

## Synthesis, Characterization and Studying Analytical Properties of 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline

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**Abstract:** In this research, we have prepared 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline, as a new quinaldine derivative by aldol condensation between quinaldine and o-vaniline and characterized by FT-IR, Ms and <sup>1</sup>H-NMR spectra. The analytical properties were studied.

This compound is colorless in acidic media, while in basic medium extremely changes to yellow color. The pKa of this compound has been calculated by using two methods and it equals to (7.73±0.11), the pH range was between (6.93 – 8.25).

The indicator was used for the end point determination of the calibration standard samples of solution (HCl) with a standard solution of NaOH, and in calibration standard samples of solution (CH<sub>3</sub>COOH) with a standard solution of NaOH.

The results were compared with the results of titrimetric methods that used known indicators for determination of end point. A statistical study of all results, shows that the determination of the end of the calibration point (strong acid with strong basis, weak acid with strong basis) using 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline as indicator, gave precision and accuracy results more than studied methods, and the change of indicator color was changed extremely from yellow to colorless.

**Keywords:** Quinaldine, O-vanilline, Acid-Base Indicator, Constant Dissociation.

### 1. Introduction:

The most prepared indicators, which used in neutralization calibrations, is few solubility in aqueous media, so it used in water-organic solvent mixtures. The organic solvents are harmful substances to the environment, very expensive and it is difficult to get rid of them after their use.

In this research, a new organic compound soluble in water was synthesized.

Even though the technical progress was developed in recent years, and the development of methods that used to determine the end point of neutralization calibrations and formation calibrations of complexes with metal cations, using modern mechanical methods [1].

However, this does not eliminate the importance of the traditional methods that used in the past, which depend on change indicator color at the end of the calibration, or determine the end point of calibration by formation complexes with cations metals. It is still searching of new organic compounds which have good analytical properties and solubility in water so that it can use as little as possible proportions of organic solvents

(sometimes up to 4% organic solvent - water) and it can be used these compounds as analytical reagents , biologically effective[2], pharmaceutical compounds and catalysts. We found that one of prepared compounds in our research has analytical properties. The aim of our research is to study the prepared compound analytically.

## 2. Experimental:

### 2.1. Materials and Equipment:

All chemicals were purchased from Sigma Aldrich Chemical Co. and Merck Chemical Co. (Germany).The infrared (FT-IR) spectroscopy of the compound was recorded in the region of 4000 -400  $\text{cm}^{-1}$  using KBr on a FT-IR Jasco-300E spectrometer. The UV spectroscopy of the compound was recorded on OP-Zen 3220,  $^1\text{H-NMR}$  spectroscopy was recorded on Bruker Specrospin ultra shield magnets 400 MHz instrument using tetramethylsilane (TMS) as an internal standard and EtOD as a solvent, the pH and conductivity changes were recorded on Martini (pH Mi 180) bench Meter.

### 2.2. Synthesis of 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline (3): [3,4]

O-vanillin 1.52 g (10 mmol) was dissolved in 8 ml of absolute ethanol with 10 ml of 10% sodium hydroxide alcoholic solution, and then added 1.35 ml (10 mmol) of quinaldine, the mixture was heated to 60°C and stirred for 1 h. The mixture was cooled to room temperature, and then the formed precipitate was filtered and washed using cyclohexane and recrystallized from ethanol, to obtain yellow crystals (it has melting point 300 °C) [5,6].

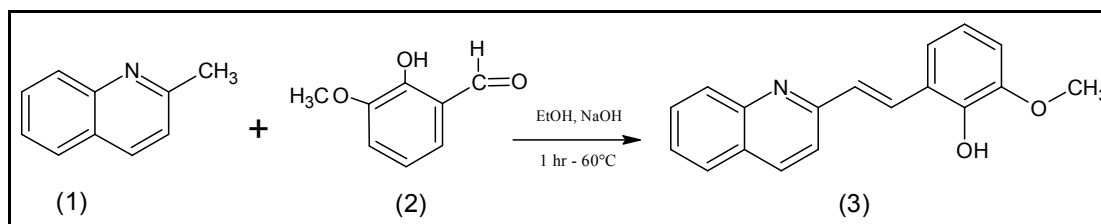


Figure (1): Synthesis of (3)

The FT-IR spectroscopy of (3) showed wideband between (3300–3600 $\text{cm}^{-1}$ ) which assigned to the (O-H) stretching vibration in this compound, absorption bands around (3000 $\text{cm}^{-1}$ ) assigned to the (C-H) stretching, the band at 1644  $\text{cm}^{-1}$  due to aromatic and aliphatic double bond and (C=N) and the band at 1270  $\text{cm}^{-1}$  due to C-O bond. Figure 2.

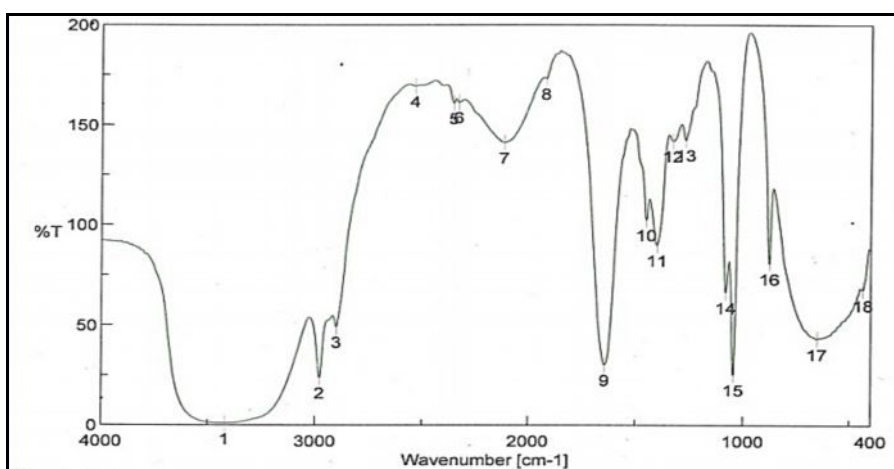


Figure (2): The FT-IR spectroscopy of (3)

MS spectroscopy of synthesized compound (3) shows a peak at ( $m/z = 276$ ) which refer to ( $\text{M-H}^+$ ), while the peak at ( $m/z = 317$ ) refer to ( $\text{M-H}^+ + \text{CH}_3\text{CN}$ ). Figure 3.

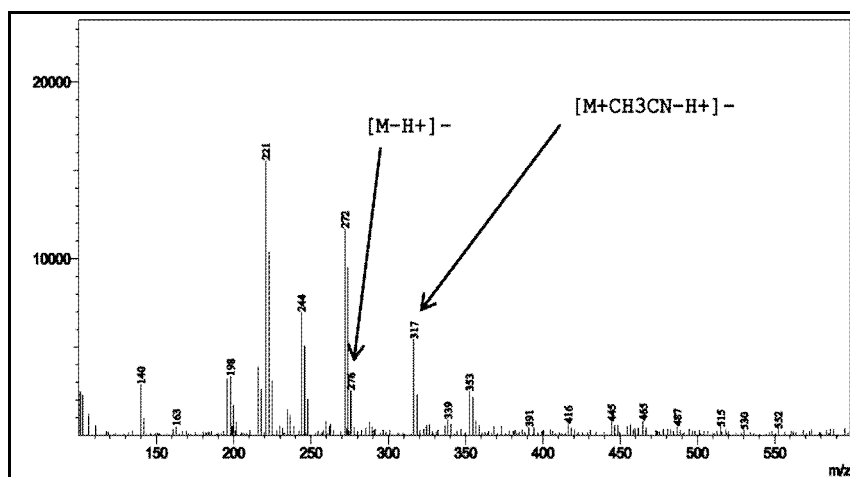


Figure (3): The MS spectroscopy of (3)

$^1\text{H-NMR}$  spectroscopy of synthesized compound shows the following chemical shifts:  $^1\text{H-NMR}$  (EtOD)  $\delta$ (ppm): 3.64 (s, 3H, O-CH<sub>3</sub>), 5.13 – 6.95 (m, 9H, Aromatic H), 6.09 (d, 1H, =CH-C-N), 6.11(d, 1H, =CH-C-Ar), 10.016(S, 1H, OH).Figure 4.

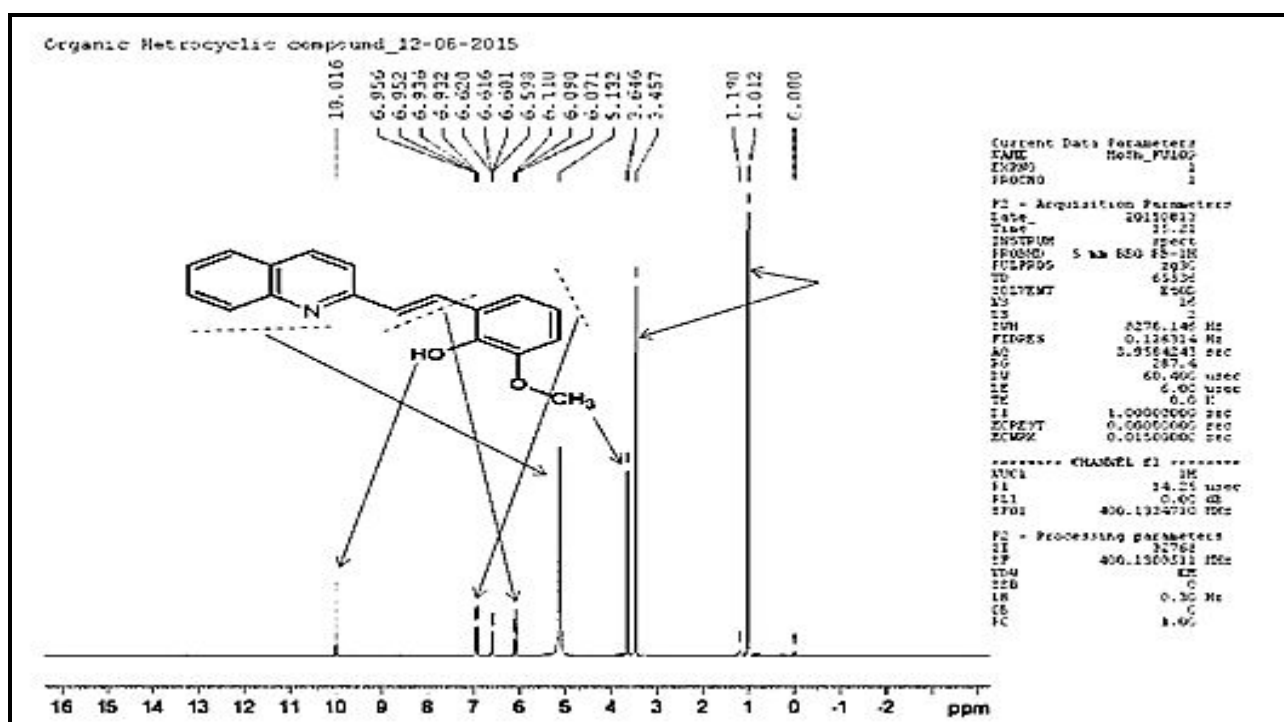


Figure (4): The  $^1\text{H-NMR}$  spectroscopy of (3)

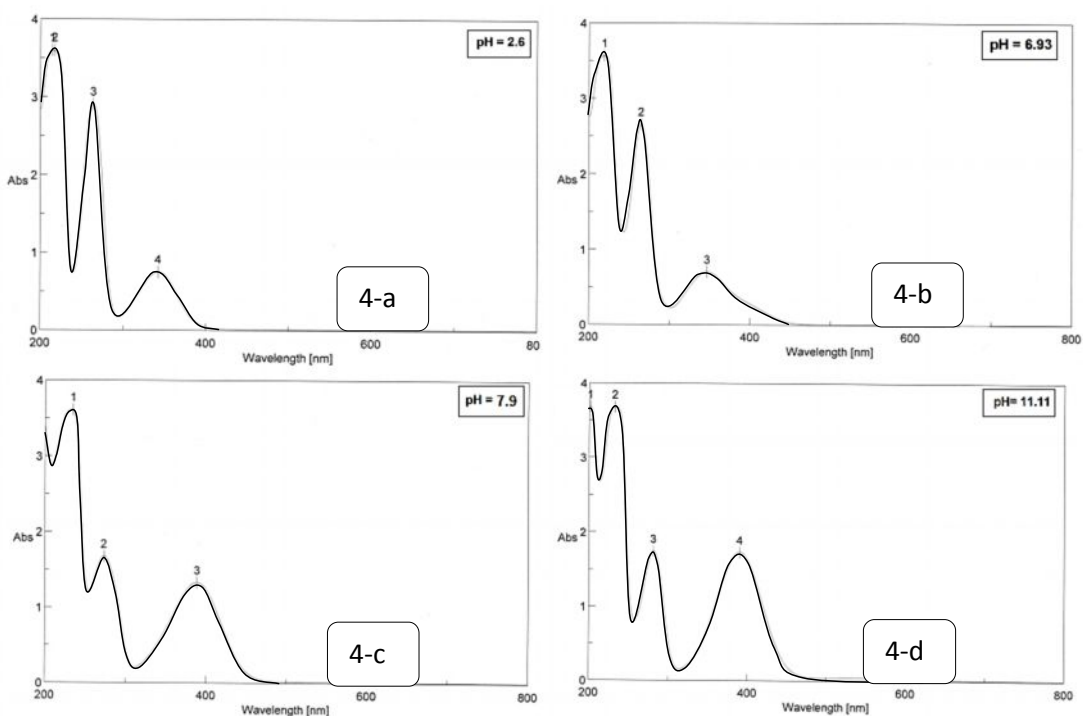
## 2.3. Analytical methods:

### 2.3.1. Preparing the reagents and standards:

1. Primary reagent solution (3) was prepared with concentration  $1 \times 10^{-3}$  M, by dissolving 0.0693 g from synthesized compound (3) with water.
2. Hydrochloric acid (0.1N) solution was prepared by taken 8.33 ml from trial hydrochloric acid (12 N,  $d=1.185$ , 37% p) in (1L) volumetric flask and then completed with distilled water to the signal.
3. Acetic acid (0.1N): solution was prepared by taken 5.714 ml from glacial acetic acid (17.5 N,  $d=1.05$ , 99.7% p) in (1L) volumetric flask and then completed with distilled water to the signal.
4. The Standardized NaOH solution (0.1N): was prepared (Vixnal).

### 2.3.2. The analytical properties study of (3):

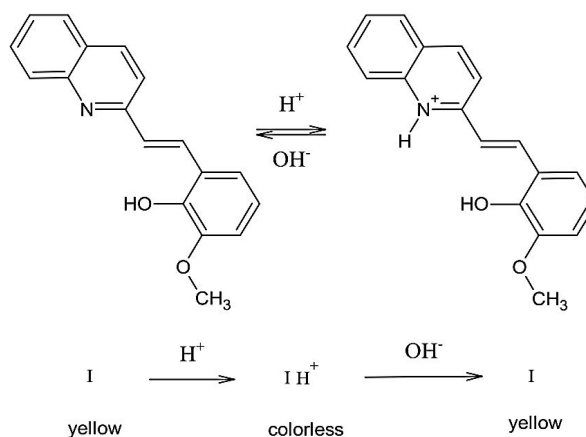
The solubility was tested against many organic solvents, this compound was slightly soluble in alcohols and acetone, whereas water is very good solvent. So analytical properties were study in aqueous solutions. The electronic spectra were studied in two areas of the electromagnetic field (UV- Visible) at various values of pH between (2.6-6.93) UV spectra were shown maximum absorption at  $\lambda_{\max}=340$  nm, as the following Figure (4a-4b) shown. The shift band toward maximum wave lengths at pH values between (7.9 -11.11) (390nm), as (4c-4d) Figure show compound (3) with n so we studied the analytical properties and  $pK_a$  for compound (3) with spectroscopic [7].



**Figure (5): Electronic spectra to compound (3)**

The compound (3) solution retained colorless in the range (6.93- 2.6) assigned to molecular formula as Figure (5) shown; while at  $pH \geq 7.8$  the color changed to yellow and that is agree with ionic formula, and the intensity of the color increased till  $pH = 11.5$ .

The spectroscopy of compound in basic media shown new absorption band at ( $\epsilon \lambda_{\max} = 1.75 \times 10^{-4}$  mol.cm<sup>-1</sup>).



**Figure (6): Molecular formula and ionization**

The ionization constant of this compound in aqueous solutions has been calculated with concentration ( $4 \times 10^{-5}$  M), by two methods (after we set the pH values by using a pH-meter with standard solutions of HCl and NaOH) [8].

We calculated the ionization constant by using the relationship:

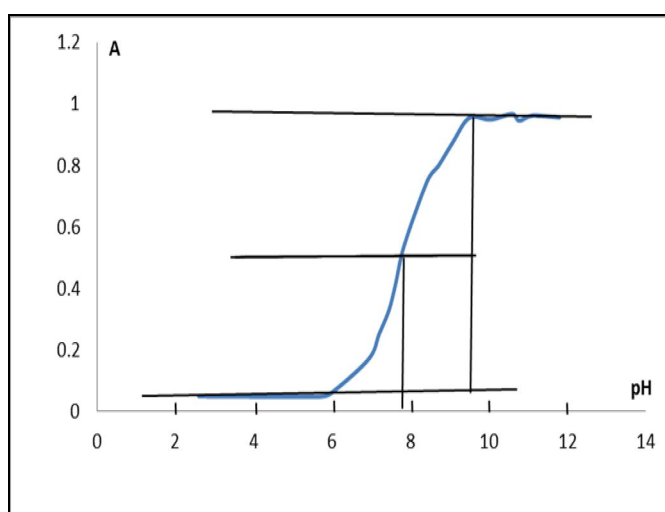
$$K_{HR} = \frac{A_{MIX} - A_{HR}}{A_{R^-} - A_{MIX}} [H^+]$$

$A_{MIX}$ : mixture absorbency.

$A_{HR}$ : Molecular shape absorbency.

$A_{R^-}$ : Ionic shape absorbency.

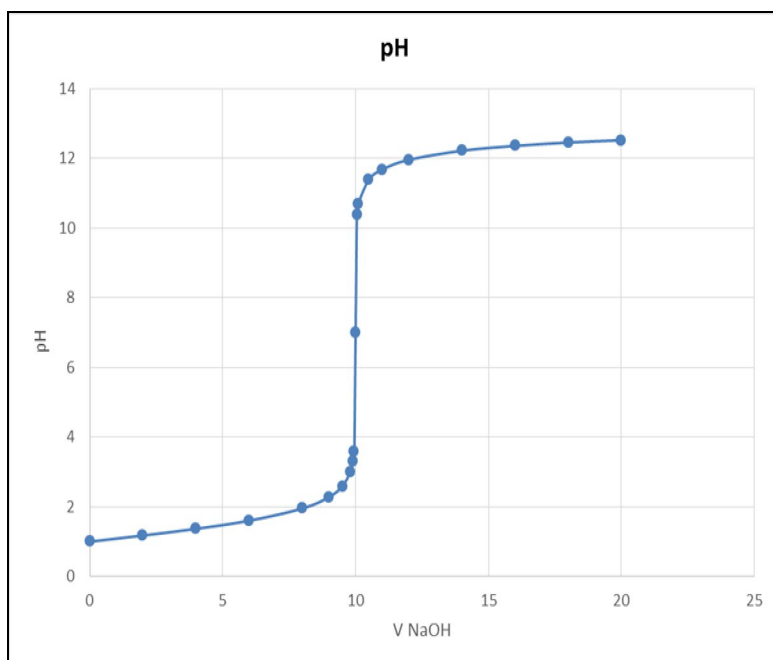
The calculated  $pK_a$  values of this method equals ( $7.72 \pm 0.21$ ) and it is very close to the values obtained graphically (7.75), as showed in Figure (6). The arithmetic average of the  $pK_a$  ( $7.74 \pm 0.11$ ).



**Figure (7): Changes in optical absorbance compound of (3) with the change in pH values in ( $\epsilon_{max} = 390$  nm)**

The table below shows that the indicator: 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline can be used successfully as acid-basis indicator in calibration of strong and weak acids with strong basis.

V NaOH	pH
0	1
2	1.1761
4	1.3679
6	1.602
8	1.9542
9	2.2787
9.5	2.591
9.8	2.9956
9.9	3.2988
9.95	3.6
10	7
10.05	10.39
10.1	10.6968
10.5	11.387
11	11.6778
12	11.9586
14	12.221
16	12.36
18	12.456
20	12.5228



**Figure(8): Calibration curve latency of HCl solution (0.5M , V=10ml) in NaOH solution (0.1M) by using 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline indicator .**

### Results and discussion:

When examining the complex interactions of the compound 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline with the following mineral ions:

( $\text{Sn}^{+4}$ ,  $\text{Sn}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Hg}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{CO}^{+2}$ ,  $\text{Bi}^{+3}$ ,  $\text{Cu}^{+2}$ ) Showed that it can not form complexes with mineral ions such as it.

It is due to its very small ionization constant, therefore it has been utilized of it as indicator in acid – basis calibrations.

It was calibrated 10ml of HCl solution (0.1N) with a standard solution of NaOH (0.1N) by using 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline as indicator, for comparison it has been used the electrical conductivity calibration method, and it was by phenolphthalein indicator.

Results were processed using statistical method as shown in [9], table (1).

**Table (1): Statistical process results of the obtained data in calibration of (10ml) HCl solution, prepared with standard solution of NaOH (0.1N), (the level of confidence 95% ,  $t=2.78$ ,  $n=5$ ).**

$\bar{V}_{\text{NaOH}} \pm \Delta V_{\text{(ml)}}$	Sr %	S	$\bar{V}_{\text{NaOH}}(\text{ml})$	The indicator or The method
$9.984 \pm 0.019$	0.10	0.014	9.984	Prepared indicator
$9.960 \pm 0.029$	0.16	0.021	9.96	Phenol
$10.012 \pm 0.074$	0.12	0.053	.01210	conductivity calibration

The results in table (1) show that it was possible to use the prepared indicator in determination of the end of the calibrations point (strong acid with strong basis), where it gives better results and more accuracy.

The prepared indicator was examined to determine the end of the calibration point of acetic acid solution with a standard solution of NaOH (0.1N), by taking 5ml of acetic acid solution (0.1N), using 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline as indicator.

For comparison it has been used the electrical conductivity calibration method, and it as by phenolphthalein indicator.

Results were processed using statistical method as shown in table (2).

**Table (2): Statistical process results of the obtained data in calibration of (5ml) acetic acid solution, with standard solution of NaOH (0.1N), (the level of confidence 95%,  $t=2.78$ ,  $n=5$ ).**

C $\pm$ ÄC	Sr%	<sup>4</sup> Sx.10	<sup>4</sup> S10	C <sub>CH<sub>3</sub>COOH</sub>	The indicator or The method
0.08299 $\pm$ 0.00030	0.36	1.08	2.41	0.08299	Phenolphthalein
0.08272 $\pm$ 0.00019	0.23	0.68	1.52	0.08272	The Synthesized indicator
0.08290 $\pm$ 0.00028	0.35	1.03	2.39	0.08290	Potential calibration

The results in table (2) show that it was possible to use the prepared indicator in determination of the end of the calibrations point (strong acid with strong basis), where it gives better results and more accuracy. The change of indicator color (from colorless to yellow) was extreme change.

### Conclusions:

1. 2-[2-(2-hydroxy-3-methoxy phenyl)-ethenyl] quinoline was synthesized.
2. This compound was diagnosed using various spectroscopic methods and structure was defined.
3. Analytical properties of this compound were studied and it showed that it can be used as indicator of calibrations acid - basis, gave better and more accuracy and validity of well-known used for such calibrations indicators results.

### References

1. Robert M. G, Pitchai P, Chandraprakash K and Palathurai S. M, Convenient and Efficient Microwave-Assisted Synthesis of a Methyl Derivative of the Fused Indoloquinoline Alkaloid Cryptosanguinolentine. *Molecules* 2010, 15, 3171-3178.
2. Avnish A. P and Arvind G. M, Synthesis of novel heterocyclic compounds and their biological Evaluation. *Der PharmaChemica*, 2010, 2(1): 215-223.
3. Andre' G, Ana C and Carlos A, Synthesis and Antileishmanial Activities of Novel 3-Substituted Quinolines. *American Society for Microbiology*, 2005, Vol. 49, No. 3, 1076–1080.
4. Grzegorz M, Jacek E. N, Ewa R, Lukasz P and Maria N, Synthesis, spectroscopy and computational studies of some biologically important hydroxyhaloquinolines and their novel derivatives. *Journal of Molecular Structure*, 2010; 130–138.
5. Mohammad A, Mohammed I. El-G and Chang-H, Optimization of the Reaction Conditions for Synthesis of (Aryloxy) quinoline Derivatives via Friedländer's Cyclization Reaction. *Bull. Korean Chem. Soc.* 2013, Vol. 34, No. 6; 1848-1853.
6. Vladimír V. K, Leonor Y. V and Carlos M. M, Recent Progress in the Synthesis of Quinolines. *Current Organic Chemistry*, 2005, 9, 141-161.
7. Abduldir Khalid Al Azrak, 2015, *Synthesis and characterization of 2',3'- Dihydroxi - 5'- nitro azobenzene - 4- sulfonic acid and studying its analytical properties*, Damascus University Journal of basic sciences.
8. Douglas, A., Skoog, D. M., West, Holle, F. J., Stanley, R. C., 2004, Fundamentals of analytical chemistry, Eighth Edition, Stanford University, San Jose State University, University of Kentucky, Michigan State University.
9. Harris, D. C., 2006, Quantitative Chemical Analysis, Eighth Edition, Michelson laboratory, China Lake, California.

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