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Synthesis of some New Schiff Bases and Hydrazones Containing Benzonaphthyridine/ Benzonaphthyridone Moiety

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ABSTRACT

The N-(4-methyl-2-pyridyl)anthranilic acid (I) was synthesized by Ullmann condensation. The compound (I) was cyclized by polyphosphoric acid (PPA) to give 4-methyl-10*H*-benzo[b][1,8]naphthyridin-5-one (II). The compound (II) was treated with selenium dioxide (SeO_2) and thionyl chloride ($SOCl_2$) to give the 4-formyl-10*H*-benzo[b][1,8]naphthyridin-5-one (III) and 4-methyl-5-chloro-benzo[b][1,8]naphthyridine (IV) respectively.The compound (III) was reacted with various substituted anilines and aliphatic amines to give the Schiff bases (Va-j). The compound (IV) was reacted with hydrazine hydrate to yield the 5-hydrazino derivative (VI), which was reacted with various aromatic aldehydes to yield the hydrazones (VIIa-j) and the R_f values reported.The reaction progress was followed by thin layer chromatography (TLC). The synthesized compounds were confirmed by spectral data (I.R, ^{1}H-NMR, ^{13}C-MNR). The possible fragmentation pattern of GC/MS for the compounds (III), (Vc) and (VIIg) were reported.

تحضير بعض قواعد شف وهيدرازونات جديدة محتوية على مجموعة البنزونفثاريدين/ البنزونفثاريدون

الملخص

حضر حامض N-(4-مثيل-2-بيريديل)الانثرانليك (I) بواسطة تفاعل أولمان. ثم حولقة المركب (I) بواسطة حامض الفسفوريك المتعدد (PPA) ليعطي 4- مثيل-10*H*- بنزو[b][8,1] نفثاردين-5-أون (II). عومل المركب (II) مع ثنائي اوكسيد السيلينيوم (SeO_2) وكلوريد الثايونيل ($SOCl_2$) ليعطي 4-فورميل-10*H*- بنزو[b][8,1] نفثاردين-5-اون (III) و 4- مثيل-5-كلورو بنزو[b][8,1] نفثاردين (IV) على التوالي.عند مفاعلة المركب (III) مع عدة أنيلينات معوضة وأمينات اليفاتية اعطى قواعد شف (V). بينما اعطى تفاعل المركب (IV) مع الهيدرازين المائي مشتق الـ 5-هيدرازينو (VI)، الذي ادخل تفاعلات مع عدة ألديهايدات أروماتيه ليعطي الهيدرازونات (VIIa-j). استخدمت تقنية كروماتوكرافيا الطبقة الرقيقة (TLC) لمتابعة سير التفاعل. كما سجلت الثوابت الفيزياوية وقيم (R_f). شخصت تراكيب المركبات المحضرة بواسطة الطرق الطيفية مثل طيف الاشعة تحت الحمراء (I.R) وطيف الرنين النووي المغناطيسي (^{1}H-NMR,^{13}C-NMR) ووضح مخطط التجزؤ المحتمل لطيف الكتلة (GC/MS) للمركبات (III, Vc, VIIg).

INTRODUCTION

Many Benzonaphthyridine derivatives have current interest due to their planner linear structure (Ivanove *et al.*, 2005). Ullmann synthesis involves the condensation of *o*-halobenzoic acid with substituted 2-aminopyridine in presence of cupric oxide and anhydrous potassium carbonate to give N-pyridylanthranilic acids (Jameel and Al-Hadedi, 2010). Cyclization of N-pyridylanthranilic acid can be achived by concentrated H_2SO_4 (Acheson, 1973), polyphosphoric acid (PPA) (Meftah *et al*., 1994) and $POCl_3$ (Al-Hadedi, 2008) to give different types of tricyclic hetero compounds. The literatures showed that the benzonaphthyridine/ benzonaphthyridone derivatives have versatile biological activities such as antitumor (Chen *et al*., 1994), trypanocidal (Mefetah *et*

al., 1994), antimicrobial (Tabart *et al*., 2001), antibacterial (Tabart *et al.,* 2003), anticancer (Deady *et al*., 2003), anticolinesterase (Marco *et al*., 2004), antimalarial (Gorlitzer *et al*., 2007), anti-HSV-1(Pincheiro *et al*., 2008), antifungal (Bhambi *et al*., 2009), anti-intestinal activity (Duan *et al*., 2011), and used as anti-inflammatory agent (Flockerzi *et al*., 2012). A new series of benzonaphthyridine/ benzonaphthyridone derivatives containing fused ring, such as imidazo (pyridino) group (Ming *et al*., 2011), pyrazolo group (Bernardino *et al*., 2012), were designed and synthesized.

In our previous work, a new benzonaphthyridine and benzonaphthyridone derivatives were synthesized, mainly sulpha drug-benzo[b][1,8]naphthyridine (Al-Hadedi, 2008), 10*H*-benzo[b][1,8]naphthyridin-5-one hydrazones (Al-Hadedi, 2009; Al- Obaydee, 2010) and 10-(alkyl, alkylhalide, benzoyl)benzo[b][1,8]naphthyridin-5-one (Al-Obaydee, 2010). The aim of the present study is preparation of new Schiff bases and hydrazones derivatives cotaining benzonaphthyridine/ benzonaphthyridone which were expected to be biologically active compounds.

EXPERIMENTAL

Melting points were determined on an electrothermal IA 9300 Digital-series (1998) apparatus, and they were uncorrected. Infrared spectra were recorded on a Bruker FT-IR spectrophotometer Tensor 27, Germany (College of Education, University of Mosul). ^{1}H, ^{13}C-NMR spectra were recorded on a Bruker 300 MHz, in (Al-Al-Bayt University, Jordan) using TMS as an internal reference, and DMSO-d_6 as a solvent, and coupling constant J(Hz) with the use of the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet and br, broad. Mass spectra (MS) were obtained from perkin Elmer Clarus 500 Gas chromatography-Mass spectrometer in (I.I.T Roorkee. Chemistry Dept., India), and from a trace 2000 series GC-MS in CH_2Cl_2 University of Southampton, Chemistry Dept., UK).

Preparation of N-(4-methyl-2-pyridyl)anthranilic acid (I).

This compound was prepared by the procedure reported in the previous work (Jameel and Al-Hadedi, 2010).

Preparation of 4-Methyl-10*H*-benzo[b][1,8]naphthyridin-5-one (II).

This compound was prepared by the procedure reported in the previous work (Al-Hadedi, 2009; Al-Obaydee, 2010).

Preparation of 4-formyl -10*H*-benzo[b][1,8]naphthyridin-5-one (III). (Chen and Deady, 1993).

In a 100 ml three-necked flask with sealed stirrer, a reflux condenser and a thermometer, 15 ml of dioxane was placed,then (1.32 g, 0.0119 mol) of selenium dioxide SeO_2 and (1 ml) water was added to the flask. The mixture was heated to 50-55˚C until the solid was dissolved. The thermometer was removed and (2.5 g, 0.0119 mol) of compound (II) was added in one partion. The mixture was refluxed with stirring for 4 hrs. The progress of the reaction was monitored by TLC. The hot solution was decanted from the precipitated (black) selenium through fluted filter paper. The dioxane and water were removed by distillation to give a solid product. The product was recrystallized from ethanol to yield a brown powder, m.p = 170-172 ˚C, R_f = 0.62, yield 2.2 g (83%).

Preparation of 4-[(1*E*)-(aryl or alkylimino)methyl]-10*H*-benzo[b][1,8]napthyri-dine-5-one, (Va-j). (kannappan *et al*., 2009).

General procedure.

In a 25 ml dry methanol, (0.1 g, 0.00044 mol) of III was dissolved by stirring and mixed with (0.00044 mol) of appropriate amine. The solution was refluxed with stirring for at least 6 hrs. The progress of the reaction was monitored by TLC. The mixture was cooled and left overnight to complete the precipitation. The product was filtered off and dried in air. Table (1) summarizes the physical data for compounds Va-j.

Table 1: Some physical data for compounds Va-j.

Compd. No.	R	m.p °C	R_f *	Color	Yield %
Va	4-$CH_3C_6H_4$-	241-242	0.27	Yellow	50
Vb	3-$CH_3C_6H_4$-	232-236	0.22	Pale yellow	42
Vc	3,4-di$CH_3C_6H_3$-	234-230	0.21	Yellow	55
Vd	2-$NO_2C_6H_4$-	> 340	0.15	Red	42
Ve	4-$NO_2C_6H_4$-	278-280	0.23	Red	40
Vf	2-$NH_2C_6H_4$-	250-252	0.11	Pale black	40
Vg	$CH_3CH_2CH_2$-	171-173	0.21	Brown	45
Vh	$CH_3CH_2CH_2CH_2$-	179-181	0.2	Brown	47
Vi	$CH_3CH_2CH_2CH_2CH_2$-	187-189	0.2	Brown	47
Vj	NH_2	199-201	0.6	Orange	35

- Elution solvent = $CHCl_3$:MeOH (9.5:0.5).

Preparation of 5-chloro-4-methylbenzo[b][1,8]naphthyridine (IV). (Atwell *et al*., 1984).

A mixture of (2.5 g, 0.012 mol) of compound II with excess (30 ml) of $SOCl_2$ containing (2 drops) DMF was refluxed for 3 hrs. The excess $SOCl_2$ was distilled off under reduced pressure, then the deep scarlet thick residue was diluted with cold chloroform, 150 ml (needs 2 hrs). The solution was slowly added with vigorous stirring to cold ammonia solution. The chloroform layer was separated and the aqueous alkaline solution was further extracted with (30ml×2) of chloroform. The combined chloroform extracts were dried by magnesium sulfate for over night. The Chloroform filtrate was evaporated until dryness. The solid residue was recrystalyzed from ethanol to yield a brown powder, m.p = 116 - 118 °C. R_f = 0.95, ($CHCl_3$:MeOH, 9.5:0.5), yield 85%. (Lit. Al-Hadedi, 2009), 118-120 °C, Rf = 0.66.

Preparation of N-{4-methylbenzo[b][1,8]naphthyridin-5-yl}hydrazine (VI). (Chandra *et al*., 2010; Al-Hadedi, 2009).

Compound IV(3g) was added with stirring to the refluxing solution of hydrazine hydrate (30 ml, 80%) in (150 ml) ethanol during 10 min, and the refluxing continued for 40 min. The completion of the reaction was monitored by TLC. The solvent was distilled under reduced pressure, then extracted by chloroform (100ml×3), and dried by magnesium sulfate overnight. Filtration and evaporation of the solvent to dryness, recrystilazation from ethanol to yield a brown powder, m.p = 103-105 °C, Rf = 0.34 ($CHCl_3$: MeOH, 9.5:0.5), yield 90%. (Lit. Al-Hadedi, 2009), m. p = 103-105 °C, Rf = 0.31, yield 73%.

Preparation of substituted (1E)-benzyliden-N-{4-methylbenzo-[b][1,8]naphthyridin-5-yl}hydrazine, (VIIa-j). (Kannappan, *et al*., 2009).

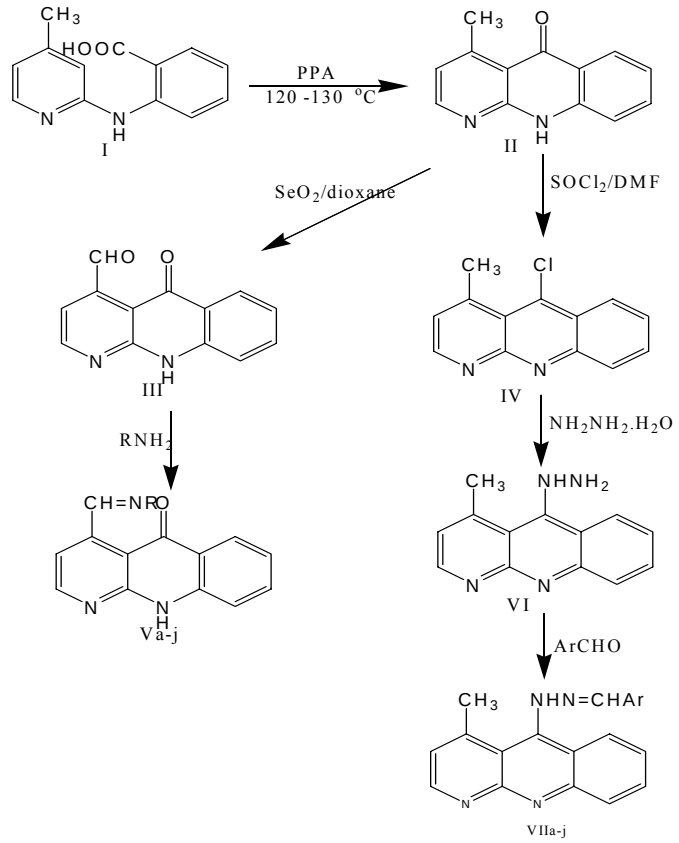
General procedure

A mixture of (0.1 g, 0.00044 mol) of VI in 25 ml of methanol was mixed with (0.00044 mol) of appropriate aldehydes. The solution was refluxed with stirring for at least 6 hrs. The progress of the reaction was monitored by TLC. The mixture was cooled and left overnight to complete the fine precipitation. The product was filtered off and dried in air. Table (2) summarizes the physical data for compounds VIIa-j.

Table 2: Some physical data for compound VIIa-j

Compd. No.	Ar	m.p °C	R_f	Color	Yield %
VIIa	C_6H_5	110-111	0.89	Yellow	45
VIIb	4-$CH_3C_6H_4$	158-160	0.96	Pale yellow	42
VIIc	2-HOC_6H_4	218-220	0.91	Yellow crystal	40
VIId	4-BrC_6H_4	228-229	0.95	Pale yellow	50
VIIe	4-$NO_2C_6H_4$	220-222	0.42	Yellow	70
VIIf	3-$NO_2C_6H_4$	128-129	0.43	Pale yellow	55
VIIg	4-ClC_6H_4	210-211	0.92	Pale yellow	38
VIIh	4-$MeOC_6H_4$	169-170	0.89	Yellow	40
VIIi	4-HO, 3-$MeOC_6H_3$	290 dec.	0.85	Brown	41
VIIj	C_6H_5-CH=CH-	150 sub.	0.57	Yellow	48

Elution solvent = $CHCl_3$:MeOH (9.5:0.5). dec. = decomposition; sub.=sublimation

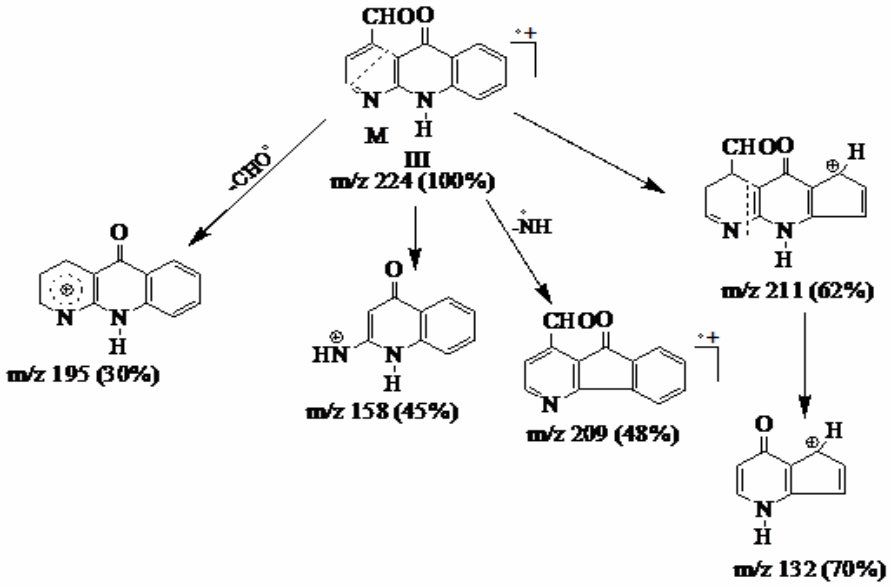


Scheme (1)

RESULTS AND DISCUSSION

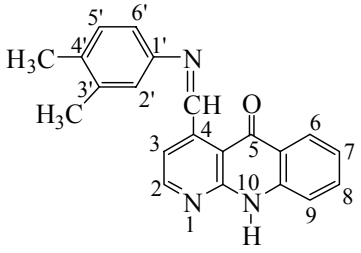
The methyl group in compound (II) was easily oxidized to the corresponding formyl group to form the compound III as shown in Scheme 1. (Chen and Deady.,1993; Deady *et al*., 2003). The

structure of compound III was confirmed via IR spectrum which showed characteristic absorption peaks in the region (3479 cm^{-1}) due to the stretching of (N-H) bond, (1705 cm^{-1}) due to the stretching of (C=O) bond of the aldehyde group, (1687 cm^{-1}) due to stretching of (C=O) bond of the ketone group, and (1637 cm^{-1}) due to stretching of (C=N) bond. The ^{1}H-NMR and ^{13}C-NMR spectral data of compound III confirmed the above results, and showed the following significant peaks: multiplet at 7.13-7.25 for 1H (H-9), multiplet at 7.43-7.65 for 2H (H-7, H-8), multiple at 7.78-7.91 for 2H (NH, H-6), multiplet at 8.11-8.29 for 1H (H-3), multiplet at 8.64-8.77 for 1H (H-2), singlet at 10.06 for 1H ($-\overset{O}{\overset{\|}{C}}-H$). The ^{13}C-NMR spectral data of the compound III showed the following significant peaks: 111.09 (C_3), 115.72(C_{5a}), 111.64 (C_9), 116.7(C_{4a}), 117.05(C_7), 128.32(C_6), 134.06(C_8), 140.06(C_4), 146.98(C_{9a}), 148.28(C_2), 158.95(C10a), 164.79(C_5), 191.93 ($-\overset{O}{\overset{\|}{C}}-H$). The mass spectral data Fig. (1) confirmed the above structure. The possible fragments (m/z) with their relative abundance (%) was reported as shown in Scheme (2). Similar data were found in Lit (Tian *et al*., 2012)



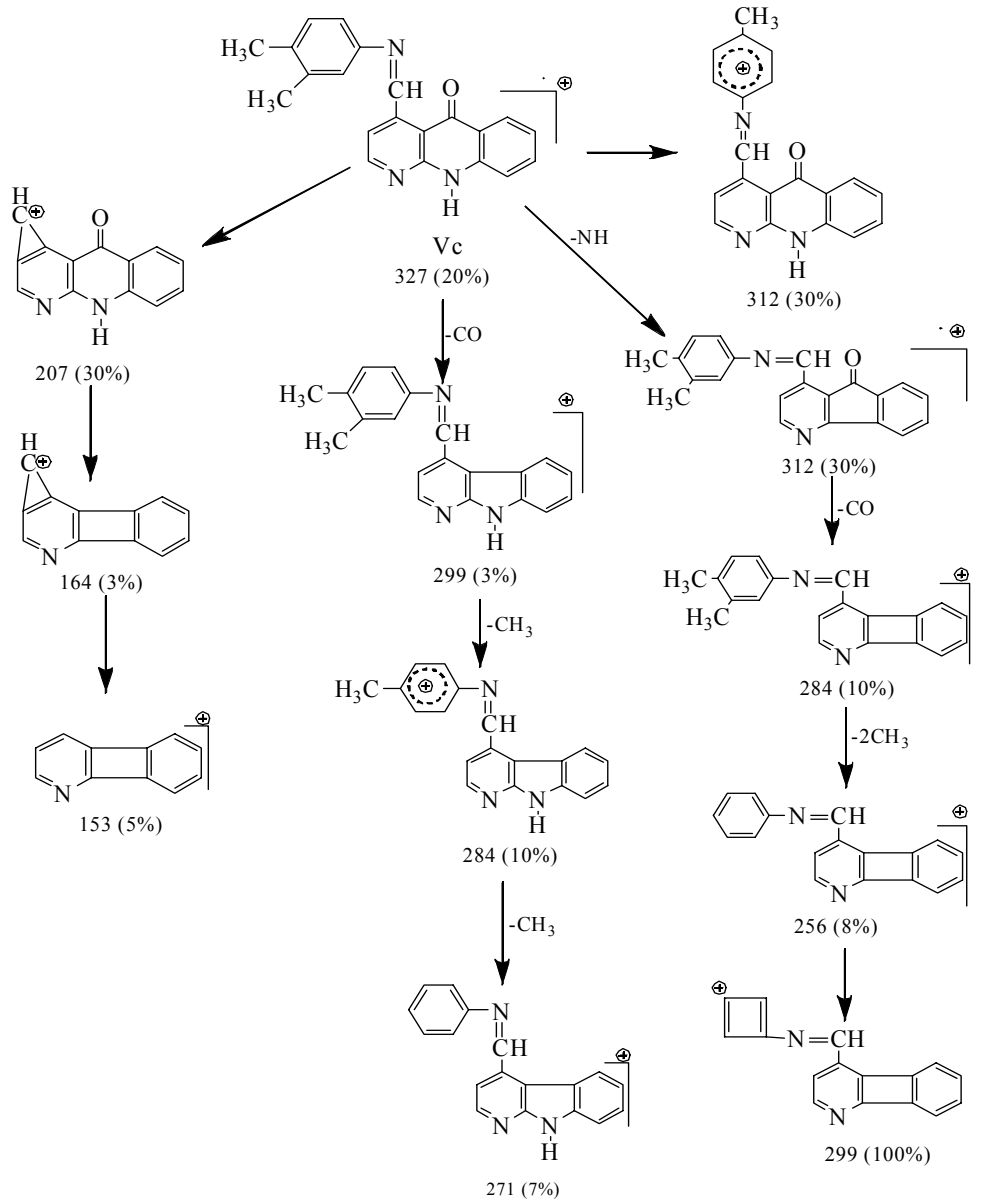
Scheme 2: Fragmentation pattern of compound (III)

The compounds Va-j(Deyanov and Konshin., 2004., Yi *et al*., 2008), have been prepared through the condensation of compound III with various substituted anilines or alkylamines. The structure of the prepared compounds Va-j, was elucidated by means of physical data Table (1) (m.p, R_f) and spectral data (Table 3). The IR spectra for compounds Va-j showed a characteristic absorption bands at (3473-3255 cm^{-1}) due to stretching of (N-H) bond, (1695-1682 cm^{-1}) due to stretching of (C=O) bond, (1645-1649 cm^{-1}) stretching of (C=N) bond. The ^{1}H-NMR and ^{13}C-NMR spectral data (DMSO-d_6, δ in ppm) confirmed the above results (Figs. 2, 3). The compound (Vc) was selected as a representative for this series, and showed the following significant ^{1}H-NMR chemical shifts Fig. (4):



Vc

Two singlet at 2.32 and 2.34, each for 3H for the two (CH_3) protons, six peaks for the nine aromatic protons: multiplet at 7.12-7.28 for 3H (H-2',H-5',H-6'), triplet at 7.54 for 1H (H-8), doublet at 7.64 for 1H(J=7Hz) (H-3), singlet at 7.70 for 1H (CH = N), multiplet at 7.85-7.89 for 2H (NH, H-7), multiplet at 8.48-8.53 for 2H (H-6, H-9), doublet at 8.90 for 1H(J=7) (H-2). The mass spectrum for compound Vc Fig. (5) showed the possible following fragmentation pattern (m/z) with the relative abundance of the fragments (%) as shown in Scheme (3).



Scheme 3: Fragmentation pattern of compound (Vc)

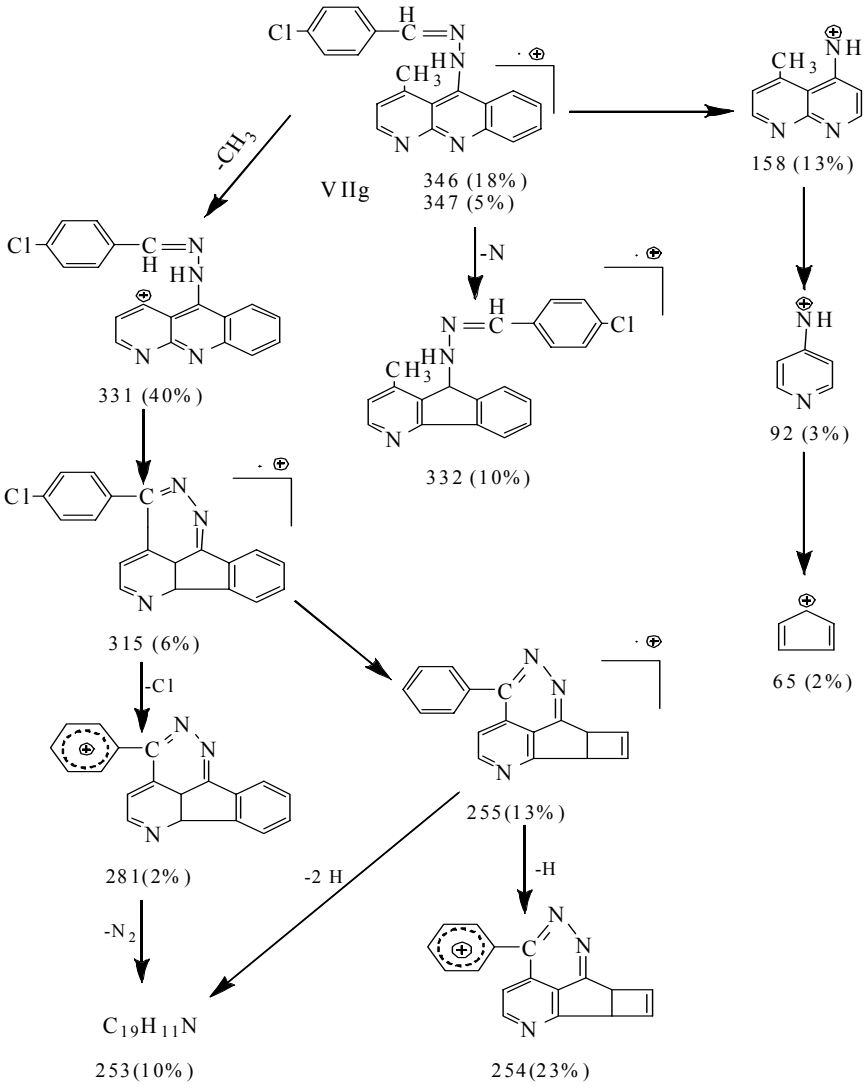
Table 3: Spectral data for compounds Va-j

Compd. No.	IR (KBr) ν(cm^{-1})		^{1}H- NMR & ^{13}C- NMR (DMSO-d_6) δ ppm
Va	C=C	1604	2.40 (s, 3H, CH_3), 7.25 (m, 4H, ArH), 7.53 (t, 1H, J=7Hz), 7.62 (d, 1H, J=7.5 Hz), 7.7 (s, 1H), 7.82-7.88 (m, 2H), 8.47-8.52 (m, 2H), 8.88(d, 1H, 7.5 Hz).
	C=N	1647	
	C=O	1685	
	NH	3422	
Vb	C=C	1605	2.37 (s, 3H, CH_3), 7.18-7.20 (m, 3H), 7.36 (m, 1H), 7.56(m, 2H), 7.83-7.95 (m, 3H), 8.34 (m, 1H), 8.81 (s,2H).
	C=N	1649	
	C=O	1682	
	NH	3417	
Vc	C=C	1608	2.32 (s, 3H, CH_3),2.34 (s. 3H, CH_3), 7.12-7.28 (m, 3H),7.54 (t, 1H), 7.64 (d,1H, J=7H), 7.70 (s,1H), 7.85-7.89 (m, 2H) 8.48-8.53 (m, 2H), 8.90 (d, 1H, J=7Hz).
	C=N	1647	
	C=O	1691	
	NH	3473	
Vd	C=C	1606	----------
	C=N	1647	
	C=O	1695	
	NH	3419	
Ve	C=C	1603	7.24-8.28 (m, 8H), 8.75-10.19 (m, 4H). 111.22, 112.80, 116.47, 116.88, 126.19, 126.48, 126.85, 126.95, 127.23, 127.56, 127.91, 128.67, 134.23, 135.70, 136.82, 147.38, 148.44, 158.52, 165.49
	C=N	1647	
	C=O	1685	
	NH	3443	
Vf	C=C	1600	4.36 (br,2H,NH_2), 6.37-7.11(m,7H), 7.30(m, 1H), 7.48-7.67 (m,3H),8.49(m,1H). 102.06, 112.52, 114.93,115.89, 116.46, 117.74, 123.54, 124.95, 126.18, 127.02,127.17, 127.44, 127.69, 128.23, 135.37, 144.52, 146.90, 147.86, 158.70, 164.70
	C=N	1645	
	C=O	1684	
	NH NH_2	3422-3260	
Vg	C=C	1605	----------
	C=N	1645	
	C=O	1685	
	NH	3422	
Vh	C=C	1606	----------
	C=N	1646	
	C=O	1684	
	NH	3418	
Vi	C=C	1604	0.85 (s,3H), 1.27 (s,4H), 1.54 (s, 2H), 2.38-2.86(m,2H), 7.37-7.49(br,2H), 7.74-7.88 (m, 3H), 8.09-8.29 (m, 2H), 8.45-8.73 (m, 1H). 14.41, 22.11, 27.25, 29.43, 30.42, 114.43, 116.48, 125.04, 125.30, 125.93, 127.16, 127.25, 128.24, 135.32, 135.61, 148.63, 158.63, 164.87
	C=N	1647	
	C=O	1684	
	NH	3430	
Vj	C=C	1607	2.9 (s, 2H, NH_2), 7.04 (d, 1H, J=4.5 Hz), 7.24 (t, 2H, J=7Hz),7.58-7.73 (m, 3H), 8.05 (d, 1H, J=7Hz) 8.39 (d, 1H, J=4.5 Hz). 114.42, 117.64, 120.88, 121.96, 122.32, 126.50, 134.12, 140.52, 146.83, 152.17, 152.61, 153.50, 179.30
	C=N	1645	
	C=O	1683	
	NH, NH_2	3417-3255	

Compound IV has been prepared through the chlorination of compound II with excess $SOCl_2$ (Al-Hadedi, 2008; Al-Hadedi, 2009) as illustrated in Scheme (1). The structure of the synthesized compound IV was confirmed by means of physical data (m.p, R_f) and spectral data. The IR spectrum showed characteristic absorbtion peaks in the region (1649 cm^{-1}) for stretching of (C=N) bond, (1606 cm^{-1}) for stretching of (C=C) bond and there is absence of stretching band of (C=O) bond at (1695 cm^{-1}).

Compound VI has been prepared through the reaction of compound IV with hydrazine hydrate (Chandra *et al*., 2010; Al-Hadedi, 2009) as shown in Scheme (1). The structure of the synthesized compound VI was confirmed by means of physical data (m.p, R_f) and spectral data. The IR spectrum showed a characteristic broad absorption peaks in the region (3422-3314 cm^{-1}) which is due to the bond stretching of (NH, NH_2) bonds, 1649 cm^{-1} for stretching of (C=N) bond, and (1590 cm^{-1}) for stretching of (C=C) bond. The ^{1}H-NMR and ^{13}C-NMR spectral data for compound VI (Fig. 6) confirmed the above results and showed significant bands: singlet at 2.38 for 3H(CH_3), singlet at 2.75 for 2H (NH_2), broad band at 3.93-3.94 for 1H (NH). The chemical shifts of the aromatic protons are shown as following: doublet at 6.92 for 1H (J=7.2 Hz) (H-3), doublet at 7.68 for 1H (J=8 Hz) (H-8), multiplet at 7.84-7.89 for 2H (H-6, H-7), doublet at 8.26 for 1H (J=8Hz)(H-9), doublet at 8.69 for 1H(J=7.2 Hz)(H-2). The ^{13}C-NMR for compound VI in (DMSO-d_6) δ in ppm, showed the following chemical shifts: 20.78(CH_3), 115.38 (C_{4a}), 115.99 (C_{5a}), 123.04 (C_6), 124.48 (C_3), 125.68 (C_7), 126.52 (C_9), 126.66 (C_8), 134.43 (C_4), 146.43 (C_{9a}), 147.37 (C_5), 148.56 (C_2), 160.61 (C_{10a}).

The compounds VIIa-j have been prepared through the condensation of compound VI with various aromatic aldehydes (Chilin *et al*., 2002; Manoj and prasad ., 2011) as illustrated in Scheme (1). The structure of the prepared compounds was elucidated by means of physical data (Table 2) (m.p, R_f) and spectral data (Table 4). The IR spectra of compounds VIIa-j showed a characteristic absorption bands at (3340-3300 cm^{-1}) for stretching of (N-H) band, (1625-1635 cm^{-1}) for stretching of (C=N) bond. The ^{1}H-NMR spectrum for compound VIIb confirmed the structure of these compounds. The mass spectrum for compound VIIg showed the possible following fragmentation (m/z) with relative abundance (%) as shown in Scheme (4).



Scheme 4: Fragmentation pattern of compound (VIIg)

Table 4: Spectral data for compounds VIIa-j

Compd. No.	IR (KBr), ν(cm^{-1})		^{1}H-NMR (DMSO-d_6) δ ppm
VIIa	C=C	1600	-------
	C=N	1624	
	NH	4430-3310	
VIIb	C=C	1602	2.36 (s, 3H,CH_3), 2.39 (s, 3H, CH_3), 7.32 (m, 5H), 7.77 (m, 3H), 8.66 (m, 2H).
	C=N	1625	
	NH	3440-3300	
VIIc	C=C	1601	2.54 (s, 3H, CH_3), 6.97-7.01 (m, 4H), 7.40-7.42 (m, 2H), 7.70-7.72 (m, 2H), 9.00-9.05 (m, 3H), 11.1 (s, 1H).
	C=N	1625	
	NH	3566-3421	
VIId	C=C	1605	-------
	C=N	1625	
	NH	3430-3310	
VIIe	C=C	1595	-------
	C=N	1635	
	NH	3435-3325	
VIIf	C=C	1597	-------
	C=N	1635	
	NH	3340-3360	
VIIg	C=C	1602	-------
	C=N	1630	
	NH	3430-3340	
VIIh	C=C	1598	2.54 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 7.05 (m, 6H), 7.08 (m, 4H), 8.63 (m, 2H).
	C=N	1628	
	NH	3435-3340	
VIIi	C=C	1600	-------
	C=N	1625	
	NH	3360-3410	
VIIj	C=C	1602	2.54 (s, 3H, CH_3), 6.93-8.40 (m, 15H).
	C=N	1630	
	NH	3435-3340	

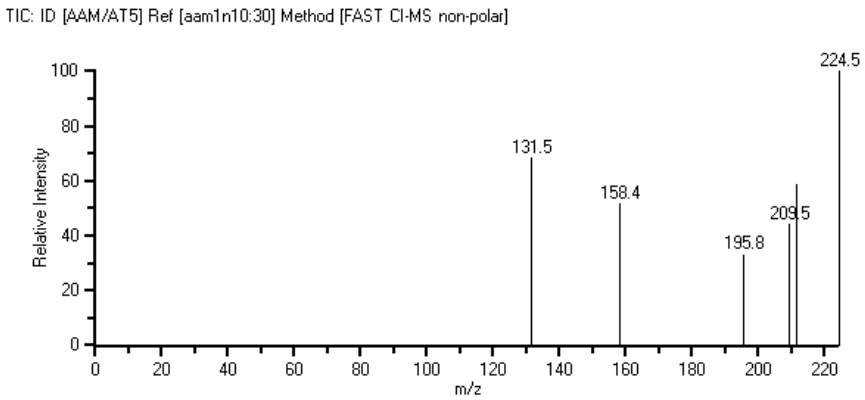


Fig. 1: Mass spectrum for compound (III)

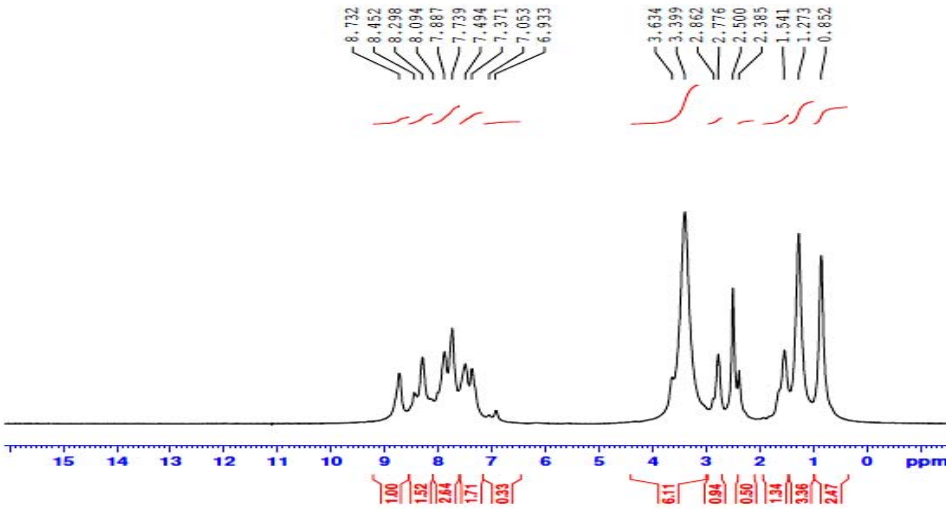


Fig. 2: ^{1}H-NMR spectrum for compound (Vi)

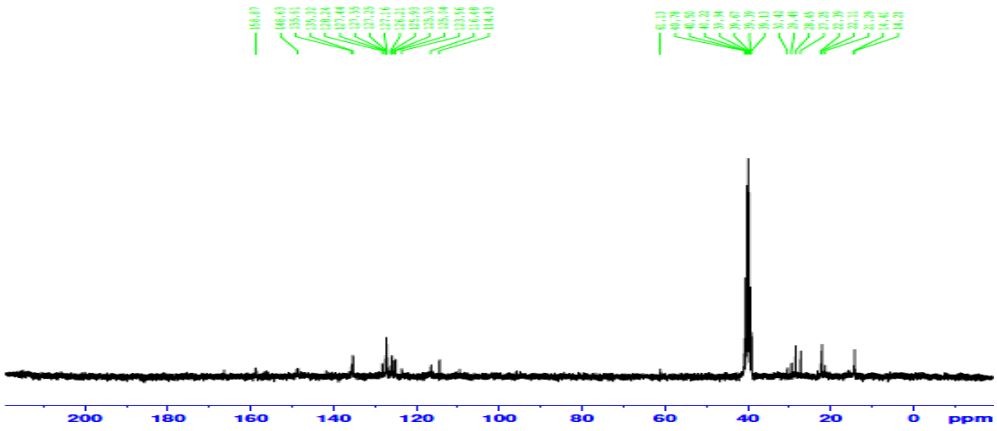


Fig. 3: ^{13}C-NMR spectrum for compound (Vi)

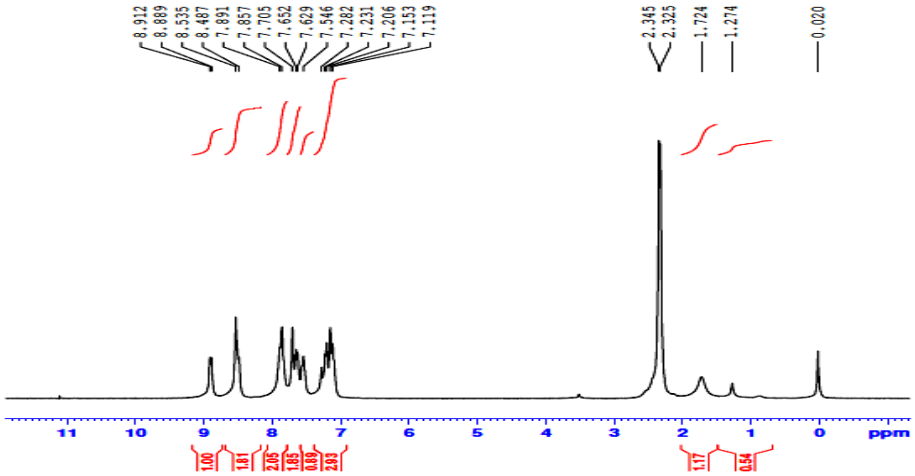


Fig. 4: 1H-NMR spectrum for compound (Vc)

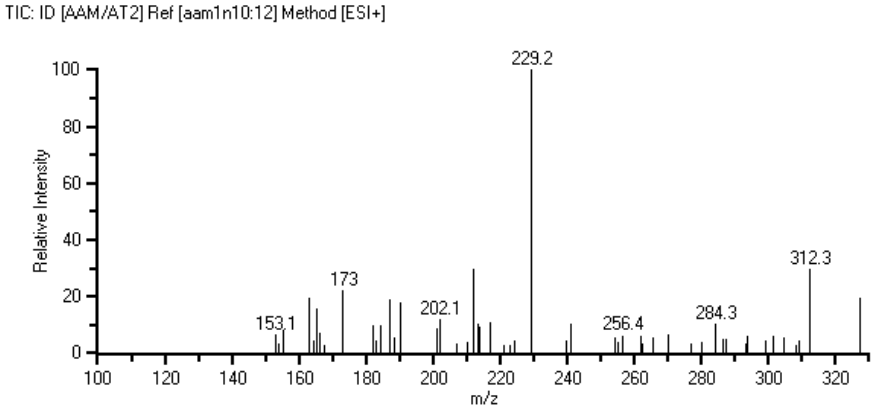


Fig. 5: Mass spectrum for compound (Vc)

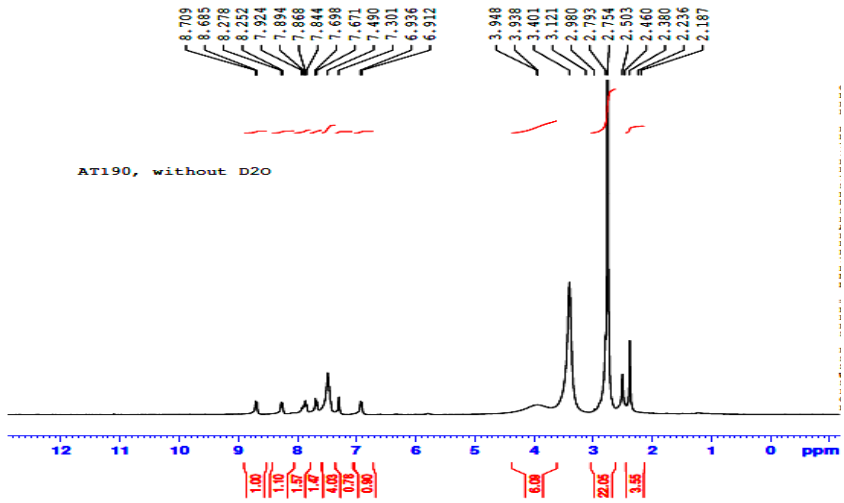


Fig. 6: ^{1}H-NMR spectrum for compound (VI)

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