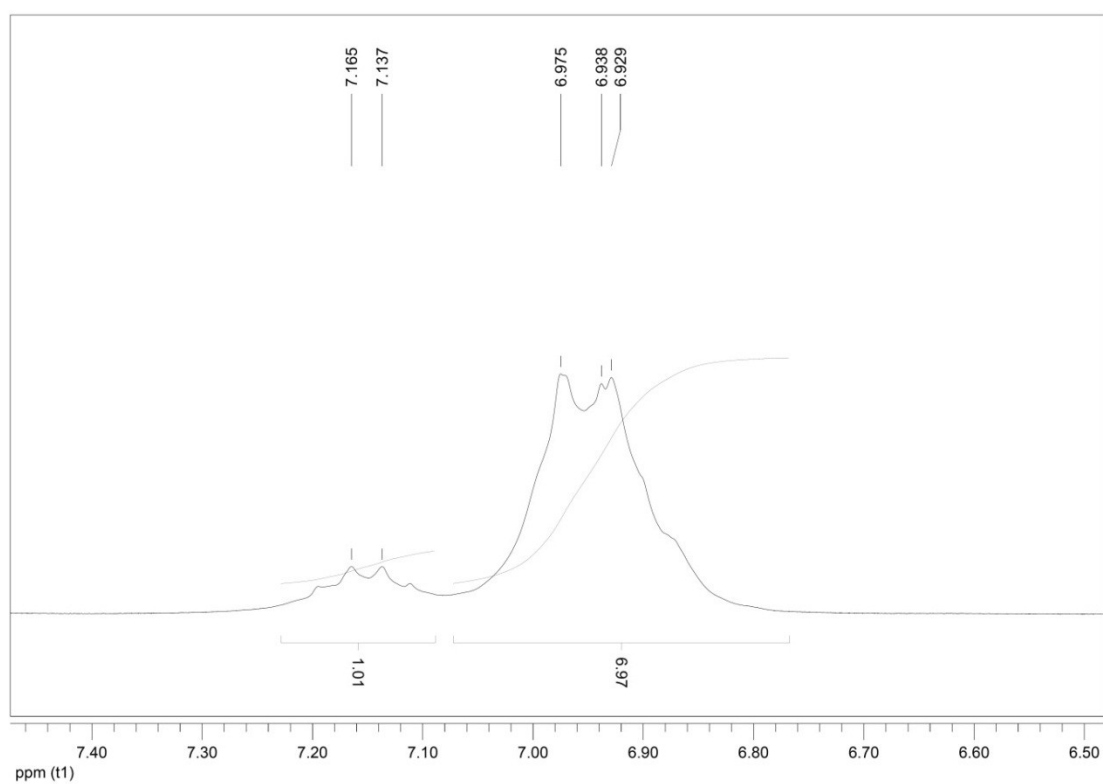
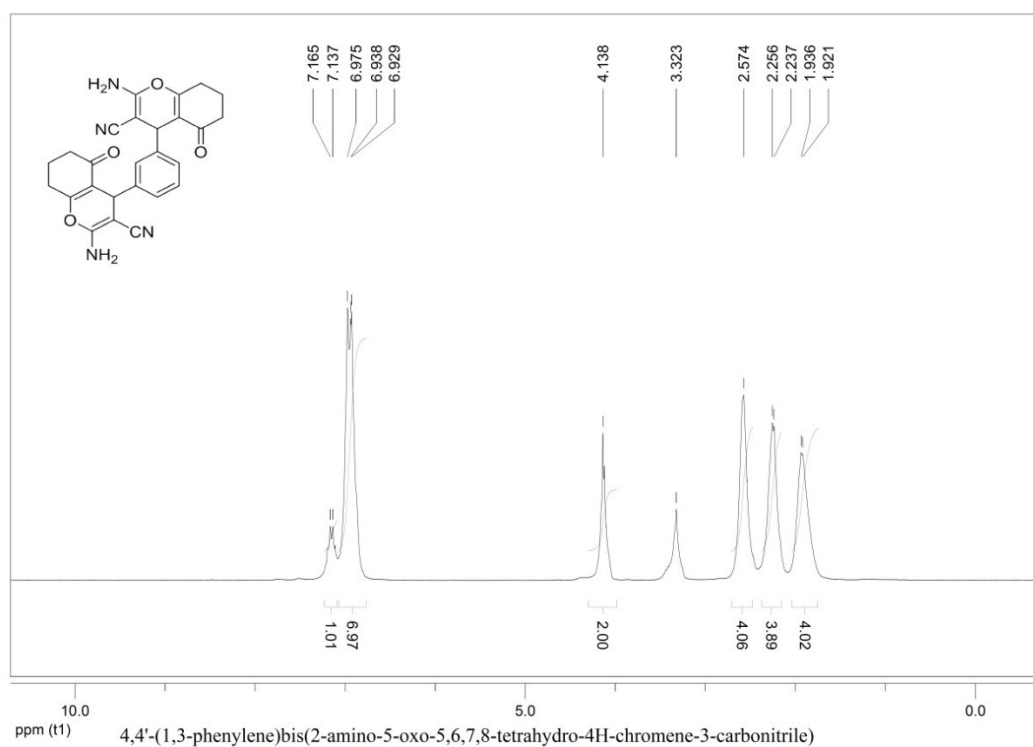
**17. 2-amino-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4q)**

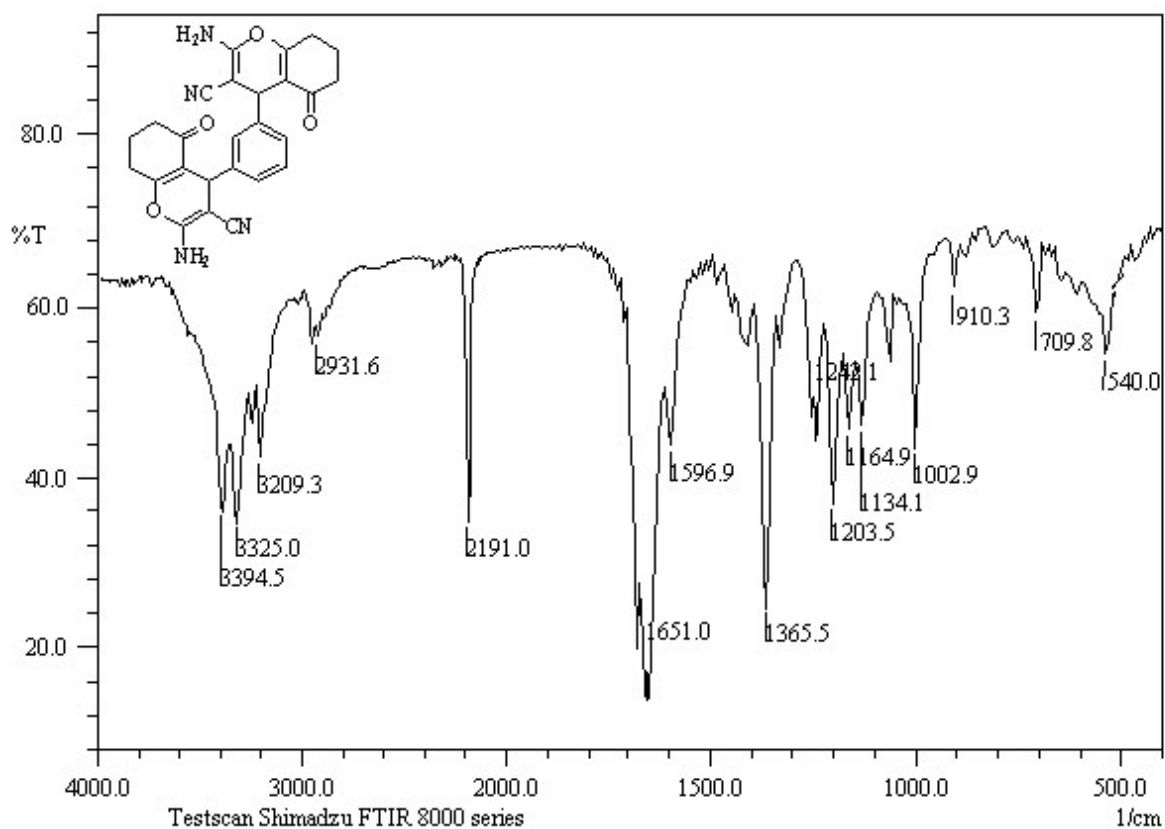
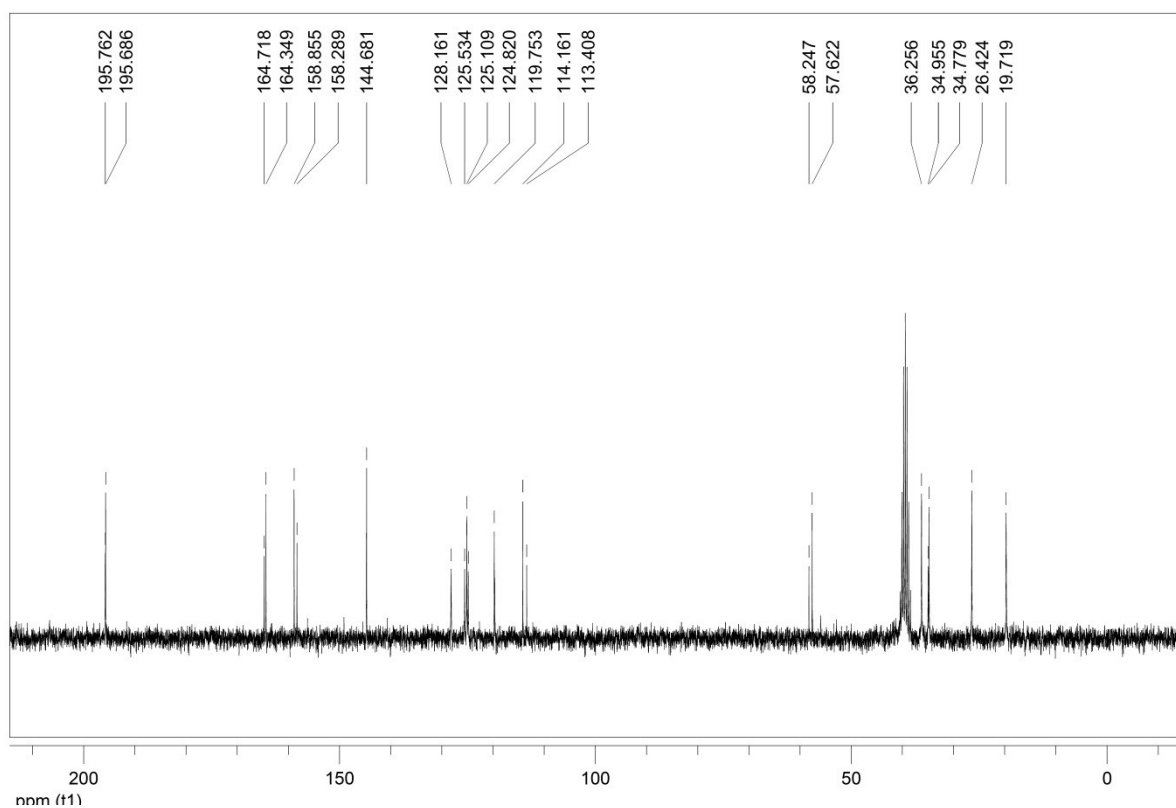




2-amino-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

**18. 4,4'-(1,3-phenylene)bis(2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile) (4r)**

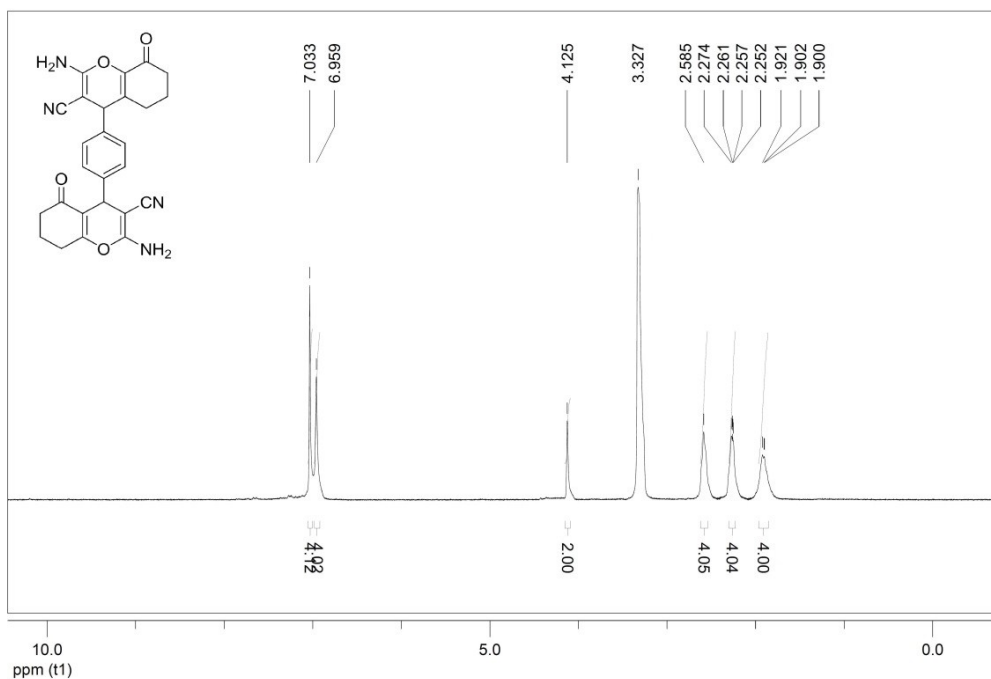




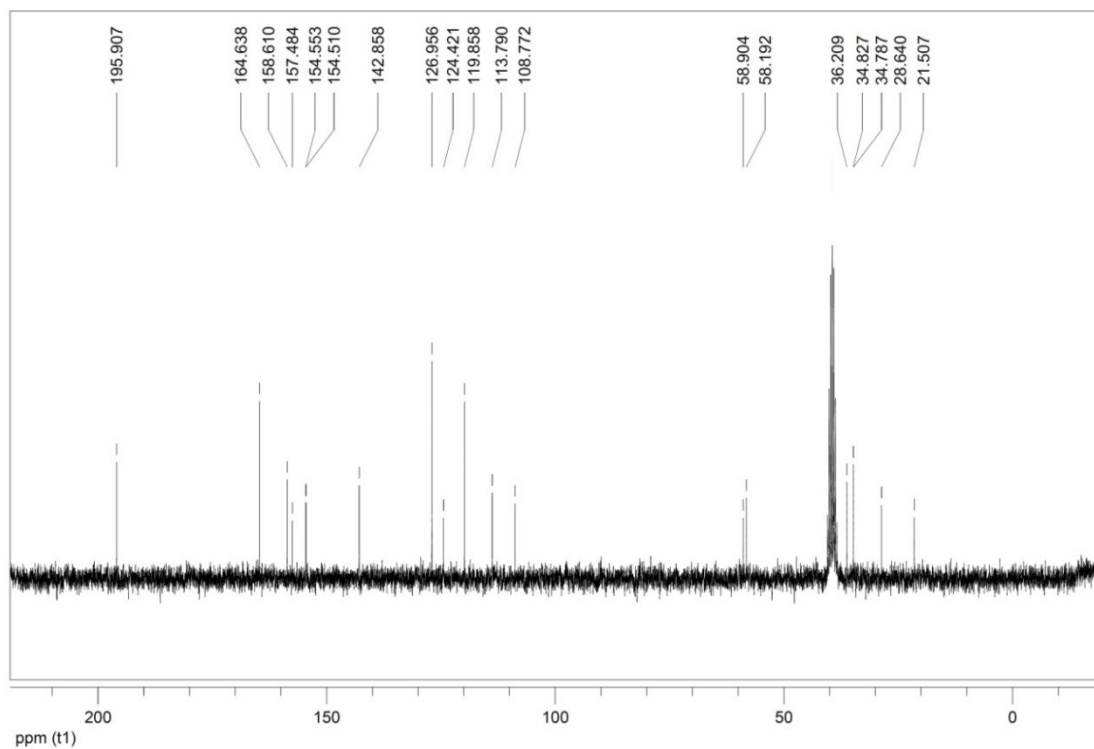
4,4'-(1,3-phenylene)bis(2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile)

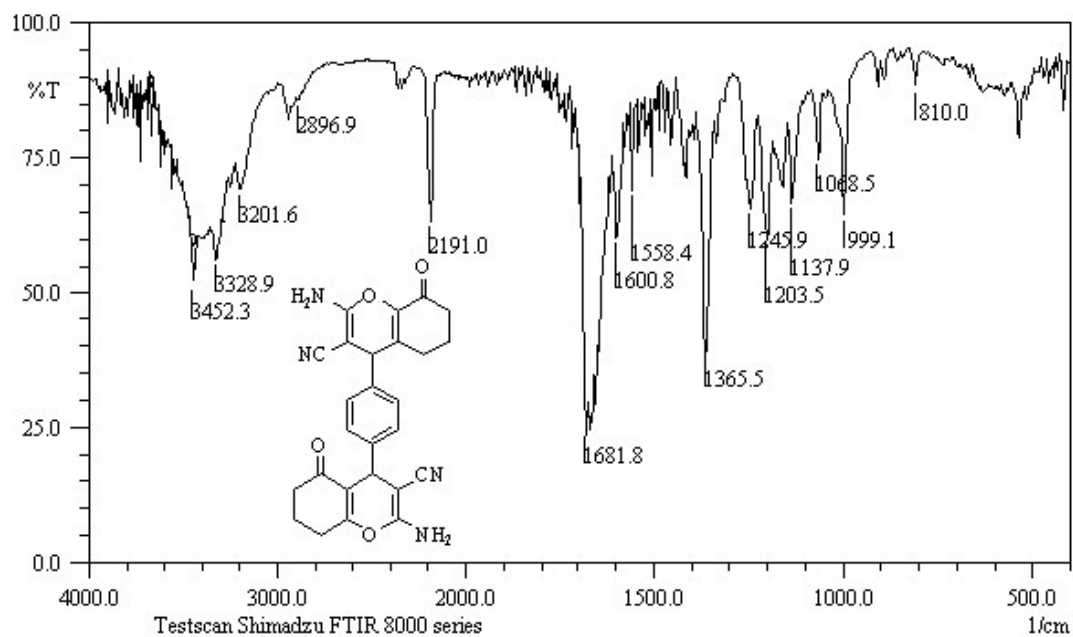


**19. 2-amino-4-(4-(2-amino-3-cyano-5-oxo-5,6,7,8-tetrahydro-4H-chromen-4-yl)phenyl)-8-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitril (4s)**



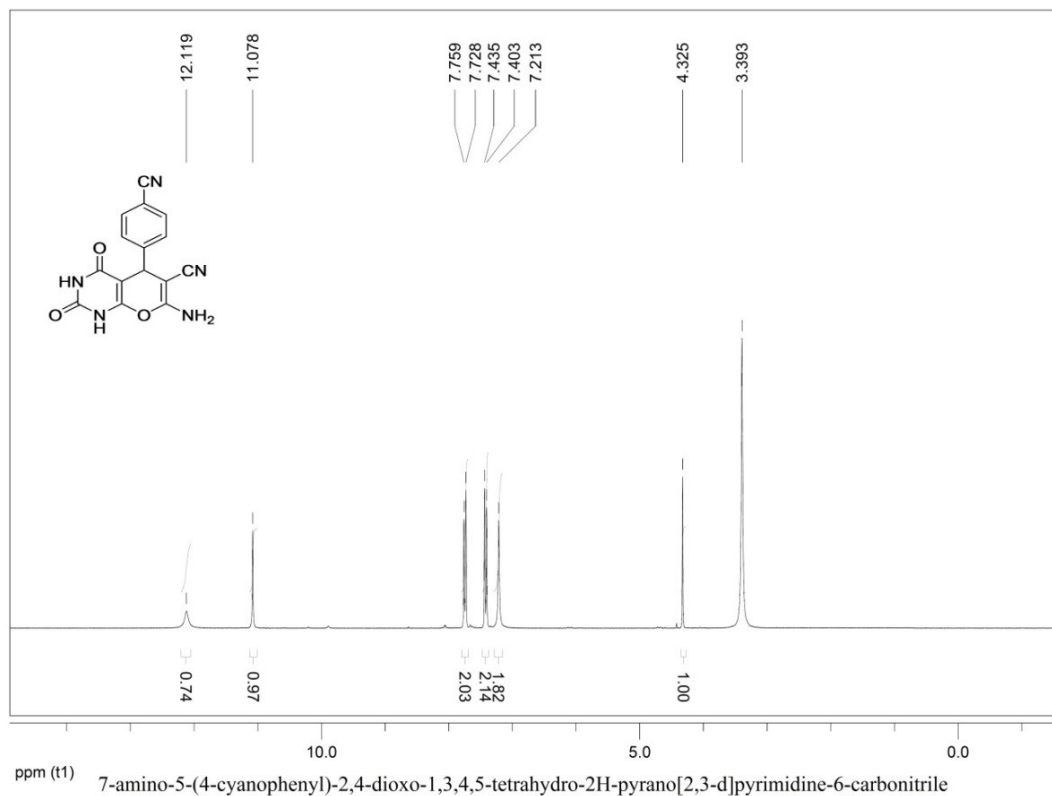
2-amino-4-(4-(2-amino-3-cyano-5-oxo-5,6,7,8-tetrahydro-4H-chromen-4-yl)phenyl)-8-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

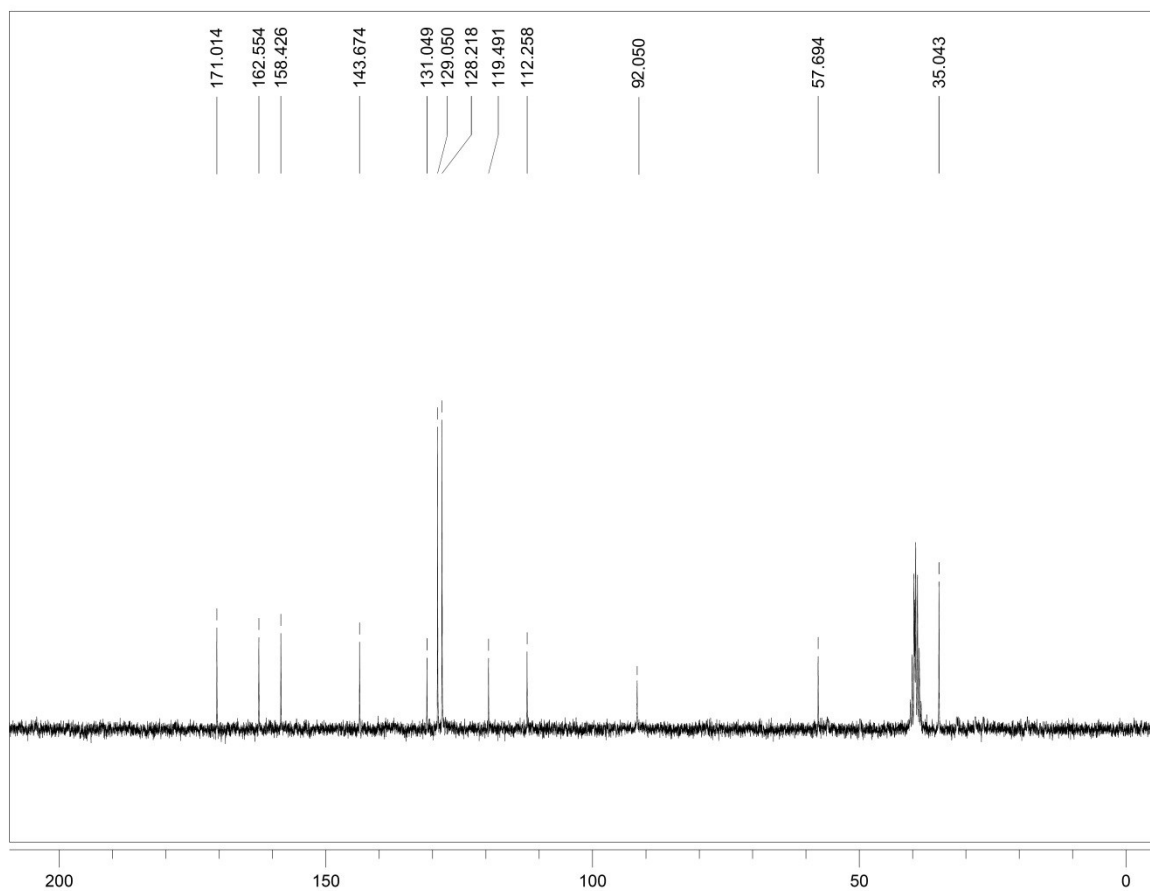
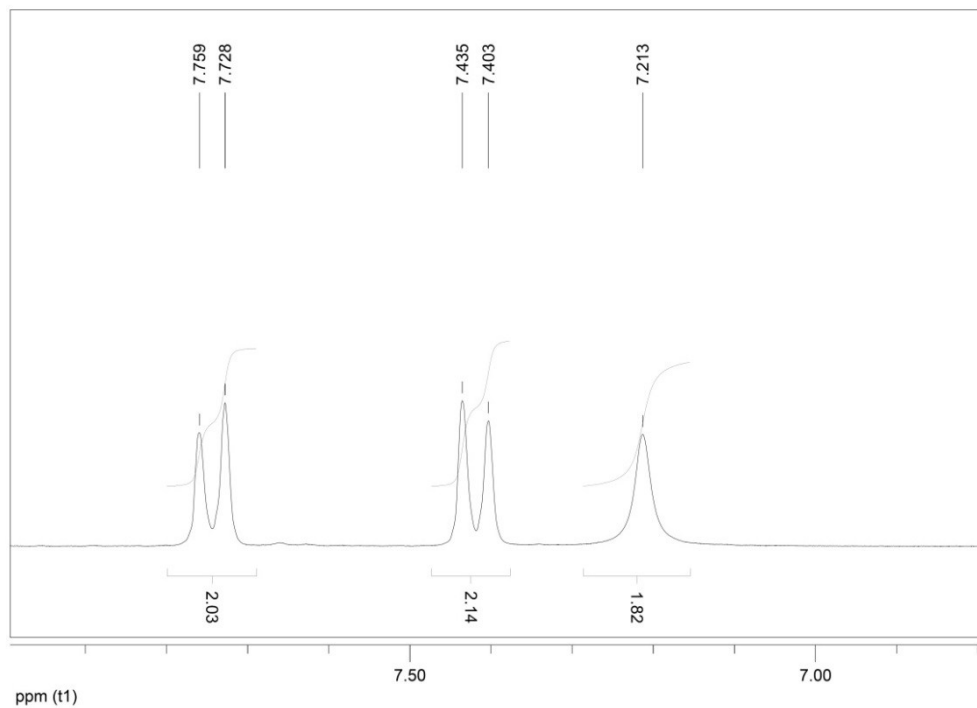


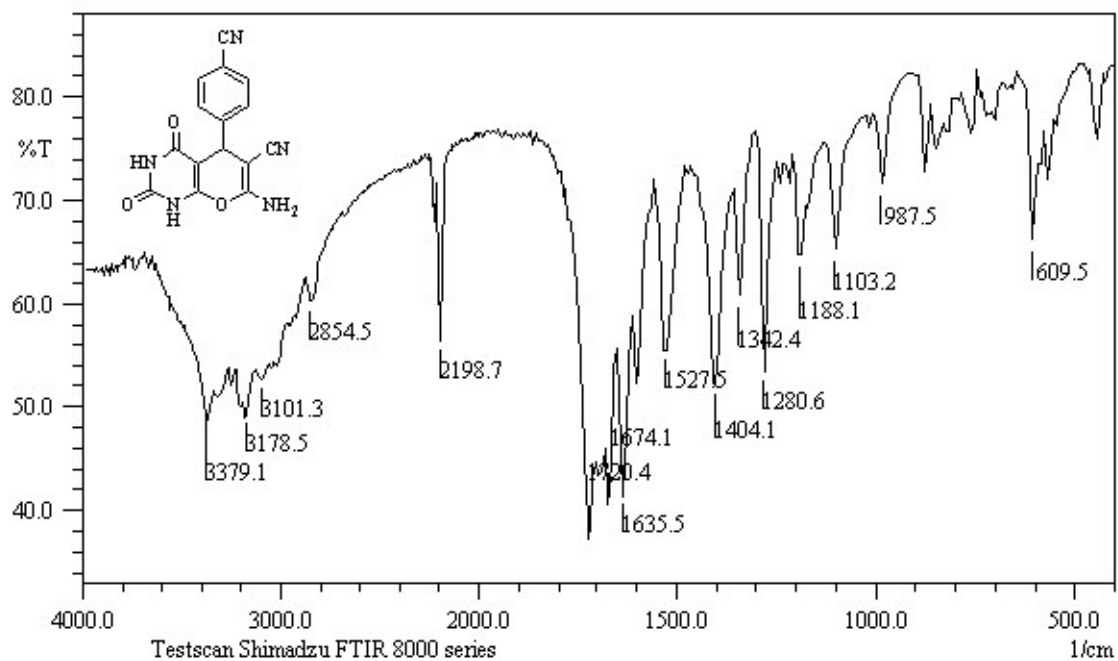


2-amino-4-(4-(2-amino-3-cyano-5-oxo-5,6,7,8-tetrahydro-4H-chromen-4-yl)phenyl)-8-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

**20. 7-amino-5-(4-cyanophenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (4t)**

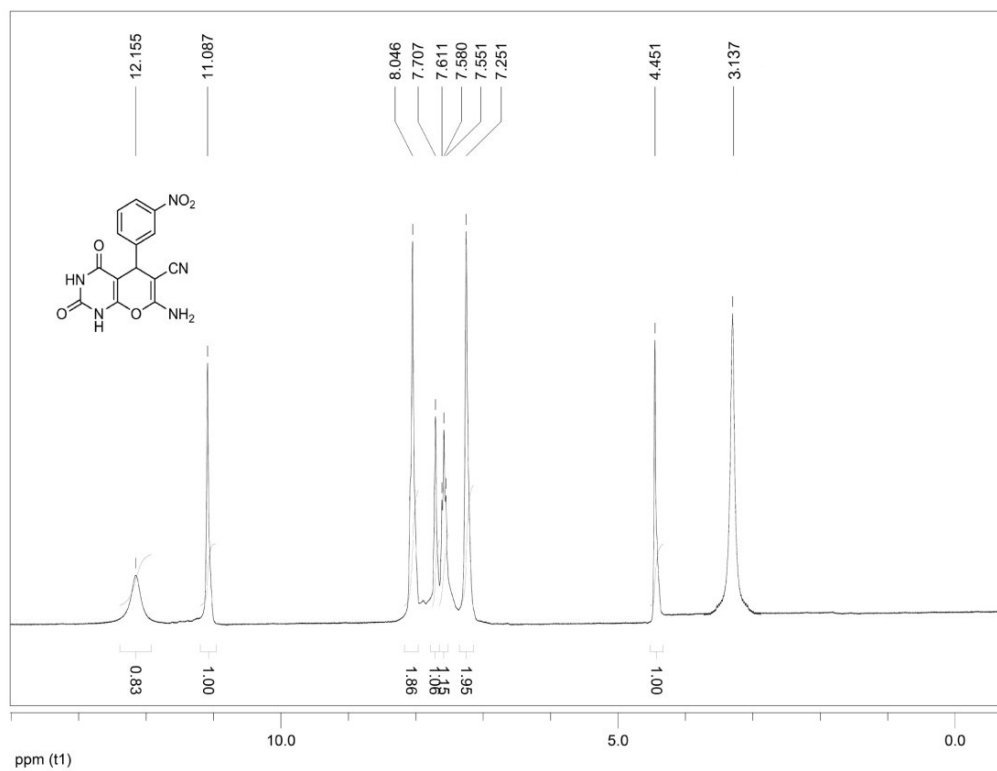




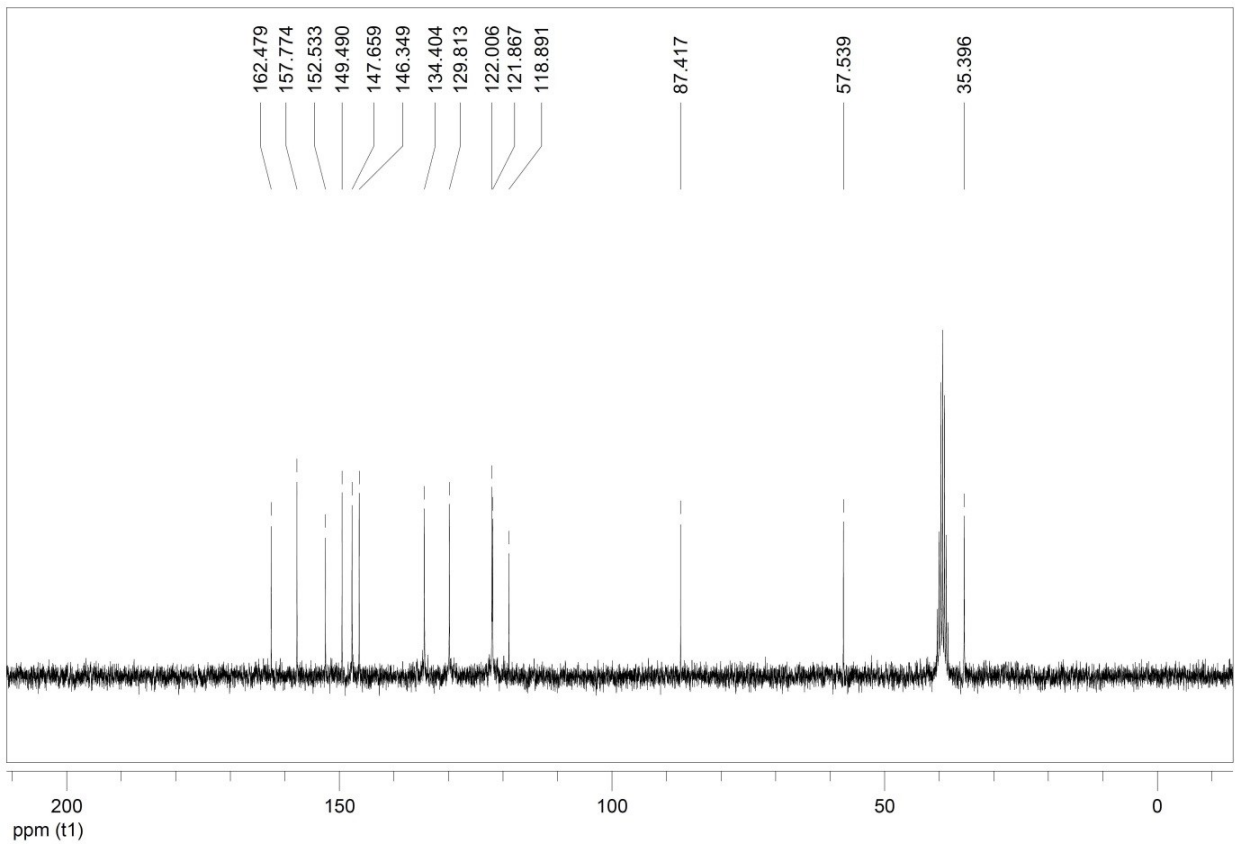
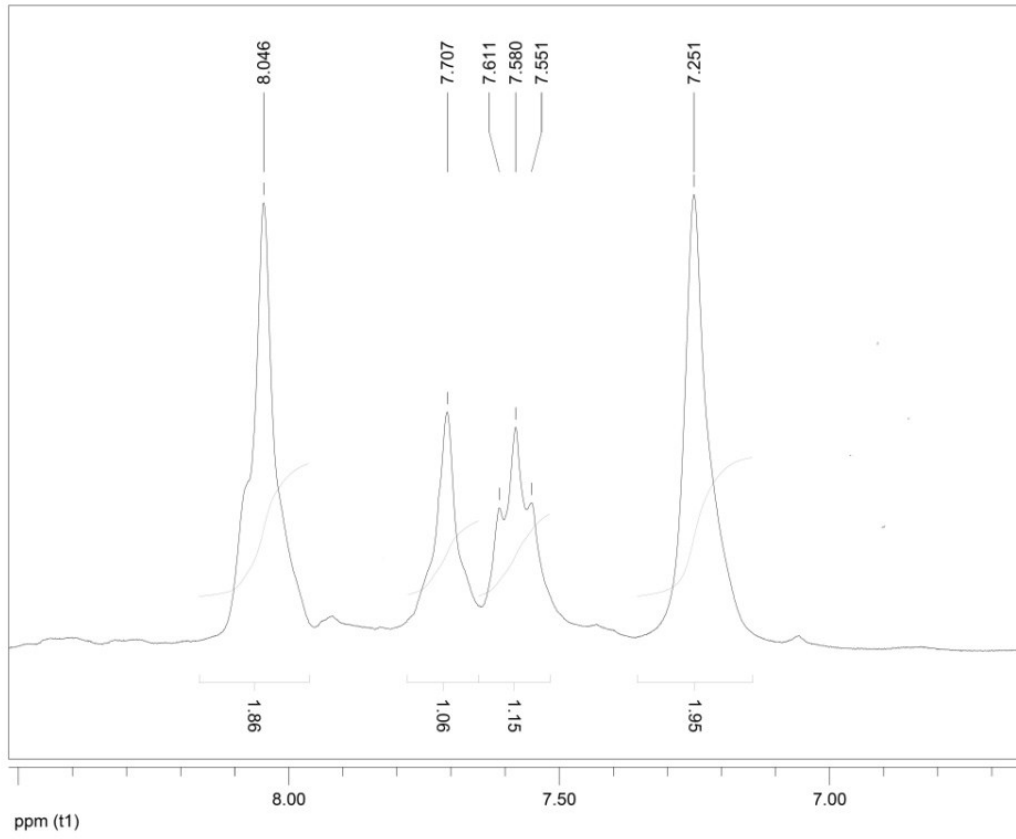


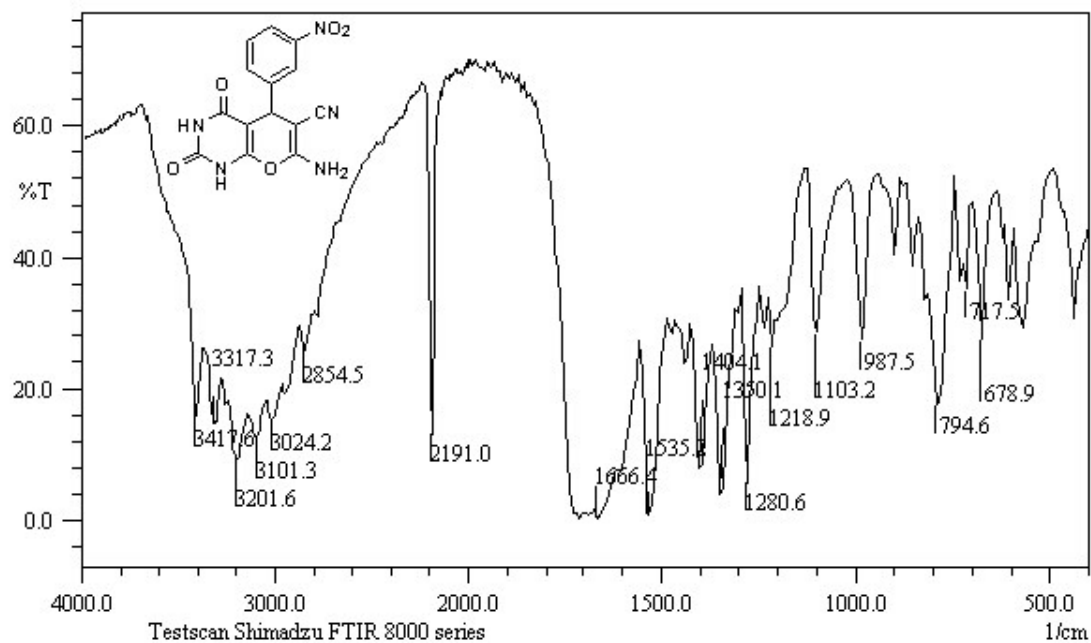
7-amino-5-(4-cyanophenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile

**21. 7-amino-5-(3-nitrophenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (4u)**

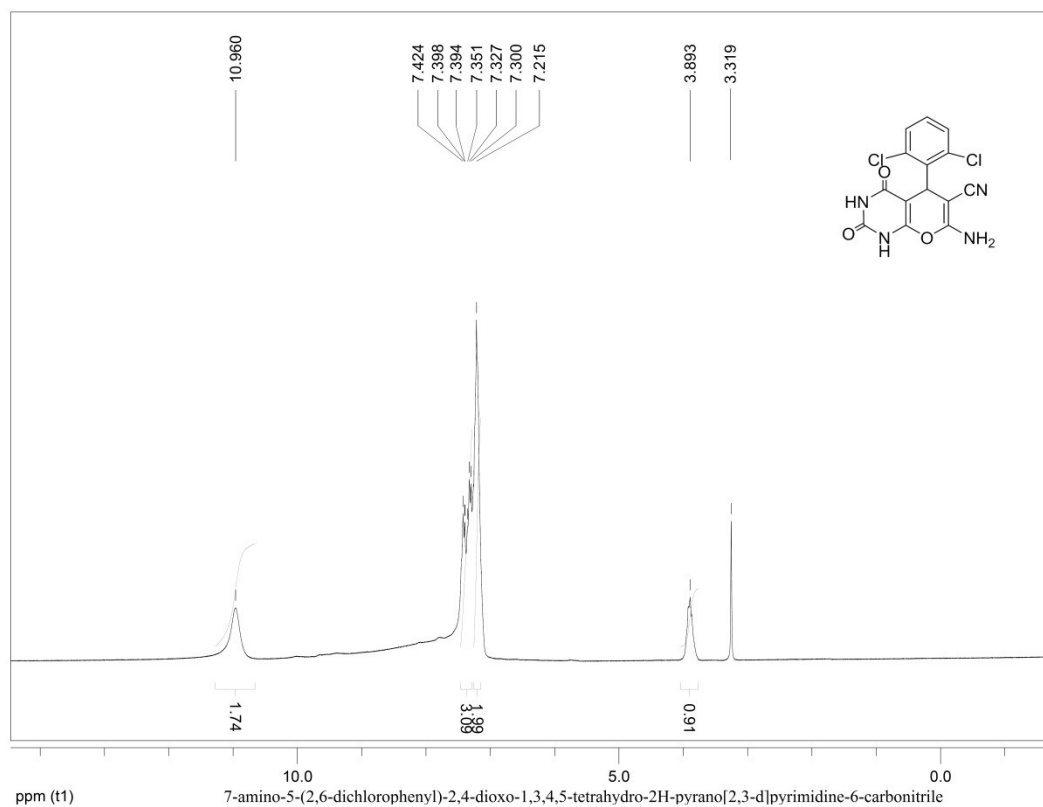


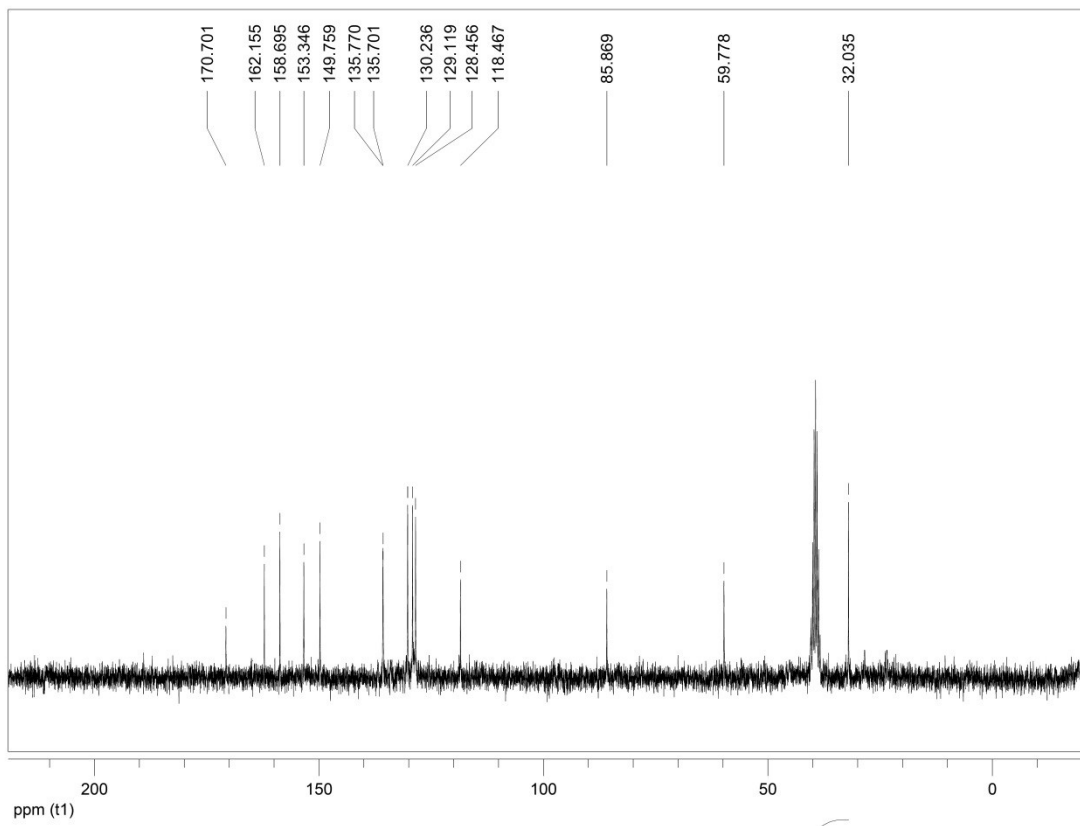
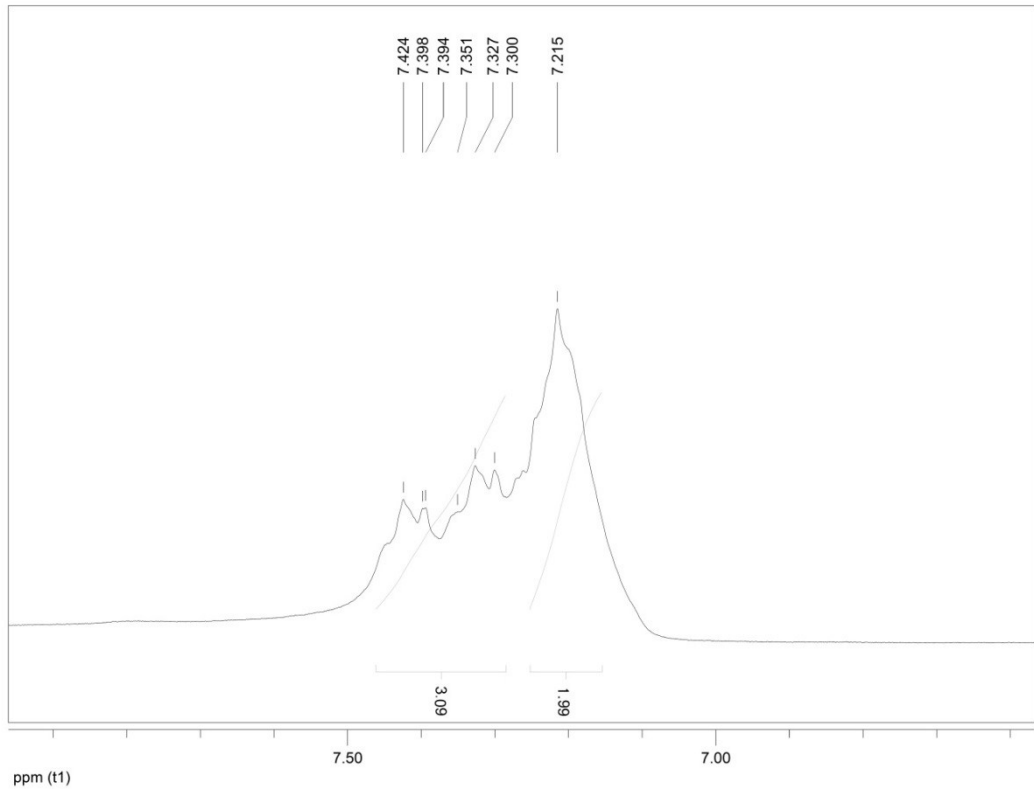
7-amino-5-(3-nitrophenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile

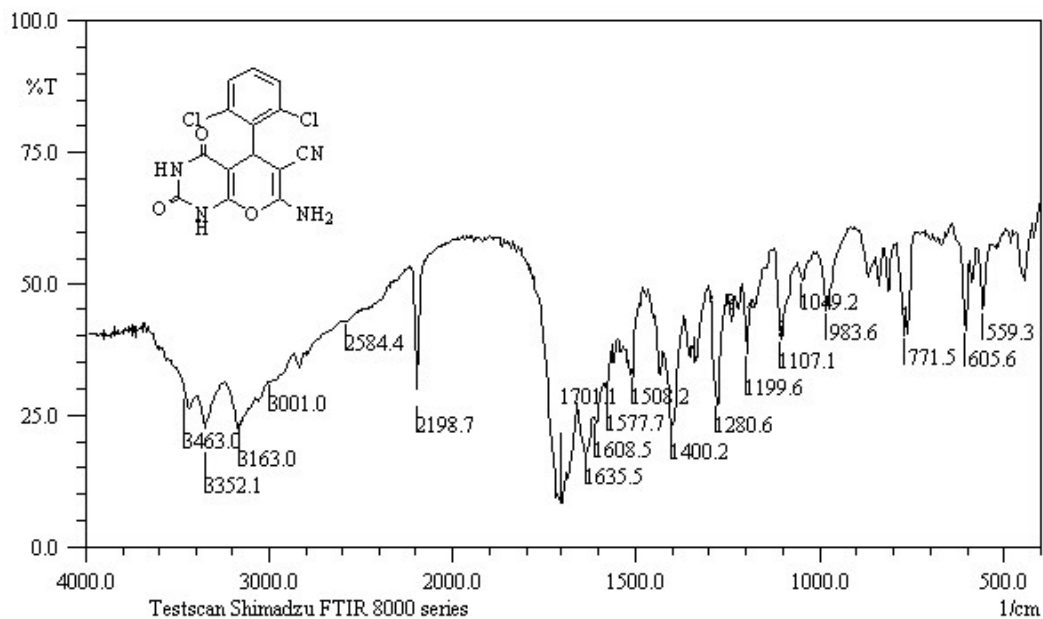




**22. 7-amino-5-(2,6-dichlorophenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrido[2,3-d]pyrimidine-6-carbonitrile (4v)**

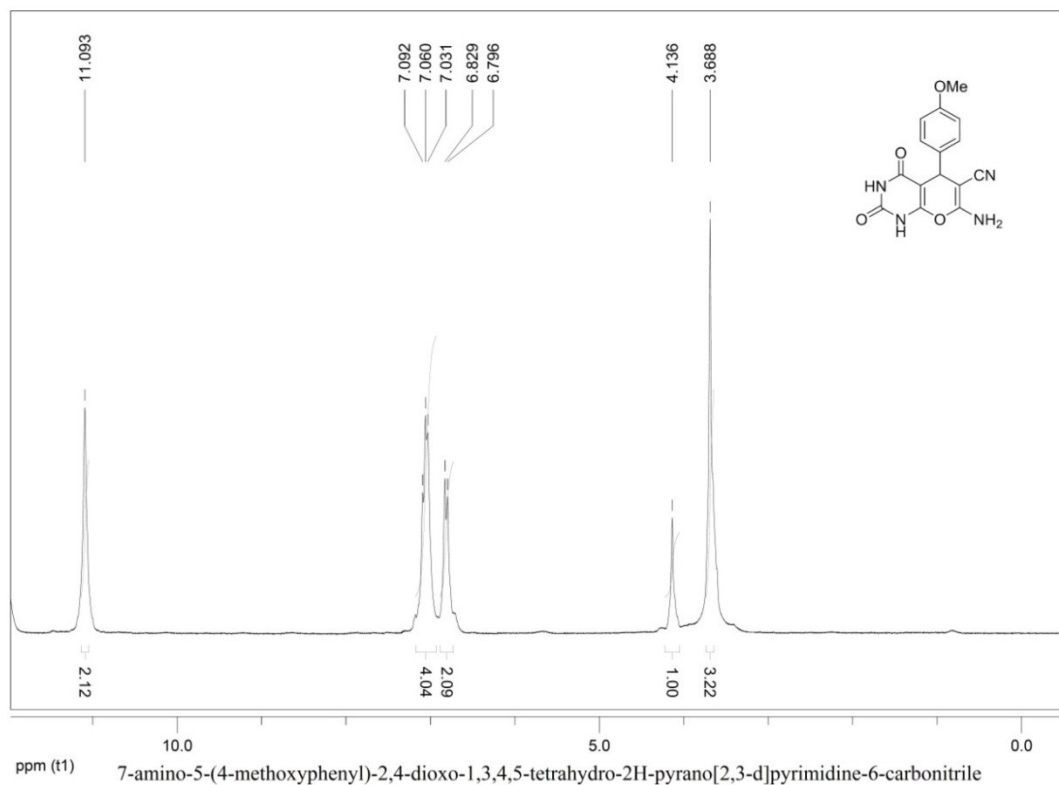




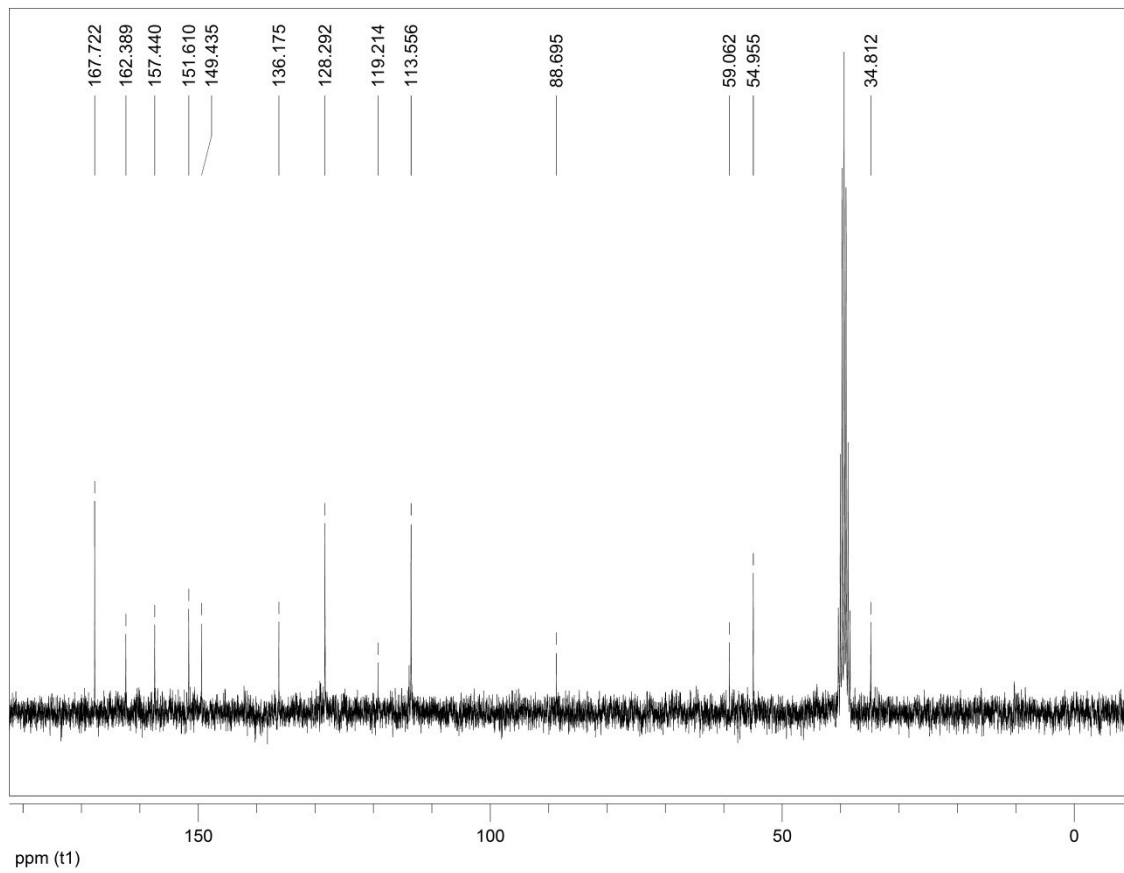
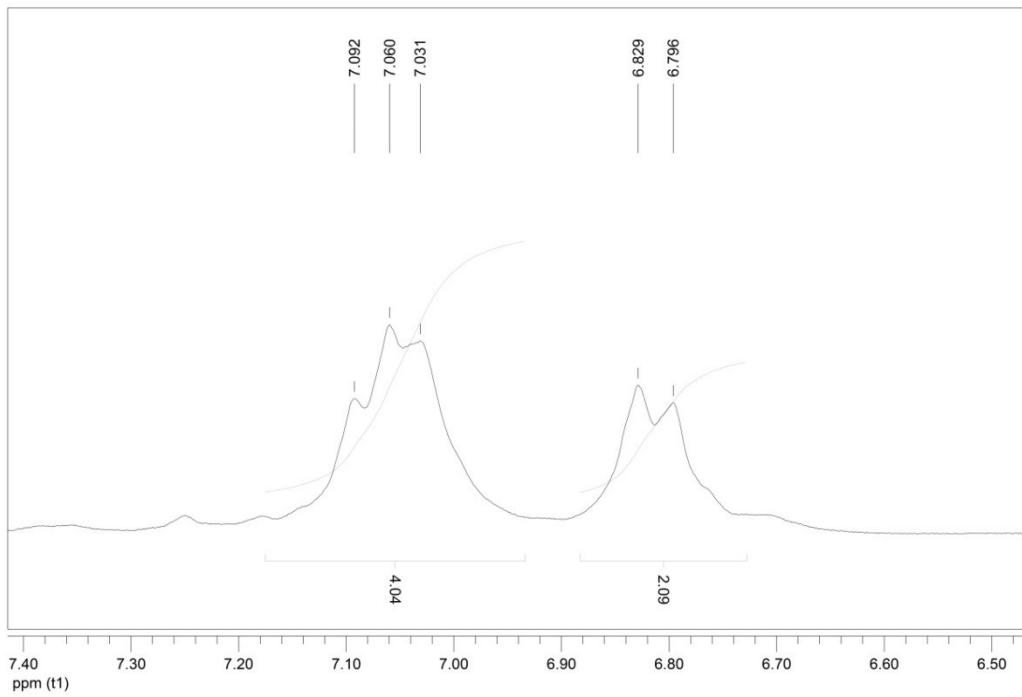


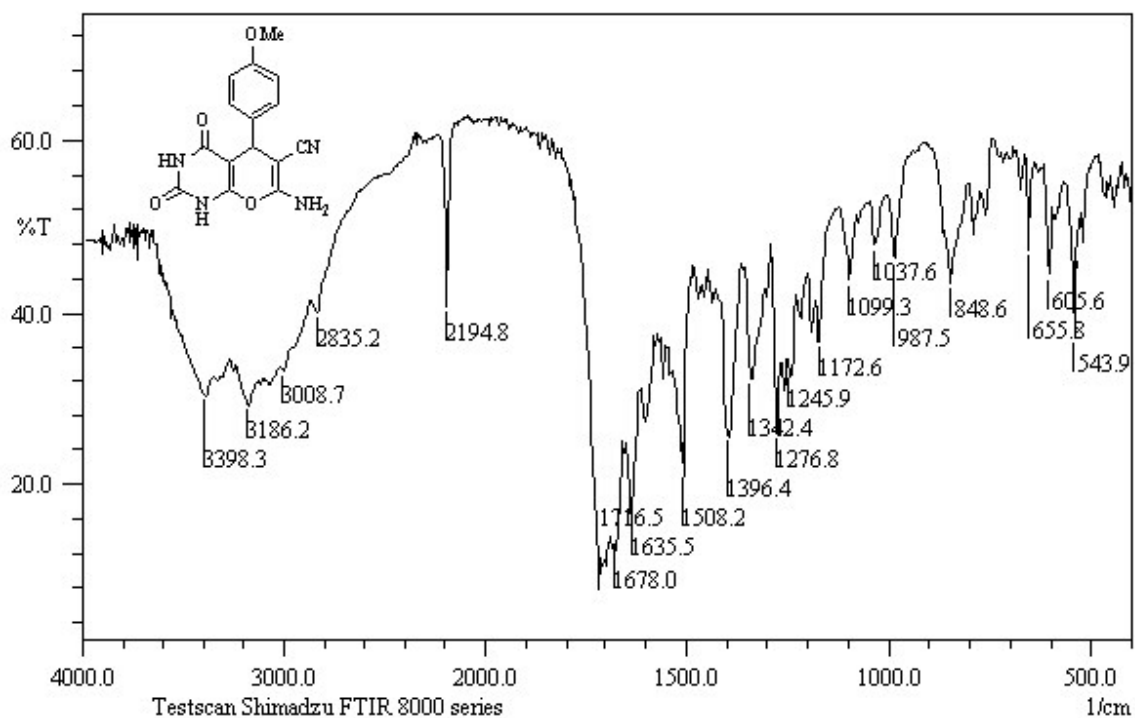
7-amino-5-(2,6-dichlorophenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile

**23. 7-amino-5-(4-methoxyphenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (4w)**



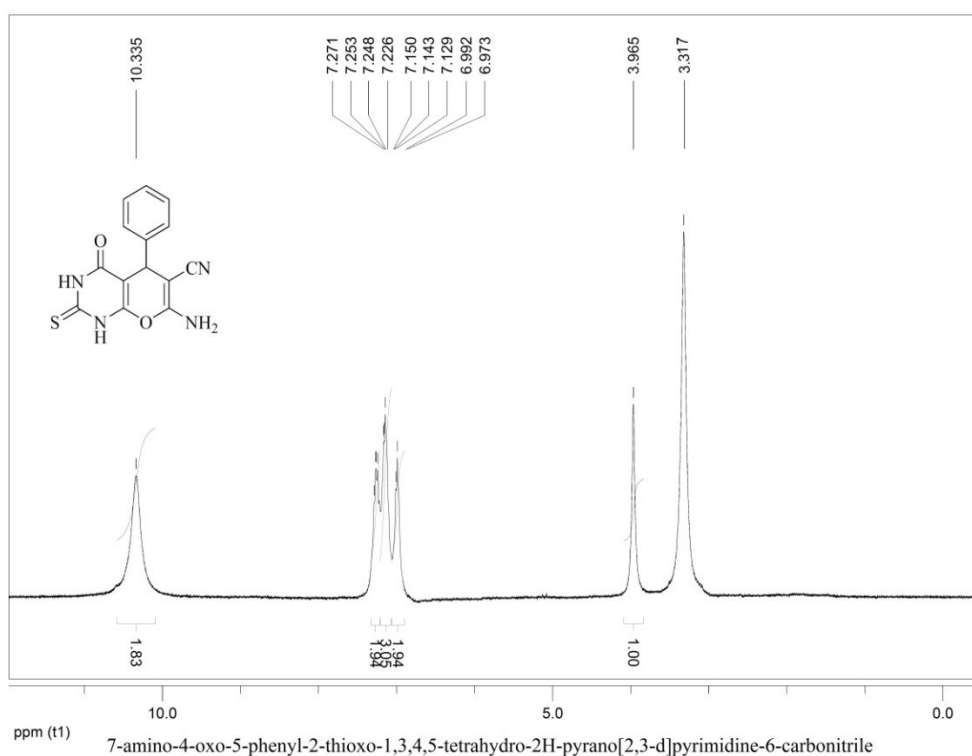


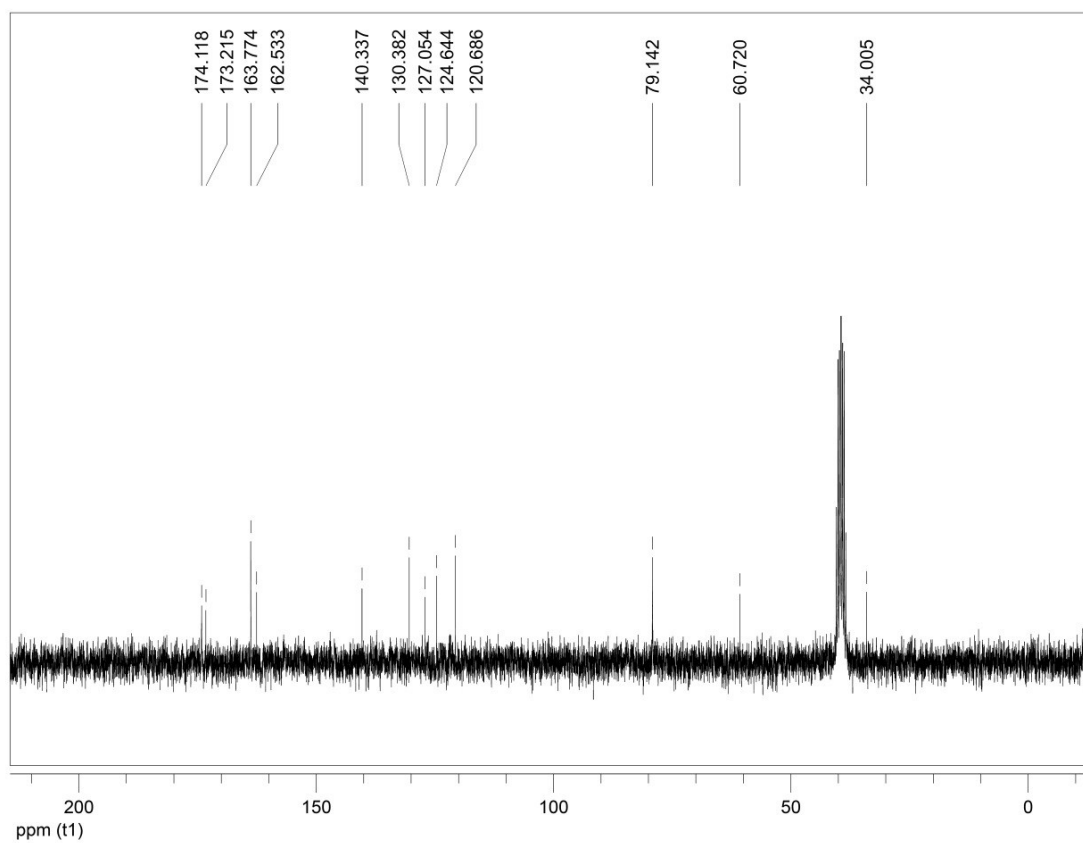
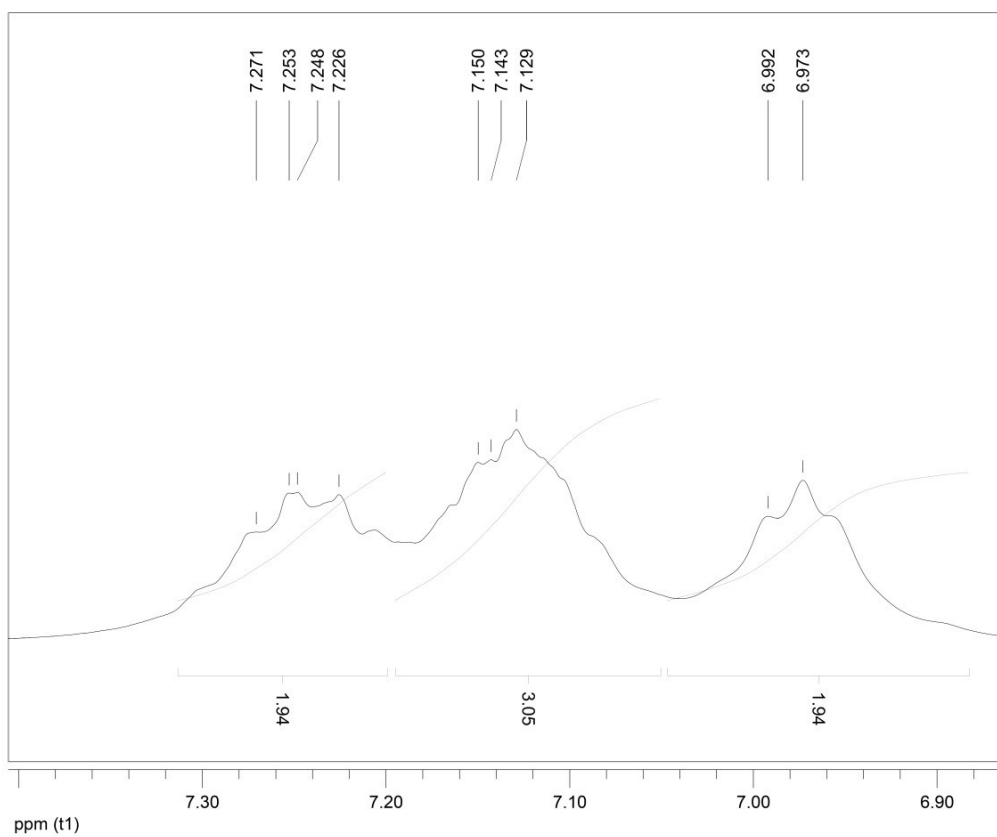


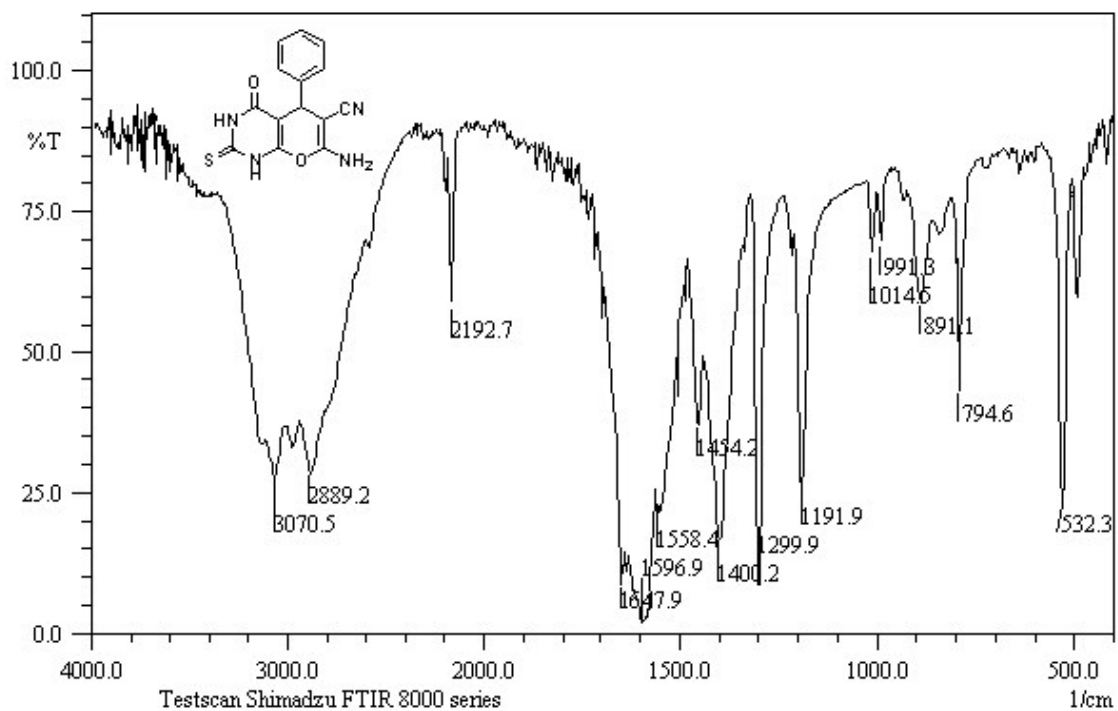


7-amino-5-(4-methoxyphenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile

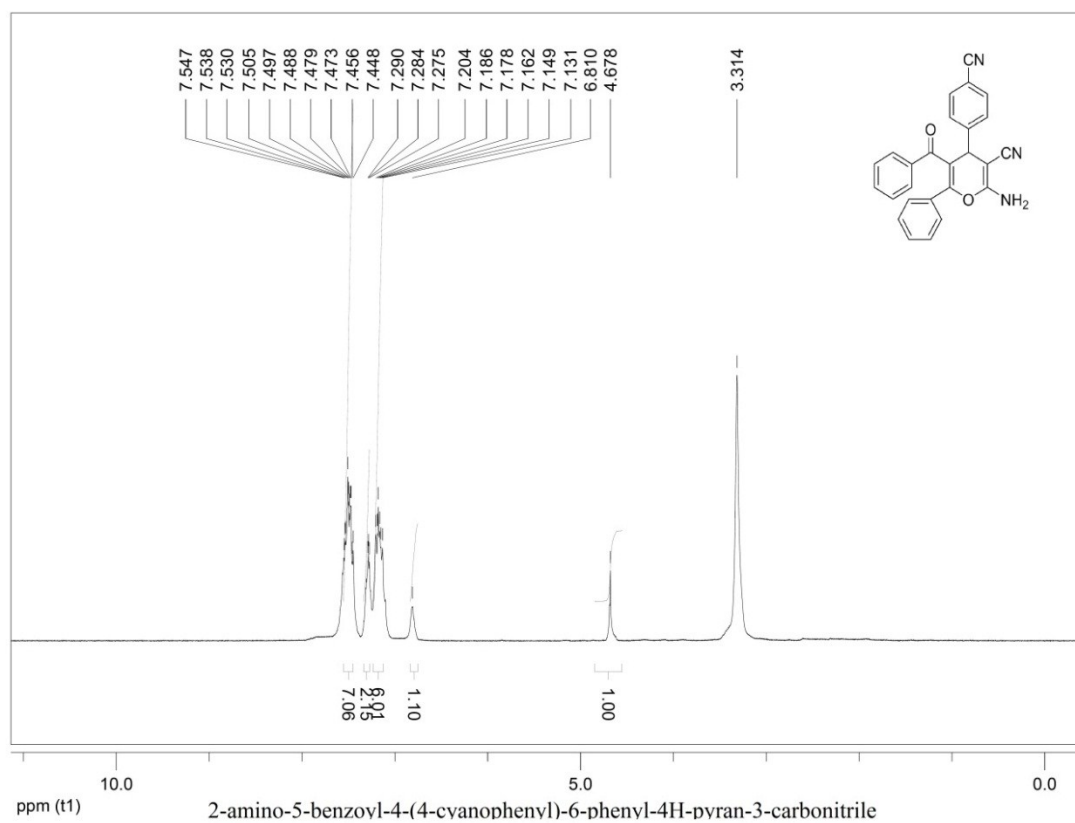
**24. 7-amino-4-oxo-5-phenyl-2-thioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (4x)**

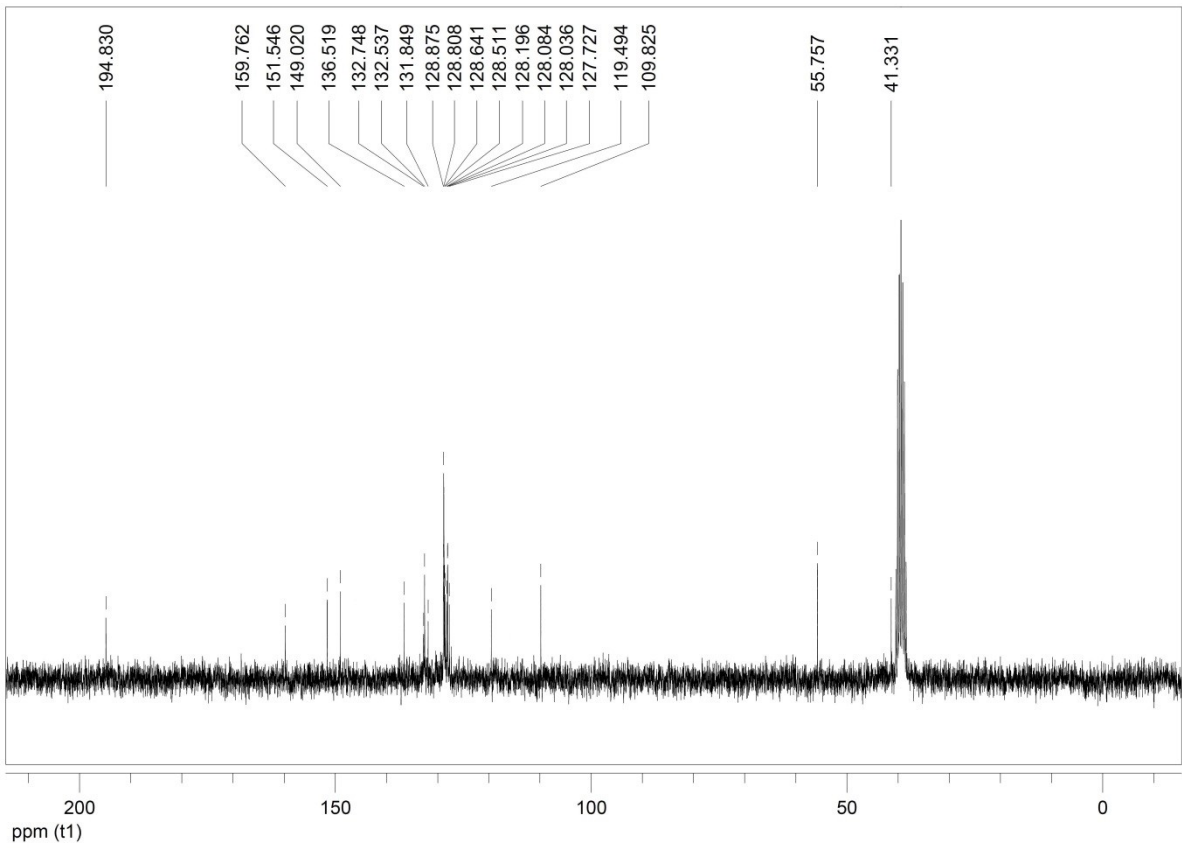
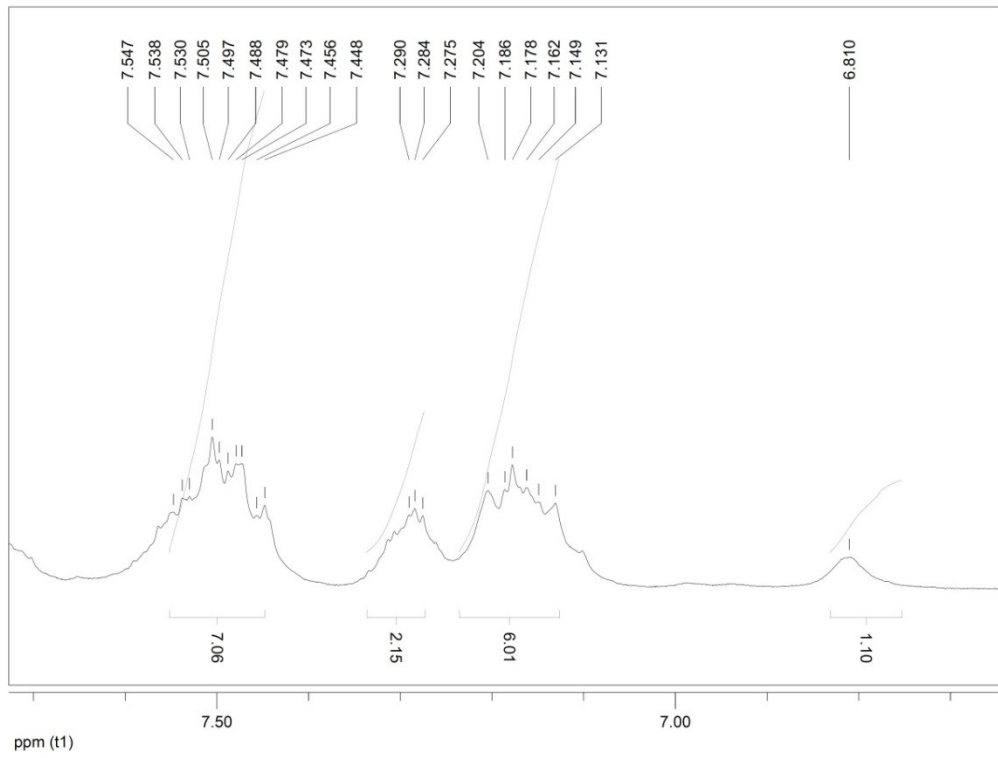


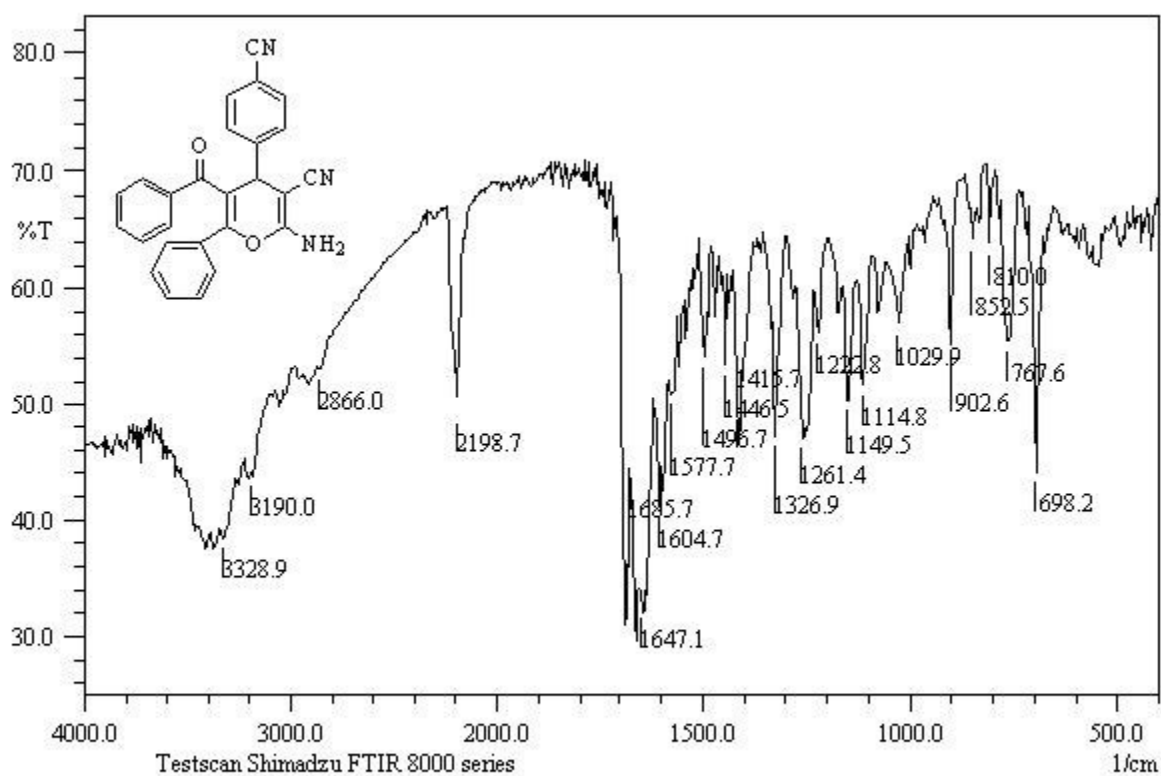




**25. 2-amino-5-benzoyl-4-(4-cyanophenyl)-6-phenyl-4H-pyran-3-carbonitrile (4y)**







2-amino-5-benzoyl-4-(4-cyanophenyl)-6-phenyl-4H-pyran-3-carbonitrile