GREEN APPROACH TO ORGANIC SYNTHESIS: MICROWAVE ASSISTED SYNTHESIS OF SCHIFF'S BASE

A project report submitted to,

Mahatma Gandhi University, Kottayam

In partial fulfillment of the requirements for the award of the

Bachelor Degree in CHEMISTRY

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Under the supervision of

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(*Affiliated to Mahatma Gandhi University, Kottayam)*

2020-2023

BHARATA MATA COLLEGE

THRIKKAKARA

CERTIFICATE

This is to certify that the project report entitled **"GREEN APPROACH TO ORGANIC SYNTHESIS: MICROWAVE ASSISTED SYNTHESIS OF SCHIFF'S BASE"** is a bonafied work carried out by Ms. FOUSIYA C M, B.Sc. Chemistry student, no portion of this has been submitted for any degree, diploma, or other comparable titles of recognition through any university, and it has been completed under my supervision and direction.

Forwarded by

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Department of Chemistry

Bharata Mata College

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Place: Thrikkakara

Date: 02/05/2023

DECLARATION

I FOUSIYA C M hereby declare that this project report entitled "GREEN APPROACH TO ORGANIC SYNTHESIS:MICROWAVE ASSISTED SYNTHESIS OF SCHIFF'S BASE" is an authentic work carried out during my course of study under the guidance of Dr. Amrutha U, Department of Chemistry,Bharata Mata College, Thrikkakara

Place: Thrikkakara

Date: 02/05/2023

ACKNOWLEDGEMENT

I have great pleasure and excitement in presenting the project report undertaken by me with the help of almighty god who done everything in our life to achieve success.

I gratefully acknowledge the help and advice of a number of people in the preparation of the project work

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FOUSIYA C M

Green Approach to Organic Synthesis: Microwave Assisted Synthesis of Schiff's Base

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Keywords: Schiff's Base, Green Synthesis, Microwave Synthesis

ABSTRACT

The main aim of the project work is a green approach for the synthesis of Schiff's Base. Highly useful and eco-friendly methods are used for this synthesis with good yield. Schiff's base is a condensation reaction in which primary amine react with carbonyl compounds.Schiff's base exhibit various biological activities such as anti-microbial, anti-cancer, anti-fungal, analgesic, anti-oxidants etc. For the current project we are trying to synthesize Schiff's base using microwave method. Here we adopted a green method for the synthesis of Schiff's bases. Several characterization techniques were used for the synthesis.The overall procession of the reaction was monitored by TLC and characterized by FTIR. These are widely used organic compounds. Since this is a green approach, reactions can be done within a short period of time without causing any harm to the environment.Compared with conventional methods, green methods are more convenient and reactions can be carried out in higher yield,and moderate conditions, without procreation of any pollutants thus pollution can be reduced to a larger extend and safer to analyst.

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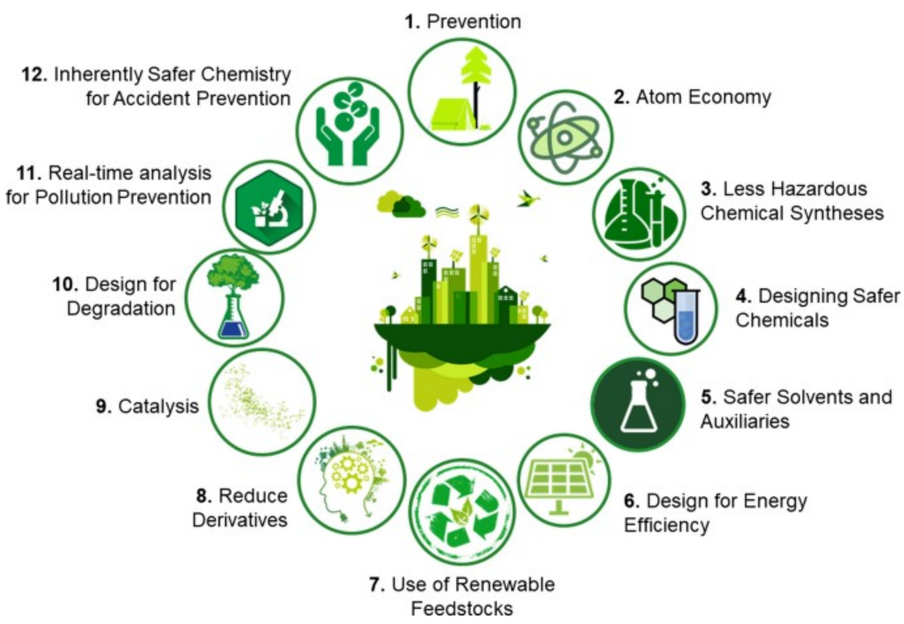
GREEN APPROACH TO ORGANIC SYNTHESIS: MICROWAVE ASSISTED SYNTHESIS OF SCHIFF'S BASE

1. INTRODUCTION

The idea of "green chemistry" was first established in the 20th century, and it uses environmentally friendly methods for compound synthesis. The creation of unique synthetic protocols was compelled by the pollution and rising energy demands to meet the needs of green and sustainable chemistry. A subfield of chemistry called "green chemistry" aims to protect the environment by developing new chemical procedures that do not harm the environment. Green chemistry aims to make synthetic processes more effective so that they utilize less harmful solvents, shorten the stages of the synthetic pathway, and generate as little trash as is practically possible.

1.1 Principles of Green Chemistry



1.2 Advantages of green synthesis

- Low cost - saves money on solvents
- Eco-friendly
- Non toxic
- Safer
- High Atom Economy
- The process and handling of reaction is simple.

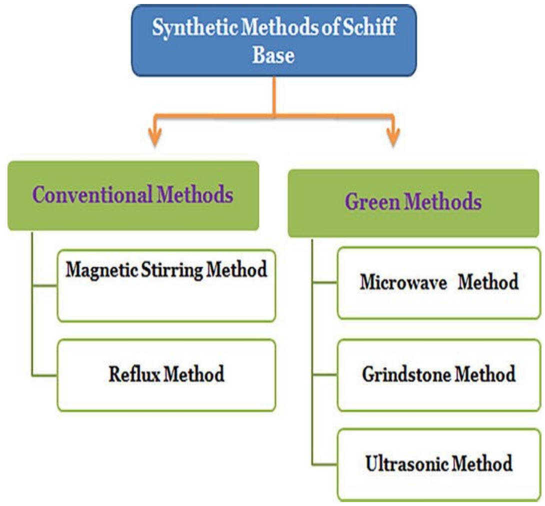
1.3 Schiff's base

Schiff base is defined by imine or azomethine group (C=N-R), are organic compounds synthesized by the condensation of primary amines with carbonyl compounds and was first reported by shiff's in 1864.ref A schiff's base is an nitrogen analogue of an aldehyde or Ketone in which C=O group is replaced by C=N-R GRP(Azomethinegrp/Imine). Schiff base reaction is a condensation reaction in which primary amine reacts with carbonyl compounds to form schiff base (SB) as a major product. SB is named after the scientist Hugo schiff and scientists were still exploring the applications of schiff's base.

The Schiff's base reaction is a group-specific reaction for aldehydes. The reaction usually occurs under basic conditions with aromatic amines to form a Schiff's base. Aniline is normally used to form a coloured anil or Schiff' bases with an aldehyde.

1.3.1 Synthesis methods of Schiff's base

The Schiff bases and its derivatives can be synthesized by various methods which include simple one step, condensation, reflux method, microwave and ultrasonication.



1.3.2 Application of Schiff base

•Schiff base exhibit various biological activities such as antimicrobial, anti cancer, antifungal, analgesic, antioxidant etc.

•Shiff's base are used as a catalyst , polymer stabilizer, pigments and dyes and corrosion inhibitors.

•It is used for the identification of compounds in different solvents.

•Application in coordination chemistry.

•Determination of strength of hydrogen bond.

•Examination of polynuclear hydrocarbons.

For the present project work we adopted microwave assisted synthesis for Schiff bases.

1.3.3 Microwave assisted synthesis

Microwave synthesis is considered as ecofriendly method for the synthesis of organic compounds. Microwave assisted synthesis has revolutionized chemical synthesis. The microwave synthesis takes place in a fraction of seconds. In conventional heating techniques, a hot plate or oil bath is used as a heat source for a chemical reaction. In chemical synthesis, microwave irradiation is frequently utilized as a source of heating. Dipolar polarization and conduction are the primary mechanisms seen in microwave aided synthesis. Many chemists have switched from conventional heating method to microwave assisted chemistry because it offers clean synthesis with the benefits of increased reaction rates, higher yields, greater selectivity, and economic for the synthesis of a large number of organic molecules.

How Microwave Heat the Substance?

The vast majority of molecular dipoles have a tendency to line up with the microwave's electric field and rotate or oscillate to follow the shifting field. Because of this movement of molecules, molecules collide and rub against one another. And thermal energy is lost along with the kinetic energy. This effect, known as dielectric heating, is a result of the bulk as a whole.

Advantages of Microwave synthesis

Atomic economy: more output, lower waste. Clean reactions produce fewer byproducts and require less purification.

H2O is a green solvent.

Less or no solvent: neat condition and 0.5–5 ml per reaction.

Only a switch is needed to start or stop the energy input into the reacting substance, which has a low energy input of 50W and a maximum of 300W.

Reduced derivatives: Blocking agents are used, and additional reagents are needed for protection and deprotection. However, MW methods either do not require such temporary modifications or allow for the use of milder conditions.

Copid responses: quick method creation

Applications of microwave synthesis

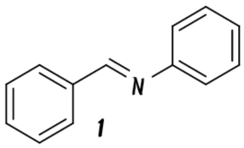
Microwave assisted synthesis is used in the synthesis of many biologically important compounds and it also replaces many conventional synthetic methods.

- ✔ Heck reaction
- ✔ Suzuki reaction
- ✔ Negishi and Kumada reaction
- ✔ Multicomponent reactions
- ✔ Solid phase synthesis
- ✔ Reactions in the absence of solvents

2.1 OBJECTIVES OF PROJECT

Schiff bases are vital in the biological field because of their structural similarity with biologically active compounds. In this perspective the synthesis and study of these types of compounds are very important.

For the present project we are trying to synthesize schiff's base using microwave method. The advantages of microwave synthesis is explained in the introduction section. Here we adopted a green method for the synthesis of following Schiff's bases.



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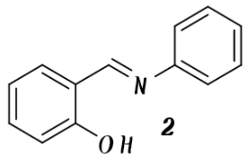

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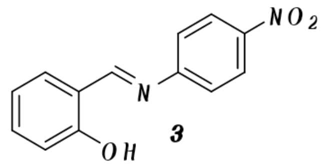

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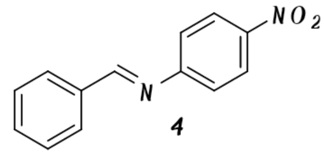


4

3 .MATERIALS REQUIRED AND METHODS

3.1MATERIALS REQUIRED

- Conical flask
- Beaker
- Measuring jar
- Microwave owen
- Glass rod
- Melting point apparatus

CHEMICALS REQUIRED

- Benzaldehyde
- Aniline
- Salicylaldehyde
- P-nitroaniline
- Distilled water

4. EXPERIMENTAL

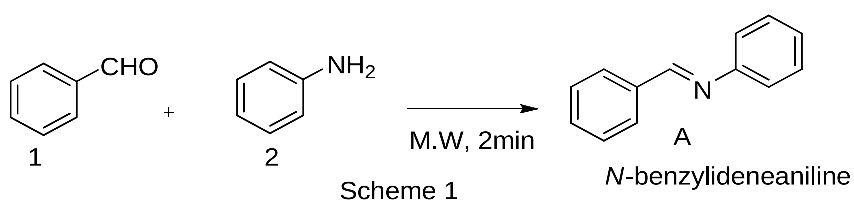
4.1 MICROWAVE METHOD

Schiff's bases are usually made by reacting aldehyde or Ketone with different types of amines. Here an aldehyde mixed with different aromatic amines which undergo

Condensation reaction. The mixture is stirred well and placed in a microwave oven and observe the changes after 2 minutes. The reaction process is monitored by TLC to check whether the reaction has taken place or not and is recrystallized to get pure samples. Melting points noted. The structure of the compound was confirmed by infrared spectroscopy. Without additional purification, analytical-grade compounds of all kinds were used. .

4.1.1 SYNTHESIS OF SCHIFF'S BASE FROM BENZALDEHYDE AND ANILINE

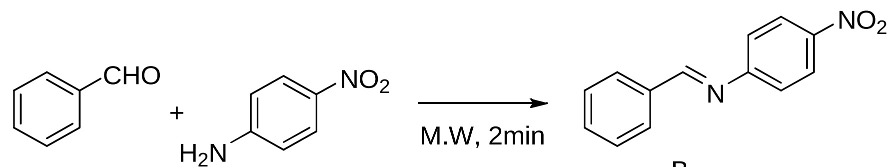
Benzaldehyde (4.6mL, 40mmol) is mixed with aniline(3.62mL, 40mmol) and 1ml water in a 250 mL conical flask. Shake well and place it in a microwave oven for about 30 sec - 2 min at 200W. Thin Layer Chromatography (TLC) is used to keep a watch on the reaction process. If it is not visible place it in a UV cabinet. The product is recrystallized using hexane and DCM (dichloromethane) to get pure samples. Then IR and melting points are recorded.



Scheme 1

4.1.2 SYNTHESIS OF SCHIFF'S BASE FROM BENZALDEHYDE AND *P*-NITROANILINE

Benzaldehyde (4.6mL, 40mmol) is mixed with *p*-nitro aniline (3.8mL, 40mmol) and 1ml water in a 250 mL conical flask. Shake well and place it in a microwave oven for about 30 sec -2 min at 200W. Thin Layer Chromatography (TLC) is used to keep a watch on the reaction process. If it is not visible, place it in a UV cabinet. The product is recrystallized using hexane and DCM (dichloromethane) to get pure samples. Then IR and melting points are recorded.



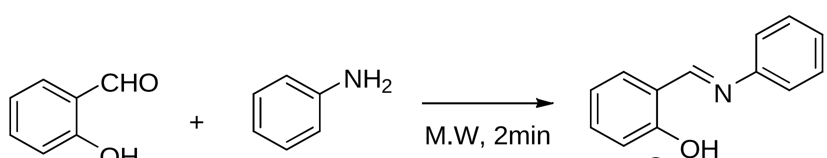
3 4 B

N-benzylidene-4-nitroaniline

Scheme 2

4.1.3 SYNTHESIS OF SCHIFF'S BASE FROM SALICYLALDEHYDE AND ANILINE

Salicylaldehyde (4.17mL, 40mmol) is mixed with aniline (3.62 mL, 40mmol) and 1ml water in a 250 mL conical flask. Shake well and place it in a microwave oven for about 30 sec -2 min at 200W. Thin Layer Chromatography (TLC) is used to keep a watch on the reaction process. If it is not visible, place it in a UV cabinet. The product is recrystallized using hexane and DCM (dichloromethane) to get pure product. Then IR and melting points are recorded.



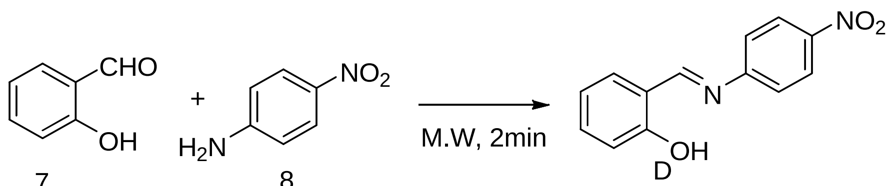
5 6 C

2-((phenylimino)methyl)phenol

Scheme 3

4.1.4 SYNTHESIS OF SCHIFF'S BASE FROM SALICYLALDEHYDE AND *P*-NITROANILINE

Salicylaldehyde (4.175mL, 40mmol) is mixed with *p*-nitro aniline (3.8mL, 40mmol) and 1ml water in a 250 mL conical flask. Shake well and place it in a microwave oven for about 30 sec -2 min at 200W. Thin Layer Chromatography (TLC) is used to keep a watch on the reaction process. If it is not visible, place it in a UV cabinet. The product is recrystallized using hexane and DCM (dichloromethane) to get pure product. Then IR and melting points are recorded.



7 8

4-nitrophenyl)imino)methyl phenol

Scheme 4

5. CHARACTERIZATION TECHNIQUES

5.1 THIN LAYER CHROMATOGRAPHY (TLC)

Thin layer chromatography is carried out to monitor the reactions. The formation of product in a reaction is confirmed by TLC. TLC plate is silica (adsorbent) coated plate. The mobile phase used is Hexane –Ethylacetate mixture. When a sample is placed on the TLC plate, the components which are more polar (strongly adsorbed to silica) will move slowly which have low R_f value. R_f value can be calculated by taking the ratio of the distance traveled by a component to distance traveled by the solvent front from the base line. It is also used to check the purity of compounds.

PROCEDURE

Firstly a TLC plate is cut off and a line is drawn as a baseline by using a pencil. Avoid using pens because there is a chance of spreading. Using a capillary tube make a spot of sample on the baseline and place TLC plate placed in the solvent system, hexane and ethyl acetate (80:20) (mobile phase) taken in a beaker and cover it with a watch glass. By capillary action the components moved up and it is separated based on its affinity towards the adsorbent (stationary phase). The solvent front, the distance travelled by each component is noted and Rf value can be calculated.

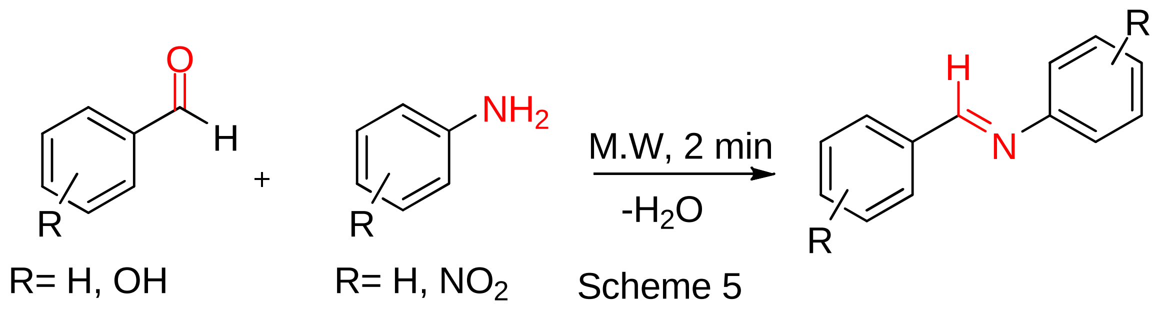
5.2 INFRARED SPECTROSCOPY

The main use of FTIR (Fourier transform infrared spectroscopy) is to examine the functional groups in organic compounds. The IR region is divided into three parts which are near IR (12500-4000 Cm-1), mid IR(4000-400 Cm^{-1}), far IR(400-50 Cm^{-1}) . It is also known as absorption or vibration Spectroscopy because the molecule absorbs radiation and it will move to an excited state and the excited molecule shows vibration.

In FT-IR graph Y axis shows absorption and X axis shows frequency or wavelength. The vibrational energy bands associated with each functional group are unique to every molecule. The FTIR spectrum of the sample was obtained by **Thermo Scientific Nicolet IS5 FTIR spectrometer**.

6.RESULTS AND DISCUSSION

Due to the good electrophilic and nucleophilic characteristics of the carbonyl and amine groups, respectively, it is noted that the condensation between a carbonyl molecule and an amine results in the creation of Schiff bases. Water has been found to be a novel, environmentally friendly solvent for the synthesis of Schiff's base. We obtained all products in 70- 80 %yield. The general reaction scheme is given below (Scheme 5). The yield, melting point and structures of product is given in table (Table 1).



Scheme 5

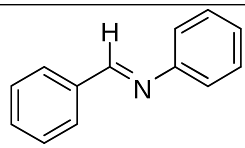
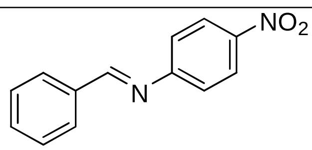
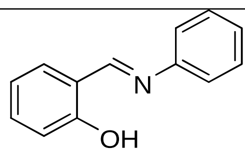
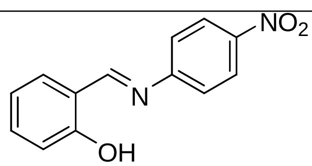
Entry	Structure	Reaction Temp	Time	Molecular Weight (g)	Yield (%)	Melting Point (°C)	Colour of product
A		200W	2 min	182	70	52.3	Dark yellow shining crystals
B		200W	2 min	227	79		Green crystals
C		200W	2 min	198	73	57.1	Light yello shining crystals
D		200W	2 min	243	78	159.6	Orange red shining crystals

Table 1- Schiff base- Structure , Yield and melting point

6.1 Yield of the Product

- ✓ Percent Yield of product = Actual Yield/Theoretical Yield × 100
- ✓ *The amount of a product produced by complete conversion of the limiting reactant in a chemical process is known as the theoretical yield.*

For example, theoretical yield of product A = 182×40/1000 = 7.28g

Actual yield = 5.1g

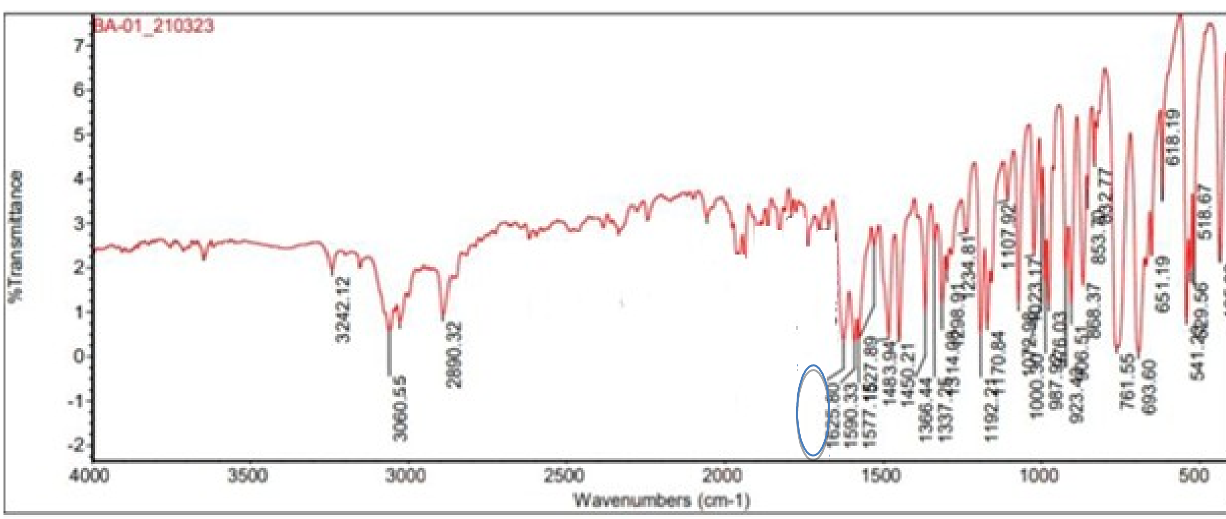
Percent Yield of product = Actual Yield/Theoretical Yield × 100

5.1/7.28 × 100 = 70.05%

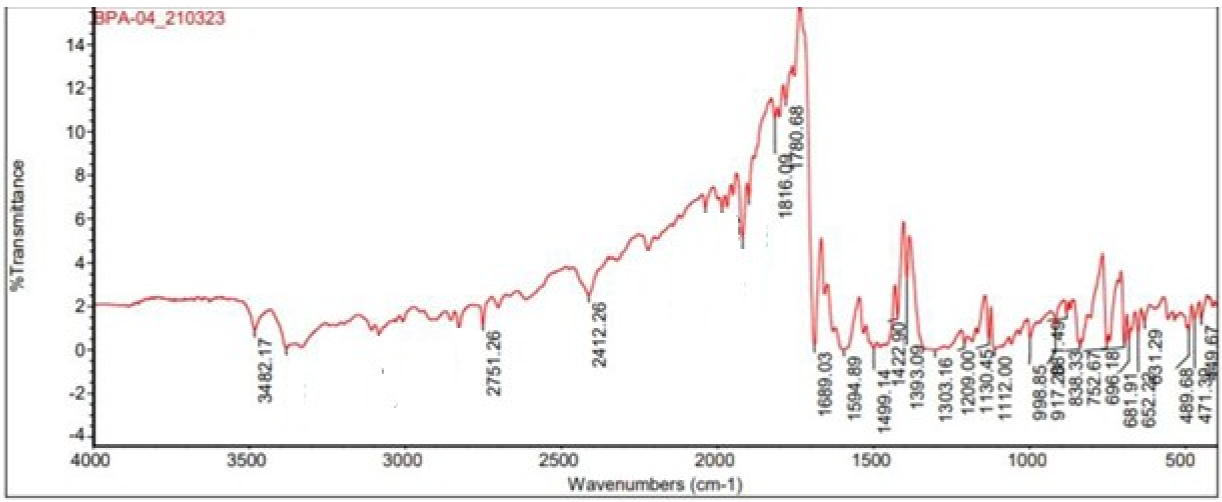
6.2 Spectral data

Medium intensity bands are visible in the infrared spectra of the substituted Schiff's bases between 1179 and 1064 cm-1. Sharp bands were discovered at 1314–1255 cm-1 because of =C–N. At 1380-1259 cm-1, CH=N- stretching bands in the Schiff's bases were visible. The band attributable to the Ar-(C-C) was visible in the IR spectra of the substituted Schiff's bases at 1597-1330 cm-1. At 1689–1488 cm–1, the C=N band was visible in the compounds.

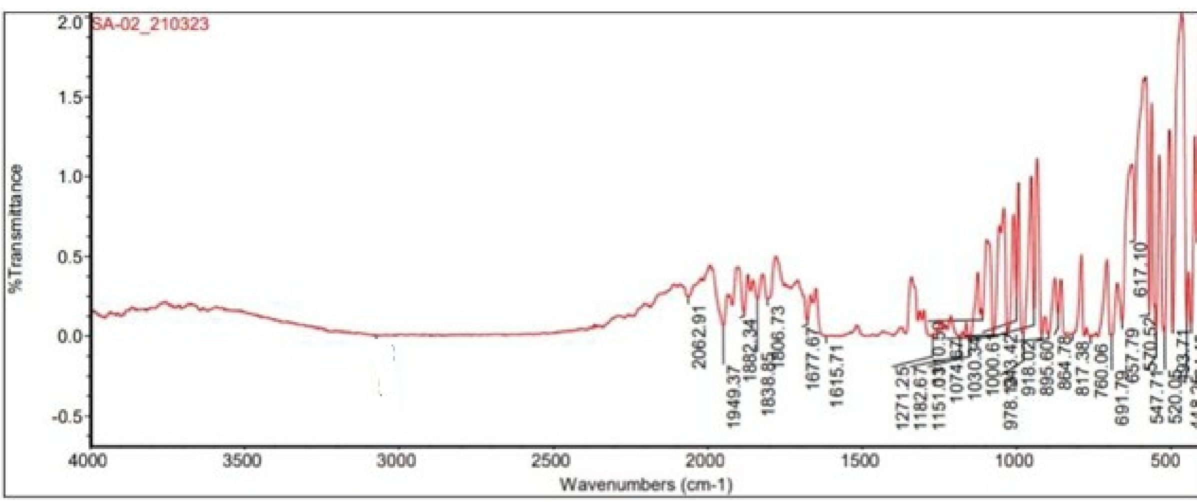
IR spectrum of A



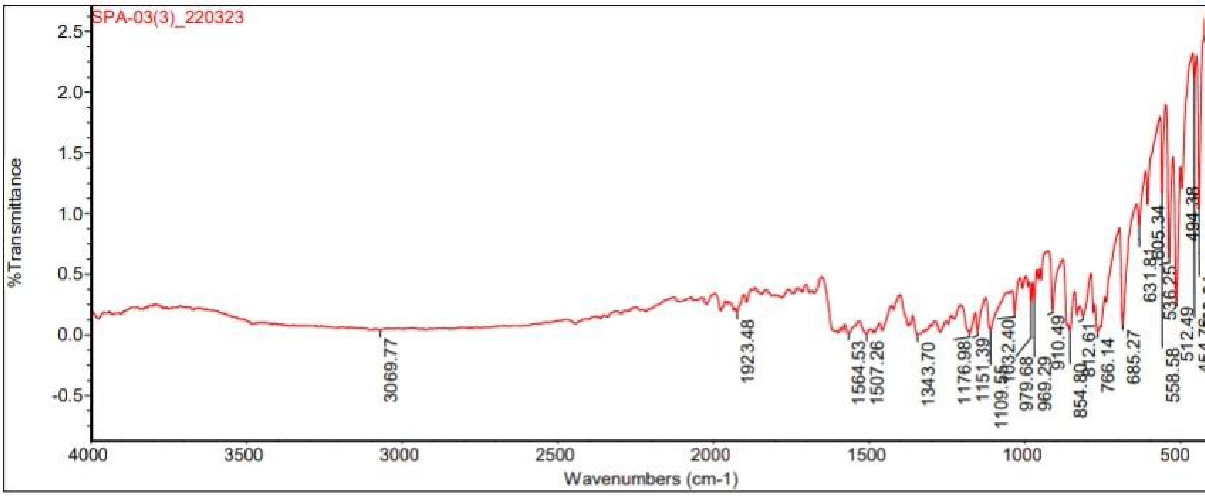
IR spectrum of B



IR spectrum of C



IR spectrum of D



7. CONCLUSION

Microwave method has proved to be better method for the synthesis of Schiff bases. Here we successfully synthesized four schiff bases using aldehyde and aniline. All the products were obtained in good yield and purity. The method is simple, efficient and ecofriendly green approach. This method's primary benefits include the use of water as a solvent, ambient reaction conditions, high yields, quick reaction times, and simple work-up procedures. This is safer and environmentally greener alternative to conventional method for the synthesis of schiff base.

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