



Review article

Different catalytic approaches of Friedländer synthesis of quinolines

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ARTICLE INFO

Keywords:

Friedländer synthesis
Polysubstituted quinolines
Ionic liquids
Nanocatalysts
Metal-organic frameworks
Organocatalysts

ABSTRACT

Friedländer quinoline synthesis is one of the most important and simplest methods among the various reported methodologies for quinoline synthesis, renowned for its efficiency and versatility. The reaction involves the condensation of a 2-aminobenzaldehyde with a ketone, forming polysubstituted quinolines. This review comprehensively examined diverse catalytic approaches developed to optimize the Friedländer reaction, highlighting recent advancements and their impact on reaction efficiency, selectivity, and environmental sustainability. The discussion encompassed traditional catalysts and emerging catalytic systems, including ionic liquids, metal-organic frameworks, polymers, and nanocatalysts. Additionally, the review addresses the influence of various catalytic environments on reaction outcomes. By collating and critically analyzing recent advancements, this review aims to provide a valuable resource for researchers seeking to leverage these catalytic strategies for synthesizing quinoline derivatives.

1. Introduction

Quinoline was initially isolated by Friedlieb Ferdinand Runge in 1834 as a colorless, hygroscopic liquid obtained from coal tar distillation [1]. This aromatic bicyclic molecule comprises a benzene ring fused ortho to a pyridine ring and is characterized as a weak tertiary base [2]. It is also referred to as azanaphthalene and benzo[b]pyridine [3]. Due to the nitrogen in the ring, it can participate in both electrophilic and nucleophilic substitution reactions, exhibiting modifications in both the pyridine and benzene rings [4]. Quinolines are distinctive natural alkaloids [5], found in numerous natural and synthetic products and hold immense importance in the pharmaceutical field [6]. Functionalized quinoline derivatives exhibit a spectrum of biological activities, including antioxidant [7], antibacterial [8], anticancer [9], antileishmanial [10], antiviral, anti-HIV [11], antimalarial [12], antitubercular [13], antiparasitic [14], antioxidant [15], antihistaminic, antidiabetic [16], antimicrobial [17], antifungal [18], and anti-inflammatory [19] Properties. Beyond these biological applications, quinolines are also utilized as photoinitiators [20], sensors, fluorescent dyes [21], photosensitizers [22], fluorescent probes [23], component in optoelectronic devices [24], and materials for nonlinear optics [25]. Additionally, they act as precursors for various heterocyclic compounds via ring-closure reactions.

Numerous synthetic techniques have been developed due to their significance in various fields [22]. One of the oldest and most reliable methods is the Skraup reaction, which involves heating aniline and glycerol with an oxidizing agent in concentrated sulfuric acid [26]. The Doebner technique, which reacts aniline, an aldehyde, and pyruvic acid, produces 2-substituted quinoline-4-carboxylic acids [24]. Introduced in 1881, the Doebner–Von Miller reaction [26] is a variant that uses ketones or α,β -unsaturated aldehydes to

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create 2- and 4-substituted quinolines in an acidic environment. Using β -ketoesters under acid reflux, the Conrad–Limpach reaction (reported in 1887) produces 2- and 3-substituted quinolin-4-ols, while the Combes synthesis produces 2,4 substituted quinoline skeletons from aryl amines and 1,3-dicarbonyl compounds. The Pfitzinger reaction [27] combines isatin with a carbonyl compound under basic conditions to produce 2- and 3-substituted quinoline-4-carboxylic acids. The Friedländer reaction, introduced by Paul Friedländer in 1882, employs 2-aminobenzaldehyde with another carbonyl component to form 2- and 3-substituted quinolines. Despite the numerous synthetic methodologies reported, a persistent demand remains for straightforward, convenient, and environmentally benign synthetic approaches [28]. These diverse methods underscore the extensive range of approaches available for constructing quinoline ring systems.

Among these methods, the Friedländer annulation is the simplest, most straightforward, and widely used approach [29,30]. The classical synthetic route involves the condensation of 2-aminobenzaldehyde with a carbonyl compound, typically a ketone (Fig. 1), under acidic or basic conditions [31]. So far, various simple and complex catalysts have been used to optimize this reaction furnishing a variety of substituted quinolines [32]. Recent advancements have focused on improving reaction efficiency, expanding substrate compatibility, and developing greener and more sustainable methods. Innovations such as microwave irradiation, ionic liquids, and solid acid catalysts have enhanced the reaction's applicability and environmental profile. The development of asymmetric Friedländer reactions has facilitated the synthesis of chiral quinolines, which are important for enantioselective drugs and catalysts. The mechanism typically involves the formation of an imine intermediate from the condensation of 2-aminobenzaldehyde with the carbonyl compound, followed by intramolecular cyclization and dehydration to yield the quinoline product.

This review comprehensively discusses various catalytic approaches and recent advancements in the Friedländer synthesis of quinolines (Fig. 2). We explore traditional methodologies alongside modern modifications, highlighting their advantages and limitations. Special attention is given to approaches and synthetic strategies that improve reaction yields, selectivity, and environmental sustainability. Additionally, we examine the applications of green chemistry techniques, emphasizing their significance in contemporary scientific research and industrial applications. This review aims to provide a detailed and nuanced understanding of available catalytic approaches for Friedländer synthesis, offering insights to aid researchers in the efficient design and synthesis of quinoline-based compounds for diverse applications.

1.1. Ionic liquids catalyzed Friedländer synthesis

Ionic liquids (ILs) have garnered significant attention as versatile and efficient catalysts in organic synthesis, particularly for Friedländer quinoline synthesis (Fig. 4). Their unique physicochemical properties—including low volatility, high thermal stability, and tunable acidity—make them highly suitable for catalytic applications [33]. A key aspect of their catalytic performance is the relationship between the basicity of the anions and overall catalytic efficiency. It is generally understood that the nature of the anion modulates the electrophilicity of the cation, which in turn influences the acidity of the ILs, thereby impacting their catalytic activity [34]. The categorization of the reported ionic liquids based on their cations.

1.1.1. Imidazolium-based cations

Most of the reported examples involve imidazolium-based ionic liquids with various anions:

1.1.1.1. Tetrafluoroborate (BF_4). In 2003, Palimkar and coworkers [34] reported two sets of ionic liquids based on N, N-di-n-butylimidazolium (bbim) and N-butylimidazolium (Hbim) salts, varying in anion basicity. The ILs investigated included 1, 3-Di-n-butylimidazolium Bromide [bbim]Br, 1,3-Di-n-butylimidazolium Chloride [bbim]Cl, 1,3-Di-n-butylimidazolium Tetrafluoroborate [bbim] BF_4 , 1,3-Di-n-butylimidazolium Hexafluorophosphate [bbim] PF_6 , 1,3-Di-n-butylimidazolium Perchlorate [bbim] ClO_4 , 1-Butylimidazolium Bromide [Hbim]Br, 1-Butylimidazolium Chloride [Hbim]Cl, 1-Butylimidazolium Hexafluorophosphate [Hbim] PF_6 , 1-Butylimidazolium Perchlorate [Hbim] ClO_4 , and 1-Butylimidazolium Tetrafluoroborate [Hbim] BF_4 . The study found that with increasing basicity of the anions (increasing pK_a of the corresponding acid), the yield progressively increased. Consequently, the ionic liquid containing tetrafluoroborate, [Hbim] BF_4 , emerged as the most efficient catalyst for Friedländer quinoline synthesis, achieving high yields of polysubstituted quinolines. Reactions were conducted under solvent-free conditions at 100 °C, with reaction times ranging from 3 to 6 h. This process yielded 93 % of the desired product, with the IL being completely recoverable and reusable over two cycles, with minimal loss in yield.

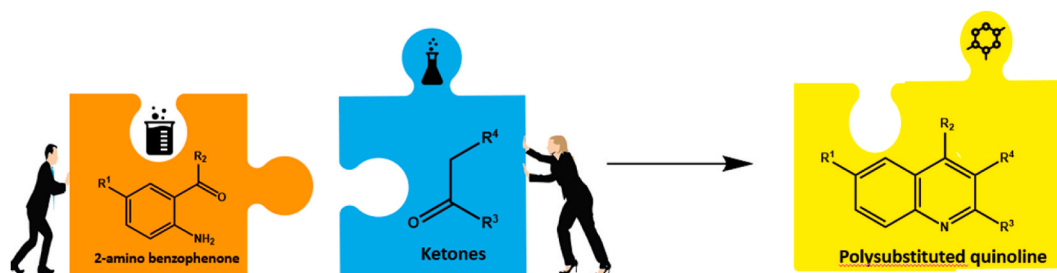


Fig. 1. General reaction scheme of Friedländer Synthesis of Quinoline.

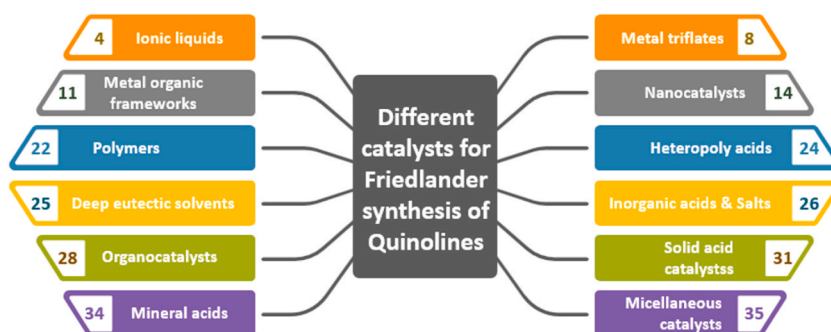


Fig. 2. Different catalytic approaches of Friedländer synthesis of Quinoline.

Later, Heravi et al. [35] also utilized [Hbim]BF₄ in the Friedländer reaction with methanol as a co-solvent under ultrasonic irradiation. This ionic liquid functioned as both a Brønsted acid catalyst and a solvent at ambient temperature. The reactions were conducted at room temperature (approximately 25 °C) for 10 min under ultrasonication, achieving an 84 % yield without additional catalysts (Scheme 1). This study highlighted the potential of ultrasonic irradiation for enhancing reaction efficiency at ambient temperatures.

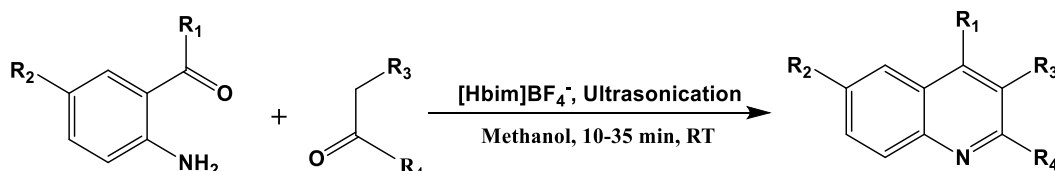
1.1.1.2. Hydrogen sulfate (HSO₄⁻). Tajik et al. [36] synthesized 1-butyl-3-methylimidazolium hydrogen sulfate ([bmim]HSO₄), an acidic IL with hydrogen sulfate anion, and used it as a catalyst (0.5 mmol%) under solvent-free conditions at 70 °C. The reaction yielded 78 % of the quinoline products after 140 min. Subsequently, Rezayati et al. [37] selected 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium hydrogen sulfate supported by Fe₃O₄ nanoparticles (Fe₃O₄-IL-HSO₄) (Fig. 3) as a Brønsted acidic ionic liquid and efficient magnetic catalyst for the same condensation reaction. Additionally, Shirini et al. [38] synthesized 1,3-disulfonic acid imidazolium hydrogen sulfate (DSIMHS), a Brønsted acid catalyst, and used it (0.25 mmol%) under solvent-free conditions at 70 °C. The reaction yielded 95 % of the quinoline product in 35 min, with the IL maintaining high yields over six cycles without pretreatment.

1.1.1.3. Bromide (Br⁻). Shirini and coworkers [39] reported a novel Brønsted acidic IL, 3,3'-(Butane-1,4-diyl)bis(1-methyl-1-H-imidazole-3-ium)-dibromide-disulfuric acid (C₄(mim)₂-2Br⁻-2H₂SO₄), containing both bromide and hydrogen sulfate anions. It was employed as a catalyst (0.05 mmol%) under solvent-free conditions at 50 °C for the Friedländer synthesis of quinolines. The reactions achieved a 90 % yield of the quinoline product in just 15 min, demonstrating the high efficiency of this novel IL.

1.1.1.4. Sulfonic acid derivatives (SO₃H⁻). Akbari et al. [40] introduced task-specific ionic liquids (TSIL) by preparing SO₃H-functionalized ILs through acidification with triflic acid. These ILs served as effective, water-tolerant acidic catalysts, achieving yields between 85 and 98 % for quinoline synthesis. Specifically, a reaction using 0.01 g of SO₃H-functionalized IL in water at 70 °C for 1 h resulted in a 92 % yield. Martos et al. [41] developed 1,3-bis(sulfomethyl)imidazole ([bsmim]), a second-generation sulfo-imidazole acid catalyst, which acted as an excellent catalyst (10 mol%) under solvent-free conditions at 80 °C. The reaction yielded 93 % of the quinoline product in 16 min, showcasing the efficiency of this IL for rapid synthesis.

Additionally, Sarma et al. [42] reported two novel acidic ILs, 3-methyl-1-sulfoimidazolium trichloroacetate ([Msim][OOCCL₃]) and 3-methyl-1-sulfoimidazolium chloride ([Msim]Cl), derived from CCl₃COOH. These ILs acted as recyclable acidic homogeneous media for Friedländer synthesis at 100 °C. Using [Msim][OOCCL₃] (0.4 mmol%), the reactions yielded 99 % of the quinoline product in 45 min, while [Msim]Cl (1.3 mmol%) yielded 98 % in 70 min, outperforming CCl₃COOH under solvent-free conditions. Khaligh et al. [43] introduced a sulfonic acid ionic liquid, 4-imidazole-1-yl-butane-1-sulfonic acid (ImBu-SO₃H), as a dual solvent-catalyst for metal-free synthesis of quinolines via Friedländer annulation. Reactions using ImBu-SO₃H under solvent-free conditions at 50 °C yielded a 92 % quinoline product in 30 min.

1.1.1.5. Trifluoromethanesulfonate (CF₃SO₃⁻). Singhal et al. [44] introduced a sulfonyl imidazolium acidic IL, 1-(4-sulfonylbutyl)-3-methylimidazolium trifluoromethanesulfonate, demonstrating its utility for quinoline synthesis under similar conditions. This study highlighted the versatility and efficiency of ILs in promoting the Friedländer synthesis of quinolines.



Scheme 1. The synthesis of polysubstituted quinolines catalyzed by [Hbim]BF₄.

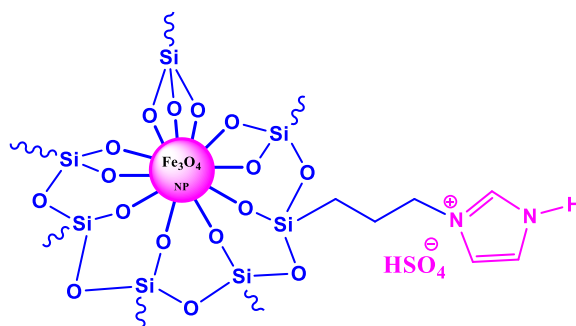


Fig. 3. Structure of magnetic-nanoparticle-supported ionic liquid (MNP-IL- HSO_4).

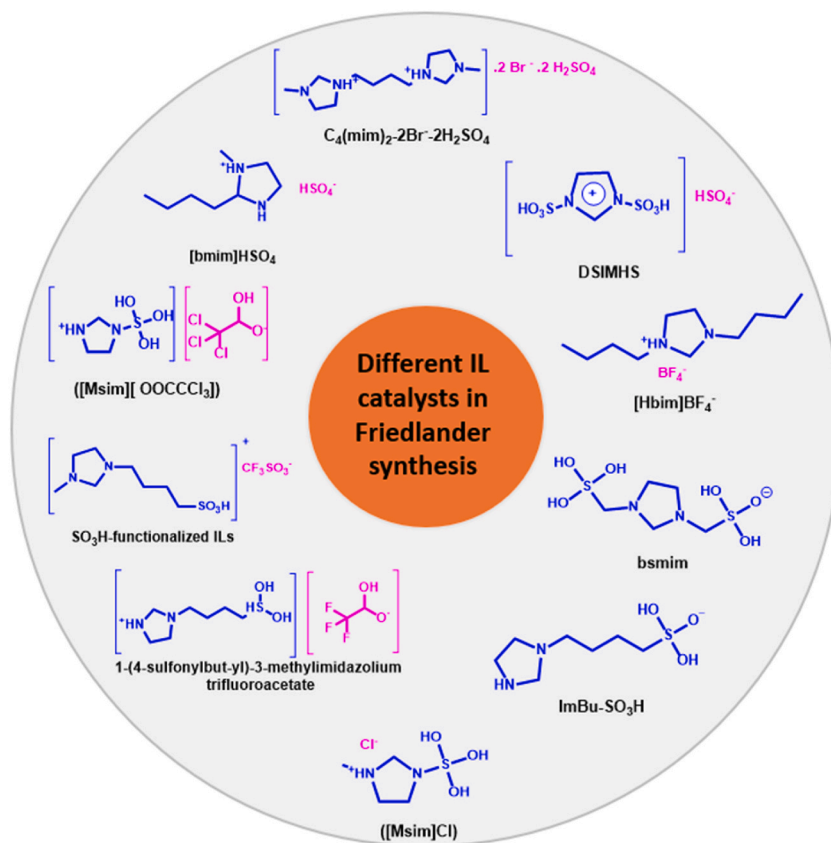


Fig. 4. Various ionic liquids used in Friedländer synthesis.

1.1.2. Ammonium-based cations

Kermani et al. [45] developed a rapid method for the Friedländer synthesis using molten triethylammonium hydrogen sulfate $[\text{Et}_3\text{NH}][\text{HSO}_4]$, a nonvolatile and non-corrosive ionic liquid that acted as a Brønsted acid catalyst under solvent-free conditions at 100°C . This method was effective for both cyclic and acyclic ketones.

This demonstrates their potential as sustainable alternatives in catalytic processes, evidenced by their high yields, recyclability, and the diverse conditions under which they operate effectively.

1.2. Metal triflates

Metal triflates, salts of trifluoromethanesulfonic acid, have exhibited high catalytic activity and stability. These catalysts are known for their high Lewis acidity, low nucleophilicity, and thermal stability, making them ideal for various organic reactions under mild conditions including Friedländer synthesis. They are derived from triflic acid (HOTf) or triflimide (HNTf_2) [46]. Based on the cations

used the metal triflates are categorized as (Fig. 5).

1.2.1. Gadolinium triflate

Wu et al. [47] reported the use of gadolinium triflate, $\text{Gd}(\text{OTf})_3$ in the ionic liquid 1-n-butyl-3-methyl-imidazolium hexafluorophosphate ($[\text{Bmim}][\text{PF}_6]$) for the Friedländer condensation. The reagent $\text{Gd}(\text{OTf})_3$ is an inexpensive, non-toxic, and moisture-stable Lewis acid. The reaction was carried at 60 °C for 15 min, achieving yields exceeding 90 %.

1.2.2. Bismuth triflate

Yadav et al. [48] demonstrated the condensation of 2-aminoaryl ketones and α -methylene ketones using 5 mol% of bismuth triflate in ethanol at room temperature (Scheme 2), yielding high product quantities. Among the various metal triflates studied for this transformation, including $\text{Cu}(\text{OTf})_2$, $\text{Yb}(\text{OTf})_3$, $\text{In}(\text{OTf})_3$ and $\text{Ce}(\text{OTf})_3$, bismuth(III) triflate $\text{Bi}(\text{OTf})_3$ was found to be the most effective in terms of conversion and reaction rates.

1.2.3. Yttrium triflate

Surya et al. [49] used the reagent Yttrium triflate, $\text{Y}(\text{OTf})_3$ as it is water-tolerable, reusable, commercially available, and significantly less expensive than $\text{Sc}(\text{OTf})_3$. In the presence of a catalytic amount of $\text{Y}(\text{OTf})_3$, the reaction was carried out in acetonitrile at room temperature, affording polysubstituted quinolines in excellent yields.

1.2.4. Zirconium triflate

Kolvari et al. [50] used Zirconium triflate, $\text{Zr}(\text{OTf})_4$ as a catalyst for the Friedländer condensation. It is easily available, less toxic, and operable under environmentally friendly conditions. The reaction resulted in a high efficiency of over 88 % yield when an ethanol and water mixture was used as a solvent, and stirred at 60 °C for 0.5–2 h.

1.2.5. Zinc triflate

Zinc triflate has attracted attention as it is inexpensive and readily prepared from commercially available trifluoromethanesulfonic acid and zinc carbonate in methanol. Lekhok and coworkers [51] used Zinc triflate, $\text{Zn}(\text{OTf})_3$ along with Indium triflate, $\text{In}(\text{OTf})_3$, under microwave irradiation and solvent-free conditions at 80 °C, achieving effective catalysis for the same condensation reaction, which could be recovered and reused efficiently.

1.2.6. Indium triflate

Tanwar et al. [52] analyzed the catalytic activity of various metal halides, tetrafluoroborates, perchlorates, and triflates. As a result, Indium triflate, $\text{In}(\text{OTf})_3$, emerged as the most effective catalyst under solvent-free conditions, yielding the desired quinolines in 75–92 %. Additionally, $\text{In}(\text{OTf})_3$ was considered based on its lower cost compared to that of $\text{Er}(\text{OTf})_3$ and $\text{Sc}(\text{OTf})_3$.

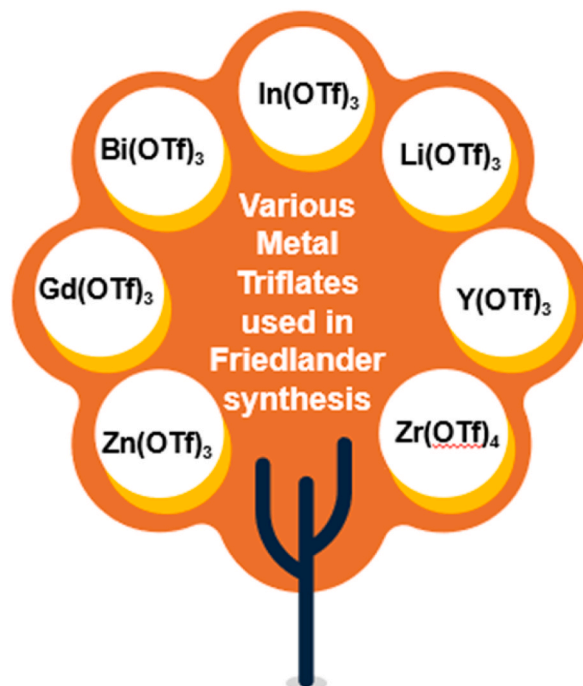
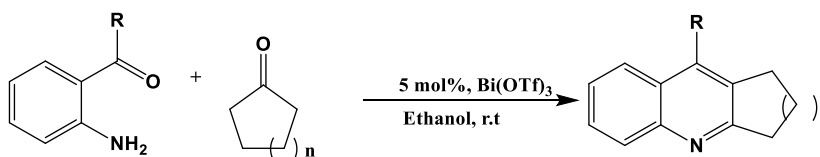


Fig. 5. Various metal triflates used in Friedländer synthesis.



Scheme 2. Y(OTf)₃ catalyzed synthesis of quinolines.

1.2.7. Lithium triflate

Recently, lithium triflate has emerged as a highly efficient, mild, reusable neutral Lewis acid catalyst. Atar et al. [53] presented a protocol using lithium triflate as a catalyst under solvent-free conditions at 80 °C, with the catalyst being easily recoverable and moisture-resistant.

1.3. Metal-organic frameworks (MOFs)

Metal Organic Frameworks are crystalline materials with a three-dimensional (3D) structure and low density, made of clusters or metal ions coordinated to rigid and multipodal organic ligands [54]. MOFs exhibit a higher level of activation as well as greater thermal and chemical stability than other classes of porous materials [55,56]. Consequently, MOFs have emerged as promising heterogeneous catalysts for Friedländer synthesis due to their tunable properties, high surface area, and diverse active sites [57].

1.3.1. Copper-based MOFs

Pérez-Mayoral [58] et al., investigated the catalytic performance of [Cu₃(BTC)₂] (BTC = benzene-1,3,5-tricarboxylate) and revealed that the presence of Lewis acid sites at the metallic center, along with the concerted effect of adjacent Cu²⁺ sites, contributed to the superior performance of [Cu₃(BTC)₂] compared to other molecular sieves, achieving an 80 % yield of quinoline in 2 h at 353 K. Tessa Whitaker et al. [59] also explored the use of CuBTC for the Friedländer synthesis of 3-acetyl-2-methyl-4-phenylquinoline, demonstrating high reusability and significant catalytic activity at 100 °C for 2 h. They further investigated the characteristics of the synthesized Basolite and the commercially available Basolite. Vivekanand Sharma [60] et al. synthesized a thermally robust Cu (II)-based MOF{[Cu₆(L)₃(H₂O)₆](14DMF)(9H₂O)}_n (Fig. 6(b–d)) with dual functionalities of Lewis acid and basic sites, using a bent amino-functionalized tetracarboxylate ligand (Fig. 6(a)) and Cu(NO₃)₂ under solvothermal conditions. The Lewis acidity of these cages increased due to the vacant coordination positions on copper. Hence, this compound was explored as a catalyst for various chemical reactions including cross-dehydrogenative coupling and Friedländer reactions. This MOF achieved high yields within 8 h under solvent-free conditions at 80 °C.

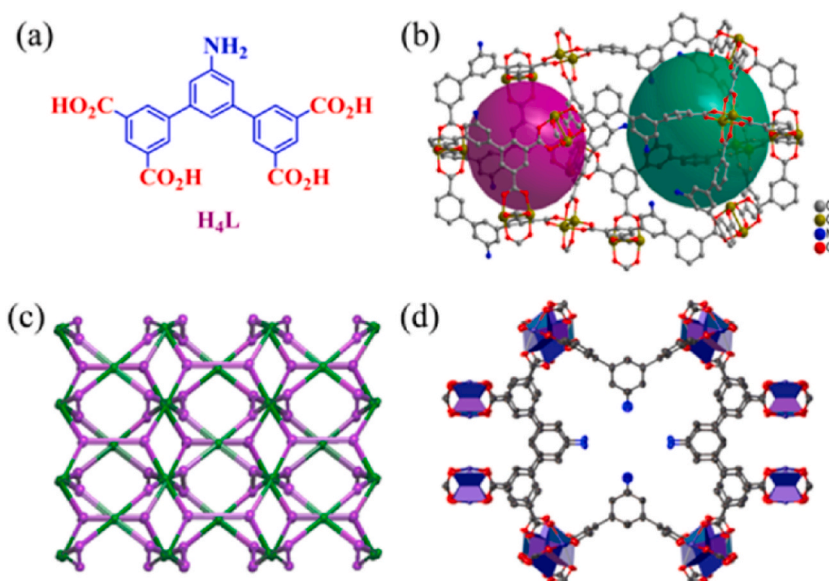


Fig. 6. synthesis of robust MOF{[Cu₆(L)₃(H₂O)₆](14DMF)(9H₂O)}_n (1) from ligand, H₄L(F), and Cu(NO₃)₂ under solvothermal conditions. (a) Ligand H₄L (b) Nanospherical cages in 1. (c) mfj topology in 1 (closely packed by nanospherical cages). (d) Replete number of open metal sites (polyhedra).

1.3.2. Hafnium-based MOFs

Ghosh et al. [61] reported the synthesis and characterization of UiO-66(Hf)-(NHCOMe)₂ (Fig. 7(a–c)) and its activated form. The central metal ion, Hf(IV), is coordinated with four μ^3 -O and four μ^3 -OH sites, as well as six 2,5-diacetamidoterephthalate linkers. The catalytic behavior of the activated form was tested in the Friedländer condensation of 2-aminoacetophenone with acetylacetone at 80 °C, yielding the desired product quantitatively within 3 h and highlighting the potential of Hf-UiO-66 as an efficient catalyst under mild conditions. Aniruddha Das et al. [62] prepared a hydrazine-functionalized Hf-UiO-66 MOF, which exhibited high chemical stability and was used as a solid heterogeneous catalyst. This MOF catalyst is composed of [Hf₆O₄(OH)₄]¹²⁺ units, with SBUs connected by twelve BDC-N₂H₃ linkers. The framework structure of the catalyst features larger octahedral and smaller tetrahedral porous cages. The catalyst produced a 95 % yield of 3-acetyl-2,4-dimethylquinoline at 100 °C in 20 h, demonstrating a broad substrate scope, excellent stability, and recyclability.

1.3.4. Silica based MOFs

Isaeva et al. [64] prepared a novel hybrid material using HKUST-1, a metal-organic framework, and mesoporous silica (MMS). This catalyst, featuring Lewis and Brønsted acid sites, effectively catalyzed the Friedländer reaction at 80 °C under reflux conditions. With a catalyst amount of 0.08 equivalents and a reaction time of 10 min, it delivered a yield of 82 %.

1.3.3. Zinc-based MOFs

Agarwal et al. [63] synthesized a novel two-dimensional, tetragonal porous MOF, {[Zn₂(TBIB)₂(HTCPB)₂].9DMF.19H₂O)}_n (Fig. 8 (a–d)), employing TBIB and H₃TCPB. a carboxylate based Zn-MOF (1). The catalytic activity is due to the presence of free protonated COOH groups in the polymer, which are decorated on the surface of the pores. This MOF demonstrated high efficiency in catalyzing the Friedländer reaction at 85 °C, with significant catalytic activity over 24 h.

1.4. Nanocatalysts

Magnetic nanoparticles (MNPs) are reusable, economical, eco-friendly, and possess many active sites, large pores, high stability, and good selectivity. The use of MNPs as a solid support for the immobilization of ionic liquids has attracted many researchers for various organic transformations [65]. The properties of nanoparticles are considerably diverse compared to their bulk counterparts due to their high surface-to-volume ratio and coordination positions, which furnish several active sites per unit area [66].

1.4.1. Metal oxide magnetic nanoparticles

1.4.1.1. Fe₃O₄@SiO₂ related nanocatalyst. Nasseri et al. [67] introduced sulfamic acid-supported Fe₃O₄@SiO₂ nanoparticles as a solid acid catalyst with large density of sulfamic acid groups for quinoline synthesis. For the preparation of the catalyst, Fe₃O₄@SiO₂ bonded N-propyl diethylene tetra sulfamic acid MNPs were washed with methanol and diethyl ether and then dried at room temperature to give Fe₃O₄@SiO₂@PDETS (Fig. 9 (a)). Then, the Friedländer reaction was carried out under reflux at 110 °C with 0.02 equivalents of catalyst, which resulted in a high yield of 83 % in 120 min.

1.4.1.2. Fe₃O₄@SiO₂-imid PMA. Esmaeilpour et al. [68] utilized Fe₃O₄@SiO₂-imid PMAⁿ and Fe₃O₄@SiO₂-imid PMA^b (Fig. 9 (b)) nanoparticles for poly-substituted quinoline synthesis. To functionalize the catalyst, Fe₃O₄@SiO₂ was refluxed with 3-chlorotriethoxypropylsilane and imidazole in p-xylene, followed by the incorporation of H₃PMO₁₂O₄₀ (PMAⁿ) under a nitrogen atmosphere. With varying catalyst amounts (0.02 and 0.03 equivalents), the reaction was carried out at 70 °C under reflux, with reaction times of 30 and 50 min, respectively, yielding 96 % and 89 % product.

1.4.1.3. Fe₃O₄@SiO₂-SO₃H. A highly active and reusable nanocatalyst, nano Fe₃O₄@SiO₂-SO₃H (Fig. 9(c)) was synthesized by Beyki

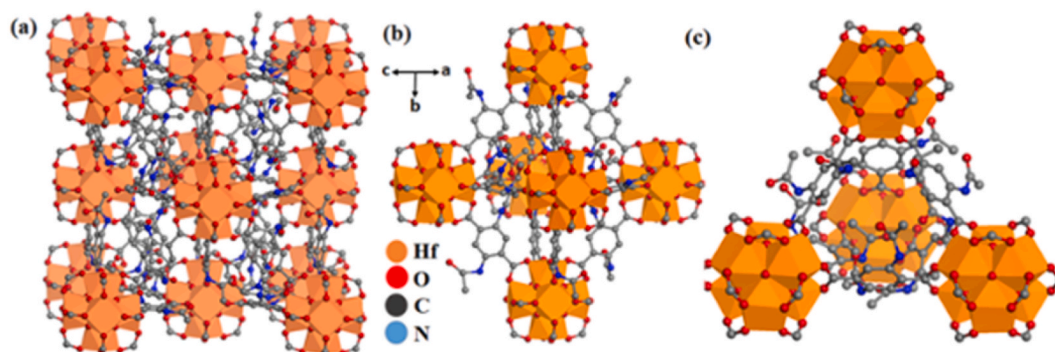


Fig. 7. (a) Structural representation of the framework UiO-66(Hf)-(NHCOMe)₂ (1) (b) octahedral and (c) tetrahedral cages of 1.

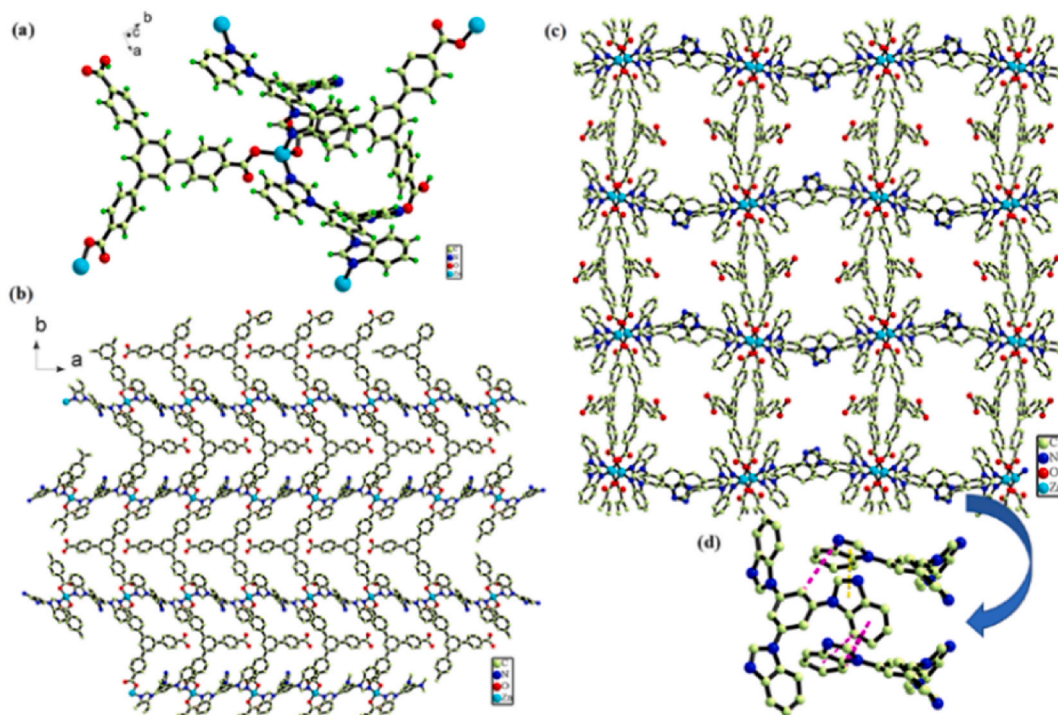


Fig. 8. (a) Coordination environment around Zn(II) metal center, (b) layered structure of the polymer, (c) 3D structure and 1D pore formation through supramolecular interactions between layers, (d) interactions between TBIB of two different layers.

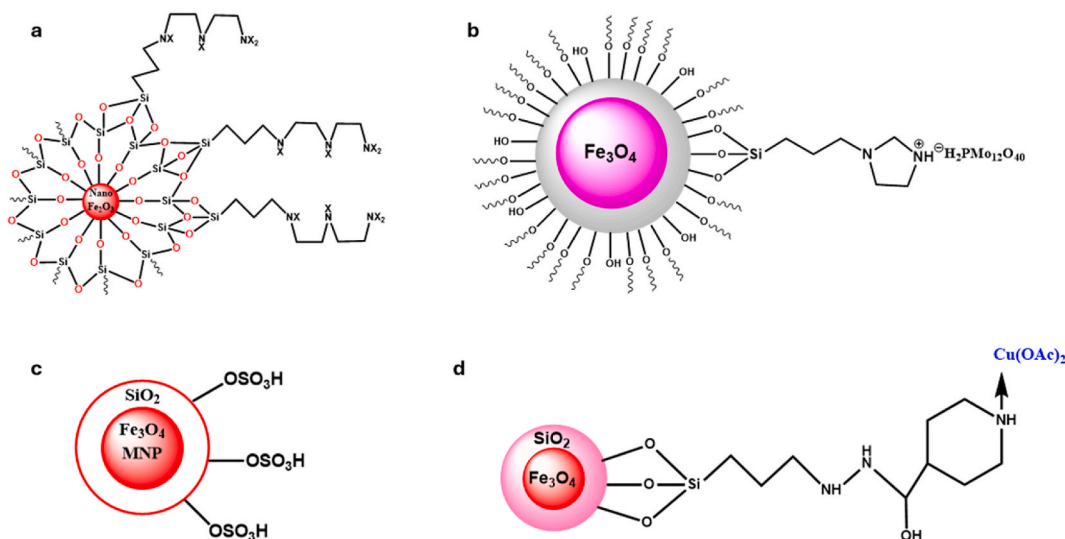


Fig. 9. schematic diagram of a. Fe₃O₄@SiO₂ bonded N-propyl diethylene tetrasulfamic acid MNPs [Fe₃O₄@SiO₂@PD TSA], b. Fe₃O₄@SiO₂-imid-PMAⁿ, c. Fe₃O₄@SiO₂-SO₃H, and d. Fe₃O₄@SiO₂/ISN/Cu(II) nanocatalysts.

et al. [69]. The chemical stability of the magnetite nanoparticles was successfully improved by the suitable deposition of silica onto the nanoparticles' surface through the ammonia-catalyzed hydrolysis of tetraethylorthosilicate (TEOS). This nanocatalyst turned out to be an excellent catalyst for the Friedländer reaction. With 0.05 equivalents of catalyst, the reaction was carried out at 110 °C for 45 min, achieving a yield of 91 %.

1.4.1.4. Fe₃O₄@SiO₂/isoniazid/Cu(II). A new nanocatalyst (Fe₃O₄@SiO₂/ISN/Cu(II)) (Fig. 9(d)) was synthesized via functionalization of silica-coated magnetic nanoparticles with Cu(OAc)₂ by Lotfi et al. [70]. This Cu(OAc)₂ functionalized nanocatalyst is used for

ethanol-mediated quinoline synthesis at 60 °C under reflux. Operating with 0.07 equivalents of catalyst, the reaction yielded over 90 % in just 2 min.

1.4.1.5. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES-TFA}$. Jafarzadeh et al. [71] developed a core-shell nanocatalyst, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES-TFA}$ (Fig. 10(a)), synthesized via chemical co-precipitation. This catalyst, immobilized with trifluoroacetic acid, exhibited excellent performance in the solvent-free Friedländer quinoline synthesis at 100 °C. With a catalyst amount of 0.2 equivalents, reflux energy source, and a reaction time of 5 min, it achieved a high yield of 96 %.

1.4.1.6. ZnCl_2 supported $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell. Soleimani et al. [72] reported on $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{ZnCl}_2$ (Fig. 10(c)) as a magnetic nanocatalyst for the Friedländer synthesis of quinolines under solvent-free conditions at 60 °C. The nanocatalyst was synthesized via co-precipitation of Fe_3O_4 magnetic nanoparticles (MNPs), followed by surface immobilization of ZnCl_2 through electronic interaction between Zn^{2+} and surface oxide species. The catalyst exhibited superior activity and reusability compared to homogeneous ZnCl_2 , delivering a yield of 95 % after 2 h of reaction time.

1.4.1.7. ZrO_2 -supported Fe_3O_4 MNPs. Zirconia is a well-known solid acid catalyst. Hejazi et al. [73] synthesized $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ magnetic nanoparticles by dispersing ZrO_2 in water, followed by the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ under an argon atmosphere. Later, this recyclable catalyst was used for quinoline synthesis in ethanol at 60 °C under reflux conditions, achieving a high yield of 92 % in just 25 min.

1.4.1.8. $\text{ZrO}_2/\text{SO}_4^{2-}/\text{Cu}$. Nasser et al. [74] developed a method utilizing copper-incorporated sulfated zirconium oxide ($\text{ZrO}_2\text{-SO}_4^{2-}/\text{Cu}$) (Fig. 10(d)) as a recyclable nanocatalyst for the Friedländer synthesis of quinolines. The catalyst operated efficiently in water at room temperature, showcasing a yield of 97 % after 45 min of reaction time.

1.4.1.9. CuFe_2O_4 nanoparticles. Seyed Baghbanian et al. [75] developed magnetically separable CuFe_2O_4 nanoparticles as a reusable catalyst for synthesizing quinoline and quinazoline derivatives in aqueous media. CuFe_2O_4 nanoparticles were synthesized by thermal decomposition of $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ in the presence of NaOH . Operated under reflux at 80 °C, the catalyst exhibited high catalytic activity (92 %) and promising green chemistry potential due to its facile recovery and recyclability without compromising efficiency.

1.4.1.10. Fe_2O_3 nanoparticles. Mehdi Sheykhani et al. [76] introduced a highly efficient and green system using magnetic nanoparticle-supported propylsulfamic acid ($\text{Fe}_2\text{O}_3\text{-HAp-(CH}_2\text{)}_3\text{-NHSO}_3\text{H}$) (Fig. 10(b)) as a heterogeneous acid catalyst. Under solvent-free conditions at room temperature, the catalyst achieved a high yield of 91 % in a short reaction time of 3.5 min. The catalyst's magnetic recoverability and stability over multiple cycles underscored its practical utility in organic synthesis.

1.4.1.11. SiO_2 nanoparticles. Hasaninejad et al. [77] reported on silica nanoparticles catalyzing the Friedländer hetero-annulation between 2-aminoaryl ketones and carbonyl compounds under microwave irradiation at 100 °C. SiO_2 is an acidic oxide. The reactions were carried out using different metal oxides such as MgO , CaO and SiO_2 , and it was found that the yields are better with silica.

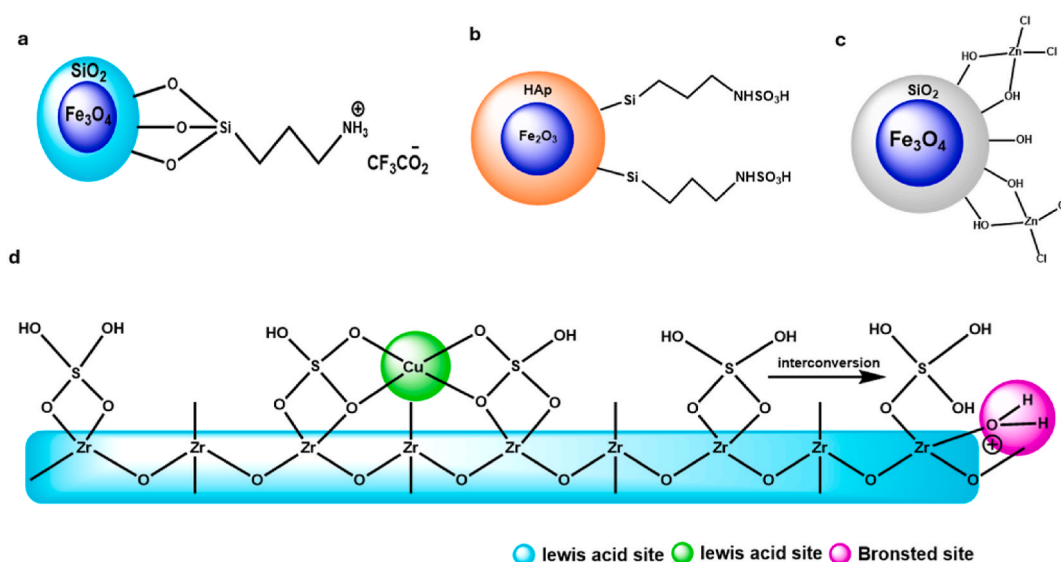


Fig. 10. schematic diagram of a. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{-TFA}$ nanocatalyst, b. $\text{Fe}_2\text{O}_3@\text{HAp-Si-(CH}_2\text{)}_3\text{-NHSO}_3\text{H}$, c. $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{ZnCl}_2$ core-shell nanoparticle, d. $\text{ZrO}_2/\text{SO}_4^{2-}/\text{Cu}$ and its potential catalytic sites.

The catalyst provided high yields (93 %) of quinoline derivatives with short reaction times and exhibited robust recyclability up to fourteen cycles without loss of activity, highlighting its efficiency and environmental benefits.

1.4.1.12. Titania. Bandyopadhyay et al. [78] employed TiO_2 nanoparticles of varying sizes (16 nm–1000 nm) as heterogeneous catalysts for quinoline synthesis at 80 °C. TiO_2 is more stable, abundant, non-toxic, and economical. The researchers synthesized TiO_2 materials of nanosize using a modified sol–gel method. It was revealed that as the particle size decreased from 1000 nm to 16 nm, there was a gradual increase in the yield of the quinoline derivatives. Using 5 equivalents of catalyst, the reaction time was 35 min, achieving a yield of 89 %.

1.4.1.13. Nano ZnO flakes. Sarvari et al. [79] investigated nano-flake ZnO as a catalyst for regiospecific quinoline synthesis under solvent-free conditions at 100 °C. Commercial ZnO was purchased, while nanoflake ZnO (NF-ZnO) and nanoparticle ZnO (NP-ZnO) were synthesized in-house. NF-ZnO was synthesized by dissolving $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and urea were in waterrefluxing the mixture, and subsequently calcining it. NP-ZnO was synthesized by dissolving $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in ethanol, adding oxalic acid dehydrate, and calcining the solid. With catalyst amounts of 0.008 equivalents, CM-ZnO and NF-ZnO achieved yields of 90 % and 98 %, respectively, with reaction times of 11 and 4 min.

1.4.1.14. NiO nanoparticles. Palakshi Reddy et al. [80] investigated NiO nanoparticles as efficient catalysts for Friedländer synthesis in ethanol under reflux conditions. The catalyst was prepared from the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Operating at 80 °C, the catalyst achieved a high yield (95 %) of quinolines in a short reaction time of 2.5 min, emphasizing its potential for rapid and sustainable organic synthesis.

1.4.1.15. Nano Al_2O_3 . Sadjadi et al. [81] employed nanocrystalline aluminum oxide in chloroform for quinoline synthesis via condensation reactions, achieving high yields under reflux conditions in just 3 min. The catalyst exhibited ease of separation and reusability, making it practical for organic synthesis. Al_2O_3 is usually prepared by decomposition of a variety of aluminium salts or aluminium hydroxide.

1.4.2. Trimetallic oxide magnetic nanoparticles

1.4.2.1. Fe-Cr-Ni oxide alloy nano belts. Kazemnejadi et al. [82] utilized magnetic Fe–Cr–Ni oxide alloy nano-belts (Fig. 11) derived from stainless steel screw decomposition as recyclable catalysts for quinoline synthesis in water at room temperature under reflux. The catalyst showed good efficiency, yielding 82 % after 85 min.

1.4.2.2. Trimetallic oxide NP (Cu/Cr/Ni). Mahmoudi et al. [83] explored Cu/Cr/Ni nanoparticles (Fig. 11) synthesized from *Echinops persicus* extract, which involved the simultaneous reduction of precursor salts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with the plant extract. The resulting catalyst demonstrated effective catalysis under reflux conditions at 100 °C, achieving a yield of 95 % over 80 min.

1.4.3. Solid acid nano catalyst

Teimouri et al. [84] developed a simple and efficient method for synthesizing poly-substituted quinolines using various solid acid catalysts, including Montmorillonite K-10, zeolite, and nano-crystalline sulfated zirconia (SZ) in ethanol under reflux conditions. These catalysts facilitated the Friedländer condensation of 2-aminoarylketones with carbonyl compounds and β -keto esters, offering advantages such as short reaction times, mild conditions, and easy work-up. The catalysts were recyclable with no significant loss of efficiency, achieving yields of 75 %, 83 %, and 89 % over varying reaction times.

1.4.4. Li^+ modified nanoporous Na^+ -MMT

Azimi et al. [85] described a novel approach using Li^+ -modified nanoporous Na^+ -montmorillonite for the solvent-free synthesis of quinolines and polycyclic quinolines via Friedländer annulation. Operating at 100 °C without solvent, the catalyst exhibited excellent catalytic activity, yielding quinoline derivatives with high efficiency (96 %) in 0.5–2 h. The method highlighted the catalyst's reusability without loss of efficacy, offering a practical and environmentally friendly route to these valuable compounds.

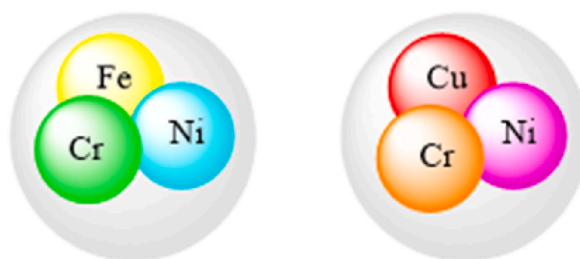


Fig. 11. Trimetallic nanocatalysts used in the Friedländer synthesis.

1.4.5. Aluminosilicate AIKIT-5

Chauhan et al. [86] utilized a nanoporous aluminosilicate catalyst (AIKIT-5) to achieve 90 % yield of quinoline derivatives via Friedländer condensation in ethanol at 80 °C. The catalyst's high surface area, large pore volume, and strong acidity enhanced selectivity and efficiency while allowing for recyclability. Among the tested AIKIT-5 variants, AIKIT-5(10) exhibited the best performance due to its superior acidity and structural properties.

1.4.6. (BSPY)HSO₄/MCM-41

M. Alibeik et al. [87] synthesized nanosized MCM-41 supported with n-butanesulfonic acid pyridinium hydrogensulfate by the sol-gel method, for the Friedländer synthesis of quinolines under solvent-free conditions at 100 °C. The catalyst demonstrated high efficiency (91 % yield) and stability.

1.4.7. Nickel nanoparticles

Angajala et al. [88] developed a green, and solvent-free protocol for synthesizing polysubstituted quinolines using biofabricated nickel nanoparticles derived from *Aegle marmelos* Correa aqueous leaf extract. The catalyst exhibited high catalytic efficacy (85–96 % yield) without the need for co-catalysts, operating at 75 °C.

1.4.8. PVA/Fe(NO₃)₃

Ziyadi et al. [89] utilized PVA/Fe(NO₃)₃ nanofiber mats as recyclable heterogeneous catalysts for Friedländer condensation in toluene at 80 °C. The catalyst showed high stability over five reuse cycles, achieving a yield of 75 % in 6–7 h.

1.4.9. Double perovskite (Bi_{1.97}Eu_{0.03}MoO₆)

Dharmana et al. [90] utilized a double perovskite catalyst, Bi_{1.97}Eu_{0.03}MoO₆, in water at 45–55 °C for the Friedländer synthesis, obtaining good yields of quinolines. This catalyst, prepared via a semi-sol-gel process by dissolving Bi₂O₃ and Eu₂O₃ in weak nitric acid, demonstrated efficient performance with a yield of 89 % after 45 min.

1.4.10. MNP@SiO₂-Pr-AP-tribromide

Kharazmi et al. [91] developed a highly active ionic liquid nano-magnetic pyridinium-tribromide catalyst, MNP@SiO₂-Pr-AP--Tribromide (Fig. 12), for synthesizing quinolines under reflux conditions with ethanol, achieving a 95 % yield in just 3 min. The catalyst's efficiency is attributed to its Br[−] content. The process involved synthesizing Fe₃O₄ nanoparticles, coating them with silica, and functionalizing them to produce the final catalyst.

1.4.11. Carbon aerogels

Godino-Ojer et al. [92] demonstrated the use of metal-free nanocatalysts based on carbon aerogels for the selective synthesis of quinoline via Friedländer reaction. Carbon aerogels were used under neat conditions under microwave irradiation at 323K for 240 min, yielding 90 % of the products.

1.5. Polymers

1.5.1. Poly(4-vinylpyridinium butane sulfonic acid) hydrogen sulfate

Kiasat et al. [93] reported the use of poly(4-vinylpyridinium butane sulfonic acid) hydrogen sulfate (P(4VPBSA)HSO₄) (Fig. 13) as an efficient dual acidic catalyst for the one-pot preparation of substituted quinolines under solvent-free conditions. The reaction, conducted at 110 °C for 40 min, resulted in a 91 % yield. This catalyst offers several advantages, including reusability, a facile work-up procedure, eco-friendly reaction conditions, short reaction time, and high product yields.

1.5.2. Sulfuric acid modified polyethylene glycol

Hasaninejad [94] et al. explored sulfuric acid-modified polyethylene glycol 6000 (PEG-OSO₃H) as an eco-friendly polymeric catalyst for the Friedländer synthesis of polysubstituted quinolines. The o-aminoarylketones and cyclic or acyclic ketones reacted with PEG-OSO₃H without any solvent under microwave irradiation at 130 °C for 5 min, achieving a 90 % yield. This method is notable for its

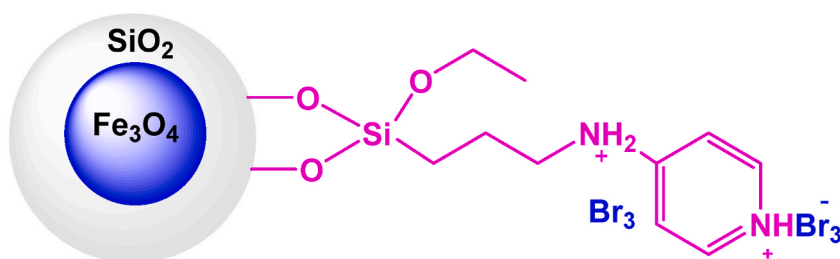


Fig. 12. Schematic diagram of MNP@SiO₂-Pr-AP-Tribromide nanocatalyst.

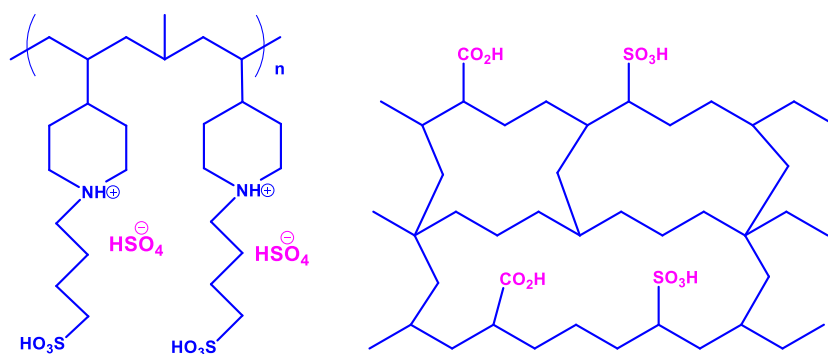


Fig. 13. Structure of P(4-VPBSA) catalyst and recyclable cross-linked AMPS-co-AA.

short reaction times and excellent yields. Zhang et al. [95] also demonstrated that 2-aminoarylketones undergo smooth condensation with α -methylene ketones in the presence of 10 mol% poly(ethylene glycol)-supported sulfonic acid (PEG-SO₃H) with water as solvent under reflux at 60 °C for 20 min, resulting in a 95 % yield. Another work was reported by same author [96] employing PEG 4000 under microwave irradiation with 2–3 drops of CH₂Cl₂ solvent at 110 °C for 5 min, producing 93 % yield. This polymer-supported synthesis method offered excellent yield and purity with a simple work-up procedure. Another efficient method for quinoline synthesis using PEG-SO₃H was developed by Nasseri et al. [97], showing high yields (75–95 %) and high purity of products, using PEG-SO₃H with DCM as the solvent under reflux for 50 min.

1.5.3. Cellulose sulfuric acid or starch sulfuric acid

Shabaani et al. [98] reported the use of sulfonated cellulose and starch as new catalysts for the Friedländer synthesis of quinolines. These catalysts, used without any solvent, were effective at 100 °C, achieving a 95 % yield in 30–40 min. This method provides high yields within a short reaction time under solvent-free conditions.

1.5.4. Chitosan-SO₃H

Subba et al. [99] has used chitosan-SO₃H, a biodegradable polymer for the synthesis of polysubstituted quinolines. It is used with ethanol solvent and, at reflux condition, provides high yields of over 90 % in a period of 20 min.

1.5.5. Nafion NR50

Chan et al. [100] described a green synthetic route for Friedländer quinoline synthesis using reusable Nafion NR50 which is a perfluorosulfonic acid. Nafion resin is primarily used as a strong solid acid with high thermal stability and chemical resistance. The reaction proceeds with reactants, and Nafion NR50 irradiated under microwave radiation (200 °C) with ethanol as the solvent for 1 h yielded 95 % of products. This method supports a high generality of functional groups and provides the desired quinolines in good to excellent yields.

1.5.6. APTPOL60

Bennardi et al. [101] proposed a new, efficient, and green methodology for obtaining quinolines using tungstophosphoric acid included in a polymeric matrix of polyacrylamide (APTPOL60). Using APTPOL60 with ethanol as the solvent, the reaction was heated under reflux conditions for 24 h, resulting in a 96 % yield. This approach demonstrated that the catalyst efficiency is not compromised after successive uses, with no leaching observed.

1.5.7. Poly(AMPS-co-AA)

Maleki et al. [102] synthesized Poly(AMPS-co-AA) (Fig. 13) by adding Cross-linked N,N-methylenebis-acrylamide to a mixture of 2-acrylamido-2-methylpropanesulfonic acid and acrylic acid. It is used for its efficiency in the synthesis of quinolines. The condensation reaction of α -methylene carbonyl compounds and o-aminoaryl ketones was facilitated without any solvent, heated to 110 °C for 20 min, achieving a 70 % yield.

1.6. Heteropoly acids

Phosphotungstic acid (H₃PW₁₂O₄₀) was used by Minoos Dabiri et al. [103] as a productive and recyclable catalyst for the Friedländer condensation of 2-aminoarylketone with carbonyl compounds, which produced polysubstituted quinolines. Conventional heating in a solvent-free environment was used to generate this reaction. Using 0.04 g of phosphotungstic acid at 80 °C for 2 min, a yield of 91 % was obtained.

Ezzat Rafiee et al. [104] explored distinct kinds of supported Keggin-type heteropoly acids (HPAs) on materials with varied textural characteristics for the Friedländer reaction to produce quinoline derivatives. On optimization, tungstophosphoric acid supported on silica (PW/SiO₂), KSF (PW/KSF), and activated carbon (PW/C) showed excellent yields and quick reaction times as catalysts. Each

catalyst was used in a 0.2 g without any solvent and heated to 100 °C. The reaction times were 10 min for PW/SiO₂ and PW/KSF, and 20 min for PW/C, achieving yields of 97 %, 74 %, and 92 %, respectively. These catalysts were reusable, maintaining significant catalytic activity after multiple runs.

J.S. Yadav et al. [105] reported the smooth condensation of o-aminoaryl ketones with α -methylene ketones using heteropoly acid, silver phosphotungstate (Ag₃PW₁₂O₄₀) as a catalyst. Under mild conditions, this catalyst produced polysubstituted quinolines with excellent yields and high selectivity. The catalyst, used in a 0.2 mmol amount with ethanol as the solvent, was heated under reflux for 6 h, yielding 81 %. Notably, the catalyst can be recovered by simple filtration and recycled for subsequent reactions.

Another keggin type heteropoly compound (HPCs) was reported by Rafiee et al. [106]. They investigated various types of cesium partially substituted phosphotungstate (Cs_xH_{3-x}PW₁₂O₄₀, x = 0 to 2.5) in the synthesis of quinoline. Cs_{2.5}H_{0.5}PW₁₂O₄₀, was found to be the efficient catalyst due to its more number of acid sites on the surface (surface acidity). The reaction was carried out under solvent-free conditions at 100 °C for 20 min, achieving a yield of 96 %.

1.7. Deep eutectic solvents (DES)

Deep eutectic solvents (DESs) are novel and more eco-friendly alternatives to ionic liquids (ILs), prepared by combining specific components that form hydrogen bonds between them. These green solvents possess unique properties, making them reliable and safe substitutes for ILs and conventional organic solvents [107]. Polysubstituted quinolines were synthesized by the Friedländer annulation reaction of 2-aminobenzophenone with ketones, mediated by choline-based DESs [108]. Among these, choline chloride-zinc chloride (ChCl-ZnCl₂) was identified as the most effective catalyst, achieving excellent yields. The reaction also demonstrated regiospecificity under basic choline hydroxide (ChOH) medium, albeit with moderate yield. These DESs serve both as solvents and catalysts, and can be recycled, offering mild reaction conditions, simple work-up procedures, and high product yields. Specifically, 2 equivalents of ChCl-ZnCl₂ and 30 equivalents of ChOH were utilized. Reactions conducted without any solvent and with water at 80 °C for 3.5 h and 4.3 h yielded 91 %. Bafti et al. [109] employed dimethylurea/citric acid as an effective method for synthesizing quinolines, aryl-4,5-diphenyl-1H-imidazoles, and bis(indolyl)methanes, using DES as both a dual catalyst and a green reaction medium. This technology is environmentally benign and efficient due to the high activity of the DES and its ease of recovery and reusability. Using 1 equivalent of the DES without any solvent, the reaction was heated to 100 °C for 25 min, achieving an 88 % yield.

1.8. Inorganic acids and salts

1.8.1. Neodymium(III) nitrate hexahydrate

The Friedländer synthesis of quinolines was efficiently catalyzed by neodymium (III) nitrate hexahydrate [Nd(NO₃)₃·6H₂O, 5 mol %] [110]. Using 5 mol% of the catalyst and ethanol as solvent at room temperature, this catalyst achieved yields ranging from 62 % to 94 %, with a maximum yield of 94 % observed in the reaction between o-amino arylketone and cyclic or acyclic ketones.

1.8.2. Boron hydrogen sulfate (BHS)

Substituted quinolines were synthesized using catalytic amounts of boron hydrogen sulfate B(HSO₄)₃ [111] under solvent-free conditions. This method offered high yield, short reaction time, low catalyst cost, and green conditions. When BHS was used at 5 mol% and heated to 90 °C for 38 min, it yielded 94 % of the products.

1.8.3. Gold(III)-catalyzed synthesis

Arcadi et al. [112] explained a novel method for achieving the Friedländer synthesis of quinolines by the sequential condensation of o-amino aromatic carbonyls and ketones with active methylene groups, which is catalyzed by gold(III). An 89 % yield was achieved by adding 2.5 mol% of NaAuCl₄·2H₂O to ethanol along with the reactants at room temperature and stirring for 6 h.

1.8.4. Tin(II) chloride dihydrate (SnCl₂·2H₂O)

Arumugam et al. [113] synthesized a variety of polysubstituted quinolines under solvent-free conditions using tin(II) chloride dihydrate. The reactions proceeded smoothly with SnCl₂·2H₂O, at room temperature, achieving high yields of around 98 % in a short time of 30 min, with excellent purity.

1.8.5. Molecular iodine

Wu et al. [114] presented a mild and efficient route for synthesizing quinolines and polycyclic quinolines using molecular iodine (1 mol%) as a catalyst and ethanol as the solvent at room temperature for 16 h, the reaction achieved a 93 % yield.

1.8.6. Cyanuric chloride

Bandgar et al. [115] reported an eco-friendly route for the synthesis of quinolines and polycyclic quinolines using cyanuric chloride under aqueous conditions. A 20 mol% of cyanuric chloride was used with water as the solvent. The reactants were stirred at room temperature for 16 h, achieving a yield of 93 %.

1.8.7. CuSO₄·5H₂O

Ravindra et al. [116] reported an efficient method for synthesizing substituted quinolines via the condensation of o-aminoaryl carbonyls with ketones in the presence of CuSO₄·5H₂O as a catalyst. The reaction was conducted at room temperature with ethanol as

the solvent, resulting in an 80 % yield after 3 h. All synthesized compounds were characterized and evaluated for antibacterial activity.

1.8.8. Niobium (V) chloride (NbCl_5) in glycerol

Nasseri et al. [117] utilized NbCl_5 in glycerol for quinoline synthesis, achieving high yields (76–98 %) under mild conditions. The reaction with 2-amino-5-chlorobenzophenone required longer times compared to 2-aminobenzophenone, while cyclic diketones reacted faster than their open-chain analogs.

1.8.9. $\text{Zr}(\text{NO}_3)_4$ and $\text{Zr}(\text{HSO}_4)_4$

Zolfigol et al. [118] introduced a green route for synthesizing polysubstituted quinolines using catalytic amounts of $\text{Zr}(\text{NO}_3)_4$ and $\text{Zr}(\text{HSO}_4)_4$. The reactants were treated with $\text{Zr}(\text{NO}_3)_4$ and water as the solvent under reflux for 6 h, resulting in an 86 % yield.

1.8.10. $\text{Zr}(\text{DS})_4$

Zolfigol et al. [119] further explored metal dodecyl sulfates, finding zirconium tetrakisdodecyl sulfate ($\text{Zr}(\text{DS})_4$) to be superior in catalyzing the synthesis of polysubstituted quinolines from o-aminoaryl ketones and ketones or β -diketones in water under reflux. $\text{Zr}(\text{DS})_4$ was used with a water/ethanol (2:1) solvent mixture, heated under reflux for 1.45 h, resulting in a 68 % yield.

1.8.11. Rice husk ash supported $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$

Shirini et al. [120] reported using rice husk ash as a support for $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ to catalyze the synthesis of polysubstituted quinolines. The catalyst reacts with the reactants under solvent-free conditions at 90 °C, achieving a yield of 93 % after 50 min.

1.9. Organocatalysts

1.9.1. Oxalic acid

Oxalic acid was used as an efficient catalyst for the Friedländer condensation under solvent-free conditions by Dabiri et al. [121]. Specifically, using 10 mol% of oxalic acid and heating the reactants to 80 °C for 2 h achieved a yield of 91 % for the corresponding quinolines.

1.9.2. Tartaric acid and urea

Fei Ping Ma et al. [122] developed a process for synthesizing quinoline derivatives using low-melting ratios of urea derivatives and L-(+)-tartaric acid as a cost-effective, safe, and biodegradable reaction medium. This melt acts as both a catalyst and a reaction medium, producing high to exceptional results. For instance, heating 1.0 mmol of tartaric acid-DMU to 70 °C for 40 h without any solvent yielded an 85 % yield.

1.9.3. Malic acid

Tufail et al. [123] discovered a malic acid-promoted, eco-friendly Friedländer approach for quinoline synthesis. When the reaction mixture was heated to 55 °C for 1.2 h in the presence of malic acid, it yielded 87 % of the corresponding quinolines. This reaction features high atom economy, short reaction times, and the recyclability of malic acid.

1.9.4. Dodecyl phosphonic acid (DPA)

Dodecylphosphonic acid (DPA) (Fig. 14) was utilized by Ghassamipour et al. [124] for Friedländer condensation. Utilizing 0.1 mmol of DPA with water at 90 °C, the reaction achieved yields of 73 %–90 % for quinolines within 45–54 min.

1.9.5. Branched fluorocarbon chains

Lei Fang et al. [125] developed a new family of branched catalysts with hydrocarbon or fluorocarbon chains (Fig. 15) for Friedländer synthesis. These catalysts, used under solvent-free conditions, exhibited temperature-dependent solubility, facilitating efficient recovery by filtration at room temperature. The reaction, which involved 2-aminoaryl ketones and carbonyl compounds with 2 mol% of the catalyst, was heated to 80 °C for 3 h, achieving a yield of 94 %.

1.9.6. Poly(*N*-bromo-*N*-ethylbenzene-1,3-disulfonamide) [PBBS] and *N,N,N',N'*-tetrabromobenzene-1,3-disulfonamide [TBBDA]

Ramin Ghorbani Vaghei et al. [126] demonstrated that PBBS and TBBDA (Fig. 16) serve as effective reagents for synthesizing quinolines from 2-aminoaryl ketones and carbonyl compounds under both aqueous and solvent-free conditions. When using water as the solvent, heating PBBS and TBBDA to 100 °C resulted in yields of 90 % and 94 %, respectively, after 7 and 5 h. Under neat conditions, these reagents yielded 83 % and 92 % under similar conditions after 4.5 and 3 h. The same authors [127] utilized these catalysts under microwave irradiation at 900 W, producing yields of 88 % and 94 % after 13 and 9 min, respectively.

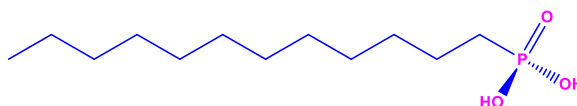


Fig. 14. Structure of dodecylphosphonic acid (DPA).

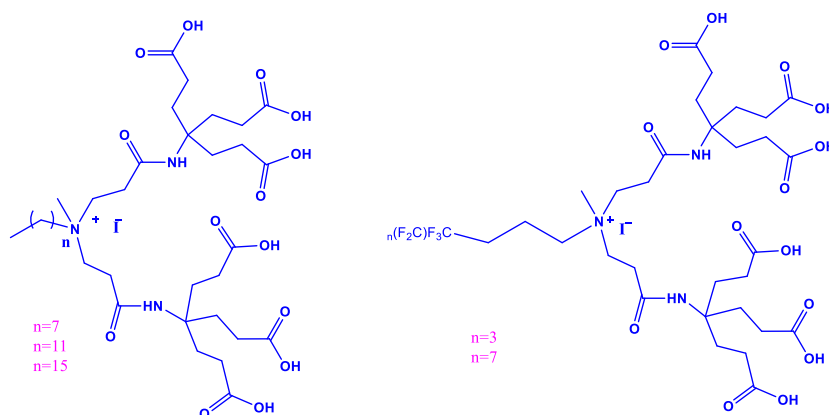


Fig. 15. Structure of branched molecules.

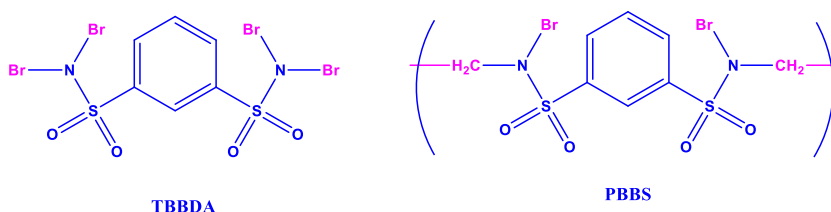


Fig. 16. Structure of TBBDA and PBBS.

1.9.7. (Bromodimethyl)sulfonium bromide (BDMS)

Venkatesham et al. [128] employed (Bromodimethyl)sulfonium Bromide BDMS (Fig. 17) for quinoline synthesis under neat conditions at 50 °C, resulting in an 80 % yield after 55 min. This method emphasizes versatility and efficiency in generating diverse quinoline structures.

1.10. Solid acid catalysts

1.10.1. Mesoporous materials

1.10.1.1. Activated carbon materials. A series of acidic activated carbon materials were used as the catalyst for the Friedländer reactions. These materials are considered environmentally friendly and cost-effective alternatives to traditional acidic mesoporous silicates or zeolites. Lopez-sanz et al. [129] reported that the activated carbon material AC MESO as an efficient catalyst. Under solvent-free conditions and heated to 363 K for 5 min, this activated mesoporous carbon achieved a yield of 79 % for quinolines in the Friedländer synthesis.

1.10.1.2. Mesoporous silicates. Dominguez-Fernandez et al. [130] synthesized and analyzed the catalytic properties of three different modified molecular sieves for the Friedländer condensation. The MCM-41 materials supporting aminopropyl (AP), methylaminopropyl (MAP), and diethylaminopropyl (DEAP) groups, along with cesium-incorporated Al-SBA-15, were examined. Among these, MAP was identified as the most effective catalyst for Friedländer condensation, attributed to the basicity of the amine groups, marking it as the

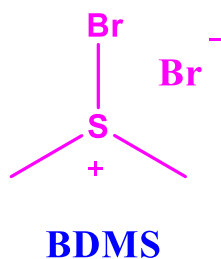


Fig. 17. Structure of (Bromodimethyl)sulfonium bromide.

first reported basic mesoporous catalyst. An equimolar ratio of o-aminoaryl ketone and ethyl acetoacetate reacted with 20 wt% of the catalyst in toluene at 100 °C for 1 h, yielding 62 %.

For enhanced selectivity in the Friedländer reaction between 2-aminobenzophenone and ethyl acetoacetate, Jesus Lopez Sanz et al. [131] introduced the first inorganic-organic hybrid mesoporous catalyst based on SBA-15, incorporating both basic and acidic sites. After heating to 363 K for 3 h in toluene, the SBA-15/APS catalyst produced an 86 % yield. Smuszkiewicz et al. [132] reported a series of mesoporous metallosilicates as efficient heterogeneous catalysts for Friedländer condensation. Using 3-Aminopropyl-trimethoxysilane (APMS) grafted on a Mesoporous Cellular Foam (MCF) under solvent-free reflux conditions for 300 min resulted in full conversion, selectively producing ethyl 6-chloro-2-methylquinoline-3-carboxylate. Notably, the 2APMS/MCF catalyst, which has a higher nitrogen content, demonstrated greater efficiency compared to APMS/MCF in this reaction.

1.10.2. Silica-supported catalysts

1.10.2.1. Silica sulfuric acid catalysts. Shaabani et al. [133] demonstrated that silica sulfuric acid is an effective catalyst for the Friedländer synthesis of quinolines. The reaction was conducted under neat conditions using 0.16 g of the catalyst, heated to 100 °C, achieving an impressive yield of 99 % after 1 h.

1.10.2.2. Silica-based sulfonic acid (MCM-41-SO₃H). Maleki et al. [134] described the use of silica-based sulfonic acid (MCM-41-SO₃H) as a modified catalyst for the Friedländer annulation. This catalyst facilitated the reaction at room temperature for 15 min, resulting in a yield of 96 %.

1.10.2.3. Sodium hydrogen sulfate silica gel (NaHSO₄-SiO₂). Desai et al. [135] synthesized 1,2,3-trisubstituted quinolines using NaHSO₄-SiO₂ as a solid acid catalyst for synthesizing 1,2,3-trisubstituted quinolines. Under neat conditions, the reaction involving 2-aminoaryl ketones and cyclic or acyclic ketones was heated to 70 °C for 6 h, achieving a yield of 90 %.

1.10.2.4. Silica-supported perchloric acid (HClO₄-SiO₂). Narasimhulu et al. [136] reported the use of silica-supported perchloric acid (HClO₄-SiO₂) as a heterogeneous recyclable catalyst for the rapid synthesis of poly-substituted quinolines via Friedländer condensation. The reaction was conducted at ambient temperature with CH₃CN as the solvent, heated to 60 °C for 2 h, resulting in a yield of 96 %.

1.10.2.5. Silica supported iodine (SiO₂/I₂). Zolfigol et al. [137] reported the synthesis of polysubstituted quinolines using Friedlander method catalyzed by the catalytic amount of iodine along with the silica. When the reaction was carried out between 2-amino 5-chlorobenzophenone and ethyl acetate in the presence of 1.0 g of silica and 0.2 mmol of iodine, stirred at 60 °C for 2 h, obtained a yield of 80 %.

1.10.2.6. Silica-supported P₂O₅ (P₂O₅/SiO₂). Hasaninejad et al. [138] described a solvent-free protocol for preparing polysubstituted quinolines via Friedländer hetero-annulation using silica-supported P₂O₅ (P₂O₅/SiO₂). The reaction mixture was heated to 80 °C for 15 min under solvent-free conditions, achieving a yield of 93 %. This green catalytic system is easily prepared by mixing and grinding P₂O₅ and SiO₂.

1.10.2.7. Silica-propylsulfonic acid. Garella et al. [139] reported a quick, solvent-free method for producing substituted quinoline derivatives via Friedländer cyclization using silica-propylsulfonic acid (Fig. 18), a reusable solid catalyst. The silica gel was refluxed in 6 M HCl, then activated by 3-mercaptopropyltrimethoxysilane (MPTMS) in dry toluene. Propylsulfonic silica (PSS) was formed by protonating the thiol groups of the resulting material with aqueous H₂SO₄ and oxidizing it with H₂O₂. This method yielded over 90 % in 30 min under microwave irradiation, though conventional heating was also applicable.

1.10.3. Zeolite

Jesus Lopez Sanz et al. [140] investigated the catalytic performance of various zeolites with different concentrations of Brønsted and Lewis acid sites, specifically H-BEA, H-MFI, H-FAU, and H-MOR, for synthesizing quinolines via Friedländer condensation. The study found that H-BEA and H-FAU exhibited superior selectivity and efficiency. When utilized under neat conditions at 363 K, these zeolites achieved yields of 90 % after 6 h.

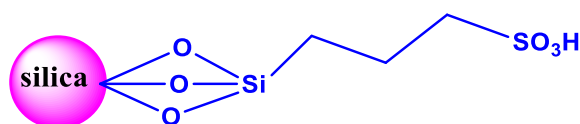


Fig. 18. Structure of propylsulfonic silica (PSS).

1.10.4. Amberlyst-15

Biswanath Das et al. [141] explored the Friedländer synthesis of quinolines using various heterogeneous solid acid catalysts, including $\text{NaHSO}_4\text{-SiO}_2$, $\text{H}_2\text{SO}_4\text{-SiO}_2$, Amberlyst-15, and $\text{HClO}_4\text{-SiO}_2$. Among these, Amberlyst-15 proved to be the most effective regarding reaction time, yield, and catalyst reusability, achieving over 85 % yield with ethanol as the solvent, heated under reflux for 2 h.

1.10.5. KSF clay

Sabitha et al. [142] utilized KSF clay (1 g) under neat conditions, employing microwave irradiation at 600 W for 5 min, resulting in a yield of 62 %.

1.10.6. Perfluorosulfonic acid

Roberto et al. [143] demonstrated the functionality of a glass microreactor with a perfluoroalkyl sulfonic acid layer (Fig. 19) for Friedländer quinoline synthesis. Using perfluorosulfonic acid and CH_3CN as the solvent, heated to 70 °C for 2.5 h, the process yielded 90 %. The catalytic monolayer was prepared by anchoring a β -sultone layer onto an activated silicon dioxide surface via a ring-opening reaction. This procedure was also applied to functionalize a glass microreactor for continuous-flow acid-catalyzed reactions.

1.11. Mineral acid

Hydrochloric acid is the typically used mineral acid for the Friedländer condensation.

1.11.1. HCl in water

Gopi et al. [144] explored a green methodology for synthesizing polysubstituted quinolines using hydrochloric acid (10 N) as a catalyst, with water as the solvent. This approach achieved a 90 % yield at room temperature after 16 h, offering an efficient alternative to more energy-intensive methods.

1.11.2. HCl with ethanol

Chavan et al. [145] utilized concentrated hydrochloric acid in combination with ethanol as a solvent for the Friedländer synthesis of quinolines, specifically between 2-amino-5-nitrobenzophenone and ethyl acetoacetate. This reaction was conducted at 80 °C for 12 h, resulting in a high yield of the corresponding quinoline. In our previous work [146], we utilized Friedländer cyclization to synthesize quinoline derivatives using the same condition of concentrated hydrochloric acid with ethanol.

1.11.3. HCl with microwave irradiation

Muscia et al. [147] employed microwave irradiation (MW) with a catalytic amount of hydrochloric acid to synthesize substituted quinolines efficiently. This reaction is subjected to microwave irradiation at 400W, under neat conditions, achieving a 64 % yield after 1.5 min.

1.12. Miscellaneous catalyst

1.12.1. Organic dye

Mohamadpour et al. [148] utilized a cationic dye, methylene blue as a SET and EnT catalyst under visible light (White LED 12W) irradiation in ethanol, achieving a 94 % yield at room temperature after 6 min.

1.12.2. Coupling reagent

Jida et al. [149] presented an eco-friendly protocol for Friedländer condensation using propyl phosphonic anhydride (T_3Ps) under mild conditions. It primarily functions as a coupling reagent or activating agent in organic synthesis. Propyl phosphonic anhydride, used in a 0.5 mmol without any solvent, heated to 60 °C for 30 min, resulted in a 95 % yield.

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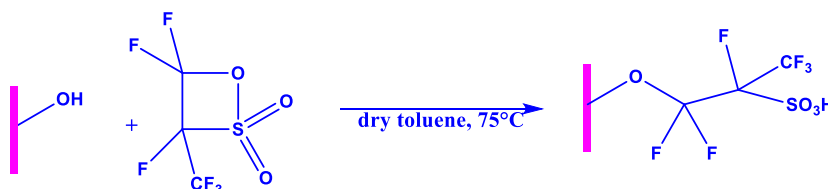


Fig. 19. Functionalization of flat silicon dioxide surface and glass microreactor by β -sultone.

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S. no	Types of catalyst	Catalyst	Amount of catalyst (a _g , b _{mmol} %, c _{wt%} , mL ^d , mol % ^e)	Solvent	Energy source	Temperature (rt = room temperature)	Time (d _h , e _{min} , f _s)	Yield (%)	Reference
S. no	Types of catalyst	Catalyst	Amount of catalyst (a _g , b _{mmol} %, c _{wt%} , mL ^d , mol % ^e)	Solvent	Energy source	Temperature (rt = room temperature)	Time (d _h , e _{min} , f _s)	Yield (%)	Reference
1	Ionic liquids	[Hbmim][BF ₄]	1 ^b	No solvent	Heat	100 °C	3.3 ^d	93	[34]
2		[Hbmim][BF ₄]	2 ^d	Methanol	Ultrasonication	25 ± 1 °C	10 ^e	84	[35]
3		[bmim]HSO ₄	0.5 ^b	No solvent	Heat	70 °C	140 ^e	78	[36]
4		Fe ₃ O ₄ -IL-HSO ₄	0.02 ^b	No solvent	Heat	90 °C	35 ^e	93	[37]
5		DSIMHS	0.25 ^b	No solvent	Heat	70 °C	35 ^e	95	[38]
6		(C ₄ mim) ₂ -2Br ⁻ -2H ₂ SO ₄	0.05 ^b	No solvent	Heat	50 °C	15 ^e	90	[39]
7	Metal triflates	TSIL	0.01 ^a	Water	Heat	70 °C	1 ^d	92	[40]
8		[bsmin]	10 ^e	No solvent	Heat	80 °C	16 ^d	93	[41]
9		[Msim][OCClCl ₃]	0.4 ^b	No solvent	Heat	100 °C	45 ^e	99	[42]
		[Msim]Cl	1.3 ^b				70 ^e	98	
10		ImBuSO ₃ H	2 ^d	No solvent	Heat	50 °C	30 ^e	92	[43]
11		SO ₃ H-functionalized IL	1.0 ^a	No solvent	Heat	45 °C	25 ^e	99	[44]
12		[Et ₃ NH][HSO ₄]	2 ^b	No solvent	Heat	100 °C	30 ^e	85	[45]
13		Gd(OTf) ₃	0.2 ^b	[Bmim][pf ₆]	Heat	60 °C	15 ^e	93	[47]
14		Bi(OTf) ₃	5 ^c	Ethanol	–	Rt	4 ^d	91	[48]
15		Y(OTf) ₃	Catalytic amount	Ch3cnAcetonitrile	–	Rt	6 ^d	81	[49]
16	Metal organic frameworks	Zr(OTf) ₄	0.2 ^b	Ethanol/water	–	Rt	90 ^e	97	[50]
17		Zn(OTf) ₄	0.01 ^a	No solvent	Microwave irradiation	85 °C	3.5 ^e	94	[51]
		In(OTf) ₄							
18		In(OTf) ₃	5 ^b	No solvent	Heat	80 °C	15 ^e	87	[52]
19		Li(OTf)	10 ^e	No solvent	Heat	80 °C	20 ^e	97	[53]
19		[Cu ₃ (BTC) ₂] activated	0.083 ^b	No solvent	Heat	353K	1 ^d	80	[58]
20		CuBTC	0.08 ^b	No solvent	Heat	100 °C	2 ^d		[59]
21		Cu(II)-Mof	1 ^c	No solvent	Heat	80 °C	8 ^d	90	[60]
22		Hafnium based UiO-66 (Hf)-(NHCOMe) ₂	0.02 ^a	No solvent	Heat	80 °C	3 ^d	98	[61]
23		UiO-66(Hf)	0.025 ^a	No solvent	Heat	100 °C	20 ^d	94	[62]
24	Nanocatalysts	Zn-Mof	5 ^c	No solvent	Heat	85 °C	24 ^d	98	[63]
25		HKUST-1	0.08 ^a	No solvent	Heat	80 °C	10 ^d	82	[64]
27		Fe ₃ O ₄ @SiO ₂ @PDESA	0.02 ^a	No solvent	Heat	110 °C	120 ^e	83	[67]
28		Fe ₃ O ₄ @SiO ₂ -imid PMA (n&b)	n-0.02 ^a b-0.03 ^a	No solvent	Heat	70 °C	30 ^e 50 ^e	96 89	[68]
29		Fe ₃ O ₄ @SiO ₂ -SO ₃ H	0.05 ^a	No solvent	Heat	100 °C	45 ^e	91	[69]
30		Fe ₃ O ₄ @ SiO ₂ /isoniazid/Cu(II)	0.07 ^a	Ethanol	Heat	60 °C	2 ^d	96	[70]
31		Fe ₃ O ₄ @SiO ₂ - APTES-TFA	0.2 ^a	No solvent	Heat	100 °C	5 ^d	96	[71]
32		ZnCl ₂ supported	0.07 ^a	No solvent	Heat	60 °C	2 ^d	95	[72]
33		Fe ₃ O ₄ @ SiO ₂ core shell							
33		ZrO ₂ supported Fe ₃ O ₄ MNPs	0.02 ^a	Ethanol	Heat	60 °C	25 ^e	92	[73]
34	TITANIA	ZrO ₂ /SO ₄ ²⁻ /CU	0.005 ^a	Water	Rt	Rt	45 ^e	97	[74]
35		CuFe ₂ O ₄ NPs	5 ^c	Water	Heat	80 °C	32 ^e	92	[75]
36		Fe ₂ O ₃ NPS	0.7 ^e	No solvent	Rt	Rt	3.5 ^d	91	[76]
37		SiO ₂ NPs	0.5 ^a	No solvent	Microwave irradiation	100 °C	8 ^e	93	[77]
38			5 ^e	No solvent	Heat	80 °C	35 ^e	89	[78]
39		NANO ZNO	0.008 ^a	No solvent	Heat	100 °C	CM-ZNO-11 ^d NF ZNO-4 ^d	90 98	[79]
40	NiO NPs		10 ^e	Ethanol	Heat	Reflux	2.5 ^e	95	[80]
41		Nano Al ₂ O ₃	0.03 ^b	Chloroform	Heat	Reflux	3 ^d	96	[81]

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S. no	Types of catalyst	Catalyst	Amount of catalyst (^a g, ^b mmol %, ^c wt%, mL ^d , mol %)	Solvent	Energy source	Temperature (rt = room temperature)	Time (^d h, ^e min, ^f s)	Yield (%)	Reference
42		Fe-Cr-Ni oxide alloy nanobelts	0.005 ^a	Water	Heat	Rt	85 ^e	82	[82]
43		Trimetallic oxide NP Cu/Cr/Ni	0.02 ^a	No solvent	Heat	100 °C	80 ^e	95	[83]
44		Solid acid nano catalyst	0.05 ^a	Ethanol	Heat		MK-10-130 ^e ZEO-100 ^e SZ-90 ^e	75 83 89	[84]
45		Li + modified nanoporous Na + -MMT	0.06 ^a	No solvent	Heat	100 °C	0.5 ^d	96	[85]
46		Aluminosilicate AIKIT-5		Ethanol	Heat	80 °C	3.5 ^d	90	[86]
47		(BSPY) HSO ₄ /MCM-41	0.07 ^a	No solvent	Heat	100 °C	45 ^e	91	[87]
48		Ni NPs	Catalytic amount	No solvent	–	75 °C	57 ^e	89	[88]
49		PVA/Fe (NO ₃) ₃	3 ^e	Toluene	Heat	80 °C	6 ^d	75	[89]
50		Double perovskite Bi _{1.97} Eu _{0.03} MoO ₆	1 ^e	Water	Heat	45–55 °C	45 ^e	89	[90]
51		MNP@SiO ₂ -Pr-AP-tribromide	0.1 ^a	Ethanol	Heat	Reflux	3 ^d	95	[91]
52		Carbon aerogels	0.025 ^a	No solvent	Heat Mw	323K	240 ^e 15 ^e	90 90	[92]
53	Polymers	P(4VPBSA)HSO ₄	0.05 ^a	No solvent	Heat	110 °C	40 ^e	91	[93]
54		PEG-6000 (PEG-OSO ₃ H)	0.18 ^a	No solvent	Mw	130 °C	5 ^e	90	[94]
55		PEG-SO ₃ H	0.2 ^a	Water	Heat	60 °C	20 ^e	95	[95]
56		PEG 4000	2- 3 drops	Dichloromethane	Mw	110 °C	5 ^e	93	[96]
58		PEG-SO ₃ H	0.1 ^b	Dichloromethane	Heat	Reflux	50 ^e	92	[97]
58		Cellulose sulfuric acid or Starch sulfuric acid		No solvent		100 °C	30 ^e 40 ^e	95	[98]
59		Chitosan-SO ₃ H	0.1 ^a	Ethanol	Heat	Reflux	20 ^e	90	[99]
60		Nafion NR50	20 ^e	Ethanol		200 °C	1 ^d	95	[100]
61		APTPO ₆₀	0.1 ^a	Ethanol	Heat	Reflux	24 ^d	96	[101]
62		AMPS-CO-AA	0.06 ^a	No solvent	Heat	110 °C	20 ^e	70	[102]
63	Heteropoly acid	Phosphotungstic Acid	0.04 ^a	No solvent	Heat	80 °C	2 ^d	91	[103]
64		PW/SiO ₂	0.2 ^a	No solvent	Heat	100 °C	10 ^d	97	[104]
		PW/KSF					10 ^d	74	
		PW/C					20 ^d	92	
65		Ag ₃ PW ₁₂ O ₄₀	0.2 ^b	Ethanol	Heat	Reflux	6 ^d	81	[105]
		Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	0.2 ^a	No solvent	Heat	100 °C	20 ^e	96	[106]
66	Deep eutectic solvent	Choline based lewis acid (ChCl.ZnCl ₂)	30 ^e	No solvent	Heat	80 °C	3.5 ^e	91	[108]
67		Dimethylurea/citric acid	1 ^a	Water	Heat	80 °C	4.3 ^e		
				No solvent	Heat	100 °C	25 ^e	88	[109]
68	Inorganic acids or salts	Nd(NO ₃) ₃	5 ^e	Ethanol	–	Rt	–	94	[110]
69		BHS (boron hydrogen sulfate)	5 ^e	No solvent	Heat	90 °C	38 ^e	94	[111]
70		NaAuCl ₄ .2H ₂ O	2.5 ^e	Ethanol	–	Rt	6 ^d	89	[112]
71		SnCl ₂ .H ₂ O		No solvent	–	Rt	30 ^e	98	[113]
72		Molecular Iodine	1 ^e	Ethanol	–	Rt	16 ^d	93	[114]
73		Cyanuric Chloride	20 ^e	Water	–	Rt	16 ^d	93	[115]
74		CUSO ₄ .5H ₂ O	0.231 ^a	Ethanol	–	Rt	3 ^d	80	[116]
75		NbCl ₅	0.1 ^b	Glycerol	Heat	110 °C	35 ^e	95	[117]
76		Zr(NO ₃) ₄	10 ^e	Water	Heat	Reflux	6 ^d	86	[118]
77		Zr(DS) ₄	0.1 ^b	Water/ethanol (2/1)	Heat	Reflux	1.45 ^d	68	[119]
78		FeCl ₂ . 2H ₂ O-RiHA (rice husk ash supported)	0.3 ^a	No solvent	Heat	90 °C	50 ^e	93	[120]
79	Organocatalyst	Oxalic acid	10 ^e	No solvent	Heat	80 °C	2 ^d	91	[121]
80		Tartaric acid-DMU	1.0 ^b	No solvent	Heat	70 °C	40 ^d	85	[122]

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S. no	Types of catalyst	Catalyst	Amount of catalyst (^a g, ^b mmol %, ^c wt%, mL ^d , mol %)	Solvent	Energy source	Temperature (rt = room temperature)	Time (^d h, ^e min, ^f s)	Yield (%)	Reference
81	Solid acid catalysts	Malic acid	50 ^e	No solvent	Heat	55 °C	1.2 ^d	87	[123]
82		DPA	0.1 ^b	Water	Heat	90 °C	45 ^e	90	[124]
83		Branched fluorocarbon chains	2 ^e	No solvent	Heat	80 °C	54 ^e	73	[125]
84		TBBDA	0.45 ^b	Water	Heat	100 °C	3 ^d	94	
84		PBBS	0.60 ^b	No solvent	Heat	100 °C	5 ^d	94	[126]
							7 ^d	90	
85							3 ^d	92	[127]
							4.5 ^d	83	
85		TBBDA	0.45 ^b	No solvent	Microwave irradiation	90W	9 ^e	94	[128]
86		PBBS	0.60 ^b		Heat	50 °C	13 ^e	88	
86		BDMS	10 ^e	No solvent	Heat	363K	55 ^e	80	[129]
87		AC MESO	0.025 ^a	No solvent	Heat	363K	5 ^d	79	[130]
88		MCM-41 MAP	20 ^c	Toluene	Heat	100 °C	1 ^d	62	[131]
89		SBA-15/APS	0.025 ^a	Toluene	Heat	363K	3 ^d	86	[132]
90		APMS/MCF	0.025 ^a	No solvent	Heat	Reflux	300 ^e	100	[133]
91		Silica sulfuric acid	0.16 ^a	No solvent	Heat	100 °C	1 ^d	99	[134]
92		(MCM-41-SO ₃ H)	0.015 ^a	No solvent	–	Rt	15 ^e	96	[135]
93		NaHSO ₄ ·SiO ₂	0.2 ^a	No solvent	Heat	70 °C	6 ^d	90	[136]
94		HClO ₄ ·SiO ₂	0.37 ^b	Ch3cn	Heat	60 °C	2 ^d	96	[137]
94		SiO ₂ /I ₂	0.2 ^b	No solvent	Heat	80 °C	2 ^d	80	[138]
		P ₂ O ₅ /SiO ₂	0.4 ^a	No solvent	Heat	80 °C	15 ^e	93	[139]
95		Silica propyl sulfonic acid	0.1 ^a	No solvent	Microwave irradiation	80 °C	0.5 ^d	90	[140]
96									[141]
97		Zeolites H-BEA	0.05 ^a	No solvent	Heat	363K	6 ^d	90	[142]
98	Amberlyst-15	10 ^c	Ethanol	Heat	Reflux	2.0 ^d	85	[143]	
99	KSF clay	1 ^a	No solvent	Microwave irradiation	600W	5 ^e	62	[144]	
100	Mineral acid	Perfluorosulfonic acid	0.3 ^a (10 ^{−6}) ^d	Acetonitrile	Heat	70 °C	2.5 ^d	90	[145]
101		Hydrochloric acid	Catalytic amount	Water	–	Rt	16 ^d	90	[146]
102		Hydrochloric acid	Catalytic amount	Ethanol	Heat	80 °C	12 ^d	90	[147]
102	Organic dye	Hydrochloric acid	Catalytic amount	Ethanol	Heat	70 °C	6 ^d	90	[148]
									[149]
103		Hydrochloric acid	Catalytic amount	No solvent	Microwave irradiation	400W	1.5 ^e	64	[150]
104	Methylene blue	1 ^e	Ethanol	Visible Light irradiation	Rt	6 ^e	94	[151]	
105	Coupling reagent	Propyl phosphonic anhydride (T ₃ Ps)	0.5 ^b	No solvent	Heat	60 °C	30 ^e	95	[152]

2. Conclusion

This review has meticulously examined a wide range of catalytic methodologies applied in the Friedländer synthesis of quinolines, revealing both their efficacy and limitations. Ionic liquids in offer significant advantages, including high yields exceeding 90 %, solvent-free conditions, recyclability, thermal stability, enhanced reaction rates, versatility, and minimized side reactions, making them efficient and sustainable catalysts. However, they also present challenges such as the necessity for elevated temperatures (45–100 °C), high initial costs, viscosity issues, complex purification processes, and the risk of decomposition under certain conditions. Metal triflates recognized for their Lewis acidic properties, offer advantages like catalyzing the reactions at room temperature, though higher temperatures (over 60 °C) can significantly reduce reaction times. They are known for their high catalytic efficiency and selectivity, often resulting in high yields. However, disadvantages include their relatively high cost and potential for moisture sensitivity, which can complicate handling and storage. Additionally, while they can operate at room temperature, reactions at lower temperatures tend to be slower, requiring extended durations to reach completion. Metal-organic frameworks (MOFs) have introduced a novel dimension to catalysis and offer significant advantages as catalysts in the Friedländer synthesis of quinolines, including high surface areas, tunable porosity, and the ability to facilitate reactions under neat conditions, which can lead to high yields and selectivity. Their structural versatility allows for incorporating various active sites, enhancing catalytic efficiency and enabling the design of catalysts tailored for specific reactions. However, MOFs also present several disadvantages, such as the requirement for high

temperatures (around 100 °C) to achieve optimal results, which can be energy-intensive. Additionally, the synthesis and activation of MOFs can be complex and costly, and their stability under reaction conditions can sometimes be a concern, potentially limiting their practical application in large-scale or industrial settings.

Nanocatalysts have revolutionized the Friedländer synthesis by providing high surface-to-volume ratios, which significantly enhance catalytic activity. Their integration into various reaction environments has demonstrated substantial improvements in reaction rates and yields. Polymer-supported catalysts offer practical benefits, particularly in terms of ease of separation and reusability. These materials provide a significant advantage over traditional homogeneous catalysts by minimizing product contamination and simplifying catalyst recovery. Solid acid catalysts, including zeolites and heteropolyacids, offer significant advantages in terms of recyclability and ease of handling. These materials facilitate Friedländer reactions effectively and are relatively straightforward to regenerate. Inorganic acids and salts are effective at room temperature, reducing energy inputs and simplifying reaction conditions. They are cost-effective and readily available, offering promising yields. However, extended reaction times along with potential side reactions require attention. Whereas organocatalysts utilise small organic molecules representing an environmentally friendly and potentially cost-effective alternative. Their application in this synthesis has yielded impressive results, particularly reaction efficiency and selectivity.

The implementation of different energy sources such as microwave irradiation, ultrasonication, and visible light irradiation has positively impacted the reaction duration and product yield. It has also avoided the need for high temperatures. Future research should focus on addressing the current limitations of each catalytic system, exploring synergistic combinations, and striving for more sustainable and economically viable solutions. By overcoming existing challenges and exploring novel catalytic strategies, researchers can contribute to more sustainable and efficient synthetic routes for quinolines. These advancements are poised to drive scientific innovation and practical utility, fostering progress across multiple industries.

CRediT authorship contribution statement

Indhu Chandrasekaran: Writing – original draft, Investigation, Formal analysis. **S. Sarveswari:** Supervision, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: S Sarveswari reports administrative support was provided by Vellore Institute of Technology. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Indhu Chandrasekaran reports administrative support was provided by Vellore Institute of Technology. Indhu Chandrasekaran reports a relationship with Vellore Institute of Technology that includes: non-financial support. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors of this paper are grateful to the administration of Vellore Institute of Technology, Vellore, India. We also thank Dr. V. Vijaykumar, Professor at Vellore Institute of Technology, Vellore, for his valuable guidance.

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