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Review

Recent Advances in the Synthesis of Quinolines: A Focus on Oxidative Annulation Strategies

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Abstract: Quinoline, a heterocyclic scaffold of paramount importance in medicinal and industrial chemistry, has garnered significant attention due to its versatile applications. Traditional synthetic methods, dating back over a century, have evolved into innovative strategies leveraging catalytic C–H bond activation, transition-metal-free protocols, and photo-induced oxidative cyclization. Recent advancements highlight the synergistic roles of catalysts, oxidants, and solvents in enhancing molecular reactivity and reaction efficiency. This review systematically summarizes state-of-the-art oxidative annulation techniques for quinoline synthesis, emphasizing mechanistic insights and practical applications.

Keywords: quinoline; oxidative annulation; photo-induced synthesis; C–H bond activation; dehydration coupling

1. Introduction

Nitrogen-containing heterocycles are a class of significant structural categories in chemical substances [1]. Among them, quinoline stands out as one of the most esteemed heterocyclic compounds due to its diverse applications across multiple fields. Quinoline derivatives exist in various natural products, especially in alkaloids. In 1834, quinoline was initially isolated from coal tar by Friedlieb Ferdinand Runge, continuing to be the primary commercial source thereof [2]. The nitrogen heterocyclic skeleton of quinoline can be easily modified by simple or complex methods, thereby providing many compounds that are commonly needed in the fields of medicine and industrial chemistry [3]. Quinoline and its derivatives have exhibited increasing significance in the pharmaceutical field compounds due to their valuable activities, such as anti-bacterial, anti-inflammatory, anti-cancer, anti-tubercular, anti-malarial, anti-HIV, and so on (Figure 1) [4,5]. Therefore, exploring new synthetic methods of quinolines is not only meaningful but also alluring, providing a multitude of pathways for discovering novel bioactive molecules. Considering the importance of the strategy for the synthesis of such compounds via oxidative annulation, this review will focus on the oxidative annulation strategies for quinoline synthesis, systematically presenting recent advances in three key aspects: (1) C–H bond activation and functionalization, (2) dehydration coupling, and (3) photocatalytic oxidative cyclization. Particular emphasis will be placed on elucidating synthetic methodologies and mechanistic investigations, aiming to provide comprehensive references for the organic chemistry community.

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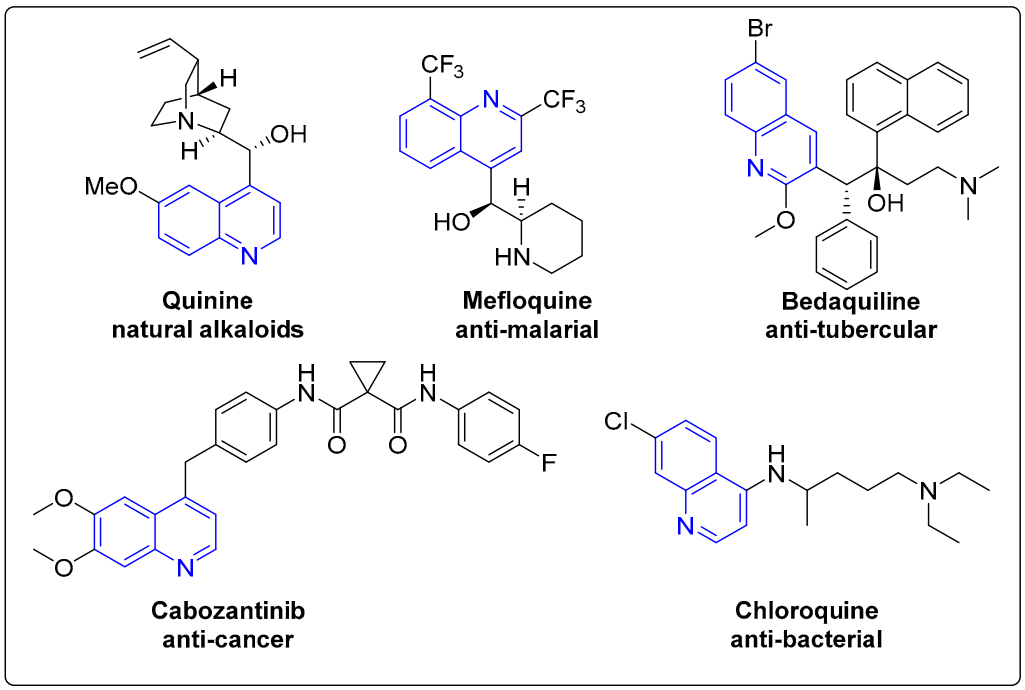
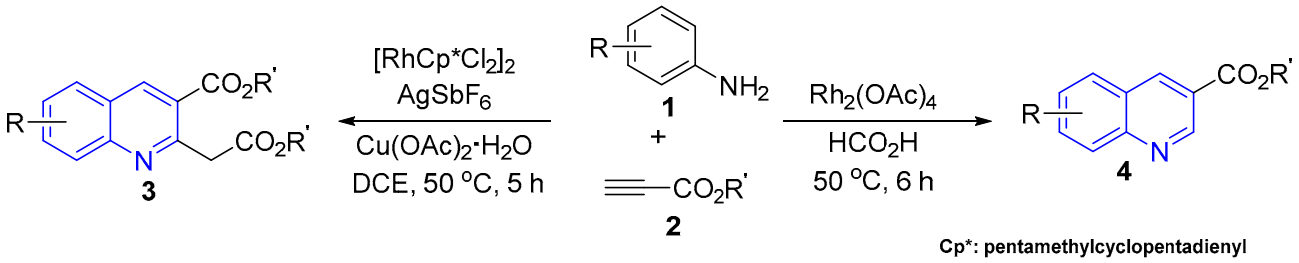


Figure 1. Natural alkaloids and drugs containing quinoline structures.

2. Oxidative Synthesis of Quinolines via C–H Transformations

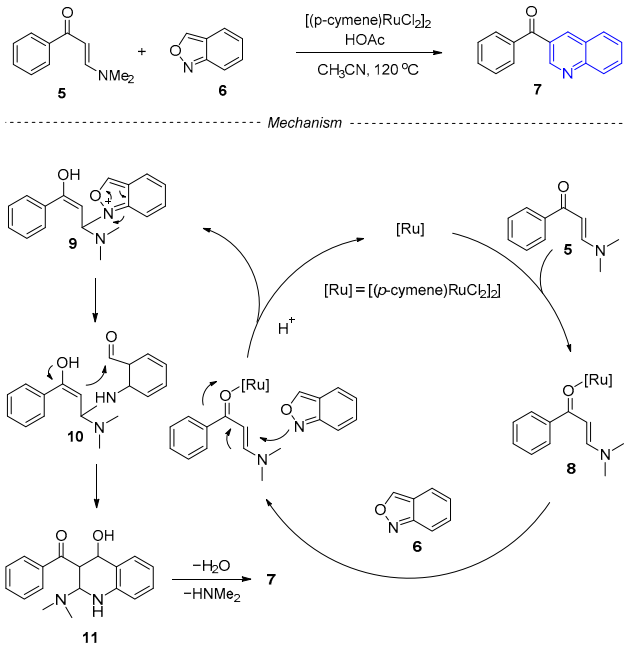
2.1. Transition Metal-Catalyzed C–H Activation Pathways

In 2016, A. Sudalai and colleagues reported a rhodium-catalyzed cyclization strategy between aniline derivatives and alkynyl esters for the regioselective synthesis of quinoline carboxylates [6]. This catalytic system involved formic acid as both a versatile C1 synthon and reducing agent, while copper(II) species served as the terminal oxidant. The rhodium catalyst played a dual role in facilitating *ortho*-C–H bond activation of aromatic amines and mediating the subsequent cyclization process under mild reaction conditions. This methodology established an efficient synthetic route to substituted quinolines through cascade C–H activation and heteroannulation reactions (Scheme 1).



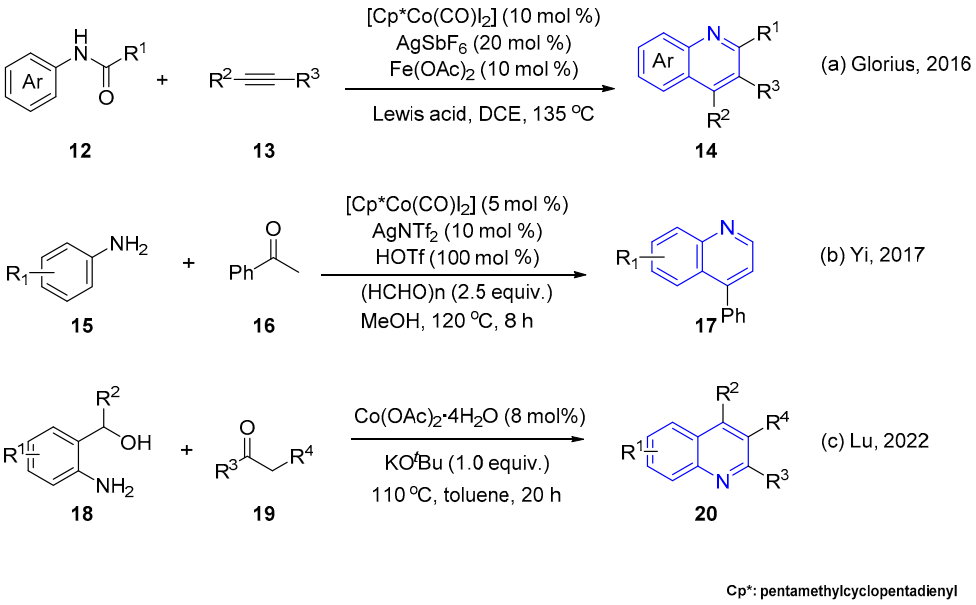
Scheme 1. Rhodium-catalyzed *ortho*-C–H bond activation for the synthesis of quinoline carboxylates.

In 2022, Xiu Wang and co-workers discovered a simple and easy-to-operate conditions to access substituted quinolines through ruthenium-catalyzed aza-Michael addition and intramolecular annulation of enaminones with anthranils (Scheme 2) [7]. The catalytic process begins with the treatment of compound **5** with [(*p*-cymene)$RuCl_2$]$_2$, a well-established ruthenium catalyst, resulting in the formation of intermediate **8**. Then, intermediate **8** passes through an aza-Michael addition-type C–N coupling with anthranil to obtain intermediate **9** and releases the ruthenium catalyst to participate in the next cycle. Intermediate **10** then undergoes an intermolecular cyclization to give intermediate **11**, which experiences the process of dehydration and deamination to give the final product **7**.



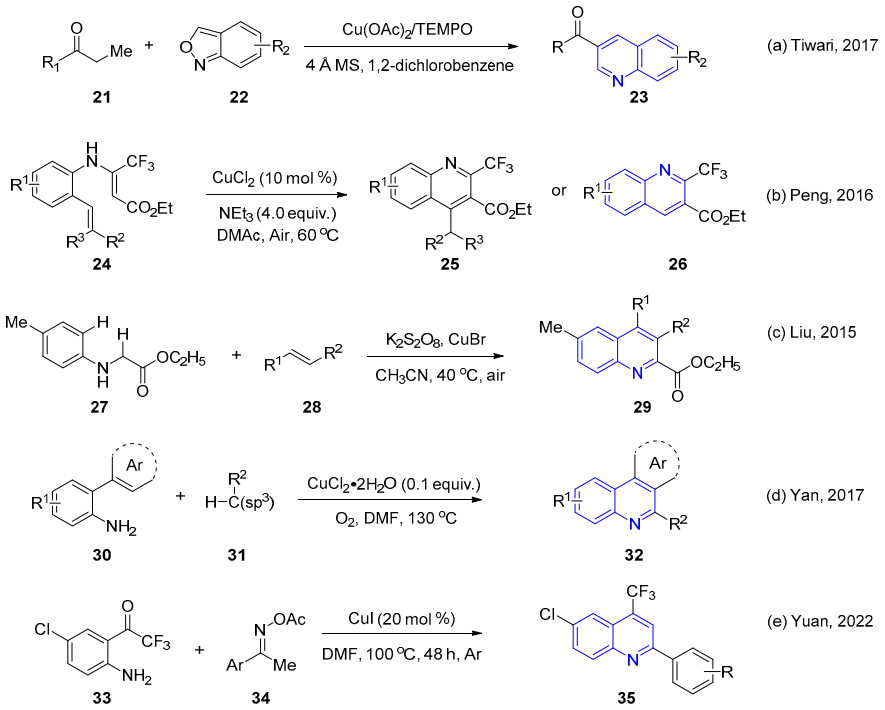
Scheme 2. Synthesis of 3-substituted quinolines by ruthenium-catalyzed annulation of enaminones with anthranils.

Frank Glorius and his colleagues used Cp*Co(III)-catalyzed C–H bond activation to control organometallic intermediates to achieve quinoline synthesis [8]. The key to this method was summarized as the following: (1) the introduction of Lewis acid accelerates dehydration cyclization and inhibits dehydrocyclization; (2) adjust the guiding group to accelerate dehydrocyclization and inhibit dehydration cyclization (Scheme 3a). The Wei Yi team discovered a Co(III)-catalyzed cyclization of acetophenone and aniline to obtain various quinoline skeletons with broad functional group tolerance and high yields (Scheme 3b) [9]. A convenient and efficient protocol to synthesize quinolines and quinazolines in one pot under mild conditions was proposed in 2022 by Guo-Liang Lu et al. via ligand-free cobalt-catalyzed cyclization of 2-aminoaryl alcohols with ketones or nitriles (Scheme 3c) [10].



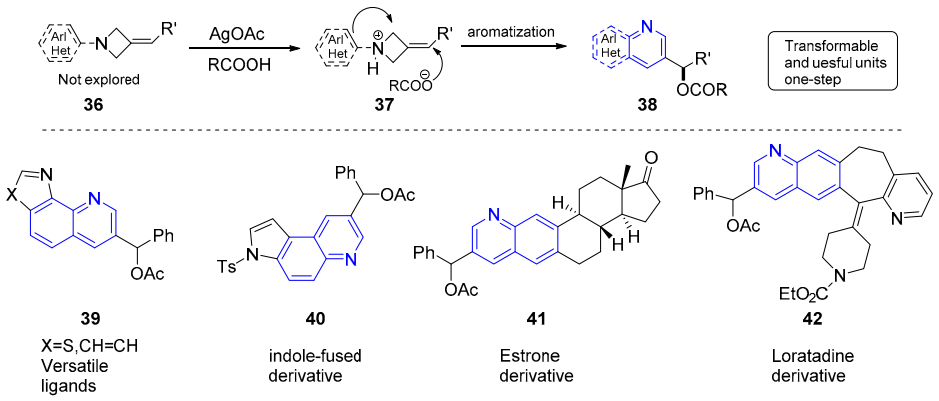
Scheme 3. Cobalt-assisted C–H bond activation to synthesize quinoline.

Tiwari group explored an efficient method to access functionalized quinolines from the readily available saturated ketones and anthranils, a one-pot reaction that generates 3-substituted quinoline derivatives in situ under the catalysis of copper acetate (Scheme 4a) [11]. Peng group discovered a method of intramolecular oxidative cyclization of *N*-(2-alkenylaryl) enamines catalyzed by cuprous iodide and 2-trifluoromethylquinolines could be obtained (Scheme 4b) [12]. In 2015, Xia Li and Lei Liu explored a kind of $K_2S_2O_8$ and cuprous bromide, taking part in the oxidative cross-dehydrogenative coupling reaction between *N*-arylglycine derivatives and olefins, yielding multifunctional quinoline dicarboxylate (Scheme 4c) [13]. The advantage of this method is that $K_2S_2O_8$ has low cost, low toxicity, and easy handling, with the absence of harmful by-products, rendering the system more cost-effective and eco-friendly. In 2017, Ru long Yan et al. reported copper-catalyzed one-pot aerobic oxidation cyclization of C(sp^3)–H/C(sp^2)–H bond functionalization, synthesized through the reaction of 2-vinylaniline or 2-arylaniline with 2-methylquinoline, utilizing oxygen as the direct oxidant (Scheme 4d) [14]. In 2022, Wei-Cheng Yuan et al. developed an efficient Cu-catalyzed annulation reaction of ketone oxime acetates with *ortho*-trifluoroacetyl anilines [15]. With the developed protocol, a series of 4-trifluoromethyl quinolines were obtained in good to excellent yields under redox-neutral conditions (Scheme 4e).

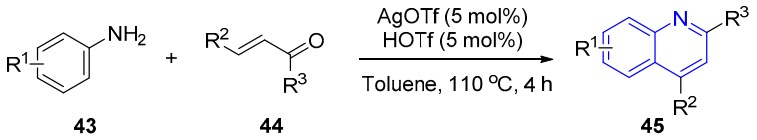


Scheme 4. Synthesis of quinoline by C–H bond activation mediated by Cu(I) or Cu(II).

In 2018, Li et al. developed a silver acetate catalyzed oxidation cascade of *N*-aryl-3-alkylideneazetidines with carboxylic acids, providing functionalized quinoline products [16]. The mechanism study indicated that silver salts played a pivotal role in achieving chemical regioselectivity and facilitating oxidative aromatization during ring expansion processes (Scheme 5). In 2014, Xu Zhang and Xue-Feng Xu reported the synthesis of quinoline by the coupling of aniline and alkenyl/alkynyl carbonyl compounds with silver trifluoroacetate [17]. They found that electron donating and electron withdrawing groups on aniline were necessary for this reaction (Scheme 6).

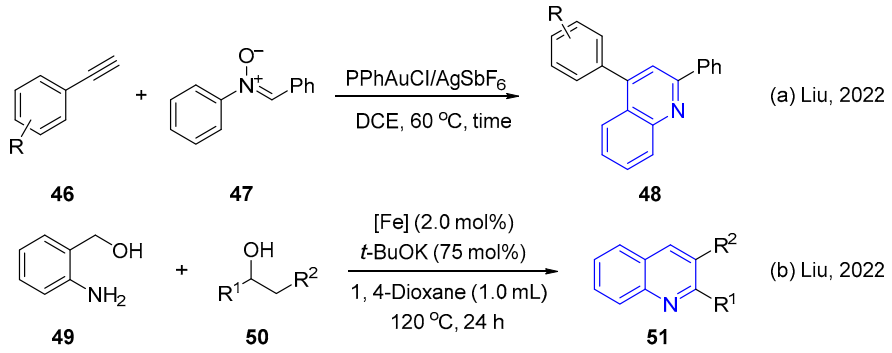


Scheme 5. Silver-promoted oxidative cascade reaction of *N*-aryl-3-alkylideneazetidines with carboxylic acids.



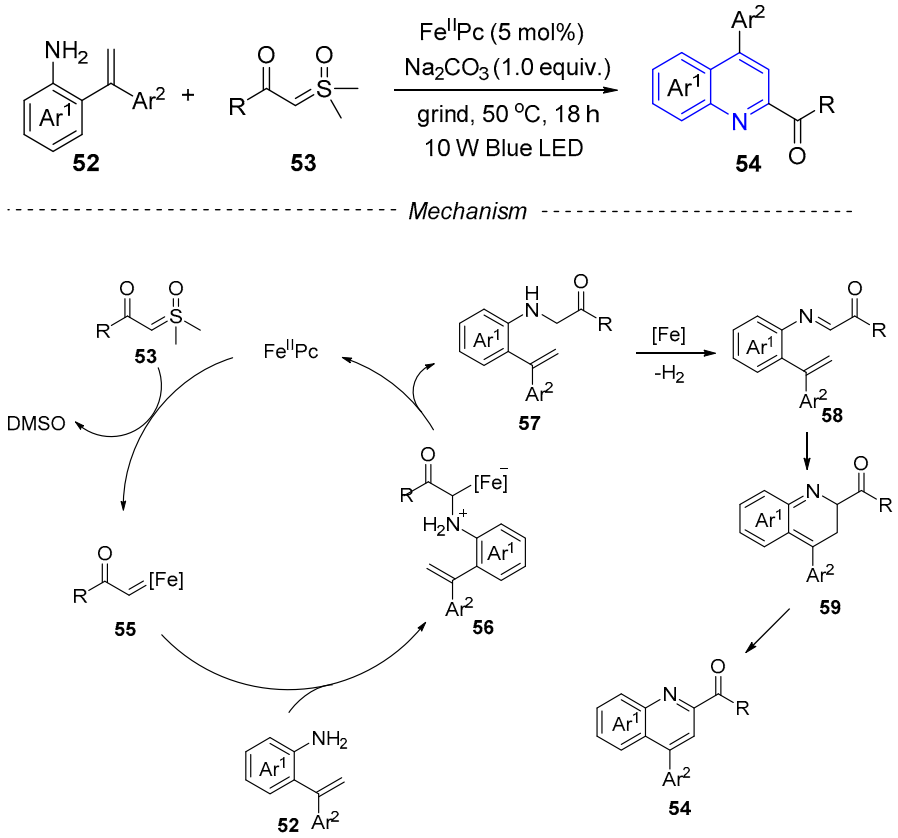
Scheme 6. Synthesis of quinoline by C–H bond activation with silver ion.

Beyond the conventional transition metal catalysis, emerging strategies have leveraged for catalytic synthesis of quinolines. For example, the gold-catalyzed synthesis of quinoline derivatives through a [4 + 2] annulation reaction between terminal arylynes and nitrones was discovered by Rai-Shung Liu and his colleagues in 2022 (Scheme 7a) [18]. In that same year, Wei-Ping Liu and his colleagues introduced a methodology for synthesizing quinolines that was both atom-economical and straightforward to enhance the yield and purity of the final product (Scheme 7b) [19].



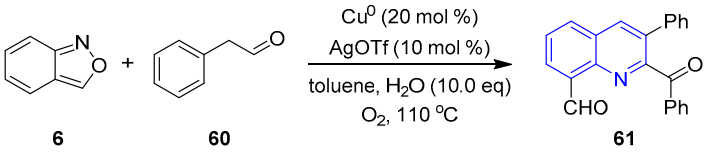
Scheme 7. Synthesis of quinoline derivatives catalyzed by other metals.

Shun Wang et al. reported a novel photo-thermo-mechanochemical approach that is free of solvent to assembling quinolines catalyzed by iron(II) phthalocyanine (Scheme 8) [20]. The proposed reaction mechanism suggests that irradiation of iron(II) phthalocyanine complexes with sulfoxonium ylide **53** can result in the formation of an Fe-carbene intermediate **55**, as supported by recent advancements in iron-catalyzed photoredox chemistry. The Fe-carbene intermediate **55** reacts with 2-vinylanilines **52** to form intermediate **56**. Protonation of intermediate **56** releases the secondary amine intermediate **57**. Intermediate **57** liberates molecular hydrogen with the aid of the Fe species to generate imine intermediate **58** followed by intramolecular electrocyclization to produce intermediate **59**. Finally, product **54** is formed through a dehydrogenation or aerobic oxidation process.



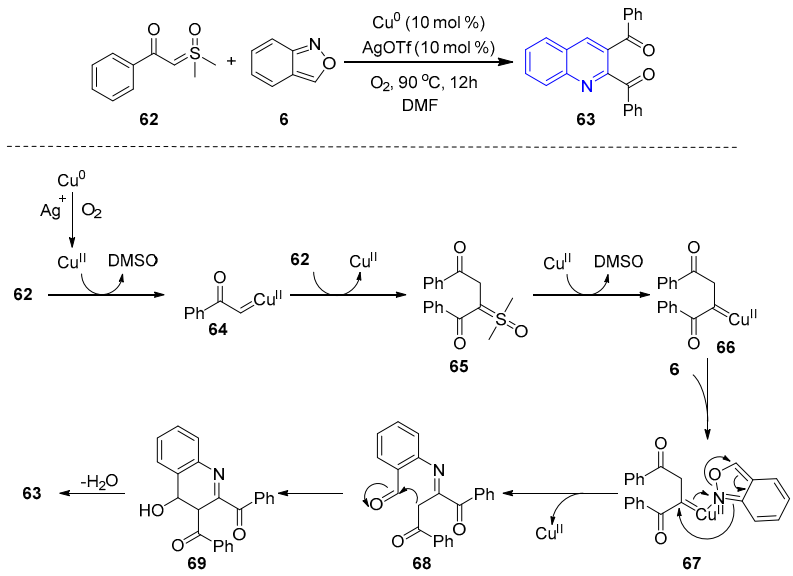
Scheme 8. Photo-thermo-mechanochemical approach to synthesize quinolines.

In 2020, Zou and coworkers developed an efficient Cu(0)-catalyzed [3 + 2 + 1] annulation strategy between anthranils and phenylacetaldehydes, enabling the synthesis of 8-acylquinolines under mild conditions (Scheme 9) [21]. The reaction, mediated by AgOTf and driven by dioxygen as the terminal oxidant, exhibited broad functional group tolerance, accommodating a variety of substituents. This method offered a straightforward and practical route to 8-acylquinolines that were valuable yet synthetically challenging scaffolds. Furthermore, the protocol allowed for subsequent aldehyde esterification, expanding its utility for the modular construction of diversely functionalized quinolines.



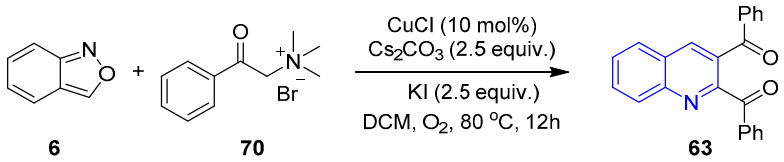
Scheme 9. Cu(0)-catalyzed [3 + 2 + 1] annulation to synthesize 8-acylquinolines.

In the same year, Zou et al. disclosed a copper-catalyzed [4 + 1 + 1] annulation of sulfoxonium ylides with anthranils to synthesize 2,3-diaroylquinolines (Scheme 10) [22]. The reaction, catalyzed by Cu(0) and AgOTf, proceeded under mild conditions with the utilization of dioxygen. The proposed mechanism for the synthesis of quinolines involved the generation of carbene intermediates from sulfoxonium ylides, which subsequently underwent cyclization with anthranils. Dioxygen played a key role in the oxidative process. For the homocoupling, a peroxy intermediate was formed, leading to tricarbonyl sulfoxonium ylides through dehydration. These transformations provided practical and efficient access to functionalized quinolines and sulfoxonium ylides.



Scheme 10. Copper-catalyzed [4 + 1 + 1] annulation to synthesize 2,3-diaroylquinolines.

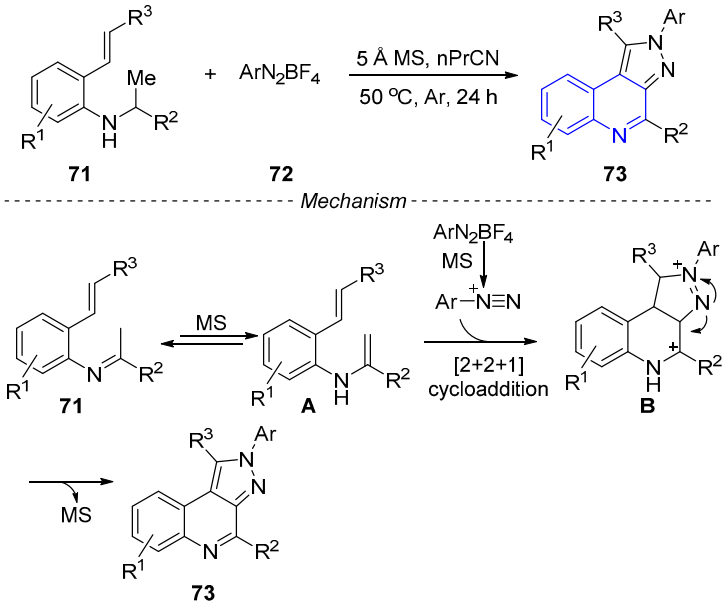
In 2024, the Zou group reported a copper(I)-catalyzed [4 + 1 + 1] annulation strategy employing ammonium salts and anthranils to access 2,3-diaroylquinolines under mild conditions (Scheme 11) [23]. This transformation, mediated solely by CuCl with molecular oxygen as the terminal oxidant, demonstrated notable advantages including readily available starting materials, broad substrate compatibility, and high product yields. The methodology provided an efficient and practical approach to construct these valuable heterocyclic scaffolds, which were otherwise challenging to synthesize through conventional routes.



Scheme 11. Copper(I)-catalyzed [4 + 1 + 1] annulation to synthesize 2,3-diaroylquinolines.

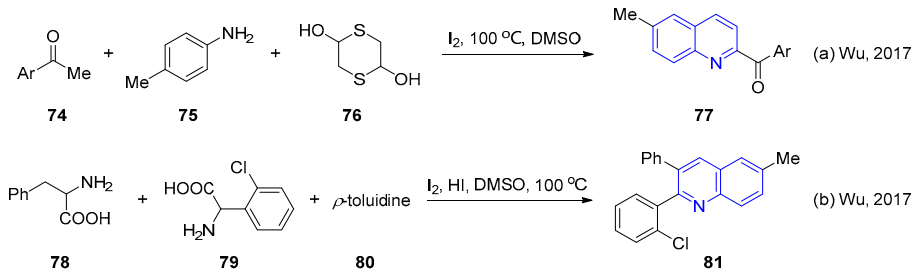
2.2. Oxidative Synthesis of Quinolines via Transition-Metal-Free C–H Transformations

Occasionally, obtaining the target molecule without the involvement of a transition metal is unnecessary. Alternatively, employing a streamlined one-pot system or approaches facilitated by molecular sieves can similarly achieve the objectives of atomic economy and environmental friendliness. For instance, a notable study by Jin-Heng Li and his team in 2016 [24] detailed a molecular sieve-mediated [2 + 2 + 1] cyclization reaction involving *N*-(*o*-alkenylaryl) imine and aryldiazonium salt. The pyrazolo quinoline skeleton could be directly synthesized, as demonstrated by the successful preparation of novel pyrazoloisoquinoline compounds, generating three new chemical bonds including one C–C bond and two C–N bonds. The research proposes a molecular sieve-mediated dehydrogenative heteroannulation mechanism: under basic 5Å MS, imine **71** isomerizes to intermediate **A**, which undergoes [2 + 2 + 1] cycloaddition with aryldiazonium (ArN_2^+) to form **B**, ultimately yielding pyrazolo[3,4-c]quinoline **73** via isomerization/dehydrogenation. The methyl C(sp^3)–H bond acts as a one-carbon unit to construct three bonds (C=C and two C–N) in one step (Scheme 12) [24].

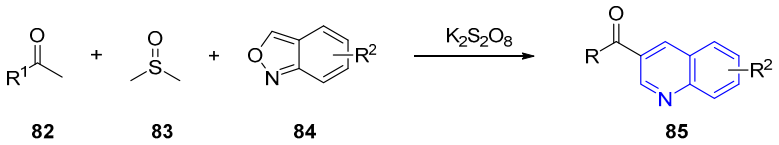


Scheme 12. Molecular sieve-mediated cyclization of imine with aryldiazonium salt.

Wu et al. proposed an efficient iodine element-induced [4 + 2] cycloaddition reaction to synthesize 2-acyl quinolines starting from aryl ketones, aromatic amines and 1,4-disulfide-2,5-diol (Scheme 13a) [25]. In 2017, they reported a method for synthesizing quinoline derivatives from aniline and two amino acids and for the first time proposed the concept of using two amino acids as heterocyclic precursors (Scheme 13b) [26]. Tiwari group reported the transition-metal-free one pot reaction of acetophenone, isoxazole, and DMSO in 2017. In this reaction, DMSO not only acted as a solvent but also as a carbon source (Scheme 14) [27].

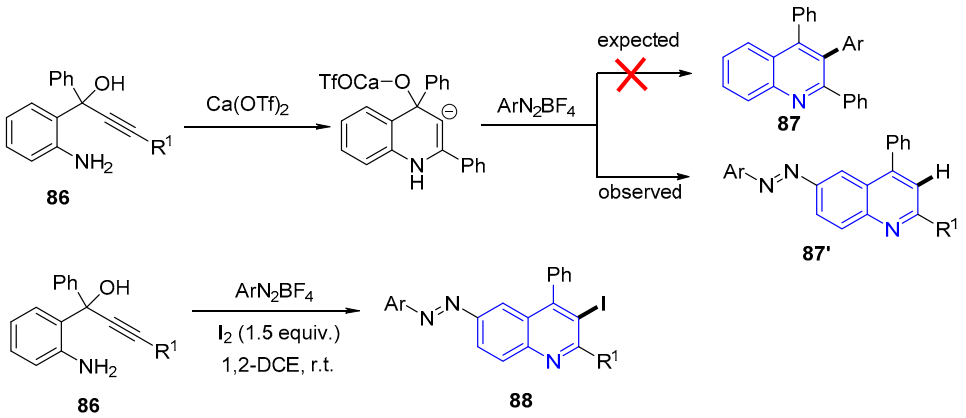


Scheme 13. Synthesis of quinolines by iodine oxidation.

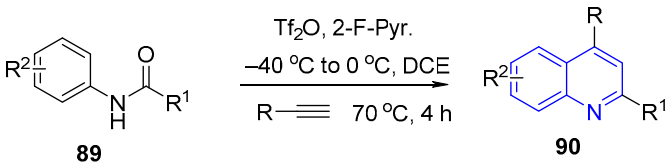


Scheme 14. One-pot reaction of DMSO as solvent and carbon source.

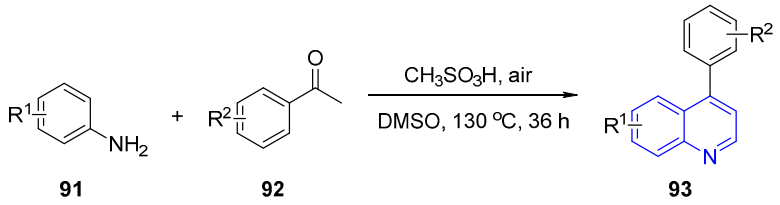
A one-pot process to synthesize 6-(aryldiazenyl)-3-iodoquinolines was also reported in 2018 by Srinivasarao Yaragorla et al., through a three-component reaction of 2-aminoaryl propargyl alcohols, aryldiazonium salts, and molecular iodine (Scheme 15) [28]. In the same year, a coupling reaction of secondary *N*-aryl amides with terminal alkynes was developed by Pei-Qiang Huang et al., synthesizing substituted quinolines under the activation system of triflic anhydride/2-fluoropyridine (Scheme 16) [29]. In 2018, compared with Anand Singh's reaction conditions, Xiu-Li Zhang et al. proposed a metal-free catalysis using CH_3SO_3H as an additive to synthesize quinoline from anilines, acetophenones, and DMSO under air (Scheme 17) [30].



Scheme 15. Synthesis of 6-(aryldiazenyl)-3-iodoquinolines by a three-component reaction.



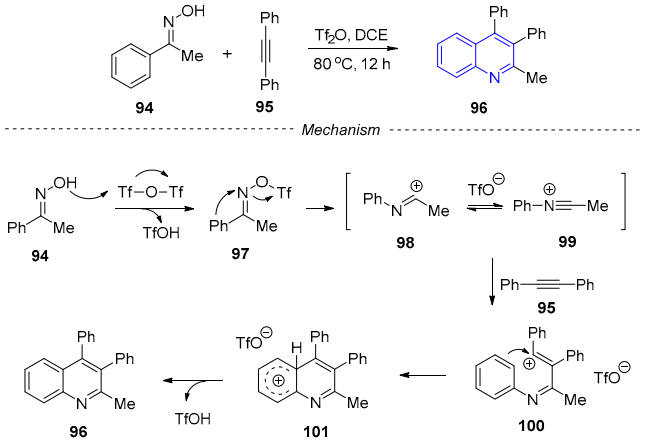
Scheme 16. Synthesis of quinolines via a coupling reaction of secondary *N*-aryl amides with terminal alkynes.



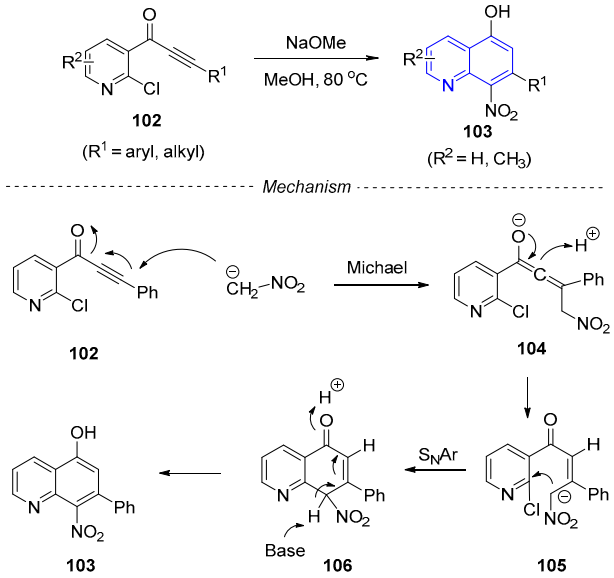
Scheme 17. Synthesis of quinolines from anilines, acetophenones, and DMSO.

In 2019, Hu's group proposed an efficient reaction to synthesize quinolines through Beckmann rearrangement of ketoximes, using Tf_2O as a catalytic agent to make the substituted ketoximes and either internal or terminal alkynes combine completely (Scheme 18) [31]. The possible pathway for the synthesis of **96** is proposed as shown in Scheme 18. Initially, the oxime **94** undergoes a Tf_2O-promoted Beckmann rearrangement, a process where ketoximes are converted into reactive nitrilium salts under acidic conditions, to yield the intermediate nitrilium salt **98**. When the salt **98** is captured by alkyne **95**, phenylsubstituted alkenyl cation intermediate **100** is formed. Finally, product **96** is obtained by an intramolecular electrophilic substitution of **100**.

In the same year, Goverdhan Mehta and his colleagues created a unique method by using substituted pyridines as a raw material without metal to explore the synthesis of quinolines [32]. They chose halopyridinyl ynones with nitromethane as a substrate in this way (Scheme 19). The plausible reaction mechanism for the new domino process is shown in Scheme 19. An initial Michael addition of the nitromethane anion to **102** leads to the intermediate **104**, which tautomerizes to the enone **105**. The recursive carbanion generated from **105** then displaces the aromatic chloride in a SNAr fashion to deliver **106**, followed by aromatization to afford **103**. The 6-π electrocyclization/halogen elimination process on the dienolate derived from **105**, leading to **103**, is less likely due to the well-documented propensity of 2-halopyridines to undergo SNAr reactions, where the reactivity order of halogens is fluorine > chlorine > bromine > iodine.

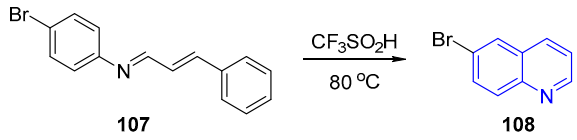


Scheme 18. Synthesis of quinolines via in situ generated nitrilium salts.



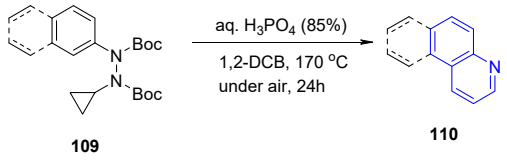
Scheme 19. Synthesis of quinolines via benzannulation of substituted pyridines.

In 2020, Klumpp and co-workers developed an efficient synthetic route to polysubstituted quinolines from vinylogous imines, employing superacids such as trifluoromethanesulfonic acid (TFA) or its anhydride (TFAA) as both the reaction medium and catalyst (Scheme 20) [33]. This methodology facilitated the construction of quinoline scaffolds via the condensation of aromatic amines with α,β-unsaturated carbonyl compounds under superacidic conditions, offering high efficiency and broad functional group compatibility.



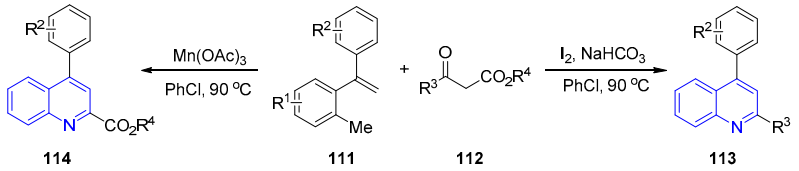
Scheme 20. Synthesis of polysubstituted quinolines from vinylogous imines.

In the same year, a novel method for quinoline synthesis promoted by a Brønsted acid via homo-diaza-Cope rearrangement of *N*-aryl-*N*′-cyclopropyl hydrazines was invented by Benjamin List et al. (Scheme 21) [34]. This method adopted a strategic combination of the classical Fischer indolization reaction and a homo-diaza-Cope rearrangement, enabling the efficient construction of quinoline scaffolds from readily available starting materials.



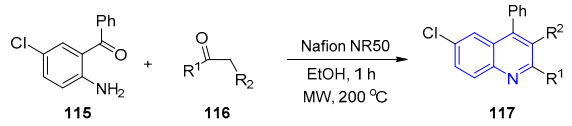
Scheme 21. Synthesis of quinolines via homo-diaza-Cope rearrangement of *N*-aryl-*N*′-cyclopropyl hydrazines.

During this year, Ze Zhang et al. developed a divergent synthetic strategy for polysubstituted quinolines from 2-styrylanilines and *β*-keto esters, controlled by promoter selection [35]. While iodine facilitated 2-alkylquinoline formation, manganese(III) acetate selectively afforded quinoline-2-carboxylates. This approach provided efficient access to both heterocyclic scaffolds under mild conditions with broad substrate scope, demonstrating the power of promoter-mediated chemoselectivity in quinoline synthesis (Scheme 22).



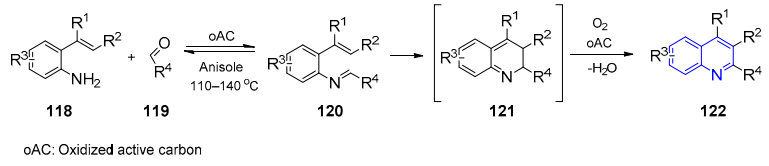
Scheme 22. Synthesis of 2-alkylquinolines via a cascade annulation of *β*-keto esters with 2-styrylanilines.

Also in 2020, a reusable solid acid catalyst called Nafion NR50 (a sulfonic acid functionalized synthetic polymer) was utilized by Wang et al. for the Friedländer quinoline synthesis in ethanol under microwave conditions [36]. This method applied a Nafion-mediated strategy under microwave irradiation to achieve the environmentally friendly synthesis of quinolines through the Friedländer reaction, utilizing 2-aminoaryl ketones and *α*-methylene carbonyl compounds as key substrates (Scheme 23).



Scheme 23. Synthesis of quinolines via the Friedländer reaction under microwave conditions.

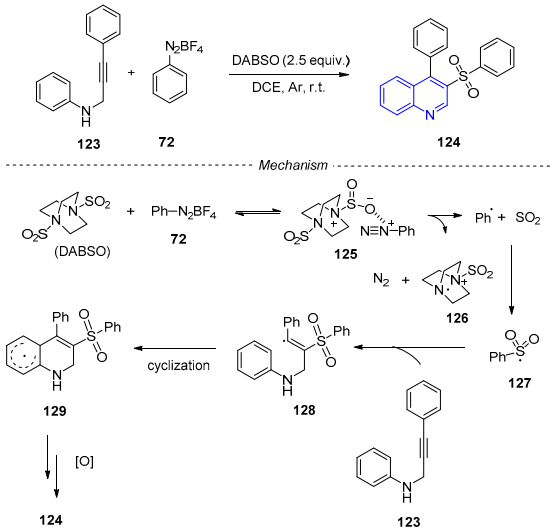
In 2021, carbocatalytic cascade synthesis of polysubstituted quinolines **122** from 2-vinyl anilines **118** and aldehydes **119** was proposed by Juho Helaja et al. [37] (Scheme 24). The reaction proceeded in a cascade manner through condensation, electrocyclization, and dehydrogenation, providing access to a wide range of quinolines with alkyl and/or aryl substituents. This method was in line with recent advancements in catalytic synthesis, such as the use of zinc iodide as a cost-effective catalyst, which has been shown to yield high rates of production and reduce the cost of synthesis significantly compared to traditional methods involving precious metal catalysts.



Scheme 24. Carbocatalytic cascade synthesis of polysubstituted quinolines from aldehydes and 2-vinyl anilines.

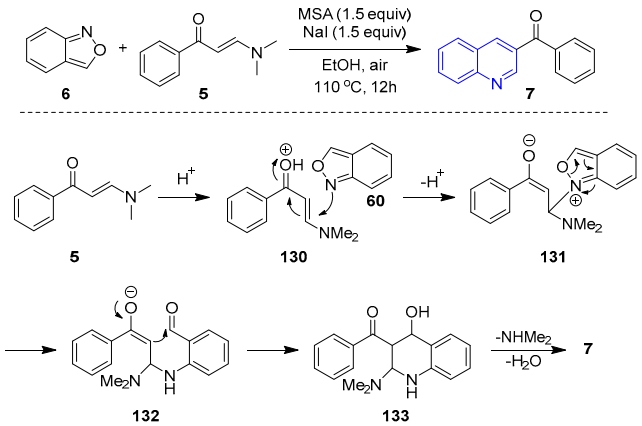
In 2022, Prasenjit Mal and his companions reported a cascaded oxidative sulfonylation of *N*-propargylamine via a three-component coupling reaction using DABCO·$(SO_2)_2$

(DABSO) [38]. 3-Arylsulfonylquinolines were obtained by mixing diazonium tetrafluoroborate, *N*-propargylamine, and DABSO under argon atmosphere in dichloroethane (DCE) without any metal and additives (Scheme 25). The mechanism involves the initial formation of a complex **125** between the aryl diazonium tetrafluoroborate and DABSO, via electrostatic interactions. Complex **125** undergoes nitrogen extrusion to generate intermediate **126**. As a result, aryl radical and sulfur dioxide, which are assumed to be formed in situ, reacted to generate an aryl sulfonyl radical **127**. Subsequently, the sulfonyl radical attacks the triple bond of *N*-propargylamine **123**, forming intermediate **128**, which promptly undergoes intramolecular cyclization to produce cyclized intermediate **129**. Lastly, rearomatization occurs through the oxidation of **129**, giving 3-aryl sulfonyl quinoline **124**.



Scheme 25. Synthesis of 3-arylsulfonylquinolines from N-propargylamines.

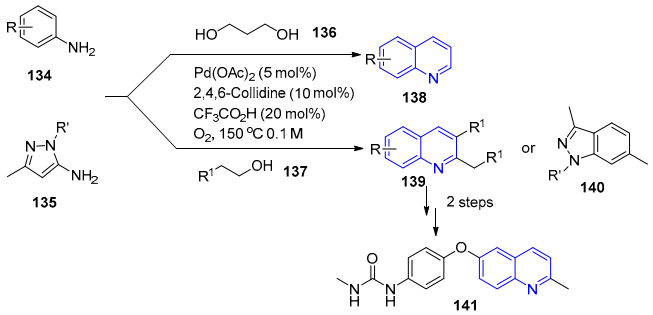
In 2023, Zou et al. developed a transition metal-free synthesis of 3-acylquinolines via annulation of anthranils and enaminones, catalyzed by methanesulfonic acid (MSA) and NaI under mild conditions [39]. The reaction accommodated diverse substrates, yielding 3-acylquinolines efficiently. The proposed mechanism involves MSA activation of enaminone **5** to form intermediate **130**, which reacts with anthranil **6** to generate intermediate **131**, stabilized by NaI. Intramolecular cyclization of intermediate **132** leads to intermediate **133**, which is converted to the final product **7**. This method was notable for its simplicity, high yields, and broad substrate scope, offering a practical and eco-friendly route to 3-acylquinolines (Scheme 26).



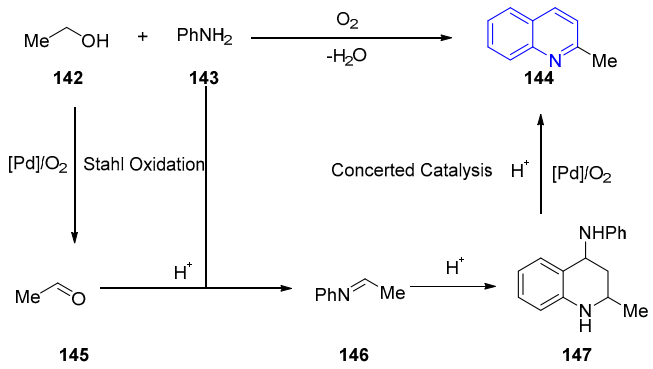
Scheme 26. Transition metal-free synthesis of 3-acylquinolines.

3. Oxidative Synthesis of Quinolines via Coupling Reaction of Aromatic Amine with Alcohol or Olefin

In recent years, the dehydration coupling reaction of aromatic amines and alcohols has also become a good choice for the construction of quinoline skeletons. Gao-Xi Jiang et al. published an article on the aerobic oxidation aromatization of simple aliphatic alcohols and anilines catalyzed by $Pd(OAc)_2$/2,4,6-Collidine/Brønsted acid in 2017 (Scheme 27) [40]. The system could be readily scaled up to the gram-scale level, offering a straightforward method for the preparation of diverse substituted quinoline derivatives in high yields. The reaction mechanism is shown in the figure below (Scheme 28).



Scheme 27. Aerobic oxidation aromatization reaction of fatty alcohol and aniline with Brønsted acid.

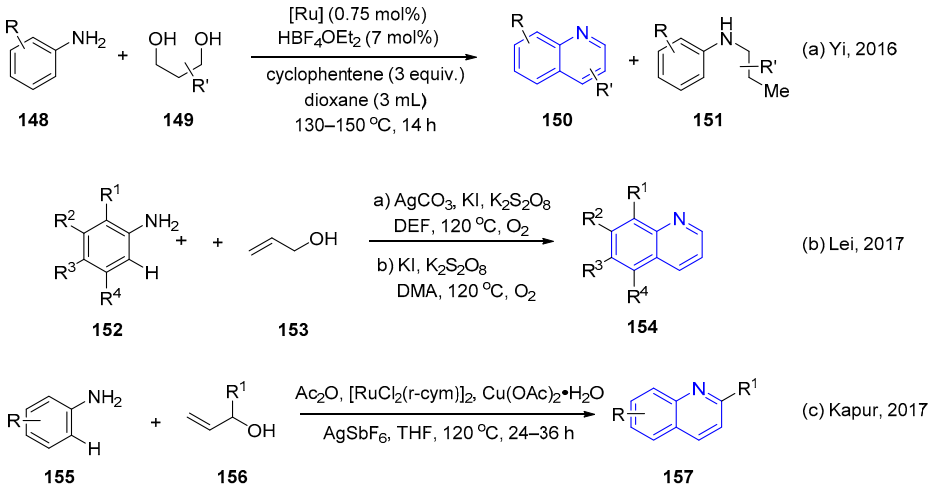


Scheme 28. A proposed mechanism for the Brønsted acid catalysis.

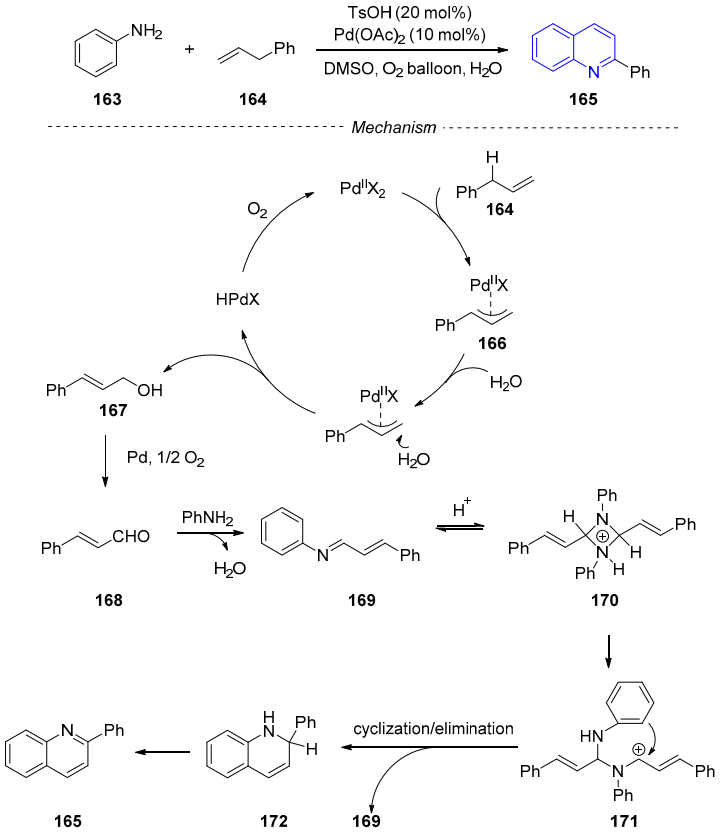
In 2016, Chae S. Yi and his colleagues discovered that arylamine and 1,3-diol could undergo dehydration C–H coupling reaction under the catalysis of ruthenium metal organic framework to obtain quinoline derivatives (Scheme 29a) [41]. Lei's group discovered the oxidative cyclization-aromatization reaction of aniline and allyl alcohol mediated by silver carbonate and iodide ion in 2017 [42]. Various types of quinolines were prepared, yielding moderate to good amounts of the derivative (Scheme 29b). In the same year, Manmohan Kapur invented a unique ruthenium-catalyzed cyclization reaction of [3 + 3] aniline and allyl alcohol, where a strategy of traceless guiding groups was employed in the activation of proximal C–H bonds (Scheme 29c) [43].

Another method for obtaining quinoline derivatives with allyl substrates participating in the reaction was developed by Jiang's group [44]. In 2016, they used a palladium-catalyzed aerobic oxidation method to obtain a variety of disubstituted quinolines (Scheme 30). The plausible mechanism is proposed as shown in Scheme 30. Initially, the corresponding π-allylpalladium species intermediate **166** is generated via coordination between the allylic C–H bond of the olefin and palladium. Subsequently, the nucleophilic attack by H_2O subsequently occurs to afford the cinnamic alcohol intermediate **167**. Oxidation of **167** by O_2 affords the cinnamaldehyde **168**. Then, the next step is a traditional condensation leading to the formation of an imine, followed by a conjugate addition of a

second molecule of imine in the presence of TsOH. Therefore, the labile diazetidinium cation intermediate **170** is formed. Then following the irreversible cyclization and elimination of **171**, 7,2-phenyl-1,2-dihydroquinolin **172** is generated. With the subsequent oxidation, the desired product **165** was afforded. Finally, Pd(0) is oxidized to regenerate the active species Pd(II) by dioxygen.



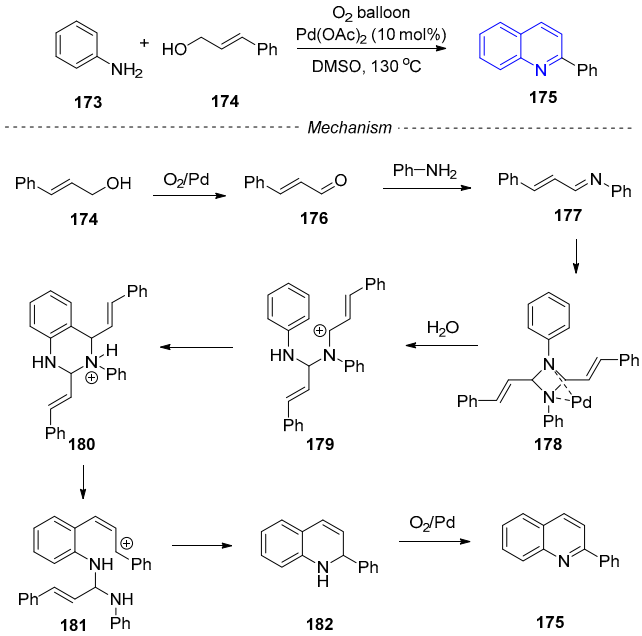
Scheme 29. Transition metal participation in the coupling of aromatic amines with alcohols or olefins.



Scheme 30. Palladium-catalyzed allylic C–H oxidative annulation for assembly of functionalized 2-substituted quinoline derivatives.

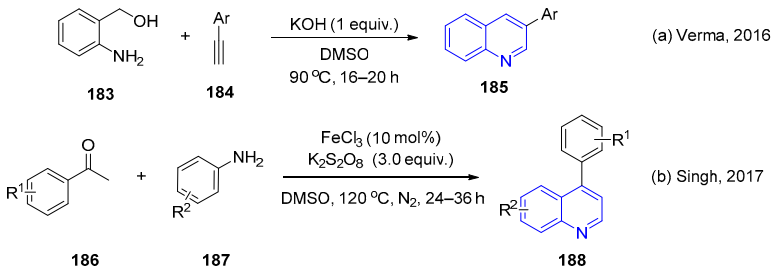
Jin-Wu Zhao et al. also discovered a method for synthesizing quinoline through palladium-catalyzed oxidative cyclization of aryl allyl alcohol and aniline in 2017 (Scheme 31) [45]. This protocol was conducted under redox-neutral conditions without the need for acids, bases, or additional additives, achieving a high yield of quinoline derivatives. It was capable of tolerating a broad range of substrates, including those with

electron-withdrawing groups such as nitryl and trifluoromethyl. The reasonable reaction pathway for palladium-catalyzed quinoline synthesis from allyl alcohols with anilines is illustrated in Scheme 31. Firstly, cinnamic alcohol **174** undergoes oxidation catalyzed by palladium, utilizing dioxygen as the oxidant to yield α,β-unsaturated aldehyde **176**. Subsequently, this aldehyde reacts through condensation with aniline, resulting in the formation of imine **177**. Under palladium catalysis, the dimerization process progresses, yielding diazetidine intermediates **178**. The C–N bond undergoes cleavage, leading to an irreversible cyclization that forms intermediate **180**. This intermediate then readily isomerizes into **181**, driven by charge interactions, followed by an intramolecular nucleophilic attack. The elimination of 1 mole of imine results in the formation of 2-phenyl-1,2-dihydroquinoline **182**. Palladium-catalyzed dehydro-aromatization subsequently occurs to yield the final product **175**.



Scheme 31. Palladium-catalyzed synthesis of quinolines from allyl alcohols and anilines.

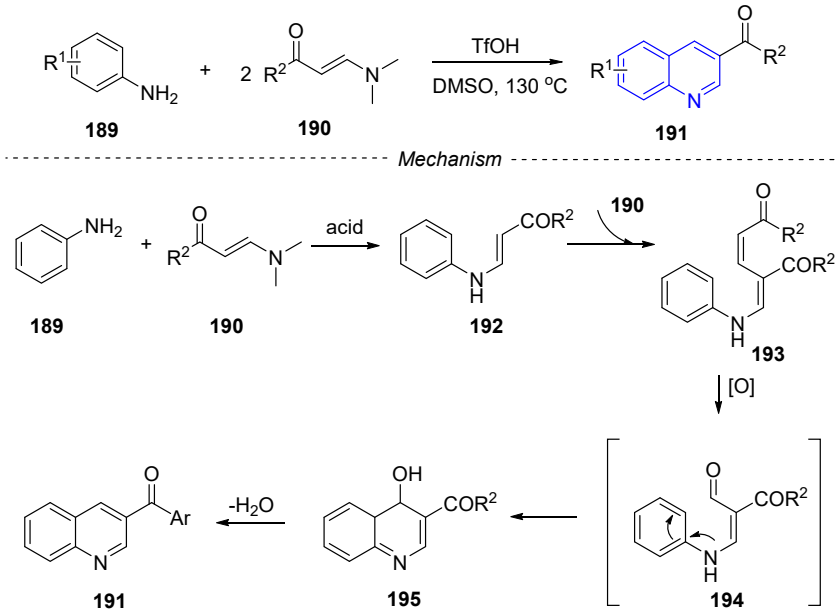
Akhilesh K. Verma and colleagues developed a regioselective synthetic route to C-3-functionalized quinolines through [4 + 2] cycloaddition of 2-aminobenzyl alcohols with terminal alkynes (Scheme 32a) [46]. In related work, Anand Singh and co-workers reported in 2017 an alternative approach for preparing 4-arylquinolines via oxidative cyclization of aryl ketones with anilines, where DMSO served as both a solvent and methylene source under $K_2S_2O_8$-mediated conditions (Scheme 32b) [47].



Scheme 32. Potassium hydroxide and potassium salt-mediated cyclization.

In the same year, Wan and co-workers explored a domino reaction between *N*,*N*-dimethyl enaminones and anilines providing 3-acyl quinolines promoted by triflic acid

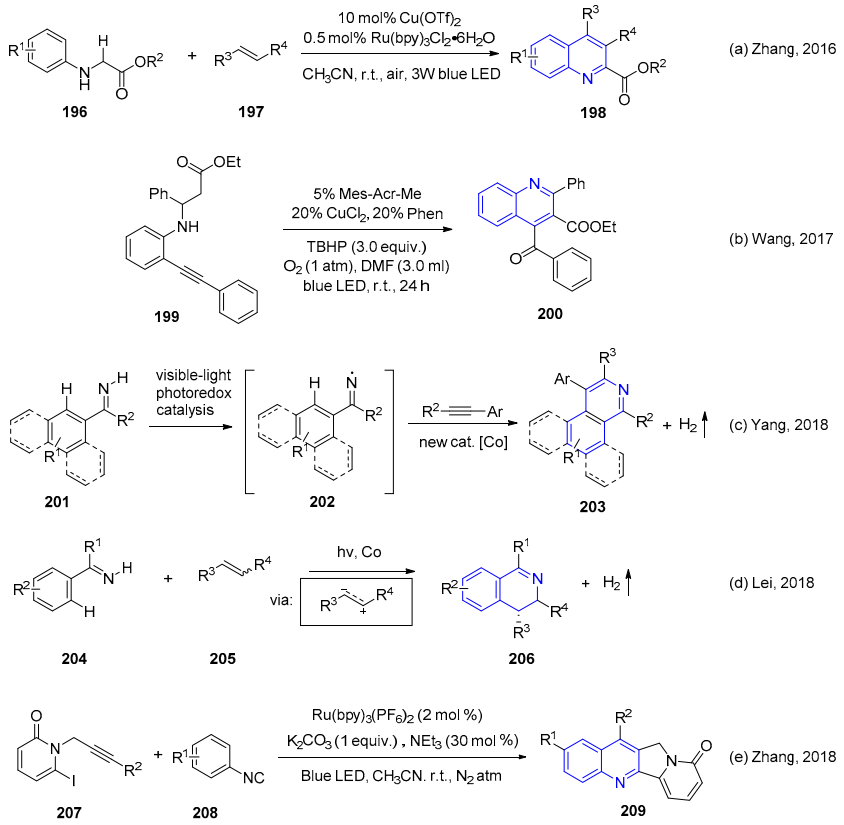
(Scheme 33) [48]. The proposed mechanism for the synthesis of quinolines **191**, as depicted in Scheme 33, involves a facile transamination reaction between anilines **189** and *N*,*N*-dimethyl enaminones **190**, leading to the formation of NH-based enaminones **192**. And the enaminone **192** might further incorporate other molecules of enaminone **190** to provide intermediate **193** via C–N bond cleavage under acidic condition. Although the exact process was not yet clear, it was well known that the C=C double bond could undergo oxygenation to yield carbonyl intermediates or equivalent species through oxidative cleavage. The phenyl ring underwent an intramolecular nucleophilic addition to the active carbonyl group, resulting in the formation of intermediate **194**. The quinoline product **191** would be generated through dehydration of compound **195**.



Scheme 33. A novel approach to synthesize quinoline without the reliance on metal catalysts.

4. Oxidative Synthesis of Quinolines via Photo-Induced Oxidative Annulation Reactions

In 2016, Yuan Zhang completed the visible light-induced aerobic oxidative dehydrogenation coupling/aromatization cascade reaction between glycine esters and olefins to produce various substituted quinoline derivatives (Scheme 34a) [49]. In 2017, the Wang group employed visible light, assisted by copper or palladium catalysts, to accomplish the direct oxidation and cyclization of aromatic enamines with alkynes or olefins under mild conditions, yielding a diverse range of polysubstituted quinoline derivative products in a moderate yield (Scheme 34b) [50]. Yang Li et al. discovered in 2018 that visible light catalyzes the formation of imino radicals [51]. This process was achieved through the cleavage of N–H bonds and the release of hydrogen, which could be used in the synthesis of various isoquinolines (Scheme 34c). In 2018, Ai-Wen Lei et al. published a study on the development of a photo-induced oxidation [4 + 2] cyclization reaction of N–H imines and olefins, utilizing photoredox/cobalt oxime dual catalytic systems, leading to the formation of multi-substituted 3,4-dihydroisoquinolines (Scheme 34d) [52]. Zhang and his colleagues constructed indolizino[1,2-b]quinolin-9(11H)-one derivatives through the method of photoredox catalyzed cyclization of isocyanoarenes **208** with *N*-(alkyl-2yn-1-yl) pyridine-2(1H)-ones **207** under 12 W blue LED irradiation (Scheme 34e) [53].

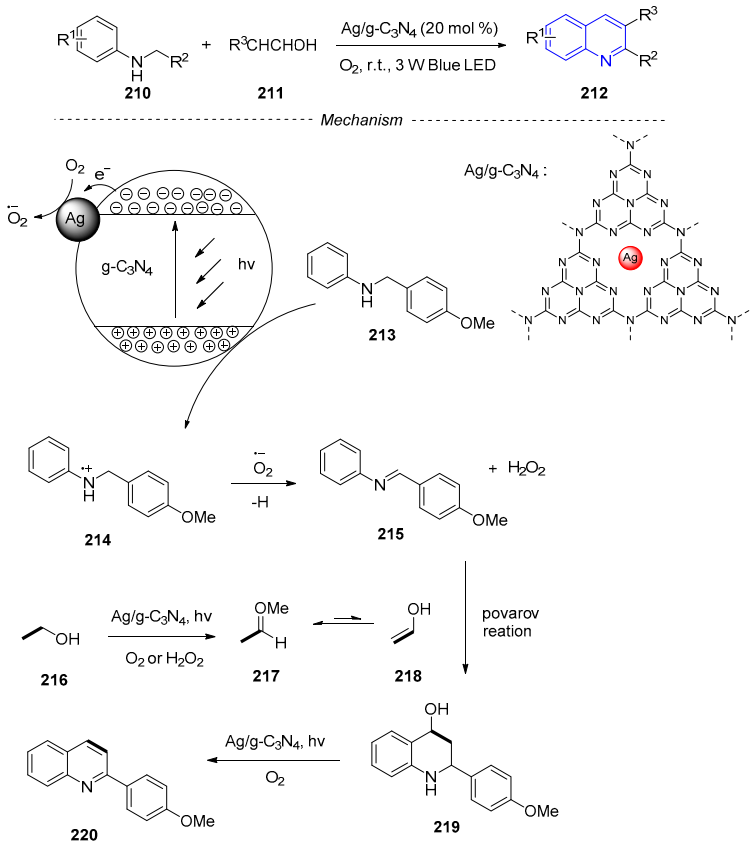


Scheme 34. Visible light-induced oxidative cyclization.

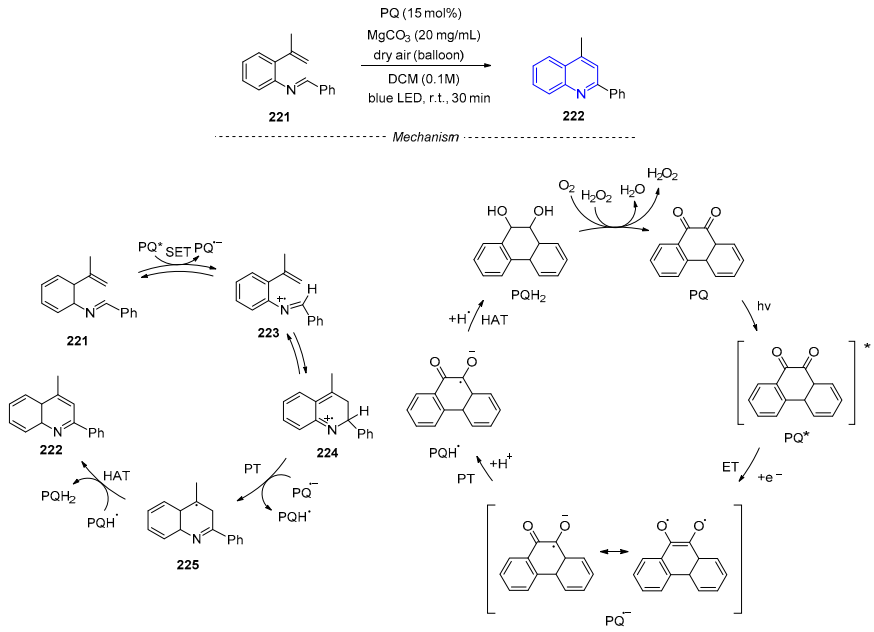
In 2020, Yao and colleagues introduced a semiconductor photocatalyzed method for the Povarov cyclization reaction, utilizing a blue LED to synthesize 2-arylquinolines. This method involved the Ag/g-C_3N_4 nanometric semiconductor as the photocatalyst, illustrated in Scheme 35 [54]. The proposed reaction mechanism is shown in Scheme 35. Initially, upon exposure to visible light, g-C_3N_4 becomes excited to generate conduction band electrons and valence band holes, and then, amine **213** releases one electron on the valence band holes to give the *N*-radical cation intermediate **214**. Furthermore, the photo-generated electrons excited to the conduction band are effectively trapped by synthesized silver nanoparticles (Ag NPs), which can then reduce the electron acceptor O_2 to form superoxide radical anions, thereby enhancing the photocatalytic activity. This process is supported by research demonstrating the photocatalytic properties of Ag NPs synthesized from plant extracts and their ability to degrade pollutants under visible light. Furthermore, with the promotion of superoxide radical anion, the photocatalytic process can effectively oxidize and degrade organic pollutants in wastewater, *N*-arylaldimine **215** is then formed. Subsequently, the in situ formed *N*-arylaldimine **215** reacts with acetaldehyde, which is produced from the photo-oxidation of ethanol catalyzed by Ag/g-C_3N_4, to generate the intermediate **219** in a Povarov process. Finally, oxidative dehydroaromatization of **219** gives the final product **220**.

In 2022, Juho Helaja and his colleagues found a new photocatalyst for the synthesis of polysubstituted quinolines via the electrocyclization of 2-vinylarylimines, which was visible-light-excited 9,10-phenanthrenequinone (PQ*) (Scheme 36) [55]. With $MgCO_3$ as an additive in DCM, various 2,4-disubstituted quinolines could be obtained in high yields. The detailed plausible reaction mechanism is also proposed. After being excited by visible light to its excited triplet state, PQ* induces single-electron transfer (SET) from 2-vinylarylimine **221**. This generates a radical cation **223** that cyclizes to a dihydroquinoline cation radical **224**. Then, the radical anion removes an acidic proton, providing intermediate **225**. Fi-

nally, the process of hydrogen-atom transfer (HAT) forms the quinoline product **222**, and 9,10-phenanthrenequinone is regenerated by molecular oxygen.



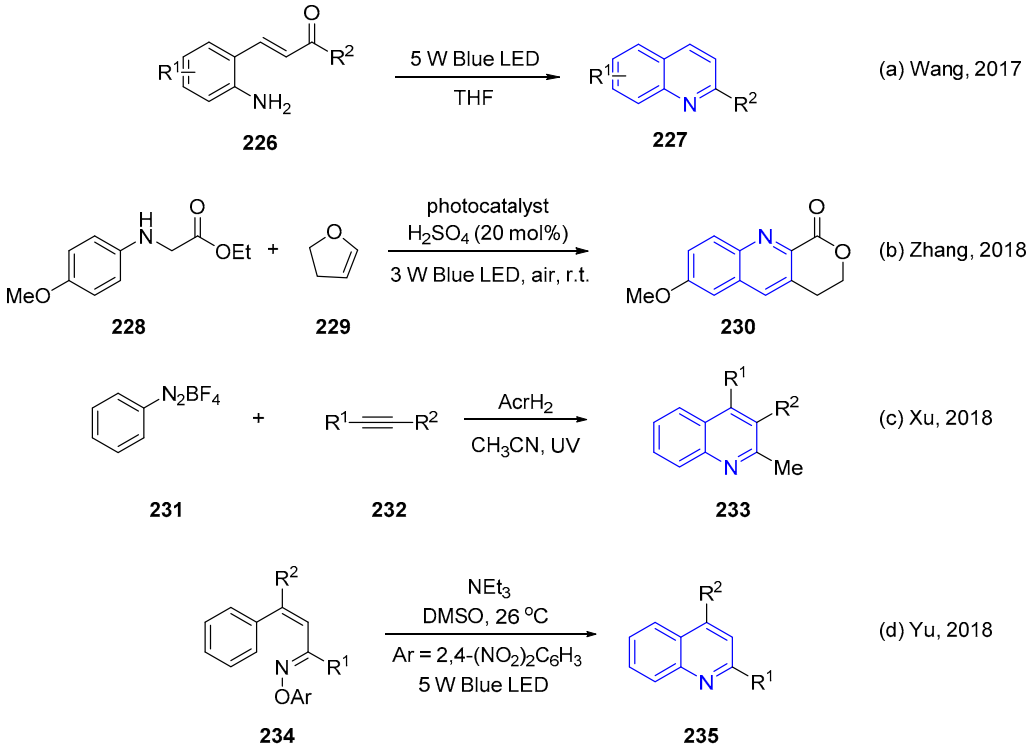
Scheme 35. Visible-light-induced photoxidation-Povarov cascade reaction.



Scheme 36. Phenanthrenequinone-sensitized photocatalytic synthesis of polysubstituted quinolines from 2-vinylarylimines.

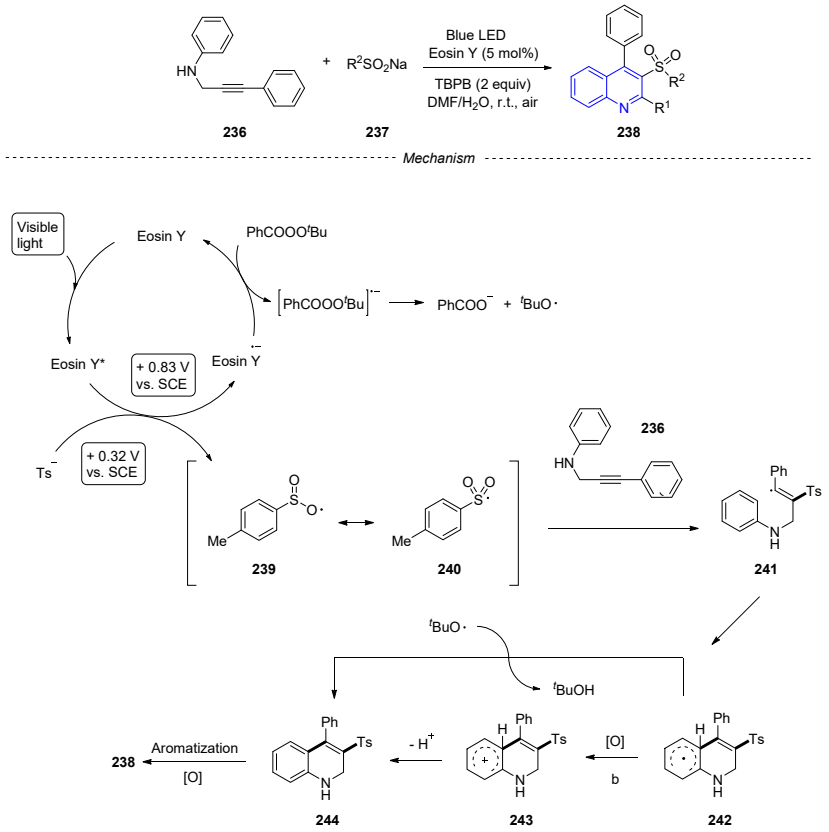
In 2017, Wang et al. discovered a photocatalyst-free, 5 W blue light-promoted approach for converting electronically diverse α,β-unsaturated ketones to various 2-aryl/-alkyl quinolines in good yields (Scheme 37a) [56]. Zhang et al. also published in 2018

about the metal-free aerobic oxidative dehydrogenation coupling/cyclization reaction of photocatalytic glycine derivatives and 2,3-dihydrofuran and the reaction could be amplified to the gram level (Scheme 37b) [57]. In 2018, an efficient metal-free photoredox catalysis for quinoline synthesis using 10-methyl-9,10-dihy-droacridine ($AcrH_2$) as the catalyst in a cascade annulation reaction was reported by the team of Xu (Scheme 37c) [58]. In the same year, Yu et al. reported a more environmentally friendly way without photocatalyst, which was an electron donor-acceptor (EDA) complex-promoted synthesis of quinolines [59]. Recently, the research of visible-light promoted metal-free protocol for sulfonylation of *N*-propargylanilines caused widespread concern (Scheme 37d).



Scheme 37. Aerobic oxidation reaction without metal photocatalysis.

Huang et al. in 2022 reported a method for synthesizing quinoline derivatives using sodium sulfinates as a green inorganic sulfur source, which complements the synthesis process [60]. Compared with the previous reports, the raw materials are obtained relatively more easily than other precursors of organic sulfonyl radicals (Scheme 38). The plausible mechanism for the formation of 3-sulfonylquinolines involving *N*-propargylanilines and sodium sulfinates is outlined in Scheme 38. Under blue LED irradiation, the photocatalyst upon excitation, Eosin Y transitions to its excited state, which is subsequently reductively quenched by the sulfinyl anion, yielding Eosin $Y^{\cdot -}$ and an oxygen-centered radical **239** that resonates with a sulfonyl radical **240**. The addition of **240** to **236** gave new radical intermediate **241**, followed by an intramolecular radical cyclization to give the cyclized radical intermediate **242**. The *t*-BuO· radical generated from the single electron transfer process between TBPB and Eosin $Y^{\cdot -}$ abstracted a hydrogen atom from **242** to afford the 1,2-dihydroquinoline **244** and *t*-BuOH. Certainly, intermediate **242** might be oxidized to the corresponding cyclohexadienyl cation **243**, which is transferred to **244** after deprotonation. Finally, an aromatization process of **244** is executed smoothly to construct the target product **238**.



Scheme 38. Visible-light promoted metal-free synthesis of 3-sulfonylquinolines.

5. Conclusions

The synthesis of quinolines through oxidative annulation has evolved significantly, driven by advancements in transition metal catalysis, photoredox chemistry, and sustainable methodologies. Key strategies include C–H bond activation, dehydration coupling, and photo-induced cyclization, offering high efficiency, broad substrate tolerance, and environmental compatibility. Future research should prioritize scalability, cost-effectiveness, and the integration of computational tools to guide catalyst design. This comprehensive review serves as a pivotal resource for researchers in the field of organic chemistry and medicine chemistry, providing critical insights for developing novel methodologies that harmonize ecological responsibility with industrial practicality. Within the current scientific paradigm characterized by intensified demands for sustainable pharmaceutical manufacturing, our systematic analysis highlights the urgent necessity to establish green chemistry solutions for scalable production of this privileged heterocyclic scaffold.

Despite notable advancements in the oxidative synthesis of quinolines, several critical challenges persist, limiting their broader applicability. A primary concern is the reliance on precious metal catalysts (e.g., palladium, gold) and stoichiometric oxidants, which not only escalate costs but also pose significant environmental and sustainability concerns. Furthermore, issues such as limited substrate scope, moderate selectivity, and unsatisfactory yields, particularly in the synthesis of complex or polysubstituted quinolines, remain unresolved. To overcome these limitations, future research should focus on three key directions: (1) developing sustainable catalytic systems employing earth-abundant transition metals (Fe, Cu) or photocatalytic protocols; (2) exploring environmentally benign oxidants (e.g., O_2, H_2O_2) and green solvents (aqueous or ionic liquid media); and (3) integrating computational chemistry with machine learning algorithms to optimize reaction parameters and predict synthetic pathways. These strategic developments promise to establish more efficient, cost-effective, and environmentally responsible synthetic routes for quinoline production.

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