Synthesis and Characterization of Some New Schiff Base Derivatives from 4-Nitro-*o*-Phenylene diamine

Afaq A.Turki[*]

*Chemistry Department Collage Of Science University Of Basrah , Iraq

Abstract

Many Schiff bases were prepared by condensation reaction of 4-nitro-o-phenylenediamine with benzaldehyde and some of its o-substituted derivatives in alcohol medium. All the ompounds were characterised by C.H.N. elemental analysis, FT-IR and ^{1}H NMR spectroscopy.

الخلاصة :

تم تحضير خمس مركبات جديدة ثنائية الايمين من خلال تفاعل 4- نايترو- اورثو- فنيلين ثنائي الامين مع البنزالديهايد وبعض مشتقاته المعوضة في الموقع أورثو. وتم تشخيص تلك المركبات بأستخدام تحليل العناصر الدقيق ومطيافية الاشعة تحت الحمراء ومطيافية الرنين النووي المغناطيسي للبروتون.

1. Introduction

Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, *e.g.*, biological, inorganic and analytical chemistry [1-5]. Application of many new analytical devices requires the presence of organic reagents as essential compounds of the measuring system. They are used, *e.g.*, in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhance selectivity and sensitivity [6-8].

Among the organic reagents actually used, Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties [9,10].

Schiff bases are widely applicable in analytical determination, using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed (determination of compounds with an amino or carbonyl group); using complex formation reactions (determination of amines, carbonyl compounds and metal ions); or utilizing the variation in their spectroscopic characteristics following changes in pH and solvent (pH of solvent polarity indicators) [1,11-13].

Unfortunately, most Schiff bases are chemically unstable and show a tendency to be involved in various equilibria, like tautomeric interconversions, hydrolysis, or formation of ionized species [14,15]. Therefore, successful application of Schiff bases requires a careful study of their characteristics.

Schiff bases of *o*-phenylenediamine derivatives have a variety of applications including biological [16], clinical [17] and analytical [18]. For many years particular attention has been paid to the synthesis and study of diimino-Schiff bases. Schiff bases are used as substrates in the preparation of a number of industrial and biologically active compounds via ring closure, cycloaddition and replacement reactions [19].

2. Expermental methods

2.1 General:

Melting points were uncorrected. NMR spectra were acquired with a Bruker Ultra Shield (^{1}H : 300 MHz) (University of AL-al-Bayt,Jordan). The chemical shifts were referenced to tetra methyl silane (TMS) as an internal standard. The elemental analysis were performed by using Euro Vector EA3000A (University of AL-al-Bayt,Jordan).

2.2 Synthesis of diimines:

General procedure:

(0.01 mole) of 4-nitro-o-phenylenediamine (1) was disolved in absolute ethanol. Then, (0.02 mole) of benzaldehyde and its derivatives (2-6) were added and heated under reflux for (3) hrs. Then, the mixture was cooled in an ice bath for 2 hrs and yielded different coloured crystals. The residue was purified by recrystallization from benzene.

N^1,N^2-dibenzylidine-4-nitrobenzene-1,2-diamine (2)

Was prepared from 4-nitro-o-phenylenediamine with benzaldehyde 80 % yield ; m.p. (195-198)^{o}c; CHN analysis for $C_{20}H_{15}N_3O_2$; C 72.94; H 4.59; N 12.76 Found; C 72.86; H 4.54; N 12.69,. FT-IR spectra $\upsilon(cm^{-1})$ 1623 cm^{-1} (C=N). $\delta_H(CDCl_3)$ 8.753 ppm(2H,s,j); (8.243-8.272) ppm (1H,d,b); 7.591 ppm (1H,s,c); (7.080-7.384) ppm (11H,m,a,d,e,f,g,h).

N^1,N^2-bis(2-methylbenzylidine)-4-nitrobenzene-1,2-diamine (3)

Was prepared from 4-nitro-o-phenylenediamine with 2-methylbenzaldehyde 79 % yield ; m.p. (196-198)^{o}c; CHN analysis for $C_{22}H_{19}N_3O_2$; C 73.93; H 5.36; N 11.76 Found; C 73.85; H 5.28; N 11.66. FT-IR spectra $\upsilon(cm^{-1})$ 1641 cm^{-1} (C=N). $\delta_H(CDCl_3)$ 8.753 ppm(2H,s,j); (8.243-8.272) ppm (1H,d,b); 7.591 ppm (1H,s,c); (7.080-7.384) (9H,m,a,d,e,f,g); 2.000 ppm (6H,s,h).

N^1,N^2-bis(2-hydroxybenzylidine)-4-nitrobenzene-1,2-diamine (4)

Was prepared from 4-nitro-o-phenylenediamine with 2-hydroxybenzaldehyde 75 % yield ; m.p. (183-185)^{o}c; CHN analysis for $C_{20}H_{15}N_3O_4$; C 66.48 ; H 4.18; N 11.63 Found; C 66.38; H 4.09; N. 11.55 FT-IR spectra $\upsilon(cm^{-1})$ 1616 cm^{-1} (C=N). $\delta_H(CDCl_3)$ 11.202 ppm (2H,s,h); 8.754 ppm (2H,s,j); (8.255-8.264) ppm (1H,d,b); 8.166 ppm (1H,s,c); (7.418-7.481) ppm (9H,m,a,d,e,f,g); 7.282 ppm (s,CDCl$_3$).

**N^1,N^2-bis(2-chlorobenzylidine)-4-nitrobenzene-1,2-diamine (5)**

Was prepared from 4-nitro-o-phenylenediamine with 2-chlorobenzaldehyde 84 % yield ; m.p. (136-138)^{o}c; CHN analysis for $C_{20}H_{13}N_3O_2Cl_2$; C 60.32; H 3.29; N 10.55 Found; C 60.23; H 3.19; N. 10.48 FT-IR spectra $\upsilon(cm^{-1})$ 1606 cm^{-1} (C=N). $\delta_H(CDCl_3)$ 9.115 ppm (2H,s,j); (8.230-8.255) ppm (1H,d,b); 7.847 ppm (1H,s,c); (7.459-7.567) ppm (9H,m,a,d,e,f,g); 7.280 ppm (s,CDCl$_3$).

**N^1,N^2-bis(2-nitrobenzylidine)-4-nitrobenzene-1,2-diamine (6)**

Was prepared from 4-nitro-o-phenylenediamine with 2-nitrobenzaldehyde 89 % yield ; m.p. (197-198)^{o}c; CHN analysis for $C_{20}H_{13}N_5O_6$; C 57.28; H 3.12; N 16.70 Found; C 57.20; H 3.11 ; N 16.62. FT-IR spectra $\upsilon(cm^{-1})$ 1618 cm^{-1} (C=N). $\delta_H(CDCl_3)$ 9.115 ppm(2H,s,j); (8.230-8.255) ppm (1H,d,b); (7.859- 7.967) ppm (10H,m,a,c,d,e,f,g); 7.280 ppm (s,CDCl$_3$).

3. Results and Discussion:

Treatment of 4-nitro-o-phenylenediamine (1) with benzaldehyde and its derivatives (2-6) in boiling ethanol gave, after purification by recrystallization from benzene, pure diimino derivatives in (75-89)% yield,as crystalline compounds, as shown in scheme 1. The structures of these products were established from their elemental analysis,FT-IR,C.H.N and ^{1}H NMR spectra.All the IR spectra of diimine showed a peak at (1606-1641) cm^{-1} which appeared due to (C=N) stretching. The^{1}H NMR spectra are represented in figures (1-5). All the ^{1}H NMR spectra of dimeric imine were characterized [20-22] by the presence of protons of at δ= (8.753-9.115) ppm, since the CH$_3$ protons appeared at δ= 2.000 ppm. The OH protons appeared at δ= 11.202 ppm. The aromatic protons rings showed doublet signal in the region δ= (8.230-8.272) ppm due to protons at b position. The other protons at c position for this rings showed singlet signal within the range (7.591-8.166) ppm. While protons at a,d,e,f,g,h for this rings showed multiplet signals within the range (7.080-7.967) ppm.
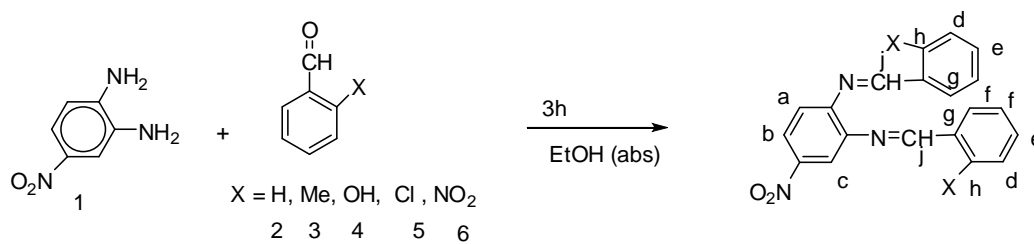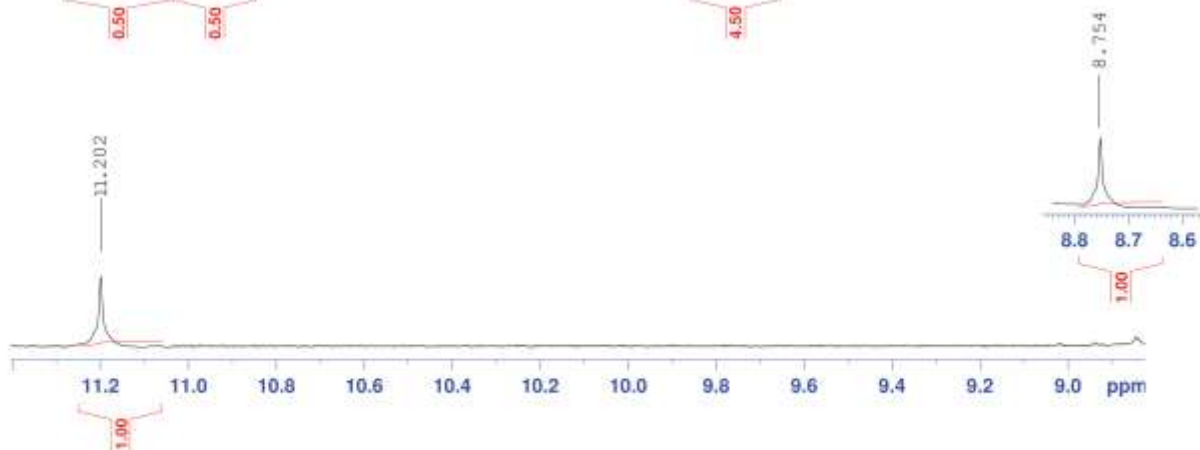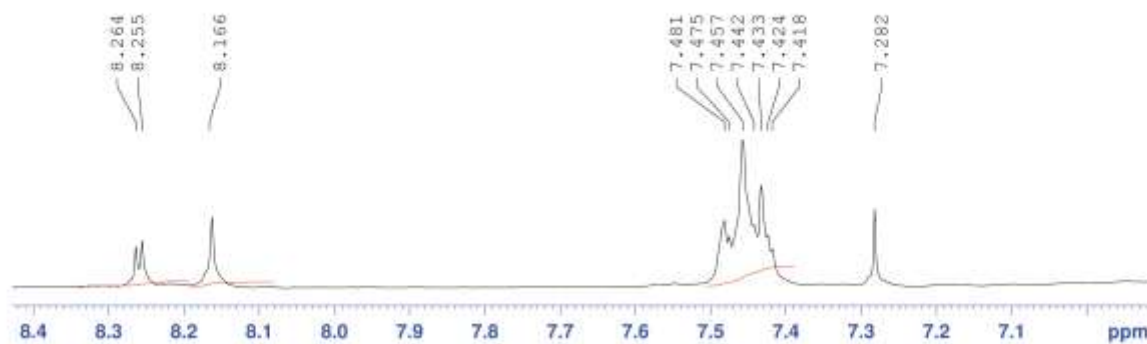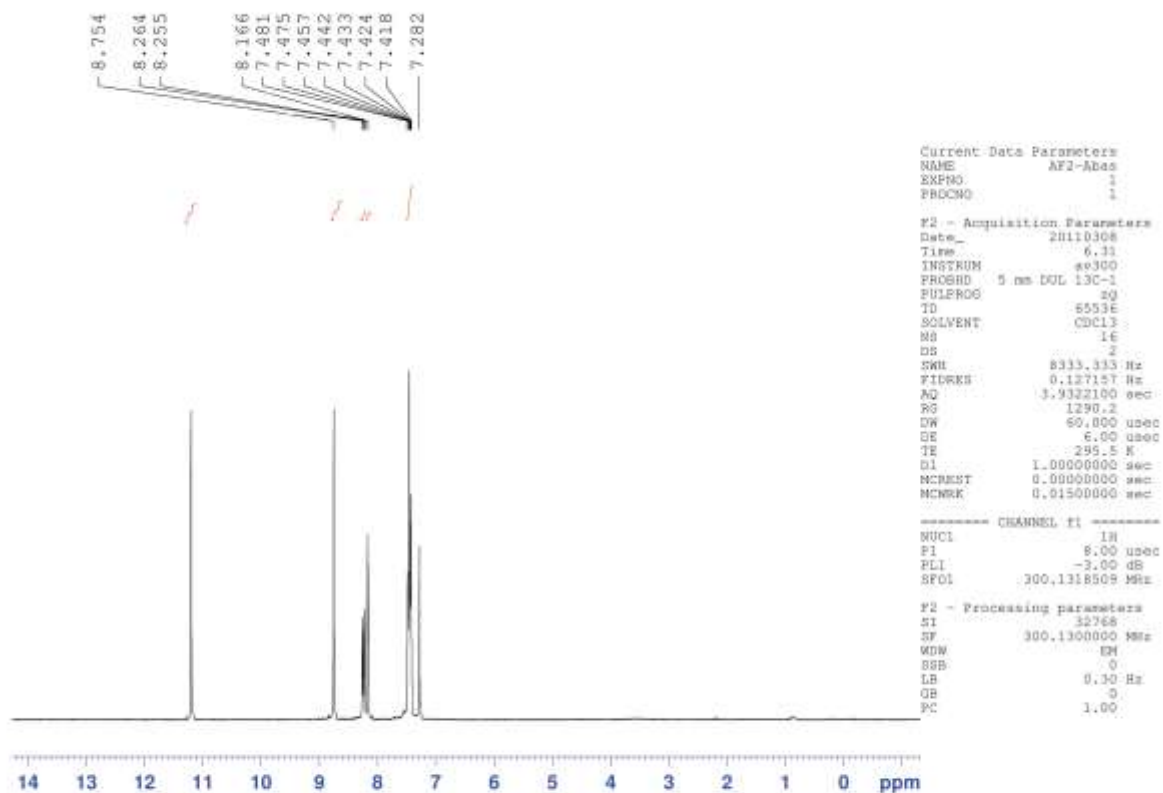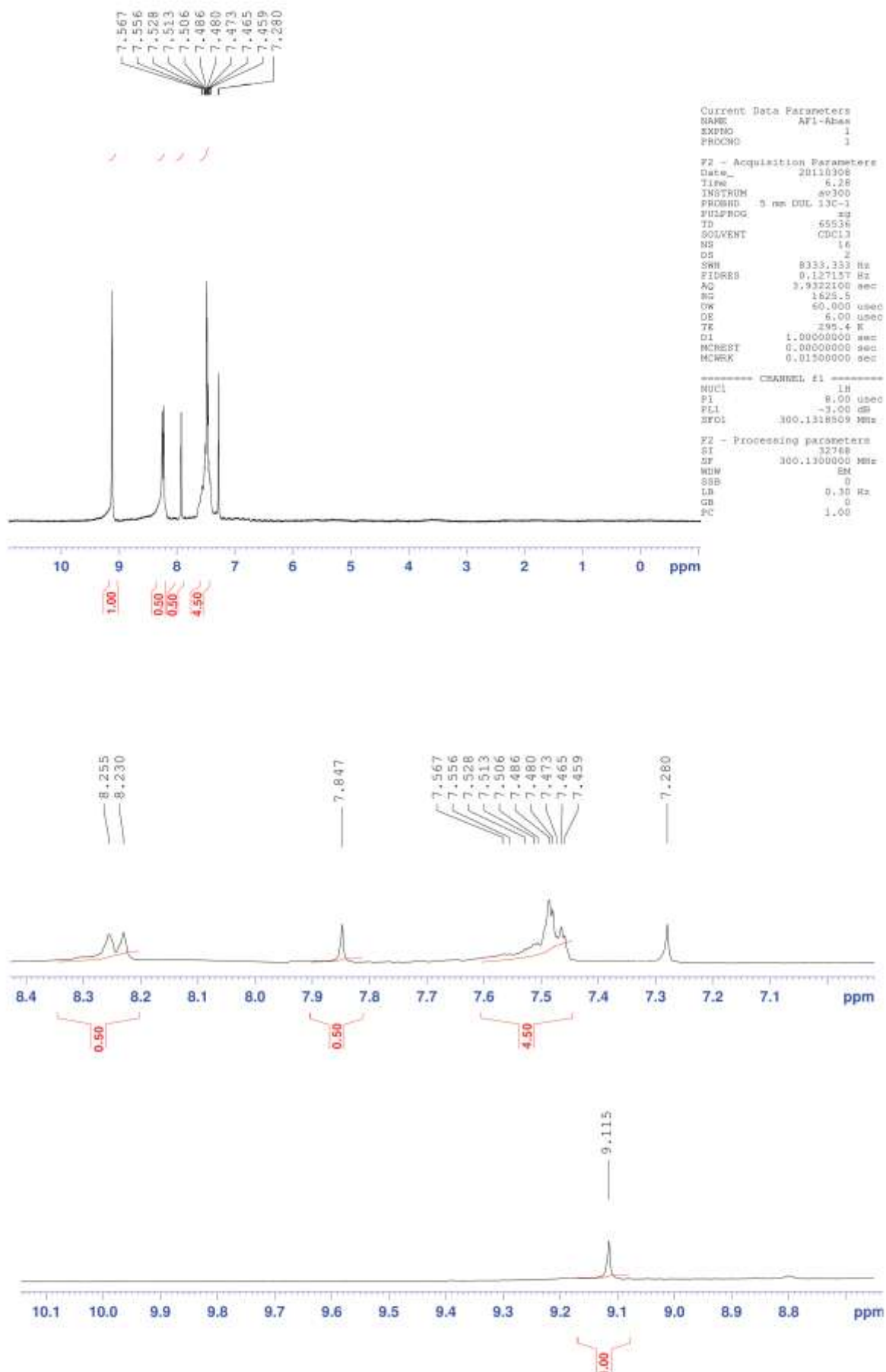
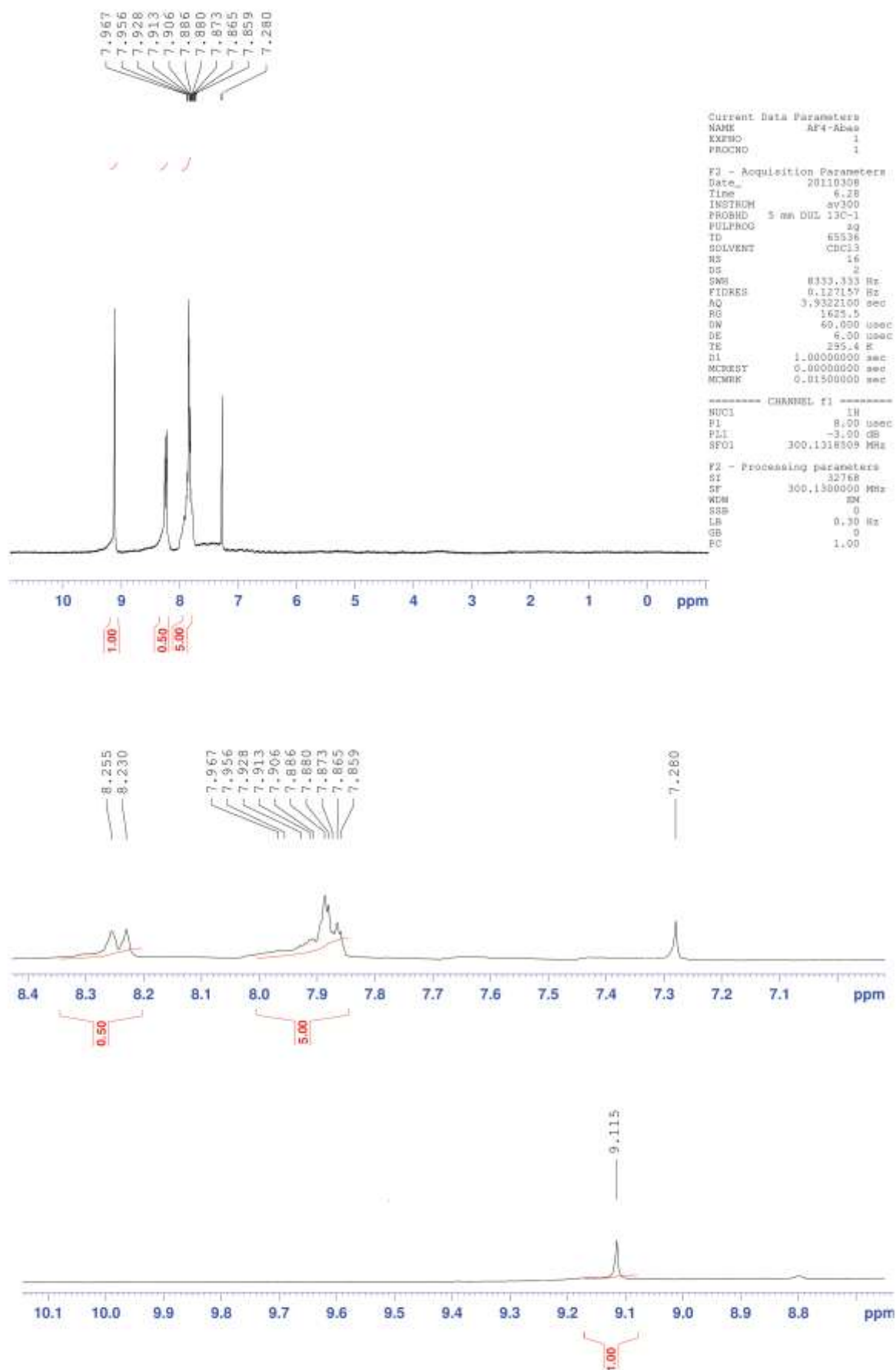**Scheme 1**
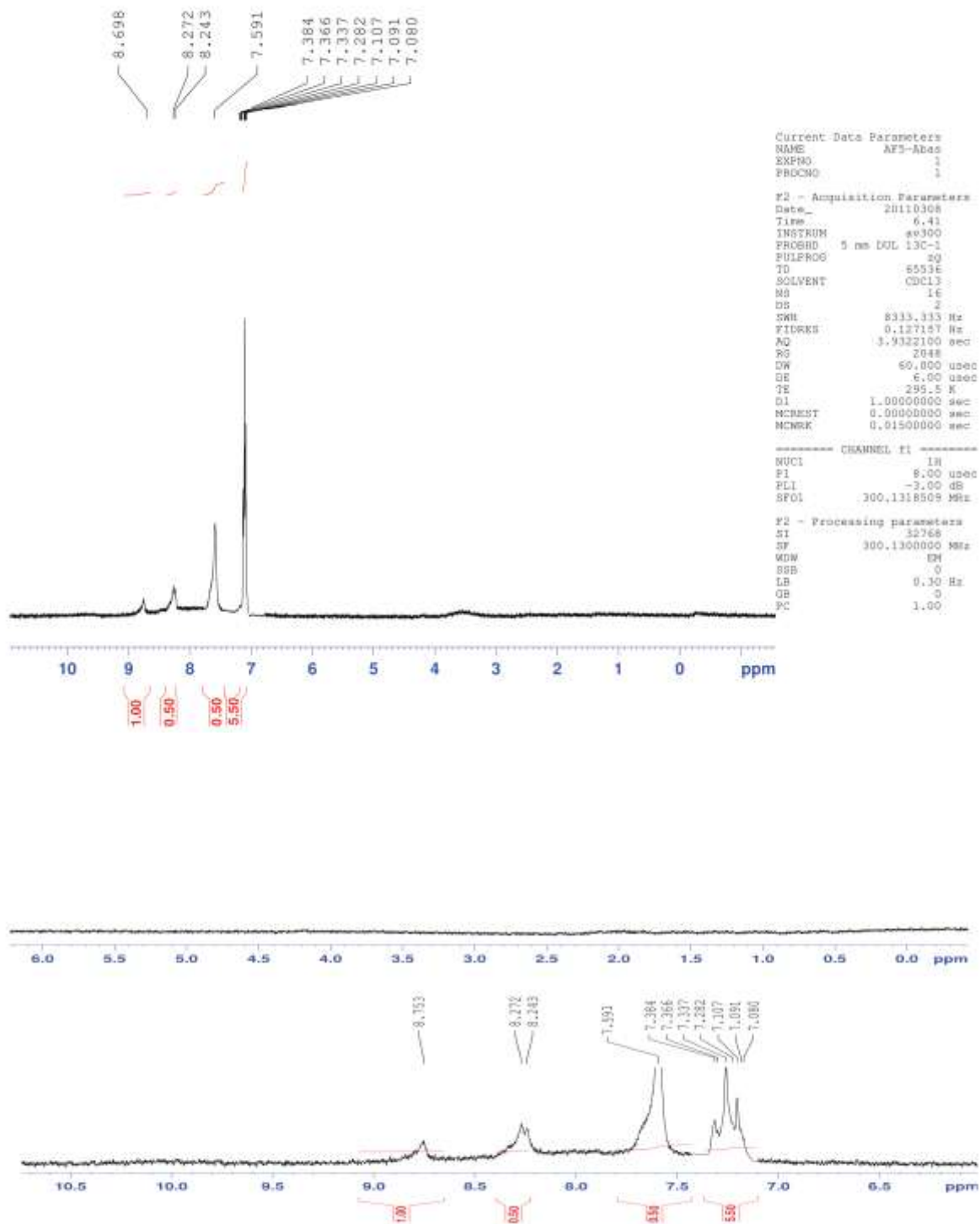
Figure (1) : ¹H NMR spectrum of diimine (2)
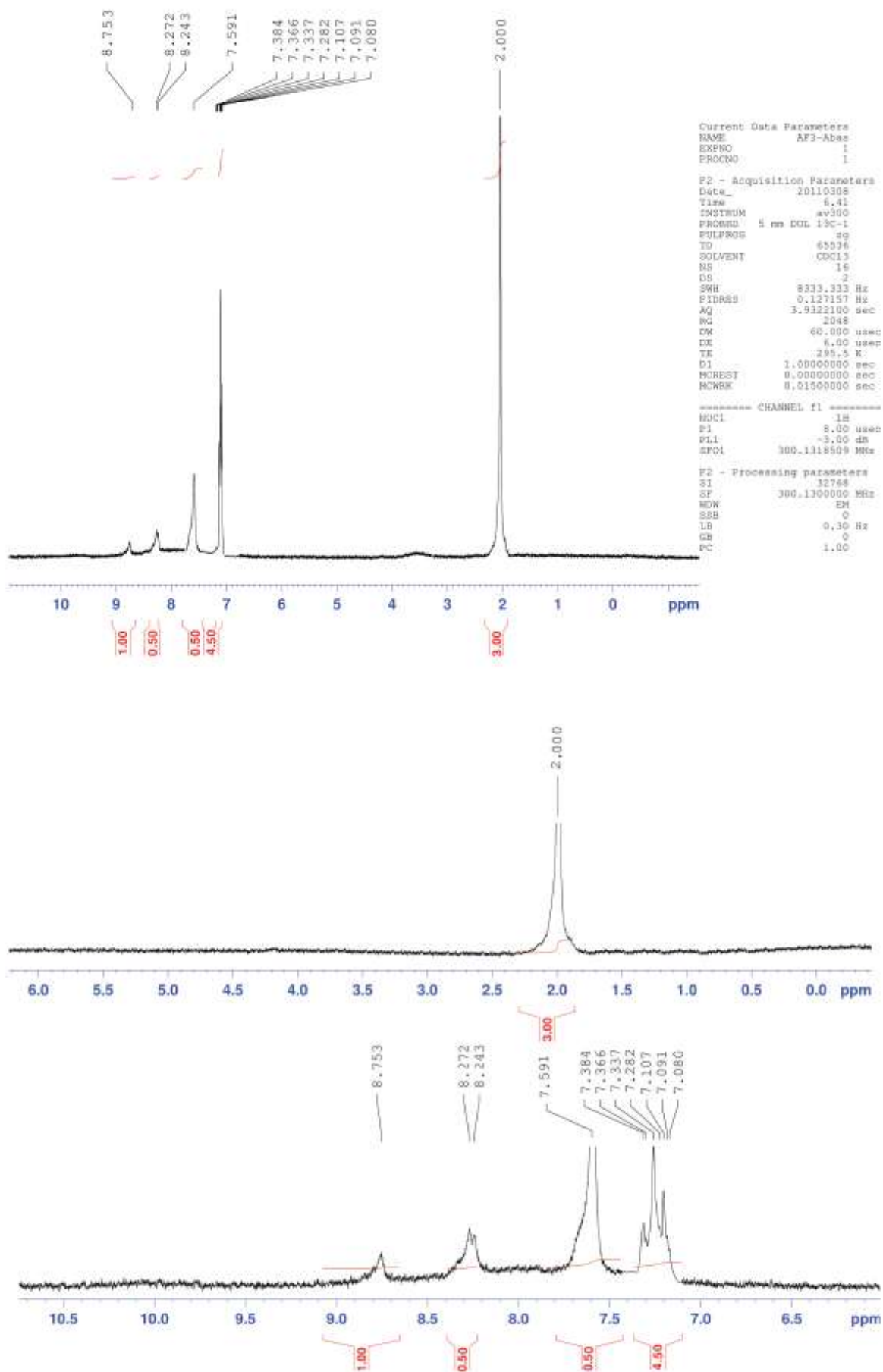
Figure (2) : ¹H NMR spectrum of diimine (3)

Figure (3) : ^{1}H NMR spectrum of diimine(4)

Figure (4) : ¹H NMR spectrum of diimine(5)

Figure (5) : ^{1}H NMR spectrum of diimine (6)

References :

1. Cimerman Z, Miljanic S, and Galic N, *Croatica Chemica Acta*, 2000, 73 (1), 81.
2. Singh P, Goel R L and Singh B P, *J. Indian Chem. Soc.*, 1975, 52, 958.
3. Perry B F, Beezer A E, Miles R J, Smith B W, Miller J and Nascimento M G,*Microbois*., 1988, 45, 181.
4. Elmali A, Kabak M and Elerman Y, *J. Mol. Struct.*, 2000, 477, 151.
5. Patel P R, Thaker B T and Zele S, *Indian J. Chem.*, 1999, 38 A, 563.
6. Valcarcel M and Laque de Castro M D, "*Flow-Throgh Biochemical Sensors*",Elsevier, 1994, Amsterdam.
7. Spichiger-Keller U, "Chemical Sesors and Biosensors for Medical and BiologicalApplications", Wiley-VCH, 1998, Weinheim.
8. Lawrence J F and Frei R W, "Chemical Derivatization in Chromatography",Elsevier, 1976, Amsterdam.
9. Patai S Ed., *"*The Chemistry of the Carbon-Nitrogen Double Bond", J. Wiley &Sons, 1970, London.
10. Jungreis E and Thabet S, "Analytical Applications of Schiff bases", Marcell Dekker, 1969, New York.
11. Metzler C M, Cahill A and Metzler D E, *J. Am. Chem. Soc.*, 1980, 102, 6075.
12. Dudek G O and Dudek E P, *Chem. Commun.*, 1965. 464.
13. Dudek G O and Dudek E P, *J. Am. Chem. Soc.*, 1966, 88, 2407.
14. Cimerman Z and Stefanac Z, *Polyhedron*, 1985, 4, 1755.
15. Galic N, Cimerman Z and Tomisic V, *Anal. Chim. Acta*, 1997, 343, 135.
16. Singh P, Goel R L and Singh B P *J. Indian Chem. Soc.,* 1975,52, 958
17. Mahindra A M, Fisher J M and Rabinovitz *Nature (London),* 1983, 303, 64
18. Palet P R, Thaker B. T. and Zele S. *Indian J. Chem.,* 1999,A38, 563
19. M. A. Baseer, V. D. Jadhav, R. M. Phule, Y. V. Archana, Y. B. Vibhute, *Orient. J. Chem.,* 2000, *16*, 553.
20. Silverstien R.M., Webster F.X., Kiemle D.J., Spectrometric Identification of Organic Compounds, sixth ed., John Wiley and Sons, 2005, New Yourk, USA.
21. Cooper J.W., Spectroscopic Techniques for Organic Chemistry, John Wiley and Sons, 1980,New Yourk, USA.
22. Shriner R.L., Hermann C.K., Spectroscopic Techniques for Organic Chemistry, John Wiley and Sons, 2004,New Yourk, USA.