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Synthesis and Characterization of Some New Schiff bases Derived from ferrocene compounds

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Abstract

Two series of Schiff base compounds were synthesized, first series synthesized by the condensation of carbonyl ferrocene derivatives with 1,6-diaminohexane in alcohol medium. The second series synthesized by the condensation of carbonyl ferrocene derivatives with 1,4-diaminobenzene in alcohol medium. All the compounds were characterized by C.H.N. elemental analysis, FT-IR and ^{1}H NMR spectroscopy

الخلاصة :

تم تحضيرسلسلتين من مركبات ثنائية الايمين الجديدة أذ تضمنت السلسلة الاولى تحضير ثلاث مركبات جديدة من خلال تفاعل مشتقات الكاربونيل للفروسين مع 1و6- ثنائي امينو هكسان , اما السلسلة الثانية فتضمنت تحضير ثلاث مركبات جديدة من خلال تفاعل مشتقات الكاربونيل للفروسين مع 1و4- ثنائي امينو بنزين. وتم تشخيص تلك المركبات بأستخدام تحليل العناصر الدقيق ومطيافية الاشعة تحت الحمراء ومطيافية الرنين النووي المغناطيسي للبروتون.

1. Introduction

One of the most attractive research areas in chemistry for recent years has involved studying the compounds which posses direct, more or less polar bonds between metal and carbon atoms. The field of organometallic chemistry and inorganic chemistry and has lead to many important applications in synthetic community[1,2].

Chemistry is increasingly influenced by biology as a result of advances in our understanding of the chemical basis of live[3]. Therefore, organometallic chemistry is beginning to make links with biochemistry. Now, it is clear that organometallic species also occour in biology, both as stable species and reaction intermediates.

Most organometallic compounds are thought to be inherently sensitive to water and oxygen, which are substances essential for biology. However, as researchers went deeper into organometallic chemistry, the began to realize that much of this field is compatible with biology. The discovery that certain inorganic complexes such as cis-platin are effective against testicular cancer has led to increase in research on metal complexes as drugs[4].

Metallocenes are organometallic compounds which consist of a metal between two planar polyhapto rings[5]. They are informally called "Sandwich compounds".

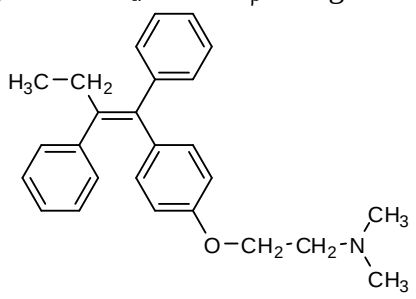
One of the ligands encountered in metallocenes is cyclopentadienyl. The cyclopentadienyl ligand (C_5H_5) has played a major role in the development of organometallic chemistry and huge number of metal cyclopentadienyl compounds are known today.

Ferrocene is $(C_5H_5)_2Fe$ is one of the well-known and most popular organometallic compounds[6]. Fortunately, ferrocene is the most stable member of the metallocene series and is not attacked by air or water[7].

Ferrocene does not appear any biological activity even if it is solubilized in water[8]. There are some other methods in the literature to overcome the water solubility problem of ferrocene derivatives. First method is to create a salt form on the organic residue of ferrocene moiety and the second one is to form salt through oxidation of central iron atom.

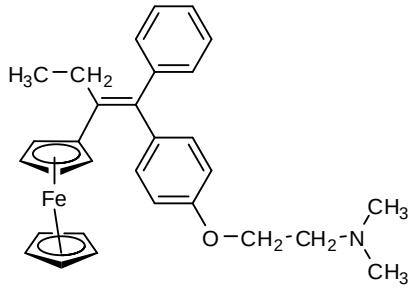
Tamoxifen (1) exhibits antitumor activity breast cancer cells that are mediated ER_α estrogen receptors[9]. However, it is not effective on cancer cells that are mediated by ER_β estrogen receptor. In 2002, Jaouen and Coworkers have investigated tomoxifen analogs that contain an organometallic

moiety. When the phenyl group, which is germinal to ethyl group in tomoxifen, is replaced by ferrocenyl group, resulting ferrocifens (2) exhibit a strong effect against Brest cancer cells that are mediated by both ER_α and ER_β estrogen receptors[10].



(1)

tamoxifens



(2)

ferrocifens

Schiff bases derived from the reaction of aromatic aldehydes and aliphatic or aromatic primary amines represent an important series of widely-studied organic ligands. The chemistry of Schiff bases is a field that is being noticed. These compounds and their metal complexes had a variety of applications, including biological [11-14], clinical [15-18], analytical [19-22] and industrial [23]. They also play important roles in catalysis [24-30]. In 2010, GaJendra Kumar et al[31]., studied antimicrobial activity of trivalent metal new Schiff base complexes derived from 2-amino-4-ethyl-5-hydroxybenzaldehyde and thiocarbohydrazide. This ligand and the complexes were also tested for their antimicrobial activity (against the bacteria *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Bacillus megaterium*, and the fungi *Kluyveromyces fragilis*, *Rhodotorula rubra*, *Candida albicans* and *Trichoderma reesei*) to assess their inhibiting potential. An attempt was also made to correlate the antimicrobial activity with the geometry of the complexes. All complexes were found to be less active against the pathogens *E. coli*, *S. aureus* and *P. aeruginosa*. The Cr(III) complex showed the best antimicrobial activity, but the ligand alone was found to be active against the fungus *T. reesei*.

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:

Potassium carbonate (7mmol), diamine derivatives (7mmol), carbonyl ferrocene derivatives (14 mmol) and dry methanol (15) ml were placed in a round bottom flask with reflux condenser and the mixture was refluxed 6 hours. At the end, the solvent were removed on a rotary evaporator. The crude product was recrystallized from ethyl alcohol to form different color crystals as a pure solid.

1,10-diferrocene-2,9-diazadeca-1,9-diene (5)

Was prepared from ferrocenecarbaldehyde with 1,6-diaminohexane 80 % yield ;oily ; CHN analysis for $C_{28}H_{32}N_2Fe_2$; C 66.17; H 6.35; N 5.51 Found; C 66.08; H 6.26; N 5.49, FT-IR spectra (KBr pellet) $\upsilon(cm^{-1})$ 1585 cm^{-1} (C=N). $\delta_H(CDCl_3)$ 7.711 ppm(2H,s,imino group); 7.281 (s, $CDCl_3$) (6.211-6.481) ppm (18H,m,cyclopentadienyl group); (1.581-1.681) ppm (4H,t,CH_2); (0.659-0.728) ppm (8H,m,CH_2).

1,10-diferrocene-2,9-diazadeca-1,10-dimethyl-1,9-diene (6)

Was prepared from 2-acetylferrocene with 1,6-diaminohexane 73 % yield ; oily; CHN analysis for $C_{30}H_{36}N_2Fe_2$; C 67.19; H 6.77; N 5.22 Found; C 67.10; H 6.72; N 5.13. FT-IR spectra (KBr pellet) $\upsilon(cm^{-1})$ 1585 cm^{-1} (C=N). $\delta_H(CDCl_3)$ 7.281 (s, $CDCl_3$) ; (6.211-6.481) ppm (18H,m,

cyclopentadienyl group); 2.175 ppm (6H,s,CH_3) (1.581-1.681) ppm (4H,t,CH_2); (0.659-0.728) ppm (8H,m,CH_2).

1,10-diferrocene-2,9-diazadeca-1,10-diphenyl-1,9-diene (7)

Was prepared from 2-benzoylferrocene with 1,6-diaminohexane 90 % yield ; oily ; CHN analysis for $C_{40}H_{40}N_2Fe_2$; C 72.74 ; H 6.10; N 4.24 Found; C 72.64; H 6.01; N 4.20 FT-IR spectra (KBr pellet) υ(cm^{-1}) 1589 cm^{-1} (C=N). δ_H($CDCl_3$) (7.744-7.750) ppm (4H,d,aromatic); (7.459-7.567) ppm(6H,m,aromatic); 7.280 (s, $CDCl_3$) ; (6.211-6.481) ppm (18H,m, cyclopentadienyl group); (3.010-3.060) ppm (4H,t,CH_2); (1.810-1.880) ppm (4H,quant,CH_2); (1.540-1.620) ppm (4H,quant,CH_2).

N^1,N^4-diferrocenylidenebenzene-1,4-diamine(8)

Was prepared from ferrocenecarbaldehyde with 1,4-diaminobenzene 81 % yield ; m.p. (172-182)^{o}c; CHN analysis for $C_{28}H_{24}N_2Fe_2$; C 67.23; H 4.84; N 5.60 Found; C 67.15; H 4.80; N 5.50 FT-IR spectra (KBr pellet) υ(cm^{-1}) 1623 cm^{-1} (C=N). δ_H($CDCl_3$) 7.711 ppm(2H,s,diimine); 7.281 (s, $CDCl_3$) ;6.821 ppm (4H,s,aromatic); (6.211-6.481) ppm (18H,m, cyclopentadienyl group).

N^1,N^4-bis(1-ferrocenylethylidene)benzene-1,4-diamine (9)

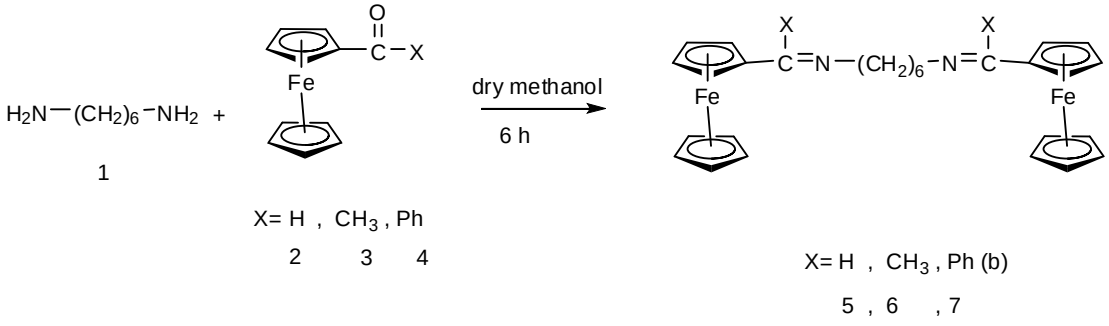
Was prepared from 2-acetylferrocene with 1,4-diaminobenzene 77 % yield ; m.p. 182^{o}c(d); CHN analysis for $C_{30}H_{28}N_2Fe_2$; C 68.21; H 5.34; N 5.30 Found; C 68.11; H 5.25 ; N 5.27. FT-IR spectra (KBr pellet) υ(cm^{-1}) 1683 cm^{-1} (C=N). δ_H($CDCl_3$) 7.281 (s, $CDCl_3$) ; 6.821 ppm(4H,s,aromatic); (6.211-6.481) ppm (18H,m, cyclopentadienyl group); 1.586 ppm (6H,s,CH_3).

N^1,N^4-bis(1-ferrocenyl (phenyl) methylene)benzene-1,4-diamine (10)

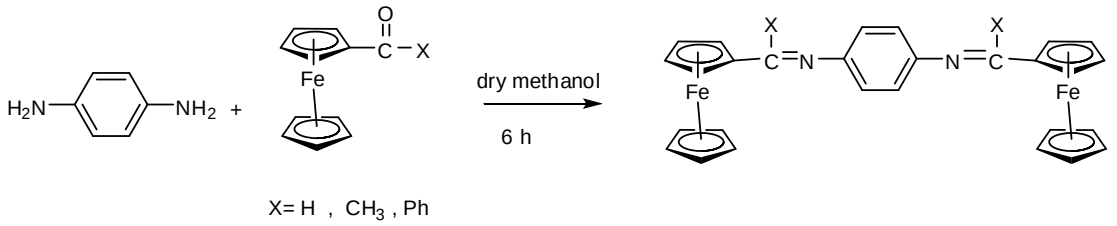
Was prepared from 2-benzoylferrocene with 1,4-diaminobenzene 91% yield ; m.p. (135-137)^{o}c; CHN analysis for $C_{40}H_{32}N_2Fe_2$; C 73.64; H 4.94; N 4.29 Found; C 73.56; H 4.91 ; N 4.20 FT-IR spectra (KBr pellet) υ(cm^{-1}) 1689 cm^{-1} (C=N). δ_H($CDCl_3$) (7.744-7.750) ppm (4H,d,aromatic); (7.459-7.567) ppm(6H,m,aromatic); 7.280 (s, $CDCl_3$) ; 6.821 ppm (4H,s,aromatic); (6.211-6.481) ppm (18H,m, cyclopentadienyl group).

Results and Discussion:

Treatment of diamine derivatives (3,4) with carbonyl ferrocene derivatives (5-10) in boiling methanol gave diimino derivatives, after purification by recrystallization from ethyl alcohol, pure diimino derivatives as shown in (scheme 1,2) in (73-91)% yield. 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 dimeric imine showed a peak at (1585-1689) cm^{-1} which appeared due to (C=N) stretching. All the ^{1}H NMR spectra of diimine were characterized [32,33,34] by the presence of protons of at δ= 7.711 ppm, since the CH_3 protons appeared at δ= (1.586-2.175) ppm.The CH_2 protons showed triplet or quartet or multiplet within the region (0.659-3.060) ppm. The cyclopentadienyl protons showed multiplet signals in the region (6.211-6.481) ppm.The aromatic protons rings b showed doublet signal in the region δ= (7.744-7.750) ppm due to protons at *ortho* position. The other protons at *meta* and *para* positions for this rings showed multiplet signal within the range (7.459-7.567) ppm. While protons at ring a showed singlet signals within the range 6.821 ppm.



Scheme 1

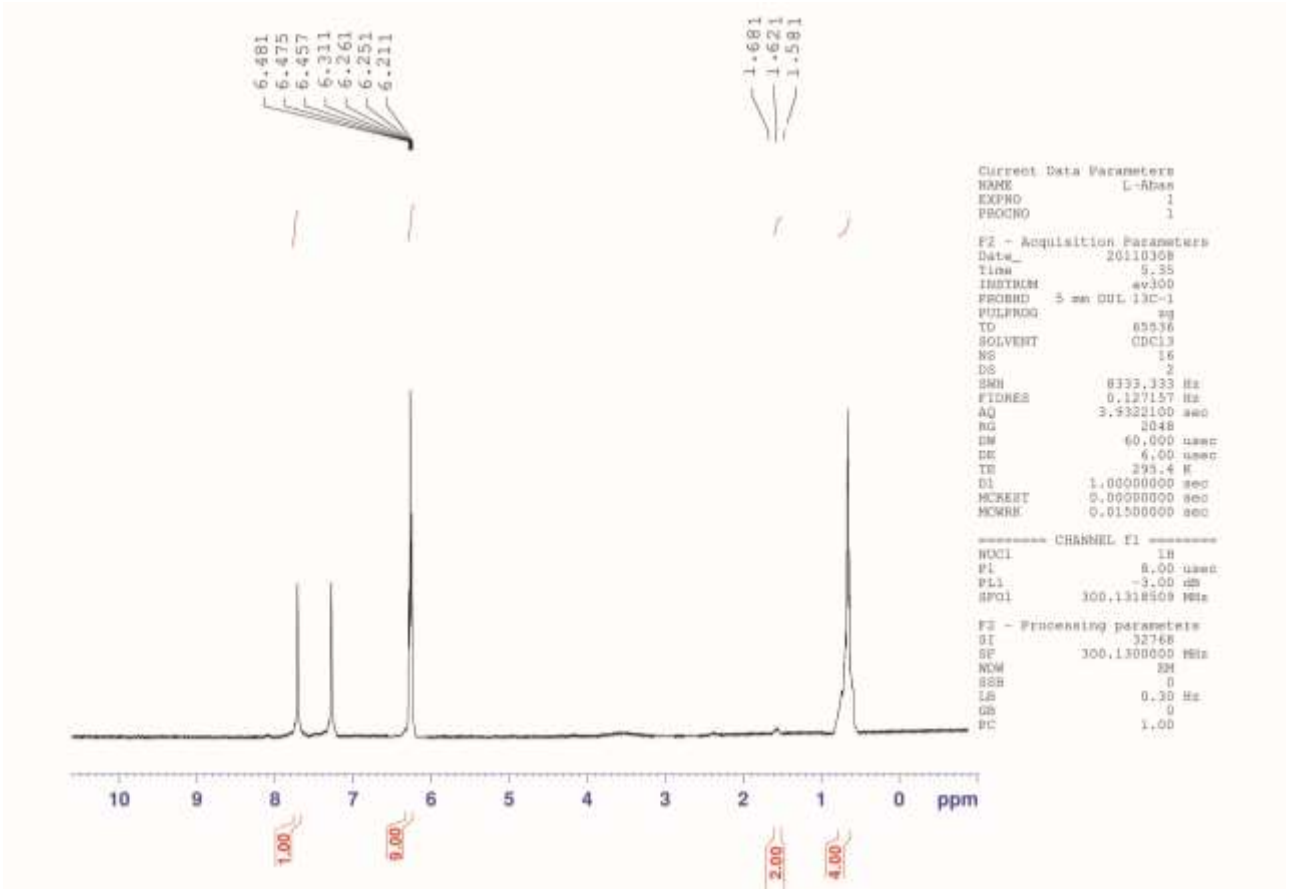


X= H , CH_3 , Ph

X= H , CH_3 , Ph (b)

8 , 9 , 10

Scheme (2)



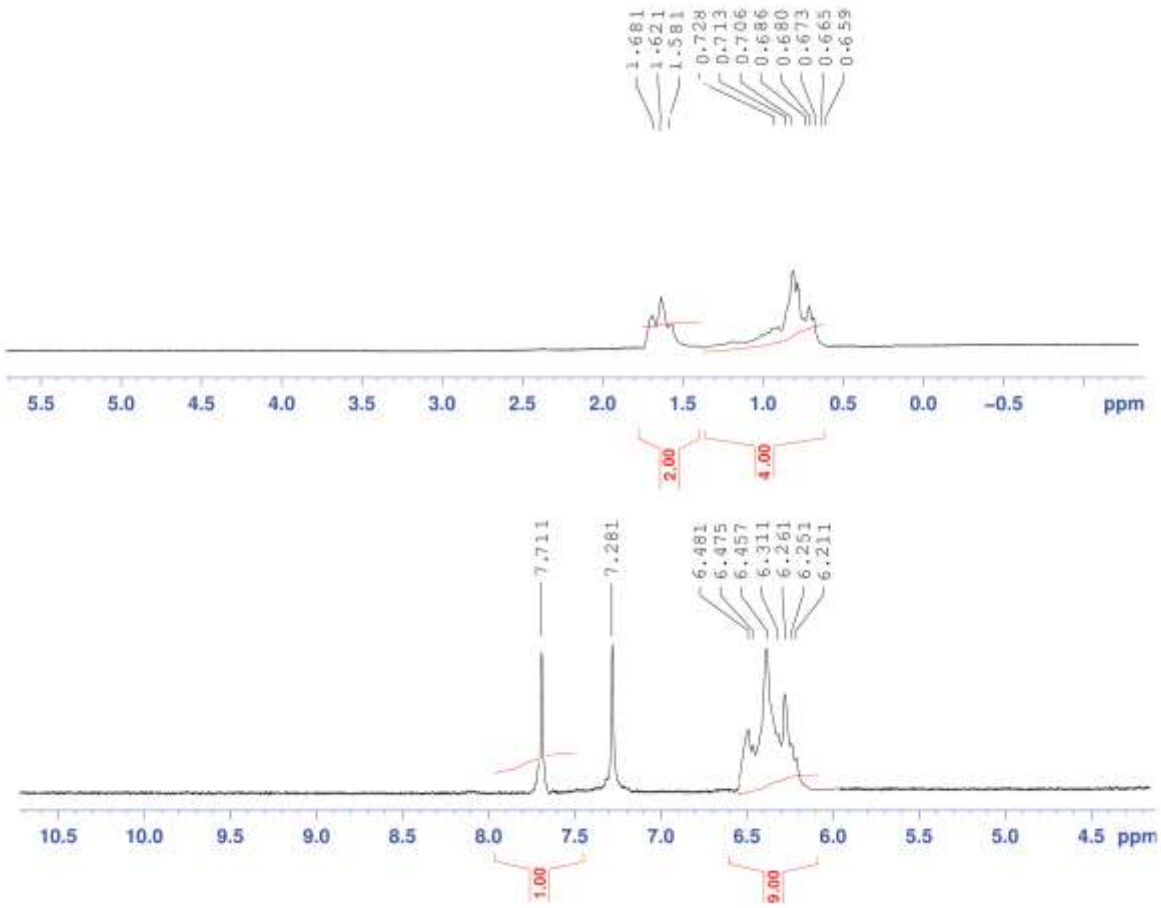
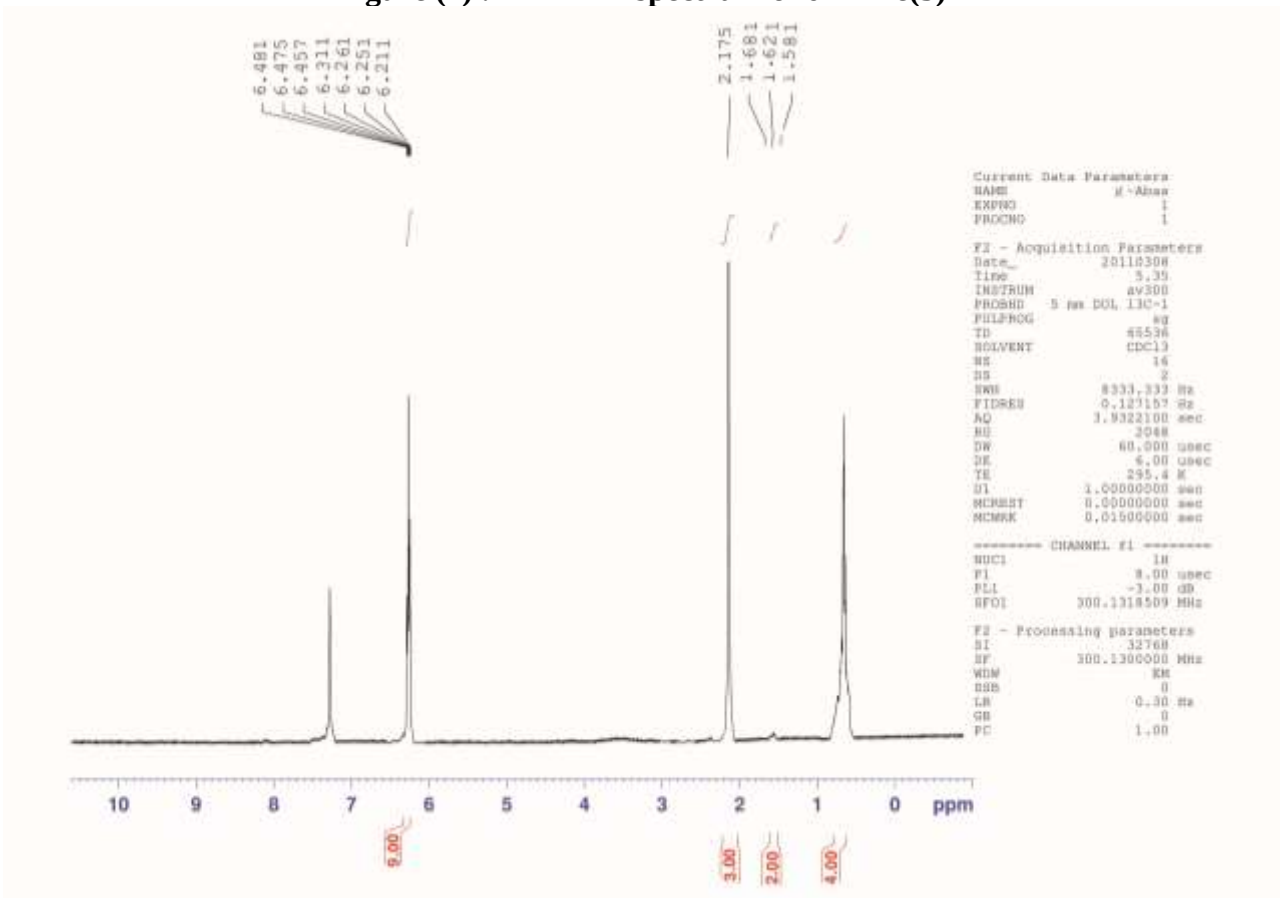


Figure (1) : ^{1}H NMR spectrum of diimine(5)



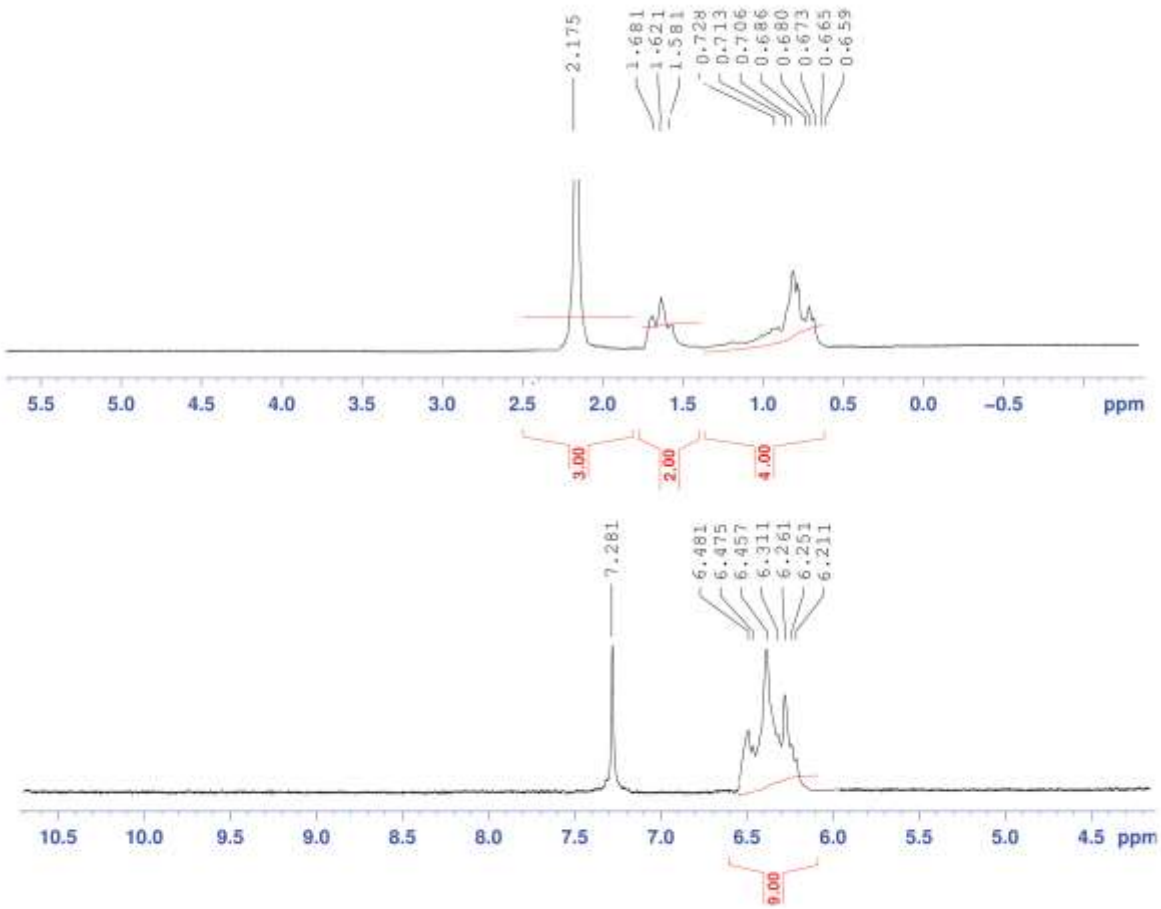
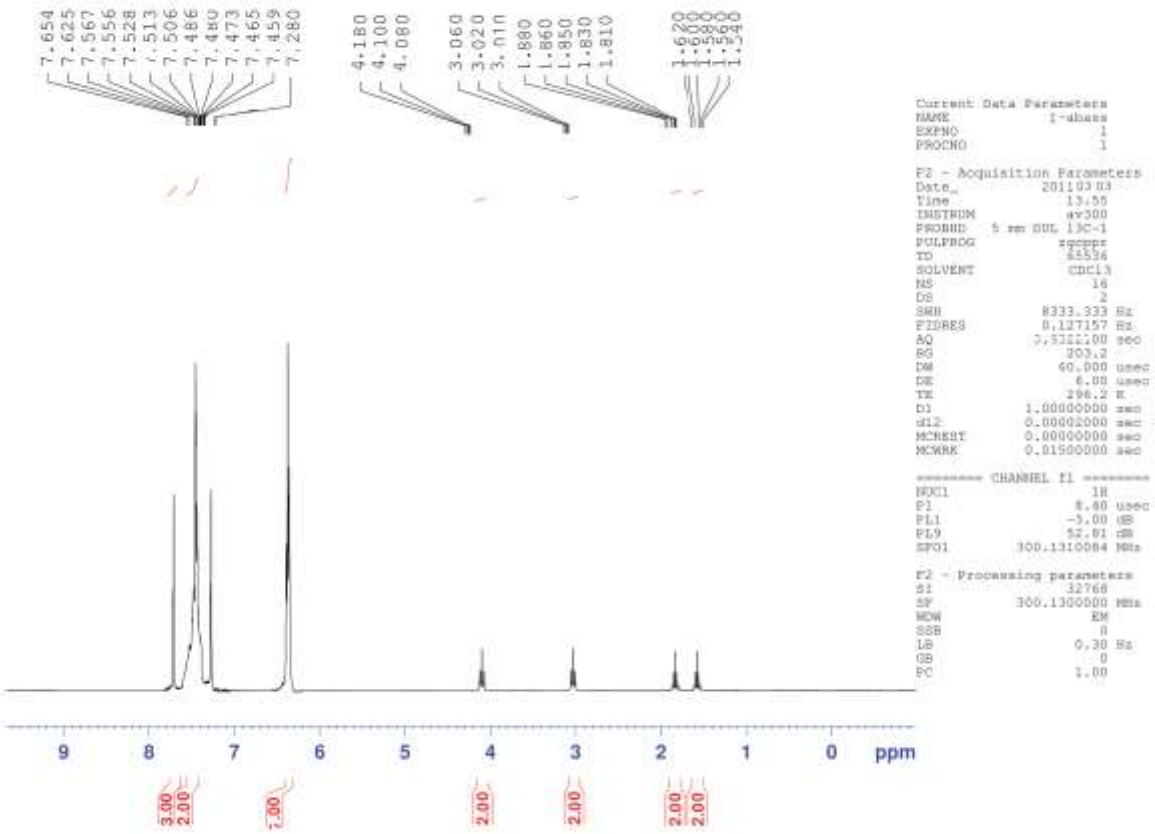


Figure (2) : ^{1}H NMR spectrum of diimine(6)



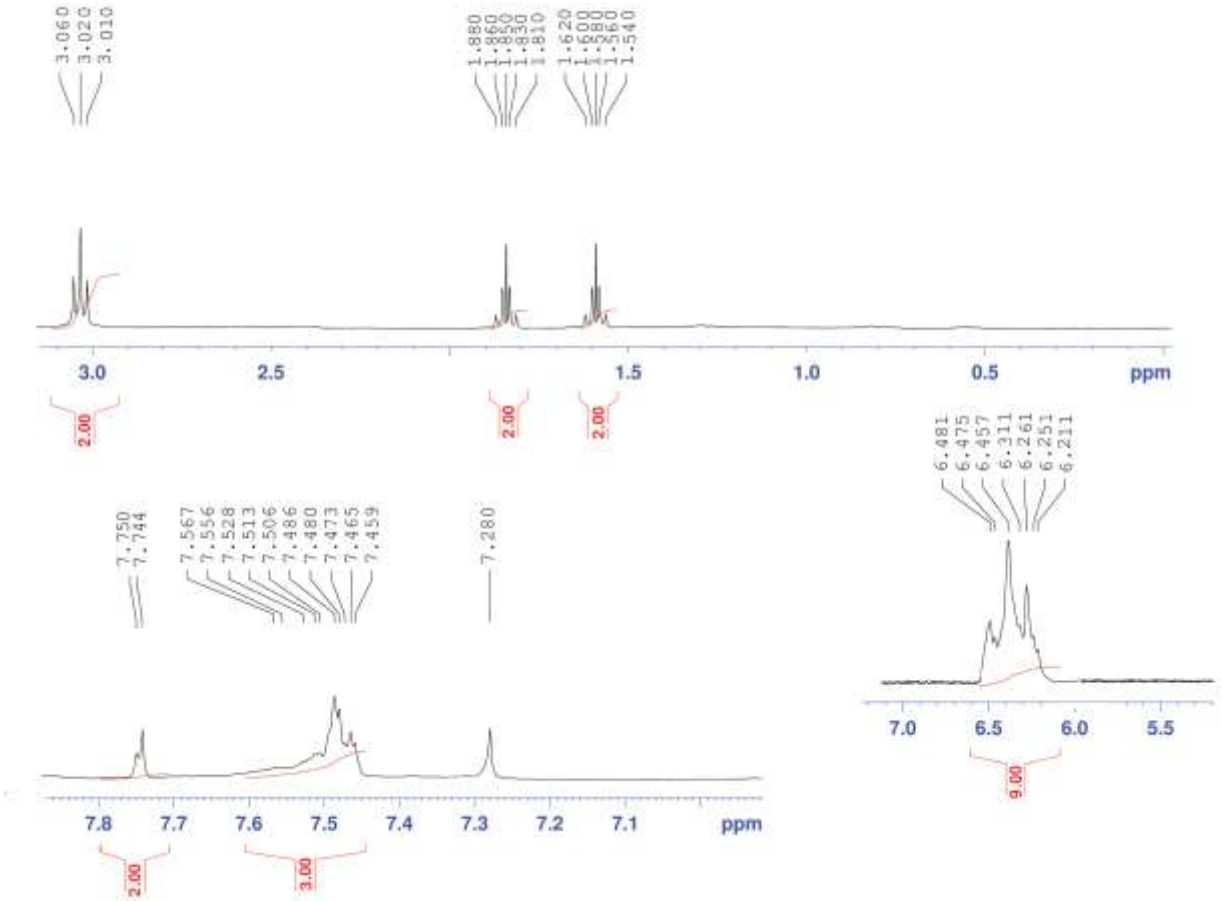


Figure (3) : ^{1}H NMR spectrum of diimine (7)

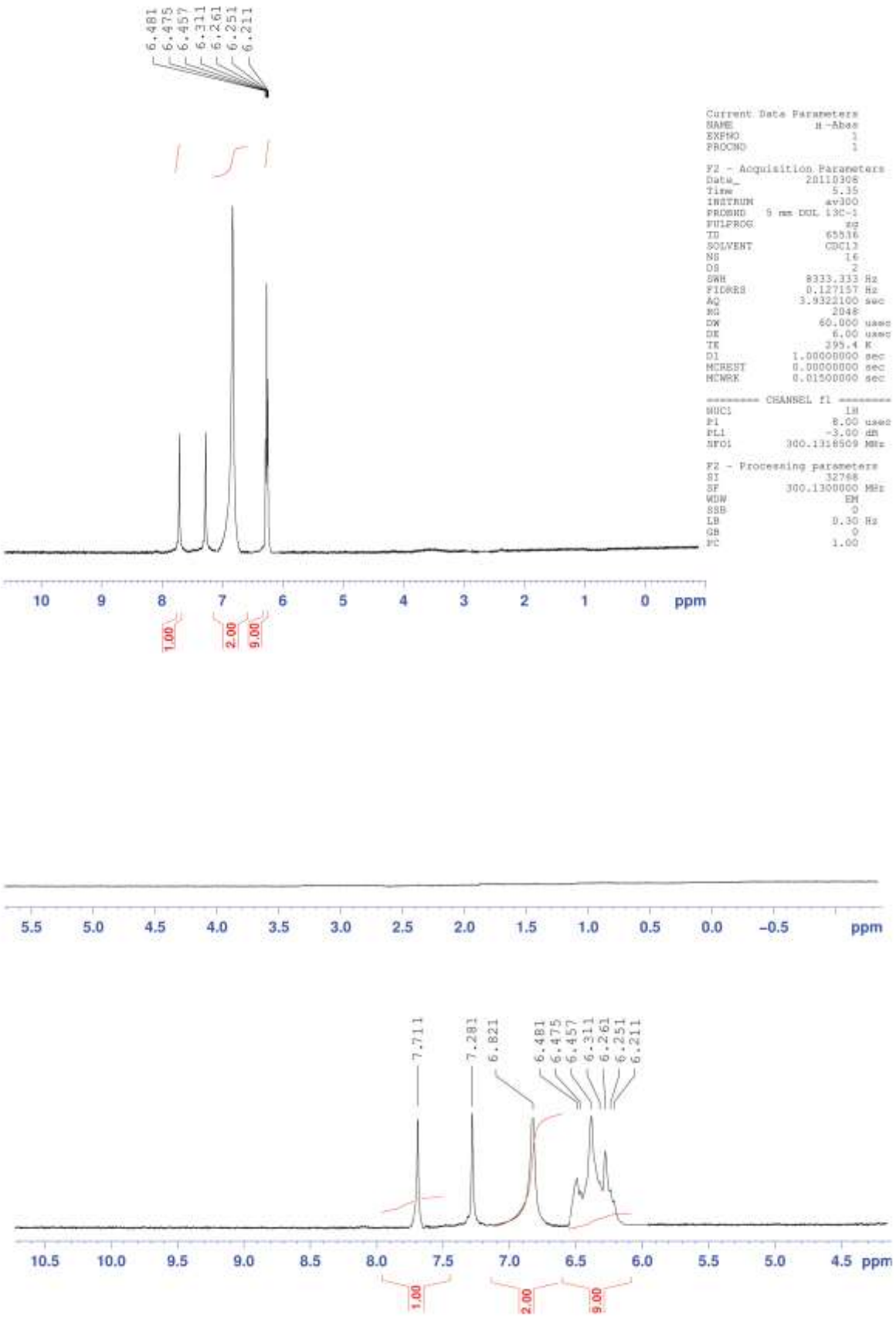


Figure (4) : ^{1}H NMR spectrum of diimine (8)

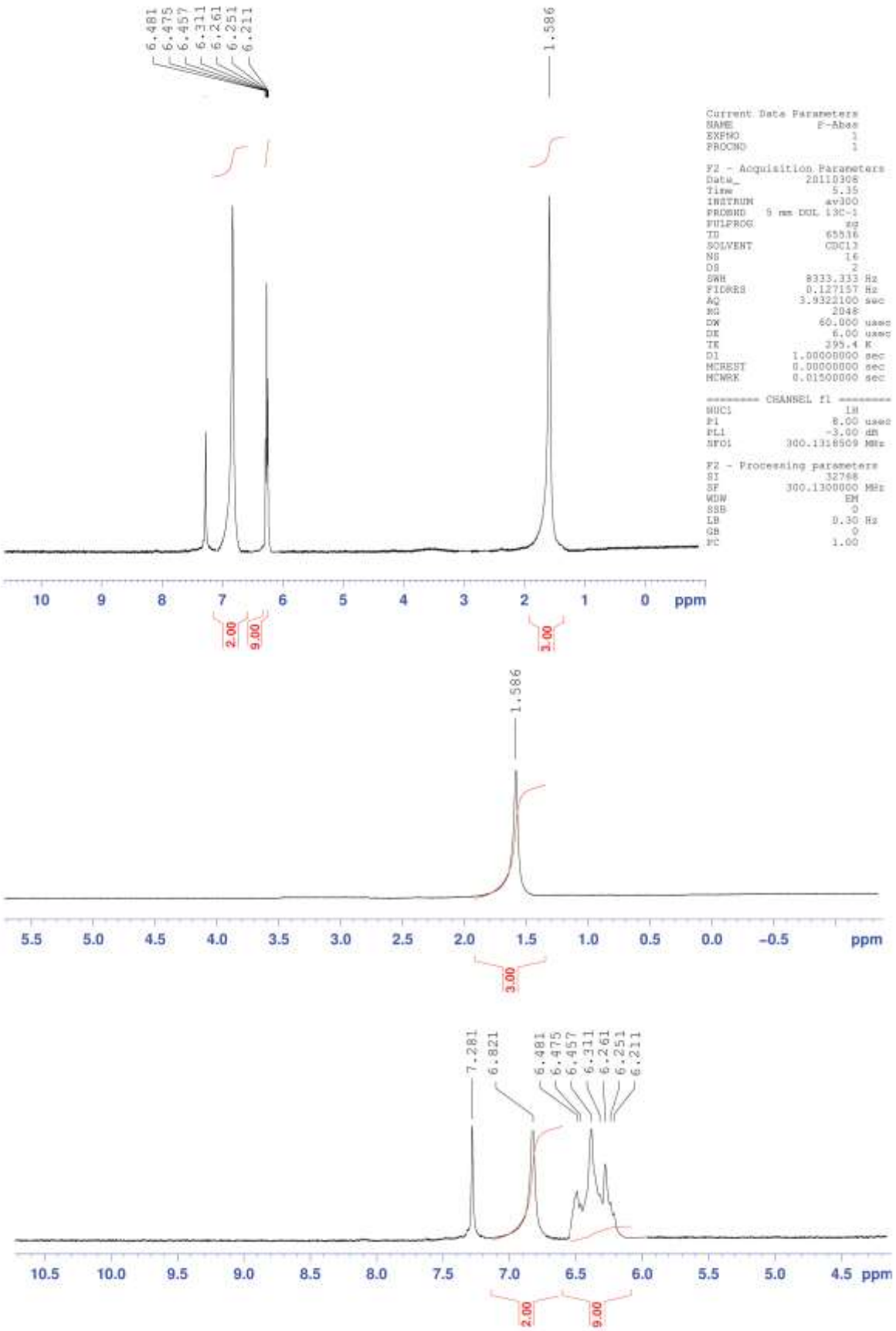


Figure (5) : ^{1}H NMR spectrum of diimine (9)

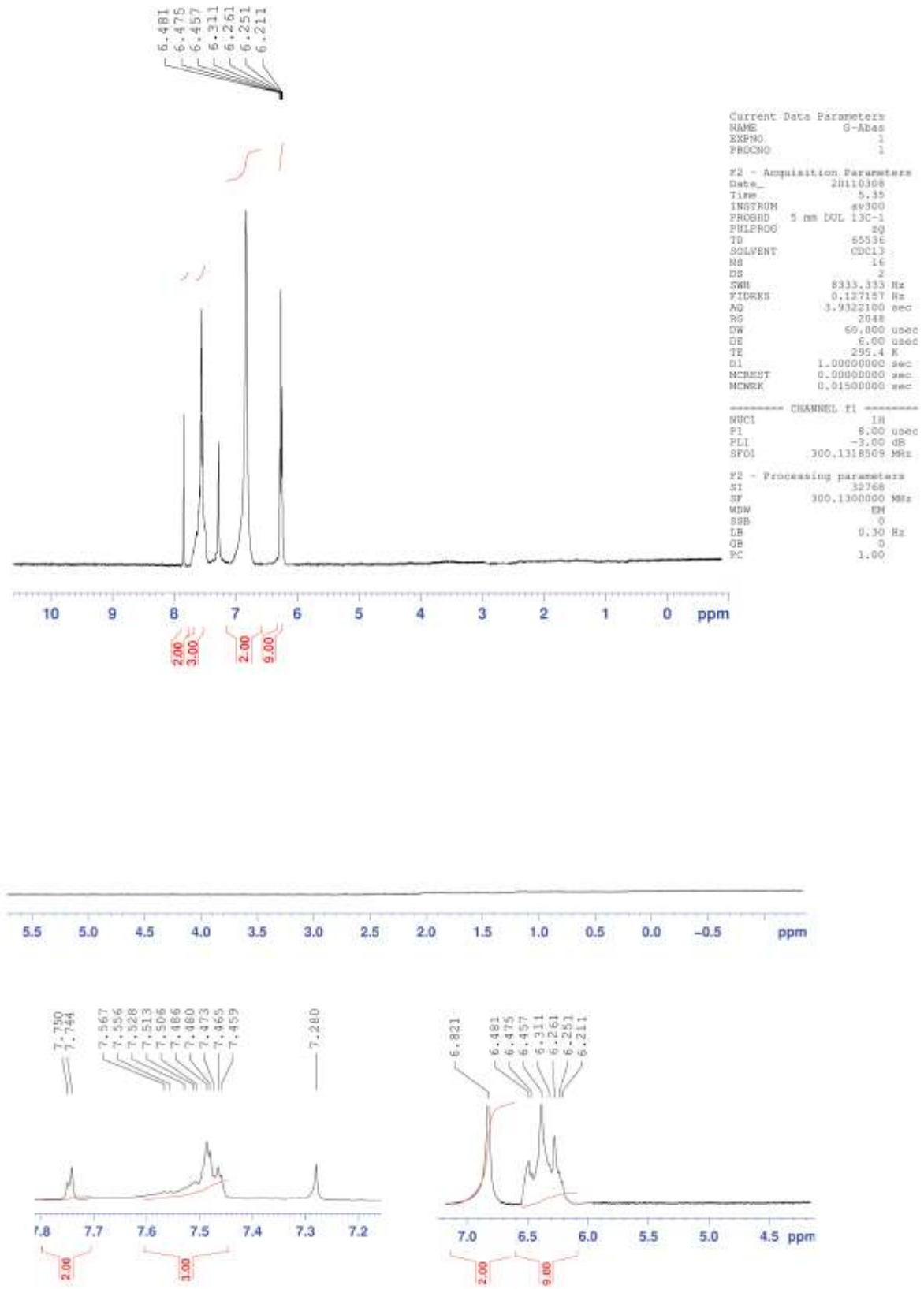


Figure (6) : ^{1}H NMR spectrum of diimine (10)

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