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Benzoquinone Ligand-Enabled Ruthenium-Catalyzed Deaminative Coupling of 2-Aminoaryl Aldehydes and Ketones with Branched Amines for Regioselective Synthesis of Quinoline Derivatives

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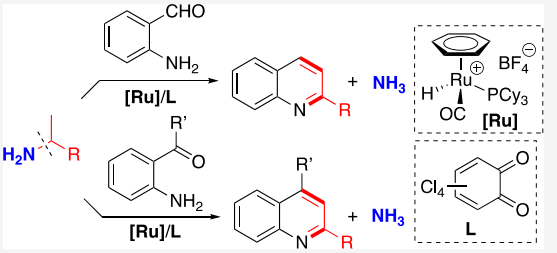
ABSTRACT: The catalytic system generated *in situ* from the cationic Ru−H complex $[(C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ (**1**) with 2,3,4,5-tetrachloro-1,2-benzoquinone (**L1**) was found to be highly effective for promoting the deaminative coupling reaction of 2-aminoaryl aldehydes with branched amines to form 2-substituted quinoline products. The analogous deaminative coupling reaction of 2-aminoaryl ketones with branched amines led to the regioselective formation of 2,4-disubstituted quinoline products. A number of biologically active quinoline derivatives including graveolinine and a triplex DNA intercalator have been synthesized by using the catalytic method.



INTRODUCTION

As one of the most prevalent organic functional groups, amines are a highly attractive class of substrates for transition metal-catalyzed deaminative coupling methods, in which the formation of ammonia would serve as the driving force.[1] Katritzky pyridinium salts have been found to be particularly effective reagents for a variety of catalytic deaminative cross electrophilic coupling reactions.[2] Since these coupling methods using Katritzky salts require preactivation of amine substrates and generate wasteful byproducts, much research effort has been devoted to develop direct deaminative coupling methods by employing simple amines and related amino compounds as the reagents.[1c,3] In a seminal work, Kakiuchi's group developed a Suzuki-type deaminative coupling method via a direct arene C−N bond cleavage of arylamines,[4] and the catalytic method has been subsequently extended to other cross coupling reactions of amides.[5] Garg's and Szostak's groups independently developed catalytic amide C−N bond cleavage methods to facilitate the synthesis of a variety of amides and related nitrogen-containing products.[6] Martin's and Zhang's groups reported a series of Ni-catalyzed site- and stereoselective deaminative alkylation and arylation of amines and amides to unactivated olefins and saturated carbons.[2d,7] A number of efficient photocatalytic deaminative coupling processes have been developed by using Katritzky-type pyridinium salts,[8] and dual Ni/photoredox catalysis methods have also been successfully utilized for the deaminative alkylation and arylation reactions of sterically hindered amines.[9] Levin's group recently devised a series of remarkably versatile direct deaminative functionalization of anomeric amides via the formation of carbon-centered radicals.[10]

We previously devised a Ru-catalyzed direct deaminative coupling method, which promotes chemoselective C−N bond cleavage of amines and α-amino acid substrates in forming 2-alkylated ketone products.[11] We subsequently discovered that a benzoquinone ligand-enabled ruthenium catalytic system, formed *in situ* from the reaction of the cationic Ru−H complex $[(C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ (**1**) with 2,3,4,5-tetrachloro-1,2-benzoquinone (**L1**), is highly effective for mediating the deaminative coupling reactions of amines to form flavanone and quinazolinone derivatives.[12] We successfully utilized the deaminative coupling protocol for promoting regioselective C−C bond cleavage reaction of enones.[13] One of the major limitations for these catalytic methods is that they typically require sterically nondemanding and linear amine substrates, although we have been able to use the branched amines in case of formation of quinozolinone derivatives.[12] In an effort to extend the scope and synthetic utility, we sought to develop suitable deaminative coupling methods for branched amine substrates. Herein, we disclose a benzoquinone-enabled Ru-catalyzed deaminative coupling method that employs branched amines as the substrates for a step-efficient synthesis of quinoline derivatives without employing any reactive reagents or forming wasteful byproducts.

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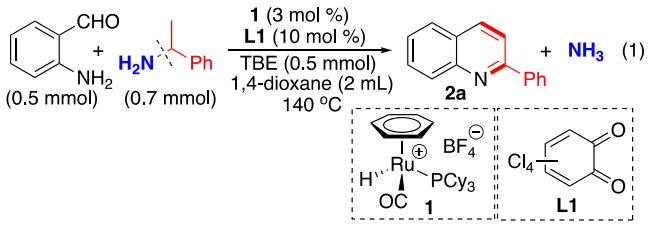
RESUTS AND DISCUSSION



We initially found that the *in situ* generated Ru catalyst system **1**/**L1** is highly effective for promoting the deaminative coupling reaction of 2-aminobenzaldehyde with branched amines. Thus, the treatment of 2-aminobenzaldehyde (0.5 mmol) with 1-phenylethanamine (0.7 mmol) in the presence of **1** (3 mol %)/**L1** (10 mol %) and *t*-butylethylene (TBE, 0.5 mmol) in 1,4-dioxane (2 mL) at 140 °C led to the formation of the 2-phenylquinoline product **2a** (eq 1). The subsequent optimization study established that the cationic Ru−H complex **1** with 2,3,4,5-tetrachloro-1,2-benzoquinone ligand (**L1**) exhibits the highest catalytic activity in promoting the coupling reaction among screened ruthenium catalysts and catechol/benzoquinone ligands (Table 1). The addition of a hydrogen scavenger *t*-butylethylene was found to further improve the coupling product yield of **2a** (entry 2), but neither common Lewis acids nor catechols and benzoquinones alone exhibited any catalytic activity in the absence of a Ru catalyst (Table S1, Supporting Information (SI)).

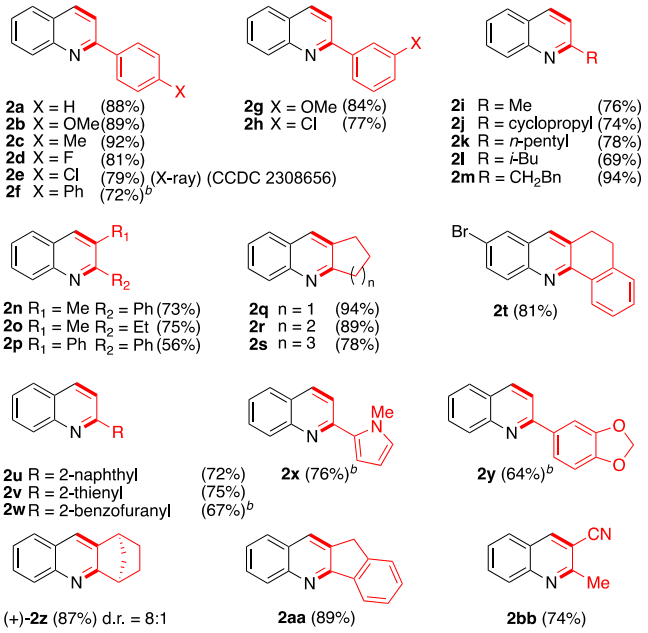
Table 1. Catalyst Screening and Optimization Study for the Deaminative Coupling Reaction of 2-Aminobenzaldehyde with 1-Phenylethanamine[a]

entry	catalyst	deviation from standard conditions	**2a** (%)[b]
1	**1**	none	92
2	**1**	without TBE	85
3	**1**	without **L1**	68
4	**1**	with 1-naphthylamine	16
5	$(PCy_3)_2(CO)RuHCl$	with $HBF_4{\cdot}OEt_2$	20
6	$[(PCy_3)_2(CO)(CH_3CN)_2RuH]^+BF_4^-$		52
7	$[(PCy_3)(CO)RuH]_4(O)(OH)_2$	with $HBF_4{\cdot}OEt_2$	56
8	$RuCl_2(PPh_3)_3$		6
9	$Ru_3(CO)_{12}$		<5
10	$[(p\text{-cymene})RuCl_2]_2$		12
11	$[(COD)RuCl_2]_x$		33
12	$RuCl_3{\cdot}3H_2O$		20
13	$BF_3{\cdot}OEt_2$		<5
14	$HBF_4{\cdot}OEt_2$		<5
15		**L1** only	<5
16		no **1** and **L1**	0

[a]Standard conditions: 2-aminobenzaldehyde (0.5 mmol), 1-phenylethanamine (0.7 mmol), catalyst (3 mol %), **L1** (10 mol %) *t*-butylethylene (TBE, 0.5 mmol), 1,4-dioxane (2 mL), 140 °C, 20 h. [b]The product yield was determined by GC-MS using hexamethylbenzene as an internal standard.

We surveyed both aldehyde and amine substrate scope under the standard conditions to examine the selectivity pattern of the deaminative coupling reaction (Scheme 1). The coupling reaction of 2-aminobenzaldehyde with *para*- and *meta*-substituted phenethylamines bearing either electron-donating or electron-withdrawing group cleanly afforded the corresponding 2-substituted quinoline products **2a**−**h**. The coupling of 2-aminobenzaldehyde with both aliphatic and benzyl-substituted branched amines predictively yielded the 2-substituted quinoline products **2i**−**m**. Notably, the coupling reaction of 2-aminobenzaldehyde with sterically demanding aliphatic- and benzyl-substituted branched amines formed a mixture of 2-substituted and 2,3-disubstituted quinoline products, favoring the 2-substituted quinolines **2k**,**m** in the 10−12:1 ratio over the 2,3-disubstituted ones (combined product yield is listed in Scheme 1). The coupling reaction of 2-aminobenzaldehyde with 1-phenylpropylamine and 1,2-diphenylethylamine selectively afforded the 2,3-disubstituted quinoline products **2n** and **2p** without a trace of other regioisomers. The coupling of 2-aminobenzaldehyde with cycloalkyl amines directly led to the formation of tricyclic quinolines **2q**−**s**. A number of heteroatom-containing amine substrates such as 1-thiophenyl-2-ethylamine and *in situ* generated enamines 1-(1-(benzofuran-2-yl)vinyl)pyrrolidine and 1-methyl-2-(1-(pyrrolidin-1-yl)vinyl)-1*H*-pyrrole predictively formed the corresponding quinoline products **2v**−**x** in good yields. In cases when the branched amine substrate is not readily available, the corresponding pyrrolidine imine, typically generated in situ from the reaction of a ketone with pyrrolidine, was used as a branched amine surrogate to form the products **2x**,**y**. The coupling of 2-aminobenzaldehyde with *exo*-2-aminonorbornane and 2-aminoindan yielded the quinoline products **2z** and **2aa**, respectively, while the coupling reaction with 3-aminocrotononitrile efficiently installed 3-cyanoquinoline product **2bb**. A preparatory scale coupling reaction of 2-aminobenzaldehyde (3 mmol) with 1-phenylethanamine (4.2 mmol) led to the isolation of product **2a** in 85% yield (0.52 g). The quinoline products were readily isolated by either crystallization or silica gel column chromato-

Scheme 1. Deaminative Coupling Reaction of 2-Aminoaryl Aldehydes with Branched Amines[a]



[a]Reaction conditions: 2-aminoaryl aldehyde (0.5 mmol), amine (0.7 mmol), **1** (3 mol %), **L1** (10 mol %), *t*-butylethylene (0.5 mmol) 1,4-dioxane (2 mL), 140 °C, 20 h. [b]The enamine substrate was generated *in situ* from the reaction of a ketone (0.5 mmol) with pyrrolidine (1.0 mmol), and **1** (5 mol %) was used.

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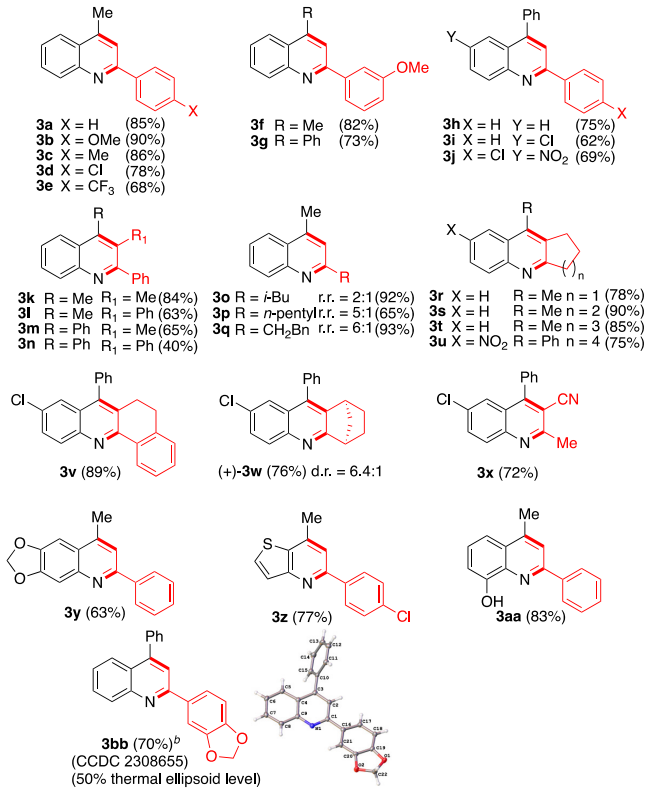
graphic methods, and their structures were completely established by spectroscopic methods. The solid-state structure of **2e** was also determined by X-ray crystallography.[14]

To extend the substrate scope of the deaminative coupling method, we explored the coupling reaction of 2-aminoaryl ketones with branched amines (Scheme 2). The coupling

Scheme 2. Deaminative Coupling Reaction of 2-Aminoaryl Ketones with Branched Amines[a]

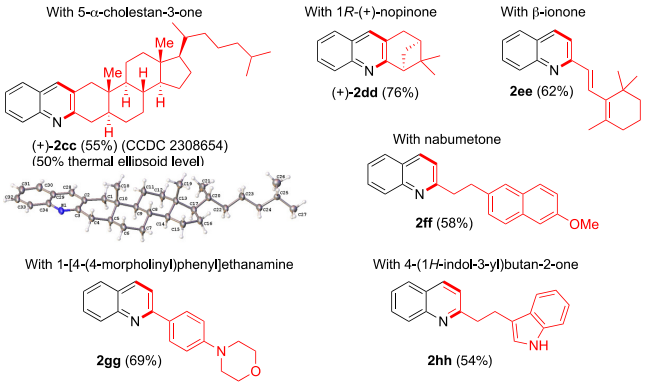


[a]Reaction conditions: 2-aminoaryl ketone (0.5 mmol), amine (0.7 mmol), **1** (3 mol %), **L1** (10 mol %), *t*-butylethylene (0.5 mmol), 1,4-dioxane (2 mL), 140 °C, 20 h. [b]The enamine substrate was generated *in situ* from the reaction of a ketone (0.5 mmol) with pyrrolidine (1.0 mmol), and **1** (5 mol %) was used.

reaction of 2-aminoacetophenone with *para*-substituted phenethylamines containing either electron-donating or electron-withdrawing group cleanly afforded the corresponding 2,4-disubstituted quinoline products **3a−e**. The coupling of 2-aminoacetophenone and 2-aminobenzophenone with *meta*- and *para*-substituted phenylethylamines led to the formation of quinolines **3f−j**. The coupling of 2-aminoaryl ketones with the branched amines, 1-phenylpropan-1-amine, 1,2-diphenylethanamine, and 1,2-diphenylethanamine, formed the 2,3,4-trisubstitued quinolines **3k−n** in a highly regioselective manner. The formation of 2,3,4-trisubstitued quinolines can be readily rationalized by invoking isomerization of initially formed enamine to a more stable internal enamine and the subsequent cyclization from the internal enamine. A mixture of the 2,4-disubstituted quinoline products **3o−q** was formed from the reaction of 2-aminoacetophenone with both aliphatic and aryl-substituted methylamines, favoring the formation of 2,4-disubstitited quinolines over 2,3,4-trisubstituted ones. The coupling with cycloalkyl amines smoothly formed the tricyclic quinoline derivatives **3r−u**, while the analogous coupling reaction of 2-aminoaryl ketones with 3-aminocrotononitrile predictively formed the 2,3,4-trisubstituted quinoline product **3x**. The coupling of a number of heteroatom-containing 2-aminoaryl ketone substrates with aryl-substituted ethanamine allowed a direct synthesis of highly functionalized quinoline products **3y−3bb**. The structure of **3bb** was determined by X-ray crystallography.

We next employed a number of biologically active ketone and amine substrates for the deaminative coupling reaction (Scheme 3). In this case, the *in situ* generated enamine

Scheme 3. Deaminative Coupling Reaction with *In Situ* Generated Enamine Substrates[a]



[a]Reaction conditions: 2-aminoaryl aldehyde (0.5 mmol), enamine (0.5 mmol), **1** (5 mol %), **L1** (10 mol %), *t*-butylethylene (0.5 mmol), 1,4-dioxane (2 mL), 140 °C, 20 h. The enamine substrate was generated *in situ* from the reaction of a ketone (0.5 mmol) with pyrrolidine (1.0 mmol), and **1** (5 mol %) was used.

substrate, which was conveniently formed from the reaction of a ketone (0.5 mmol) with pyrrolidine (1.0 mmol), was found to be a suitable surrogate for the branched amine substrate. Thus, the treatment of 2-aminobenzaldehyde with an *in situ* generated steroidal pyrrolidine derivative led to the corresponding quinoline product (+)-**2cc**. The structure of (+)-**2cc** was established by X-ray crystallography. The coupling of 2-aminobenzaldehyde with *in situ* generated enamine substrate from the reaction of (*R*)-(+)-nopinone with pyrrolidine yielded the coupling product (+)-**2dd** in 76% yield. The analogous coupling reaction of 2-aminobenzaldehyde with *in situ* generated (*E*)-1-(4-(2,6,6-trimethylcyclohex-1-en-1-yl)-buta-1,3-dien-2-yl)pyrrolidine and 1-(4-(6-methoxynaphthalen-2-yl)but-1-en-2-yl)pyrrolidine afforded the quinoline products **2ee** and **2ff**, respectively, while the direct deaminative coupling reaction of 2-aminobenzaldehyde with 1-[4-(4-morpholinyl)phenyl]ethanamine yielded the quinoline product **2gg** in 69% yield. The coupling of 2-aminobenzaldehyde with an *in situ* formed enamine substrate 3-(3-(pyrrolidin-1-yl)but-3-en-1-yl)-1*H*-indole smoothly yielded the coupling product **2hh**.

A number of biologically active quinoline target molecules were synthesized by using the deaminative coupling method to further exemplify its synthetic utility (Scheme 4). Following the literature procedure,[15] the oxidation reaction of **2u** with *m*-CPBA followed by the treatment with oxalyl chloride in DMF formed the chlorinated quinoline product **4u**. The substitution reaction of **4u** with NaOMe yielded graveolinine **5u** in 90% yield from **2u**. The naphthyl-substituted quinoline **4y** was synthesized in a similar fashion from **2y**, and the amination

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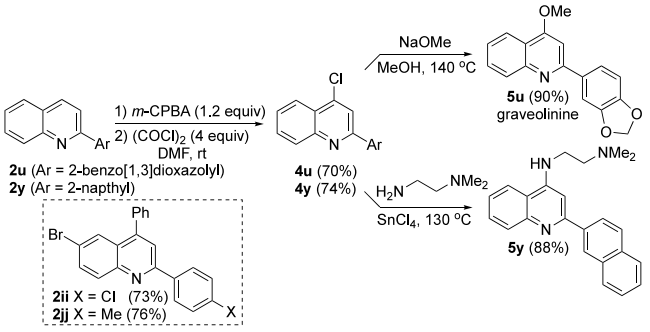
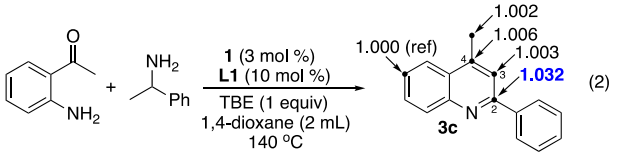
Scheme 4. Synthesis of Graveolinine and Related Quinoline Derivatives



reaction of **4y** with N^1,N^1-dimethylethane-1,2-diamine in the presence of $SnCl_4$ afforded the amino-substituted quinoline product **5y** in 88% yield. Graveolinine has been found to exhibit a broad spectrum of antibacterial, antitumor, and spasmolytic activities, and it has been studied as a potential drug for Alzheimer's disease.[16] The amino-substituted quinoline product **5y** has been found to selectively bind to a triplex DNA and has been used as a therapeutic gene expression modulator.[17] In addition, the 2,4-disubstituted quinoline products **2ii** and **2jj**, which have been shown to exhibit anticancer and antituberculosis activities, were directly synthesized from the reaction of 2-amino-5-bromobenzophenone with 1-(4-chlorophenyl)ethylamine and 1-(4-methyl)-ethylamine, respectively.[18] The synthesis of these target molecules clearly illustrates synthetic versatility of the deaminative catalytic method in attaining a library of biologically active 2-substituted quinoline products.



To discern the rate-limiting step of the coupling reaction, we measured the carbon kinetic isotope effect (KIE) of the coupling reaction by using Singleton's high precision NMR method at natural abundance.[19] The high conversion sample of **3c** was obtained from the treatment of 2-aminoacetophenone (0.5 mmol) with 1-phenylethanamine (0.7 mmol) in 1,4-dioxane (2 mL) in the presence of **1** (3 mol %)/**L1** (10 mol %) and *t*-butylethylene (1.0 equiv) at 140 °C for 20 h (avg. 90% conversion) (eq 2). The low conversion sample was similarly isolated from three separate reactions after 2 h (avg. 13% conversion). The most significant carbon isotope effect was observed on C(2) of the product **3c** when the ^{13}C ratio of the high conversion sample was compared with the low conversion sample (^{13}C(avg 90% conversion)/^{13}C(avg 13% conversion) at C(2) = 1.032; average of two runs) (Table S3, SI). The observation of the carbon KIE on C(2) suggests the C−N bond cleavage as the turnover-limiting step of the coupling reaction.

To examine the electronic influence of amine substrate, we compared the reaction rate of 2-aminoacetophenone with a series of *para*-substituted phenylethylamines (X = OMe, Me, H, F, Cl). The rate of the coupling reaction of 2-aminobenzaldehyde (0.10 mmol) with *para*-substituted phenylethylamine (0.14 mmol) in the presence of **1** (3 mol %)/**L1** (10 mol %) and *t*-butylethylene (1 equiv) in dioxane-d_8 was monitored by ^1H NMR. The appearance of the product peak was normalized against an internal standard (C_6Me_6) in 40 min intervals, and the k_{obs} of each catalytic reaction was determined from a first-order plot of $-\ln([C_7H_7NO]_t/[C_7H_7NO]_0)$ vs time. The Hammett plot of $\log(k_X/k_H)$ vs σ_p showed a linear correlation, in which the coupling reaction was promoted by an electron-rich phenylethylamine substrate (ρ = −0.6 ± 0.2) (Figure 1). The promotional effect by the

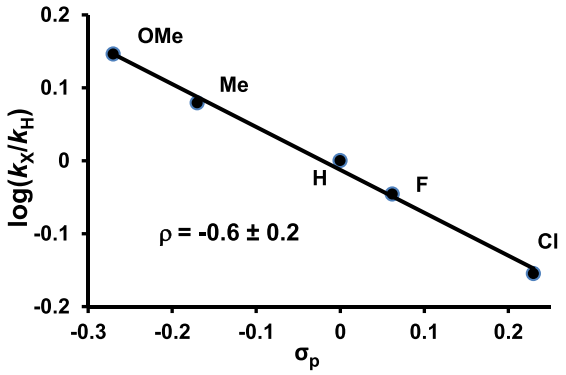
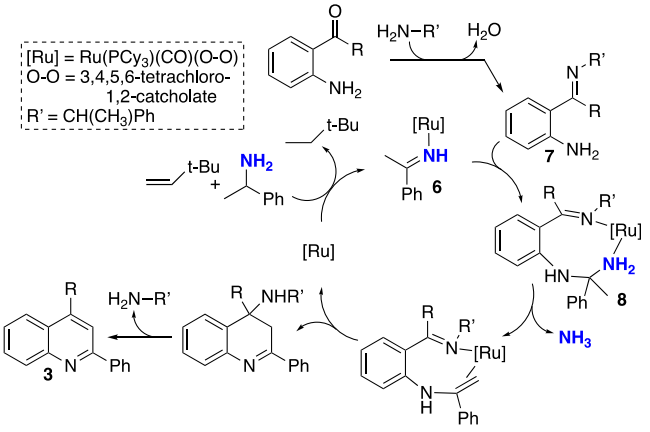


Figure 1. Hammett plot from the reaction of 2-aminobenzaldehyde with a series of *para*-substituted phenylethylamines (X = OMe, Me, H, F, Cl).

electron-releasing group of the amine substrates is also consistent with the C−N bond cleavage as the most energetically demanding step for the coupling reaction.

Although details of the coupling reaction still remain to be established, we offer a plausible mechanistic sequence for the formation of quinoline products on the basis of these preliminary results (Scheme 5). We propose that the Ru-

Scheme 5. Plausible Mechanistic Pathway for the Deaminative Coupling Reaction



imine species **6** is initially formed from the dehydrogenation of the amine substrate. In support of this notion, we have been able to detect a Ru-amine complex from the reaction mixture of **1**, 2-aminoacetophenone, and 1-phenylethanamine by NMR and LC-MS.[20] Meanwhile, 2-aminoacetophenone would readily undergo the dehydrative coupling reaction with the amine substrate to form the 2-aminoaryl imine substrate **7**. The nucleophilic attack of the imine substrate **7** to the imine-coordinated Ru catalyst **6** would form an elaborated Ru-amine species **8**. The observation of the significant carbon KIE on

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C(2) of **3c** as well as the Hammett correlation data suggest that the C−N bond cleavage (deamination) is the rate-determining step of the coupling reaction. The subsequent cyclization and proton transfer steps would form the 4-aminoquinoline derivative, which is expected to rapidly undergo deamination to form the quinoline product **3**.

While the current deaminative coupling reaction shares some mechanistic features with the Friedländer quinoline synthesis,[21] one of the distinguishing features of our proposed mechanism is the formation of an imine intermediate species **7**. To establish if imine **7** is a viable substrate, we performed the coupling reaction of a presynthesized imine substrate (*E*)-2-(1-((1-phenylethyl)imino)ethyl)aniline with 1-phenylethanamine under standard conditions, which led to the product **3a** in 45% yield. The Ru catalyst was found to be essential for the coupling reaction, as the reaction did not give **3a** in the absence of the Ru catalyst. While the result clearly supports that imine **7** is a viable substrate for the coupling reaction, we have not been able to completely rule out an alternate mechanism via the formation of an enone intermediate bearing the 2-aminoaryl group that has been considered a key intermediate for the Friedländer quinoline synthesis. We also observed the formation of *t*-butylethane in the crude reaction mixture, which validates TBE as the hydrogen acceptor for the dehydrogenation of the amine substrate. In support of this notion, we previously found that the Ru−H complexes exhibit a high activity for the dehydrogenation of saturated amines in the presence of TBE.[22]

We have not been able to decipher the exact role of **L1**. We previously showed that an isolated Ru-catecholate complex exhibits considerably higher activity toward deaminative coupling reactions compared to the in situ generated one.[11b] However, in the current study, we failed to isolate the similar Ru-catecholate complex from the reaction of **1** with **L1**, despite our best efforts. In an effort to detect a Ru-catecholate complex, the reaction mixture of **1**, 2-aminoacetophenone, and 1-phenylethanamine was analyzed by NMR and LC-MS. The formation of two new phosphorus peaks was observed by $^{31}P\{^{1}H\}$ NMR at δ 45.4 (s) and 41.5 (s) ppm after 2 min of heating the reaction mixture at 120 °C. The ESI-LC-MS analysis of the mixture showed that the parent mass ions of these complexes match with Ru-amine and -quinoline complexes without the catecholate ligand (Figure S2, SI). Since the Ru catalyst without **L1** still exhibits a reasonable activity for the reaction as delineated in Table 1, we suspect that both the Ru complexes with and without the catecholate (or 1,2-benzoquinone) ligand may be catalytically active for the deaminative coupling reaction.

CONCLUSIONS

In summary, we have successfully devised a Ru-catalyzed deaminative coupling method for 2-aminoaryl aldehydes and ketones with readily available branched amine substrates, which efficiently leads to a regioselective synthesis of 2-substituted and 2,4-disubstituted quinoline derivatives. We have been able to synthesize a number of biologically active quinoline derivatives including graveolinine and a triplex DNA intercalator by using the catalytic method. The preliminary kinetic and mechanistic studies indicate that the reaction proceeds via the coupling reaction between initially formed imine and 2-aminoarylimine substrates, in which the C−N bond cleavage is the rate-determining step of the coupling reaction. Efforts to examine detailed mechanisms as well as to explore synthetic utility of the deaminative coupling methods are continuing in our laboratory.

EXPERIMENTAL SECTION

All operations were carried out in a nitrogen-filled glovebox or by using standard high vacuum and Schlenk techniques unless otherwise noted. Solvents were freshly distilled over appropriate drying reagents. Benzene, toluene, and hexanes were distilled from purple solutions of sodium and benzophenone, and dichloromethane was dried over calcium hydride prior to use. All organic substrates were received from commercial sources and were used without further purification. Column chromatography was performed on a silica gel P60 (40−63 μm particle size), and thin layer chromatography was performed on EMD Millipore glass back TLC plates precoated with silica gel 60 GF_{254}. The ^{1}H, ^{2}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian 300 or 400 MHz FT-NMR spectrometer, and the data are reported in parts per million (ppm) relative to TMS, with the residual solvent peak as an internal reference. Multiplicities are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constant(s) in Hz. Mass spectra were recorded from the Shimadzu GC-MS-QP2010 SE spectrometer with an SH-Rxi-5sil MS, fused silica (crossbond 1,4-*bis*(dimethylsiloxy)-phenylene dimethyl polysiloxane) column (30 m, 0.25 mm, 0.25 μm). High-resolution mass spectra (HRMS) were obtained at the Mass Spectrometry/ICP Lab, Department of Chemistry and Biochemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin, and at the Analytical Instrumentation Center, School of Pharmacy, University of Wisconsin-Madison, Madison, Wisconsin.

General Procedure for the Coupling Reaction of a 2-Aminoaryl Aldehyde with a Branched Amine. In a glovebox, 2-aminoaryl aldehyde (0.5 mmol), an amine (0.7 mmol), *t*-butylethylene (TBE, 0.5 mmol), complex **1** (3 mol %), and **L1** (10 mol %) were dissolved in anhydrous 1,4-dioxane (6 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the glovebox and was stirred in an oil bath set at 140 °C for 20 h. The reaction tube was taken out of the oil bath and was cooled to room temperature. After the tube was open to air, the solution was filtered through a short silica gel column by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC-MS. The analytically pure product was isolated by column chromatography on silica gel (40−63 μm particle size, hexanes/EtOAc). The product was completely characterized by NMR and GC-MS spectroscopic methods. Caution! Although no problems were encountered during the course of this work, care should always be taken when heating a sealed reaction vessel above the boiling point of the solvent. This procedure includes heating the reaction mixture above the boiling point of 1,4-dioxane.

Preparatory Scale Synthesis of 2a. In a glovebox, complex **1** (52 mg, 3 mol %) and **L1** (73 mg, 10 mol %) were dissolved in anhydrous 1,4-dioxane (2 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The resulting solution was stirred for 5−10 min. 2-Aminobenzaldehyde (363 mg, 3.0 mmol), an amine (508 mg, 4.2 mmol), and 3,3-dimethyl-1-butene (252 mg, 3.0 mmol) were dissolved in 1,4-dioxane (2 mL), and the solution was added to the reaction tube. The tube was brought out of the glovebox and was stirred in an oil bath set at 140 °C for 20 h. The reaction tube was taken out of the oil bath and was cooled

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to room temperature. After the tube was open to air, the solution was filtered through a short silica gel column by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC-MS. The analytically pure product was isolated by column chromatography on silica gel (40−63 μm particle size, hexanes/EtOAc). Yield = 523 mg (85%).

Synthesis of Graveolinine (5u). The synthesis of quinoline *N*-oxide was conducted following the literature procedure.[15] In a 250 mL RB flask, **2u** (249 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (5 mL) and 3-chloroperbenzoic acid (206 mg, 1.2 mmol) was added to the solution. After the reaction mixture was stirred overnight at room temperature, the product mixture was concentrated under vacuum, and the resulting residue was purified by flash column chromatography (9:1 EtOAc/MeOH) to obtain the quinoline *N*-oxide. The quinoline *N*-oxide (133 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (1 mL) and $(COCl)_2$ (2 mmol) in DMF (2 mmol) was added at 0 °C. The reaction mixture was stirred for 12 h at room temperature. The product mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography to give **4u** (104 mg, 70%). The **4u** (57 mg, 0.2 mmol) was dissolved in MeOH (2 mL), and NaOMe (0.24 mmol) was added to the solution, and the reaction mixture was heated at 140 °C for 10 h under nitrogen atmosphere. The resulting product mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography to give graveolinine **5u** (50 mg, 90%).

*2-Phenylquinoline (**2a**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-phenylethanamine (85 mg, 0.7 mmol) was stirred at 140°C for 20 h. The product **2a** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 90 mg (88%). Data for **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.61 (m, 4H), 7.34−7.25 (m, 2H), 7.22−7.17 (m, 1H), 7.05−6.89 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.3, 148.2, 139.6, 136.7, 129.7, 129.6, 129.2, 128.8, 127.5, 127.4, 127.1, 126.2, 118.9 ppm; GC-MS for $C_{15}H_{11}N$, m/z = 205 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*2-(4-Methoxyphenyl)quinoline (**2b**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-(4-methoxyphenyl)ethanamine (106 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2b** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 105 mg (89%). Data for **2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21−8.09 (m, 4H), 7.83−7.75 (m, 2H), 7.72 (tt, J = 8.5, 1.6 Hz, 1H), 7.55−7.44 (m, 1H), 7.09−7.01 (m, 2H), 3.86 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.7, 156.7, 148.1, 136.5, 132.0, 129.5, 129.4, 128.8, 127.3, 126.8, 125.8, 118.4, 114.1, 55.2 ppm; GC-MS for $C_{16}H_{13}NO$, m/z = 235 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*2-(p-Tolyl)quinoline (**2c**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-(*p*-tolyl)ethanamine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2c** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 101 mg (92%). Data for **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 15.9, 8.5 Hz, 2H), 8.10 (dd, J = 8.4, 2.1 Hz, 2H), 7.88−7.78 (m, 2H), 7.73 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.52 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 2.45 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.2, 148.1, 139.4, 136.6, 129.5, 129.5, 127.4, 127.4, 127.0, 126.0, 118.8, 21.3 ppm; GC-MS for $C_{16}H_{13}N$, m/z = 219 (M_+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*2-(4-Fluorophenyl)quinoline (**2d**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-(4-fluorophenyl)ethanamine (97 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2d** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 90 mg (81%). Data for **2d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21−8.11 (m, 4H), 7.84−7.76 (m, 2H), 7.73 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.52 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.26−7.16 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.0, 162.5, 156.1, 148.1, 136.6, 135.6 (d, J_{CF} = 3.3 Hz), 129.6 (d, J_{CF} = 14.0 Hz), 129.3 (d, J_{CF} = 8.5 Hz), 127.4, 127.0, 126.3, 118.5, 115.7 (d, J_{CF} = 21.3 Hz) ppm; GC-MS for $C_{15}H_{10}FN$, m/z = 223 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[23]

*2-(4-Chlorophenyl)quinoline (**2e**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-(4-chlorophenyl)ethanamine (109 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2e** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 94 mg (79%). Data for **2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21−8.14 (m, 2H), δ 8.13−8.09 (m, 2H), 7.82 (d, J = 8.3, Hz, 2H), 7.74 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.56−7.52 (m, 1H), 7.51−7.47 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.9, 148.2, 138.0, 136.9, 135.5, 129.8, 129.6, 129.0, 128.8, 127.4, 127.2, 126.5, 118.5 ppm; GC-MS for $C_{15}H_{10}ClN$, m/z = 281 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[24]

*2-([1,1′-Biphenyl]-4-yl)quinoline (**2f**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and in situ generated 1-(1-([1,1′-biphenyl]-4-yl)vinyl)pyrrolidine (174 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2f** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 101 mg (72%). Data for **2f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29−8.19 (m, 4H), 7.93 (dd, J = 8.5, 2.3 Hz, 1H), 7.84 (dd, J = 8.2, 1.5 Hz, 1H), 7.76 (dd, J = 15.2, 7.9 Hz, 3H), 7.71−7.67 (m, 2H), 7.57−7.46 (m, 3H), 7.42−7.36 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.8, 148.3, 142.0, 140.5, 138.5, 136.8, 129.7, 129.7, 128.8, 127.9, 127.6, 127.5, 127.5, 127.2, 127.1, 126.3, 118.9 ppm; GC-MS for $C_{21}H_{15}N$, m/z = 281 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[23]

*2-(3-Methoxyphenyl)quinoline (**2g**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-(3-methoxyphenyl)ethanamine (106 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2g** was isolated by column

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chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 99 mg (84%). Data for **2g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.16 (m, 2H), 7.89−7.72 (m, 3H), 7.77−7.68 (m, 2H), 7.53 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.44 (t, J = 7.9 Hz, 1H), 7.03 (dd, J = 8.2, 2.5 Hz, 1H), 3.93 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1, 157.0, 148.0, 141.0, 136.8, 129.7, 129.6, 129.6, 127.4, 127.2, 126.3, 119.9, 119.0, 115.4, 112.6, 55.3 ppm; GC-MS for $C_{16}H_{13}NO$, m/z = 235 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[25]

*2-(3-Chlorophenyl)quinoline (**2h**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and in situ generated 1-(1-(3-chlorophenyl)vinyl)pyrrolidine (145 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2h** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 92 mg (77%). Data for **2h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.20 (m, 1H), δ 8.18 (d, J = 8.5 Hz 1H) 8.00 (d, J = 8.6 Hz, 1H), 7.94 (dt, J = 7.6, 1.6 Hz, 1H), 7.70 (ddd, J = 8.3, 6.3, 1.7 Hz, 2H), 7.62 (d, J = 8.6 Hz, 1H), 7.50−7.42 (m, 1H), 7.41−7.31 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.0, 147.8, 140.9, 136.5, 134.6, 129.7, 129.5, 129.4, 128.9, 127.3, 127.2, 126.9, 126.2, 125.2, 118.1 ppm; GC-MS for $C_{15}H_{10}ClN$, m/z = 239 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[26]

*2-Methylquinoline (**2i**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and propan-2-amine (41 mg, 0.7 mmol) was stirred at 140°C for 20 h. The product **2i** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 54 mg (76%). Data for **2i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 2H), 7.80−7.73 (m, 1H), 7.68 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.52−7.44 (m, 1H), 7.32−7.24 (m, 1H), 2.76 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.8, 147.6, 136.0, 129.3, 128.4, 127.3, 126.3, 125.5, 121.8, 25.2 ppm; GC-MS for $C_{10}H_9N$, m/z = 143 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[27]

*2-Cyclopropylquinoline (**2j**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and cyclopropylamine (40 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2j** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Light-yellow oil, yield = 63 mg (74%). Data for **2j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.72 (dd, J = 8.3, 1.4 Hz, 1H), 7.64 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.42 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.15 (d, J = 8.5 Hz, 1H), 2.25 (tt, J = 8.3, 4.9 Hz, 1H), 1.19−1.14 (m, 2H), 1.12−1.06 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 147.9, 135.8, 129.2, 128.6, 127.4, 126.6, 125.1, 119.2, 18.0, 10.2 ppm; GC-MS for $C_{12}H_{11}N$, m/z = 169 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*2-Pentylquinoline (**2k**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and heptan-2-amine (81 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2k** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Light-yellow oil, yield = 78 mg (78%). Data for **2k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.00 (m, 2H), 7.75 (d, J = 8.3 Hz, 1H), 7.71−7.62 (m, 1H), 7.50−7.42 (m, 1H), 7.28 (dt, J = 9.1, 1.6 Hz, 2H), 3.00−2.92 (m, 2H), 1.87−1.75 (m, 1H), δ 1.46−1.29 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0, 147.8, 136.1, 129.2, 128.7, 127.4, 126.6, 125.6, 121.3, 39.3, 31.7, 29.7, 22.5, 14.0 ppm; GC-MS for $C_{14}H_{17}N$, m/z = 199 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[27]

*2-Isobutylquinoline (**2l**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 4-methylpentan-2-amine (71 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2l** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Light yellow oil, yield = 64 mg (69%). Data for **2l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.2 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 2.83 (d, J = 7.6 Hz, 2H), 2.19 (nonet, J = 6.8 Hz, 1H), 0.96 (d, J = 6.8 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.2, 147.9, 135.9, 129.2, 128.8, 127.4, 126.7, 125.6, 122.0, 48.3, 29.4, 22.5 ppm; GC-MS for $C_{13}H_{15}N$, m/z = 185 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[28]

*2-Phenethylquinoline (**2m**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 4-phenylbutan-2-amine (104 mg, 0.7 mmol) was stirred at 140°C for 20 h. The product **2m** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow liquid, yield = 110 mg (94%). Data for **2m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−7.96 (m, 2H), 7.77−7.63 (m, 2H), 7.46 (q, J = 7.7 Hz, 1H), 7.25 (d, J = 9.3 Hz, 4H), 7.20−7.12 (m, 2H), 3.27 (t, J = 7.4 Hz, 2H), 3.14 (t, J = 7.6 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7, 147.8, 141.4, 136.2, 129.4, 128.7, 128.4, 128.3, 127.5, 126.7, 125.9, 125.8, 121.5, 40.9, 35.9 ppm; GC-MS for $C_{17}H_{15}N$, m/z = 233 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[29]

*3-Methyl-2-phenylquinoline (**2n**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-phenylpropan-1-amine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2n** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow liquid, yield = 80 mg (73%). Data for **2n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 8.4, 1.1 Hz, 1H), 8.02 (d, J = 1.1 Hz, 1H), 7.78 (dd, J = 8.0, 1.4 Hz, 1H), 7.72−7.64 (m, 1H), 7.62−7.59 (m, 2H), 7.55−7.51 (m, 1H), 7.50−7.47 (m, 2H), 7.47−7.43 (m, 1H), 2.47 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.4, 146.5, 140.7, 136.8, 129.2, 128.8, 128.7, 128.3, 128.2, 127.5, 126.7, 126.4, 76.7, 20.6 ppm; GC-MS for $C_{16}H_{13}N$, m/z = 219 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[23]

*2-Ethyl-3-methylquinoline (**2o**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and pentan-3-amine (61 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2o** was isolated by column chromatography on silica gel (hexanes/

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EtOAc = 100:1−5:1). Yellow liquid, yield = 64 mg (75%). Data for **2o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.83 (s, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.66−7.57 (m, 1H), 7.44 (t, J = 7.5 Hz, 1H), 3.00 (q, J = 7.6 Hz, 2H), 2.48 (s, 3H), 1.38 (t, J = 7.6 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.2, 146.4, 135.9, 133.8, 129.4, 128.3, 127.3, 126.6, 125.6, 29.4, 19.1, 12.8 ppm; GC-MS for $C_{12}H_{13}N$, m/z = 171 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[26]

*2,3-Diphenylquinoline (**2p**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1,2-diphenylethanamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2p** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 79 mg (56%). Data for **2p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.5 Hz, 1H), 8.18 (s, 1H), 7.87 (dd, J = 8.2, 1.6 Hz, 1H), 7.79−7.71 (m, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.52−7.45 (m, 2H), 7.33−7.23 (m, 8H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 147.2, 140.4, 139.9, 137.5, 134.5, 130.0, 129.7, 129.6, 129.4, 128.2, 127.9, 127.9, 127.4, 127.2, 127.1, 126.7 ppm; GC-MS for $C_{21}H_{15}N$, m/z = 281 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*2,3-Dihydro-1H-cyclopenta[b]quinoline (**2q**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and cyclopentylamine (60 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2q** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 79 mg (94%). Data for **2q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 2.1 Hz, 1H), 7.67 (dt, J = 8.1, 1.5 Hz, 1H), 7.58 (tt, J = 8.3, 1.1 Hz, 1H), 7.45−7.36 (m, 1H), 3.12 (td, J = 7.6, 1.0 Hz, 2H), 3.02 (td, J = 7.4, 1.6 Hz, 2H), 2.15 (pd, J = 7.6, 1.3 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.8, 147.3, 135.5, 130.2, 128.4, 128.2, 127.3, 127.2, 125.4, 34.5, 30.4, 23.5 ppm; GC-MS for $C_{12}H_{11}N$, m/z = 169 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[24]

*1,2,3,4-Tetrahydroacridine (**2r**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and cyclohexylamine (69 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2r** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 81 mg (89%). Data for **2r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.5 Hz, 1H), 7.75 (s, 1H), 7.66 (dd, J = 8.2, 1.5 Hz, 1H), 7.62−7.54 (m, 1H), 7.40 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 3.11 (t, J = 6.5 Hz, 2H), 2.93 (t, J = 6.4 Hz, 2H), 2.05−1.90 (m, 2H), 1.86 (p, J = 6.2 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.2, 146.4, 135.0, 130.9, 128.4, 128.1, 127.1, 126.8, 125.4, 33.4, 29.1, 23.1, 22.8 ppm; GC-MS for $C_{13}H_{13}N$, m/z = 183 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[24]

*7,8,9,10-Tetrahydro-6H-cyclohepta[b]quinoline (**2s**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and cycloheptylamine (79 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2s** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 77 mg (78%). Data for **2s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.66 (dd, J = 8.0, 1.4 Hz, 1H), 7.59 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.42 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 3.22−3.15 (m, 2H), 2.93−2.85 (m, 2H), 1.86 (p, J = 5.8 Hz, 2H), 1.82−1.74 (m, 2H), 1.73−1.67 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 146.1, 136.4, 134.5, 128.3, 128.3, 127.2, 126.7, 125.6, 39.9, 35.3, 32.1, 28.7, 26.9 ppm; GC-MS for $C_{14}H_{15}N$, m/z = 197 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[27]

*9-Bromo-5,6-dihydrobenzo[c]acridine (**2t**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-amino-5-bromobenzaldehyde (99 mg, 0.5 mmol) and 1,2,3,4-tetrahydronaphthalen-1-amine (103 mg, 0.7 mmol) was stirred at 140°C for 20 h. The product **2t** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 125 mg (81%). Data for **2t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 7.5 Hz, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.75 (s, 1H), 7.66 (s, 1H), 7.62−7.55 (m, 1H), 7.34−7.25 (m, 2H), 7.16 (d, J = 6.9 Hz, 1H), 2.98 (t, J = 7.1 Hz, 2H), 2.88 (t, J = 7.0 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.7, 146.0, 139.3, 134.2, 132.7, 132.0, 131.5, 131.0, 130.0, 128.9, 128.0, 127.3, 126.0, 119.8, 28.7, 28.1 ppm; GC-MS for $C_{17}H_{12}BrN$, m/z = 310 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[30]

*2-(Naphthalen-2-yl)quinoline (**2u**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-(naphthalen-2-yl)ethanamine (120 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2u** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 92 mg (72%). Data for **2u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32−8.21 (m, 2H), 8.18−8.11 (m, 1H), 8.00−7.88 (m, 3H), 7.83−7.69 (m, 3H), 7.66−7.57 (m, 2H), 7.55−7.44 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 148.1, 138.7, 136.2, 134.0, 131.2, 129.7, 129.7, 129.1, 128.4, 127.7, 127.5, 127.0, 126.6, 125.9, 125.7, 125.4, 123.2 ppm; GC-MS for $C_{19}H_{13}N$, m/z = 255 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*2-(Thiophen-2-yl)quinoline (**2v**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-thiophen-yl-2-ethylamine (89 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2v** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 79 mg (75%). Data for **2v**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.75−7.66 (m, 4H), 7.50−7.43 (m, 2H), 7.14 (ddd, J = 5.2, 3.6, 1.6 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.1, 147.9, 145.2, 136.4, 129.6, 129.0, 128.4, 127.9, 127.3, 127.0, 125.9, 125.7, 117.4 ppm; GC-MS for $C_{13}H_9NS$, m/z = 211 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[27]

*2-(Benzofuran-2-yl)quinoline (**2w**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and in situ generated 1-(1-(benzofuran-2-yl)vinyl)pyrrolidine (149 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2w** was isolated by

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column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 82 mg (67%). Data for **2w**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dt, J = 8.3, 1.0 Hz, 1H), 8.11−8.06 (m, 1H), 7.90 (dt, J = 8.7, 1.2 Hz, 1H), 7.74−7.67 (m, 2H), 7.66−7.61 (m, 2H), 7.56 (d, J = 0.9 Hz, 1H), 7.50−7.45 (m, 1H), 7.36 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.27 (td, J = 7.4, 1.0 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.4, 154.9, 148.7, 148.0, 136.5, 129.8, 129.3, 128.6, 127.4, 127.4, 126.5, 125.4, 123.1, 121.6, 117.9, 111.6, 106.1 ppm; GC-MS for $C_{17}H_{11}NO$, m/z = 245 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[31]

*2-(1-Methyl-1H-pyrrol-2-yl)quinoline (**2x**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and in situ generated 1-methyl-2-(1-(pyrrolidin-1-yl)vinyl)-1*H*-pyrrole (123 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2x** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 79 mg (76%). Data for **2x**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.6, 0.9 Hz, 2H), 7.77−7.65 (m, 3H), 7.47 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 6.85−6.80 (m, 2H), 6.27 (td, J = 2.7, 1.3 Hz, 1H), 4.23 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.2, 147.6, 135.8, 132.1, 129.3, 129.0, 127.6, 127.4, 126.0, 125.4, 120.0, 112.3, 107.8, 37.6 ppm; GC-MS for $C_{14}H_{12}N_2$, m/z = 208 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[32]

*2-(Benzo[d][1,3]dioxol-5-yl)quinoline (**2y**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and in situ generated 1-(1-(benzo[*d*][1,3]dioxol-5-yl)vinyl)pyrrolidine (152 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2y** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Light-yellow solid, yield = 80 mg (64%). Data for **2y**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.11 (m, 2H), 7.79−7.74 (m, 3H), 7.71 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.65 (dd, J = 8.1, 1.8 Hz, 1H), 7.49 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.03 (s, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.5, 148.7, 148.3, 148.0, 136.6, 133.9, 129.6, 129.4, 127.3, 126.9, 126.0, 121.7, 118.5, 108.4, 107.8, 101.3 ppm; GC-MS for $C_{16}H_{11}NO_2$, m/z = 249 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[33]

*1,2,3,4-Tetrahydro-1,4-methanoacridine (**2z**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and bicyclo[2.2.1]-heptan-2-amine (78 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2z** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow liquid, yield = 85 mg (87%). Data for **2z**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.2, 1.2 Hz, 1H), 7.74−7.66 (m, 2H), 7.59 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.47−7.39 (m, 1H), 3.56−3.48 (m, 2H), 2.12−1.97 (m, 2H), 1.92 (dt, J = 9.3, 2.0 Hz, 1H), 1.71 (dt, J = 9.3, 1.5 Hz, 1H), 1.47−1.40 (m, 1H), 1.34−1.28 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 146.5, 139.9, 128.5, 127.9, 127.7, 127.5, 125.6, 125.3, 46.7, 45.3, 42.1, 27.4, 25.6 ppm; GC-MS for $C_{14}H_{13}N$, m/z = 195 (M^+); $[\alpha]_D$ = +59 (c = 0.07 g/100 mL in CH_2Cl_2). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[34]

*11H-Indeno[1,2-b]quinoline (**2aa**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 2,3-dihydro-1*H*-inden-1-amine (93 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2aa** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 97 mg (89%). Data for **2aa**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 4.7 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.83 (ddd, J = 9.6, 4.8, 3.0 Hz, 2H), 7.66 (ddd, J = 8.5, 5.2, 1.7 Hz, 1H), 7.58−7.54 (m, 1H), 7.53−7.47 (m, 1H), 7.43−7.36 (m, 2H), 4.09 (s, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.6, 147.2, 141.5, 138.6, 133.3, 128.7, 128.3, 128.0, 127.3, 127.2, 126.0, 125.4, 125.2, 121.0, 38.5 ppm; GC-MS for $C_{16}H_{11}N$, m/z = 217 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[27]

*2-Methylquinoline-3-carbonitrile (**2bb**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 3-aminobut-2-enenitrile (57 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2bb** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 62 mg (74%). Data for **2bb**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.83−7.76 (m, 2H), 7.56 (t, J = 7.6 Hz, 1H), 2.88 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.9, 148.2, 142.2, 132.6, 128.8, 127.7, 127.3, 124.6, 117.1, 106.8, 24.1 ppm; GC-MS for $C_{11}H_8N_2$, m/z = 168 (M^+); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{11}H_8N_2$ 169.0760, found 169.0758.

*(1R,3aS,3bR,5aS,13aS,13bS,15aR)-13a,15a-Dimethyl-1-((R)-6-methylheptan-2-yl)2,3,3a,3b,4,5,5a,6,13,13a,13b,14,-15,15a-tetradecahydro-1H-cyclopenta[5,6]naphtho[1,2-b]-acridine (**2cc**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (31 mg, 0.25 mmol), and in situ generated 1-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*] phenanthren-3yl)pyrrolidine (153 mg, 0.35 mmol) was stirred at 140 °C for 20 h. The product **2cc** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 65 mg (55%). Data for **2cc**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 1H), 7.78 (s, 1H), 7.67 (dd, J = 8.1, 1.4 Hz, 1H), 7.58 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.41 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 3.06 (dd, J = 18.4, 5.5 Hz, 1H), 2.96 (d, J = 16.2 Hz, 1H), 2.77 (dd, J = 18.4, 12.6 Hz, 1H), 2.56 (d, J = 16.1 Hz, 1H), 2.05 (dt, J = 12.5, 3.4 Hz, 1H), 1.83 (ddd, J = 13.0, 6.5, 3.6 Hz, 1H), 1.72 (d, J = 3.5 Hz, 2H), 1.67−1.58 (m, 3H), 1.52 (d, J = 6.7 Hz, 2H), 1.43−1.31 (m, 5H), 1.31−0.95 (m, 11H), 0.93 (d, J = 6.4 Hz, 3H), 0.87 (dd, J = 6.6, 1.8 Hz, 6H), 0.78 (s, 3H), 0.69 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.5, 146.5, 135.8, 130.2, 128.5, 128.1, 127.2, 126.8, 125.4, 56.4, 56.3, 53.5, 43.5, 42.4, 42.1, 39.9, 39.5, 37.4, 36.1, 35.8, 35.5, 35.2, 31.6, 28.7, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.3, 18.7, 12.0, 11.6 ppm; GC-MS for $C_{34}H_{49}N$, m/z = 471 (M^+); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{34}H_{49}N$ 472.3938, found 472.3936; $[\alpha]_D$ = +59 (c = 0.05 g/100 mL in CH_2Cl_2).

*(2S,4S)-3,3-Dimethyl-1,2,3,4-tetrahydro-2,4-methanoacridine (**2dd**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol),

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and in situ generated 1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)pyrrolidine (134 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2dd** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 89 mg (76%). Data for **2dd**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.5, 1.3 Hz, 1H), 7.79 (s, 1H), 7.70−7.63 (m, 1H), 7.57 (ddt, J = 9.9, 6.9, 1.6 Hz, 1H), 7.44−7.33 (m, 1H), 3.17 (t, J = 5.6 Hz, 1H), 3.08 (dd, J = 3.1, 1.6 Hz, 2H), 2.76 (dt, J = 9.9, 5.9 Hz, 1H), 2.34 (tt, J = 5.9, 2.9 Hz, 1H), 1.42 (s, 3H), 1.34 (dd, J = 10.1, 1.6 Hz, 1H), 0.67 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.1, 145.4, 133.8, 128.9, 128.3, 128.2, 127.7, 126.8, 125.3, 51.1, 39.7, 39.4, 31.1, 30.5, 25.9, 21.2 ppm; GC-MS for $C_{16}H_{17}N$, m/z = 223 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}N$ 224.1434, Found 224.1426; $[\alpha]_D$ = +23 (c = 0.08 g/100 mL in CH_2Cl_2).

*(E)-2-(2-(2,6,6-Trimethylcyclohex-1-en-1-yl)vinyl)-quinoline (**2ee**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and in situ generated (*E*)-1-(4-(2,6,6-trimethylcyclohex-1-en-1-yl)buta-1,3-dien-2-yl)pyrrolidine (172 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2ee** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 86 mg (62%). Data for **2ee**: ^{1}H NMR (400 MHz, $CDCl_3$) (ddd, J = 8.4, 6.2, 2.2 Hz, 2H), 7.73 (dt, J = 8.1, 2.1 Hz, 1H), 7.67 (ddt, J = 9.7, 7.0, 1.4 Hz, 1H), 7.58 (dd, J = 8.6, 2.4 Hz, 1H), 7.45 (ddt, J = 8.3, 6.9, 1.4 Hz, 1H), 7.31 (d, J = 16.4 Hz, 1H), 6.73 (dd, J = 16.4, 2.1 Hz, 1H), 2.08 (d, J = 6.8 Hz, 2H), 1.85 (s, 3H), 1.70−1.63 (m, 2H), 1.52 (dt, J = 8.7, 2.5 Hz, 2H), 1.14 (d, J = 2.2 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.6, 148.1, 137.0, 136.0, 133.8, 133.2, 131.6, 129.4, 129.1, 127.3, 127.1, 125.7, 118.6, 39.6, 34.2, 33.1, 28.9, 21.8, 19.1 ppm; GC-MS for $C_{20}H_{23}N$ m/z = 277 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{23}N$ 278.1903, found 278.1904.

*2-(2-(6-Methoxynaphthalen-2-yl)ethyl)quinoline (**2ff**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and in situ generated 1-(4-(6-methoxynaphthalen-2-yl)but-1-en-2-yl)-pyrrolidine (197 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2ff** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 91 mg (58%). Data for **2ff**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.85−7.78 (m, 1H), 7.81−7.66 (m, 3H), 7.64 (s, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.40 (dd, J = 8.5, 1.9 Hz, 1H), 7.31−7.24 (m, 1H), 7.19−7.12 (m, 2H), 3.94 (s, 3H), 3.42 (dd, J = 10.0, 6.4 Hz, 2H), 3.32 (dd, J = 9.1, 5.6 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.8, 157.1, 147.8, 136.6, 136.3, 133.0, 129.4, 129.0, 128.9, 128.7, 127.8, 127.5, 126.8, 126.7, 126.4, 125.8, 121.5, 118.6, 105.5, 55.2, 40.9, 35.9 ppm; GC-MS for $C_{22}H_{19}NO$, m/z = 313 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}NO$ 314.1539, found 314.1534.

*4-(4-(Quinolin-2-yl)phenyl)morpholine (**2gg**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 1-[4-(4-morpholinyl)phenyl]ethanamine (144 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2gg** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 100 mg (69%). Data for **2gg**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dt, J = 8.7, 4.6 Hz, 4H), 7.81 (dd, J = 15.9, 8.4 Hz, 2H), 7.70 (ddd, J = 8.5, 6.9, 1.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.06−6.99 (m, 2H), 3.92−3.85 (t, J = 4.8 Hz, 4H), 3.31−3.22 (t, J = 4.8 Hz, 4H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.8, 152.0, 148.2, 136.5, 130.6, 129.5, 129.3, 128.4, 127.4, 126.8, 125.7, 118.4, 115.1, 66.7, 48.6 ppm; GC-MS for $C_{19}H_{18}N_2O$, m/z = 290 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{18}N_2O$ 291.1492, found 291.1488.

*2-(2-(1H-Indol-3-yl)ethyl)quinoline (**2hh**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzaldehyde (61 mg, 0.5 mmol), and 3-(3-(pyrrolidin-1-yl)but-3-en-1-yl)-1*H*-indole (168 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2hh** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 73 mg (54%). Data for **2hh**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.13 (dd, J = 8.5, 1.2 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.79 (dd, J = 8.1, 1.4 Hz, 1H), 7.74−7.65 (m, 2H), 7.51 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.34 (dt, J = 8.1, 1.0 Hz, 1H), 7.27 (d, J = 8.3 Hz, 1H), 7.20 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.14 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.92 (dd, J = 2.3, 1.1 Hz, 1H), 3.47−3.38 (m, 2H), 3.38−3.28 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4, 147.8, 136.2, 136.1, 129.4, 128.6, 127.5, 127.4, 126.8, 125.7, 121.8, 121.6, 121.5, 119.1, 118.8, 115.5, 111.1, 39.5, 25.4 ppm; GC-MS for $C_{19}H_{16}N_2$, m/z = 272 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{16}N_2$ 273.1386, found 273.1388.

*4-Methyl-2-phenylquinoline (**3a**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 1-phenylethanamine (85 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3a** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Light-yellow oil, yield = 91 mg (85%). Data for **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (ddd, J = 12.9, 7.9, 1.6 Hz, 3H), 8.00 (dd, J = 8.3, 1.5 Hz, 1H), 7.77−7.68 (m, 2H), 7.59−7.50 (m, 3H), 7.50−7.42 (m, 1H), 2.76 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.0, 148.1, 144.8, 139.8, 130.2, 129.3, 129.2, 128.7, 127.5, 127.2, 126.0, 123.6, 119.7, 19.0 ppm; GC-MS for $C_{16}H_{13}N$, m/z = 219 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[35]

*2-(4-Methoxyphenyl)-4-methylquinoline (**3b**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 1-(4-methoxyphenyl)ethanamine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3b** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 112 mg (90%). Data for **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22−8.10 (m, 3H), 7.97−7.90 (m, 1H), 7.70 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.64 (t, J = 1.3 Hz, 1H), 7.50 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.07−7.00 (m, 2H), 3.86 (s, 3H), 2.70 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.6, 156.4, 147.9, 144.6, 132.1, 129.8, 129.2, 128.7, 126.9, 125.6, 123.5, 119.1, 114.0, 55.2, 18.9 ppm; GC-MS for $C_{17}H_{15}NO$, m/z = 249 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[35]

*4-Methyl-2-(p-tolyl)quinoline (**3c**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 1-(*p*-tolyl)ethanamine (95 mg,

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0.7 mmol) was stirred at 140 °C for 20 h. The product **3c** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 100 mg (86%). Data for **3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.5 Hz, 1H), 8.07 (dd, J = 8.3, 1.6 Hz, 2H), 7.99 (d, J = 8.3 Hz, 1H), 7.75−7.68 (m, 2H), 7.57−7.50 (m, 1H), 7.33 (d, J = 7.8 Hz, 2H), 2.76 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.9, 147.8, 144.9, 139.3, 136.7, 130.0, 129.5, 129.3, 127.4, 127.1, 125.9, 123.6, 119.6, 21.3, 19.0 ppm; GC-MS for $C_{17}H_{15}N$, m/z = 233 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[35]

*2-(4-Chlorophenyl)-4-methylquinoline (**3d**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 1-(4-chlorophenyl)ethanamine (109 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3d** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 94 mg (78%). Data for **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.4, 1.2 Hz, 1H), 8.15−8.06 (m, 2H), 7.98 (dd, J = 8.3, 1.5 Hz, 1H), 7.73 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.65 (t, J = 1.3 Hz, 1H), 7.59−7.51 (m, 1H), 7.55−7.44 (m, 2H), 2.75 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 147.9, 145.2, 138.0, 135.4, 130.2, 129.6, 128.9, 128.8, 127.3, 126.3, 123.6, 119.3, 19.0 ppm; GC-MS for $C_{16}H_{12}ClN$, m/z = 253 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[36]

*4-Methyl-2-(4-(trifluoromethyl)phenyl)quinoline (**3e**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 1-(4-(trifluoromethyl)phenyl)ethanamine (132 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3e** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 98 mg (68%). Data for **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21−8.10 (m, 3H), 7.98 (dq, J = 8.3, 0.9 Hz, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.65 (t, J = 1.2 Hz, 1H), 7.54 (ddt, J = 7.9, 6.8, 1.0 Hz, 1H), 7.25−7.15 (m, 2H), 2.75 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.0, 162.5, 155.8, 147.9, 145.1, 135.8 (d, J_{CF} = 3.3 Hz), 130.1, 129.5, 129.4, 129.3, 127.1, 126.1, 123.6, 119.3, 115.7 (d, J_{CF} = 21.2 Hz), 19.0 ppm; GC-MS for $C_{17}H_{12}F_3N$, m/z = 287 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[36]

*2-(3-Methoxyphenyl)-4-methylquinoline (**3f**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 1-(3-methoxyphenyl)ethanamine (106 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3f** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Red oil, yield = 102 mg (82%). Data for **3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.5 Hz, 1H), 8.00−7.94 (m, 1H), 7.80 (d, J = 2.1 Hz, 1H), 7.74−7.66 (m, 3H), 7.58−7.50 (m, 1H), 7.43 (t, J = 7.9 Hz, 1H), 7.03 (dd, J = 8.3, 2.6 Hz, 1H), 3.93 (s, 3H), 2.72 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 156.6, 147.8, 144.8, 141.0, 130.1, 129.6, 129.2, 127.2, 126.0, 123.5, 119.9, 119.7, 115.2, 112.5, 55.3, 18.9 ppm; GC-MS for $C_{17}H_{15}NO$, m/z = 249 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[35]

*2-(3-Methoxyphenyl)-4-phenylquinoline (**3g**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzophenone (99 mg, 0.5 mmol), and 1-(3-methoxyphenyl)ethanamine (106 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3g** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 114 mg (73%). Data for **3g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.83 (s, 1H), 7.82−7.71 (m, 3H), 7.62−7.41 (m, 7H), 7.04 (dd, J = 8.2, 2.2 Hz, 1H), 3.94 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.1, 156.6, 149.1, 148.7, 141.1, 138.3, 130.1, 129.8, 129.5, 129.5, 128.6, 128.4, 126.3, 125.8, 125.6, 120.0, 119.4, 115.4, 112.6, 55.4 ppm; GC-MS for $C_{22}H_{17}NO$, m/z = 311 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[37]

*2,4-Diphenylquinoline (**3h**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzophenone (99 mg, 0.5 mmol), and 1-phenylethanamine (85 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3h** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Light yellow oil, yield = 105 mg (75%). Data for **3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, J = 8.5, 1.4 Hz, 1H), 8.22 (dt, J = 8.1, 1.3 Hz, 2H), 7.93 (dd, J = 8.4, 1.5 Hz, 1H), 7.84 (d, J = 1.1 Hz, 1H), 7.75 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.62−7.51 (m, 6H), 7.55−7.44 (m, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.9, 149.2, 148.8, 139.6, 138.4, 130.1, 129.5, 129.5, 129.3, 128.8, 128.6, 128.4, 127.6, 126.3, 125.7, 125.6, 119.3 ppm; GC-MS for $C_{21}H_{15}N$, m/z = 281 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[35]

*6-Chloro-2,4-diphenylquinoline (**3i**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-amino-5-chlorobenzophenone (116 mg, 0.5 mmol), and 1-phenylethanamine (85 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3i** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 98 mg (62%). Data for **3i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (ddd, J = 8.9, 4.3, 1.4 Hz, 3H), 7.88 (d, J = 2.1 Hz, 1H), 7.85 (d, J = 1.2 Hz, 1H), 7.67 (dt, J = 9.0, 1.7 Hz, 1H), 7.59−7.48 (m, 8H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.0, 148.4, 147.2, 139.1, 137.7, 132.2, 131.7, 130.4, 129.6, 129.4, 128.8, 128.8, 128.7, 127.5, 126.4, 124.4, 120.0 ppm; GC-MS for $C_{21}H_{14}ClN$, m/z = 315 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[38]

*2-(4-Chlorophenyl)-6-nitro-4-phenylquinoline (**3j**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), (2-amino-5-nitrophenyl)(phenyl)methanone (121 mg, 0.5 mmol), and 1-(4-chlorophenyl)ethanamine (109 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3j** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 124 mg (69%). Data for **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 2.5 Hz, 1H), 8.51 (dd, J = 9.3, 2.5 Hz, 1H), 8.34 (d, J = 9.2 Hz, 1H), 8.22 (d, J = 8.6 Hz, 2H), 7.95 (s, 1H), 7.68−7.58 (m, 3H), 7.61−7.50 (m, 4H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.6, 151.7, 150.8, 145.5, 136.9, 136.7, 131.7, 129.5, 129.4, 129.4, 129.3, 129.2, 129.1, 124.9, 123.3, 122.9, 120.3, 110.0 ppm; GC-MS for $C_{21}H_{13}ClN_2O_2$, m/z = 360 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{13}ClN_2O_2$ 361.0738, found 361.0740.

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*3,4-Dimethyl-2-phenylquinoline (**3k**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 1-phenylpropan-1-amine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3k** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 98 mg (84%). Data for **3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 8.4, 1.3 Hz, 1H), 8.09−7.92 (m, 1H), 7.66 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.58−7.47 (m, 5H), 7.46−7.41 (m, 1H), 2.67 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4, 145.8, 142.2, 141.7, 130.0, 128.8, 128.2, 128.1, 127.8, 127.1, 127.0, 126.0, 123.2, 17.4, 14.7 ppm; GC-MS for $C_{17}H_{15}N$, m/z = 233 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[39]

*4-Methyl-2,3-diphenylquinoline (**3l**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 1,2-diphenylethanamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3l** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 93 mg (63%). Data for **3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31−8.24 (m, 1H), 8.10 (ddd, J = 8.4, 1.5, 0.7 Hz, 1H), 7.76 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.68−7.58 (m, 1H), 7.45−7.22 (m, 5H), 7.24−7.15 (m, 3H), 7.18−7.08 (m, 2H), 2.56 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.7, 146.5, 142.6, 141.0, 138.9, 133.9, 130.7, 130.0, 129.7, 129.2, 128.9, 128.0, 127.5, 127.1, 127.0, 126.5, 125.1, 124.1, 16.3 ppm; GC-MS for $C_{22}H_{17}N$, m/z = 295 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*3-Methyl-2,4-diphenylquinoline (**3m**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzophenone (99 mg, 0.5 mmol), and 1-phenylpropan-1-amine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3m** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 96 mg (65%). Data for **3m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dt, J = 8.4, 1.0 Hz, 1H), 7.70−7.61 (m, 3H), 7.59−7.48 (m, 5H), 7.47−7.40 (m, 3H), 7.36−7.31 (m, 2H), 2.18 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.8, 147.7, 146.2, 141.5, 137.7, 129.4, 129.3, 128.9, 128.6, 128.4, 128.2, 128.0, 127.8, 127.0, 126.6, 126.2, 125.9, 18.5 ppm; GC-MS for $C_{22}H_{17}N$, m/z = 295 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[40]

*2,3,4-Triphenylquinoline (**3n**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzophenone (99 mg, 0.5 mmol), and 1,2-diphenylethanamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3n** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 51 mg (40%). Data for **3n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 7.75 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.61 (dd, J = 8.5, 1.5 Hz, 1H), 7.50−7.45 (m, 1H), 7.41−7.38 (m, 2H), 7.33−7.28 (m, 3H), 7.24−7.21 (m, 3H), 7.18−7.14 (m, 2H), 7.08−6.95 (m, 3H), 6.94−6.86 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.9, 147.8, 147.1, 140.9, 138.2, 136.9, 132.9, 131.3, 130.2, 129.9, 129.5, 129.4, 128.2, 127.8, 127.7, 127.6, 127.3, 127.2, 126.6, 126.5, 126.3 ppm; GC-MS for $C_{27}H_{19}N$, m/z = 357 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[41]

*2-Isobutyl-4-methylquinoline (**3o**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 4-methylpentan-2-amine (78 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3o** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 92 mg (92%). Data for **3o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.10 (s, 1H), 2.80 (d, J = 7.4 Hz, 2H) 2.66 (m, 3H), 2.20 (dt, J = 13.6, 6.7 Hz, 1H), 0.97 (d, J = 6.7 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 147.7, 143.8, 129.3, 128.9, 126.7, 125.3, 123.5, 122.7, 48.2, 29.4, 22.5, 18.7 ppm; GC-MS for $C_{14}H_{17}N$, m/z = 199 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[42]

*4-Methyl-2-pentylquinoline (**3p**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and heptan-2-amine (81 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3p** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 69 mg (65%). Data for **3p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.5 Hz, 1H), 7.98−7.90 (m, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.54−7.45 (m, 1H), 7.14 (s, 1H), 2.92 (dd, J = 9.1, 6.8 Hz, 2H), 2.66 (s, 3H), 1.86−1.73 (m, 2H), 1.45−1.26 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.7, 147.4, 144.4, 129.1, 129.0, 126.7, 125.4, 123.5, 122.0, 39.1, 31.7, 29.8, 22.5, 18.7, 14.0 ppm; GC-MS for $C_{15}H_{19}N$, m/z = 213 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[43]

*4-Methyl-2-phenethylquinoline (**3q**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and 4-phenylbutan-2-amine (104 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3q** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 115 mg (93%). Data for **3q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 7.0 Hz, 1H), 7.71−7.62 (m, 1H), 7.53−7.45 (m, 1H), 7.32−7.23 (m, 4H), 7.21−7.15 (m, 1H), 7.07 (s, 1H), 3.27−3.23(t, J = 6.8 Hz, 2H), 3.14 (t, J = 4.1 Hz, 2H), 2.63 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4, 147.6, 144.4, 141.6, 129.2, 129.1, 128.4, 128.3, 126.8, 125.9, 125.5, 123.6, 122.2, 40.8, 35.9, 18.6 ppm; GC-MS for $C_{18}H_{17}N$, m/z = 247 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[44]

*9-Methyl-2,3-dihydro-1H-cyclopenta[b]quinoline (**3r**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and cyclopentylamine (60 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3r** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Colorless oil, yield = 71 mg (78%). Data for **3r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−7.99 (m, 1H), 7.93 (dt, J = 8.4, 2.0 Hz, 1H), 7.61 (ddd, J = 8.4, 5.2, 1.7 Hz, 1H), 7.48 (ddd, J = 8.1, 5.1, 3.6 Hz, 1H), 3.18 (td, J = 7.8, 2.5 Hz, 2H), 3.05 (td, J = 7.4, 2.7 Hz, 2H), 2.58 (d, J = 3.0 Hz, 3H), 2.20 (pd, J = 7.6, 2.3 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.7,

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147.2, 138.0, 133.8, 128.9, 127.8, 126.9, 125.1, 123.2, 34.9, 29.5, 22.8, 14.7 ppm; GC-MS for $C_{13}H_{13}N$, m/z = 183 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature values.[45]

*9-Methyl-1,2,3,4-tetrahydroacridine (**3s**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and cyclohexylamine (69 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3s** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 89 mg (90%). Data for **3s**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.5, 1.3 Hz, 1H), 7.88 (dd, J = 8.7, 3.3 Hz, 1H), 7.56 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.40 (tt, J = 8.2, 1.4 Hz, 1H), 3.08 (t, J = 6.0 Hz, 2H), 2.80 (t, J = 5.6 Hz, 2H), 2.45 (s, 3H), 1.88 (dq, J = 7.2, 2.8, 2.3 Hz, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 145.6, 141.1, 128.7, 128.5, 127.9, 126.7, 125.1, 123.1, 34.3, 26.9, 23.0, 22.6, 13.3 ppm; GC-MS for $C_{14}H_{15}N$, m/z = 197 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature values.[27]

*11-Methyl-7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoline (**3t**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminoacetophenone (68 mg, 0.5 mmol), and cycloheptylamine (79 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3t** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 90 mg (85%). Data for **3t**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.3, 1.3 Hz, 1H), 7.89 (dd, J = 8.4, 1.5 Hz, 1H), 7.61−7.52 (m, 1H), 7.43 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 3.22−3.15 (m, 2H), 2.97−2.89 (m, 2H), 2.56 (s, 3H), 1.87−1.79 (m, 2H), 1.78−1.71 (m, 2H), 1.69−1.61 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.2, 145.4, 139.0, 134.0, 129.0, 127.7, 127.0, 125.3, 123.6, 39.7, 31.6, 29.1, 27.6, 26.8, 13.9 ppm; GC-MS for $C_{15}H_{17}N$, m/z = 211 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature values.[46]

*2-Nitro-12-phenyl-6,7,8,9,10,11-hexahydrocycloocta[b]-quinoline (**3u**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), (2-amino-5-nitrophenyl)(phenyl)-methanone (121 mg, 0.5 mmol), and cyclooctylamine (89 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3u** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 125 mg (75%). Data for **3u**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, J = 9.2, 1.7 Hz, 1H), 8.15 (d, J = 1.7 Hz, 1H), 8.11 (d, J = 9.2 Hz, 1H), 7.66−7.45 (m, 3H), 7.27−7.18 (m, 2H), 3.24 (t, J = 6.1 Hz, 2H), 2.78 (t, J = 6.1 Hz, 2H), 1.99−1.90 (m, 2H), 1.55−1.42 (m, 4H), 1.40−1.29 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.8, 148.5, 148.2, 144.8, 135.8, 134.2, 130.2, 129.1, 128.7, 128.5, 126.3, 123.2, 121.8, 36.6, 31.2, 31.1, 28.2, 26.5, 25.7 ppm; GC-MS for $C_{21}H_{20}N_2O_2$, m/z = 332 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}N_2O_2$, 333.1598 Found 333.1566.

*9-Chloro-7-phenyl-5,6-dihydrobenzo[c]acridine (**3v**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-amino-5-chlorobenzophenone (116 mg, 0.5 mmol), and 1,2,3,4-tetrahydronaphthalen-2-amine (103 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3v** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 152 mg (89%). Data for **3v**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 7.6 Hz, 1H), 8.14 (d, J = 8.9 Hz, 1H), 7.61−7.50 (m, 4H), 7.48−7.42 (m, 1H), 7.41−7.35 (m, 2H), 7.33−7.28 (m, 2H), 7.27−7.22 (m, 1H), 2.86 (ddt, J = 11.8, 8.1, 4.0 Hz, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.3, 145.4, 144.6, 139.2, 136.1, 134.6, 131.6, 131.1, 129.8, 129.3, 129.3, 129.0, 128.7, 128.1, 127.9, 127.7, 127.2, 126.3, 124.7, 28.0, 26.4 ppm; GC-MS for $C_{23}H_{16}ClN$, m/z = 341 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature values.[47]

*7-Chloro-9-phenyl-1,2,3,4-tetrahydro-1,4-methanoacridine (**3w**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-amino-5-chlorobenzophenone (116 mg, 0.5 mmol), and bicyclo[2.2.1]heptan-2-amine (78 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3w** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow oil, yield = 116 mg (76%). Data for **3w**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.9, 2.3 Hz, 1H), 7.63 (d, J = 2.3 Hz, 1H), 7.59−7.46 (m, 4H), 7.42 (d, J = 7.1 Hz, 1H), 7.32 (d, J = 7.0 Hz, 1H), 3.60 (d, J = 4.3 Hz, 1H), 3.42−3.36 (m, 1H), 2.17−1.91 (m, 3H), 1.69 (dt, J = 9.4, 1.5 Hz, 1H), 1.53 (tt, J = 11.6, 2.6 Hz, 1H), 1.41−1.30 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 145.0, 138.7, 137.6, 135.3, 131.2, 130.2, 129.7, 129.4, 128.6, 128.2, 127.4, 124.7, 46.5, 45.8, 40.9, 27.3, 25.7 ppm; GC-MS for $C_{20}H_{16}ClN$, m/z = 305 (M^+); $[\alpha]_D$ = +59 (c = 0.09 g/100 mL in CH_2Cl_2). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}ClNH$ 306.1044 found 306.1013.

*6-Chloro-2-methyl-4-phenylquinoline-3-carbonitrile (**3x**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), (2-amino-5-chlorophenyl)(phenyl)methanone (116 mg, 0.5 mmol), and 3-aminobut-2-enenitrile (57 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3x** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 100 mg (72%). Data for **3x**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dt, J = 9.0, 2.5 Hz, 1H), 7.78−7.70 (m, 1H), 7.66−7.57 (m, 4H), 7.45 (dd, J = 4.3, 2.2 Hz, 2H), 2.98 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.5, 154.2, 146.3, 133.5, 133.2, 130.5, 130.1, 129.3, 129.2, 129.1, 129.0, 125.5, 116.3, 108.0, 24.5 ppm; GC-MS for $C_{17}H_{11}ClN_2$, m/z = 278 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{11}ClN_2$ 279.0684, found 279.0679.

*8-Methyl-6-phenyl-[1,3]dioxolo[4,5-g]quinoline (**3y**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 1-(6-aminobenzo[*d*][1,3]dioxol-5-yl)ethanone (90 mg, 0.5 mmol), and 1-phenylethanamine (85 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3y** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 83 mg (63%). Data for **3y**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.75−7.59 (m, 4H), 7.52 (tt, J = 6.9, 1.3 Hz, 1H), 6.94 (dd, J = 8.1, 1.4 Hz, 1H), 6.03 (s, 2H), 2.73 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.2, 148.7, 148.2, 144.8, 129.9, 129.3, 125.7, 123.5, 121.6, 119.2, 117.2, 108.3, 107.8, 101.3, 18.9 ppm; GC-MS for $C_{17}H_{13}NO_2$, m/z = 263 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature values.[48]

*5-(4-Chlorophenyl)-7-methylthieno[3,2-b]pyridine (**3z**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5

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mmol), 1-(3-aminothiophen-2-yl)ethenone (71 mg, 0.5 mmol), and 1-(4-chlorophenyl)ethanamine (109 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3z** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 100 mg (77%). Data for **3z**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−7.97 (m, 2H), 7.77 (d, J = 5.5 Hz, 1H), 7.67 (d, J = 5.5 Hz, 1H), 7.51−7.42 (m, 3H), 2.66 (d, J = 0.8 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.5, 154.3, 142.7, 137.6, 135.2, 133.0, 130.7, 129.0, 128.7, 125.5, 116.8, 110.0, 20.3 ppm; GC-MS for $C_{14}H_{10}ClNS$, m/z = 259 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{10}ClNS$ 260.0295, found 260.0293.

*4-Methyl-2-phenylquinolin-8-ol (**3aa**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 1-(2-amino-3-hydroxyphenyl)ethenone (76 mg, 0.5 mmol), and 1-phenylethanamine (85 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3aa** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 98 mg (83%). Data for **3aa**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.18−8.11 (m, 2H), 7.73 (t, J = 1.1 Hz, 1H), 7.56−7.46 (m, 3H), 7.45−7.43 (m, 2H), 7.20 (dd, J = 4.9, 3.8 Hz, 1H), 2.73 (t, J = 1.0 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.3, 152.6, 145.8, 138.7, 137.6, 129.4, 128.8, 127.4, 127.3, 127.0, 120.1, 114.0, 109.9, 19.1 ppm; GC-MS for $C_{16}H_{13}NO$, m/z = 235 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{13}NO$ 236.1070, found 236.1067.

*2-(Benzo[d][1,3]dioxol-5-yl)-4-phenylquinoline (**3bb**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (14 mg, 5 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), 2-aminobenzophenone (99 mg, 0.5 mmol), and in situ generated 1-(1-(benzo[*d*][1,3]dioxol-5-yl)vinyl)pyrrolidine (152 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **3bb** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). Yellow solid, yield = 114 mg (70%). Data for **3bb**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 1.6 Hz, 1H), 7.74 (s, 1H), 7.73−7.66 (m, 2H), 7.59−7.48 (m, 5H), 7.46 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.04 (s, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.2, 149.0, 148.8, 148.6, 148.3, 138.4, 134.0, 129.9, 129.5, 129.5, 128.5, 128.4, 126.1, 125.6, 125.6, 121.7, 118.9, 108.4, 107.9, 101.3 ppm; GC-MS for $C_{22}H_{15}NO_2$, m/z = 325 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{15}NO_2$ 326.1176, found 326.1156.

*6-Bromo-2-(4-chlorophenyl)-4-phenylquinoline (**2ii**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), (2-amino-5-bromophenyl)(phenyl)methanone (137 mg, 0.5 mmol), and 1-(4-chlorophenyl)ethanamine (109 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2ii** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 143 mg (73%). Data for **2ii**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 15.1, 8.7 Hz, 3H), 8.03 (d, J = 2.2 Hz, 1H), 7.83−7.78 (m, 2H), 7.53 (ddt, J = 20.6, 8.6, 4.6 Hz, 7H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.7, 148.5, 147.2, 137.4, 135.8, 133.1, 131.7, 129.7, 129.4, 129.0, 128.8, 128.8, 128.7, 127.7, 126.9, 120.6, 119.5 ppm; GC-MS for $C_{21}H_{13}BrClN$, m/z = 392 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[49]

*6-Bromo-4-phenyl-2-(p-tolyl)quinoline (**2jj**).* A 1,4-dioxane (2.0 mL) solution of complex **1** (9 mg, 3 mol %), **L1** (12 mg, 10 mol %), 3,3-dimethyl-1-butene (42 mg, 0.5 mmol), (2-amino-5-bromophenyl)(phenyl)methanone (137 mg, 0.5 mmol), and 1-(*p*-tolyl)ethanamine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **2jj** was isolated by column chromatography on silica gel (hexanes/EtOAc = 100:1−5:1). White solid, yield = 142 mg (76%). Data for **2jj**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−8.07 (m, 3H), 8.04 (d, J = 2.2 Hz, 1H), 7.81 (s, 1H), 7.78 (dd, J = 9.0, 2.2 Hz, 1H), 7.58−7.48 (m, 5H), 7.34 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.9, 148.1, 147.2, 139.7, 137.6, 136.1, 132.8, 131.6, 129.5, 129.3, 128.7, 128.6, 127.6, 127.3, 126.7, 120.1, 119.7, 21.3 ppm; GC-MS for $C_{22}H_{16}BrN$, m/z = 374 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[49]

*2-(Benzo[d][1,3]dioxol-5-yl)-4-chloroquinoline (**4u**).* The synthesis of quinoline *N*-oxide was conducted following the literature procedure.[15] In a 250 mL of RB flask, **2u** (249 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (5 mL) and 3-chloroperbenzoic acid (206 mg, 1.2 mmol) was added to the solution. After the reaction mixture was stirred overnight at room temperature, the product mixture was concentrated under vacuum and the resulting residue was purified by flash column chromatography (9:1 EtOAc/MeOH) to obtain the quinoline *N*-oxide. The quinoline *N*-oxide (133 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (1 mL) and the solution of DMF (2 mmol) and $(COCl)_2$ (2 mmol) was added at 0 °C, and the reaction mixture was stirred for 12 h at room temperature. The product **4u** was isolated by silica gel column chromatography (white solid, 104 mg, 70%). Data for **4u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 8.4, 1.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.89 (s, 1H), 7.80−7.69 (m, 2H), 7.66−7.55 (m, 2H), 6.95 (d, J = 8.1 Hz, 1H), 6.05 (s, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.5, 149.2, 148.8, 148.5, 143.0, 132.9, 130.6, 129.8, 127.0, 125.1, 123.9, 121.8, 118.7, 108.5, 107.8, 101.5 ppm; GC-MS for $C_{16}H_{10}ClNO_2$, m/z = 283 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*2-(Benzo[d][1,3]dioxol-5-yl)-4-methoxyquinoline (**5u**).* The compound **4u** (57 mg, 0.2 mmol) was dissolved in MeOH (2 mL), and NaOMe (0.24 mmol) was added to the solution, and the reaction mixture was heated at 140 °C for 10 h under a nitrogen atmosphere. The resulting product mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography to give graveolinine **5u** (white solid, 50 mg, 90%). Data for **5u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 8.3, 1.5 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.74−7.66 (m, 2H), 7.61 (dd, J = 8.1, 1.8 Hz, 1H), 7.50−7.44 (m, 1H), 7.09 (s, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.04 (s, 2H), 4.11 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.9, 158.0, 148.8, 148.2, 134.4, 130.1, 128.7, 125.3, 121.7, 121.6, 120.2, 108.4, 108.0, 101.4, 97.6, 55.7 ppm; GC-MS for $C_{17}H_{13}NO_3$, m/z = 279 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*4-Chloro-2-(naphthalen-2-yl)quinoline (**4y**).* The synthesis of **4y** was carried out by following the same experimental procedure used for the synthesis of **4u** (white solid, 107 mg, 74%). Data for **4y**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.32 (dd, J = 8.6, 1.9 Hz, 1H), 8.22 (dd, J = 10.7, 8.1 Hz, 2H), 8.06 (d, J = 2.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.92−7.85 (m, 1H), 7.82−7.73 (m, 1H), 7.64−7.55 (m, 1H), 7.59−7.49 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.8, 148.9, 143.0, 135.6, 133.9, 133.2, 130.5, 129.9, 128.8, 128.6, 127.6, 127.1, 126.9, 126.3, 125.2, 124.6, 123.8, 119.0

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ppm; GC-MS for $C_{19}H_{12}ClN$, m/z = 289 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

*N^1,N^1-Dimethyl-N^2-(2-(naphthalen-2-yl)quinolin-4-yl)-ethane-1,2-diamine (**5y**).* The compound **4y** (58 mg, 0.2 mmol) was dissolved in N^1,N^1-dimethylethane-1,2-diamine (1 mL), and $SnCl_4$ (0.02 mmol) was added to the solution. The reaction mixture was heated at 130 °C for 4 h under an inert atmosphere. The resulting mixture was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography to give **5y** (yellow solid, 60 mg, 88%). Data for **5y** ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 1.9 Hz, 1H), 8.29 (dd, J = 8.8, 1.8 Hz, 1H), 8.18−8.11 (m, 1H), 7.96 (d, J = 8.5 Hz, 2H), 7.91−7.81 (m, 2H), 7.67 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.56−7.48 (m, 2H), 7.44 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 6.98 (s, 1H), 6.01 (s, 1H), 3.46−3.40 (m, 2H), 2.74 (t, J = 5.9 Hz, 2H), 2.34 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.1, 150.5, 148.4, 138.1, 133.6, 133.4, 129.9, 129.3, 128.7, 128.2, 127.6, 126.8, 126.3, 126.1, 125.3, 124.4, 119.7, 118.0, 96.9, 57.0, 45.0, 40.0 ppm; GC-MS for $C_{23}H_{23}N_3$, m/z = 341 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature values.[15]

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.4c00063.

Experimental procedures, characterization data, and NMR spectra for organic products (PDF)

Accession Codes

CCDC 2308654−2308656 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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