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Synthesis and Characterization of Some New Schiff Bases Derived from 7-hydroxy-4-methyl Coumarin

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Abstract: ***Coumarins induce researchers for further developments in organic synthesis because of their pharmaceutical and biological activities. The current research aimed to synthesize new Schiff bases derived from 7-hydroxy-4-methyl-coumarin containing amide, hydrazine carbothioamide, ethylidene moieties. Compound (1) (7-hydroxy-4-methyl coumarin) was converted into quinolin-2(H)-one derivative (2) by the reaction with acetamide. Reaction of derivative (2) with thiosemicarbazide in ethanol leads to the synthesize of (7-hydroxy-4-methyl-2-oxoquinolin-1(2H)-yl)ethylidene)hydrazinecarbothioamide derivative (3).Schiff bases(4-6) are prepared through the reaction of (3) with one of aldehydes or ketone. Newcoumarin derivatives are characterized by their physical properties and various spectral analysis like: FTIR, [1]HNMR, GC-Ms spectra and micro elemental analysis (C.H.N.S) technique for some of them.***

Keywords: Synthesis, Coumarin, Quinolin, Schiff bases.

1. Introduction

Compounds containing imine group (–C=N–) typically known as Schiff bases. They discovered by the scientist Schiff in (1864) and he named them imines[1].They have been synthesized by the reaction of equal quantities from primary amines with active carbonyl group (aldehydes or ketons).They are known by several names like imines, ketimines, aldimines, azomethines and anils which are related to condensation products from aromatic amines with aromatic aldehydes and ketones [2].Schiff bases are reported to show a variety of interesting biological activities, including antifungal[3], antibacterial[4-6], anti-mouse hepatitis virus (MHV)[7], anticancer[8] and herbicidal activities[9].The possession of schiff bases for this event biological activities are caused by the presence of azomethines group (-CH=N) that are present within their structures[10].

2. Materials and Methods

Initial chemical compounds were obtaind from BDH, Merck and Fluka companies. Mellting point was determined in an capillary tubes on Sturat Scientific Melting Point SMPLU-K and are uncorrected. Infrared spectra were recorded on Shimadzu FTIR (8300) spectrophotometer by using KBr pellet technique in Ibn Sina State Company (ISSC). ^{1}HNMR spectra were recorded on {Bruker DMX -500 NMR spectrophotometer in Al- al Bayt University (Jordan)} infrequency 300 MHz, using TMS as the internal standard in (DMSO-d_6). Mass spectrum was recorded on Ultra Shimadzu (GCHS-QP 2010) in Al-Mustansiriyh University. Also micro elemental analysis (C.H.N.S) was measured by using a device (Euro Vectro -3000A Element Analyzer)in Ibn Al-Haitham College -University of Baghdad. The reactions were monitored by TLC on silica gel thin layer plates.

3. Experimental

a) Preparation of 7-Hydroxy-4-Methyl Coumarin [11] (1)
Powdered resorcinol (3.7g, 0.033mol) was added to (4.4 ml, 3.46 mol) of ethyl acetoacetate and stirred, then it was added slowly to (15 ml) of conc. H_2SO_4 with stirring at (5-10)^{o}C for 30 mins. Then it was left for 1 hr. the mixture was poured into crushed ice, the precipitatewas filtered then dried and recrystallized from ethanol.

b) Preparation of 1-acetyl-7-hydroxy-4-methyl quinolin-2(1H)-one [12](2)
A mixture of compound (1) (7.04g , 0.04mol) and (2.36g , 0.04mol) acetamide in (40ml) dry benzene was refluxed for 8hrs. Then the precipitate was filtered, dried and recrystallized from chloroform.

c) Preparation of 2-(1-(7-hydroxy-4-methyl-2-oxo quinolin-1(2H)-yl) ethylidene) hydrazine carbothioamide[13](3)
A mixture of compound (2) (1.08g , 0.01mol) and thiosemicarbazide (0.91g , 0.01mol) were dissolved in (50ml) ethanol and refluxed for 4hrs. The resulting crystalscooled, filtered and washed with distilled water then dried and recrystallized from ethanol.

d) Preparation of Schiff bases [14] (4-6)
A mixture of compound (3) (0.29g , 0.001mol) and (0.001mol) from various aldehydes and keton was dissolved in (15ml) abs. ethanol, (3) drops of glacial acetic acid was added then the mixture was refluxed for 6hrs. The solid product was filtered, dried and recrystallized from ethanol**.**

4. Results and Discussion

Treatment of ethyl acetoacetate with resorcenol in cooled medium in the presence of sulfuric acid leads to yielded coumarin. The new derivatives prepared following the reactions sequence depicted in Scheme (2). The structures of compounds (1-6) were confirmed by physical properties and spectral data which are listed in Table (1) and Table (2).

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The FTIR spectrum of compound (1), Figure (1), shows the (C=O) lactone stretching frequency near (1678)cm^{-1}. The frequency of the (C=C) group appears at about (1597) cm^{-1}, and absorption band at (3155) cm^{-1} due to the stretching vibration of the hydroxyl group, other bands are shown in Table (1).

Reaction of compound (1) with acetamide leads to obtain quinolin derivative (2).The FTIR spectrum of (2), Figure (2) show absorption bands :(C=O)at (1701)$cm^{-1}$for amide and at (1774) cm^{-1} for lactam, (C=C) at (1616) cm^{-1} and (OH) at (3448) cm^{-1}.

^{1}HNMR spectrum of compound (2), Figure (5) shows (δppm) : 1.64 (s, 3H, CH_3 lactam) ; 3.40 (s, 3H, CH_3amide); 4.65(s, 1H, CH lactam); (7.04-8.42)(m, 3H, Ar-H); 9.15 (b.s, 1H, OH).

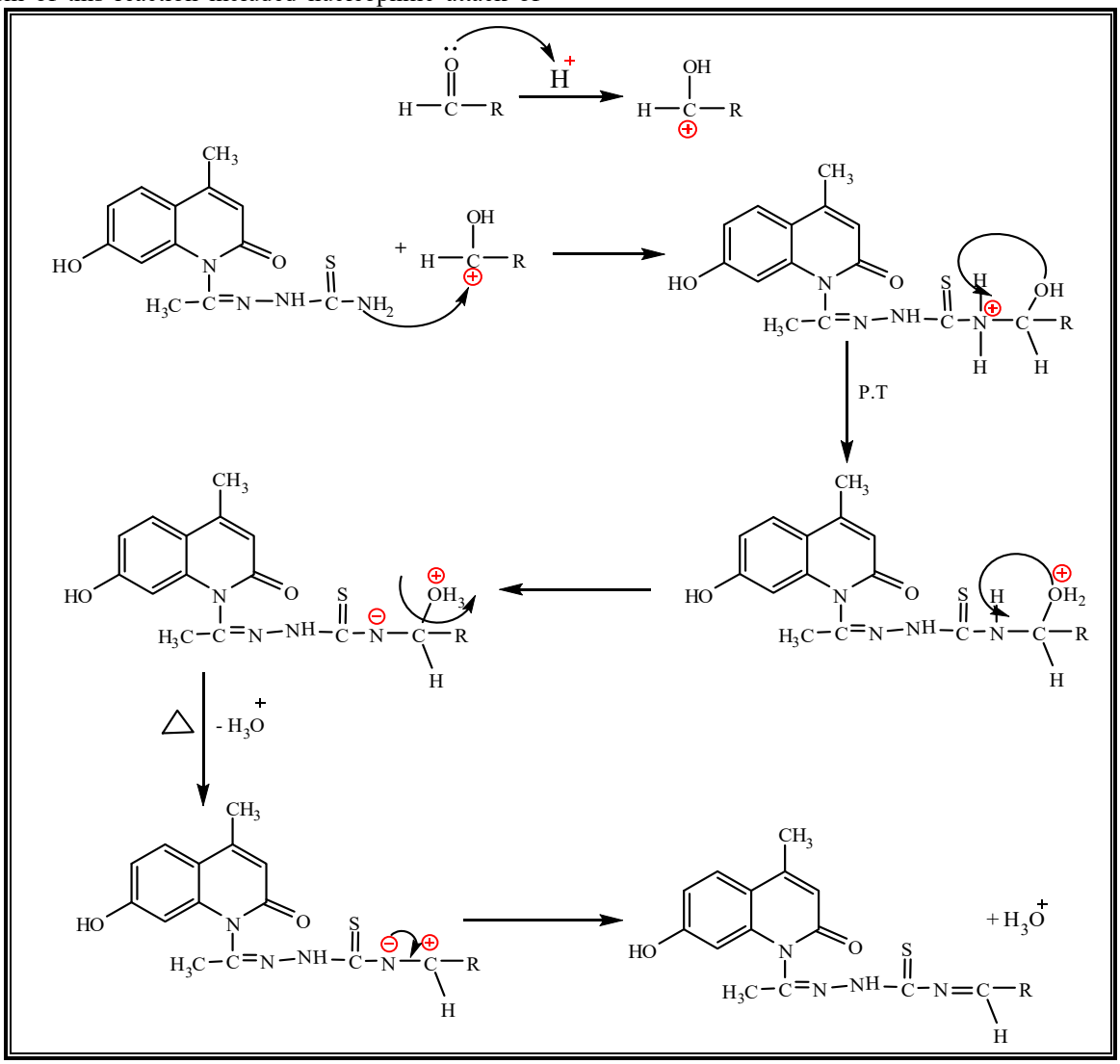
Refluxing of compound(2) with thiosemicarbazide leads to obtain compound (3).The mass spectrum of compound (3), Figure(3)shows the molecular ion peak for formula $C_{13}H_{14}N_4O_2S$ at m/z=292.

Condensation of compound (3) with various aldehydes or ketone in abs. ethanol in the presence of few drops from glacial acetic acid leads to production schiff bases (4-6).The mechanism of this reaction included nucleophilic attack of amine group on the carbonium ion of carbonyl group of aldehyde or ketone to form unstable compounds followed by losing H_3O molecule to give an imine compounds, Scheme(1) [15].

Schiff bases have been characterized and confirmed using FT-IR spectrum besides the ^{1}H.NMR spectrum for some of them. The FT-IR spectrum of compound (5), Figure (4) shows the disappearance absorption band at (3251, 3282) cm^{-1} due to the asymmetric and symmetric stretching vibration of the (NH_2) group and appearance bandat (1600) cm^{-1} for (C=N) imine group, other bands are shown in Table (1).

The ^{1}H.NMR spectrum of compound (6) in Figure(6), shows characteristic signals at: δ2.20 (s, 3H, CH_3)lactam; δ3.43(s, 6H, $2CH_3$)imine; δ7.12(s, 1H, CH) lactam; δ7.92 (s, 8H, Ar-H); δ8.26(s, 1H, NH); δ10.20(s, 1H, OH).

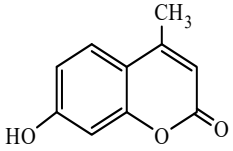
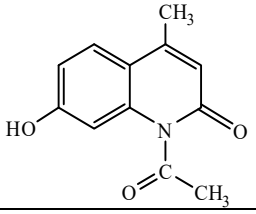
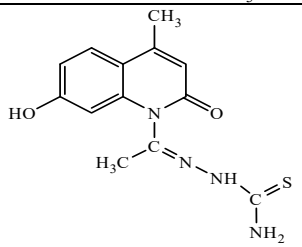
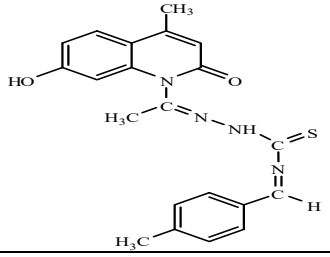
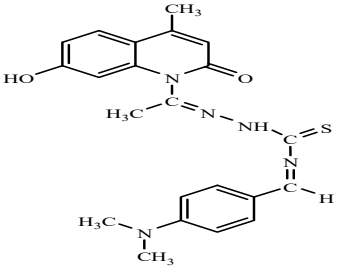
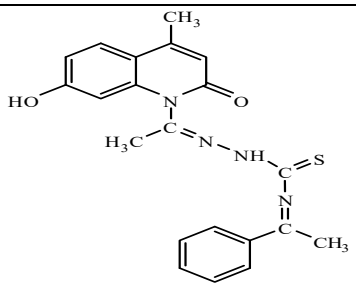
Also elemental analysis (C.H.N.S) for compound (4) was measured. Calcd for [$C_{21}H_{20}N_4O_2S$]: C, 64.22; H, 5.09; N, 14.27; S, 8.15. Found: C, 64.11; H, 4.88; N, 14.12; S, 8.10.



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Scheme 1: The mechanism steps for the synthesis of Schiff bases.

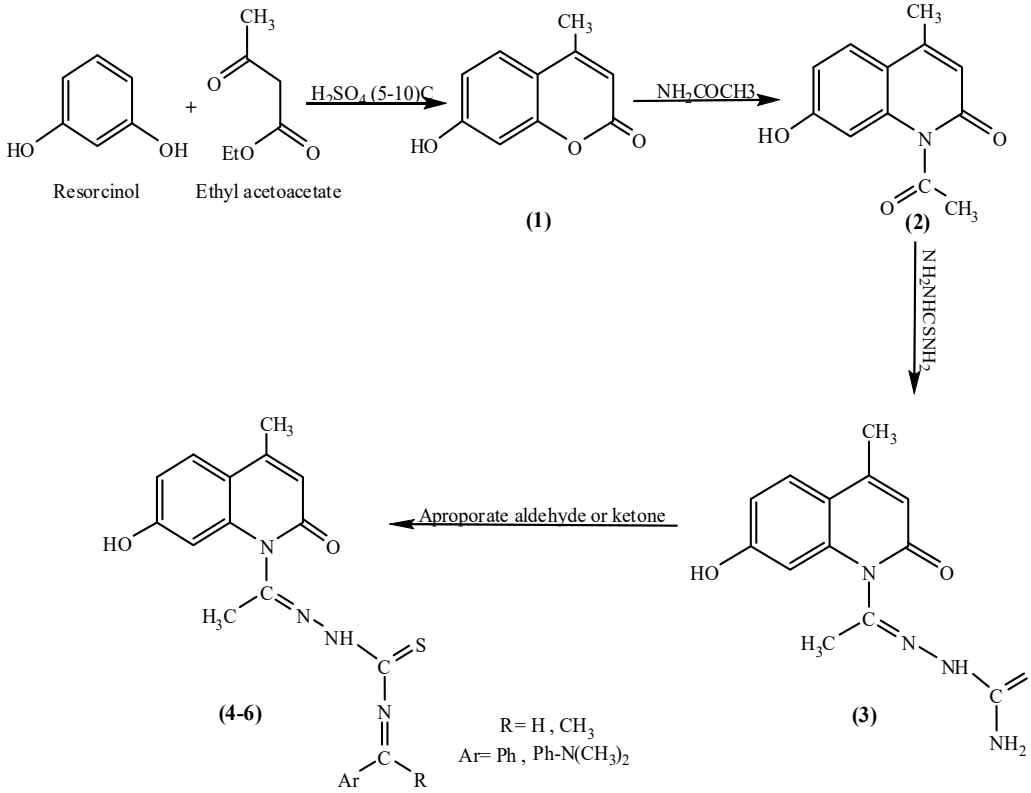
Table 1: Physical Properties and Spectral Data of the Prepared Compounds

Comp NO.	Nomenclature and Chemical formula	Structure	M. P.°C	Yield %	Color	Infrared data cm^{-1}
1	7-Hydroxy-4- Methyl Coumarin **[$C_{10}H_8O_3$]**		173-175	89	White	1678(C=O) , 3155(O-H) , 3012(C-H) ar. , (2808-2939) (C-H) al. , 1597(C=C) , 1273(C-O)
2	1-acetyl-7-hydroxy-4-methyl quinolin-2(1H)-one **[$C_{12}H_{11}NO_3$]**		172-174	79	Yellow	1701 (C=O) amide , 1774(C=O) lactam , 1616(C=C) , 3101(C-H) ar., (2927-2997) (C-H)al. , 3448(O-H) , 1145 (C-O)
3	2-(1-(7-hydroxy-4-methyl-2-oxoquinolin-1(2H)-yl)ethylidene)hydrazinecarbothioamide **[$C_{13}H_{14}N_4O_2S$]**		171-173	71	Colorless Crys.	(3159-3251)(NH_2) , 3136(N-H) , (2804-2981)(C-H)al. , (3024-3066)(C-H)ar. , 1612(C=N) , 1465(C-N) , 1045(C=S) , 3414(O-H)
4	2-(1-(7-hydroxy-4-methyl-2-oxo quinolin-1(2H)-yl) ethylidene)-N-(4-methyl benzylidene) hydrazinecarbo thioamide **[$C_{21}H_{20}N_4O_2S$]**		167-169	79	Yellow	3259(NH) , 3375(O-H) , 1610(C=N) , 2816(C-H)al. , 1540(C=C) , 1083(C=S) , 1176(C-O) , 1408(C-N)
5	N-(4-(dimethyl amino)benzylidene)-2-(1-(7-hydroxy-4-methyl-2-oxo quinolin-1(2H)-yl)ethylidene) hydrazinecarbothioamide **[$C_{22}H_{23}N_5O_2S$]**		193-195	92	Yellow	3263(NH) , 3352(O-H) , 1600(C=N) , 1519(C=C) , (2800-2897)(C-H)al. , 1067(C=S) , 1184(C-O) , 1361(C-N)
6	2-(1-(7-hydroxy-4-methyl-2-oxo quinolin-1(2H)-yl)ethylidene)-N-(1-phenylethylidene) hydrazinecarbothioamide **[$C_{21}H_{20}N_4O_2S$]**		94-96	78	Light Orange	3209(N-H) , 3406(O-H) , 1585(C=N) , 3143(C-H)al. , 1512(C=C) , 1095(C=S) , 1292(C-O) , 1489(C-N)

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Table 2: Chemical Schiff's ^{1}HNMR spectra

Comp. No	^{1}HNMR (DMSO-d_6) δppm
2	1.64(s, 3H, CH_3 lactam) ; 3.40(s, 3H, CH_3 amide) ; 4.65(s, 1H, CH lactam); (7.04-8.42)(m, 3H, Ar-H); (9.15)(b.s, 1H, OH).
6	2.20 (s, 3H, CH_3 lactam);3.43(s, 6H, $2CH_3$ imine);7.12(s, 1H, CH lactam); 7.92(s, 8H, Ar-H); 8.26(s, 1H, NH); 10.20 (s, 1H, OH



Scheme 2: The synthetic route for new compounds

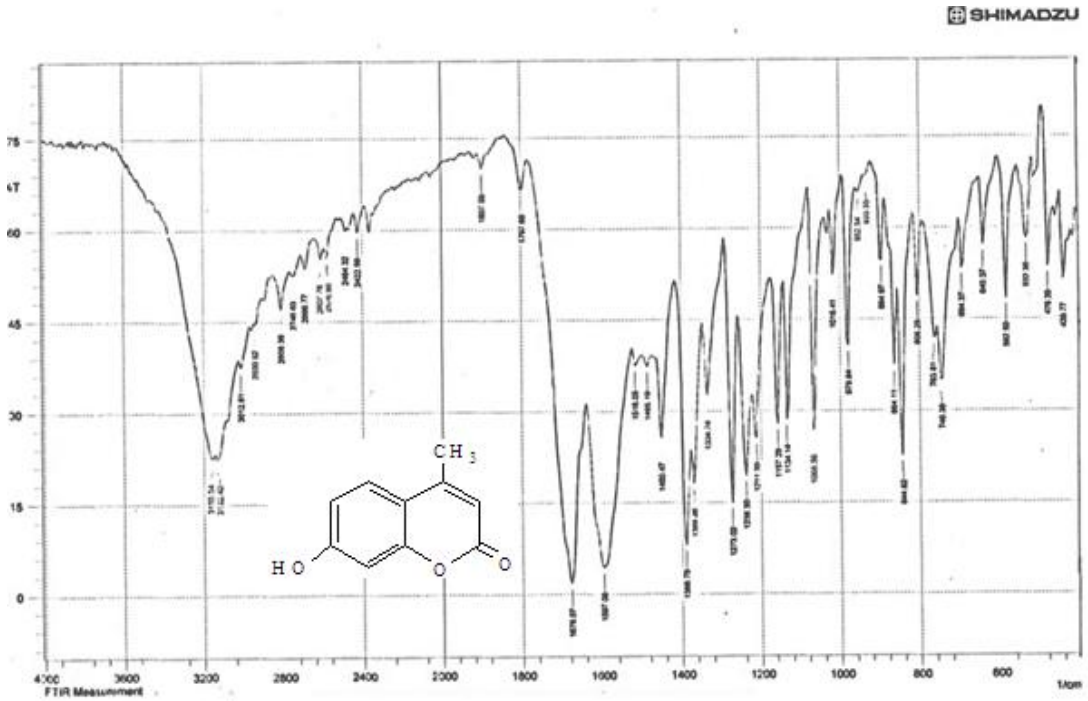


Figure 1: FTIR Spectrum of Compound (1)

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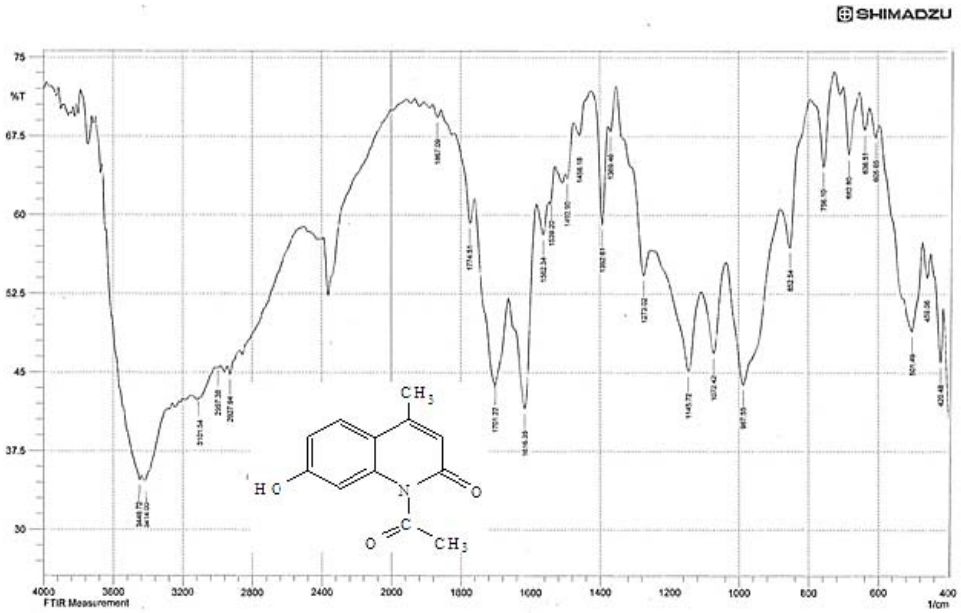


Figure 2: FTIR Spectrum of Compound (2)

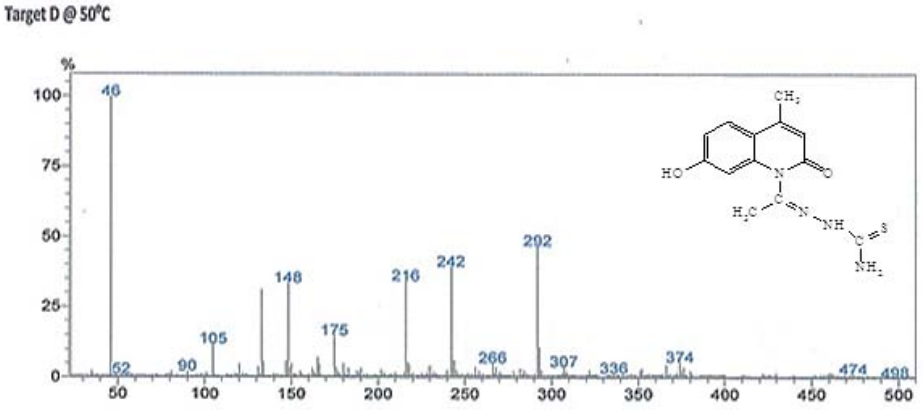


Figure 3: GC-MsSpectrum of Compound (3)

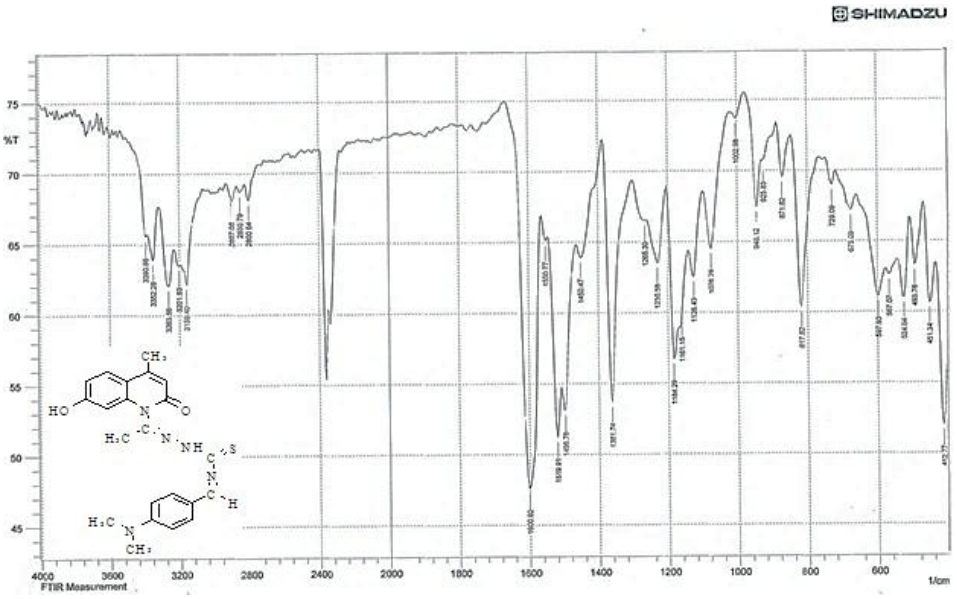


Figure 4: FTIR Spectrum of Compound (5)

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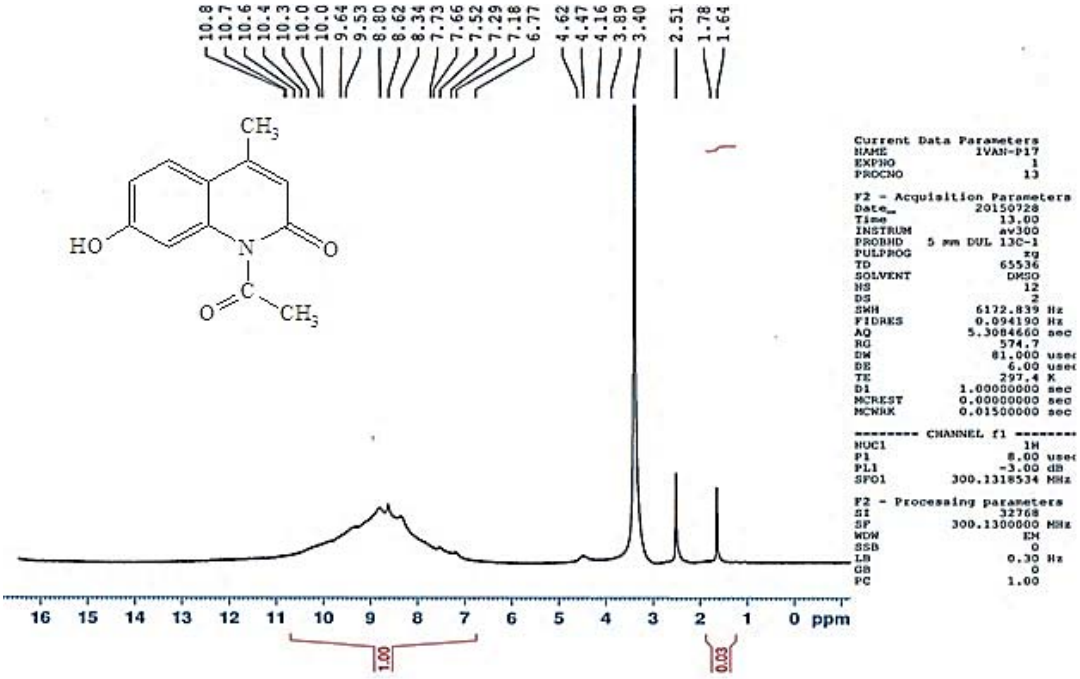


Figure 5: [1]H.NMR Spectrum of Compound (2)

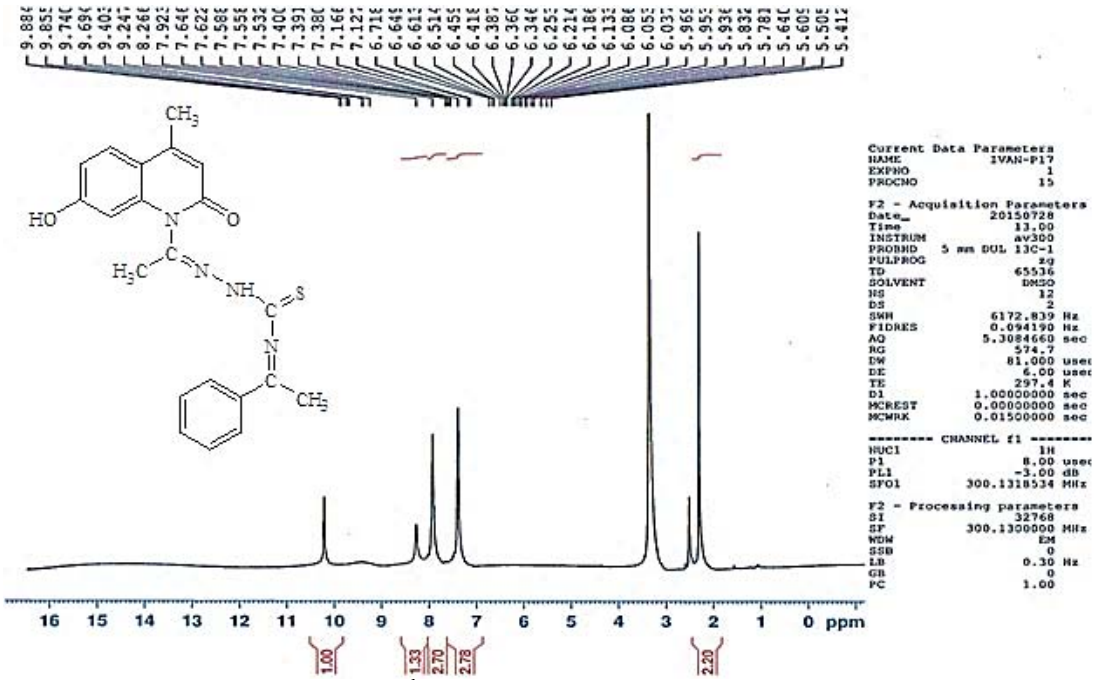


Figure 6: [1]H.NMR Spectrum of Compound (6)

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