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Silver-Mediated C−H Activation: Oxidative Coupling/Cyclization of *N*-Arylimines and Alkynes for the Synthesis of Quinolines

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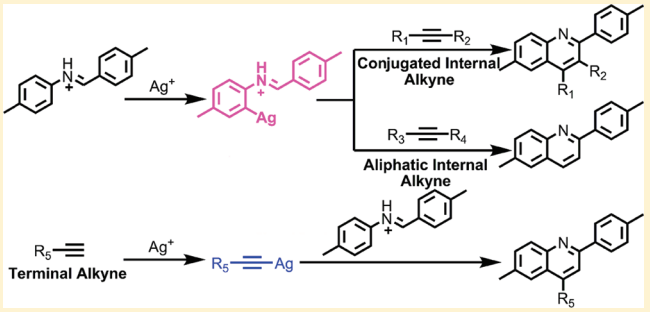
Supporting Information

ABSTRACT: A silver-mediated tandem protocol for the synthesis of quinolines involving the oxidative coupling/cyclization of *N*-arylimines and alkynes has been developed. We demonstrated that scenario-dependent metalation could occur either at the *ortho* C−H bond of an *N*-arylimine through protonation-driven enhancement of acidity or at the terminal C−H bond of an alkyne by virtue of the carbophilic π-acidity of silver. The diverse set of mechanistic manifolds implemented with a single type of experimental protocol points toward the importance of stringent reactivity analysis of each individual potentially reactive molecular site. Importantly, the direct arene C−H bond activation provides a unique and distinct mechanistic handle for the expansion of reactivity paradigms for silver. As expected, the protocol allows for the incorporation of both internal and terminal alkynes into the products, and in addition, both electron-withdrawing and -donating groups are tolerated on *N*-arylimines, thus enabling the vast expansion of substituent architectures on quinoline framework. Further, an intriguing phenomenon of structural isomerization and chemical bond cleavage has been observed for aliphatic internal alkynes.

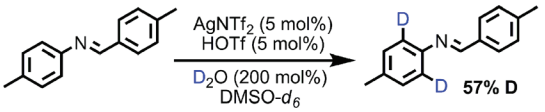


INTRODUCTION

Silver has received increased attention in the organic synthesis arena by virtue of its expanding reactivity patterns that have been discovered recently.[1] Indeed, silver-mediated organic transformations have emerged as an important synthetic tool for the construction of many architecturally intriguing molecules.[1b] In particular, the carbo-, oxo-, and azaphilicity associated with this precious metal have enabled the generation of functionally diverse heterocycles.[1c] The Lewis acidity is typically exploited to activate the bound functionality for viable reactivity either through the depletion of electron density,[1d] or in the case of terminal alkynes, based on the deprotonation process.[1e] In an effort to pursue the diversification of silver chemistry, we have turned our attention to the possibility of achieving disparate mechanistic manifolds within a single type of reaction system. *N*-arylimines and alkynes are the substrates of our particular interest for activating and coupling. We hypothesized that scenario-dependent metalation could occur either at the *ortho* C−H bond of an *N*-arylimine through protonation-driven enhancement of acidity or at the terminal C−H bond of an alkyne by virtue of the carbophilic π-acidity of silver. Herein, we wish to report a silver-mediated tandem protocol for the synthesis of quinolines involving the oxidative coupling/cyclization of *N*-arylimines and alkynes. This protocol allows for the incorporation of both internal and terminal alkynes into the products and both electron-withdrawing and -donating groups are tolerated on *N*-arylimines. Further, an intriguing phenomenon of structural isomerization and chemical bond cleavage has been observed for aliphatic internal alkynes. Most importantly, the direct arene C−H bond activation mode provides a unique and distinct mechanistic handle for the expansion of reactivity paradigms for silver.

RESULTS AND DISCUSSION

Our study began with the evaluation on the feasibility of activating the *ortho* C−H bond of protonated imine with silver. Indeed, a rapid H/D exchange between an *N*-arylimine and D_2O could be observed with the participation of $AgNTf_2$ and HOTf (eqs S1, Supporting Information, and 1). The process



(1)

became extremely sluggish in the absence of either $AgNTf_2$ or HOTf. The requisite use of HOTf and selective C−H activation at *N*-aryl carbon argues against either chelation-assisted or proximal site mechanism.[2] Indeed, typical chelation-based C−H activation would occur with the formation of a stable five-membered metalacycle and preferred coordination of Ag^I with the imine nitrogen should be translated to the *C*-aryl C−H bond activation.[1b,3] In addition, protonation at the imine

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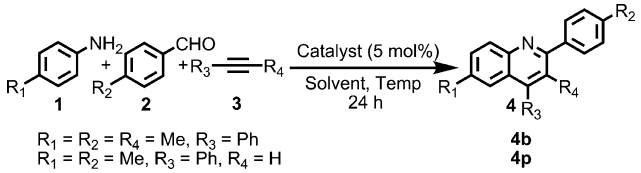
Table 1. Optimization of Reaction Conditions



entry	catalyst	solvent	temp (°C)	isolated yield 4b	isolated yield 4p
1	$AgNTf_2$/HOTf	Toluene	80	78%	96%
2	$AgNTf_2$	Toluene	80	23%	40%
3	HOTf	Toluene	80	NR	10%
4	$AgNTf_2/AlMe_3$	Toluene	80	65%	70%
5	$AgNTf_2/CF_3COOH$	Toluene	80	68%	75%
6	$AgNTf_2$/HOTf	CH_2Cl_2	50	12%	NR
7	$AgNTf_2$/HOTf	DMF	120	NR	NR
8	$AgNTf_2$/HOTf	THF	60	32%	NR
9	$AgNTf_2$/HOTf	CCl_4	76	NR	NR
10	$AgNTf_2$/HOTf	Toluene	60	68%	75%
11	HOTf	Toluene	60	NR	NR

nitrogen would render the functional group highly electron deficient and a less likely coordination site for Ag^I. Further, acidic conditions have been postulated to be beneficial to the enhancement of electrophicility of cationic metals.[4] However, it is unlikely to be operative here since NTf_2^- is already a highly noncoordinating anionic species. Taking into account above considerations and acidity enhancement of *ortho* C−H bond upon imine protonation, the activation process therefore favors a mechanistic interpretation by the concerted metalation-deprotonation (CMD) mechanism.[5] Transition metal-mediated C−H functionalization has become an active research area due to the ability to achieve conceptually distinct reaction modes.[2] For arene type of substrates, the C−H bond functionalization is most successfully achieved via electrophilic aromatic substitution (EAS), which entails the requisite use of an electrophilic metal catalyst and an electron-rich aromatic structure. As an alternative pathway, CMD mechanism has been recently proposed to account for the unusual reactivity of electron-deficient, C−H acidic aromatic rings.[5] The positive correlation between the acidity and reactivity is furnished by the initial agostic interaction of C−H bond with metal and subsequent facile deprotonation by the counterion (through either σ-bond metathesis or base assistance), thus complementing the reaction pattern through the Wheland intermediate. For such a CMD-based strategy, the research is directed largely toward the exploitation of high-valent cationic species and only recently has the direct evidence for a low-valent Au^I-mediated stoichiometric C−H activation been identified.[6] We envisioned that the novel reactivity mode could be imparted on silver with otherwise unattainable C−H activation-driven, synthetically useful reaction patterns. With the encouraging C−H activation result in hand, we theorized that the carbon nucleophile generated thereof could be used for the attack on a Ag^I-activated alkyne. Gratifyingly, reaction of an *N*-arylimine and an internal alkyne allows for the generation of a quinoline derivative. Further screening of the reaction conditions indicates that an amine/aldehyde/alkyne combination (Table 1) is as effective as an imine/alkyne mix for the transformation, offering evidence that the product formation proceeds through the same reaction pathway. Notably, the desired product is formed in high yield only in the presence of both $AgNTf_2$ and HOTf (entry 1). The lack of substantial reaction in the exclusive presence of HOTf (entry 3) suggests that Ag^I is an indispensable species driving the catalytic coupling/cyclization process. The ability to generate quinoline derivative from the internal alkyne is consistent with a pathway involving the initial carbometalation of alkyne and a subsequent cyclization of carbometalated product with the iminium unit (Scheme 1). Since alkyne could be activated by Ag^I, and migratory insertion is not a common process in coinage metal-mediated reactions, the carbometalation should be achieved through the nucleophilic attack of Ag^I-linked *N*-aryl carbon on Ag^I-activated alkyne. It should be noted that the proposed transformation from dihydroquinoline to quinoline is a commonly observed process,[7] which presumably proceeds through the oxidation by air during the postreaction workup step. The electron-deficient nature of the iminium group allows the cyclization process to proceed through nucleophilic attack of Ag^I-attached alkenyl bond on the partially positively charged iminium carbon. Further evidence for the protonation-enabled C−H acidity enhancement mechanism comes from the observation that an increased product yield could be obtained through the assistance of a main-group Lewis acid (entry 4). Indeed, such a Lewis acid-based C−H acidity enhancement has been employed previously on a site-selective alkenylation/alkylation of heterocycles.[8] Toluene is the solvent of choice for the oxidative coupling/cyclization tandem sequence and the reaction can be carried out at a relatively low temperature (80 °C). Other reaction media tested, including CH_2Cl_2, DMF, THF, and CCl_4 (entries 6−9), could not effect the desired transformation with a yield comparable to that in toluene. Further lowering the temperature to more benign 60 °C still enables the product formation with a reasonably high yield (entry 10). The reaction gets completely suppressed in the absence of $AgNTf_2$ at such a temperature (entry 11). Without the participation of silver, no product was observed for the internal alkyne even at higher temperatures (e.g., 110 °C), while the corresponding quinoline derivative could be obtained for the terminal alkyne. Therefore, Ag^I is absolutely essential for the transformation involving internal alkynes and it can also contribute to the quinoline formation for terminal alkynes under more benign settings. Interestingly, under the experimental

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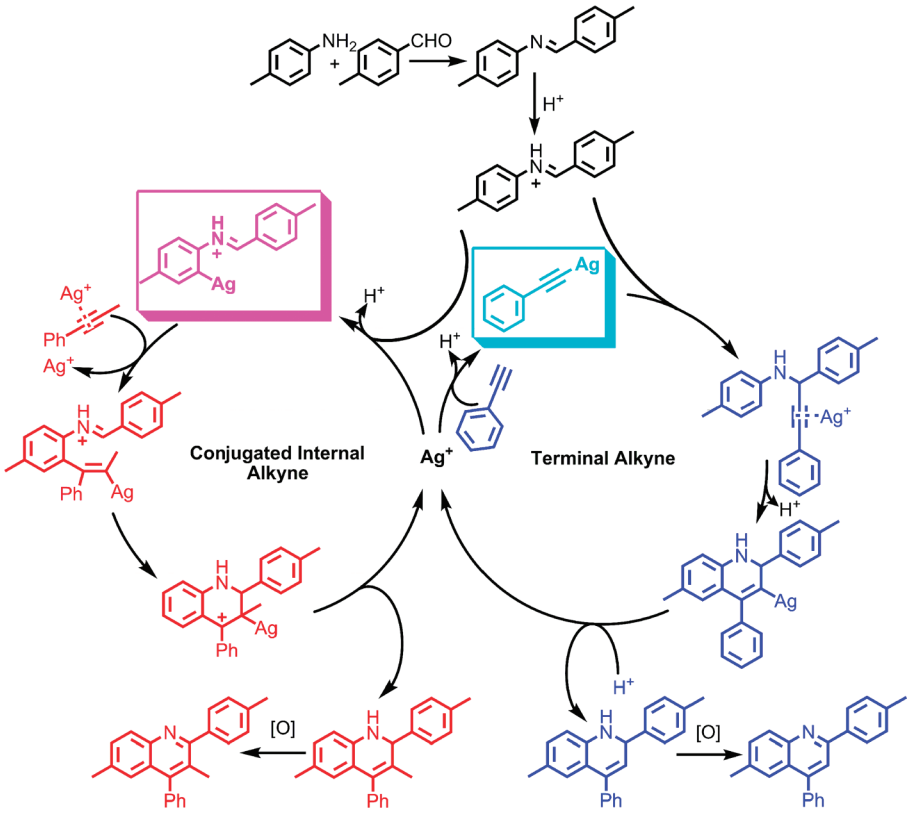
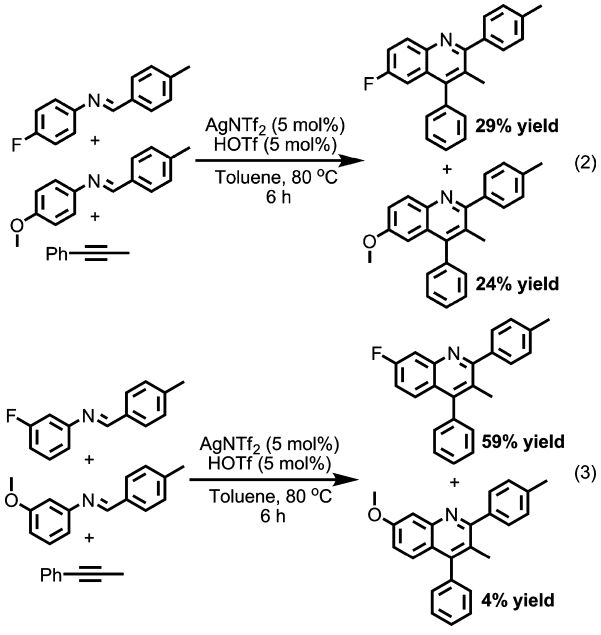
Scheme 1. Proposed Transformation Mechanisms for Conjugated Internal Alkynes and Terminal Alkynes



conditions employed herein, terminal alkynes generally offer better yields than those from internal alkynes (entries 1, 4, 5, and 10). However, in spite of similarity in the frameworks of end products, the reactions with internal and terminal alkynes most likely proceed through distinctly different mechanistic pathways (*vide infra*).

To further probe the reaction mechanism and explore the substrate scope, a range of substituted amines, aldehydes, and alkynes were examined under the optimized conditions (Table 2). For internal aryl-substituted alkynes, good yields are obtainable irrespective of the electronic property of the *N*-aryl ring substituent (**4a**–**4f**). Specifically, the efficient product formation from aniline with an electron-withdrawing group (**4e** and **4f**) favors an acidic C–H bond activation mechanism and argues against ring closure through the EAS pathway. In further support of this, a competition experiment carried out with anilines bearing electron-withdrawing and -donating groups indicates that the electron-withdrawing aniline slightly dominates the product formation (eq 2). Since a group *meta* to the C–H bond is expected to exert less electronic influence on the activation process, an additional competition experiment was carried out on two substrates with substituents on the *para* positions of the C–H bonds (eq 3). A much more pronounced electronic effect has indeed been observed for an *N*-arylimine containing such a substitution pattern, with product formation substantially dominated by the electron-withdrawing structure. Notably, the reaction is not sensitive to steric hindrance, as the transformation can be effected for an alkyne with two phenyl substituents (**4g**). The alkyne scope is manifested by a high-yield product formation for electron-poor substrates (bearing two electron-withdrawing ester groups) (**4h**–**4l**). Under this circumstance, quinoline derivatives with both the retention of ester groups and the loss of one ester group could be observed, depending on the imine substrate. The loss of



ester group in the quinoline derivative is speculated to occur after the C–H activation step and before the cyclization process. Although the exact mechanism has yet to be elucidated, acidic conditions likely contribute to the destabilization of the ester group. It should be noted that no product of **4j**–**4l** was observed in the absence of Ag^{I}, confirming the essential role played by the metal species. To examine the feasibility of C–H bond activation pathway, an imine substrate with bulky, cyclization-blocking *C*-substituents was challenged with an internal alkyne (eq 4). Indeed an intermediate product with the

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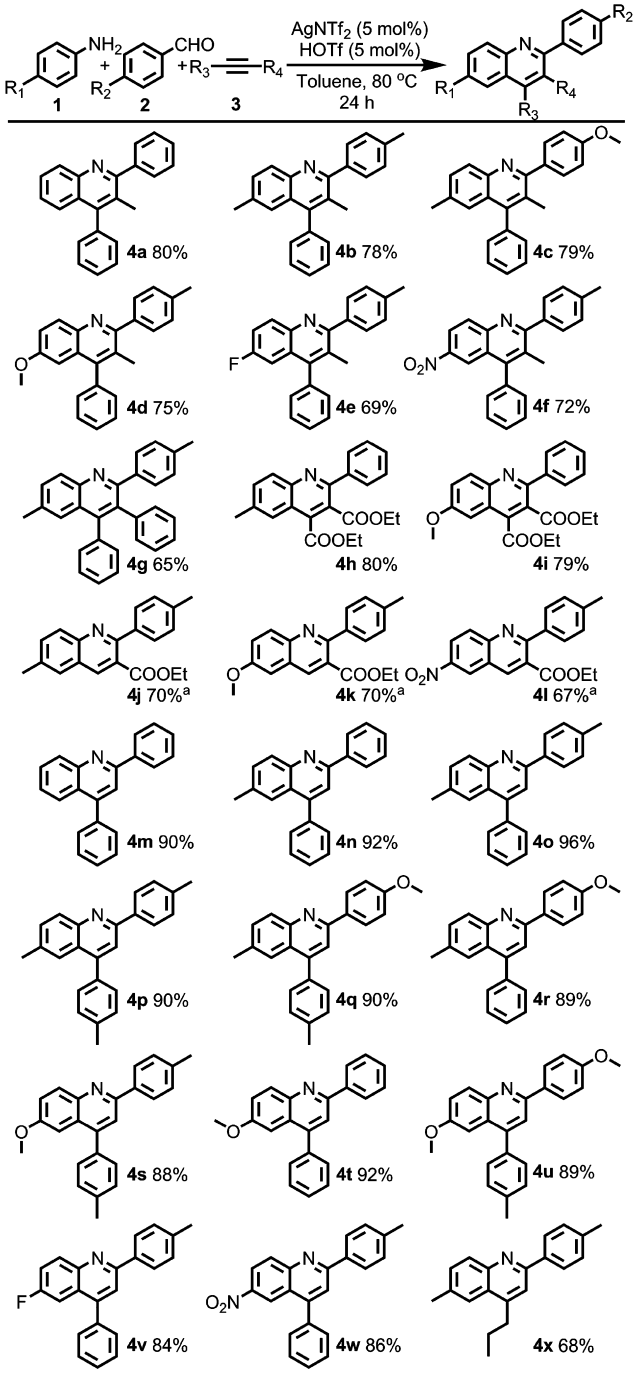
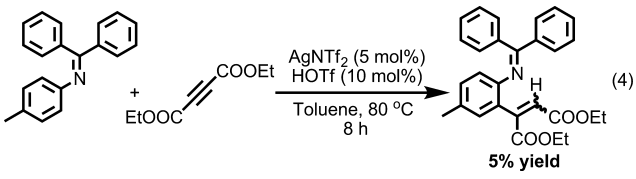
Table 2. Reaction Scope for Conjugated Internal Alkynes and Terminal Alkynes

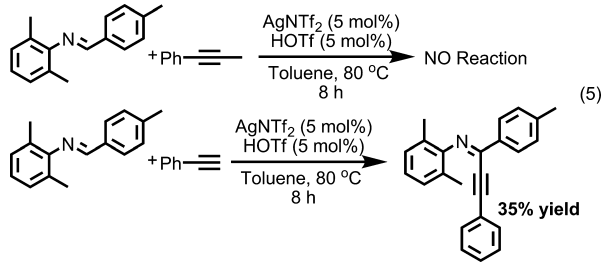


[a]The alkyne substrate: R_3 = R_4 = COOEt. The quinoline products: R_3 = H, R_4 = COOEt.



(4)

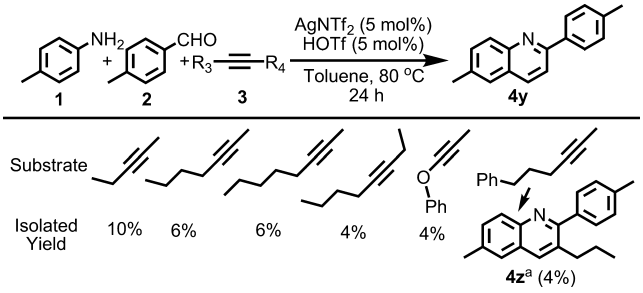
alkenylation of imine *N*-aryl ring was trapped, offering evidence for the possibility of alkyne carbometalation-initiated reaction sequence. It should be noted however that, when a subsequent ring closure reaction is possible as in the case of less hindered imine substrates employed herein, proto-demetalation reaction does not take place at this stage (*vide infra*). On a final note, no reaction occurs between an internal alkyne and a C−H activation-blocking imine substrate (bearing two *o*-methyl groups on *N*-aryl ring) (eq 5), indicating that the transformation might not be initiated through such an alkyne/imine coupling step.



(5)

For aliphatic internal alkynes, an interesting C−C bond cleavage reaction was observed, furnishing quinoline products with shortened carbon skeletons (Table 3, **4y**). One striking

Table 3. Reaction Scope for Aliphatic Internal Alkynes



[a]Trace amount of **4y** was observed.

feature of the reaction is that the two carbon atoms incorporated into the heterocycle might not come from those of the initial triple bond, as indicated by the bond-shifted product (**4z**) and ^{13}C labeling experiment (eq 6). Further evidence for the triple bond shift comes from several deuterium labeling studies. Reaction of aliphatic internal alkynes with an imine bearing an *o*-deuterated *N*-aryl ring, or a nondeuterated imine in the presence of deuterated acid or deuterated water (eqs 7 and 8), afforded the quinoline product with apparent deuterium incorporation. The internal alkyne is therefore proposed to be isomerized to a terminal alkyne before the carbometalation step (Scheme 2), at which stage the deuterium exchange is achieved on the acidic C−H bond. To test whether C−C bond cleavage occurs after the initial proto-demetalation formation of alkenylated imine and during the cyclization process, two independently synthesized substrates with an alkyl substituent on the alkene group were examined (eq 9). No C−C bond-cleaved product was observed, offering evidence that attachment of Ag^I to the alkenyl group might be required for the C−C bond cleavage following the cyclization step (Scheme 2). Aromatization resulting from the Ag^I-mediated *β*-alkyl elimination[9] could be potentially responsible for the occurrence of C−C bond cleavage reaction. Several observations for the reactions with aliphatic internal alkynes deserve comments: (1) Spheres with bright metallic luster were observed after the reaction, indicating the reduction of Ag^I to Ag^0. (2) An attempted stabilization of Ag^I with a coordinating ligand (e.g., PPh_3 and

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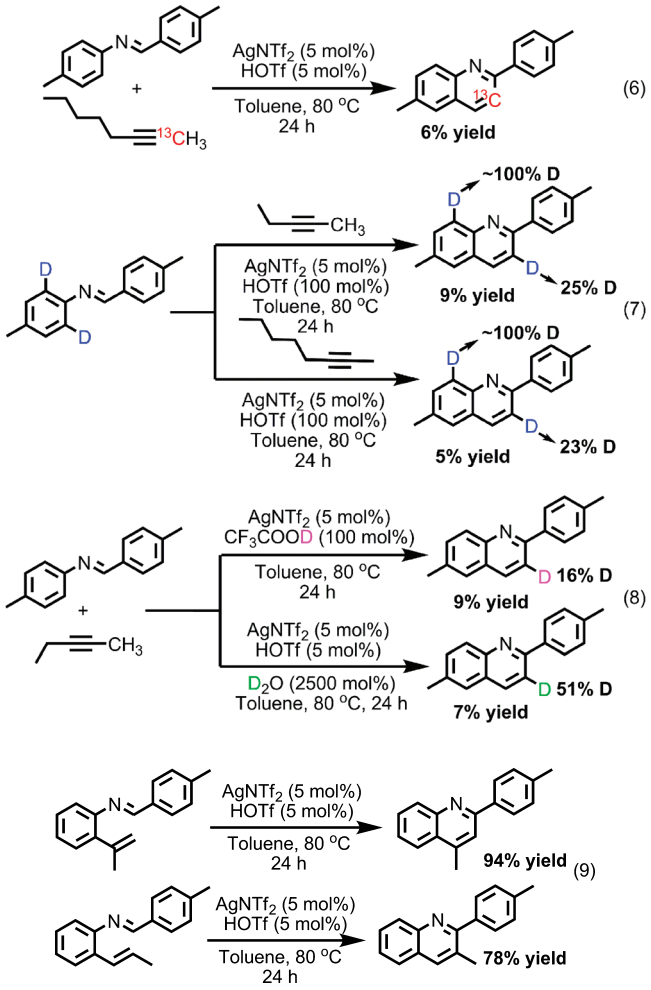
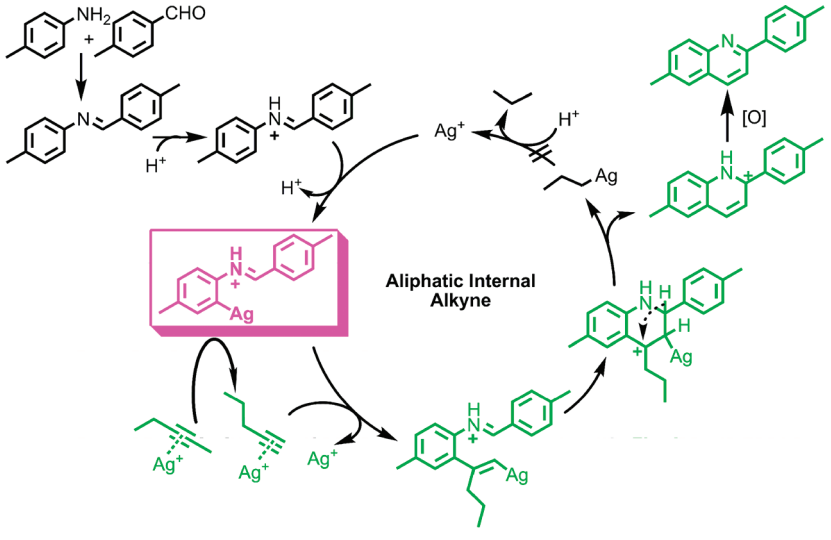


PCy_3) during the transformation proved unsuccessful. (3) Reaction in the presence of air or 1 equivalent of oxidant (e.g., 1,2-dibromoethane), which should presumably enable the reoxidation of Ag^0 back to Ag^I and furnish a conceptually valid catalytic cycle, did not result in the improvement of yield. (4) The addition of 1 equivalent of either $AgNTf_2$ or acid (e.g., HOTf) was not effective for the achievement of a quantitative transformation. (5) A fluorescent product other than the target compound (e.g., **4y**), with polarity similar to aliphatic internal alkynes according to thin layer chromatography, could be consistently observed in either the absence or presence of an *N*-arylimine. The low product yield of quinoline for an aliphatic internal alkyne is therefore derived from two factors: a speculated high-yield competing side reaction and reduction of Ag^I to Ag^0 metal by β-eliminated alkyl group (the proto-demetalation release of active Ag^I species apparently did not occur, Scheme 2). In spite of the unsatisfactory performance of aliphatic internal alkynes, the intriguing phenomenon observed herein provides important insight into the potentially new reaction patterns for Ag^I and might serve as the basis for the exploration of mechanistically distinct synthetic possibilities. A slight kinetic isotope effect[10] is identified (k_H/k_D = 1.12 and 1.10) (eq S2, Supporting Information), indicating that C–H bond activation is not a kinetically significant event in the reaction. It should be noted that, however, kinetic isotope effect depends on a variety of factors, with possibly consistently low values under certain circumstances (e.g., for sufficiently non-linear transition-state configurations[10c]).

As mentioned above, our synthetic scheme has been demonstrated on a terminal alkyne. Previous methods for the preparation of quinolines are generally restricted to this type of substrates, although distinct mechanistic hypotheses have been proposed (e.g., initial attack of imine carbon by alkyne, direct Diels–Alder reaction).[7a,11] Gratifyingly, the versatility of our silver-based system is manifested by the broad terminal alkyne substrate scope, with the formation of desired quinoline derivatives regardless of electron-donating or -withdrawing character of the functionality on aniline (Table 2, **4m**-**4w**). Also noteworthy is the achievement of a relatively high yield for an aliphatic terminal alkyne (**4x**), in marked contrast with the reactivity pattern for aliphatic internal alkynes. Two mechanistically relevant phenomena deserve special attention for the terminal alkyne substrates: (1) A reaction carried out with an imine substrate bearing two *o*-methyl groups on *N*-aryl ring indicates that an initial attack of terminal alkyne on iminium carbon is possible (eq 5). (2) A competition experiment with electron-withdrawing and -donating imines provides the dominant product from the electron-donating imine (eqs 10 and 11). Therefore, although an arene C–H bond

Scheme 2. Proposed Transformation Mechanism for Aliphatic Internal Alkynes



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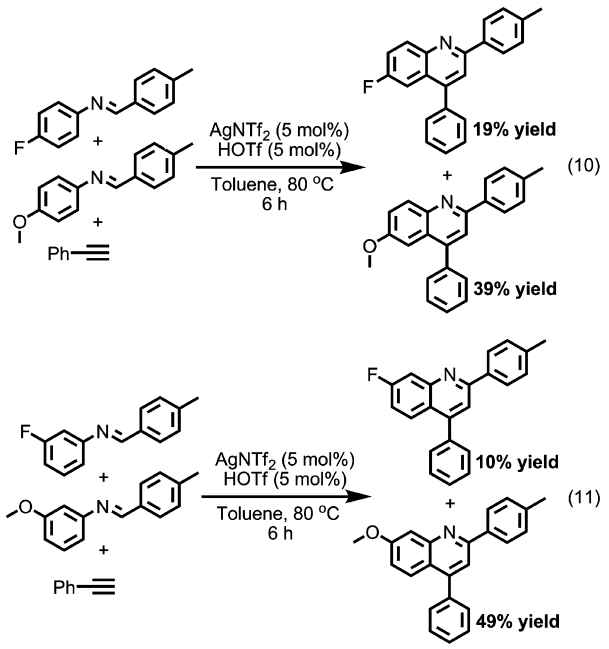
activation mechanism might still be operative here, an alternative reaction sequence involving the initial addition of Ag^I-activated terminal alkynes to iminium ions and a subsequent



nucleophilic cyclization attack of *N*-aryl ring on alkyne-Ag^I complex (Scheme 1) is more likely occurring. Such a distinct mechanism is warranted by the preferred deprotonation of terminal alkyne C−H bond over *ortho* C−H bond of protonated *N*-arylimine due to the difference in acidity.

CONCLUSION

In conclusion, a silver-based system for the synthesis of quinolines via oxidative coupling/cyclization of *N*-arylimines and alkynes has been uncovered. The transformation is effective for a broad range of substrates, thus enabling the expansion of substituent architectures on the heterocyclic framework. The acidity enhancement-based C−H activation strategy reported herein should be generally applicable to the coupling chemistry with other functional partners. The diverse set of mechanistic manifolds implemented with a single type of experimental protocol points toward the importance of stringent reactivity analysis of each individual potentially reactive molecular site.

EXPERIMENTAL SECTION

General Information. NMR (^{1}H and ^{13}C) spectra were recorded in $CDCl_3$ or DMSO-d_6 solutions on a 500 MHz NMR spectrometer. High resolution mass spectra were obtained on a mass spectrometry facility. $AgNTf_2$ was prepared according to the literature procedure.[12] All other reagents were facilely prepared or used as received from commercial sources except that toluene, THF, CCl_4, DMF and CH_2Cl_2 were distilled to the dry and oxygen-free state under the protection of nitrogen. All the reactions were performed with the standard Schlenk technique.

General Catalytic Procedure. Aniline (0.093 g, 1 mmol) and benzaldehyde (0.106 g, 1 mmol) were added to a Schlenk flask. After stirring for 10 min, $AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), and 1-phenyl-1-propyne (0.128 g, 1.1 mmol) were further added to the Schlenk flask containing 5 mL of toluene. The mixture was stirred at 80 °C for 24 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane, and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 1/1, v/v) to afford 0.236 g of 2,4-diphenyl-3-methylquinoline (**4a**, yield 80%). All other compounds are synthesized in a similar manner, with the yields calculated from the isolated, pure products.

Procedure for Demonstrating *ortho* C−H Bond Activation of an *N*-Arylimine. *N*-(4-methylbenzylidene)aniline (0.098 g, 0.5 mmol) was dissolved in D_2O/DMSO-d_6 (D_2O/DMSO-d_6 = 1/1, v/v). The solution was added to a NMR tube. Then the catalyst $AgNTf_2$ (0.01 g, 0.025 mmol) and HOTf (0.0038 g, 0.025 mmol) was added. The reaction mixture was heated at 80 °C for 3 h. The H/D molar ratio was measured by ^{1}H NMR, see eq S1, Supporting Information.

4-Methyl-*N*-(4-methylbenzylidene)aniline (0.104 g, 0.5 mmol) was dissolved in D_2O/DMSO-d_6 (D_2O/DMSO-d_6 = 1/1, v/v). The solution was added to a NMR tube. Then the catalyst $AgNTf_2$ (0.01 g, 0.025 mmol) and HOTf (0.0038 g, 0.025 mmol) was added. The reaction mixture was heated at 80 °C for 3 h. The H/D molar ratio was measured by ^{1}H NMR, see eq 1.

The analysis of the H/D exchange ratio was described as follows. In the case of *N*-(4-methylbenzylidene)aniline, the quantitative NMR integration of the H signal area at the *ortho* position of *N*-arylimine (with the *para* Me group on the *C*-aryl moiety as the internal reference) equals 3.58 for pure *N*-(4-methylbenzylidene)aniline. The area is decreased to 0.93 + 1.78 (2.71) after the reaction is performed in the presence of both $AgNTf_2$ and D_2O/DMSO-d_6. Assuming that the H with a signal area of 0.93 is assigned as the *para* H on the *N*-aryl moiety and that the integration value corresponds to 1 H, the decrease from 3.58 to 2.71 is derived from the D incorporation into the *ortho* position. Therefore D% = (3.58−0.93−1.78)/(3.58−0.93) × 100% = 33%. However, since the exact integration area for the *para* H in the original total of 3.58 is not clear, and there is a partial overlap between the signals with areas of 0.93 and 1.78, we cannot strictly exclude the possibility of H/D exchange at the *para* H on the N-aryl moiety. The *ortho* H/D exchange can be unambiguously observed with the substitution of the *para* position with a Me group. In the case of 4-methyl-*N*-(4-methylbenzylidene)aniline, the quantitative NMR integration of the H signal area at the *ortho* position of *N*-arylimine (with the *para* Me group on the *C*-aryl moiety as the internal reference, which exhibits a signal area of 3.00) equals 1.84 for pure 4-methyl-*N*-(4-methylbenzylidene)aniline. The area is decreased to 0.80 after the reaction is performed in the presence of both $AgNTf_2$ and D_2O/DMSO-d_6. Therefore D% = (1.84−0.80)/1.84 × 100% = 57%.

Procedure for Competition Experiments Involving an Internal Alkyne. $AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), 1-phenyl-1-propyne (0.058 g, 0.5 mmol), and imine substrates of 4-fluoro-*N*-(4-methylbenzylidene)aniline (0.105 g, 0.5 mmol), 4-methoxy-*N*-(4-methylbenzyli dene)aniline (0.113 g, 0.5 mmol) were added to a Schlenk flask containing 5 mL of toluene. The reaction mixture was stirred at 80 °C for 6 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 3/2, v/v) to afford the product, see eq 2.

$AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), 1-phenyl-1-propyne (0.058 g, 0.5 mmol), and imine substrates of 3-fluoro-*N*-(4-methylbenzylidene)aniline (0.105 g, 0.5 mmol), 3-methoxy-*N*-(4-methylbenzylidene)aniline (0.113 g, 0.5 mmol) were added to a Schlenk flask containing 5 mL of toluene. The reaction mixture was stirred at 80 °C for 6 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 3/2, v/v) to afford the product, see eq 3.

Procedure for Trapping an Alkenylation Product on a Bulky *N*-Arylimine. *p*-Toluidine (0.75 g, 7 mmol) and diphenylketone (1.82 g, 10 mmol) was dissolved in benzene, to which zinc chloride

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(0.134 g, 1 mmol) was added. The reaction mixture was heated under boiling conditions for 24 h to afford the imine product of *N*-(diphenylmethylene)-4-methylaniline. Subsequently, diethyl acetylenedicarboxylate (0.17 g, 1 mmol), $AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.015 g, 0.1 mmol), and chromatography-purified imine were added to a Schlenk flask. The reaction mixture was heated at 80 °C for 8 h and the resulting solvent-free residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 1/1, v/v) to afford the product, see eq 4.

Procedure for Investigating the Reactivity of an Alkyne toward an *ortho*-Methylated *N*-Arylimine. 2,6-Dimethyl-*N*-(4-methylbenzylidene)aniline (0.223 g, 1 mmol), $AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), and 1-phenyl-1-propyne (0.128 g, 1.1 mmol) were added to a Schlenk flask containing 5 mL of toluene. The mixture was stirred at 80 °C for 8 h, then cooled down to room temperature. No product was observed, see eq 5.

2,6-Dimethyl-*N*-(4-methylbenzylidene)aniline (0.223 g, 1 mmol), $AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), and phenylacetylene (0.112 g, 1.1 mmol) were added to a Schlenk flask containing 5 mL of toluene. The mixture was stirred at 80 °C for 8 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 1/1, v/v) to afford the product, see eq 5.

Procedure for ^{13}C Labeling for the Investigation of Reaction Mechanism Involving an Aliphatic Internal Alkyne. 4-Methyl-*N*-(4-methylbenzylidene)aniline (0.209 g, 1 mmol), $AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), and 2-octyne-^{13}C (0.122 g, 1.1 mmol) were added to a Schlenk flask containing 5 mL of toluene. The mixture was stirred at 80 °C for 24 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 1/1, v/v) to afford the product, see eq 6.

Procedure for Deuterium Labeling for the Investigation of Reaction Mechanism Involving an Aliphatic Internal Alkyne. 4-Methyl-*N*-(4-methylbenzylidene)aniline-d_2 (0.211 g, 1 mmol), $AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), and 2-pentyne (0.075 g, 1.1 mmol) or 2-octyne (0.121 g, 1.1 mmol) were added to a Schlenk flask containing 5 mL of toluene. The mixture was stirred at 80 °C for 24 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 1/1, v/v) to afford the product, see eq 7.

Procedure for Investigation of Reaction Mechanism Involving an Aliphatic Internal Alkyne through the Addition of a Deuterated Species. 4-Methyl-*N*-(4-methylbenzylidene)aniline (0.209 g, 1 mmol), $AgNTf_2$ (0.02 g, 0.05 mmol), CF_3COOD (0.0058 g, 0.05 mmol) or HOTf (0.075 g, 0.05 mmol)/D_2O (0.5 mL, 25 mmol), and 2-pentyne (0.075 g, 1.1 mmol) were added to a Schlenk flask containing 5 mL of toluene. The mixture was stirred at 80 °C for 24 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether =1/1, v/v) to afford the product, see eq 8.

Procedure for Investigation of the C−C Bond Cleavage Mechanism Involving an Aliphatic Internal Alkyne through an Intramolecular Cyclization Reaction. 2-Isopropenylaniline (0.133 g, 1 mmol) and *p*-tolualdehyde (0.12 g, 1 mmol) were added to a Schlenk flask. After stirring for 10 min, the Schlenk flask was further charged with $AgNTf_2$ (0.02 g, 0.05 mmol) and HOTf (0.0075 g, 0.05 mmol) and 5 mL of toluene. The mixture was stirred at 80 °C for 24 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 1/1, v/v) to afford the product, see eq 9.

(*E*)-2-(prop-1-enyl)aniline (0.133 g, 1 mmol) and *p*-tolualdehyde (0.12 g, 1 mmol) were added to a Schlenk flask. After stirring for 10 min, the Schlenk flask was further charged with $AgNTf_2$ (0.02 g, 0.05 mmol) and HOTf (0.0075 g, 0.05 mmol) and 5 mL of toluene. The mixture was stirred at 80 °C for 24 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 1/1, v/v) to afford the product, see eq 9.

Procedure for Kinetic Isotope Effect Experiments. $AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), 1-phenyl-1-propyne (0.058 g, 0.5 mmol) or 2-pentyne (0.034 g, 0.5 mmol), and 4-methyl-*N*-(4-methylbenzylidene)aniline (0.105 g, 0.5 mmol), 4-methyl-*N*-(4-methylbenzylidene)-aniline-d_2 (0.106 g, 0.5 mmol) were added to a Schlenk flask containing 5 mL of toluene. The tube was capped and stirred at 80 °C for 24 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 1/1, v/v) to afford the product. The resulting residue was analyzed by ^1H NMR. In the case of 1-phenyl-1-propyne, the quantitative NMR integration of the H signal area at the eighth position of the quinoline derivative (with the Me group at the third position of the quinoline as the internal reference) equals 0.91 for reaction with pure 4-methyl-*N*-(4-methylbenzylidene)aniline. The area is decreased to 0.48 when the reaction is carried out in the presence of both 4-methyl-*N*-(4-methylbenzylidene)aniline and 4-methyl-*N*-(4-methylbenzylidene)aniline-d_2. Therefore KIE = k_H/k_D = 0.48/(0.91−0.48) = 1.12. In the case of 2-pentyne, the quantitative NMR integration of the H signal area at the eighth and second (two *o*-H on the *p*-tolyl group) positions of the quinoline derivative (with one of the Me groups as the internal reference) equals 2.71 for reaction with pure 4-methyl-*N*-(4-methylbenzylidene)aniline. The area is decreased to 2.37 when the reaction is carried out in the presence of both 4-methyl-*N*-(4-methylbenzylidene)aniline and 4-methyl-*N*-(4-methylbenzylidene)aniline-d_2. Therefore KIE = k_H/k_D = (2.37−2)/(2.71−2.37) = 1.10. The experiments were repeated three times, see eq S2, Supporting Information.

Procedure for Competition Experiments Involving a Terminal Alkyne. $AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), phenylacetylene (0.051 g, 0.5 mmol), and 4-fluoro-*N*-(4-methylbenzylidene)aniline (0.105 g, 0.5 mmol), 4-methoxy-*N*-(4-methylbenzylidene)aniline (0.113 g, 0.5 mmol) were added to a Schlenk flask containing 5 mL of toluene. The reaction mixture was stirred at 80 °C for 6 h, then cooled down to room temperature, diluted with 10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 3/2, v/v), see eq 10.

$AgNTf_2$ (0.02 g, 0.05 mmol), HOTf (0.0075 g, 0.05 mmol), phenylacetylene (0.051 g, 0.5 mmol), and 3-fluoro-*N*-(4-methylbenzylidene)aniline (0.105 g, 0.5 mmol), 3-methoxy-*N*-(4-methylbenzyl idene)aniline (0.113 g, 0.5 mmol) were added to a Schlenk flask containing 5 mL of toluene. The reaction mixture was stirred at 80 °C for 6 h, then cooled down to room temperature, diluted with

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10 mL of dichloromethane and washed with 10 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel chromatography (dichloromethane/petroleum ether = 3/2, v/v), see eq 11.

Compound Characterization Data. *2,4-Diphenyl-3-methylquinoline (**4a**).*[7a] ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.26 (d, J = 8.5 Hz, 1H), 7.66−7.71 (m, 3H), 7.51−7.60 (m, 5H), 7.42−7.50 (m, 3H), 7.36 (t, 2H), 2.21 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 160.9, 147.9, 146.3, 141.5, 137.8, 129.41, 129.35, 129.0, 128.7, 128.6, 128.3, 128.1, 127.9, 127.1, 126.8, 126.3, 126.0, 18.6; HRMS (EI) Calcd. for $C_{22}H_{17}N$: [M$^+$], 295.1361. Found: m/z 295.1360.

*2-p-Tolyl-3,6-dimethyl-4-phenylquinoline (**4b**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.12 (d, J = 8.5 Hz, 1H), 7.51−7.56 (m, 6H), 7.33−7.35 (m, 4H), 7.18 (s, 1H), 2.46 (s, 3H), 2.43 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 160.0, 147.1, 145.0, 138.8, 138.0, 137.7, 136.0, 130.7, 129.4, 129.2, 128.97, 128.95, 128.7, 127.7, 127.0, 126.7, 124.7, 21.8, 21.3, 18.7; HRMS (EI) Calcd. for $C_{24}H_{21}N$: [M$^+$], 323.1674. Found: m/z 323.1675.

*2-(4-Methoxyphenyl)-3,6-dimethyl-4-phenylquinoline (**4c**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.10 (d, J = 8.5 Hz, 1H), 7.56−7.62 (m, 4H), 7.50−7.53 (m, 2H), 7.33 (d, J = 7.0 Hz, 2H), 7.16 (s, 1H), 7.05 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H), 2.43 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 159.6, 159.5, 147.1, 145.0, 138.1, 135.9, 134.2, 130.7, 130.4, 129.4, 129.1, 128.7, 127.7, 126.9, 126.8, 124.7, 113.4, 55.4, 21.80, 18.8; HRMS (EI) Calcd. for $C_{24}H_{21}NO$: [M$^+$], 339.1623. Found: m/z 339.1622.

*2-p-Tolyl-3-methyl-4-phenyl-6-methoxyquinoline (**4d**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.10 (d, J = 9.0 Hz, 1H), 7.49−7.59 (m, 5H), 7.31−7.35 (m, 5H), 6.66 (d, J = 2.5 Hz, 1H), 3.72 (s, 3H), 2.45 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 158.5, 157.5, 146.5, 142.5, 138.7, 138.1, 137.6, 130.9, 129.3, 129.0, 128.9, 128.7, 127.9, 127.8, 127.0, 120.6, 104.2 55.3, 21.3, 18.7; HRMS (EI) Calcd. for $C_{24}H_{21}NO$: [M$^+$], 339.1623. Found: m/z 339.1622.

*2-p-Tolyl-3-methyl-4-phenyl-6-fluoroquinoline (**4e**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.17−8.19 (q, 1H), 7.57−7.60 (t, 2H), 7.51−7.53 (m, 3H), 7.41−7.45 (m, 1H), 7.28−7.35 (q, 4H), 7.02 (q, 1H), 2.47 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 167.2, 148.5, 141.7, 139.9, 139.1, 132.9, 129.6, 129.5, 129.0, 128.3, 127.9, 127.8, 127.6, 126.2, 123.0, 120.1, 100.0, 21.3, 18.1; HRMS (EI) Calcd. for $C_{23}H_{18}NF$: [M$^+$], 327.1423. Found: m/z 327.1424.

*2-p-Tolyl-3-methyl-4-phenyl-6-nitroquinoline (**4f**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.42 (q, 1H), 8.37 (d, J = 2.0, 1H), 8.28 (d, J = 9.0, 1H), 7.61 − 7.64 (t, 2H), 7.59−7.60 (t, 3H), 7.34−7.37 (m, 4H), 2.47 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 164.4, 149.7, 148.4, 145.4, 138.8, 137.8, 136.2, 131.2, 129.2, 129.12, 129.08, 128.8, 128.7, 128.0, 126.1, 123.0, 122.0, 21.3, 18.9; HRMS (EI) Calcd. for $C_{23}H_{18}N_2O_2$: [M$^+$], 354.1368. Found: m/z 354.1366.

*2-p-Tolyl-3,4-diphenyl-6-methylquinoline (**4g**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.18 (d, J = 8.5 Hz, 1H), 7.58 (d, J = 10.0 Hz, 1H), 7.29−7.34 (m, 6H), 7.14−7.16 (m, 2H), 7.03−7.04 (m, 5H), 6.91−6.93 (m, 2H), 2.45 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 158.0, 147.0, 146.0, 138.7, 138.3, 137.2, 136.3, 132.9, 131.6, 131.4, 130.4, 129.9, 129.4, 128.4, 127.7, 127.3, 127.1, 126.5, 126.2, 125.3, 113.8, 21.9, 21.2; HRMS (EI) Calcd. for $C_{29}H_{23}N$: [M$^+$], 385.1830. Found: m/z 385.1827.

*Diethyl 2-Phenyl-6-methylquinoline-3,4-dicarboxylate (**4h**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.12 (d, J = 9.0 Hz, 1H), 7.85 (s, 1H), 7.67 (t, 3H), 7.44−7.50 (m, 3H), 4.53−4.57 (q, 2H), 4.13−4.17 (q, 2H), 2.59 (s, 3H), 1.44−1.46 (t, 3H), 1.02−1.05 (t, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 167.6, 166.3, 155.9, 146.9, 140.2, 138.6, 138.4, 133.7, 129.7, 128.8, 128.5, 128.4, 124.5, 124.0, 122.2, 62.4, 61.8, 21.9, 14.0, 13.5; HRMS (EI) Calcd. for $C_{22}H_{21}NO_4$: [M$^+$], 363.1471. Found: m/z 363.1476.

*Diethyl 2-Phenyl-6-methoxyquinoline-3,4-dicarboxylate (**4i**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.11 (d, J = 9.0 Hz, 1H), 7.65 (q, 2H), 7.45−7.50 (m, 5H), 4.51−4.56 (q, 2H), 4.13−4.18 (q, 2H), 3.97 (s, 3H), 1.43−1.46 (t, 3H), 1.02−1.05 (t, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 167.8, 166.3, 159.1, 154.2, 144.7, 140.1, 137.2, 131.5, 128.7, 128.5, 128.3, 125.3, 124.3, 123.5, 102.7, 62.3, 61.8, 55.6, 14.0, 13.5; HRMS (EI) Calcd. for $C_{22}H_{21}NO_5$: [M$^+$], 379.1420. Found: m/z 379.1422.

*Ethyl 2-p-Tolyl-6-methylquinoline-3-carboxylate (**4j**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.52 (s, 1H), 8.35 (s, 1H), 8.12 (q, 3H), 7.61 (d, J = 8.0 Hz, 1H), 7.36 (q, 2H), 4.54−4.59 (q, 2H), 2.60 (s, 3H), 2.46 (s, 3H), 1.51−1.54 (t, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 166.7, 155.8, 147.9, 139.6, 137.7, 136.2, 135.3, 132.0, 129.9, 129.6, 127.2, 124.2, 123.9, 119.9, 61.8, 22.1, 21.3, 14.4; HRMS (EI) Calcd. for $C_{20}H_{19}NO_2$: [M$^+$], 305.1416. Found: m/z 305.1420.

*Ethyl 2-p-Tolyl-6-methoxyquinoline-3-carboxylate (**4k**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.30 (d, J = 7.5 Hz, 1H), 8.10 (s, 1H), 7.47 (d, J = 8.0 Hz, 3H), 7.38 (d, J = 7.5 Hz, 2H), 7.28 (s, 1H), 4.56 (q, 2H), 3.84 (s, 3H), 2.50 (s, 3H), 1.49−1.52 (t, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 165.7, 159.5, 148.2, 145.4, 144.3, 138.6, 135.0, 132.7, 129.5, 129.33, 129.26, 122.8, 121.8, 103.4, 62.1, 55.6, 21.3, 14.4; HRMS (EI) Calcd. for $C_{20}H_{19}NO_3$: [M$^+$], 321.1365. Found: m/z 321.1368.

*Ethyl 2-p-Tolyl-6-nitroquinoline-3-carboxylate (**4l**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 9.7 (d, J = 2.5 Hz, 1H), 8.50 (s, 1H), 8.45 (d, J = 2.5 Hz, 1H), 8.23 (d, J = 9.0 Hz, 1H), 8.12 (d, J = 8.5 Hz, 2H), 7.36 (q, 2H), 4.60 (q, 2H), 2.47 (s, 3H), 1.55−1.58 (t, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 165.3, 159.8, 151.1, 146.0, 141.4, 137.1, 134.8, 131.6, 129.8, 127.6, 123.2, 122.9, 122.8, 121.7, 62.5, 21.4, 14.3; HRMS (EI) Calcd. for $C_{19}H_{16}N_2O_4$: [M$^+$], 336.1110. Found: m/z 336.1114.

*2,4-Diphenylquinoline (**4m**).*[7a,11c,13] ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.43 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 8.5 Hz, 1H), 7.92 (s, 1H), 7.80 (t, 1H), 7.51−7.64 (m, 9H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 156.9, 149.2, 149.1, 139.8, 138.6, 130.4, 129.7, 129.6, 129.5, 129.0, 128.7, 128.5, 127.8, 126.5, 125.9, 125.8, 119.4; HRMS (EI) Calcd. for $C_{21}H_{15}N$: [M$^+$], 281.1204. Found: m/z 281.1207.

*2,4-Diphenyl-6-methylquinoline (**4n**).*[7a,11c,13] ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.85 (d, J = 9.0 Hz, 1H), 8.15 (t, 2H), 7.97 (d, J = 3.5 Hz, 2H), 7.88 (s, 1H), 7.62−7.73 (m, 8H), 2.61 (s, 3H); ^{13}C NMR (500 MHz, DMSO-d_6) δ ppm: 155.7, 153.4, 140.0, 139.4, 136.2, 136.1, 132.9, 132.7, 130.5, 130.2, 129.8, 129.6, 129.5, 125.9, 125.5, 123.1, 121.8, 21.8; HRMS (EI) Calcd. for $C_{22}H_{17}N$: [M$^+$], 295.1361. Found: m/z 295.1357.

*2-p-Tolyl-4-phenyl-6-methylquinoline (**4o**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.30 (d, J = 9.0 Hz, 1H), 8.23 (s, 1H), 8.18 (d, J = 7.5 Hz, 2H), 7.93 (d, J = 8.5 Hz, 1H), 7.80 (s, 1H), 7.67−7.72 (m, 5H), 7.51 (d, J = 8.0 Hz, 2H), 2.52 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 158.5, 153.0, 144.6, 140.7, 137.7, 137.1, 135.2, 130.8, 129.40, 129.36, 129.0, 127.2, 126.0, 125.8, 121.8, 121.529, 120.9, 21.9, 21.5; HRMS (EI) Calcd. for $C_{23}H_{19}N$: [M$^+$], 309.1517. Found: m/z 309.1521.

*2,4-Di-p-tolyl-6-methylquinoline (**4p**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.61 (d, J = 14.5 Hz, 1H), 8.00 (d, J = 13.5 Hz, 2H), 7.89 (d, J = 12.0 Hz, 2H), 7.70 (d, J = 14.5 Hz, 1H), 7.53 (d, J = 13.5 Hz, 2H), 7.45 (d, J = 13.0 Hz, 2H), 7.32 (d, J = 13.0 Hz, 2H), 2.54 (s, 3H), 2.47 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 158.5, 152.6, 144.4, 141.4, 140.5, 137.5, 136.9, 132.2, 130.6, 130.1, 129.5, 128.9, 127.1, 126.0, 125.8, 121.2, 120.6, 21.8, 21.39, 21.36; HRMS (EI) Calcd. for $C_{24}H_{21}N$: [M$^+$], 323.1674. Found: m/z 323.1679.

*2-(4-Methoxyphenyl)-4-p-tolyl-6-methylquinoline (**4q**).*[14] ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.38 (d, J = 9.0 Hz, 1H), 8.00 (d, J = 4.5 Hz, 2H), 7.73 (d, J = 6.0 Hz, 2H), 7.66 (d, J = 9.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 3.67 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 163.3, 156.4, 152.5, 140.7, 139.3, 138.9, 135.8, 132.8, 130.5, 129.9, 129.5, 125.6, 125.4, 123.4, 122.3, 119.9, 115.2, 55.5, 21.7, 21.3; HRMS (EI) Calcd. for $C_{24}H_{21}NO$: [M$^+$], 339.1623. Found: m/z 339.1620.

*2-(4-Methoxyphenyl)-4-phenyl-6-methylquinoline (**4r**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.20 (d, J = 8.5 Hz, 2H), 7.91 (t, 2H), 7.81 (s, 1H), 7.68 (d, J = 3.5 Hz, 3H), 7.61−7.62 (m, 2H), 7.18−7.21 (t, 3H), 3.95 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (500 MHz, DMSO-d_6) δ

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ppm: 163.4, 155.8, 152.8, 139.7, 138.7, 136.14, 136.06, 131.7, 130.5, 130.2, 129.5, 128.6, 125.6, 124.3, 122.4, 121.4, 115.4, 56.2, 21.8; HRMS (EI) Calcd. for $C_{23}H_{19}NO$: [M^+], 325.1467. Found: m/z 325.1468.

2,4-Di-p-tolyl-6-methoxyquinoline (**4s**). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.17 (t, 3H), 7.77 (s, 1H), 7.71 (s, 1H), 7.58 (d, J = 10.5 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.00 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 3.91 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 160.7, 155.7, 148.4, 147.4, 138.2, 135.83, 135.77, 132.4, 131.7, 129.6, 129.5, 129.3, 128.8, 125.6, 124.5, 119.0, 114.2, 55.4, 21.8, 21.3; HRMS (EI) Calcd. for $C_{24}H_{21}NO$: [M^+], 339.1623. Found: m/z 339.1617.

2,4-Diphenyl-6-methoxyquinoline (**4t**). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.20 (t, 3H), 7.81 (t, 1H), 7.53−7.56 (m, 3H), 7.57−7.62 (m, 4H), 7.42−7.49 (m, 2H), 7.22 (d, J = 3.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 157.9, 154.5, 147.8, 145.1, 139.8, 138.9, 131.8, 129.5, 129.1, 128.9, 128.8, 128.4, 127.4, 126.8, 121.9, 119.6, 103.8, 55.4; HRMS (EI) Calcd. for $C_{22}H_{17}NO$: [M^+], 311.1310. Found: m/z 311.1308.

2-(4-Methoxyphenyl)-4-p-tolyl-6-methoxyquinoline (**4u**). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.16 (d, J = 8.5 Hz, 3H), 7.76 (s, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.38−7.42 (m, 3H), 7.25 (d, J = 2.5 Hz, 1H), 7.06−7.07 (d, J = 8.50 Hz, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 160.6, 157.5, 154.3, 147.8, 144.9, 138.2, 135.9, 132.4, 131.4, 129.4, 129.3, 128.6, 126.5, 121.6, 119.2, 114.2, 103.9, 55.43, 55.35, 21.3; HRMS (EI) Calcd. for $C_{24}H_{21}NO_2$: [M^+], 355.1572. Found: m/z 355.1571.

2-p-Tolyl-4-phenyl-6-fluoroquinoline (**4v**). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.24 (q, 1H), 8.11 (d, J = 8.5 Hz, 2H), 7.85 (s, 1H), 7.50−7.61 (m, 7H), 7.36 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 161.5, 159.5, 156.3, 148.6, 145.9, 139.5, 138.1, 136.6, 132.5, 129.6, 129.4, 128.8, 128.6, 127.4, 119.7, 119.4, 108.9, 21.3; HRMS (EI) Calcd. for $C_{22}H_{16}NF$: [M^+], 313.1267. Found: m/z 313.1271.

2-p-Tolyl-4-phenyl-6-nitroquinoline (**4w**). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.87 (d, J = 2.0 Hz, 1H), 8.51 (d, J = 11.0 Hz, 1H), 8.38 (d, J = 8.5 Hz, 1H), 8.19 (d, J = 8.0 Hz, 2H), 7.99 (s, 1H), 7.59−7.65 (m, 5H), 7.39(d, J = 8.0 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 159.9, 151.1, 145.2, 140.9, 137.0, 135.7, 131.6, 129.8, 129.5, 129.3, 129.1, 127.7, 124.7, 123.0, 122.9, 120.5, 21.5; HRMS (EI) Calcd. for $C_{22}H_{16}N_2O_2$: [M^+], 340.1212. Found: m/z 340.1217.

2-p-Tolyl-4-propyl-6-methylquinoline (**4x**). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.02−8.07 (t, 3H), 7.75 (s, 1H), 7.64 (s, 1H), 7.50−7.52 (d, J = 10.5 Hz, 1H), 7.31 (d, J = 10.0 Hz, 2H), 3.03−3.07 (t, 2H), 2.55 (s, 3H), 2.42 (s, 3H), 1.81−1.86 (m, 2H), 1.05−1.08 (q, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 156.1, 148.1, 147.0, 139.0, 137.2, 135.5, 131.3, 129.5, 128.2, 127.4, 126.5, 122.4, 118.6, 34.5, 23.3, 22.0, 21.3, 14.2; HRMS (EI) Calcd. for $C_{20}H_{21}N$: [M^+], 275.1674. Found: m/z 275.1677.

2-p-Tolyl-6-methylquinoline (**4y**). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.14 (d, J = 8.5 Hz, 1H), 8.07 (d, J = 8.5 Hz, 3H), 7.84 (d, J = 8.5 Hz, 1H), 7.58 (q, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.57 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 156.5, 147.6, 146.8, 143.8, 139.2, 136.0, 131.9, 129.5, 129.3, 128.8, 127.3, 126.3, 118.8, 21.6, 21.3; HRMS (EI) Calcd. for $C_{17}H_{15}N$: [M^+], 233.1204. Found: m/z 233.1199.

2-p-Tolyl-3-propyl-6-methylquinoline (**4z**). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.10 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 2H), 7.66 (q, 2H), 7.55 (s, 1H), 7.33 (d, J = 8.0 Hz, 2H), 3.12−3.16 (t, 2H), 2.81−2.84 (m, 2H), 2.55 (s, 3H), 2.45 (s, 3H), 2.15−2.21 (q, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 160.0, 156.7, 141.7, 135.7, 131.4, 129.5, 128.53, 128.45, 127.4, 126.3, 126.0, 122.3, 118.6, 35.7, 24.6, 21.9, 21.3, 13.1; HRMS (EI) Calcd. for $C_{20}H_{21}N$: [M^+], 275.1674. Found: m/z 275.1675.

2-p-Tolyl-3-methyl-4-phenyl-7-fluoroquinoline. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.16 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 9.0 Hz, 2H), 7.53−7.61 (m, 5H), 7.41 (d, J = 9.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 1H), 2.46 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 157.8, 154.6, 147.7, 145.0, 139.0, 138.9, 137.0, 131.6, 129.6, 129.4, 128.7, 127.6, 127.2, 126.6, 121.7, 119.5, 103.9, 21.3, 18.2; HRMS (MALDI/DHB) Calcd. for $C_{23}H_{19}NF$: [M + H]$^+$, 328.1496. Found: m/z 328.1487.

2-p-Tolyl-3-methyl-4-phenyl-7-methoxyquinoline. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.22 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 2H), 7.55−7.64 (m, 5H), 7.45 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 2.0 Hz, 1H), 3.82 (s, 3H), 2.48 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 161.2, 157.3, 150.7, 148.9, 139.3, 138.7, 137.1, 129.54, 129.52, 128.6, 128.3, 127.5, 126.7, 119.2, 117.3, 115.5, 108.1, 55.6, 21.3, 18.4; HRMS (MALDI/DHB) Calcd. for $C_{24}H_{22}NO$: [M + H]$^+$, 340.1696. Found: m/z 340.1697.

Diethyl-2-(2-(diphenylmethyleneamino)-5-methylphenyl)-maleate. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.33−7.35 (m, 3H), 7.25−7.28 (m, 1H), 7.15−7.18 (t, 2H), 6.98−7.04 (m, 4H), 6.75−6.76 (d, J = 8.5 Hz, 2H), 6.61−6.63 (d, J = 8.0 Hz, 2H), 4.34−4.39 (q, 2H), 3.92−3.96 (q, 2H), 2.28 (s, 3H), 1.34−1.36 (t, 3H), 0.92−0.95 (t, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 165.4, 164.6, 152.8, 137.7, 137.4, 137.0, 136.0, 130.3, 129.6, 129.1, 128.7, 128.2, 128.1, 125.0, 92.5, 59.8, 59.6, 20.9, 14.4, 14.2; HRMS (EI) Calcd. for $C_{28}H_{27}NO_4$: [M^+], 441.1940. Found: m/z 441.1941.

(Z)-2,6-Dimethyl-N-(3-phenyl-1-p-tolylprop-2-ynylidene)-aniline. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.79 (m, 1H), 7.53 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.10 (t, 4H), 6.94−6.99 (m, 2H), 6.60−6.63 (d, J = 16.5 Hz, 1H), 2.34 (s, 3H), 2.13 (s, 6H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 167.2, 148.5, 141.7, 139.9, 132.9, 129.6, 129.0, 128.3, 127.9, 127.6, 126.2, 123.0, 120.1, 21.3, 18.1; HRMS (EI) Calcd. for $C_{24}H_{21}N$: [M^+], 323.1674. Found: m/z 323.1671.

2-p-Tolyl-4-methylquinoline. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.78 (d, J = 9.0 Hz, 1H), 8.19 (t, 1H), 8.02−8.07 (m, 3H), 7.97 (s, 1H), 7.86 (t, 1H), 7.42 (d, J = 8.0 Hz, 2H), 3.03 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (500 MHz, DMSO-d_6) δ ppm: 156.7, 153.4, 143.4, 138.4, 134.0, 130.1, 129.2, 128.9, 128.8, 126.8, 125.6, 122.1, 121.7, 21.2, 19.5; HRMS (EI) Calcd. for $C_{17}H_{15}N$: [M^+], 233.1204. Found: m/z 233.1207.

2-p-Tolyl-3-methylquinoline. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.16 (d, J = 8.5 Hz, 1H), 8.02 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.68 (t, 1H), 7.53 (d, J = 8.0 Hz, 3H), 7.33 (d, J = 7.5 Hz, 2H), 2.50 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 160.6, 146.7, 138.1, 138.0, 136.7, 129.4, 129.3, 129.0, 128.8, 128.7, 127.6, 126.7, 126.3, 21.4, 20.7; HRMS (EI) Calcd. for $C_{17}H_{15}N$: [M^+], 233.1204. Found: m/z 233.1201.

2-p-Tolyl-4-phenyl-6-methoxyquinoline. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.28 (d, J = 8.5 Hz, 1H), 8.21 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.81 (s, 1H), 7.74 (q, 1H), 7.46−7.50 (m, 3H), 7.38 (d, J = 7.50 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 3.90 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 157.0, 146.0, 144.9, 137.7, 136.2, 135.3, 130.5, 130.4, 129.3, 128.8, 128.4, 127.3, 126.7, 126.3, 126.1, 125.1, 124.3, 54.3, 20.8; HRMS (EI) Calcd. for $C_{23}H_{19}NO$: [M^+], 325.1467. Found: m/z 325.1468.

2-p-Tolyl-4-phenyl-7-fluoroquinoline. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.17 (d, J = 9.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 2H), 7.79 (s, 1H), 7.53−7.61 (m, 5H), 7.41 (d, J = 9.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 2.0 Hz, 1H) 2.46 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 157.7, 154.7, 147.7, 144.9, 139.0, 138.9, 137.0, 131.5, 129.5, 129.4, 128.7, 128.3, 127.2, 126.6, 121.7, 119.5, 103.8, 21.3; HRMS (MALDI/DHB) Calcd. for $C_{22}H_{17}NF$: [M + H]$^+$, 314.1340. Found: m/z 314.1333.

2-p-Tolyl-4-phenyl-7-methoxyquinoline. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.09 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 9.5 Hz, 1H), 7.67 (s, 1H), 7.50−7.58 (m, 6H), 7.33 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 1H), 4.00 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 160.7, 157.3, 150.7, 148.9, 139.3, 138.7, 137.0, 129.6, 129.5, 128.6, 128.3, 127.4, 126.8, 120.8, 119.3, 117.3, 107.9, 55.6, 21.4; HRMS (MALDI/DHB) Calcd. for $C_{23}H_{20}NO$: [M + H]$^+$, 326.1539. Found: m/z 326.1541.

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■ ASSOCIATED CONTENT

Supporting Information

Compound characterization data and mechanistic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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