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## Preparation and Characterization of novel 3-(4-chloro phenyl)-1- nitro phenyl-5-(substituted phenyl)-formazans

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### ABSTRACT

In the present research, a series of 3-(4-chloro phenyl)-1- nitro phenyl-5-(substituted phenyl)-formazans (5a-d) were synthesized by the condensation of schiff base(3)and diazonium salt of various substituted aromatic amines (4a-d). The Schiff base (3) was itself synthesized by the condensation of 4-nitro aniline(1) with 4-chloro benzaldehyde(2). All the reaction were routinely monitored and purity was determined on thin layer chromatography using coated aluminum plates and spots were visualized by exposing the dry plates in iodine vapours. The structures of the compounds have been confirmed by elemental analysis, Mass spectroscopy ,  $^1\text{H}$  NMR, U.V, IR spectral data and melting points.

### 1. INTRODUCTION

Formazans have been found to possess important medical applications[1].Formazans are known for their spectrum of biological activities such as antibacterial[2,3] anti-fertility[4] and antifungal[5]. Several formazans show promising anticonvulsant and therapeutic agents[6,7] Furthermore, Formazans were studied as corrosion inhibitor .The result showed that the corrosion inhibition efficiency of these compounds was found to vary with the temperature and acid concentration[8,9]. Schiff bases are utilized as starting material in the synthesis of

pharmaceutically important compounds such as formazans derivatives which have already attracted considerable attention in the analytical chemistry because of their high sensitivity toward many metals and organometals[10]. Our idea was to combine Azomethine group and azo group in one single molecule to get formazan derivatives.Target compounds(5a-d) were prepared according to Scheme-1.The aim of this study was to prepare a series of 3-(4-chloro phenyl)-1- nitro phenyl-5-(substituted phenyl)-formazans

## 2. EXPERIMENTAL

All chemicals were obtained from commercial sources and purified by distillation or recrystallization before use. All melting points were determined in open Capillary tubes using Electrothermal (Gallen Kamp) apparatus were uncorrected. All the reactions were routinely monitored and purity was determined on thin layer chromatography using coated aluminum plates and spots were visualized by exposing the dry plates in iodine vapours. Elemental analysis was performed with a Thermo Finnigan Eger 300F in Iran. <sup>1</sup>H-NMR spectra were

recorded on a Bruker's 500 FT MHz NMR instrument using DMSO-d<sub>6</sub> as solvent and TMS as internal reference (chemical shifts in  $\delta$  ppm) in Iran. IR spectra were recorded on Shimadzu FTIR-8400S spectrophotometer in Iraq. Electronic spectra were measured in the region (200-600 nm) for solution in DMF at room temperature using (Spectro Scan 80D) Uv.Vis Spectrophotometer-U.K in Iraq. Mass spectra were recorded on MSD Direct probe using Acq method test dp.M in Iran.

### 2.1. Preparation of Schiff bases (3).

A mixture of equimolar amount (0.01 mmol) of 4-nitro aniline(1), 4-chloro benzaldehyde(2) in ethanol (20ml) and glacial acetic acid (2-3 drops) was refluxed for 3hrs on water bath. The reaction

mixture was concentrated, cooled, the solid obtained was filtered and recrystallized from ethanol to give Schiff bases(3) of N-(4-chlorobenzylidene)-4-nitroaniline[11]. It was obtained 80% yield.

### 2.2. Diazotization of amine (4a-d).

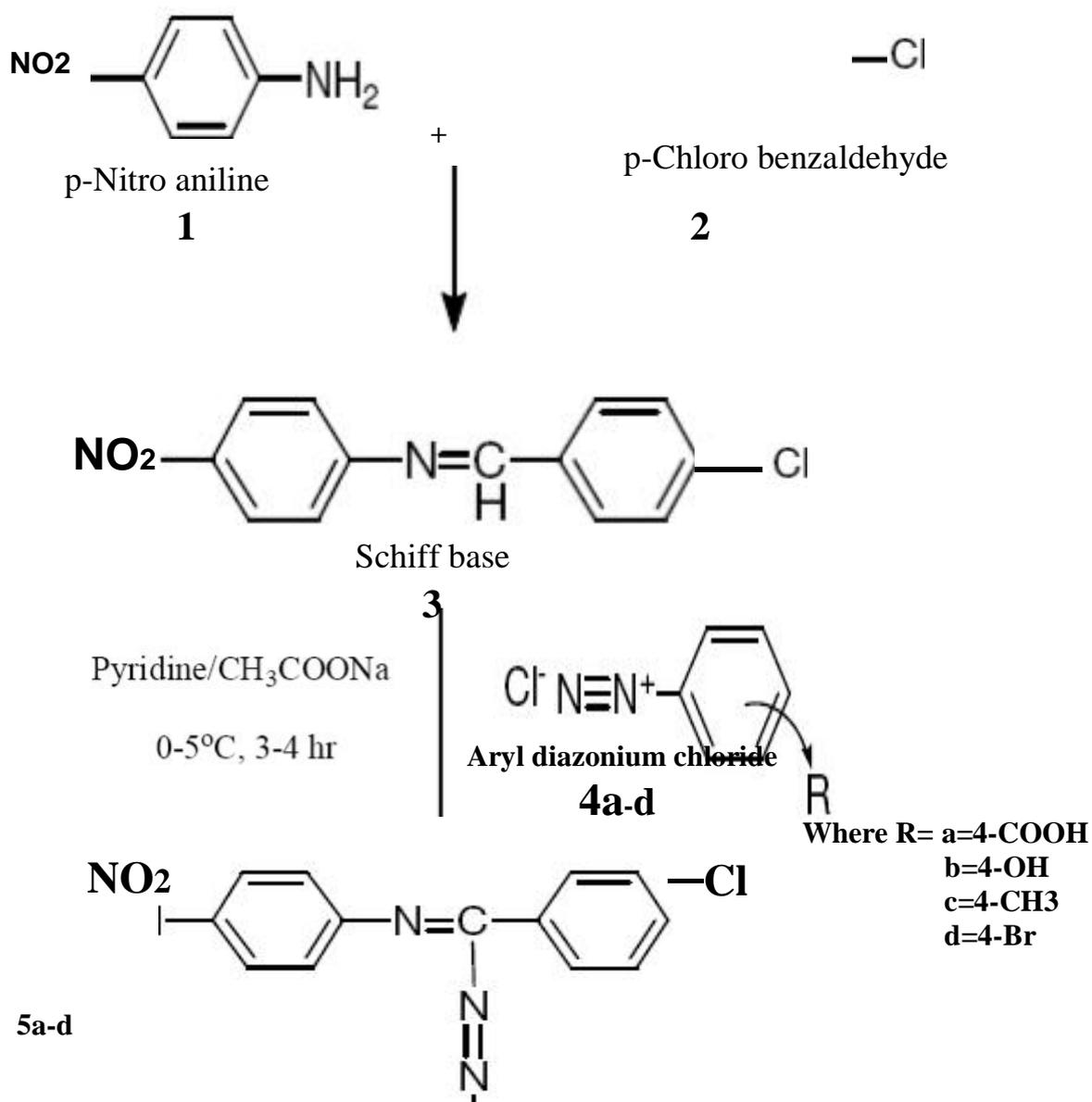
A finely ground powder of the (10 mmol) amine dissolved in water was cooled to (0-5 °C) and diazotized with 1M sodium nitrite solution (10 ml) at 0 °C and 3M HCl (10 ml). The rate of addition was adjusted so

that the temperature of the solutions remains below 10 °C. The solution was kept in an ice bath and used immediately in the next step [12].

### 2.3. Preparation of 3-(4-chloro phenyl)-1- nitro phenyl-5-(substituted phenyl)-formazans (5a-d).

The solution of Schiff bases (3) (0.01 mole) in pyridine (10ml) was reacted with cold diazonium chloride of aniline (4a) (0.01mole) in the presence of sodium acetate (0.3gm) in ice bath at 0-5 °C for 3 hours. Coloured product obtained was filtered

and washed with water till it was free from excess pyridine and crystallized from ethanol [13], yield 62%. Other compounds, (5b-e) were prepared in similar manner and the characterization data for different substituted formazans are given in Table-1.



**Scheme 1:** Synthetic route to formazan derviatives

### 3. RESLUT AND DISCUSSION

The physical properties of Schiff base and novel formazans derivatives are Presented in Table1. The compounds are quite stable in dry air and they are soluble in most organic solvent. Synthetic routes

leading to target compounds are summarized in Scheme1. The structure of these compounds were proven on the basis of melting points and spectral data.

### 3.1 Elemental analysis

The characterization was carried out for one formazans derivatives (5c) through elemental analysis calculated :C : 63.40 ; H

:3.96 ; N :14.79 % ,found :C :63.57 ; H :3.82 ; N :14.81 %.

### 3.2. <sup>1</sup>H-NMR spectra

<sup>1</sup>H-NMR spectra a singlet peak at  $\delta$  8.75 ppm due to N=CH- (1H) of Schiff base( 3 ) and disappearance shows of signal at  $\delta$  2.60 ppm due to -NH<sub>2</sub> (2H) of 4-nitro aniline(1) and  $\delta$  9.5 ppm due to

-CHO (1H) of 4-chloro benzaldehyde(2)[14] , <sup>1</sup>H-NMR spectra of formazans derivatives (5a-b) shows the disappearance of singlet at  $\delta$  8.75 ppm due to CH=N- [15].

### 3.3. IR spectra

The IR spectra of all compounds and the study are recorded in the solid state using the KBr disk technique.selected bands of diagnostic importance are collected in Table 2.The formation of Schiff base ( 3 ) was indicated by their IR spectra from the appearance of azomethine CH=N stretching band at 1625 cm<sup>-1</sup> combined with the disappearance of IR band in region 3378 cm<sup>-1</sup> and 1710 cm<sup>-1</sup> corresponding to

NH<sub>2</sub> group and C=O group of 4-nitro aniline(1) and 4-chloro benzaldehyde(2) respectively [16,17].While formazans derivatives (5a-d) confirmed by the appearance of IR band in the region 1570-1585 cm<sup>-1</sup> due to -N=N- group and the disappearance of bands at 1625 cm<sup>-1</sup> (-N=CH-)[18]. .

### 3.4. UV-Visible spectra

The electronic absorption spectra of Schiff base( 3 ) exhibit two bands within the 284 nm due to the excitation of the electrons (  $\pi$ - $\pi^*$  transitions ) of aromatic rings and 338 nm is assigned to (  $\pi$ - $\pi^*$  transitions ) within the C=N

group[19].While compounds (5a-d) have two bands (380-416nm) and (434-530nm) due to an intramolecular charge transfer involving the whole molecule [20].

### 3.5. Mass spectra

The mass spectra of formazans (5c) exhibit parent peak m/z 381.As per the even electron rule the 381 ion cleaves to fragment with even mass at fragment peaks at m/z 257 formed by the loss of Ph-NO<sub>2</sub> from the

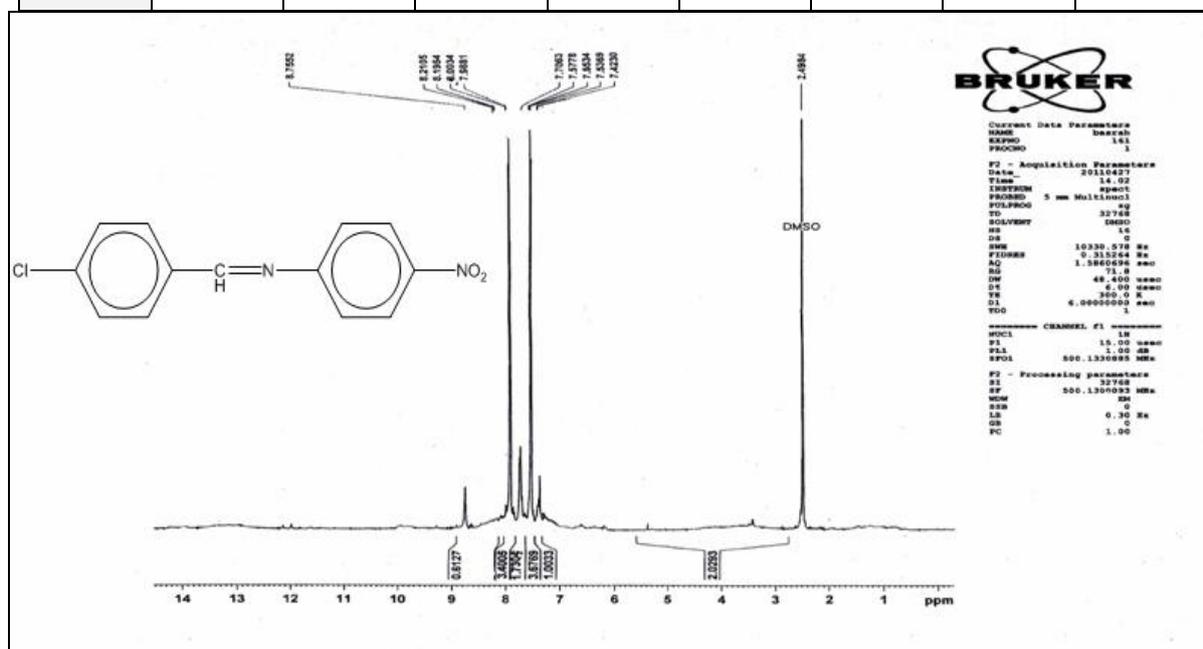
base peak, m/z 271 due to the removal of Ph-Cl [21] and m/z 290 due to fragment of Ph-N<sup>+</sup> [22].The other peaks of mass prove the structure of compound.

**Table 1: physical properties and analytical data of Compounds Synthesized**

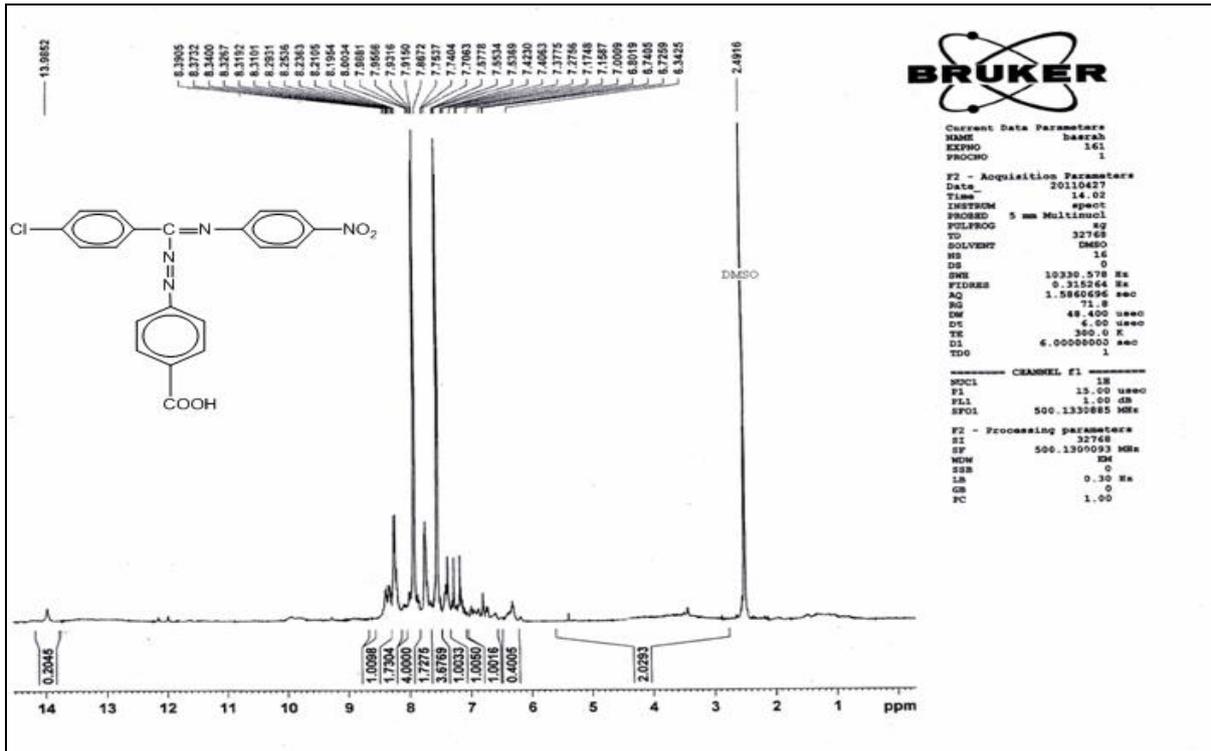
Comp	R	M.P (°C)	Color	M.Wt	M.formula	Yield %	$\lambda$ (nm)	$\epsilon_{\max}$ L . mol <sup>-1</sup> .cm <sup>-1</sup>
3	—	141-142	Yellow	260.5	C13O2N2H9Cl	80 %	284 338	1905 3115
5a	COOH	214-215	Buff	408.5	C20O4N4H13Cl	62 %	380 434	2300 1900
5b	OH	168-169	Brown	380.5	C19O3N4H13Cl	81 %	408 530	2258 1850
5c	CH3	170-172	Red	378.5	C20O2N4H15Cl	70 %	402 523	2252 1700
5d	Br	160-161	Red Dark	443.5	C19O2N4H12ClBr	73 %	416 515	2100 1677

Table 2 : Major IR absorption bands (cm<sup>-1</sup>) of Compounds Synthesized

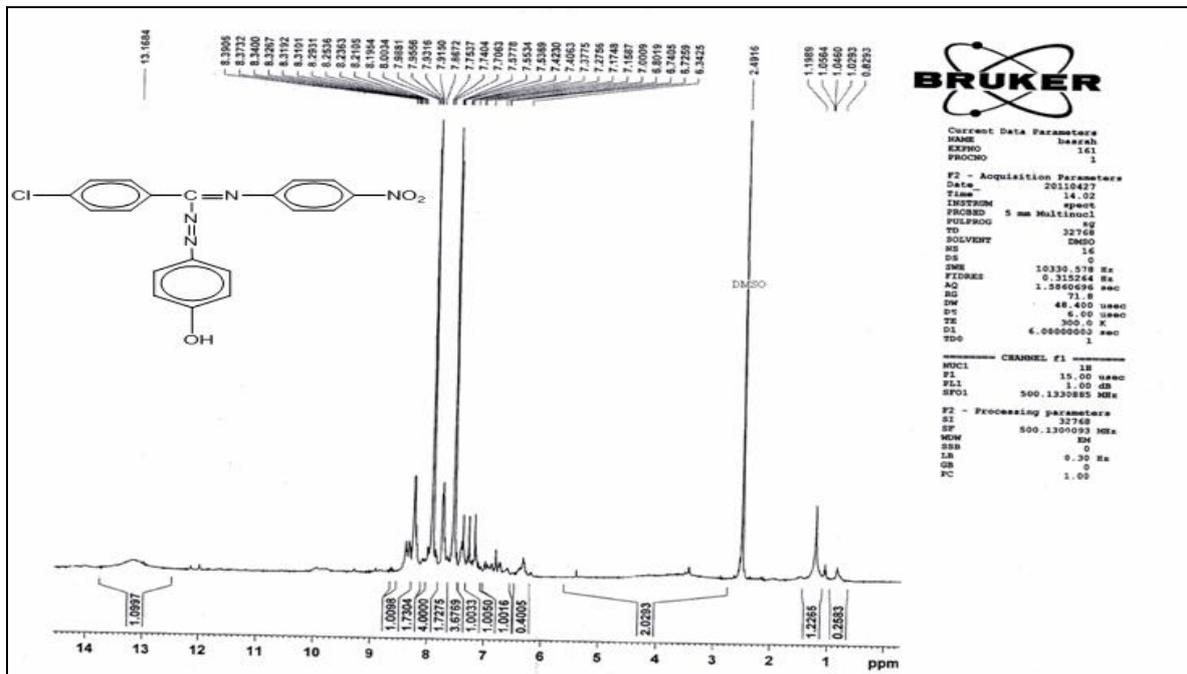
Comp	V(O-H)	V(C-H) aromatic	V(C-H) aliphatic	V(C=O)	V(CH=N)	V(C=N)	V(N=N)	V(C-N)
3	-	3070	-	-	1625	-	-	-
5a	3350	3040	-	1710	-	1610	1585	1334
5b	3340	3030	-	-	-	1615	1580	1330
5c	-	3030	2920	-	-	1610	1570	1335
5d	-	3345	-	-	-	1615	1580	1345



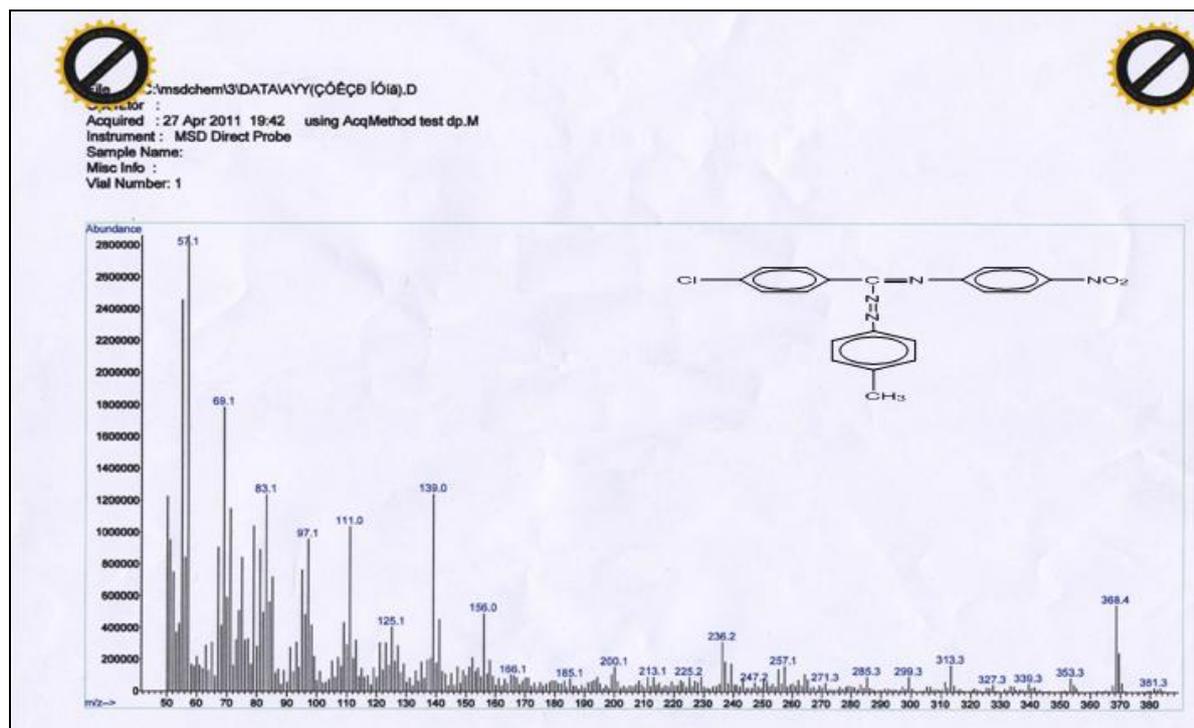
Fig(1) <sup>1</sup>H NMR of Compound 3



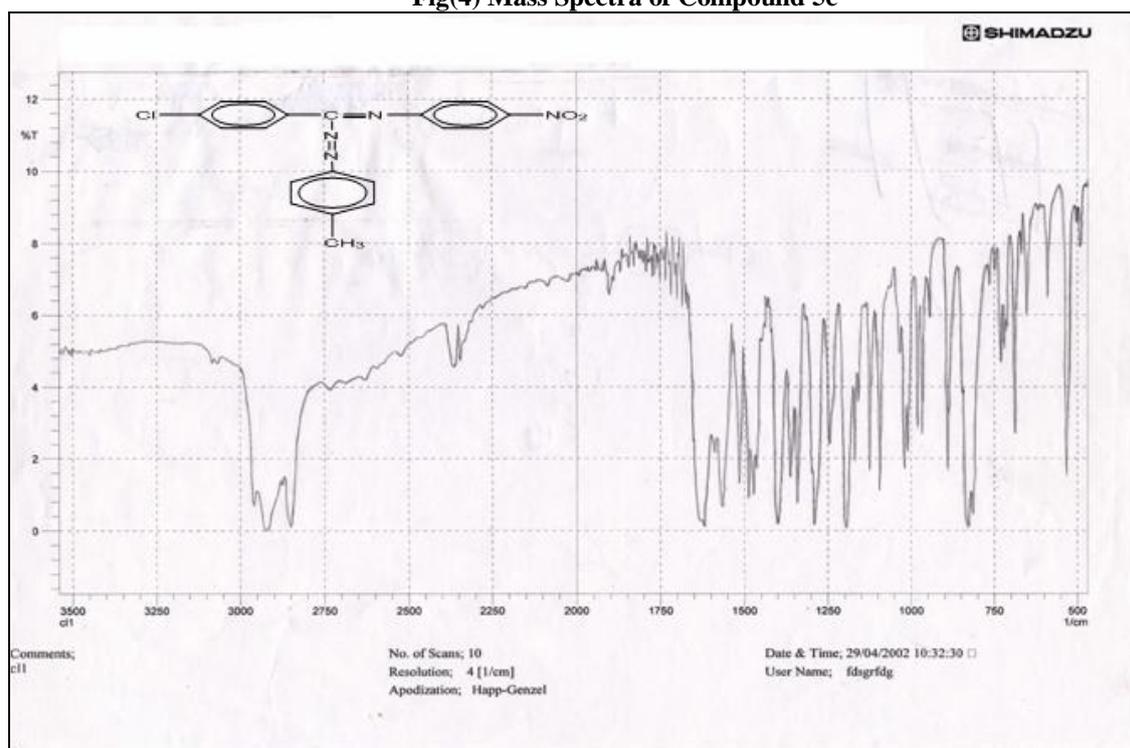
Fig(2) <sup>1</sup>HNMR of Compound 5a



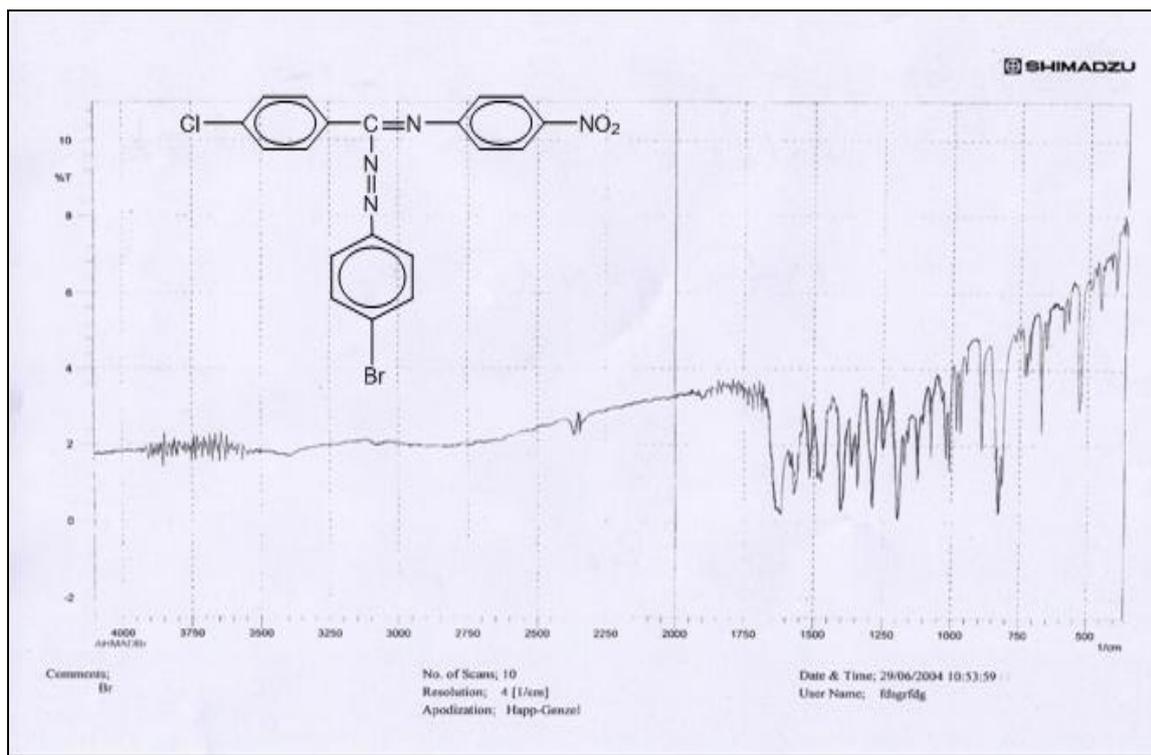
Fig(3) <sup>1</sup>HNMR of Compound 5b



Fig(4) Mass Spectra of Compound 5c



Fig(5) FT- IR of Compound 5c



Fig(6) FT- IR of Compound 5d

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## تحضير مشتقات جديدة ٣ - (٤ - كلورو فنيل) - ١ - نايترؤ فنيل - ٥ - ( فنيل معوض بموقع بارا) فورمازين وتشخيصها

أحمد مجيد جاسم  
جامعة البصرة ، كلية التربية، قسم الكيمياء

### الملخص

في هذا البحث حضرت سلسلة من مشتقات جديدة لمركب ٣ - (٤ - كلورو فنيل) - ١ - نايترؤ فنيل - ٥ - ( فنيل معوض بموقع بارا) فورمازين بوساطة تكاثف قاعدة شف (مركب وسطي) N - (٤ - كلورو بنزليدين) - ٤ - نايترؤانليين مع ملح الدايازونيوم لامينات اورماتية معوضة بمجاميع مختلفة بالموقع بارا، وقاعدة شف حضرت من تكاثف بارا نايترؤانلين مع بارا كلورو بنزاليهايد. تمت متابعة التفاعلات باستخدام تقنية كروموتوغرافيا الطبقة الرقيقة وشخصت المركبات المحضرة بوساطة اطياف الرنين النووي المغناطيسي للبرتون، الاشعة تحت الحمراء، الاطياف المرئية وفوق البنفسجية، طيف الكتلة وقيست درجات الانصهار لجميع المركبات المحضرة.