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Efficient Approach To Construct Unsymmetrical Biaryls through Oxidative Coupling Reactions of Aromatic Primary Alcohols and Arylboronic Acids with a Rhodium Catalyst

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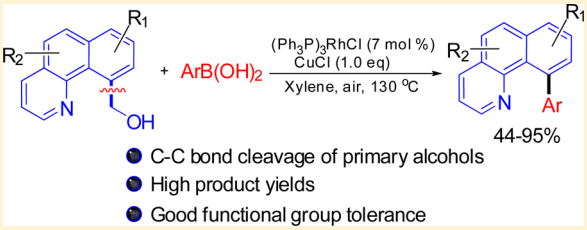
Supporting Information

ABSTRACT: Unsymmetrical biaryls were synthesized by oxidative coupling reactions between aromatic primary alcohols and arylboronic acids through the C−C bond cleavage of the primary alcohols chelated with a rhodium catalyst. The desired unsymmetrical biaryl products were obtained in good to excellent yields under the optimized reaction conditions. A wide variety of functionalities are compatible with the reaction under the optimized conditions. This new coupling strategy provides a favorable method to construct valuable biaryl compounds from aromatic primary alcohols which are cheap, environmentally friendly, and easily accessible substrates.



INTRODUCTION

Biaryl compounds have always drawn the attention of synthetic chemists due to their wide range of pharmaceutical, material, and biological applications.[1] Transition-metal-catalyzed cross-coupling reactions are powerful and reliable methods for C−C bond formation, especially for the synthesis of unsymmetrical biaryls.[2,3] The Suzuki−Miyaura reaction is one of the more widely used cross-coupling reactions.[3m,4] However, traditional coupling reactions have some drawbacks associated with the use of organohalides and organometallic reagents.

In the last two decades, scientists have been developing more atom economical and greener coupling reactions. For example, direct arylation reactions using C−H bond activation by transition-metal catalysts have been developed, and impressive progress has been made in this area.[5,6] The direct arylation method does not require prefunctionalization of the reactants, which offers an attractive alternative to conventional cross-coupling reactions.

In comparison to synthetic methods based on C−H bond activation, the synthesis of complex molecules via C−C bond activation using nontraditional retrosynthetic disconnections can have higher efficiencies.[7−9] Furthermore, coupling reactions based on C−C bond activation often use commercially available, cheap, nontoxic, and environmentally friendly substrates, such as aldehydes, ketones, esters, and alcohols as the coupling counterparts. This has greatly enriched the diversity of coupling reactions and has provided chemists with alternative coupling methods for the construction of biaryl compounds.

However, C−C bonds are not easily activated, because they are kinetically inert and thermodynamically stable. Therefore, C−C bonds often have to be activated by forming stable metallacyclic intermediates via ring-opening reactions of strained three- or four-membered rings.[9m−o,10] Directing a metal to a particular C−C bond using a chelating group is a method to cleave unstrained carbon−carbon bonds.[11,12] Recently, catalytic selective C−C bond cleavage has been used to form stable organometallic intermediates by using sterically congested tertiary alcohols. For example, Miura and co-workers successfully coupled tertiary alcohols with aryl halides[11a−c] and with internal alkynes[12b] using C−C activation strategies. Yorimitsu and Oshima's group have explored C−C bond cleavage using tertiary alcohols with aryl halides,[11d−g] aldehydes,[12c,d] and Boc-protected allyl alcohols.[12e]

In comparison, secondary alcohols for C−C bond cleavage generally are not thermodynamically favorable. However, secondary alcohols have been employed in C−C bond activation reactions.[9l,13,14] Chiba et al. reported the Pd(II)-catalyzed ring expansion of cyclic 2-azido alcohols which involved unprecedented C−C bond cleavages and C−N bond formations.[13] Wang and Kang demonstrated allylic esterification of secondary homoallyl alcohols with acids using palladium-catalyzed selective C−C bond cleavage.[9l] Shi and co-workers reported several novel examples of coupling reactions which used rhodium-catalyzed C−C bond cleavage of secondary alcohols.[14]

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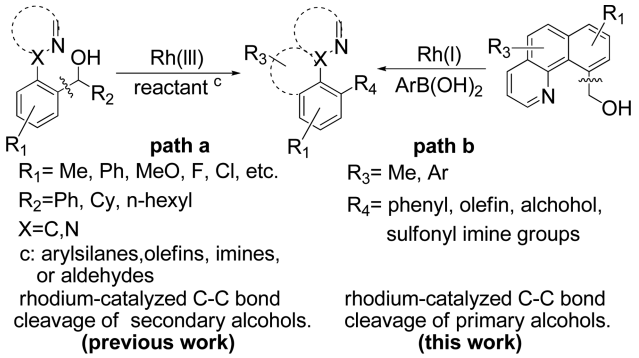
Directing a rhodium metal close to a particular C−C bond by chelation with a N group to generate a thermodynamically stable five-membered rhodacyclic intermediate is the key to successful C−C bond cleavage in secondary alcohols (Scheme 1a). However, when this method was applied to primary alcohols, the desired coupling products were only obtained in very low yields.[14d] Thus, the efficient cleavage of a C−C bond in a primary alcohol remains a challenge.

Scheme 1. Rhodium-Catalyzed Coupling Reaction of Alcohols through C−C Bond Cleavage: (a) Secondary Alcohols; (b) Primary Alcohols

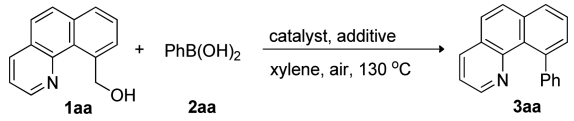


Our group has reported efficient rhodium-catalyzed coupling reactions for quinoline and arylboronic acid C−C[9e] or C−O[15] bond cleavages. Decarbonylation coupling reactions of ethyl benzo[*h*]quinoline-10-carboxylate and arylboronic acids through chelate-assisted sp^2 C−COOEt bond activation have been achieved.[9e] The DFT calculations of this bond activation process indicated that a lower energy and more stable rhodacyclic intermediate was generated by the rhodium-catalyzed C−C bond cleavage of the benzoquinoline reactants with the assistance of a N-containing directing group. From this result, we envisioned that (benzo[*h*]quinolin-10-yl)methanol could be applied to study rhodium-catalyzed C−C bond activation, since the generation of a more stable rhodacyclic intermediate might facilitate C−C bond cleavage by avoiding the subtraction of the primary alcohol α-H. Thus, herein the reaction of (benzo[*h*]quinolin-10-yl)methanols, primary alcohols, with arylboronic acids in the presence of metal catalysts was investigated for C−C bond activation (Scheme 1b).

RESULTS AND DISCUSSION

To achieve these reactions, (benzo[*h*]quinolin-10-yl)methanol (**1aa**) and phenylboronic acid (**2aa**) were initially used as the cross -coupling partners to optimize the reaction conditions in the presence of different transition-metal catalysts. The results are shown in Table 1. Several Pd and Ir complexes completely failed to catalyze the transformation under various reaction conditions (entries 1−5). However, when $(PPh_3)_3RhCl$ was used as the catalyst at 130 °C in xylene for 15 h, 10-phenylbenzo[*h*]quinoline (**3aa**) was obtained in 45% yield (entry 6). The use of an additive with $(PPh_3)_3RhCl$ significantly improved the reaction yield (i.e., the efficiency). Using CuCl as an additive gave **3aa** in 90% yield (entry 7), and CuI gave **3aa** in 82% yield (entry 8). However, the reaction yield did not significantly improve using $CuCl_2$ or $Cu(OAc)_2$ as an additive (entries 9 and 10). Notably, the cross-coupling reaction did not proceed at all when CuCl was used without $(PPh_3)_3RhCl$ (entry 11). These results show that $(PPh_3)_3RhCl$ together with CuCl play an important role in achieving this transformation. Increasing the reaction time to 20 h did not improve the reaction yield when $(PPh_3)_3RhCl$ and CuCl were both used at 130 °C (entry 12). However, when the reaction time was shortened to 12 h, the yield of **3aa** decreased to 85% (entry 13). Several other solvents, such as tolune, NMP, DCE, and CH_3CN, were tested at different temperatures with $(PPh_3)_3RhCl$ as the catalyst and CuCl as the additive (entires 14−17). None of these solvents gave results better than those with xylene.

Table 1. Optimization of Reaction Conditions for the Cross-Coupling Reaction of (Benzo[*h*]quinolin-10-yl)methanol (a Primary Alcohol) and Phenylboronic Acid[a]



entry	catalyst	additive[b]	solvent	time (h)	yield (%)[e]
1	$Pd(OAc)_2$		xylene	15	0
2	$Pd(dba)_2$		xylene	15	0
3	$Pd(PPh_3)_4$		xylene	15	0
4	$lrCl_3{\cdot}3H_2O$		xylene	15	0
5	lrCp*Cl		xylene	15	0
6	$(PPh_3)_3RhCl$		xylene	15	45
7	$(PPh_3)_3RhCl$	CuCl	xylene	15	90
8	$(PPh_3)_3RhCl$	CuI	xylene	15	82
9	$(PPh_3)_3RhCl$	$CuCl_2$	xylene	15	67
10	$(PPh_3)_3RhCl$	$Cu(OAc)_2$	xylene	15	50
11		CuCl	xylene	15	0
12	$(PPh_3)_3RhCl$	CuCl	xylene	20	89
13	$(PPh_3)_3RhCl$	CuCl	xylene	12	85
14	$(PPh3)_3RhCl$	CuCl	tolune	15	78
15	$(PPh_3)_3RhCl$	CuCl	NMP	15	0
16[c]	$(PPh_3)_3RhCl$	CuCl	DCE	15	0
17[c]	$(PPh_3)_3RhCl$	CuCl	CH_3CN	15	0
18	$Rh_2(COD)_2Cl_2$		xylene	15	23
19[d]	$Rh_2(COD)_2Cl_2$	PPh_3	xylene	15	35
20	$RhCl_3{\cdot}3H_2O$		xylene	15	trace
21	RhCp*Cl		xylene	15	trace
22	$[Ru(COD)Cl_2]_n$		xylene	15	trace
23	$RuCl_3{\cdot}nH_2O$		xylene	15	0
24	$NiCl_2(dppe)$		xylene	15	0

[a]Reaction conditions unless specified otherwise: **1aa** (0.1 mmol), **2aa** (0.2 mmol), catalyst (7 mol %) in 1 mL of xylene in air at 130 °C. [b]Additive (0.1 mmol). [c]Reaction temperature: 90 °C. [d]Additive (0.01 mmol). [e]Yields were determined by ^1H NMR using trimethylphenylsilane as the internal standard.

When the catalyst $(PPh_3)_3RhCl$ was replaced by $Rh_2(COD)_2Cl_2$, the cross-coupling reaction proceeded slowly (15 h) to give the desired **3aa** in low yield (23%; Table 1, entry 18). Adding the additive PPh_3 did not significantly improve the product yield (entry 19). $RhCl_3{\cdot}3H_2O$ and RhCp*Cl were also tested as catalysts, but both gave very low (<5%) yields (entries 20 and 21). Finally, Ru and Ni complexes were tested as the catalyst under similar reaction conditions, but again no **3aa** was obtained (entries 22−24). On the basis of these results, the optimized catalytic system for this transformation is 7 mol % of $(PPh_3)_3RhCl$ with 1 equiv of CuCl in xylene at 130 °C.

Next the optimized reaction conditions were used to investigate the reaction of (benzo[*h*]quinolin-10-yl)methanol

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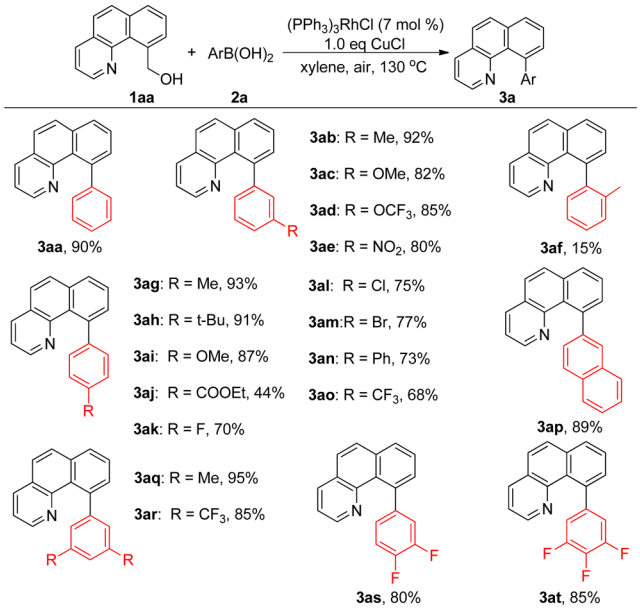
(**1aa**) with various arylboronic acids bearing electron-donating or electron-withdrawing groups. The results are shown in Scheme 2. When **1aa** was reacted with phenylboronic acid, the

Scheme 2. Arylative Coupling Reaction of (Benzo[*h*]quinolin-10-yl)methanol and Various Arylboronic Acids[a]



[a]Reaction conditions: **1aa** (0.1 mmol), **2a** (0.2 mmol), $Rh(PPh_3)_3Cl$ (7 mol %), CuCl (0.1 mmol) in 1 mL of xylene in air at 130 °C for 15 h. Yields were determined by ^1H NMR using trimethylphenylsilane as the internal standard.

desired product **3aa** was obtained in 90% yield (Table 1, entry 7). Meta-substituted phenylboronic acids, including −Me, −OMe, $-OCF_3$, and $-NO_2$, were well-tolerated and afforded the corresponding products **3ab**−**ae** in moderate to good yields (80−92% yield). The phenylboronic acid with a methyl group had the highest yield (92% of **3ab**). However, the coupling reaction between **1aa** and phenylboronic acid containing a methyl group at the ortho position produced a yield of **3af** of only 15%, indicating that the reaction is very sensitive to steric hindrance in the arylboronic acid.

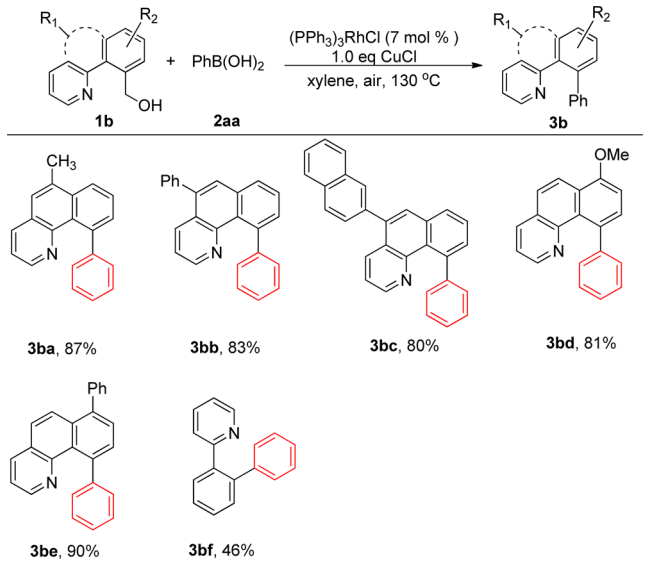
Next, various para-substituted phenylboronic acids were subjected to the coupling reaction. Both 4-methyl- and 4-*tert*-butylphenylboronic acids exhibited good reactivities, giving **3ag**, **ah** in 93% and 91% yields, respectively. The reaction of **1aa** with a phenylboronic acid bearing a methoxy group proceeded smoothly to give **3ai** in 87% yield. However, phenylboronic acid with a −COOEt substituent gave the coupling product **3aj** in low yield (44%): The ester group may act as a directing group to induce C−H activation, which would significantly reduce the yield of the main reaction.

Not surprisingly, when (benzo[*h*]quinolin-10-yl)methanol (**1aa**) was reacted with arylboronic acids bearing −F, −Cl, or −Br groups under the standard reaction conditions, the corresponding products **3ak**−**am** were obtained in 70−77% yields. The halide substituents on the substrates survived these coupling reactions, and thus this offers possibilities for additional functionalization reactions.[2b,16] In addition, the coupling reactions of **1aa** with phenylboronic acids containing other groups, such as −Ph or $-CF_3$ on the phenylboronic acid aryl rings, afforded the desired products **3an**, **ao** in 73% and 68% yields, respectively.

(Naphthalen-2-yl)boronic acid also exhibited good reactivity under the standard conditions to give **3ap** in 89% yield. Notably, (benzo[*h*]quinolin-10-yl)methanol (**1a**) reacted with arylboronic acid bearing methyl groups at the two meta positions to give **3aq** in 95% yield. Di- and trisubstituted −F and $-CF_3$ also gave the corresponding products **3ar**−**at** in 80−85% yields.

To gain further insight into the scope of the reaction, various aromatic primary alcohols were also surveyed (Scheme 3). A

Scheme 3. Arylative Coupling Reactions of Various Primary Alcohols and Boronic Acid[a]



[a]Reaction conditions: **1b** (0,1 mmol), **2aa** (0.2 mmol), $Rh(PPh_3)_3Cl$ (7 mol %), CuCl (0.1 mmol) in 1 mL of xylene in air at 130 °C for 15 h. Yields were determined by ^1H NMR using trimethylphenylsilane as the internal standard.

substrate with a methyl substituent at the 6-position of the benzo[*h*]quinoline ring worked well in this catalytic system, giving the desired product **3ba** in 87% yield. Moreover, a −Ph substituent at the 5-position also did not affect the reaction with phenylboronic acid; the corresponding coupling product **3bb** was obtained in 83% yield. However, the reaction of (5-(naphthalen-2-yl)benzo[*h*]quinolin-10-yl)methanol and phenylboronic acid under the standard conditions afforded the product **3bc** in a slightly lower yield of 80%. Reactions between phenylboronic acid and (7-methoxybenzo[*h*]quinolin-10-yl)-methanol with an electron-donating −OMe group at the 7-position on the benzo[*h*]quinoline ring and (7-phenylbenzo-[*h*]quinolin-10-yl)methanol with a −Ph group at the 7-position proceeded smoothly to give the products **3bd**, **be** in 81% and 90% yields, respectively. These results show that substitutions on the benzo[*h*]quinoline ring have little effect on this reaction.

Finally (2-(pyridin-2-yl)phenyl)methanol was subjected to the coupling reaction under the standard conditions. The corresponding product **3bf** was obtained in a yield of only 46%. This indicates that the benzo[*h*]quinoline ring can generate a stable rhodacyclic intermediate which facilitates the C−C bond cleavage during the coupling reaction.

Initially, we theorized that this reaction proceeded directly through a C−C bond cleavage mechanism in which the

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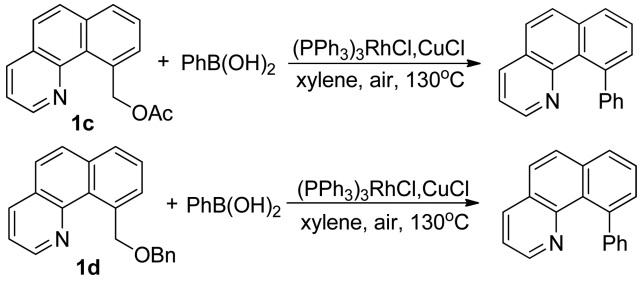
rhodium metal center was directed close to the α C−C bond of the primary alcohol via coordination with the alcohol N atom. The C−C bond cleavage would then occur through the oxidative addition of rhodium to the C−C bond. If this hypothesis were true, the breakage of the C−C bond would not be directly related to the hydroxyl group. In order to prove this, the hydroxyl group on **1aa** was replaced with an acetyl or benzyl group to give (benzo[*h*]quinolin-10-yl)methyl acetate (**1c**) and 10-(phenoxymethyl)benzo[*h*]quinoline (**1d**) respectively. However, mixtures of **1c**, **d** with phenylboronic acid did not give the desired product **3aa** under the standard reaction conditions (Scheme 4). These results indicate that a free

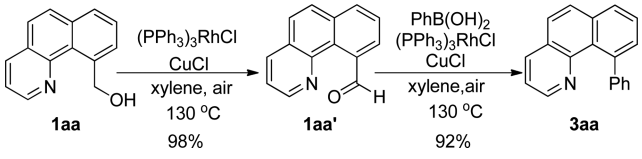
Scheme 4. Rhodium-Catalyzed Reactions of (Benzo[*h*]quinolin-10-yl)methyl Acetate and 10-(Phenoxymethyl)benzo[*h*]quinoline with Phenylboronic Acid



hydroxyl group is crucial for the cross-coupling reaction. This suggests that the cross-coupling does not proceed directly through a C−C bond cleavage but rather that the reaction proceeds via another reaction mechanism.

To further explore the reaction mechanism, **1aa** was mixed with $(PPh_3)_3RhCl$ (7 mol %) and CuCl (1 equiv) in air under the standard reaction conditions in the absence of phenylboronic acid. The reaction was stopped after 3 h. The major product was isolated from the reaction mixture and was identified as benzo[*h*]quinoline-10-carbaldehyde (Scheme 5).

Scheme 5. Rhodium-Catalyzed Reaction of (Benzo[*h*]quinolin-10-yl)methanol with Phenylboronic Acid To Obtain 10-Phenylbenzo[*h*]quinoline by Intermediate Benzo[*h*]quinoline-10-carbaldehyde



This suggests that the oxidation of the primary alcohol to an aldehyde may be the key step in this cross-coupling reaction. Next, the isolated benzo[*h*]quinoline-10-carbaldehyde was mixed with phenylboronic acid in the presence of $(PPh_3)_3RhCl$ and CuCl in air under the standard reaction conditions. This produced **3aa** as the only product in high yield (Scheme 5).

On the basis of the above findings and previous reports,[9e,u] a plausible mechanism is proposed in Figure 1. First, $(PPh_3)_3RhCl$ dehydrogenates **1aa** to **1aa′** in air.[17] Subsequently, **1aa′** interacts with $(PPh_3)_3RhCl$ with the help of CuCl, known to cleave phosphines,[9e,18] to give the five-membered rhodacyclic intermediate **A**.[9e] This occurs when the rhodium coordinates with the N atom, bringing the Rh metal

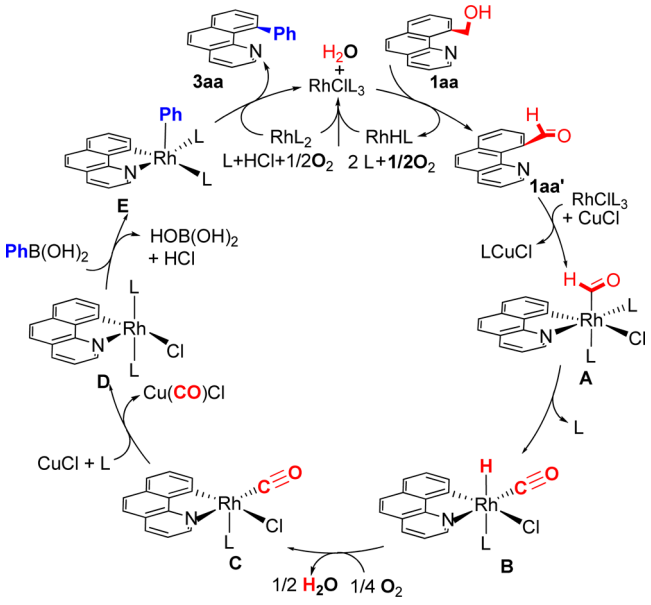


Figure 1. Proposed mechanism for the reaction of primary alcohols and arylboronic acids catalyzed by $(PPh_3)_3RhCl$.

center close to the α C−C bond of the primary alcohol. The oxidative addition of rhodium to that C−C bond causes it to break and **A** is formed. The migration of the aldehyde H to the Rh(III) metal center then produces intermediate **B**. The H coordinated to the metal center is then oxidized to H_2O,[19] which gives intermediate **C**. The CO ligand in **C** is then eliminated with the assistant of CuCl to give intermediate **D**.[9e] The subsequent reductive elimination of **E** affords the desired product and a rhodium(0) complex. Finally, the rhodium(0) complex is oxidized to $(PPh_3)_3RhCl$ in the presence of HCl and O_2, and it then re-enters another catalytic cycle.

CONCLUSION

In summary, direct arylated coupling reactions between primary alcohols and arylboronic acids can be performed through C−C bond cleavage with the assistance of an N-containing directing group in the presence of $(PPh_3)_3RhCl$ and CuCl. Various functionalities are tolerated under the standard reaction conditions, and the reaction proceeds with high efficiency. This catalytic system may also be applicable to other coupling reactions. Further work on the applications of this reaction for building aromatic compounds with biological activities is currently underway in our laboratory.

EXPERIMENTAL SECTION

General Information. The starting materials were synthesized and purified according to the literature procedures.[20−23] Other chemicals and reagents were obtained from commercial sources. All reactions were monitored by analytical thin-layer chromatography on 0.20 mm Yantai Huagong silica gel plates and spots were detected by UV absorption. Silica gel (200−300 mesh) (from Yantai Huagong Chemical Co. Ltd.) was used for flash chromatography.

NMR spectra were obtained on a 400 MHz spectrometer with $CDCl_3$ as solvent. The chemical shifts are reported in ppm relative to $CDCl_3$ (δ 7.26) for ^1H NMR and relative to the central $CDCl_3$ resonance (δ 77.0) for ^{13}C NMR. For ^{19}F NMR, (trifluoromethyl)-benzene was used as an external standard. Coupling constants (J) are quoted in Hz for ^1H. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Conversions were obtained by ^1H NMR analysis of the

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sample. NMR data of known compounds are in agreement with literature values. Infrared spectra were recorded on an FT-IR spectrophotometer. Elemental analyses were performed by the Elemental Analysis Section of Tianjin University.

(Benzo[*h*]quinolin-10-yl)methanol (1aa). The product was prepared according to the literature.[20,21] Yellow solid (yield 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 4.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.74−7.67 (m, 3H), 7.52 (dd, J = 4.4 Hz, 8.0 Hz, 1H), δ 4.60 (q, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 146.3, 139.5, 136.7, 135.3, 130.2, 129.6, 129.0, 128.8, 127.9, 127.6, 125.1, 121.0, 66.6; IR (KBr) ν 3467, 2923, 1630, 1447, 1383, 1199, 1025, 752, 698 cm^{-1}. Anal. Found (calcd) for $C_{14}H_{11}NO$: C, 80.31 (80.36); H, 5.32 (5.30); N, 6.71 (6.69).

(6-Methylbenzo[*h*]quinolin-10-yl)methanol (1ba). The product was prepared according to the literature.[20,21] Yellow solid (yield 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J = 2.0 Hz, 1H), 8.16 (d, J = 5.2 Hz, 1H), 8.07 (dd, J = 1.6 Hz, 4.8 Hz, 1H), 7.70 (d, J = 4.8 Hz, 2H), 7.53−7.52 (m, 2H), 5.20 (s, 2H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 146.1, 140.0, 136.0, 135.4, 134.8, 130.4, 130.0, 128.0, 127.7, 125.4, 124.8, 121.3, 67.0, 29.7; IR (KBr) ν 3424, 2925, 1723, 1425, 1383, 1263, 1026, 797, 732 cm^{-1}. Anal. Found (calcd) for $C_{15}H_{13}NO$: C, 80.65 (80.69); H, 5.91 (5.87); N, 6.29 (6.27).

(5-Phenylbenzo[*h*]quinolin-10-yl)methanol (1bb). The product was prepared according to the literature.[20−23] Yellow solid (yield 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06−9.03 (m, 1H), 8.37−8.33 (m, 1H), 7.92 (d, J = 4.8 Hz, 1H), 7.77−7.63 (m, 2H), 7.55−7.41 (m, 6H), 7.17−7.13 (m, 1H), 5.28−5.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 141.2, 139.2, 137.2, 135.3, 135.2, 130.5, 130.2, 130.0, 129.8, 129.1, 128.6, 128.5, 128.4, 127.7, 127.4, 127.0, 121.3, 121.1, 66.9; IR (KBr) ν 3323, 3055, 2925, 1923, 1725, 1493, 1265, 1175, 1032, 756, 702 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{15}NO$: C, 84.14 (84.19); H, 5.32 (5.30); N, 4.89 (4.91).

(5-(Naphthalen-2-yl)benzo[*h*]quinolin-10-yl)methanol (1bc). The product was prepared according to the literature.[20−23] Yellow solid (yield 58%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05−9.04 (m, 1H), 8.40−8.38 (m, 1H), 8.02−7.92 (m, 6H), 7.74−7.68 (m, 2H), 7.64−7.52 (m, 4H), 5.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.0, 139.8, 137.4, 136.6, 135.4, 135.0, 133.4, 132.8, 130.6, 129.8, 129.5, 129.1, 128.9, 128.5, 128.11, 128.06, 128.0, 127.8, 127.4, 126.6, 126.5, 121.1, 66.9; IR (KBr) ν 3320, 2926, 2780, 1923, 1723, 1522, 1195, 1042, 763, 709 cm^{-1}. Anal. Found (calcd) for $C_{24}H_{17}NO$: C, 85.88 (85.94); H, 5.13 (5.11); N, 4.18 (4.18).

(7-Methoxybenzo[*h*]quinolin-10-yl)methanol (1bd). The product was prepared according to the literature.[20,21] Yellow solid (yield 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (dd, J = 1.6 Hz, 4.0 Hz, 1H), 8.40 (d, J = 9.2 Hz, 1H), 8.25 (dd, J = 1.6 Hz, 6.4 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.57−7.54 (m, 1H), 7.05−7.00 (m, 1H), 5.14 (d, J = 7.6 Hz, 2H), 4.03 (S, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 147.7, 146.4, 136.8, 131.8, 130.8, 130.7, 128.0, 126.5, 124.5, 122.5, 121.3, 107.0, 66.6, 55.8; IR (KBr) ν 3415, 2928, 1734, 1427, 1396, 1241, 1023, 765, 713 cm^{-1}. Anal. Found (calcd) for $C_{15}H_{13}NO_2$: C, 75.34 (75.30); H, 5.46 (5.48); N, 5.85 (5.85).

(7-Phenylbenzo[*h*]quinolin-10-yl)methanol (1be). The product was prepared according to the literature.[20,21] Yellow solid (yield 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, J = 4.4 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 9.2 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H),7.65−7.61 (m, 2H), 7.52−7.46 (m, 6H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 146.8, 141.2, 140.9, 139.2, 136.8, 133.5, 130.4, 130.2, 130.1, 129.4, 128.4, 127.6, 127.5, 127.1, 125.1, 121.5, 67.1; IR (KBr) ν 3326, 2923, 2860, 1726, 1576, 1518, 1497, 1182, 1033, 948, 743, 694 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{15}NO$: C, 84.16 (84.19); H, 5.33 (5.30); N, 4.89 (4.91)

(2-(Pyridin-2-yl)phenyl)methanol (1bf). The product was prepared according to the literature.[21] Yellow solid (yield 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 2.4 Hz, 1H), 7.85−7.83 (m, 1H), 7.62 (d, J = 5.2 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.53−7.48 (m, 1H), 7.42 (d, J = 2.4 Hz, 2H), 7.41−7.32 (m, 1H), 4.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 148.0, 140.3, 139.8, 137.5, 131.1, 130.0, 129.3, 128.1, 123.8, 122.2, 64.6; IR (KBr) ν 3282, 2923, 2860, 1726, 1576, 1518, 1497, 1182, 1033, 948, 743, 694 cm^{-1}. Anal. Found (calcd) for $C_{12}H_{11}NO$: C, 77.83 (77.81); H, 5.98 (5.99); N, 7.58 (7.56).

(Benzo[*h*]quinolin-10-yl)methyl Acetate (1c). The product was prepared according to the literature.[20,21] Yellow solid (yield 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, J = 3.6 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 7.91−7.82 (m, 3H), 7.71−7.68 (m, 2H), 7.51−7.48 (m, 1H), 6.38 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 147.8, 147.5, 135.7, 135.3, 135.0, 128.9, 128.5, 128.3, 127.5, 127.3, 126.4, 125.7, 120.9, 68.0, 21.3.

10-(Benzyloxymethyl)benzo[*h*]quinoline (1d). The product was prepared according to the literature.[20,21] Yellow solid (yield 53%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03−9.01 (m, 1H), 8.29 (d, J = 7.6 Hz, 1H), 8.17−8.15 (m, 1H), 7.90−7.83 (m, 2H), 7.78−7.74 (m, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 7.2 Hz, 2H), 7.49−7.33 (m, 4H), 5.92 (s, 2H), 4.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 147.2, 139.2, 139.1, 135.2, 134.9, 128.7, 128.6, 128.3, 127.7, 127.6, 127.54, 127.48, 127.4, 125.7, 125.3, 120.6, 73.8, 72.9.

Benzo[*h*]quinoline-10-carbaldehyde (1aa′). (Benzo[*h*]-quinoline-10-yl)methanol (20.9 mg, 0.1 mmol), $(PPh_3)_3RhCl$ (6.5 mg, 0.007 mmol), and CuCl (9.9 mg, 0.1 mmol) were added to 1 mL of xylene. Then the mixture was stirred at 130 °C for 7 h in air, and the product was purified by column chromatography to provide a pale yellow solid (20.3 mg, yield 98%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.26 (s, 1H), 9.02−9.01 (m, 1H), 8.24 (dd, J = 0.8 Hz, 5.2 Hz, 1H), 8.07 (d, J = 5.2 Hz, 1H), 7.93 (d, J = 4.8 Hz, 1H), 7.88 (d, J = 6.0 Hz, 1H), 7.78−7.76 (m, 2H), 7.57−7.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.7, 148.6, 145.9, 138.0, 135.8, 134.1, 131.6, 129.8, 127.9, 127.8, 127.6, 127.3, 126.1, 121.9. IR (KBr) ν 3449, 2925, 2854, 1637, 1384, 1121, 836, 710 cm^{-1}. Anal. Found (calcd) for $C_{14}H_9NO$: C, 81.10 (81.14); H, 4.41 (4.38); N, 6.75 (6.76).

Experimental Procedure for Rhodium-Catalyzed Direct Arylation with Organoboron Compounds via Primary Alcohols. In an oven-dried screw-top vial were placed the primary alchohol (0.1 mmol), substituted phenylboronic acid (0.2 mmol), copper(I) chloride (9.9 mg, 0.1 mmol), $Rh(PPh_3)_3Cl$ (6.5 mg, 0.007 mmol), and xylene (1 mL) in an air atmosphere. The mixture was vigorously stirred at 130 °C 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.

The compounds **3aa−ag,ai−at,ba−bf** are known, and the ^{1}H NMR and the ^{13}C NMR spectra of these compounds are in agreement with previous reports.[9e,24]

*10-Phenylbenzo[h]quinoline (**3aa**).* Pale yellow solid (23.0 mg, yield 90%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (dd, J = 4.4 Hz, 1.6 Hz, 1H), 8.09 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.71−7.67 (m, 2H), 7.55 (d, J = 7.2 Hz, 1H), 7.40−7.33 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.8, 146.4, 141.8, 135.1, 135.0, 131.4, 129.0, 128.7, 128.2, 127.9, 127.3, 127.2, 127.0, 125.9, 125.6, 121.0. IR (KBr) ν 3051, 1584, 1511, 1441, 1420, 816, 757, 701, 621 cm^{-1}. Anal. Found (calcd) for $C_{19}H_{13}N$: C, 89.32 (89.38); H, 5.14 (5.13); N, 5.51 (5.49).

*10-m-Tolylbenzo[h]quinoline (**3ab**).* Pale yellow solid (24.8 mg, yield 92%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.45 (dd, J = 4.0, 1.2 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.70−7.66 (m, 2H), 7.55 (d, J = 7.2 Hz, 1H), 7.32−7.28 (m, 3H), 7.21−7.16 (m, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.9, 146.3, 141.9, 139.5, 135.1, 131.5, 129.3, 128.8, 128.3, 128.2, 127.8, 127.1, 127.0, 126.4, 126.0, 125.9, 121.0, 21.6; IR (KBr) ν 3030, 2942, 1555, 1367, 1258, 1022, 846, 767, 687 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{15}N$: C, 89.13 (89.19); H, 5.63 (5.61); N, 5.23 (5.20).

*10-(3-Methoxyphenyl)benzo[h]quinoline (**3ac**).* Pale yellow solid (23.4 mg, yield 82%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 8.09 (dd, J = 8.0 Hz, 1.2 Hz,1H), 7.93 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.71−7.66 (m, 2H), 7.57 (d, J = 7.2 Hz, 1H), 7.36−7.30 (m, 2H), 6.97−6.91 (m, 3H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.0, 147.0, 146.9, 141.4, 138.9, 135.2, 135.1, 131.7, 129.8, 129.2, 128.3, 127.7, 127.2, 127.0, 125.9, 121.0, 112.8,

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55.3; IR (KBr) ν 3044, 2923, 1564, 1224, 1036, 829, 793, 725, 608 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{15}NO$: C, 84.17 (84.19); H, 5.27 (5.30); N, 4.92 (4.91).

*10-(3-(Trifluoromethoxy)phenyl)benzo[h]quinoline (**3ad**).* Yellow solid (28.8 mg, yield 85%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 4.4 Hz, 1.6 Hz, 1H), 8.10 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.73−7.68 (m, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.36−7.32 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.6, 148.3, 147.0, 146.5, 140.0, 135.2, 135.0, 131.2, 128.9, 128.7, 128.5, 128.2, 127.3, 127.0, 126.9, 126.1, 122.1, 122.0, 121.2, 119.4 (q, J_{C-F} = 254.7 Hz), 118.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −57.6 (s, 3F); IR (KBr) ν 3045, 2921, 1578, 1418, 1221, 1155, 913, 832, 695, 613 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{12}F_3NO$: C, 70.83 (70.79); H, 3.58 (3.56); N, 4.10 (4.13).

*10-(3-Nitrophenyl)benzo[h]quinoline (**3ae**).* Yellow solid (24.1 mg, yield 80%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.37−8.24 (m, 3H), 8.12 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.75−7.68 (m, 3H), 7.56−7.51 (m, 2H),7.34 (dd, J = 7.6 Hz, 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.0, 147.8, 147.0, 146.2, 139.0, 135.4, 135.1, 135.0, 131.1, 129.0, 128.7, 128.2, 127.9, 127.4, 127.1, 126.3, 123.9, 121.4, 120.8; IR (KBr) ν 3047, 1526, 1345, 835, 805, 743, 676, 615 cm^{-1}. Anal. Found (calcd) for $C_{19}H_{12}N_2O_2$: C, 76.04 (75.99); H, 4.05 (4.03); N, 9.31 (9.33).

*10-o-Tolylbenzo[h]quinoline (**3af**).* Yellow viscous oil (4.04 mg, yield 15%): ^1H NMR ($CDCl_3$, 400 MHz) δ 8.41 (dd, J = 4.0, 1.6 Hz, 1H), 8.08 (dd, J = 8.0, 1.6 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.72−7.68 (m, 2H), 7.47 (d, J = 7.2 Hz, 1H), 7.32−7.25 (m, 4H), 7.18−7.16 (m, 1H), 1.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.4, 147.1, 146.4, 141.1, 135.8, 135.0, 134.7, 130.7, 128.7, 128.4, 127.9, 127.8, 127.2, 127.0, 125.9, 125.8, 125.4, 125.1, 120.9, 20.1; IR (KBr) ν 3045, 2920, 1419, 1261, 1134, 925, 753, 734 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{15}N$: C, 89.21 (89.19); H, 5.59 (5.61); N, 5.22 (5.20).

*10-p-Tolylbenzo[h]quinoline (**3ag**).* Pale yellow solid (25.0 mg, yield 93%): ^1H NMR ($CDCl_3$, 400 MHz) δ 8.44 (d, J = 2.4 Hz, 1H), 8.15 (d, J = 6.8 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.70 (t, J = 8.0 Hz, 2H), 7.57 (d, J = 7.2 Hz, 1H), 7.33−7.20 (m, 5H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.0, 146.8, 143.5, 141.8, 135.1, 135.0, 131.6, 129.1, 128.6, 128.3, 128.1, 127.8, 127.2, 127.0, 125.8, 121.0, 21.3; IR (KBr) ν 3044, 2918, 1603, 1555, 1442, 1419, 1326, 1261, 925, 813, 716, 663 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{15}N$: C, 89.24 (89.19); H, 5.60 (5.61); N, 5.21 (5.20).

*10-(4-tert-Butylphenyl)benzo[h]quinoline (**3ah**).* Pale yellow solid (28.3 mg, yield 91%):^1H NMR ($CDCl_3$, 400 MHz) δ 8.43 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 8.08 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.70−7.66 (m, 2H), 7.59 (d, J = 7.2 Hz, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.33−7.30 (m, 3H), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.4, 147.0, 146.8, 143.3, 141.8, 135.1, 135.0, 131.5, 129.2, 128.4, 128.3, 127.7, 127.2, 127.0, 125.8, 124.2, 121.0, 34.5, 31.6; IR (KBr) ν 3051, 2945, 1637, 1573, 1418, 1332, 927, 833, 813, 662 cm^{-1}; HRMS (ESI) m/z 312.1734 [M + H^+] (calcd 312.1752). Anal. Found (calcd) for $C_{23}H_{21}N$: C, 88.67 (88.71); H, 6.79 (6.80); N, 4.50 (4.50).

*10-(4-Methoxyphenyl)benzo[h]quinoline (**3ai**).* Pale yellow solid (23.7 mg, yield 87%): ^1H NMR ($CDCl_3$, 400 MHz) δ 8.46 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 8.10 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.94 (dd, J = 8.0 Hz,1.2 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.71−7.67(m, 2H), 7.54−7.52 (m, 1H), 7.36−7.29 (m, 3H), 7.12−7.08 (m, 2H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.0, 147.0, 146.9, 139.0, 135.2, 135.1, 131.7, 129.8, 129.2, 128.3, 127.7, 127.2, 127.0, 125.9, 121.0, 112.8, 55.3; IR (KBr) ν 3028, 2920, 1513, 1242, 1172, 821, 736, 660 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{15}NO$: C, 84.22 (84.19); H, 5.29 (5.30); N, 4.92 (4.91).

*Ethyl 4-(Benzo[h]quinolin-10-yl)benzoate (**3aj**).* Yellow solid (14.4 mg, yield 44%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.39−8.38 (m, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 7.6 Hz, 2H), 7.32 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 4.43 (dd, J = 11.6 Hz, 7.2 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 151.5, 146.9, 144.3, 135.2, 134.9, 130.9, 130.1, 130.0, 128.7, 128.4, 128.2, 127.2, 127.1, 127.0, 126.0, 121.2, 61.0, 14.3; IR (KBr): 3046, 2950, 2915, 2862, 1711, 1606, 1398, 1271, 1174, 1021, 832, 758, 731, 705 cm^{-1}. Anal. Found (calcd) for $C_{22}H_{17}NO_2$: C, 80.68 (80.71); H, 5.24 (5.23); N, 4.30 (4.28).

*10-(4-Fluorophenyl)benzo[h]quinoline (**3ak**).* Pale yellow solid (19.1 mg, yield 70%): ^1H NMR ($CDCl_3$, 400 MHz) δ 8.45 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 8.09 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.71−7.66 (m, 2H), 7.52 (d, J = 7.2 Hz, 1H), 7.37−7.28 (m, 3H), 7.08 (t, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.5 (d, $^1J_{C-F}$ = 241.7 Hz), 146.8, 146.7, 142.2 (d, $^3J_{C-F}$ = 3.3 Hz), 140.7, 135.2, 135.0, 131.5, 130.1 (d, $^3J_{C-F}$ = 7.7 Hz), 129.1, 128.3, 128.1, 127.2, 127.0, 126.0, 121.1, 114.2 (d, $^2J_{C-F}$ = 21.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −118.1 (m, 1F); IR (KBr) ν 3045, 1594, 1423, 1213, 1157, 834, 756, 729 cm^{-1}. Anal. Found (calcd) for $C_{19}H_{12}FN$: C, 83.53 (83.50); H, 4.41 (4.43); N, 5.11 (5.12).

*10-(4-Chlorophenyl)benzo[h]quinoline (**3al**).* Pale yellow solid (21.7 mg, yield 75%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 2.8 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.72−7.68 (m, 2H), 7.52 (d, J = 7.2 Hz, 1H),7.41−7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.9, 146.8, 146.5, 144.9, 140.3, 135.2, 135.0, 131.5, 131.3, 130.1, 130.0, 128.9, 128.2, 127.4, 127.2, 127.1, 127.0, 126.0, 121.1; IR (KBr) ν 3045, 2926, 1510, 1421, 1395, 1086, 840, 822, 728 cm^{-1}. Anal. Found (calcd) for $C_{19}H_{12}ClN$: C, 78.72 (78.76); H, 4.16 (4.17); N, 4.81 (4.83).

*10-(4-Bromophenyl)benzo[h]quinoline (**3am**).* Pale yellow solid (25.6 mg, yield 77%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 2.8 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.72−7.66 (m, 2H), 7.53−7.49 (m, 3H), 7.35 (dd, J = 8.0, 4.0 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.9, 146.6, 145.4, 140.4, 135.3, 135.0, 131.2, 130.5, 130.4, 128.8, 128.3, 128.2, 127.2, 127.0, 126.0, 121.2, 119.6; IR (KBr) ν 3045, 1592, 1487, 1422, 1394, 1015, 920, 816, 730 cm^{-1}. Anal. Found (calcd) for $C_{19}H_{12}BrN$: C, 68.32 (68.28); H, 3.61 (3.62); N, 4.17 (4.19).

*10-(Biphenyl-4-yl)benzo[h]quinoline (**3an**).* Pale yellow solid (24.2 mg, yield 73%): ^1H NMR ($CDCl_3$, 400 MHz) δ 8.46 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 8.11 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.76−7.66 (m, 7H), 7.51−7.44 (m, 4H),7.39−7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.9, 145.6, 141.5, 141.4, 138.4, 135.2, 135.1, 131.5, 129.2, 129.1, 128.7, 128.3, 128.0, 127.3, 127.0, 126.9, 126.0, 125.9, 121.1; IR (KBr) ν 3045, 2924, 1483, 1419, 835, 752, 711 cm^{-1}. Anal. Found (calcd) for $C_{25}H_{17}N$: C, 90.63 (90.60); H, 5.17 (5.17); N, 4.21 (4.23).

*10-(4-(Trifluoromethyl)phenyl)benzo[h]quinoline (**3ao**).* Pale yellow solid (22.0 mg, yield 68%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 2.8 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.74−7.64 (m, 4H), 7.52−7.45 (m, 3H),7.35 (dd, J = 8.0 Hz, 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.2, 146.9, 146.4, 140.3, 135.3, 135.0, 131.1, 129.0, 128.9, 128.5, 128.2, 128.0, 127.7 (q, J_{C-F} = 31.8 Hz), 127.3, 127.1, 126.1, 124.8 (q, J_{C-F} = 273.6 Hz), 124.2 (q, J_{C-F} = 3.7 Hz), 121.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.0 (s, 3F); IR (KBr) ν 3043, 2928, 1523, 1402, 1162, 1075, 926, 742, 693, 607 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{12}F_3N$: C, 74.32 (74.30); H, 3.75 (3.74); N, 4.34 (4.33).

*10-(Naphthalen-2-yl)benzo[h]quinoline (**3ap**).* Yellow solid (27.2 mg, yield 89%): ^1H NMR ($CDCl_3$, 400 MHz) δ 8.33 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 8.10 (dd, J = 8.0, 1.6 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.94−7.89 (m, 4H), 7.79−7.72 (m, 3H), 7.66 (d, J = 6.4 Hz, 1H), 7.53−7.49 (m, 2H), 7.46 (dd, J = 8.4 Hz, 1.6 Hz, 1H),7.30 (dd, J = 8.0 Hz, 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.9, 146.7, 144.5, 141.5, 135.1, 135.0, 133.7, 132.1, 131.9, 129.4, 129.0, 128.3, 128.1, 128.0, 127.6, 127.2, 127.1, 125.9, 125.6, 125.5, 125.4, 125.1, 121.0; IR (KBr) ν 3047, 1560, 1418, 1013, 831, 817, 749, 642 cm^{-1}. Anal. Found (calcd) for $C_{23}H_{15}N$: C, 90.42 (90.46); H, 4.96 (4.95); N, 4.57 (4.59).

*10-(3,5-Dimethylphenyl)benzo[h]quinoline (**3aq**).* Pale yellow solid (26.9 mg, yield 95%): ^1H NMR ($CDCl_3$, 400 MHz) δ 8.48 (dd, J = 4.0, 1.6 Hz, 1H), 8.09 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.70−7.66 (m, 2H), 7.56 (d, J = 6.4 Hz, 1H), 7.34 (dd, J = 8.0 Hz, 4.4 Hz, 1H), 7.01 (s, 3H), 2.37 (s,

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6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.9, 146.8, 146.1, 141.9, 136.6, 135.1, 135.0, 131.5, 129.0, 128.3, 127.7, 127.3, 127.1, 127.0, 126.6, 125.8, 121.0, 21.4; IR (KBr) ν 3046, 2925, 1556, 1413, 1328, 905, 830, 733, 636 cm^{-1}. Anal. Found (calcd) for $C_{21}H_{17}N$: C, 89.05 (89.01); H, 6.04 (6.05); N, 4.92 (4.94).

*10-(3,5-Bis(trifluoromethyl)phenyl)benzo[h]quinoline (**3ar**).* Pale yellow solid (33.2 mg, yield 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 2.4 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.85−7.72 (m, 6H), 7.53 (d, J = 6.8 Hz, 1H),7.37 (dd, J = 8.0 Hz, 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.1, 146.9, 146.0, 138.4, 135.5, 135.0, 131.2, 130.4, 129.2, 128.6, 127.3, 127.1, 126.4, 125.2, 122.5, 121.6, 119.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.6 (s, 6F); IR (KBr) ν 3043, 1640, 1516, 1375, 1278, 1167, 1127, 895, 836, 735, 626 cm^{-1}. Anal. Found (calcd) for $C_{21}H_{11}F_6N$: C, 64.50 (64.46); H, 2.82 (2.83); N, 3.59 (3.58).

*10-(3,4-Difluorophenyl)benzo[h]quinoline (**3as**).* Pale yellow solid (23.3 mg, yield 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 8.11 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.95 (d, J = 7.2 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.73−7.66 (m, 2H), 7.52−7.49 (m, 1H), 7.36 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 7.21−7.12 (m, 2H), 7.06−7.03 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7 (dd, $^1J_{C-F}$ = 244.2 Hz, 12.6 Hz), 149.0 (dd, $^1J_{C-F}$ = 243.6 Hz, 12.6 Hz), 146.9, 146.4, 143.1 (dd, $^3J_{C-F}$ = 6.5 Hz, 4.2 Hz), 139.4, 135.3, 134.9, 131.2, 128.8, 128.5, 128.2, 127.3, 126.9, 126.1, 124.5 (dd, $^3J_{C-F}$ = 5.7 Hz, 3.4 Hz), 121.2, 117.9 (d, $^2J_{C-F}$ = 17.3 Hz), 116.0 (d, $^2J_{C-F}$ = 16.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −140.3 (m, 1F), −143.0 (m, 1F); IR (KBr) ν 3052, 2926, 1665, 1519, 1423, 1257, 1123, 837, 816, 772, 733, 628 cm^{-1}. Anal. Found (calcd) for $C_{19}H_{11}F_2N$: C, 78.37 (78.34); H, 3.80 (3.81); N, 4.83 (4.81).

*10-(3,4,5-Trifluorophenyl)benzo[h]quinoline (**3at**).* Pale yellow solid (26.3 mg, yield 85%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 8.12 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.74−7.66 (m, 2H), 7.48 (d, J = 7.2 Hz, 1H), 7.38 (dd, J = 8.0 Hz, 4.4 Hz, 1H), 6.96−6.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 149.4, 147.1, 146.2, 142.3, 139.5, 138.5, 135.4, 134.9, 130.8, 128.9, 128.7, 128.1, 127.4, 127.0, 126.3, 121.4, 112.9, 112.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −137.3 (m, 1F), −165.8 (m, 2F); IR (KBr) ν 3052, 1611, 1527, 1423, 1244, 1031, 833, 732, 659, 631 cm^{-1}. Anal. Found (calcd) for $C_{19}H_{10}F_3N$: C, 73.75 (73.78); H, 3.28 (3.26); N, 4.51 (4.53).

*6-Methyl-10-phenylbenzo[h]quinoline (**3ba**).* Pale yellow solid (23.4 mg, yield 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37−8.36 (m, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.00 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.60−7.55 (m, 2H), 7.44−7.40 (m, 2H), 7.38−7.36 (m, 3H), 7.28 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 146.3, 146.0, 142.1, 134.8, 134.3, 133.6, 131.2, 128.6, 127.4, 127.1, 126.9, 125.8, 125.5, 123.8, 121.1, 20.5; IR (KBr) ν 3052, 1587, 1573, 1442, 1424, 1382, 1021, 871, 828, 786, 760, 732, 696 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{15}N$: C, 89.22 (89.19); H, 5.60 (5.61); N, 5.18 (5.20).

*5,10-Diphenylbenzo[h]quinoline (**3bb**).* Yellow solid (27.5 mg, yield 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43−8.42 (m, 1H), 8.15 (dd, J = 8.4, 1.2 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.83 (s, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.58−7.55 (m, 5H), 7.46−7.37 (m, 6H), 7.28−7.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 141.7, 139.5, 138.0, 134.4, 133.5, 131.4, 130.3, 130.0, 128.7, 128.6, 128.5, 128.3, 128.0, 127.7, 127.4, 127.3, 126.4, 125.9, 125.6, 120.8; IR (KBr) ν 3055, 3025, 1567, 1513, 1492, 1386, 806, 758, 735, 703 cm^{-1}. Anal. Found (calcd) for $C_{25}H_{17}N$: C, 90.64 (90.60); H, 5.20 (5.17); N, 4.21 (4.23).

*5-(Naphthalen-2-yl)-10-phenylbenzo[h]quinoline (**3bc**).* Yellow solid (30.5 mg, yield 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 7.6 Hz, 1H), 8.08−8.03 (m, 1H), 7.90−7.81 (m, 3H), 7.61−7.54 (m, 2H), 7.48−7.43 (m, 5H), 7.33−7.26 (m, 6H), 7.16−7.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 147.0, 146.6, 146.5, 141.7, 141.6, 137.9, 134.4, 133.5, 131.5, 131.4, 130.0, 128.8, 128.7, 128.5, 128.1, 128.0, 127.8, 127.7, 127.4, 127.3, 125.6, 120.8, 119.1; IR (KBr) ν 3051, 1597, 1513, 1412, 1383, 804, 738, 709 cm^{-1}. Anal. Found (calcd) for $C_{29}H_{19}N$: C, 91.27 (91.31); H, 5.01 (5.02); N, 3.68 (3.67).

*7-Methoxy-10-phenylbenzo[h]quinoline (**3bd**).* Pale yellow solid (23.1 mg, yield 81%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43−8.40 (m, 2H), 8.09 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.39−7.31 (m, 6H), 7.13 (d, J = 8.0 Hz, 1H), 4.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 146.7, 146.6, 146.5, 135.1, 133.9, 131.4, 130.0, 129.0, 127.4, 127.2, 125.7, 125.3, 125.1, 121.5, 121.1, 106.5, 55.8; IR (KBr) ν 3052, 1590, 1510, 1455, 1419, 1318, 1246, 1112, 1072, 1024, 834, 812, 764, 736, 699 cm^{-1}. Anal. Found (calcd) for $C_{20}H_{15}NO$: C, 84.24 (84.19); H, 5.30 (5.30); N, 4.92 (4.91).

*7,10-Diphenylbenzo[h]quinoline (**3be**).* Pale yellow solid (29.8 mg, yield 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.8 Hz, 1H), 7.66−7.55 (m, 7H), 7.50−7.47 (m, 1H), 7.43−7.37 (m, 5H),7.33 (dd, J = 8.0 Hz, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 146.8, 146.8, 141.2, 141.0, 140.1, 134.9, 132.8, 130.8, 130.3, 129.5, 128.7, 128.6, 128.4, 127.4, 127.3, 126.9, 125.9, 125.7, 125.6, 121.2; IR (KBr) ν 3053, 1574, 1523, 1496, 1394, 1146, 1035, 812, 766, 735, 708 cm^{-1}. Anal. Found (calcd) for $C_{25}H_{17}N$: C, 90.65 (90.60); H, 5.17 (5.17); N, 4.21 (4.23).

*2-(Biphenyl-2-yl)pyridine (**3bf**).* White solid (10.6 mg, yield 46%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 3.6 Hz, 1H), 7.75−7.73 (m, 1H), 7.51−7.48 (m, 3H), 7.41−7.38 (m, 1H), 7.52−7.19 (m, 5H), 7.13−7.10 (m, 1H), 6.91 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 149.3, 141.3, 140.6, 139.4, 135.2, 130.4, 129.7, 128.5, 128.0, 127.6, 126.6, 125.4, 121.3; IR (KBr) ν 3053, 1572, 1521, 1491, 1394, 1146, 1035, 812, 761, 735, 709 cm^{-1}. Anal. Found (calcd) for $C_{17}H_{13}N$, 88.27 (88.28); H, 5.68 (5.67); N, 6.04 (6.06).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00238.

NMR spectra of materials and products (PDF)

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Notes

The authors declare no competing financial interest.

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