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Microwave- Assisted Green Synthesis of Quinoline-Schiff Base Metal Complexes: A Review

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Abstract: The creation of quinoline–Schiff base metal complexes by microwave-assisted green synthesis has attracted a lot of interest because it is an effective and environmentally friendly method. According to the principles of green chemistry, microwave irradiation permits quick, energy-efficient reactions with little or no solvent. Schiff bases, which are renowned for their exceptional metal-chelating capabilities, and quinoline derivatives, which are known for their varied pharmacological characteristics, combine to produce stable complexes with increased biological potential. Incorporating metal ions like Cu (II), Ni (II), Zn (II), and Co (II) further alters the complexes' physicochemical and biological characteristics. Compared to traditional approaches, this approach has the following benefits: quicker reaction times, higher yields, less solvent use, and less environmental effect. Because of their improved membrane permeability, enhanced lipophilicity, and synergistic actions between the metal and ligand, these complexes show encouraging antibacterial activity. The synthesis methods, structural characteristics, and biological uses of microwave-assisted quinoline–Schiff base metal complexes are highlighted in this review as viable options for the creation of antimicrobial drugs.

Keywords: Microwave heating, Schiff base, Metal complexes, Green synthesis.

INTRODUCTION:

The increasing interest in microwave-assisted green synthesis of Schiff base metal complexes, especially those that incorporate quinoline scaffolds, is highlighted by recent studies. There are many benefits to this environmentally friendly method, such as quick reaction times, large yields, and less of an influence on the environment [(1)].These complexes frequently have greater efficiency than free ligands and display a variety of biological actions, including antibacterial, antifungal, and anticancer qualities [(2)].Schiff bases containing azomethine groups can more easily coordinate with transition metals to form complexes that have a variety of uses in the domains of biology, analysis, and catalysis [(3)].Green solvents, photo catalysts, and solvent-free conditions are some of the sustainable synthetic processes that have been the focus of recent study. The pressing demand for safer, more effective, and ecologically friendly methods of creating pharmaceutically active chemicals is met by these developments.

Role of metal complexes in enhancing biological activity:

Biologically active ligand metal complexes are essential for boosting a variety of biological processes. Transition metals are especially well-suited for creating complexes that can alter redox processes and possibly function as pro oxidants or antioxidants due to their varied coordination abilities [4]. Numerous biological actions, such as anti- inflammatory, antioxidant, anticancer, and antibacterial qualities, are displayed by metal complexes with heterocyclic nitrogen-containing molecules such as pyrazoles, aziridines, and diaziridines [5].One quinolone derivative, ciprofloxacin, for example, can potentially increase its antibacterial effectiveness by forming compounds with different transition metals [6].Developing more potent medicinal medicines requires an understanding of the structure-activity correlations of these metal complexes.

Importance of green chemistry:

- Developing ecologically friendly chemical processes and products to minimize pollution and environmental damage is the emphasis of the new area of "green chemistry".
- Throughout a product's lifecycle, it seeks to minimize waste production and the usage of hazardous substances while optimizing resource efficiency [7].
- The design of safer and more sustainable chemical processes is guided by the twelve principles of green chemistry, which were first presented by Anastas and Warner
- Among the many advantages of green chemistry include reduced pollution, enhanced worker safety, and possible economic gains for businesses [8].

Advantage of microwave assisted methods over conventional methods:

Figure 1:

Table 1: Difference between conventional and microwave assisted methods of heating[9 to 11]

S.NO	CONVENTIONAL HEATING	MICROWAVE ASSISTED HEATING
1.	The heat or thermal reaction starts from surface of material only.	The heat or thermal reaction start from uniformly and simultaneously form surface to bulk of the material.
2.	The heat transfer requires physical contact between materials surface and vessel.	Physical contact between materials surface and vessel is not required.
3.	Heating takes place by electric or thermal source.	Heating takes place by microwaves.
4.	Heating of material involves thermal conduction mechanism.	Heating of material involves dielectric polarization of material.

LITERATURE REVIEW:

Sinkar et al 2024.., Surveys contemporary green and high-efficiency methods for preparing Schiff bases and their transition-metal complexes, with an emphasis on non-traditional activation and solvent-minimizing techniques. Example-rich review that usefully compiles green synthetic methods for Schiff bases and their metal complexes, but it would be stronger with standardized quantitative comparisons, scale-up guidance, and deeper mechanistic and environmental analysis.

Sonawane *et al* 2023.., A useful, up-to-date, scaffold-focused review that compiles synthetic and activity data for quinoline Schiff-base metal complexes - excellent as a discovery handbook - but it would be stronger with standardized comparative data, deeper mechanistic critique, and translational (in vivo/ADMET) perspective. Restricting to quinoline-based Schiff bases gives useful depth for researchers interested in this scaffold.

Kumar *et al* 2023.., present a comprehensive review focused on microwave-assisted synthesis of Schiff base metal complexes and their biological activities, particularly anticancer and antimicrobial properties. The paper emphasizes how microwave irradiation has revolutionized traditional synthetic methods by offering shorter reaction times, higher yields, cleaner products, and better reproducibility.

Kostova and Balkansky 2013 present a comprehensive review of metal complexes formed with biologically active ligands (especially Schiff bases, flavonoids, coumarins, thiosemicarbazones, and other heterocyclic ligands) that demonstrate antioxidant potential. The paper summarizes synthetic approaches, characterization techniques, biological evaluations, and the structure–activity relationship (SAR) between coordination chemistry and antioxidant behavior.

Khan and colleagues et al.., 2017 Present a focused review on the coordination chemistry of ciprofloxacin (CIP)-a widely used fluoroquinolone antibiotic-and its metal complexes with various transition and main-group metals. The paper compiles previous research highlighting the synthesis, characterization, and biological significance of ciprofloxacin-metal complexes, emphasizing their enhanced antibacterial and pharmacological activities compared to the parent drug

Dr. Mallikarjun Kote et al.., 2022 presents an insightful discussion on the role of green chemistry in environmental protection and pollution control. The work emphasizes how the principles of green chemistry-focused on minimizing hazardous substances and optimizing resource efficiency-can be implemented in chemical industries to mitigate air, water, and soil pollution.

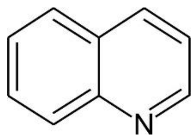
Majedul Hoque et.al.., 2023 this article outlines the principles of green chemistry, their relevance, and how implementing green chemistry can help maintain and improve environmental health. It explores methods, strategies, and practices industries, governments, and communities can adopt to reduce pollution, manage waste, minimize harmful by-products, and promote sustainable resource use.

Kappe, C. O. et al.., 2004 Kappe explores the evolution and application of microwave-assisted organic synthesis (MAOS), emphasizing its advantages over traditional heating methods. The paper provides a thorough examination of the underlying principles, including microwave dielectric heating, and discusses various applications in organic synthesis.

Lidström et al.., 2001 Provide a comprehensive examination of microwave-assisted organic synthesis (MAOS), focusing on its principles, applications, and advantages over traditional heating methods. The paper consolidates literature up to 2000, offering insights into the rapid adoption of microwave technology in synthetic organic chemistry.

Gupta, M., & Singh, B. et al.., 2005 Provides an in-depth analysis of microwave-assisted organic synthesis (MAOS), emphasizing its alignment with green chemistry principles. They discuss how microwave irradiation accelerates chemical reactions by directly interacting with polar molecules, leading to rapid and uniform heating. This method contrasts with traditional heating techniques, which rely on external heat sources and often result in uneven temperature distribution.

CHEMISTRY OF QUINOLINE SCHIFF BASE METAL COMPLEXES:



QUINOLINE

Because of its many uses in medicinal chemistry, materials science, and catalysis, quinoline-based metal complexes have attracted a lot of interest [12].These complexes can be created using a variety of transition metals and have special physicochemical properties that enable adjustable optical and structural features [13].Quinoline-derived metal complexes have demonstrated encouraging outcomes in antimalarial research, with some of them outperforming conventional medications like chloroquine [14].Complexes of gold, ruthenium, and iridium have shown especially strong efficacy against several forms of malaria.

QUINOLINE FRAMEWORK:

Quinoline:

Quinoline is a heterocyclic aromatic substance made up of a benzene ring bonded to pyridine. It acts as a valuable framework in medicinal chemistry because of its various pharmacological actions, such as antimalarial, antibacterial, anti-inflammatory, and anticancer effects .Compounds based on quinoline have demonstrated potential in blocking tyrosine kinases, proteasomes, and the polymerization of tubulin [15].

Moreover, quinoline derivatives demonstrate anticorrosive characteristics because of their elevated electron density and capacity to create stable complexes with metal surfaces [16].

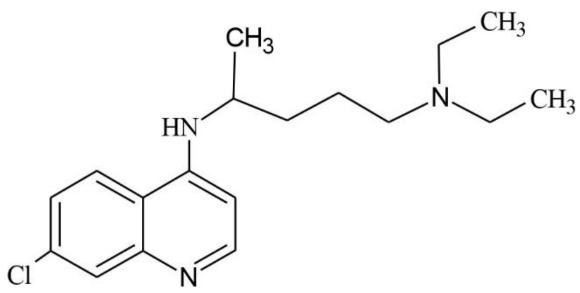
- **Chemical formula:** C_9H_7N
- **IUPAC Name:** 1-benzazine or benzo[b]pyridine

Important characteristics include:

- Aromatic: 10 π-electron system (Hückel's rule).
- The heterocyclic ring's first nitrogen atom offers planarity and electrical characteristics that are perfect for drug-receptor interactions.

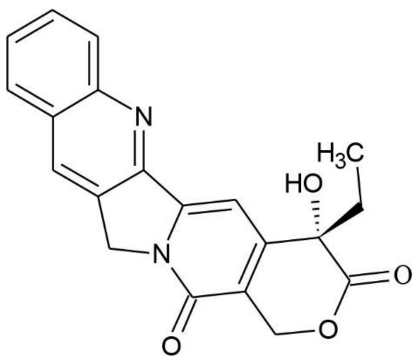
Example of substituted quinoline derivatives:

1. Antimalarial medication



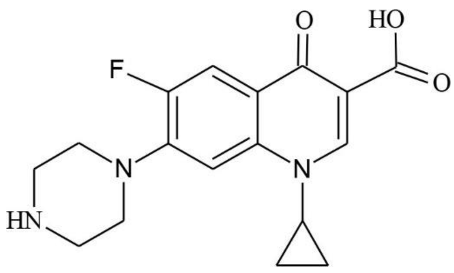
Chloroquine

2. Anticancer properties



Camptothecin

3. Antibacterial mediction



Ciprofloxacin

Application:

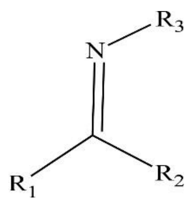
- Anti malarial
- Anti inflammatory
- Anticancer
- Antibaterial
- Fluroscent dyes and sensors (17,18)

SCHIFF BASE:

The German chemist Hugo Schiff, who was the first to characterize the results of the reaction between primary amines and carbonyl compounds in 1864, is the source of the term Schiff base (19).

The diversity of schiff bases, a broad class of compounds distinguished by the presence of a double bond connecting carbon and nitrogen atoms, is produced by the numerous ways in which a range of alkyl or aryl substituents can be combined.

These kinds of compounds can be created in a lab or discovered in nature. Chemical compounds [imines] with a hyrocarbyl group on the nitrogen atom (R2C=NR'(R' ≠ H)) are known as Schiff bases (20).



SCHIFF BASE

METAL COMPLEXATION:

The process by which a metal ion combines with one or more ligands-atoms, ions, or molecules that have the ability to donate electrons-to create a coordination complex or metal complex is known as metal complexation. In many industrial, biological, and chemical processes, this interaction is essential.

The Essential Elements of Metal Complexation:

- Ion of metal: most often a transition metal (such as Fe^{3+}, Cu^{2+}, and Co^{2+}).
- Ligand: An ion or molecule that gives one or more electron pairs (e.g., NH_3, H_2O, Cl^-, EDTA).
- Coordination Bond: A kind of covalent bond that is created when ligands give the metal ion lone pairs.

Type of ligand:

1. Donate one pair of electrons (for example, H_2O, NH_3) to become monodentate.
2. Bidentate: Give two pairs of electrons (ethylenediamine, for example).
3. Polydentate (Chelating agents): Provide several pairings (EDTA, for example).

Metal Complexation Application:

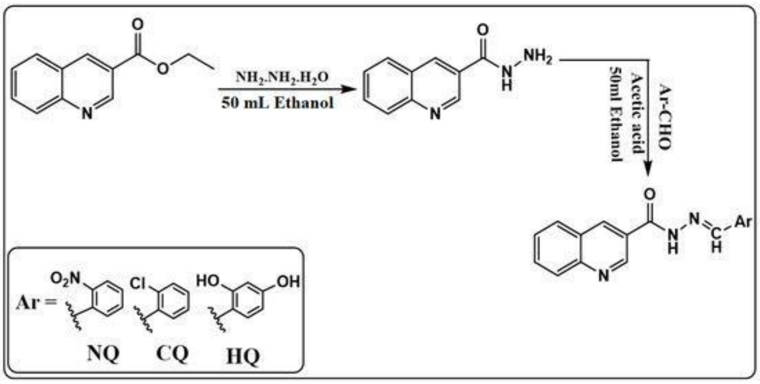
- Metal-based medications (such as cisplatin for cancer) are a part of medicinal chemistry .
- Catalysis: Industrial reactions employ metal complexes.

- Environmental Chemistry: Metal mobility in soil and water is impacted by metal complexation.
- Hemoglobin (Fe2+ complex) and vitamin B12 (Co2+ complex) are examples of bioinorganic chemistry [21, 22].

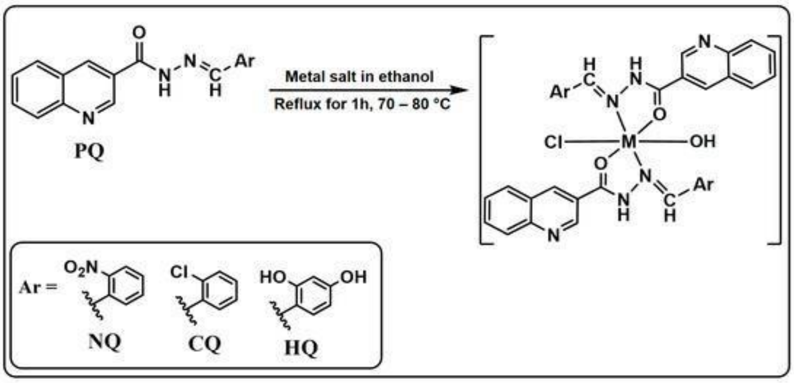
Example reaction:

$$Cu^{2+} + 4NH_3 \rightarrow [Cu\ (NH_3)4]^{2+}$$

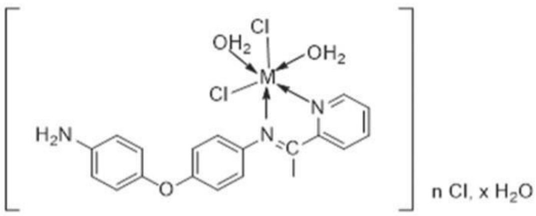
SYNTHESIS OF SCHIFF BASE LIGAND



SYNTHESIS OF METAL COMPLEXES:



STRUCTURES OF SCHIFF BASE METAL COMPLEXES:



M = Cr(III);	n = 1, x = 3
Mn(II); Cu(II);	n = 0, x = 2
Fe(III);	n = 1, x = 2
Co(II);	n = 0, x = 4
Zn(II); Cd(II);	n = 0, x = 0

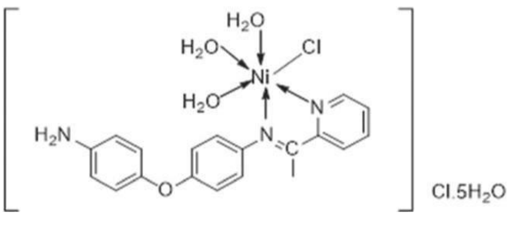


Table 2: Example of quinoline Schiff base metal complexes and their structural characteristics [23 to 27]

Complex Code	Metal Ion	Schiff Base Ligand Components	Coordination Mode	Geometry	Key Structural Features
[Cu(QSB1)]	Cu(II)	Quinoline-2-carbaldehyde + aniline	N, O (bidentate)	Square planar	Aromatic π- system, planar, Cu coordinated to N (azomethine) and O (phenolic)
[Zn(QSB2)]	Zn(II)	8-Hydroxy quinoline + salicylaldehyde	N, O, O (tridentate)	Tetrahedral	Stable chelate, enhanced lipophilicity, Zn–O and Zn–N bonds
[Co(QSB3)$_2$]	Co(II)	Quinoline-2-carbaldehyde + 4-chloroaniline	N, O (bidentate x2)	Octahedral	Two Schiff base ligands, electron-withdrawing Cl enhances planarity
[Ni(QSB4)]	Ni(II)	5-nitro salicylaldehyde + 8-amino quinoline	N, O (bidentate)	Square planar	Planar, H-bond acceptor, NO_2 group increases polarity
[Fe(QSB5)(Cl)$_2$]	Fe(III)	Quinoline + 2-hydroxy acetophenone	N, O (bidentate) + 2 Cl^-	Octahedral	Mixed-ligand complex, Fe–O, Fe–N, and Fe–Cl bonds
[Mn(QSB6)(H_2O)$_2$]	Mn(II)	6-Methoxy quinoline + salicylaldehyde	N, O (bidentate)	Octahedral	Axial aqua ligands, methoxy group improves solubility
[Cu(QSB7)$_2$]	Cu(II)	Quinoline hydrazone Schiff base	N, N, O (tridentate)	Square planar	Hydrazone moiety, increased chelation stability
[Cd(QSB8)$_2$]	Cd(II)	5-bromo quinoline-2-carbaldehyde + 2-aminophenol	N, O (bidentate)	Distorted tetrahedral	Bulky Br group affects geometry and activity

GREEN CHEMISTRY:

The goal of the new area of "green chemistry" is to create environmentally friendly chemical processes and products .It is governed by 12 principles that prioritize the use of safer solvents and reagents, waste minimization, and atom economy [28].

The idea began with projects like the Brundtland report and Responsible Care®, and it developed via scholarly work and legislation [29].By rethinking synthesis techniques and selecting ecologically friendly starting materials, solvents, and catalysts, green chemistry seeks to reduce the pollution that the chemical industry causes [30].

Catalysis, biocatalysis, the use of renewable feedstocks, alternative reaction media (like water or ionic liquids), and new reaction conditions (like microwave irradiation) are some of the current trends in green chemistry .Green chemistry aims to accomplish both economic and environmental benefits by putting these ideas and trends into practice [31].

Principle of green chemistry:

The twelve guiding principles of green chemistry are designed to reduce or eliminate hazardous materials from the synthesis, manufacturing, and use of chemical products. This, intern, aims to reduce or eliminate the use of materials that are harmful to the environment and human health. The term "green chemistry" was initially coined in the early 1990s.The Green Chemistry Institute was created in 1997 [32].The first volume of the reputable Royal Society of Chemistry's green chemistry journal was published in 1999 [33].

Predicated on twelve principles that seek to limit or remove hazardous compounds from the synthesis, manufacture, and usage of chemical products, and therefore the use of materials that are harmful to the environment and human health. They are entirely made of chemicals and chemical procedures that don't harm the environment. Its foundation is the creation or replication of molecules, reaction materials, and procedures that are safer for the environment and human health [34]

MICROWAVE ASSISTED SYNTHESIS:

Microwave-assisted eco-friendly synthesis is a novel method in organic chemistry that adheres to green chemistry ideals by minimizing harmful substances and enhancing efficiency

This method employs electromagnetic waves to produce heat, resulting in quicker reactions and greater yields than traditional techniques [35].These nanostructures may be utilized in catalysis, antimicrobial functions, and cancer therapies [36].

Microwave-assisted synthesis is especially beneficial in drug discovery and development, providing shorter reaction times and eco-friendly processes. The method's benefits, including increased reaction rates, improved yields, and better selectivity, have resulted in its extensive use in chemical synthesis, polymer production, and nanotechnology [37].

REACTION PROTOCOL:

General Procedure: Green Synthesis Assisted by Microwave

1. Materials Needed:

- Primary amine (such as quinoline-amine derivative
- Aldehyde that is aromatic (for Schiff base formation)
- Metal salt (such as $Zn(OAc)2$, $CuCl_2$, and $Ni(NO_3)_2$)
- Green solvents include ethanol, water, or a combination of ethanol and water.
- Reactor for microwaves (or home microwave with safety control)
- Round-bottom flask, magnetic stirrer, and optional TLC setup Microwave

2. Stepwise Procedure

Step 1: Schiff Base Ligand Synthesis

- Mix 1 mmol of aldehyde and 1 mmol of quinoline-amine in 10–15 mL of ethanol.
- To pre-mix, stir the mixture for five minutes at room temperature.
- Put the reaction mixture in a sealed receptacle that is suitable to use in a microwave.
- Apply microwave radiation to it:
- 200–400 W of power
- Duration: two to five minutes
- Temperature range: 80 to 120 °C (depending on microwave settings)
- The reaction mixture should be cooled.
- Filter the resulting Schiff base and, if required, recrystallize [38]

Step 2: Complexation of Metals

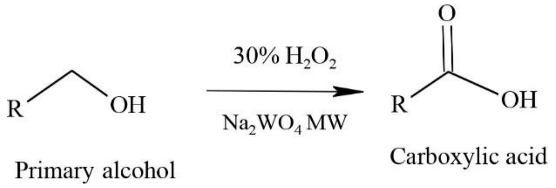
- The Schiff base ligand should dissolve in very little ethanol.
- Add metal salt in an equimolar or slightly excess amount (1.2 mmol, for example).
- Put the mixture in the microwave:
- 300–500 W of power
- Duration: three to six minutes
- Climate: 100–130 °C
- The precipitated metal complex should be cooled and filtered.
- Dry with a vacuum after washing with cold ethanol [39].

3. Important Notes:

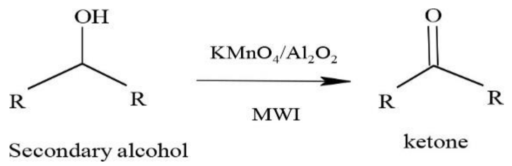
- Use ethanol, water, or PEG as green solvents instead of harmful ones.
- For most Schiff base reactions, catalysts are not required.
- If necessary, track the reaction's progress using TLC or UV-Vis.
- When compared to traditional heating (hours), reaction completion is usually quicker (minutes) [40]

4. Example Reaction

1.



2.



FLOW CHART

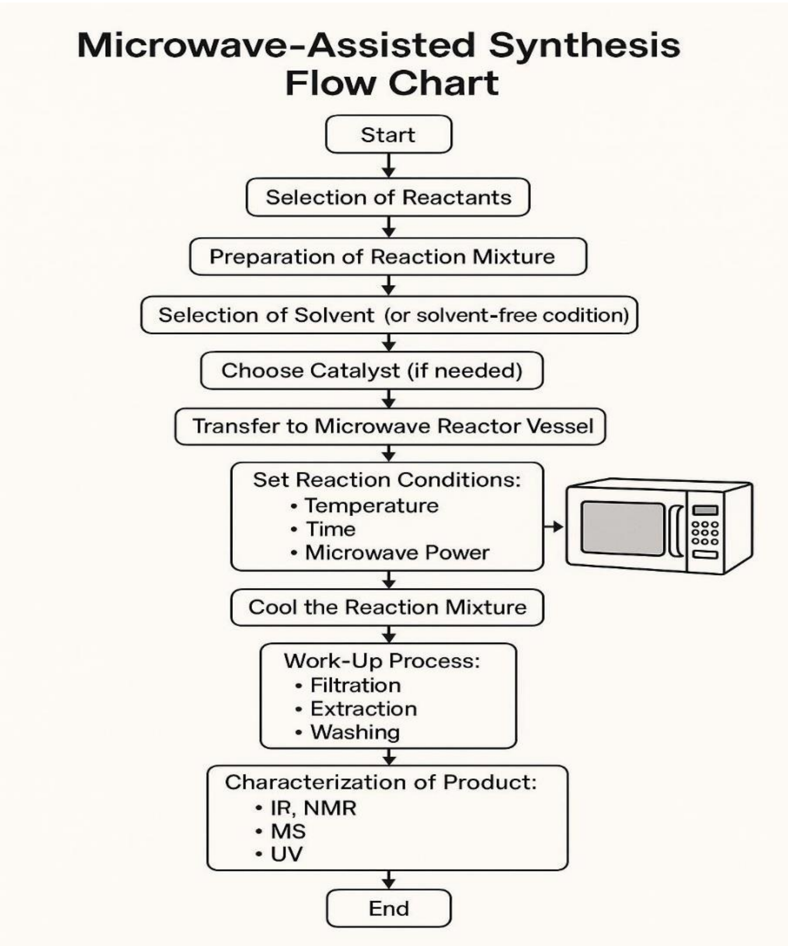


Figure 2:

Table 3: Microwave assisted synthesis vs conventional synthesis [Time/Yield/solvent] (41 to 46)

Parameter	Microwave-Assisted Synthesis	Conventional Synthesis
Reaction Time	5–15 minutes	4–24 hours
Reaction Temperature	80–120 °C (controlled & rapid heating)	Reflux temperature (slow ramp- up)
Product Yield (%)	80–95%	50–75%
Solvent Usage	Minimal or solvent-free (green solvents)	Large volumes of organic solvents
Energy Efficiency	High (focused heating)	Low (bulk heating, heat loss)
Purity of Product	Often higher due to fewer by- products	May require extensive purification
Reaction Control	Precise (time/temp controlled)	Less control; uneven heating possible
Environmental Impact	Low (green chemistry compliant)	Higher due to solvent and energy use

Discussion:

Microwave-assisted green synthesis has proven to be a rapid, efficient, and eco-friendly method for developing quinoline–Schiff base metal complexes. By using benign solvents and minimizing reaction times, this technique not only improves yield and purity but also reduces energy consumption and chemical waste compared with conventional approaches. The versatility of this strategy allows the preparation of diverse metal complexes with potential applications in catalysis, medicine, and material science.

However, most studies remain limited to laboratory scale, with insufficient attention to scalability, mechanistic clarity, and environmental assessments. Future research should emphasize standardized green metrics, continuous or flow microwave platforms, eco-friendly metal sources, and detailed structure–activity investigations. Addressing these gaps will enable the translation of microwave-assisted green methods into robust, sustainable, and industrially relevant technologies.

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