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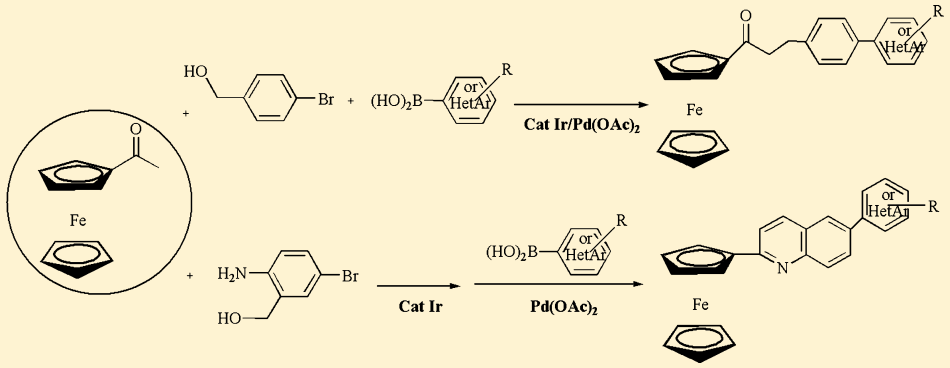
One-Pot Synthesis of Ferrocenyl Ketones Containing Biaryls and 6-Aryl-2-ferrocenylquinolines via Ir/Pd-Cocatalyzed α-Alkylation/Suzuki Reaction

Chen Xu,*[,†,‡] Xin-Qi Hao,[‡] Zhi-Qiang Xiao,[‡] Zhi-Qiang Wang,[†] Xiao-Er Yuan,[‡] Wei-Jun Fu,[†] Bao-Ming Ji,[†] and Mao-Ping Song*[,‡]

[†]College of Chemistry, Chemical Engineering, Luoyang Normal University, Luoyang, Henan 471022, China

[‡]College of Chemistry, Molecular Engineering, Zhengzhou University, Zhengzhou, Henan 450052, China

Supporting Information



ABSTRACT: An efficient PPh_3-cyclometalated iridium(III) benzo[*h*]quinoline hydride **1**/$Pd(OAc)_2$-cocatalyzed three-component α-alkylation/Suzuki reaction has been developed. The three-component reaction of 4-bromobenzyl alcohol, acetylferrocene, and arylboronic acids gives ferrocenyl ketones containing biaryls in moderate to good yields. This method was successfully applied to a one-pot synthesis of 6-aryl-2-ferrocenyl quinolines, using (2-amino-5-bromophenyl)methanol instead of 4-bromobenzyl alcohol.

INTRODUCTION

The multicomponent reactions (MCRs) are one-pot processes that offer significant advantages over classical step-by-step approaches, allowing the formation of several bonds and construction of complex molecules from readily available starting materials in a single synthetic operation.[1] For the design of a MCR, it is important to study the catalyst compatibility with materials from the catalytic steps comprising the overall process. In most cases, two (or more) different metals/ligands were added to the reaction medium to afford the two (or more) transformations.[2] Because there are many different reactions that can be catalyzed by the same ligand, it is possible for the catalyst (two different metals based on a same ligand) to initiate two or more mechanistically distinct reactions in a MCR. This alternative is highly desirable in view of economic and practical points. Transition-metal-catalyzed reactions such as α-alkylation and Suzuki reaction have become an extremely powerful method in organic synthesis for the formation of carbon−carbon bonds.[3] In these reactions, halides are the most commonly used electrophiles. Recently, there has been significant interest in the transition-metal-catalyzed hydrogen autotransfer process by alcohols as a more benign alternative to potentially genotoxic halides.[4] This strategy can improve both the atom efficiency and the regioselectivity of the process, producing only water as a side product. To our knowledge, there are no reports concerning a three-component reaction that consists of α-alkylation and Suzuki reaction catalyzed by two metals based on a same ligand.

Several groups have reported the use of Ru,[5] Pd,[6] and Ni[7] catalysts for the α-alkylation of ketones with alcohols. In addition, Ir complexes serve as efficient catalysts for hydrogen transfer from alcohols to aldehydes,[8] and they have been utilized in α-alkylation of ketones. Among them, $[Ir(cod)Cl]_2$ has been the most commonly employed Ir catalyst for this reaction.[9] Ishii and co-workers reported direct α-alkylation of ketones and acetates with primary alcohols catalyzed by an $[Ir(cod)Cl]_2/PPh_3$/base system.[10] We have also found that PPh_3-cyclometalated iridium(III) pyrimidine complexes were very efficient catalysts for α-alkylation.[11] Considering that PPh_3 is the most common ligand in the Suzuki reaction,[12] we speculate that $Pd(OAc)_2$ in combination with PPh_3-cyclometalated iridium(III) complex can cocatalyze α-alkylation and Suzuki reaction. Since the discovery of ferrocene in 1951,[13] the

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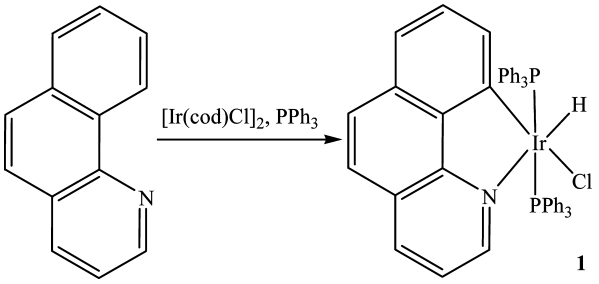
preparation of functionalized ferrocenyl derivatives has been extensively studied, especially with respect to applications in organic synthesis, materials chemistry, and biochemistry.[14] As a continuation of our interest in the synthesis and application of ferrocenyl derivatives,[15] we prepared a new PPh_3-cyclometalated iridium(III) benzo[*h*]quinoline hydride **1** and described the first Ir/Pd-cocatalyzed one-pot reaction of bromoarylmethanols, acetylferrocene, and arylboronic acids, providing a series of ferrocenyl ketones containing biaryls and 6-aryl-2-ferrocenylquinolines.

RESULTS AND DISCUSSION

The preparation of new PPh_3-cyclometalated iridium(III) hydride **1** is as follows (Scheme 1): A reaction mixture of

Scheme 1. Preparation of PPh_3-Cyclometalated Iridium(III) Hydride 1

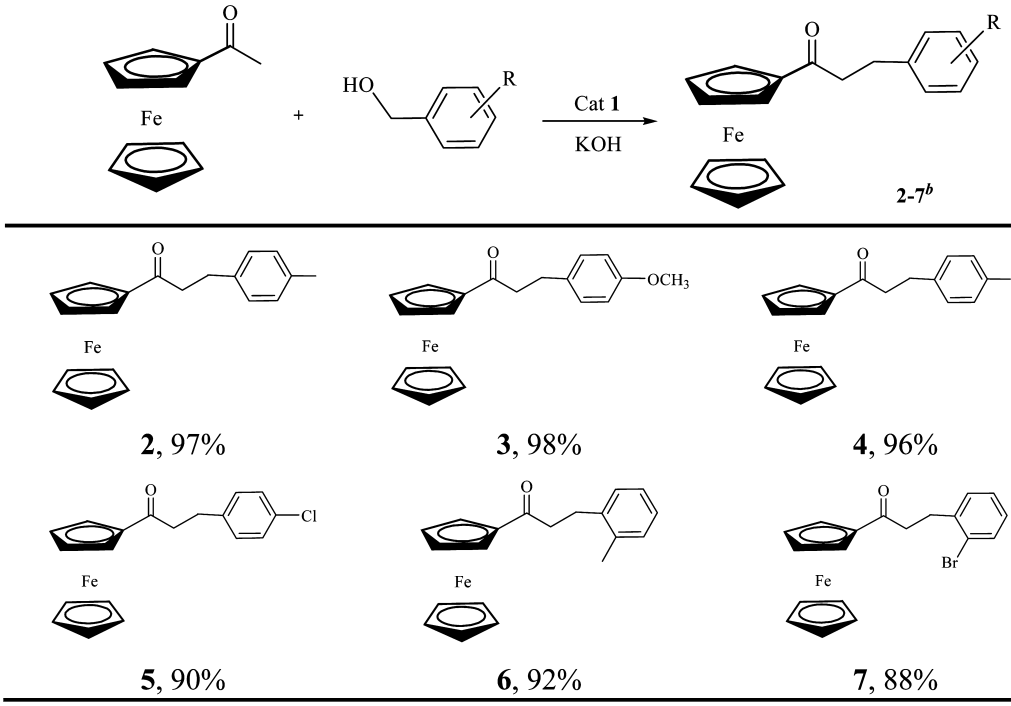


$[Ir(cod)Cl]_2$, PPh_3, and benzo[*h*]quinoline in 2-ethoxyethanol was refluxed under N_2 for 12 h and then cooled to room temperature. The yellow precipitate was filtered and washed with ethanol several times, and the crude product was recrystallized from CH_2Cl_2, giving yellow crystals of **1**. It was characterized by elemental analysis, IR, NMR, and also by X-ray diffraction analysis. The IR spectrum of **1** show ν_{Ir-H} at 2133 cm^{-1}, and the ^1H NMR spectrum reveals a triplet of hydride resonances at −16.86 ppm (t, J_{P-H} = 16.3 Hz). The crystal structure of **1** shows the H being trans to the nitrogen of benzo[*h*]quinoline (Figure S1 in Supporting Information). The Ir−C, Ir−Cl, and Ir−H bond lengths of **1** are similar to those of related cyclometalated iridium(III) hydrides.[16]

In 2006, Yus and co-workers reported direct α-alkylation of acetylferrocene with phenylmethanol catalyzed by $RuCl_2(DMSO)_4$, while the reaction gave the expected product only in a very low yield (17%).[5c] We have previously shown that PPh_3-cyclometalated iridium(III) complexes effectively catalyzed the above reaction, giving 83% yield.[11] On the basis of the success of this approach, we were interested to see whether the obtained PPh_3-cyclometalated iridium(III) hydride **1** would be an efficient catalyst for α-alkylation of acetylferrocene with arylmethanols. Fortunately, the α-alkylations of acetylferrocene with a variety of arylmethanols were carried out with catalytic loadings of 2 mol % (relative to acetylferrocene) in the presence of KOH as base in dioxane at 110 °C, affording the products in excellent yields (Table 1). Furthermore, the coupling of hindered arylmethanols with acetylferrocene also gave the desired products **6** and **7** in good yields (92 and 88%, respectively).

Since it is known that simple catalyst $Pd(OAc)_2/PPh_3$ can catalyze organic halides and arylboronic acids to form a variety of biaryls,[12] we hypothesized that $Pd(OAc)_2$ in combination with PPh_3-cyclometalated iridium(III) hydride can cocatalyze one-pot α-alkylation/Suzuki reaction. The three-component reaction of acetylferrocene, 4-bromobenzyl alcohol, and phenylboronic acid was carried out with various bases and solvents in the presence of Ir/Pd catalysts. The results from this

Table 1. α-Alkylation of Acetylferrocene with Arylmethanols Catalyzed by 1[a]



[a]Reaction conditions: acetylferrocene (0.5 mmol), arylmethanols (0.6 mmol), **1** (2 mol %), KOH (0.5 mmol), dioxane (3 mL), 110 °C, 12 h, nitrogen atmosphere. [b]Yield (average of two runs).

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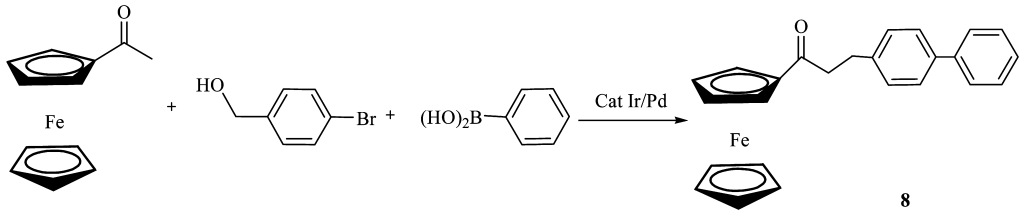
Table 2. Optimization of the Three-Component Reaction Conditions[a]



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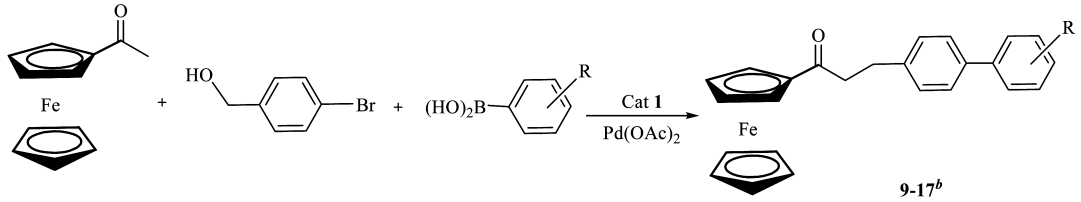
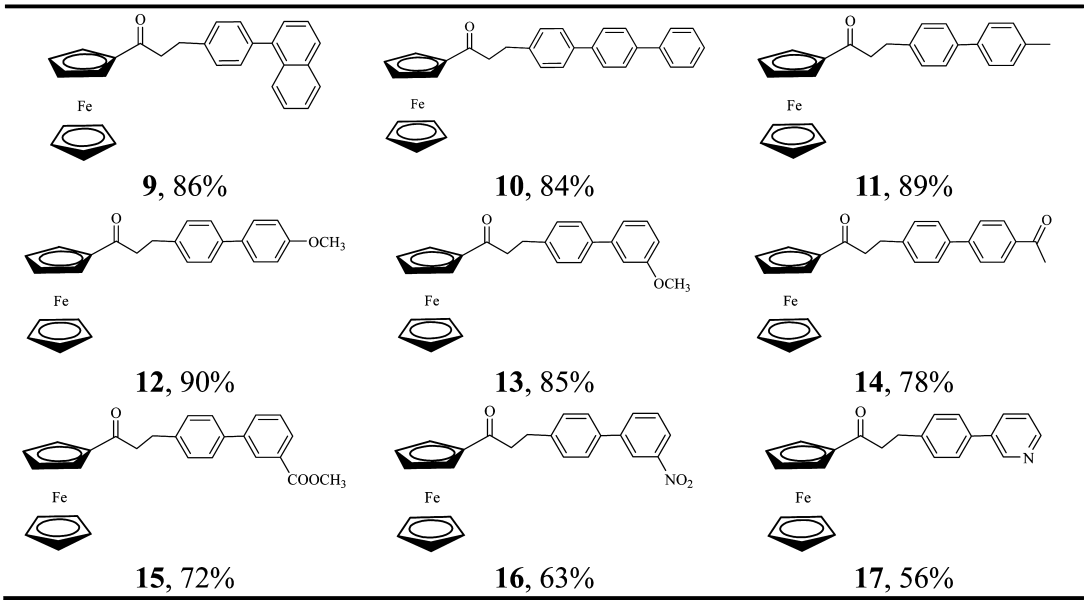
entry	catalyst (mol %)	base (equiv)	solvent	yield (%)[b]
1	**1**/$Pd(OAc)_2$ (2/3)	KOH (3)	dioxane	38
2	**1**/$Pd(OAc)_2$ (2/3)	K_2CO_3 (3)	dioxane	30
3	**1**/$Pd(OAc)_2$ (2/3)	Cs_2CO_3 (3)	dioxane	43
4	**1**/$Pd(OAc)_2$ (2/3)	KOH/Cs_2CO_3 (1/2)	dioxane	87
5	**1**/$Pd(OAc)_2$ (2/3)	KOH/Cs_2CO_3 (1/2)	toluene	57
6	**1**/$Pd(OAc)_2$ (2/3)	KOH/Cs_2CO_3 (1/2)	THF	14
7[c]	**1** (2)	KOH/Cs_2CO_3 (1/2)	dioxane	trace
8[d]	$Pd(OAc)_2/PPh_3$ (3/6)	KOH/Cs_2CO_3 (1/2)	dioxane	trace
9	**1**/$PdCl_2$ (2/3)	KOH/Cs_2CO_3 (1/2)	dioxane	76
10	**1**/$Pd(dba)_2$ (2/3)	KOH/Cs_2CO_3 (1/2)	dioxane	85
11	$[Ir(cod)Cl]_2/PPh_3/Pd(OAc)_2$ (1/4/3)	KOH/Cs_2CO_3 (1/2)	dioxane	40
12	$IrCl_3/Pd(OAc)_2$ (2/3)	KOH/Cs_2CO_3 (1/2)	dioxane	trace

[a]Reaction conditions: acetylferrocene (0.5 mmol), 4-bromobenzyl alcohol (0.6 mmol), phenylboronic acid (0.75 mmol), solvent (3 mL), 110 °C, 18 h, nitrogen atmosphere. [b]Yield (average of two runs). [c]Main product is **4** (98%). [d]Main product is biphenyl-4-methanol (38%).

Table 3. One-Pot Synthesis of Ferrocenyl Ketones Containing Biaryls[a]



9-17[b]



9, 86% **10**, 84% **11**, 89%

12, 90% **13**, 85% **14**, 78%

15, 72% **16**, 63% **17**, 56%

[a]Reaction conditions: acetylferrocene (0.5 mmol), 4-bromobenzyl alcohol (0.6 mmol), arylboronic acids (0.75 mmol), **1**/$Pd(OAc)_2$ (2–3 mol %), KOH/Cs_2CO_3 (0.5 mmol/1 mmol), dioxane (3 mL), 110 °C, 18 h, nitrogen atmosphere. [b]Yield (average of two runs).

study are summarized in Table 2. It was disappointing to find at the beginning that the isolated yields of the product **8** were only 30–43% with 2–3 mol % of **1**/$Pd(OAc)_2$ in dioxane using single base (KOH, K_2CO_3, and Cs_2CO_3). However, when the dual bases KOH/Cs_2CO_3 were used, the yield increased to 87% (entry 4). Among the tested solvents, dioxane was much better than other solvents such as toluene and THF (entries 5 and 6). Only complex **1** is used as catalyst for the above reaction (entry 7); the expected product **8** was not isolated, and the main product was α-alkyl product **4** (98%). Using $Pd(OAc)_2/PPh_3$ as

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catalyst in the absence of the Ir complex **1** provided the main product (38%) biphenyl-4-methanol[15d] (entry 8). In addition, the activities of several related catalytic systems in the same model reaction were investigated. **1**/$PdCl_2$ and **1**/$Pd(dba)_2$ also showed comparable activity, producing the product in 76−85% yields (entries 9 and 10). $[Ir(cod)Cl]_2/PPh_3/Pd(OAc)_2$ generated the product in low yield (40%, entry 11). However, $IrCl_3/Pd(OAc)_2$ was almost inactive under the same reaction conditions (entry 12), suggesting that PPh_3 participated in the catalytic cycles.

To test this procedure, the scope of the reaction was then investigated with various arylboronic acids under the established protocol (Table 3). Similar to the result of phenylboronic acid, good yields (84−86%) were also obtained in the cases of 1-naphthylboronic acid and 4-biphenylboronic acid. For electron-rich arylboronic acids, they could provide the corresponding products **11**−**13** in good to excellent yields (85−90%). In cases of electron-deficient arylboronic acids containing −CO−, $-COOCH_3$, or $-NO_2$ groups, an obvious decrease in yield was observed (63−78%). This three-component coupling was found also to proceed successfully with heteroarylboronic acid, such as pyridin-3-ylboronic acid, furnishing **17** in a moderate yield (56%).

The exact structures of products **9** and **13** were further determined by single-crystal X-ray crystallography and shown in Figure 1 and Figure S2 (see Supporting Information). The

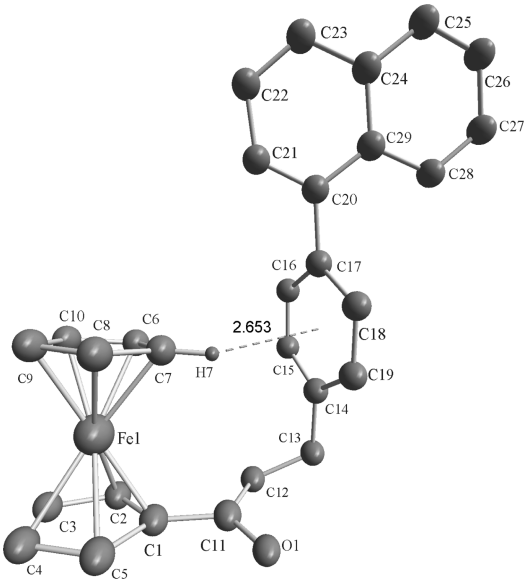

Figure 1. Molecular structure of compound **9**. Non-hydrogen bonding H atoms are omitted for clarity.

crystal structures of the two compounds are similar; the middle benzene ring plane is almost perpendicular to the Cp ring (dihedral angles of 84.7 and 95.8° for **9** and **13**, respectively). The most striking common features are intramolecular (unsubstituted Cp) C−H···π (the middle benzene ring) interactions[17] of 2.653 and 2.608 Å for **9** and **13**, respectively.

Quinolines and their derivatives are well-known as important natural products which are often endowed with many pharmacological properties.[18] In spite of the existence of many synthetic routes, there are limited reports involving ferrocenylquinolines.[5c,19] Among them, the metal-catalyzed modified Friedlaender reaction[20] is one of the simplest methods, where 2-aminobenzyl alcohol, which is cheaper and more stable than 2-aminobenzaldehyde, is allowed to react with carbonyl compounds via hydrogen transfer reaction and cyclization to form quinoline derivatives.[5c,21] To date, only one account has been reported concerning the synthesis of quinolines from amino alcohols and ketones catalyzed by Ir catalysts.[21d] However, this reaction has not involved ferrocenylquinolines. Thus, the development of efficient methodologies for the synthesis of substituted ferrocenylquinolines from simple, readily available starting materials is still desired.

Prompted by the good results obtained in the synthesis of ferrocenyl ketones containing biaryls, we explored whether this strategy would allow the preparation of substituted ferrocenylquinolines. The direct three-component reaction of acetylferrocene, (2-amino-5-bromophenyl)methanol, and phenylboronic acid was selected as the model reaction. Disappointingly, the expected three-component coupled product **19** was not isolated; the main product was α-alkyl product 2-ferrocenyl-6-bromoquinoline **18** (78%), clearly showing that Suzuki reaction did not proceed. Thus, we carried out the **1**-catalyzed α-alkylation of acetylferrocene and (2-amino-5-bromophenyl)-methanol, let it reach completion (98% yield), and then added the $Pd(OAc)_2$, Cs_2CO_3, and phenylboronic acid dissolved in the same solvent, and the reaction was continued. To our delight, 6-phenyl-2-ferrocenylquinoline **19** could be synthesized in high yield (91%) by a one-pot, two-step procedure (Scheme 2). This protocol was equally efficient compared to the combined individual reactions but without any workup or isolation of the intermediate.

The scope of the procedure was further investigated by varying the arylboronic acids (Table 4). Good yields were obtained for the coupling of naphthylboronic acids or 4-biphenylboronic acid to give **20**, **21**, and **22** in 90, 88, and 87% yields, respectively. The electronic nature of the substituents on the arylboronic acids did have an effect on the reaction. Electron-donating substrates reacted to give the correponding products **23** and **24**, and the yields (92 and 93%) are slightly higher than the yields of electron-withdrawing substrates. Reaction with *para*-, *ortho*-, and *meta*-arylboronic acids proceeded efficiently to form the expected products **23** and **34** in moderate to good yields (43−93%). A slight decrease in the yields of *meta*-substitution products **28**−**30** was observed.

Scheme 2. Synthesis of 6-Aryl-2-ferrocenylquinoline 19

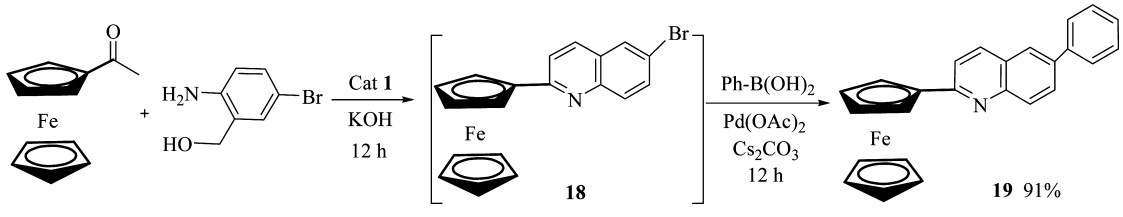

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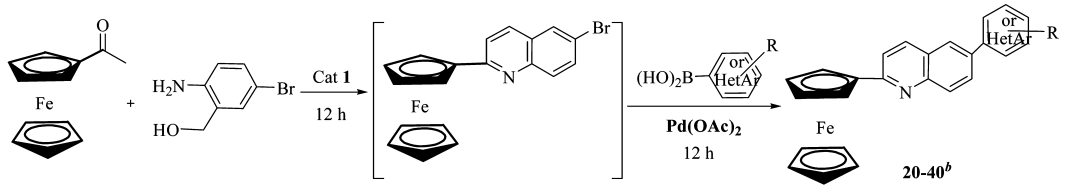
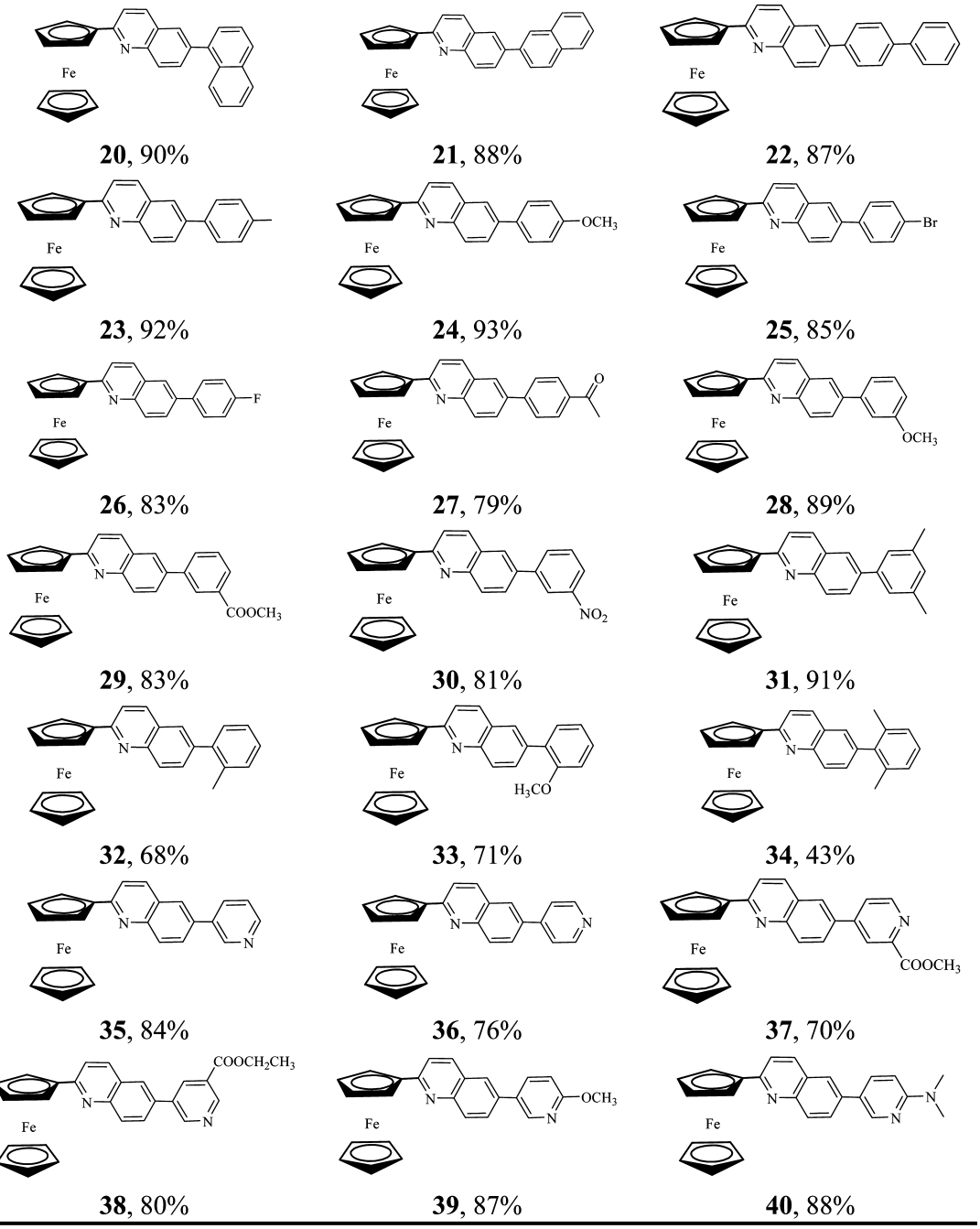
Table 4. One-Pot Synthesis of 6-Aryl-2-ferrocenylquinolines[a]





[a]Reaction conditions: acetylferrocene (0.5 mmol), (2-amino-5-bromophenyl)methanol (0.6 mmol), arylboronic acids (0.75 mmol), **1**/$Pd(OAc)_2$ (2–3 mol %), KOH/Cs_2CO_3 (0.5 mmol/1 mmol), dioxane (3 mL), 110 °C, nitrogen atmosphere. [b]Yield (average of two runs).

In the same manner, switching the methyl or methoxy group from the *para*-position to the *ortho*-position on the benzene ring does obviously influence the yields of **32** and **33** (68 and 71%), demonstrating that steric factors have an influence on the Suzuki reaction. The very sterically hindered 2,6-dimethylphenylboronic acid only provided the corresponding product **34** in a 43% yield.

Finally, we examined the one-pot three-component reactions of heteroarylboronic acids. Compared with the yield of **17** (56%), the yield (84%) of **35** starting from the same pyridin-3-

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ylboronic acid increased obviously. The method proved to be effective for pyridinylboronic acids bearing a variety of functional groups, including esters (**37** and **38**), ethers (**39**), and amines (**40**). The detailed structures of **23**, **29**, **32**, and **40** were confirmed by single-crystal X-ray crystallography (Figure S3 in Supporting Information). In each compound, the substituent Cp ring and the quinoline ring are approximately coplanar.

In conclusion, we have developed a PPh_3-cyclometalated iridium(III) hydride/$Pd(OAc)_2$-cocatalyzed three-component reaction of acetylferrocene, bromoarylmethanols, and arylboronic acids. This one-pot protocol provides efficient access to a variety of ferrocenyl ketones containing biaryls and 6-aryl-2-ferrocenylquinolines via α-alkylation and Suzuki reaction. The advantages of this method include simple operation, high efficiency, good functional tolerance, diversity of the starting material, and that an additional ligand is not required.

EXPERIMENTAL SECTION

General Information. The IR spectra were recorded on an FT-IR spectrometer on KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a spectrometer in $CDCl_3$ at 400 and 100 MHz, respectively, with TMS as internal standard. MS experiments were performed with EI source. All new compounds were further characterized by elemental analysis. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. All other chemicals were commercially available except for (2-amino-5-bromophenyl)methanol, which was prepared according to the published procedures.[22] Compounds **3**,[23] **5**,[23] and **18**[19e] are known compounds, and other compounds are new compounds.

Preparation of Compound 1. A reaction mixture of $[Ir(cod)Cl]_2$ (0.5 mmol), benzo[*h*]quinoline (1.2 mmol), and PPh_3 (2.2 mmol) in 2-ethoxyethanol (15 mL) was refluxed under an nitrogen atmosphere for 10 h and then cooled to room temperature. A yellow precipitate was filtered and washed with water and ethanol several times, recrystallized in CH_2Cl_2, and dried under vacuum as a yellow solid (838.4 mg, 90%): IR (KBr, cm^{-1}) 3049, 2133, 1568, 1482, 1432, 1403, 1330, 1188, 1090, 836, 742, 722; ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, J = 6.4 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.45−7.52 (m, 3H), 7.21−7.27 (m, 11H), 6.95−7.10 (m, 19H), 6.65 (d, J = 7.3 Hz, 1H), 6.44 (t, J = 8.4 Hz, 1H), −16.86 (t, J = 16.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 148.4, 140.4, 134.1, 133.8, 131.7, 131.4, 129.5, 128.8, 127.1, 127.0, 125.7, 122.6, 119.8, 117.6; MS (EI, 70 eV) m/z = 896.2 $(M - Cl)^+$. Anal. Calcd (%) for $C_{49}H_{39}ClIrNP_2$: C, 63.18; H, 4.22; N, 1.50. Found: C, 63.41; H, 4.03; N, 1.67.

General Procedure for α-Alkylation of Acetylferrocene with Arylmethanols. To a solution of Ir(III) complex **1** (0.01 mmol) in solution (3 mL) were added acetylferrocene (0.5 mmol), the corresponding alcohol (0.6 mmol), and base (0.5 mmol) under nitrogen. The reaction mixture was then placed in an oil bath and heated at 110 °C for 12 h, cooled, and quenched with water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate, then the combined organic layers were washed with water, dried over $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator. The resulting residue was purified by flash chromatography on silica gel using CH_2Cl_2 as eluent. The second band was collected and afforded the red solids **2**−**7**.

1-Ferrocenyl-3-(4-methylphenyl)propan-1-one (2): Yield 161.1 mg, 97%; IR (KBr, cm^{-1}) 2921, 1652, 1515, 1452, 1378, 1255, 1105, 1023, 1002, 817, 809; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 4.75 (s, 2H), 4.46 (s, 2H), 4.08 (s, 5H), 2.99 (s, 4H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 138.7, 135.8, 129.3, 128.6, 79.1, 72.3, 69.8, 69.4, 41.8, 29.9, 21.6; MS (EI, 70 eV) m/z = 333.1 $(M + H)^+$. Anal. Calcd (%) for $C_{20}H_{20}FeO$: C, 72.31; H, 6.07. Found: C, 72.50; H, 5.92.

3-(4-Bromophenyl)-1-ferrocenylpropan-1-one (4): Yield 190.6 mg, 96%; IR (KBr, cm^{-1}) 2927, 1666, 1584, 1486, 1455, 1408, 1377, 1254, 1105, 1071, 1010, 876, 814; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 4.75 (s, 2H), 4.48 (s, 2H), 4.09 (s, 5H), 2.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 140.6, 131.5, 130.4, 119.8, 78.8, 72.3, 69.7, 69.2, 41.1, 29.4; MS (EI, 70 eV) m/z = 397.0 $(M + H)^+$. Anal. Calcd (%) for $C_{19}H_{17}BrFeO$: C, 57.47; H, 4.32. Found: C, 57.59; H, 4.23.

1-Ferrocenyl-3-(2-methylphenyl)propan-1-one (6): Yield 198.2 mg, 92%; IR (KBr, cm^{-1}) 2926, 1663, 1571, 1491, 1454, 1403, 1378, 1253, 1104, 1002, 879, 831, 761; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 6.4 Hz, 1H), 7.13−7.18 (m, 3H), 4.77 (s, 2H), 4.48 (s, 2H), 4.11 (s, 5H), 3.03 (t, J = 6.8 Hz, 2H), 2.98 (t, J = 6.8 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 139.8, 136.0, 130.5, 129.1, 126.5, 126.3, 79.1, 72.4, 69.8, 69.4, 40.2, 27.7, 19.5; MS (EI, 70 eV) m/z = 333.1 $(M + H)^+$. Anal. Calcd (%) for $C_{20}H_{20}FeO$: C, 72.31; H, 6.07. Found: C, 72.45; H, 5.96.

3-(2-Bromophenyl)-1-ferrocenylpropan-1-one (7): Yield 174.8 mg, 88%; IR (KBr, cm^{-1}) 2923, 1667, 1565, 1469, 1451, 1377, 1293, 1227, 1107, 1083, 1020, 815, 758, 745; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.4 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 4.79 (s, 2H), 4.49 (s, 2H), 4.10 (s, 5H), 3.17 (t, J = 7.0 Hz, 2H), 3.06 (t, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 140.9, 133.1, 131.5, 128.2, 127.8, 124.4, 79.0, 72.4, 69.9, 69.4, 39.6, 31.0; MS (EI, 70 eV) m/z = 397.0 $(M + H)^+$. Anal. Calcd (%) for $C_{19}H_{17}BrFeO$: C, 57.47; H, 4.32. Found: C, 57.36; H, 4.41.

General Procedure for Synthesis of Ferrocenyl Ketones Containing Biaryls. The reaction of the acetylferrocene (0.5 mmol), 4-bromobenzyl alcohol (0.6 mmol), arylboronic acids (0.75 mmol), KOH (0.5 mmol), and Cs_2CO_3 (1.0 mmol) at 110 °C for 18 h in dioxane (3 mL) in the presence of **1**/$Pd(OAc)_2$ (0.01 mmol/0.015 mmol) under nitrogen affords the red products **8**−**17** after evaporation of the solvent and purification on silica gel using dichloromethane as eluent.

3-Biphenyl-1-ferrocenylpropan-1-one (8): Yield 171.5 mg, 87%; IR (KBr, cm^{-1}) 2922, 1663, 1484, 1453, 1405, 1377, 1253, 1105, 1077, 1026, 1009, 877, 816, 762, 696; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, J = 8.0 Hz, 4H), 7.30−7.43(m, 5H), 4.78 (s, 2H), 4.48 (s, 2H), 4.09 (s, 5H), 3.07 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 141.2, 140.9, 139.3, 129.2, 128.9, 127.4, 127.2, 127.1, 79.1, 72.4, 69.8, 69.4, 41.6, 29.9; MS (EI, 70 eV) m/z = 395.1 $(M + H)^+$. Anal. Calcd (%) for $C_{25}H_{22}FeO$: C, 76.15; H, 5.62. Found: C, 76.24; H, 5.55.

1-Ferrocenyl-3-phenyl-4-(1-naphthyl)propan-1-one (9): Yield 191.1 mg, 86%; IR (KBr, cm^{-1}) 2921, 1665, 1502, 1448, 1410, 1394, 1375, 1251, 1107, 1075, 1022, 1002, 875, 802, 778; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.85 (m, 3H), 7.34−7.49 (m, 8H), 4.78 (s, 2H), 4.46 (s, 2H), 4.08 (s, 5H), 3.09−3.13 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 140.9, 140.3, 138.8, 133.9, 131.8, 128.7, 128.4, 127.6, 127.0, 126.2, 126.0, 125.8, 125.5, 79.2, 72.4, 69.8, 69.4, 41.6, 30.0; MS (EI, 70 eV) m/z = 445.1 $(M + H)^+$. Anal. Calcd (%) for $C_{29}H_{24}FeO$: C, 78.39; H, 5.44. Found: C, 78.23; H, 5.56.

1-Ferrocenyl-3-(1,4-terphenyl)propan-1-one (10): Yield 197.6 mg, 84%; IR (KBr, cm^{-1}) 2924, 1653, 1485, 1456, 1379, 1270, 1231, 1084, 1028, 1002, 897, 839, 758, 690; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.65 (m, 8H), 7.45 (t, J = 7.8 Hz, 2H), 7.39 (d, J = 8.0 Hz, 3H), 4.79 (s, 2H), 4.49 (s, 2H), 4.10 (s, 5H), 3.09 (t, J = 4.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 140.9, 140.7, 140.0, 139.9, 138.7, 129.1, 128.8, 127.5, 127.4, 127.3, 127.1, 127.0, 79.0, 72.3, 69.7, 69.3, 41.4, 29.8; MS (EI, 70 eV) m/z = 471.1 $(M + H)^+$. Anal. Calcd (%) for $C_{31}H_{26}FeO$: C, 79.16; H, 5.57. Found: C, 79.33; H, 5.45.

1-Ferrocenyl-3-(4-methylbiphenyl)propan-1-one (11): Yield 181.7 mg, 89%; IR (KBr, cm^{-1}) 2918, 1657, 1498, 1449, 1375, 1264, 1223, 1108, 1079, 1037, 1002, 896, 822, 808, 742; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 4.77 (s, 2H), 4.48 (s, 2H), 4.09 (s, 5H), 3.06 (s, 4H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 140.4, 139.1, 138.1, 136.8, 129.4, 128.9, 127.0, 126.8, 78.9, 72.2, 69.7, 69.2, 41.4, 29.7, 21.1; MS (EI, 70 eV) m/z = 409.1 (M

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+ H)$^+$. Anal. Calcd (%) for $C_{26}H_{24}FeO$: C, 76.48; H, 5.92. Found: C, 76.32; H, 5.99.

1-Ferrocenyl-3-(4-methoxybiphenyl)propan-1-one (12): Yield 190.9 mg, 90%; IR (KBr, cm^{-1}) 2939, 1658, 1606, 1498, 1450, 1406, 1374, 1248, 1222, 1181, 1109, 1079, 1035, 899, 817, 800, 749; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 4H), 7.33 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 4.78 (s, 2H), 4.48 (s, 2H), 4.09 (s, 5H), 3.83 (s, 3H), 3.06 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 159.2, 140.2, 138.9, 133.7, 129.1, 128.2, 127.0, 114.3, 79.1, 72.4, 69.9, 69.4, 55.5, 41.6, 29.9; MS (EI, 70 eV) m/z = 425.1 (M + H)$^+$. Anal. Calcd (%) for $C_{26}H_{24}FeO_2$: C, 73.60; H, 5.70. Found: C, 73.74; H, 5.58.

1-Ferrocenyl-3-(3-methoxybiphenyl)propan-1-one (13): Yield 180.3 mg, 85%; IR (KBr, cm^{-1}) 2931, 1660, 1608, 1580, 1479, 1447, 1407, 1374, 1251, 1208, 1168, 1106, 1054, 870, 827, 776; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.4 Hz, 2H), 7.15 (d, J = 7.6 Hz, 1H), 7.10 (s, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.48 (t, J = 8.0 Hz, 1H), 4.77 (s, 2H), 4.48 (s, 2H), 4.09 (s, 5H), 3.84 (s, 3H), 3.07 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 160.0, 142.6, 141.0, 139.1, 129.8, 129.1, 127.4, 119.6, 112.9, 112.5, 79.0, 72.4, 69.8, 69.4, 55.4, 41.5, 29.9; MS (EI, 70 eV) m/z = 425.1 (M + H)$^+$. Anal. Calcd (%) for $C_{26}H_{24}FeO_2$: C, 73.60; H, 5.70. Found: C, 73.77; H, 5.56.

3-(4-Acetylbiphenyl)-1-ferrocenylpropan-1-one (14): Yield 170.2 mg, 78%; IR (KBr, cm^{-1}) 2923, 1678, 1656, 1601, 1451, 1376, 1355, 1265, 1227, 1107, 1079, 1003, 898, 811, 730; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 4.78 (s, 2H), 4.49 (s, 2H), 4.10 (s, 5H), 3.08 (br, 4H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 197.9, 145.7, 142.1, 137.9, 135.9, 129.4, 129.1, 127.5, 127.2, 79.1, 72.4, 69.9, 69.4, 41.4, 29.9, 26.8; MS (EI, 70 eV) m/z = 437.1 (M + H)$^+$. Anal. Calcd (%) for $C_{27}H_{24}FeO_2$: C, 74.32; H, 5.54. Found: C, 74.18; H, 5.70.

1-Ferrocenyl-3-(3-methoxycarbonylbiphenyl)propan-1-one (15): Yield 162.9 mg, 72%; IR (KBr, cm^{-1}) 2949, 1712, 1668, 1453, 1443, 1403, 1380, 1384, 1309, 1242, 1227, 1104, 1087, 1022, 896, 812, 759; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 4.78 (s, 2H), 4.49 (s, 2H), 4.10 (s, 5H), 3.94 (s, 3H), 3.08 (t, J = 4.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 167.2, 141.4, 138.1, 131.6, 130.8, 129.3, 128.9, 128.7, 128.3, 128.2, 127.4, 52.3, 41.5, 29.9; MS (EI, 70 eV) m/z = 453.1 (M + H)$^+$. Anal. Calcd (%) for $C_{27}H_{24}FeO_3$: C, 71.69; H, 5.35. Found: C, 71.81; H, 5.17.

1-Ferrocenyl-3-(3-nitrobiphenyl)propan-1-one (16): Yield 138.4 mg, 63%; IR (KBr, cm^{-1}) 2929, 1660, 1527, 1518, 1455, 1408, 1347, 1255, 1105, 1076, 1029, 867, 833, 737, 721; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 3H), 7.43 (d, J = 7.6 Hz, 2H), 4.79 (s, 2H), 4.50 (s, 2H), 4.10 (s, 5H), 3.10 (t, J = 6.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 148.9, 142.8, 142.5, 136.7, 133.0, 129.8, 129.6, 128.4, 127.4, 121.9, 79.0, 72.5, 69.9, 69.4, 41.3, 29.8; MS (EI, 70 eV) m/z = 440.1 (M + H)$^+$. Anal. Calcd (%) for $C_{25}H_{21}FeNO_3$: C, 68.35; H, 4.82; N, 3.19. Found: C, 68.48; H, 4.61; N, 3.32.

1-Ferrocenyl-3-(pyridin-3-ylphenyl)propan-1-one (17): Yield 110.7 mg, 56%; IR (KBr, cm^{-1}) 2925, 1659, 1454, 1408, 1390, 1255, 1105, 1079, 1027, 1001, 880, 822, 806, 716; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.55 (s, 1H), 7.83 (d, J = 7.2 Hz, 1H), 7.51 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 7.2 Hz, 2H), 4.76 (s, 2H), 4.47 (s, 2H), 4.08 (s, 5H), 3.07 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 148.5, 148.4, 141.9, 136.6, 135.9, 134.3, 129.6, 127.4, 123.7,79.1, 72.4, 69.9, 69.4, 41.4, 29.9; MS (EI, 70 eV) m/z = 396.1 (M + H)$^+$. Anal. Calcd (%) for $C_{24}H_{21}FeNO$: C, 72.93; H, 5.35; N, 3.54. Found: C, 72.85; H, 5.26; N, 3.68.

General Procedure for Synthesis of 6-Aryl-2-ferrocenylquinolines. In a Schlenk tube, a mixture of the acetylferrocene (0.5 mmol), (2-amino-5-bromophenyl)methanol (0.6 mmol), KOH (0.5 mmol), and **1** (0.01 mmol) in dioxane (3 mL) was evacuated and charged with nitrogen. The mixture was heated at 110 °C for 12 h and then allowed to cool to room temperature. The vessel was opened, and arylboronic acids (0.75 mmol), Cs_2CO_3 (1.0 mmol), and $Pd(OAc)_2$ (0.015 mmol) were added to it under nitrogen. The mixture was heated at 110 °C for another 12 h. After removal of the solvent, the residue was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to give the red solid 6-aryl-2-ferrocenylquinolines **19**−**34**. Eluent CH_2Cl_2/ethyl acetate (2:1) for **35**−**40**.

2-Ferrocenyl-6-phenylquinoline (19): Yield 171.1 mg, 91%; IR (KBr, cm^{-1}) 2961, 1593, 1575, 1499, 1485, 1449, 1378, 1337, 1260, 1093, 1020, 799, 757, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−8.12 (m, 2H), 7.92 (d, J = 6.4 Hz, 2H), 7.71 (d, J = 7.6 Hz, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 5.08 (s, 2H), 4.47 (s, 2H), 4.06 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 147.8, 140.8, 138.3, 135.8, 129.5, 129.2, 129.1, 127.6, 127.4, 127.0, 125.4, 120.0, 84.0, 70.6, 69.8, 68.1; MS (EI, 70 eV) m/z = 390.1 (M + H)$^+$. Anal. Calcd (%) for $C_{25}H_{19}FeN$: C, 77.14; H, 4.92; N, 3.60. Found: C, 77.27; H, 4.81; N, 3.69.

2-Ferrocenyl-6-(1-naphthyl)quinoline (20): Yield 197.7 mg, 90%; IR (KBr, cm^{-1}) 2922, 1595, 1498, 1379, 1282, 1105, 1092, 1016, 1001, 819, 791, 773, 734; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.88−7.96 (m, 3H), 7.79−7.84 (m, 2H), 7.41−7.61 (m, 5H), 5.11 (s, 2H), 4.48 (s, 2H), 4.08 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 147.8, 139.8, 138.1, 135.7, 134.0, 132.1, 131.8, 128.8, 128.5, 128.0, 127.4, 126.8, 126.4, 126.1, 126.0, 125.9, 125.6, 120.0, 84.0, 70.6, 69.8, 68.2; MS (EI, 70 eV) m/z = 440.1 (M + H)$^+$. Anal. Calcd (%) for $C_{29}H_{21}FeN$: C, 79.28; H, 4.82; N, 3.19. Found: C, 79.17; H, 4.76; N, 3.32.

2-Ferrocenyl-6-(2-naphthyl)quinoline (21): Yield 193.3 mg, 88%; IR (KBr, cm^{-1}) 2922, 1589, 1502, 1455, 1379, 1272, 1103, 1095, 1000, 878, 842, 812, 742; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.15 (m, 3H), 8.06 (s, 2H), 7.95 (t, J = 9.2 Hz, 2H), 7.88 (m, 2H), 7.61 (d, J = 8.4 Hz, 1H), 7.52 (br, 2H), 5.10 (s, 2H), 4.49 (s, 2H), 4.08 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 147.9, 138.2, 135.9, 133.9, 132.9, 129.5, 129.4, 128.8, 128.4, 127.9, 127.1, 126.6, 126.5, 126.3, 126.2, 125.7, 125.6, 120.1, 83.9, 70.7, 69.9, 68.2; MS (EI, 70 eV) m/z = 440.1 (M + H)$^+$. Anal. Calcd (%) for $C_{29}H_{21}FeN$: C, 79.28; H, 4.82; N, 3.19. Found: C, 79.37; H, 4.68; N, 3.25.

6-Biphenyl-2-ferrocenylquinoline (22): Yield 202.5 mg, 87%; IR (KBr, cm^{-1}) 2924, 1596, 1499, 1485, 1400, 1337, 1262, 1104, 1093, 1026, 1000, 889, 826, 763; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.14 (m, 2H), 7.98 (s, 2H), 7.81 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 7.6 Hz, 2H), 7.67 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 5.10 (s, 2H), 4.49 (s, 2H), 4.08 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 147.9, 140.8, 140.5, 139.6, 137.7, 135.8, 135.6, 129.6, 129.1, 129.0, 127.8, 127.6, 127.5, 127.2, 127.1, 125.3, 120.1, 119.6, 84.0, 70.6, 69.8, 68.1; MS (EI, 70 eV) m/z = 466.1 (M + H)$^+$. Anal. Calcd (%) for $C_{31}H_{23}FeN$: C, 80.01; H, 4.98; N, 3.01. Found: C, 80.13; H, 4.82; N, 3.09.

2-Ferrocenyl-6-(4-methylphenyl)quinoline (23): Yield 185.5 mg, 92%; IR (KBr, cm^{-1}) 2919, 1592, 1516, 1499, 1377, 1335, 1284, 1181, 1105, 1012, 914, 858, 824; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (t, J = 9.6 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 7.6 Hz, 2H), 5.07 (s, 2H), 4.47 (s, 2H), 4.06 (s, 5H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 147.8, 138.2, 137.4, 135.7, 129.8, 129.5, 129.1, 127.3, 127.0, 125.0, 119.9, 84.2, 70.6, 69.8, 69.1, 21.3; MS (EI, 70 eV) m/z = 404.1 (M + H)$^+$. Anal. Calcd (%) for $C_{26}H_{21}FeN$: C, 77.43; H, 5.25; N, 3.47. Found: C, 77.56; H, 5.14; N, 3.53.

2-Ferrocenyl-6-(4-methoxyphenyl)quinoline (24): Yield 195.0 mg, 93%; IR (KBr, cm^{-1}) 2918, 1607, 1517, 1501, 1458, 1283, 1242, 1177, 1104, 1024, 818; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−8.07 (m, 2H), 7.87 (d, J = 12.4 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 12.4 Hz, 1H), 7.01 (d, J = 8.2 Hz, 2H), 5.06 (s, 2H), 4.46 (s, 2H), 4.05 (s, 5H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.4, 147.6, 137.9, 135.6, 133.3, 129.5, 129.0, 128.5, 127.1, 124.6, 119.9, 114.5, 84.1, 70.5, 69.8, 68.1, 55.5; MS (EI, 70 eV) m/z = 420.1 (M + H)$^+$. Anal. Calcd (%) for $C_{26}H_{21}FeNO$: C, 74.48; H, 5.05; N, 3.34. Found: C, 74.62; H, 4.91; N, 3.46.

6-(4-Bromophenyl)-2-ferrocenylquinoline (25): Yield 199.0 mg, 85%; IR (KBr, cm^{-1}) 2917, 1597, 1557, 1508, 1423, 1260, 1103, 1091, 1022, 906, 811, 757; ^{1}H NMR (400 MHz, $CDCl_3$) δ

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8.02−8.08 (m, 3H), 7.74 (d, J = 7.6 Hz, 2H), 7.65 (m, 1H), 7.57 (m, 2H), 7.44−7.49 (m, 2H), 5.07 (s, 2H), 4.46 (s, 2H), 4.05 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 148.4, 135.6, 132.2, 129.5, 129.1, 129.0, 128.9, 128.7, 127.6, 126.8, 125.5, 119.6, 84.1, 70.5, 69.8, 68.1; MS (EI, 70 eV) m/z = 468.0 $(M + H)^+$. Anal. Calcd (%) for $C_{25}H_{18}BrFeN$: C, 64.14; H, 3.88; N, 2.99. Found: C, 64.28; H, 3.75; N, 3.10.

2-Ferrocenyl-6-(4-fluorophenyl)quinoline (26): Yield 169.0 mg, 83%; IR (KBr, cm^{-1}) 2924, 1599, 1514, 1499, 1411, 1281, 1218, 1160, 1106, 1001, 816; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−8.11 (m, 2H), 7.87 (br, 2H), 7.65−7.69 (m, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.18 (t, J = 8.4 Hz, 2H), 5.09 (s, 2H), 4.49 (s, 2H), 4.07 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.5, 159.8, 147.8, 137.2, 136.9, 135.6, 129.6, 129.0, 125.3, 120.1, 116.0, 115.8, 84.0, 70.7, 69.8, 68.1; MS (EI, 70 eV) m/z = 408.1 $(M + H)^+$. Anal. Calcd (%) for $C_{25}H_{18}FFeN$: C, 73.73; H, 4.45; N, 3.44. Found: C, 73.64; H, 4.37; N, 3.62.

6-(4-Acetylphenyl)-2-ferrocenylquinoline (27): Yield 170.4 mg, 79%; IR (KBr, cm^{-1}) 2921, 1673, 1595, 1499, 1413, 1356, 1273, 1258, 1196, 1104, 1014, 961, 821; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.13 (m, 2H), 7.92−7.97 (m, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 8.4 Hz, 1H), 5.09 (s, 2H), 4.50 (s, 2H), 4.07 (s, 5H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 160.4, 148.2, 145.3, 136.8, 136.1, 135.8, 129.8, 129.2, 128.8, 127.5, 126.9, 126.0, 120.2, 83.8, 70.8, 69.8, 68.2, 26.8; MS (EI, 70 eV) m/z = 432.1 $(M + H)^+$. Anal. Calcd (%) for $C_{27}H_{21}FeNO$: C, 75.19; H, 4.91; N, 3.25. Found: C, 75.33; H, 4.88; N, 3.41.

2-Ferrocenyl-6-(3-methoxyphenyl)quinoline (28): Yield 186.6 mg. 89%; IR (KBr, cm^{-1}) 2924, 1595, 1578, 1502, 1479, 1212, 1174, 1104, 1092, 815, 761; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 9.2 Hz, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.91 (s, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 2H), 7.24 (s, 1H), 6.92 (d, J = 8.0 Hz, 1H), 5.07 (s, 2H), 4.46 (s, 2H), 4.05 (s, 5H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 159.7, 147.9, 142.3, 138.1, 135.7, 130.0, 129.5, 129.2, 126.9, 125.5, 120.0, 119.9, 113.2, 113.0, 84.0, 70.6, 69.8, 68.1, 55.5; MS (EI, 70 eV) m/z = 420.1 $(M + H)^+$. Anal. Calcd (%) for $C_{26}H_{21}FeNO$: C, 74.48; H, 5.05; N, 3.34. Found: C, 74.59; H, 4.93; N, 3.42.

2-Ferrocenyl-6-(3-methoxycarbonylphenyl)quinoline (29): Yield 185.3 mg, 83%; IR (KBr, cm^{-1}) 2946, 1718, 1596, 1580, 1504, 1430, 1303, 1236, 1104, 1085, 818, 755, 692; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.05−8.13 (m, 3H), 7.90−7.98 (m, 3H), 7.54−7.61 (m, 2H), 5.09 (s, 2H), 4.49 (s, 2H), 4.07 (s, 5H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 160.1, 148.0, 141.1, 137.1, 135.8, 131.8, 131.0, 129.8, 129.2, 128.9, 128.7, 128.5, 127.0, 125.7, 120.2, 83.9, 70.7, 69.8, 68.2, 52.4; MS (EI, 70 eV) m/z = 448.1 $(M + H)^+$. Anal. Calcd (%) for $C_{27}H_{21}FeNO_2$: C, 72.50; H, 4.73; N, 3.13. Found: C, 72.67; H, 4.54; N, 3.19.

2-Ferrocenyl-6-(3-nitrylphenyl)quinoline (30): Yield 175.9 mg, 81%; IR (KBr, cm^{-1}) 2922, 1597, 1525, 1499, 1347, 1282, 1137, 1093, 1000, 888, 845, 818, 763; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.08−8.15 (m, 2H), 8.03 (d, J = 7.6 Hz, 1H), 7.98 (s, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.60−7.66(m, 2H), 5.09 (s, 2H), 4.51 (s, 2H), 4.08 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 149.0, 148.3, 142.5, 135.8, 135.5, 133.2, 130.1, 130.0, 128.5, 126.9, 126.0, 122.3, 122.1, 120.4, 83.7, 70.8, 69.9, 68.2; MS (EI, 70 eV) m/z = 435.1 $(M + H)^+$. Anal. Calcd (%) for $C_{25}H_{18}FeN_2O_2$: C, 69.14; H, 4.18; N, 6.45. Found: C, 69.07; H, 4.09; N, 6.63.

6-(3,5-Dimethylphenyl)-2-ferrocenylquinoline (31): Yield 189.9 mg, 91%; IR (KBr, cm^{-1}) 2918, 1667, 1592, 1501, 1379, 1278, 1242, 1133, 1093, 1001, 885, 831, 819, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (t, J = 10.0 Hz, 2H), 7.5 (br, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.36 (s, 2H), 7.05 (1, 1H), 5.10 (s, 2H), 4.49 (s, 2H), 4.09 (s, 5H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 147.8, 140.7, 138.6, 138.5, 135.7, 129.4, 129.3, 129.2, 127.0, 125.4, 125.3, 119.9, 84.1, 70.6, 69.8, 68.1, 21.6; MS (EI, 70 eV) m/z = 418.1 $(M + H)^+$. Anal. Calcd (%) for $C_{27}H_{23}FeN$: C, 77.71; H, 5.56; N, 3.36. Found: C, 77.84; H, 5.47; N, 3.31.

2-Ferrocenyl-6-(2-methylphenyl)quinoline (32): Yield 137.0 mg, 68%; IR (KBr, cm^{-1}) 2922, 1595, 1483, 1455, 1378, 1268, 1104, 1094, 1005, 842, 818, 761; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 10.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.29−7.33 (m, 4H), 5.08 (s, 2H), 4.47 (s, 2H), 4.07 (s, 5H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 147.5, 141.5, 139.2, 135.6, 131.4, 130.6, 128.6, 127.6, 127.5, 126.6, 126.0, 119.9, 84.1, 70.6, 69.8, 68.1, 20.7; MS (EI, 70 eV) m/z = 404.1 $(M + H)^+$. Anal. Calcd (%) for $C_{26}H_{21}FeN$: C, 77.43; H, 5.25; N, 3.47. Found: C, 77.51; H, 5.12; N, 3.56.

2-Ferrocenyl-6-(2-methoxyphenyl)quinoline (33): Yield 148.9 mg, 71%; IR (KBr, cm^{-1}) 2921, 1596, 1506, 1484, 1455, 1253, 1179, 1115, 1028, 817, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−8.07 (m, 2H), 7.88 (s, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 5.09 (s, 2H), 4.47 (s, 2H), 4.06 (s, 5H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 156.8, 147.6, 135.9, 135.7, 131.8, 131.2, 130.3, 129.0, 1228.4, 127.8, 126.7, 121.1, 119.6, 111.5, 84.2, 70.5, 69.8, 68.1, 55.8; MS (EI, 70 eV) m/z = 420.1 $(M + H)^+$. Anal. Calcd (%) for $C_{26}H_{21}FeNO$: C, 74.48; H, 5.05; N, 3.34. Found: C, 74.42; H, 4.94; N, 3.47.

6-(2,6-Dimethylphenyl)-2-ferrocenylquinoline (34): Yield 89.7 mg, 43%; IR (KBr, cm^{-1}) 2922, 1595, 1503, 1470, 1378, 1282, 1179, 1129, 1106, 1092, 1001, 891, 819, 769; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 6.4 Hz, 1H), 7.46 (dd, J = 8.4 Hz, 1H), 7.20 (d, J = 7.0 Hz, 1H), 7.15 (d, J = 6.8 Hz, 2H), 5.08 (s, 2H), 4.48 (s, 2H), 4.10 (s, 5H), 2.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 147.3, 141.2, 138.3, 136.2, 135.4, 131.3, 129.0, 127.4, 127.3, 127.2, 126.8, 119.5, 84.1, 70.4, 69.7, 68.0, 21.0; MS (EI, 70 eV) m/z = 418.1 $(M + H)^+$. Anal. Calcd (%) for $C_{27}H_{23}FeN$: C, 77.71; H, 5.56; N, 3.36. Found: C, 77.85; H, 5.43; N, 3.29.

2-Ferrocenyl-6-pyridin-3-ylquinoline (35): Yield 163.9 mg, 84%; IR (KBr, cm^{-1}) 2928, 1596, 1503, 1475, 1420, 1396, 1340, 1247, 1180, 1105, 1050, 1016, 822, 801, 707; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.63 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.91(s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 6.0 Hz, 1H), 5.08 (s, 2H), 4.48 (s, 2H), 4.06 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 148.7, 148.5, 148.1, 136.2, 135.7, 134.7, 134.5, 130.0, 128.6, 126.9, 125.8, 123.8, 120.2, 83.7, 70.7, 69.8, 68.1; MS (EI, 70 eV) m/z = 391.1 $(M + H)^+$. Anal. Calcd (%) for $C_{24}H_{18}FeN_2$: C, 73.86; H, 4.65; N, 7.18. Found: C, 73.97; H, 4.52; N, 7.24.

2-Ferrocenyl-6-pyridin-4-ylquinoline (36): Yield 148.3 mg, 76%; IR (KBr, cm^{-1}) 2925, 1595, 1501, 1420, 1396, 1340, 1246, 1104, 1093, 1016, 891, 821, 801, 706; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 4.8 Hz, 2H), 8.09−8.15 (m, 2H), 8.01 (d, J = 2.8 Hz, 1H), 7.92−7.95 (m, 1H), 7.61−7.65 (m, 3H), 5.10 (s, 2H), 4.51 (s, 2H), 4.08 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 150.4, 148.5, 147.8, 135.8, 134.8, 129.9, 128.1, 126.7, 126.0, 121.7, 120.2, 83.5, 70.8, 69.8, 68.1; MS (EI, 70 eV) m/z = 391.1 $(M + H)^+$. Anal. Calcd (%) for $C_{24}H_{18}FeN_2$: C, 73.86; H, 4.65; N, 7.18. Found: C, 73.99; H, 4.54; N, 7.11.

2-Ferrocenyl-6-(3-methoxycarbonylpyridin-4-yl)quinoline (37): Yield 156.9 mg, 70%; IR (KBr, cm^{-1}) 2927, 1715, 1593, 1501, 1440, 1416, 1303, 1259, 1106, 1012, 918, 829, 808, 742; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.4 Hz, 1H), 8.52 (s, 1H), 8.08−8.16 (m, 3H), 7.97 (d, J = 8.4 Hz, 1H), 7.82 (br, 1H), 7.62 (d, J = 8.4 Hz, 1H), 5.10 (s, 2H), 4.52 (s, 2H), 4.08 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 161.2, 150.3, 149.2, 148.8, 148.7, 135.9, 130.2, 127.9, 126.8, 126.4, 124.7, 123.2, 120.5, 83.5, 70.9, 69.9, 68.2, 53.2; MS (EI, 70 eV) m/z = 449.1 $(M + H)^+$. Anal. Calcd (%) for $C_{26}H_{20}FeN_2O_2$: C, 69.66; H, 4.50; N, 6.25. Found: C, 69.85; H, 4.41; N, 6.17.

2-Ferrocenyl-6-(5-ethoxycarbonylpyridin-3-yl)quinoline (38): Yield 184.9 mg, 80%; IR (KBr, cm^{-1}) 2923, 1714, 1597, 1504, 1455, 1368, 1291, 1239, 1162, 1104, 1023, 835, 823, 807; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 9.12 (s, 1H), 8.60 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.98 (s, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 5.09 (s, 2H), 4.46−4.50 (m, 4H), 4.07 (s, 5H), 1.45 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 160.7, 151.8, 149.6, 148.2, 136.1, 135.7, 135.4, 133.6, 130.2,

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128.4, 126.9, 126.5, 126.1, 120.3, 83.6, 70.8, 69.8, 68.2, 61.7, 14.4; MS (EI, 70 eV) m/z = 463.1 $(M + H)^+$. Anal. Calcd (%) for $C_{27}H_{22}FeN_2O_2$: C, 70.14; H, 4.80; N, 6.06. Found: C, 70.27; H, 4.74; N, 6.01.

2-Ferrocenyl-6-(4-methoxypyridin-3-yl)quinoline (39): Yield 182.8 mg, 87%; IR (KBr, cm^{-1}) 2926, 1597, 1567, 1507, 1458, 1407, 1385, 1341, 1284, 1134, 1091, 1027, 993, 915, 822, 752; ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.05−8.10 (m, 2H), 7.90 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 9.2 Hz, 2H), 7.58 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 5.07 (s, 2H), 4.48 (s, 2H), 4.06 (s, 5H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 159.9, 147.8, 145.4, 137.7, 135.6, 135.0, 129.8, 129.7, 128.6, 127.1, 124.9, 120.1, 111.1, 83.9, 70.7, 69.8, 68.1, 53.7; MS (EI, 70 eV) m/z = 421.1 $(M + H)^+$. Anal. Calcd (%) for $C_{25}H_{20}FeN_2O$: C, 71.44; H, 4.80; N, 6.67. Found: C, 71.60; H, 4.73; N, 6.59.

6-(4-Dimethylaminopyridin-3-yl)-2-ferrocenylquinoline (40): Yield 190.7 mg, 88%; IR (KBr, cm^{-1}) 2921, 1605, 1519, 1497, 1393, 1332, 1267, 1220, 1103, 1092, 1022, 1012, 842, 804; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.01−8.07 (m, 2H), 7.79−7.85 (m, 3H), 7.55 (d, J = 8.4 Hz, 1H), 6.60 (d, J = 8.8 Hz, 1H), 5.06 (s, 2H), 4.46 (s, 2H), 4.05 (s, 5H), 3.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 158.8, 147.4, 146.5, 135.9, 135.8, 135.5, 129.6, 128.3, 127.2, 123.9, 123.6, 119.9, 105.9, 84.1, 70.5, 69.8, 68.0, 38.3; MS (EI, 70 eV) m/z = 434.1 $(M + H)^+$. Anal. Calcd (%) for $C_{26}H_{23}FeN_3$: C, 72.07; H, 5.35; N, 9.70. Found: C, 72.21; H, 5.27; N, 9.79.

■ ASSOCIATED CONTENT

Supporting Information

Copy of ^1H and ^{13}C NMR spectra for all products. X-ray CIF files for **1**, **9**, **13**, **23**, **29**, **32**, and **40**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xubohan@163.com (C.X.), maopingsong@zzu.edu.cn (M.-P.S.).

Notes

The authors declare no competing financial interest.

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