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Palladium-Catalyzed Desulfitative Cross-Coupling of Sodium Arylsulfinates with Aryl Bromides and Chlorides: An Alternative Convenient Synthesis of Biaryls

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An alternative method for synthesis of biaryls has been developed through the Pd catalyzed desulfitative coupling reaction of sodium arylsulfinates with aryl bromides and chlorides. The procedure tolerates a variety of functional groups, such as cyano, formyl, acetyl, chloro, methoxy, trifluoromethyl and heteroaromatic unit. The desired products were obtained in moderate to excellent yields under relatively mild reaction conditions without additives, base or co-catalyst.

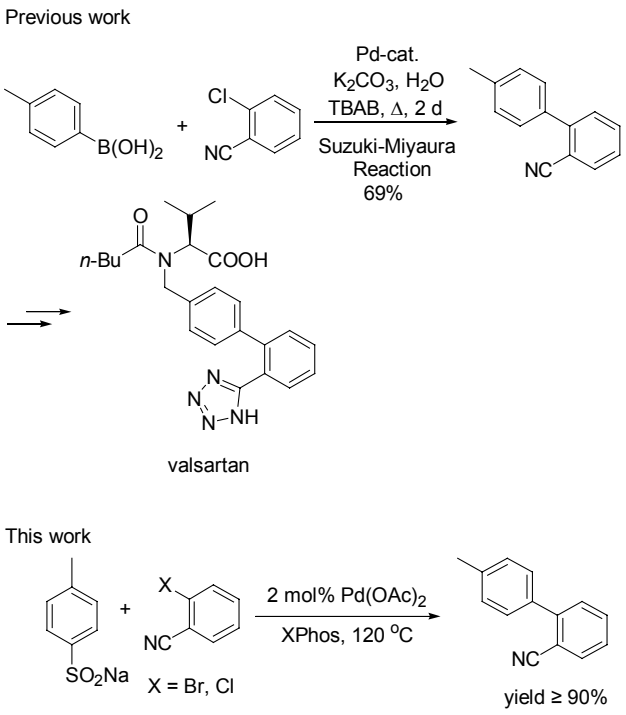
Keywords cross-coupling, desulfination, aryl bromides, aryl chlorides, palladium

Introduction

The biaryl structural motif is a predominant substructure of many pharmaceuticals, biologically active compounds, natural products and functional materials.[1] Among the biphenyl compounds, 2-cyanobiphenyl compounds are key intermediates in the synthesis of angiotensin II receptor antagonists, such as Losartan, Irbesartan, Valsartan and Candesartan.[2] Consequently, many research groups in organic chemistry field have paid attention to developing new and more efficient aryl-aryl bond formation methods for over a century. The Suzuki cross-coupling reaction has been proven to be a powerful method for combining aryl halides and arylboronic acid by giving ready access to biaryl motifs and has been widely applied in various industrial and academic researches (Scheme 1).[2b,3]

As a replacement of organoboron reagents, aryl sulfinic acids and their salts were introduced in the biaryl synthesis through the transition-metal-catalyzed desulfitative coupling in the last decade.[4] Pioneering studies of desulfitative biaryl coupling were reported in 1970 by Garves.[5] In 1992, Sato and Okoshi[6] reported an efficient palladium-catalyzed desulfitative synthesis of biaryls with sodium arylsulfinates and aromatic bromides at 150 ℃ using *N*-methyl-2-pyrrolidone as solvent. In the past decade, a series of desulfitative coupling reactions were reported for the C—C bond formation,[7] which were used to compose sulphones.[8] For example, sodium arylsulfinates were coupled with olefins,[9] azoles,[10] indoles[11] and heteroarenes[12] through C—H activation, and reacted with nitriles[13] and α,β-unsaturated carbonyl compounds[14] via addition reaction. Moreover, Li *et al*.[15] developed another highly efficient catalyst system through rhodium-cata-

Scheme 1 Methods for the synthesis of 4'-methylbiphenyl-2-carbonitrile



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lyzed coupling of aldehydes with sodium arylsulfinates at high temperature (165 ℃). Recently, Forgione *et al.* investigated the desulfitative coupling of lithium thiophene-2-sulfinate with 4-bromobenzonitrile at 170 ℃ under microwave irradiation[16] and also reported the Pd/dppf catalyzed reaction between sodium arylsulfinates and aryl bromides at 185 ℃.[17]

The palladium-catalyzed desulfitative conjugate addition of arylsulfinic acids with α,β-unsaturated carbonyl compounds and the mechanistic studies by ESI-MS have recently been reported by our group.[14] Furthermore, we have developed the palladium-catalyzed desulfitative arylation by C—O bond cleavage of aryl triflates with sodium arylsulfinates.[18] Herein, we aimed to expand the scope of desulfitative coupling reaction with aryl bromides and chlorides to form biaryls under mild conditions. The reaction system has been successfully applied for the synthesis of 4'-methylbiphenyl-2-carbonitrile, an important intermediate for the production of Sartans, under relatively mild reaction conditions without additives, base, or co-catalyst (Scheme 1).

Experimental

General experimental procedures

All reagents were obtained from commercial sources (>99%) and used without further purification unless otherwise noted. Analytical thin layer chromatography (TLC) was carried out with silica gel GF 254 precoated plates. Visualization was accomplished with a UV lamp. The reactions were carried out under N_2 atmosphere and the products were isolated by column chromatography on silica gel (300—400 mesh) using petroleum ether (b.p. 60—90 ℃) and ethyl acetate. All compounds were characterized by ^{1}H NMR, ^{13}C NMR and Mass spectroscopy. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra in $CDCl_3$ with TMS as internal standard were determined. Gas chromatography analyses were performed with an FID detector. GC-MS data were also performed.

Typical procedure for the synthesis of biphenyl-2-carbonitrile (3a)

A flame-dried reaction vessel with a magnetic stirring bar was charged with $Pd(OAc)_2$ (0.9 mg, 0.004 mmol), XPhos (3.8 mg, 0.008 mmol), sodium phenylsulfinate (**1a**, 39.4 mg, 0.24 mmol), 2-bromobenzonitrile (**2a**, 36.2 mg, 0.2 mmol), toluene (1 mL). The mixture was stirred at 120 ℃ under N_2 for 40 h and cooled to room temperature. The resulting solution was extracted with ethyl acetate (25 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under vacuum, the crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, V∶V=1∶10) to give **3a** (32.6 mg, 91%) as a colorless oil. Compounds **3b**—**3o** were prepared using the same method.

Biphenyl-2-carbonitrile (**3a**):[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42—7.52 (m, 5H), 7.54—7.59 (m, 2H), 7.64 (t, J=7.7 Hz, 1H), 7.76 (d, J=7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.4, 118.9, 127.7, 128.9, 130.2, 133.0, 133.9, 145.6, 138.3; GC-MS (EI) *m*/*z*: 179 $[M]^+$.

Biphenyl (**3b**):[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, J=7.2 Hz, 4H), 7.44 (t, J=8.0 Hz, 4H), 7.36—7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.2, 128.7, 127.2, 127.1; GC-MS (EI) *m*/*z*: 154 $[M]^+$.

Biphenyl-4-carbonitrile (**3c**):[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (t, J=7.2 Hz, 1H), 7.49 (t, J=7.2 Hz, 2H), 7.59 (d, J=7.2 Hz, 2H), 7.70 (q, J=8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.0, 119.1, 127.4, 127.9, 128.8, 129.3, 132.7, 139.3, 145.8; GC-MS (EI) *m*/*z*: 179 $[M]^+$.

Biphenyl-4-carbaldehyde (**3d**):[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (t, J=7.2 Hz, 1H), 7.48 (t, J=7.4 Hz, 2H), 7.63 (d, J=7.4 Hz, 2H), 7.75 (d, J=8.2 Hz, 2H), 7.95 (d, J=8.2 Hz, 2H), 10.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 127.5, 127.8, 128.62, 129.2, 130.4, 135.3, 139.8, 147.3, 192.1; GC-MS (EI) *m*/*z*: 181 $[M-H]^+$.

Biphenyl-2-carbaldehyde (**3e**):[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, J=8.0 Hz, 2H), 7.43—7.53 (m, 5H), 7.64 (td, J=7.2, 1.2 Hz, 1H), 8.03 (dd, J=8.0, 0.8 Hz, 1H), 9.98 (d, J=0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 127.7, 128.0, 128.3, 128.6, 130.3, 130.9, 133.7, 133.9, 137.9, 146.2,192.6; GC-MS (EI) *m*/*z*: 181 $[M-H]^+$.

1-(Biphenyl-4-yl)ethanone (**3f**):[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.64 (s, 3H), 7.40 (t, J=7.0 Hz, 1H), 7.47 (t, J=7.6 Hz, 2H), 7.63 (d, J=7.8 Hz, 2H), 7.68 (d, J=8.1 Hz, 2H), 8.03 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.9, 127.39, 127.44, 128.40, 129.09, 129.12, 136.0, 140.0, 145.9, 198.0; GC-MS (EI) *m*/*z*: 196 $[M]^+$.

4-Methoxybiphenyl (**3g**):[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.85 (s, 3H), 6.97 (t, J=8.9 Hz, 2H), 7.30 (t, J=7.3 Hz, 1H), 7.42 (t, J=7.6 Hz, 2H), 7.47—7.56 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 127.9, 55.5, 114.4, 126.8, 126.9, 128.3, 128. 9, 133.9, 141.0, 159.3; GC-MS (EI) *m*/*z*: 184 $[M]^+$.

2-Methoxybiphenyl (**3h**):[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.79 (s, 3H), 6.94—7.05 (m, 2H), 7.31 (t, J=6.6 Hz, 3H), 7.40 (t, J=7.2 Hz, 2H), 7.52 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.7, 55.7, 111.4, 121.0, 127.1, 128.1, 128.8, 129.7, 130.9, 131.0, 138.7, 156.6; GC-MS (EI) *m*/*z*: 184 $[M]^+$.

4'-Methylbiphenyl-2-carbonitrile (**3j**):[2b] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.41 (s, 3H), 7.29 (d, J=8.0 Hz, 2H), 7.51—7.38 (m, 4H), 7.62 (t, J=8.0 Hz, 1H), 7.74 (d, J=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 127.4, 128.8, 129.6, 130.1, 132.9, 133.9, 135.4, 138.8, 145.7; GC-MS (EI) *m*/*z*: 193 $[M]^+$.

4'-Methoxybiphenyl-2-carbonitrile (**3k**):[25] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.86 (s, 3H), 6.96—7.09 (m, 2H), 7.39 (t, J=8.0 Hz, 1H), 7.47—7.52 (m, 3H), 7.61 (t, J=8.0 Hz, 1H), 7.74 (d, J=8.0 Hz, 1H); ^{13}C NMR (100

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MHz, $CDCl_3$) δ: 55.5, 111.2, 114.4, 119.2, 127.2, 130.0, 130.2, 130.7, 132.9, 133.9, 145.4, 160.2; GC-MS (EI) *m*/*z*: 209 $[M]^+$.

4'-Chlorobiphenyl-2-carbonitrile (**3l**):[26] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44—7.52 (m, 6H), 7.65 (t, J= 7.7 Hz, 1H), 7.76 (d, J=7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.3, 118.6, 128.0, 129.1, 130.1, 130.2, 133.1, 134.0, 135.2, 136.7, 144.3; GC-MS (EI) *m*/*z*: 213 $[M]^+$.

4'-(Trifluoromethoxy)biphenyl-2-carbonitrile (**3m**):[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J=8.0 Hz, 2H), 7.45—7.52 (m, 2H), 7.59 (d, J=8.0 Hz, 2H), 7.67 (t, J=7.6 Hz, 1H), 7.78 (d, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.4, 118.6, 121.3, 128.2, 130.2, 130.5, 133.2, 134.0, 136.8, 144.2, 149.8; GC-MS (EI) *m*/*z*: 263 $[M]^+$.

2-(Thiophen-2-yl)benzonitrile (**3n**):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15 (td, J=5.2, 0.8 Hz, 1H), 7.38 (td, J=8.0, 0.8 Hz, 1H), 7.43 (dd, J=5.2, 0.8 Hz, 1H), 7.58—7.65 (m, 3H), 7.73 (d, J=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.2, 119.0, 127.5, 127.7, 128.4, 129.9, 133.1, 134.5, 137.7, 139.6; GC-MS (EI) *m*/*z*: 185 $[M]^+$.

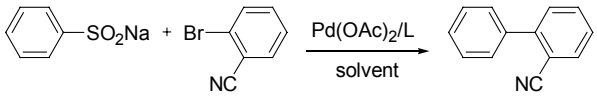
4-(Trifluoromethyl)biphenyl (**3o**):[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (t, J=7.3 Hz, 1H), 7.48 (t, J=7.3 Hz, 2H), 7.57—7.63 (m, 2H), 7.70 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.9, 125.87, 125.90, 127.5, 127.6, 128.4, 129.2, 140.0, 144.9; GC-MS (EI) *m*/*z*: 222 $[M]^+$.

Results and Discussion

Initially, the potential of Pd-catalyzed desulfitative cross-coupling reaction of sodium phenylsulfinate (**1a**) with 2-bromobenzonitrile (**2a**) under nitrogen gas atmosphere has been investigated as a model reaction (Table 1). However, only 25% desired coupling product was detected by GC from the experiment performed by using $Pd(OAc)_2$/dppe in diglyme at 120 ℃ (Table 1, Entry 1). Next, various ligands were screened. Phosphine-type ligands, such as dppp, were found to be more active than nitrogen-type ligands 2,2'-bipyridine (Table 1, Entries 6, 8—10). Screening of solvents revealed that toluene was the best solvent by achieving 82% GC yield at 130 ℃ (Table 1, Entries 1—6, 12). Further experiments showed that the yields were not improved by addition of the base, such as CaO, Na_2CO_3 and K_2CO_3 (Table 1, Entries 13—15). Using the biaryl phosphine-type ligand XPhos and prolonging the reaction time resulted in biphenyl-2-carbonitrile (**3a**) in 99% GC yield (Table 1, Entry 16).

With the optimized reaction conditions in hand (Table 1, Entry 16), we tested a wide range of sodium arylsulfinates and aryl bromides to evaluate the group tolerance (Table 2). As shown in Table 2, the system tolerated many strong electron-withdrawing groups, such as cyano, formyl and acetyl, and gave the corresponding coupling products in moderate to good yields (Table 2, **3a**, **3c—3f**). Phenyl bromide gave the desired product

Table 1 Optimization of the reaction conditions[a]



1a **2a** **3a**

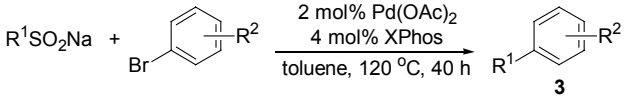
Entry	Ligand	Dosage of ligand/mol%	Solvent (V : V)	Yield[b]/%
1	dppe	2	Diglyme	25
2	dppe	2	NMP	43
3	dppe	2	NMP/diglyme (1 : 3)	28
4	dppe	2	NMP/diglyme (1 : 1)	33
5	dppe	2	NMP/diglyme (3 : 1)	46
6	dppe	2	Dioxane	47
7	dppe	2	DMF	31
8	dppf	2	Dioxane	24
9	dppp	2	Dioxane	77
10	2,2'-Bipyridine	2	Dioxane	N.R
11[c]	dppp	2	Dioxane	99 (90[d])
12[e]	dppp	2	Toluene	82
13[f]	dppp	2	Toluene	34
14[g]	dppp	2	Toluene	81
15[h]	dppp	2	Toluene	33
16[i]	XPhos	4	Toluene	99 (91[d])

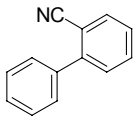
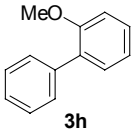
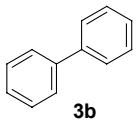
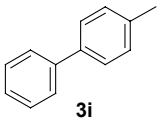
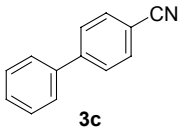
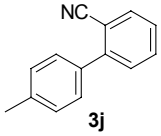
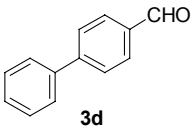
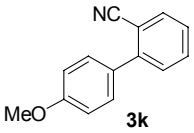
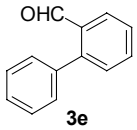
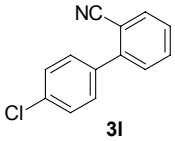
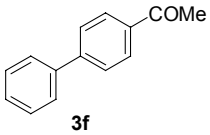
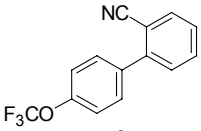
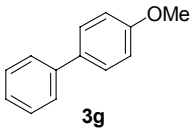
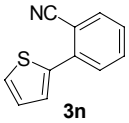
[a] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (2 mol%), and ligand in a solvent (1 mL) under N_2 for 24 h at 120 ℃ unless otherwise noted. [b] GC yield based on **2a**. [c] 150 ℃ for 12 h. [d] Yield after column chromatography. [e] 130 ℃. [f] 2 equiv. CaO, 130 ℃. [g] 2 equiv. Na_2CO_3, 130 ℃. [h] 2 equiv. K_2CO_3, 130 ℃. [i] 40 h.

in excellent yield (Table 2, **3b**). In addition, steric effects of groups at the *ortho*-position did not show much influence on the reaction. Aryl bromides bearing electron-donating groups, such as methoxy, methyl were tolerated well and generated the desired products in moderate yields (Table 2, **3g—3i**). Relatively low yields observed with the presence of the methoxy group were due to the precipitation of Pd black, which could be improved by increasing the amount of catalyst and the reaction temperature. Furthermore, a series of functional groups of sodium arylsulfinates were investigated under the given conditions and proven to react smoothly with 2-cyanophenyl bromide, giving the products **3m** and **3n** in yields of 92% and 75%, respectively. The electron-withdrawing group chloro was also tolerated well and generated **3l** in 80% yield.

The cross-coupling reactions of less active aryl chlorides have also been investigated under the optimized conditions (2 mol% $Pd(OAc)_2$, 4 mol% XPhos, toluene, N_2, 120 ℃, 40 h) (Table 3). The protocol has been proven to be effective for the coupling of a range of aryl

Table 2 Reaction scope of various aryl bromides[a]

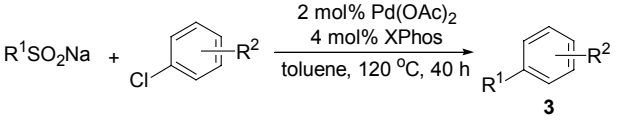


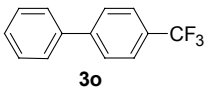
Product	Yield/%	Product	Yield/%
 **3a**	91	 **3h**	53[b]
 **3b**	95	 **3i**	68[c]
 **3c**	51	 **3j**	90
 **3d**	76	 **3k**	45
 **3e**	65	 **3l**	80
 **3f**	68	 **3m**	92
 **3g**	67[b]	 **3n**	75

[a] Reaction conditions: aryl bromides (0.2 mmol), sodium arylsulfinates (0.24 mmol), $Pd(OAc)_2$ (2 mol%), XPhos (4 mol%) and toluene (1 mL) in a sealed tube stirred at 120 ℃ for 40 h under N_2, yield after column chromatography. [b] $Pd(OAc)_2$ (3 mol%), XPhos (6 mol%) at 130 ℃. [c] GC yield based on aryl bromide.

chlorides bearing strong electron-withdrawing groups including cyano, formyl, acetyl and trifluoromethyl, giving the corresponding products in moderate to excellent yields (Table 3, **3a**, **3d**—**3f**, **3o**). Phenyl chloride also gave the desired product in moderate yield (Table 3, **3b**). **3a** was generated in 84% yield with 2-cyanophenyl chloride as substrate, indicating that steric hindrance has little effect on the reaction. Similarly, the reaction of substrate bearing methoxy group resulted in lower yield of 43% (Table 3, **3k**). Gratifyingly, this method was

Table 3 Reaction scope of various aryl chlorides[a]



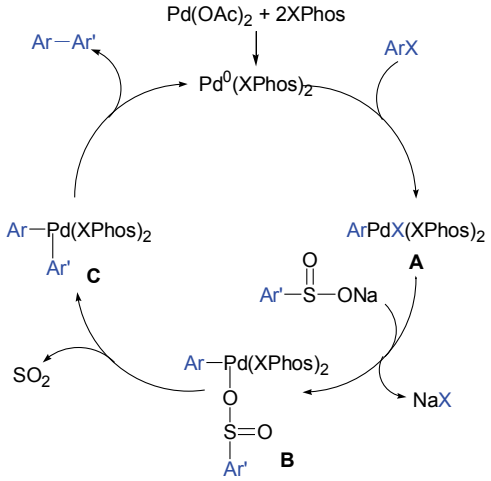
Product	Yield/%	Product	Yield/%
3a	84	**3k**	43
3b	55	**3l**	78
3d	70	**3m**	93
3e	62	**3n**	79
3f	58	 **3o**	77
3j	95		

[a] Reaction conditions: aryl chlorides (0.2 mmol), sodium arylsulfinates (0.24 mmol), $Pd(OAc)_2$ (2 mol%), XPhos (4 mol%) and toluene (1 mL) in a sealed tube stirred at 120 ℃ for 40 h under N_2, yield after column chromatography.

suitable for the coupling reaction of substituted arylsulfinates and heterocyclic aromatic sulfinate with 2-cyanophenyl chloride and resulted in desired products in good to excellent yields (Table 3, **3l**—**3n**).

A plausible mechanism to rationalize this transformation is illustrated in Scheme 2. At first, catalyst $Pd^0(XPhos)_2$, is generated in situation from the anions $Pd(OAc)_2$ and the phosphine XPhos.[27] Initial oxidative addition of the Pd(0) complex into the aryl halide bond followed by a ligand exchange from halide to sulfinate produces Pd(II) sulfinic intermediate **B**.[14] Next, **B** undergoes desulfination to generate the four-coordinate palladium(II) **C**. At last, the catalytic cycle is completed by reductive elimination of intermediate **C**, generating the aryl-aryl and $Pd^0(XPhos)_2$.

Scheme 2 Proposed mechanism for palladium-catalyzed reaction of sodium arylsulfinates with aryl halides



Conclusions

In summary, we have reported a novel palladium-

catalyzed desulfitative coupling reaction of sodium arylsulfinates with aryl bromides and chlorides for the construction of C—C bonds. In the presence of only 2 mol% amount of $Pd(OAc)_2$ as catalyst and XPhos as ligand, either aryl bromides or chlorides easily reacted with sodium arylsulfinates at 120 ℃, and resulted in corresponding biaryls in moderate to excellent yields. Broad functional groups, such as cyano, formyl, acetyl, chloro, methoxy, trifluoromethyl and heteroaromatic are tolerated under relatively mild conditions. This method provided an alternative route for the synthesis of unsymmetrical biaryls.

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