



Synthesis and Characterization of Novel Bis-Schiff Bases Based O-Tolidine

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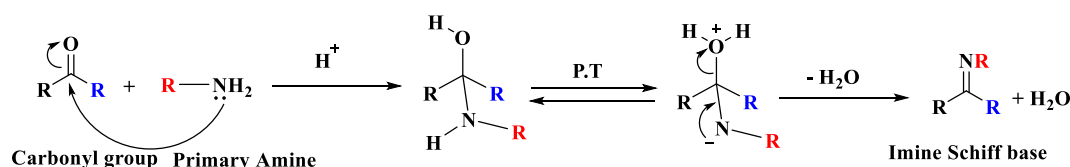
Abstract. Three novel Schiff base (A-C) was reported in this study by reaction of o-tolidine with three different aldehydes 2-bromobenzaldehyde, 3-hydroxybenzaldehyde, and 2,4-dihydroxybenzaldehyde to attain three novel Bis-Schiff Bases ligands in high yield (86-97%). Thin-layer chromatography (TLC) technique is used to monitor the reaction. These agents were characterized by ^{13}C , ^1H NMR, HRMS, FTIR, and melting point. The synthesized compounds (A-C) are expected to have considerable biological activity owing to their molecular structure, which incorporates essential imine functional groups.

Keywords Schiff Base, O-Tolidine, Ligands, Synthesis

1. INTRODUCTION

In 1864 Hugo Schiff was the first to report the Schiff base, which formed by direct reaction of a primary amine with an aldehydes and ketones.[1]

Schiff base are high thermal stability and colorful organic compounds, the azomethine ($-\text{C}=\text{N}-$) is consider the functional group of the Schiff bases. [2] Under specific chemical conditions, Schiff base can be synthesis by reacting of a primary amines with an activated carbonyl groups in aldehydes or a ketones. Scheme 1 shown General reaction to synthesis of Schiff base. [3]



Scheme 1. General reaction to synthesis of Schiff base.

Recently, the interest in Schiff base was increased and there are many studies have reported [4] the synthesis of new Schiff bases compounds because of their unique and wide range of applications such as semiconductor, [5, 6] antimicrobial [7] anticancer [8], catalytic reactions[9] and many biological activates[10] especially o-tolidine many studies have been reported and show optical properties and others applications[11]. Additionally, there are several industrial uses for Schiff bases, such as corrosion inhibitors, analytical chemistry, metal complex ligands, and dyes. In this study, we report the synthesis, and characterization of novel Schiff base derivatives for o-tolidine.

2. METHODS

General Information

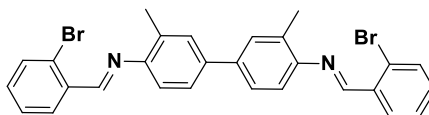
The starting materials for this study *o*-tolidine, 2-bromobenzaldehyde, 3-hydroxybenzaldehyde, and 2,4-dihydroxybenzaldehyde, absolute ethanol, and glacial acetic acid were used as starting materials are supplied by Sigma Aldrich. An DMSO- d_6 , $CDCl_3$, and $MeOD-d_3$ was used as solvent for 1H NMR and ^{13}C NMR.

General experimental procedure

General procurer to Preparation of Schiff bases (A,B,C):

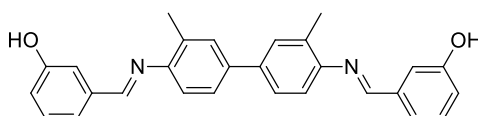
A solution of *o*-tolidine (0.5 g, 2.355 mmol) dissolved in (6 mL) absolute ethanol was added dropwise for 5 minutes to a solution of 2-bromobenzaldehyde, 3-hydroxybenzaldehyde, and 2,4-dihydroxybenzaldehyde (4.710 mmol, 2.0 eq.) in absolute ethanol (5 mL). After adding two drops of acetic acid, the reaction mixture was stirred for two hours to produce a yellow precipitate. At r.t. the reaction mixture was filtered and washed with ethanol to get a shiny yellow target compound (A-C). The following data confirmed the structure of the Schiff base (A-C).

(N4E,N4'E)-N4,N4'-bis(2-bromobenzylidene)-3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (A)



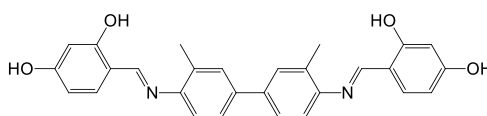
Yield 97%, yellow. **m.p.** 161-162 °C; **FT-IR** (ATR): ν max/ cm^{-1} 3033 cm^{-1} aromatic (C-H) stretch), 2955 cm^{-1} (Aliphatic (C-H) stretch), 1612 cm^{-1} (CH=N stretch Imine), 1593 cm^{-1} aromatic (C=C) stretch, 1021 cm^{-1} (C-Br). **1H NMR** (400 MHz, $CDCl_3$) δ 8.84 (s, 2H, 2 \times -N=CH), 8.30 (d, J = 7.7 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.54 – 7.47 (m, 4H), 7.43 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 2.47 (s, 6H, 2 \times CH₃). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.23 (–CH=N), 149.93, 138.84, 134.97, 133.38, 132.93, 132.40, 129.29, 129.07, 127.85, 126.13, 125.40, 118.39, 18.27. **HRMS** (ESI+) (m/z): $[M+H]^+$ calculated for C₂₈H₂₂Br₂N₂ 546.01, found 547.0197.

3,3'-((1E,1'E)-((3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)bis(azanylylidene))bis(methanylylidene))diphenol (B)



Yield 86%, yellow. **m.p.** 186-187 °C; **IR** (diamond-ATR): $\nu_{\text{max}}/\text{cm}^{-1}$ 3368 cm^{-1} (OH), 3043 cm^{-1} (Aromatic (C-H) stretch), 2918 cm^{-1} (Aliphatic (C-H) stretch), 1621 cm^{-1} (CH=N stretch Imine), 1579 cm^{-1} aromatic (C=C) stretch. **^1H NMR** (400 MHz, MeOD- d_3) δ 8.37 (s, 2H, $2 \times \text{N}=\text{CH}$), 7.51 – 7.29 (m, 10H), 7.02 (d, $J = 8.1$ Hz, 2H), 6.98 – 6.93 (m, 2H), 3.32 (s, $2 \times \text{OH}$, 2H), 2.41 (s, 6H, $2 \times \text{CH}_3$). **^{13}C NMR** (101 MHz, MeOD) δ 161.58, 159.08 ($-\text{CH}=\text{N}$), 151.24, 139.61, 139.17, 133.38, 130.87, 129.58, 126.23, 121.87, 119.76, 119.39, 115.42, 18.18. **HRMS** (ESI+) (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2$ 420.18, found 421.1909.

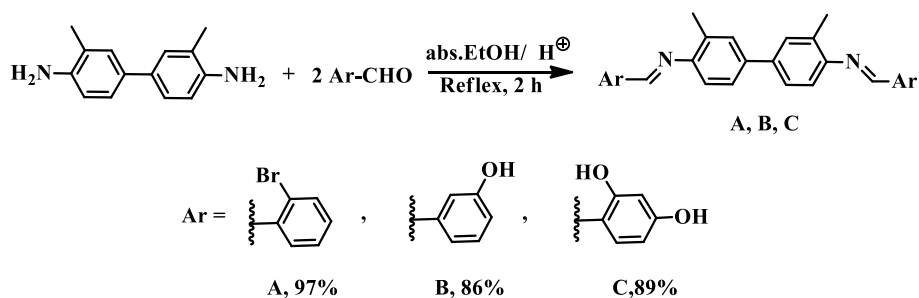
4,4'-((1E,1'E)-((3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)bis(azanylylidene))bis(methanylylidene))bis(benzene-1,3-diol) (C)



Yield 89%, Brown. **m.p.** 280-281 °C ; **IR** (diamond-ATR): $\nu_{\text{max}}/\text{cm}^{-1}$ 3040 cm^{-1} (OH), 3031 cm^{-1} (Aromatic (C-H) stretch), 2977 cm^{-1} (Aliphatic (C-H) stretch), 1621 cm^{-1} (CH=N stretch Imine), 1583 cm^{-1} aromatic (C=C) stretch. **^1H NMR** (400 MHz, DMSO- d_6) δ 13.89 (s, 2H, $2 \times \text{OH}$), 10.28 (s, $2\text{H} \times \text{OH}$), 8.80 (s, 2H, $2 \times \text{N}=\text{CH}$), 7.66 – 7.58 (m, 4H), 7.43 (dd, $J = 22.2, 8.4$ Hz, $2 \times 2\text{H}$), 6.42 (m, 2H), 6.32 (m, 2H), 2.38 (s, 6H, $2 \times \text{CH}_3$). **^{13}C NMR** (101 MHz, DMSO- d_6) δ 163.41, 162.54, 161.68, 145.90, 137.24, 134.46, 132.05, 128.47, 125.06, 118.16, 112.31, 107.89, 102.41, 18.02. **HRMS** (ESI+) (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{25}\text{N}_2\text{O}_4^+$ 453.18 ; found 453.1781.

3. RESULTS AND DISCUSSION:

This work described the synthesis of three novel Schiff compounds (A-C) Bis-Schiff Bases ligands in high yield (89-97%). These compounds were attained by reacting o-tolidine with three aldehydes, 2-bromobenzaldehyde, 3-hydroxybenzaldehyde, and 2,4-dihydroxybenzaldehyde. Scheme 1 shows the general reaction for synthesizing novel compounds A, B, and C. Table 1 shows the compounds' chemical structure and other physical properties (A-C).



Scheme 1: Synthesis of novel compounds A-C.

Table 1: Physical characteristics of bis Schiff bases A,B,C					
Compound	Structure	M.Wt g/mol	Color	Yield (%)	m.p. (°C)
A		546.30	yellow	97%	161-162 °C
B		420.50	yellow	86%	186-187 °C
C		452.50	brown	89%	280-281 °C

FT-IR results of compounds A,B, C

The FT-IR spectra of compounds (A-C) are presented in Table 2, highlighting the principal significant bands such as (C=N) azomethine group. The sharp band of the stretching vibrations of amino (-NH₂) groups in the o-tolidine around 3468, 3410 cm⁻¹, and 3373, 3338 cm⁻¹ disappeared and this provides strong evidence that the condensation reactions between o-tolidine and the aldehydes occurred successfully. Also, a strong band at (1612-1621) cm⁻¹ appeared related to the ν (-C=N-) azomethine group vibrations for Schiff bases (A-C). Table 2 shows spectra data for compounds (A-C).

Table 2: important Spectral data of FT-IR (ν, cm ⁻¹) of Schiff base (A-C).						
Comp.	OH	Aromatic (C-H)	Aliphatic (C-H)	azomethine (-C=N-)	Aromatic (-C=C-)	(=C-Br)
A	-	3033	2955	1612	1593	1021
B	3368	3043	2918	1621	1579	-
C	3040	3031	2977	1621	1583	-

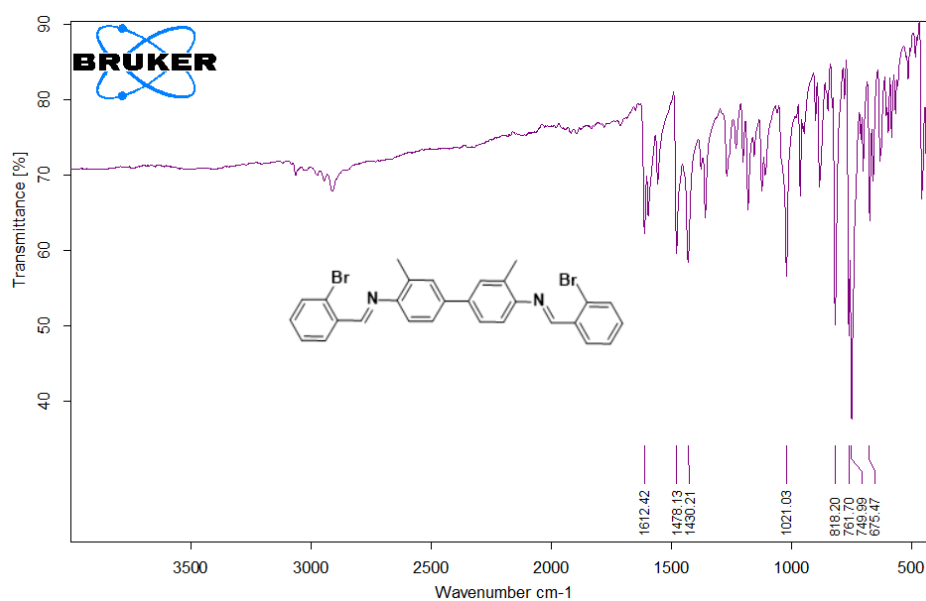


Figure 1. FT-IR spectra of (A)

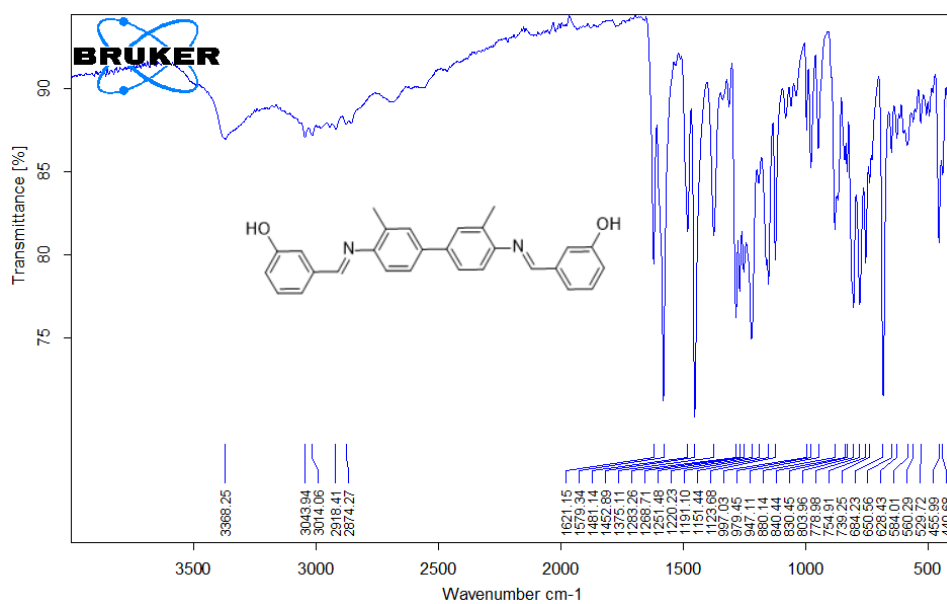


Figure 2. FT-IR spectra of (B)

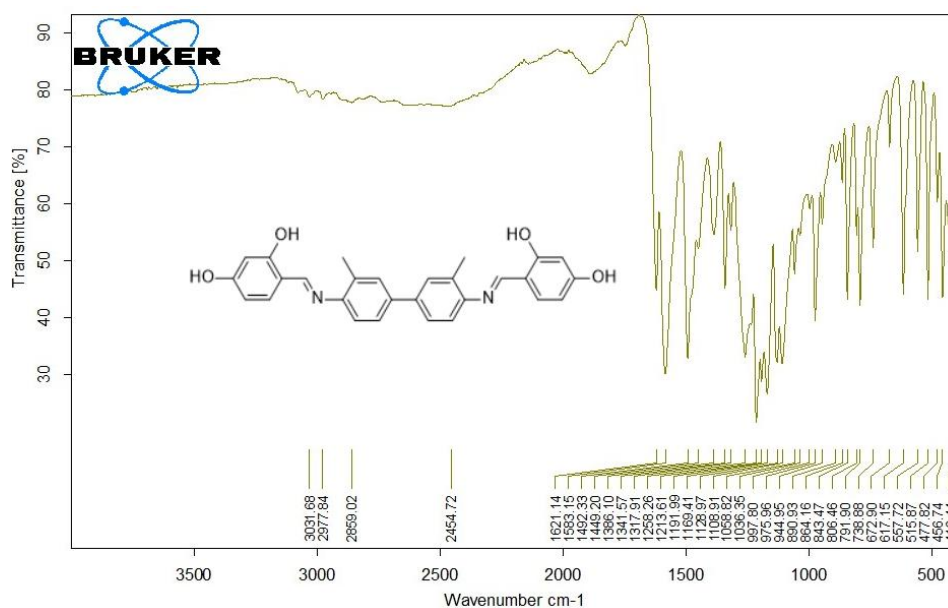


Figure 3. FT-IR spectra of (C)

^1H NMR and ^{13}C NMR spectra of the synthesized compounds A,B,C:

The ^1H NMR and ^{13}C NMR together with FT-IR and HRMS were employed to validate the structures of the synthesized compounds. Hence, ^1H NMR spectra of the **A-C** compounds show chemical shift of the **azomethine** proton ($-\text{CH}=\text{N}$) in 8.84, 8.37 and 8.80 ppm respectively for compounds (**A-C**) as shown in Table 3 and figures (1,3, and 5).

The peaks of the aromatic protons for (**A-C**) compounds appeared in the ranges 8.30-6.32 ppm as expected.

It is clear from the structure of compounds B and C holding hydroxyl groups. Symmetric compound **B** which holds two hydroxyl groups shows a peak appearing at δ 3.32 ppm. Compound **C**, which holds 4 hydroxyl groups, showed two signals at 13.89 and 10.28 and each single related to two hydroxyl groups. Table 3 shows the ^1H NMR spectral data for bis Schiff base (**A-C**).

Table 3: ^1H NMR spectrum data (δ , ppm) of compounds (A-C)	
Compound	^1H NMR spectrum data
A	8.84 (s, 2H, $2\times\text{N}=\text{CH}$), 8.30 (d, $J = 7.7$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.54 – 7.47 (m, 4H), 7.43 (t, $J = 7.5$ Hz, 2H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 2.47 (s, 6H, $2\times\text{CH}_3$).
B	δ 8.37 (s, 2H, $2\times\text{N}=\text{CH}$), 7.51 – 7.29 (m, 10H), 7.02 (d, $J = 8.1$ Hz, 2H), 6.98 – 6.93 (m, 2H), 3.32 (s, $2\times\text{OH}$, 2H), 2.41 (s, 6H, $2\times\text{CH}_3$).
C	13.89 (s, 2H, $2\times\text{OH}$), 10.28 (s, 2H, $2\times\text{OH}$), 8.80 (s, 2H, $2\times\text{N}=\text{CH}$), 7.66 – 7.58 (m, 4H), 7.43 (dd, $J = 22.2, 8.4$ Hz, $2\times\text{H}$), 6.42 (m, 2H), 6.32 (m, 2H), 2.38 (s, 6H, $2\times\text{CH}_3$).

Table 4: ^{13}C NMR spectrum data (δ , ppm) of compounds (A-C)	
Compound	^{13}C NMR spectrum data
A	In CDCl_3 : δ 158.23 ($-\text{CH}=\text{N}$), 149.93, 138.84, 134.97, 133.38, 132.93, 132.40, 129.29, 129.07, 127.85, 126.13, 125.40, 118.39, 18.27.
B	In MeOD : δ 161.58, 159.08 ($-\text{CH}=\text{N}$), 151.24, 139.61, 139.17, 133.38, 130.87, 129.58, 126.23, 121.87, 119.76, 119.39, 115.42, 18.18.
C	In $\text{DMSO}-d_6$: δ 163.41, 162.54, 161.68 ($-\text{CH}=\text{N}$), 145.90, 137.24, 134.46, 132.05, 128.47, 125.06, 118.16, 112.31, 107.89, 102.41, 18.02.

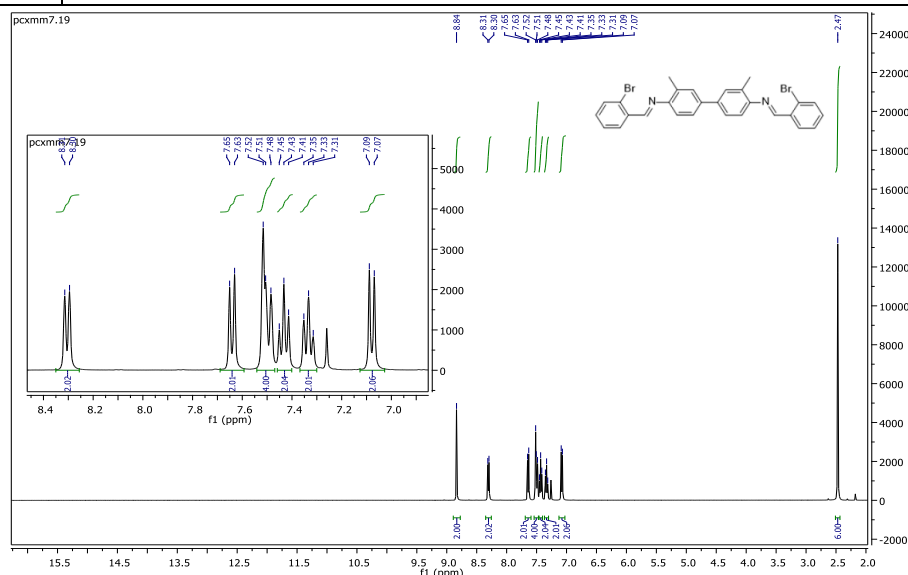


Figure 5. ^{13}C NMR of **A** (100.1 MHz, in CDCl_3).

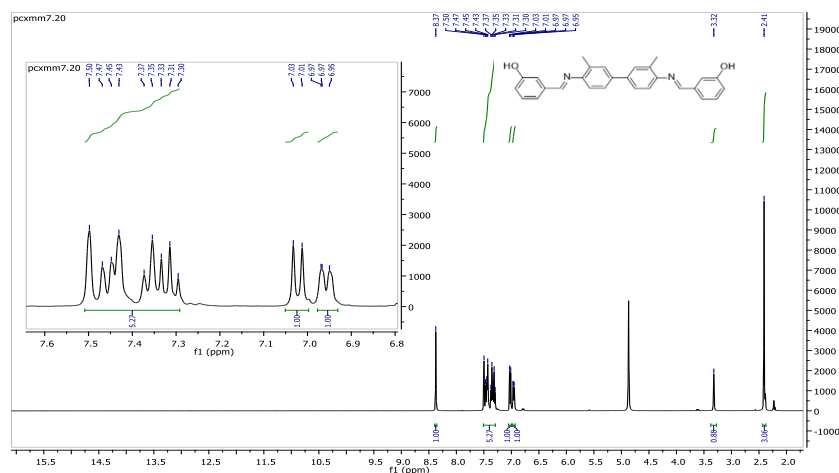


Figure 6. ^1H NMR spectrum of **B** (400 MHz, in MeOD-d_3)

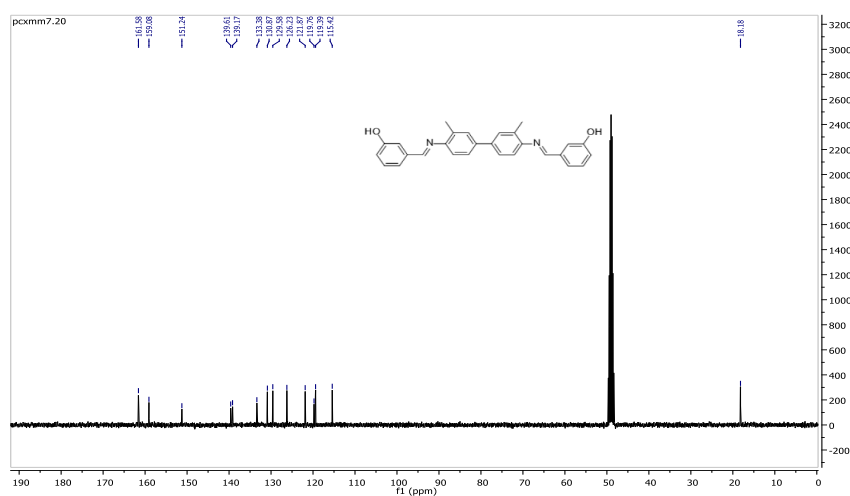


Figure 7. ^{13}C NMR of **B** (100.1 MHz, in MeOD-d_3).

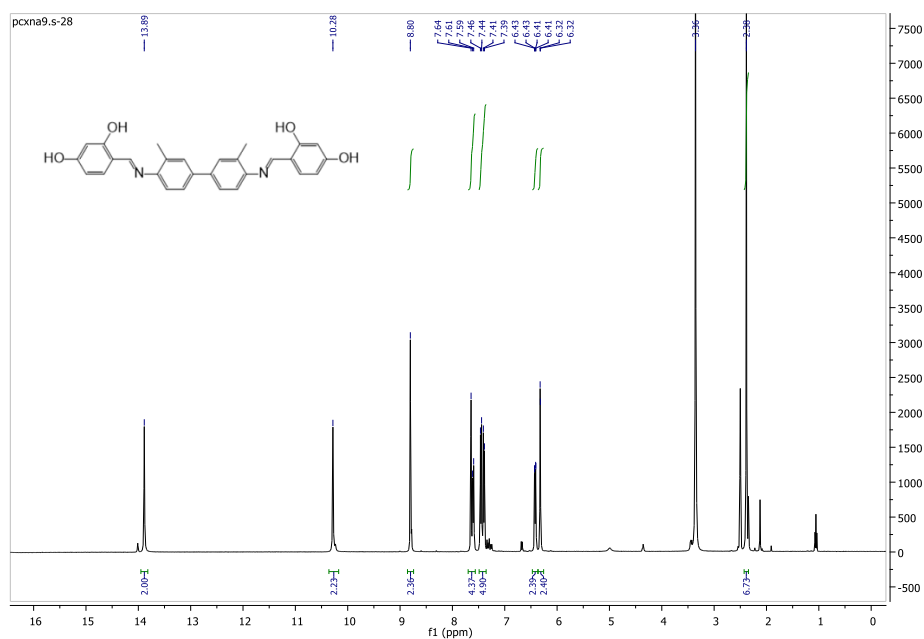


Figure 8. ^1H NMR of **C** (400 MHz, in DMSO-d_6)

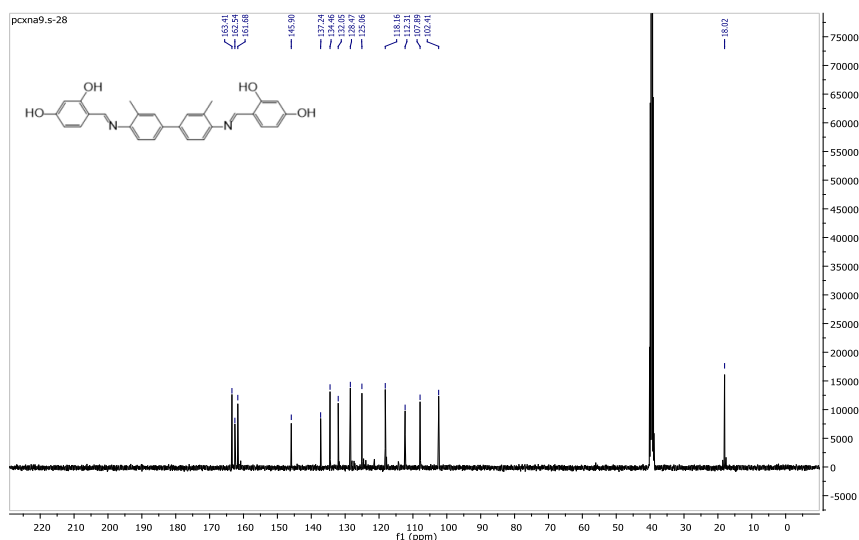


Figure 9. ^{13}C NMR of C (100.1 MHz, in DMSO-d_6).

4. CONCLUSION

The three new Schiff compounds (**A-C**) derived from o-tolidine and three different aldehydes 2-bromobenzaldehyde, 3-hydroxybenzaldehyde, and 2,4 dihydroxybenzaldehyde have been prepared with optimal yield 89-97%. These compounds were fully characterized using ^{13}C NMR, ^1H NMR, mass spectroscopy, FTIR Spectroscopy, and M.P spectroscopy techniques. ^1H NMR for the three prepared compounds (**A-C**) showed a sharp singlet within the 8.37-8.80 ppm corresponding to the azomethine ($-\text{CH}=\text{N}-$) proton. The signal's position of the azomethine ($-\text{CH}=\text{N}-$) proton mainly depends on the chemical environment of the substituents in the benzene ring. The ^{13}C NMR peaks observed ranged from 158.23 to 161.68 ppm, indicative of the azomethine ($-\text{CH}=\text{N}-$) carbon.

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