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# Palladium catalyzed reductive homocoupling reactions of aromatic halides in dimethyl sulfoxide (DMSO) solution

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ABSTRACT

Biaryls were obtained in good to excellent yields from the palladium catalyzed reductive homocoupling reactions of various aryl iodides and bromides in dimethyl sulfoxide (DMSO) solution without the need for any additional reducing reagents. $Pd(dppf)Cl_2$ is the most effective among the screened palladium catalysts for the homocoupling reactions. Fluorides, carbonates, acetates and hydroxides can be used as bases at promoting the palladium catalyzed reductive homocoupling of aryl halides in DMSO solution. X-ray photoelectron spectroscopic (XPS) analysis shows that the oxidative $Pd^{2+}$(dppf) species can be reduced into the $Pd^0$(dppf) active species by solvent DMSO molecules to furnish the catalytic cycle, indicating that DMSO plays a dual role as both solvent and reducing reagent. A plausible reaction mechanism has been discussed. Elimination of additional reducing reagents will not only reduce the reaction operation cost, but will also simplify the product separation and purification.



## 1. Introduction

Biaryl is a key building block for many biologically significant agrochemicals, pharmaceuticals, and natural products [1]. Also, the biaryl moiety is a valuable building block (monomer) for conductive polymers [2], and is a core structure for liquid crystals [3]. The copper-mediated Ullmann reductive coupling reactions of aromatic halides have been traditionally used to synthesize symmetrical biaryls for over one century [4,5], but these reactions require both high temperature (over 200 °C) and the consumption of a stoichiometric amount of copper. As a result, many functional groups cannot survive such drastic reaction conditions and have had very limited applications in synthesizing the highly functionalized biaryls [6,7].

The palladium catalyzed homocoupling of aromatic halides has been shown as a more convenient and straightforward method for biaryl synthesis than the traditional copper-mediated Ullmann reactions, and it is believed to be catalyzed by palladium (0) ($Pd^0$) active species [8–10], which can be *in situ* regenerated using suitable reducing reagent as the hydrogen-donor and/or electron source [11–13]. A wide variety of reducing reagents have been used to regenerate *in situ* the $Pd^0$ active species, including hydroquinone [8], formate salt [14], hydrogen gas [15], amines [9,16], alcohols [17], zinc [18], indium [19], triphenylarsine [20], etc. The $Pd^0$ active species can also be regenerated using electrochemical reduction [21].

Lemaire and co-workers [22] found that the reductive homocoupling of aromatic halides could be catalyzed by $Pd(OAc)_2$ in dimethylformamide (DMF) solution without the need for any additional reducing reagent. But DeShong and co-workers [23] found that no homocoupling product was formed from the $Pd(OAc)_2$ catalyzed reaction of 4-iodotoluene in DMF solution in the absence of triphenylphosphine. However, the presence of triphenylphosphine was found to have strongly deleterious effect on the $Pd(dba)_2$ catalyzed homocoupling of 4-iodotoluene in DMF solution [23]. Moreover, tetraalkylammonium fluorides were required at promoting the palladium catalyzed reductive homocoupling, and the alkali ($Na^+$, $K^+$ and $Cs^+$) fluoride salts were shown to be ineffective at promoting the homocoupling reactions in DMF solution [23]. On the other hand, little attention has been paid to dimethyl sulfoxide (DMSO) solvent as the reducing reagent for the palladium catalyzed reductive homocoupling of aromatic halides. Albanese et al. [24] reported the allylpalladium dimer catalyzed homocoupling of four aryl iodides and two aryl bromides using anhydrous tetrabutylammonium fluoride base in DMSO solution. As far as we know, this is the only report in the literature for the palladium catalyzed reductive homocoupling in DMSO solution without the need for additional reducing reagents.

In the course of our interests in biaryl intermediate synthesis and its industrial application [25], we found that the palladium catalyzed reductive homocoupling of various aryl iodides and bromides could be carried out in DMSO solution using bases such as

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fluorides, acetates, carbonates and hydroxides without the need for any additional reducing reagents. Elimination of additional reducing reagents will not only reduce the reaction operation cost, but will also simplify the product separation and purification.

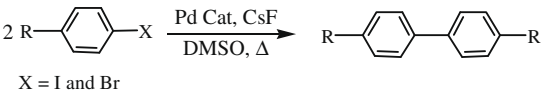
## 2. Results and discussion

A series of the palladium catalysts were tested for the reductive homocoupling reaction of iodobenzene in DMSO solution as a model reaction. In our initial experiments, a set of reaction conditions were selected consisting of 1.0 mmol iodobenzene, 0.10 mmol palladium catalyst, 7.5 mmol cesium fluoride (CsF) in 5.0 ml DMSO under an atmosphere of argon for 3 h. These reaction conditions proved to be highly effective for the homocoupling of aryl iodides and bromides. The biphenyl product was isolated and characterized using NMR and MS analytical techniques (see Section 3 for the detail). Gas chromatography/mass spectroscopy (GC/MS) analysis of the reaction mixtures clearly revealed gradual disappearance of the starting material (aryl halide) and formation of the biphenyl product. The biphenyl yields from the GC/MS analysis are summarized in Table 1 for the tested palladium catalysts. Examination of Table 1 shows that the biphenyl yields are 58.3%, 63.9%, 81.5%, 82.3%, and 96.7% for $PdCl_2$, $Pd(dba)_2$ (dba = dibenzylideneacetone), $Pd(PPh_3)_4$, $Pd(OAc)_2$, and $Pd(dppf)Cl_2$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene], respectively. $Pd(dppf)Cl_2$ is clearly the most effective among the screened palladium catalysts for the reductive homocoupling reactions in DMSO solution. Similar results were also obtained for other aryl iodides and bromides using these palladium catalysts as shown in Scheme 1. In addition, $Pd(dppf)Cl_2$ catalyst is more stable and less air-sensitive, and also has a relatively longer shelf-life compared to the other palladium catalysts, thus it was chosen for the subsequent studies.

Palladium catalyzed reductive reactions usually need suitable bases to neutralize the acidic products generated, otherwise the acidic products will increase the medium acidity and suppress the reactions [8,13,26]. Examination of entry 1 of Table 2 shows that no reductive homocoupling product (biphenyl) was formed in the absence of base, indicating that a suitable base is also essential for the success of the palladium catalyzed reductive homocoupling of aromatic halides in DMSO solution. Although alkali fluoride salts were ineffective at promoting the palladium catalyzed reductive homocoupling of aryl halides in DMF [23], Table 2 clearly shows that the alkali fluorides can be used as efficient bases for the $Pd(dppf)Cl_2$ catalyzed reductive homocoupling of iodobenzene in DMSO. Interestingly, acetates, carbonates, bicarbonates and hydroxides can also be used as bases for the reductive homocoupling reactions. The reaction conditions used in Table 2 were chosen not for the total completion of the homocoupling, so that the biphenyl yields will also represent the relative effectiveness of the bases used. Examination of entries 2–12 of Table 2 shows that fluorides, acetates, carbonates, bicarbonates and hydroxides are comparable as bases at promoting the $Pd(dppf)Cl_2$ catalyzed homocoupling of iodobenzene in DMSO solution. For example, the biphenyl yields of the $Pd(dppf)Cl_2$ catalyzed homocoupling of iodobenzene are 51.0%, 45.7%, and 49.8% for cesium fluoride (CsF), cesium carbonate ($Cs_2CO_3$) and cesium acetate (CsOAc), respectively.

Interestingly, the cesium salts are always more effective than the corresponding potassium salts, which in turn are better than the corresponding sodium salts at promoting the palladium catalyzed reductive homocoupling reactions. The relative effectiveness of these salts is presumably associated with the size of the metal cations as the diameters of the sodium, potassium and cesium cations are 0.90 Å, 1.33 Å and 1.66 Å, respectively [27]. The relatively larger size of the potassium and cesium cations leads to weaker ion-pairing interactions, resulting in higher solubility and basicity. Tetraalkylammoniums ($R_4N^+$) are even larger in size than the cesium cation ($Cs^+$), and indeed their fluorides are excellent bases for the palladium catalyzed reductive reactions [22–24]. The ineffectiveness of the alkali fluoride salts at promoting the palladium catalyzed homocoupling reactions in DMF solution could be caused by the relatively lower solubility of the alkali fluoride salts [23].

In a sharp contrast to when alkali fluoride salts were used as bases, the alkali chloride and bromide salts (Table 2, entries 13–15) have no effect at promoting the $Pd(dppf)Cl_2$ catalyzed reductive homocoupling in DMSO solution. Surprisingly, pyridine (Table 2, entry 16) has also no effect at promoting the palladium catalyzed reductive homocoupling. These results indicate that the basicities of chloride, bromide and pyridine are too weak to neutralize the acidic product(s) generated from the palladium catalyzed reductive homocoupling reactions. Nevertheless, these results are consistent with the equilibrium acidities ($pK_a$) of their conjugate acids in DMSO solution, as the $pK_a$ values of hydrofluoric acid, acetic acid and water are 15.0, 12.3 and 32, respectively [28], whereas the $pK_a$ values of hydrobromic acid, hydrochloric acid and pyridinium cation are 0.9, 1.8 and 3.4, respectively [28]. In other words,




**Scheme 1.**

**Table 1**
Reductive homocoupling reactions of iodobenzene in DMSO solution catalyzed by different palladium catalysts.[a]

| Palladium catalyst | Biphenyl yield (%)[b] |
|---|---|
| $PdCl_2$ | 58.3 |
| $Pd(dba)_2$[c] | 63.9 |
| $Pd(PPh_3)_4$ | 81.5 |
| $Pd(OAc)_2$ | 82.3 |
| $Pd(dppf)Cl_2$[d] | 96.7 |

[a] *Reaction conditions*: 1.0 mmol iodobenzene, 0.10 mmol palladium catalyst, 7.5 mmol cesium fluoride in 5.0 ml DMSO at 120 °C for 3.0 h.
[b] Biphenyl yields, based on the amount of iodobenzene (1.0 mmol), were determined from the GC/MS measurements.
[c] dba: dibenzylideneacetone.
[d] dppf: 1,1′-bis(diphenylphosphino)ferrocene.

**Table 2**
Base effects on $Pd(dppf)Cl_2$ catalyzed reductive homocoupling of iodobenzene in DMSO solution.[a]

| Entry | Base | Biphenyl yield (%)[b] |
|---|---|---|
| 1 | No base | 0 |
| 2 | CsF | 51.0 |
| 3 | KF | 37.9 |
| 4 | NaF | 19.6 |
| 5 | $Cs_2CO_3$ | 45.7 |
| 6 | $K_2CO_3$ | 23.6 |
| 7 | $Na_2CO_3$ | 15.4 |
| 8 | CsOAc | 49.8 |
| 9 | KOAc | 41.5 |
| 10 | NaOAc | 41.0 |
| 11 | NaOH | 31.2 |
| 12 | $NaHCO_3$ | 24.9 |
| 13 | KCl | 0 |
| 14 | KBr | 0 |
| 15 | NaBr | 0 |
| 16 | Pyridine | 0 |

[a] *Reaction conditions*: 1.0 mmol iodobenzene, 0.03 mmol $Pd(dppf)Cl_2$ catalyst, 7.5 mmol base (except for entry 1) in 5.0 ml DMSO at 120 °C for 3.0 h.
[b] Biphenyl yields, based on the amount of iodobenzene (1.0 mmol), were determined from the GC/MS measurements.

fluoride, acetate or hydroxide is at least about 9 p$K$ units ($\sim 10^9$ times) more basic than bromide, chloride or pyridine, implying that the acidic product(s) generated from the palladium catalyzed reductive homocoupling might have p$K_a$ values in the range of 4–12 in DMSO solution.

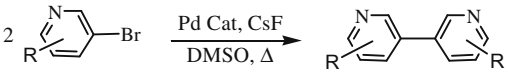
The Pd(dppf)$Cl_2$ catalyzed reductive homocoupling protocol of iodobenzene in DMSO solution is applicable to a wide array of aryl iodides and bromides as evident from Table 3. Examination of Table 3 shows that the Pd(dppf)$Cl_2$ catalyzed reductive homocoupling reactions work well for the aryl halides bearing with either an electron-withdrawing group such as *o*-F (entry 13), *p*-F (entries 4 and 14), *p*-Cl (entries 5 and 15), *p*-$NO_2$ (entry 6), *p*-$CO_2$Et (entry 7) and *p*-$CF_3$ (entry 16), or an electron-donating group such as *o*-$CH_3$ (entry 9), *p*-$CH_3$ (entries 2, 10 and 18), and *p*-$OCH_3$ (entries 3, 11 and 19). For a sterically congested substrate, 2-bromotoluene (Table 3, entry 9), a 2,2′-dimethylbiphenyl yield of 94% was obtained. Furthermore, excellent biaryl yields were also obtained from the Pd(dppf)$Cl_2$ catalyzed reductive homocoupling of the heteroaryl bromides (Table 3, entries 17–19) as shown in Scheme 2.

Attempts to extend the Pd(dppf)$Cl_2$ catalyzed reductive homocoupling to chlorobenzene and fluorobenzene failed, clearly due to the much stronger carbon–chlorine and carbon–fluorine bond strength. The carbon–chlorine (96 kcal/mol) of chlorobenzene and carbon–fluorine (126 kcal/mol) of fluorobenzene are much stronger than the carbon–iodine (65 kcal/mol) of iodobenzene and carbon–bromine (81 kcal/mol) of bromobenzene [29,30]. Therefore, it is not unexpected to find that 2,2′-difluorobiphenyl is formed as the sole homocoupling product from 2-fluorobromobenzene (Table 3, entry 13), and that 4,4′-difluorobiphenyl is formed from 4-fluoroiodobenzene (Table 3, entry 4) and 4-fluorobromobenzene (Table 3, entry 14), respectively. Similarly, 4,4′-dichlorobiphenyl is formed as the sole homocoupling product from 4-chloroiodobenzene (Table 3, entry 5) and 4-chlorobromobenzene (Table 3, entry 15), respectively. Our results presented in Table 3 compare favorably to those obtained by Lemaire and co-workers [22] and DeShong and co-workers [23]. Interestingly, the clean formation of biaryls (Tables 1–3) stands in sharp contrast

**Table 3**
Pd(dppf)$Cl_2$ catalyzed reductive homocoupling of various aryl iodides and bromides in DMSO solution.[a]

| Entry | Substrate | Temperature (°C) | Time (h) | Biaryl yield (%)[b] |
|---|---|---|---|---|
| 1 | $C_6H_5I$ | 120 | 5 | 100 (95) |
| 2 | 4-$CH_3C_6H_4I$ | 120 | 8 | 98.8 (94) |
| 3 | 4-$CH_3OC_6H_4I$ | 120 | 8 | 92.7 (89) |
| 4 | 4-$FC_6H_4I$ | 100 | 8 | 100 (96) |
| 5 | 4-$ClC_6H_4I$ | 100 | 5 | 98.4 (95) |
| 6 | 4-$O_2NC_6H_4I$ | 100 | 12 | 100 (96) |
| 7 | 4-$EtO_2CC_6H_4I$ | 100 | 5 | 92.6 (91) |
| 8 | $C_6H_5Br$ | 120 | 10 | 100 (96) |
| 9 | 2-$CH_3C_6H_4Br$ | 140 | 44 | 94.0 (90) |
| 10 | 4-$CH_3C_6H_4Br$ | 140 | 44 | 84.2 (81) |
| 11 | 4-$CH_3OC_6H_4Br$ | 140 | 44 | 74.2 (71) |
| 13 | 2-$FC_6H_4Br$ | 100 | 1.5 | 94.3 (90) |
| 14 | 4-$FC_6H_4Br$ | 120 | 10 | 100 (98) |
| 15 | 4-$ClC_6H_4Br$ | 140 | 1.5 | 95.8 (93) |
| 16 | 4-$CF_3C_6H_4Br$ | 100 | 5 | 100 (97) |
| 17 | 2-$BrC_5H_4N$[c] | 120 | 8 | 100 (96) |
| 18 | 2-Me-5-$BrC_5H_3N$[d] | 120 | 8 | 95.0 (91) |
| 19 | 2-MeO-5-$BrC_5H_3N$[e] | 120 | 8 | 92.3 (89) |

[a] *Reaction conditions*: 1.0 mmol aromatic halide, 0.1 mmol Pd(dppf)$Cl_2$ catalyst, 7.5 mmol cesium fluoride in 5.0 ml DMSO.
[b] Biaryl yields, based on the amount of aromatic halide (1.0 mmol), were determined from the GC/MS measurements. The isolated yields are listed in the parentheses.
[c] 2-Bromopyridine.
[d] 2-Methyl-5-bromopyridine.
[e] 2-Methoxy-5-bromopyridine.




**Scheme 2.**

to Dyker's observed formation of triaryl products under similar reaction conditions [8,31].

During the reductive homocoupling of aromatic halides, the $Pd^0$ active complex acts as a reducing reagent, and it needs to be regenerated *in situ* from the oxidative $Pd^{2+}$ species in order to continue the catalytic redox cycle, otherwise it needs a stoichiometric amount of the $Pd^0$ active complex [5–14]. Since no additional reducing reagents were added, we first speculated that the formation of halogen such as iodine ($I_2$) or bromine ($Br_2$) resulted from the oxidation of the corresponding iodide or bromide anion. After careful examination of the reaction product mixture, no formation of halogen was detected. Also, no oxidizing products were observed from ligands of the palladium catalysts.

We then turned our attention to the DMSO solvent to regenerate the $Pd^0$ active species from the corresponding oxidative $Pd^{2+}$ species. In order to test this hypothesis, we used X-ray photoelectron spectroscopic (XPS) technique to examine the oxidation states of the palladium catalyst prepared under different reaction conditions. Formation of black precipitate has always been observed from the Pd(dppf)$Cl_2$ catalyzed reductive homocoupling of aromatic halides in DMSO solution (Tables 1–3). The XPS spectrum of the black precipitate is shown in curve **C** of Fig. 1. Interestingly, the same black precipitate could also be obtained from the DMSO solution of Pd(dppf)$Cl_2$ with cesium fluoride at 120 °C for 3 h, and the corresponding XPS spectrum of the black precipitate is shown in curve **B** of Fig. 1. However, no black precipitate was observed for the DMSO solution of Pd(dppf)$Cl_2$ in the absence of cesium fluoride at 120 °C for 3 h, and the XPS spectrum of the treated Pd(dppf)$Cl_2$ catalyst is shown in the curve **A** of Fig. 1. Examination of the curve **A** shows that the treated Pd(dppf)$Cl_2$ catalyst has the identical binding energy ($\sim$338 eV), a characteristic binding energy for the $Pd^{2+}$ species [32], with the fresh Pd(dppf)$Cl_2$ catalyst. But the binding energy peak for the curve **B** just like that for the curve **C** shifts to around 336 eV, a characteristic binding energy for the $Pd^0$ metal [32,33], indicating that the oxidative $Pd^{2+}$ complex has been reduced into the $Pd^0$ active species by solvent DMSO, and the presence of a suitable base (CsF) is essential for the reduction even at

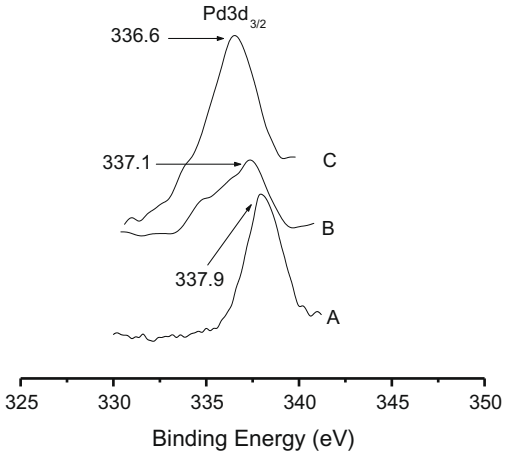
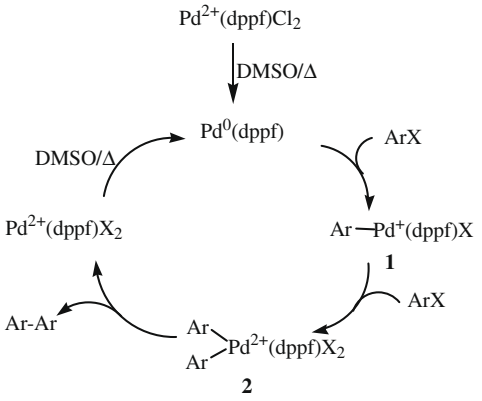



**Fig. 1.** X-ray photoelectron spectra of the palladium catalyst samples prepared under different reaction conditions. (**A**) Pd(dppf)$Cl_2$ in DMSO at 120 °C for 3.0 h. (**B**) Pd(dppf)$Cl_2$ + CsF in DMSO at 120 °C for 3.0 h. (**C**) Pd(dppf)$Cl_2$ + CsF + Iodobenzene in DMSO at 120 °C for 3.0 h.




**Scheme 3.**

the elevated temperature. DMSO solvent has been reported as a reducing reagent in other reaction systems [34–36]. For example by persulfate ion, DMSO could be oxidized into the corresponding radical cation, which could be used as a polymerization catalyst for acrylonitrile [36]. These results provide the conclusive evidence that the $Pd^0$ active complex could be regenerated *in situ* from reduction of the oxidative $Pd^{2+}$ complex in the presence of a suitable base (such as CsF) by solvent DMSO at the elevated temperature for the palladium catalyzed reductive homocoupling as shown in Eq. (1)

$$Pd^{2+}(dppf)Cl_2 + DMSO \xrightarrow[Base]{\Delta} Pd^0(dppf) \quad (1)$$

Formation of the dehalogenation product seems to be negligible for the Pd(dppf)$Cl_2$ catalyzed reductive homocoupling of aromatic halides in DMSO solution (Tables 1 and 3). This conclusion is further supported by the Pd(dppf)$Cl_2$ catalyzed reductive homocoupling of iodobenzene in a sealed reaction system to prevent evaporation of the homocoupling product (benzene). The yields for the hydrogen atom abstraction product (benzene) were determined to be 0.030%, 0.042% and 0.12% for 3 h at temperatures of 80, 100 and 120 °C, respectively. Negligible hydrogen atom abstraction has also been reported in other palladium catalyzed coupling reactions [37–40]. These results suggest that the biphenyl formation proceeds via the concerted mechanism rather than the stepwise mechanism through the aryl radical intermediate, followed by radical dimerization [13,41], since the hydrogen atom abstraction of aryl radicals from solvent DMSO is diffusion-controlled ($1 \times 10^8\ M^{-1}\ s^{-1}$) [42].

A plausible mechanism for the palladium catalyzed reductive homocoupling of aromatic halides is shown in Scheme 3. The $Pd^0$ active complex is regenerated from reduction of the oxidative $Pd^{2+}$ active complex by solvent DMSO, followed by oxidative insertion of aromatic halides to form monoarylpalladium (**1**) and diarylpalladium (**2**) intermediates, similar to the intermediates proposed by Jutand and Mosleh [13] and Rawal and co-workers [8]. Elimination of the biaryl product from the diarylpalladium intermediate **2** yields the oxidative $Pd^{2+}$ species to furnish the catalytic redox cycle.

## 3. Experimental

### 3.1. Chemicals

Solvents and chemicals were all analytical grade or the highest grade commercially available, and they were used without further purification unless otherwise indicated. Palladium compounds [$PdCl_2$, Pd(dppf)$Cl_2$, Pd(OAc)$_2$, Pd($PPh_3$)$_4$ and Pd(dba)$_2$] were purchased from Zhejiang Metallurgical Research Institute. DMSO solvent was treated with potassium hydroxide (KOH) pellet overnight, and then distilled under a reduced pressure before use.

### 3.2. General procedures

The quantitative analysis was performed on an Agilent GC/MS instrument with a programmable split/splitless injector. The injector-port temperature was set at 270 °C. The oven-temperature program was initially set at 140 °C and ramped to 270 °C at 10 °C/min, and maintained for 2 min at every step. NMR spectra were recorded in $CDCl_3$ on an AVANCE III 400 MHz spectrometer. $^1H$ NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak as the internal reference. Multiplicities are reported as: singlet (s), doublet (d), and multiplet (m). Melting points were measured on a Buchi 510 in open capillary tubes and were not calibrated. X-ray photoelectron spectra (XPS) were recorded using a PHI 5000C ESCA spectrometer (PHI Company, USA.).

### 3.3. Sample preparation for X-ray photoelectron spectroscopic (XPS) measurements

A 1.5 inch silicon (100) slice with single polishing face was boiled in sulfuric acid/hydrogen peroxide (v/v, 2/1) for 5 min after rinsed with water, and then dipped in 10% hydrofluoric acid for half a minute. The silicon slice was further cleaned by sonication in ethanol and water for 5 min, respectively. The palladium catalyst samples were then applied on the polished surface of the cleaned slice for XPS measurement. Relative elemental ratios were determined on an Al/Mg anode with a power of 250 W (14.0 kV). The pressure of the analysis chamber was maintained at $<1 \times 10^{-8}$ Torr. The complete scan diagram of 0–12000 eV (currency energy 93.9 eV) was obtained by RBD147 data collecting fiche from US RBD using Auger Scan 3.21 software. The final binding energies were calibrated using C1s of 284.6 eV as the internal reference and the binding energy peaks were secluded using the XPS Peak 4.1 software.

### 3.4. General procedure for palladium catalyzed reductive homocoupling reactions

To a 20 ml of tabular reactor containing 5.0 ml DMSO, aromatic halide (1.0 mmol), a proper amount of palladium catalyst and a proper amount of base were added under an argon atmosphere. The reaction mixture was allowed to stir at 120 °C for 3 h for the optimization studies. GC/MS or/and TLC were used to monitor the homocoupling reaction until the disappearance of the aryl halide starting materials for Table 3. The reaction mixture was quenched with 10 ml water after cooled down to room temperature, and then extracted three times with ethyl acetate ($3 \times 20$ ml). The combined organic layer was washed with water, saturated brine, and then dried with anhydrous $Na_2SO_4$. Solvent was removed under a reduced pressure, and the reaction product was purified by silica gel chromatography with a mixture of petroleum ether and ethyl acetate (v:v, 1:1) as eluent. All of the homocoupling products are known, and they were identified by comparison with their literature melting point, NMR and MS spectral results.

### 3.5. Physical and spectral data of the reductive homocoupling reaction products

Biphenyl is a white solid, m.p. 70–71 °C (lit. 69–70 °C) [43], $^1H$ NMR: $\delta$ 7.60 (d, 4H, $J$ = 7.4 Hz), 7.44 (d, 4H, $J$ = 7.8 Hz), 7.35 (d, 2H, $J$ = 7.3); MS (EI) $m/e$ (%) = 154 ($M^+$, 100%), 76 (7%).

4,4′-Difluorobiphenyl is a white solid, m.p. 87–88 °C (lit. m.p. 89–90 °C) [44], $^1$H NMR: $\delta$ 7.48 (m, 4H), 7.09 (t, 4H, $J$ = 8.6); MS (EI): $m/z$ (%) = 190 ($M^+$, 100%), 170 (20%).

2,2′-Difluorobiphenyl is a white solid, m.p. 117–118 °C (lit. m.p. 119 °C) [45], $^1$H NMR: $\delta$ 7.4–7.35 (m, 4H), 7.24–7.14 (m, 4H); MS (EI): $m/z$ (%) = 190 ($M^+$, 100%), 170 (20%).

4,4′-Dichlorobiphenyl is white solid, m.p. 146–147 °C (lit. 147–148 °C) [13], $^1$H NMR: $\delta$ 7.45 (d, 4H, $J$ = 10.8 Hz), 7.40 (d, 4H, $J$ = 10.8 Hz). MS (EI): $m/z$ (%) = 222 ($M^+$, 100%), 186 (15%), 152 (51%), 111 (5%).

4,4′-Dimethylbiphenyl is white solid, m.p. 122–123 °C (lit. 118–120 °C) [46], $^1$H NMR: $\delta$ 7.66 (d, 4H, $J$ = 8.0 Hz), 7.41 (d, 4H, $J$ = 8.0 Hz), 2.56 (s, 6H); MS (EI): $m/z$ (%) = 182 ($M^+$, 100%), 167 (55%), 152 (12%), 89 (11%).

4,4′-Dimethoxybiphenyl is white solid, m.p. 178–180 °C (lit. 178–179 °C) [44], $^1$H NMR: $\delta$ 7.47 (q, 4H, $J$ = 6 Hz), 6.95 (q, 4H, $J$ = 6 Hz), 3.84 (s, 6H); MS (EI): $m/z$ (%) = 182 ($M^+$, 100%), 167 (55%), 152 (12%), 89 (11%).

4,4′-Dinitrobiphenyl is yellow solid, m.p. 235–237 °C, (lit. 238–239 °C) [47], $^1$H NMR: $\delta$ 8.37 (d, 4H, $J$ = 8.0 Hz), 7.79 (d, 4H, $J$ = 8.0 Hz); MS (EI): $m/z$ (%) = 244 ($M^+$, 100%), 214 (35%), 225 (25%), 152 (65%), 126 (15%).

4,4′-Dicarbethoxybiphenyl is white solid, m.p. 223–225 °C (lit. 224–226 °C) [44], $^1$H NMR: $\delta$ 8.13 (q, 4H, $J$ = 6.0 Hz), 7.7 (q, 4H, $J$ = 6.0 Hz), 4.40 (q, 4H, $J$ = 8.0 Hz), 1.40 (q, 6H, $J$ = 8.0 Hz); MS (EI): $m/z$ (%) = 298 ($M^+$, 100%), 242(15%), 152 (32%).

2,2′-Dimethylbiphenyl is white solid, m.p. 16–17 °C (lit. 18 °C) [48], $^1$H NMR: $\delta$ 7.27–7.20 (m, 6H), 7.11–7.09 (d, 2H, $J$ = 7.2 Hz), 2.05 (s, 6H); MS (EI): $m/z$ (%) = 182 ($M^+$, 70%), 167 (100%), 152 (20%), 89 (11%).

4,4′-Bis(trifluoromethyl)biphenyl is white solid, m.p. 91–93 °C (lit. 92–93 °C) [13], $^1$H NMR: $\delta$ 7.72 (q, 8H, $J$ = 16 Hz). MS (EI): $m/z$ (%) = 190 ($M^+$, 100%), 172 (50%), 85 (10%).

2,2′-Bipyridinyl is white solid, m.p. 71–72 °C (lit. 70–71 °C) [13], $^1$H NMR: $\delta$ 8.67 (q, 2H, $J$ = 1.5 Hz), 8.39 (q, 2H, $J$ = 2.5 Hz), 7.81 (m, 2H), 7.30 (m, 2H); MS (EI): $m/z$ (%) = 156 ($M^+$, 100%), 154 (9%), 153 (15%), 66 (15%).

6,6′-Dimethyl-3,3′-bipyridinyl is white solid, m.p. 118–119 °C (lit. 118–119 °C) [49], $^1$H NMR: $\delta$ 8.39 (d, 2H), 7.80 (q, 2H, $J$ = 8 Hz), 7.394 (t, 2H, $J$ = 7.2 Hz), 2.627 (s, 6H); MS (EI): $m/z$ (%) = 184 ($M^+$, 100%), 156(10%).

6,6′-Dimethoxy-3,3′-bipyridinyl is pinkish solid, m.p. 105–106 °C (lit. 104.5–106 °C) [50], $^1$H NMR: d 8.3 (d, 2H), 7.67 (d, 2H, $J$ = 10 Hz), 6.84 (d, 2H, $J$ = 8.0 Hz), 4.0 (d, 6H, $J$ = 4.0 Hz); MS (EI): $m/z$ (%) = 216 ($M^+$, 100%), 187 (37%), 146 (10%), 78 (9%).

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