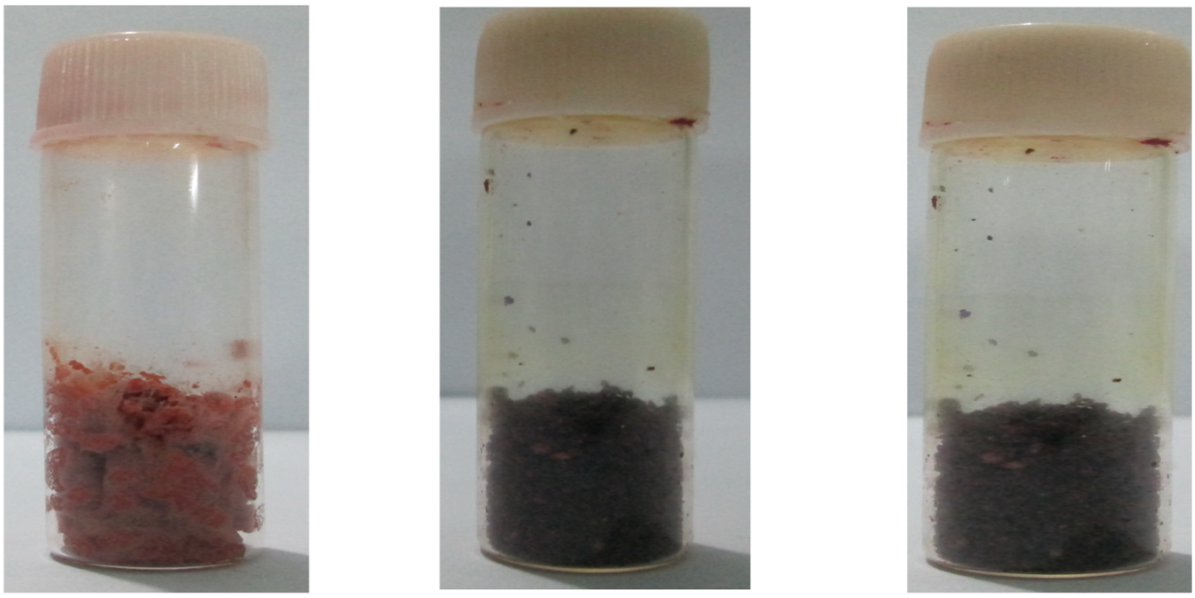
Electronic Supplementary Material (ESI) for RSC Advances.

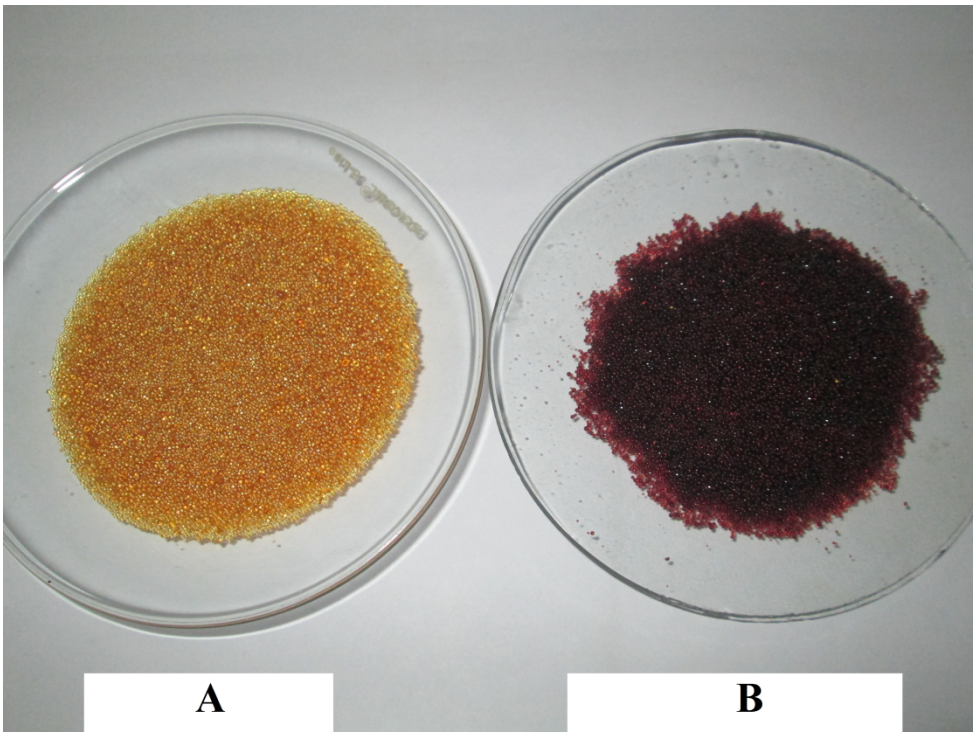
Reaction sequence in Ionic liquid. A one pot procedure



A B C

A- After mixing the reactants aromatic aldehyde, aromatic amine, phenylhydrazine, $NaNO_2$ and ionic liquid
B- After grinding the mixture thoroughly for 5 mins
C- After exposure of the imtimate mixture to microwave radiation.

Reaction sequence in Solid Phase procedure.



A: Colour of Amberlite IRA 120(Na^+) after immobilization of diazonium ions

B: Colour of the Amberlite IRA 120(Na^+) after reaction with phenylhydrazines of various aldehydes

Experimental: Chemicals were purchased from Loba chieme (India) and purified by procedures reported in literature[49]. Acidic ionic liquids prepared from dialkylamines by a procedure reported earlier[47]. Formazans obtained were confirmed by comparing their melting points with those reported in literature. Melting points were recorded in open caplliaries and are uncorrected. Products were purified by repeated column chromatography. All products were characterized by spectroscopic methods. UV-vis spectra were recorded were recorded in UV-1800 Shimadzu UV spectrophotometer, IR spectra were recorded in KBr pallets in a Perkin Elmer FT-IR 1600 spectrophotometer and ^1H and ^{13}C NMR were recorded in Bruker Bio Spin 300MHz spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra of new compounds were recorded in Micromass QTOF ESI-MS instrument (model

HAB273) and Microwave irradiation of reaction mixture was performed in reactor procured from Catalyst^{TM}(India) reactor.

Preparation of ionic liquids: Ionic liquids of dialkylamines: $[Et_2NH]HSO_4$,$[(n\text{-propyl})_2NH]HSO_4$ and $[(n\text{-isopropyl})_2NH]HSO_4$ were prepared by a procedure describe earlier.

General procedure for the synthesis of ionic liquids: Under vigorous stirring 0.05 mol of sulphuric acid was added dropwise to an ice cold solution of 0.04 mol of the appropriate dialkylammoniumbromide in 15 mL of chloroform. Removal of chloroform under reduced pressure gave a white solid which was dried in vacuo**.**

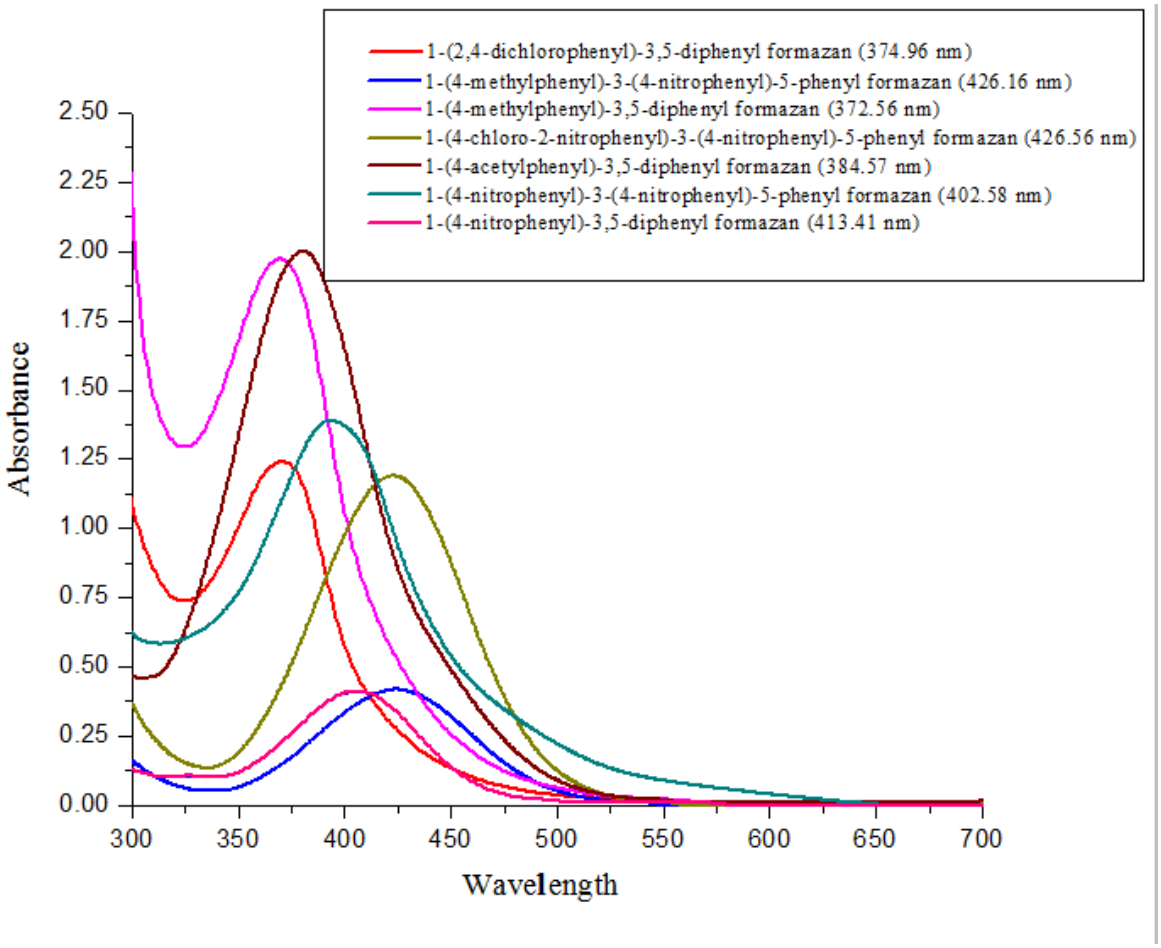
For physical properties of the $[Et_2NH]HSO_4$,$[(n\text{-propyl})_2NH]HSO_4$ and $[(n\text{-isopropyl})_2NH]HSO_4$ report appearing in **Tetraheron Letters 53, (2012) 4718-4720** may be referred

General procedure for synthesis of formazan in ionic liquid:

A mixture of aromatic aldehyde (1mmol), phenylhydrazine (1 mmol), aromatic amine(1 mmol) and $NaNO_2$ (1.2mmol) , 10 mol% of $[Et_2NH]HSO_4$ and 1 mL of deionized water was ground to a homogeneous mixture. The bright coloured mixture was exposed to microwave irradiation (240 Watt) for a 1-1.5 mins. After completion of the reaction , the solid mass obtained was washed with water till the washings were free of of IL. The remaining solid was dissolved in ethylacetate , dried using anhydrous Na_2SO_4 and product obtained reduced pressure evaporation of solvent . Finally the products were recrystallized from 95% v/v EtOH.

General method for synthesis of formazan in solid phase: Resin immobilized diazonium ions was prepared by a procedure described earlier, recovered and dried[44-46]. The phenylhydrazone of the aromatic aldehydes were prepared by reported methods[23]. The hydrazones(1mmol) were dissolved in 50mL of cyclohexane and the solution percolated through a column slurry packed with 15g of immobilized diazonium ions. On formation of the formazan dyes , the beads turned deep red. The beads were recovered , dried at room temperature and the product obtained by extraction of the beads with ethylacetate in a soxhlet extraction apparatus. The products were tested for their purity by TLC using prepared silica gel plates and ethylacetate: petroleum ether (40-60) in the ration 10:1 as the eluent . TLC indicated purity of the product. Reduced pressure evaporation of the products gave the formazans .

UV Spectra of all some selected formazans in EtOH (95% v/v)



Entry 9: Mass spectra of 1-(4-nitrophenyl)-3,5-diphenylformazan

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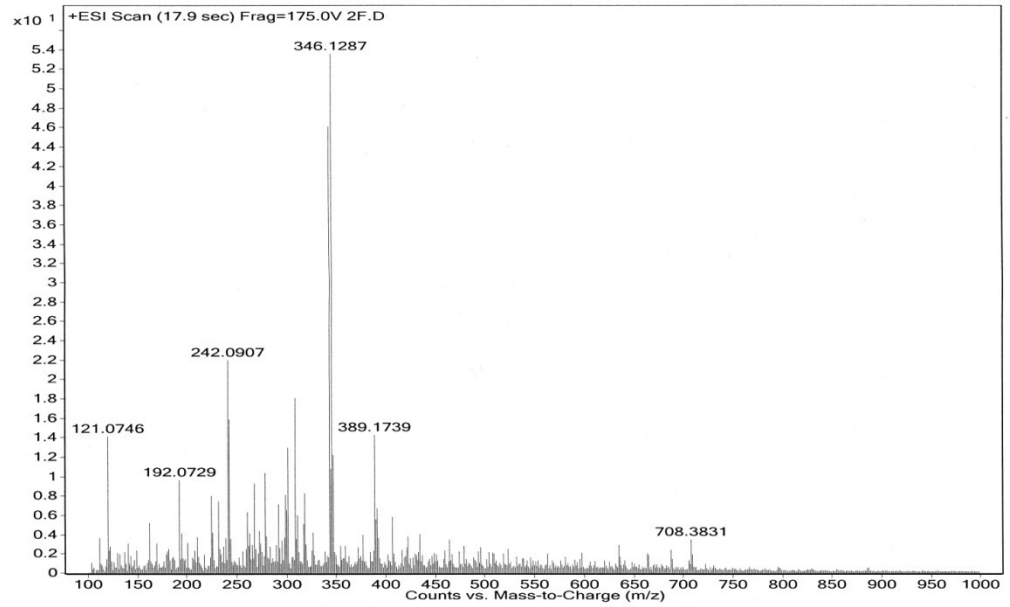
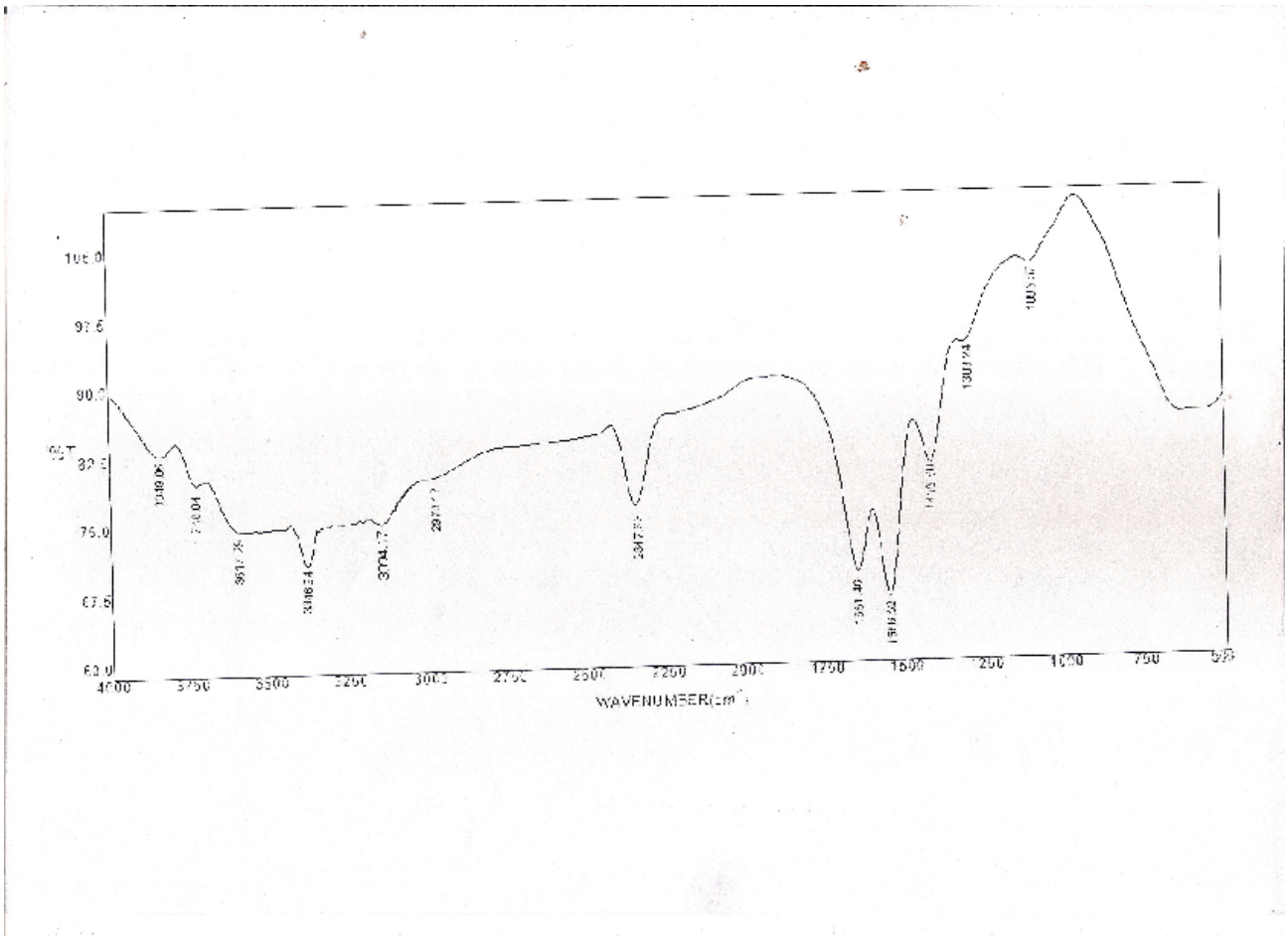
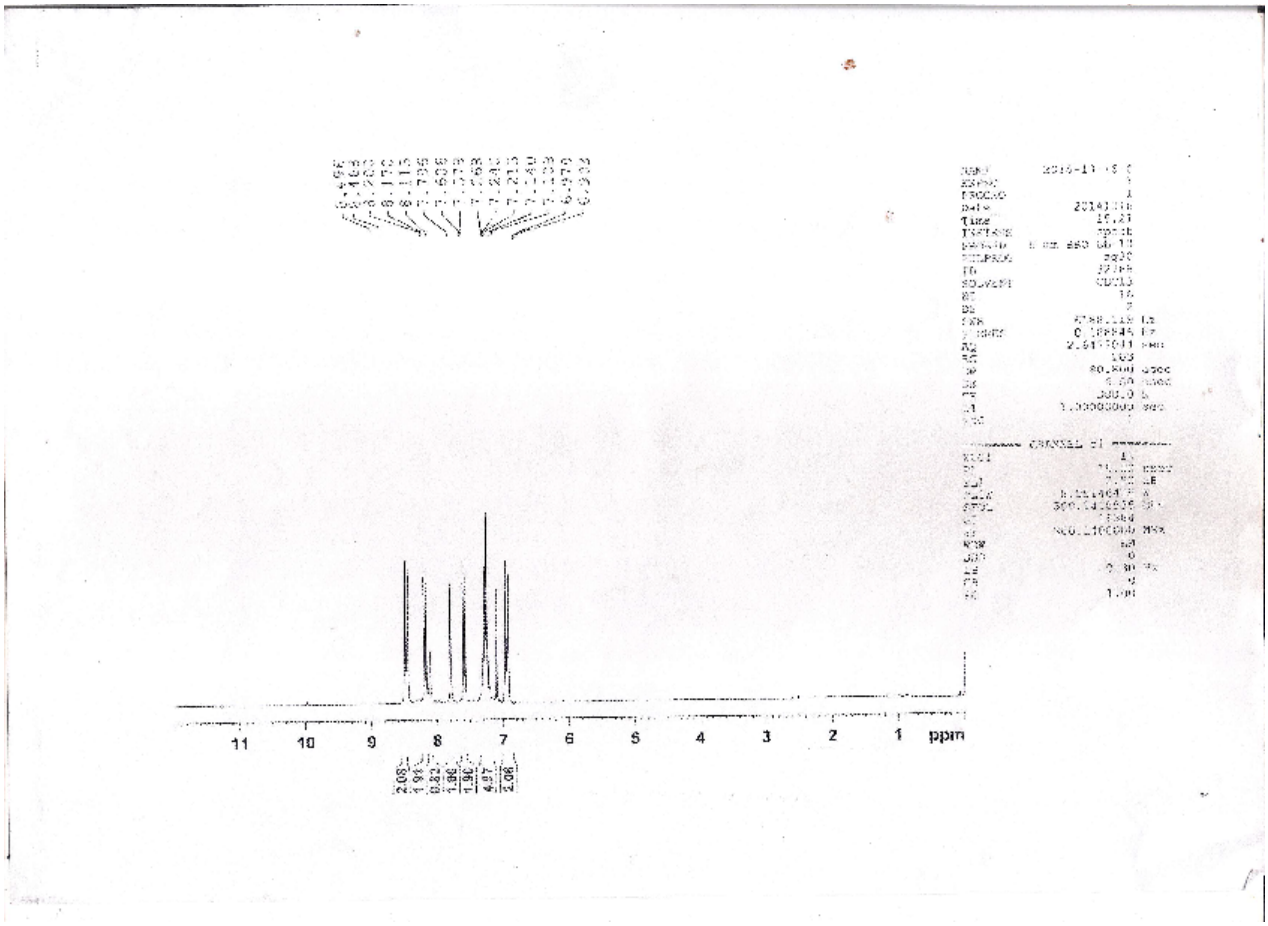
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	2F.D	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



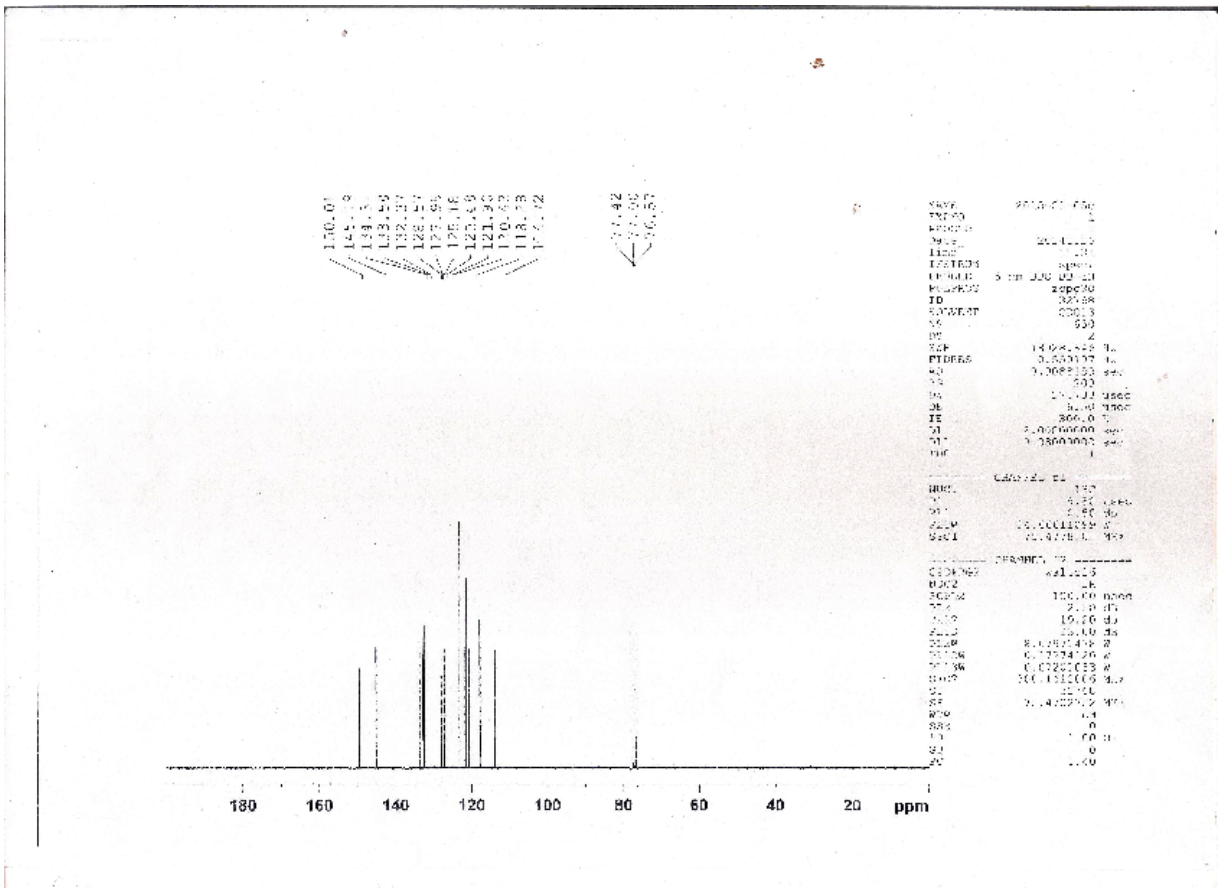
Entry 9: IR (in KBr) spectra of 1-(4-nitrophenyl)-3,5-diphenylformazan



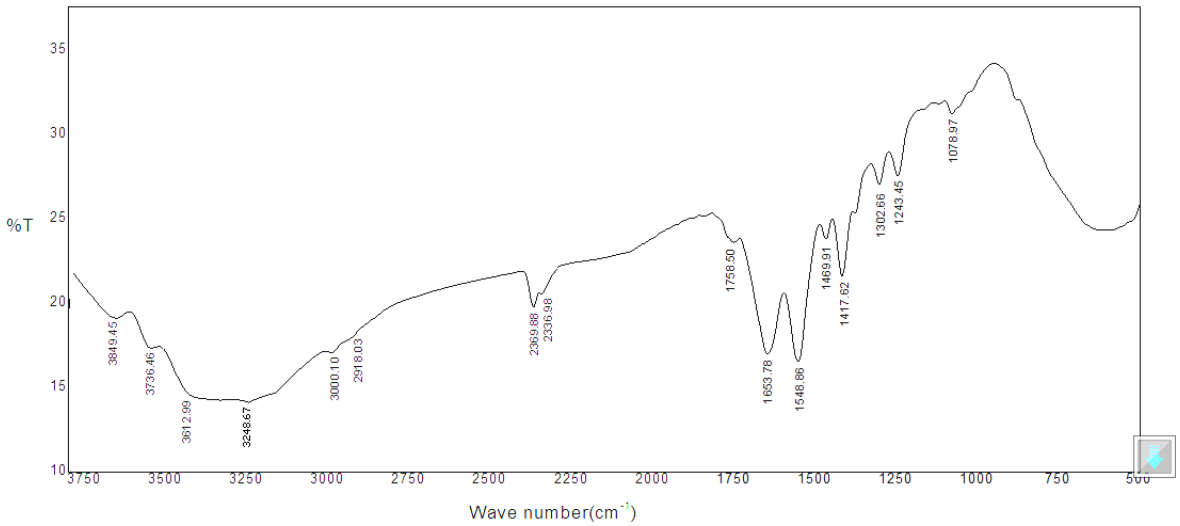
Entry 9 : 1H NMR spectra (300 MHz, $CDCl_3$) of 1-(4-nitrophenyl)-3,5-diphenylformazan



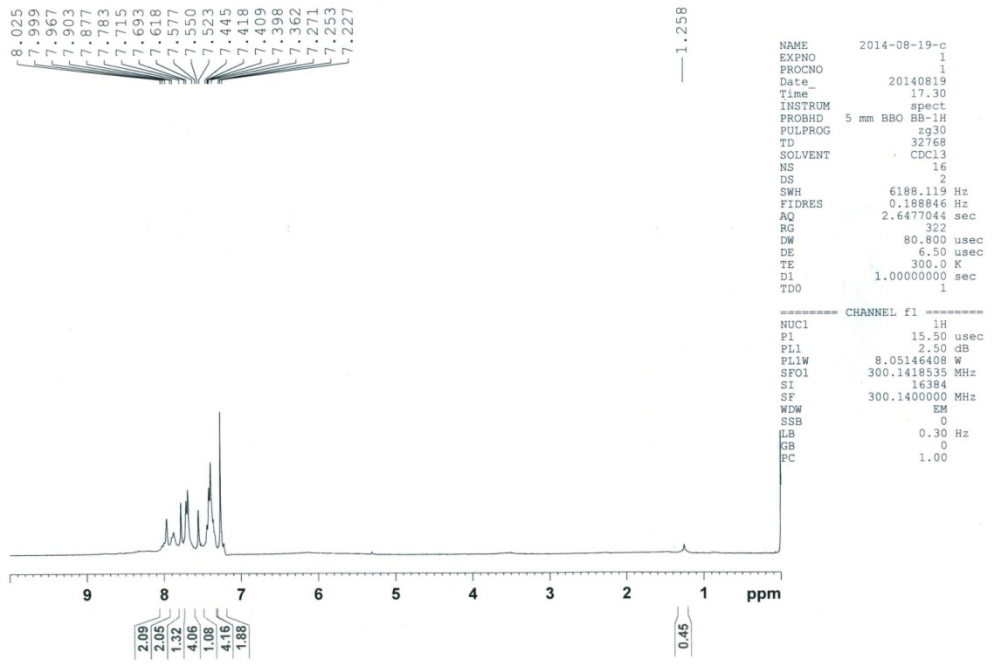
Entry 9: ^{13}C NMR (75 MHz, $CDCl_3$) of 1-(4-nitrophenyl)-3,5-diphenylformazan



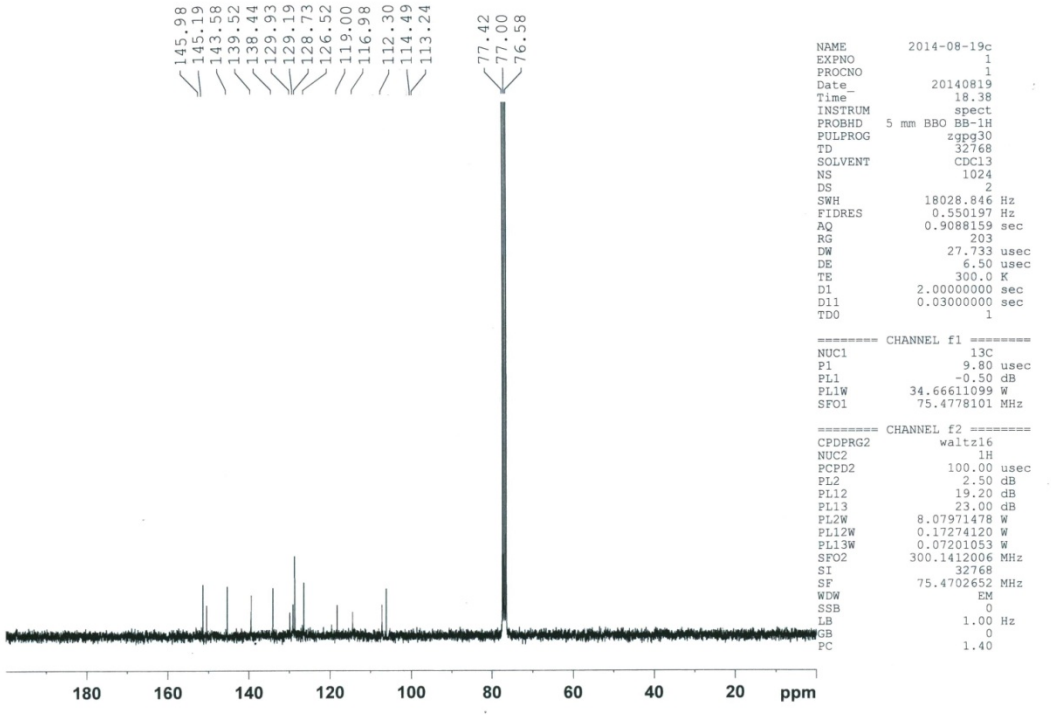
IR Spectra in KBr of 1-(3-nitrophenyl)-3,5-diphenylformazan (entry 10)



^{1}H NMR spectra (300 MHz, $CDCl_3$) of 1-(3-nitrophenyl)-3,5-diphenylformazan (entry 10)



^{13}C-NMR spectra (75 MHz, $CDCl_3$) of 1-(3-nitrophenyl)-3,5-diphenylformazan (entry 10)



Mass spectra of 1-(3-nitrophenyl)-3,5-diphenylformazan (entry 10)

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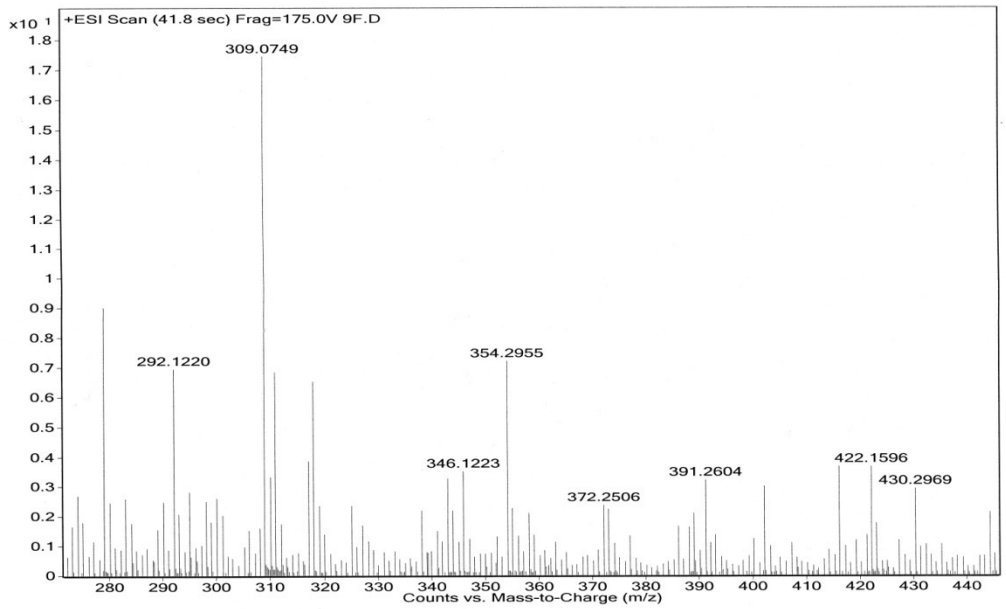
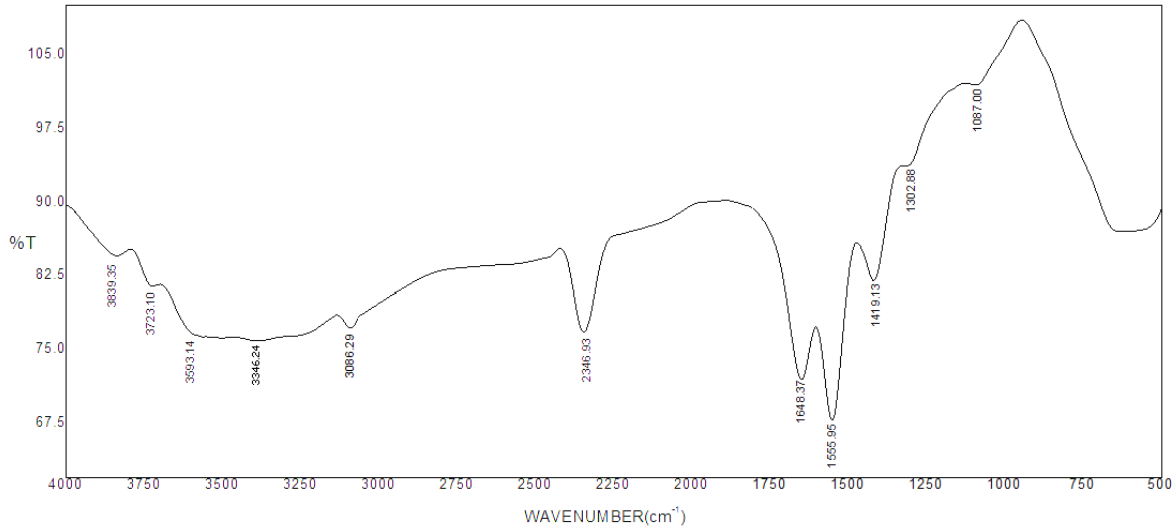
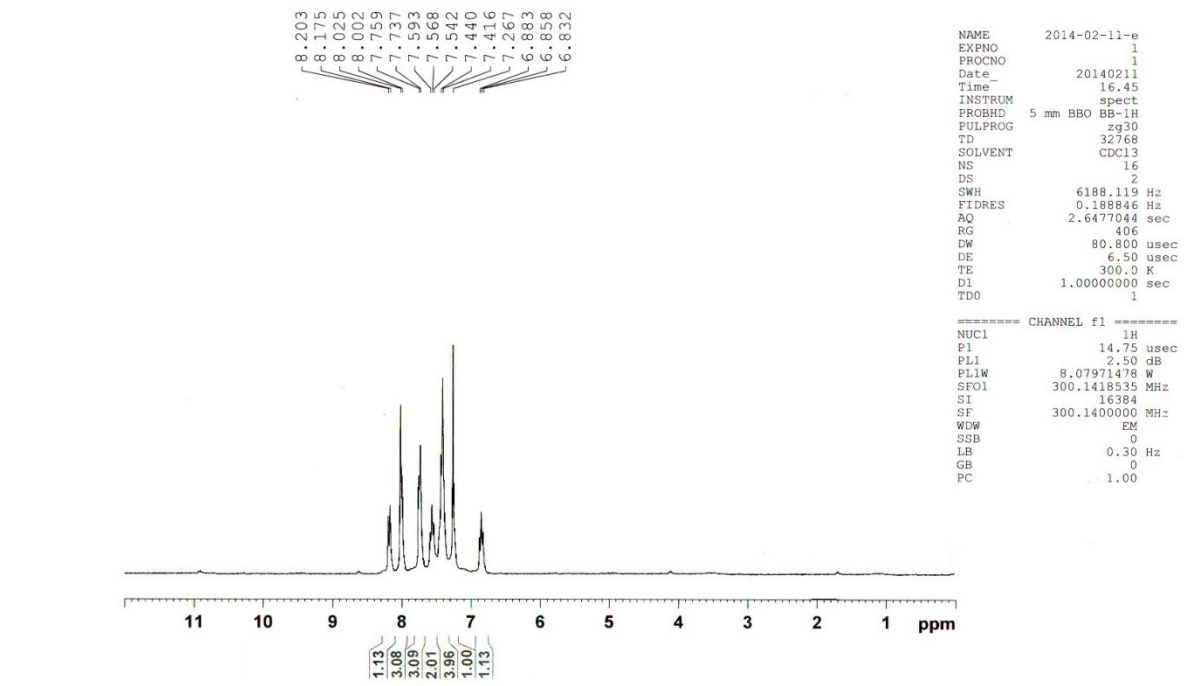


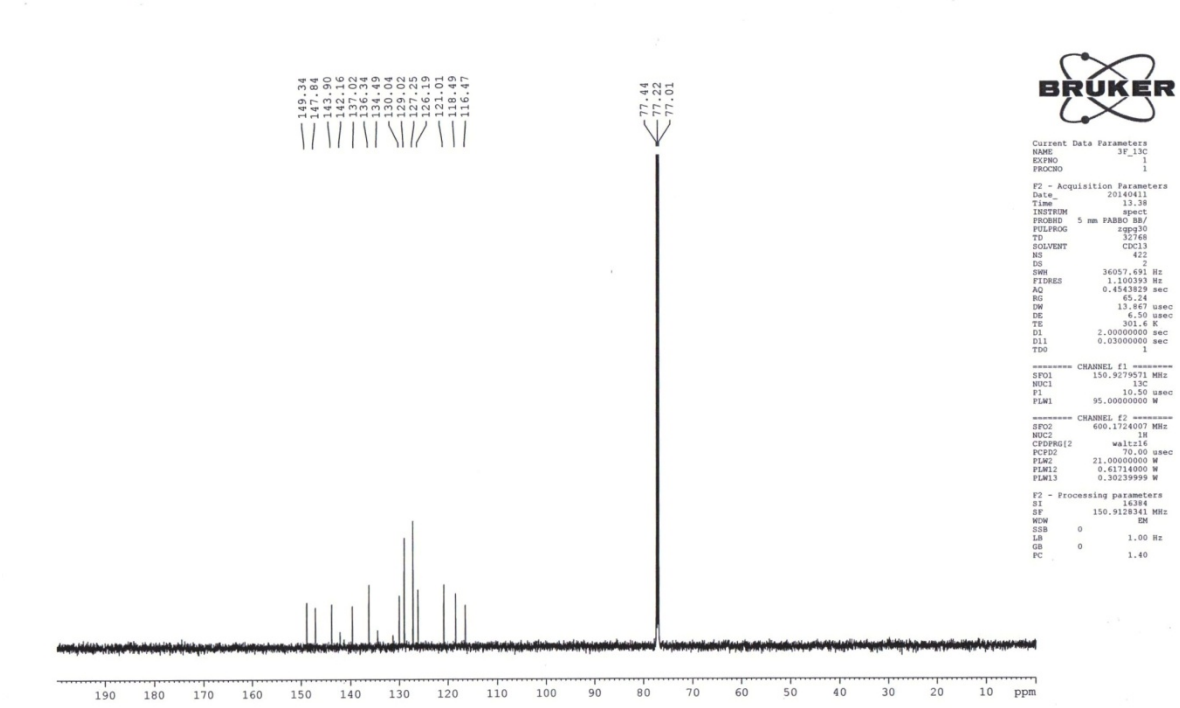
IR spectra (KBr) (entry 11) of 1-(2-nitrophenyl)-3,5-diphenylformazan



^{1}H-NMR (300 MHz, $CDCl_3$, Entry 11) of 1-(2-nitrophenyl)-3,5-diphenylformazan

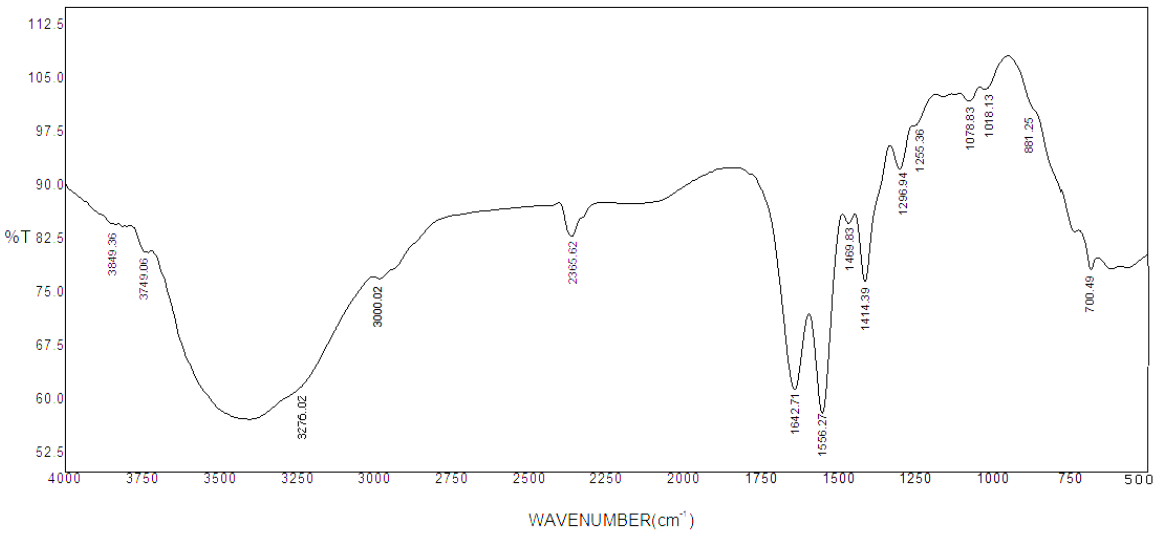


^{13}C NMR spectra (75 MHz, $CDCl_3$, Entry 11) of 1-(2-nitrophenyl)-3,5-diphenylformazan

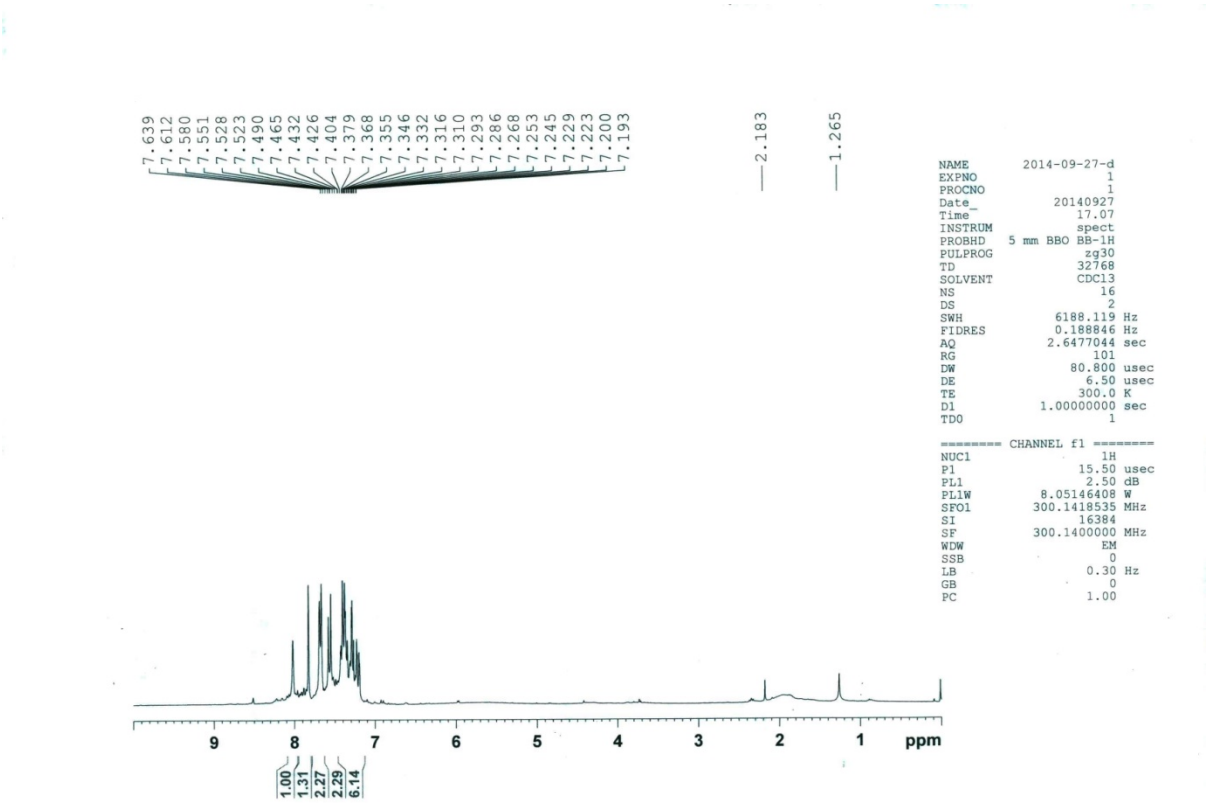


IR spectra of Entry 12: 1-(2,4-dichlorophenyl)-3,5-diphenylformazan

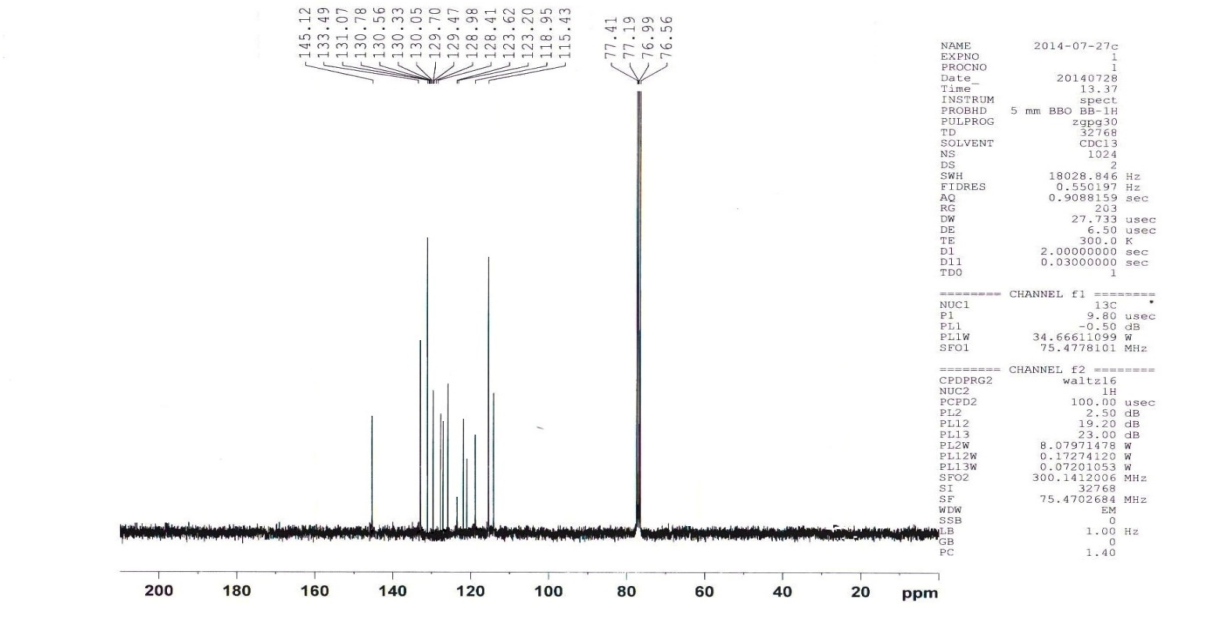
IR spectra in KBr



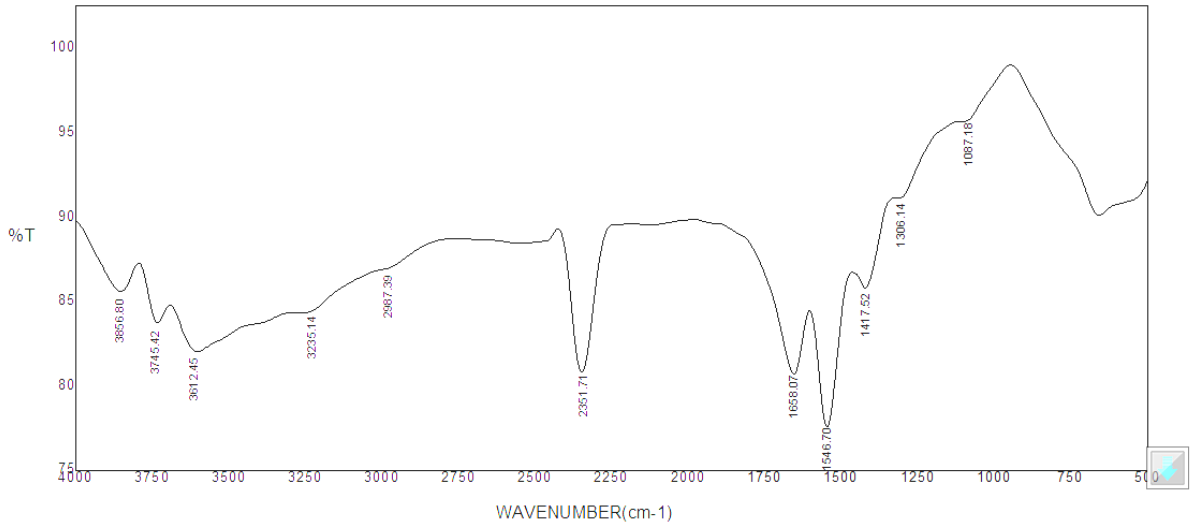
^{1}H –NMR spectra ($CDCl_3$, Entry 12) of 1-(2,4-dichlorophenyl)-3,5-diphenylformazan



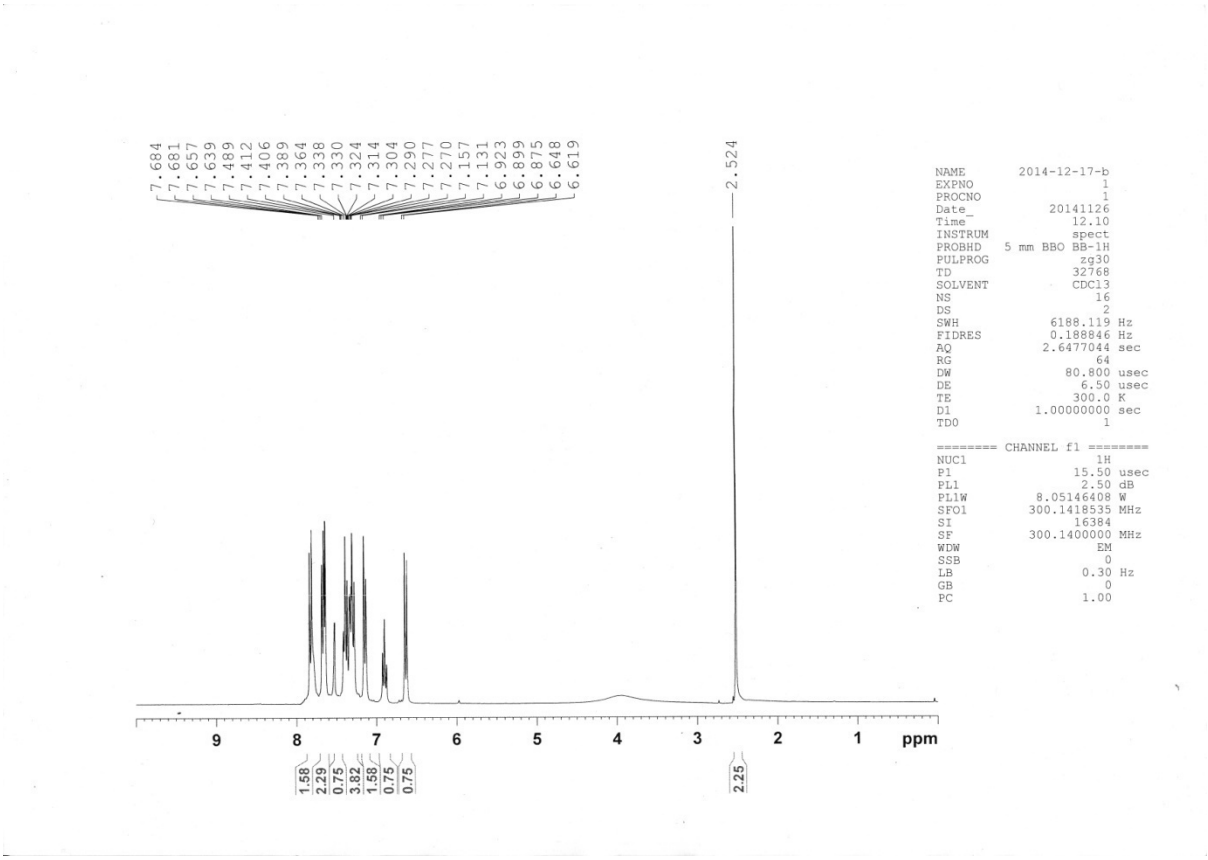
^{13}C NMR spectra (75 MHz in $CDCl_3$, Entry 12) of 1-(2,4-dichlorophenyl)-3,5-diphenylformazan



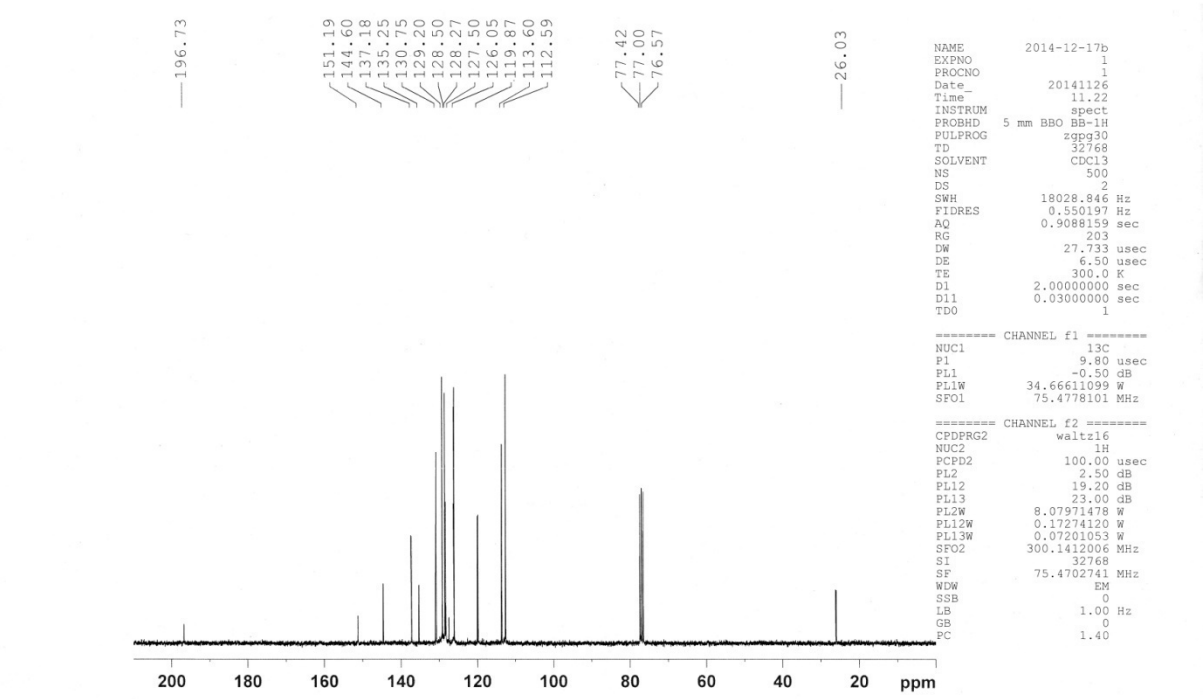
IR spectra in KBr of 1-(4-acetoxyphenyl)-3,5-diphenylformazan(entry 13)



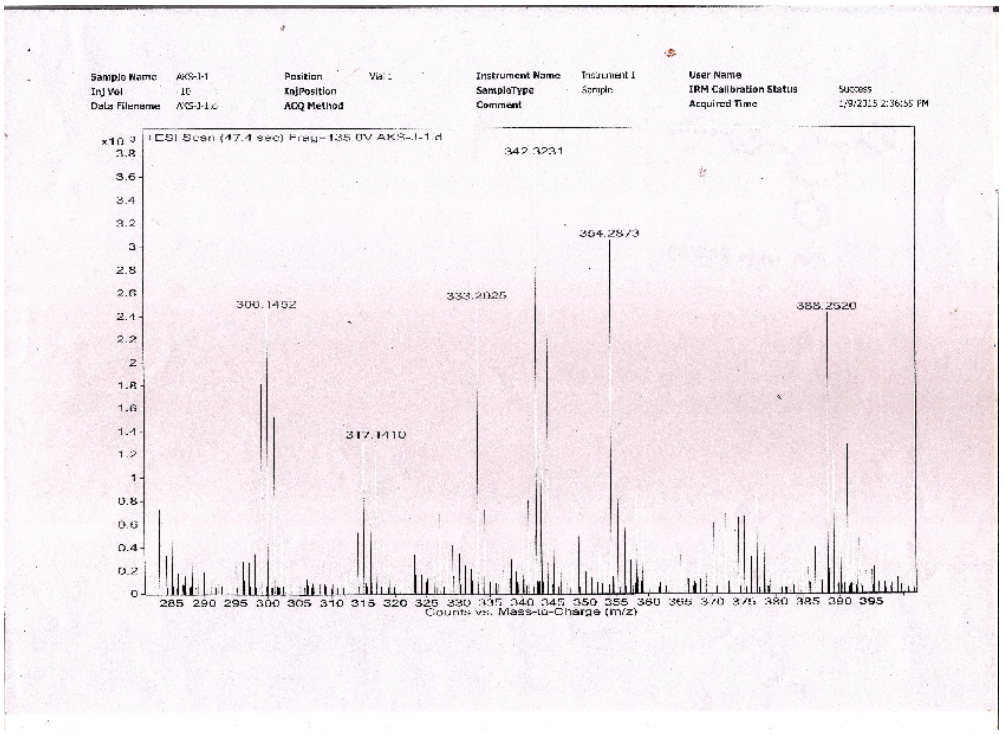
^{1}H NMR spectra in $CDCl_3$, 300MHz (Entry 13) of 1-(4-acetoxyphenyl)-3,5-diphenylformazan



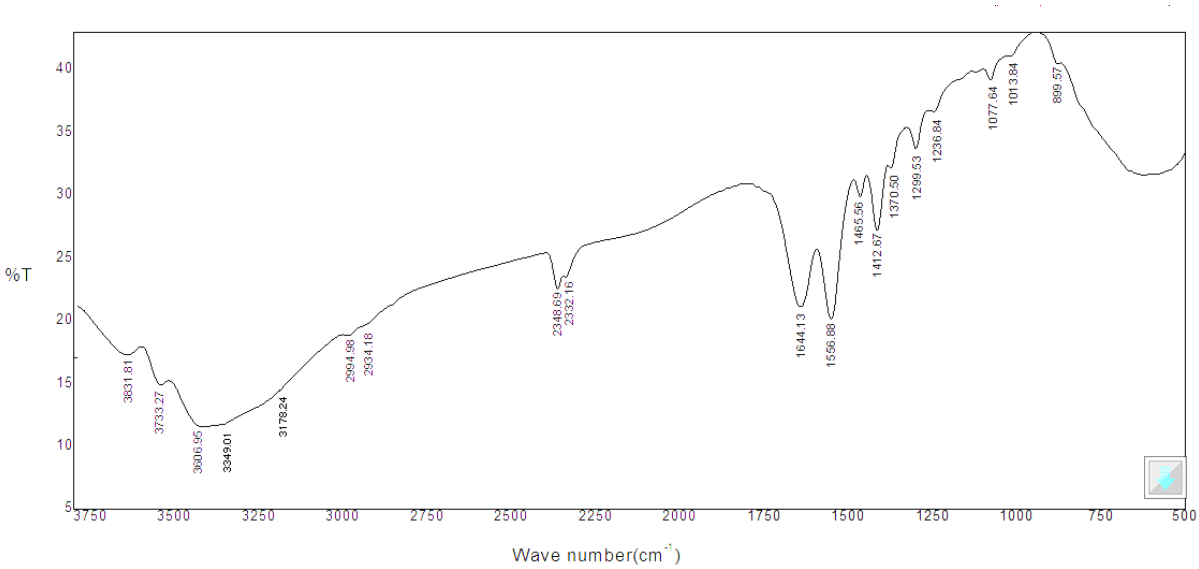
^{13}C NMR in $CDCl_3$ (75 MHz) of 1-(4-acetoxyphenyl)-3,5-diphenylformazan(Entry 13)



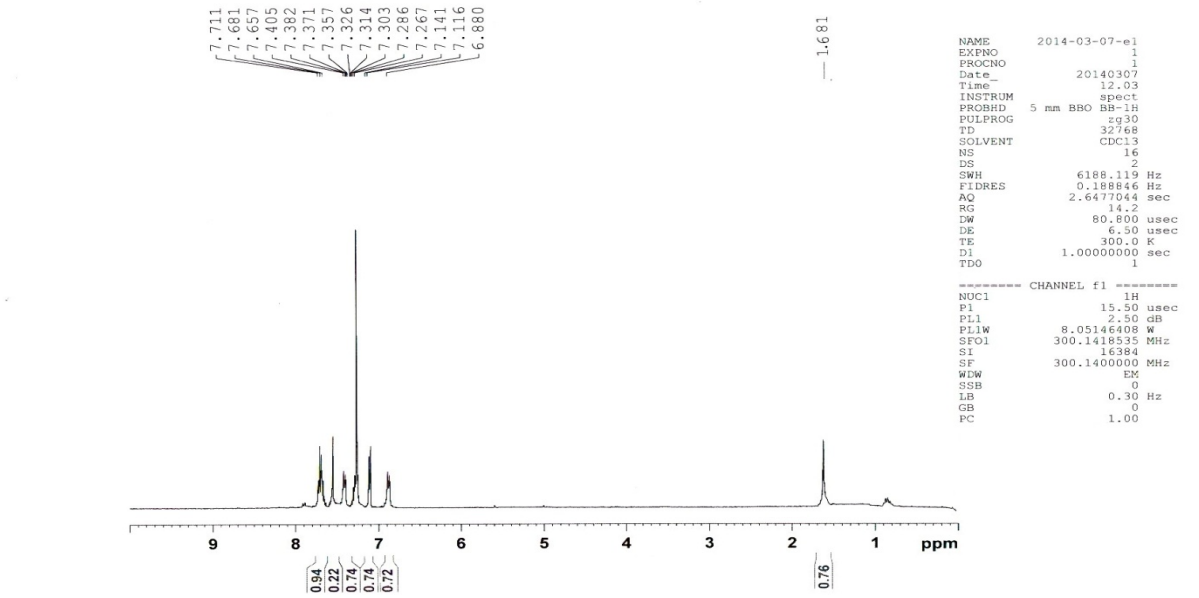
Mass spectra of 1-(4-acetoxyphenyl)-3,5-diphenylformazan(Entry 13)



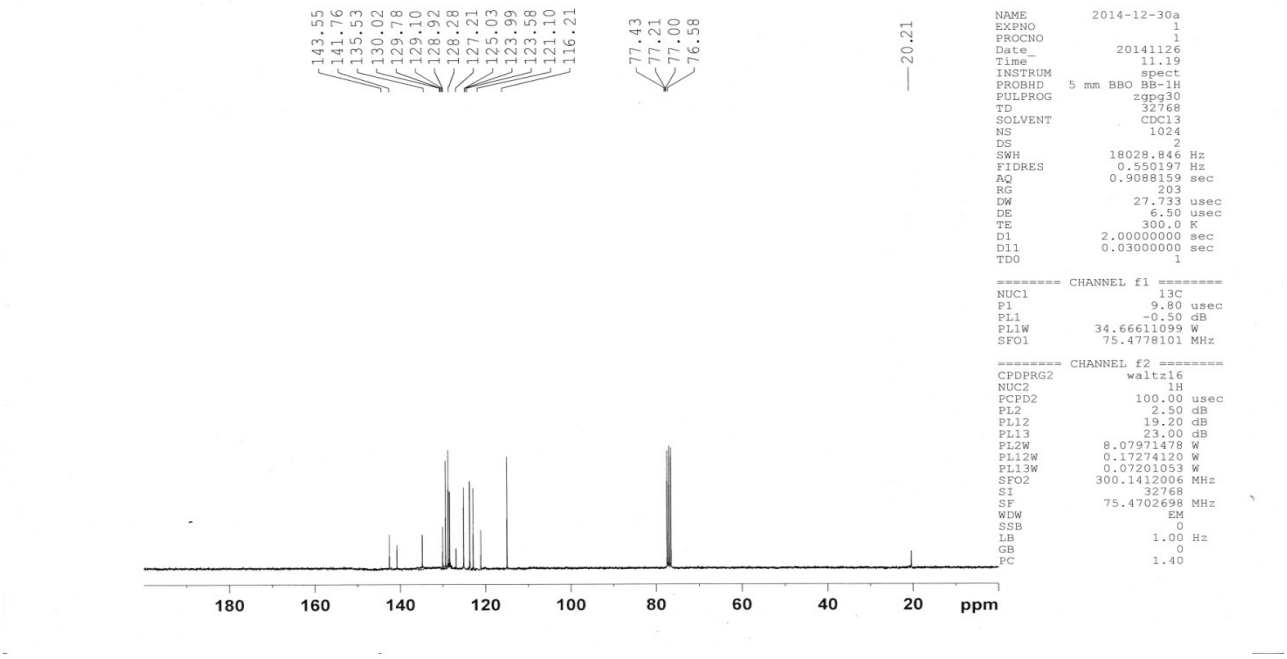
Entry 14 IR spectra of 1-(4-methylphenyl)-3,5-diphenylformazan



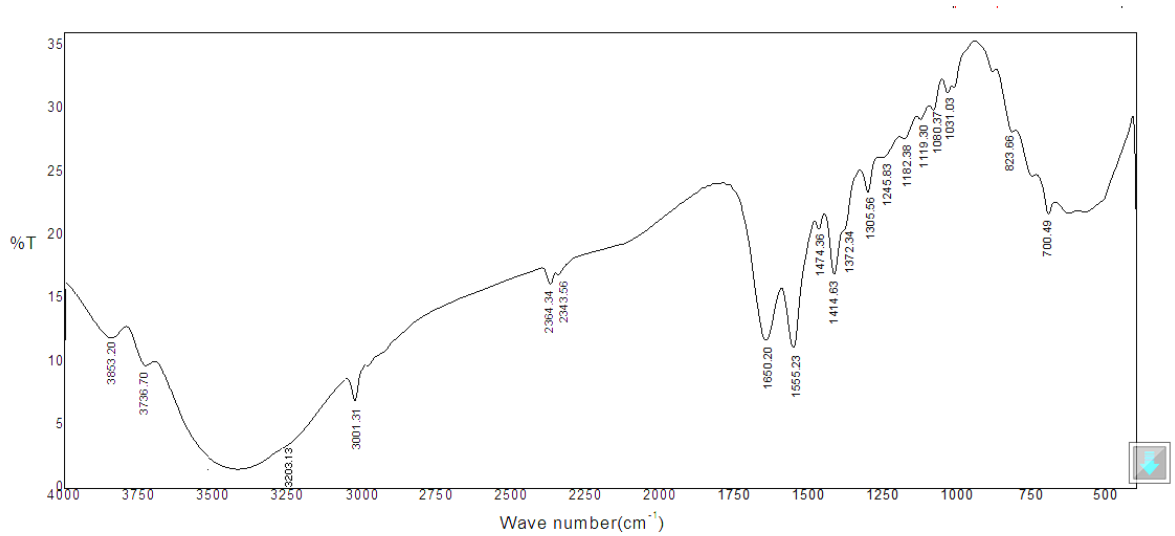
Entry 14 : 1H-NMR (300 MHz, $CDCl_3$) spectra of 1-(4-methylphenyl)-3,5-diphenylformazan



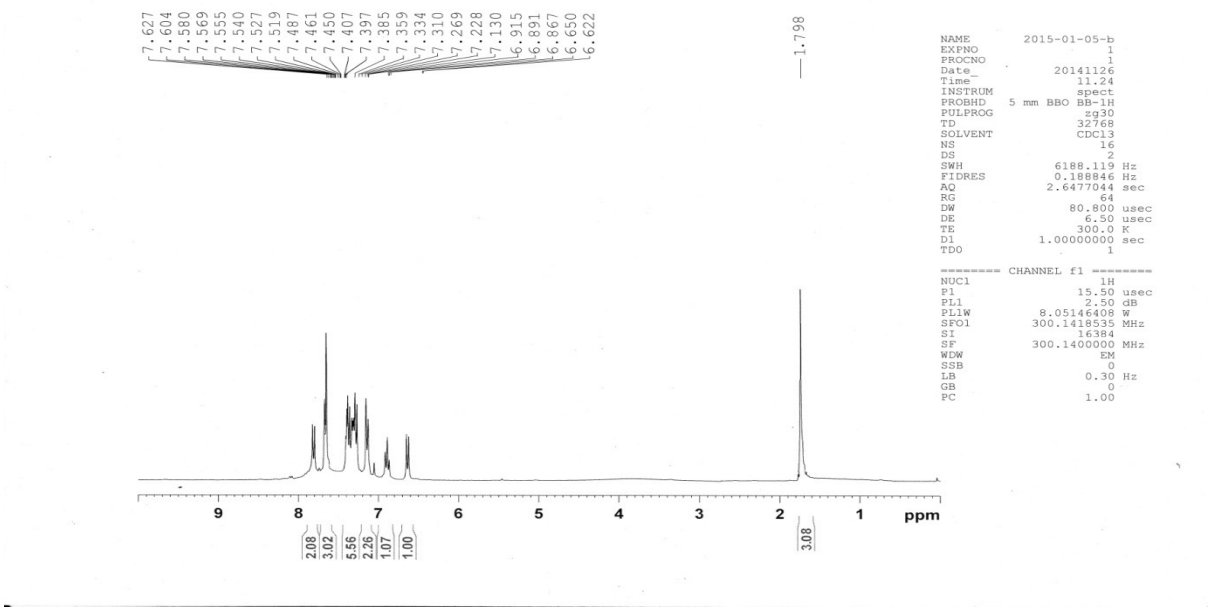
Entry 14 : ^{13}C-NMR (75 MHz, $CDCl_3$) spectra of 1-(4-methylphenyl)-3,5-diphenylformazan



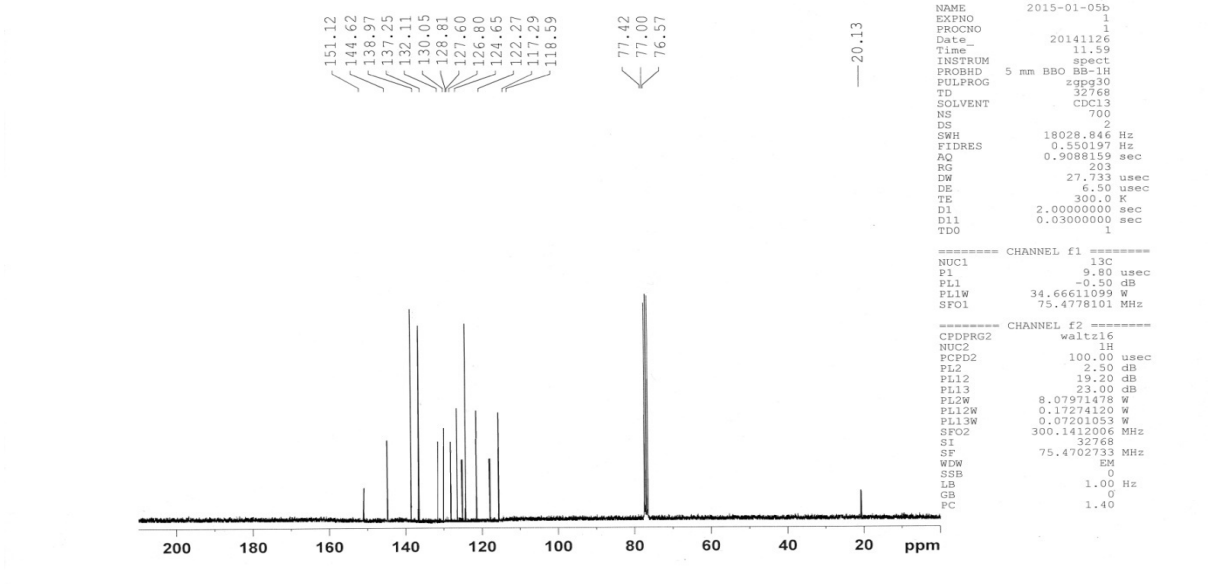
IR spectra in KBr of 1-(4-chlorophenyl)-3-(4-methyl)-5-diphenyl formazan (Entry 15)



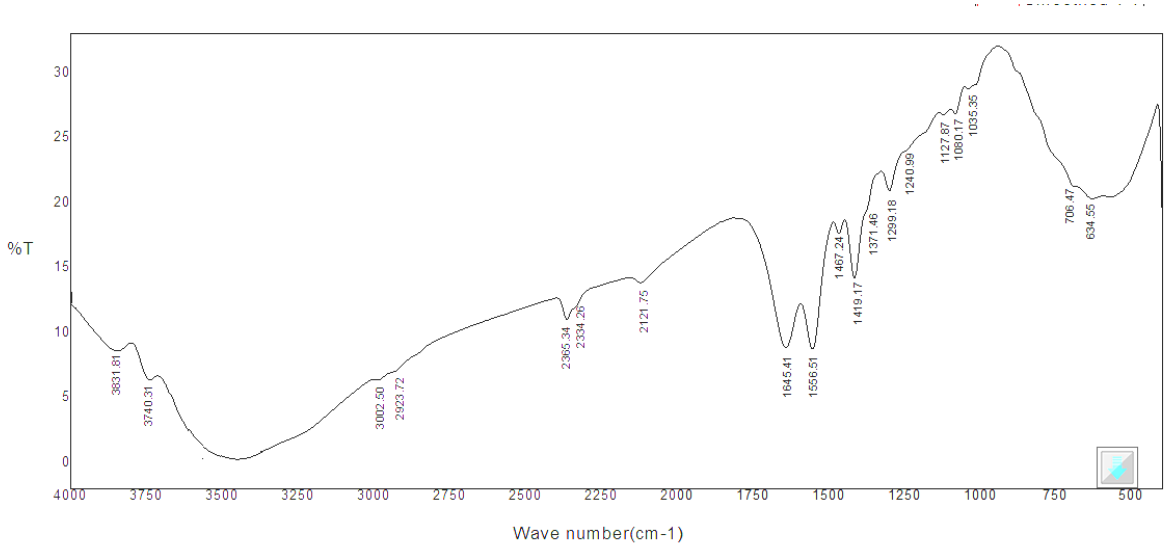
^{1}H NMR spectra in $CDCl_3$ (300 MHz) of 1-(4-chlorophenyl)-3-(4-methyl)-5-diphenyl formazan (Entry 15)



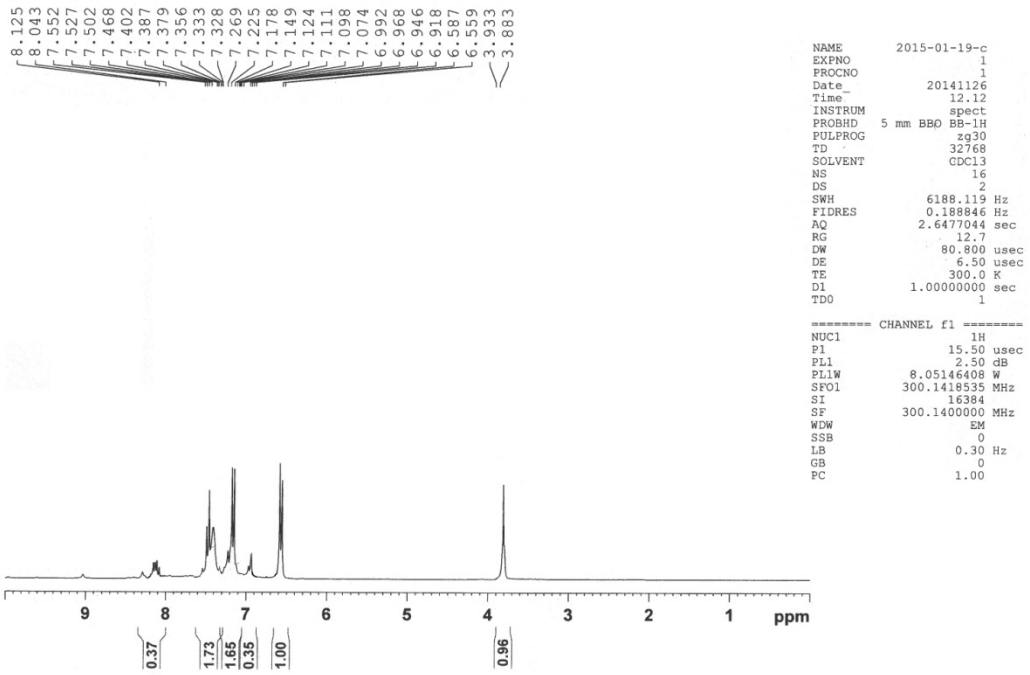
^{13}C NMR spectra in $CDCl_3$ (75 MHz) of 1-(4-chlorophenyl)-3-(4-methyl)-5-diphenyl formazan (Entry 15)



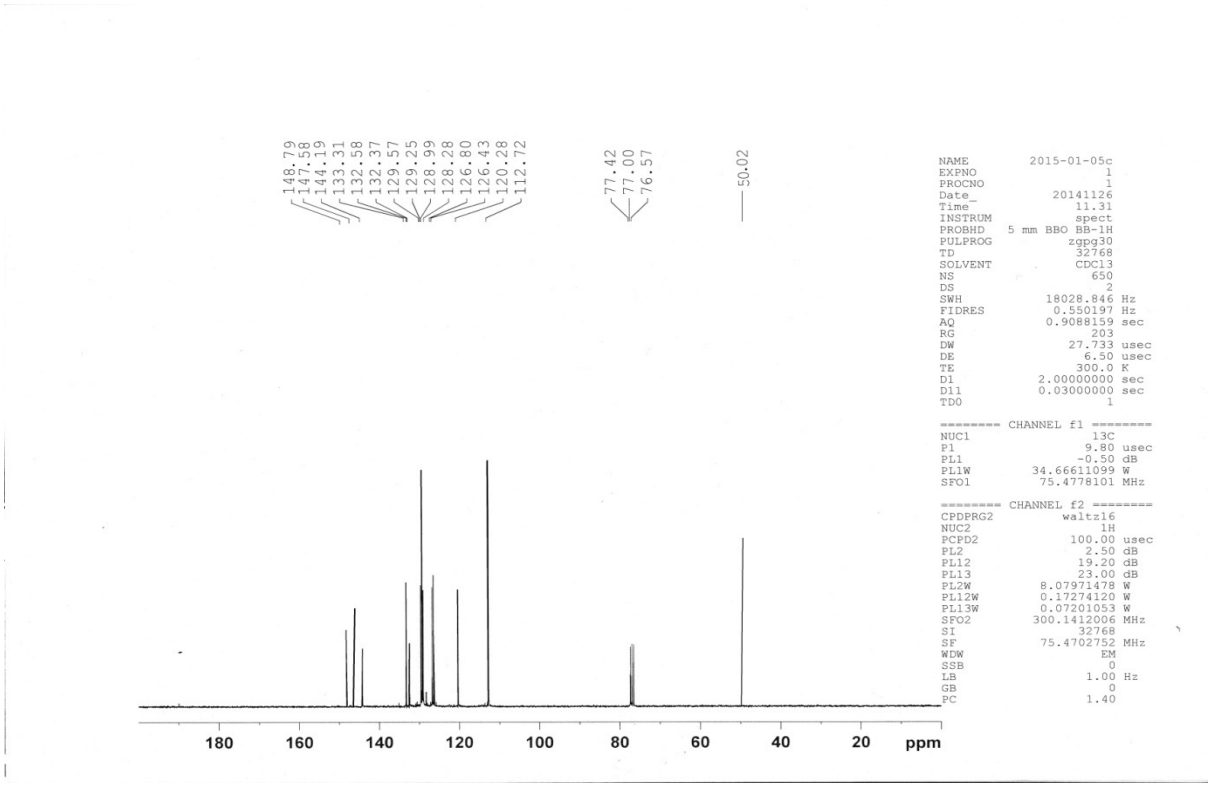
IR spectra of 1-(4-chlorophenyl)-3-(2-methoxyphenyl)-5-phenylformazan(Entry 16)



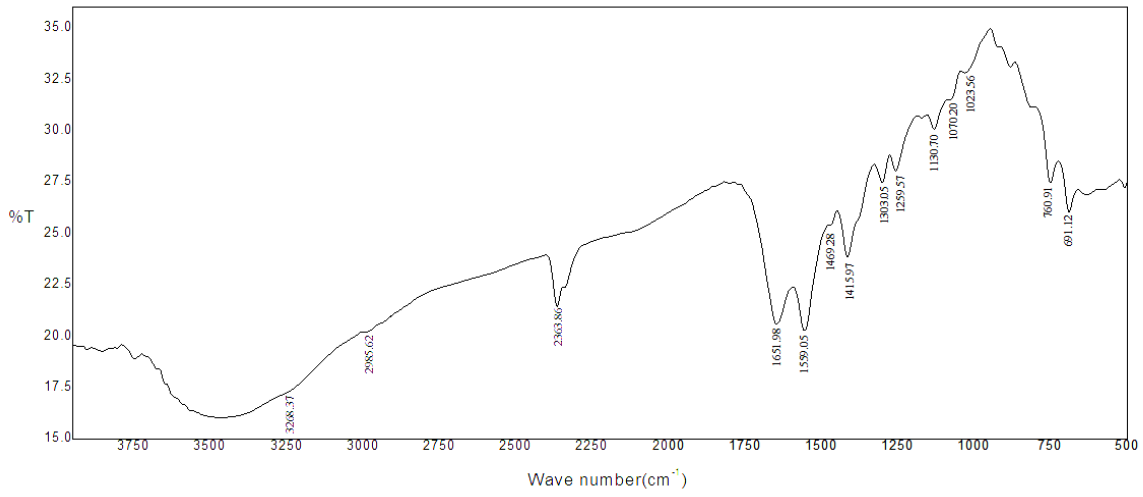
1H NMR spectra of 1-(4-chlorophenyl)-3-(2-methoxyphenyl)-5-phenylformazan(Entry 16)



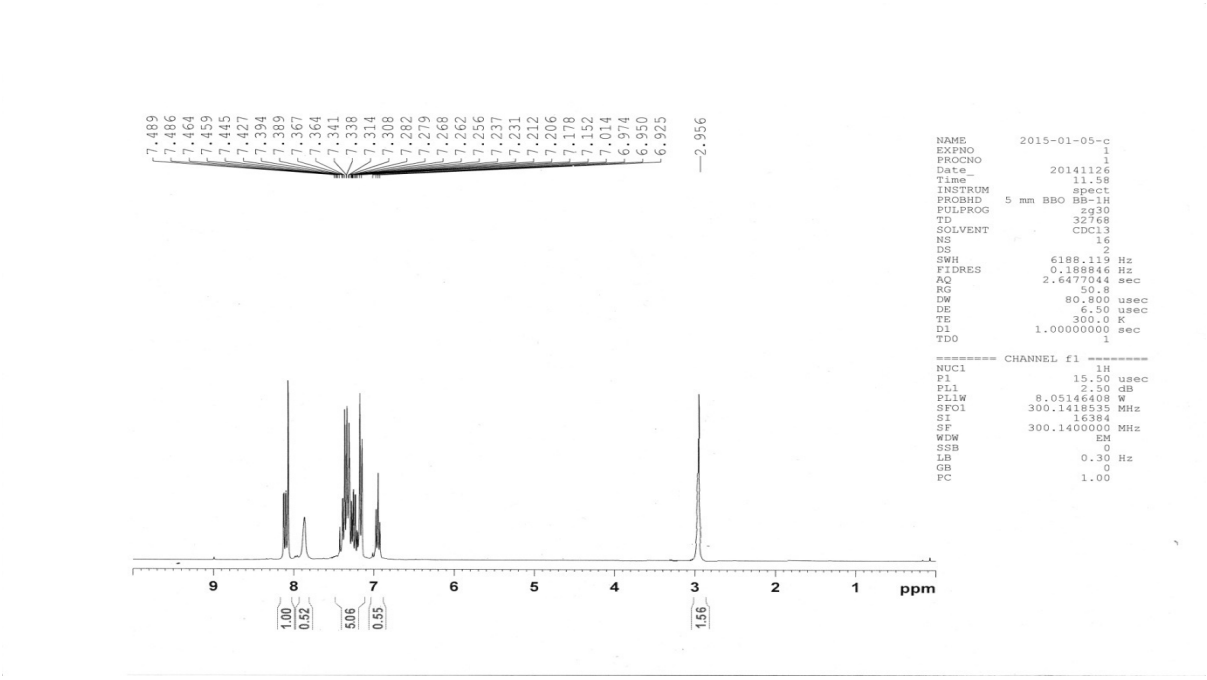
^{13}C NMR spectra of 1-(4-chlorophenyl)-3-(2-methoxyphenyl)-5-phenylformazan(Entry 16)



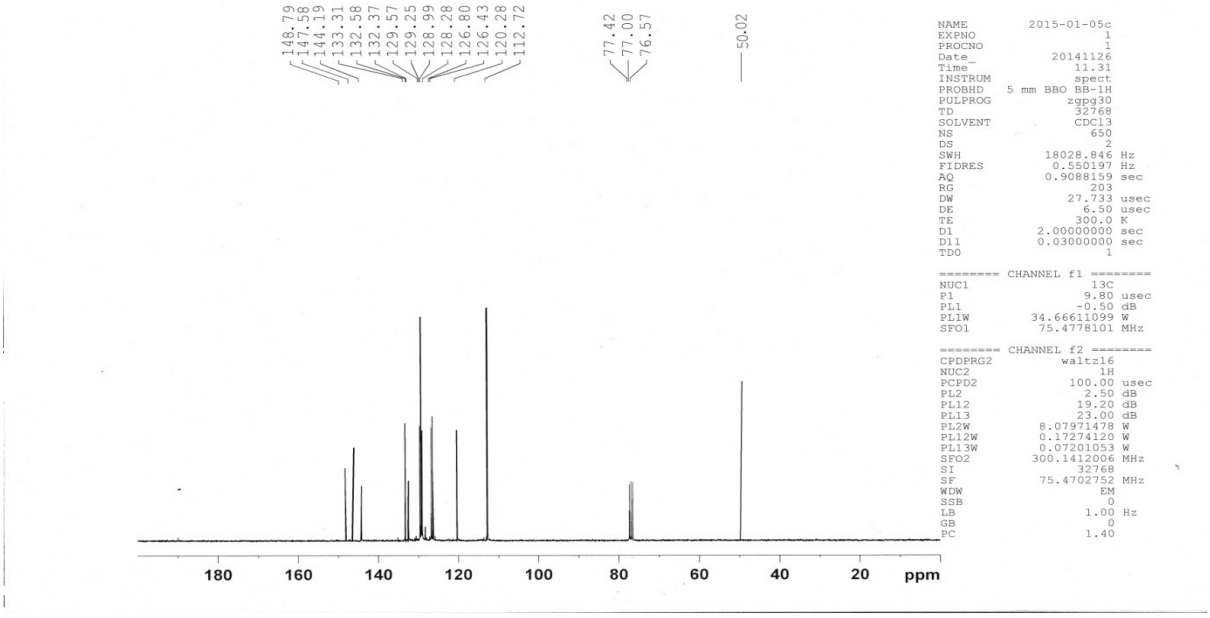
IR Spectra in KBr of 1-(4-methoxyphenyl)-3(2-chlorophenyl-5-phenyl formazan (Entry 17)



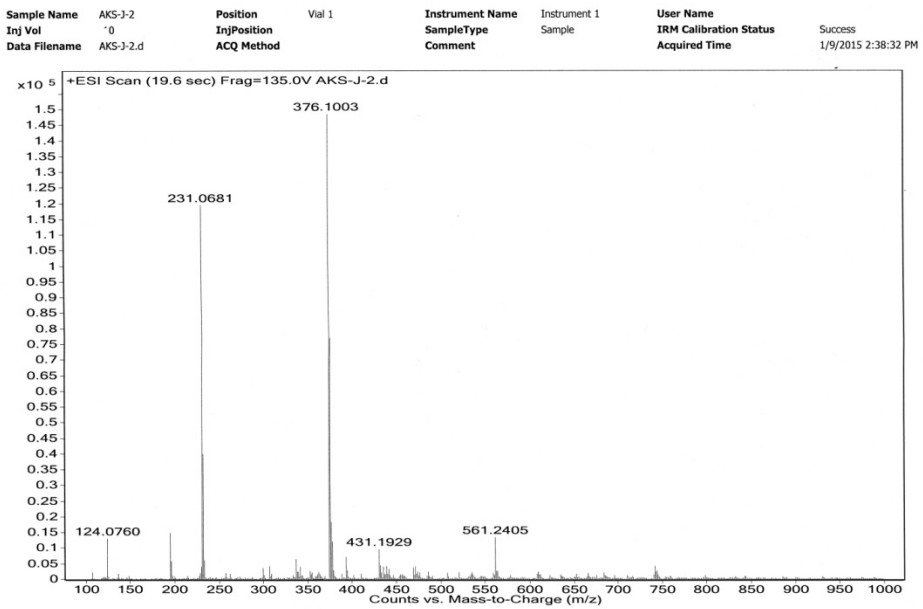
^{1}H NMR spectra in $CDCl_3$, 300MHz of 1-(4-methoxyphenyl)-3(2-chlorophenyl-5-phenyl formazan (Entry 17)



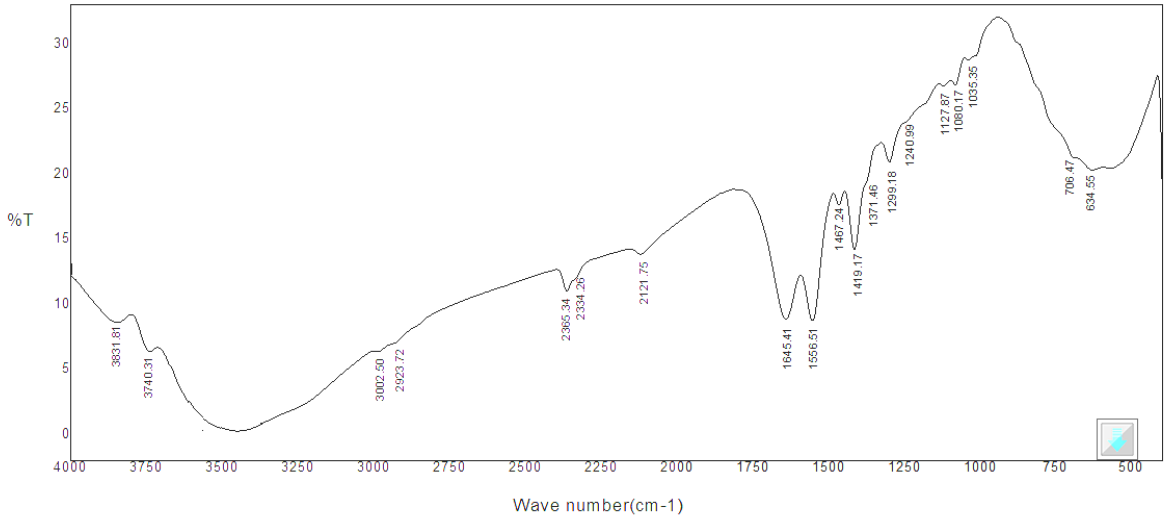
^{13}C NMR spectra (75 MHz, $CDCl_3$) of 1-(4-methoxyphenyl)-3(2-chlorophenyl-5-phenyl formazan (Entry 17)



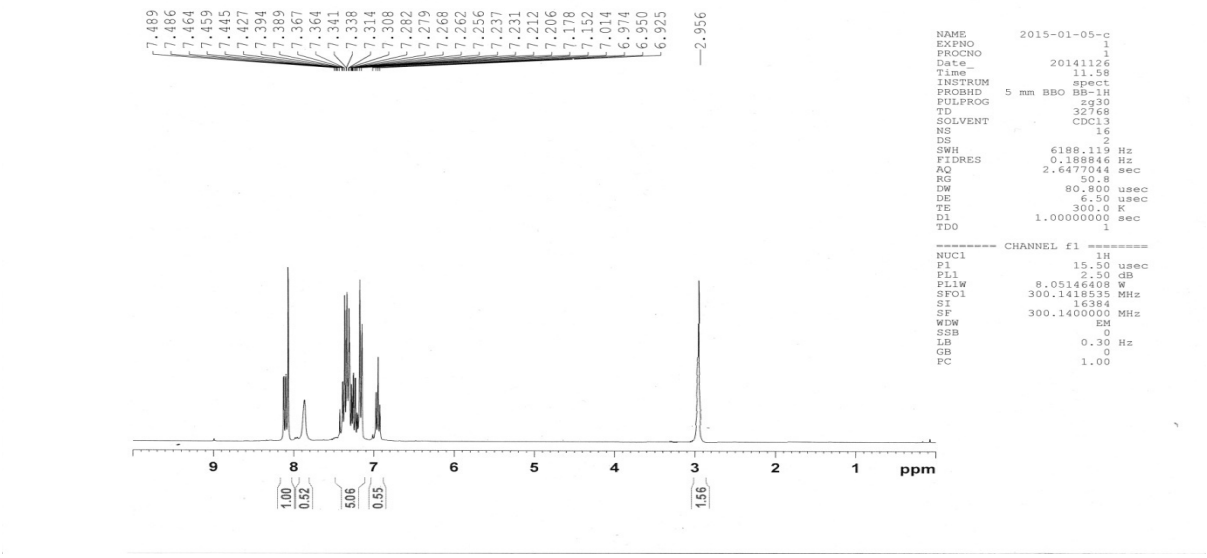
Mass spectra of 1-(4-methoxyphenyl)-3(2-chlorophenyl-5-phenyl formazan (Entry 17)



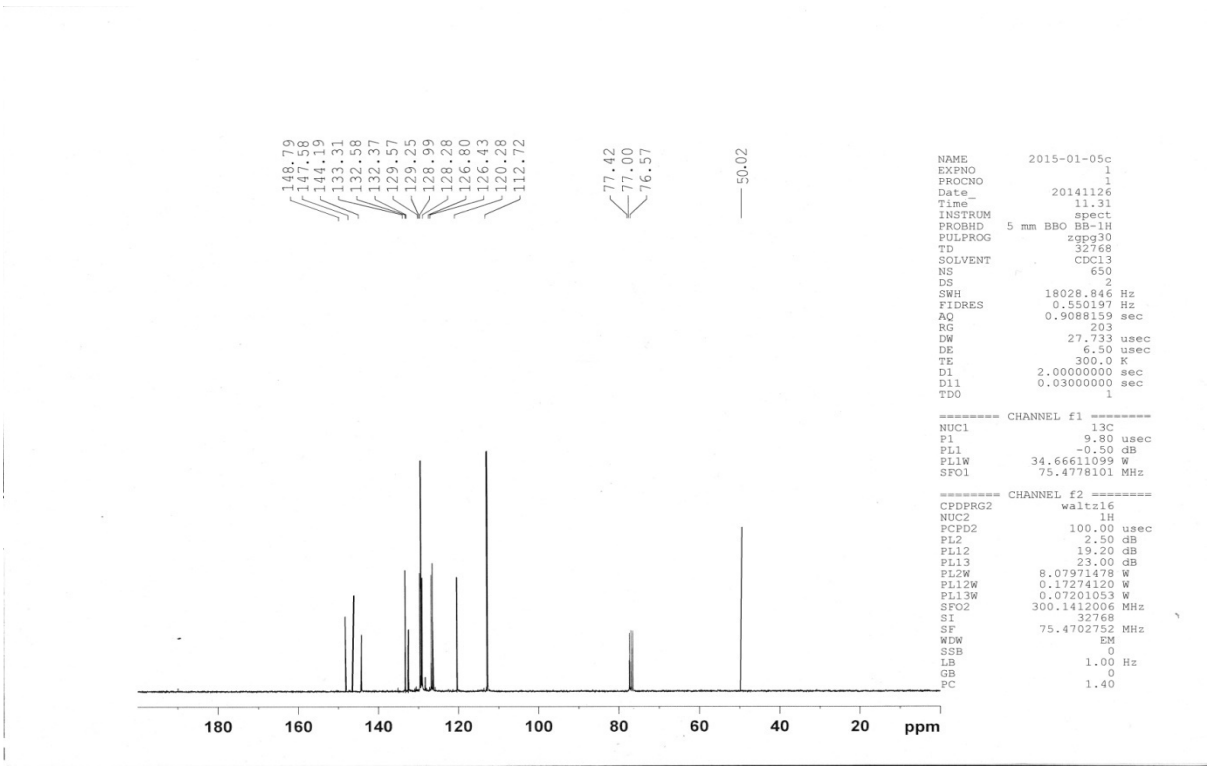
IR spectra of 1-(4-methoxyphenyl)-3-(2-chlorophenyl-5-phenyl formazan(Entry 17):



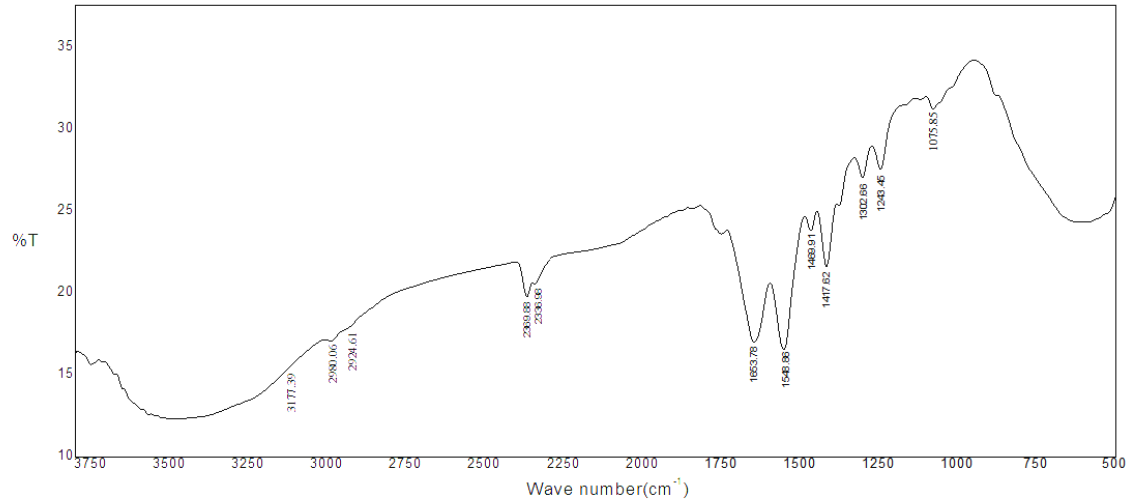
^{1}H NMR spectra of 1-(4-methoxyphenyl)-3-(2-chlorophenyl-5-phenylformazan(Entry 17)



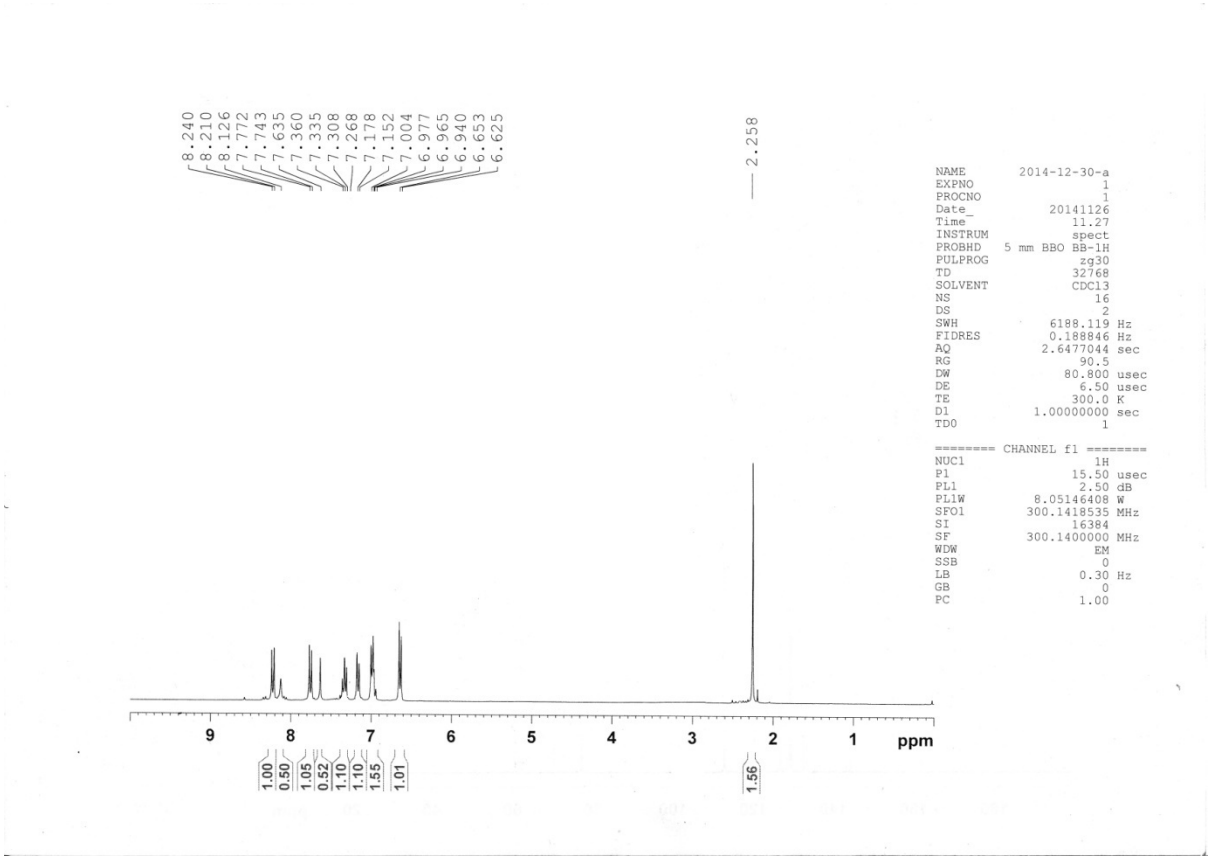
^{13}C NMR spectra of 1-(4-methoxyphenyl)-3-(2-chlorophenyl-5-phenylformazan(Entry 17)



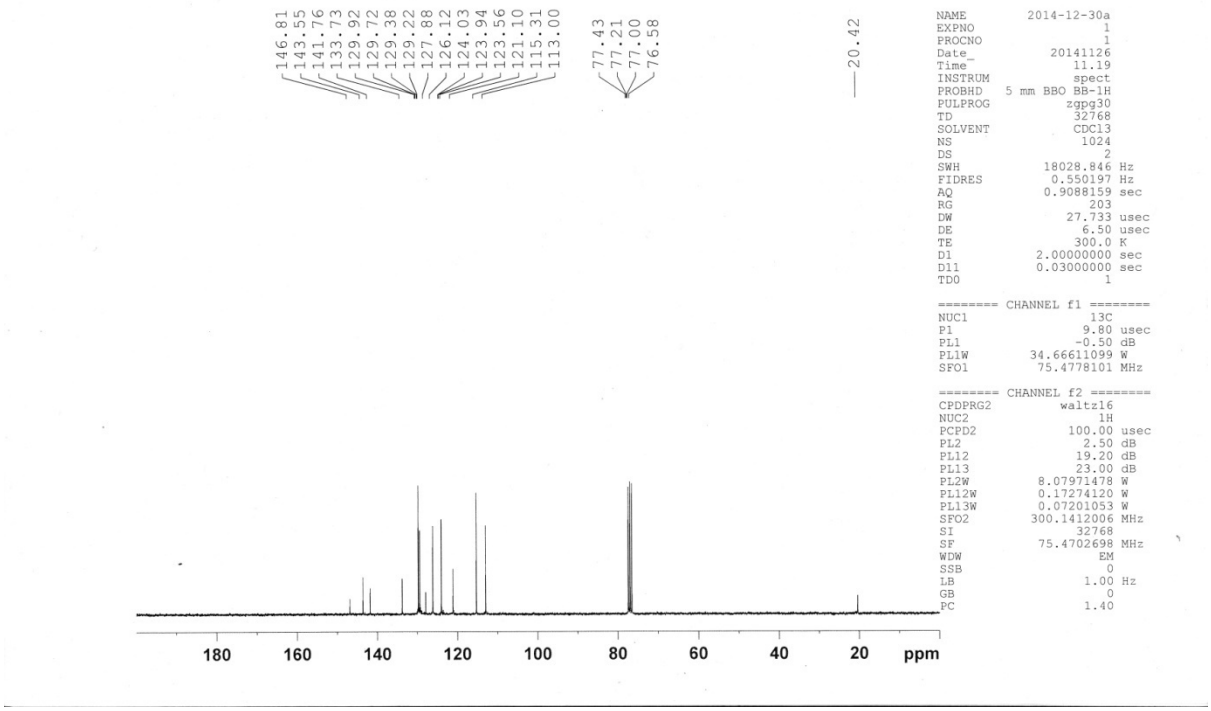
IR spectra of 1-(4-methylphenyl)-3-(4-nitrophenyl)-5-phenylformazan(Entry 18):



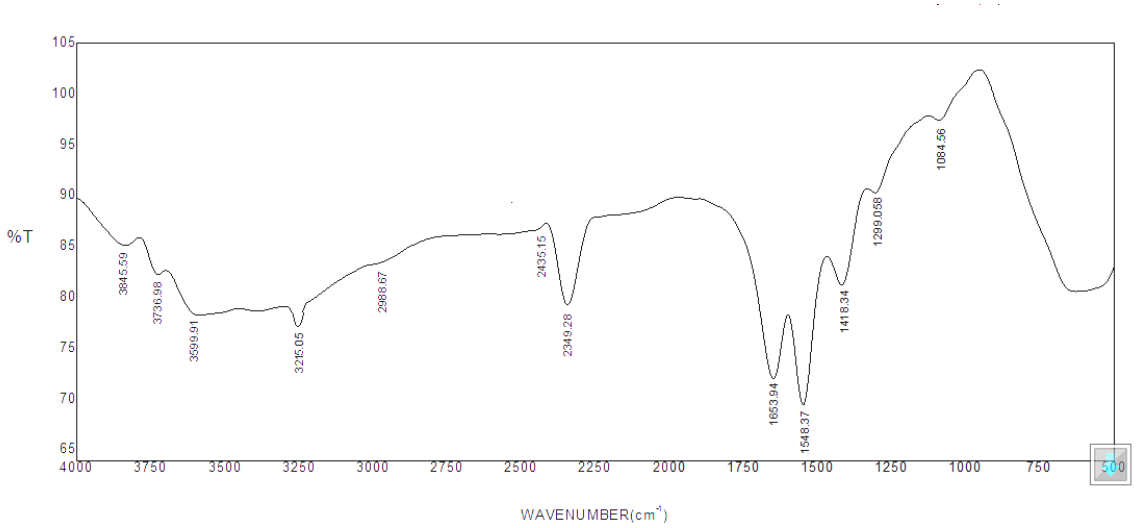
^{1}H NMR (300 MHz, $CDCl_3$) of 1-(4-methylphenyl)-3-(4-nitrophenyl)-5-phenyl formazan(Entry 18):



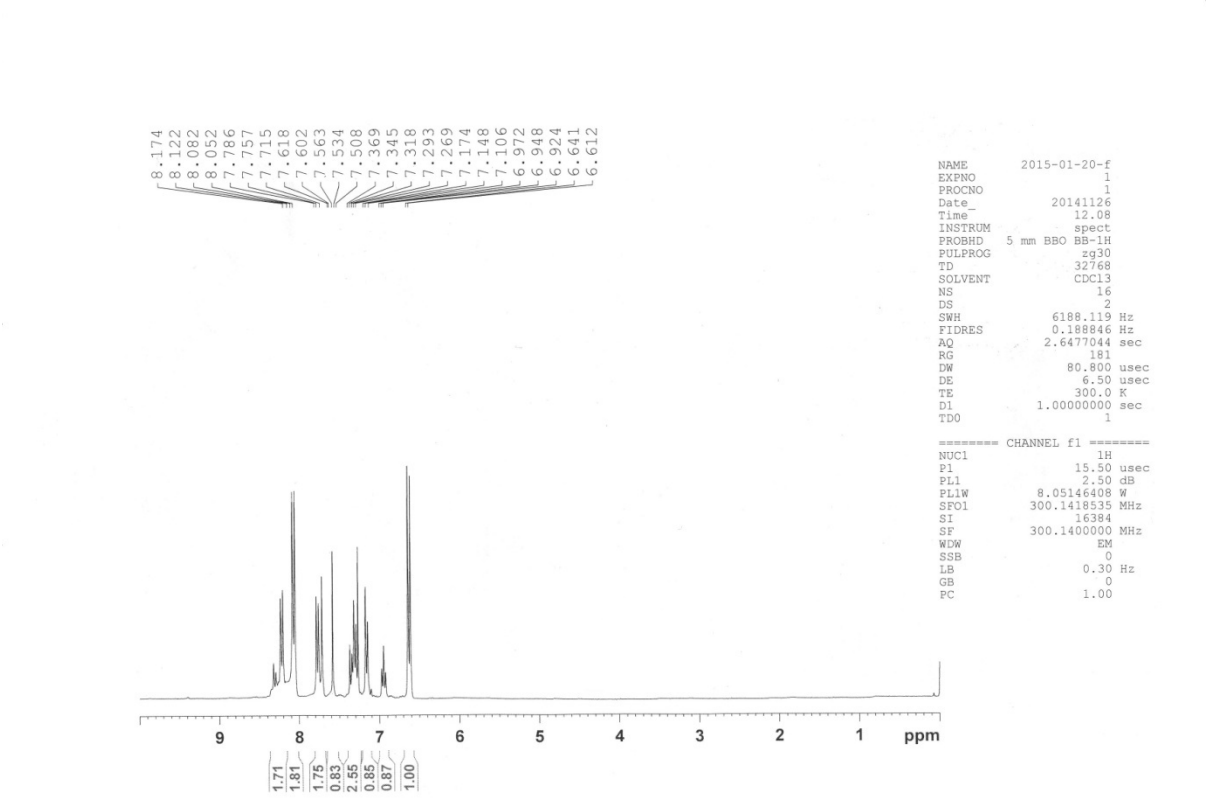
^{13}C NMR spectra of 1-(4-methylphenyl)-3-(4-nitrophenyl)-5-phenylformazan(Entry 18):



IR spectra of 1-(4-nitrophenyl)-3-(4-nitrophenyl)-5-phenyl formazan (entry 19)



^{1}H NMR spectra(300 MHz, $CDCl_3$) of 1-(4-nitrophenyl)-3-(4-nitrophenyl)-5-phenyl formazan (entry 19)



^{13}C NMR spectra(300 MHz, $CDCl_3$) of 1-(4-nitrophenyl)-3-(4-nitrophenyl)-5-phenyl formazan (entry 19)