Synthesis, Characterization and Corrosion Inhibition Properties of Synthesized Schiff Bases

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MS THESIS WORK

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Dedication

To my mother and husband

To my siblings

Acknowledgments

First and foremost, I am thankful to Almighty Allah, who always blesses me and guides me to the right path.

I would like to thank my mother for her constant support and prayers without which my success would not be possible.

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Abbreviations	Explanation
AIDS	Acquired Immune Deficiency Syndrome
cm^{-1}	Per centimeter
FT-IR	Fourier Transform Infrared Spectroscopy
mL	Mililitre
Mm	Millimeter
MPa	Mega Pascal Pressure unit
mpy	Mills Per Year
MRI	Magnetic Resonance Imaging
nm	Nanometer
ppm	Parts Per Million
RNA	Ribonuleic Acid
TLC	Thin Layer Chromatography
UV	Ultraviolet

Abstract

During the past few years, much attention is drawn by corrosion inhibitors. Schiff bases are promising corrosion inhibitors of mild steel, copper and zinc in acidic media. Apart from corrosion inhibitors, these can be used as drugs, catalysis of reactions, in dyes and pigments and in sensors. They have also been used as anti-bacterial, anti-viral and anti-fungal agents. Six different Schiff bases were synthesized by condensation of 4-Nitro-o-phenylenediamine with different aldehydes and then characterized by different spectroscopic techniques. These Schiff bases were then tested for their corrosion inhibition properties along with biological potential including anti-fungal and anti-bacterial.

Chapter 1

1.1 Introduction:

Schiff bases are organic compounds which are synthesized by condensing together primary amines and carbonyl compounds which may be an aldehyde or a ketone. They are also known as imines due to the characteristic C=N bond present in them. Schiff bases are considered as one of the most important organic compounds and are used as regulators of plant growth hormones, catalysts, and dyes etc. Schiff bases are also known for their biological activities such as anti-fungal, anti-epileptic, anti-bacterial, anti-malarial, and anti-tumor, racemization and transamination activities [1].

Due to the increase in industrial applications in corrosive environments and acidic solution, mild steel phenomenon has given much interest. The corrosion inhibition of mild steel ,zinc and copper can be done by using Schiff bases [2]. Schiff bases are excellent corrosion inhibitors compared to the individual reactants i.e amines and aldehydes from which they are synthesized. A good inhibitor possesses two main properties, firstly it should be inexpensive and can be easily made from comparatively cheap raw materials, and secondly, it should contain oxygen and nitrogen which are highly electronegative atoms and should contain an aromatic ring as it is surrounded by an electron cloud. Schiff bases are also a good corrosion inhibitor owing to the presence of >C=N group present in them [3]. They get themselves adsorbed on the surface of metal owing to C=N and form a monolayer on the metal surface by forming linkages, thereby terminating all kinds of cathodic and anodic reactions and thus preventing the metal from corrosion [4].

Schiff bases protect the metal from corrosion by forming a protective thin film on the surface of the metal and prevent water molecules to form bonds with metal and corrode it. The mechanism of action of inhibitor is related to the surface of metal and functional group of inhibitors. The adsorption is governed by the chemistry of inhibitor molecule and its structure, composition of metal surface, charge distribution in inhibitor molecule, the adsorption mode and the type of aggressive media. Furthermore a Schiff base has shown to be a better corrosion inhibitor than the individual constituents from which it is synthesized [5].

Schiff bases have found many exciting properties that is why they show many applications in various aspects of human life. They are not only biological active compound but also used in other fields such as catalysis, sensors and model compounds for active centers of metallo-enzymes [6].

1.1.1 History of Schiff bases:

Imines were synthesized by the condensation reaction of aldehydes with primary amines for the first time in 1864 by a German chemist named Hugo Schiff. Due to condensation reaction H_2O molecule is also eliminated. Although these are not bases but designation for these compounds as bases is still used. The imines were named Schiff bases after Hugo Schiff [7].

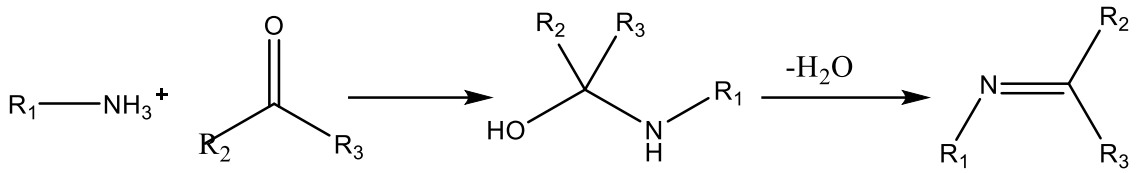
1.1.2 Chemistry of Schiff Bases:

The general formula for the Schiff bases is represented as $R_3R_2C=NR_1$ and these are also known as imines or azomethine. Schiff base becomes a stable imine when the substituent may be alkyl or aryl. Schiff base can be synthesized by the reaction of primary amine and a carbonyl compound. The reaction is nucleophilic addition reaction forming a carbinolamine which is followed by release of water molecule to generate an imine [8].

For more than hundred years the physical properties and reactivity of Schiff bases have been studied. Cellulose which is widely used material of paper, clothes and construction material and its complexation with chitosan produces new Schiff bases of various physical properties [9]. The stabilization of metals in different oxidation states is also done by Schiff bases [10]. The lone pair of electrons on nitrogen are responsible for the chemical and biological importance of the Schiff bases and has been shown through several studies. Schiff bases that contain imino functionality have shown to be quite efficient in biological activities like anti-tumor, anti-bacterial, anti-inflammatory, anti-corrosive and anti-diabetic [11].

Schiff bases show excellent properties when they are in complexation with some metal ions than alone as a ligand. The property of lipophilicity is enhanced when Schiff base is a coordinated one than it is in a ligand form [12]. Schiff bases are conceived as excellent chelating ligands due to their synthetic flexibility, easy formation and properties of C=N group [13].

The general reaction for the synthesis of Schiff base ligand is shown **(Scheme 1)**



Amine Aldehyde Hemiaminal Schiff Base

Scheme 1: General reaction of Schiff Base Formation

1.1.3 Properties of Schiff Bases:

Schiff bases have shown extended applications in different fields of biology which include anti-bacterial, anti-viral, anti-tumor, antifungal, antioxidant, anti-HIV, anti-malarial and anti-inflammatory activity and also catalyze different reactions such as oxygenation of alkenes, electro-reduction, hydrosilylation reactions, polymerization reaction, decomposition reaction, hydrolysis reaction, oxidation of organic compounds, aldol reaction, Henry reaction, epoxidation of alkenes, synthesis of bis(indolyl) methane and Diels-Alder reaction [14].

Removal of uranium (VI) from aqueous solution is done by magnetic Schiff bases through adsorption process [15]. Schiff base complexes of zinc have been proved for their excellent activity in hydrosilylation of ketones as catalysts for the reaction of benzaldehydes and oxazole to yield oxazoline adducts which are optically active [16]. Schiff bases act as an efficient anti-cancer agents by interacting with the cell constituents by their nitrogen atom of azomethine and thus a hydrogen bond is formed which tends to change the normal processes of cell [17].

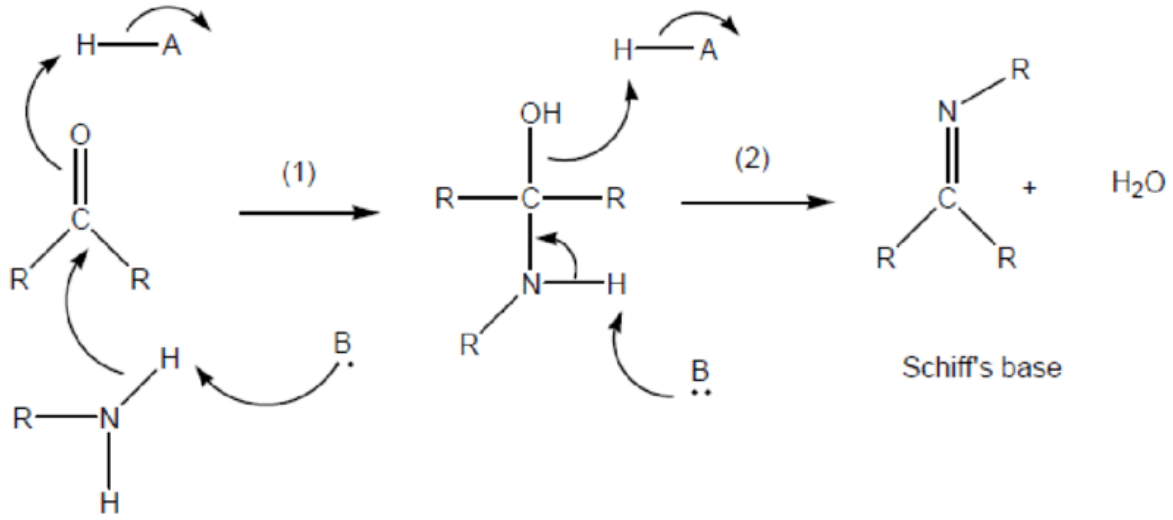
Schiff bases derived from 4-aminoantipyrine and benzaldehyde show activity against anti-inflammatory diseases which are caused by oxidative stress and inflammation [18]. Schiff base complexes of cobalt and chromium are used for dying leather, wools and food packages. Some complexes are used for dying of polyfibers. Schiff base metal complexes having azo groups are used for dying of textiles [19]. Cu (II) metal complexes of Schiff base show comparatively more antifungal activity than other Schiff base complexes as because Cu (II) complexes possesses higher stability constant compared to other complexes [20].

Schiff base metal complexes derived from the reaction of aldehyde and benzoic acid and UO_2 or Ni (II) or Co (II) showed an excellent antibacterial activity against pseudomonas aeruginosa,

E.Coli , Staphylococcus Pyogenes. Due to which Schiff base complexes can be safely used for the treatment of infections caused by these specific bacterial strains [21].

1.1.4 Formation of Schiff Bases

The Schiff base ligands can be synthesized by the condensation reaction of aldehyde/ketone and amines in the presence of various solvents and specified reaction conditions. The most common solvents to be used for the formation of Schiff bases are methanol and ethanol and the reactions are mostly carried out either by stirring or under reflux **(Scheme 2)**.



Scheme 2: Mechanism Of Schiff Base formation

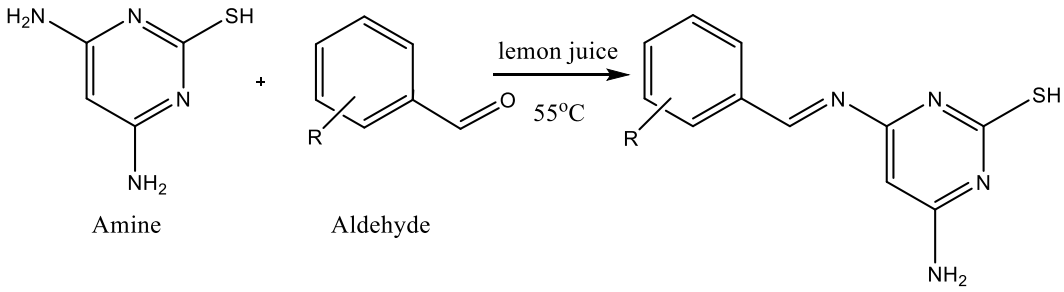
1.1.5 Methods of Schiff Base Synthesis:

Synthesis of Schiff Bases can be done by the following different methods:

1.1.5.1 From Lemon Juice:

Schiff bases can be prepared by using lemon juice which is a natural catalyst also known as green catalyst. Lemon juice is a potential organic solvent and used due to its cost effectiveness, non-toxicity, safe nature and being environment friendly. This process simply involves the condensation of amine with aldehyde with the addition of lemon acid as catalyst [22].

Azadeh Alikhani et al. synthesized Schiff base by reacting 4,6-diamino 2-thiol pyrimidine and aldehyde in equimolar ratio. Lemon juice was added as catalyst. Reaction progress was monitored through TLC and final product was achieved in good yields **(Scheme 3)** [23].



Scheme 3: Synthesis of Schiff base in the presence of lemon juice as catalyst

1.1.5.2 Solvent free method:

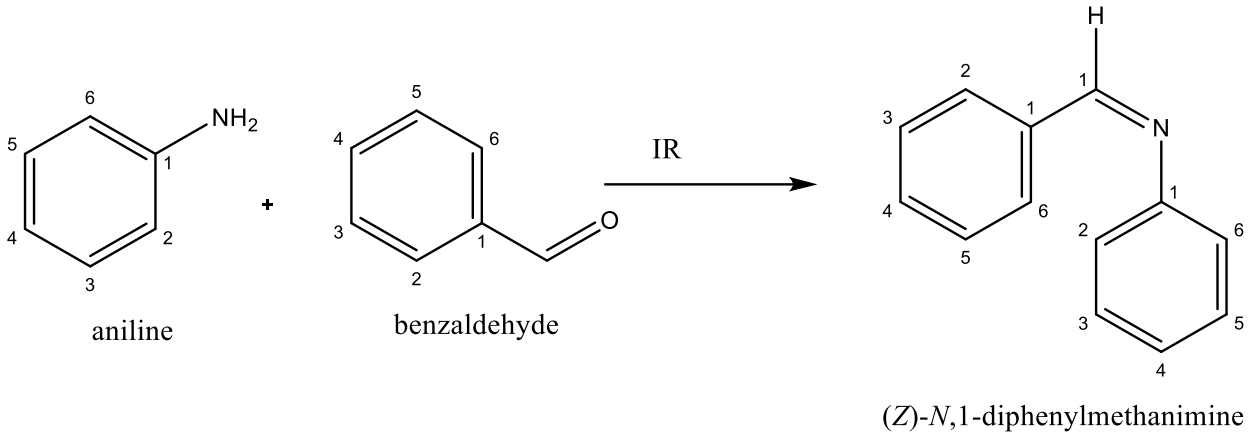
Schiff bases have also been synthesized by solvent free method. This is one of the convenient method due to the use of an efficient and inexpensive catalyst, short reaction times, high product yields, simplicity in reaction and workup.

Hossein Naemi et al (2007) reported the formation of Schiff base using P_2O_5/SiO_2 as catalyst in solvent free state under mild conditions [24].

1.1.5.3 Microwave Irradiations:

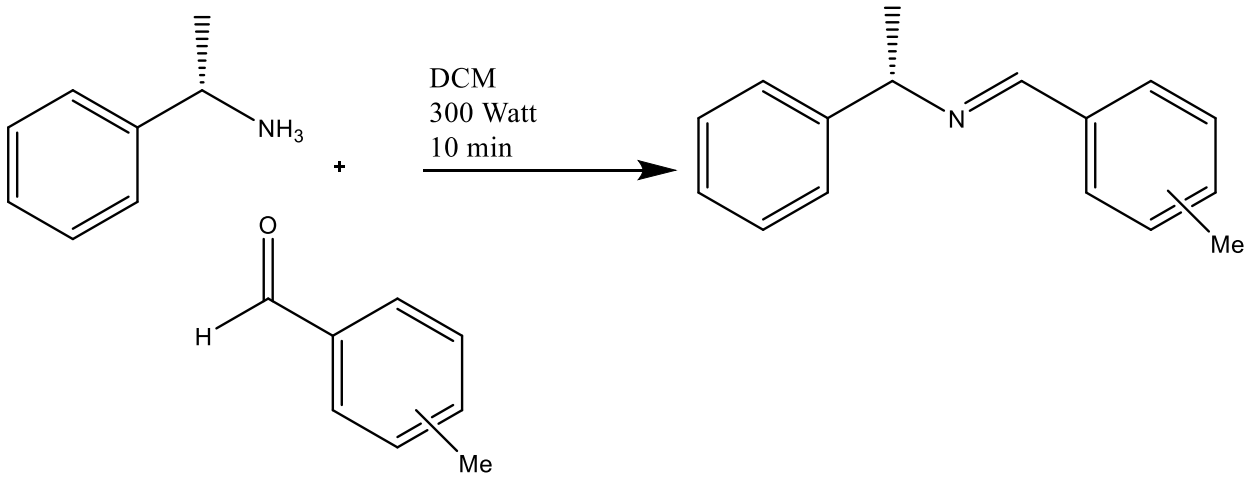
Schiff bases have also been synthesized under microwave irradiations and this method is preferred over conventional refluxing method due to its effectiveness and economicity, it is also called as (MAOS) method. The percentage and purity of obtained product is quite high as compared to the conventional methods [25].

M. A. Va Zaquez et al. in 2004 synthesized a series of Schiff bases by the condensation of anilines with benzaldehyde at room temperature in the absence of a solvent. He utilized IR radiations which acted as a source of energy and an effective promoter. The use IR radiations yielded high reaction yields and reduced the longer reaction times **(Scheme 4)** [26].



Scheme 4: Synthesis of Schiff base by microwave irradiations

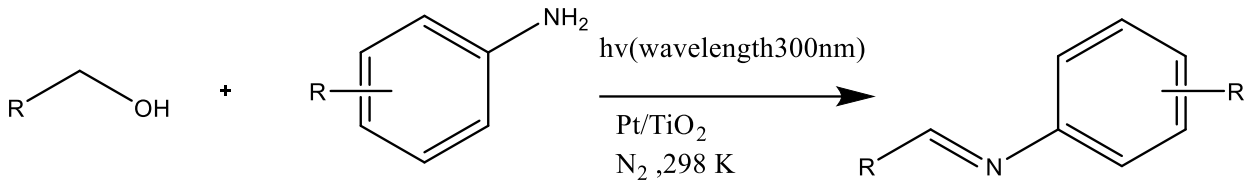
Emily C. Border et al. in 2015 , synthesized Schiff bases by using amines and different functionalized and unfunctionalized aldehydes in DCM catalyzed by microwave radiations by using molecular sieves **(Scheme 5)** [27].



Scheme 5: Synthesis of Schiff base under microwave radiations

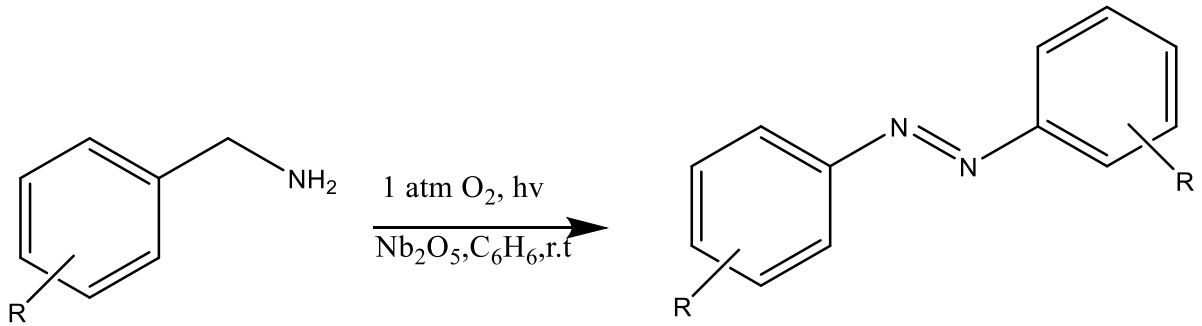
1.1.5.4 Photocatalyzed Oxidation:

Y. Shiraishi et al. in 2011, synthesized Schiff bases by the reaction of amines with alcohols catalyzed by TiO_2 loaded Pt nanoparticles under UV radiations. The reaction was initiated by TiO_2 nanoparticles which resulted in the formation of hole pairs and electron pairs. The hole pair results in oxidizing alcohol to aldehyde which then get condensed with amines **(Scheme 6)** [28].



Scheme 6: Schiff base synthesis by photocatalyzed oxidation

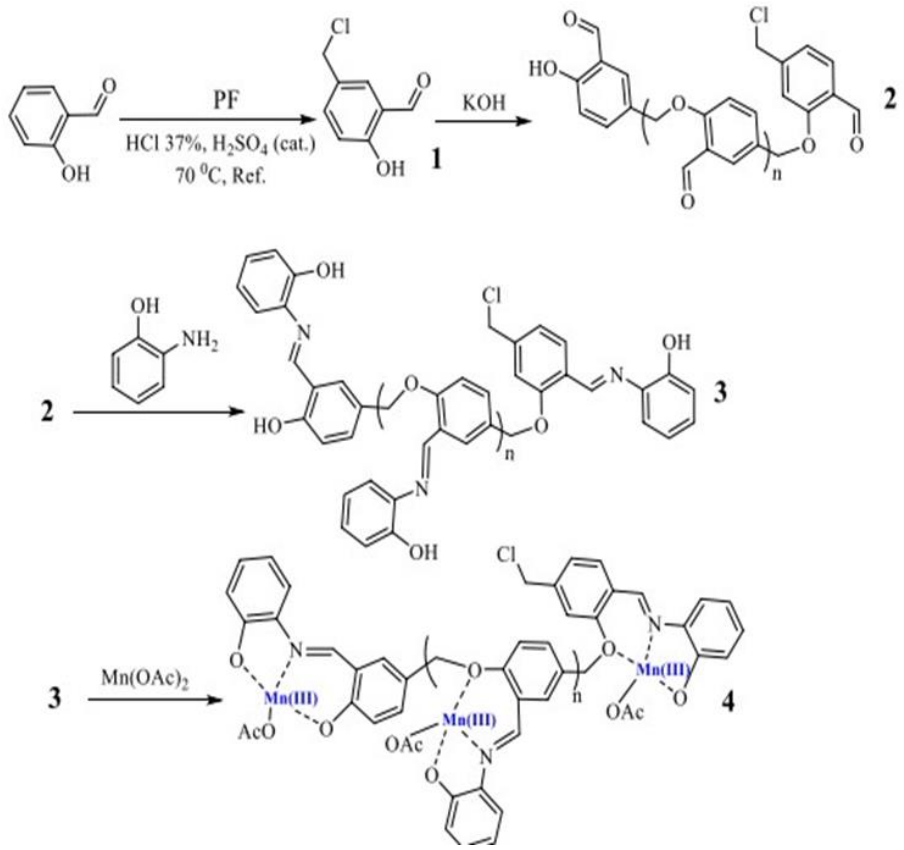
Furukawa et al. in 2013 , used Nb_2O_5 , which is an effective and heterogenous catalyst, for the synthesis of imines under visible light radiations either in the presence or absence of O_2 .For the conversion of benzylamines to imines, a wavelength of 390nm was used, through active electron transfer mechanism by dehydrogenation, then hydrolysis is done with the help of water to aldehyde and its condensation with adsorbed amines resulted in the formation of imines **(Scheme 7)** [29].



Scheme 7: Schiff base synthesis under visible light radiations

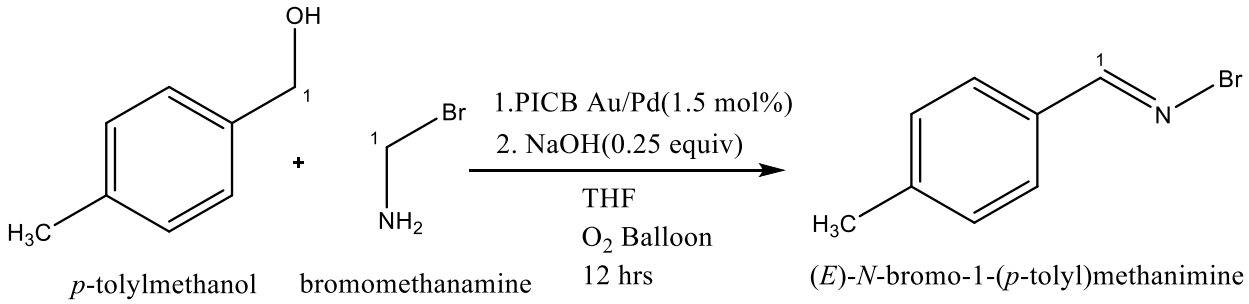
1.1.5.5 Oxidation of Alcohols:

Milad Kazemnejadi et al. in 2017 synthesized 5-hydroxy-5-chloromethyl-benzaldehyde by reacting together primary benzylic alcohols and primary amines using HCl as catalyst **(Scheme 8)** [30].



Scheme 8: Synthesis of PSA-Schiff Base-Mn (III) complex

J. F. Soule et al in 2013, synthesized Schiff bases by using THF as a solvent in the presence of NaOH base and carbon black incarcerated PICB-Au/Pd nanoparticles as reusable and heterogenous catalyst **(Scheme 9)** [31].



Scheme 9: Synthesis of Schiff base in the presence of NaOH

1.1.5.6 From Amino Acids:

Mohammad Shakir and co-workers (2011) had synthesized Schiff bases from glyoxal and leucine in the presence of methanol and NaOH over constant stirring at room temperature. The solid product was washed with methanol and dried in vacuum over anhydrous $CaCl_2$. The yield of the products obtained varied [32].

Har Lal Singh in 2010 synthesized Schiff base ligand by refluxing together 3-methyl-4-fluoro acetophenone and amino acids (phenylalanine, glycine, tryptophan, alanine) for 6-8hrs in methanol which acted as a reaction medium [33].

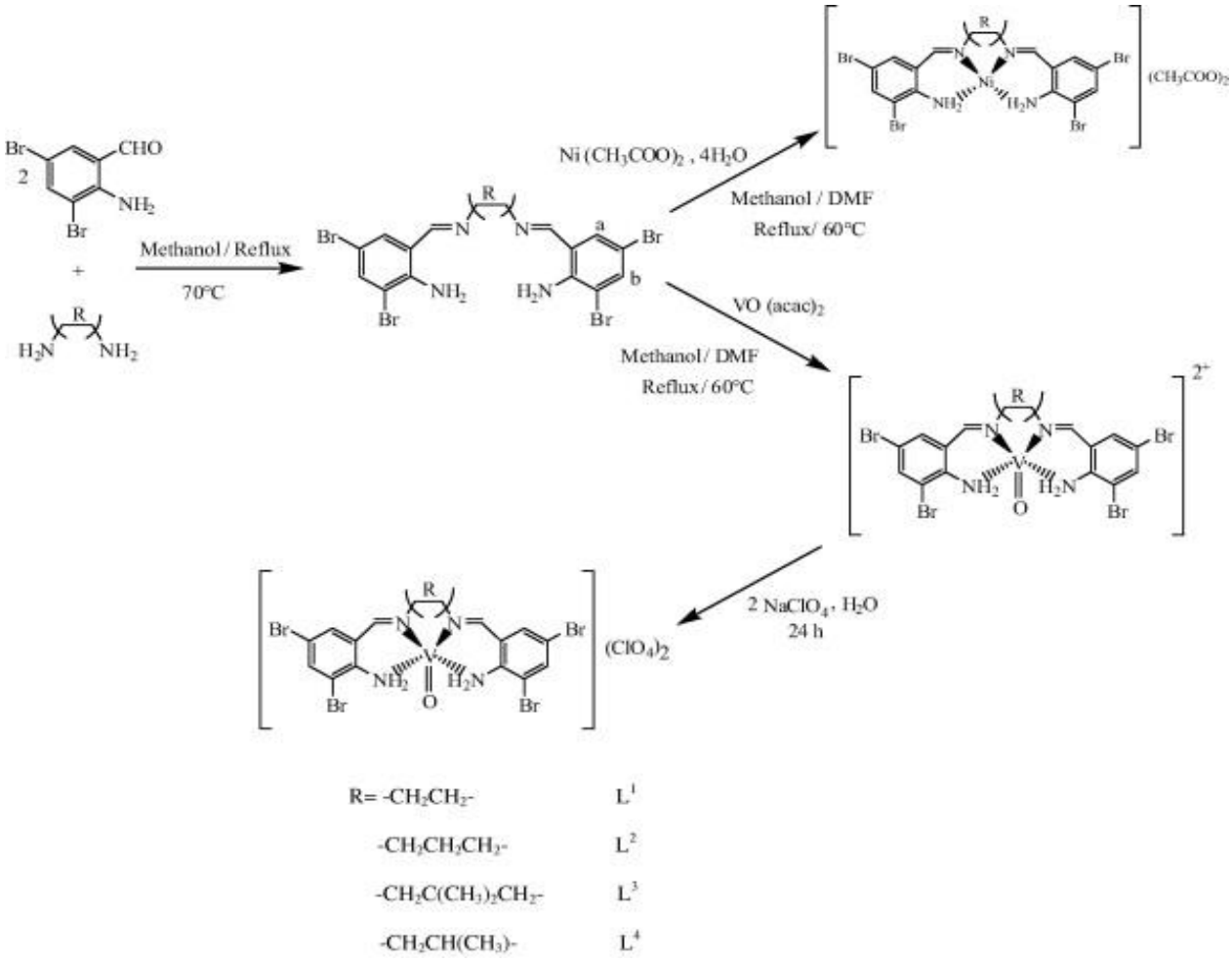
In 2008, Jan Vanco and co-workers synthesized Potassium salt of Schiff base ligand in 79% yield by reacting together equimolar mixture of Salicylaldehyde and alanine and potassium hydroxide dissolved in 10mL of water in the presence of ethanol at room temperature for 24 hours. The product obtained was re-crystallized from methanol [34].

Jianyong Mao and co-workers (2006) had synthesized Schiff bases by reacting equimolar quantities of salicylaldehyde and various amino acids upon reflux at 65 degrees Celsius for 30 minutes. The filtration and washing of final product with ethanol was done. The yield was 88 % [35].

In 2005, WEI Danyi and co-workers synthesized Schiff base ligand by reacting together equimolar quantities of tetra glycol aldehyde and phenylalanine and 3mmol $LiOH.H_2O$. The solvents used were methanol and ethanol mixture and reflux was done for 40 minutes. The product obtained was recrystallized from anhydrous methanol. The product was obtained in good yield [36].

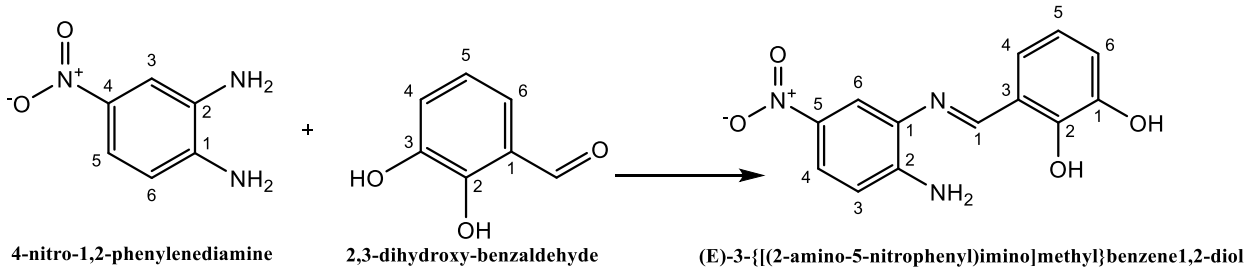
1.1.5.7 From Diamines:

Khosro Mohammadi et al. in 2015 reported the synthesis of Schiff base by reacting together 2-amino-3,5-dibromobenzaldehyde and aliphatic diamine at a reflux for about 12hrs **(Scheme 10)** [37].



Scheme 10: Synthesis of Schiff base from Diamines

W.A.K Mahmood and coworkers (2016) synthesized Schiff bases by reacting 4-Nitro-1,2-Phenylenediamine with 2,3-dihydroxy-benzaldehyde with constant stirring and then their Cu and Ni complexes were made and the yield obtained was 94% Mahmood, Kianfar [38] **(Scheme 11)**.



Scheme 11: Schiff base synthesis from 4-Nitro-o-Phenylenedamines

1.2 Applications of Schiff Bases:

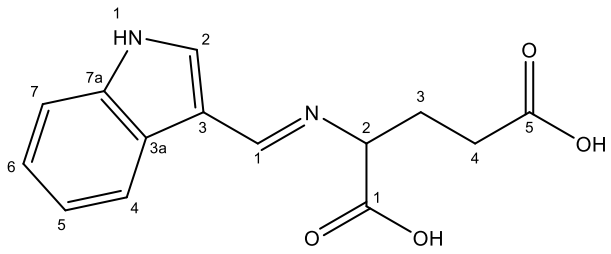
Schiff bases have large number of applications.

1.2.1 Medicines and Pharmacy:

Schiff base complexes have their extensive use in human organism i.e radiopharmaceuticals and MRI (Magnetic resonance imaging) [39]. Schiff bases have been generally used for the treatment of diabetes and AIDS. They have also been helpful in structure elucidation of biomolecules and biological processes of living organism. They are used as antimalarial and cancer drug resistance. They have also been used to immobilize enzyme [40].

1.2.2 Biological Activity:

Schiff bases show excellent biological activity due to the presence of >C=N present in them. The imine group explains the process of racemization and transamination in different biological systems. 2-[(1H-Indol-3-ylmethylene)-amino]-pentanedioic acid is an active antifungal and anti-bacterial agent **(Figure 1)** [41].



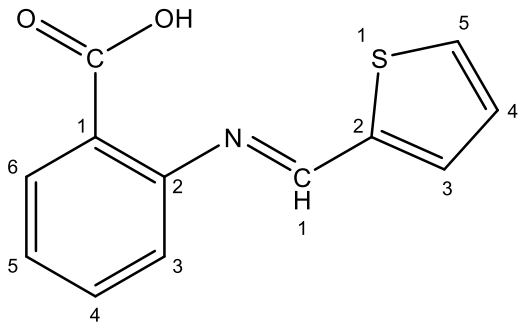
2-[(1H-Indol-3-ylmethylene)-amino]-pentanedioic acid

Figure 1: Bio-active 2-[(1H-Indol-3-ylmethylene)-amino]-pentanedioic acid

Schiff bases are used because of their antibacterial and antifungal properties. Schiff Base complexes of Cu(II) and Cd(II) are active antimicrobial agents against *Staphylococcus aureus* [42].

1.2.3 Anti-bacterial Properties:

Schiff bases are efficient antibacterial agents. They are used against various gram positive and gram negative strains of bacteria e.g. (E)-2-((thiophen-2-ylmethylene)amino)benzoic acid **(Figure 2)** [43].



(*E*)-2-((thiophen-2-ylmethylene)amino)benzoic acid

Figure 2: Anti-bacterially active (E)-2-((thiophen-2-ylmethylene) amino) benzoic acid

As for the treatment of tuberculosis that is caused by mycobacterium tuberculosis, N-(Salicylidine)-2-hydroxyaline is used [44].

1.2.4 Anti-fungal Properties:

Schiff bases are promising antifungal medicines. Quinazolinones derivatives of Schiff bases possess antifungal properties against T.mentagrophytes and Microsporum gypseum. Co (III) complexes have been shown to be effective antifungal agents against *P. aeruginosa and K. pneumoniae* and their activity is comparable with that of standard drugs e.g., ketoconazole. The structure of Co (III) complex is shown in the figure **(Figure 3)** [45].

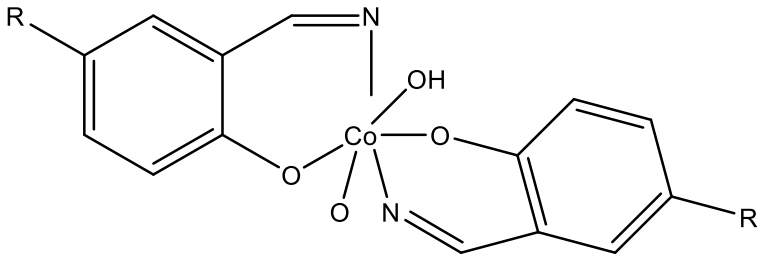


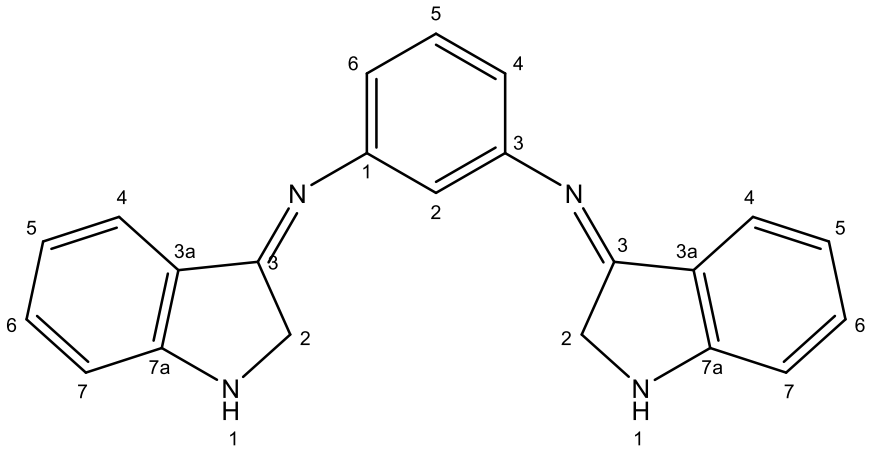
Figure 3: Antifungally active of Co (II) complex of schiff base

1.2.5 Biocidal Properties:

Schiff bases of Isatin derivatives are employed to destruct parasites and protozoa. Schiff bases of β-keto esters and O-aminobenzoic acid have been used biocidally against E. coli, A.niger and B.cinera.

1.2.6 Anti-viral Properties:

Schiff bases possess excellent antiviral properties. Isatin schiff bases are used against HIV **(Figure 4)**. These Schiff bases also show anti-convulsant activity and are used in anti-epileptic drugs [46].



(3*Z*,3'*Z*)-*N*,*N*'-(1,3-phenylene)bis(indolin-3-imine)

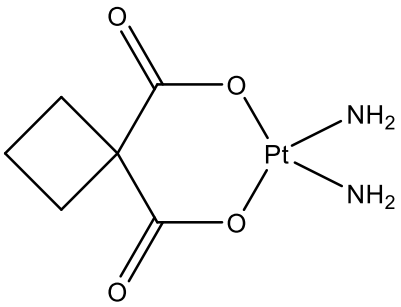
Figure 4: Antivirally active Isatin derived Schiff base

1.2.7 Anti-malarial Properties:

Malaria is a disease caused by biting of female anopheles mosquito. It has been known for centuries and serious health problems are caused by it. Schiff bases are also used as antimalarial drugs. [47]

1.2.8 Anti-cancer Properties:

Schiff bases have high anti-cancer activity. Some Schiff bases derivatives block ribonucleotide reductases in cancer cells to treat leukemia. Schiff bases of Pt (II) complexes are well known for their anti-tumor activity, so their drugs have got a worldwide approval to be used **(Figure 5)** [48].



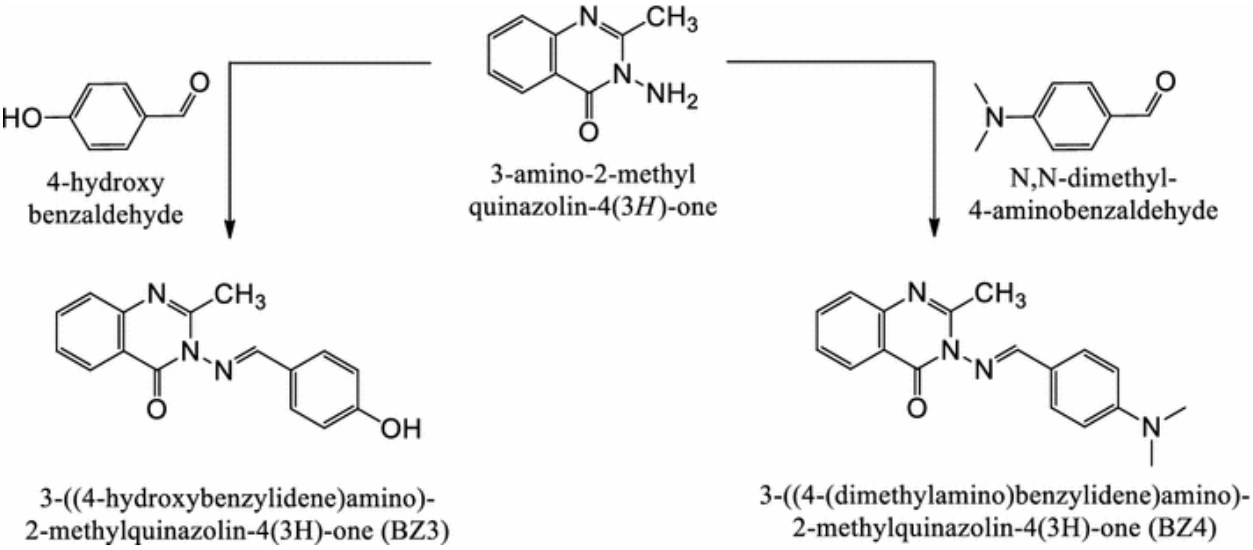
carboplatin

Figure 5: Anti-cancer drug Carboplatin

1.2.9 Corrosion Inhibitors:

Schiff bases have wide applications in inhibition of corrosion in corrosive environments and are also economically feasible. Inhibitor molecules adsorb themselves on the surface of metal or alloy and prevent all kinds of cathodic and anodic reactions thereby protecting mild steel from corrosive environments.

Dalia M. Jamil synthesized 3-((4-(dimethylamino)benzylidene)amino)-2-methylquinazolin-4(3*H*)-one (BZ4) which acted as efficient corrosion inhibitor of mild steel in acidic media by reacting 3-amino-2-methylquinazolin-4(3*H*)-one with 4-hydroxybenzaldehyde and *N*,*N*-dimethyl-4-aminobenzaldehyde at reflux **(Scheme 12**) [49]. The mechanism of adsorption of synthesized Schiff on the surface of metal is shown in figure **(Figure 6).**



Scheme 12: Synthesis of corrosion inhibitor

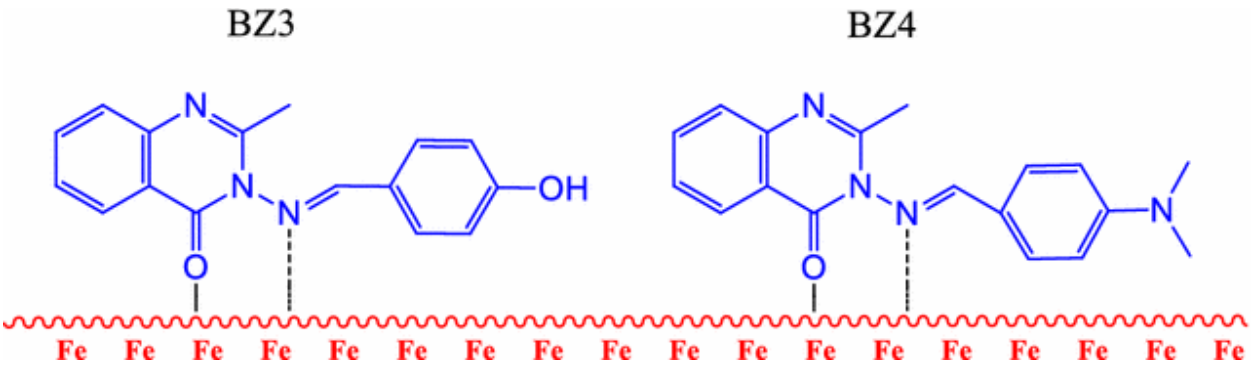
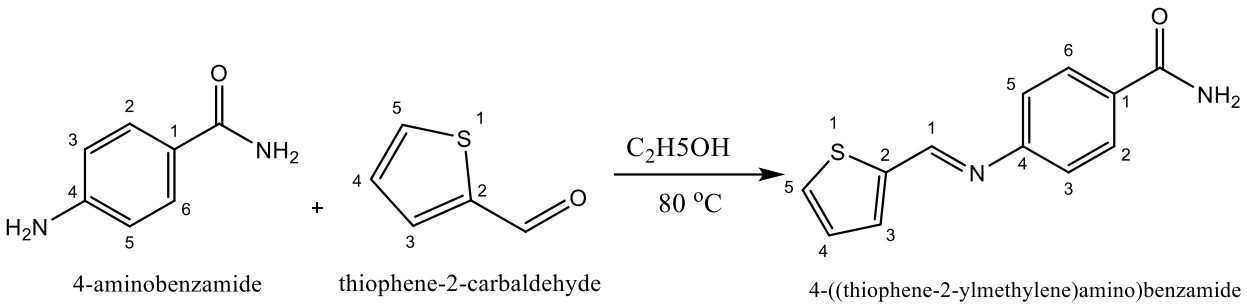


Figure 6: Adsorption of Schiff base ligand on metal surface

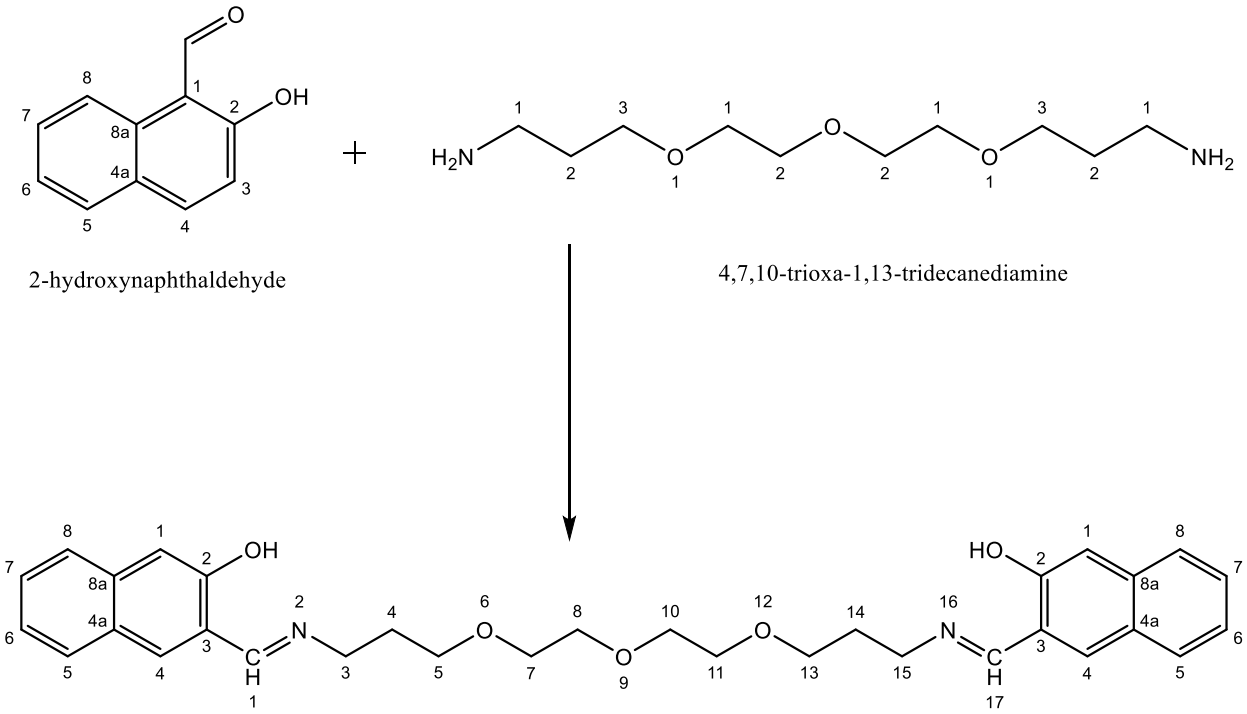
Fatih Tezcan and his coworkers in 2018 synthesized Schiff base by reacting together 4-aminobenzamide and thiophene-2-carbaldehyde in equimolar ratio under reflux at 353 K for 5 hrs. The resulting Schiff base 4-((thiophene-2-ylmethylene)amino)benzamide showed excellent corrosion inhibition activity of 96% against mild steel in 1.0M HCl **(Scheme 13)** [50].



4-aminobenzamide + thiophene-2-carbaldehyde → 4-((thiophene-2-ylmethylene)amino)benzamide

Scheme 13: Synthesis of corrosion inhibitor of mild steel

Sonia Benabid et al in 2017 synthesized anti-corrosive Schiff base by the reaction of 2-hydroxynaphtaldehyde and 4,7,10-trioxa-1,13-tridecanediamine in molar ratio of 1:2 and the reaction mixture was refluxed for 14 hrs. in methanol. The brown colored Schiff base was obtained in 61% yield **(Scheme 14)** [51].

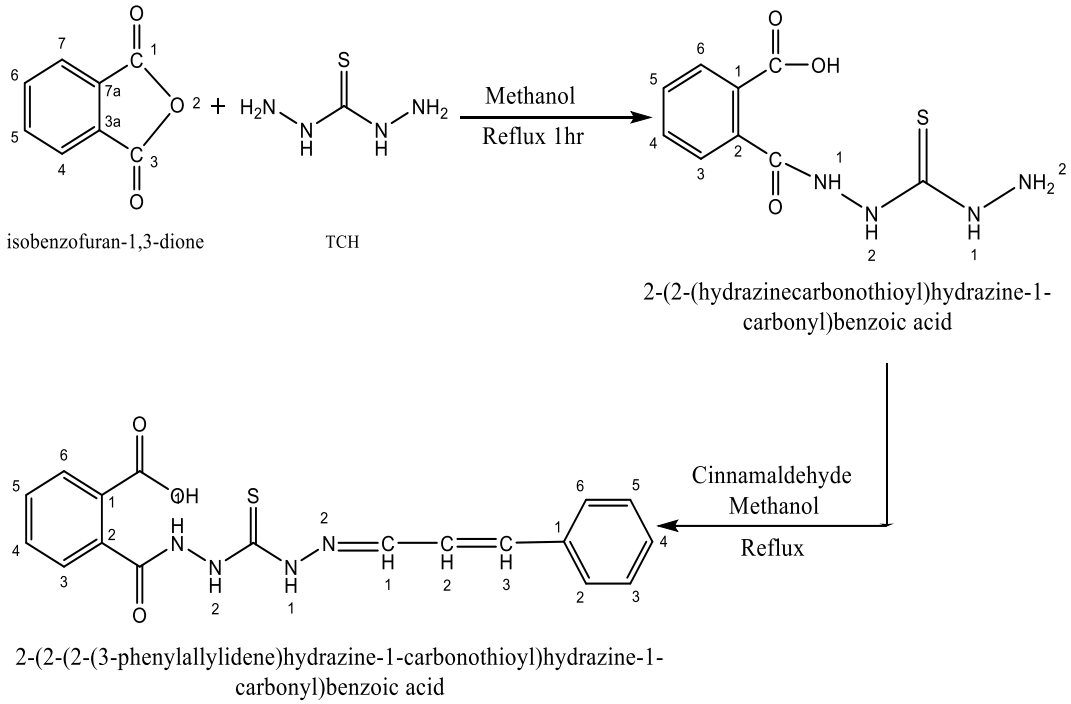


2-hydroxynaphthaldehyde + 4,7,10-trioxa-1,13-tridecanediamine → 3,3'-((1*E*,16*E*)-6,9,12-trioxa-2,16-diazaheptadeca-1,16-diene-1,17-diyl)bis(naphthalen-2-ol)

Scheme 14: Synthesis of anti-corrosive Schiff base HNTTD

Ahamad et al. in 2010 synthesized 2-(2-(2-(3-phenylallylidene)hydrazine-1-carbonothioyl)hydrazine-1-carbonyl)benzoic acid Schiff base by reacting together isobenzofuran-1,3-dione and TCH in equimolar ratio

under reflux for 1hr. The yield of the product obtained was 91% and acted as efficient corrosion inhibitor on the surface of mild steel in HCl and the corrosion inhibition efficiency was 99.5% **(Scheme 15)** [52].



Scheme 15: Synthetic route of anti-corrosive Schiff base

Chapter 2

2 Experimental:

2.1 Chemicals and Reagents:

The reagents used were benzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde, 4-hydroxybenzaldehyde, propionaldehyde, 4-(diethylamino)salicylaldehyde, 4-nitro-1,2-phenylenediamine and glacial acetic acid.

2.2 Solvents:

All the solvents ethanol, methanol, chloroform, ethyl acetate, n-hexane, tetrahydrofuran were of analytical grade and used without further purification.

2.3 Instrumentation:

Electronic analytical balance ATY224 was used to weigh different chemicals. The reaction progress was monitored through TLC which was analyzed under UV lamp. The solvents were evaporated using rotary evaporator R-210. The melting points of products were recorded in open capillary in melting point apparatus SMP10. The functional groups of compounds were identified through FT-IR equipped with ATR model ALPHA 20488. Elemental analysis of the sample was done through CHN analyzer.

2.4 Chemical composition of carbon steel alloy for anti-corrosion activity

The carbon steel alloy utilized as Working Electrodes belongs to the grade AISI 1040 of carbon steel and the surface area of the sample was 1 cm^2. Supplier has provided the list of mechanical properties of the chosen carbon steel sample to be tested, presented as following: Yield strength is given as 415 MPa, tensile strength is mentioned as 620 MPa and 18% is elongation to failure. The carbon steel working electrodes' chemical composition (wt.%) was S ≤ 0.050 %, Mn 0.60-0.90%,

C 0.370-0.440%, P ≤ 0.040, and Fe 98.6-99% was balanced. Data is obtained from the Octal Steel (China).

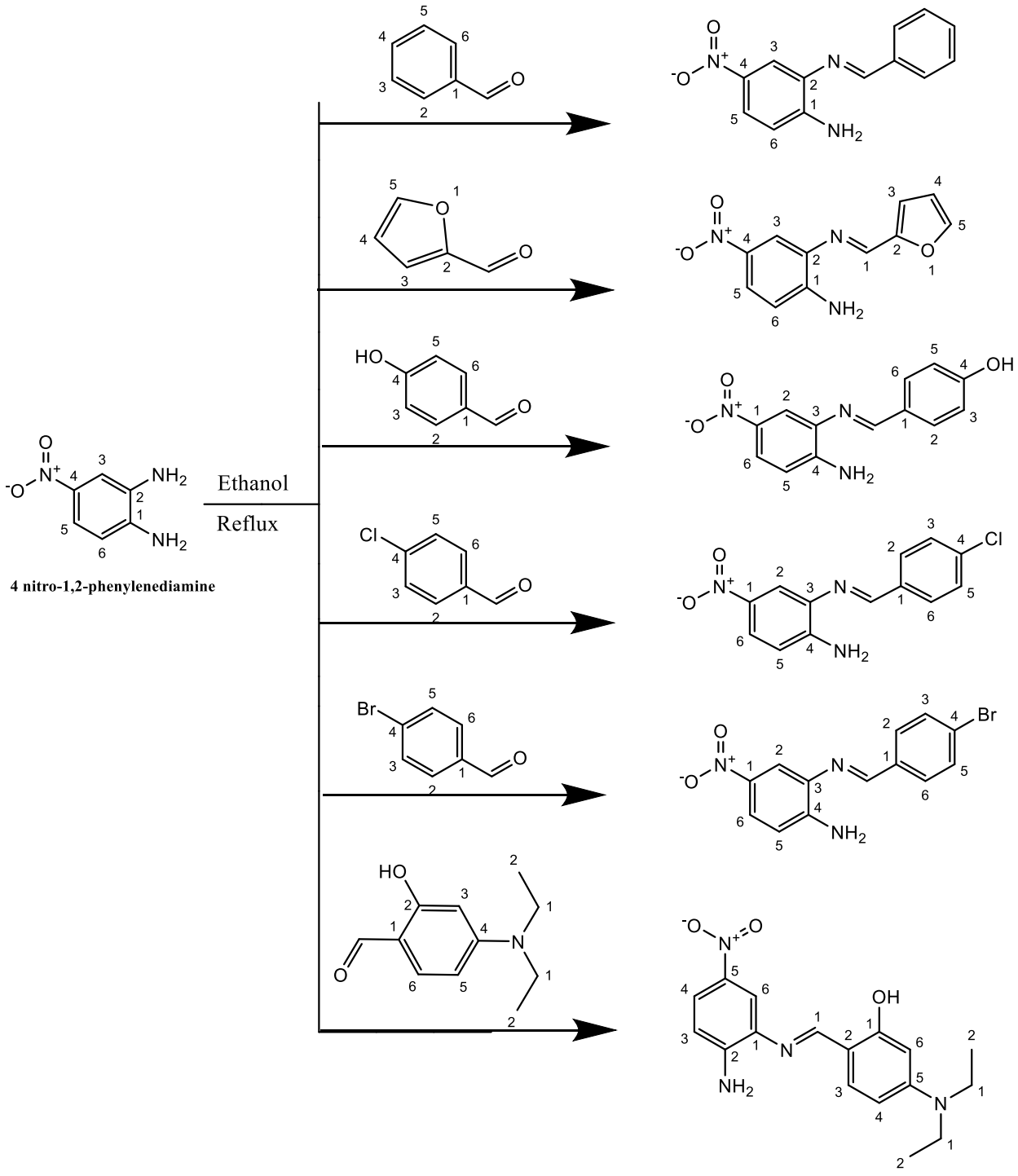
2.4.1 Test solution for Anti-corrosion activity

Two different solutions were prepared, 5% SCME soil solution and 5% Wah soil solution. These solutions were prepared by the 1:1 soil-to-water method, where 200 g of scoop of soil was put into the 500 ml beaker and then 200 ml of distilled water was added, the solution is stirred for 20 minutes. Then transfer the paste to the filter funnel to get the extract. This extract was then placed on the hot plate and leave it for evaporation to obtain the concentrated soil salt solution, which then was used to make the 5% solution of soil using distilled water. The 300-ppm concentration for each inhibitor were used. Inhibitors were organic in nature, so they were soluble in (methanol and ethanol), hence by using the 300-ppm using 5% soil solution.

2.5 Synthesis of Different Schiff Bases:

2.5.1 General Procedure for Schiff Base Synthesis

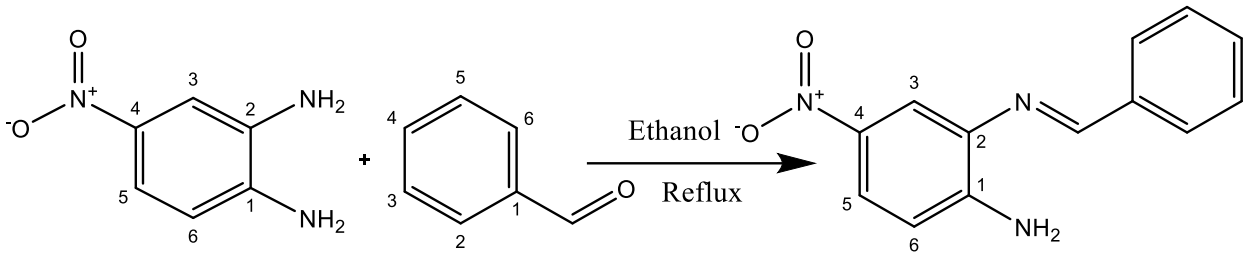
The amine (0.5 g, 3.26mmol) was dissolved in 5ml of ethanol. (1.2g, 6.53mmol) of aldehyde was dissolved separately in 3ml of ethanol. For the synthesis of Schiff base, 4-nitro-1,2-phenylenediamine was condensed with seven different aldehydes namely benzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde, 4-hydroxybenzaldehyde, propionaldehyde and 4-(diethylamino)salicylaldehyde in ethanol or methanol whether at room temperature or high temperature. The reaction time varied from 1hr-24hrs either at constant stirring or reflux. The extra solvent was evaporated using a rotary evaporator. The precipitates obtained were then filtered and washed with suitable solvent over filter paper to remove impurities. The impure products were further purified by repeated recrystallizations. The final products were dried in open air.



Scheme 16: Synthesis of Schiff bases by using 4-Nitro-1,2-Phenylenediamine

2.5.1.1 2-(benzylideneamino)-4-nitroaniline (ASB-1)

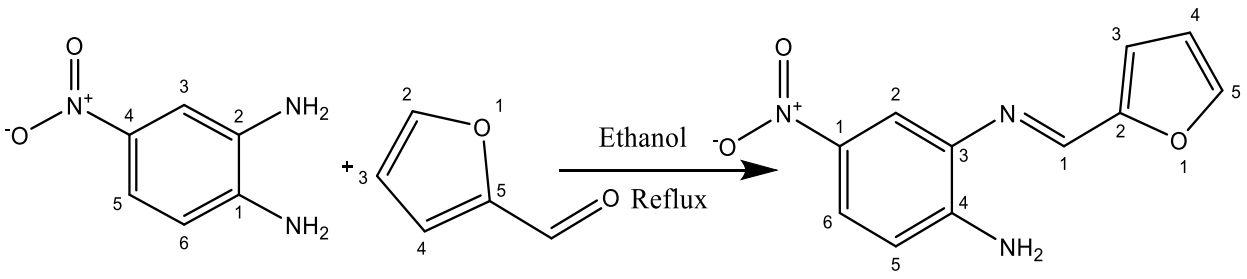
Physical appearance: Yellow Crystals, Reaction time: 7hrs, Yield: 75%, TLC System: 2% ($CH_3OH:CHCl_3$), Melting point: 198-200 ^oC, FT-IR (ν_{max}, cm^{-1}): 3352-3470 (N-H), 1608 (C=N), 1571 (NO_2), 1478 (C=C).



4-nitro-1,2-phenylenediamine benzaldehyde (*E*)-2-(benzylideneamino)-4-nitroaniline

2.5.1.2 2-((furan-2-ylmethylene)amino)-4-nitroaniline (ASB-2)

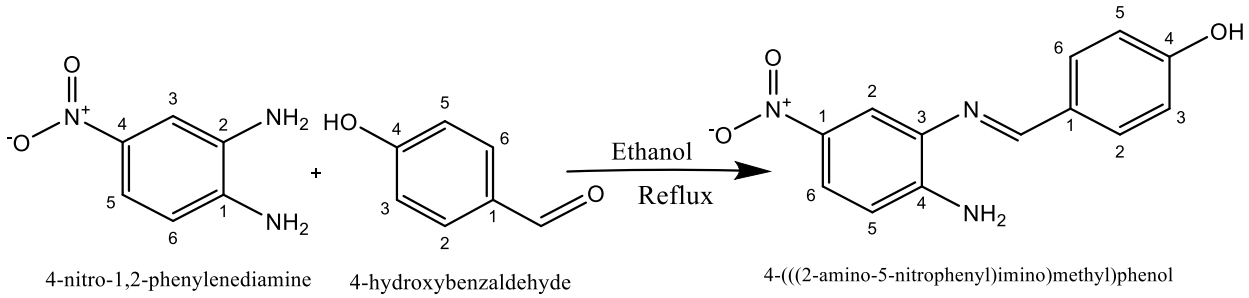
Physical appearance: Blackish Brown Crystals, Reaction time: 24hrs, Yield: 80%, TLC System: 2% ($CH_3OH:CHCl_3$), Melting point: 202-204 ^oC, FT-IR (ν_{max}, cm^{-1}): 3301-3444 (N-H), 1611 (C=N), 1574 (NO_2), 1477 (C=C), 1181(C=O).



4-nitro-1,2-phenylenediamine furfural 2-((furan-2-ylmethylene)amino)-4-nitroaniline

2.5.1.3 4-(((2-amino-5-nitrophenyl)imino)methyl)phenol (ASB-3)

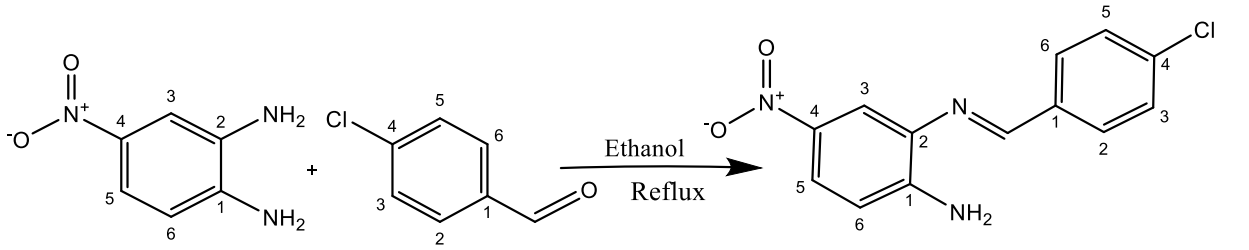
Physical appearance: Yellow Powder, Reaction time: 5hrs, Yield: 77%, TLC System: 2% ($CH_3OH:CHCl_3$), Melting point:224-226 ^oC, FT-IR (ν_{max}, cm^{-1}): 3312 (O-H), 1586 (C=N), 1505 and 1334 (NO_2), 1446 (C=C).



4-nitro-1,2-phenylenediamine 4-hydroxybenzaldehyde 4-(((2-amino-5-nitrophenyl)imino)methyl)phenol

2.5.1.4 2-(4-chlorobenzylidene)-5-nitrobenzene-1,2-diamine (ASB-4)

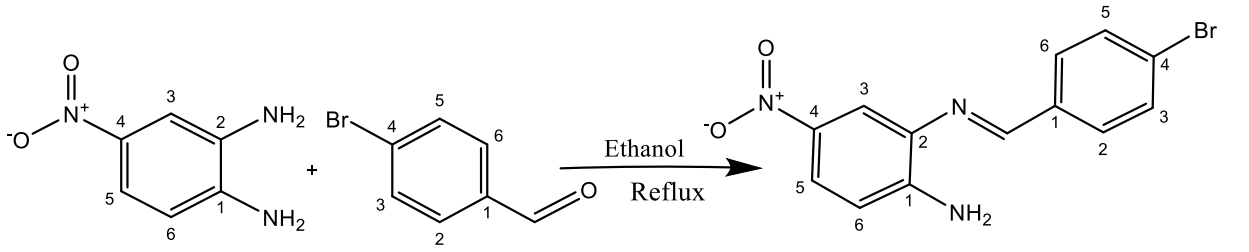
Physical appearance: Yellow Powder, Reaction time: 4hrs, Yield:80%, TLC System: 2% (CH_3OH:$CHCl_3$), Melting point: 192-194 ^oC, FT-IR (ν_{max}, cm^{-1}): 3374 3484 (N-H), 1589 (C=N), 1328 and 1486 (NO_2), 745 (C-Cl).



4-nitro-1,2-phenylenediamine 4-chlorobenzaldehyde (*E*)-2-((4-chlorobenzylidene)amino)-4-nitroaniline

2.5.1.5 2-(4-bromobenzylidene)-5-nitrobenzene-1,2-diamine (ASB-5)

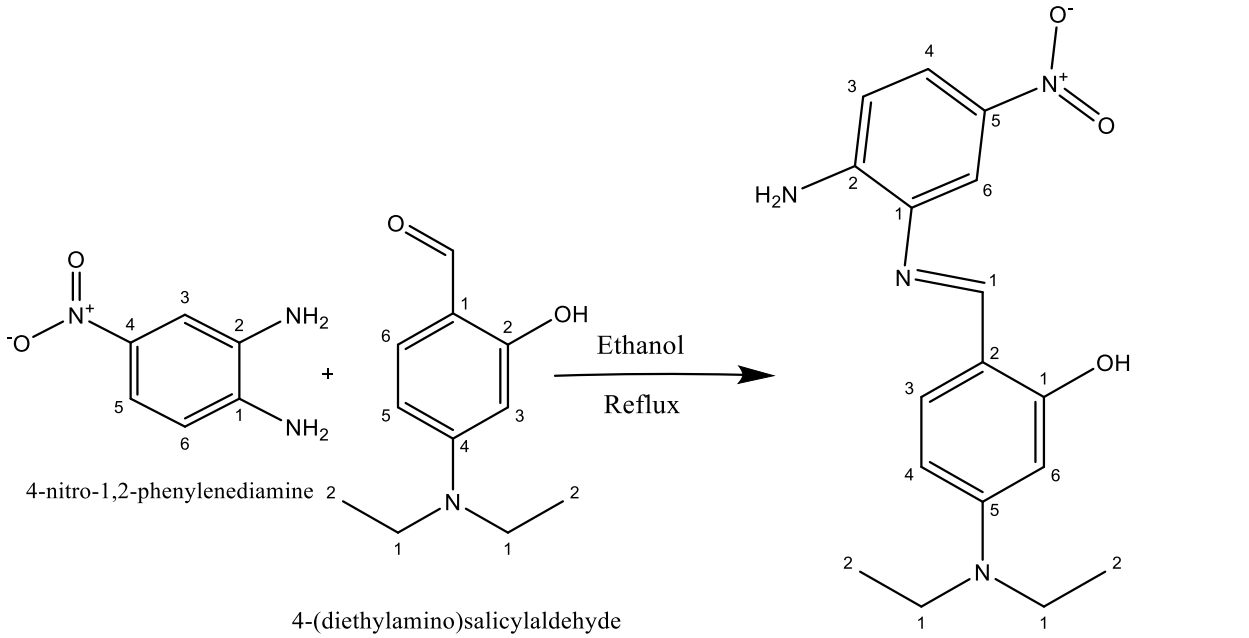
Physical appearance: Yellow Powder, Reaction time: 9hrs, Yield: 70%, TLC System: 2% (CH_3OH:$CHCl_3$), Melting point: 221-223 ^oC, FT-IR (ν_{max}, cm^{-1}): 3369 3481 (N-H), 1588 (C=N), 1485 (C=C), 1327(C-N), 745(C-Br).



4-nitro-1,2-phenylenediamine 4-bromobenzaldehyde (*E*)-2-((4-bromobenzylidene)amino)-4-nitroaniline

2.5.1.6 2-(((2-amino-5-nitrophenyl)imino)methyl)-5-(diethylamino)phenol (ASB-6)

Physical appearance: Brownish Powder, Reaction time: 3hrs, Yield: 75%, TLC System: 2% (CH_3OH:$CHCl_3$), Melting point:205-207 ^oC, FT-IR (ν_{max}, cm^{-1}): 3330 (O-H), 1575 (C=N), 1485 (C=C), 1296 (C-N).



4-nitro-1,2-phenylenediamine 4-(diethylamino)salicylaldehyde

(*E*)-2-(((2-amino-5-nitrophenyl)imino)methyl)-5-(diethylamino)phenol

Chapter 3

3 Results and Discussion

This chapter deals with the results and discussion of the target molecules, synthesized using a specific scheme.

The reaction was carried out by reacting the amine with aldehyde in ethanol under reflux. The aldehydes used to synthesize Schiff bases were benzaldehyde, furaldehyde, 4-hydroxybenzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde, 4(diethylamino)Salicylaldehyde. The reaction progress was monitored by TLC. FT-IR was performed after completion of reaction. The appearance of C=N at around 1600 cm^{-1} indicated the formation of imine linkage which is the characteristic of Schiff base.

3.1 Synthesis of Schiff Base:

Schiff bases were synthesized by reacting together aromatic aldehydes with diamine. The characterization of products was done through physical and spectroscopic studies. The physical and data of compounds are given in the table **(Table 1).**

Table 1: Physical data of synthesized Schiff bases

Ligand	Molecular weight (g/mol)	Texture	Colour	Melting point (ºC)	Yield (%)
ASB-1	**112.16**	**Powder**	**Yellow**	**198-200**	**75**
ASB-2	**98.0846**	**Crystals**	**Brownish black**	**202-204**	**80**
ASB-3	**122.123**	**Crystals**	**Yellow**	**224-226**	**77**
ASB-4	**140.567**	**Powder**	**Yellow**	**192-194**	**80**
ASB-5	**185.02**	**Powder**	**Yellow**	**221-223**	**70**
ASB-6	**193.24**	**Powder**	**Yellow**	**205-207**	**75**

In the FT-IR of the compounds (ASB-1 – ASB-6) the characteristic imine band appeared at 1575-1611 cm^{-1} which is the main functional group of Schiff base and so it indicated the formation of Schiff base.

3.1.1 Characterization of 2-(benzylideneamino)-4-nitroaniline (ASB-1)

The indication of completion of reaction was obtained through FT-IR and difference in melting point of final product from that of individual reactants also confirmed the product formation. The band at 1608 cm^{-1} also confirmed the formation of Schiff base. The band of primary amine was observed at 3352-3470, NO_2 at 1571 and C=C at 1478 **(Figure 7).**

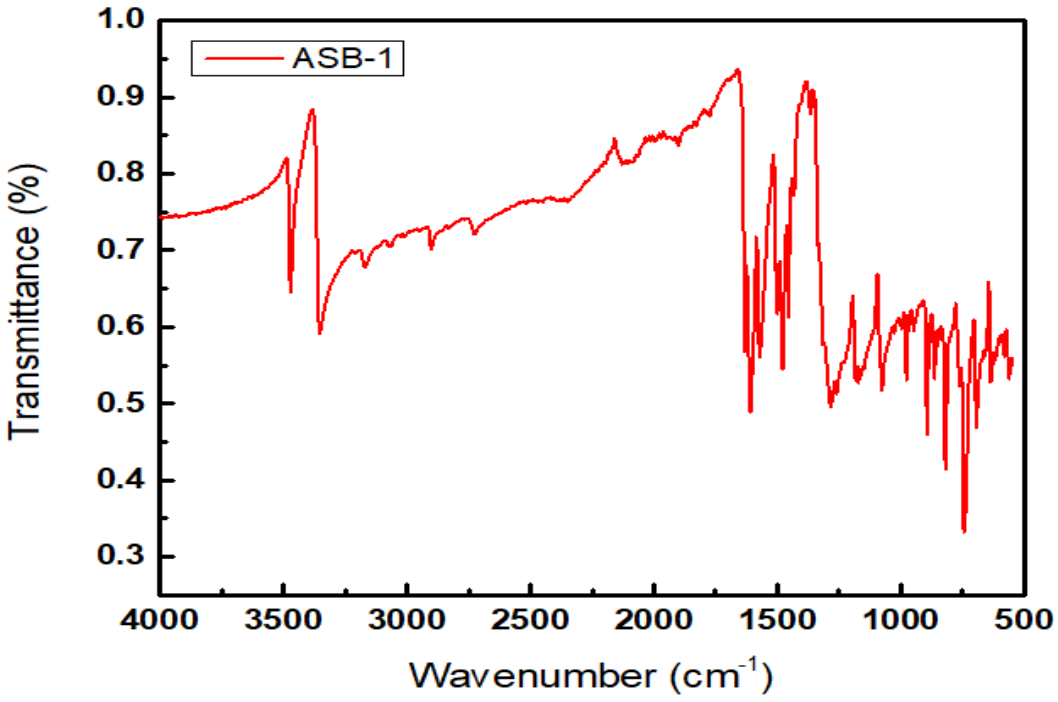


Figure 7: FTIR Spectrum of ASB-1

CHN analysis was also performed to check the percentage composition of synthesized Schiff bases. The following table shows the calculated and found percentage composition of elements which are in close approximation and so they confirm the formation of Schiff base **(Table 2).**

Table 2: CHN Analysis of ASB-1

Molecular Formula	Found			Calculated		
$C_{13}H_{11}N_3O_2$	C%	H%	N%	C%	H%	N%
	63.28	3.20	14.45	64.72	4.60	17.42

3.1.2 Characterization of 2-((furan-2-ylmethylene)amino)-4-nitroaniline (ASB-2)

The indication of completion of reaction was obtained through FT-IR and difference in melting point of final product from that of individual reactants also confirmed the product formation. The band at 1611 cm^{-1} also confirmed the formation of Schiff base. The band of N-H was observed at 3301-3444, NO_2 band at 1574, C=C at 1477 and C-O at 1181 cm^{-1} **(Figure 8).**

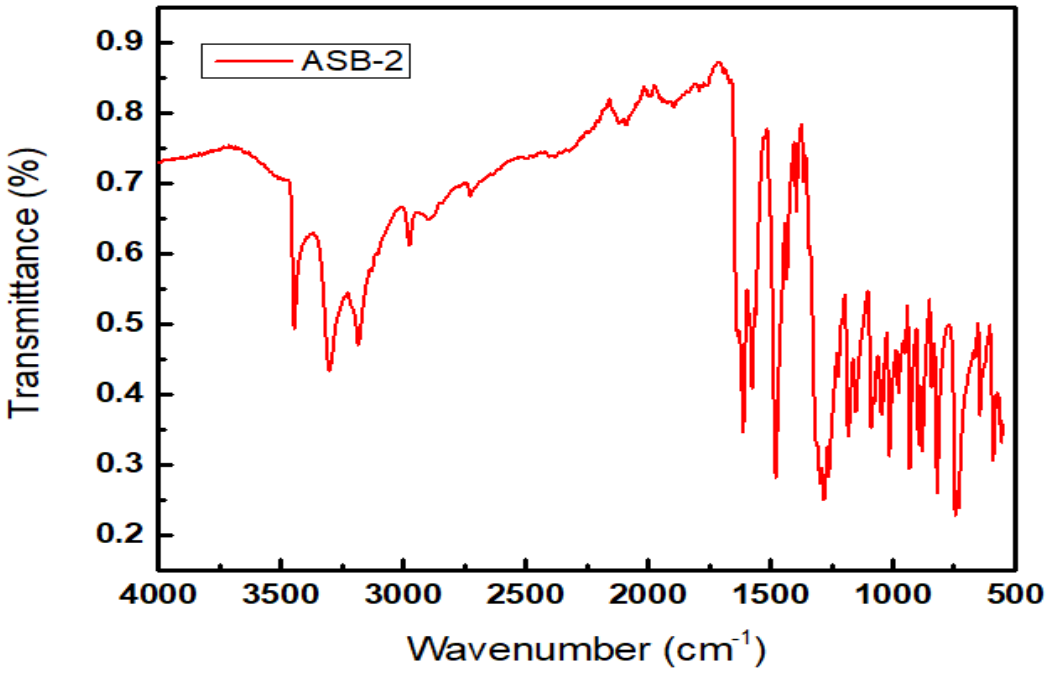


Figure 8: FTIR Spectrum of ASB-2

CHN analysis was also performed to check the percentage composition of synthesized Schiff bases. The following table shows the calculated and found percentage composition of elements which are in close approximation and so they confirm the formation of Schiff base **(Table 3)**.

Table 3: CHN Analysis of ASB-2

Molecular Formula	**Found**			**Calculated**		
$C_{11}H_9N_3O_3$	C %	H %	N%	C %	H %	N %
	57.14	3.92	18.17	56.01	1.18	16.42

3.1.3 Characterization of 4-(((2-amino-5-nitrophenyl)imino)methyl)phenol (ASB-3)

The indication of completion of reaction was obtained through FT-IR and difference in melting point of final product from that of individual reactants also confirmed the product formation. The band at 1586 cm^{-1} also confirmed the formation of Schiff base. The O-H band was observed at 3312, NO_2 at 1505 and C=C at 1446 cm^{-1} **(Figure 9).**

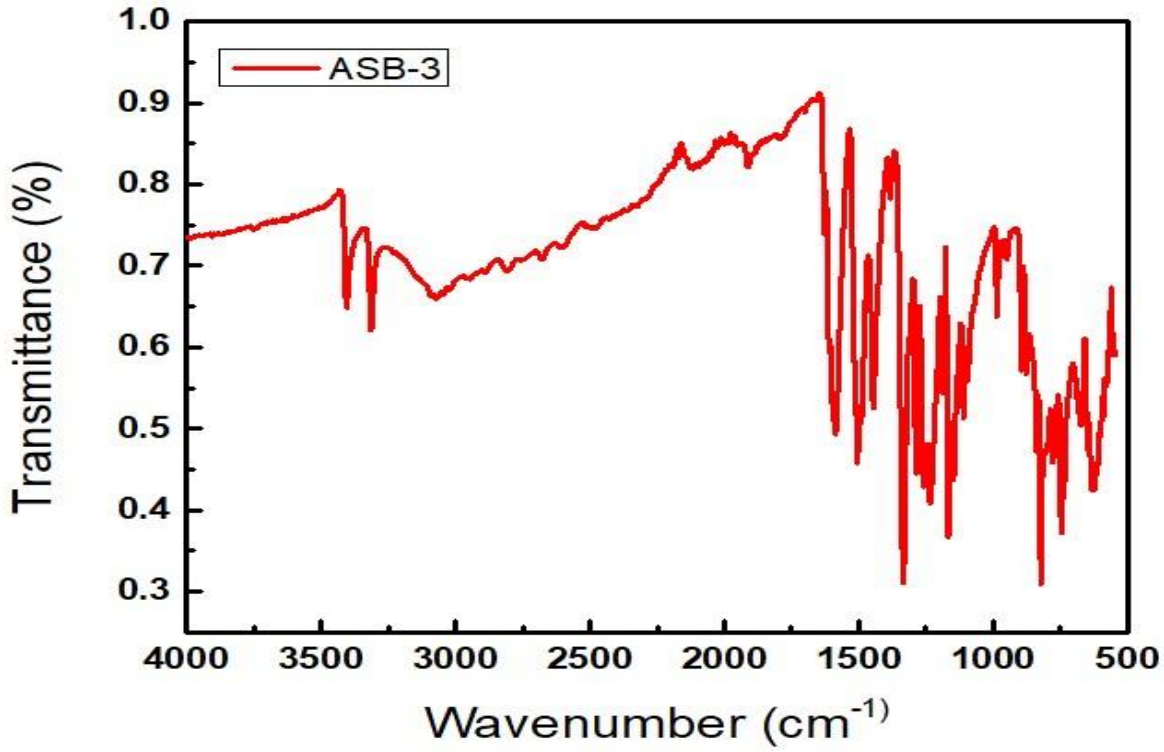


Figure 9: FTIR Spectrum Of ASB-3

CHN analysis was also performed to check the percentage composition of synthesized Schiff bases. The following table shows the calculated and found percentage composition of elements which are in close approximation and so they confirm the formation of Schiff base **(Table 4).**

Table 4: CHN Analysis of ASB-3

Molecular Formula	**Found**			**Calculated**		
$C_{13}H_{11}N_3O_3$	C %	H %	N %	C %	H %	N %
	61.22	1.97	13.48	60.70	4.31	16.33

3.1.4 Characterization of N1-(4-chlorobenzylidene)-5-nitrobenzene-1,2-diamine (ASB-4)

The indication of completion of reaction was obtained through FT-IR and difference in melting point of final product from that of individual reactants also confirmed the product formation. The band near 1589 cm^{-1} also confirmed the formation of Schiff base. The N-H band was observed at 3374-3484, NO_2 at 1328 and C-Cl at 745 cm^{-1} **(Figure 10).**

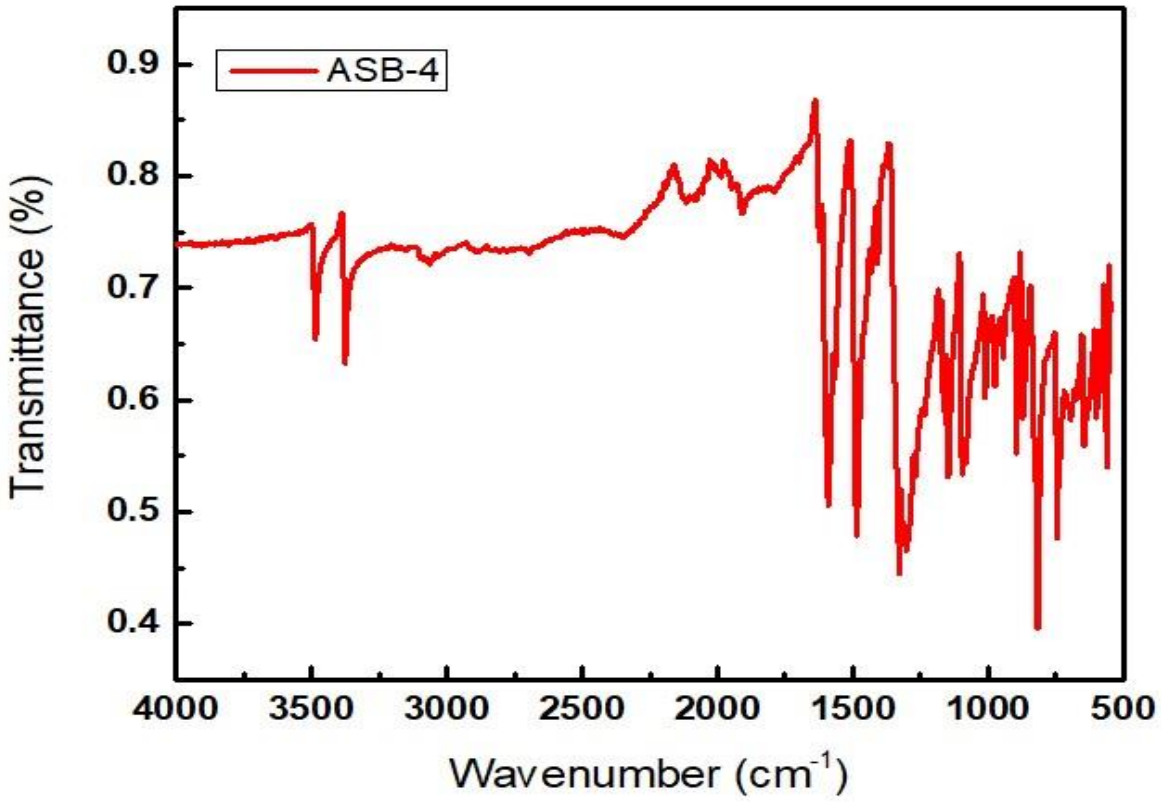


Figure 10: FTIR Spectrum of ASB-4

CHN analysis was also performed to check the percentage composition of synthesized Schiff bases. The following table shows the calculated and found percentage composition of elements which are in close approximation and so they confirm the formation of Schiff base **(Table 5).**

Table 5: CHN Analysis of ASB-4

Molecular Formula	Found			Calculated		
$C_{13}H_{10}ClN_3O_2$	C%	H%	N%	C%	H%	N%
	59.22	1.88	12.47	56.64	3.66	15.24

3.1.5 Characterization of N1-(4-bromobenzylidene)-5-nitrobenzene-1,2-diamine (ASB-5)

The indication of completion of reaction was obtained through FT-IR and difference in melting point of final product from that of individual reactants also confirmed the product formation. The band near 1588 cm^{-1} also confirmed the formation of Schiff base. The N-H band was observed at 3369-3481, C=C at 1485, C-N at 1327, C-Br at 745 cm^{-1} **(Figure 11).**

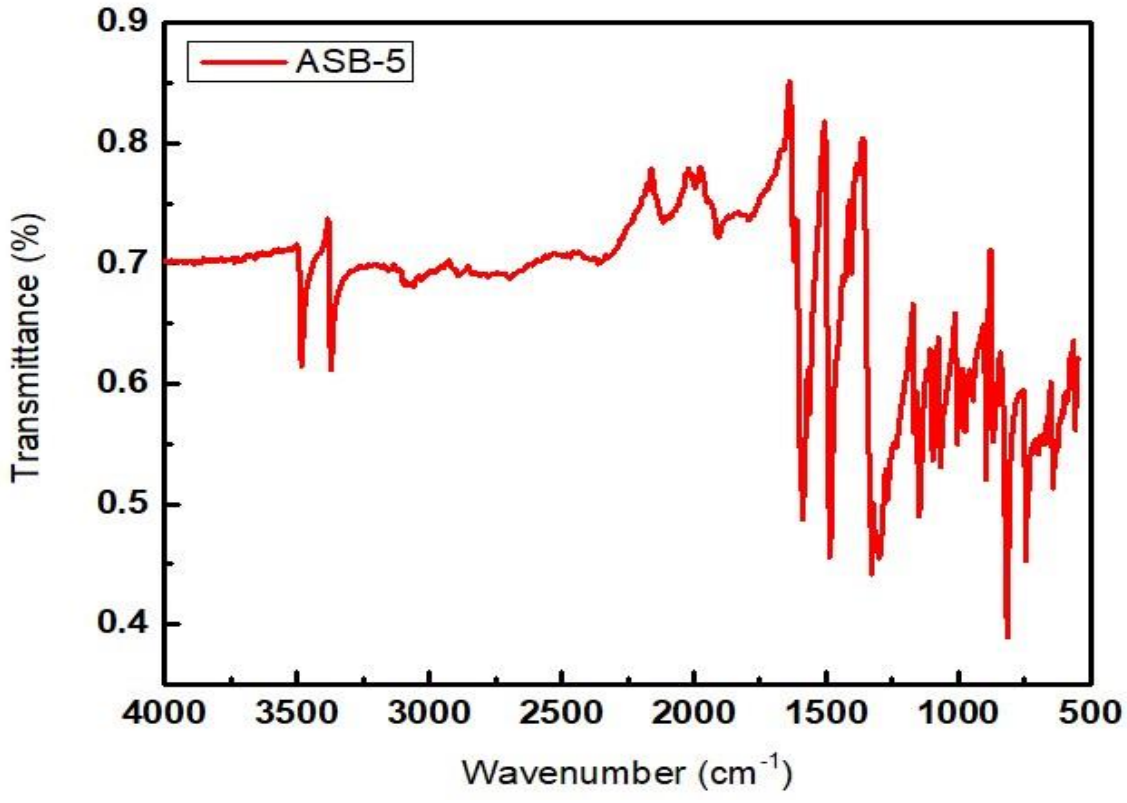


Figure 11: FTIR Spectrum of ASB-5

CHN analysis was also performed to check the percentage composition of synthesized Schiff bases. The following table shows the calculated and found percentage composition of elements which are in close approximation and so they confirm the formation of Schiff base **(Table 6).**

Table 6: CHN Analysis of ASB-5

Molecular Formula	**Found**			**Calculated**		
$C_{13}H_{10}BrN_3O_2$	C%	H%	N%	C%	H%	N%
	50	1.47	13.53	48.77	3.15	13.13

3.1.6 2-(((2-amino-5-nitrophenyl)imino)methyl)-5-(diethylamino)phenol (ASB-6)

The indication of completion of reaction was obtained through FT-IR and difference in melting point of final product from that of individual reactants also confirmed the product formation. The band at 1575 cm^{-1} also confirmed the formation of Schiff base. The O-H band was observed at 3330, C=C at 1485 and C-N at 1296 cm^{-1} **(Figure 12)**.

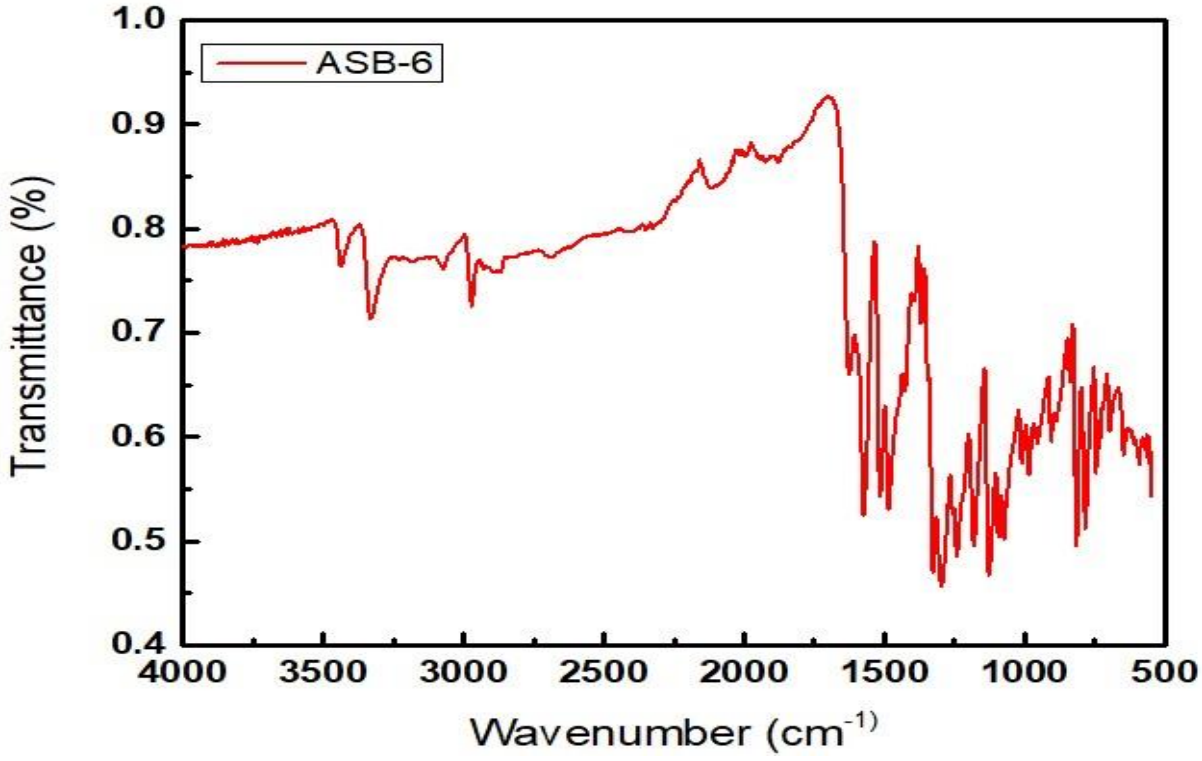


Figure 12: FTIR Spectrum of ASB-6

CHN analysis was also performed to check the percentage composition of synthesized Schiff bases. The following table shows the calculated and found percentage composition of elements which are in close approximation and so they confirm the formation of Schiff base **(Table 7).**

Table 7: CHN Analysis of ASB-6

Molecular Formula	**Found**			**Calculated**		
$C_{17}H_{20}N_4O_3$	C%	H%	N%	C%	H%	N%
	59.22	1.88	12.47	62.18	6.14	17.06

3.2 Applications

3.2.1 Corrosion Inhibition

The corrosion inhibition properties of synthesized Schiff bases were studied on carbon steel alloy in basic soil solutions.

3.2.1.1 Corrosion inhibition study of ASB-1

It can be seen from the table 8 that the value of corrosion current (I_{corr}) is decreased upon the addition of inhibitor (ASB-1) which shows the adsorption of inhibitor molecules on the metal surface and thus blocking the active sites and inhibiting the anodic and cathodic reactions. This is attributed to the presence of azomethine group which has blocked the anodic and cathodic sites. The value of I_{corr} can be obtained by extrapolation of tafel lines to corrosion potential (E_{corr}). The inhibition efficiency (Z%) and surface coverage (θ) can be calculated from the following equation:

$$Z\% = i_{uninh} - i_{inh} \div i_{uninh} \times 100$$

$$\theta = i_{uninh} - i_{inh} \div i_{uninh}$$

Table 8: Corrosion inhibition efficiency of ASB-1

Inhibitors Code	**Current density i_{corr}/nAcm^{-2}**	**β_a (mV e^{-3})**	**- β_c (mV e^{-3})**	**CR (e-3 mpy)**	**Surface coverage (Θ)**	**The inhibition efficiency (Ɛ%)**
Blank	50.29	133	92	22.74	-	-
ASB-1	29.50	237	179	13.42	0.41	41.34

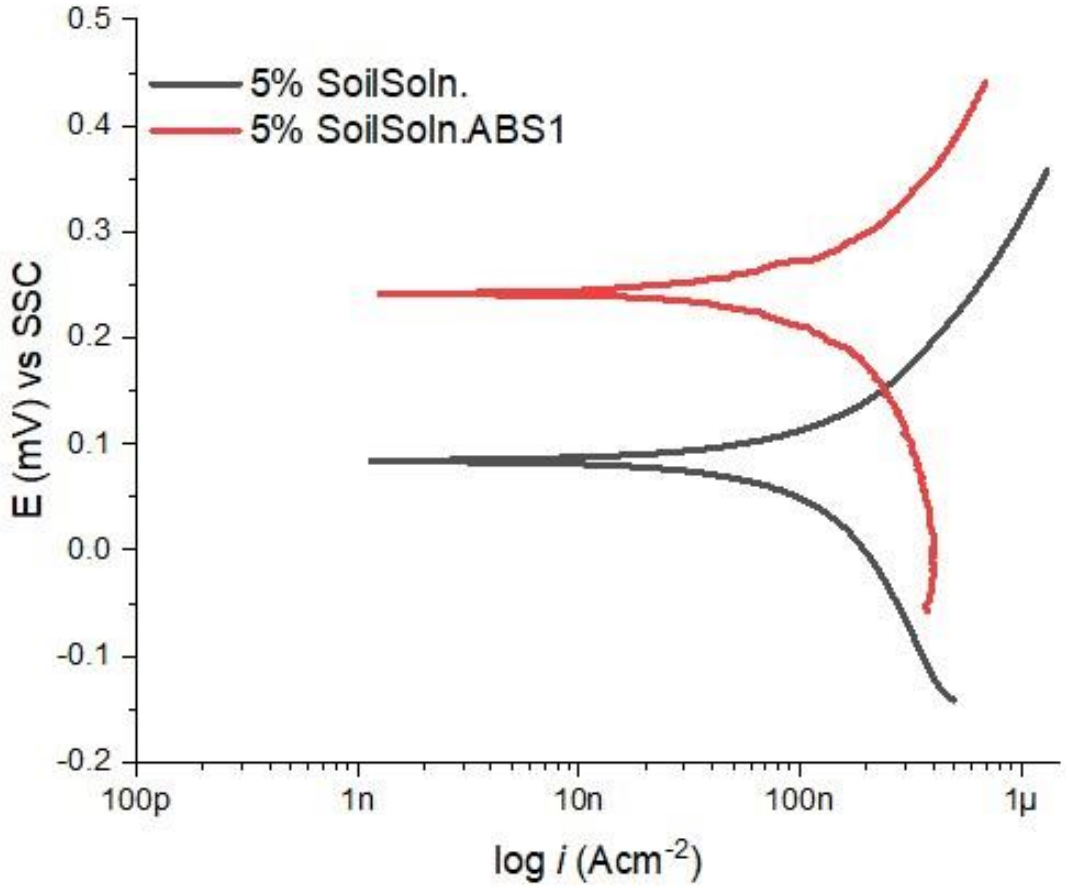


Figure 13: Tafel Plot of ASB-1

It can be seen from the tafel plot of ASB-1 that both the anodic and cathodic currents decreases upon the addition of inhibitor. As a result of which active sites on metal are blocked and there will be decrease in corrosion rate. This fact is attributed to the presence of azomethine group in inhibitor molecule which tends to bind the active sites on metal surface thereby preventing the metal from corrosive environment.

3.2.1.2 Corrosion Inhibition study of ASB-2

It can be seen from table 9 and tafel plot of ASB-2 that there is no decrease in corrosion current upon the addition of inhibitor which results in non-blockage of active sites on metal surface and so there will be no inhibition from corrosive media. The corrosion rate is also the same as that of blank which resulted in no surface coverage and ultimately zero inhibition efficiency.

Table 9: Corrosion inhibition efficiency of ASB-2

Inhibitors Code	Current density i_{corr}/nAcm^{-2}	β_a (mV e^{-3})	- β_c (mV e^{-3})	CR (e-3 mpy)	Surface coverage (θ)	The inhibition efficiency ($Z\%$)
Blank	46.21	153	121	20.90	0	0
ASB-2	46.21	70.3	111	20.90	0	0

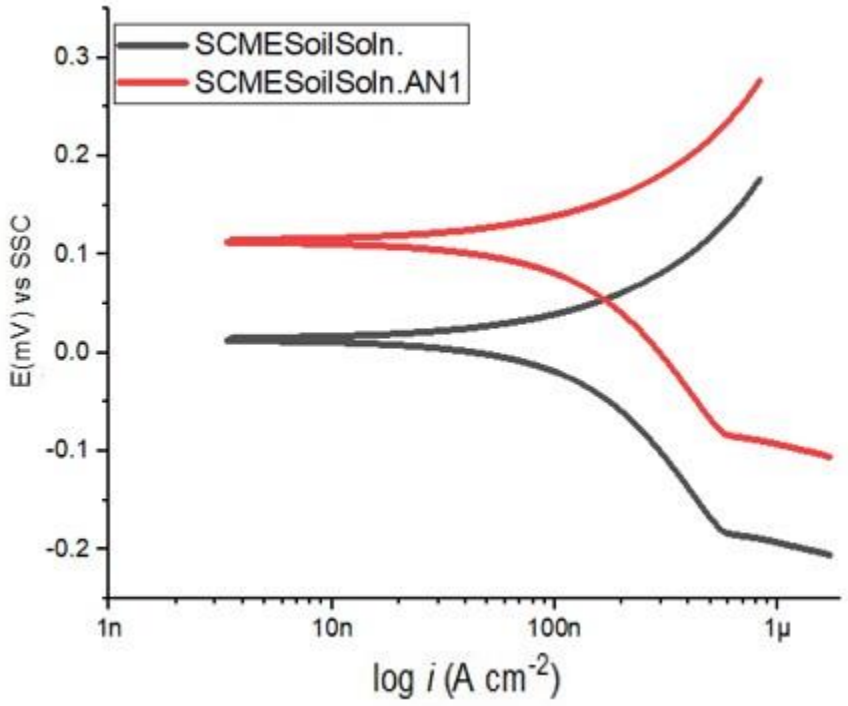


Figure 14: Tafel plot of ASB-2

It can be seen from the tafel plot that there is no decrease in corrosion current upon the addition of inhibitor which might be attributed to the presence of ions and halides in soil which blocked the activity of inhibitor molecules.

3.2.1.3 Corrosion Inhibition study of ASB-3

It can be seen from the table 10 that the value of corrosion current (I_{corr}) is decreased upon the addition of inhibitor (ASB-3) which shows the adsorption of inhibitor molecules on the metal

surface and thus blocking the active sites and inhibiting the anodic and cathodic reactions. The value of I_{corr} can be obtained by extrapolation of tafel lines to corrosion potential (E_{corr}). The inhibition efficiency (Z%) and surface coverage (θ) can be calculated from the following equation:

$$Z\% = i_{uninh} - i_{inh} \div i_{uninh} \times 100$$

$$\theta = i_{uninh} - i_{inh} \div i_{uninh}$$

Table 9: Corrosion inhibition efficiency of ASB-3

Inhibitors Code	**Current density i_{corr}/nAcm^{-2}**	**β_a (mV e^{-3})**	**- β_c (mV e^{-3})**	**CR (e-3 mpy)**	**Surface coverage (θ)**	**The inhibition efficiency (*Z%*)**
Blank	41.41	74.88	102	18.5	0	0
ASB-3	32.65	77.15	136	14.5	0.25	21.5

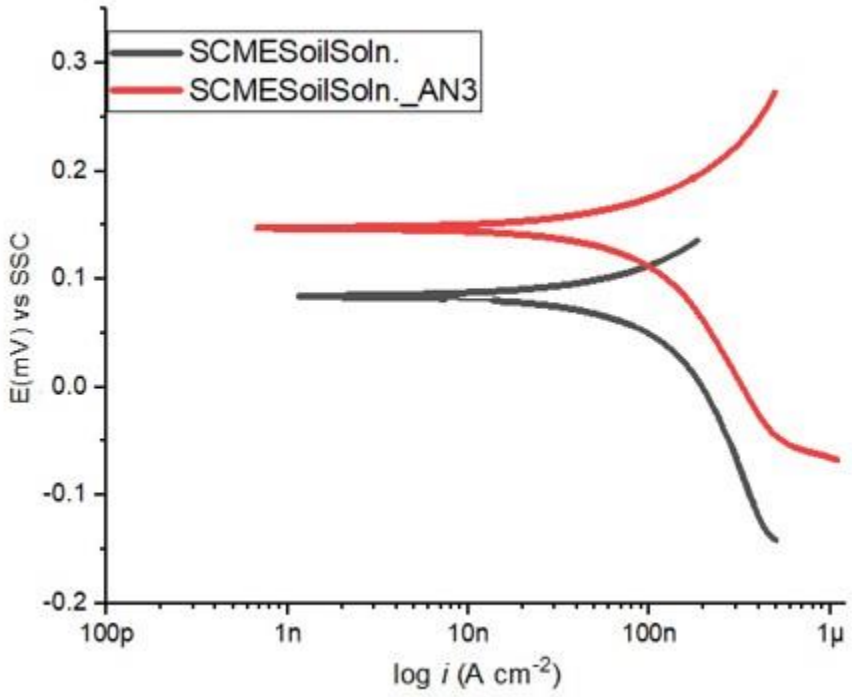


Figure 15: Tafel plot of ASB-3

A well-defined tafel region is obtained which shows the anodic and cathodic curves for ASB-3. There is a decrease in anodic and cathodic current in the presence of inhibitor which is attributed to the presence of azomethine group (-C=N) which has increased electronic density and OH group in inhibitor molecule which is strongly activating due to the presence of single pair of electrons on oxygen atom.

3.2.1.4 Corrosion Inhibition study of ASB-4

It can be seen from the table 11 that the value of corrosion current (I_{corr}) is decreased upon the addition of inhibitor (ASB-4) which shows the adsorption of inhibitor molecules on the metal surface and thus blocking the active sites and inhibiting the anodic and cathodic reactions. The value of I_{corr} can be obtained by extrapolation of tafel lines to corrosion potential (E_{corr}). The inhibition efficiency (Z%) and surface coverage (θ) can be calculated from the following equation:

$$Z\% = i_{uninh} - i_{inh} \div i_{uninh} \times 100$$

$$\theta = i_{uninh} - i_{inh} \div i_{uninh}$$

Table 10: Corrosion inhibition efficiency of ASB-4

Inhibitors Code	**Current density i_{corr}/nAcm^{-2}**	**β_a (mV e^{-3})**	**- β_c (mV e^{-3})**	**CR (e-3 mpy)**	**Surface coverage (θ)**	**The inhibition efficiency (Z%)**
Blank	71.24	84.1	79	32.35	0	0
ASB-4	32.96	104	155	14.96	0.53	53.75

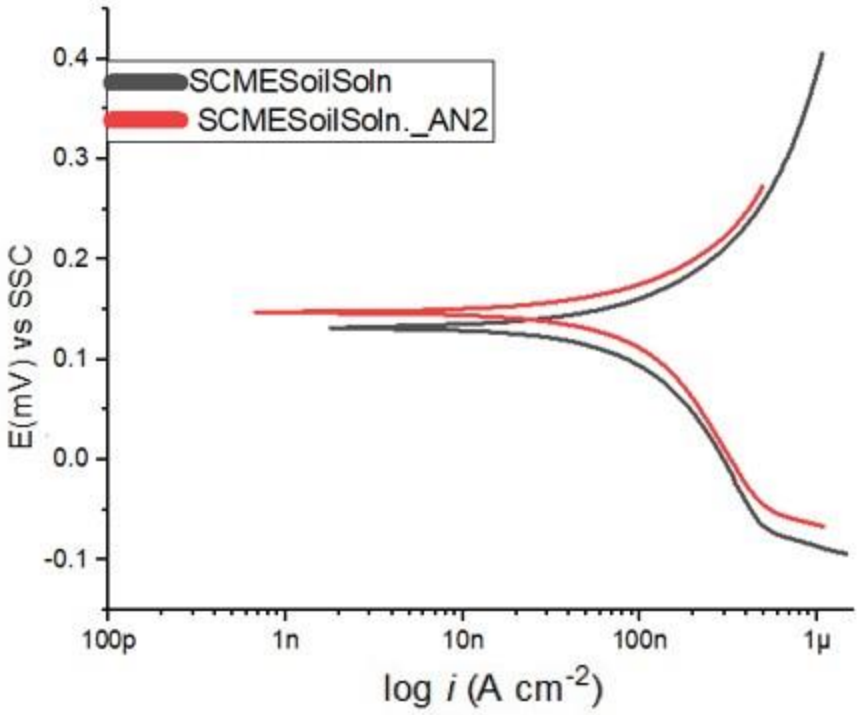


Figure 16: Tafel plot of ASB-4

A well-defined tafel region is obtained which showed the anodic and cathodic curves for ASB-4. The tafel plot is also known as E log I diagram. It shows a decrease in corrosion current upon the addition of inhibitor which is the result of blockage of active sites of metal surface The corrosion inhibition efficiency of ASB-4 is attributed to the presence of aromatic ring, azomethine group -C=N and halogen atom (Cl). The electronic cloud on the inhibitor molecule tends to bind to the active sites of metal surface and so blocks the anodic and cathodic currents.

3.2.1.5 Corrosion Inhibition study of ASB-5

It can be seen from the table 12 that the value of corrosion current (I_{corr}) is decreased upon the addition of inhibitor (ASB-5) which shows the adsorption of inhibitor molecules on the metal surface and thus blocking the active sites and inhibiting the anodic and cathodic reactions. This is attributed to the presence of azomethine group which has blocked the anodic and cathodic sites. The value of inhibition efficiency is also enhanced due to the presence of halogen bromine. The value of I_{corr} can be obtained by extrapolation of tafel lines to corrosion potential (E_{corr}). The inhibition efficiency (Z%) and surface coverage (θ) can be calculated from the following equation:

$$Z\% = i_{uninh} - i_{inh} \div i_{uninh} \times 100$$

$$\theta = i_{uninh} - i_{inh} \div i_{uninh}$$

Table 11: Corrosion inhibition efficiency of ASB-5

Inhibitors Code	**Current density i_{corr}/nAcm^{-2}**	**β_a (mV e^{-3})**	**- β_c (mV e^{-3})**	**CR (e-3 mpy)**	**Surface coverage (θ)**	**The inhibition efficiency (Z%)**
Blank	63.7	176	205	28.98	0	0
ASB-5	26.2	137	157	11.41	0.60	60.62

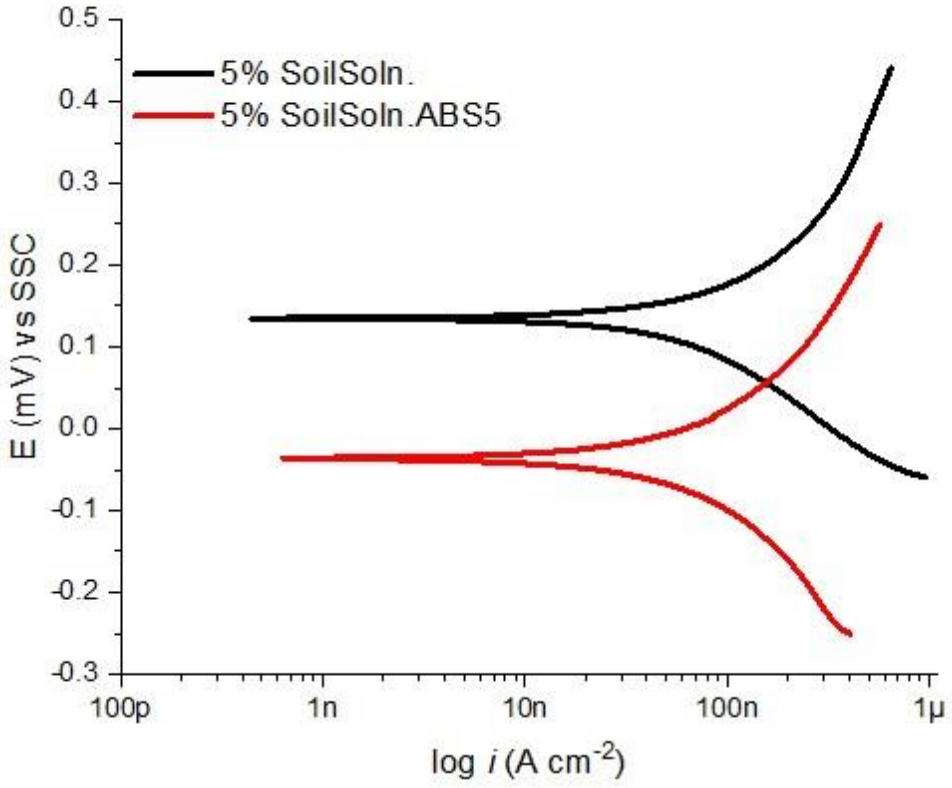


Figure 17: Tafel plot of ASB-5

A well-defined tafel region is obtained which showed the anodic and cathodic curves for ASB-5. The tafel plot is also known as E log I diagram. It shows a decrease in corrosion current upon the addition of inhibitor which is the result of blockage of active sites of metal surface The corrosion inhibition efficiency of ASB-5 is attributed to the presence of aromatic ring, azomethine group -C=N and halogen atom (Br). The electronic cloud on the inhibitor molecule tends to bind to the active sites of metal surface and so blocks the anodic and cathodic currents.

3.2.1.6 Corrosion Inhibition study of ASB-6

It can be seen from the table 12 that there is a drastic increase in corrosion current upon the addition of inhibitor which means that the Schiff base has made the environment more corrosive instead of inhibiting the corrosion. The corrosion rate has also increased.

Table 12: Corrosion inhibition efficiency of ASB-6

Inhibitor Code	**Current density i_{corr}/nAcm^{-2}**	**β_a (mV e^{-3})**	**- β_c (mV e^{-3})**	**CR (e-3 mpy)**	**Surface coverage (Ɵ)**	**The inhibition efficiency (Z%)**
Blank	11.41	98.7	136	5.23	-	-
ASB-6	88.71	115	197	40.72	-	-

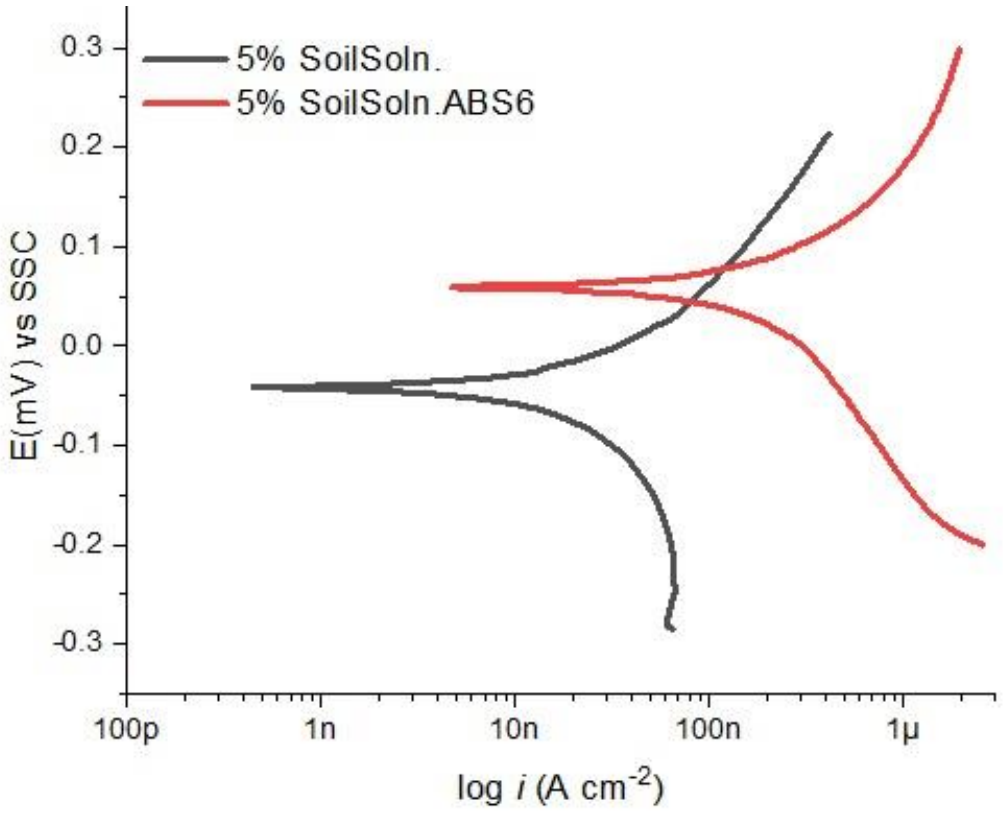


Figure 18: Tafel plot of ASB-6

It can be seen from the tafel plot that there is an increase in anodic and cathodic currents upon the addition of inhibitor. The value of corrosion rate has also increased to a greater extent. As a result of which the Schiff base, instead of inhibition, causes more corrosion to the metal. This affect is due to the high acidic nature of the Schiff base as compared to the corrosive environment.

3.2.2 Biological Activity

Schiff bases are biologically active compounds. The loan pair of electrons on nitrogen atom imine group are a reason behind biological activity of Schiff bases. Schiff bases various biological activities including antifungal, anti-bacterial and anti-tumor activities. They are used in biological processes for structure elucidation, racemization and transamination. Biological activities including anti-fungal and anti-bacterial activities of synthesized Schiff bases were carried out.

3.2.2.1 Antibacterial Activity

Table 13: Antibacterial activity results of Schiff bases

Sample Name	*Escherichia coli*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*
ASB-1	6.7±0.82	6.4±0.47	6.3±0.47
ASB-2	6.3±0.47	6.7±0.82	6.5±0.47
ASB-3	9.3±1.25	6.3±0.47	6.8±0.47
ASB-4	6.4±0.47	6.5±0.47	6.7±0.82
ASB-5	6.5±0.47	6.7±0.82	6.4±0.47
ASB-6	6.8±0.47	6.8±0.47	6.7±0.47
Moxifloxacin	**35±0.47**	**23±0.82**	**35±0.94**

Results of anti-bacterial activity of synthesized Schiff bases are shown in table 13 which shows moderate activity of Schiff bases against three different bacterial strains and moderate to efficient activity of ASB-3 against *Escherichia coli*. The anti-bacterial activity of Schiff bases is related to the presence of azomethine group which forms hydrogen bonds with the active centres of cell constituents thereby causing an interference with the normal cell processes.

3.2.2.2 Antifungal Activity

Table 14: Anti-Fungal activity results of synthesized Schiff bases

Sample Name	*Candida Albicans*	*Candida Parasilosis*
ASB-1	12.3±0.94	13.3±0.94
ASB-2	6.8±0.82	6.5±0.47
ASB-3	6.7±0.82	6.5±0.82
ASB-4	6.3±0.47	6.3±0.47
ASB-5	6.5±0.82	6.7±0.82
ASB-6	6.4±0.82	6.4±0.47
Amphotericin B	**18±0.47**	**22±0.82**

Results of anti-fungal activity of synthesized Schiff bases are shown in table 14 which shows the moderate activity of Schiff bases against two different species of fungi and moderate to efficient activity of ASB-1. The antifungal activity of Schiff bases is attributed to the presence of azomethine group which forms hydrogen bonds with active centres of cell constituents thereby interfering with normal cell processes. Also, it deactivates various enzymes which play an important role in metabolic pathways of these microorganisms.

Anti-microbial Activity of Schiff Bases

Although the exact mechanism is not understood biochemically, mode of action of anti-microbials may involve following targets in microorganisms:

- They may interfere with the cell wall synthesis, damage it as a result of which cell permeability may be altered or they may disorganize lipoprotein leading to cell death.
- They may deactivate cellular enzymes which play a vital role in different metabolic pathways in these microorganisms.
- They may denature one or more proteins in the cell, as a result of which normal cell processes may be altered.
- They may form hydrogen bonds through their azomethine group with the active centres of the cell constituents thereby interfering in normal cell processes.
- They may form bonds with trace elements present in the cell and thus inhibits the microbial growth to a great extent.

Conclusion

Schiff bases were synthesized in good yields by condensation of 4-Nitro-1,2-Phenylenediamine with six different aldehydes namely benzaldehyde, furaldehyde, 4-hydroxybenzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde and 4(Diethylamino)Salicylaldehyde. FT-IR and CHNS analysis were used for indication to confirmation of synthesized Schiff bases. Corrosion Inhibition studies of Schiff bases indicated that ASB-4 showed corrosion inhibition efficiency of 53% due to the presence of halogen. Biological activity results indicated that ASB-3 showed efficient antibacterial activity due to the presence of OH group and ASB-1 showed efficient antifungal activity.

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