Nat. Volatiles & Essent. Oils, 2021; 8(4): 4513-4522

NVEO
Natural Volatiles &
Essential Oils

Preparation And Characterization Of New B-Ketoimine Schiff Base Compounds

Israa A. Alkhayyat[1] , Mohammed A. Altahan[2]

[1,2] Department of Chemistry, College of Science, University of Thi-Qar/Iraq moh.altahan@sci.utq.edu.iq

Abstract

In this paper (E)-4-((1-(2-hydroxycyclopent-1-en-1-yl)ethylidene) amino)phenol **L_1** and (E)-2-((1-(2-hydroxycyclopent-1-en-1-yl)ethylidene) amino)phenol **L_2** Schiff base ligands have been prepared by acidic catalysed reaction of 2-acetylcyclopentanone with p-amino phenol and o-amino phenol, respectively. The two new compounds were identified by H-NMR, C-NMR Mass Spect. Uv-Vis. Spect., I.R spect. and C.H.N. analysis.

Keywords: Schiff base, b-diketone, ketoimine, aniline, phenol

1-Introduction

Schiff base compounds represent a major class of organic compounds and these have attracted a great deal of attention. These compounds are a wide and important class of organic chemistry.(1) They were firstly reported by Hugo Schiff in 1864.(2) Schiff base compound are generally prepared by condensation of primary amines with carbonyl compounds.(3) The general formula for these compounds is RHC = N-R_1, where R and R_1 are alkyl or aryl groups, with common structural feature azomethine group.(4) Many papers relating to Schiff base compounds have been published and many synthetic novel Schiff base compounds have greatly contributed to the organic chemistry. This steady interest is due to their intriguing variety of Schiff base compounds and their potential applications in many different fields e.g. biological activities, including antifungal, antibacterial, antimalarial, anti-proliferative, anti-inflammatory, antiviral, and antipyretic properties.(5,6) The imine group present in such compounds has been shown to be critical to their biological activities.(7-9)

Schiff's base compounds are widely used in photo-stabilization to improve the stability of poly vinyl chloride polymers PVC against photo-degradation by ultraviolet radiation(10-12) and are also used to

prevent poly methyl methacrylate from degradation[13] and to prevent polystyrene from photo-degradation by their addition to polymer films.[14, 15]

2-Experimental

2-1-Material

All chemicals used were reagent grade and were used without further purification unless otherwise stated.

2-2-Measurements

The new Schiff base compounds have been identified by several techniques. Proton and carbon NMR spectra were recorded on a Bruker DRX System AL 500 (500 MHZ) operating at 400 MHz for ^{1}H and 101 MHz for ^{13}C-NMR d9 DMSO used as internal standard, using TMS as an external standard. Mass Specta were obtained with range 1-1000 m/z and type network mass selective detector 5973. I.R. spectra were recorded on 800S Fourier Transformer Infrared Spectrophotometer/ Shimadzo (FT-IR) in the region 600-4000 cm^{-1} using KBr pellets. Elemental analysis for C, H, and N were performed on a CHNS-Elements Analyzer in Iran Polymer and petrochemical institute. The Uv-Vis. Spectra were recorded in methanol on a spectroscan 80D UV-Vis. Spectrophotometer with quartz cell of a 1cm path length..The electro thermal melting point model 9300 was used to measure the melting point of ligands.

2-3-Synthesis of ligands

- (E)-4-((1-(2-hydroxycyclopent-1-en-1-yl)ethylidene) amino)phenol **L1**

p-hydroxy aniline (1.8 g, 0.016 mol) was dissolved in absolute ethanol (20ml) with stirring until a clear solution was obtained. 2-acetylcyclopentanone (2 ml, 0.016 mol) was then added drop wise with stirring. The mixture was acidified with few drops of glacial acetic acid, and then heated with stirring for 2 hours. The resulting solution volume was reduced by gentle evaporation on a water bath before being cooled in an ice bath to give a pale yellow precipitate of $\mathbf{L_1}$. The product were removed by filtration, recrystallized from ethanol, filtered off and dried in vacuum. The compound are characterized as ($C_{13}H_{15}NO_2$) by Mass spectra, ^{1}H-NMR, ^{13}C-NMR, FTIR,and elemental analysis; Yield 58.8%.

- (E)-2-((1-(2-hydroxycyclopent-1-en-1-yl)ethylidene) amino)phenol $\mathbf{L_2}$

The preparation of $\mathbf{L_2}$ was carried out by dissolving o-hydroxy aniline (3.6 g, 0.032 mol) in absolute ethanol (20ml) with stirring until a clear solution was obtained. 2-acetylcyclopentanone (4 ml, 0.032

mol) was then added drop wise with stirring. The product was acidified with few drops of glacial acetic acid, and then heated with stirring for 2 hours. The resulting product was concentrated by gentle evaporation on a water bath before being cooled in an ice bath to give a yellow precipitate of **L_2** compound. The precipitate were removed by filtration, recrystallized from ethanol, filtered off and dried in vacuum. The compound are characterized as ($C_{13}H_{15}NO_2$) by Mass spectra, ^{1}H-NMR, ^{13}C-NMR, FTIR,and elemental analysis; Yield 57%.

3-Result and discussion

The elemental analysis data of the new compounds **L_1** and **L_2** and their physical properties of the new compounds are listed in Table **3-1**. Elemental analysis data of the compounds were consistent with their formulation.

Table 3-1. Analytical data, Physical properties of the compounds

Compounds	M.Wt. g/mol.	m.p °C	Color	Elemental analysis		
				C	H	N
L_1	217.27	195	Pale yellow	Fou. 70.93 Cal. 71.87	7.2 6.96	6.22 6.45
L_2	217.27	287	yellow	Fou. 70.99 Cal. 71.87	7.16 6.96	6.22 6.45

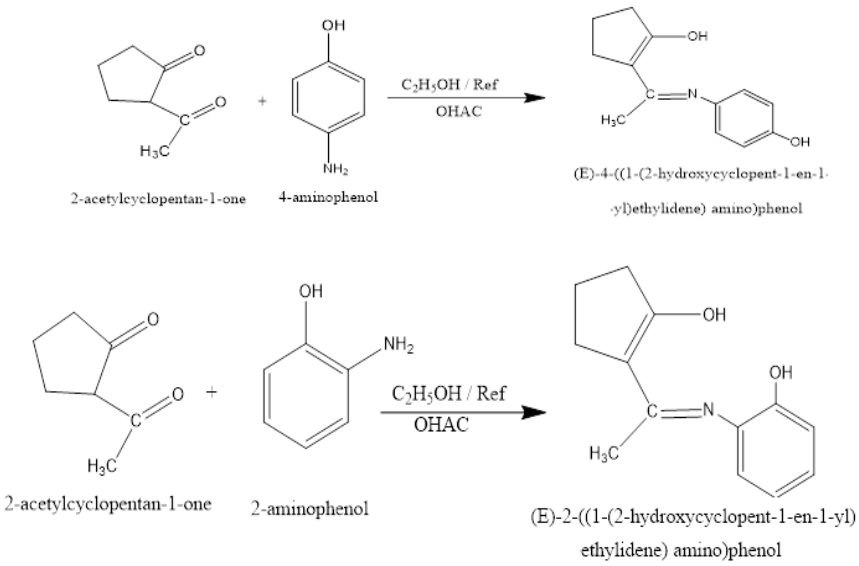

Figure 3-1: The reaction equation of the new compounds.

H NMR analysis of compounds **L_1** showed doublet of doublet at 6.73, 6.93 ppm belong to para substituted benzene ring. The CH_2 groups of cyclopentanone ring showed several peaks at 1.79, 2.21, and 2.5 ppm. Singlet peaks belong to CH_3, OH-Ar, and OH enolate groups appear at 1.97, 9.44, and 11.72 ppm, respectively. While ^{1}H NMR analysis of compounds **L_2** showed a multipate signals at 7.16, 6.87 ppm belong to ortho substituted benzene ring. The CH_2 groups of cyclopentanone ring showed several peaks at 1.83, 2.58, and 2.84 ppm. Singlet peaks belong to CH_3, OH-Ar, and OH enolate groups appear at 2.02, 9.91, and 11.3 ppm, respectively. All the ^{1}H NMR and ^{13}C-NMR data of compounds **L_1** and **L_2** are listed in Table 3-2 and showed in Figures 3-2 and 3-3.

Table 3-2 ^{1}H, and ^{13}C-NMR data for compounds **L_1** and **L_2**

المركب	^{1}H ppm	^{13}C ppm
L_1	6.73, 6.93(dd, 4H, CH of Ar), 1.79 (pentate, 2H, CH_2 of Cp), 2.21(triplate, 2H, CH_2 of Cp), 2.50 (triplate, 2H, CH_2 of Cp), 1.97 (singlate, 3H, CH_3), 9.44 (singlate, 1H, OH-Ar), 11.72 (singlate, 1H, OH enolate)	19 (CH_3), 22 (CH_2 of Cp), 29 (CH_2 of Cp), 42 (CH_2 of Cp), 106 (CH= of Cp), 163 (enolic CH= of Cp), 110 (CH Ar), 117 (CH Ar), 121 (CH Ar), 122 (CH Ar), 150 (C phenolic), 126 (C-N= Ar), 139 (C=N acelic)

L_2	7.16- 6.87 (m, 4H, CH of Ar), 1.83 (pentate, 2H, CH_2 of Cp), 2.58(triplate, 2H, CH_2 of Cp), 2.84 (triplate, 2H, CH_2 of Cp), 2.02 (singlate, 3H, CH_3), 9.91 (singlate, 1H, OH-Ar), 11.3 (singlate, 1H, OH enolate)	24 (CH_3), 30 (CH_2 of Cp), 31 (CH_2 of Cp), 35 (CH_2 of Cp), 42 (CH= of Cp), 163 (enolic CH= of Cp), 110 (CH Ar), 117 (CH Ar), 121 (CH Ar), 122 (CH Ar), 150 (C phenolic), 126 (C-N= Ar), 139 (C=N acelic)

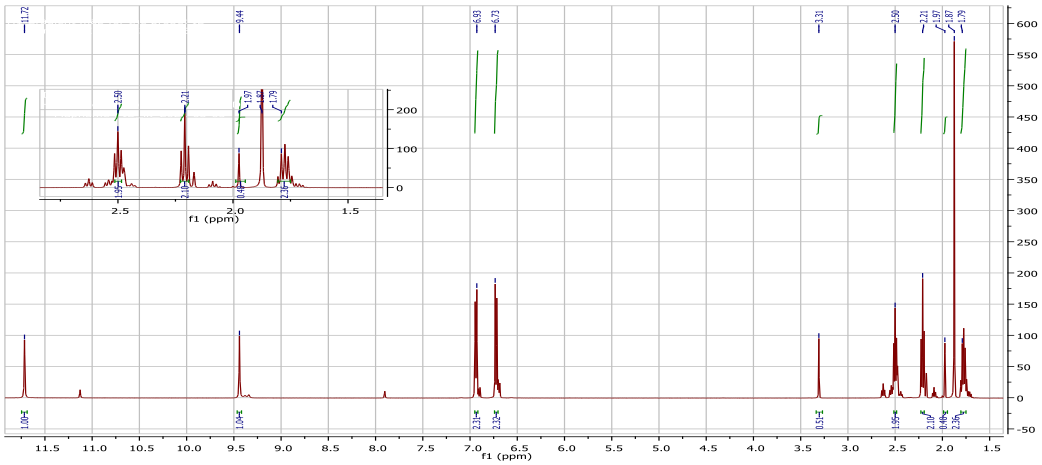

Figure 3-2 ^{1}H-NMR for **L_1**

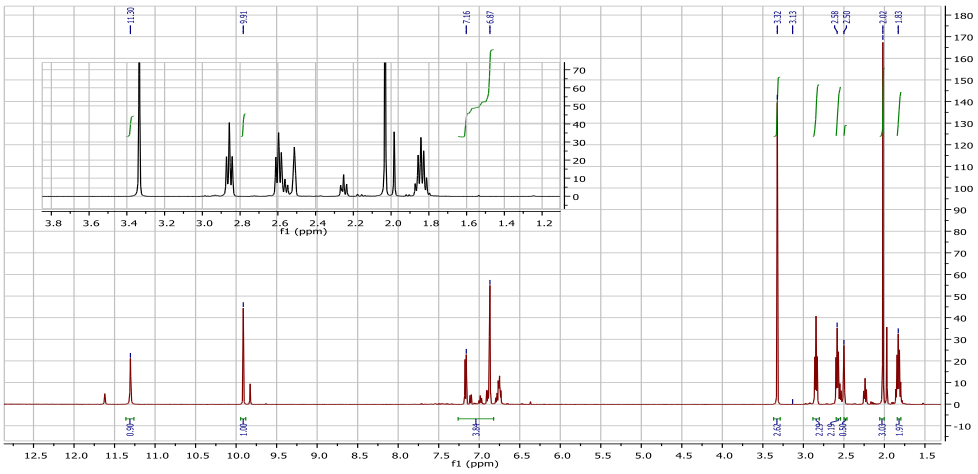

Figure 3-3 ^{1}H-NMR for **L_2**

The Mass spectra and their tentative assignment for the new compounds **L_1** and **L_2** are presented in Table 3.3 and showed in Figures 3-4, 3-5, and 3-6.

Table 3.3 The mass data for compounds **L_1** and **L_2**

L_1		L_2	
ions	m/z	ions	m/z
$C_{12}H_{15}NO_2$	202	$C_{12}H_{15}NO_2$	202
$C_{11}H_{10}NO_2$	188	$C_{11}H_{10}NO_2$	188
$C_{10}H_8NO_2$	174	$C_{10}H_8NO_2$	174
$C_9H_6NO_2$	160	$C_{10}H_7O_2$	159
$C_9H_6O_2$	146	$C_9H_6O_2$	146
$C_8H_6O_2$	134	$C_8H_5O_2$	133
$C_7H_{10}NO$	124	C_7H_6NO	120
C_6H_7NO	109	C_6H_8NO	110
C_6H_5N	91	C_6H_5N	91
C_5H_7N	81	C_5H_6N	80
C_5H_5	65	C_5H_5	65
C_4H_7	55	C_4H_5	53

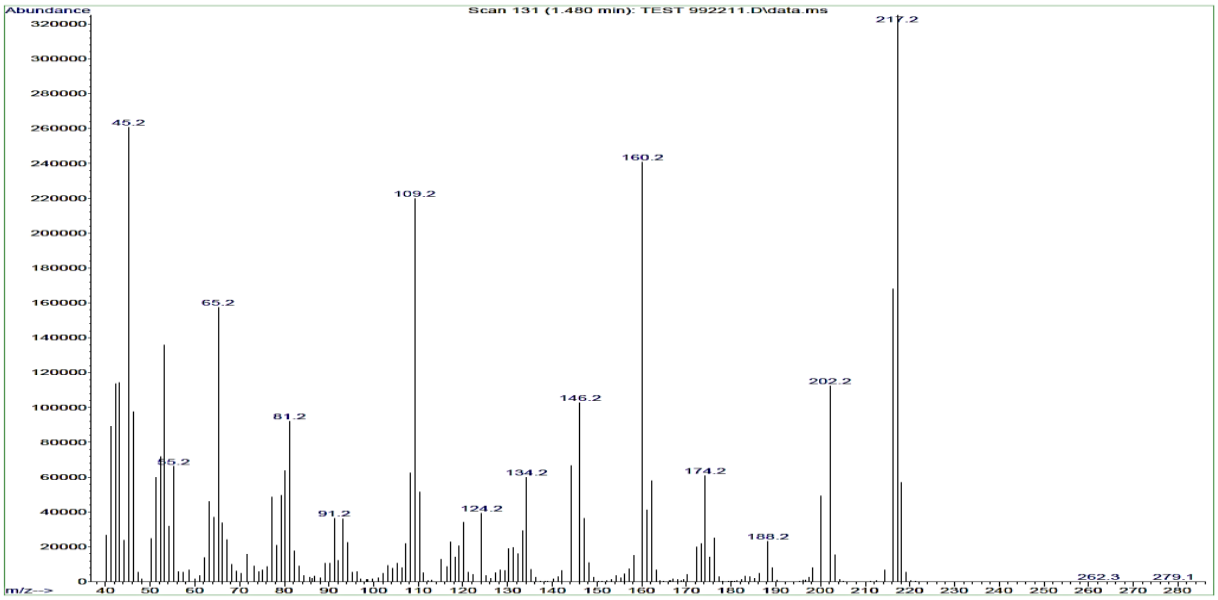

Figure 3-4 Mass spectra of **L_1**

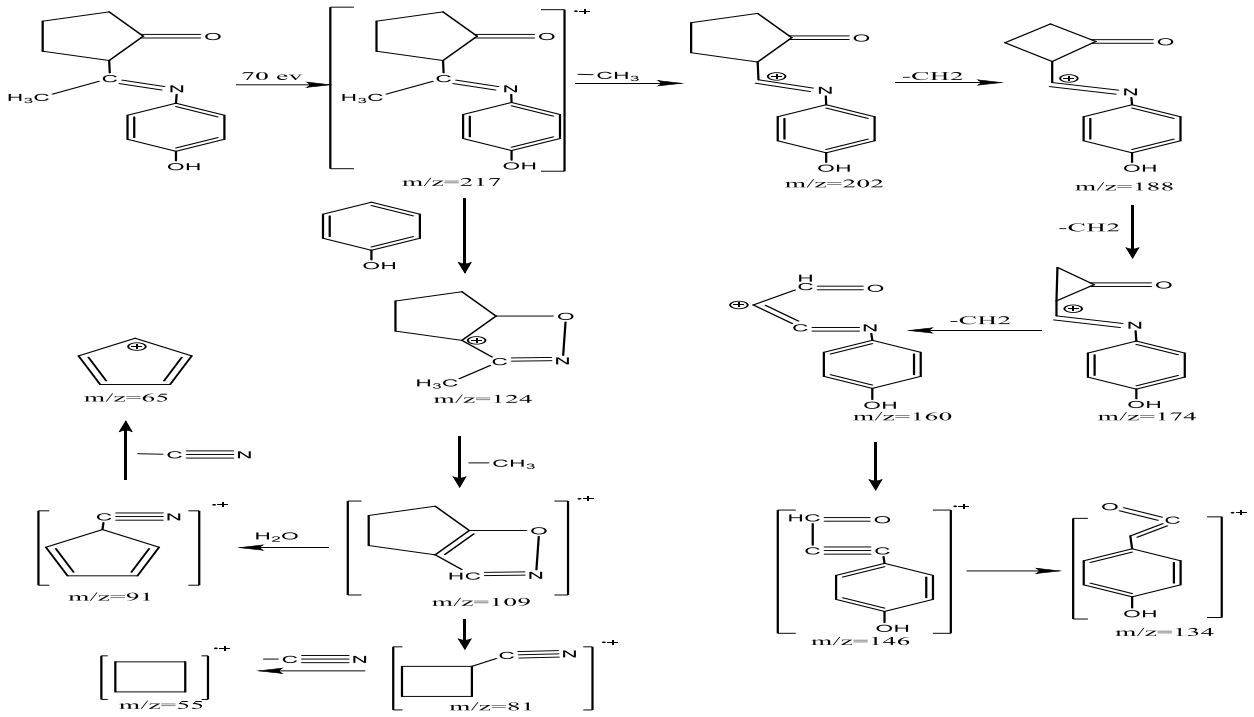

Figure 3-5 Mass fragmentation for **L_1**

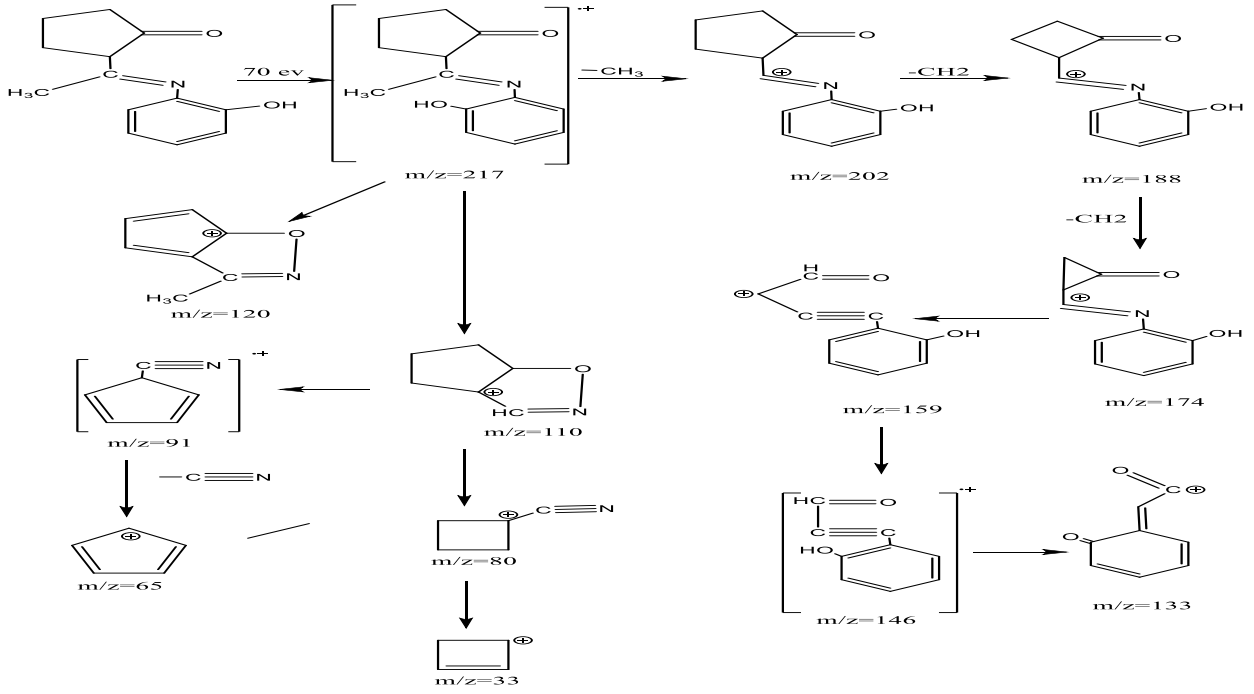

Figure 3-6 Mass fragmentation for **L_2**

The peaks in the region 2900-3100 can be assigned to $\upsilon(C\text{-}H)_{aromatic}$ and $\upsilon(C\text{-}H)_{aliphatic}$ for both compounds,[16,17]. The υ(C=O) and υ(C-O) stretching frequencies were observed in the 1509 cm^{-1} and 1229 cm^{-1} region for L_1, while in 1505 cm^{-1} and 1262 cm^{-1} region for L_2, respectively. The I.R spectrum of compound L_1 shows strong peaks at 1558 cm^{-1} and 1509 cm^{-1} belong to υ(C=N) and υ(C=C) stretching frequencies, respectively, while in L_2 compound appears at 1567 $cm^{-1}$and 1505 cm^{-1}, respectively. The vibrational data for both compounds are presented in the Table 3-4 and showed in figures 3-7 and 3-8.

Table 3-4, Infrared spectra (cm^{-1}) for the compounds **L_1 and L_2**.

Com.	$\upsilon(C\text{-}H)_{aromatic}$	$\upsilon(C\text{-}H)_{aliphatic}$	υ(C=O)	υ(C=N)	υ(C=C)	υ(C-O)
L1	3064(m) 3022 (m)	2968 (m) 2947 (m)	1609 (s)	1558 (s)	1509 (s)	1269 (w)
L2	3049 (m) 3010 (m)	2989 (m) 2948 (m)	1620 (s)	1567 (s)	1505 (s)	1262 (w)

Where s=strong; m=medium; w=weak;

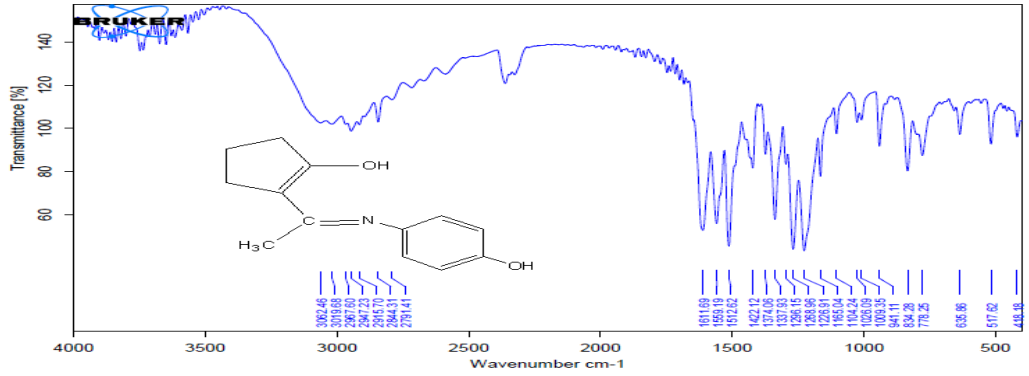

Figure 3-7 I.R. spectrum of compound **L_1**

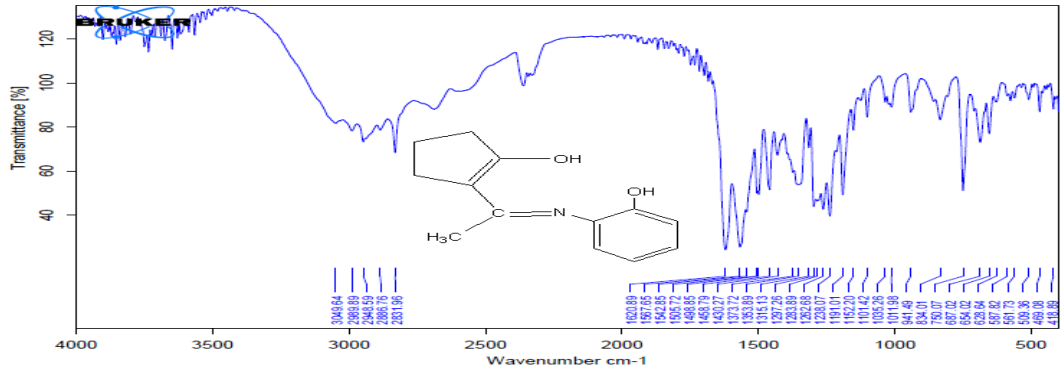

Figure 3-8 I.R. spectrum of compound **L_2**

4-References

1- Arulmurugan S, Kavitha PH, Venkatraman RP. "Biological activities of Schiff base and its complexes: a review". Rasayan J Chem. 2010; **3**(3); p385–410.

2- Schiff H. Mitteilungen aus dem universitats laboratorium in Pisa: Eineneue reihe organischer basen. Justus Liebigs Ann Chem. 1864;131; p118–119.

3- Sykes P. A Guidebook to Mechanism in Organic Chemistry. Pearson Education India, 1986.

4- Rauf A, Shah A, Munawar KS, et al. Synthesis, spectroscopic characterization, DFT optimization and biological activities of Schiff bases and their metal (II) complexes. J Mol Struct. 2017;1145; p132-140.

5- Dhar DN, Taploo CL. Schiff bases and their applications. J Sci Ind Res. 1982;41:501–506.

6- Przybylski P, Huczyński A, Pyta K, Brzezinski B, Bartl F. Biological properties of Schiff bases and azo derivatives of phenols. Curr. Org Chem. 2009;13; p124–148.

7- Bringmann G, Dreyer M, Faber JH, Dalsgaard PW, Staerk D, Jaroszewski JW. Ancistrotanzanine C and related 5,1'- and 7,3'-coupled naphthylisoquinoline alkaloids from Ancistrocladus tanzaniensis. J Nat Prod. 2004;67(5); p743–748.

8- Salimon J, Salih N, Ibraheem H, Yousif E. Synthesis of 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole as potential antimicrobial agents. Asian J Chem. 2010;22(7); p5289–5296.

9- Guo Z, Xing R, Liu S, Zhong Z, Ji X, Wang L. Antifungal properties of Schiff bases of chitosan, N-substituted chitosan and quaternized chitosan. Carbohydr Res. 2007;342(10); p1329–1332.

10- Li Y, Yang ZS, Zhang H, Cao BJ, Wang FD. Artemisinin derivatives bearing Mannich base group: synthesis and antimalarial activity. Bioorg Med Chem. 2003;11; p4363–4368.

11- Yousif E, Salih N, Salimon J. Improvement of the photostabilization of PVC films in the presence of 2 N-salicylidene-5-(substituted)-1,3,4-thiadiazole. J Appl Polym Sci. 2011;120; p2207–2214

12- Yousif E, Ahmed A, Mahmoud M. New organic photostabilizers for rigid PVC against photodegradation. Saarbrücken: Lambert Academic; 2012.

13- Yousif E. Photostabilization of PVC: principles and applications. Saarbrücken: Lambert Academic; 2012.

14- Yousif E, Salimon J, Salih N, Ahmed A. Improvement of the photostabilization of PMMA films in the presence 2 N-salicylidene-5-(substituted)-1,3,4-thiadiazole. J King Saud University Sci. 2012;24; p131–137.

15- Yousif E, Salimon J, Salih N. New stabilizers for polystyrene based on 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds. J Saudi Chem Soc. 2012;16; p299–306.

16- Sakthilatha, D., and R. Rajavel. Chemical Science Transactions (2013): p 711.

17- A.K.Szikszai, T. Patonay, J. Jeko, Arkivoc,2001; p 40-50.