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# Transition Metal-Free Homocoupling of Unactivated Electron-Deficient Azaarenes

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**Abstract:** This work has established the first direct homocoupling of unactivated electron-deficient azaarenes in the presence of TMPMgCl (2,2,6,6-tetramethylpiperidinylmagnesium chloride) and TMEDA (tetramethylethylenediamine). In this process, no transition metal was used while freely available air was employed as the oxidant. The investigated successful substrates included quinolines, isoquinoline, 3-phenylated pyridines, and 2-phenylated quinoxalines, giving moderate to high yields. The homocoupling of quinolines was effectively scaled up to one gram in high yield. Additionally, an iridium complex of 6,6′-dimethyl-2,2′-biquinoline was prepared and characterized as an efficient red-emitting material.

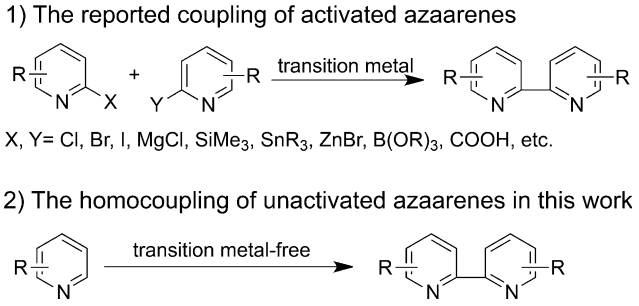
**Keywords:** azaarenes; C–C homocoupling; tetramethylethylenediamine (TMEDA); 2,2,6,6-tetramethylpiperidinylmagnesium chloride (TMPMgCl); transition metal-free conditions

## Introduction

Symmetrical homodimers of electron-deficient azaarenes, such as 2,2′-bipyridines and 2,2′-biquinolines, belong to an array of considerably important compounds with versatile utilities. They are extensively used in light-emitting materials,[1] for labeling biomacromolecules,[2] for bioanalysis,[3] and as ideal ligands in metal-catalyzed organic transformations.[4] The dimers and their derivatives also exhibit various appealing bioactivities.[5]

The methods to prepare these dimers are primarily dependent on transition metal-catalyzed procedures, involving Ullmann,[6] Still,[7] Negishi,[8] Suzuki,[9] and Hiyama couplings,[10] as well as other coupling methods of activated or pre-functionalized electron-deficient azaarenes (Scheme 1).[11] Many transition metals are expensive and toxic to the environment. Removing traces of transition metals from such dimers is challenging, laborious and expensive because of the extremely strong metallic coordination. Therefore, transition metal-free coupling methods are particularly of interest for preparing these homodimers. However, compared to the ever-growing transition metal-free coupling transformations,[12,13] only a few examples of homodimers have been reported to be prepared *via* transition metal-free cross-coupling[14] or homocoupling[15] of activated electron-deficient azaarenes.

Activated or pre-functionalized azaarenes are more inaccessible and expensive than simple unactivated azaarenes. However, only activated azaarenes were successful starting materials for homodimers of electron-deficient azaarenes in previous reports. Direct




**Scheme 1.** Methods for the synthesis of symmetrical dimers of azaarenes.

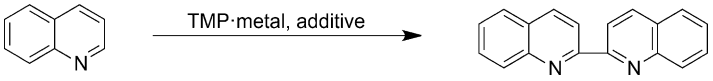
homocoupling of unactivated azaarenes has always been very difficult. Indeed, there are few reports on bipyridines synthesized directly from the homocoupling of unactivated pyridines, and the yields are poor even when using transition metal catalysts.[16] Therefore, the straightforward transition metal-free homocoupling of unactivated azaarenes still remains challenging, though highly desirable. In this work, we report for the first time that TMPMgCl (2,2,6,6-tetramethylpiperidinylmagnesium chloride) can effectively promote the direct transition metal-free homocoupling of unactivated azaarenes (Scheme 1). This new procedure represents a cost-effective, environmentally benign and practical method to prepare homodimers of electron-deficient azaarenes.

## Results and Discussion

We recently demonstrated that the direct transition metal-free coupling of aryl Grignard reagents and electron-deficient azaarenes effectively occurred in the presence of TMEDA (tetramethylethylenediamine).[17] After that work, the homocoupling of quinoline was serendipitously found, while TMPMgCl and TMEDA were occasionally introduced into quinoline. In the report by Knochel and co-workers, we note that the electron-deficient azaarenes are quickly metallated in the presence of the complex TMPMgCl·LiCl, and subsequently, effectively functionalized. However, homodimers are absent in their products,[18] which is dramatically different from our results. This difference in results demonstrates the profound influence of the reaction conditions on the outcome of azaarenes.

Optimization of the reaction conditions began with screening of several complexes of TMP and different basic metallic reagents (Table 1, entries 1–5). The results indicated that the complexes of TMP and MgX (X = Cl, Br) performed much better than the complexes of TMP and lithium or zinc and that the complex TMPMgCl produced the highest yield. The opti-

**Table 1.** Optimization of the reaction conditions.[a]




| Entry | TMP-Metal (equiv.) | Additive (equiv.)[b] | Solvent | Temperature [°C] | Yield [%][c] |
|---|---|---|---|---|---|
| 1 | TMPLi (1.2) | TMEDA (1.0) | THF | r.t. | 40 |
| 2 | TMPMgCl (1.2) | TMEDA (1.0) | THF | r.t. | 71 |
| 3 | TMPMgBr (1.2) | TMEDA (1.0) | THF | r.t. | 55 |
| 4 | TMPMgCl·LiCl (1.2) | TMEDA (1.0) | THF | r.t. | 65 |
| 5 | TMPZnCl·LiCl (1.2) | TMEDA (1.0) | THF | r.t. | -[d] |
| 6 | TMPMgCl (1.0) | TMEDA (1.0) | THF | r.t. | 42 |
| 7 | TMPMgCl (1.5) | TMEDA (1.0) | THF | r.t. | 73 |
| 8 | TMPMgCl (1.8) | TMEDA (1.0) | THF | r.t. | 68 |
| 9 | TMPMgCl (1.5) | TMEDA (1.0) | toluene | r.t. | 64 |
| 10 | TMPMgCl (1.5) | TMEDA (1.0) | $Et_2O$ | r.t. | 11 |
| 11 | TMPMgCl (1.5) | TMEDA (1.0) | dioxane | r.t. | 15 |
| 12 | TMPMgCl (1.5) | TMEDA (1.0) | *t*-BuOMe | r.t. | 10 |
| 13 | TMPMgCl (1.5) | TMEDA (1.0) | THF | 50 | 62 |
| 14 | TMPMgCl (1.5) | TMEDA (1.0) | THF | 60 | 46 |
| 15 | TMPMgCl (1.5) | TMEDA (1.0) | toluene | 60 | 88 |
| 16 | TMPMgCl (1.5) | TMEDA (1.0) | toluene | 80 | 52 |
| 17 | TMPMgCl (1.5) | BDMAEE (1.0) | toluene | 60 | 61 |
| 18 | TMPMgCl (1.5) | HMTA (1.0) | toluene | 60 | 59 |
| 19 | TMPMgCl (1.5) | NMM (1.0) | toluene | 60 | 66 |
| 20 | TMPMgCl (1.5) | DMAP (1.0) | toluene | 60 | 49 |
| 21 | TMPMgCl (1.5) | TEEDA (1.0) | toluene | 60 | 68 |
| 22 | TMPMgCl (1.5) | TMEDA(0) | toluene | 60 | 62 |
| 23 | TMPMgCl (1.5) | TMEDA(0.8) | toluene | 60 | 85 |
| 24 | TMPMgCl (1.5) | TMEDA(1.2) | toluene | 60 | 91 |
| 25 | TMPMgCl (1.5) | TMEDA(1.5) | toluene | 60 | 89 |

[a] 1 mmol quinoline was used. The reaction time was 3 days at room temperature whereas the time was 20 h at elevated temperatures.
[b] BDMAEE = 2,2′-oxybis(*N*,*N*-dimethylethanamine), HMTA = hexamethylenetetramine, DMAP = 4-dimethylamino pyridine, TEEDA = *N*,*N*,*N*′,*N*′-tetraethylethane-1,2-diamine.
[c] Isolated yield.
[d] No coupling product was detected.

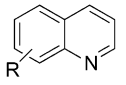
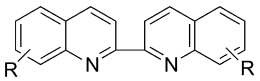
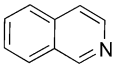
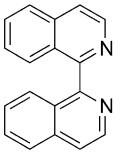
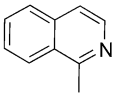
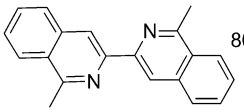
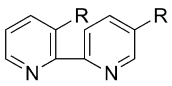
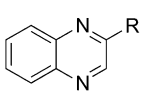
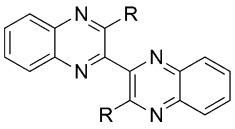
mal TMPMgCl loading of 1.5 equivalents (equiv.) to quinoline was subsequently determined by experiments (entries 2, 6–8). Then, a series of solvents were tested at room temperature, proving THF to be the best solvent (entries 7, 9–12). However, increasing the reaction temperature gradually reduced the homocoupling yield in THF (entries 7, 13 and 14). On the other hand, toluene improved the yield at the elevated temperature of 60 °C, while at 80 °C, the yield decreased (entries 9, 15 and 16). Therefore, toluene was selected as the optimal solvent in view of the yield (entry 14 *vs.* 15). Screening a variety of additives indicated that TMEDA achieved the highest yield (entries 15, 17–21). The ideal TMEDA loading was then experimentally determined to be 1.2 equiv. to quinoline (entries 15, 22–25).

With the optimized reaction conditions in hand, we then investigated the scope of the azaarenes with this new protocol (Table 2). Quinolines with aliphatic substituents achieved high yields except for the 4-methyl substituent (entries 1–5). Quinolines with aromatic substituents led to very complicated results.[19] Similarly, isoquinoline produced 1,1′-biisoquinoline with 87% yield (entry 6). However, the 1-methyl-substituted isoquinoline produced 3,3′-biisoquinoline only in low yield despite the elevated temperature and prolonged reaction time (entry 7). Bipyridine was not produced when starting with only pyridine. 3-Phenylated and chlorinated pyridines could successfully couple to give less sterically hindered symmetrical 2,6′-bipyridines, a series of rarely reported dimers, resulting in good to high yield when using high temperature and long reaction time (entries 8–14). However, coupling of 3-naphthylpyridine became very sluggish and achieved a very low yield with complicated side products (entry 10). Replacing toluene with a mixture of xylenes and raising the temperature increased the coupling yield of 3-(*p*-methylphenyl)pyridine, whereas these effects were not found for other pyridine derivatives (entry 12). Quinoxaline itself is not a suitable substrate because of the very complicated results.[20] 2-Phenylated quinoxalines homocoupled with moderate to good yields (entries 15–20). The electron-withdrawing and electron-donating groups in the benzene rings did not obviously influence the yield of quinoxaline homocoupling. To the best of our knowledge, this is the first report of quinoxaline homocoupling.

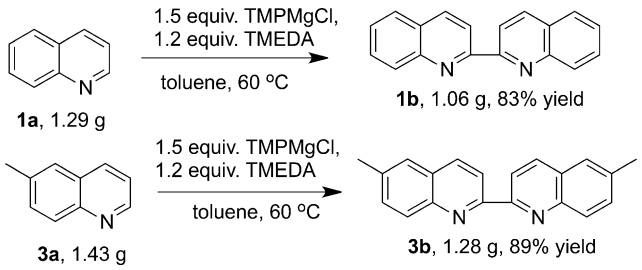
The homocoupling of quinolines was subsequently tested on the gram scale (from 1.0 mmol to 10 mmol). The results showed that this method is practical for preparing 2,2′-biquinolines in a green manner (Scheme 2).

Light-emitting materials are currently very attractive due to their versatile functionalities. Symmetrical homodimers of electron-deficient azaarenes are well-coordinated to numerous metals and are attractive ligands for organic light-emitting materials.[2,21] We then

**Table 2.** The TMPMgCl-promoted homocoupling of azaarenes.[a]

| Entry | Substrate | Product | Conditions and Yield[b] |
|---|---|---|---|
| |  |  | |
| 1 | **1a:** R = H | **1b** | 60 °C, 20 h, 91% |
| 2 | **2a**: R = 4-Me | **2b** | 60 °C, 20 h, 42% |
| 3 | **3a:** R = 6-Me | **3b** | 60 °C, 24 h, 92% |
| 4 | **4a:** R = 7-Me | **4b** | 60 °C, 24 h, 81% |
| 5 | **5a:** R = 6-*n*-Bu | **5b** | 60 °C, 24 h, 90% |
| 6 |  **6a** |  **6b** | 60 °C, 24 h, 87% |
| 7 |  **7a** |  **7b** | 80 °C, 48 h, 17%[c] |
| |  |  | |
| 8 | **8a**: R = Ph | **8b** | 80 °C, 48 h, 87% |
| 9 | **9a**: R = Cl | **9b** | 80 °C, 48 h, 39% |
| 10 | **10a**: R = 2-naphthyl | **10b** | 80 °C, 4 d, 16%[d] |
| 11 | **11a**: R = 4-MeOC$_6$H$_4$ | **11b** | 90 °C, 4 d, 44% |
| 12 | **12a**: R = 4-MeC$_6$H$_4$ | **12b** | 90 °C, 4 d, 64% (78%)[e] |
| 13 | **13a**: R = 3,5-Me$_2$C$_6$H$_3$ | **13b** | 90 °C, 4 d, 42% |
| 14 | **14a**: R = 3-MeOC$_6$H$_4$ | **14b** | |
| |  |  | |
| 15 | **15a**: R = Ph | **15b** | 60 °C, 4 h, 54% |
| 16 | **16a**: R = 4-MeC$_6$H$_4$ | **16b** | 60 °C, 4 h, 62% |
| 17 | **17a**: R = 3,5-Me$_2$C$_6$H$_3$ | **17b** | 60 °C, 36 h, 40% |
| 18 | **18a**: R = 4-MeOC$_6$H$_4$ | **18b** | 60 °C, 36 h, 41% |
| 19 | **19a**: R = 3-MeC$_6$H$_4$ | **19b** | 60 °C, 12 h, 56% |
| 20 | **20a**: R = 3-FC$_6$H$_4$ | **20b** | 60 °C, 18 h, 39% |

[a] *Reaction conditions:* azaarenes 1.0 mmol, TMPMgCl 1.5 mmol, TMEDA 1.2 mmol, toluene as the solvent.
[b] Isolated yield.
[c] Starting material was recovered in 60%. The side products were complicated mixtures.
[d] The side products were complicated mixtures and the starting material was recovered in 26%.
[e] The yield in the parenthesis was achieved in xylene at 110 °C for 4 days.




**Scheme 2.** Gram-scale homocoupling of quinolines.

readily prepared the red-light-emitting Ir-DMBQ(NBT)$_2$ complex **B** from 6,6′-dimethyl-2,2′-biquinoline **3b** and the cyclometallated diiridium complex **A** (Scheme 3).

The iridium complex **B** obviously displays four bands in the UV-vis absorption spectrum at 230, 277, 358 and 456 nm (Figure 1), corresponding to spin-allowed π→π* transition of the ligands and both spin-orbit coupling enhanced $^3$(π→π*) and spin-forbidden $^3$MLCT transitions, respectively.[22] Moreover, the photoluminescence (PL) spectra of the complex clearly exhibit strong red-light emission, with a main peak at 607 nm and a shoulder at 661 nm.

We propose a homocoupling process on the basis of the previous studies (Scheme 4).[14,15,23] Quinoline **1a** is first metallated to form quinolinyl Grignard reagent **I**. The Grignard reagent **I** is then added to the non-metallated quinoline. TMEDA strongly promotes the addition to form intermediate **II**. Finally, isodimer **II** is quickly oxidized to form the symmetrical homodimer, 2,2′-biquinoline **1b**, after the completed reaction mixture is exposed to air. The coupling results of 3-phenylated pyridines to 2,6′-bipyridines strongly support this assumption.

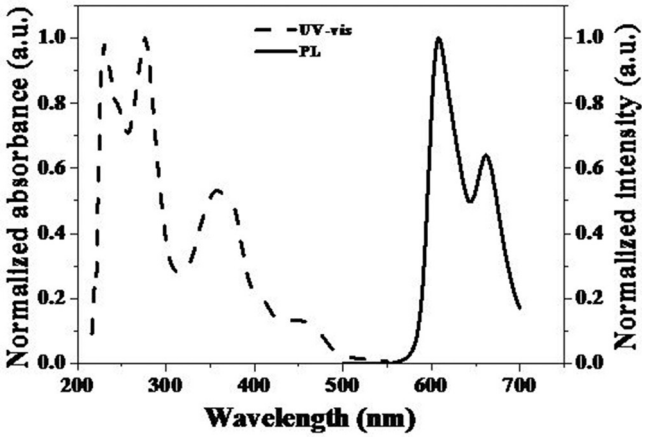
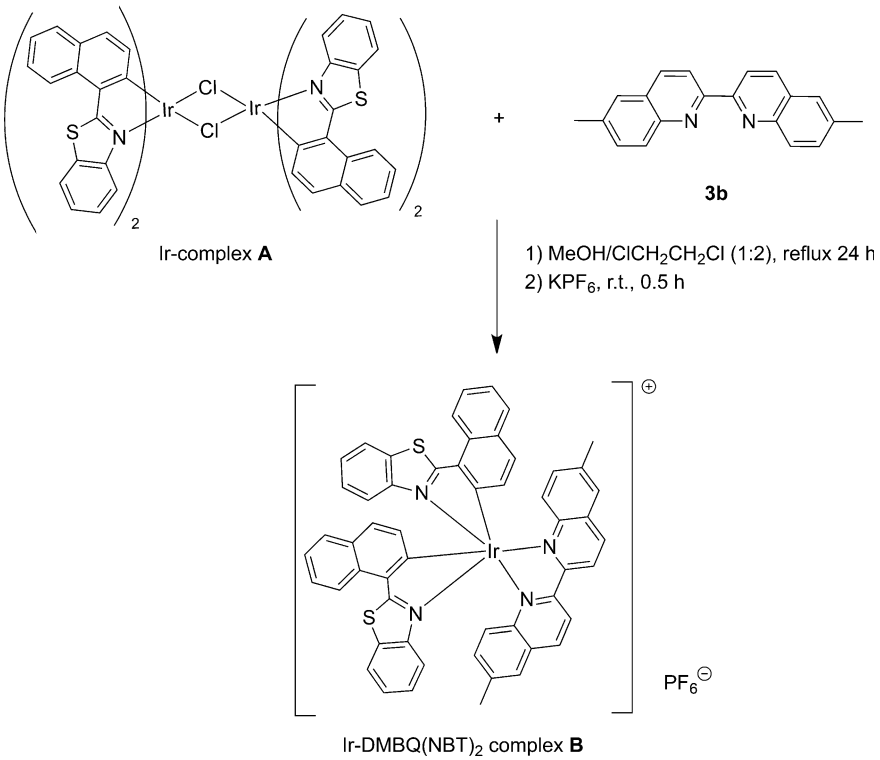


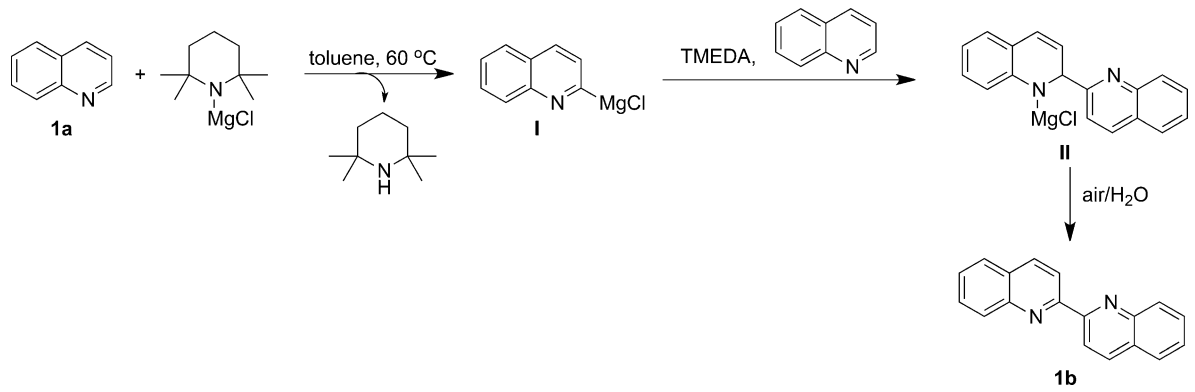

**Figure 1.** Absorption of UV-vis (left axis) and PL (right axis) spectra of the Ir-DMBQ(NBT)$_2$ complex **B** in dichloromethane ($1.0\times10^{-6}$ mol/L).

To further verify the assumption, we introduced excess acetic anhydride and *n*-BuCl into the completed coupling reaction of quinoline and allowed the stirring to proceed for 2 h (Scheme 5). After the usual work-up, the crude product was analyzed directly

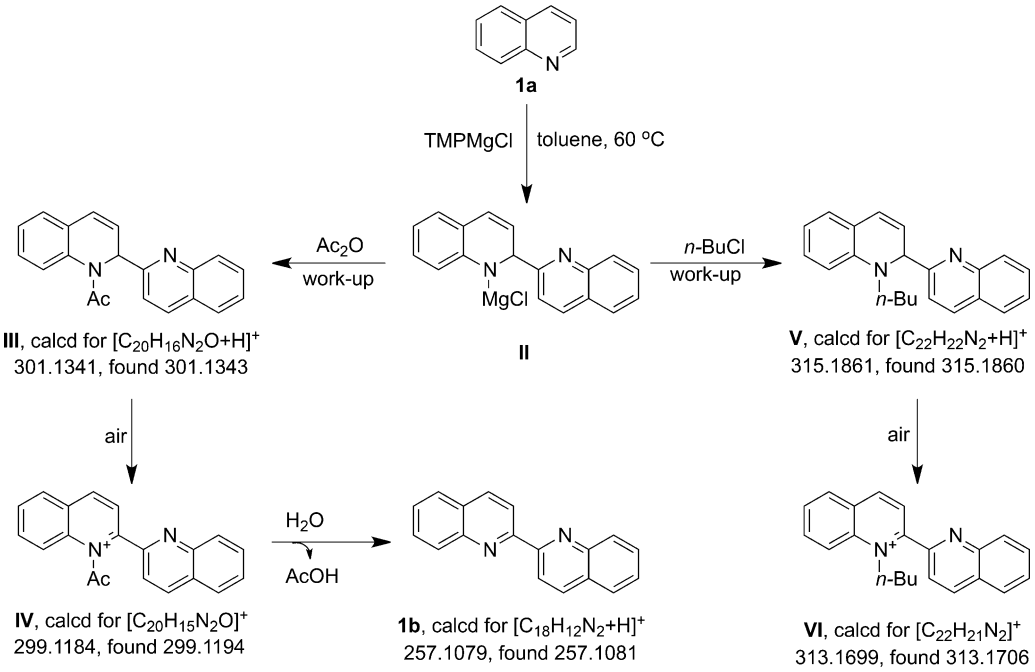



**Scheme 3.** The preparation of iridium complex **B**.




**Scheme 4.** The assumed homocoupling process.




**Scheme 5.** Experiments to confirm intermediate **II**.

with HR-MS (see the Supporting Information, S44 and S45). The process can be explained on the basis of the HR-mass spectrum. For the addition of acetic anhydride, intermediate **II** is transformed into acetated heterodimer **III**, and most of **III** is then quickly oxidized to produce **IV** in air. Subsequently, the acetate group very easily leaves the quinolinyl framework to generate homodimer **1b**. When *n*-BuCl is introduced into the completed coupling reaction, intermediate **II** transforms to **V**, and then **V** is partially oxidized to generate quaternary ammonium salt **VI** by air. These two experiments completely show the presence of intermediate **II** and strongly support the assumption in Scheme 4.

## Conclusions

This is the first time the direct efficient transition metal-free homocoupling of electron-deficient unactivated azaarenes has been successfully demonstrated. The coupling is effectively promoted by readily available TMPMgCl and the additive, TMEDA. The coupled heterodimer is then oxidized in air to form the symmetrical homodimer. This protocol is evidently cost-efficient because unactivated azaarenes as starting materials are inexpensive and easily accessible. Air is used as an effective oxidant, and no transition metal is needed. This not only greatly reduces the expense and waste of the process but also facilitates the purification of the product. In addition, the process can be run on the gram scale, and the dimeric products can be readily used to prepare light-emitting ma-

terials. The homocoupling yields of quinolines and isoquinoline in this work are comparable to yields of the most commonly used Ullmann coupling of halogenated quinolines and isoquinoline.[6] The process in this work also achieved higher yields than the transition metal-catalyzed homocoupling of unactivated electron-deficient azaarenes.[16] In addition, the homocoupling of quinoxalines has not been disclosed in the catalysis of transition metals, and their homocoupling is achieved for the first time in this work. Furthermore, the rarely reported synthesis of symmetrical 2,6′-homodimers of 3-phenylated pyridines is also achieved for the first time using this method. Therefore, this work provides an environmentally benign, cost-efficient and practical alternative method to prepare symmetrical homodimers of electron-deficient azaarenes.

## Experimental Section

### General Remarks

All reactions were performed under an argon or nitrogen atmosphere. Solvents were dried according to the established procedures prior to use. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel. All reagents were purchased from commercial corporations unless otherwise stated. TMPMgCl was freshly prepared from *n*-BuMgCl and TMPH (2,2,6,6-tetramethylpiperidine). Melting points are uncorrected and were recorded on a XT5 melting point apparatus. HR-MS were measured with a Thermo Scientific Orbitrap Elite or a Bruker MaXis 4G mass spectrometer. $^1$H NMR and $^{13}$C NMR spectra were measured on 400 MHz and 100 MHz spectrometers (NMR in $CDCl_3$ with TMS as an internal standard), respectively, and recorded as ppm. UV-vis absorption and photoluminescent spectra were recorded on a Shimadzu UV-2550 spectrometer and on a PerkinElmer LS-55 spectrometer, respectively.

### General Procedure for Homocoupling of Azaarenes

TMPMgCl was freshly prepared from *n*-BuMgCl in THF and TMPH (2,2,6,6-tetramethylpiperidine).[24] Under an argon atmosphere, TMPMgCl (1.5 mmol, 0.8 mmol mL$^{-1}$) in THF was introduced into a dry round-bottom flask and THF was evaporated off under the reduced pressure. The argon was again charged into the flask and 2.0 mL dry toluene were added. TMEDA (1.2 mmol, 91 μL) was introduced at room temperature. The mixture was stirred for 30 min. Then the azaarene (1 mmol) was added. The reaction mixture was vigorously stirred in an oil bath at the temperature stated in Table 2. After completion of the reaction, as checked with TLC, the reaction mixture was cooled to 0 °C and cold water was added dropwise to quench the reaction. The mixture was extracted with dichloromethane three times. The organic layers were combined, washed with brine, dried with anhydrous $Na_2SO_4$. After filtration, the combined filtrates were concentrated in vacuum to give the crude product. The resulting product was purified by silica gel column chromatography (petroleum ether/ethyl acetate).

**2,2′-Biquinoline (1b):**[6] column chromatography, silica gel (petroleum ether/ethyl acetate, 15:1); pale yellow solid; yield: 91% (116.5 mg); mp 190.1–191.4 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.87 (d, $J$ = 8.8 Hz, 2H), 8.35 (d, $J$ = 8.8 Hz, 2H), 8.25 (d, $J$ = 8.4 Hz, 2H), 7.90 (d, $J$ = 8.0 Hz, 2H), 7.77 (t, $J$ = 7.4 Hz, 2H), 7.59 (t, $J$ = 7.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 156.3, 148.0, 136.9, 130.0, 129.7, 128.5, 127.8, 127.1, 119.5.

**4,4′-Dimethyl-2,2′-biquinoline (2b):**[25] column chromatography, silica gel (petroleum ether/ethyl acetate, 15:1); pale yellow solid; yield: 42% (58.3 mg); mp 180.5–181.9 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.68 (s, 2H), 8.26 (d, $J$ = 8.4 Hz, 2H), 8.08 (d, $J$ = 8.4 Hz, 2H), 7.76 (t, $J$ = 7.4 Hz, 2H), 7.60 (t, $J$ = 7.8 Hz, 2H), 2.85 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 156.3, 148.0, 144.3, 130.1, 129.6, 128.5, 127.7, 127.0, 20.0.

**6,6′-Dimethyl-2,2′-biquinoline (3b):**[26] column chromatography, silica gel (petroleum ether/ethyl acetate, 15:1); pale yellow solid; yield: 92% (130.8 mg); mp 253.8–256.8 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.79 (d, $J$ = 8.8 Hz, 2H), 8.24 (d, $J$ = 8.8 Hz, 2H), 8.12 (d, $J$ = 8.8 Hz, 2H), 7.64 (s, 2H), 7.60 (d, $J$ = 8.8 Hz, 2H), 2.57 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 155.7, 146.6, 136.9, 136.1, 131.9, 129.6, 128.5, 126.7, 119.5, 21.8.

**7,7′-Dimethyl-2,2′-biquinoline (4b):**[27] column chromatography, silica gel (petroleum ether/ethyl acetate, 15:1); pale yellow solid; yield: 81% (115.2 mg); mp 273.2–274.9 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.77 (d, $J$ = 8.4 Hz, 2H), 8.29 (d, $J$ = 8.4 Hz, 2H), 8.01 (s, 2H), 7.79 (d, $J$ = 8.4 Hz, 2H), 7.42 (d, $J$ = 8.4 Hz, 2H), 2.61 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 156.4, 148.2, 139.9, 136.5, 129.3, 129.0, 127.4, 126.6, 118.7, 22.0.

**6,6′-Dibutyl-2,2′-biquinoline (5b):** column chromatography, silica gel (PE/EA, 15:1); pale yellow solid; yield: 90% (165.8 mg); mp 135.4–136.4 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.79 (d, $J$ = 8.0 Hz, 2H), 8.25 (d, $J$ = 8.0 Hz, 2H), 8.14 (d, $J$ = 8.0 Hz, 2H), 7.63–7.59 (m, 4H), 2.82 (t, $J$ = 8.0 Hz, 4H), 1.76–1.69 (m, 4H), 1.47–1.39 (m, 4H), 0.97 (t, $J$ = 8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 155.7, 146.8, 141.9, 136.3, 131.3, 129.7, 128.5, 126.1, 119.4, 35.8, 33.5, 22.5, 14.1; HR-ESI MS: $m/z$ = 369.2322, calcd. for $C_{26}H_{28}N_2$ ([M + H]$^+$): 369.2325.

**1,1′-Biisoquinoline (6b):**[6a] column chromatography, silica gel (petroleum ether/ethyl acetate, 5:1); pale yellow solid; yield: 87% (111.5 mg); mp 312.4–315.3 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.73 (d, $J$ = 5.6 Hz, 2H), 7.96 (d, $J$ = 8.0 Hz, 2H), 7.83 (d, $J$ = 5.6 Hz, 2H), 7.77–7.70 (m, 4H), 7.49 (t, $J$ = 7.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 158.2, 142.0, 136.9, 130.5, 127.9, 127.7, 127.3, 127.0, 121.2.

**1,1′-Dimethyl-3,3′-biisoquinoline (7b):** column chromatography, silica gel (petroleum ether/ethyl acetate, 15:1); pale yellow solid; yield: 17% (24.2 mg); mp 217.1–218.5 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.50 (d, $J$ = 5.6 Hz, 2H), 8.27 (d, $J$ = 8.4 Hz, 2H), 7.82 (d, $J$ = 8.4 Hz, 2H), 7.67–7.61 (m, 2H), 7.56 (d, $J$ = 5.6 Hz, 2H), 3.91 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.2, 141.9, 136.2, 129.8, 127.2, 127.1, 125.3, 119.4, 22.8; HR-ESI MS: $m/z$ = 285.1388, calcd. for $C_{20}H_{16}N_2$ ([M + H]$^+$): 285.1386.

**3,3′-Diphenyl-2,6′-bipyridine (8b):** column chromatography, silica gel (petroleum ether/ethyl acetate, 3:1); pale

yellow solid; yield: 87% (134.2 mg); mp 100.1–101.5 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.83 (s, 1H), 8.76 (d, $J$ = 1.0 Hz, 1H), 7.81–7.75 (m, 2H), 7.59 (d, $J$ = 7.2 Hz, 2H), 7.48–7.36 (m, 5H), 7.29–7.28 (m, 3H), 7.23–7.21 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 156.8, 155.6, 148.5, 147.8, 139.5, 138.6, 137.5, 136.6, 135.1, 134.0, 129.3, 129.2, 129.0, 128.3, 128.1, 127.2, 127.0, 124.7, 123.1; HR-ESI MS: $m/z$ = 309.1388, calcd. for $C_{22}H_{16}N_2$ ([M+H]$^+$): 309.1386.

**3,3′-Dichloro-2,6′-bipyridine (9b):**[28] column chromatography, silica gel (petroleum ether/ethyl acetate, 10:1); pale yellow solid; yield: 39% (43.9 mg); mp 114.7–115.9 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.84 (s, 1H), 8.62 (s, 1H), 7.54–7.46 (m, 3H), 7.41 (d, $J$ = 5.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 157.6, 154.9, 149.0, 146.1, 139.0, 132.1, 128.9, 124.8, 123.1.

**3,3′-Di(naphthalen-2-yl)-2,6′-bipyridine (10b):** column chromatography, silica gel (petroleum ether/ethyl acetate, 3:1); pale yellow solid; yield: 16% (33 mg); mp 107.6–109.9 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.93 (s, 1H), 8.82 (d, $J$ = 3.6 Hz, 1H), 8.01 (s, 1H), 7.96–7.82 (m, 7H), 7.72–7.61 (m, 2H), 7.48 (s, 6H), 7.26–7.09 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 156.6, 155.6, 148.6, 148.0, 139.0, 137.2, 136.6, 135.1, 134.7, 134.4, 133.4, 132.8, 132.3, 128.8, 128.2, 128.1, 127.7, 127.6, 126.5, 126.4, 126.3, 126.1, 124.9, 123.2; HR-ESI MS: $m/z$ = 409.1682, calcd. for $C_{30}H_{20}N_2$ ([M+H]$^+$): 409.1680.

**3,3′-Bis(4-methoxyphenyl)-2,6′-bipyridine (11b):** column chromatography, silica gel (petroleum ether/ethyl acetate, 3:1); pale yellow solid; yield: 44% (81.1 mg); mp 143.8–146.8 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.83 (s, 1H), 8.73 (d, $J$ = 3.6 Hz, 1H), 7.78–7.71 (m, 2H), 7.54 (d, $J$ = 8.4 Hz, 2H), 7.40–7.37 (m, 1H), 7.31 (d, $J$ = 8.4 Hz, 1H), 7.15 (d, $J$ = 8.0 Hz, 2H), 7.01 (d, $J$ = 8.4 Hz, 2H), 6.84 (d, $J$ = 8.4 Hz, 2H), 3.85 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 159.8, 158.9, 156.2, 148.2, 147.5, 138.5, 136.2, 134.6, 133.5, 131.8, 130.5, 129.9, 128.1, 124.7, 123.0, 114.5, 113.8, 55.3, 55.2; HR-ESI MS: $m/z$ = 369.1591, calcd. for $C_{24}H_{20}N_2O_2$ ([M+H]$^+$): 369.1593.

**3,3′-Di-*p*-tolyl-2,6′-bipyridine (12b):** column chromatography, silica gel (petroleum ether/ethyl acetate, 3:1); pale yellow solid; yield: 64% (107.7 mg); 78% (131.2 mg); mp 109.2–112.9 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.85 (s, 1H), 8.75 (d, $J$ = 3.6 Hz, 1H), 7.79–7.73 (m, 2H), 7.50 (d, $J$ = 7.2 Hz, 2H), 7.50–7.41 (m, 1H), 7.40–7.26 (m, 3H), 7.10 (s, 4H), 2.40 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 156.4, 155.5, 148.3, 147.7, 138.6, 138.0, 137.0, 136.5, 135.0, 134.6, 133.8, 129.7, 129.2, 129.1, 126.8, 124.7, 123.0, 21.1; HR-ESI MS: $m/z$ = 337.1688, calcd. for $C_{24}H_{20}N_2$ ([M+H]$^+$): 337.1686.

**3,3′-Bis(3,5-dimethylphenyl)-2,6′-bipyridine (13b):** column chromatography, silica gel (petroleum ether/ethyl acetate, 3:1); yellow solid; yield: 42% (76.5 mg); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.83 (s, 1H), 8.74 (d, $J$ = 4.4 Hz, 1H), 7.79–7.74 (m, 2H), 7.39–7.33 (m, 2H), 7.19 (s, 2H), 7.03 (s, 1H), 6.90 (s, 1H), 6.82 (s, 2H), 2.38 (s, 6H), 2.22 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 156.6, 155.6, 148.2, 147.7, 139.3, 138.6, 138.5, 137.7, 137.5, 136.8, 135.2, 133.9, 129.7, 128.8, 127.2, 124.8, 124.6, 122.9, 21.3, 21.2; HR-ESI MS: $m/z$ = 365.2005, calcd. for $C_{26}H_{24}N_2$ ([M+H]$^+$): 365.2012.

**3,3′-Bis(3-methoxyphenyl)-2,6′-bipyridine (14b):** column chromatography, silica gel (petroleum ether/ethyl acetate, 3:1); pale yellow solid; yield: 57% (104.9 mg); mp 36.1–37.4 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.85 (s, 1H), 8.77 (d, $J$ = 4.4 Hz, 1H), 7.82–7.75 (m, 2H), 7.43–7.35 (m, 3H), 7.22–7.16 (m, 2H), 7.10 (s, 1H), 6.94 (d, $J$ = 8.0 Hz, 1H), 6.79 (t, $J$ = 7.2 Hz, 2H), 6.75 (s, 1H), 3.86 (s, 3H), 3.66 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.0, 159.3, 156.8, 155.5, 148.5, 147.8, 140.7, 138.8, 138.4, 136.4, 135.0, 134.1, 130.0, 129.3, 124.6, 123.0, 121.8, 119.5, 114.7, 113.3, 113.2, 112.8, 55.3, 55.0; HR-ESI MS: $m/z$ = 369.1596, calcd. for $C_{24}H_{20}N_2O_2$ ([M+H]$^+$): 369.1598.

**3,3′-Diphenyl-2,2′-biquinoxaline (15b):** column chromatography, silica gel (petroleum ether/ethyl acetate, from 15/1 to 10/1); white solid; yield: 54% (110.8 mg); mp 210.2–211.2 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.39–8.37 (m, 2H), 8.19–8.17 (m, 2H), 7.88–7.85 (m, 4H), 7.21 (t, $J$ = 7.4 Hz, 2H), 7.02 (t, $J$ = 7.6 Hz, 4H), 6.80 (d, $J$ = 7.6 Hz, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 153.2, 152.0, 141.9, 141.1, 137.3, 130.9, 130.2, 129.7, 129.3, 129.0, 128.7, 128.1; HR-ESI MS: $m/z$ = 411.1608, calcd. for $C_{28}H_{18}N_4$ ([M+H]$^+$): 411.1604.

**3,3′-Di-*p*-tolyl-2,2′-biquinoxaline (16b):** column chromatography, silica gel (petroleum ether/ethyl acetate, from 15/1 to 10/1); white solid; yield: 62% (135.9 mg); mp 204.8–205.2 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.37–8.34 (m, 2H), 8.18–8.15 (m, 2H), 7.86–7.84 (m, 4H), 6.84 (d, $J$ = 7.6 Hz, 4H), 6.70 (d, $J$ = 8.0 Hz, 4H), 2.27 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 153.4, 152.2, 141.9, 140.9, 138.8, 134.5, 130.7, 129.9, 129.6, 129.2, 128.9, 128.7, 21.1; HR-ESI MS: $m/z$ = 439.1917, calcd. for $C_{30}H_{22}N_4$ ([M+H]$^+$): 439.1917.

**3,3′-Bis(3,5-dimethylphenyl)-2,2′-biquinoxaline (17b):** column chromatography, silica gel (petroleum ether/ethyl acetate, from 15/1 to 10/1); white solid; yield: 40% (94 mg); mp 199.6–201.3 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.38–8.36 (m, 2H), 8.18–8.16 (m, 2H), 7.87–7.84 (m, 4H), 6.85 (s, 2H), 6.38 (s, 4H), 2.02 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 153.7, 152.4, 141.7, 140.9, 137.4, 137.0, 130.7, 130.3, 129.9, 129.5, 129.1, 127.1, 21.0; HR-ESI MS: $m/z$ = 467.2233, calcd for $C_{32}H_{26}N_4$ ([M+H]$^+$): 467.2230.

**3,3′-Bis(4-methoxyphenyl)-2,2′-biquinoxaline (18b):** column chromatography, silica gel (petroleum ether/ethyl acetate, from 10/1 to 5/1); white solid; yield: 41% (97 mg); mp 152.5–153.5 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.30–8.22 (m, 2H), 8.16–8.11 (m, 2H), 7.87–7.81 (m, 4H), 7.48 (d, $J$ = 8.8 Hz, 4H), 6.85 (d, $J$ = 8.4 Hz, 4H), 3.79 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 153.3, 152.4, 141.9, 141.0, 131.3, 131.2, 130.6, 130.5, 130.4, 130.1, 130.0, 129.6, 55.3; HR-ESI MS: $m/z$ = 471.1815 calcd. for $C_{30}H_{22}N_4O_2$ ([M+H]$^+$): 471.1813.

**3,3′-Di-*m*-tolyl-2,2′-biquinoxaline (19b):** column chromatography, silica gel (petroleum ether/ethyl acetate, from 15/1 to 10/1); white solid; yield: 56% (122.8 mg); mp 207.3–208.0 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.39–8.37 (m, 2H), 8.19–8.17 (m, 2H), 7.87–7.85 (m, 4H), 7.04 (d, $J$ = 7.6 Hz, 2H), 6.85 (t, $J$ = 7.6 Hz, 2H), 6.64 (s, 2H), 6.51 (d, $J$ = 7.6 Hz, 2H), 2.11 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 153.5, 152.2, 141.9, 141.1, 138.0, 137.1, 130.8, 130.0, 129.9, 129.7, 129.4, 129.2, 127.6, 126.0, 21.1; HR-ESI MS: $m/z$ = 439.1923, calcd. for $C_{30}H_{22}N_4$ ([M+H]$^+$): 439.1917.

**3,3′-Bis(3-fluorophenyl)-2,2′-biquinoxaline (20b):** column chromatography, silica gel (petroleum ether/ethyl acetate, from 15/1 to 10/1); green solid; yield: 39% (104.5 mg); mp 125.6–132.4 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.39–8.37

(m, 2H), 8.20–8.18 (m, 2H), 7.92–7.88 (m, 4H), 7.09–6.93 (m, 2H), 6.83 (d, $J=7.6$ Hz, 2H), 6.62 (d, $J=9.2$ Hz, 2H), 6.55 (d, $J=6.8$ Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=$ 164.7, 162.2, 150.4, 143.0, 142.2, 141.8, 139.0, 130.7, 130.6, 130.5, 129.9, 129.7, 129.2, 123.0; HR-ESI MS: $m/z=$ 447.1420, calcd. for $C_{28}H_{16}N_4F_2$ ($[M+H]^+$): 447.1416.

### Synthesis of Ir-DMBQ(NBT)$_2$ Complex B[21]

$IrCl_3\cdot n H_2O$ (1 g, 3.12 mmol) and 2-(naphthalen-1-yl)benzo[*d*]thiazole (NBT, 2.04 g, 7.79 mmol) were introduced into the mixture of 30 mL 2-ethoxyethanol and 10 mL water under nitrogen at room temperature. The reaction temperature was gradually elevated to 135 °C and the reaction was allowed to stir for 24 h at this temperature. The mixture was cooled to room temperature and 30 mL water was added. The red precipitate was collected by filtration, washed twice with water and then a methanol/water mixture (1:2, v/v). The solid was pumped dry to give the crude dimer $[Ir(NBT)_2Cl]_2$ **A**. The crude dimer was directly used for subsequent preparation of Ir-DMBQ(NBT)$_2$ complex **B** without further purification.

6,6′-Dimethyl-2,2′-biquinoline (DMBQ; 142.5 mg, 0.5 mmol) and the prepared dimer $[Ir(NBT)_2Cl]_2$ **A** (0.30 g, 0.2 mmol) were added in a mixed solvent of 1,2-dichloroethane (20 mL) and methanol (10 mL) under the nitrogen atmosphere. The mixture was heated to reflux for 24 h in the dark. After cooling to room temperature, solid $KPF_6$ (1.84 g, 10 mmol) was carefully added in one portion and the mixture was stirred for another 0.5 h at room temperature. A small quantity of water was then added. The mixture was extracted with dichloromethane (50 mL×3). The combined organic phase was washed with water (50 mL×2) and dried over anhydrous $Na_2SO_4$. After filtration, the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by chromatography on silica gel using dichloromethane/methanol (10:1, v/v) as the eluent to give the red powdery Ir-DMBQ(NBT)$_2$ complex **B**; yield: 35% (160 mg). $^1$H NMR (400 MHz, $CDCl_3$): $\delta=9.03$ (d, $J=$ 8.0 Hz, 2H), 8.65 (d, $J=8.0$ Hz, 2H), 8.39 (d, $J=8.0$ Hz, 2H), 7.90 (d, $J=8.0$ Hz, 2H), 7.75 (d, $J=8.0$ Hz, 2H), 7.65–7.59 (m, 4H), 7.44 (t, $J=8.0$ Hz, 2H), 7.33–7.25 (m, 6H), 6.95 (t, $J=8.0$ Hz, 2H), 6.73 (dd, $J=20.0$, 8.0 Hz, 4H), 6.51 (d, $J=8.0$ Hz, 2H), 2.20 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=177.6$, 160.0, 158.4, 147.8, 146.4, 141.2, 139.2, 133.9, 133.0, 132.4, 131.0, 130.9, 130.8, 130.5, 130.2, 129.8, 128.4, 128.2, 127.5, 127.0, 125.9, 124.4, 123.0, 122.7, 121.5, 118.0, 21.1; HR-ESI MS: $m/z=997.2025$, calcd. for $C_{54}H_{36}IrN_4S_2PF_6$ ($[M-PF_6]$): 997.2005.

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## References

[1] a) H.-C. Su, H.-F. Chen, F.-C. Fang, C.-C. Liu, C.-C. Wu, K.-T. Wong, Y.-H. Liu, S.-M. Peng, *J. Am. Chem. Soc.* **2008**, *130*, 3413–3419; b) H. C. Moon, T. P. Lodge, C. D. Frisbie, *J. Am. Chem. Soc.* **2014**, *136*, 3705–3712; c) B. J. Coe, N. R. M. Curati, E. C. Fitzgerald, S. J. Coles, P. N. Horton, M. E. Light, M. B. Hursthouse, *Organometallics* **2007**, *26*, 2318–2329; d) S. Zhang, K. Dokko, M. Watanabe, *Chem. Mater.* **2014**, *26*, 2915–2926; e) A. G. De Crisci, A. J. Lough, K. Multani, U. Fekl, *Organometallics* **2008**, *27*, 1765–1779.

[2] a) E. Wachter, D. K. Heidary, B. S. Howerton, S. Parkin, E. C. Glazer, *Chem. Commun.* **2012**, *48*, 9649–9651; b) K. Adamson, C. Dolan, N. Moran, R. J. Forster, T. E. Keyes, *Bioconjugate Chem.* **2014**, *25*, 928–944; c) A. Chouai, S. E. Wicke, C. Turro, J. Bacsa, K. R. Dunbar, D. Wang, R. P. Thummel, *Inorg. Chem.* **2005**, *44*, 5996–6003; d) K. Suntharalingam, T. C. Johnstone, P. M. Bruno, W. Lin, M. T. Hemann, S. J. Lippard, *J. Am. Chem. Soc.* **2013**, *135*, 14060–14063; e) Q. Zhao, M. Yu, L. Shi, S. Liu, C. Li, M. Shi, Z. Zhou, C. Huang, F. Li, *Organometallics* **2010**, *29*, 1085–1091; f) H. Huang, P. Zhang, B. Yu, Y. Chen, J. Wang, L. Ji, H. Chao, *J. Med. Chem.* **2014**, *57*, 8971–8983.

[3] a) P. D. Compton, J. V. Strukl, D. L. Bai, J. Shabanowitz, D. F. Hunt, *Anal. Chem.* **2012**, *84*, 1781–1785; b) S. Shinoda, K. Yanoa, H. Tsukube, *Chem. Commun.* **2010**, *46*, 3110–3112; c) Z. Xiao, J. Brose, S. Schimo, S. M. Ackland, S. La Fontaine, A. G. Wedd, *J. Biol. Chem.* **2011**, *286*, 11047–11055.

[4] a) J. J. Walsh, G. Neri, C. L. Smith, A. J. Cowan, *Chem. Commun.* **2014**, *50*, 12698–12701; b) K. J. Cavell, M. C. Elliott, D. J. Nielsen, J. S. Paine, *Dalton Trans.* **2006**, 4922–4925; c) Y. Hayashi, S. Santoro, Y. Azuma, F. Himo, T. Ohshima, K. Mashima, *J. Am. Chem. Soc.* **2013**, *135*, 6192–6199; d) K. K. Toh, A. Biswas, Y.-F. Wang, Y. Y. Tan, S. Chiba, *J. Am. Chem. Soc.* **2014**, *136*, 6011–6020; e) X. Mi, M. Huang, J. Zhang, C. Wang, Y. Wu, *Org. Lett.* **2013**, *15*, 6266–6269; f) Y. Suna, M. Z. Ertem, W.-H. Wang, H. Kambayashi, Y. Manaka, J. T. Muckerman, E. Fujita, Y. Himeda, *Organometallics* **2014**, *33*, 6519–6530; g) F. Shirini, M. Abedini, M. Seddighi, O. G. Jolodar, M. Safarpoor, N. Langroodi, S. Zamani, *RSC Adv.* **2014**, *4*, 63526–63532; h) J. C. Tellis, D. N. Primer, G. A. Molander, *Science* **2014**, *345*, 433–436.

[5] a) I. Murakami-Kubo, K. Doh-ura, K. Ishikawa, S. Kawatake, K. Sasaki, J.-i. Kira, S. Ohta, T. Iwaki, *J. Virol.* **2004**, *78*, 1281–1288; b) T. Fukuuchi, K. Okuda, S. Yoshihara, S. Ohta, *J. Health Sci.* **2009**, *55*, 586–592; c) T. Fukuuchi, K. Doh-ura, S. Yoshiharab, S. Ohta, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5982–5987; d) R. Cao, J. Jia, X. Ma, M. Zhou, H. Fei, *J. Med. Chem.* **2013**, *56*, 3636–3644; e) V. Gandin, M. Porchia, F. Tisato, A. Zanella, E. Severin, A. Dolmella, C. Marzano, *J. Med. Chem.* **2013**, *56*, 7416–7430; f) J. López-Ogalla, G. Saiz, F. E. Palomo, *Org. Process Res. Dev.* **2013**, *17*, 120–126; g) B. A. Albani, B. Peña, N. A. Leed, N. A. B. G. de Paula, C. Pavani, M. S. Baptista, K. R. Dunbar, C. Turro, *J. Am. Chem. Soc.* **2014**, *136*, 17095–17101.

[6] a) M. Iyoda, H. Otsuka, K. Sato, N. Nisato, M. Oda, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80–87; b) R. N. Dhital, C. Kamonsatikul, E. Somsook, H. Sakurai, *Catal. Sci. Technol.* **2013**, *3*, 3030–3035; c) A. V. Aksenov, V. I. Goncharov, *Chem. Heterocycl. Compd.* **2008**, *44*, 1491–

  

1492; d) M. Zeng, Y. Du, C. Qi, S. Zuo, X. Li, L. Shao, X.-M. Zhang, *Green Chem.* **2011**, *13*, 350–356; e) K. Masui, H. Ikegami, A. Mori, *J. Am. Chem. Soc.* **2004**, *126*, 5074–5075; f) L.-Y. Liao, X.-R. Kong, X.-F. Duan, *J. Org. Chem.* **2014**, *79*, 777–782; g) L. Jiao, E. Hao, M. Gracüa, H. Vicente, K. M. Smith, *J. Org. Chem.* **2007**, *72*, 8119–8122; h) J. Hassan, V. Penalva, L. Lavenot, C. Gozzi, M. Lemaire, *Tetrahedron* **1998**, *54*, 13793–13804.

[7] a) G. Verniest, X. Wang, N. De Kimpe, A. Padwa, *J. Org. Chem.* **2010**, *75*, 424–433; b) M. Heller, U. S. Schubert, *J. Org. Chem.* **2002**, *67*, 8269–8272; c) U. S. Schubert, C. Eschbaumer, M. Heller, *Org. Lett.* **2000**, *2*, 3373–3376; d) P. F. H. Schwab, F. Fleischer, J. Michl, *J. Org. Chem.* **2002**, *67*, 443–449.

[8] a) J. R. Colombe, S. Bernhardt, C. Stathakis, S. L. Buchwald, P. Knochel, *Org. Lett.* **2013**, *15*, 5754–5757; b) S. A. Savage, A. P. Smith, C. L. Fraser, *J. Org. Chem.* **1998**, *63*, 10048–10051; c) L. R. Moore, D. A. Vicic, *Chem. Asian J.* **2008**, *3*, 1046–1049; d) S.-H. Kim, R. D. Rieke, *Tetrahedron* **2010**, *66*, 3135–3146.

[9] a) S. Sakashita, M. Takizawa, J. Sugai, H. Ito, Y. Yamamoto, *Org. Lett.* **2013**, *15*, 4308–4311; b) H. Matondo, N. Ouhaja, S. Souirti, M. Baboulene, *Main Group Met. Chem.* **2002**, *25*, 163–167.

[10] a) F. Louërat, H. Tye, S. Napier, M. Garrigou, M. Whittaker, P. C. Gros, *Org. Biomol. Chem.* **2011**, *9*, 1768–1773; b) A. S. Manoso, P. DeShong, *J. Org. Chem.* **2001**, *66*, 7449–7455.

[11] a) X. Li, D. Zou, F. Leng, C. Sun, J. Li, Y. Wu, Y. Wu, *Chem. Commun.* **2013**, *49*, 312–314; b) C. K. Haley, C. D. Gilmore, B. M. Stoltz, *Tetrahedron* **2013**, *69*, 5732–5736; c) J.-B. Liu, L. Nie, H. Yan, L.-H. Jiang, J. Weng, G. Lu, *Org. Biomol. Chem.* **2013**, *11*, 8014–8017; d) W. Liu, Y. Li, Y. Wang, C. Kuang, *Org. Lett.* **2013**, *15*, 4682–4685; e) G. Cahiez, C. Chaboche, F. Mahuteau-Betzer, M. Ahr, *Org. Lett.* **2005**, *7*, 1943–1946; f) B.-J. Deelman, W. M. Stevels, J. H. Teuben, M. T. Lakin, A. L. Spek, *Organometallics* **1994**, *13*, 3881–3891.

[12] For recent reviews on transition metal-free coupling reactions, see: a) C.-L. Sun, Z.- J. Shi, *Chem. Rev.* **2014**, *114*, 9219–9280; b) V. P. Mehta, B. Punji, *RSC Adv.* **2013**, *3*, 11957–11986; c) S. S. Bhojgude, A. T. Biju, *Angew. Chem.* **2012**, *124*, 1550–1552; *Angew. Chem. Int. Ed.* **2012**, *51*, 1520–1522; d) T. L. Chan, Y. Wu, P. Y. Choy, F. Y. Kwong, *Chem. Eur. J.* **2013**, *19*, 15802–15814; e) S. Yanagisawa, K. Itami, *ChemCatChem* **2011**, *3*, 827–829; f) Z. Shao, H. Zhang, *Chem. Soc. Rev.* **2012**, *41*, 560–572; g) R. Kumar, E. V. Van der Eycken, *Chem. Soc. Rev.* **2013**, *42*, 1121–1146; h) J. A. Murphy, *J. Org. Chem.* **2014**, *79*, 3731–3746; i) S. Roscales, A. G. Csákÿ, *Chem. Soc. Rev.* **2014**, *43*, 8215–8225.

[13] Z. Peng, N. Li, X. Sun, F. Wang, L. Xu, C. Jiang, L. Song, Z.-F. Yan, *Org. Biomol. Chem.* **2014**, *12*, 7800–7809.

[14] a) S. Wakabayashi, Y. Kubo, T. Takeda, J.-i. Uenishi, S. Oae, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2338–2341; b) W.-C. Chen, Y.-C. Hsu, W.-C. Shih, C.-Y. Lee, W.-H. Chuang, Y.-F. Tsai, P. P.-Y. Chen, T.-G. Ong, *Chem. Commun.* **2012**, *48*, 6702–6704.

[15] a) A. Krasovskiy, A. Tishkov, V. del Amo, H. Mayr, P. Knochel, *Angew. Chem.* **2006**, *118*, 5132–5136; *Angew. Chem. Int. Ed.* **2006**, *45*, 5010–5014; b) K. Inamoto, Y. Araki, S. Kikkawa, M. Yonemoto, Y. Tanaka, Y. Kondo, *Org. Biomol. Chem.* **2013**, *11*, 4438–4441; c) L. G. Vaughan, *J. Organomet. Chem.* **1980**, *190*, C56–C58.

[16] a) T. Kawashima, T. Takao, H. Suzuki, *J. Am. Chem. Soc.* **2007**, *129*, 11006–11007; b) W. H. F. Sasse, *Org. Synth.* **1966**, *46*, 5–10.

[17] a) F.-F. Zhuo, W.-W. Xie, Y.-X. Yang, L. Zhang, P. Wang, R. Yuan, C.-S. Da, *J. Org. Chem.* **2013**, *78*, 3243–3249; b) L. Zhang, L. Sun, Y.-Y. Li, Y. Liu, Y.-X. Yang, R. Yuan, P. Wang, C.-S. Da, *ChemCatChem* **2013**, *5*, 3516–3519; c) Y.-X. Yang, Y. Liu, L. Zhang, Y.-E. Jia, P. Wang, F.-F. Zhuo, X.-T. An, C.-S. Da, *J. Org. Chem.* **2014**, *79*, 10696–10702.

[18] a) A. Krasovskiy, V. Krasovskaya, P. Knochel, *Angew. Chem.* **2006**, *118*, 3024–3027; *Angew. Chem. Int. Ed.* **2006**, *45*, 2958–2961; b) B. Haag, M. Mosrin, H. Ila, V. Malakhov, P. Knochel, *Angew. Chem.* **2011**, *123*, 9968–9999; *Angew. Chem. Int. Ed.* **2011**, *50*, 9794–9824.

[19] 6-Phenylated quinoline was explored as the substrate, but very complicated results were detected. The homocoupling product could not been prepared. It could be detected only with HR-MS: $m/z = 409.1707$, calcd. for $[C_{30}H_{20}N_2+H]^+$: 409.1705 (see the Supporting Information S46).

[20] Complicated product mixtures were detected when quinoxaline was used as the starting material. The homodimer could be detected with HR-MS but could not be prepared for further characterization: $m/z = 259.0978$, calcd. for $[C_{16}H_{10}N_4+H]^+$ 259.0984; $m/z = 281.0794$, calcd. for $[C_{16}H_{10}N_4+Na]^+$ 281.0803 (see the Supporting Information S47).

[21] a) T. Yu, P. Liu, H. Chai, J. Kang, Y. Zhao, H. Zhang, D. Fan, *J. Fluoresc.* **2014**, *24*, 933–943; b) T. Yu, Y. Cao, W. Su, C. Zhang, Y. Zhao, D. Fan, M. Huang, K. Yue, S. Z. D. Cheng, *RSC Adv.* **2014**, *4*, 554–562; c) T. Yu, Y. Shi, H. Chai, L. Niu, P. Liu, Y. Zhao, J. Kang, B. Gao, H. Zhang, *RSC Adv.* **2014**, *4*, 11680–11688; d) G.-G. Shan, H.-B. Li, H.-Z. Sun, H.-T. Cao, D.-X. Zhu, Z.-M. Su, *Dalton Trans.* **2013**, *42*, 11056–11065.

[22] a) H. Rho, G. Park, Y. Ha, Y. Kim, *Jpn. J. Appl. Phys.* **2006**, *45*, 568–573; b) Z. Bao, A. Lovinger, J. Brown, *J. Am. Chem. Soc.* **1998**, *120*, 207–208; c) Y. Wang, N. Herron, V. Grushin, D. LeCloux, V. Petrov, *Appl. Phys. Lett.* **2001**, *79*, 449–451.

[23] a) M. Tobisu, I. Hyodo, N. Chatani, *J. Am. Chem. Soc.* **2009**, *131*, 12070–12071; b) I. Hyodo, M. Tobisu, N. Chatani, *Chem. Asian J.* **2012**, *7*, 1357–1365.

[24] W. Schlecker, A. Huth, E. Ottow, J. Mulzer, *J. Org. Chem.* **1995**, *60*, 8414–8416.

[25] S. Wakabayashi, T. Tanaka, Y. Kubo, J. Uenishi, S. Oae, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3848–3850.

[26] A. G. Osborne, M. L. Staley, *J. Chem. Res.* **1989**, *12*, 388–389.

[27] A. K. Sheinkman, V. N. Kalafat, V. A. Ivanov, N. A. Klyuev, *Khim. Geterotsikl. Soedin.* **1977**, *3*, 385–390.

[28] J. S. Dhau, A. Singh, Y. Kasetti, S. Bhatia, P. V. Bharatam, P. Brandão, V. Félix, K. N. Singh, *Tetrahedron* **2013**, *69*, 10284–10291.

  