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SYNTHESIS AND ^{1}HNMR SPECTROSCOPIC CHARACTERIZATION OF LONG ALKOXY CHAINS BEARING SCHIFF BASE LIGAND

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Abstract

Three new long alkoxy chain bearing schiff base ligands have been prepared by the condensation of long alkoxy chain (C_6 and C_8) bearing azo derivatives of salicylaldehyde with widely used biological buffering agent tris(hydroxymethyl)aminomethane (ligand L_2 and L_3) and 2-amino-2-ethyl-1,3-propanediol (ligand L_1) respectively. The synthesized Schiff base ligands have been characterized by ^{1}H NMR spectra.

Key words: Schiff base, Synthesis, Characterization, TRIS, TRIS AMINO, Salicylaldehyde derivatives.

Introduction

A Schiff base is a functional group that contains carbon-nitrogen double bond with nitrogen connected to an aryl or alkyl group but not hydrogen (Golcu, *et al.*, 2005). Schiff base is the product yield from the condensation reaction of primary amines with carbonyl compounds may contain a variety of substituent's with different electron-donating or electron-withdrawing groups, and therefore may have interesting chemical properties (Blagus, *et al*., 2010). The wide variety of possible structures for the ligands, made the field of Schiff base complexes is fast developing, depending on the aldehyde and amine used (Kumar, *et al*., 2010). Schiff bases are the important compound owing to their wide range of biological activities and industrial application (Wang, *et al*., 2008). Transition and non-transition metals with Schiff bases have been investigated extensively for many years because of their important contribution in the development of catalysis, magnetism, molecular architectures and materials chemistry (Priyarega, *et al.*, 2011). A comprehensive review covers much of the applications of metal complexes formed with Schiff base ligand (Kumar, *et al*., 2009). Some Schiff bases were tested for fungicidal activity, which is related to their chemical structure (Al-Shiri, *et al.*, 2003).

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 (Cimerman, *et al*., 2000; Singh, *et al.*, 1975 & Perry, *et al*., 1988). They have been found to posses the pharmacological activities such as antimalarial, anticancer, antibacterial, antifungal, antitubercular, antiinflammetery, antimicrobial, antiviral, anticonvulsant, anti-hypertensive and hypnotic activities (Li ,*et al*., 2003; Villar, *et al*., 2004; Venugopal, *et al*., 2008; pandey, *et al*., 2003; Bhat, *et al*., 2005; Wadher, *et al*., 2009; Karthikeyan, *et al*., 2006; Shah, *et al*., 1992 & More, *et al*., 2001). Now a day's biochemists have also been paid their attention towards the studies of a new kind of chemotherapeutic Schiff bases

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(Choi, *et al*., 1995 & Katia, *et al*., 1996). Several studies have also shown that azo ligands containing salicylaldimine-based side chains can be used in the production of chemical sensors because they show a significant change of color of the solution and maxima of the absorption band when they interact with transition metal ions. Transition metal-complexed azo methine compounds have been studied in great detail in the literature for understanding their optical and electronic properties, structure–redox relationships, mesogenic characteristics (Hoshino, *et al*., 1990, Baena, *et al*., 1994, Gegiou, *et al*., 1996; Tascioglu, *et al*., 2006 & Sheikhshoaie, *et al*., 2006).

Schiff base ligand derived from TRIS and their complexes have been reported by several researchers (Sui, *et al*., 2007; Cannon, *et al*., 1976; Sui, *et al*., 2005; Martinez, *et al*., 2011; Lihua, *et al*., 2000; Alan *et al*., 1988; & Breet, *et al*., 1987). Our present investigation deals with the synthesis and characterization of some new Schiff bases resulting from the general condensation of long alkoxy chain (C_6, C_8) and azo-linked bearing salicylaldehyde derivatives with extensively used biological buffer and good complexing agents tris (hydroxymethyl)aminomethane (TRIS) and 2-amino-2-ethyl-1,3-propanediol (TRIS AMINO) (Gomori, *et al*., 1955 & Bai, *et al*., 2000). All the synthesized compounds have been characterized on the basis of TLC and ^{1}H NMR spectral data.

Materials and Methods

The entire compound salicylaldehyde, 4-acetamidophenol, 1-bromohexane 1-bromo heptane, tris(hydroxymethyl)aminomethane(TRIS) and 2-amino-2-ethyl-1,3-propanediol (TRIS AMINO) used in this study were reagent grade, purchased from commercial sources and used as received. The purity of the compounds was checked using precoated TLC plates (MERCK, 60F) using dichloromethane: methanol (8:2) solvent system. The developed chromatographic plates were visualized under UV at 254 nm. and ^{1}HNMR spectra in DMSO on a 400 MHz BRUKER FT-NMR instrument using TMS as internal standard.

Synthesis

The long alkoxy chain bearing azo-linked salicylaldehyde derivatives **C** were prepared by the following three steps, using 4-acetaaminophenol as starting material.

1st step

4-acetaaminophenol (8 gm, 53 mmol) and K_2CO_3 (7.7gm, 58 mmol) was dissolved in 150 ml acetone with heating. To this solution was added alkylbromide (56 mmol) drop by drop. The resulting reaction mixture was refluxed for 24 hour and the solvent was removed under reduced pressure. To the residue was added water and the white precipitate formed were separated by filtration and washed several times with water and finally air dried.

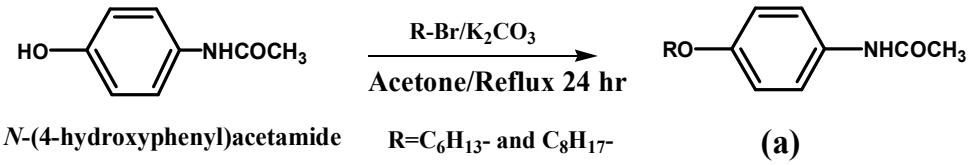

Figure1a: Synthesis scheme of *N*-(4-(alkyloxy) phenyl)acetamide (a)

2nd step

To 150 ml of water was added product (**a**) and to it was then added conc. HCl (30 ml) and refluxed for 10 hour. After refluxing the pH of the reaction mixture was adjusted to 3.5 using 4M NaOH solution. The greenish pink precipitate formed were separated by filtration, washed with water and dried under vacuum. Yield: 1.98 gm.

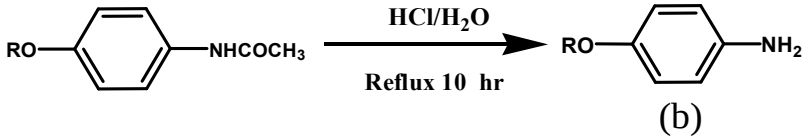

Figure1b: Synthesis scheme of *N*-(4-(alkyloxy)aniline (b)

3rd step

Compound **(b)** 10.23 mmol was dissolved in methanol 20 ml, Conc. HCl 2ml, 30 mmol and water 10 ml with heating. The clear orange solution were then placed on ice bath (0-5^{0}C) and added $NaNO_2$ (0.966 gm, 14 mmol) drop wise and stirred 30 minutes. To it was then added salicylaldehyde (1.248 gm, 10.23 mmol) in methanol 10 ml and stirred 1 hour. The reaction mixture was then filtered and to the filtrate 4 M NaOH solutions was added until the completion of the formation of yellow precipitate and stirred another 2 hours. The yellow product was then separated by filtration with washing using cold ethanol and dried under vacuum.

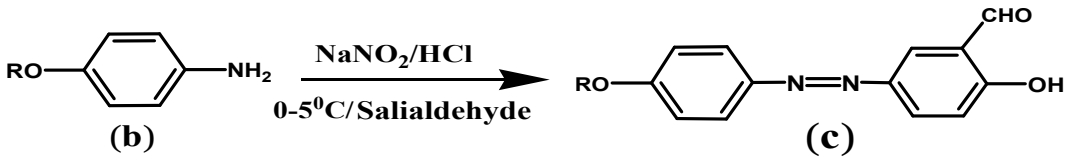

Figure1c: Synthesis scheme of *N*-(4-(alkyloxy)azo-linked salicylaldehyde (C)

Synthesis of the Schiff base ligand L_1, L_2 and L_3

The condensation of 6 and 8-alkoxy azo-linked salicylaldehyde ***(c)*** *with 2-amino-2-ethyl-1,3-propanediol and tris (hydroxymethyl)aminomethane in ethanol yields the desired schiff base ligand* ***L_1***, ***L_2*** *and* ***L_3*** *according to following condensation reaction:*

Ligand L_1

To an (0.72 gm, 2.209 mmol) hot ethanol (80 ml) solution of the compound **(c)** was added 2-amino-2-ethyl-1,3-propanediol (0.263 gm, 2.209 mmol) with constant stirring. The reaction mixture was left under refluxed for 2 hours. After refluxing the clear orange solution was left overnight. The yellow crystalline precipitate obtained was separated by filtration and washed with cold ethanol. Re-crystallization of the yellow compound from ethanol yield 0.696 gm solid product dried under vacuum and kept dry in desiccators.

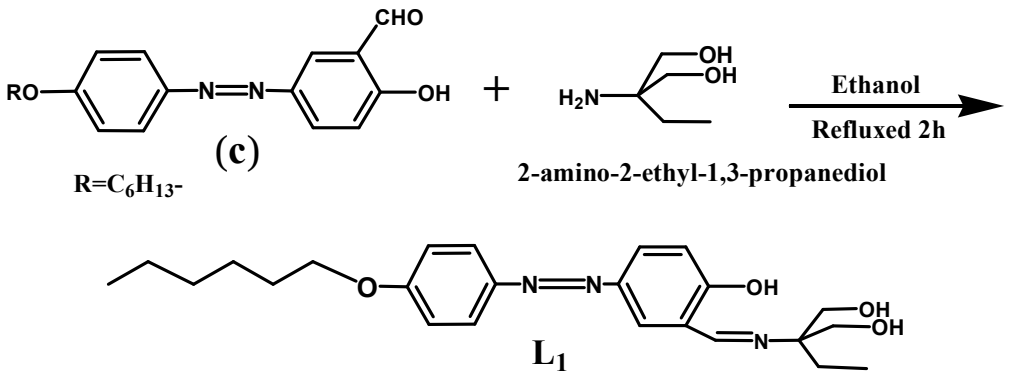

Figure 2a: Synthesis scheme of the Schiff base ligand L_1

Ligand L_2

The Schiff base ligand **L_2** and **L_3** were prepared using 1:1 molar ratio of salicylaldehyde derivatives and ammine (TRIS and TRIS AMINO) with the same procedure described above

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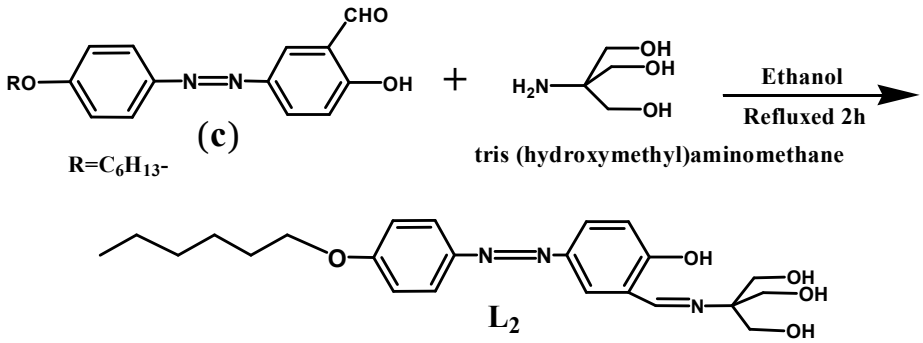


Figure 2b: Synthesis scheme of the Schiff base ligand L_2

Ligand L_3

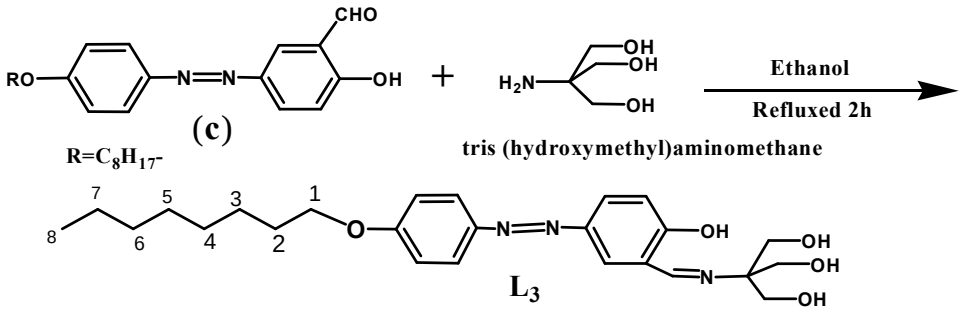


Figure 2c: Synthesis scheme of the Schiff base ligand L_3

Results and Discussions

All the synthesized Schiff base compounds (**L_1-L_3**) were purified by successive re-crystallization using ethanol. The purity of the synthesized compounds was checked by performing TLC. The structures of the synthesized compounds were determined on the basis of their ^{1}HNMR data.

The ^{1}H NMR spectrum of the ligand in DMSO shown in Figure (3a.b-5a.b) and their signals given in Table 1-5. The phenyl multiplet of the Schiff base ligand **L_1** and **L_2** is seen at 6.4 – 8.0 ppm whereas the phenyl muliplet of the ligand **L_3** is seen at 6.7-8.0 ppm. The azomethine proton in all the Schiff base ligand is seen at 8.7 ppm (singlet, J=8.387). The peak at 0.98 ppm which is a triplet, is assigned to -CH_3 groups of TRIS AMINO part of the ligand **L_1** and alkoxy substituent on the benzene ring (**L_1-L_3**) . The multiplet peak at 1.3-1.8 ppm in all the Schiff base ligand which, is assigned to –CH_2 group of alkoxy substituent on the bezene ring. In all the Schiff base ligand the ethoxy substituent –OCH_2 peak on the benzene ring is seen at 4.1 ppm (J=7.118) as triplet (Mounika et al., 2010). The singlet peak at 3.6 ppm is attributed to –CH_2 protons attached to OH group of the TRIS and TRIS AMINO part of the ligand **L_1-L_3**. The singlet peak at 5.1 ppm is tentatively attributed for 3 OH protons of the TRIS part of the ligand **L_3**.

Table1. ^{1}HNMR Spectral data of the ligand L_1

Chemical shift ppm	Multiplicity	Number of protons	Functional group assigned
6.4-8.0	Multiplet	7	Aromatic protons
8.7	Singlet	1	-HC=N-
4.1	triplet	2	-OCH_2-
3.6	singlet	4	-CH_2- of TRIS AMINO
0.98-1.8	multiplet	16	-CH_3(2) and -CH_2-(5)

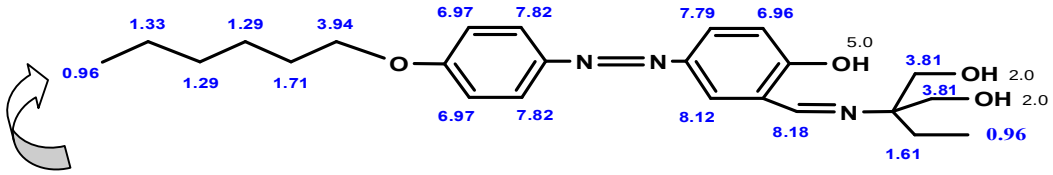
Table 2. ^{1}HNMR Spectral data of the ligand L_2

Chemical shift ppm	Multiplicity	Number of protons	Functional group assigned
6.4-8.0	Multiplet	7	Aromatic protons
8.7	Singlet	1	-HC=N
4.1	triplet	2	-OCH_2-
3.6	singlet	4	-CH_2- of TRIS
0.98-1.8	multiplet	11	-CH_3(1) and -CH_2-(4)

Table 3. ^{1}HNMR Spectral data of the ligand L_3

Chemical shift ppm	Multiplicity	Number of protons	Functional group assigned
6.7-8.0	Multiplet	7	Aromatic protons
8.7	Singlet	1	-HC=N
4.1	triplet	2	-OCH_2-
3.6	singlet	6	-CH_2- of TRIS
0.98-1.8	multiplet	15	-CH_3(1) and -CH_2-(6)
5.1	singlet	3	Tentatively attributed to 3 OH protons of TRIS part

Ligand L_1



Chemical shift value (ppm) from software Chem Office Ultra (2004)

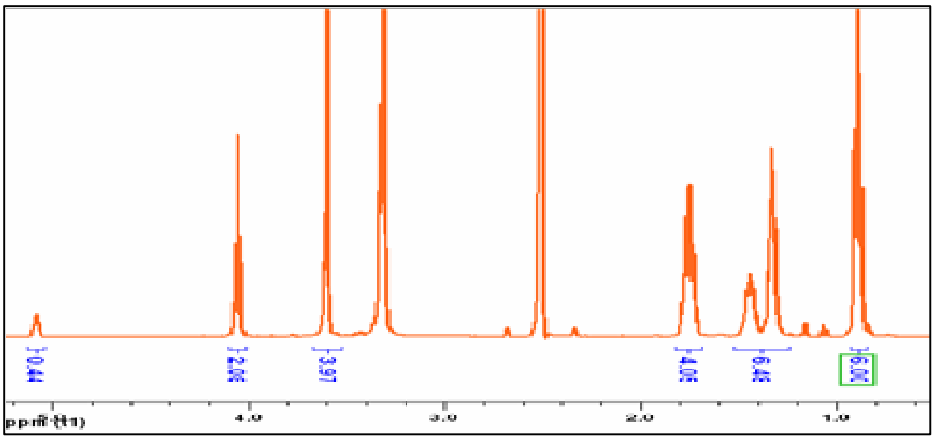


Figure 3a: ¹HNMR of the Schiff base ligand L_1 (alkoxy chain part)

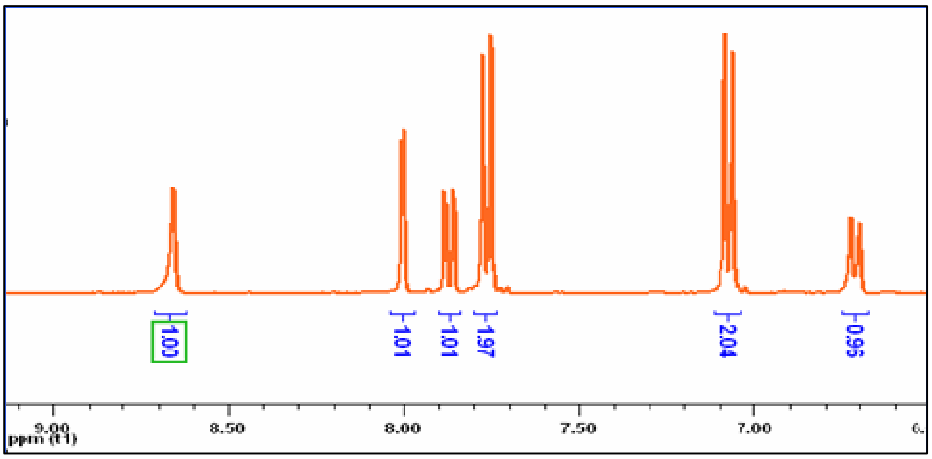
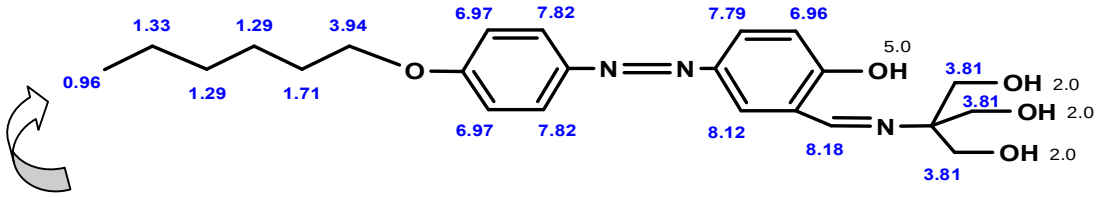


Figure 3b: ¹HNMR of the Schiff base ligand L_1 (aromatic part)

Ligand L_2



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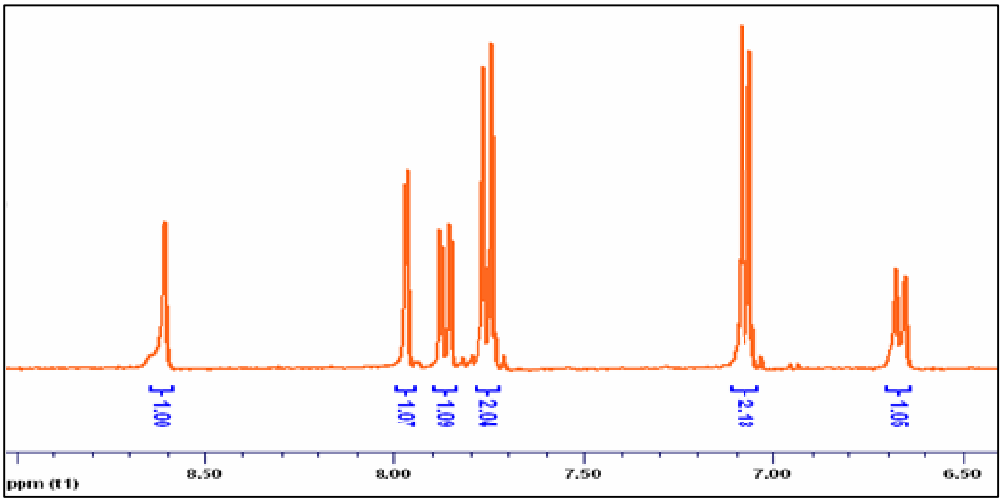


Figure 4a. ^{1}HNMR of the Schiff base ligand L_2 (alkoxy chain part)

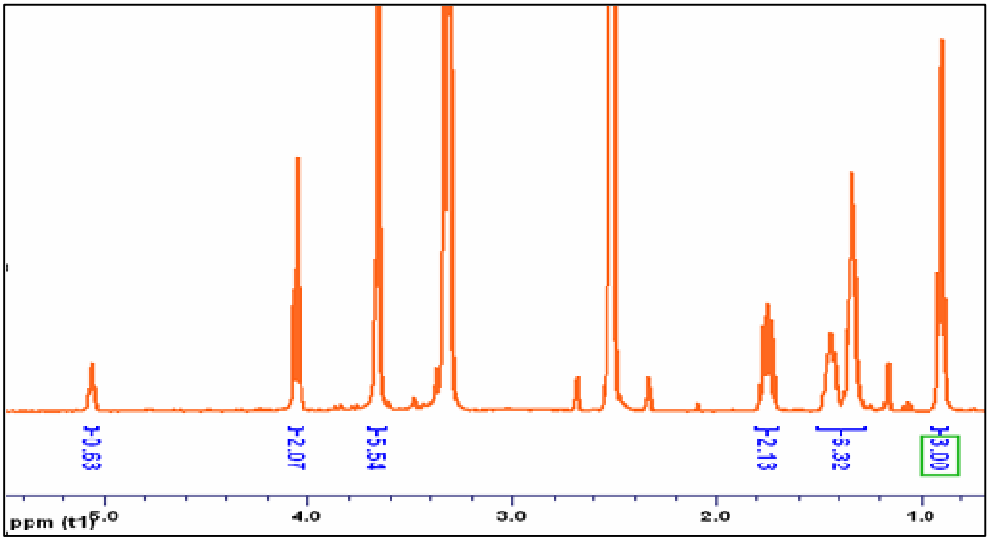
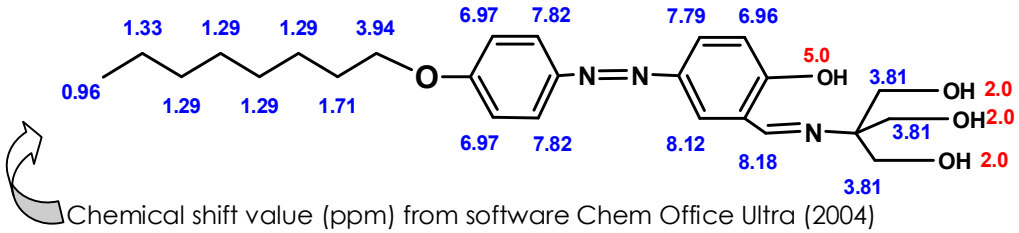


Figure 4b: ^{1}HNMR of the Schiff base ligand L_2 (aromatic part)

Ligand L_3



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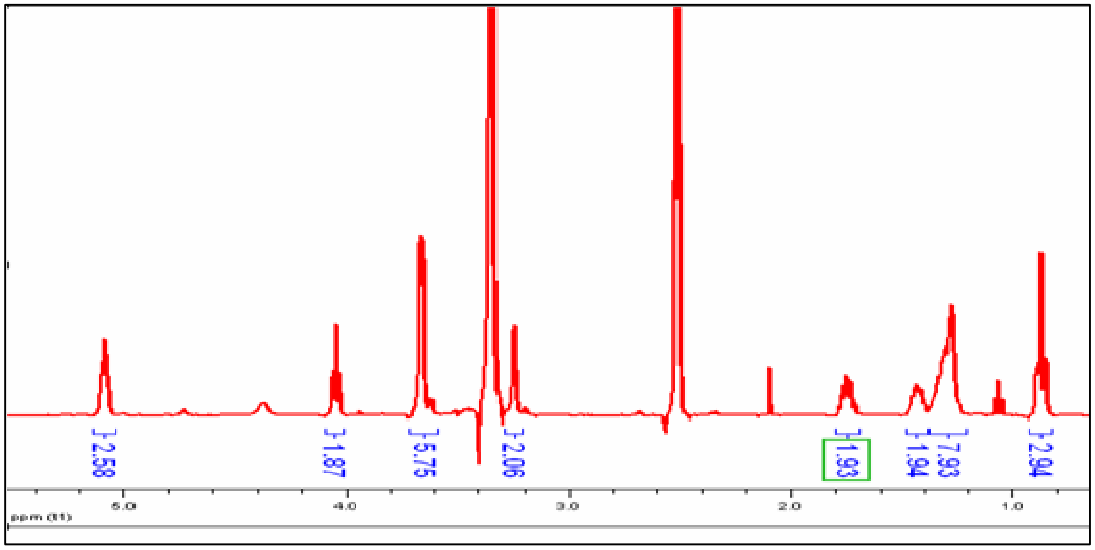

Figure 5a. [1]HNMR of the Schiff base ligand L_3 (alkoxy chain part)

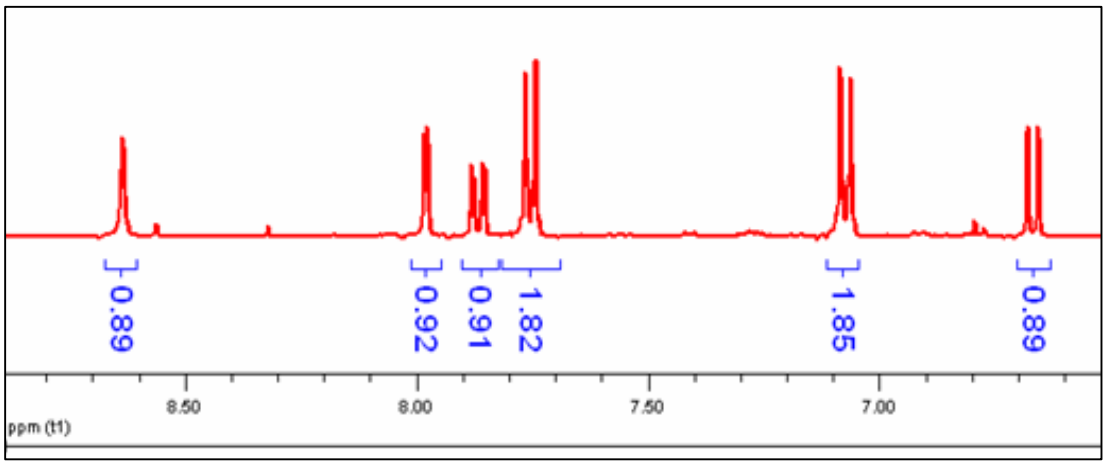

Fig. 5b. [1]HNMR of the Schiff base ligand L_3 (aromatic part)

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