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Review

# Quinoline Synthesis: Nanocatalyzed Green Protocols—An Overview

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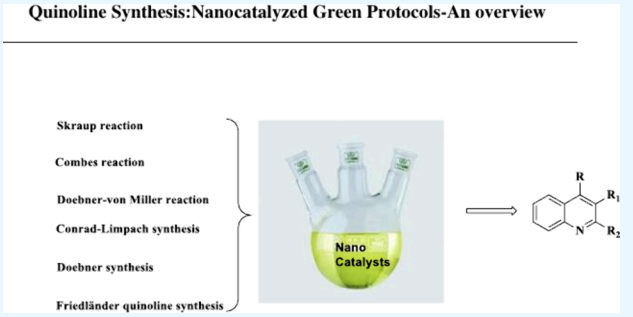
**ABSTRACT:** Heterocyclic compounds are of great interest in our daily lives. They are widely distributed in nature and are synthesized in laboratories. Heterocycles play an important role in the metabolism of all living cells, including vitamins and coenzyme precursors like thiamine and riboflavin. Furthermore, heterocyclic systems are essential building blocks for creating innovative materials with intriguing electrical, mechanical, and biological properties. Also, more than 85% of all biologically active chemical entities comprise a heterocycle. As a result, heterocycle synthesis piqued researchers' curiosity, and in recent decades, chemists have concentrated more on nitrogen-containing cyclic nuclei in structures. Quinoline and its derivatives exhibit several biological functions, including antimicrobial, anticancer, antimalarial, anti-inflammatory, antihypertensive, and antiasthmatic effects. In addition, over a hundred quinoline-based drugs are available to treat a variety of disorders. Because of its biological importance, researchers developed one-pot synthetic methods employing effective acid/base catalysts (Lewis acids, Brønsted acids, and ionic liquids), reagents, and transition-metal-based catalysts. These methods have some downsides, including longer reaction times, harsher reaction conditions, creation of byproducts, costly catalysts, use of hazardous solvents, an unacceptable economic yield, and catalyst recovery. Researchers' focus has switched to creating environmentally friendly and effective methods for the synthesis of quinoline derivatives as a result of these methodologic shortcomings. Because of its special qualities, the use of nanocatalysts or nanocomposites offers an option for the effective synthesis of quinolines. This review focuses on the published research articles on nanocatalysts to synthesize substituted quinoline derivatives. This review covers all contributions until May 2024, focusing on quinoline ring building and mechanistic issues. With the aid of this review, we anticipate that synthetic chemists will be able to develop more effective methods of synthesizing quinolines.




## 1. INTRODUCTION

One of the most significant areas of chemistry is heterocyclic chemistry, which yields a wide range of molecules of biological significance. In nature, heterocyclic compounds are abundant and necessary for life.[1] In the fields of biochemistry, materials chemistry, drug development, and other sciences, heterocycles are essential. They are essential to every living cell's metabolism. Numerous heterocyclic compounds possess pharmacological activity, with many of them having frequent therapeutic use.[2] The bulk of heterocyclic compounds discovered in nature are nitrogen-containing, making them the most abundant class of compounds when compared to those containing oxygen or sulfur. Among the N-containing hetercocyles, quinoline (**3**) and its derivatives are significant themes among pharmacologically significant heterocyclic compounds because of their wide variety of biological activities and natural presence in substances.[3] Quinoline is a bicyclic heterocyclic molecule containing a benzene ring (**1**) fused with pyridine (**2**) at two adjacent carbon atoms. This core is also known as 1-azanaphthalene, benzazine, 1-benzazine benzopyridine, and benzo[*b*]pyridine[4,5] (Figure 1).

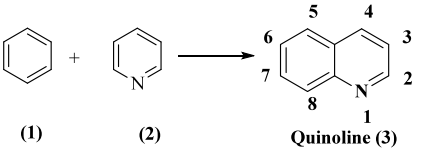



**Figure 1.** Structure of quinoline.

The compounds with a quinoline motif demonstrate a variety of biological and pharmacological activities, such as antitubercular,[4] antimalarial,[6] anticancer,[7] antihuman immunodeficiency virus (HIV),[8] antiviral,[9] anti-inflammatory,[10] analgesic,[11] antibacterial,[12] antihypertensive,[13] anti-Alzheimer activity,[14] antibiotic,[15,16] antileishmanial,[17] antioxidant,[18] antiprotozoal,[19] DNA binding,[20] inhibition of tyrosine kinase[21]

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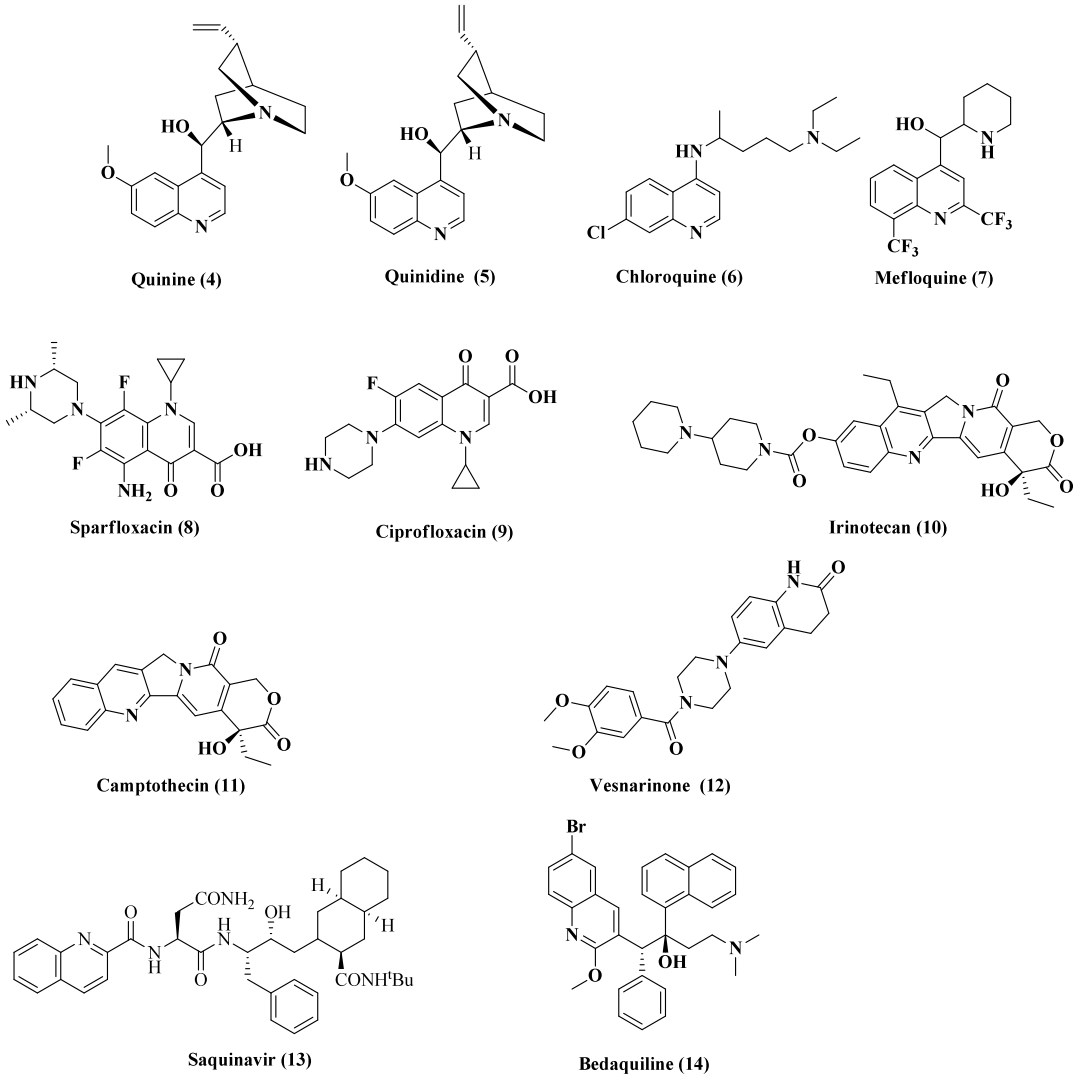


**Figure 2.** Examples of clinically used quinoline derivatives.

properties, and tyrokinase PDGF-RTK inhibition.[22] Also, 2-trifluoromethyl quinoline scaffolds have also been used as organic ligands[23,24] and fluorescence probes.[25,26] Currently, few quinoline based drugs booming in the market, *viz*., quinine (**4**), quinidine (**5**), chloroquine (**6**), and mefloquine (**7**), are used as antimalarial drugs.[27,28] Sparfloxacin (**8**) and ciprofloxacin (CPFX) (**9**) act as antimicrobial drugs.[29,30] Irinotecan (**10**) and camptothecin (**11**) act as anticancer agents.[31−33] Vesnarinone (**12**) (cardiotonic) and Saquinavir (**13**) act as an HIV-1 protease enzyme.[34] Also, Bedaquiline (**14**), a quinoline-based drug, acts as an antimycobacterial drug in the market[35] (Figure 2).

Therefore, quinoline synthesis is gaining popularity among synthetic organic chemists and biologists due to its wide range of biological/pharmacological applications. A variety of methods for the synthesis of quinoline derivatives are available through a number of classical synthetic route/name reactions from commercially available reagents such as substituted anilines. The most important among them are (a) Skraup synthesis, (b) Combes reaction, (c) Doebner−von Miller reaction, (d) Riehm synthesis, (e) Conrad−Limpach synthesis, (f) Doebner, (g) Gould−Jacobs synthesis, and (h) Pavarov reaction. Also the other methods like (i) Friedländer synthesis (from 2-aminobenzaldehyde with carbonyl compounds), (j) Knorr quinoline synthesis (from $\beta$-ketoanilide using sulfuric acid), (k) Pfitzinger reaction (isatin with a base and a carbonyl compound), (l) Niementowski quinoline synthesis (anthranilic acid with carbonyl compounds), (m) Camps quinoline synthesis (*o*-acylaminoacetophenone with base), and (n) Meth−Cohn synthesis (acylanilides and DMF/$POCl_3$) use different starting materials for the synthesis of quinoline. Figure 3 summarizes the synthesis approaches for these traditional procedures (Figure 3).[36−40]

Even though a lot of these methods work quite well, they frequently require the use of other acids and more expensive reagents and oxidants and generate a lot of waste and require longer reaction times, the use of toxic solvents, the need to separate the catalyst from the reaction system, and the reusability of homogeneous catalysts. Furthermore, several of these processes produce relatively high amounts of unwanted byproducts, which must be removed tediously and frequently wastefully.[41] They are also unsatisfactory in terms of operational ease and yield. As a result, it is now crucial to adhere to what may be regarded as superior and environmentally sustainable "green synthetic methods". Thus, the development of novel, environmentally friendly methods for


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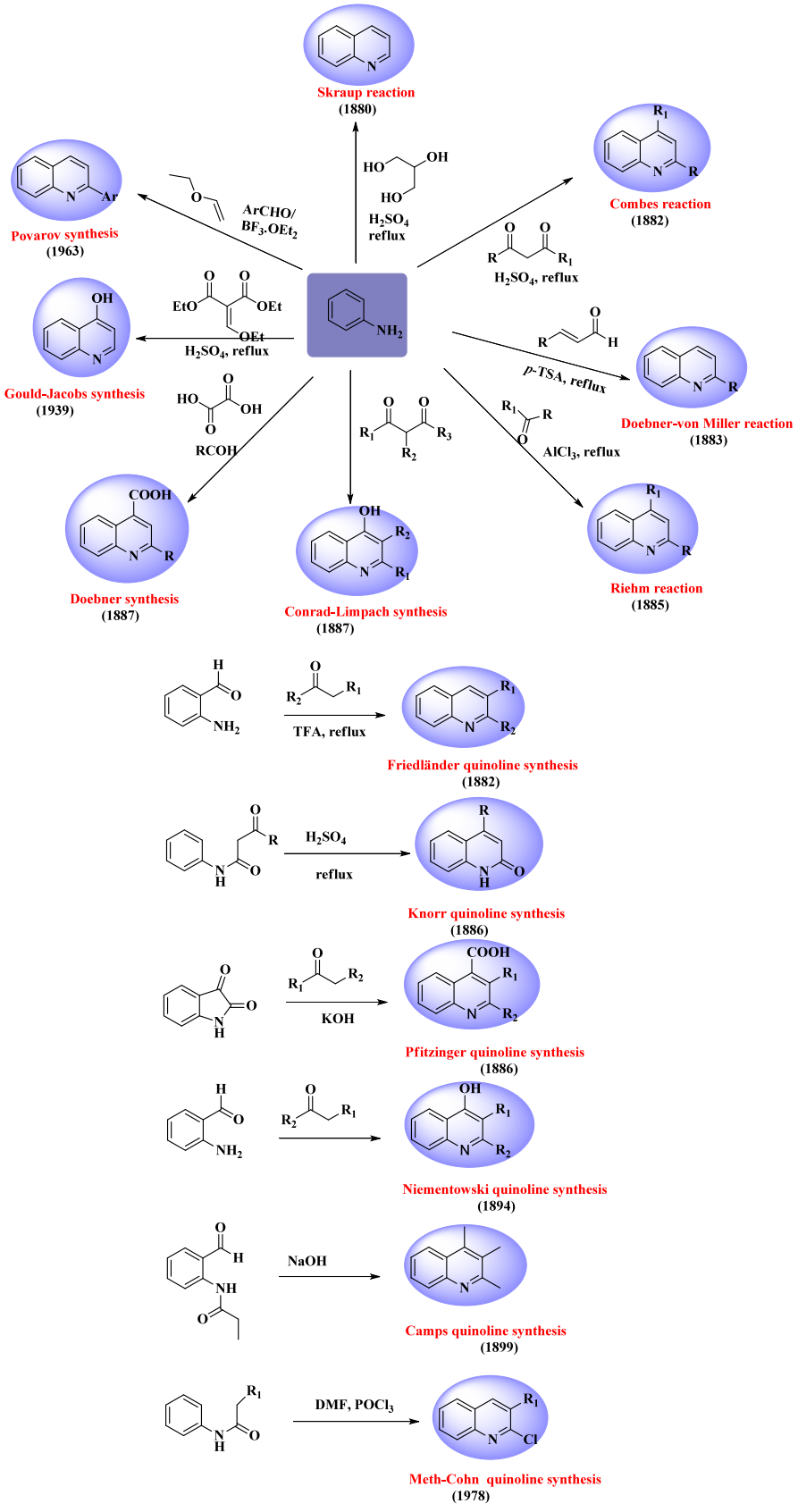


**Figure 3.** Conventional routes for the synthesis of quinoline derivatives.

producing chemical entities can significantly lessen the chemical industry's environmental effect while also lowering the expenses of using high temperatures and handling generated trash. In the last decade, nanomaterials/nanocatalysts have emerged as superior alternatives to traditional materials for a wide range of catalytic organic reactions/



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transformations.[42] In addition to being utilized in the transformation of organic compounds, nanocatalysts find extensive applications in photocatalysis, semiconductors, energy conversion and storage in nanobots, chemical production, biological applications, and environmental technologies.[43−46] Nanocatalysts come in a variety of forms, including nanomixed metal oxides, graphene-based nanocatalysts, magnetic nanocatalysts, nanosupported catalysts, and core−shell nanocatalysts, which have been used in catalytic applications.[47] When compared to homogeneous/heterogeneous catalysts, nanocatalysts can provide significant benefits. These include exceptional specificities in many chemistries based on their outstanding features (high surface areas, degenerated density of energy states, and plasmon), good reusability combined with high activities, cheap preparation costs, remarkable selectivity, strong mechanical strengths, high resistance to temperature, high stability, and superb activity (Figure 4).[48−50]

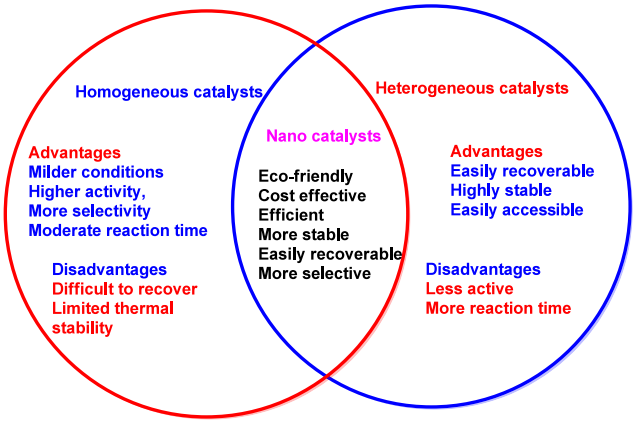


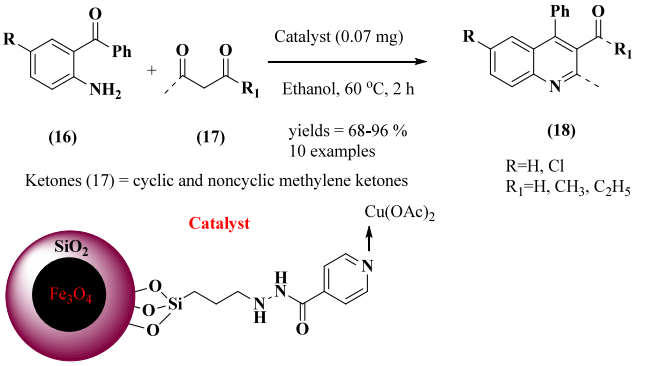

**Figure 4.** Advantages of nanocatalysts over homogeneous and heterogeneous catalysts.

As a result, organic chemists and process development professionals are interested in employing these nanocatalysts for organic transformations and heterocyclic synthesis. Several heterocyclic compounds, including quinoxaline,[51] benzimidazole,[52] pyrazole,[53] acridine,[54] triazole,[55] coumarin,[56] 1,4-dihydropyridine,[57] diazepines,[58] benzo[*b*]furan,[59] and quinoline,[60] as well as other heterocycles,[42] have already been synthesized using nanocatalysts. Several review articles have previously been published, demonstrating several pharmacological/biological uses of quinoline and its derivatives.[4,10,61−66] Also, for the application of transition metal/metal-free synthesis, environmentally benign approaches have been reported for the synthesis of quinoline.[67−72] These catalysts have some drawbacks like recovery and low yield. As an alternative, nanobased recyclable catalysts were introduced. To overcome these disadvantages, this review gives comprehensive insight into the application of nanobased catalysts for one-pot protocols for quinoline synthesis with plausible reaction mechanisms (until May 2024). This review has been divided into sections based on the nanocatalysts used to synthesize quinolines (such as Fe, Cu, Zn, Ni, Co, Au, Ag, $SiO_2$, Ti, Al, Sn, Zr, Ru, 12-phosphotungstic acid, and Hg-based nanocatalysts).

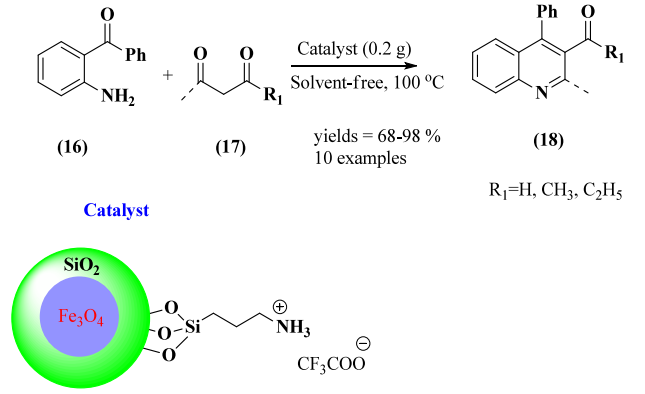
## 2. SYNTHESIS OF QUINOLINES USING VARIOUS NANOCATALYSTS

**2.1. Iron-Based Nanocatalysts for the Synthesis of Quinolines.** The scientific and industrial communities have shown a great deal of interest in iron-based nanoparticles as effective catalysts and supports because of their special qualities, which include efficient recyclability, size, low toxicity, high surface area, abundance, good biocompatibility, easy accessibility, high surface-to-volume ratio, and coordinated parts that provide more active sites per unit area than their corresponding bulk materials.[73] Additionally, a lot of organic transformations and heterocyclic syntheses were carried out using Fe-based nanomaterials.[74] Also, numerous Fe-based catalysts and materials were utilized to synthesize quinolines, which are addressed in this section. The $Fe_3O_4$@$SiO_2$/isoniazid/Cu(II) has been synthesized by Lotfi and co-workers as a recoverable magnetic nanocatalyst. The material has been characterized using a variety of techniques, including transmission electron microscopy (TEM), scanning electron microscopy (SEM), powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), a vibrating sample magnetometer (VSM), energy dispersive spectroscopy (EDS), and X-ray and Fourier transform infrared (FT-IR). This material has a spherical shape with an average size of 20−30 nm and was produced on the surface of modified $Fe_3O_4$ nanoparticles with amino groups acting as organic shells. The newly developed nanocatalyst was used to synthesize quinoline derivatives from $\alpha$-methylene ketones and 2-aminoaryl ketones

**Scheme 1. Synthesis of Quinolone Using $Fe_3O_4$@$SiO_2$/Isoniazid/Cu(II) as a Catalyst**




**Scheme 2. Synthesis of Quinoline Using $Fe_3O_4$@$SiO_2$-APTES-TFA as a Catalyst**



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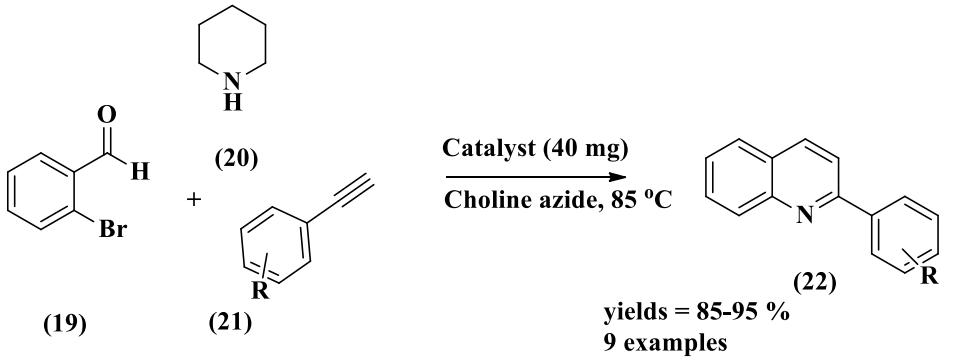
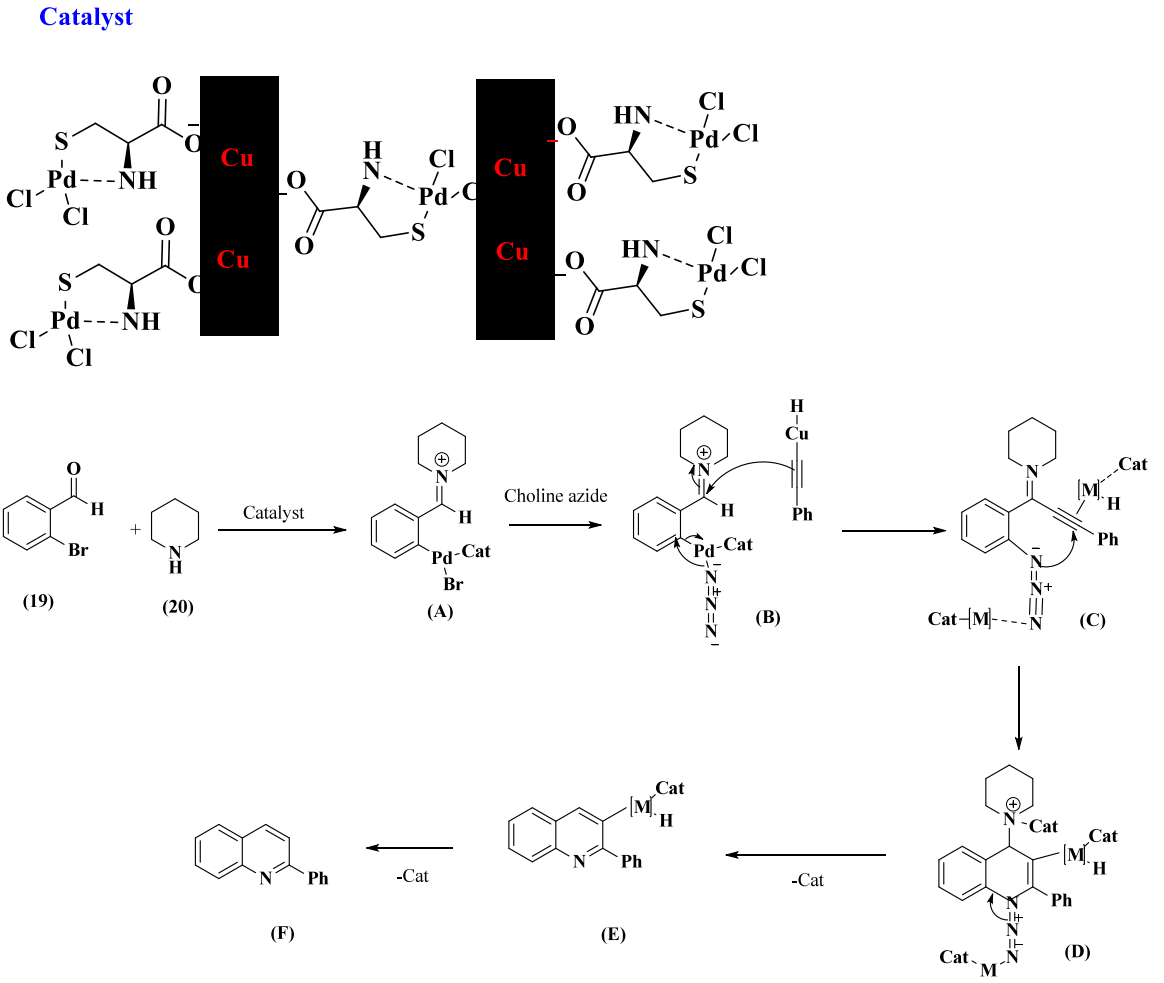
**Scheme 3. Synthesis of Quinoline Using Magnetic $\gamma$-$Fe_2O_3$@Cu-LDH@Cysteine-Pd as a Catalyst and Their Plausible Mechanism**




via the Friedlander protocol. The diverse quinoline derivatives were produced in good yield (68−96%) utilizing cyclic and noncyclic methylene ketones, with a catalyst load of 0.07 mg, at 60 °C for 2 h, with ethanol serving as the reaction solvent. The use of cyclohexanone decreased the yield, and the author notes that the amino aryl ketones with and without substituents did not exhibit any discernible influence on yields. Up to four recycling cycles are possible with a 24% activity reduction in the catalyst. The protocol's primary benefits are its high catalytic activity, ease of separation using an external magnet, and high reusability (Scheme 1).[75] A subsequent study by Jafarzadeh and co-workers produced an $Fe_3O_4$@$SiO_2$-APTES-TFA core−shell nanocatalyst that is magnetically recoverable and immobilized with trifluoroacetic acid. It was characterized using FTIR, XRD, TGA, CHN, TEM, and DLS. In $Fe_3O_4$@$SiO_2$−$CH_2CH_2CH_2NH_3^+OOCCF_3$, strong ionic interactions between quaternary ammonium and trifluoroacetate groups can produce an ion pair with distinct behavior alkaline to ionic liquids. The agglomerated nanomaterial has cores that are smaller than 50 nm on average. Additionally, this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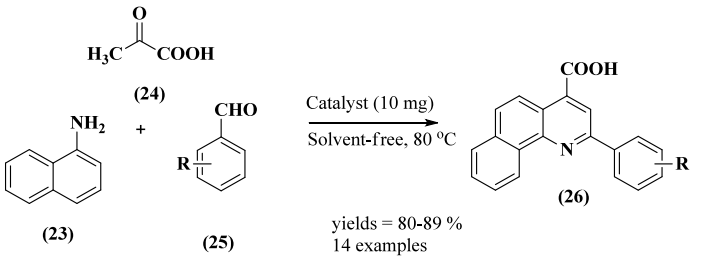
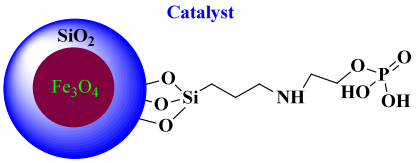
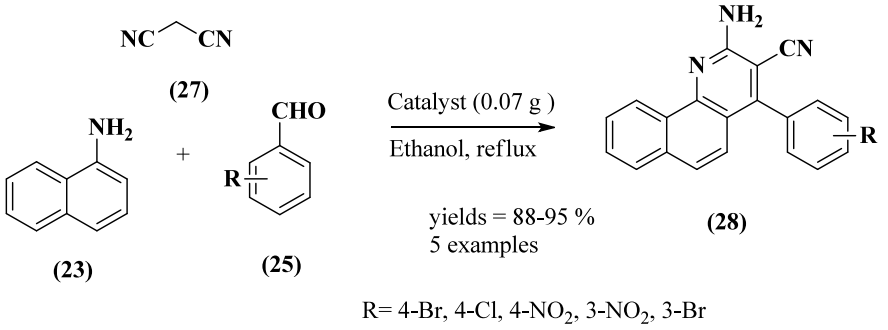
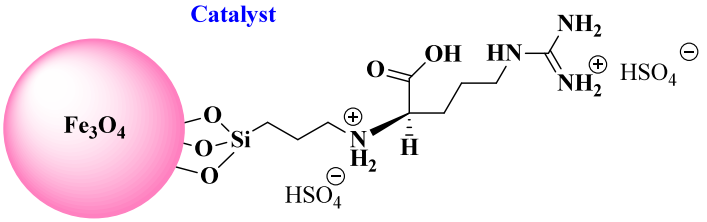
**Scheme 4. Synthesis of Quinoline Using $Fe_3O_4@SiO_2@(CH_2)_3NH(CH_2)_2O_2P(OH)_2$ as a Catalyst**

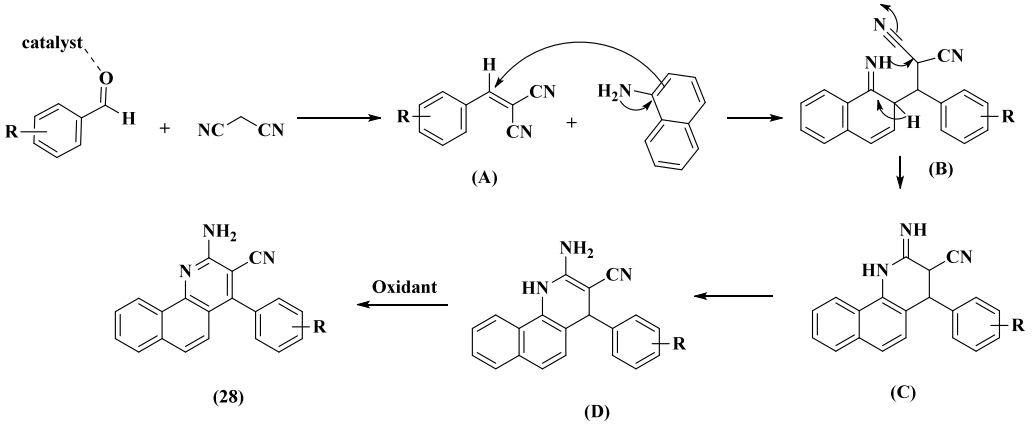



**Scheme 5. Synthesis of Quinolone Using $Fe_3O_4$@PS-Arginine Magnets as a Catalyst and Their Plausible Mechanism**




substance/catalyst is employed in the solvent-free Friedlander annulation process to prepare quinolines, employing a variety of cyclic and acyclic dicarbonyl compounds. At 100 °C under solvent-free conditions, a good yield (68−98%) of quinoline was achieved with 0.2 g of catalyst. The authors noted that nearly equal yields of comparable quinoline compounds were



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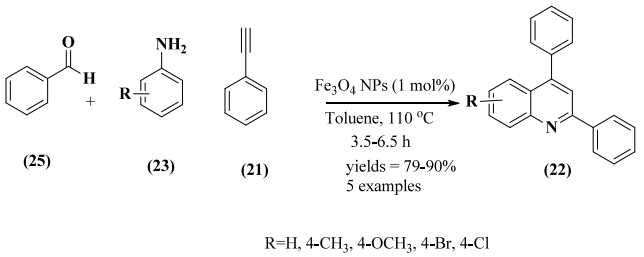
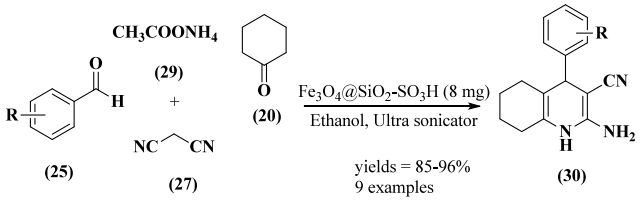
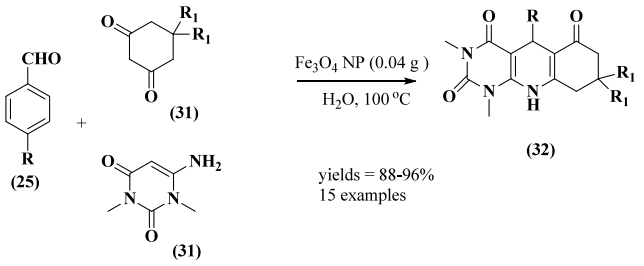
**Scheme 6. Synthesis of Quinoline Using $Fe_3O_4$ Nanoparticles Supported by Perylene Bisimide As a Catalyst**



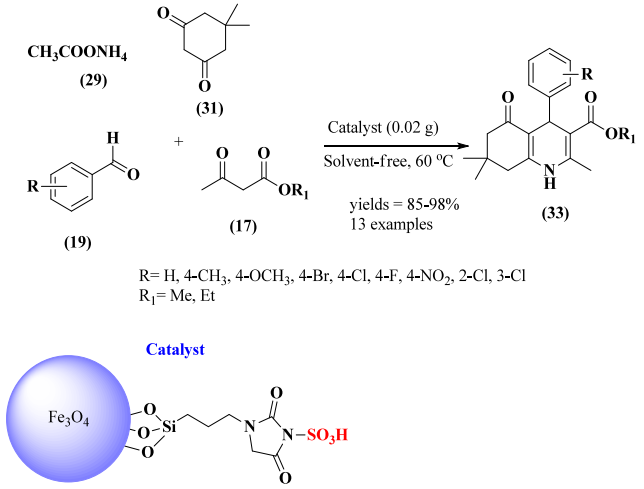

**Scheme 7. Synthesis of Quinoline Using $Fe_3O_4$@$SiO_2$−$SO_3H$ Nanoparticles As a Catalyst**




**Scheme 8. Synthesis of Quinoline Using $Fe_3O_4$ NP−Cellulose As a Catalyst**




**Scheme 9. Synthesis of Quinoline Using Sulfamic Acid-Functionalized $Fe_{3-x}Ti_xO_4$ MNPs as a Catalyst**




obtained from both aromatic and aliphatic ketones. With the aid of an external magnet, the catalyst may be readily retrieved after the reaction and utilized again for at least four runs without seeing a discernible drop in catalytic activity (Scheme 2).[76]

A dual nanocatalyst, magnetic $\gamma$-$Fe_2O_3$@Cu-LDH@Cysteine-Pd was developed by Heydari et al. These nanoparticles, which range in size from 17 to 29 nm, resemble cauliflowers in appearance and contain a porous, interconnected network. After further intercalation, the average size of $\gamma$-$Fe_2O_3$@Cu-LDH@Cysteine and $\gamma$-$Fe_2O_3$@Cu-LDH@Cysteine-Pd rose to around 22−46 and 18−53 nm, respectively. Additionally, this catalyst was used to synthesize quinolones by intramolecular cyclization, C−N coupling, and $A^3$-coupling. Phenylacetylene derivatives were converted to the required quinolines with excellent yields (85−95%) at 40 mg of catalyst at 85 °C in choline azide medium in 4 h after the reaction was adjusted using varied quantities of catalyst, solvent, and temperature. This approach is applied to aromatic alkynes with various substituents, and it is discovered that *para*-substituted electron-donating groups had a little higher efficiency on the reactivity than the *ortho*-substitution of the $-OCH_3$ group on phenylacetylene, which exhibited a minor drop in reactivity. Following the process, the catalyst can be retrieved and utilized for up to four cycles with minimal degradation. According to a probable mechanism put out by the author, the reaction between 2-bromo benzaldehyde and piperidine in situ forms the iminium ion (B) in the first step. The active palladium-containing catalyst inserts between the C−Br bond in the subsequent oxidative addition phase to create palladium complex (A). There is an azide group exchange with Br and C−N coupling during the reductive elimination process. In the third stage, activated phenylacetylene will combine with an iminium intermediate (B) to generate an *N*-benzyl propargyl amine molecule (C) by an $A^3$-coupling reaction. Subsequently, quinoline is generated by intramolecular cyclization and the removal of a secondary molecule (Scheme 3).[77] The $Fe_3O_4$@$SiO_2$@$(CH_2)_3NH(CH_2)_2O_2P(OH)_2$, a new nanomagnetic/heterogeneous catalyst developed by Zolfigol and co-workers, is made with 2-aminoethyl dihydrogen phosphate. The catalyst has particle sizes that are less than 30 nm. Further, the catalyst is used in the multicompount synthesis of benzo-[*h*]quinoline-4-carboxylic acid derivatives by the reaction of pyruvic acid, naphthylamine, and benzaldehydes. Following reaction parameter adjustment, 80 °C and 10 mg of the new catalyst were used without the use of a solvent. In a shorter amount of time (20−35 min), the necessary benzo-[*h*]quinoline-4-carboxylic acid derivatives were produced with high yields (80−89%). Without losing its catalytic activity, the catalyst may be retrieved using an external magnet and utilized for a minimum of six consecutive runs. The protocol's advantages include quick reaction durations, high product yields, environmentally friendly and temperate reaction temperatures, smooth and simple separation, and catalyst reusability (Scheme 4).[78]

$Fe_3O_4$@propylsilane-argenine ($Fe_3O_4$@PS-Arg) magnetic nanoparticles (MNPs) were prepared from $Fe_3O_4$, propylsilan, and arginine, as described by Kefayati et al. These materials have a consistent size of 70−90 nm and a spherical shape. Utilizing $\alpha$-naphthilamine and aromatic aldehydes in a one-pot reaction with malononitrile, these nanoparticles served as an environmentally safe solid acid magnetic nanocatalyst for the production of 2-amino-4-arylbenzo[*h*]quinoline-3-carbonitrile derivatives. The best product yield (95%) was achieved by employing 0.07 g of catalyst and EtOH, a suitable solvent for the reaction, although the process was optimized using various loads of catalysts and solvents. In minimal time (5−15 min),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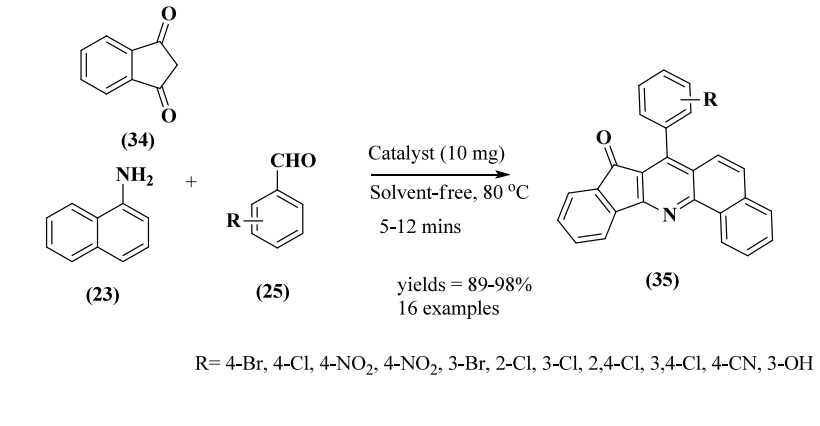
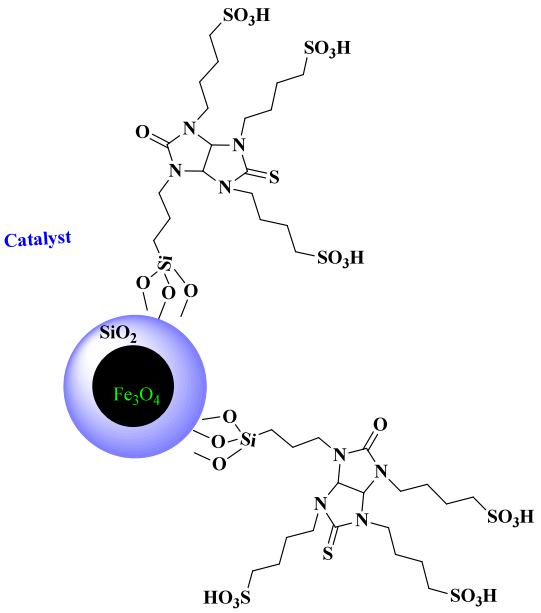
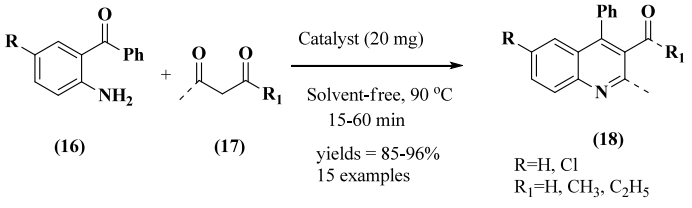
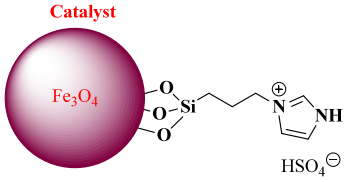
**Scheme 10. Synthesis of Quinoline Using $Fe_3O_4$@Urea/HITh-$SO_3H$ MNPs as a Catalyst**




**Scheme 11. Synthesis of Quinoline Using $Fe_3O_4$–IL-$HSO_4$ as a Catalyst**




many benzo[*h*]quinoline-3-carbonitrile compounds were produced with excellent yields (88−95%). Without significantly lowering its activity or the reaction yield, the catalyst can be extracted from the reaction mixture and employed up to five more times. The author put out a tenable mechanism for quinoline synthesis. Condensing malononitrile with aldehyde in the first stage produces product (A) by Knoevenagel condensation. It then reacts with $\alpha$-naphthilamine via a Michael addition to produce intermediate (B), which is then intramolecularly cyclized to produce quinoline (Scheme 5).[79] Using sequential three-component coupling/hydroarylation/dehydrogenation processes of aldehyde, alkyne, and aromatic amine, Bhalla and colleagues synthesized quinoline derivatives using superparamagnetic $Fe_3O_4$ nanoparticles supported by



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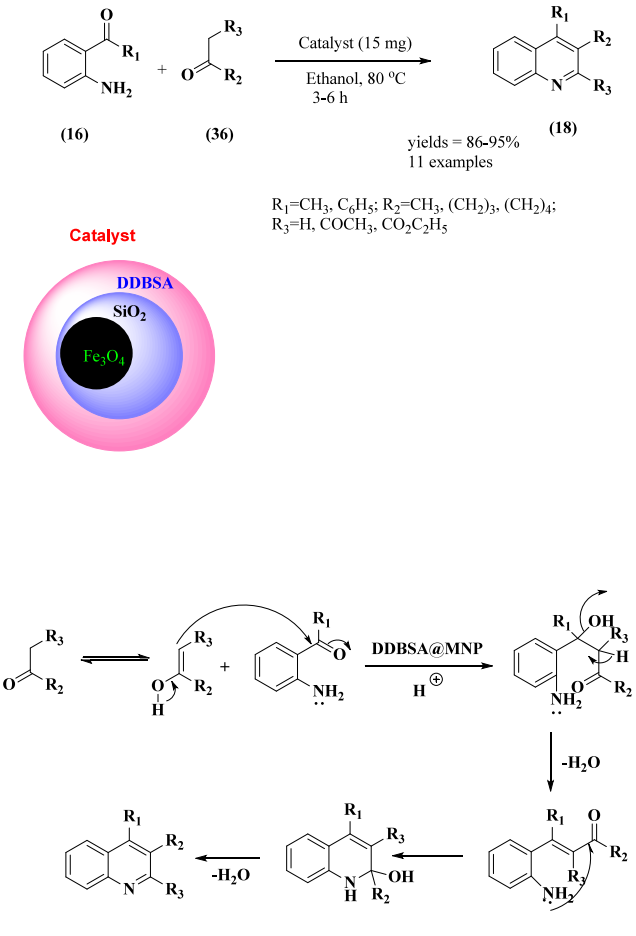
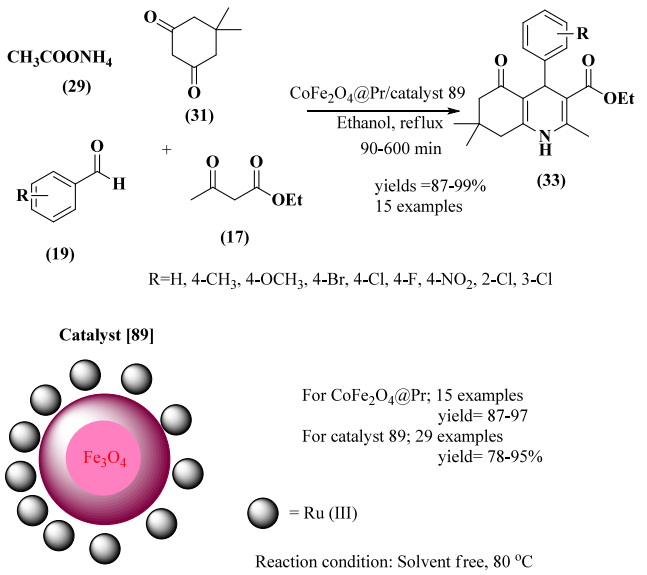
**Scheme 12. Synthesis of Quinoline Using DDBSA@MNP as a Catalyst and Their Plausible Mechanism**

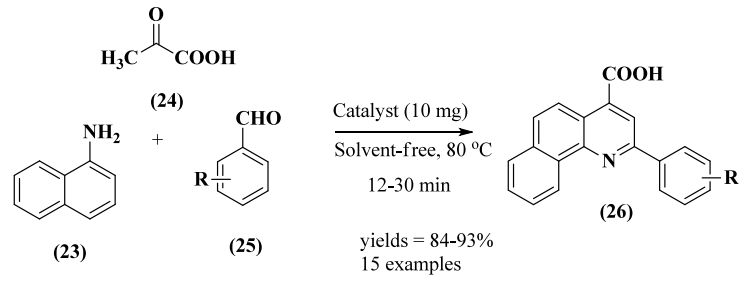


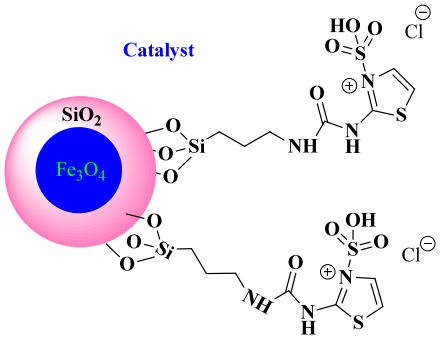

**Scheme 14. $CoFe_2O_4$@Pr and RuIII@CMC/$Fe_3O_4$ Catalyzed the One-Pot Synthesis of Polyhydroquinoline Derivatives**




perylene bisimide. These materials are in the form of nanorods with sizes in the range of 80−130 nm. The aniline with electron-donating (EDGs) and electron-withdrawing groups (EWGs) worked well, producing the respective compounds in high yields (79−90%). $Fe_3O_4$ NPs were magnetically isolated after the reaction and may be employed again up to five times without significantly losing their catalytic activity. The author put out a tenable method that adheres to the previously mentioned protocol. $Fe_3O_4$ nanoparticles interact with alkyne to produce a propargylamine intermediate by reaction with an *in situ* created imine derivative. Intramolecular hydroarylation

**Scheme 13. Synthesis of Quinoline Using $Fe_3O_4$@$SiO_2$@$(CH_2)_3$-Urea-Thiazole Sulfonic Acid Chloride As a Catalyst**



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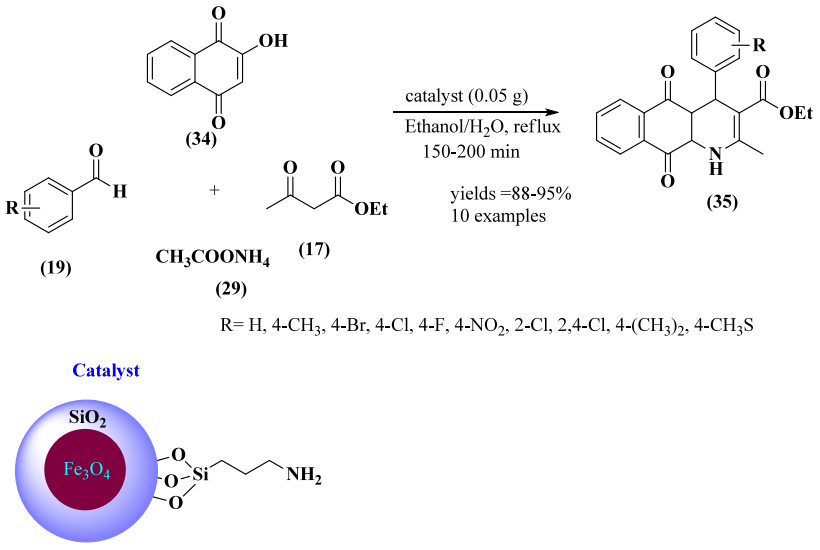
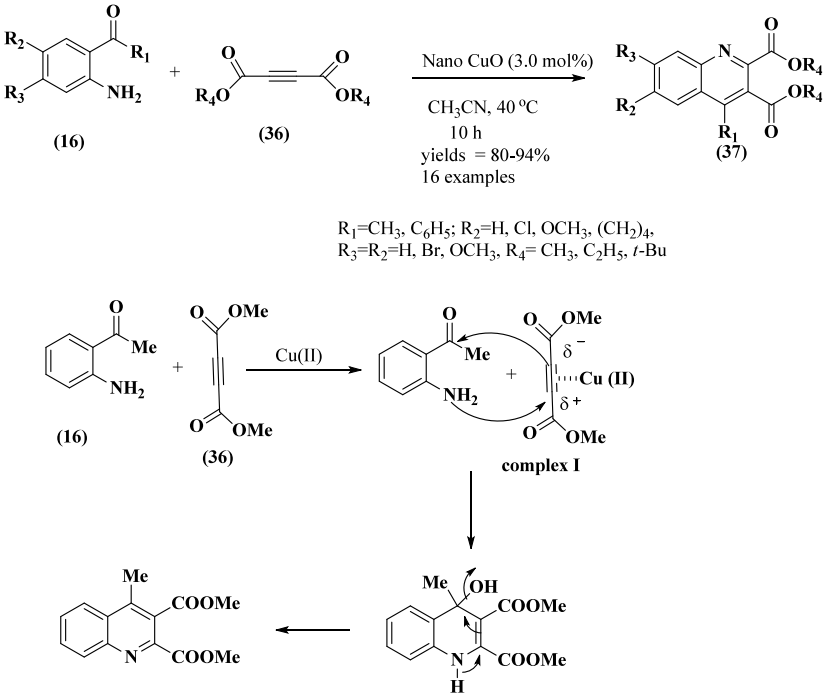
ACS Omega 2024, 9, 42630−42667

**Scheme 15. $Fe_3O_4$@$SiO_2$-$NH_2$ Catalyzed the One-Pot Synthesis of Polyhydroquinoline Derivatives**




**Scheme 16. Synthesis of Quinoline Using Nano-CuO as a Catalyst and Their Plausible Mechanism**




of a propargylamine intermediate followed by air oxidation produced the quinoline derivative (Scheme 6).[80]

Ghomi and co-workers employed $Fe_3O_4$@$SiO_2$−$SO_3H$ nanoparticles in the four-component condensation process of aromatic aldehydes, cyclohexanone, malononitrile, and ammonium acetate under ultrasonic irradiation to synthesize hexahydro-4-phenylquinoline-3-carbonitriles. These MNPs range in size from 30 to 40 nm on average. Variations in the catalyst amount and solvents improve the reaction. When 10 mg of catalyst was used in ethanol, the greatest results were obtained. Under these circumstances, a variety-oriented library of quinolines with a decent yield (85−96%) were synthesized using a wide range of substrates in a reduced reaction time (5−10 min). The catalyst was recovered and reused. Product yields were found to slightly decline with each reuse of the catalyst (run 1, 94%; run 2, 94%; run 3, 93%; run 4, 93%; run 5, 92%; run 6, 92%). The advantages of the technique include great atom economy, high yields, low reaction times, little catalyst loading, good catalyst recoverability, a straightforward method, and enhanced catalyst utilization. The author supported the tenable mechanism, which agrees with previous reports. After benzaldehydes and malononitrile undergo Knoevenagel condensation, an intermediate is formed. Michael addition of cyclohex-1-enamine to the intermediate is then carried out, and the product is cyclized to produce derivatives of quinolines (Scheme 7).[81] The $Fe_3O_4$ NPs supported on cellulose were synthesized by Edjlali and co-workers. Following deposition, a significant number of $Fe_3O_4$ NPs with particle sizes ranging from 11 to 24 nm were created and evenly dispersed throughout the surface of the cellulose. Using water as a


https://doi.org/10.1021/acsomega.4c07011
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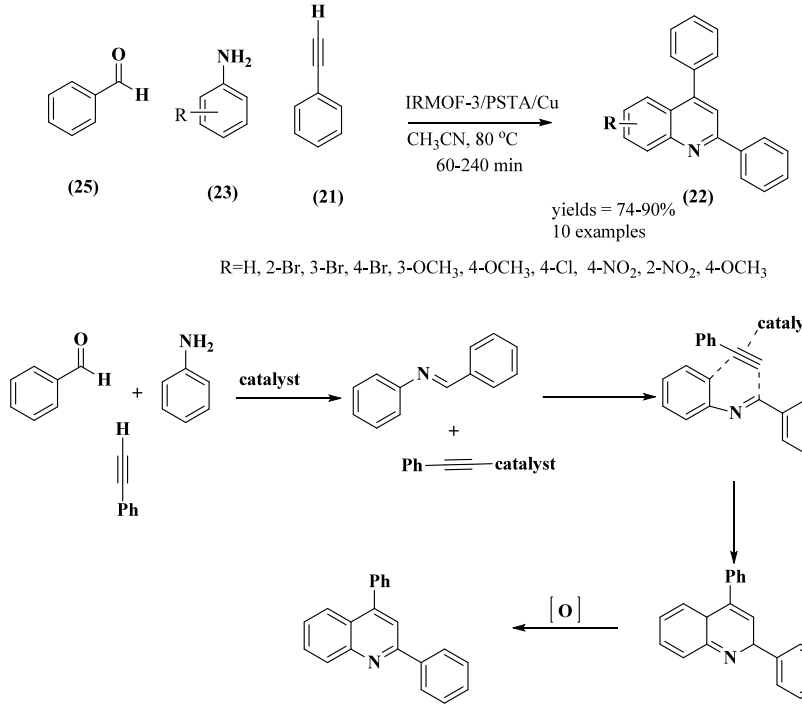
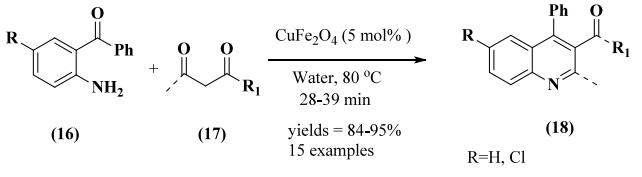
**Scheme 17. Synthesis of Quinoline Using IRMOF-3/PSTA/Cu as a Catalyst and Their Plausible Mechanism**

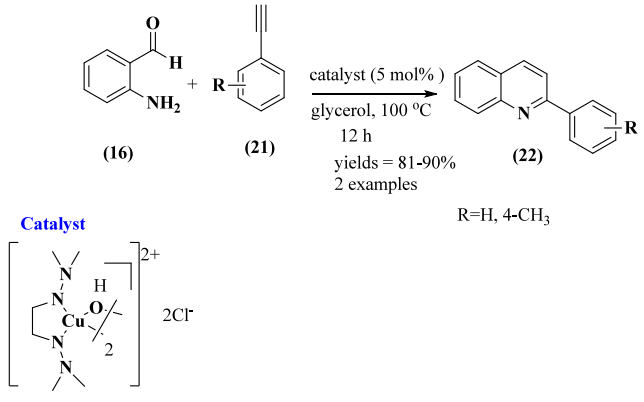



**Scheme 18. Synthesis of Quinoline Using $CuFe_2O_4$ as a Catalyst**



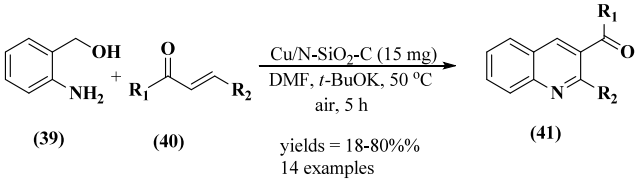

carbonyl sources ($R_1$)= pentane-2,4-dione, cyclic ketones (cyclohexanone, cyclopentanone, and acetophenone), and β-ketoesters (methyl and ethyl acetoacetate)

**Scheme 19. Synthesis of Quinoline Using Cu NPs as a Catalyst**



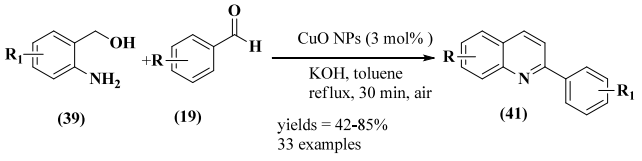

green solvent under reflux conditions for 2 h, a three-component reaction involving different aromatic aldehydes, 6-amino-1,3-dimethyluracil, and dimedone or 1,3-cyclohexadione was used to synthesize pyrimido[4,5-*b*]quinolones using the catalytic activity of an $Fe_3O_4$ NP-cell. Pyrimidinedo-[4,5-*b*]quinoline synthesis is best achieved using 0.04 g of $Fe_3O_4$ NPs-cell (0.9 mol % of $Fe_3O_4$ NP) in water under reflux

**Scheme 20. Synthesis of Quinoline Using Cu/N-$SiO_2$−C as a Catalyst**



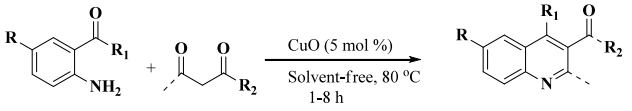

$R_1$=Ph, 4-$OCH_3$-$C_6H_4$, 4-$CH_3$-$C_6H_4$, 4-$NO_2$-$C_6H_4$, *t*-Bu
$R_2$=Ph, 4-$CH_3$-$C_6H_4$, 4-$NMe_2$-$C_6H_4$, 4-Br-$C_6H_4$, 4-F-$C_6H_4$, 4-Cl-$C_6H_4$, 4-$CF_3$-$C_6H_4$, 3-$OCH_3$-$C_6H_4$

**Scheme 21. Synthesis of Quinoline Using CuO as a Catalyst**




R=H, $OCH_3$, $CH_3$, F, Cl, Br, I
$R_1$=2-$CH_3$, 2-$OCH_3$, 4-$CH_3$, pyridine, thiophene,furan, and dioxole

**Scheme 22. CuO-Catalyzed Synthesis of Quinoline**




carbonyl sources ($R_2$)= pentane-2,4-dione, cyclic ketones (cyclohexanone, cyclopentanone, and acetophenone), and β-ketoesters (methyl and ethyl acetoacetate)

conditions, yielding high-quality library products in high yields (88−96%). The catalyst can be retrieved and reused five times



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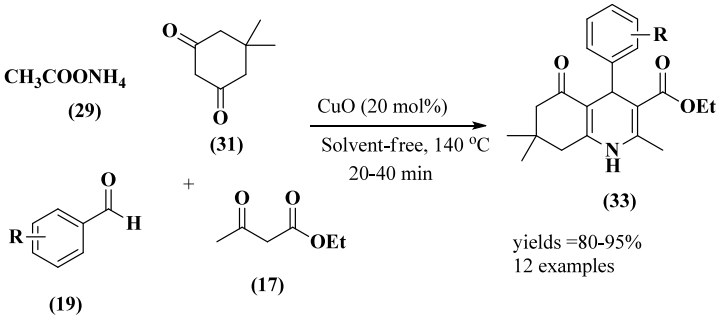
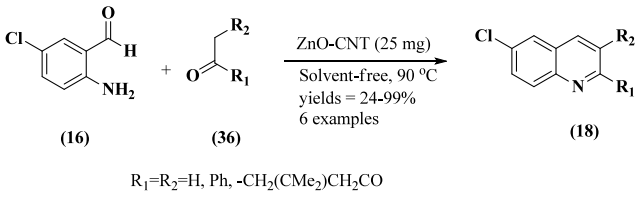
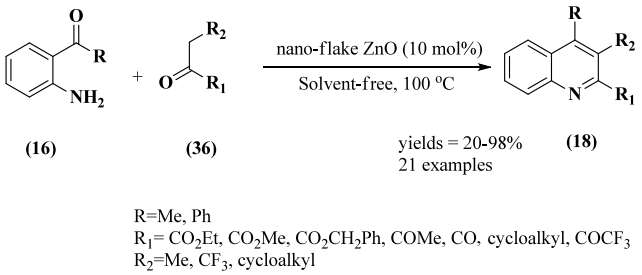
**Scheme 23. Synthesis of Polyhydroquinolines Using CuO NPs as a Catalyst**




**Scheme 24. Synthesis of Quinoline Using ZnO−CNT NPs as a Catalyst**




**Scheme 25. Synthesis of Polysubstituted Quinolines under Solvent-Free Conditions Using Nanoflake ZnO as a Catalyst**




without losing activity. The approach has several benefits, including reusable catalysts, low catalyst quantities, and catalysts that use natural bases and water as solvent (Scheme 8).[82]

Abbasi and Jaymand et al. synthesized $Fe_{3-x}Ti_xO_4$ MNPs functionalized with sulfamic acid by using imidazolidine-2,4-dione and 3-chloropropyltrimethoxysilane. Later, they functionalized the MNPs with chlorosulfonic acid. The spherical core−shell shape of these NPs is characterized, and the average sizes of NPs are around 60−70 nm, respectively. Additionally, the catalyst's efficacy was assessed in a one-pot, four-component condensation process using aromatic aldehydes, ammonium acetate, dimedone, and alkyl acetoacetates to synthesize hexahydroquinoline derivatives. The range of quinoline derivatives was synthesized in high to excellent yield (85−98%) using the ideal catalyst loading (0.02 g) and reaction temperature (rt) of 60 °C for the reaction period (20 min). For up to four cycles, the nanocatalyst can be recovered and utilized again with just a little decrease in activity. The mechanism of the reaction was the same as that which was previously discussed: Knoevenagel condensation between aldehyde and the enolized form of dimedone. Conversely, in the presence of the catalyst, alkyl acetoacetate experiences nucleophilic condensation with ammonium acetate to generate the enamine intermediate, which then proceeds through intramolecular nucleophilic cyclization and dehydration to provide the quinoline derivative (Scheme 9).[83] $Fe_3O_4$@urea/HITh-$SO_3H$ MNPs were synthesized by Jiang and co-workers, and their size was around 50 nm. The key characteristic of MNP morphology is the bonding of acidic groups to the catalytic surface. Moreover, this catalyst is employed under solvent-free conditions to prepare 7-aryl-8*H*-benzo[*h*]indeno-[1,2-*b*]quinoline-8-one. After the reaction conditions were optimized, the optimum outcomes were attained under solvent-free circumstances at a temperature of 80 °C and a catalyst load of 10 mg. This optimization allowed for the efficient synthesis of many quinoline derivatives in high yield and at a reduced reaction time. Moreover, the catalyst may be extracted and reused for six runs without significantly lowering the product yield (Scheme 10).[84]

The development of $Fe_3O_4$ NPs supported by 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium hydrogen sulfate ($Fe_3O_4$-IL-$HSO_4$), a Brønsted acidic ionic liquid, was described by Rezayati and co-workers. Using this catalyst, 2-aminoaryl ketones underwent condensation with 1,3-dicarbonyl compounds under solvent-free conditions to generate polysubstituted quinolines in a single pot by Friedlander reaction. The reaction conditions like solvent, temperature, and catalyst concentration were optimized. The greatest results were achieved with a 20 mg catalyst load at 90 °C in solvent-free circumstances. A fast reaction time (15−60 min) and a good to high yield (85−96%) were achieved by synthesizing several quinoline derivatives. Several carbonyl sources were employed in this process, including pentane-2,4-dione, cyclic ketones (cyclohexanone, cyclopentanone, and acetophenone), and *β*-ketoesters (methyl and ethyl acetoacetate). The catalyst is recoverable when the reaction is finished, and it may be utilized six times in a row without significantly losing its catalytic activity (Scheme 11).[85] Dodecylbenzenesulfonic acid (DDBSA@MNP) supported by magnetite ($Fe_3O_4$) nanoparticles was developed by Katheriya, Patel, and co-workers. This material has an average particle size of around 16 nm and the catalyst's core−shell structure. Using ethanol as a solvent and 0.15 g of catalyst at 80 °C, the catalyst is optimized for the one-pot condensation of 2-aminobenzophenones and ketones to provide good isolated yields of substituted quinolines. Shorter reaction durations, great isolated yields, simple workup, and purification are some of the benefits of the procedures. The catalyst may be easily recovered and reused for up to five reaction cycles. The method's likely mechanism, as suggested by the author, entails a catalyst that activates the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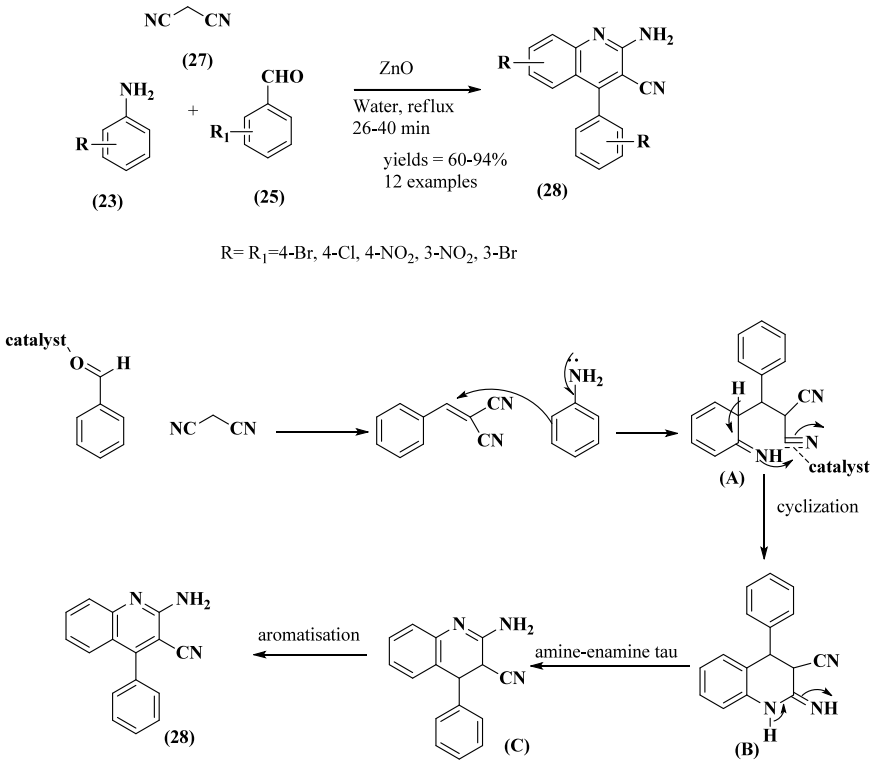
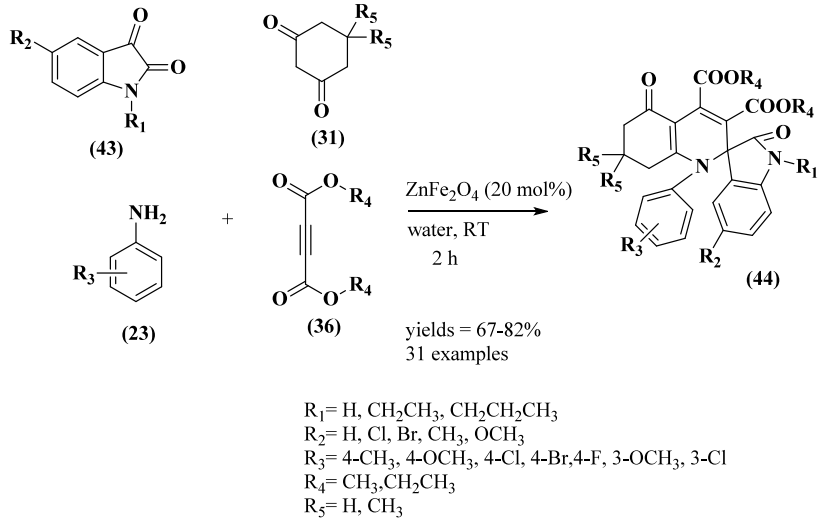
**Scheme 26. Synthesis of Quinoline Using ZnO as a Catalyst and Its Plausible Mechanism**




**Scheme 27. Synthesis of Spiro[indoline-3,2′-quinoline] Derivatives Using $ZnFe_2O_4$ as a Catalyst**




carbonyl carbon of 2-aminoaryl ketone, allowing active methylene of $\beta$-ketoester or ketone to nucleophilically attack and generate a product by a cross-aldol reaction. After losing water molecules, the resulting $\beta$-hydroxy ketone becomes an $\alpha,\beta$-unsaturated ketone. Cyclization of this ketone yields a specific quinoline derivative (Scheme 12).[86]

Yarie, Taherpour, and co-workers synthesized ionically tagged MNPs with urea linkers ($Fe_3O_4$@$SiO_2$@$(CH_2)_3$-urea-thiazole sulfonic acid chloride) and characterized them using SEM, TEM, IR, EDX, and other techniques. This catalyst has a spherical form and is composed of nanoscale particles. Moreover, catalysts are used in the synthesis of derivatives of 2-aryl-quinoline-4-carboxylic acid such as pyruvic acid, 1-naphthylamine, and various benzaldehydes. The best conditions for the reactions were 10 mg of catalyst for 30 min at 80 °C without the use of a solvent. This resulted in a variety of 2-aryl-quinoline-4-carboxylic acid derivatives being produced in short reaction times in good yields. The approach works with various aromatic aldehydes that include electron-releasing or -withdrawing substituents and halogens on their aromatic ring. After the reaction, the catalyst was collected, washed with ethanol, dried, and reused in the next cycle. After six cycles, the catalyst efficiency did not decline much (Scheme 13).[87] Tamoradi and co-workers developed the 3,5-pyrazoledicarboxylic acid monohydrate functionalized with Pr (praseodymium complex), grafted on magnetic $CoFe_2O_4$. The synthesis of polyhydroquinoline derivatives using this catalyst involves combining different benzaldehydes, dimedones, ethyl acetoa-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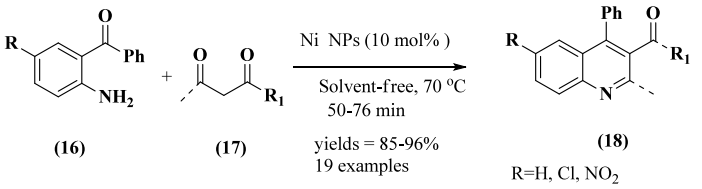
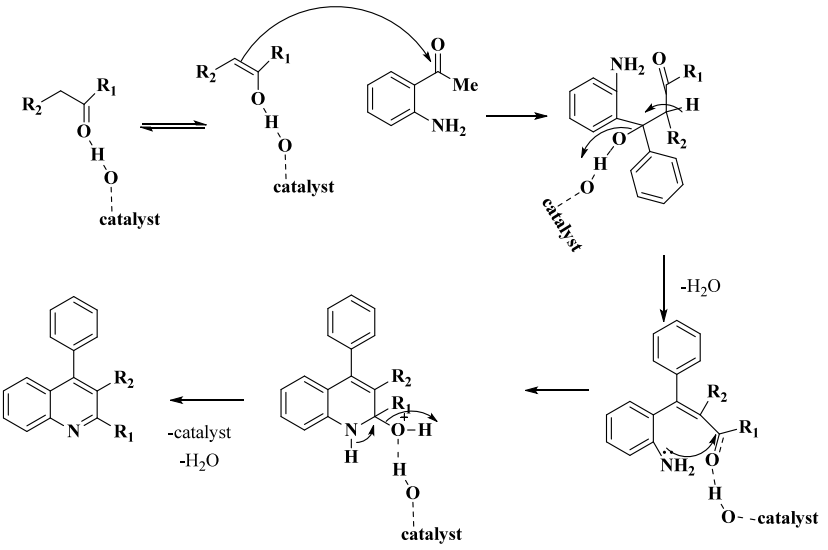
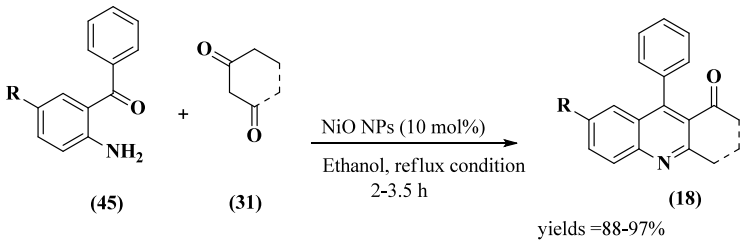
**Scheme 28. Synthesis of Quinoline Using Ni NPs as a Catalyst and Their Plausible Mechanism**




carbonyl sources ($R_1$)= pentane-2,4-dione, cyclic ketones (cyclohexanone, cyclopentanone, and acetophenone), and β-ketoesters (methyl and ethyl acetoacetate




**Scheme 29. Synthesis of Quinoline Using NiO NPs**




carbonyl sources =aliphatic and aromatic β-diketones, cyclic and acyclic ketones, and β-ketoesters

cetate, and ammonium acetate in a multicomponent synthesis. A variety of polyhydroquinolines have been synthesized with fast reaction times and high yields (15 examples, 87−97%) by using the optimum conditions, such as 0.04 g of catalyst in ethanol under reflux conditions. Easy workups, recycling exploitation, high catalytic activity, ease of preparation, simple catalyst separation, and good to exceptional isolated yields are some of the protocol's benefits. The author reported a tenable mechanism based on previously published works. First, an *α,β*-unsaturated molecule is produced in the presence of the catalyst during the Knoevenagel condensation between dimedone and ethyl acetoacetate. The polyhydroquinolines were generated by a subsequent Michael addition reaction between the active methylenes on the *α,β*-unsaturated carbonyl compounds (the nucleophilic attack), which were activated by Pr (Scheme 14).[88] Li and co-workers synthesized the same derivatives (29 examples, yield 78−95%) using Ru (III) incorporated with a magnetic nanosized carboxymethyl-cellulose (CMC)/$Fe_3O_4$ hybrid (RuIII@CMC/$Fe_3O_4$). The Ru (III) species are evenly distributed over the $Fe_3O_4$ MNPs, and the catalyst's nanoparticles gathered into clusters and took on a quasi-spherical shape. This results in an increase in the catalyst's surface area, improving mass transfer and expanding its region of interaction with substrates. The fresh and recovered catalysts had average particle sizes of 28 and 16 nm in diameter, respectively. The catalyst retains a large amount of its catalytic activity, even after being retrieved using an external magnet and reused several times. This protocol's benefits include its quick reaction time, strong reactivity, moderate condition, and reusable catalyst.[89] $Fe_3O_4$@$SiO_2$−$NH_2$ nanocomposites (CMs) were developed by Ghasemzadeh and co-workers; on average, these materials are between 50 and 60 nm in size and resemble stars. Tetrahydrobenzo[*g*]-quinoline-5,10-dione derivatives were synthesized with these MNP nanocatalysts under optimum circumstances, including the catalyst, solvent, and temperature. Additionally, the author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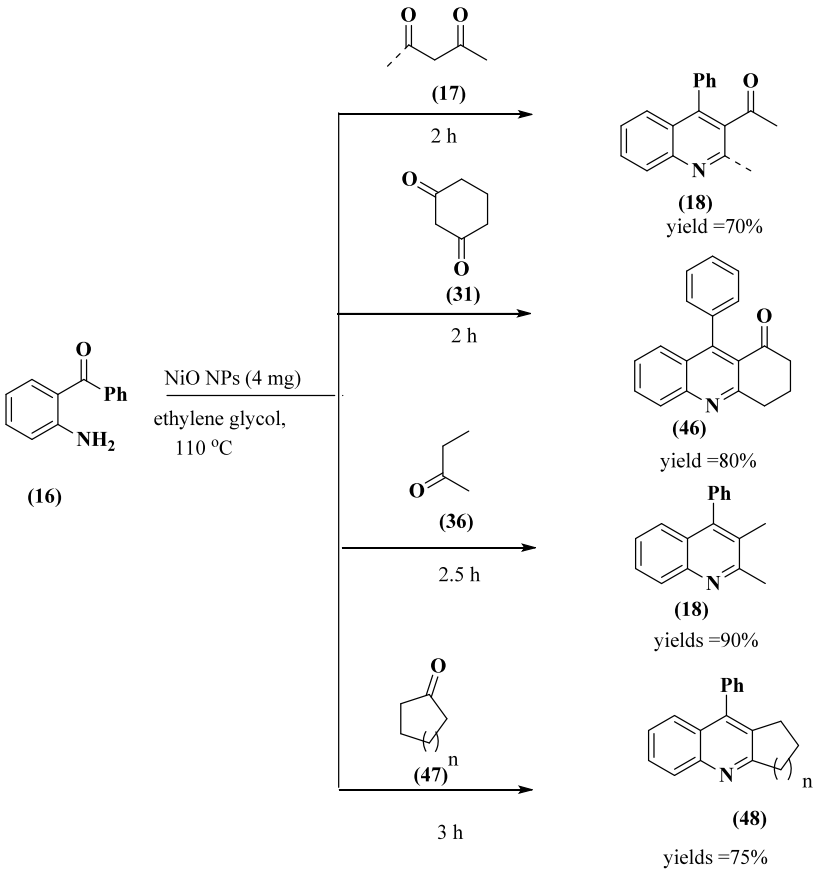
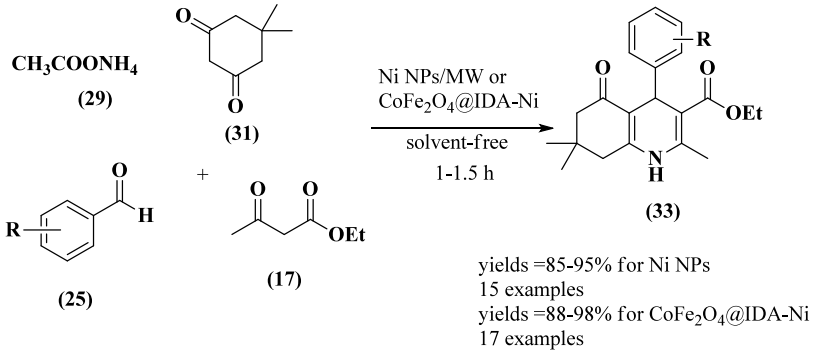
**Scheme 30. NiO NP-Catalyzed Synthesis of Quinolines**




**Scheme 31. Ni NP-Catalyzed Synthesis of Polyhydroquinoline Derivatives under Solvent-Free Conditions**




R=H, 4-$CH_3$, 4-$OCH_3$, 4-Br, 4-Cl, 4-F, 4-$NO_2$, 2-Cl, 3-Cl, 3-$NO_2$, 2-furyl, 2-thienyl

successfully produced the desired compounds in ethanol and water for 150 min at a catalyst concentration of 0.05 g. The author observed that compounds with electron-donating groups like OH and $OCH_3$ interacted extremely easily with aromatic aldehydes that had EWGs like $NO_2$, Cl, and Br at the *para*-position. This catalyst was also retrieved and reused several times without losing its activity, similar to the techniques mentioned above (Scheme 15).[90]

**2.2. Copper-Based Nanocatalysts for the Synthesis of Quinolines.** Because of their unique optical, mechanical, electrical, and catalytic capabilities, copper nanoparticles are of tremendous interest. As a novel class of heterogeneous catalysts in a variety of chemical reactions, copper nanoparticles have been investigated.[91,92] A wide range of reactions have been demonstrated by Cu-based nanocatalysts with different morphologies, such as those using Cu, CuO, $Cu_2O$, $Cu_3N$, and supported Cu catalysts. Cu-based nanocatalysts are used in a wide range of nanotechnology applications, such as photocatalysis, electrocatalysis, and catalytic organic transformations.[93] This section discusses the numerous copper-based nanocatalysts used in the quinoline synthesis. Rao and colleagues synthesized CuO NPs, and these are spherical in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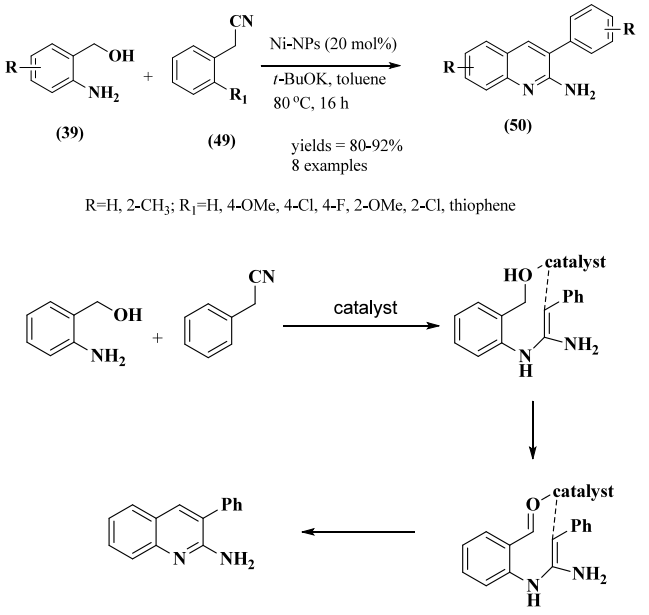
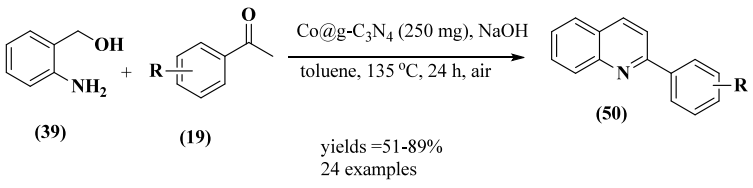
**Scheme 32. Synthesis of 2-Aminoquinoline from 2-Aminobenzyl Alcohol and Benzyl Nitriles Using Ni NPs and Their Plausible Mechanism**




shape and less than 50 nm in size. These CuO NPs were used to synthesize quinoline-2,3-dicarboxylates from different 2-aminoacetophenones and dimethylacetylenedicarboxylates. The optimized conditions, such as 3.0 mol % nano-CuO, 2.0 mL of acetonitrile, and 40 °C, allowed for the good yield (80−94%) and prolonged synthesis time (10 h) of the required quinolines. When compared with 2-aminoacetophenone molecules, the author found that 2-aminobenzophenone produced lower yields. Also, electron-donating methoxy-substituted 2-aminoacetophenone and unsubstituted 2-amino-acetophenone gave a fair yield; this yield will also be the same for 2-aminobenzophenone. Additionally, compared to 2-aminocarbonyl compounds containing diethylacetylenedicar-boxylate, those containing dimethylacetylenedicarboxylate had better yields. The amine group first attacks the polarized unsaturated diester; then the carbonyl group attacks it; and finally a water molecule is eliminated. This coordinated action of the catalyst nano-CuO results in complex I, which yields the desired product. With a high degree of activity, the catalyst can be retrieved and utilized up to four more times (Scheme 16).[94] Ghorbani-Vaghei et al. developed a CuI nanoparticle-immobilized hybrid material of an amino-functionalized zinc metal−organic (IRMOF-3) and poly(sulfonamidetriazine) (PSTA) (IRMOF-3/PSTA/Cu) by reacting IRMOF-3 with porous PSTA and then immobilizing CuI NPs. This material features a spherical CuI particle distribution on IRMOF-3/PSTA and a cubic and uniform nanostructure that is 75 nm in size. The nanocatalyst has great significance due to its high porosity, huge surface area, and multifunctional MOF with stability and durability. Aniline derivatives, benzaldehyde, and phenylacetylene were incorporated in a one-pot multi-component procedure to generate quinoline derivatives using nanomaterial IRMOF-3/PSTA/Cu. The reaction was opti-mized concerning its catalytic potential and the influence of the solvent concentration, temperature, and catalyst. At the optimized process with 10 mg of nanocatalyst and $CH_3CN$ as the solvent at 80 °C, the different quinoline derivatives were synthesized in excellent yield (85−96%). After observing the electrostatic effect, the authors discovered that the electron-withdrawing groups in aniline increased the reactivity of Cu-catalyzed domino reactions mediated by IRMOF-3/PSTA, compared to those containing electron-donating groups. The catalyst increases the activity of phenylacetylene binding to iminium ions produced in situ by the interaction between amines and benzaldehydes, according to the author's conceivable mechanism. After this, the dihydroquinoline is produced by a coordinated cyclization reaction between phenylacetylene and a Schiff base by the Diels−Alder process. Ultimately, the oxidation forms the desired products (Scheme 17).[95]

The synthesis of $CuFe_2O_4$ NPs was described by Baghbanian and co-workers, and the materials have a tiny, agglomerated nanoparticle morphology with a disordered surface morphology, with an average particle size of 5−15 nm. Additionally, in ideal circumstances, such as 5 mol % of $CuFe_2O_4$ NPs in water at 80 °C, this catalyst was employed to synthesize quinolines, producing good yields and quick reaction times. Additionally, 2-aminoaryl ketones interacted with relevant cyclic ketones, such as cyclopentanone and cyclohexanone, to produce large quantities of quinolines. The catalyst was isolated from the reaction mixture using an external magnet and was subsequently reused five times without exhibiting any appreciable catalytic activity. The possible mechanism is the same as previously documented or discussed (like Scheme 12): the catalyst activates the carbonyl groups, followed by aldol condensation, which generates an intermediate with lost water, then protonation, and finally ring closure between the amine group and the protonated carbonyl group. Finally, water removal of intermediates yields quinoline compounds (Scheme 18).[96] With the help of polyvinylpyrro-lidone as a stabilizer, Favier et al. synthesized tiny zerovalent copper NPs (CuNPs) from Cu(I) and Cu(II) precursors in glycerol. Crystalline zerovalent nanoparticles with the antici-pated face-centered cubic shape for bulk copper were formed by the catalyst. This catalyst is employed in the synthesis of heterocycles such as benzofurans, indolizines, and quinolines via C−N couplings, as well as the production of C−C and C−heteroatom bonds. More than five cycles of the catalytic phase

**Scheme 33. Synthesis of Quinoline from 2-Aminobenzyl Alcohol and Ketones Using Co@g-$C_3N_4$**





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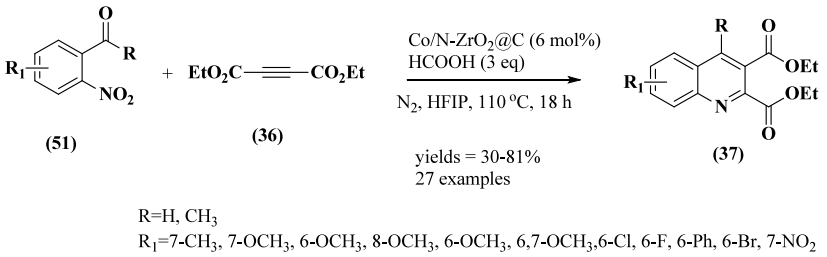
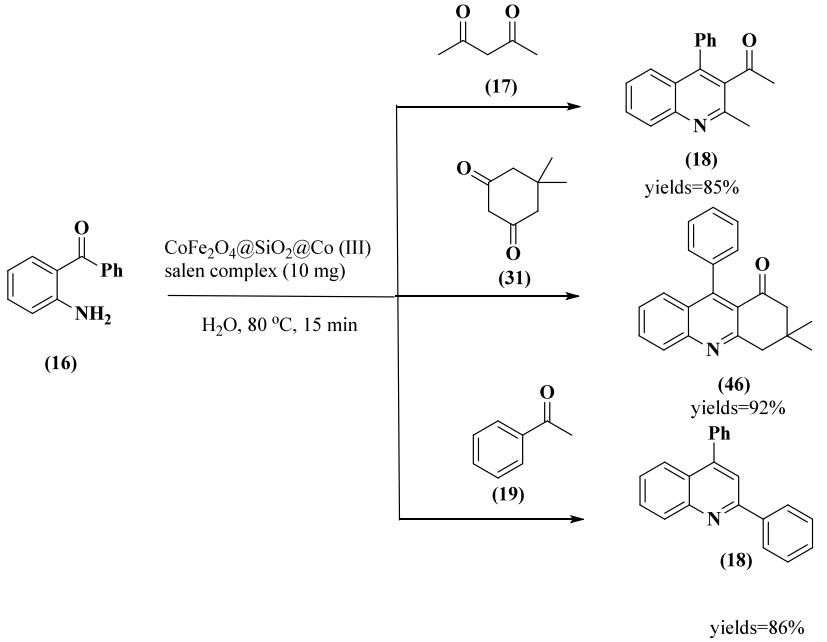
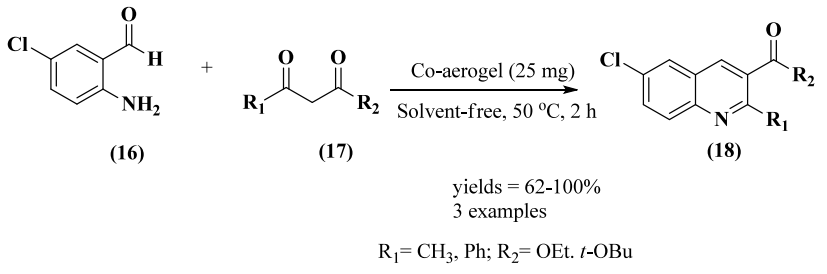
**Scheme 34. Synthesis of Quinoline by Reductive Annulation with Alkynoates and Alkynones**




**Scheme 35. Synthesis of Quinoline Derivatives Catalyzed by the $CoFe_2O_4$@$SiO_2$@Co(III) Salen Complex and Their Plausible Mechanism**




**Scheme 36. Synthesis of Quinoline by Friedländer Condensation from 2-Amino-5-chlorobenzaldehyde and Ethyl Acetoacetate Using Co-aerogel as a Catalyst**




maintained activity without revealing a detectable level of copper in the organic compounds that were isolated (Scheme 19).[97]

A copper nanocatalyst supported on nitrogen-silica-doped carbon (Cu/N-$SiO_2$−C) was employed by Xiong, Zhou, and co-workers to synthesize 3-acylquinolines from 2-aminoaryl alcohols and $\alpha,\beta$-unsaturated ketones in a single pot. Cu/N-$SiO_2$−C has an uneven, largely homogeneous shape resembling a sphere. The addition of silica to Cu/N−C results in improved catalytic activity (Cu/N-$SiO_2$−C), and only the Cu/N−C component of the catalyst yields the least amount of product (66%). The copper particles in the catalyst are grouped, and part of the copper particles, silicon, and nitrogen are dispersed evenly throughout the catalyst. The intended results were obtained in good yield when the catalyst (15 mg), solvent (DMF), and additive (*t*-BuOK) were optimized and used for one hour at 50 °C. According to the author, the protocol's advantages include its straightforward operation, moderate operating temperatures, the copper catalyst's durability and reusability, strong functional tolerance, and its use of molecular $O_2$ as the only oxidant (Scheme 20).[98] Colloidal CuO NPs were developed by Kundu and co-workers and further utilized to synthesize quinolines, pyridines, and pyrroles *via* an alcohol dehydrogenative coupling. The CuO NPs had an average particle size of 3.2 nm and an uneven shape and were mesoporous. Using different 2-aminobenzyl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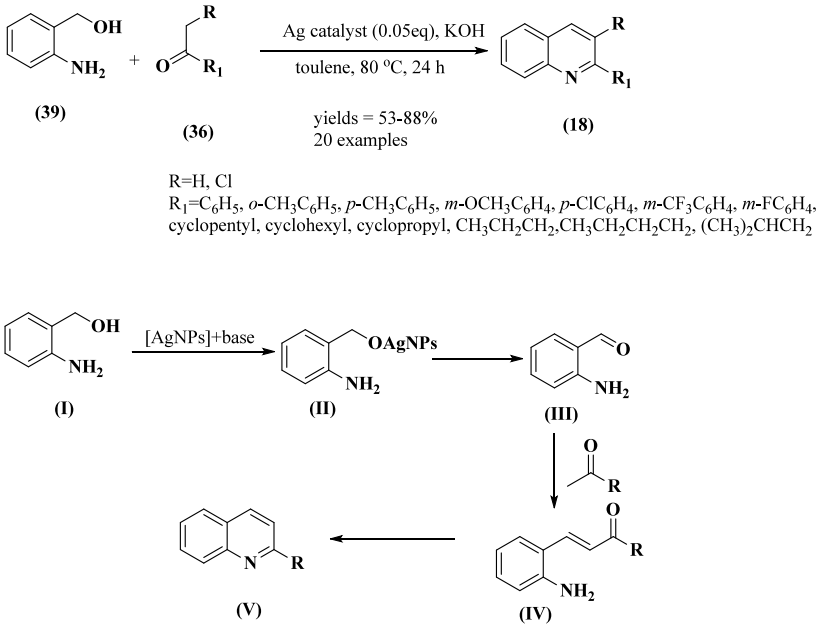
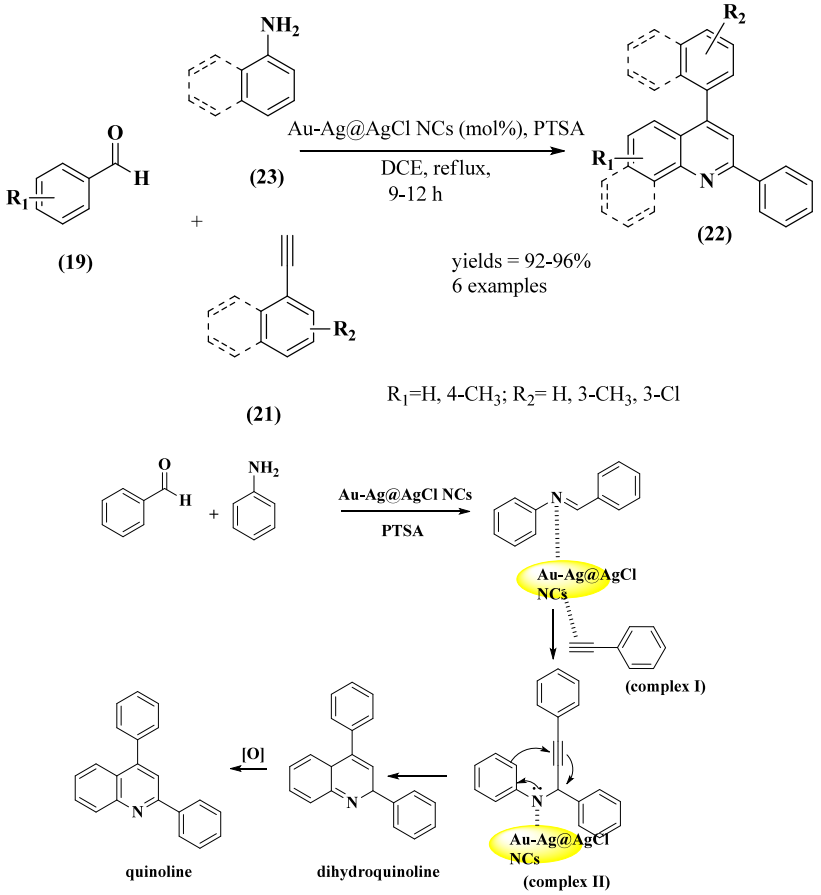
**Scheme 37. Synthesis of Quinoline Using Silver-Based Nanocatalyst**




**Scheme 38. Synthesis of Quinoline Using Au−Ag@AgCl NCs as a Catalyst and Its Plausible Mechanism**




alcohol and carbonyl sources, the quinoline derivative was produced under ideal reaction conditions, such as 3 mol % CuO NPs and 0.5 equiv of KOH in toluene at 120 °C for 30 min. The author noted that high to exceptional yields of the necessary quinolines were obtained from 2-aminobenzyl alcohol in combination with electron-donating substituted ketones (4-OMe, 4-Me) and substituted ketones containing halogens (4-F, 4-Cl, 4-Br, 4-I). As demonstrated, the CuO NPs may be recycled and utilized again for the sixth run without losing their catalytic activity. The mechanism worked in the same way as previously mentioned, involving the following steps: aldol condensation, intramolecular cyclization, and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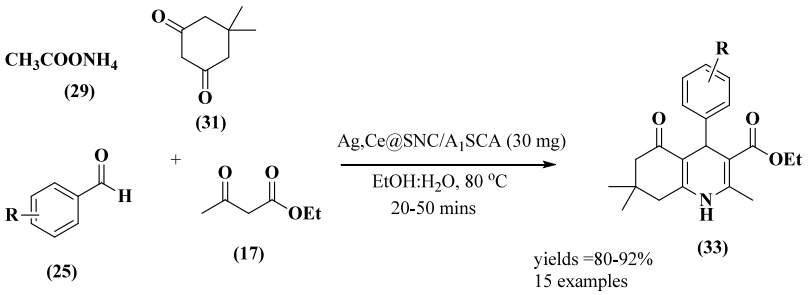
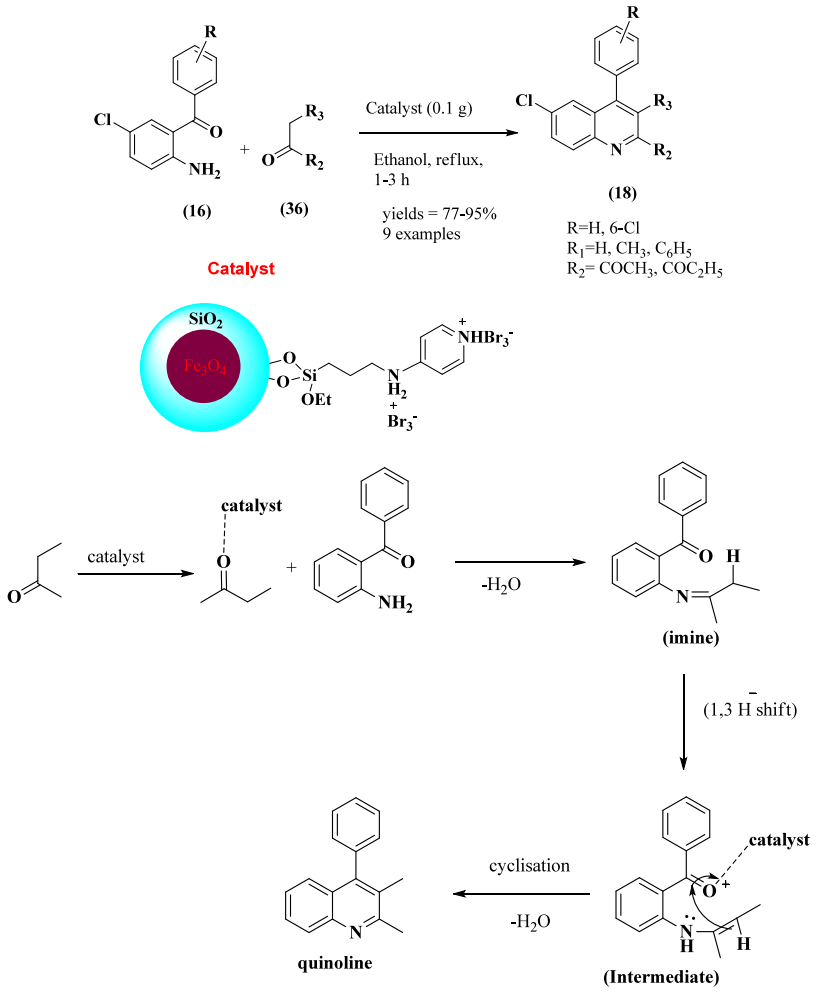
**Scheme 39. Synthesis of Polyhydroquinolines Using Ag,Ce@SNC/A1SCA as a Catalyst**




R=H, 4-$CH_3$, 4-$OCH_3$, 4-Br, 4-Cl, 4-F, 4-$NO_2$, 4-OH, 2-aldehyde with indole, quinoline, thiophene, furan

**Scheme 40. Synthesis of Quinoline Derivatives Using MNPs@$SiO_2$-Pr-AP-Tribromide as a Catalyst**




dehydration (Scheme 21).[99] In the same array, the CuO NP was employed by Akbari and co-workers for the Friedlander quinoline synthesis in a single pot. The CuO catalyst's dimensions are determined to be 25−27 nm in size and 214 $m^2/g$ in surface area. The methodology offers several benefits, including solvent-free conditions; a safe, nonvolatile, and noncorrosive catalyst; high yields; simple and gentle reaction conditions; and catalyst recovery (Scheme 22).[100] In another study, Safaei-Ghomi et al. employed CuO NPs to synthesize polyhydroquinolines using MCRs of aldehydes, dimedone, ethyl acetoacetate, and ammonium acetate. These nanoparticles are spherical in form with an average diameter of 40−50 nm. Under ideal circumstances, such as catalyst concentrations of 20 mol % at 140 °C in a solvent-free environment, a variety of polyhydroquinolines were produced in 20−40 min with an outstanding yield (80−95%). The aldehydes containing EWGs at the *para*-position, such as $NO_2$, Br, and Cl, interacted easily and produced the intended product with a good yield in a shorter amount of time (Scheme 23).[101] An identical set of polyhydroquinoline derivatives were synthesized with chitosan-decorated copper nanoparticle (CS/Cu NP) catalysts. SEM confirms the absence of copper nanoparticles, which might be attributable to their excellent dispersion across chitosan. The CuO NPs assist the electro-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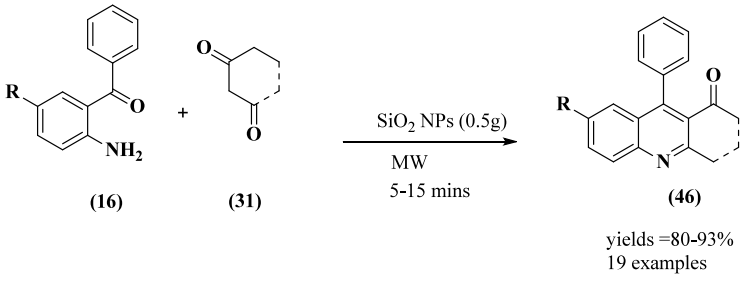
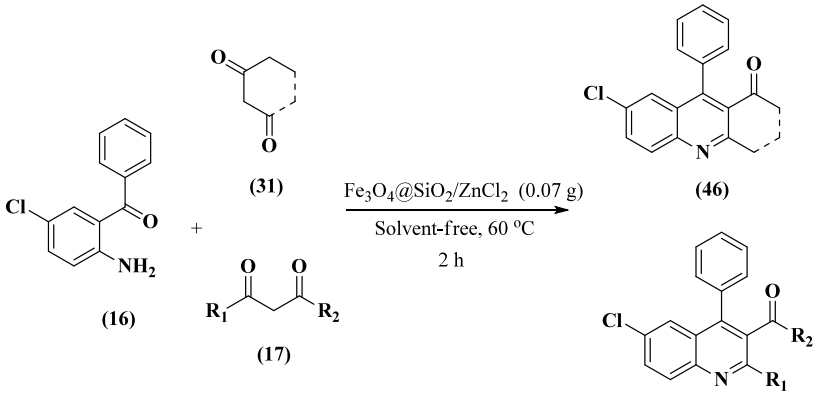
**Scheme 41. Synthesis of Quinolines in the Presence of $SiO_2$ NPs under Microwave Irradiation**



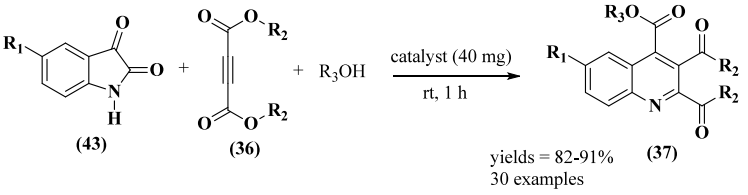

R= H, Cl
carbonyl sources =aliphatic and aromatic β-diketones, cyclic and acyclic ketones, and β-ketoesters

**Scheme 42. Synthesis of Quinolines Using $Fe_3O_4$@$SiO_2$/$ZnCl_2$ NPs**

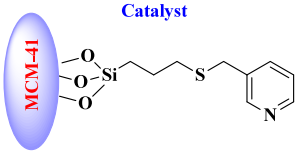



$R_1$=$CH_3$, $C_2H_5$, Pr, iPr, $CH_2Cl$, $CH_2COCH_3$; $R_2$= $CH_3$, $OC_2H_5$, $OCH_3$, $CH_2COCH_3$
cyclic ketones=cyclohexanone, dimedone, tetronic acid

**Scheme 43. Synthesis of 2,3,4-Trisubstituted Quinoline Derivatives Using Mesoporous MCM-41 Silica-Supported Pyridine NPs**




$R_1$= H, $OCH_3$, Cl, Br, I, $NO_2$; $R_2$= $CH_3$, $CH_2CH_3$; $R_3$= methyl, ethyl, *n*-propyl, *n*-butyl, benzyl




philicity of the aldehyde's carbonyl group by the reduction of $Cu^{2+}$ ions into $Cu^{+}$, resulting in the condensation of active methylene carbon of ethylacetoacetate followed by dehydration. Michael addition is then carried out, facilitated by the catalyst's basic sites, before the last step in the ionic process (Scheme 23).[102]

**2.3. Zinc-Based Nanocatalysts for the Synthesis of Quinolines.** The zinc-based NPs have garnered a lot of attention due to their distinct chemical and physical characteristics, which include high chemical stability, high catalysis, acid−base character, biocompatibility, UV screening performance, porosity based on their various morphologies, high photostability, large excitation binding energy, a broad radiation absorption range, photochemical activity, and low toxicity.[103−107] These nanostructures are helpful in a variety of material applications, including flexible hybrid nanoceramics, gas sensors, solar cells, advanced optoelectronics development, and biomedical applications.[108] With a focus on the synthesis of pertinent biologically active heterocyclic systems, several zinc-based NP catalysts have been developed and described as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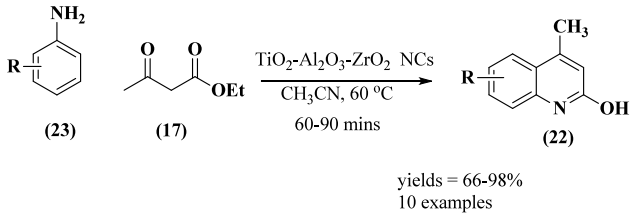
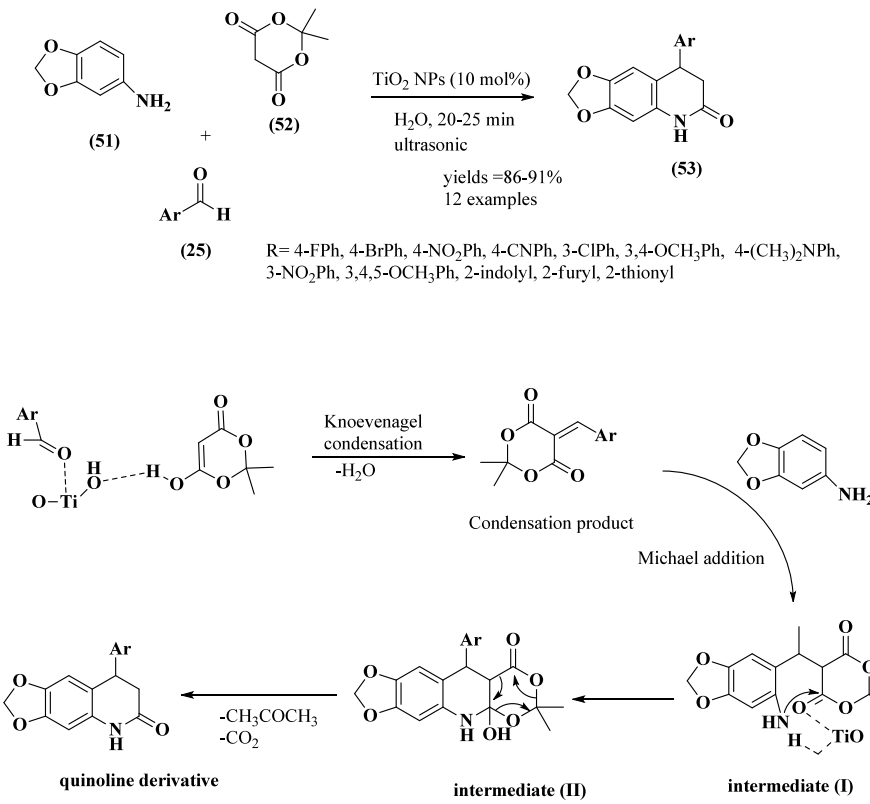
**Scheme 44. Synthesis of Polysubstituted Quinoline in the Presence of $TiO_2$−$Al_2O_3$−$ZrO_2$**




intriguing catalysts for an array of organic transformations throughout the past decade.[109] The use of the Zn-based catalyst for the synthesis of quinoline and its derivatives is covered in this section. Godino-Ojer, Pérez-Mayaral, and co-workers synthesized ZnO NPs via incipient wetness impregnation with various carbon supports, such as a carbon aerogel (CA), activated carbon (AC), and multiwalled carbon nanotubes (MWCNTs). ZnO with CA demonstrated the 3D-overlapping of roughly spherical carbon nanoparticles, but the morphology of the CNT support exhibits a strong cross-linking between them, generating huge bundles of carbon nanotubes. Additionally, these ZnO/carbon catalysts have been used in solvent-free Friedlander condensation to synthesize quinolines from 2-amino-5-chlorobenzaldehyde and other carbonylic chemicals. Because of its increased Zn concentration, the CNT exhibits significantly improved catalytic activity among the three carbon catalysts. Moderate to good yields (24−99%) of different quinolines were produced, employing carbonyl compounds under solvent-free conditions and optimized conditions, such as 25 mg of catalyst (ZnO/CNT) (Scheme 24).[110] Hosseini-Sarvari reported the synthesis of substituted quinolines under solvent-free conditions by using the nanoflake ZnO NP. Two varieties of ZnO NP were synthesized by the author: NF-ZnO (highest activity and regioselectivity) and CM-ZnO. Lewis acid sites ($Zn^{2+}$) and Lewis base sites ($O^{2-}$) are present in the NF-ZnO. In the Friedlander synthesis, the proton of the $\alpha$-methylene group can therefore occupy a Lewis base site ($O^{2-}$) of NF-ZnO, and the Lewis acid moiety ($Zn^{2+}$) can activate the carbonyl group for imine production. The desired quinoline derivatives were obtained in moderate yield (20−95%) under optimized conditions, such as catalyst load (10 mol %) and solvent-free conditions at 100 °C, with various 1,3-dicarbonyl compounds, such as alkyl acetoacetates, acetyl acetone, cyclic $\beta$-diketones, such as 5,5-dimethylcyclohexandione (dimedone), and cyclic ketones reacted with 2-aminoaryl ketones (Scheme 25).[111] ZnO NPs were utilized by Anbhule and co-workers to synthesize quinoline derivatives using the MCR reaction. Malononitrile, various substituted anilines, and substituted aromatic aldehydes (EWGs/ERGs) may all be used in this reaction to provide excellent yields of the products in water at shorter reaction times. The author postulated a tenable mechanism in which intermediate (A) is produced in the first stage of the reaction by Knoevenagel condensation between aromatic aldehyde and malononitrile. The Michael addition product (B) between aromatic amines and intermediates (A) is created in the next step. To produce the final product, intermediate (B) is subjected to further cyclization and aromatization. The protocols' good yields, quick reaction times, ease of setup, and ease of operation are its strong points (Scheme 26).[112] The $ZnFe_2O_4$ nanopowder, which functions as a dual Lewis acid−base combination

**Scheme 45. Synthesis of Quinoline Derivatives Using $TiO_2$ NPs under Ultrasonic Irradiation and Their Plausible Mechanism**



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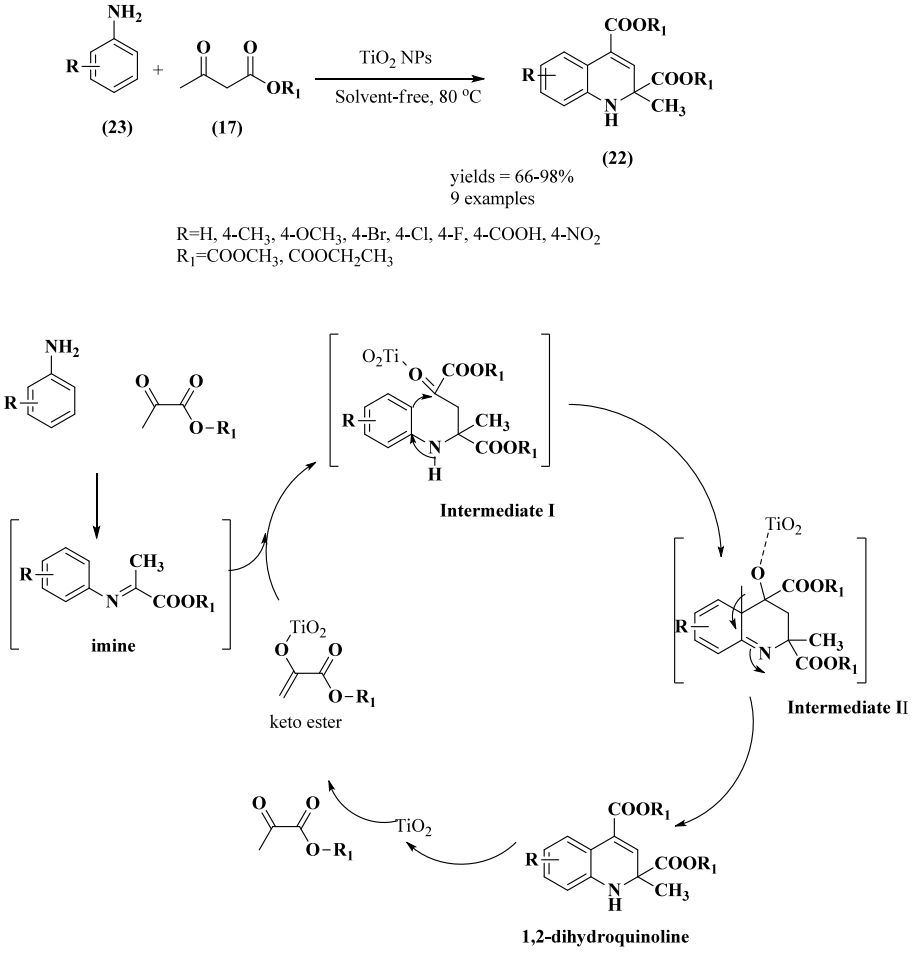
Scheme 46. Synthesis of 1,2-Dihydroquinoline Derivatives Using $TiO_2$ NPs and Their Plausible Mechanism




catalyst, was developed by Pramanik and co-workers. This NP is a compact arrangement with an approximate diameter of 95−150 nm and a spherical form. Additionally, tetrahydrospiro[indoline-3,2-quinoline] was synthesized utilizing this catalyst in a water medium at room temperature via MCR from isatin, dimedone, *p*-toluidine, and dimethyl acetylenedicarboxylate. Excellent yields of the prodcuts were produced under optimal circumstances, such as a catalyst load of 20 mol % and water as a solvent for 2 h at rt. Up to five times, the catalyst is recovered and utilized again with nearly the same catalytic activity. The current approach, according to the author, has many advantages over the previously published method. These include a shorter reaction period (from 2 to 24 h), the use of water as a green solvent instead of AcOH, and simpler product separation and purification (Scheme 27).[113]

**2.4. Quinoline Synthesis Using Nickel-Based Nanocatalysts.** The enormous surface area and tiny size of nickel-based NPs make them extremely useful for catalysis in organic synthesis. As catalysts, Ni-based NPs are widely used and have excellent possibilities for a variety of organic reactions and chemical production processes,[114] such as the synthesis of heterocycles,[115] synthesizing thioesters,[116] styrene oxide,[117] reducing aldehydes,[118] ketones,[119] hydrogenating citral,[120] and chemoselective oxidative coupling of thiols.[121] Consequently, the exceptional catalytic activity, facile synthesis, straightforward operation, environmental friendliness, and reversibility of the Ni-based NPs prompted scientists to investigate this subject. This section discusses the Ni-based nanocatalyst used to synthesize quinoline. Subashini and co-workers synthesized a nickel nanocatalyst from *Aegle Marmelos Correa* aqueous leaf extract, and it is crystalline, with an average particle size of 80−100 nm and a triangular shape. These NPs were used in solvent-free synthesis to produce polysubstituted quinoline derivatives by Friedlander annulation. The nickel nanocatalyst's Lewis acid sites efficiently engage with the ketone's carbonyl oxygen by forming surface-bound hydrogen-bonded species. These species then proceed through intramolecular cyclization to produce the target molecules in a fair yield. The catalyst can be extracted and utilized again in the same form for up to five cycles of additional tests. Selectivity, environmental compatibility, and reusability are some of the protocol's benefits (Scheme 28).[122] The nickel oxide NPs, which have a size range of less than 100 nm and are rod-shaped, were developed by Vijayakumar and co-workers. The polysubstituted quinolines were synthesized from these NPs from aminoaryl ketones and *β*-ketoesters/ketones (including aliphatic and aromatic *β*-diketones, cyclic and acyclic ketones, and *β*-ketoesters), with the aid of NiO NPs acting as a catalyst. When the reaction was run under ideal circumstances, such as with a 10% mol catalyst load and ethanol as a solvent, it proceeded quickly and produced the intended products in large quantities. Lewis acid sites ($Ni^{2+}$) and Lewis base sites ($O^{2-}$) are present in the NiO NPs. Therefore, the *α*-methylene group of NiO NPs is deprotonated by a Lewis base site ($O^{2-}$), and the carbonyl group can be activated for imine production by a Lewis acid site ($Ni^{2+}$). The protocol's benefits include low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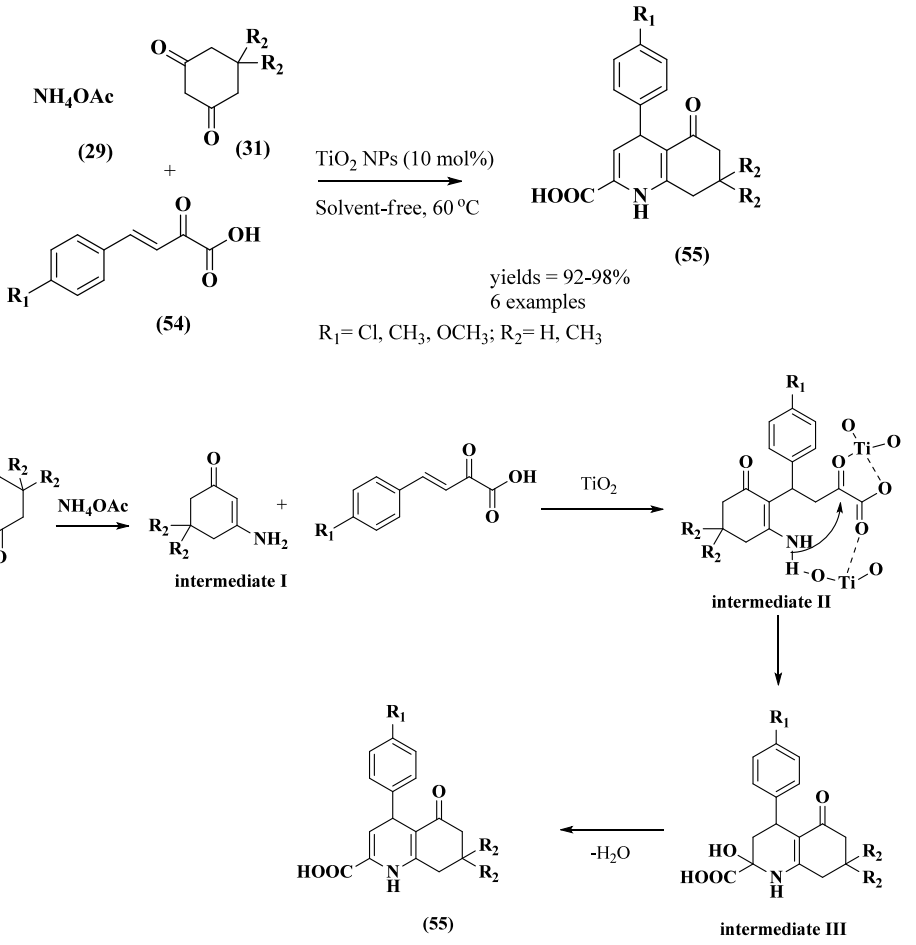
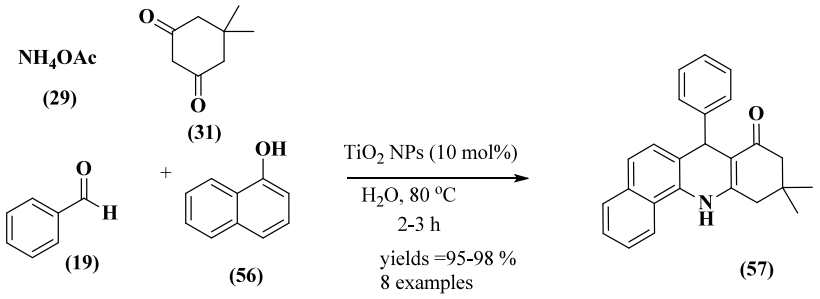
**Scheme 47. Synthesis of Hexahydro-2-quinolinecarboxylic Acids in Solvent-Free Conditions Using $TiO_2$ NPs and Their Plausible Mechanism**




**Scheme 48. Synthesis of Quinolone Derivatives in Aqueous Conditions Using $TiO_2$ NPs**




R= 4-$CH_3$, 4-Br, 4-Cl, 4-OH, 2-Cl, 2,4-Cl, 3,4-Cl, 3-$NO_2$

cost, excellent yields with quick reaction times, a clear product profile, simplicity, and ease of catalyst preparation. The likely process is the same as previously mentioned, including Knoevenagel condensation, dehydration, and Michael addition followed by cyclization (Scheme 29).[123]

Nasseri and co-workers have synthesized NiO NPs by employing nickel nitrate as a precursor and *Tamarix serotina* flower extract. The typical size of NiO NPs is between 10 and 14 nm, and their shape is aggregation. Further using these NPs for a one-pot reaction between 2-aminobenzophenone and different carbonyl compounds (ketones, diketones, and cyclic ketones) produced a variety of quinoline derivatives in good to high yields (60−90%) under the ideal conditions, which included a catalyst load of 4 mg, a temperature of 110 °C, and ethylene glycol as a solvent. The author noted that cyclic diketones respond more quickly than their open-chain counterparts. Ketone derivatives are also involved in these reactions; however, they take longer to complete. This could be because dicarbonyl molecules have more activity than ketone derivatives. The catalyst's catalytic activity is only marginally decreased after four cycles, allowing for its recovery and reuse (Scheme 30).[124] Shingare et al. reported that polyhydroquinoline compounds were synthesized under solvent-free conditions by Hantzsch condensation with nickel NPs using MCR from aromatic aldehydes, dimedone, and ethyl acetoacetate. The Ni NPs have a particle size of around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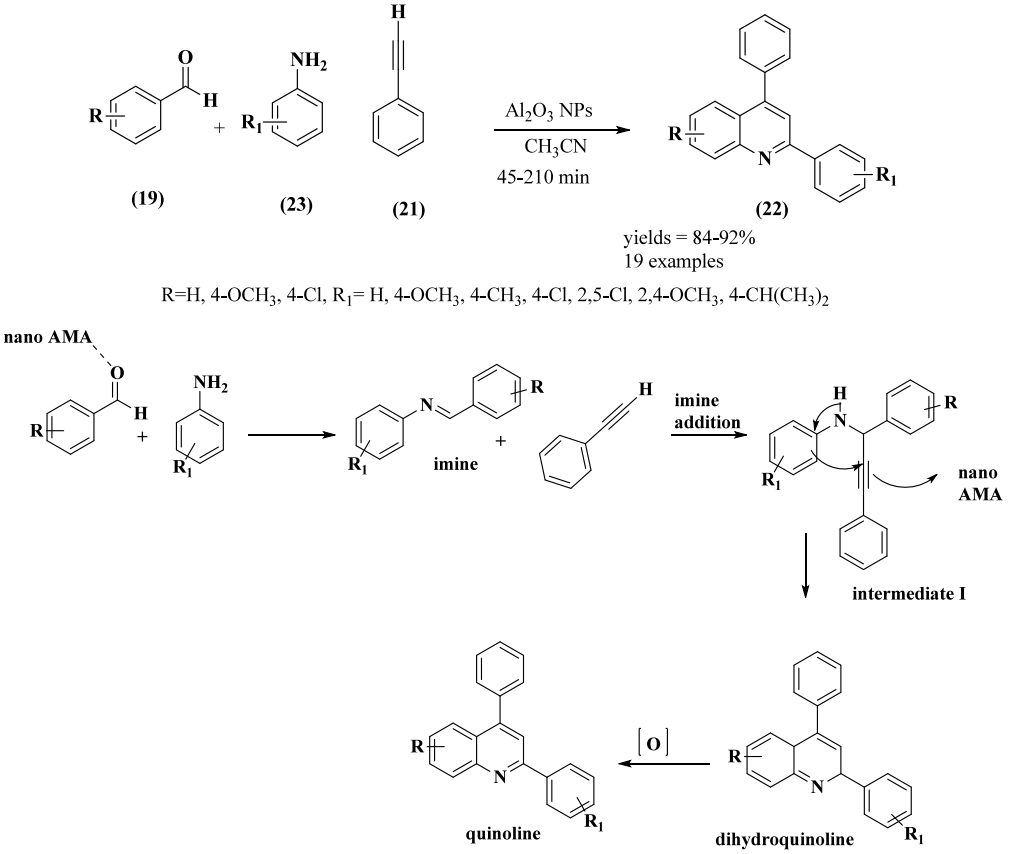
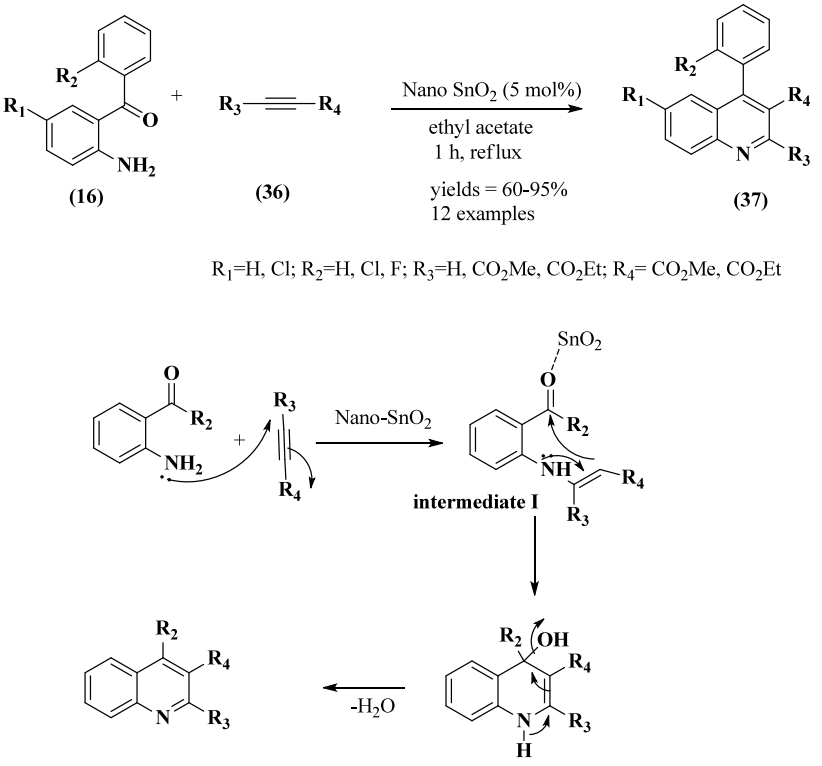
**Scheme 49. Synthesis of 2,4-Disubstituted Quinoline Using $Al_2O_3$ NPs**




**Scheme 50. Synthesis of Disubstituted Quinoline Using $SnO_2$ NPs**




80 nm. By employing this technique, heterocyclic systems such as thiophene-2-carboxaldehydes and furan-2-carboxaldehydes, as well as electron-rich and electron-deficient aldehydes, reacted smoothly to give a substantial amount of products



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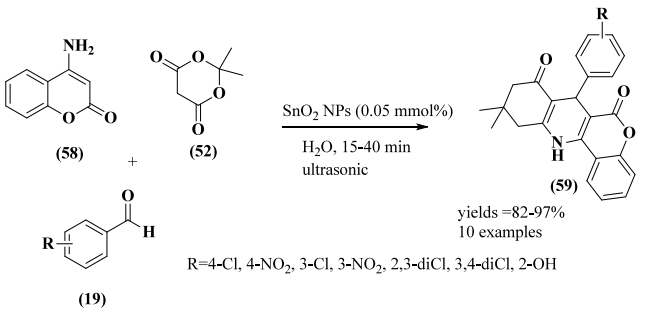
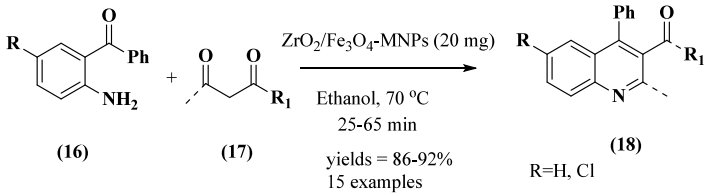
**Scheme 51. Synthesis of Chromeno[4,3-*b*]quinoline Using $SnO_2$ NPs from Marine Diatom Extract**




(85−95%). The protocols' advantages include superior yields, quicker reaction times, a simple workup process, and group compatibility (Scheme 31).[125] Tamoradi and colleagues synthesized the same set of compounds (88−98%) in the same array, but they used a Ni complex supported on $CoFe_2O_4$ ($CoFe_2O_4$@IDA-Ni nanocomposite) as the MNP catalyst. NPs are homogeneous nanometers in a quasispherical shape with a diameter of around 25 nm. Highly active sites are accessible for Ni immobilization on the surface of $CoFe_2O_4$ NPs.[126] Dateer and co-workers revealed the biogenic synthesis of Ni NPs employing leaf extract from *Portulaca oleracea*. The average size of these NPs is 40.09 nm, which have an uneven flake-like shape and are agglomerated. Further NPs were used for the synthesis of N-heterocycles such as quinazolines and quinolines. By using *t*-BuOK as the base, catalyst load (20 mol %), and toluene as the solvent, several 2-aminoquinoline derivatives were synthesized from 2-aminobenzyl alcohol and benzyl nitriles under optimum circumstances, which included 16 h at 80 °C. The catalyst retains its catalytic activity even after being retrieved and utilized up to six times. The author put up a tenable process in which a metallacycle is generated by tautomerization when the amine group combines with nitrile. Quinoline was produced by condensation and catalyst-mediated dehydrogenation (Scheme 32).[127]

**2.5. Cobalt-Based Nanocatalysts for the Synthesis of Quinolines.** Cobalt, a late 3D transition metal, has complex coordination and organometallic chemistry. Co-based NPs are appealing to researchers because of their physicochemical qualities and tiny size, and they may be employed as catalysts, in energy storage, in medicine, in microelectronics, in contrast agents, and as a foundation for drug delivery systems[128−131] and hav been investigated for synthetic and catalytic applications.[132] We address the use of Co-based NPs for the effective synthesis of quinoline in this section, as they are currently the most significant and effective NPs in catalysis. Wang et al. reported the synthesis of cobalt-doped g-$C_3N_4$ (Co@g-$C_3N_4$) NPs with thin layers stacked in clusters. The synthesized NPs were used for quinoline preparation using 2-aminobenzyl alcohols with ketones under optimal reaction conditions, including a catalyst (50 mg), NaOH as an additive (0.5 mmol), and toluene as a solvent (2.0 mL) for 24 h at 135 °C. The various quinolines were produced with a high yield (57−87%) and a variety of substrate options. During this transformation, the reactants with EDGs may be more advantageous. Following the reaction, the catalyst Co@g-$C_3N_4$ may be recovered and recycled up to six times with a little reduction in activity; that is, the yield gradually drops with longer recycling durations (Scheme 33).[133] Using a template approach, Zhang et al. synthesized an octahedral cobalt nanocatalyst based on nitrogen-doped $ZrO_2$@C. The carbon and zirconia matrix in which the Co nanoparticles are embedded is present in the NPs. Using these NPs, 2-nitroaryl carbonyls are reductively annulated with alkynoates and alkynones to produce quinoline. Quinolines, the intended product, are achieved in moderate to outstanding isolated yields under optimized conditions, such as solvent as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), catalyst (6 mol %), and HCOOH as the hydrogen donor at 110 °C. The intended product was produced in comparatively larger yields by the reactants with EWGs than by the substrates with strong EDGs in comparatively lower yields. The protocols' broad substrate scope, reusable metal catalyst that is abundant on Earth, selectivity, ease of operation, strong functional compatibility, and efficient transfer hydrogenation are their main features (Scheme 34).[134] The Co(III) salen complex immobilized on a cobalt ferrite-silica nanoparticle ($CoFe_2O_4$@$SiO_2$@Co(III) salen complex) magnetic nanocatalyst was synthesized by Nasseri et al. The average size of the NPs was 11.76−15.00 nm. Moreover, quinolines were synthesized from 2-amino-benzophenone and carbonyl compounds using these recyclable NPs. Optimal reaction conditions, such as a 10 mg of catalyst loaded into water as a solvent for 15 min at 80 °C, result in high to excellent yields (85−96%) of the respective quinolines. The catalyst can be retrieved and reused again with the external permanent magnet catalyst for as many as five runs without causing the catalyst's catalytic activity to diminish (Scheme 35).[135] Maldonado-Hódar and Pérez-Mayaral et al. synthesized several series of novel zerovalent cobalt nano-carbons as supported and doped aerogels; they are three-dimensional networks of 15−17 nm-sized primary carbon particles. The coexistence of oxygen surface groups and zerovalent Co NPs causes both catalytic species to work in concert. Additionally, this Co-catalyst was employed in the Friedlander reaction to synthesize quinolines utilizing various substituted *β*-keto esters and 2-amino-5-chlorobenzaldehyde. According to the author's conclusion, the carbon aerogels

**Scheme 52. Synthesis of Various Quinolines Using $ZrO_2/Fe_3O_4$-MNPs as the Catalyst and Its Plausible Mechanism**




carbonyl sources ($R_1$)= pentane-2,4-dione, cyclic ketones (cyclohexanone, cyclopentanone, and acetophenone), and β-ketoesters (methyl and ethyl acetoacetate)



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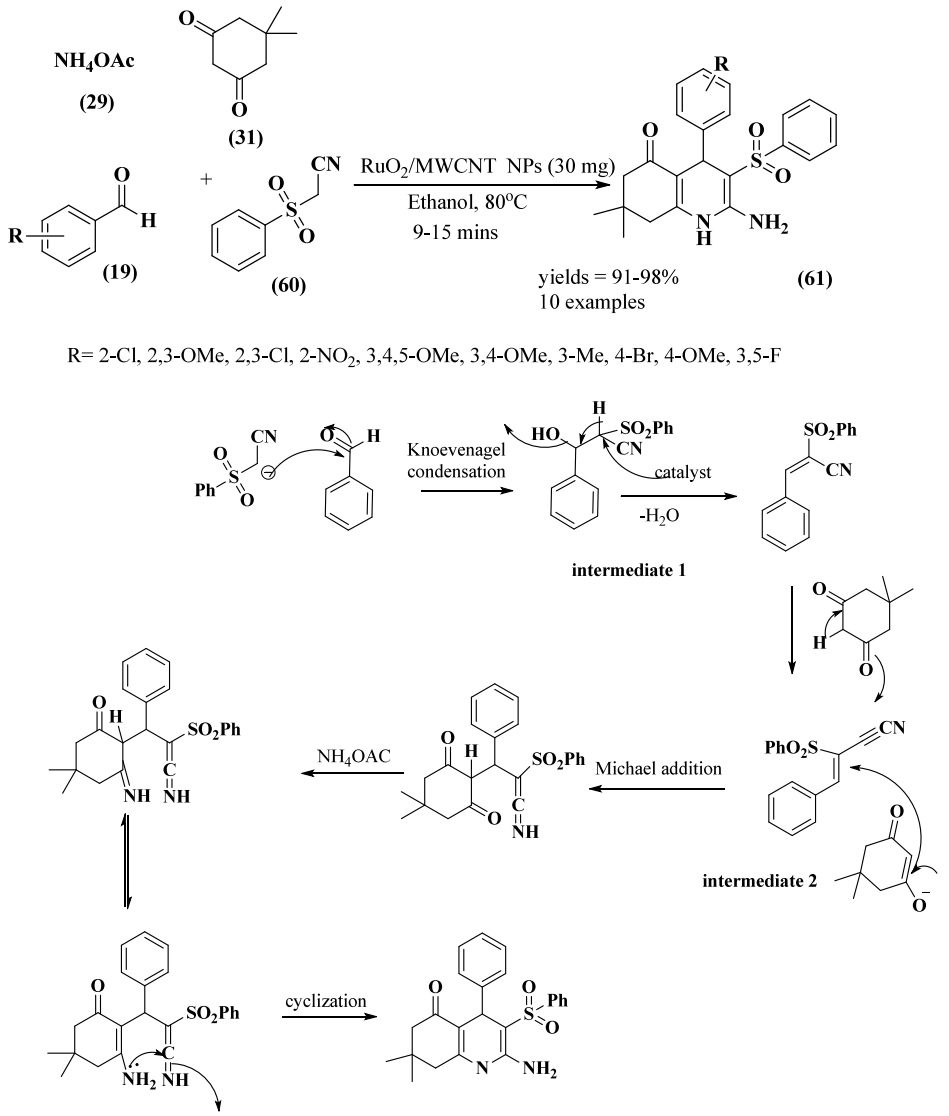
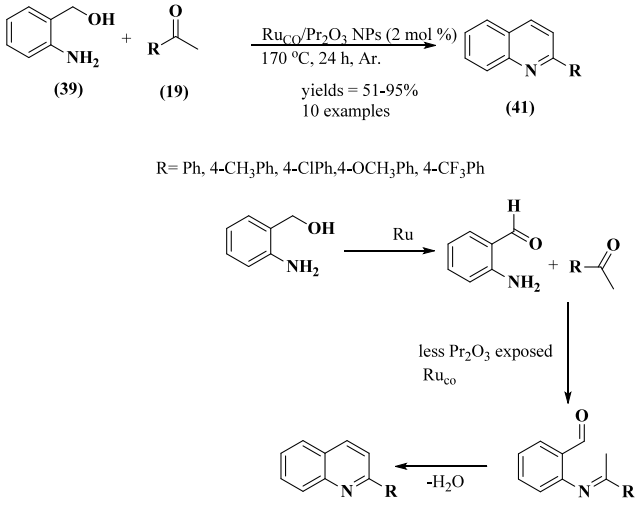
**Scheme 53. Synthesis of Various Quinolines Using $RuO_2$/MWCNT as the Catalyst and Its Plausible Mechanism**




**Scheme 54. Synthesis of 2-Substituted Quinolines Using $Ru_{co}/Pr_2O_3$ as the Catalyst and Its Plausible Mechanism**




based on Co(0) significantly improve their catalytic performance in the preparation of quinolines (Scheme 36).[136]

**2.6. Silver/Gold Nanocatalysts for the Synthesis of Quinolines.** Researchers are drawn to Ag-based NPs because of their biological potential, minimal production of hazardous byproducts, advantageous economic properties, friendly nature, and less side effects. Additionally, a variety of sectors have shown interest in these NPs because of their unique, customizable physical and chemical characteristics, especially those where an antiseptic effect is highly desired. Thus, Ag-based NPs were employed in the power sector[137] and the food, textile, construction, medical, cosmetology, pharmacy, and other industries,[138,139] as well as in biomedicine,[140] where they function as receptors in the tagging of biological materials. Ag nanoparticles are used in reduction and oxidation processes as well as C−C, C−N, C−S, and C−O bond formation reactions in a variety of chemical transformations.[141] Small-sized AuNPs, on the other hand, have outstanding catalytic activity in a wide range of chemical processes. Examples include the reduction of carbon−carbon triple bonds or nitroarenes, aerobic alcohol oxidation, and carbon−carbon bond creation.[142] In this section, we covered silver- and gold-based nanocatalysts for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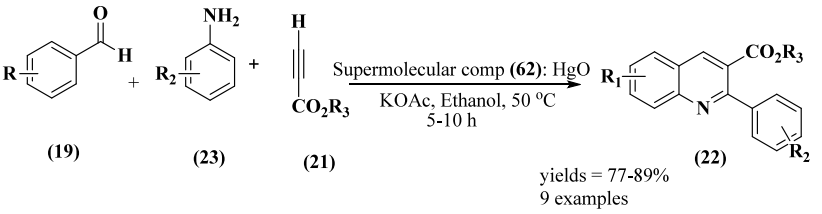
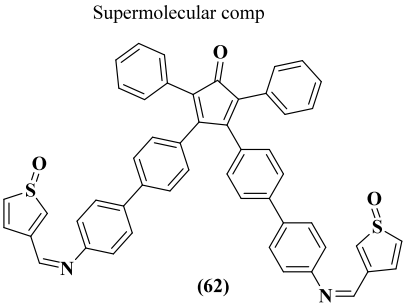
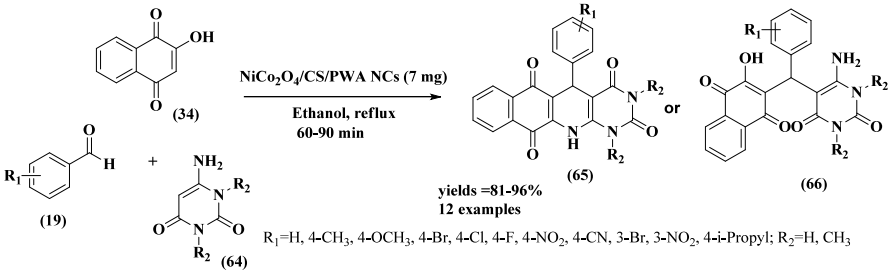
**Scheme 55. Synthesis of a Quinoline Derivative Catalyzed by a Supramolecular Ensemble Compound: HgO**



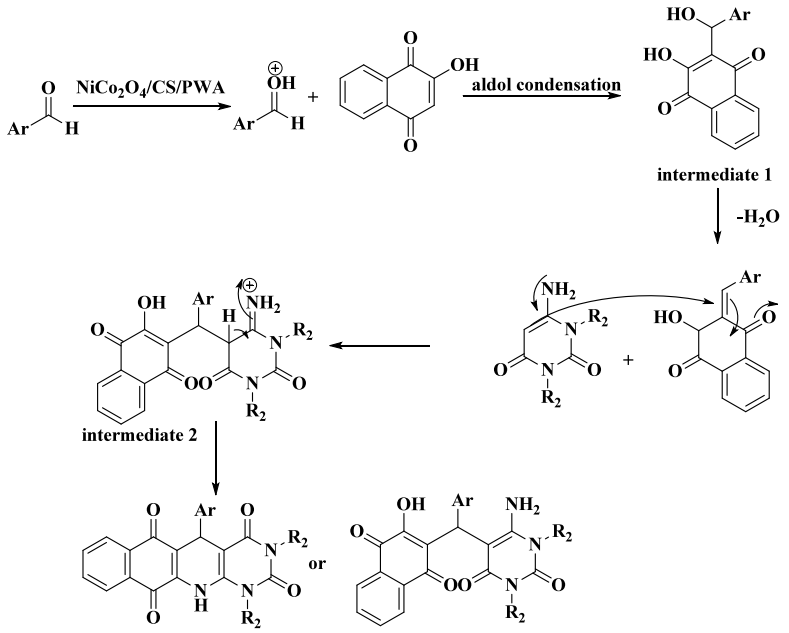

$R_1$=H, 4-$CH_3$, 4-$OCH_3$, 4-Br, 4-Cl, 3,4-$CH_3$;$R_2$= H, $CH_3$, $NO_2$; $R_3$=$CH_3$, $CH_2CH_3$




**Scheme 56. Synthesis of Pyrimido[4,5-*b*]quinoline-tetraone Derivatives Using the $NiCo_2O_4$/CS/PWA Nanocomposite and Their Plausible Mechanism**




$R_1$=H, 4-$CH_3$, 4-$OCH_3$, 4-Br, 4-Cl, 4-F, 4-$NO_2$, 4-CN, 3-Br, 3-$NO_2$, 4-i-Propyl; $R_2$=H, $CH_3$




quinoline production. Using green algae (*Chlorella vulgaris*), Chundawat and colleagues synthesized Ag-NPs and used UV, FTIR, X-ray, and SEM to characterize them. The size of these NPs, which had a truncated triangular, spherical, and cubic form, was determined to be between 40 and 90 nm. Ag NPs were employed in the one-pot synthesis of quinolines using



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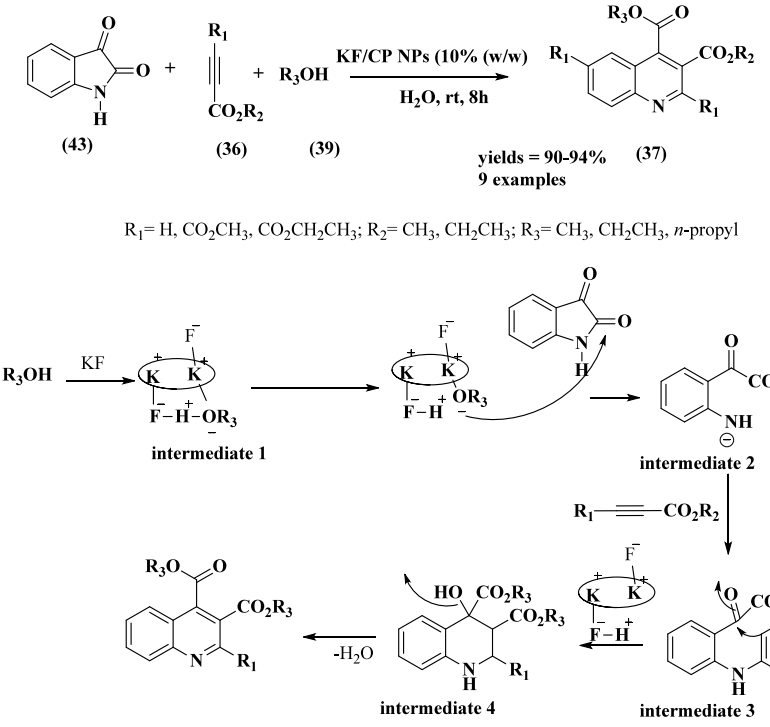
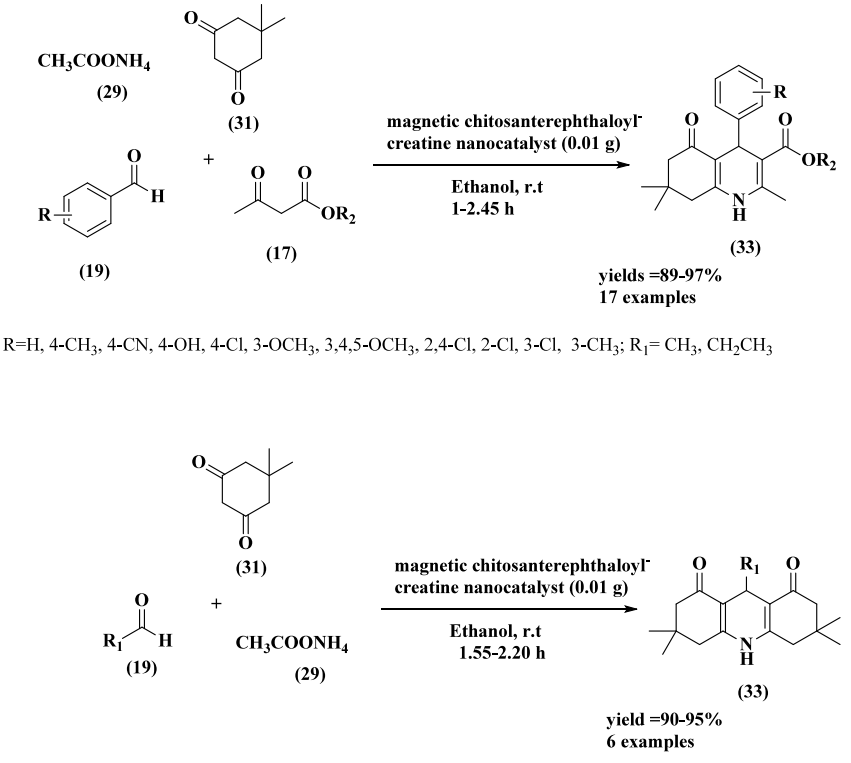
**Scheme 57. Synthesis of Substituted Quinoline Using KF/CP NPs and Their Plausible Mechanism**




**Scheme 58. Synthesis of Polyhydroquinoline Derivatives Catalyzed by a Magnetic Chitosan-Terephthaloyl-Creatine Nanocatalyst**




acetyl derivatives and 2-aminobenzyl alcohol. The author has proposed a plausible approach, In the presence of a base, the reactant alcohol (**I**) reacts with catalysts (AgNPs) to form the Ag-complex intermediate (**II**) followed by 2-aminobenzaldehyde (**III**), which then reacts with an acetyl derivative to form intermediate (**IV**); ultimately, it goes through cyclization; and the removal of water molecules results in the formation of quinoline (**V**). The approach has the advantages of being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inexpensive, producing no harsh or hazardous waste, and being appropriate for industrial use (Scheme 37).[143] A simple, environmentally friendly, and additive-free method for producing Au−Ag@AgCl NCs employing *Nephrolepis cordifolia* tuber extract as the capping and reducing agent is described by Sapkota and Han. These NCs had an average diameter of 30 nm, were spherical, and included a small number of hexagonal and polydispersed particles with sizes ranging from 10 to 50 nm. The synthesized NCs are used to catalyze the multicomponent (aniline, benzaldehyde, and phenyl acetylene derivatives) domino annulation−aromatization reaction during the quinoline synthesis. Many quinolines were synthesized in a good to outstanding yield (92−96%) under the ideal circumstances, which included the catalyst concentration (2 mol %) and 1,2-dichloroethane (DCM) as a solvent in the presence of *p*-toluenesulfonic acid (PTSA) (10 mol %). The Au−Ag@AgCl NC was recycled and reused five times with no noticeable loss of catalytic activity. The author postulated a feasible method for imine formation, including the condensation of aldehydes and amines in the presence of PTSA. The imine combines with Au−Ag@AgCl NCs, forming a coordination complex, and then reacts with alkynes to yield the propargylamine intermediate (complex II). This intermediate undergoes intramolecular hydroarylation of the alkyne to produce dihydroquinoline, which, following air oxidation, yields the required quinoline (Scheme 38).[144] The green method for grafting Ag and Ce nanoparticles atop silane-modified mesoporous nitrogen-doped graphitic carbon (Ag,Ce@SNC/A1SCA) was described by Gupta and co-workers. The material has a porous, layered structure with dimensions between 4 and 5 nm in size. These NPs were also employed in the one-pot synthesis of derivatives of polyhydroquinolines. A well-suited mixture of ethanol/water (1:1) and nanocatalyst (30 mg) at 80 °C produced a satisfactory yield of the intended polyhydroquinoline derivative. The authors observed that heterocyclic and aromatic aldehydes having electron-withdrawing functional groups delivered better yields than their electron-releasing counterparts. Without witnessing any significant decrease in activity, the catalyst might be retrieved and used five more times until being redeemed following the fifth run (Scheme 39).[145]

**2.7. Quinoline Synthesis Employing Silica-Based Nanocatalysts.** The silica nanoparticle ($SiO_2$) is a readily accessible, recyclable, and reasonably priced oxide that is often utilized as a support in organic transformations in conjunction with a catalyst The composition of a $SiO_2$ is silicon (46.83%) and oxygen (53.33%).[146,147] Promising characteristics of these $SiO_2$ NPs include excellent mechanical, chemical, and thermal durability; regulated porosity; large surface area; robust framework; and nanoscale size.[148,149] $SiO_2$-coated metal nanoparticles are now among the most significant catalysts of this kind, with applications across several industries. Numerous industries, including semiconductor manufacture, solar cell production, photovoltaic (Li-ion) battery production, biomedical engineering and medicine, and heterogeneous nanocatalysis, require $SiO_2$.[150−153] In contemporary organic synthesis, $SiO_2$ is employed in a wide range of modifications and synthetic approaches, particularly in catalytic activities. We discuss the use of $SiO_2$ in quinoline synthesis in this section. An ionic liquid nanomagnetic pyridinium-tribromide (MNPs@$SiO_2$−Pr-AP-tribromide) was synthesized by Ghorbani-Vaghei and co-workers as a novel nanocatalyst for the one-pot synthesis of quinoline derivatives from 2-amino aryl ketones and dicarbonyl compounds. These NPs have a spherical form with particle diameters ranging from 35 to 83 nm. The catalytic activity of MNPs@$SiO_2$−Pr-AP-tribromide is increased by the addition of $Br_3^-$. Several quinolines were found to have a good to excellent yield (77−95%) when the catalyst concentration (0.1 g) and solvent (ethanol) were optimized. Six consecutive reuses of the catalyst are possible without noticeably decreasing its catalytic activity once it has been retrieved and cleaned with ethanol. Bromine atoms are bound to nitrogen atoms in the nanocatalyst (MNPs@SiO2-Pr-AP-tribromide); it is likely that they will release $Br^+$ *in situ*. The author provided a reasonable mechanism: in the first stage, dicarbonyl is activated by $Br^+$ and combines with the amino acid aryl ketone, and imine is generated by the removal of water. In the following step, $Br^+$ activates the carbonyl group of 2-aminoarylketones, which undergoes intramolecular cyclization before forming the required quinoline ring via the hydration process. The procedure has several advantages, including shorter reaction times, higher product efficiency, ease of preparation and separation, and catalyst recyclability (Scheme 40).[154] By employing silicon NPs as catalysts in the Friedlander heteroannulation reaction between 2-aminoaryl ketones and carbonyl compounds under microwave conditions, Hasaninejad, Zare, and co-workers have devised a successful approach for the synthesis of quinoline. Different oxides (MgO, CaO, $SiO_2$ (60−120 mesh), and neutral $Al_2O_3$) were used in the reactions. The yield and reaction times of the $SiO_2$ nanoparticles were quite good. The catalytic activity of silica NPs is largely dependent on the presence of reactive OH groups on their surface. Various quinolines were synthesized with high yields and short reaction times from *α*-methylene ketones (cyclic 1,3-diketones, acyclic 1,3-diketones, and *β*-ketoesters) that reacted with 2-aminoarylketones under microwave irradiation, using optimized conditions such as a catalyst load of 0.5 g of silica NPs at 600 W of microwave power (100 °C). The mechanism is the same as that described in previous literature (Scheme 18): an intermediate is formed when 2-aminoarylketone condenses with the *α*-methylene group of a carbonyl compound (aldol condensation), and further, by intermediate dehydration, protonation, and intramolecular cyclization, the quinoline derivatives are formed (Scheme 41).[155] The $Fe_3O_4$@$SiO_2$/$ZnCl_2$ MNP was developed by Soleimani and co-workers by functionalizing MNPs coated in silica with $ZnCl_2$. These NPs have a core−shell structure with a noticeable difference between the silica shells and the $Fe_3O_4$ cores, with an average core size of ∼25−30 nm. Furthermore, under solvent-free conditions, these MNPs were employed as an acid catalyst for the synthesis of various quinolines in good to outstanding yield under optimum circumstances, such as catalyst concentration of 0.07 g at solvent-free conditions for 2 h at 60 °C using 2-aminoaryl ketone and various cyclic or acyclic *β*-dicarbonyls. The catalyst is recycled and utilized five more times after the reaction, each time losing 20% of its activity (Scheme 42).[156] Mesoporous MCM-41 silica-supported pyridine NPs were designed by Mukhopadhyay and co-workers, and these NPs are 2D hexagonal arrays of pore channels with a large surface area and a limited distribution of mesoporosity. Additionally, this material is employed in the one-pot, three-component synthesis of 2-, 3-, and 4-trisubstituted quinolines from dialkylacetylenedicarboxylates and substituted isatins. The desired products were obtained in good yield (82−91%) using ideal reaction conditions, such as catalyst concentration


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(40 mg), at room temperature, and a variety of alcohols, such as methanol, ethanol (EtOH), propyl alcohol (*n*-PrOH), *n*-butyl alcohol (*n*-BuOH), benzyl alcohol, and 2-phenyl ethyl alcohol (alcohols act as both reacting partners and solvents). The catalyst is recovered once the reaction is complete and can be utilized again for up to seven cycles without experiencing a major reduction in catalytic activity. The procedure has several advantages, including a recoverable catalyst, minimal catalyst loading, great yields in quick reactions, clean reaction conditions, and cost efficiency (Scheme 43).[157]

**2.8. Titanium Dioxide (Nano-$TiO_2$)-Based Nanocatalysts for Quinoline Synthesis.** In the past few years, titanium dioxide nanoparticles (TiO NPs) have gained a lot of interest due to their high activity, potent oxidizing capacity, nontoxicity, ease of availability, reusability, and long-term stability.[158] Nano-$TiO_2$ has a range of commercial uses in photocatalysis to remove pollutants, photovoltaics, or catalysis; moreover, it is used for sensors, paints, papers, sunscreen lotions, plastics, inks, food coloring, and toothpaste.[159,160] In addition, $TiO_2$ is employed as a catalyst in organic reactions like cyclization processes[161] and cross-coupling reactions, which include C−C,[162] C−O,[163] and C−N couplings.[164] We covered the use of $TiO_2$ NPs for quinoline synthesis in this section. $TiO_2$−$Al_2O_3$−$ZrO_2$ NCs were synthesized by our group in 2018 using the coprecipitation approach. These are spherical structures with a diameter ranging from 100 to 350 nm. With different anilines and ethylacetoacetate, several quinolines were synthesized in good to outstanding yield (66−98%) under optimal reaction conditions, such as catalyst load (5 mol %) and acetonitrile as a solvent at 60 °C. Comparing anilines with EDGs to those with EWGs, the author found that the latter produced higher amounts of quinoline. The benefits of this technique include quick reaction times and high yields, a pure product profile, simple catalyst production, affordable and eco-friendly catalyst, and easy reaction conditions (Scheme 44).[165] Singh and co-workers used titanium(IV) isopropoxide and *Origanum majorana* leaf extract as the reducing and capping agents to create TiO NPs under ultrasonic irradiation. These NPs have a particle size of less than 20 nm and are spherical in form. Additionally, the NPs were employed in a three-component reaction involving Meldrum's acid, 3,4-(methylenedioxy)aniline, and different aromatic aldehydes under ultrasonic irradiation to generate quinoline hybrids. Using 10 mol % of $TiO_2$ NPs in an aqueous media under 50 W of sonication under optimized reaction conditions, different 8-aryl-7,8-dihydro-dioxolo[4,5-g] quinolin-6(5*H*)-ones (85−91%)[1,3] was obtained. The catalyst can be recovered and reused for another cycle without losing its catalytic activity when the reaction is finished. According to the author's conceivable process, aldehyde and Meldrum's acid first undergo Knoevenagel condensation, resulting in the formation of an intermediate (**I**). Further, this undergoes Michael addition reaction with 3,4-(methylenedioxy) aniline to generate an additional intermediate (**II**). Furthermore, the required quinoline derivatives are produced via intramolecular cyclization and the removal of acetone and $CO_2$ (Scheme 45).[166] El-Remaily and Abu-Dief et al. synthesized $TiO_2$ NPs from Neem leaf extract, resulting in crystalline particles with an anatase phase, homogeneous spherical shape, and a size of around 19 nm. This NPs were employed in the synthesis of 1,2-dihydroquinoline derivatives from quinolarylamines and ethyl/methyl pyruvate, with the utilization of solvent-free conditions and optimum reaction conditions, such as a catalyst concentration of 2 mol %. A good to outstanding yield (66−98%) of the different dihydroquinolines was produced, and the catalyst could be recovered and reused up to four times without losing its catalytic activity. The author postulated a mechanism for the synthesis of 1,2-dihydroquinoline that is compatible with earlier discussions. When aniline combines with a ketoester, imine is formed. This imine then reacts with activated $\alpha$-ketoesters to generate an electrophile. The keto ester group's second mole combines with the intermediate, resulting in water elimination and proton shift to generate the desired 1,2-dihydroquinoline (Scheme 46).[167] Using $TiO_2$ NPs, an efficient heterogeneous catalyst that functions as both a Lewis acid and a Lewis base, Abdolmohammadi reported the synthesis of 2-quinolinecarboxylic acid from arylmethylidenepyruvic acids, 1,3-cyclohexandiones, and ammonium acetate in a one-pot, three-component process. Various quinoline derivatives were reported to have a good to excellent yield (92−98%) under the optimal reaction conditions, such as a catalyst concentration of 10 mol % under solvent-free conditions. According to the author's conceivable process, 1,3-cyclohexandiones react with ammonium acetate in the first step to generate an intermediate (**I**). This intermediate next goes through Michael addition and is coordinated with $TiO_2$ NPs to form intermediate (**II**). After intermediate (**III**) is dehydrated, quinoline is formed by the intramolecular cyclization of intermediate (**II**) (Scheme 47).[168] In the same array, the author used $TiO_2$ NPs for the synthesis of 7-aryl-10,10-dimethyl-7,10,11,12-tetrahydrobenzo[*c*]acridin-8(9*H*)-ones using 1-naphthol, aromatic aldehydes, dimedone, and ammonium acetate in aqueous conditions. The procedures' benefits include moderate reaction conditions, excellent yields, quick reaction periods, and a high degree of catalyst recyclability (Scheme 48).[169]

**2.9. Aluminum/Tin Nanoparticles for Quinoline Synthesis.** Researchers have been interested in Al-based NPs because of their size, excellent thermal conductivity, and unique physical and chemical characteristics. Because of their higher reactivity, Al NPs find extensive use in sectors such as explosives, propellants, and pyrotechnics.[170] These Al-based NPs are also used in many organic transformations including quinoline and those discussed in this section. $Al_2O_3$ nanoparticles were synthesized by Sharghi and co-workers, who then employed them as a catalyst in a multicomponent process involving aryl amines, aryl aldehydes, and phenylacetylene to synthesize 2,4-disubstituted quinoline. The typical size of these NPs is less than 100 nm. With optimal catalyst and solvent conditions, a good yield (84−92%) of the different quinolines was produced. The catalyst retains its catalytic activity for up to five cycles after reaction and can be recovered. Some of the advantages of the procedures, according to the authors, are cheap catalysts, quick reaction times, large yields, and reusable catalysts. Based on existing literature, the author posited a tenable mechanism wherein imine is formed through the interaction of aniline and aldehyde when Al NPs are present. A propargylamine intermediate (**I**) is formed when phenylacetylene is further mixed with imines. The dihydroquinoline produced by this cyclization is then oxidized by atmospheric air to produce desired quinoline derivatives (Scheme 49).[171]

Tin-based NPs/tin oxide NPs, on the other hand, are one of the most thoroughly investigated materials because of their wide range of applications in semiconductors. They have been widely employed as lithium batteries,[172] solar cells,[173] gas sensors,[174] and catalysts.[175] Furthermore, these NPs are


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employed in chemical synthesis,[176] and quinolines are synthesized using these NPs, as detailed in this section. Qandalee et al. employed nano-$SnO_2$ to synthesize quinoline from 2-aminobenzophenones and acetylenic mono- or diesters. These NPs feature a tetragonal rutile structure with a size of 70 to 95 nm. Under optimum circumstances such as ethyl acetate as a solvent, a catalyst concentration of 5 mol %, and a reaction time of 1 h, the different quinolines were produced in good to outstanding yield. Based on the literature, the author proposed a plausible mechanism: in the first step, the reaction between the nucleophilic amine and the acetylenic ester produces intermediate I on the surface of nano-$SnO_2$, which can act as a Lewis acid to increase the electrophilicity of the carbonyl group of 2-aminobenzophenone. Furthermore, it undergoes intramolecular cyclization, followed by water elimination, to produce quinolines (Scheme 50).[177] The preparation of $SnO_2$ NPs, from marine diatom extract, has been shown to be more environmentally friendly by Buazar and colleagues in another publication. The average size of these NPs is 20 nm, and they have a spherical form. Additionally, these NPs are employed as efficient catalysts in MCR processes involving dimedone, aromatic aldehyde, and 4-aminocoumarin to synthesize derivatives of chromeno[4,3-*b*]quinoline under ultrasound assistance. With the right parameters, such as a catalyst load of 0.05 mmol % and water as the solvent, several quinoline derivatives can be produced in a shorter reaction time with high yields (82−97%). The catalytic efficacy of $SnO_2$ NPs remained unaffected, even after undergoing up to six separate catalytic cycles. The suggested procedure is the same as in other previous publications (Scheme 45); it involves the carbonyl of the aryl aldehyde that has been activated by the catalyst and dimedone by Knoevenagel condensation. The required quinoline is generated when the intermediate combines with aminocoumarin by Michael addition, cyclization, and dehydration (Scheme 51).[178]

**2.10. Zirconium and Ruthenium Based Nanocatalysts for Quinoline Synthesis.** Zirconium is a strong transition metal that has several applications when present in its oxide state, often known as zirconia or zirconium oxide. Zirconium-based NPs have drawn the attention of material scientists in recent decades because of their chemical stability, high specific area, thermal stability, biocompatibility, luminescence, refractive index, and substantial antibacterial, antioxidant, and antifungal characteristics.[179] Zirconia-based NPs have several uses, including semiconductors,[180] catalysts,[181] sensors,[182] cutting tool coatings, ceramics,[183] and implants.[184] Also, the substantial literature on zirconium compounds as catalysts or reagents in synthetic organic chemistry also reveals that zirconium compounds have found an ever-increasing importance in organic synthesis.[185] In this section, we cover the Zr-based NPs used in the quinoline synthesis. $ZrO_2$-supported $Fe_3O_4$-MNPs ($ZrO_2$/$Fe_3O_4$-MNPs) were developed by Shojaei and co-workers. These NPs have a porous structure, uniform shape and size distribution, and particle sizes between 5 and 25 nm. Additionally, these NPs are employed as an eco-friendly and productive heterogeneous nanocatalyst in the Friedlander annulation process, which produces quinolines from a variety of benzophenones and ketones/$\beta$-diketones. Using ethanol as the solvent and a catalyst concentration of 20 mg at 70 °C, optimal circumstances allowed for the synthesis of several quinolines in high to excellent yields (87−92%) in a shorter reaction time of 25−65 min. This approach is effective for $\beta$-ketoesters, cyclic ketones such as cyclohexanone and cyclopentanone, and cyclic and acyclic diketones such as 5,5-dimethylcyclohexanedione and acetylacetone. Once the reaction is completed, the catalyst can be retrieved and reused three times with no significant drop in activity (Scheme 52).[186,187]

Conversely, researchers were drawn to ruthenium-based NPs because of their characteristics, including size, dispersion, shape, composition, and surface state. It has been shown that Ru-based NPs can be used as catalysts in solutions for a variety of processes. The main ones include hydrogen synthesis by amine borane dehydrogenation or water-splitting processes, reduction, oxidation, Fischer−Tropsch, C−H activation, and $CO_2$ transformation.[188] In this section, we explored the uses of Ru-based NPs in the synthesis of quinolines. The preparation of $RuO_2$/MWCNT nanocatalysts was described by Maddila and co-workers; these NPs are white, fluffy-looking particles with a size of 15−25 nm. The dispersion of $RuO_2$ NPs over a multiwalled carbon nanotube backbone is confirmed by TEM. Additionally, these NPs were studied in the efficient green synthesis of sulfonyl-quinoline derivatives from dimedone, $NH_4OAc$, phenylsulfonyl acetonitrile, and substituted aldehydes in a one-pot, four-component reaction in ethanol. Many quinoline derivatives were synthesized in good yield using the optimal reaction conditions of 2.5% $RuO_2$/MWCNT (30 mg) as a catalyst in the presence of an ethanol solvent solution at a shorter reaction time. Additionally, the catalyst retains its catalytic activity even after being retrieved and employed up to eight times. Using the literature, the author hypothesized the mechanism. Phenylsulfonylpropanenitrile (intermediate **1**) is produced in the first step when phenylsulfonyl acetonitrile and aldehyde undergo Knoevenagel condensation in the presence of a rapid $RuO_2$/MWCNT catalyst. Additionally, this forms intermediate **2** when it combines with dimedone via the Michel addition reaction. The following stage involves cyclization, which yields the desired product, derivatives of quinoline (Scheme 53).[189] Chaudhari et al. synthesized 2-substituted quinolines from 2-aminobenzyl alcohol and other ketones using Ru nanolayers supported by praseodymium oxide ($Pr_2O_3$) and Ru NP catalysts. The required quinoline was produced in moderate to good yield (51−95%) at 170 °C for 24 h using optimum reaction conditions, such as catalyst (2 mol %) and mesitylene (1 g). When compared to that bearing EWG, acetophenone bearing EDG provides a fair yield, according to the author's study of the electrical impact. This procedure is effective for methyl, nonmethyl, cyclic, and heteroaryl (methyl) ketone. The catalyst's catalytic activity will decline during the course of three cycles of recovery and reuse. The authors confirmed that the $Pr_2O_3$-supported Ru nanolayer catalyst outperformed conventional $Pr_2O_3$-supported Ru nanoparticle catalysts in synthesizing 2-substituted quinolines. In the plausible mechanism, the first step is Ru-catalyzed acceptorless dehydrogenation, which converts 2-aminobenzyl alcohol to 2-aminobenzaldehyde. Then, $Pr_2O_3$-promoted condensation of 2-aminobenzaldehyde and ketone yields a cyclized end product (quinoline) (Scheme 54).[190]

**2.11. Mecury/12-Phosphotungstic Acid-Based Nanocatalysts for the Synthesis of Quinolines.** Supramolecular ensemble tetraphenylcyclopentadienone derivatives and HgO NPs, which are specular in form and have nanospheres ranging in size from 25 to 32 nm, have been synthesized by Bhalla and colleagues. Additionally, these NPs were used in a multicomponent quinoline synthesis, including different anilines, aldehydes, and electron-deficient alkynes. Many quinoline


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derivatives were reported in a good yield (77−89%) at a longer duration (5−10 h) under the optimized reaction conditions, which included a catalyst concentration of 0.05 mol %, ethanol as a solvent, and 0.5 equiv of KOAc as a base at 50 °C. According to the author, aggregates of derivative tetraphenylcyclopentadienone sufficiently enhance the Lewis acidity of HgO NPs, increasing their efficiency for the C−H activation reaction. Additionally, the small size and spherical shape of in situ generated HgO NPs provide a large surface area for catalytic reactions. These factors may be responsible for the C−H activation reactions. Finally, tetraphenylcyclopentadienone derivative aggregates helped to move the reactant molecules toward the catalytic sites (Scheme 55).[191] Twelve phosphotungstic acid functionalized chitosan@$NiCo_2O_4$ NCs (PWA/CS/$NiCo_2O_4$) were developed by Safari and co-workers. NCs have a spherical shape and a typical diameter of around 30 nm. A variety of pyrimido[4,5-*b*]quinoline-tetraone derivatives were synthesized with an excellent yield (81−96%) in 60−90 min by using optimized reaction conditions, such as catalyst (7 mg) and ethanol as solvent under reflux conditions. The aldehyde with EDGs has a lower yield and requires more time for synthesis of the product when compared to EWGs. The catalyst may be retrieved using an external magnet and reused five times without significantly reducing the catalytic activity. Based on the existing literature, a feasible process is presented that involves aldol condensation, Michael addition, and cyclization to produce the desired product. In the first stage, 2-hydroxy-1,4-naphthoquinone combines with the aldehyde via aldol condensation, followed by dehydration, yielding intermediate (**I**). In the following step, the third reagent attacks, producing intermediate (**II**) by Michael addition. Finally, this intermediate (**II**) is cyclized, yielding the desired products (Scheme 56).[192]

**2.12. Other Types of Nanocatalysts for Quinoline Synthesis.** Javanshir and co-workers developed potassium fluoride-impregnated clinoptilolite (a natural zeolite) (KF/CP) NPs as a heterogeneous base nanocatalyst. These NPS are spherical in form and have a particle size of 41 nm. Furthermore, these NPs were used in the MCR reaction of alcohols, activated acetylene compounds, and isatin in water at room temperature to synthesize quinolines. A variety of quinoline derivatives are synthesized in good yields (90−94%) under optimum reaction conditions, such as catalyst concentrations of 10% (w/w) and water as a solvent at room temperature. Low catalyst loading, the utilization of natural catalysts, gentle and clean reaction conditions, and cost-effectiveness are the procedures' key benefits. According to the author's plausible hypothesis, the intermediate **1** is created when a hydrogen bond forms between the alcohol's proton and fluoride ion. Intermediate (**I**) combines with isatin's C-2 in the following phase. Anion intermediate **III** can develop when intermediate (**II**), which is produced after the nucleophilic substitution process, opens the heterocyclic ring. The ring-opened intermediate (**III**)'s nucleophilic assault on the acetylic molecule in the next stage results in the creation of anionic intermediate **IV**, which then goes through intramolecular *exo*-trig cyclization to produce functionalized quinoline derivatives (Scheme 57).[193] The magnetic chitosan-terephthaloyl-creatine bionanocomposite was synthesized by Maleki and co-workers. The NC structure exhibits a spherical shape, uniform distribution, and average size of 25−30 nm. Additionally, using MCR (four-component synthesis) with substituted aldehydes, ethyl/methyl acetoacetate, dimedone, and ammonium acetate, these NCs were employed to synthesize polyhydroquinoline derivatives. A good yield (90−97%) of several quinoline derivatives was achieved using optimized reaction conditions, such as a catalyst load of 0.01 g and ethanol as a solvent at rt (Scheme 58).[194]

## 3. CONCLUSION

The quinoline ring is a key pharmacophore in current drug research. Quinoline has several biological properties, spanning antimalarial, antimicrobial, antiprotozoal, antitumor, antitubercular, anti-inflammatory, antibacterial, antifungal, antihypertensive, anticancer, anti-HIV, anti-inflammatory, antiproliferative, antioxidant, and DNA binding. As a result, syntheses of this core have become an increasingly prevalent subject among researchers worldwide. The conventional methods for quinoline synthesis have a few drawbacks; thus, researchers have been interested in developing novel procedures, particularly greener ones, in recent decades, mostly employing nanocatalysts. In this work, we have compiled and organized the catalytic protocols utilizing nanocatalysts, and their plausible reaction mechanistic pathways have been discussed. Researchers who worked on nanocatalysts for quinoline synthesis found several advantages, including mild reaction conditions with high yield, easy reaction workup, short reaction time, minimal waste, economic (low cost), atom efficiency, safety, the use of greener solvents or solvent-free methods (some methods), exceptional tolerance to functional groups, recoverability, and reuse. Almost all of the approaches (nanocatalysts) for quinoline synthesis exploited the same mechanistic routes, such as Knoevenagel condensation (sometimes aldol condensation), Michael addition, and intramolecular cyclization, followed by the application of an oxidant or water removal. The results provided in this study will motivate synthetic chemists to develop an intuitive and easy tool for the researcher to organize additional exploration of this problem.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

Data are contained in the manuscript. More data can be obtained from the corresponding author through an email request.

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Rangappa S. Keri: Methodology, Conceptualization, Supervision. Srinivasa Budagumpi: Conceptualization, Methodology. Vinayak Adimule: Conceptualization, Supervision.



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## Notes

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## ■ ABBREVIATIONS

AC, Activated carbon
APTES, 3-(Aminopropyl)triethoxysilane
BET, Brunauer−Emmett−Teller
CA, Carbon aerogel
CMC, Carboxymethylcellulose
CNT, Carbon nanotube
DCM, Dichloromethane
DDBSA, Dodecylbenzenesulfonic acid
DMF, Dimethylformamide
DNA, Deoxyribonucleic acid
EDG, Electron-donating groups
EDS, Energy-dispersive spectroscopy
EWG, Electron-withdrawing groups
$Fe_3O_4$, Iron(II, III) oxide
FTIR, Fourier transform infrared spectroscopy
g, Gram
GO, Graphene oxide
HITh, 4,5-Dihydroxyimidazolidine-2-thione
HFIP, 1,1,1,3,3,3-Hexafluoro-2-propanol
LDH, Lactate dehydrogenase
ICP, Inductively coupled plasma
IRMOF-3, Isoreticular metal−organic framework-3
MCR, Multicomponent reaction
mg, Milligram
mL, Milliliter
MOF, Metal−organic frameworks
MNPs, Magnetic nanoparticles
MWCNT, Multiwalled carbon nanotubes
NBQX, 2,3-Dioxo-6-nitro-7-sulfamoyl-benzo[*f*]quinoxaline
nm, Nanometer
NCs, Nanocomposites
NPs, Nanoparticles
PBA, Bisphosphonic acid
$POCl_3$, Phosphorus oxychloride
PSTA, Polysulfonamidetriazine
PTSA, *p*-Toluenesulfonic acid
Pr, Praseodymium complex
pXRD, Powder X-ray diffraction
rt, Room temperature
SBA-15, Santa Barbara Amorphous-15
SEM, Scanning electron microscopy
SiCN, Siliconcarbonitrite
TEM, Transition electron microscopy
TFA, Trifluoroacetic acid
TGA, Thermogravimetric analysis
UV, Ultraviolet
VSM, Vibrating sample magnetometer
XPS, X-ray photoelectron spectroscopy

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