Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

A Benign synthesis of 2-amino-4H-chromene in aqueous medium using hydrotalcite (HT) as a heterogeneous base catalyst

Sandip R. Kale,[a] Sandeep S. Kahandal,[a] Anand S. Burange,[a] Manoj B. Gawande[b] and Radha V. Jayaram[a]*

[a]*Department of Chemistry, Institute of Chemical Technology, N. Parekh Marg, Matunga, Mumbai 400 019, India*
[b]*Department of Chemistry, Faculty of Science and Technology, Universidade Nova de Lisboa, 2829–516 Caparica, Portugal Tel - +351-964223243, Fax: +351 21 2948550, Tel: +351 21 2948300*

Basicity measurement by phenol adsorption method[1]

The base strength of the catalysts was determined by phenol adsorption method. Standard solutions of phenol in cyclohexane were prepared at room temperature (100, 200, 300, 400, 500, 600 ppm). After plotting calibration curve, fifty milliliters of 100 ppm solution was taken in separate conical flasks to which 0.2 g of the Mg/Al hydrotalcite catalyst was added and the mixture was kept in a shaker for 3 h. After equilibrium was reached, the catalyst was removed by filtration. The procedure was repeated for other catalysts. The amount of phenol adsorb by the catalysts was determined using following formula,

$$q_e = \frac{(Co-Ce) \times V}{W}$$

Catalyst	Surface area (m^2g^{-1})	Basicity (mmol g^{-1})
Mg/Al:2.0 hydrotalcite	145	0.087
Mg/Al:3.0 hydrotalcite	189	0.095
Mg/Al:4.0 hydrotalcite	236	0.117
Mg/Al:5.0 hydrotalcite	269	0.151

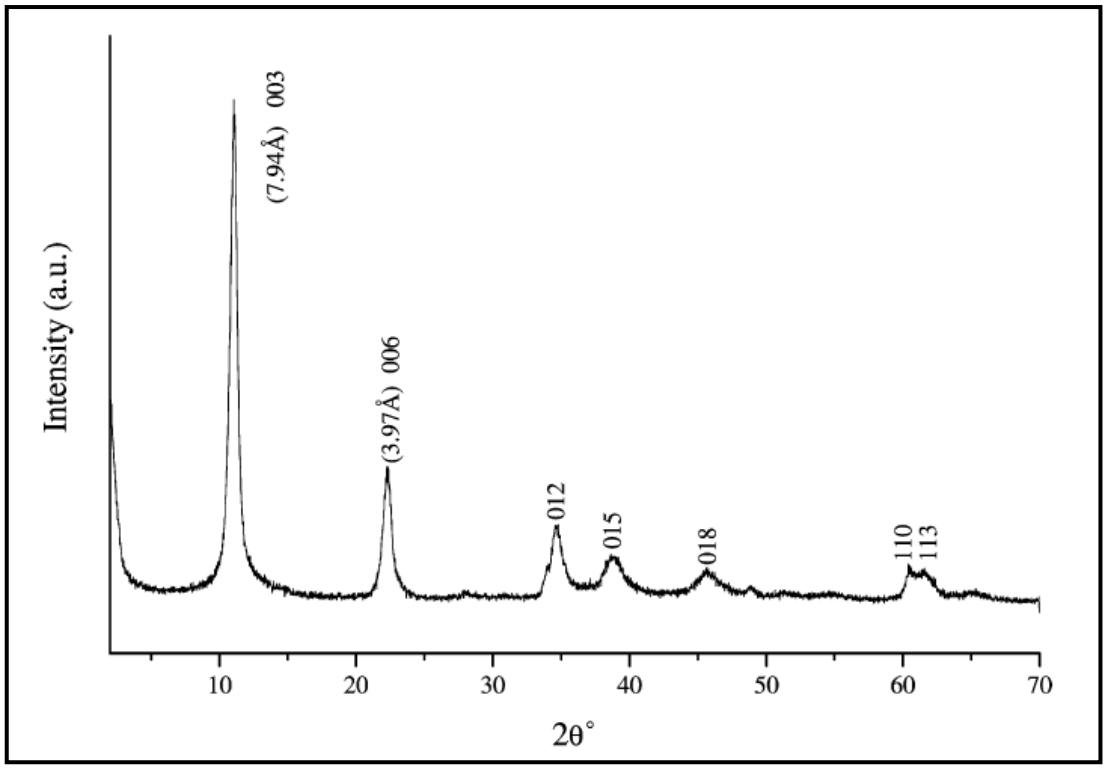
Where, qe – quantity of phenol adsorb,

Co- initial conc. of phenol,

Ce- conc. of phenol at equilibrium,

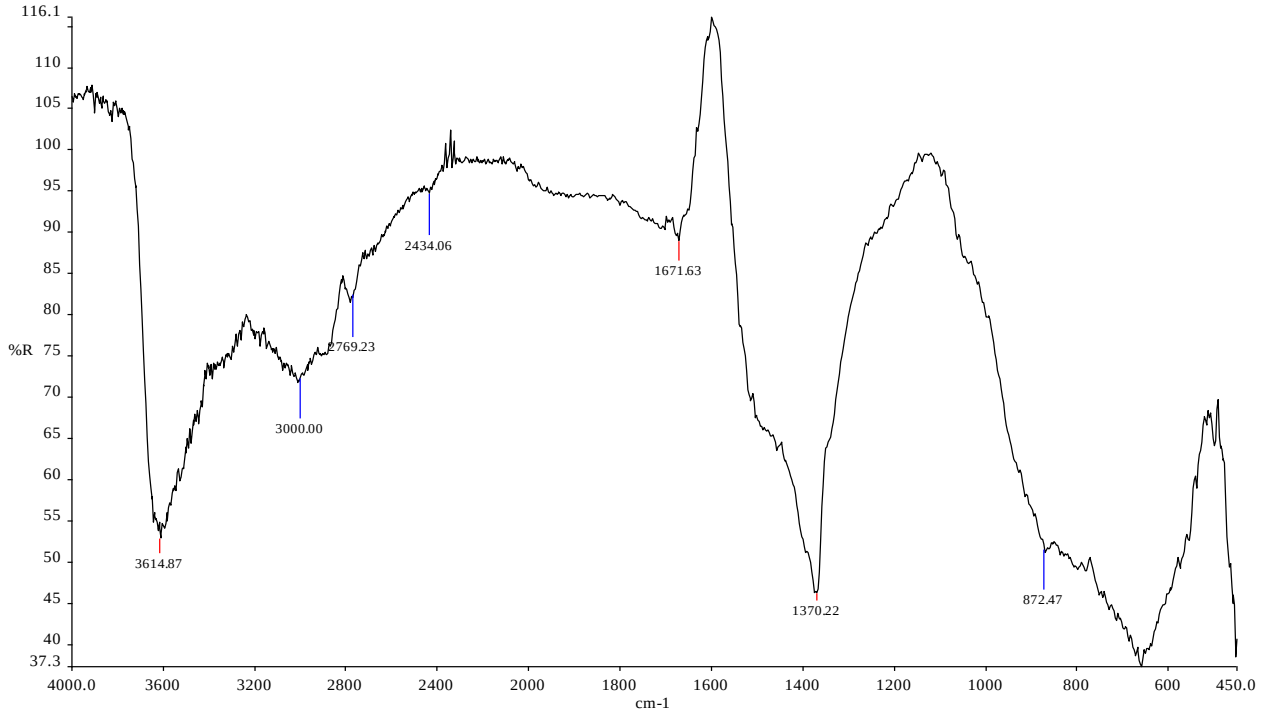
W- wt. of the catalyst (gm)

From the phenol adsorption experiment, it was observed that Mg/Al= 5 shows maximum total basicity (0.131 mmol/g).



XRD of Mg/Al: 5.0 hydrotalcite

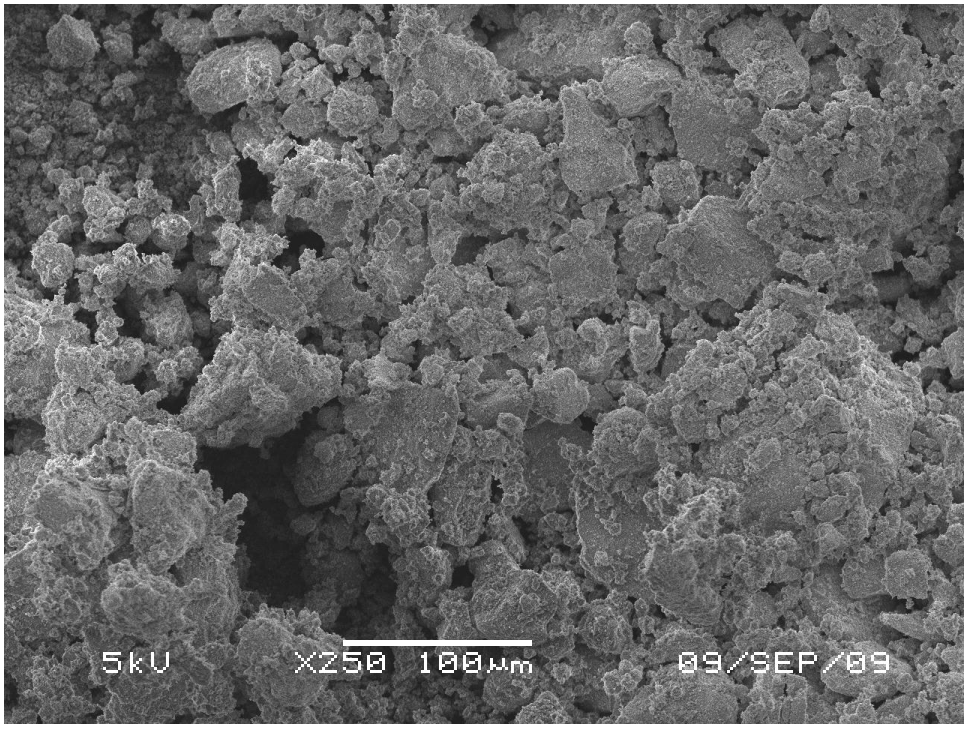
XRD of the Mg/Al: 5.0 hydrotalcite clearly indicate the crystalline nature of the catalyst. The presence of both sharp and diffuse non-basal reflections was taken as indication of a partially disordered structure.



FTIR spectra of Mg/Al: 5.0 hydrotalcite

The peak present around 3000 cm^{-1} can be attributed to hydrogen bonding between H_2O and the anion in the interlayer; an H_2O bending vibration also occurs at 1670 cm^{-1}. The intensity of these latter two bands depends on the type of anion and the amount of water.

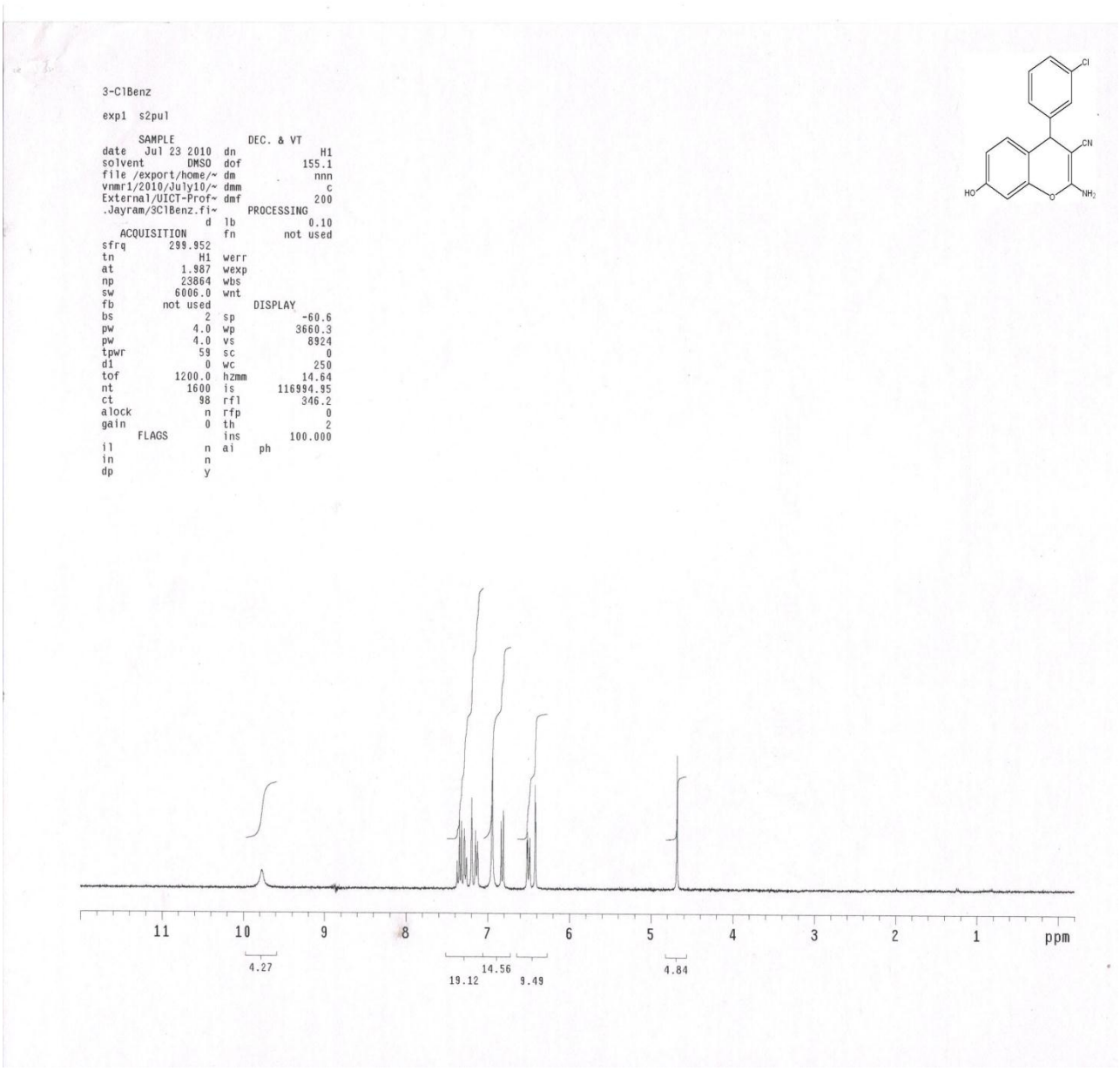
In the 600-1000 cm^{-1}, region there are some bands related to vibrations of the anions, and some related to cation-oxygen vibration. This region has been thoroughly studied only by Sema (Serna et al. 1985). IR frequency value at 1360 cm^{-1} is related to the carbonate ion present in the interlayer.



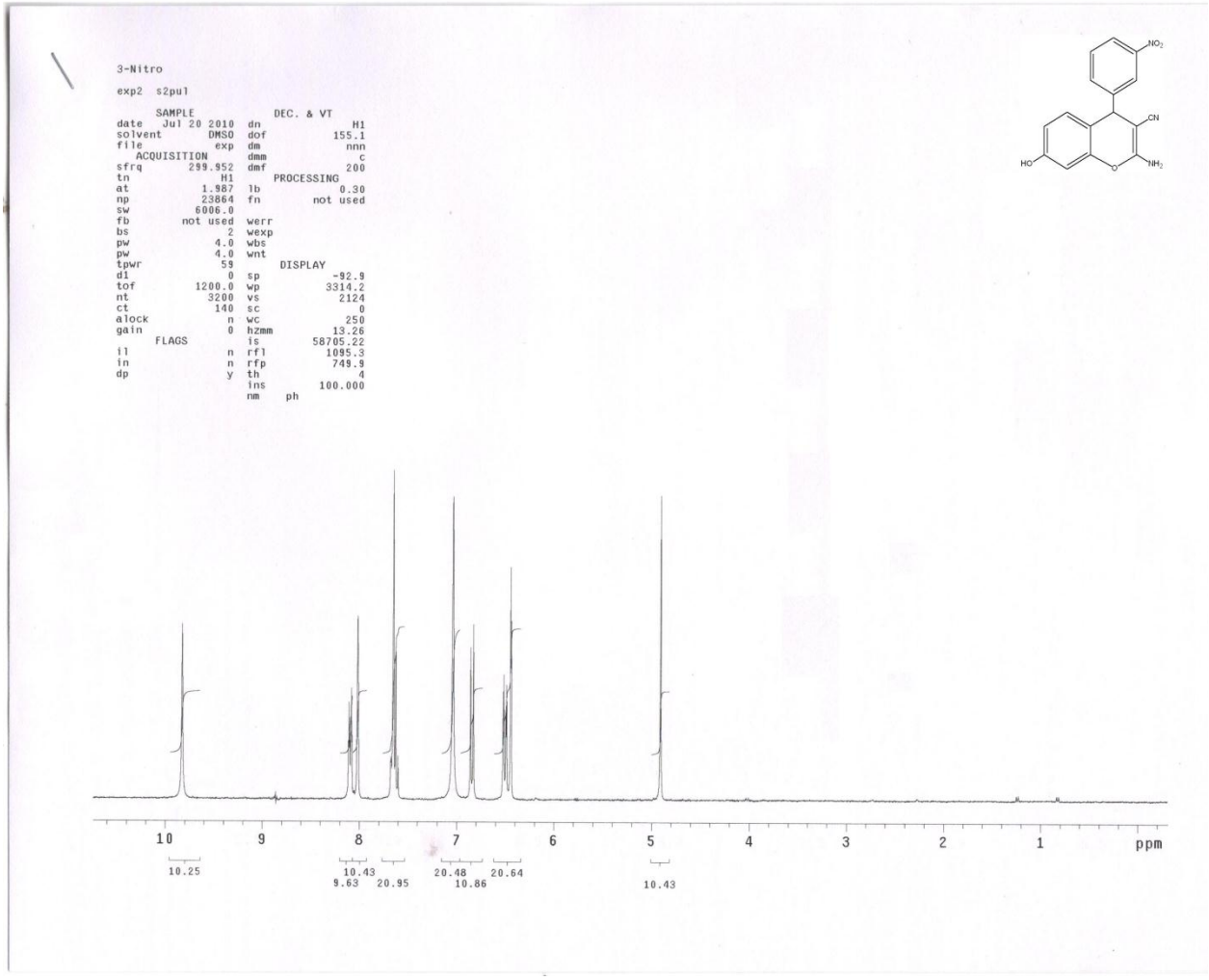
SEM image of Mg/Al: 5.0 hydrotalcite

Observations at the scanning electron microscope showed that the particles are formed by almost spherical aggregates of hexagonal platelets.

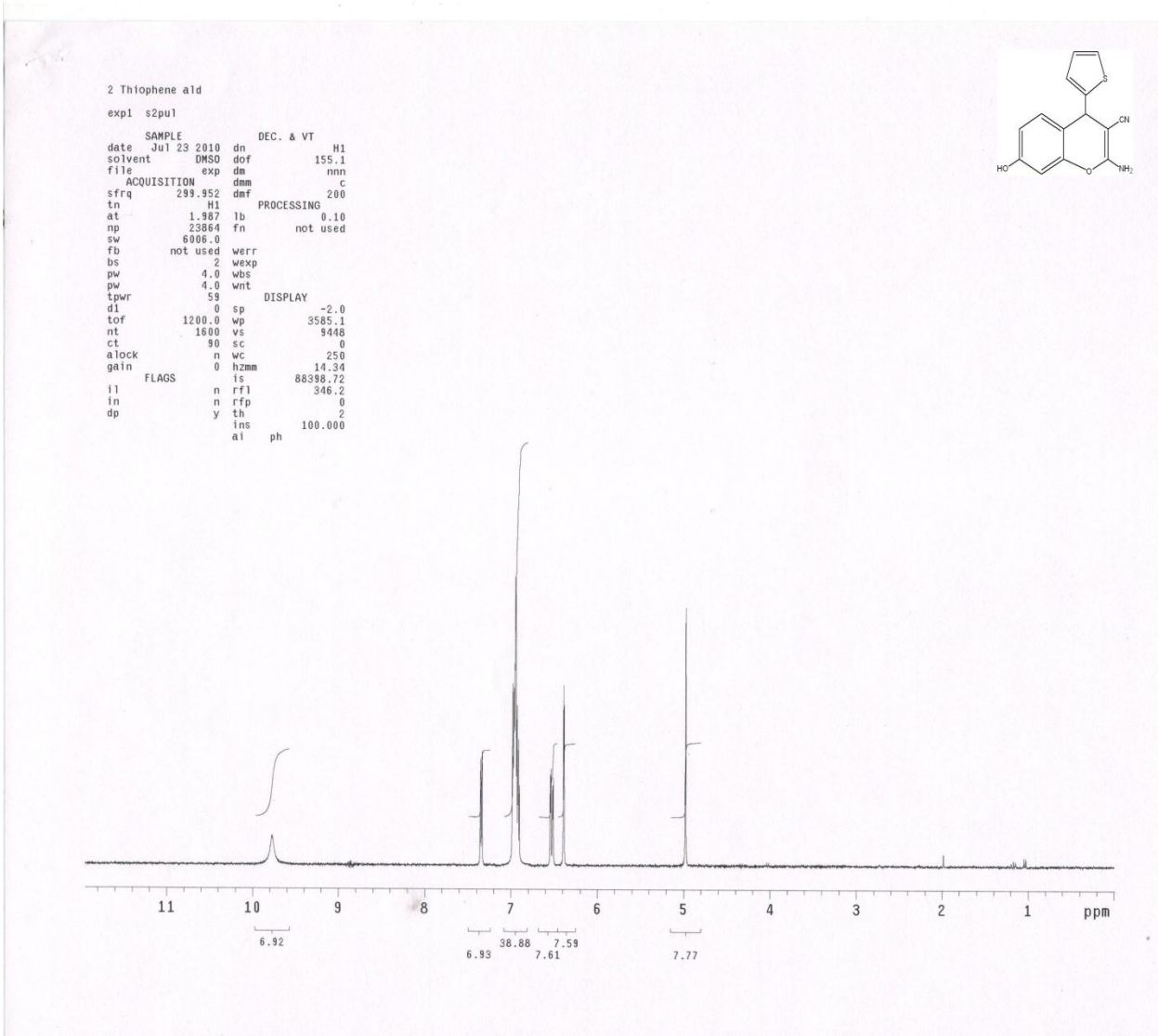
^{1}H NMR spectra of 2-Amino-3-cyano-7-hydroxy-4-(3-chlorophenyl)-4Hchromene:



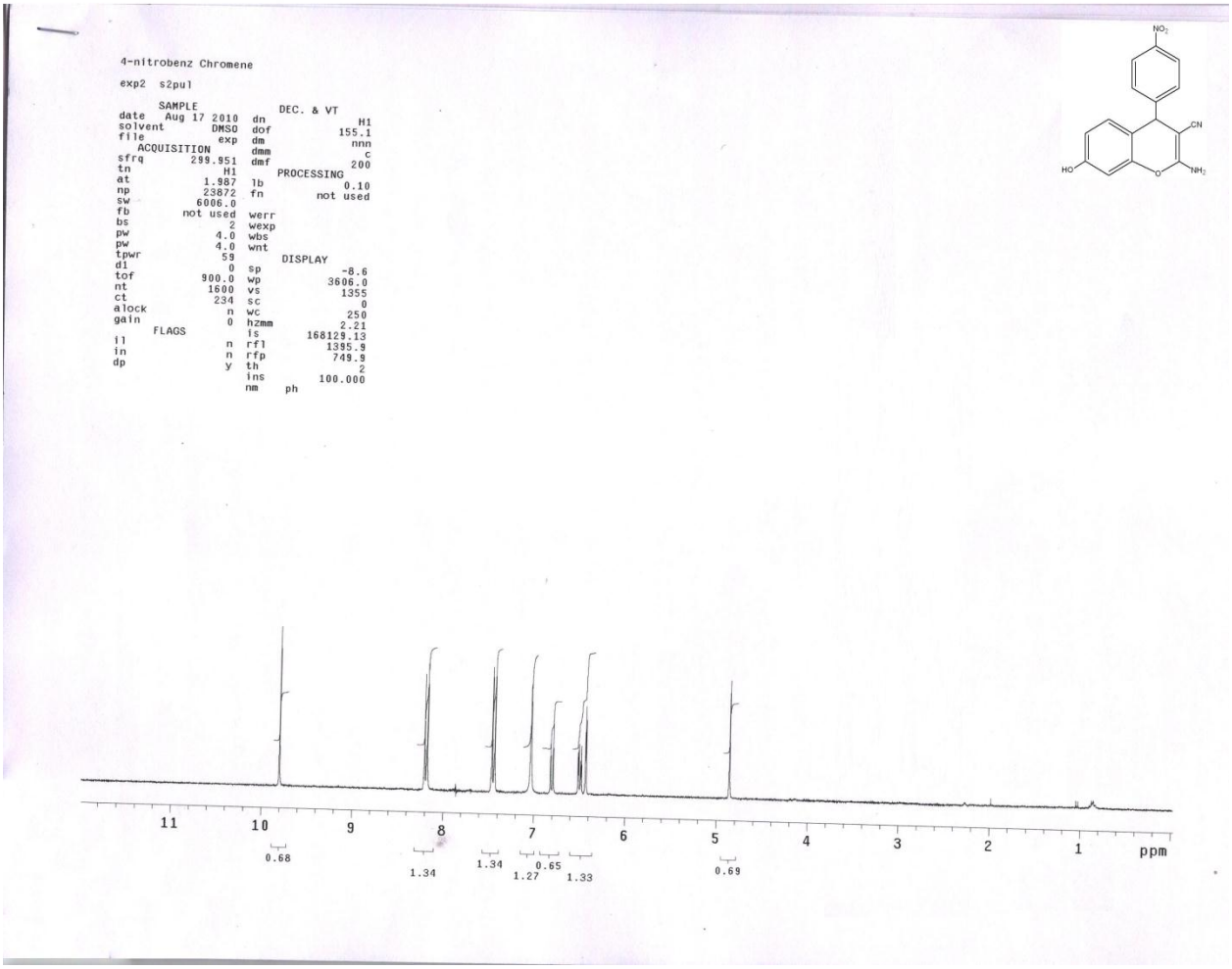
^{1}H NMR spectra of 2-Amino-3-: cyano-7-hydroxy-4-(3-nitrophenyl)-4Hchromene



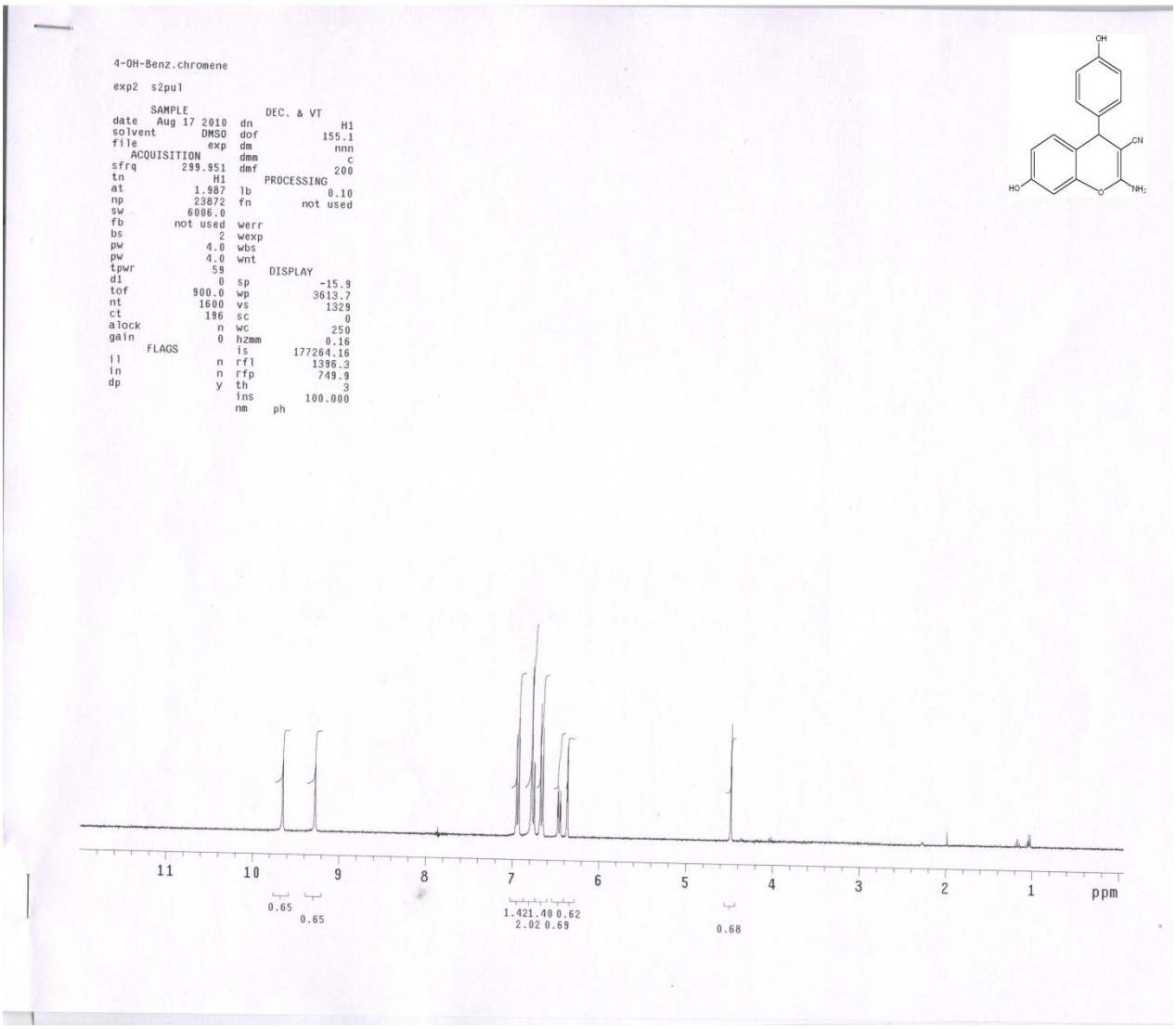
^{1}H NMR spectra of 2-Amino-3-cyano-7-hydroxy-4-(2-thiophene)-4Hchromene:



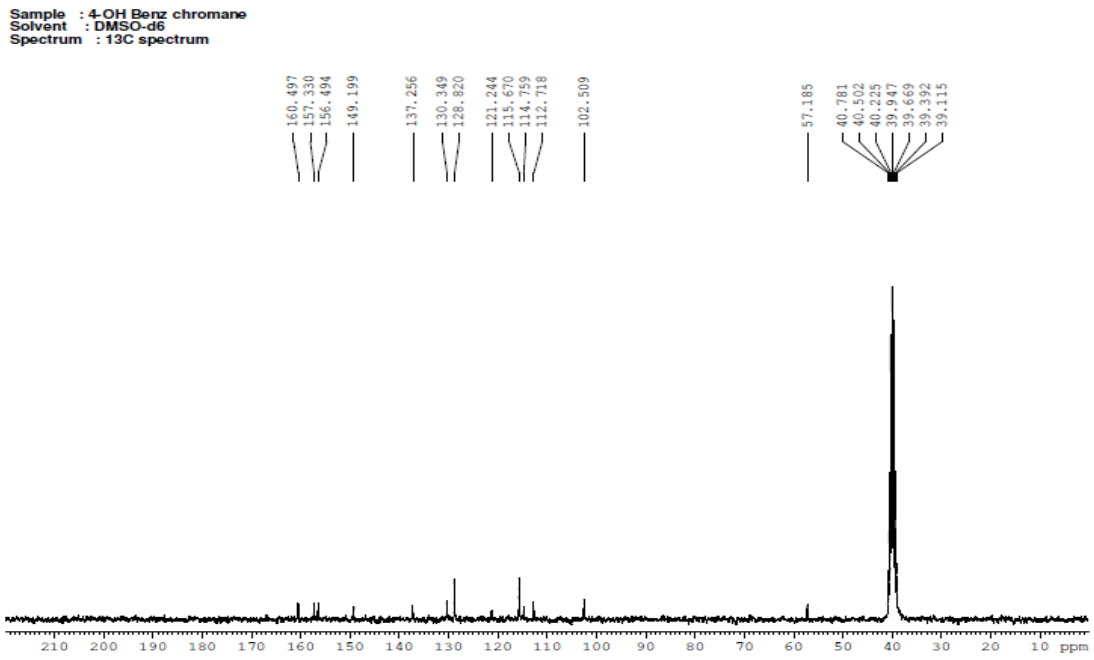
^{1}H NMR spectra of 2-Amino-3-cyano-7-hydroxy-4-(4-nitrophenyl)-4Hchromene:



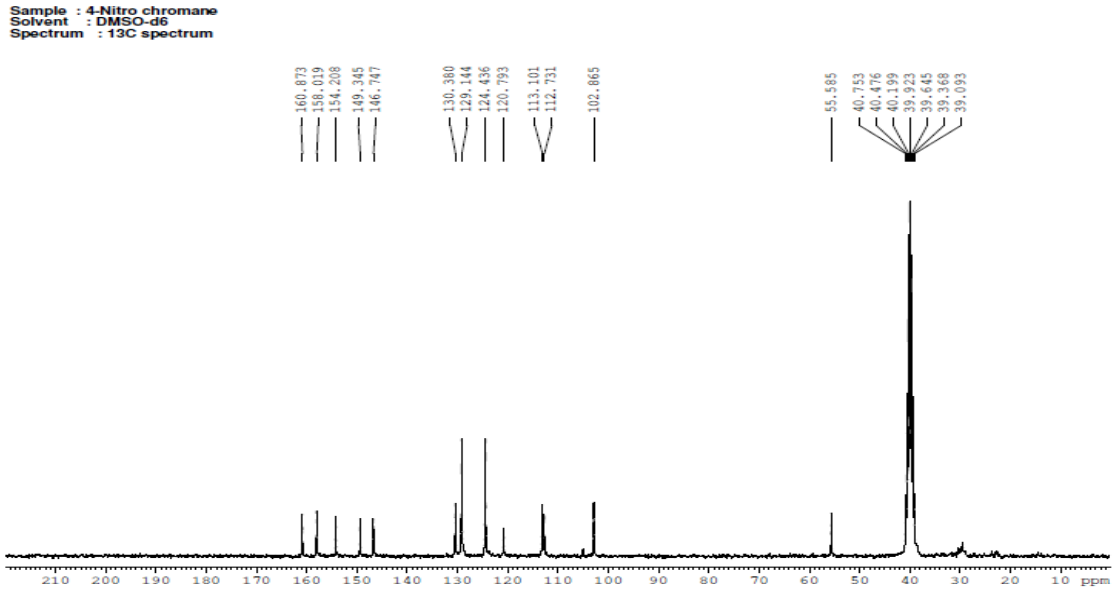
^{1}H NMR spectra of 2-Amino-3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-4Hchromene



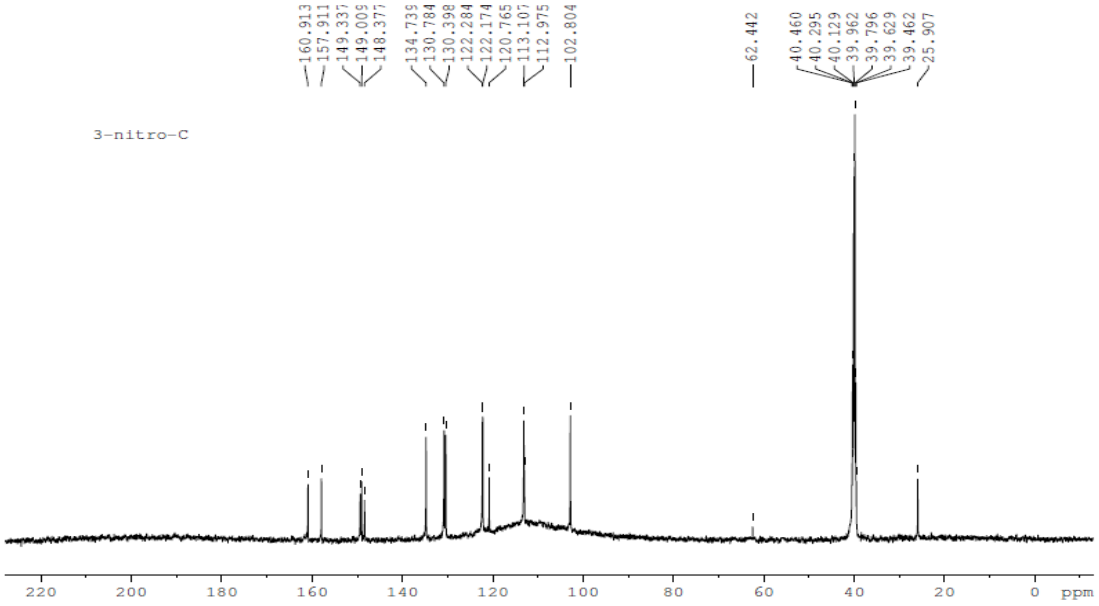
^{13}C NMR spectra of 2-Amino-3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-4Hchromene:



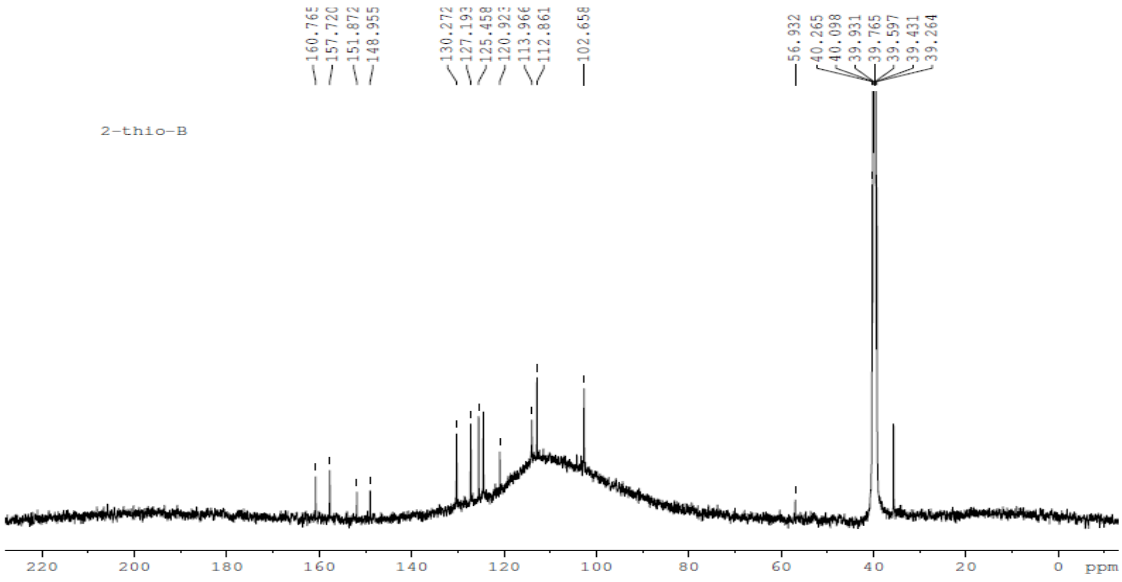
^{13}C NMR spectra of 2-Amino-3-cyano-7-hydroxy-4-(4-nitrophenyl)-4Hchromene:



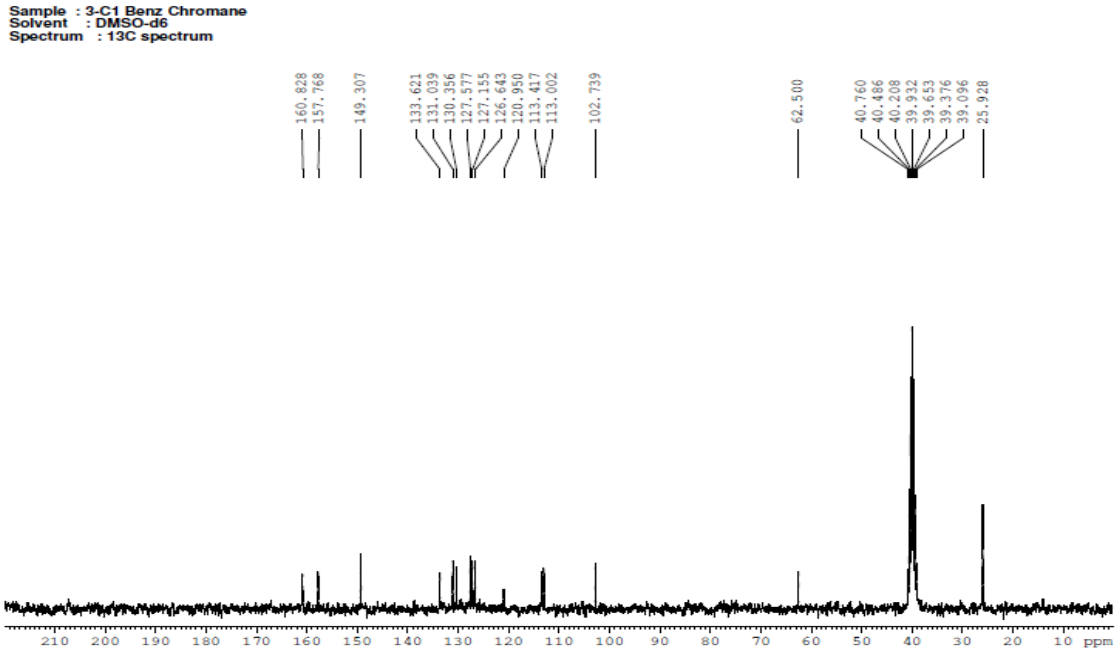
^{13}C NMR spectra of 2-Amino-3-cyano-7-hydroxy-4-(3-nitrophenyl)-4Hchromene:



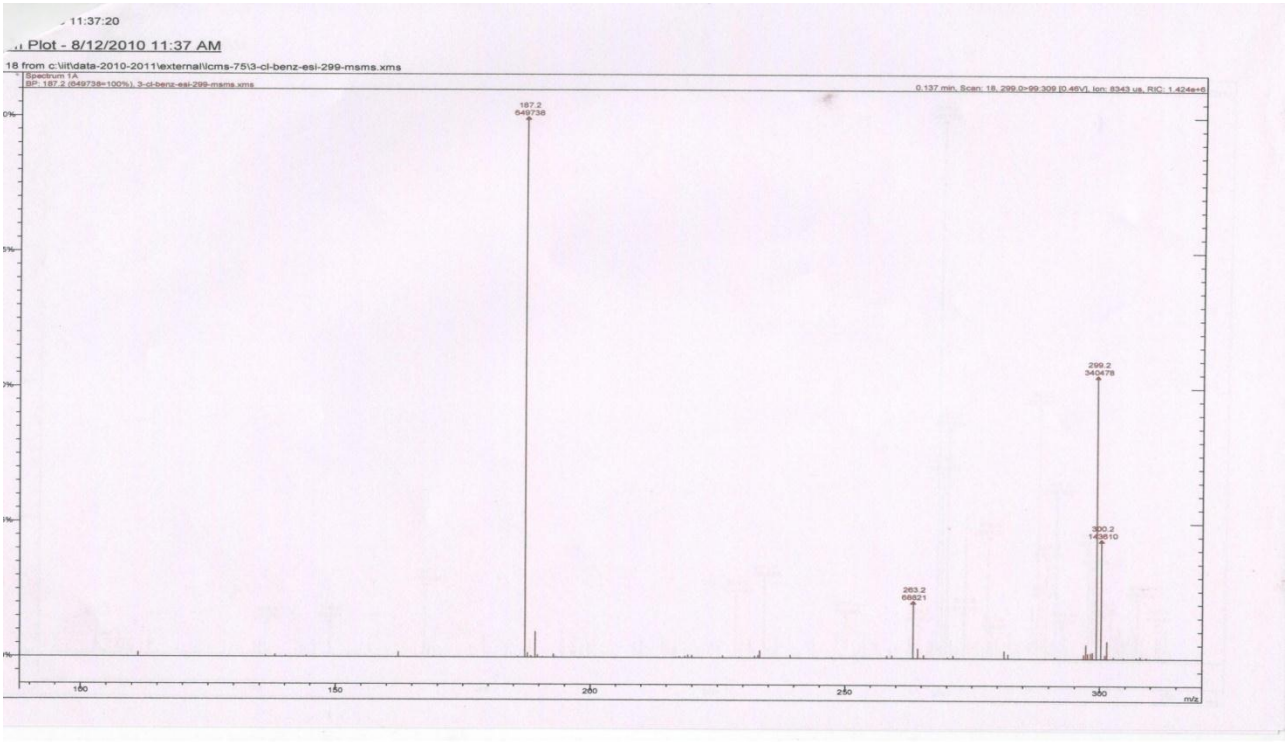
^{13}C NMR spectra of 2-Amino-3-cyano-7-hydroxy-4-(2-thiophene)-4Hchromene:



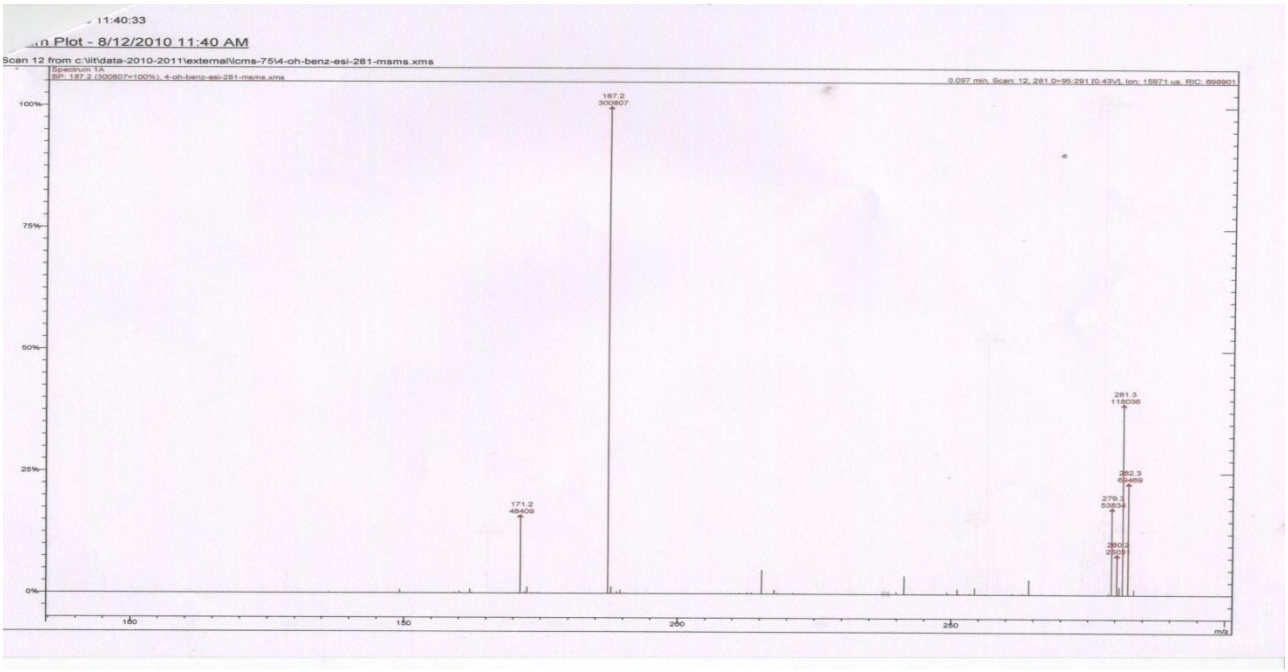
^{13}C NMR spectra of 2-Amino-3-cyano-7-hydroxy-4-(3-chlorophenyl)-4Hchromene:



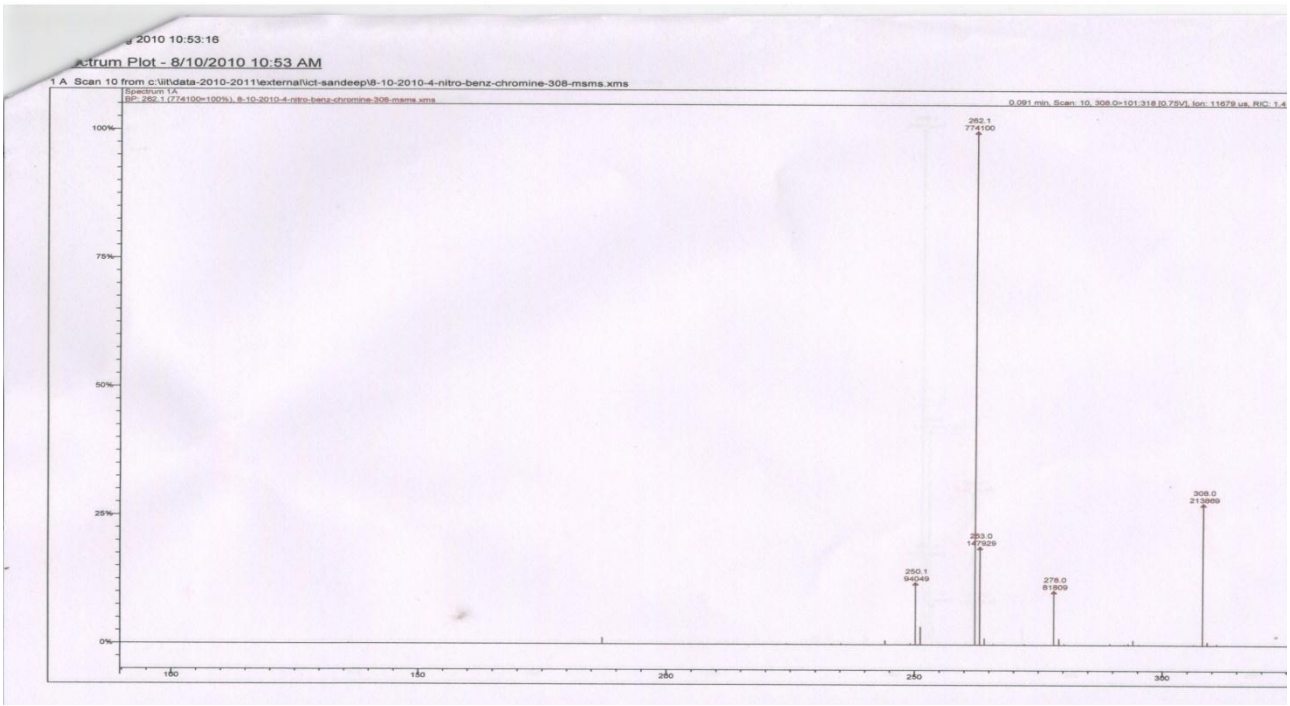
Mass spectra of 2-Amino-3-cyano-7-hydroxy-4-(3-chlorophenyl)-4Hchromene:



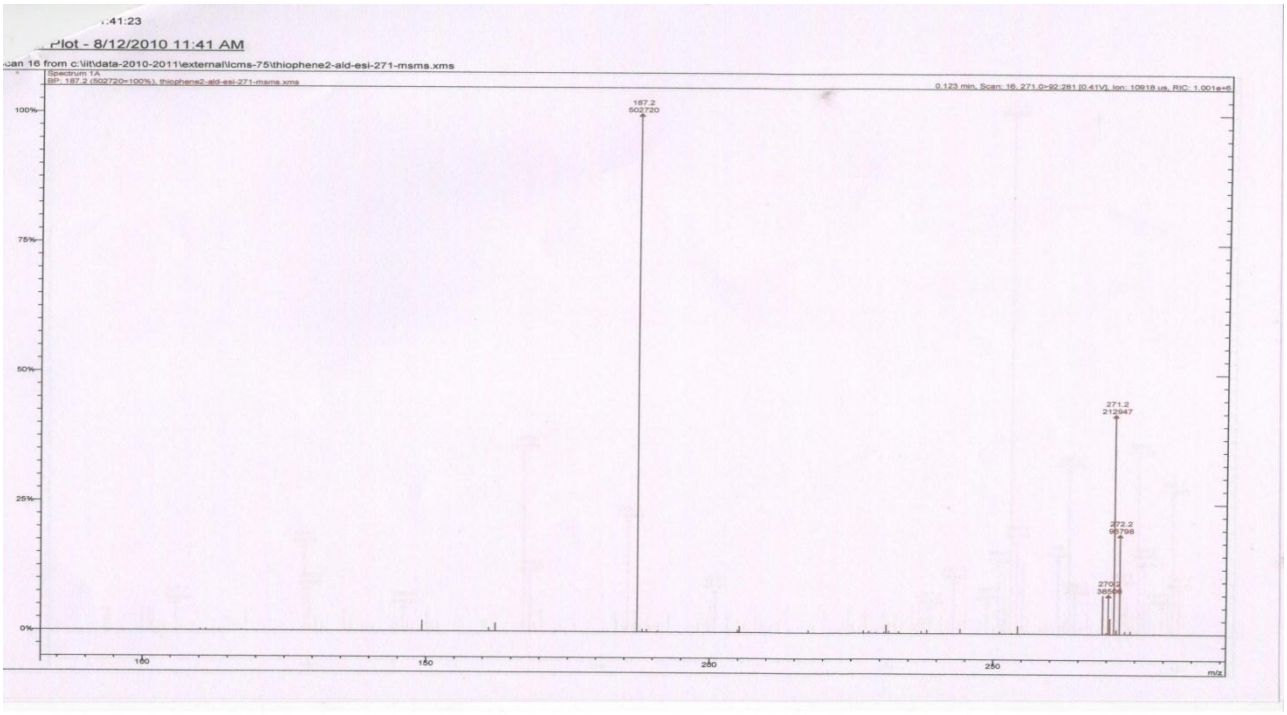
Mass spectra of 2-Amino-3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-4Hchromene:



Mass spectra of 2-Amino-3-cyano-7-hydroxy-4-(4-nitrophenyl)-4Hchromene:



Mass spectra of 2-Amino-3-cyano-7-hydroxy-4-(2-thiophene)-4Hchromene:



Reference

1. (a) Parida, K.; Das, J.; *J. Mol. Catal., A* **2000**,*151*, 185.

   (b) Antonyraj, C.A.; Kannan, S., *Applied Catalysis A: General*, **2008,** *338*, 121–129.