Ag NPs decorated on a COF in the presence of DBU as an efficient catalytic system for the synthesis of tetramic acids via CO_2 fixation into propargylic amines at atmospheric pressure

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Materials and Equipments

Phloroglucinol (M = 126.11 g/mol), hexamine (M = 140.18 g/mol) and *p*-phenylenediamine (M = 108.14 g/mol) were purchased from Sigma-Aldrich. Trifluoroacetic acid (99.5%) was obtained from TCI Chemicals (India). HCl (Hydrochloric acid) and anhydrous DMF (dimethylformamide) was utilized without any purification.

A D8 Advance SWAX diffractometer from Bruker-AXS utilizing a constant current (40 mA) and voltage (40 kV) was used to obtain the powder XRD pattern of the Ag@TpPa-1 catalyst. The XRD machine was calibrated with silicon sample utilizing Ni-filtered Cu Kα radiation (λ=0.15406 nm). Quantachrome Autosorb-iQ (USA) surface area analyser was used for N_2 adsorption/desorption analysis at 77 K. The sample was activated at 403 K for 12 h under high vacuum before the adsorption of gas. Pore size distribution was obtained by using NLDFT method employing the carbon/cylindrical pore model as reference. For the analysis of HR TEM, 10 mg of the Ag@TpPa-1 catalyst was dispersed into absolute EtOH under the application of sonication for 5 min, followed by the sample coating on a carbon coated Cu-grid and dried in air. JEOL JEM 6700 field emission-scanning electron microscope (FE SEM) was employed to analyze particle size and morphology of Ag@TpPa-1. UV-visible diffuse reflectance spectroscopy (UV 2401PC) and FT-IR (Nicolet MAGNA-FT IR 750 spectrometer Series II) were used to understand the framework and coordination. A TA Instruments thermal analyser (TA-SDT Q-600) was used for the differential thermal analysis (DTA) and thermogravimetric (TGA) of Ag@TpPa-1 with a temperature (ramped at 10^{o}C/min) under continuous air flow. A CHNOS elemental analyser (Vario EL III) was used to determine the contents of C, N and H in Ag@TpPa-1. ^{1}H and^{13}C NMR spectra of the TFP monomer and products were kept on a Bruker DPX-300/500 NMR spectrometer.

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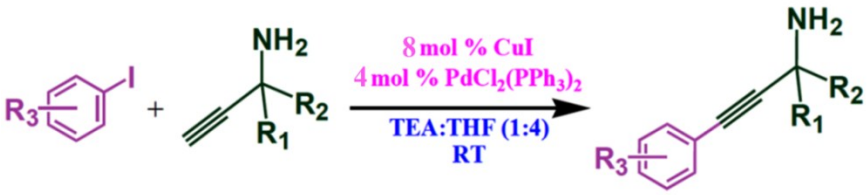
Section S1: Experimental section

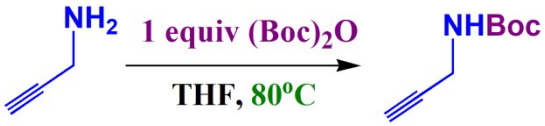
1.1. General method for synthesis of various substituted propargylic amine derivatives with substitution on the propargylic positions

The substituted propargylic amine derivatives were synthesized by Sonogashira Coupling following the previously reported method. The terminal propargylic amines (10 mmol) were poured into a reaction mixture of the aryl iodide (11 mmol), CuI (76.2 mg, 0.40 mmol) and $PdCl_2(PPh_3)_2$ (140.4 mg, 0.20 mmol) in 4:1 mixture of THF/Et_3N under inert atmosphere at room temperature and allowed to stay overnight under continuous stirring. Saturated aqueous solution of ammonium chloridewas poured into the solution at the end of the reaction followed by extraction with diethyl ether three times. The brine solution was used to wash combined layer of organic nature and anhydrous Na_2SO_4 was utilized to get rid of moisture followed by a filtration and concentrated under the application of reduction of pressure. Purification of the resulting residue was performed by column chromatography (Petroleum ether/ EtOAc = 4 / 1).The desired propargylic amines were separated in excellent yields (75-99 %).

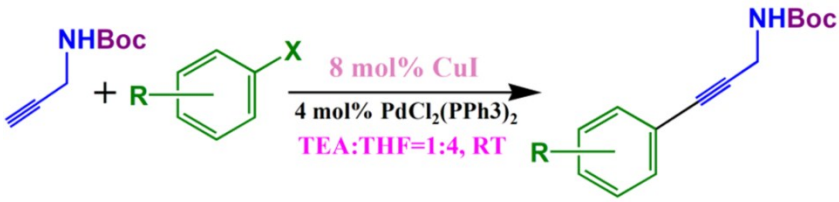


1.2. General method for the synthesis of various substituted propargylic amines with no substitution on the propargylic position

The desired substrates were synthesized by previously reported literatures[53]in three step strategies. To 3-aminopropyne solution (20 mmol) in THF (40 ml) was added di-tert-butyl dicarbonate (20 mmol) and allowed to stir at 80 °C for 1 hour.

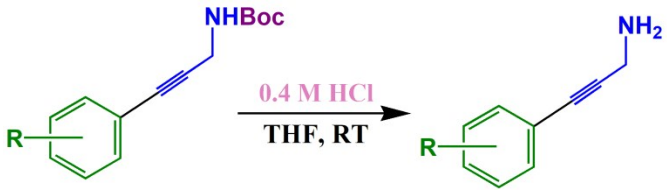


At the end, the pressure was reduced to concentrate the solution followed by purification of the residue by silica gel column chromatography (Petroleum ether / EtOAc = 9 / 1). The tert-butyloxycarbonyl (Boc) protected carbamate was observed in excellent yield.



The prepared carbamate (10 mmol) was poured into a solution of $PdCl_2(PPh_3)_2$ (0.20 mmol), the aryl halides (11 mmol) and CuI (0.40 mmol) in Et_3N/THF = 1:4 solution under the application of nitrogen gas at room temperature and allowed to stir overnight. Saturated aqueous solution of ammonium chloride was poured into the mixture at the end of the reaction, followed by extraction with diethyl ether three times. The brine solution was used to wash combined layer of organic nature and anhydrous Na_2SO_4 was utilized to get rid of moisture followed by a filtration and concentrated under the application of reduction of pressure. The purification of the residue was performed by silica gel column chromatography (Petroleum

ether/ EtOAc= 20: 2). The desired propargylic amines were observed in excellent yields (82-90 % yield).



The solution of 4.0 M HCl dioxane (16 mmol) was poured into a solution of the BOC protected coupling product (4.0 mmol) in THF (5 ml) at room temperature and allowed to stirr overnight. The dilution of reaction mixture was performed with diethyl ether upon completion. The solution of organic nature was isolated by decantation, and the washing of the precipitate was performed with diethyl ether three times. The aqueous NaOH solution (1.0 M) was poured into the suspension of the precipitate in diethyl ether, followed by extraction with diethyl ether three times. The washing of combined organic layer was performed with brine solution, and allowed to dry out with anhydrous Na_2SO_4. The desired primary propargylic amine was produced after solvent evaporation without any purification in satisfactory yield (73- 92 % yield).

1.3. Synthesis of tetramic Acids

1.3.1 General method for the Synthesis of tetramic acid derivatives with substitution on the propargylic position

DBU (5.2 mmol) was poured into a solution of starting material (2.6 mmol) and Ag@TpPa-1 (40 mg) in MeCN (5 ml).After purge of carbon dioxide inside the flask, the solution was allowed to stir at 60 °C. The aqueous solution of hydrochloric acid (2.0 M) was added after the end of the reaction followed by extraction with ethyl acetate five times. The combined organic layer was washed with HCl aqueous solution (2.0 M), and then dried over anhydrous Na_2SO_4. After concentration under reduced pressure, the residue was purified by reprecipitation. The residue was dissolved in small portion of $CHCl_3$. Then, to the solution was

added excess amount of hexane to precipitate the tetramic acid. After removal of solvent by decantation, the corresponding tetramic acid was obtained.

1.3.2 General procedure for the Synthesis of tetramic acid derivatives with no substitution on the propargylic position

To a flask was added Ag@TpPa-1 (40 mg) starting substrate (2.4mmol), and MeCN (5 mL), and CO_2 purged inside the flask. The reaction mixture was stirred at 25 °C until the starting substrate disappeared. After completion, the solution was degassed by freeze-deaeration. To the degassed solution was added DBU (2.4mmol) at 25 °C, and the mixture was stirred until the oxazolidinone disappeared. Upon completion, the reaction mixture was dropped into HCl aqueous solution at 0 °C with vigorously stirring, and then extracted with dichloromethane five times. The combined organic layer was dried over anhydrous Na_2SO_4. After concentration, the corresponding tetramic acid was afforded.

Section S2: HR-TEM analysis

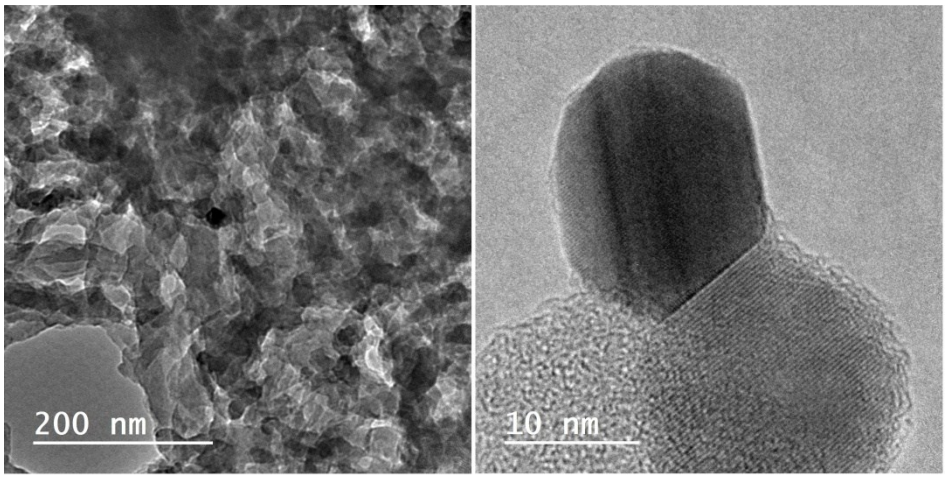


Figure S1. HR-TEM image of reused Ag@TpPa-1.

Section S3: FE-SEM analysis

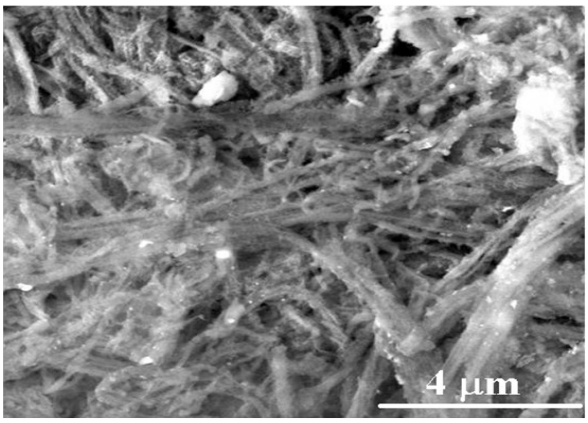


Figure S2. FE-SEM image of reused Ag@TpPa-1.

Section S4: Thermogravimetric and CHN analysis

To develop a conception about the thermal stability of TpPa-1 and Ag@TpPa-1TGA analysishas been performed from 25 °C to 600 °C in a flow of air. As noticed from TG/DTA curves, the initial loss of weight begins at 328 °C owing to the breakage of various functional groups of organic nature in the covalent organic frameworkand further loss of weight at above 430 °C temperature is attributable to the thermal disintegration of residual part of the skeleton.The TG/DTA analysis indicates that material has excellent thermal stability.[56]The data of CHN analysis suggested the percentages of carbon, hydrogen and nitrogen in material. The data of CHN analysis exhibited C= 67.25, H= 5.5 and N= 7.76 %, which agrees with the structure of Ag@TpPa-1.

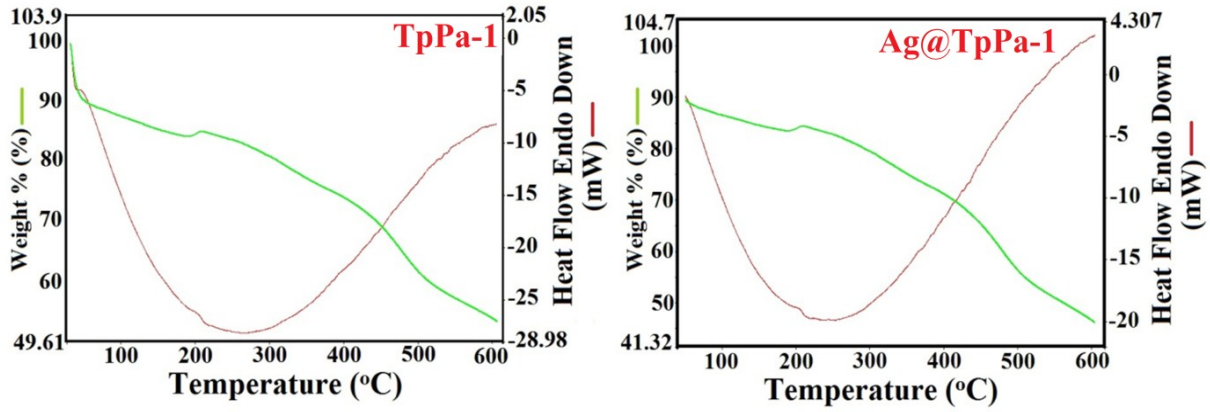


Figure S3. TG/DTA plot ofTpPa-1 and Ag@TpPa-1

Section S5: ^{1}H NMR and FT IR spectra of 2,4,6-triformylphloroglucinol

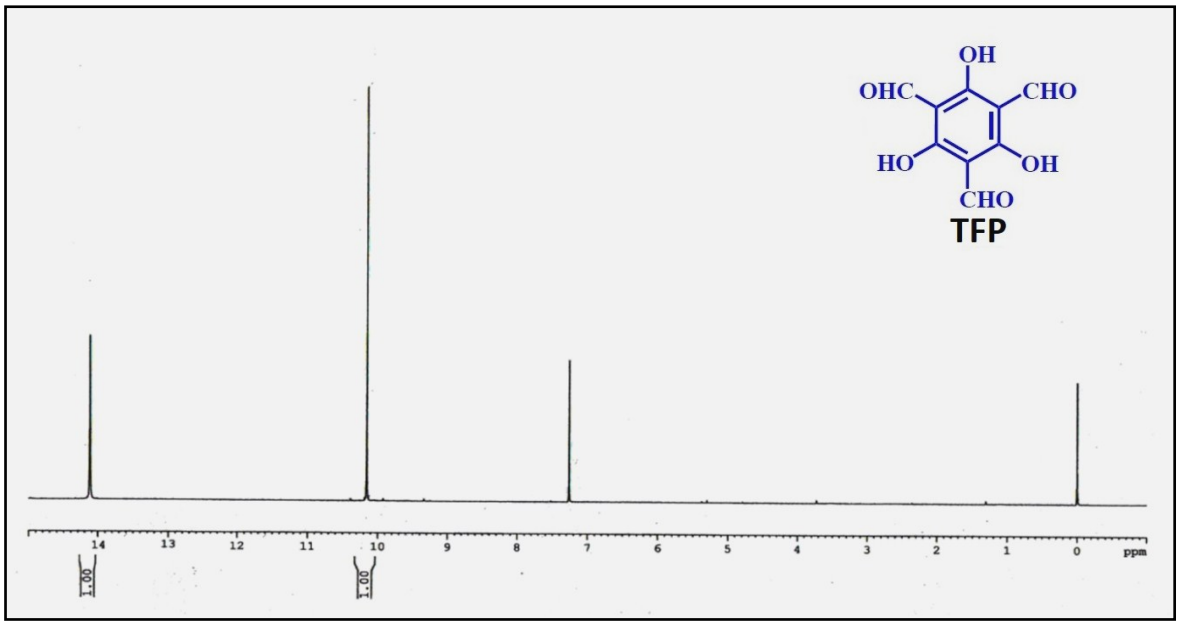


Figure S4.[1]H NMR spectra of 2,4,6-triformylphloroglucinol

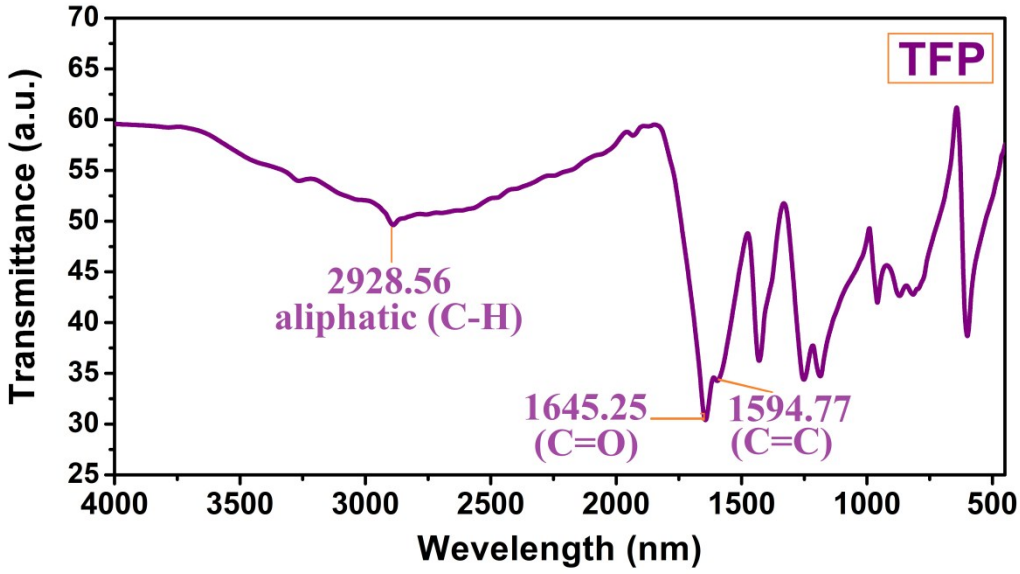


Figure S5. FT IR spectra of 2,4,6-triformylphloroglucinol

Section S6: FT IR spectra

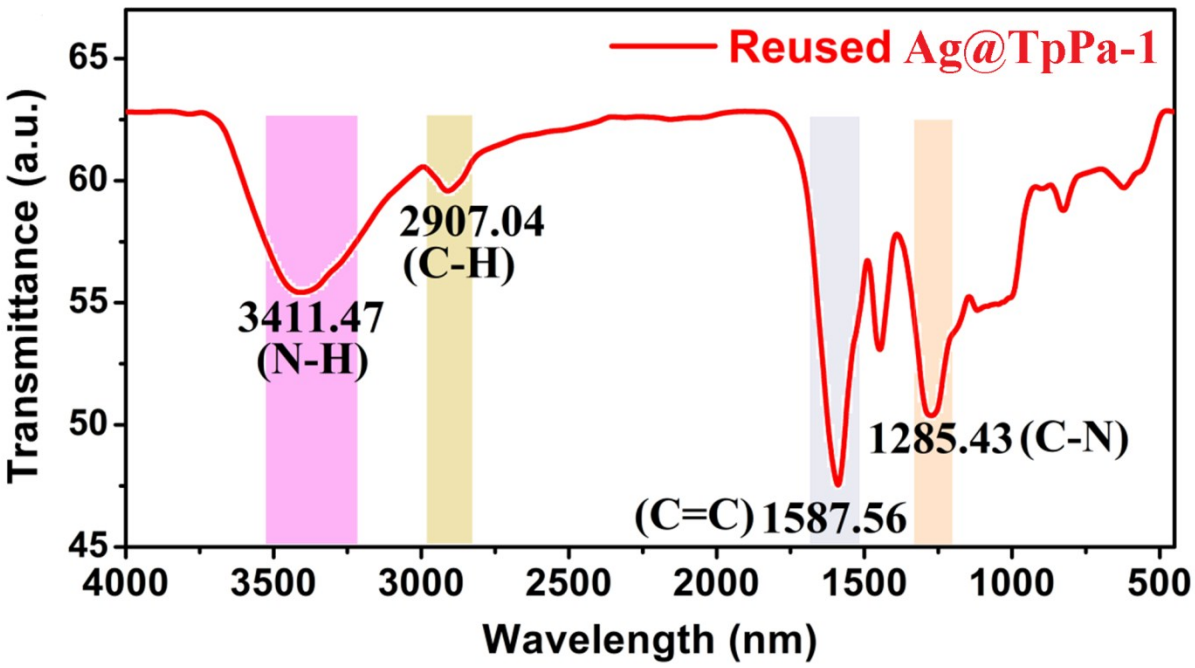


Figure S6. FT IR spectra of reused Ag@TpPa-1 after five runs.

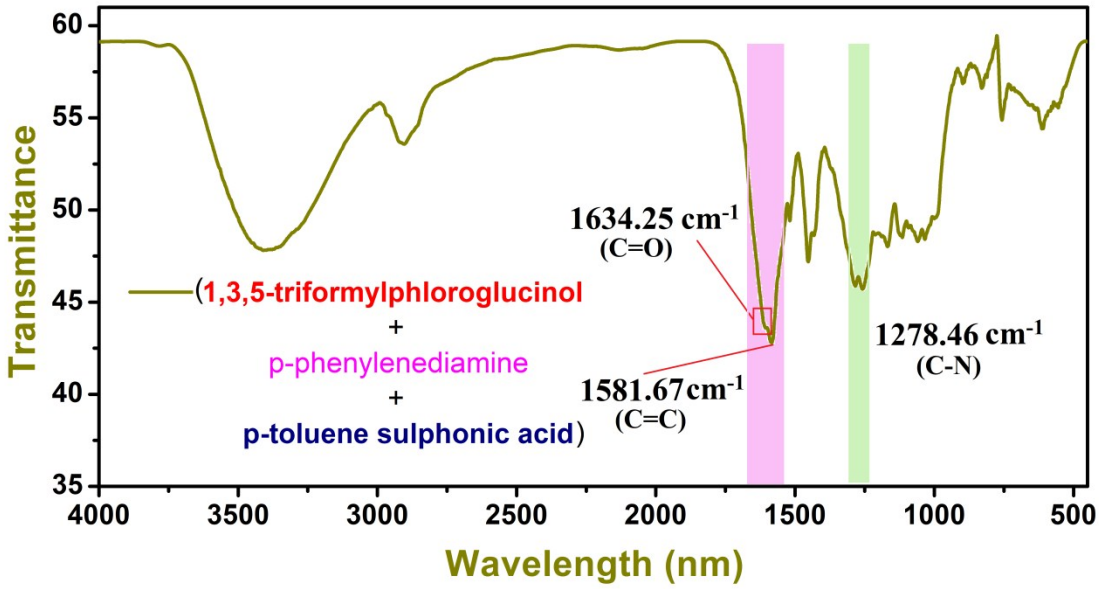


Figure S7. FT IR spectra of the intermediate (PTSA + Pa1 + Tp) before heating.

Section S7: UV-Vis DRS analysis

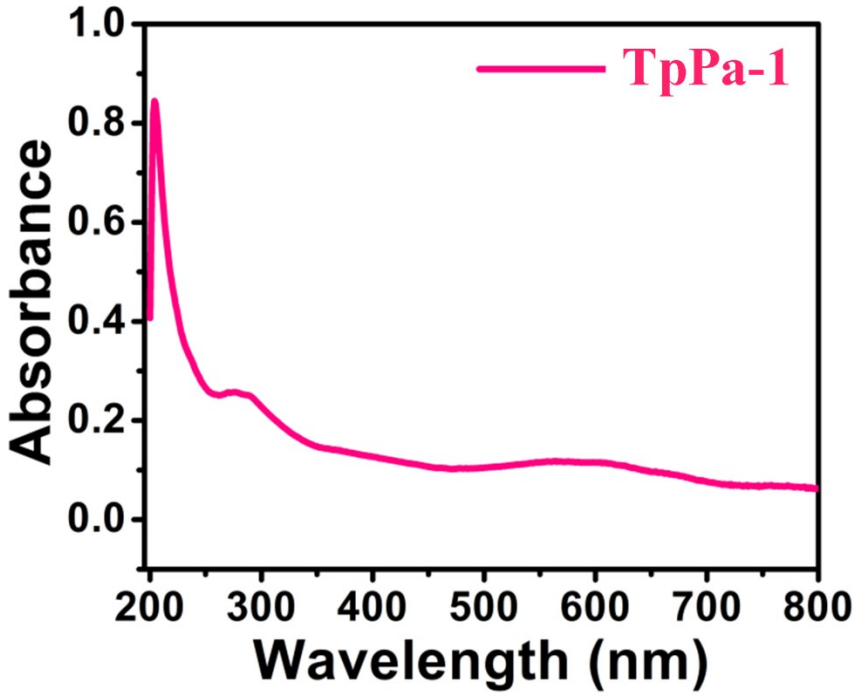
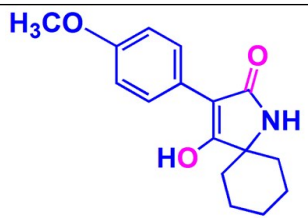
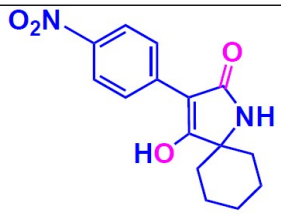
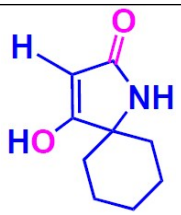
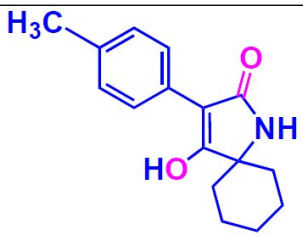
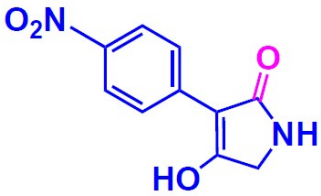
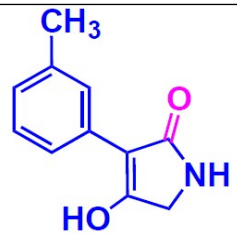


Figure S8. The DRS-UV-visible absorption spectrum of TpPa-1.

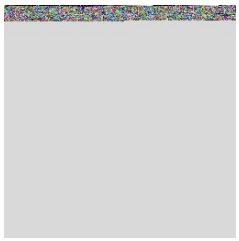
Section S8: NMR Spectra

^{1}H NMR data of isolated pure tetramic acid derivatives:

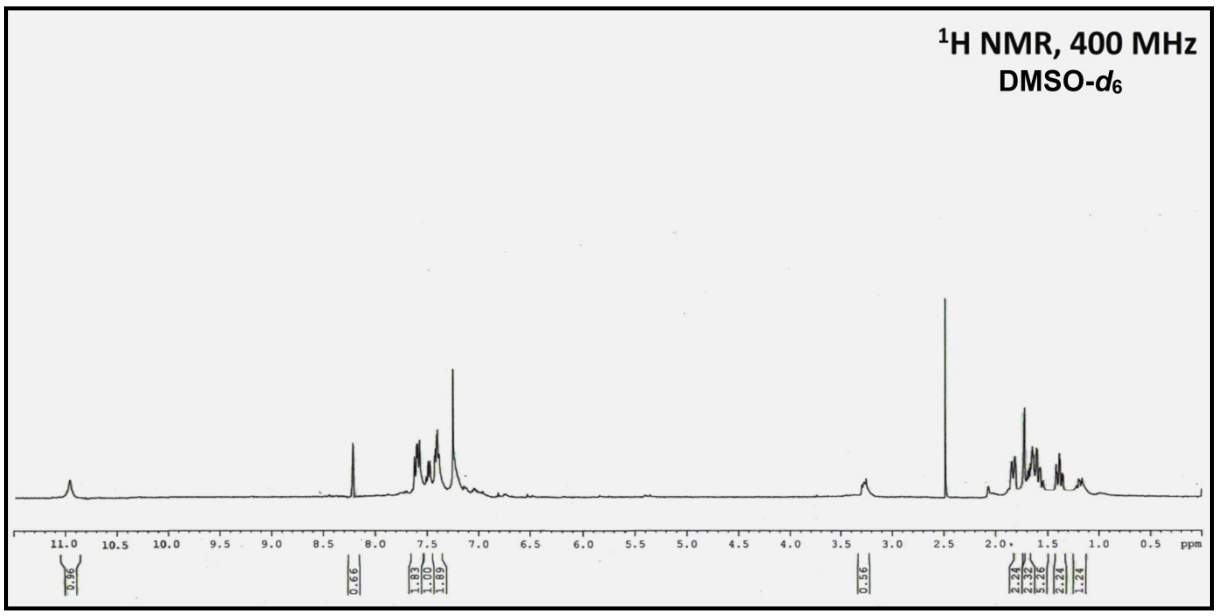
	Pale yellowish solid; m.p.: 214.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.10-1.17 (m, 1H), 1.24-1.27 (d, J = 12.1 Hz, 2H), 1.49-1.62 (m, 5H), 1.87 (dd, J = 12.8 Hz, 8.5 Hz, 2H), 7.24 (t, J = 7.7 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H), 7.79 (t, J = 4.1 Hz, 2H), 8.26 (s, 1H) 10.27 (s, 1H);^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.7, 24.6, 33.2, 59.2, 101.5, 125.6, 126.9, 127.4, 132.3, 169.2, 174.4.
	Pale yellowish solid; m.p.: 226.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.09-1.16 (m, 1H), 1.24-1.27 (d, J = 12.1 Hz, 2H), 1.47-1.72 (m, J = 5H), 1.92-1.97 (m, 2H), 3.71 (s, 3H), 6.79 (d, J = 9.3 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 8.22 (s, 1H), 10.23 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.7, 24.4, 33.2, 56.1, 59.2, 101.4, 113.3, 125.8, 128.6, 157.2, 171.8, 174.1.
	Pale orange yellowish solid; m.p.: 272.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.13-1.21 (m, 1H), 1.28 (d, J = 12.8 Hz, 2H), 1.48-1.99 (m, 7H),7.27-7.69 (m, 5H),8.41 (s, 1H);^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.7, 24.3, 32.6, 59.1, 100.4, 123.2, 127.1, 140.4, 145.3, 170.2, 180.3.
	Orange solid; m.p.: 213.8 °C; 1H NMR (400 MHz, DMSO-d_6): keto form; δ = 1.47-1.88 (m, 10H), 3.03 (s, 2H), 8.72 (s, 1H); enol form; d = 1.23-1.31 (m, 10H), 4.61 (s, 1H), 7.72 (s, 1H), 11.28 (s, 1H);^{13}C NMR (100 MHz, DMSO-d_6): keto form and enol form; δ = 20.6, 21.8, 24.5, 32.9, 33.2, 60.9, 66.7, 91.8, 169.9, 172.7, 211.9.
	Pale yellow solid; m.p.: 193.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.19-1.23 (m, 1H), 1.27-1.74 (m, 7H), 1.87 (dd, J = 12.9 Hz, 8.4 Hz, 2H), 2.32 (s, 3H), 7.12 (d, J = 8.3 Hz, 2H), 7.40-7.54 (d, J 8.2 Hz, 2H), 8.16 (s, 1H), 10.76 (s, 1H);^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.1, 22.2, 24.6, 32.2, 59.2, 101.5, 127.1, 128.3,

	129.6, 135.9, 170.5, 173.8.
	Yellow solid; m.p.: 134.3 °C; 1H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 2H), 6.13 (s, 1H), 7.35-7.59 (m, 5H), 10.78 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.4, 108.2, 127.2, 128.6, 128.8, 133.9, 141.1, 159.4.
	Pale yellowish solid; m.p.: 134.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.71 (s, 2H), 6.15 (s, 1H), 6.82-6.83 (d, 2H), 7.22-7.23(d, 2H) 9.27 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.4, 108.2, 128.1, 131.7, 136.8, 141.2, 157.5.
	Yellow solid; m.p.: 122.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 3.64 (s, 2H), 6.13 (s, 1H), 7.12-7.14 (s, 2H), 7.40-7.55, 8.96 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 31.4, 108.1, 129.6, 130.3, 132.8, 136.6, 141.1, 157.9.
	Yellow solid; m.p.: 78.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3H), 3.66 (s, 2H), 5.92 (s, 1H), 6.80-6.84 (m, 1H), 7.20-7.25 (m, 2H), 7.82-7.83 (d,1H), 8.96 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1, 31.1, 108.2, 126.9, 127.2, 129.8, 130.4, 132.4, 137.3, 141.1, 157.5.
	Pale yellowish solid; m.p.: 134.3 °C; 1H NMR (400 MHz, CDCl3): δ = 3.67 (s, 2H), 6.17 (s, 1H), 7.27-7.69 (m, 4H), 9.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.4, 108.2, 123.1, 126.4, 126.9, 141.2, 143.7, 158.0.
	Brown solid; m.p.: 162.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 3.67 (s, 2H), 6.15 (s, 1H), 7.33-7.65 (m, 4H), 9.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 31.8, 108.2, 129.8, 130.8, 132.1, 136.4, 141.3, 157.5.

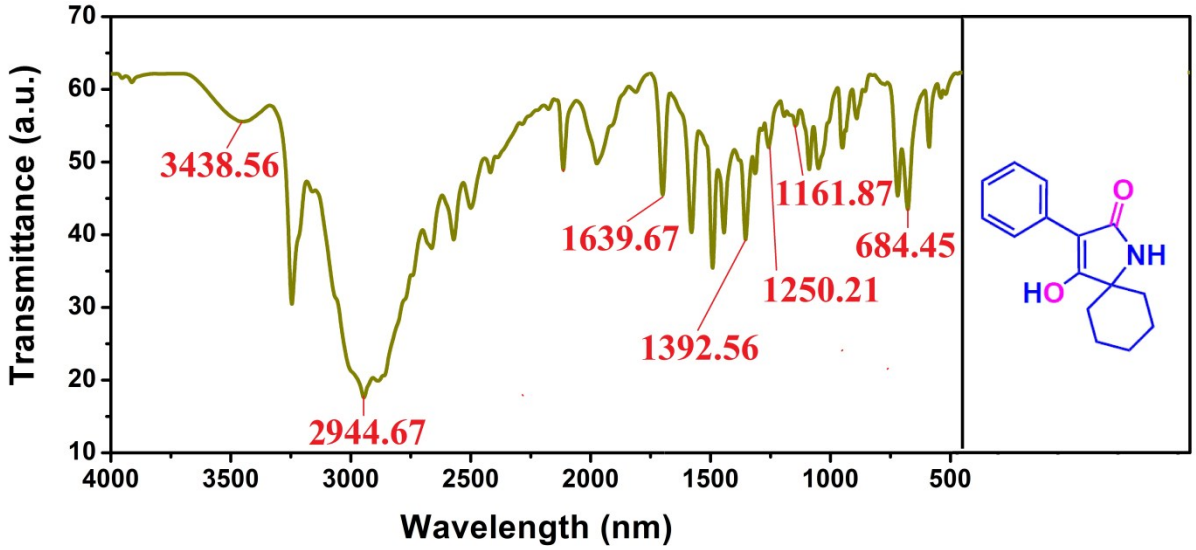
4-Hydroxy-3-phenyl-1-azaspiro[4.5]dec-3-en-2-one (Table 3, entry 1)



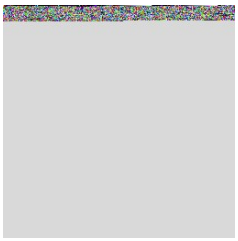
^{1}H NMR spectra:



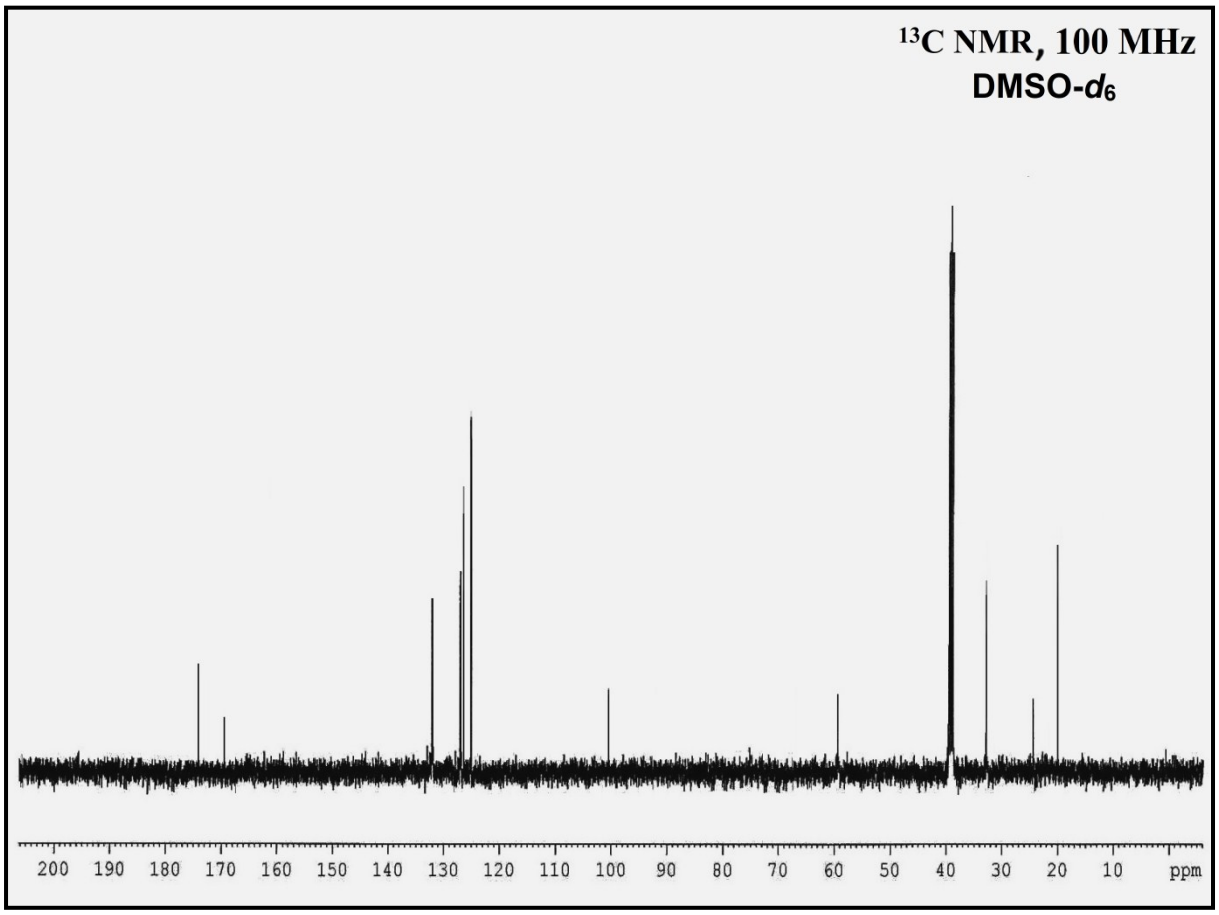
IR spectra:



4-Hydroxy-3-phenyl-1-azaspiro[4.5]dec-3-en-2-one (Table 3, entry 1)

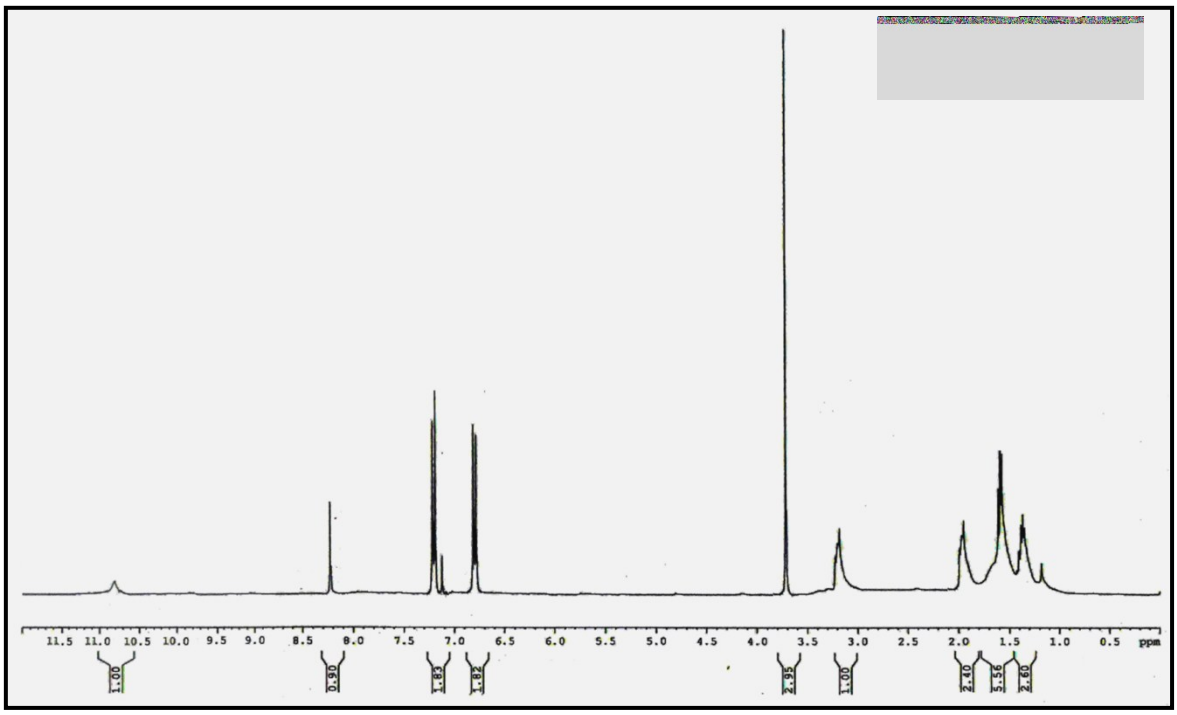


^{13}C NMR spectra:

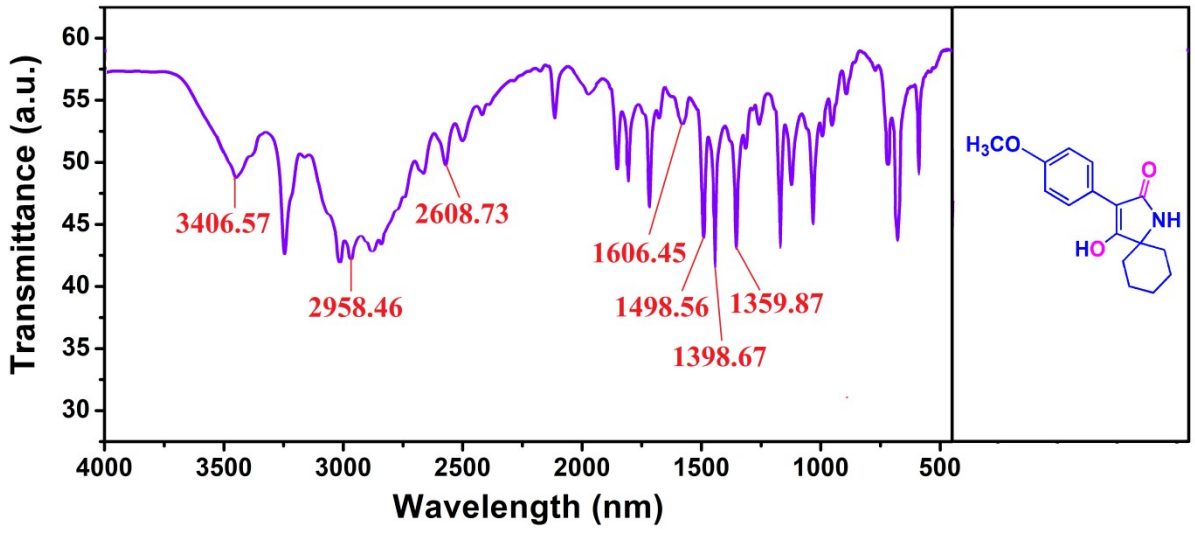


4-Hydroxy-3-(4-methoxyphenyl)-1-azaspiro[4.5]dec-3-en-2-one (Table 3, entry 2)

^{1}H NMR spectra:

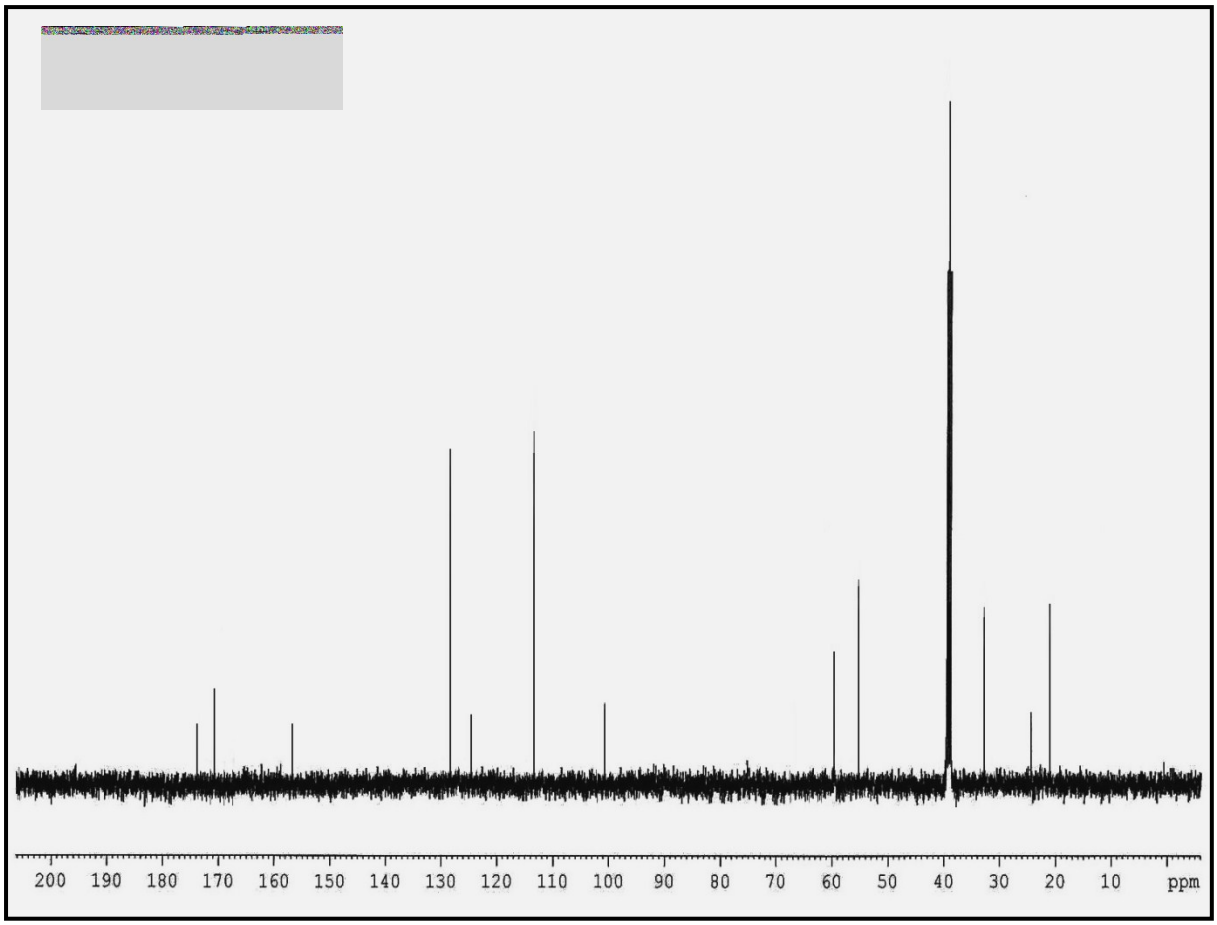


IR spectra:



4-Hydroxy-3-(4-methoxyphenyl)-1-azaspiro[4.5]dec-3-en-2-one (Table 3, entry 2)

^{13}C NMR spectra:



4-Hydroxy-3-(4-nitrophenyl)-1-azaspiro[4.5]dec-3-en-2-one (Table 3, entry3)

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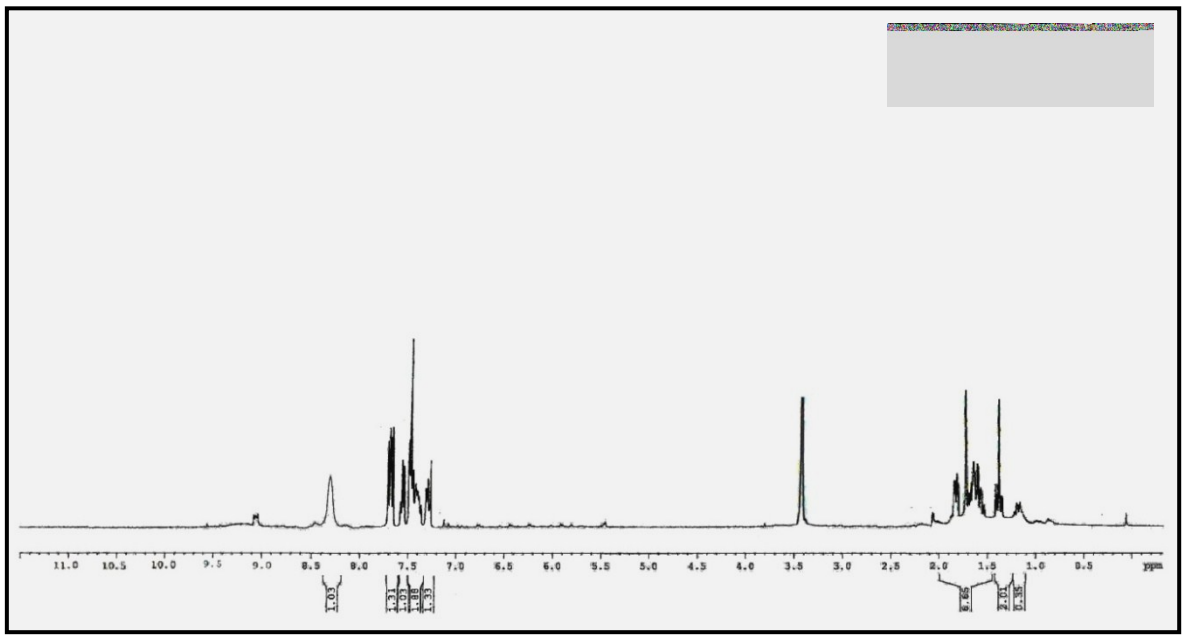
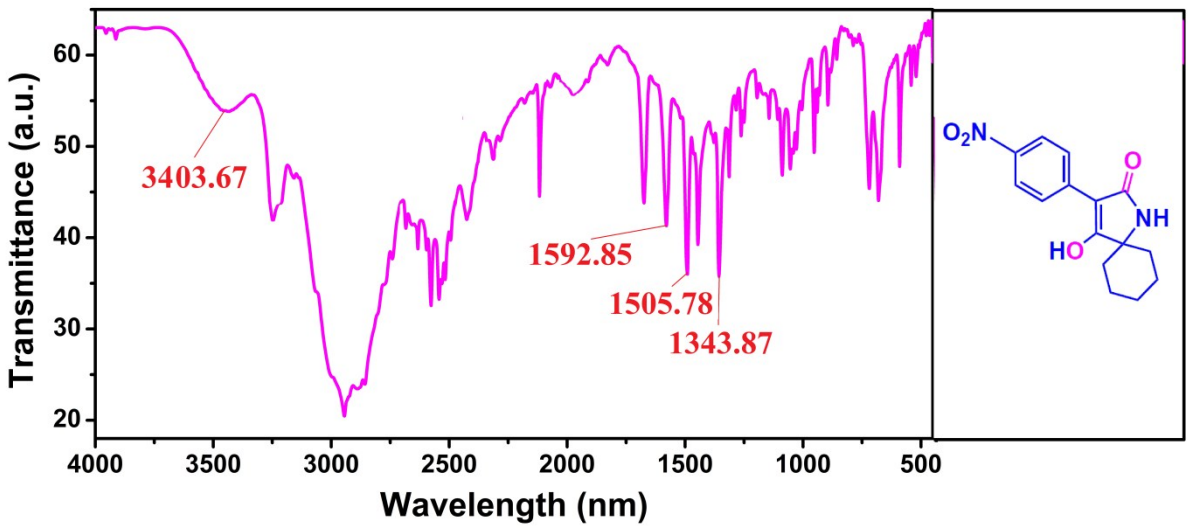
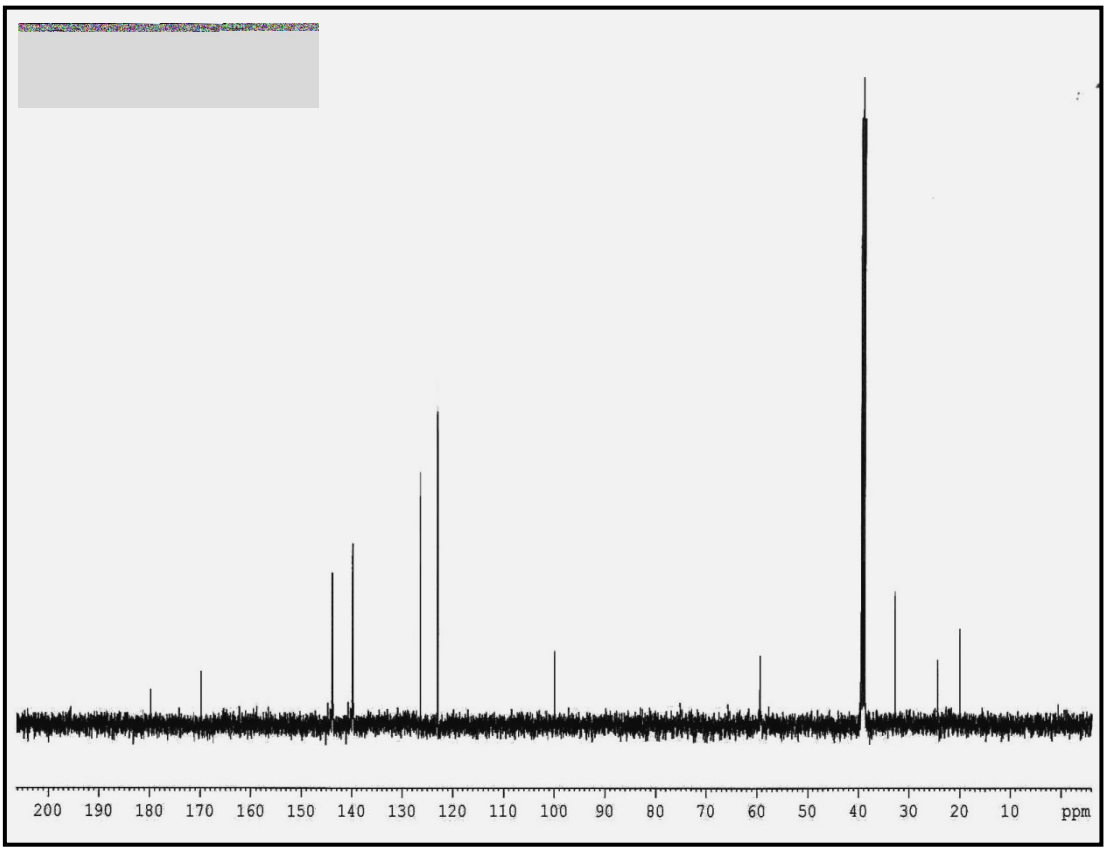


IR spectra:



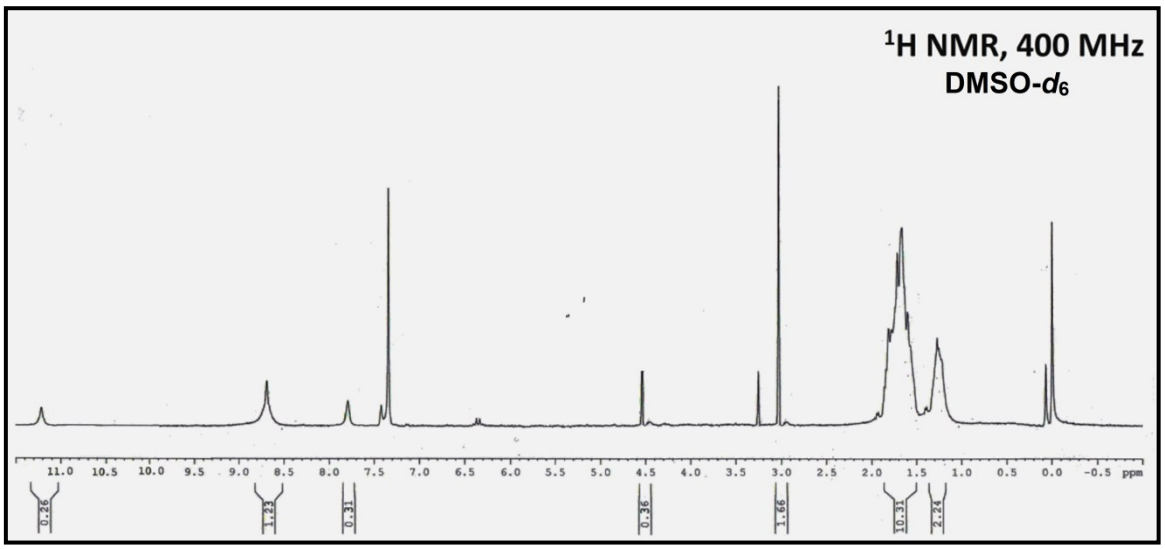
4-Hydroxy-3-(4-nitrophenyl)-1-azaspiro[4.5]dec-3-en-2-one (Table 3, entry 3)

^{13}C NMR spectra:

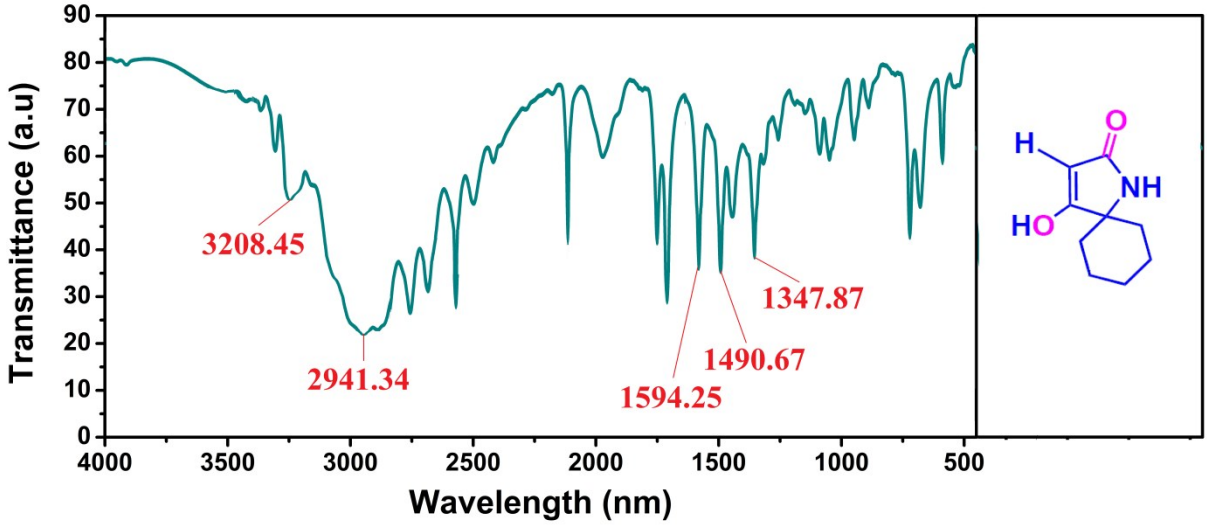


4-Hydroxy-1-azaspiro[4.5]dec-3-en-2-one (Table 3, entry 4)

^{1}H NMR spectra:

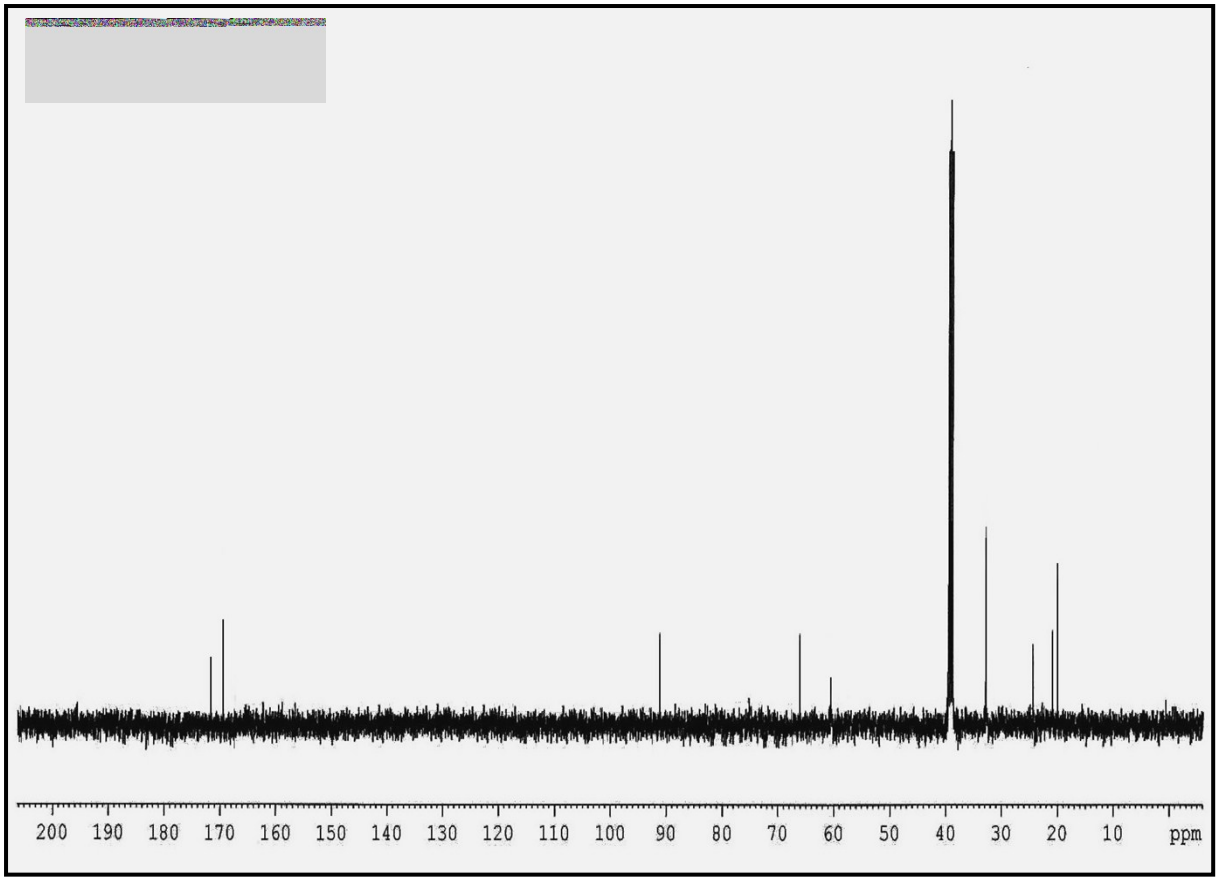


IR spectra:



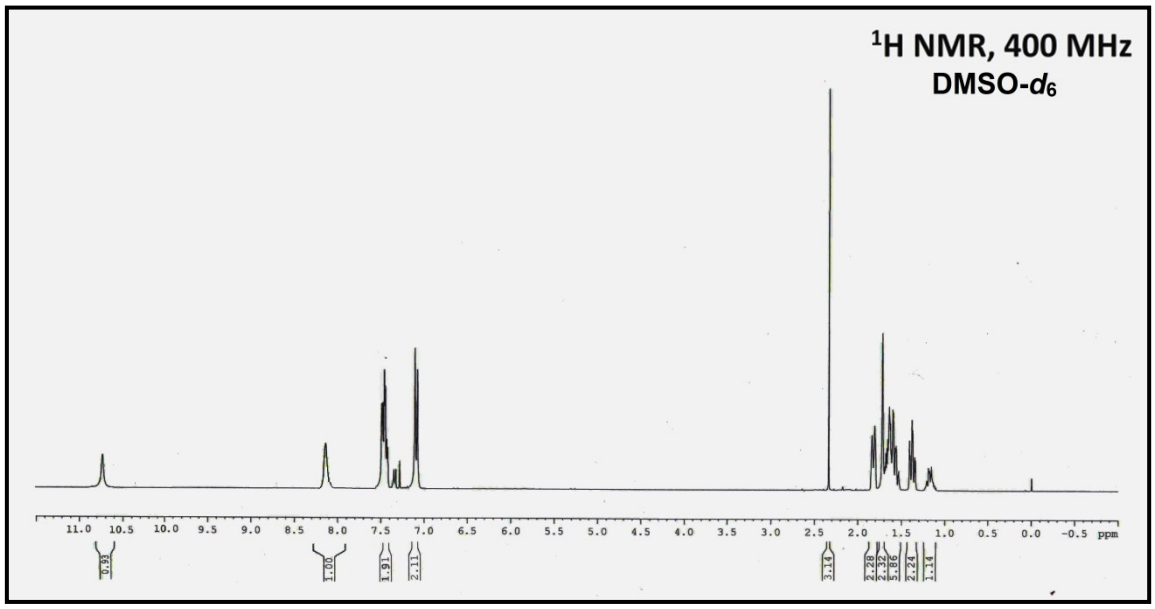
4-Hydroxy-1-azaspiro[4.5]dec-3-en-2-one (Table 3, entry 4)

^{13}C NMR spectra:

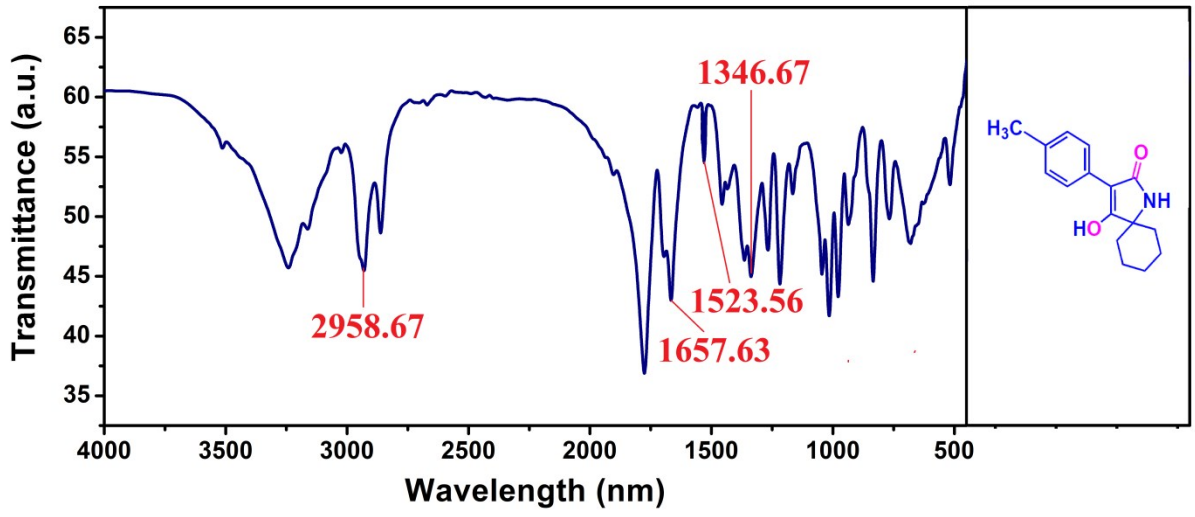


4-Hydroxy-3-(4-methylphenyl)-1-azaspiro[4.5]dec-3-en-2-one(Table 3, entry 5)

^{1}H NMR spectra:

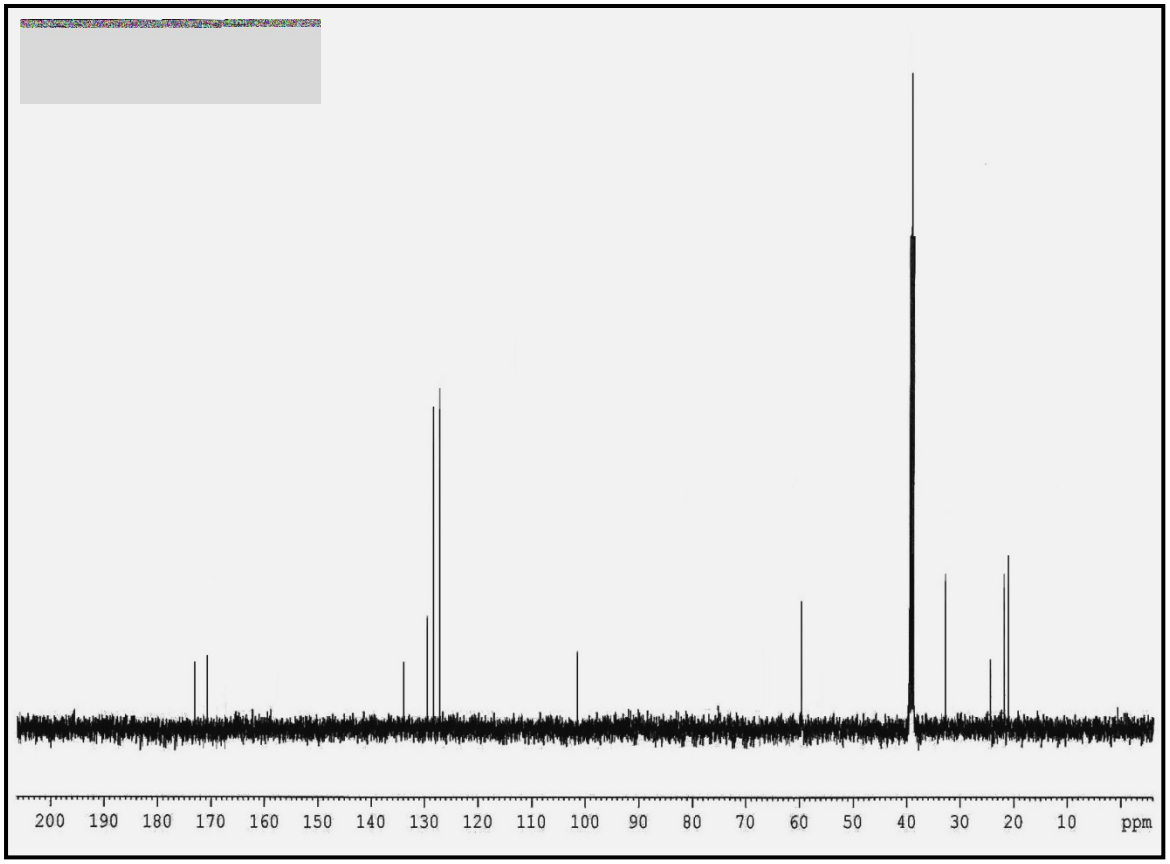


IR spectra:



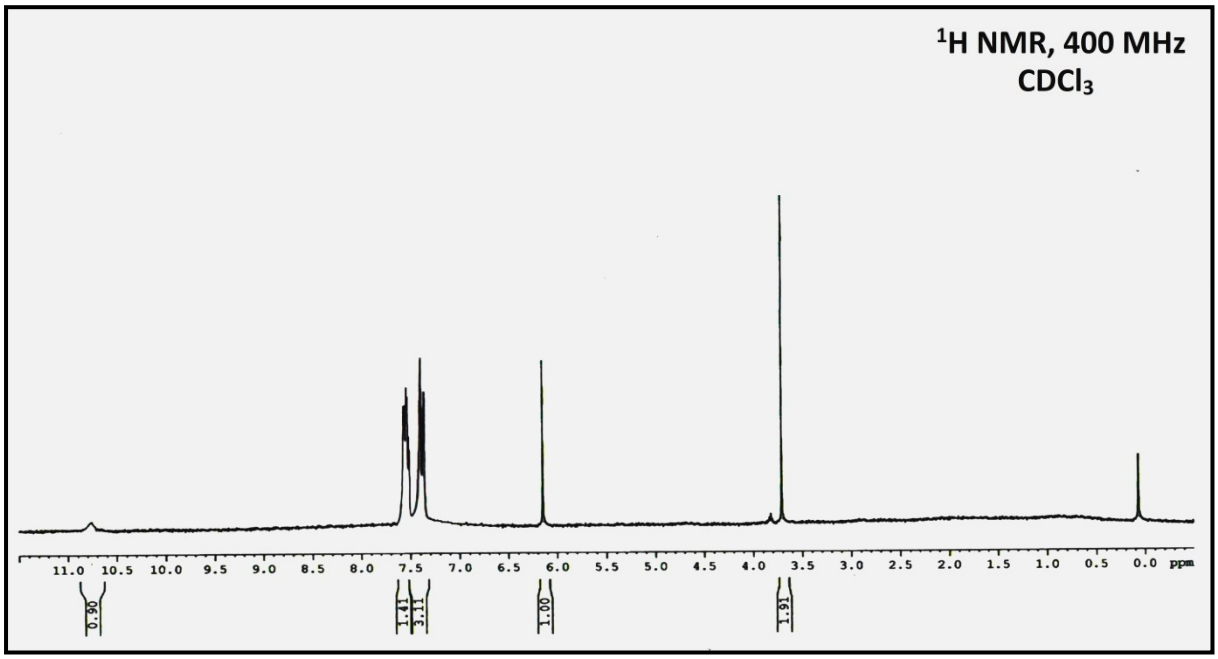
4-Hydroxy-3-(4-methylphenyl)-1-azaspiro[4.5]dec-3-en-2-one(Table 3, entry 5)

^{13}C NMR spectra:

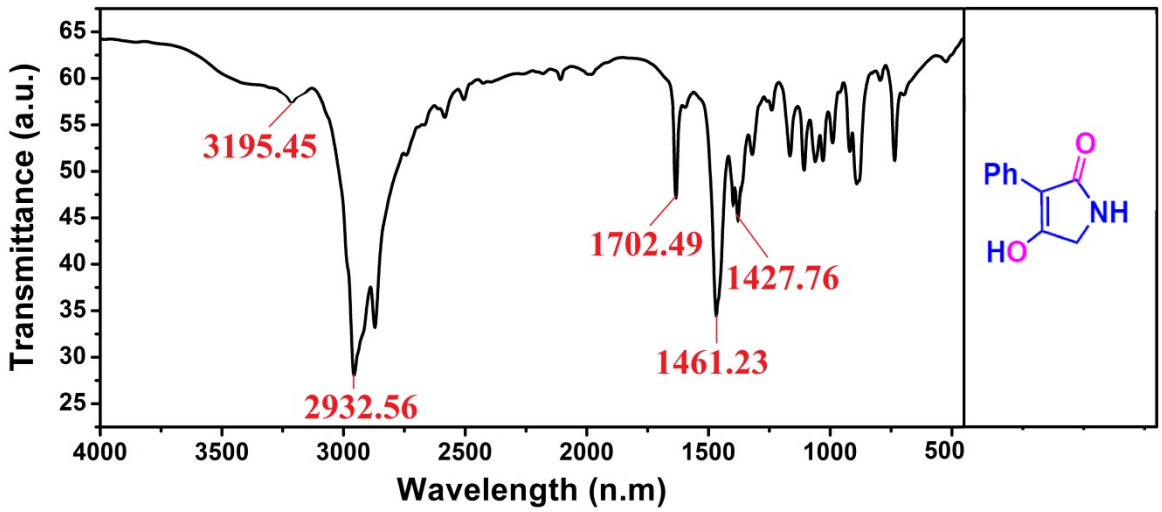


1,5-Dihydro-4-hydroxy-3-phenyl-2H-pyrrol-2-one (Table 4, entry 1)

^{1}H NMR spectra:

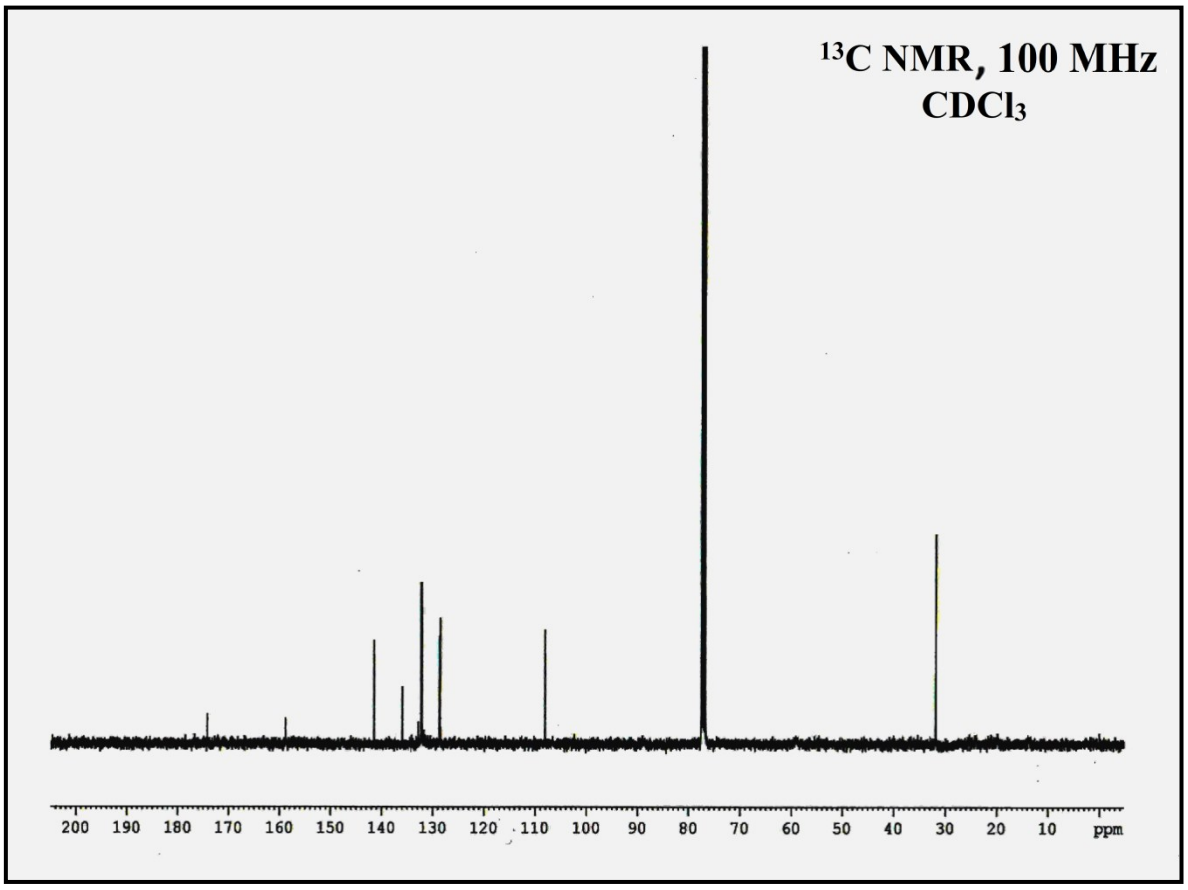


IR spectra:



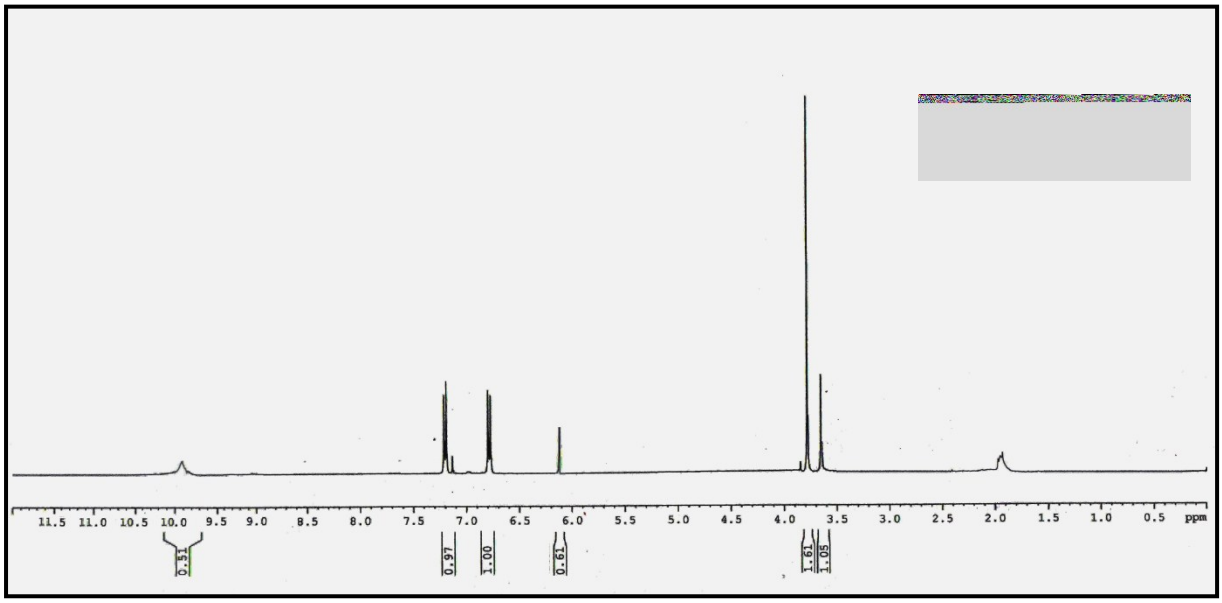
1,5-Dihydro-4-hydroxy-3-phenyl-2H-pyrrol-2-one (Table 4, entry 1)

^{13}C NMR spectra:

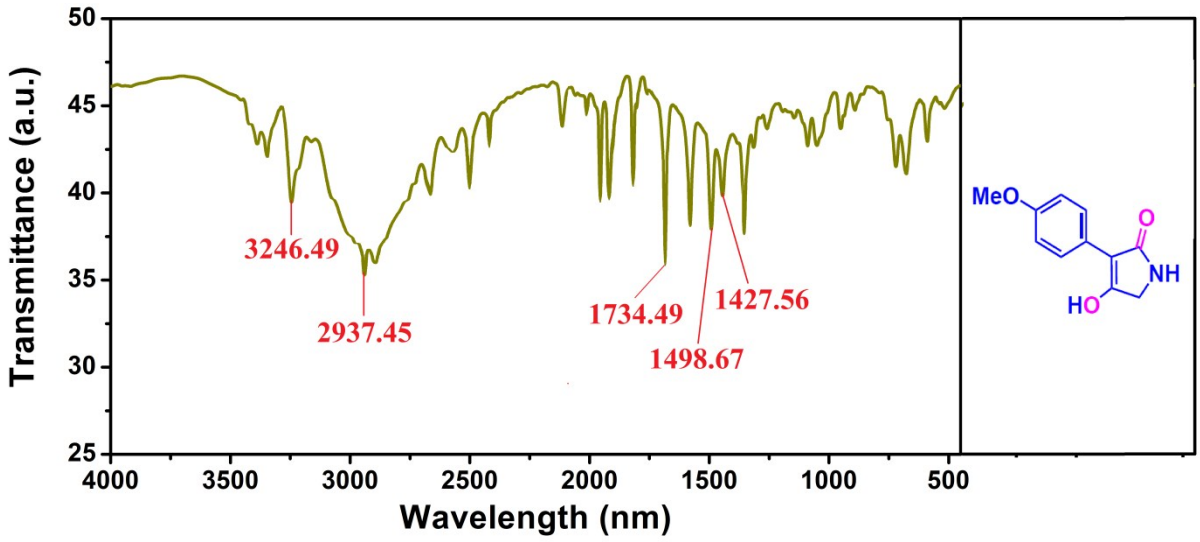


<u>1,5-Dihydro-4-hydroxy-3-(4-methoxyphenyl)-2H-pyrrol-2-one</u> (Table 4, entry 2)

^{1}H NMR spectra:

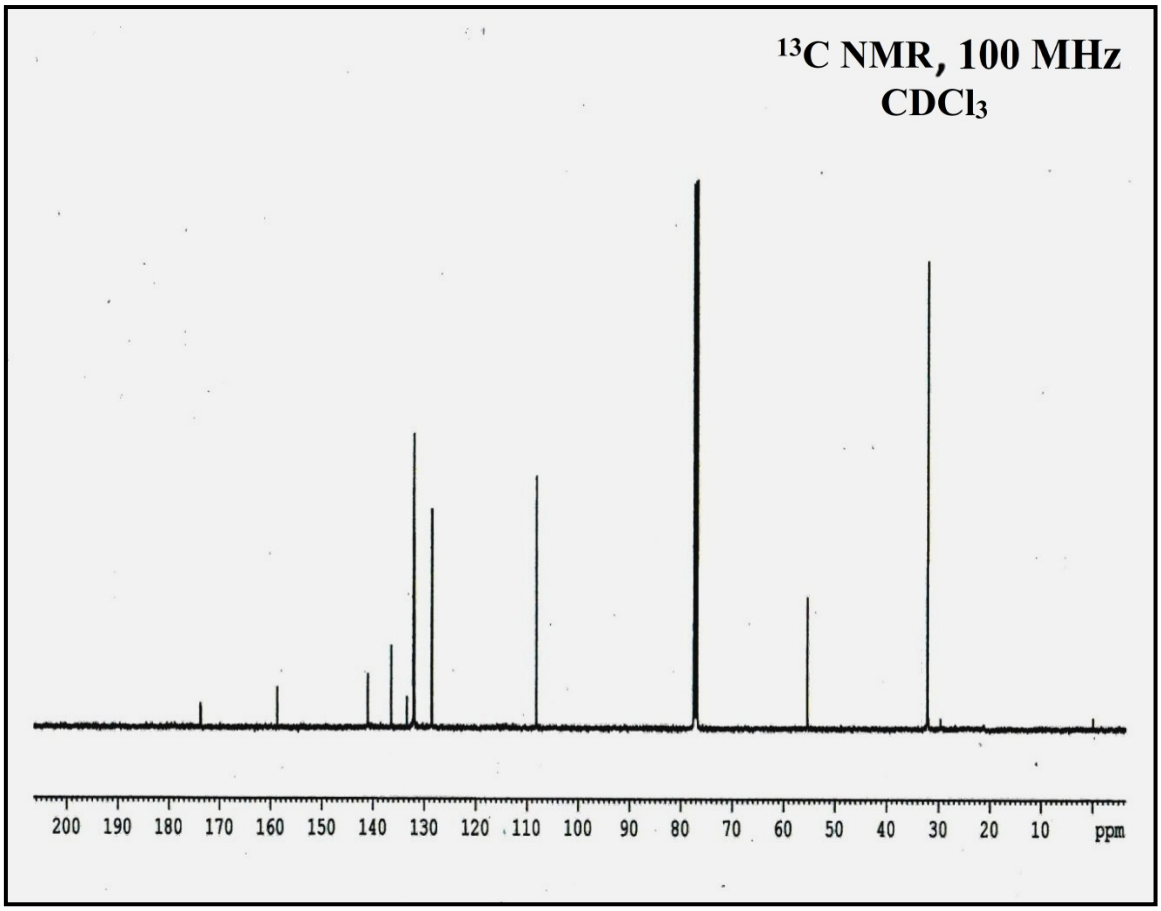


IR spectra:



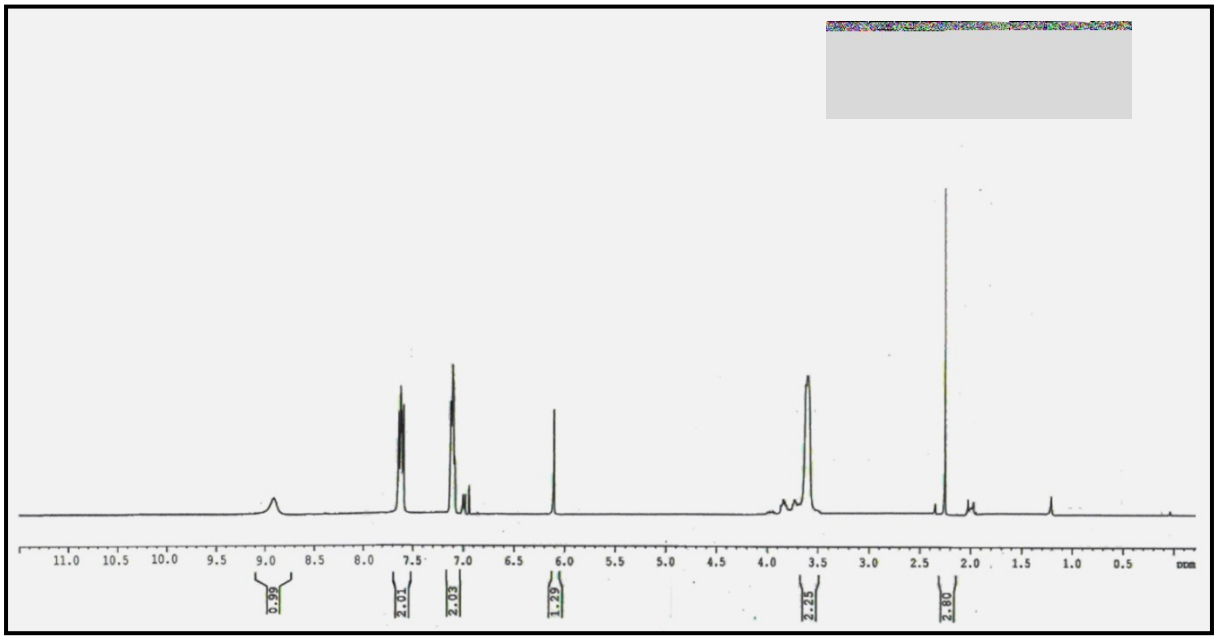
<u>1,5-Dihydro-4-hydroxy-3-(4-methoxyphenyl)-2H-pyrrol-2-one</u> (Table 4, entry 2)

^{13}C NMR spectra:

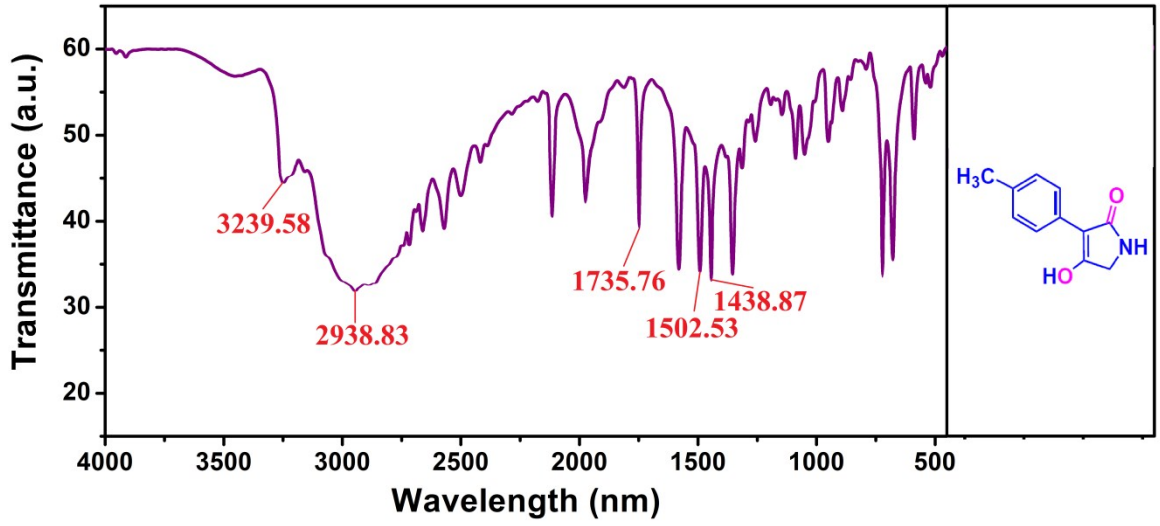


1,5-Dihydro-4-hydroxy-3-(4-methylphenyl)-2H-pyrrol-2-one (Table 4, entry 3)

^{1}H NMR spectra:

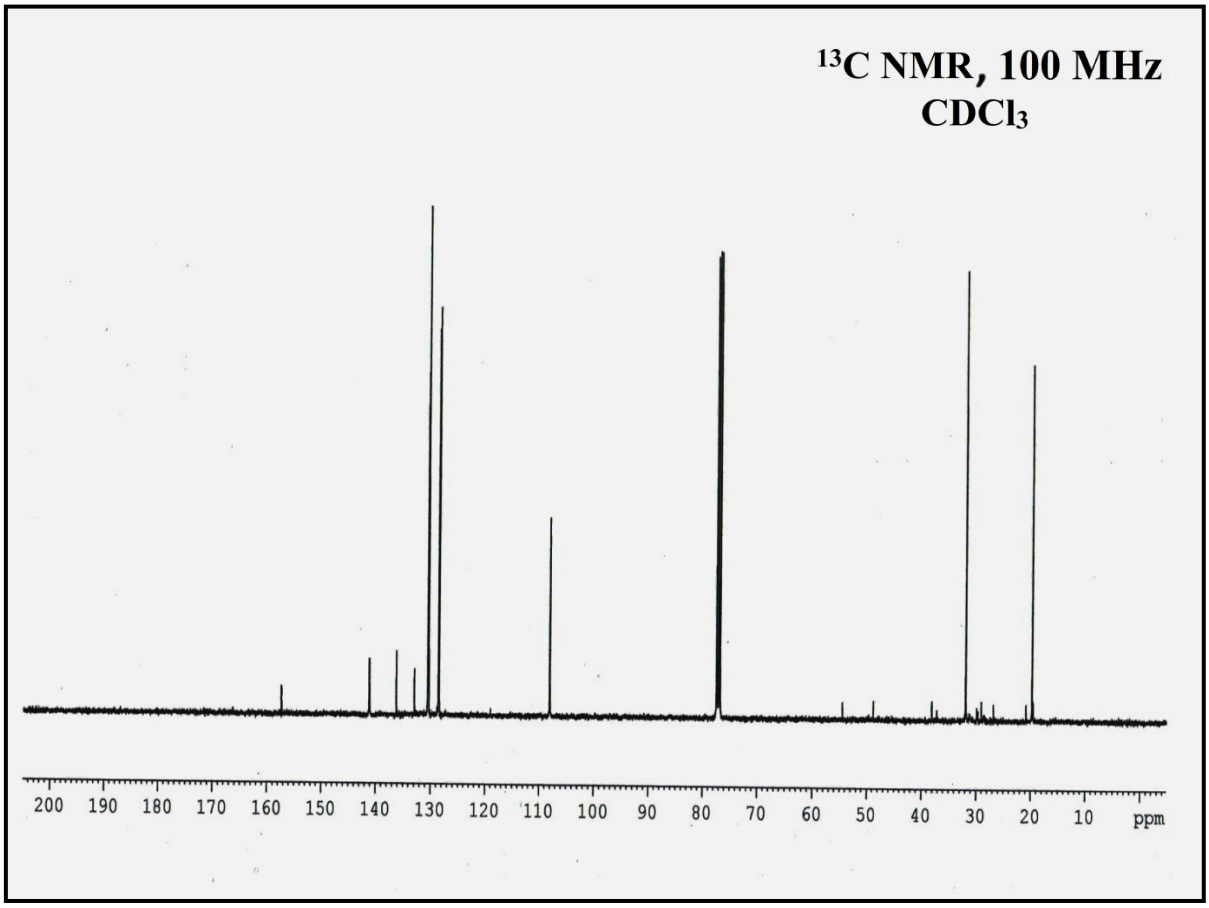


IR spectra:



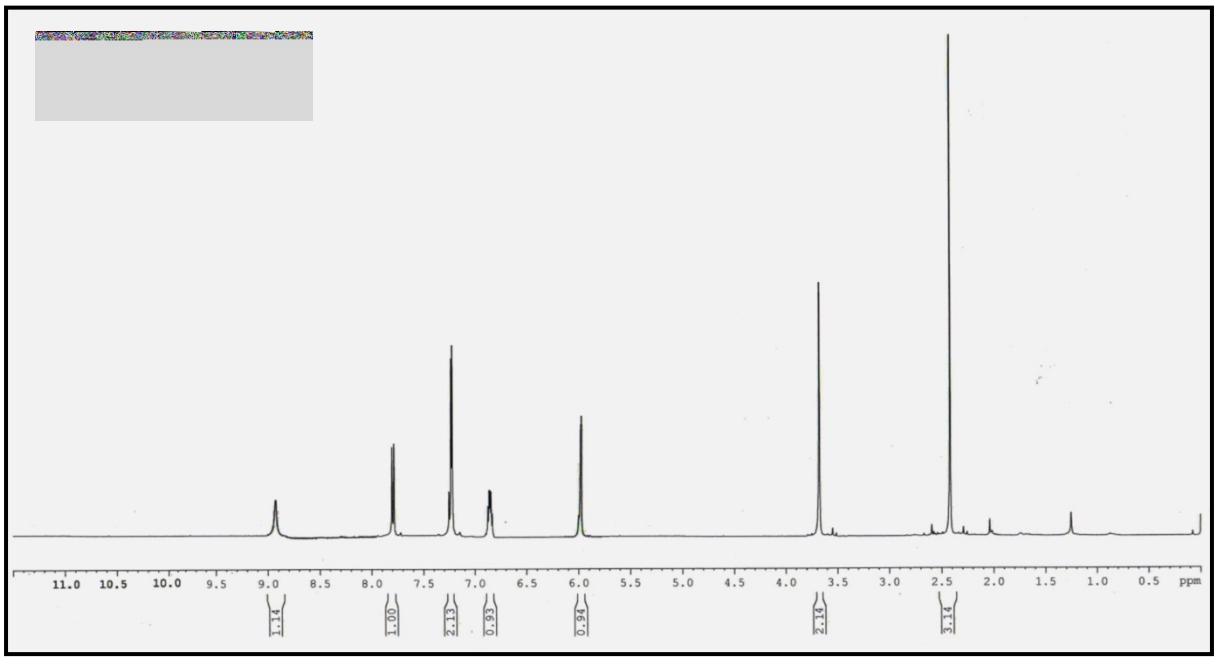
<u>1,5-Dihydro-4-hydroxy-3-(4-methylphenyl)-2H-pyrrol-2-one</u> (Table 4, entry 3)

^{13}C NMR spectra:

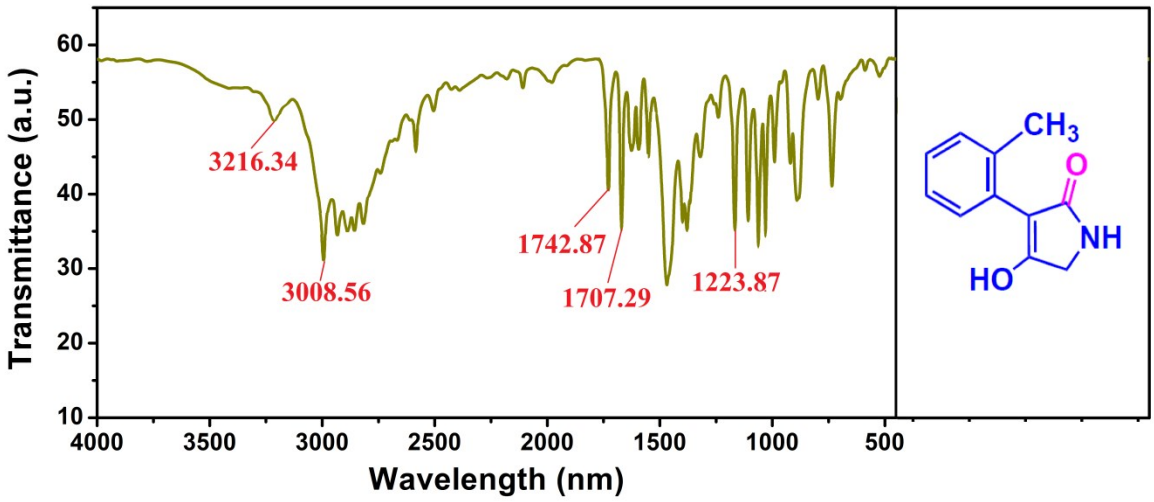


<u>1,5-Dihydro-4-hydroxy-3-(2-methylphenyl)-2*H*-pyrrol-2-one</u>(Table 4, entry 4)

^{1}H NMR spectra:

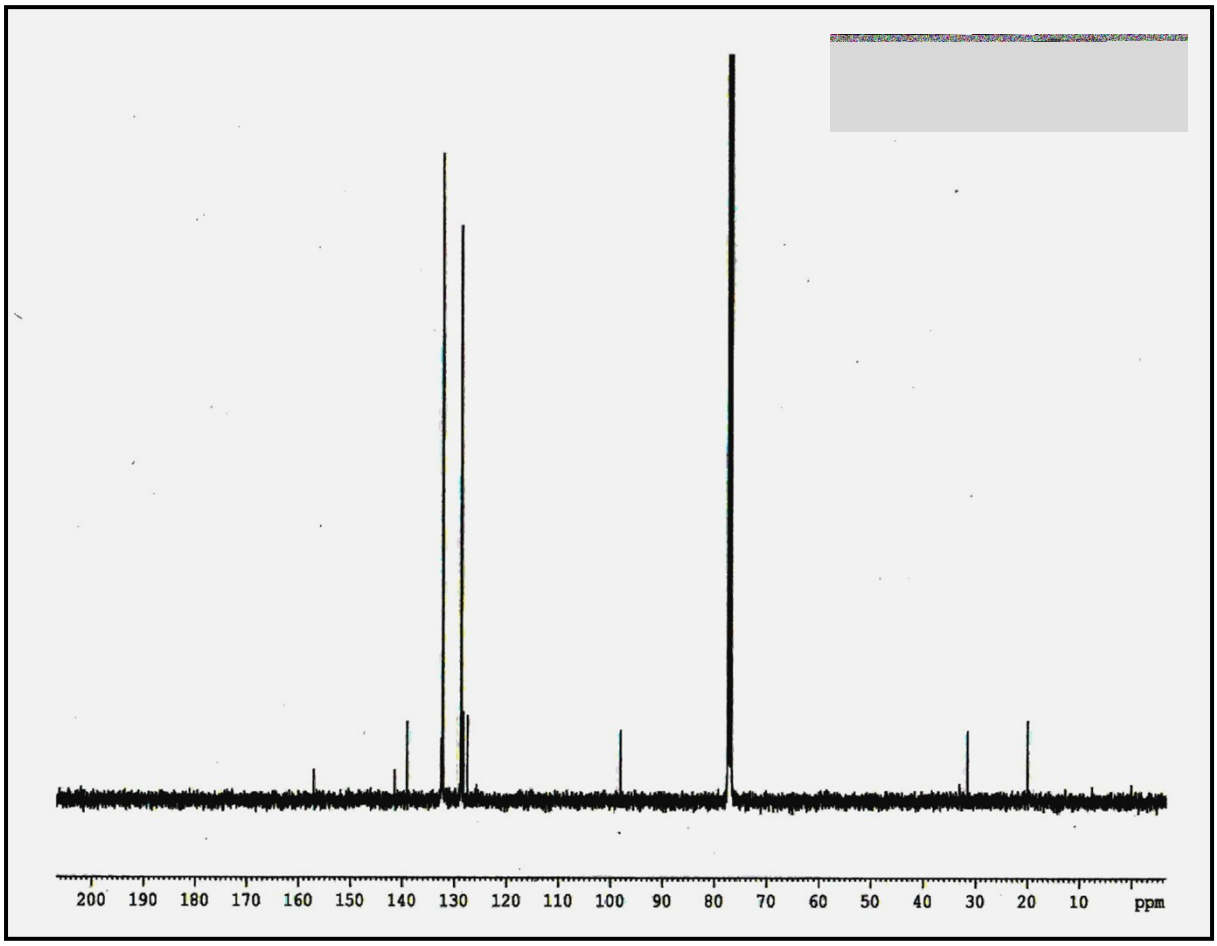


IR spectra:



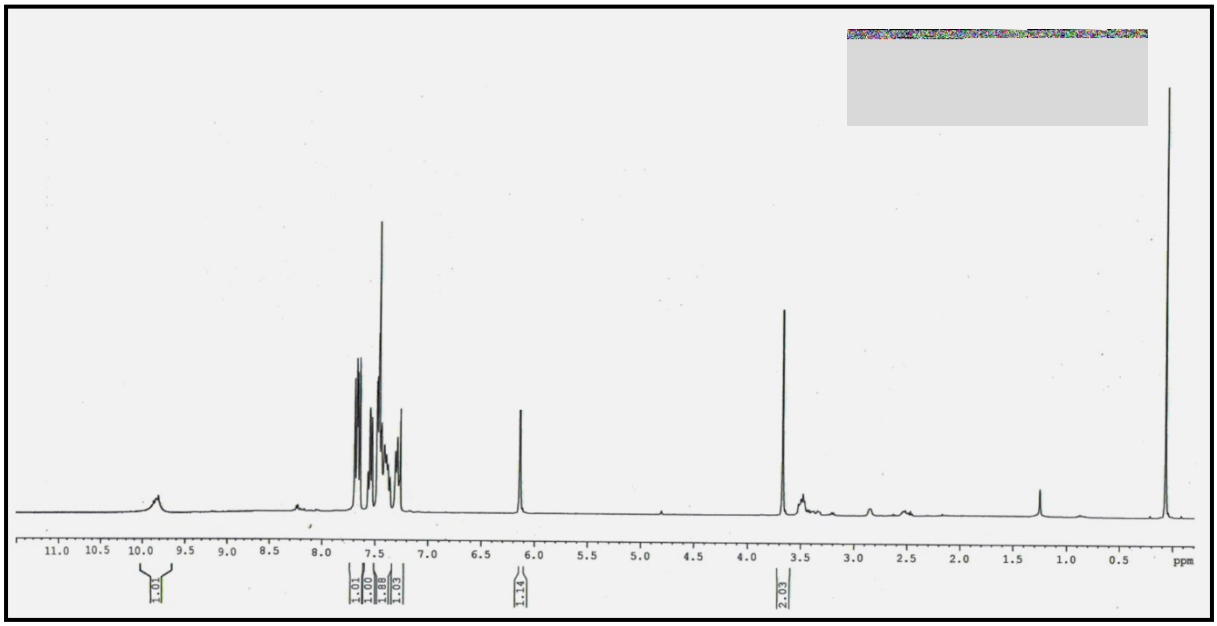
1,5-Dihydro-4-hydroxy-3-(2-methylphenyl)-2*H*-pyrrol-2-one(Table 4, entry 4)

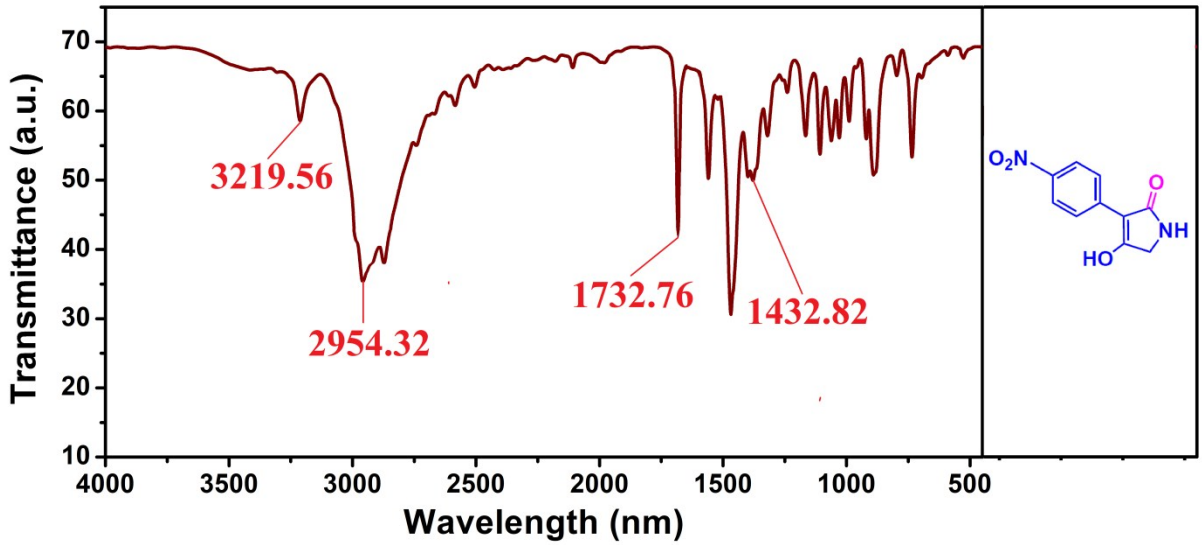
^{13}C NMR spectra:



1,5-Dihydro-4-hydroxy-3-(4-nitrophenyl)-2H-pyrrol-2-one (Table 4, entry 5)

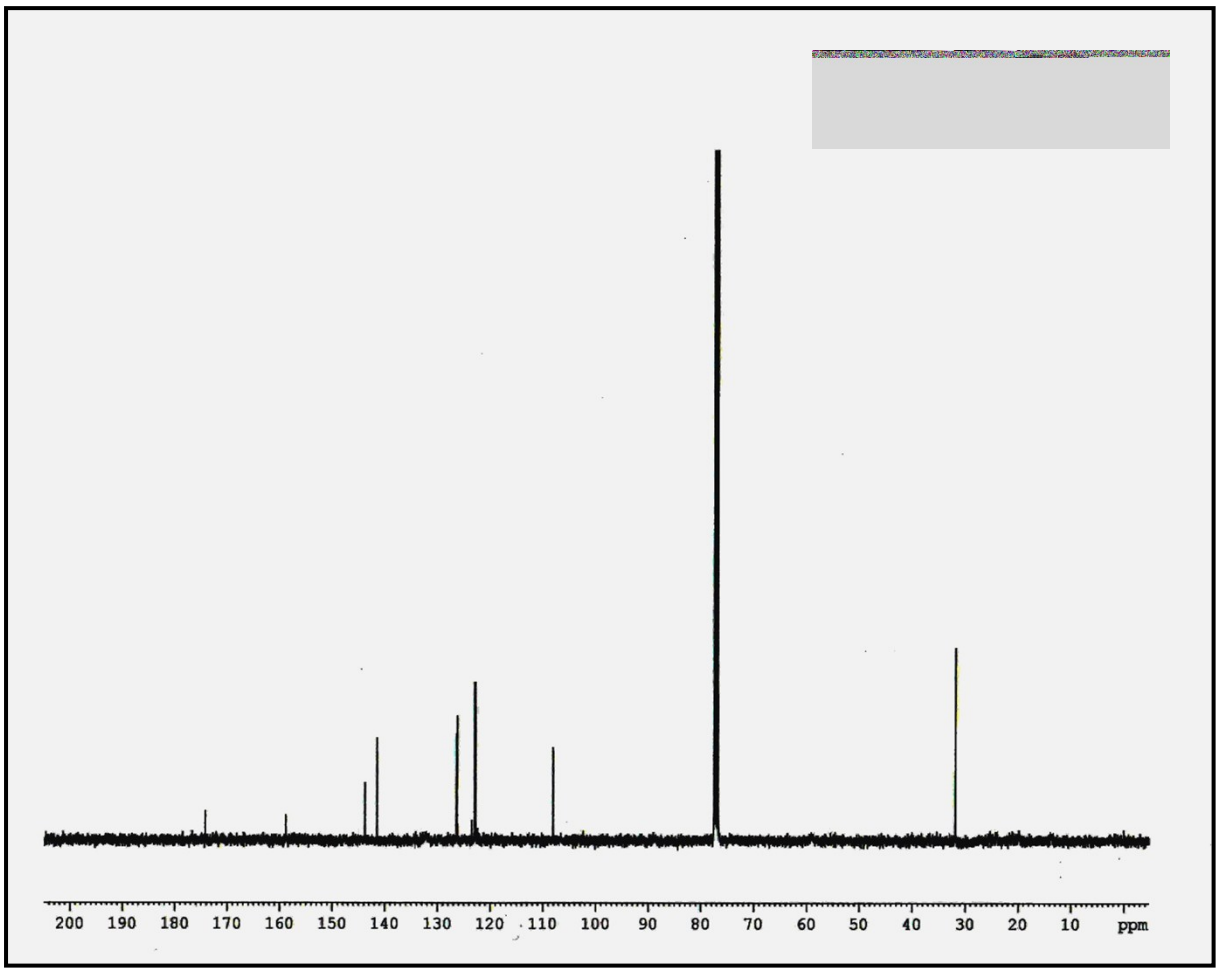
^{1}H NMR spectra:



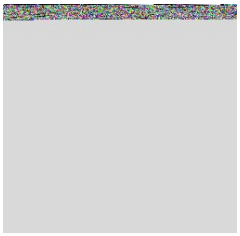


1,5-Dihydro-4-hydroxy-3-(4-nitrophenyl)-2H-pyrrol-2-one (Table 4, entry 5)

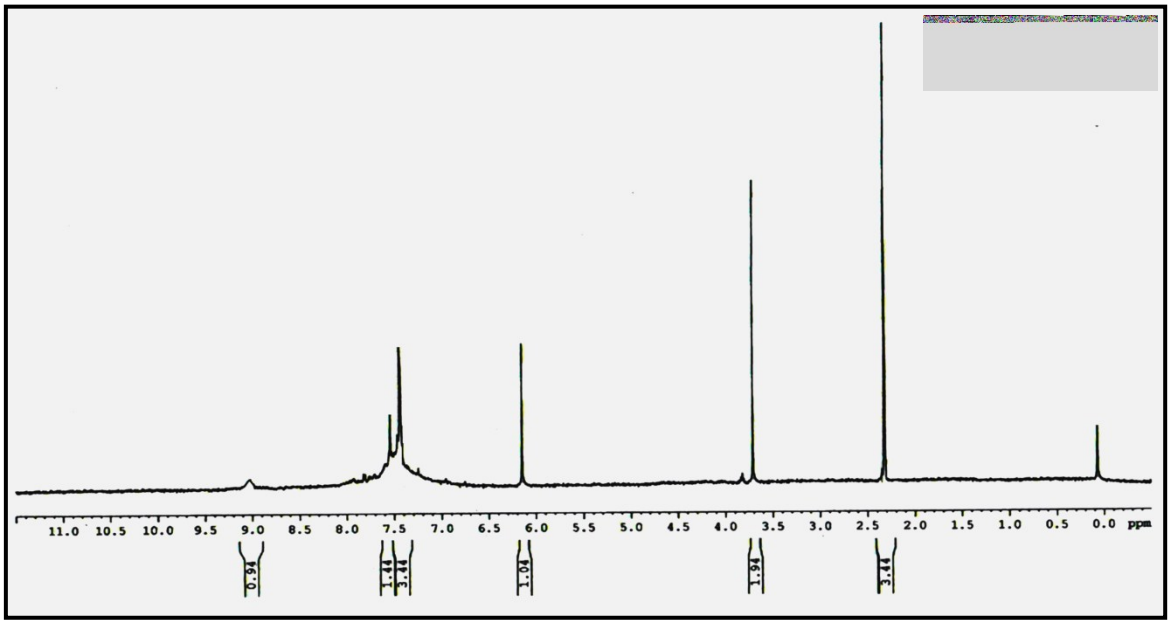
^{13}C NMR spectra:

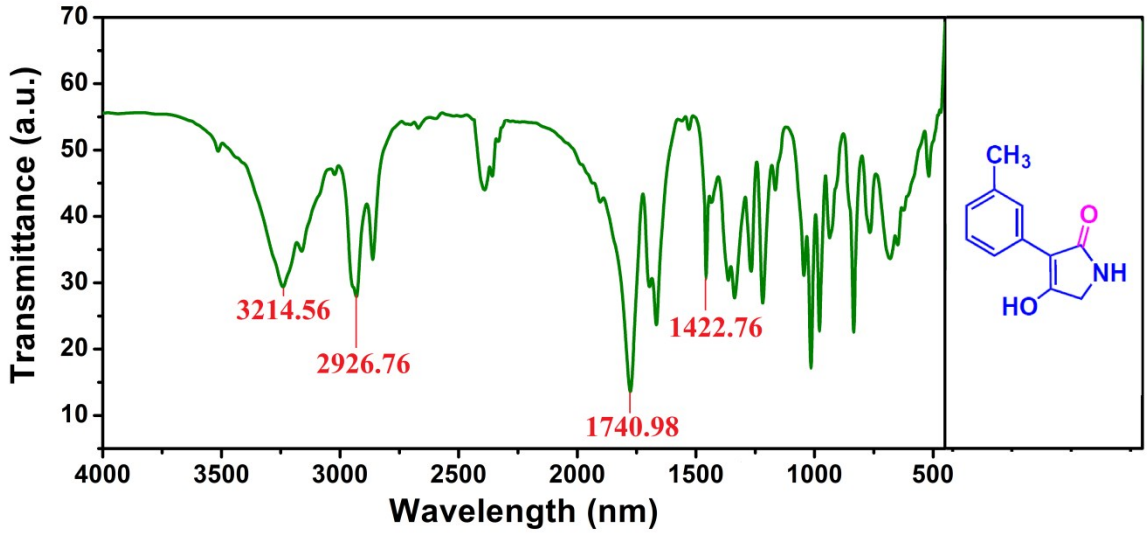


1,5-Dihydro-4-hydroxy-3-(3-methylphenyl)-2H-pyrrol-2-one (Table 4, entry 6)

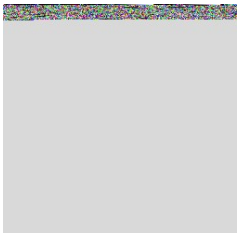


^{1}H NMR spectra:





<u>1,5-Dihydro-4-hydroxy-3-(3-methylphenyl)-2H-pyrrol-2-one</u> (Table 4, entry 6)



^{13}C NMR spectra: