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Nickel(0)-Catalyzed Decarbonylative Cross-Coupling of Aromatic Esters with Arylboronic Acids via Chelation Assistance

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ABSTRACT: 10-Arylbenzo[*h*]quinolines were synthesized by cross-coupling of ethyl benzo[*h*]quinoline-10-carboxylate with arylboronic acids *via* group-directed Ni(0) catalyzation. The catalytic system combining Ni(COD)$_2$ (10 mol %) with PCy$_3$ (20 mol %) and *t*-BuOK (3 equiv) was optimal for the above transformations. A series of arylboronic acids reacted with ethyl benzo[*h*]quinoline-10-carboxylates for the production of various substituted 10-phenyl[*h*]quinolines in moderate and good yields under optimized reaction conditions.
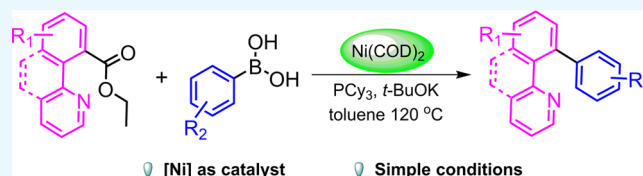
INTRODUCTION

Transition-metal-mediated cross-coupling of aryl halides and arylboronic acids, namely, the Suzuki−Miyaura reaction, has been widely applied in the construction of organic materials, pharmaceuticals, and natural products as a powerful and reliable C−C bond formation method.[1] Although the use of organic halides as electrophiles dominates for these cross-coupling reactions, in the past few decades, some other compounds have also been found to react with arylboronic acids as alternative electrophiles for the C−C bond formation.[2] For example, several advanced methods have been developed to use phenols or anilines as the electrophiles for cross-coupling with arylboronic acids.[3] The *in situ* generated intermediates of aromatic nitriles, tertiary alcohols, aromatic aldehydes, and amides have also been found to react with arylboronic acids to form C−C bonds in the presence of transition metals.[4] The transition-metal-mediated decarboxylation intermediates of aromatic acids and anhydrides were found to react with arylboronic acids to give cross-coupling products smoothly.[5] The use of these substrates other than aryl halides as electrophiles in coupling reactions has the following advantages: First, these reactions do not produce metal halide wastes that exert a strong corrosive effect on metal reactors and thus are conducive to future industrial production. Second, considering that these reactions use readily available raw materials to construct useful complex molecules through rapid transformation, production costs are considerably reduced.[6] Hence, the development of new synthetic strategies and routes that use different electrophiles for cross-coupling with arylboronic acids is a continuous pursuit in synthetic organic chemistry.

Esters are cheap and abundant in nature and are the most commonly used organic substrates. Therefore, there is a growing interest in using esters as electrophiles for coupling with arylboronic acids.[7] One such effort involves the cross-coupling of this *O*-acetylated phenol derivative with phenyl-

boronic acid to selectively oxidize the aryl C−O bond of the *O*-acetylated phenol in the presence of a metal (Scheme 1, i).[8] In

Scheme 1. Reaction of Esters with Arylboronic Acids
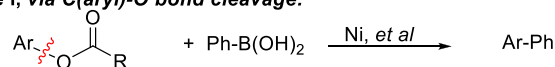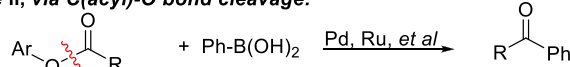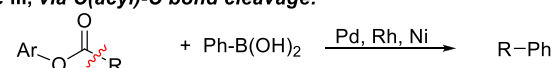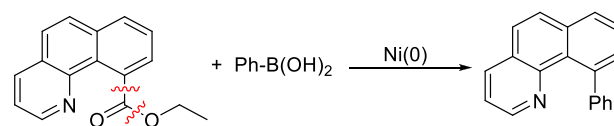
addition, some active esters, such as 4-nitrophenyl esters, benzoic acid phenyl esters, and 2-pyridyl esters, when there is a suitably positioned directing group, are used as coupling electrodes to arylboronic acids, which are converted to ketones by the activation of acyl C−O bonds (Scheme 1, ii).[9] As far as we know, esters can also form carbon−carbon bonds through

direct carbon−carbon bond activation or decarbonylation pathways, which involves the loss of the carbonyl group in the form of carbon monoxide (Scheme 1, iii).[10] Cavallo and Rueping found that ligands play an important role in the chemoselective C(acyl)−O bond *vs* C(aryl)−C bond cleavage of aromatic esters in nickel-catalyzed C(sp^2)−C(sp^3) cross-couplings with alkyl boron compounds.[11] In 2012, our group reported a chelation-assisted rhodium-catalyzed C−C bond activation of ethyl benzo[h]quinoline-10-carboxylate that provided a cross-coupling biaryl compound when reacted with organoboron compounds.[12] Although the use of a rhodium catalyst gives high yields in this reaction, there is a lack of methods that are inexpensive and with readily accessible catalysts and can be performed with high cross-coupling selectivity.[13] Herein, we report the cross-coupling of ethyl benzo[h]quinoline-10-carboxylate with arylboronic acids in the presence of a Ni(0) catalyst.

■ RESULTS AND DISCUSSION

After screening the decarbonylative cross-coupling reaction of ethyl benzo[h]quinoline-10-carboxylate (**1a**) and phenyl-boronic acid (**2a**), Ni(COD)$_2$ (10 mol %) and PCy$_3$ (20 mol %) as the catalyst in combination with t-BuOK (3.0 equiv) as the base were selected as the optimal catalytic system for the current transformation (Table 1). In the optimal catalytic system, the reaction of **1a** and **2a** in toluene at 120 °C for 20 h gave the desired decarbonylative cross-coupling biaryl product **3a** in 81% yield. Replacing phenylboronic acid with phenyl-boronic acid pinacol ester (PhBpin) and triphenylboroxine

Table 1. Optimization of the Reaction Conditions for the Cross-Coupling of Ethyl Benzo[h]quinoline-10-carboxylate with Phenylboronic Acid[a]
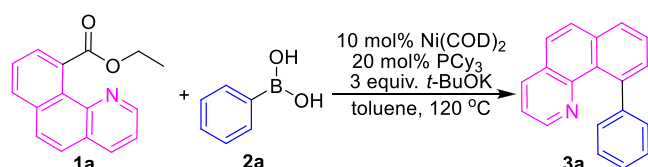


deviation from "standard conditions"		yield (%)[a]
substrate in place of **2a**	none	81
	PhBpin	72
	(PhBO)$_3$	75
precatalyst in place of Ni(COD)$_2$	NiI$_2$, NiCl$_2$, Ni(OAc)$_2$, Ni(acac)$_2$	0−10
	Ni(OAc)$_2$ + Zn (3 equiv)	15
	Ni(PPh3)$_4$	0
ligands in place of PCy$_3$	dppe, dppp, BINAP, xantphos	43−55
	IMeS·HCl, IPr·HCl	60−61
base in place of t-BuOK	K$_3$PO$_4$	55
	K$_2$CO$_3$	57
	t-BuONa	71
	Cs$_2$CO$_3$	76
reduce the usage of base	0 equiv	0
	2 equiv	73
additive CuI	10 mol %	61
	1 equiv	18
replace toluene with other solvents	acetonitrile	0
	1,4-dioxane	70

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (2.3 equiv), catalyst (10 mol %), ligand (20 mol %), and base (3.0 equiv) in 0.5 mL of toluene, 120 °C, 20 h under N$_2$; isolated yields.

(PhBO)$_3$ resulted in 72 and 75% product yields, respectively, under similar reaction conditions. The use of other nickel compounds, such as NiI$_2$, NiCl$_2$, Ni(OAc)$_2$, and Ni(acac)$_2$, as catalysts in place of Ni(COD)$_2$ provided low yields (0−10%) of the decarbonylative cross-coupling products, indicating that Ni(0) plays a catalytic role in such a reaction. However, the *in situ* generation of Ni(0) *via* the reduction of Ni(OAc)$_2$ with Zn powder showed low catalytic activity in this reaction, and the desired product was isolated in 15% yield. Notably, no decarbonylative cross-coupling product was isolated when Ni(PPh$_3$)$_4$, a frequently used Ni(0) complex, was utilized in the reaction. This phenomenon implied that the ligand plays an important role in this nickel-catalyzed reaction. Therefore, different ligands were applied in the coupling reaction. When a bisphosphine ligand, such as 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), or 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos), was introduced into the reaction mixture to substitute for PCy$_3$, the desired coupling products were obtained in moderate yields that ranged from 43 to 55%. The substitution of PCy$_3$ with 1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride (IMes·HCl) or 1,3-bis(2,6-diisopropyl phenyl)-imidazolium chloride (IPr·HCl), which could generate additional electron-donating NHC ligands in the presence of t-BuOK, did not give positive results and resulted in the isolation of the desired coupling product in 60 and 61% yields, respectively. The type and amount of the base also had a significant effect on the yield of this catalytic coupling reaction. The coupling reactions gave product **3a** in 55 and 57% yields when K$_3$PO$_4$ and K$_2$CO$_3$ were used instead of t-BuOK, respectively. When t-BuONa and Cs$_2$CO$_3$ were used as bases in this reaction, the yields of **3a** were 71 and 76%, which were lower than the yields when t-BuOK was used as the base. Reducing the amount of the base t-BuOK to 2 equiv caused the product yield to drop to 73%. The coupling reaction yielded no product when the base was completely removed from the reaction mixture. Notably, the self-coupling product of phenylboronic acid significantly increased when the amount of the base applied exceeded 3 equiv. This result was very different from that obtained for a similar reaction catalyzed by rhodium,[12] which give high product yields in the absence of a base. This difference may indicate that this coupling reaction may have a different mechanism. Futhermore, copper salt was an effective additive to promote decarbonylation in the rhodium system,[12] so we tried to add CuI as an additive and the results suggested that the yield of the product was not ideal. Different solvents also provided different coupling product yields. The reaction furnished **3a** in 70% yield in 1,4-dioxane but was inhibited completely in acetonitrile.

With the optimal catalytic conditions in hand, the effects of various substituted groups on arylbononic acids and ethyl benzo[h]quinoline-10-carboxylate on this decarbonylative cross-coupling reaction were investigated, and the results are shown in Table 2. When phenylboronic acids with a methyl group at the *p*-, *m*-, or *o*-position were applied in coupling with **1a**, the desired products **3b**, **3c**, and **3d** were obtained with 78, 70, and 50% yields, respectively. These results demonstrated that the yields of the corresponding products were decreased by slightly increasing the steric hindrance of phenylboronic acids. The yield of the desired product **3e** acquired with phenylboronic acids with the 2,5-Me substitution was 69%, which was lower than that obtained with phenylboronic acids

Table 2. Cross-Coupling of Ethyl Benzo[h]quinoline-10-carboxylates with Arylboronic Acid[a,b]
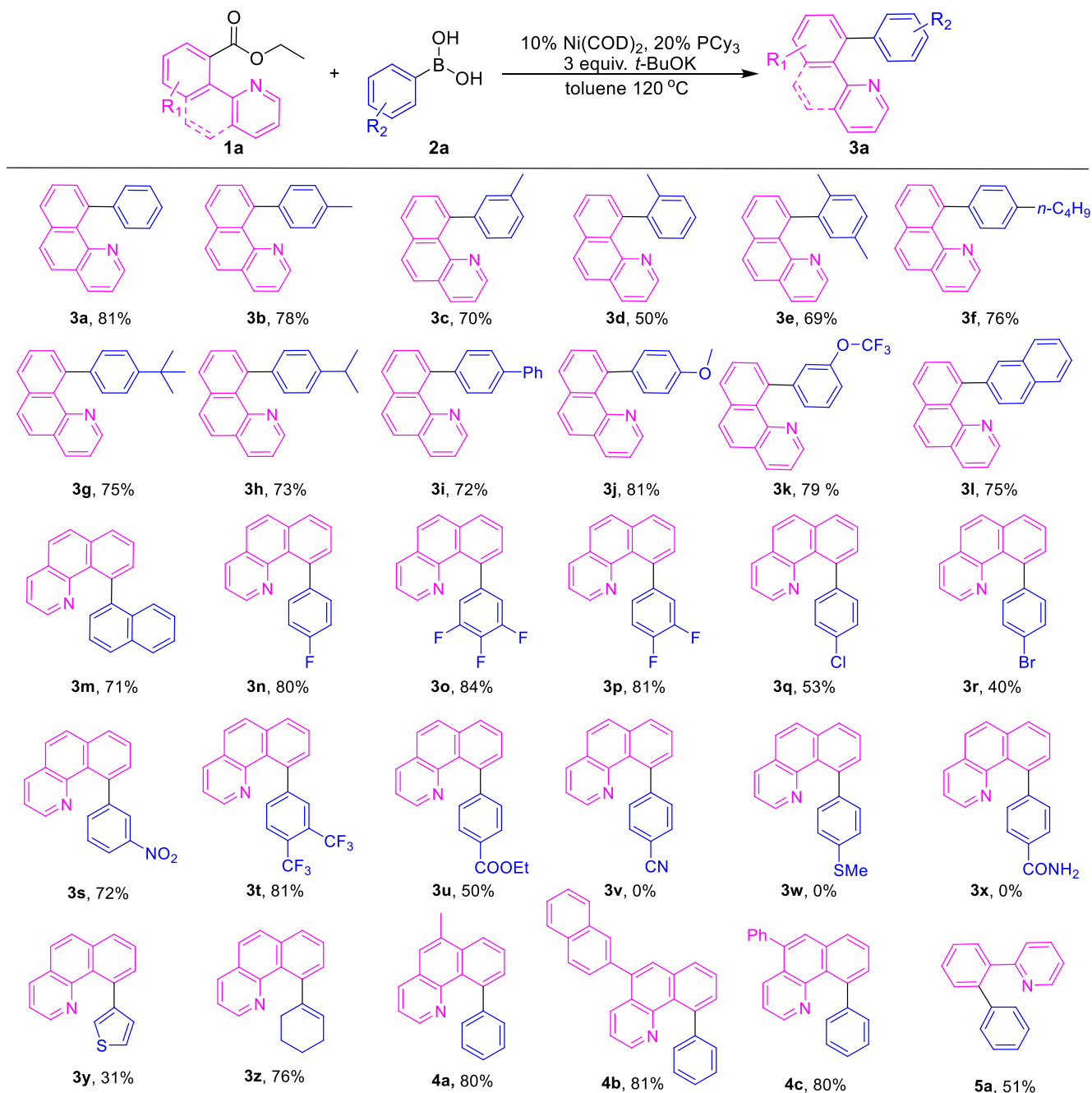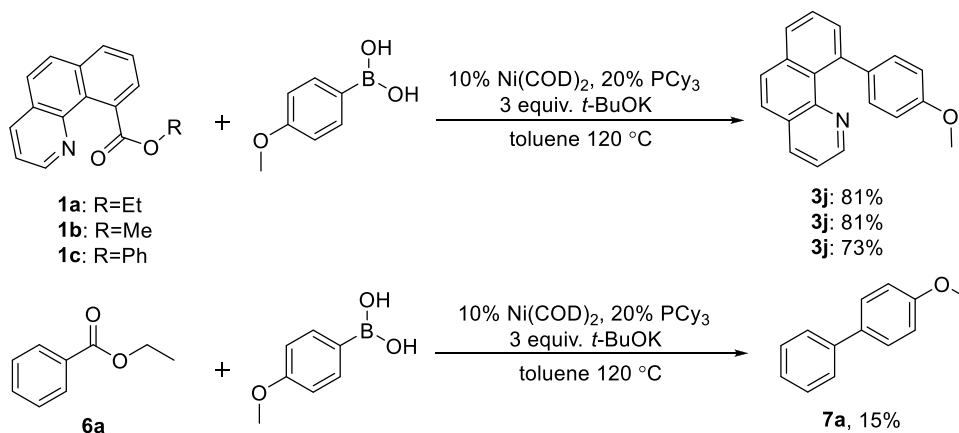

[a] Reaction conditions: **1** (0.10 mmol), **2** (0.23 mmol), Ni(COD)$_2$ (10 mol%), PCy$_3$ (20 mol%), t-BuOK(3 equiv.) in 0.5 mL toluene at 120 °C for 20 h under N$_2$; [b] Isolated yields.

[a]Reaction conditions: **1** (0.10 mmol), **2** (0.23 mmol), Ni(COD)$_2$ (10 mol %), PCy$_3$ (20 mol %), t-BuOK(3 equiv) in 0.5 mL toluene at 120 °C for 20 h under N$_2$. [b]Isolated yields.

without substitution. Steric hindrance may affect the transmetalation of phenylboronic acids to the metal center, thereby decreasing the product yield. Phenylboronic acids with n-Bu at the p-position reacted with **1a** to produce **3f** with 76% yield. **1a** could also react with phenylboronic acids containing a t-Bu and i-Pr groups to produce the corresponding products **3g** and **3h** with 75 and 73% yields. In addition, the reaction of 4-Ph-substituted phenylboronic acid with **1a** yielded product **3i** in 72% yield. These results indicated that the substitution of a bulky alkyl or aryl at the p-position of phenylboronic acid has little effect on the product yield of the reaction. The product **3j**

was obtained in 81% yield using a phenylboronic acid with an electron-donating p-MeO group. Phenylboronic acid with an electron-withdrawing −CF$_3$O group at the m-position produced the desired product **3k** with good yield (79%). These experiments indicated that the lack or enrichment of the electricity of phenylboronic acid has little effect on the coupling reaction. Other boronic acids, such as naphthalen-2-ylboronic acid and naphthalen-1-ylboronic acid, also reacted with **1a** smoothly to produce **3l** and **3m** in yields of 75 and 71%, respectively. Penylboronic acids with fluorine substitutions, such as 4-F, 3,4,5-F, or 3,4-F, produced **3n**, **3o**, and **3p**

Scheme 2. Reactivities of 1a, 1b, 1c, and 6a with (4-Methoxyphenyl) Boronic Acid

1a: R=Et
1b: R=Me
1c: R=Ph

10% Ni(COD)$_2$, 20% PCy$_3$
3 equiv. t-BuOK
toluene 120 °C

3j: 81%
3j: 81%
3j: 73%

6a

10% Ni(COD)$_2$, 20% PCy$_3$
3 equiv. t-BuOK
toluene 120 °C

7a, 15%

with 80, 84, and 81% yields, respectively. The F-substituent was shown to have little effect on the yield. However, when phenylboronic acids with 4-Cl and 4-Br substitutions were utilized in the reaction with **1a**, the corresponding coupling products **3q** and **3r** were furnished in 53 and 40% yields. The low yields may be due to the serious self-coupling side reactions of phenylboronic acid with a −Cl or −Br substituent in the presence of a Ni(0) catalyst. Phenylboronic acid with m-NO$_2$, a strong electron-withdrawing group, could also react with **1a** smoothly to give the desired product **3s** in 72% yield.

A 3,4-CF$_3$-substituted phenylboronic acid also gave the desired product **3t** in 81% yield. The two examples indicated that this decarbonylative cross-coupling reaction was compatible with strongly electron-deficient boronic acids. The 4-COOEt-substituted phenylboronic acid also produced the desired product **3u** but with moderate yield (50%). The coordination of the COOEt group may prevent the transmetalization of phenylboronic acid to the metal center, thereby decreasing the product yield. Unfortunately, when the −CN, −SMe, and −CONH$_2$-substituted phenylboronic acids were used as substrates, the desired cross-coupling products were all not observed. Heterocyclic and alkenyl-substituted phenylboronic acids were suitable candidates and gave the desired products **3y** and **3z** in 31 and 76% yields, respectively. Other ethyl benzo[h]quinoline-10-carboxylate derivatives, such as 5-methyl, 6-(naphthalen-2-yl), or 6-phenyl substitutes, also reacted with phenylboronic acid smoothly to produce **4a**, **4b**, and **4c** in yields of 80, 81, and 80%, respectively, indicating that alkyl or aryl substitutions at the benzo[h]quinoline framework has little effect on the coupling reaction. This result is consistent with the observation for the rhodium (I) catalytic system in our previous report. The reaction was also applied to ethyl 2-(2-pyridinyl)benzoate (**5**) as a coupling partner to give product **5a** in 51% yield.

As a leaving group of the ester group via the C−C bond cleavage of benzoquinoline esters, phenyl benzo[h]quinoline-10-carboxylate (**1c**) is somewhat less reactive compared to ethyl benzo[h]quinoline-10-carboxylate (**1a**) and methyl benzo[h]quinoline-10-carboxylate (**1b**). However, the reaction of ethyl benzoate (**6a**) with 4-methoxyphenylboronic acid under the same optimal reaction conditions gave only 15% of the coupling product (**7a**). It is proved that the presence of the guide group in this substrate facilitates carbon−carbon bond activation (Scheme 2).

A plausible catalytic mechanism is proposed and shown in Figure 1, which is based on the current experiments and
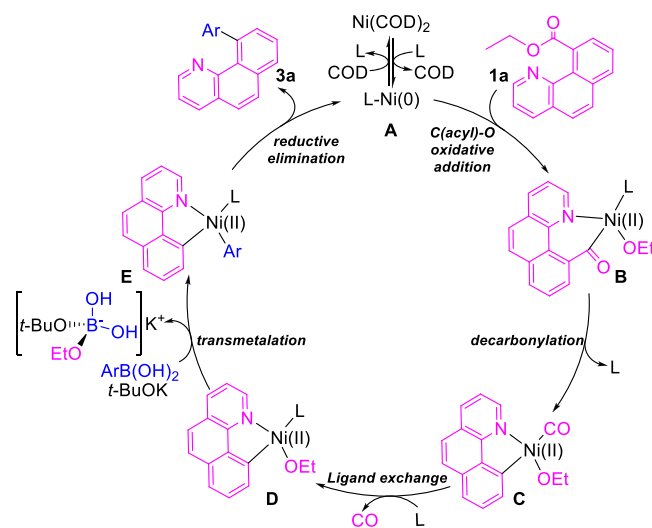
Figure 1. Plausible mechanism for the decarbonylative cross-coupling reaction of ethyl benzo[h]quinoline-10-carboxylate and arylboronic acids via chelation-assisted nickel(0)-catalyzed C(acyl)−C bond cleavage

previous reports on decarbonylative coupling of ester and boronic acids. The formation mechanism of **3** includes the following steps: First, the highly catalytically active catalyst **A** is formed through the ligand exchange of Ni(COD)$_2$, the catalytic precursor, with PCy$_3$. Then, the nitrogen of ethyl benzo[h]quinoline-10-carboxylate coordinates with the metal center of catalyst **A**. In this case, the Ni(0) metal center and the C(acyl)−O bond are brought into proximity. The following oxidative addition between the C(acyl)−O bond and the Ni(0) metal center produces the six-membered cyclic chelated Ni(II) complex **B**. Subsequently, the carbonyl group of the ester fragment in **B** migrates to the Ni(II) metal center to give the five-membered cyclic chelated Ni(II) intermediate **C**. This process is accompanied by the departure of a PCy$_3$ ligand. Next, CO is exchanged and released with the PCy$_3$ ligand to produce the intermediate **D**. The transmetalation of arylboronic acid into the Ni(II) metal center in the presence of t-BuOK yields the aryl nickel complex **E** and releases a K[B(OH)$_2$(OEt)(O-t-Bu)] complex at the same time. Finally, the reductive elimination of the aryl and the benzo[h]quinolin-10-yl group from intermediate **E** yields the desired cross-coupling product **3a**, and the regenerated intermediate **A** can further coordinate with **1a** to enter another catalytic cycle. It is

worth to note that the use of 3 equiv of the base and an excess amount of arylboronic acid are beneficial to the transmetalation of **D** into **E**, thereby providing a high yield of the cross-coupling product. This reaction is significantly different from a similar reaction catalyzed by rhodium without the use of an additional base. This difference implies that the rate-determining steps of these two catalytic reactions may be different. In the proposed reaction mechanism, the slow process from **D** to **E** coincides with the reaction that requires a large excess amount of base and arylboronic acids. PCy$_3$ may play an important role in the release of CO by re-cooperating with the Ni (II) metal center of intermediate **C**.

■ CONCLUSIONS

We have developed a new method for the synthesis of biaryl derivatives through decarbonylative cross-coupling of aromatic esters and arylboronic acids *via* chelation-assisted Ni(0)-catalyzed C(acyl)−C bond cleavage. Ni(COD)$_2$ (10 mol %) and PCy$_3$ (20 mol %) catalysts in combination with *t*-BuOK (3.0 equiv) were selected as the best catalytic system for the current conversion. Under optimal catalytic conditions, a series of arylbononic acids bearing various substituted groups reacted with ethyl benzo[*h*]quinoline-10-carboxylate derivatives to produce various 10-aryl-substituted benzo[*h*]quinolines with moderate-to-good yields. Although these reactions were sensitive to hindrance, arylboronic acids with electron-withdrawing or electron-donating groups were compatible with this reaction. The ligand was observed to play an important role in achieving high yields. A large and more electron-donating phosphine ligand, PCy$_3$, was identified to be the best ligand for this transformation. A reasonable catalytic mechanism, which included C(acyl)−O oxidation, decarbonylation, ligand exchange, transmetalization, and reductive elimination, was proposed to explain the formation of cross-coupling products. Although the yield of the nickel-catalyzed reaction is slightly lower, it is more competitive than the rhodium-catalyzed reaction because nickel catalysts are cheap and readily available. Our laboratory is currently further studying the application of this reaction in the generation of benzoquinoline derivatives with fluorescence properties.

■ EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all commercially available reagents were used as received without further purification. Toluene was dried from sodium/benzophenone under a nitrogen (N$_2$) atmosphere and distilled prior to use. All reactions were carried out under an atmosphere of N$_2$ with oven-dried glassware and anhydrous solvents. Reactions were monitored by TLC with silica gel 60 F254. Silica gel (200−300 mesh) was used for column chromatography. ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR were recorded in deuterated solvents on a 400 MHz Bruker DRX-400 spectrometer. Electrospray mass spectra (ESI-MS) of products were recorded on Bruker MiorOTOF-Q II. The starting materials were synthesized and purified according to the corresponding literature procedures, and the ^{1}H NMR and ^{13}C NMR data were consistent with the literature.[14−16]

Ethyl Benzo[h]quinoline-10-carboxylate (1a). The product was prepared according to the literature[14] as a yellow solid (86% yield). ^{1}**H NMR** (400 MHz, chloroform-*d*) δ 8.90 (dd, *J* = 4.4, 1.8 Hz, 1H), 8.17 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.97 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.74−7.65 (m, 3H),

7.51 (dd, *J* = 8.1, 4.3 Hz, 1H), 4.60 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (101 MHz, chloroform-*d*) δ 172.36, 147.73, 145.12, 135.55, 134.02, 132.55, 129.33, 127.76, 127.72, 127.45, 126.97, 126.18, 126.11, 121.99, 61.50, 14.28.

Ethyl 2-(2-Pyridinyl)benzoate (5). The product was prepared according to the literature[17] as a yellow solid (86% yield). ^{1}**H NMR** (400 MHz, chloroform-*d*) δ 8.63 (dt, *J* = 5.0, 1.2 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.74 (td, *J* = 7.7, 1.9 Hz, 1H), 7.59−7.42 (m, 4H), 7.29−7.19 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (101 MHz, chloroform-*d*) δ 168.82, 158.87, 149.00, 140.98, 136.21, 131.79, 131.09, 129.77, 128.31, 122.85, 122.02, 60.96, 13.82.

Experimental Procedure for the Ni-Catalyzed Benzo-[*h*]-quinoline-10-carboxylic Acid Ethyl Ester with Substituted Phenylboronic Acids. Substituted ethyl benzo[*h*]-quinoline-10-carboxylate (0.1 mmol), substituted phenylboronic acid (0.23 mmol), PCy$_3$ (0.02 mmol), *t*-BuOK (0.3 mmol), and Ni(COD)$_2$ (0.01 mmol) were successively added into a 10 mL sealed tube using anhydrous toluene (0.5 mL) as the solvent. The mixture was vigorously stirred at 120 °C under a nitrogen atmosphere to the end of the reaction. Organic solvents were removed in vacuo, and then the residue was purified by silica gel column chromatography to give the desired product.

10-Phenylbenzo[h]quinolone (3a). White solid, 20.5 mg (yield: 81%). ^{1}**H NMR** (400 MHz, chloroform-*d*) δ 8.45 (dd, *J* = 4.3, 2.1 Hz, 1H), 8.09 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.87 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.74−7.64 (m, 2H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.42 (ddd, *J* = 11.8, 8.9, 6.7 Hz, 5H), 7.32 (dt, *J* = 6.1, 3.2 Hz, 1H). ^{13}**C NMR** (101 MHz, chloroform-*d*) δ 146.93, 146.86, 146.48, 141.74, 135.25, 135.03, 131.55, 129.06, 128.77, 128.34, 128.01, 127.44, 127.27, 127.09, 125.99, 125.74, 121.13.

10-(p-Tolyl)benzo[h]quinolone (3b). Colorless oil, 21 mg (yield: 78%). ^{1}**H NMR** (400 MHz, chloroform-*d*) δ 8.45 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.65 (dd, *J* = 8.3, 5.8 Hz, 2H), 7.53 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.32−7.18 (m, 5H), 2.45 (s, 3H). ^{13}**C NMR** (101 MHz, chloroform-*d*) δ 146.90, 146.85 143.46, 141.73, 135.10, 135.05, 131.68, 129.09, 128.65, 128.33, 128.12, 127.81, 127.23, 127.06, 125.90, 121.04, 21.34.

10-(m-Tolyl)benzo[h]quinolone (3c). White solid, 18.8 mg (yield: 70%). ^{1}**H NMR** (400 MHz, chloroform-*d*) δ 8.49 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.10 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.94 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.75−7.66 (m, 2H), 7.59 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.38−7.29 (m, 2H), 7.26 (t, *J* = 2.0 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 3H). ^{13}**C NMR** (101 MHz, chloroform-*d*) δ 146.91, 146.31, 141.87, 136.87, 135.21, 135.05, 131.58, 129.37, 129.07, 128.35, 127.90, 127.25, 127.23, 127.07, 126.47, 126.06, 125.92, 121.10, 21.67.

10-(o-Tolyl)benzo[h]quinolone (3d). Yellow oil, 13.4 mg (yield: 50%). ^{1}**H NMR** (400 MHz, chloroform-*d*) δ 8.40 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.92 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.71−7.61 (m, 2H), 7.45 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.32−7.21 (m, 4H), 7.17 (dd, *J* = 7.0, 1.9 Hz, 1H), 1.84 (s, 3H). ^{13}**C NMR** (101 MHz, chloroform-*d*) δ 147.50, 147.06, 146.48, 141.06, 135.91, 135.10, 134.67, 130.75, 129.48, 128.76, 128.46, 127.97, 127.93, 127.28, 126.98, 125.96, 125.87, 125.15, 121.00, 20.25.

10-(2,5-Dimethylphenyl)benzo[h]quinolone (3e). White solid, 19.5 mg (yield: 69%). ^{1}**H NMR** (400 MHz, chloroform-*d*) δ 8.43 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.06 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.92 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.85 (d, *J* = 8.8 Hz,

1H), 7.71−7.64 (m, 2H), 7.46 (dd, J = 7.2, 1.4 Hz, 1H), 7.29 (dd, J = 8.0, 4.3 Hz, 1H), 7.13−7.07 (m, 2H), 7.02 (d, J = 1.7 Hz, 1H), 2.36 (s, 3H), 1.77 (s, 3H). **13C NMR** (101 MHz, chloroform-d) δ 147.50, 147.06, 146.25, 141.20, 135.06, 134.62, 134.35, 132.82, 130.87, 129.48, 128.67, 128.57, 128.47, 127.82, 127.23, 126.93, 126.54, 125.80, 120.97, 21.20, 19.72. **ESI-MS** [M + H]$^+$ calcd for $C_{21}H_{17}N$: 284.1439, found: 284.1440.

10-(4-Butylphenyl)benzo[h]quinolone (3f). White solid, 23.6 mg (yield: 76%). **1H NMR** (400 MHz, chloroform-d) δ 8.41 (dd, J = 4.3, 1.9 Hz, 1H), 8.03 (dd, J = 8.0, 1.9 Hz, 1H), 7.87 (dd, J = 7.9, 1.5 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.67−7.62 (m, 2H), 7.55 (dd, J = 7.3, 1.5 Hz, 1H), 7.30−7.24 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 2.71 (t, J = 7.7 Hz, 2H), 1.77−1.64 (m, 2H), 1.44 (q, J = 7.4 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H). **13C NMR** (101 MHz, chloroform-d) δ 146.98, 146.84, 143.65, 141.86, 140.19, 135.21, 135.07, 131.61, 129.17, 128.61, 128.36, 127.81, 127.50, 127.24, 127.08, 125.91, 121.06, 35.54, 33.82, 22.48, 14.15. **ESI-MS** [M + H]$^+$ calcd for $C_{23}H_{21}N$: 312.1752, found: 312.1756.

10-(4-(tert-Butyl)phenyl)benzo[h]quinolone (3g). White solid, 23.3 mg (yield: 75%). **1H NMR** (400 MHz, chloroform-d) δ 8.44 (dd, J = 4.3, 1.9 Hz, 1H), 8.08 (dd, J = 8.0, 1.9 Hz, 1H), 7.92 (dd, J = 7.8, 1.5 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.72−7.66 (m, 2H), 7.60 (dd, J = 7.3, 1.4 Hz, 1H), 7.45 (d, J = 8.1 Hz, 2H), 7.32 (dt, J = 8.2, 2.0 Hz, 3H), 1.46 (d, J = 1.0 Hz, 9H). **13C NMR** (101 MHz, chloroform-d) δ 148.47, 146.97, 146.90, 146.88, 143.35, 141.77, 135.21, 135.06, 131.63, 129.19, 128.38, 128.35, 127.20, 127.08, 125.91, 124.28, 121.05, 34.58, 31.62. **ESI-MS** [M + H]$^+$ calcd for $C_{23}H_{21}N$: 312.1752, found: 312.1750.

10-(4-Isopropylphenyl)benzo[h]quinolone (3h). White solid, 21.4 mg (yield: 73%). **1H NMR** (400 MHz, chloroform-d) δ 8.40 (dd, J = 4.3, 1.9 Hz, 1H), 7.98 (dd, J = 8.0, 1.9 Hz, 1H), 7.86−7.75 (m, 2H), 7.64−7.51 (m, 3H), 7.30−7.20 (m, 5H), 3.21−2.71 (m, 1H), 1.34 (d, J = 7.0 Hz, 6H). **13C NMR** (101 MHz, chloroform-d) δ 147.03, 146.93, 146.24, 143.83, 141.90, 135.25, 135.13, 131.71, 129.23, 128.75, 128.41, 127.87, 127.27, 127.13, 125.95, 125.50, 121.09, 34.00, 24.33.

10-([1,1′-Biphenyl]-4-yl)benzo[h]quinolone (3i). White solid, 23.8 mg (yield: 72%). **1H NMR** (400 MHz, chloroform-d) δ 8.45 (dd, J = 4.3, 1.9 Hz, 1H), 8.10 (dd, J = 8.0, 1.9 Hz, 1H), 7.95 (dd, J = 7.9, 1.5 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.77−7.64 (m, 6H), 7.60 (dd, J = 7.2, 1.5 Hz, 1H), 7.51−7.42 (m, 4H), 7.39−7.31 (m, 2H). **13C NMR** (101 MHz, chloroform-d) δ 146.89, 146.83, 145.56, 141.44, 141.30, 138.36, 135.25, 135.06, 131.52, 129.22, 129.06, 128.75, 128.32, 128.04, 127.26, 127.10, 127.06, 126.95, 126.08, 125.98, 121.14.

10-(4-Methoxyphenyl)benzo[h]quinolone (3j). White solid, 23.1 mg (yield: 81%). **1H NMR** (400 MHz, chloroform-d) δ 8.46 (dd, J = 4.3, 1.9 Hz, 1H), 8.04 (dd, J = 8.0, 1.9 Hz, 1H), 7.87 (dd, J = 8.0, 1.5 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.68−7.60 (m, 2H), 7.53 (dd, J = 7.3, 1.5 Hz, 1H), 7.29 (dd, J = 8.3, 4.8 Hz, 3H), 7.02−6.90 (m, 2H), 3.88 (s, 3H). **13C NMR** (101 MHz, chloroform-d) δ 157.98, 147.03, 146.92, 141.41, 138.96, 135.26, 135.13, 131.76, 129.85, 129.17, 128.37, 127.81, 127.25, 127.09, 125.93, 121.07, 112.86, 55.34.

10-(3-(Trifluoromethoxy)phenyl)benzo[h]quinolone (3k). Yellow solid, 26.8 mg (yield: 79%). **1H NMR** (400 MHz, chloroform-d) δ 8.41 (dd, J = 4.3, 1.8 Hz, 1H), 8.08 (dd, J = 8.0, 1.9 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.68 (t, J = 8.6 Hz, 2H), 7.52 (dd, J = 7.3, 1.4 Hz, 1H),

7.42 (t, J = 8.1 Hz, 1H), 7.32 (dd, J = 7.5, 4.9 Hz, 2H), 7.21 (d, J = 7.7 Hz, 2H). **19F NMR** (376 MHz, chloroform-d) δ −57.57. **13C NMR** (101 MHz, chloroform-d) δ 148.55, 148.31, 147.00, 146.44, 139.96, 135.31, 134.98, 131.21, 128.86, 128.76, 128.54, 128.21, 127.29, 127.07, 126.85, 126.16, 122.20, 121.97, 121.28, 119.42 (q, J = 254.7 Hz), 118.36.

10-(Naphthalen-2-yl)benzo[h]quinolone (3l). White solid, 22.9 mg (yield: 75%). **1H NMR** (400 MHz, chloroform-d) δ 8.33 (dd, J = 4.3, 1.9 Hz, 1H), 8.10 (dd, J = 8.1, 1.9 Hz, 1H), 8.00−7.86 (m, 5H), 7.78 (d, J = 8.5 Hz, 1H), 7.75−7.70 (m, 2H), 7.65 (dd, J = 7.3, 1.5 Hz, 1H), 7.48 (ddd, J = 23.5, 7.3, 2.5 Hz, 3H), 7.30 (dd, J = 8.0, 4.3 Hz, 1H). **13C NMR** (101 MHz, chloroform-d) δ 146.97, 146.72, 144.53, 141.51, 135.22, 135.07, 133.82, 132.20, 131.98, 129.49, 129.09, 128.36, 128.19, 128.13, 127.64, 127.27, 127.24, 126.01, 125.71, 125.57, 125.43, 125.20, 121.14. **ESI-MS** [M + H]$^+$ calcd for $C_{23}H_{15}N$: 306.1283, found: 306.1284.

10-(Naphthalen-1-yl)benzo[h]quinolone (3m). White solid, 21.6 mg (yield: 71%). **1H NMR** (400 MHz, chloroform-d) δ 8.07−7.98 (m, 3H), 7.91 (q, J = 8.2 Hz, 3H), 7.80−7.69 (m, 2H), 7.64−7.51 (m, 2H), 7.41−7.33 (m, 2H), 7.22 (d, J = 8.6 Hz, 1H), 7.16−7.04 (m, 2H). **13C NMR** (101 MHz, chloroform-d) δ 147.24, 146.48, 144.97, 139.61, 134.96, 134.69, 133.24, 133.08, 131.69, 130.34, 128.36, 128.31, 127.92, 127.29, 127.12, 126.43, 126.22, 126.08, 125.58, 125.10, 125.02, 124.64, 120.85.

10-(4-Fluorophenyl)benzo[h]quinolone (3n). White solid, 21.8 mg (yield: 80%). **1H NMR** (400 MHz, chloroform-d) δ 8.46 (dd, J = 4.4, 1.9 Hz, 1H), 8.10 (dd, J = 8.0, 1.9 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.69 (dd, J = 10.9, 8.2 Hz, 2H), 7.53 (d, J = 7.3 Hz, 1H), 7.33 (ddd, J = 13.5, 8.2, 4.9 Hz, 3H), 7.10 (t, J = 8.7 Hz, 2H). **19F NMR** (376 MHz, chloroform-d) δ −118.10. **13C NMR** (101 MHz, chloroform-d) 161.59 (d, J = 244.42 Hz), 146.89, 146.76, 142.26 (d, J = 4.0 Hz), 140.67, 135.32, 135.04, 131.52, 130.17 (d, J = 8.0 Hz), 129.06, 128.32, 128.18, 127.29, 127.05, 126.04, 121.17, 114.14 (d, J = 21.2 Hz).

10-(3,4,5-Trifluorophenyl)benzo[h]quinolone (3o). White solid, 25.9 mg (yield: 84%). **1H NMR** (400 MHz, chloroform-d) δ 8.51 (dd, J = 4.3, 1.8 Hz, 1H), 8.12 (dd, J = 8.0, 1.9 Hz, 1H), 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.75−7.59 (m, 2H), 7.48 (dd, J = 7.2, 1.4 Hz, 1H), 7.38 (dd, J = 8.0, 4.3 Hz, 1H), 6.94 (dd, J = 8.6, 6.6 Hz, 2H). **19F NMR** (376 MHz, chloroform-d) δ −137.30 (d, J = 20.5 Hz), −165.78 (t, J = 20.7 Hz). **13C NMR** (151 MHz, chloroform-d) δ 151.49 (dd, J = 10.6, 4.5 Hz), 149.85 (dd, J = 10.6, 4.5 Hz), 147.23, 146.26, 142.82−142.09 (m), 139.26 (t, J = 15.5 Hz), 138.59, 137.61 (t, J = 15.5 Hz), 135.52, 135.02, 130.95, 128.98, 128.79, 128.23, 127.46, 127.09, 126.39, 121.51, 112.93 (dd, J = 16.6, 3.0 Hz).

10-(3,4-Difluorophenyl)benzo[h]quinolone (3p). White solid, 23.5 mg (yield: 81%). **1H NMR** (400 MHz, chloroform-d) δ 8.48 (dd, J = 4.3, 1.9 Hz, 1H), 8.11 (dd, J = 8.0, 1.9 Hz, 1H), 7.95 (dd, J = 8.0, 1.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.75−7.62 (m, 2H), 7.50 (dd, J = 7.3, 1.4 Hz, 1H), 7.36 (dd, J = 8.1, 4.3 Hz, 1H), 7.21−7.10 (m, 2H), 7.04 (dddd, J = 8.3, 4.4, 2.1, 1.4 Hz, 1H). **19F NMR** (376 MHz, chloroform-d) δ −140.45 (d, J = 21.7 Hz), −143.07 (d, J = 21.7 Hz). **13C NMR** (101 MHz, chloroform-d) δ 149.7 (dd, J = 245.4 Hz, 12.8 Hz), 148.1 (dd, J = 243.6 Hz, 12.8 Hz), 147.03, 146.45, 143.22 (d, J = 10.8 Hz), 139.45, 135.39, 134.97, 131.25, 128.87, 128.56, 128.24, 127.33, 127.03, 126.18, 124.50 (dd, J =

6.0 Hz, 3.5 Hz), 121.32, 117.85 (d, J = 17.2 Hz), 116.03 (d, J = 17.1 Hz).

10-(4-Chlorophenyl)benzo[h]quinolone (3q). White solid, 15.3 mg (yield: 53%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.46 (dd, J = 4.3, 1.8 Hz, 1H), 8.09 (dd, J = 8.0, 1.9 Hz, 1H), 7.93 (dd, J = 7.9, 1.4 Hz, 1H), 7.85 (d, J = 8.7 Hz, 1H), 7.72–7.64 (m, 2H), 7.53–7.46 (m, 3H), 7.35–7.32 (m, 1H), 7.26–7.19 (m, 2H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 146.66, 146.30, 145.10, 140.05, 135.07, 134.71, 131.09, 131.02, 130.23, 130.15, 129.84, 128.55, 128.05, 127.99, 127.22, 126.99, 126.81, 125.82, 120.97, 119.40.

10-(4-Bromophenyl)benzo[h]quinolone (3r). Colorless oil, 13.3 mg (yield: 40%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.46 (dd, J = 4.3, 1.9 Hz, 1H), 8.10 (dd, J = 8.0, 1.9 Hz, 1H), 7.93 (dd, J = 7.9, 1.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.72–7.64 (m, 2H), 7.50 (td, J = 6.8, 1.7 Hz, 3H), 7.34 (dd, J = 8.0, 4.3 Hz, 1H), 7.26–7.21 (m, 3H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 146.94, 146.58, 145.37, 140.33, 135.36, 134.99, 131.31, 130.50, 130.43, 128.83, 128.33, 128.27, 127.27, 127.09, 126.10, 121.25, 119.68.

10-(3-Nitrophenyl)benzo[h]quinolone (3s). White solid, 21.6 mg (yield: 72%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.36 (dd, J = 4.3, 1.9 Hz, 1H), 8.23 (ddq, J = 5.0, 2.4, 1.2 Hz, 2H), 8.12 (dd, J = 8.0, 1.9 Hz, 1H), 8.00 (dd, J = 8.0, 1.4 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.76–7.72 (m, 2H), 7.68 (dt, J = 7.6, 1.3 Hz, 1H), 7.57–7.50 (m, 2H), 7.35 (dd, J = 8.0, 4.3 Hz, 1H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 147.96, 147.73, 146.95, 146.23, 138.95, 135.54, 135.10, 135.01, 131.22, 129.01, 128.72, 128.25, 128.02, 127.38, 127.16, 126.32, 123.98, 121.45, 120.83.

10-(3,4-Bis(trifluoromethyl)phenyl)benzo[h]quinolone (3t). White solid, 31.6 mg (yield: 81%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.36 (dd, J = 4.3, 1.9 Hz, 1H), 8.12 (dd, J = 8.0, 1.9 Hz, 1H), 8.01 (dd, J = 8.0, 1.4 Hz, 1H), 7.91–7.85 (m, 2H), 7.83 (s, 2H), 7.77–7.70 (m, 2H), 7.52 (dd, J = 7.2, 1.4 Hz, 1H), 7.36 (dd, J = 8.0, 4.3 Hz, 1H). **¹⁹F NMR** (376 MHz, chloroform-*d*) δ −62.59. **¹³C NMR** (151 MHz, chloroform-*d*) δ 148.14, 146.97, 146.11, 138.47, 135.61, 135.11, 131.31, 130.30 (q, J = 32.7 Hz), 129.40, 129.36, 128.70, 128.30, 127.43, 127.26, 126.46, 123.93 (q, J = 272.8 Hz), 121.68, 119.69–119.49 (m).

Ethyl 4-(benzo[h]quinolin-10-yl)benzoate (3u). White solid, 16.3 mg (yield: 50%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.38 (dd, J = 4.3, 1.9 Hz, 1H), 8.12–8.05 (m, 4H), 7.93 (dd, J = 7.9, 1.4 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.71–7.65 (m, 2H), 7.49 (dd, J = 7.2, 1.4 Hz, 1H), 7.43–7.38 (m, 2H), 7.30 (dd, J = 8.0, 4.3 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 167.18, 151.54, 146.92, 146.46, 140.63, 135.29, 134.94, 131.03, 130.19, 128.85, 128.80, 128.75, 128.45, 128.22, 127.75, 127.28, 127.22, 127.07, 126.12, 121.26, 60.80, 14.48.

10-(Thiophen-3-yl)benzo[h]quinolone (3y). White solid, 8.1 mg (yield: 31%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.60–8.51 (m, 1H), 8.13–8.05 (m, 1H), 7.94–7.89 (m, 1H), 7.84 (dd, J = 8.8, 1.7 Hz, 1H), 7.73–7.59 (m, 3H), 7.40–7.33 (m, 1H), 7.30–7.22 (m, 2H), 7.04 (d, J = 4.9 Hz, 1H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 147.20, 146.86, 146.50, 136.25, 135.26, 135.00, 131.75, 130.72, 129.44, 128.32, 128.28, 127.21, 127.18, 125.94, 122.74, 121.20, 119.72.

10-(Cyclohex-1-en-1-yl)benzo[h]quinoline (3z). Colorless oil, 20.4 mg (yield: 76%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.99 (dd, J = 4.3, 1.9 Hz, 1H), 8.10 (dd, J = 8.1, 1.9 Hz, 1H), 7.80 (dd, J = 9.6, 7.7 Hz, 2H), 7.61 (dd, J = 16.4, 8.4 Hz, 2H),

7.54–7.35 (m, 2H), 5.63 (t, J = 3.7 Hz, 1H), 2.58 (d, J = 14.8 Hz, 1H), 2.40–2.21 (m, 2H), 1.89 (dd, J = 79.1, 45.4 Hz, 5H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 147.70, 146.93, 145.26, 144.25, 135.26, 134.85, 129.98, 129.01, 128.63, 127.55, 127.46, 127.20, 125.55, 120.86, 120.29.

6-Methyl-10-phenylbenzo[h]quinolone (4a). White solid, 21.5 mg (yield: 80%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.33 (dd, J = 4.3, 1.9 Hz, 1H), 8.11–8.04 (m, 1H), 7.97 (dd, J = 8.0, 1.9 Hz, 1H), 7.76–7.69 (m, 1H), 7.59–7.51 (m, 2H), 7.45–7.29 (m, 7H), 7.28–7.21 (m, 1H), 2.82–2.79 (m, 3H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 146.91, 146.31, 146.06, 142.07, 134.86, 134.36, 133.68, 131.22, 129.11, 128.69, 128.63, 127.43, 127.09, 126.96, 125.89, 125.54, 123.84, 121.15, 20.62.

5-(Naphthalen-2-yl)-10-phenylbenzo[h]quinolone (4b). White solid, 30.8 mg (yield: 81%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.41 (dd, J = 4.2, 1.8 Hz, 1H), 8.15 (dd, J = 8.3, 1.9 Hz, 1H), 8.02–7.87 (m, 6H), 7.69 (t, J = 7.6 Hz, 1H), 7.63 (dd, J = 8.4, 1.7 Hz, 1H), 7.55 (td, J = 6.7, 2.4 Hz, 3H), 7.44–7.36 (m, 4H), 7.22 (dd, J = 8.1, 4.4 Hz, 1H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 147.11, 146.66, 146.55, 141.75, 137.93, 137.04, 134.48, 133.66, 133.50, 132.80, 131.57, 128.84, 128.74, 128.70, 128.16, 128.13, 128.09, 128.02, 127.86, 127.46, 127.43, 126.58, 126.55, 126.36, 125.70, 120.95.

5,10-Diphenylbenzo[h]quinolone (4c). White solid, 26.5 mg (yield: 80%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.41 (dd, J = 4.2, 1.8 Hz, 1H), 8.14 (dd, J = 8.3, 1.8 Hz, 1H), 7.92 (dd, J = 7.9, 1.4 Hz, 1H), 7.82 (s, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.58–7.46 (m, 6H), 7.44–7.34 (m, 5H), 7.26 (d, J = 6.0 Hz, 1H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 147.02, 146.57, 146.52, 141.66, 139.49, 137.96, 134.40, 133.57, 131.48, 130.01, 128.68, 128.59, 128.53, 128.37, 128.02, 127.71, 127.42, 127.36, 126.40, 125.65, 120.88.

2-([1,1′-Biphenyl]-2-yl)pyridine (5a). Yellow oil, 11.8 mg (yield: 51%). **¹H NMR** (400 MHz, chloroform-*d*) δ 8.65–8.60 (m, 1H), 7.70 (dd, J = 5.7, 3.3 Hz, 1H), 7.46 (dq, J = 7.8, 3.6 Hz, 3H), 7.38 (td, J = 7.7, 1.8 Hz, 1H), 7.26–7.20 (m, 3H), 7.16 (dd, J = 6.7, 2.9 Hz, 2H), 7.10 (dd, J = 7.4, 4.9 Hz, 1H), 6.88 (d, J = 7.9 Hz, 1H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 159.27, 149.44, 141.36, 140.63, 135.22, 130.52, 130.50, 129.73, 128.55, 128.08, 127.67, 126.72, 125.44, 121.37.

4-Methoxy-1,1′-biphenyl (7a). White solid, 2.8 mg (yield: 15%). **¹H NMR** (400 MHz, chloroform-*d*) δ 7.57–7.50 (m, 4H), 7.41 (t, J = 7.7 Hz, 2H), 7.33–7.27 (m, 1H), 7.00–6.95 (m, 2H), 3.85 (s, 3H). **¹³C NMR** (101 MHz, chloroform-*d*) δ 159.15, 140.85, 133.79, 128.75, 128.19, 126.77, 126.69, 114.21, 55.37.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

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NMR spectra for compounds and complexes synthesized (PDF)

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Notes

The authors declare no competing financial interest.

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