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Synthesis of 4-sulfonatobenzylphosphines and their application in aqueous-phase palladium-catalyzed cross-coupling

Jane N. Moore, Nicholas M. Laskay, Kevin S. Duque, Steven P. Kelley, Robin D. Rogers, Kevin H. Shaughnessy*

Department of Chemistry, The University of Alabama, Box 870336, Tuscaloosa, AL 35487-0336, USA

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ABSTRACT

Aqueous-biphasic catalysis offers the potential for safer and more environmentally sustainable synthetic processes. In addition, hydrophilic supporting ligands allow homogeneous catalysts to be readily separated from organic products and potentially reused. The synthesis of two new water-soluble ligand precursors, di-*tert*-butyl(4-sulfonatobenzyl)phosphonium and di-1-adamantyl(4-sulfonatobenzyl)phosphonium, are reported. The air-stable, zwitterionic phosphonium salts were prepared by the reaction of dialkylphosphines with ethyl 4-bromomethylbenzenesulfonate, which results in a one-pot alkylation followed by deprotection of the ethyl sulfonate. This methodology provides an operationally simpler route to sulfonated benzylphosphines than electrophilic sulfonation. The new phosphine ligands were applied to aqueous-phase Suzuki and Sonogashira couplings of aryl bromides.

Introduction

Water has received significant attention as a reaction medium in metal-catalyzed reactions because of its numerous attractive properties compared to traditional organic solvents [1–4]. Water is nonflammable, nontoxic, renewable, and widely available. Water has also been considered as an environmentally friendly solvent due these many beneficial properties. Reactions run in water are not inherently environmentally friendly, however; as aqueous waste streams with organic contaminants represent their own disposal challenges. For metal-catalyzed reactions, water offers the potential to easily separate hydrophilic precious metal catalysts from organic product streams for potential reuse. Finally, water has been shown to promote organic reactions of hydrophobic substrates in many reactions [5].

Palladium-catalyzed cross-coupling reactions have become widely used tools for construction of carbon–carbon and carbon-heteroatom bonds [6,7]. Significant research effort has identified several highly effective classes of ligands, such as sterically demanding trialkylphosphines (P*t*-Bu_3, Ad_2PBu) [8], dialkylbiarylphosphines (X-phos) [9], and *N*-heterocylic carbenes (IMes, IPr) [10]. Common features among these ligands are large steric demands and strong σ-electron donating ability. These properties favor low-coordination, electron-rich active species that are highly active towards oxidative addition [11]. The steric bulk can also favor challenging reductive eliminations [12,13].

The use of water-soluble phosphine ligands in palladium-catalyzed cross-coupling reactions dates to Casalnuovo's pioneering report of the use of $Pd(TPPMS)_3$ (TPPMS = sodium diphenyl(3-sulfonato)phenylphosphine) for Suzuki, Heck, and Sonogashira couplings of aryl halides in water/organic solvent mixtures [14]. Since that initial report, numerous examples of hydrophilic ligands have been disclosed to provide effective cross-coupling catalysts [2,15]. Early hydrophilic ligands, such as TPPTS (Fig. 1) [16], were based on modified triphenylphosphine scaffolds. Catalysts derived from these ligands showed modest activity and were limited to aryl iodides or in some cases aryl bromides at elevated temperatures (>100 °C). Our group reported the first examples of hydrophilic, sterically demanding trialkylphosphine ligands for cross-coupling reactions [17,18]. Since these initial reports, we and others have developed hydrophilic phosphines [19–25] and *N*-heterocyclic carbene precursors [26,27] that provide high activity catalysts capable of coupling aryl bromides and chlorides under mild conditions (Fig. 1).

In designing more effective water-soluble phosphine ligands, we were interested in exploring alkylaryl substituents, such as

* Corresponding author. Tel.: +1 205 348 4435; fax: +1 205 348 9104.
E-mail address: kshaughn@ua.edu (K.H. Shaughnessy).

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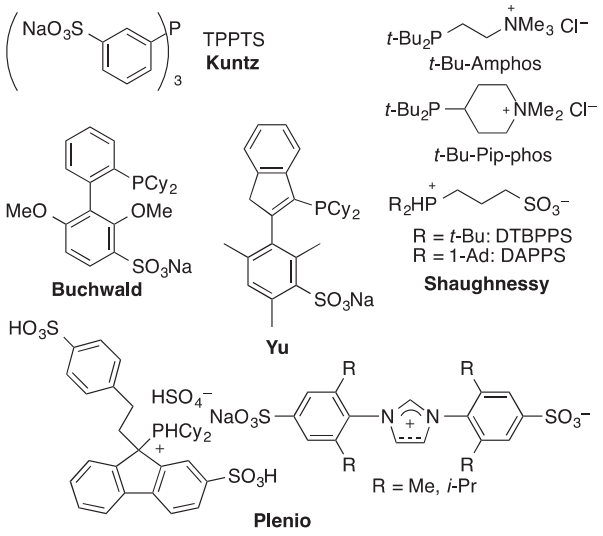


Fig. 1. Examples of water-soluble ligands previously reported.

benzyl or phenethyl. We envisioned that these substituents would be an easily introduced group that would provide the potential for incorporation of hydrophilic substituents through well-established arene functionalization chemistry. Electrophilic sulfonation of benzylphosphines have been previously reported, for example [28,29]. In addition, we hypothesized that the nearby aromatic substituent could provide additional stabilization of the palladium center. This hemilabile coordination is thought to play a key role in the success of the 2-biarylphosphine class of ligands (Fig. 2) [30,31]. Herein, we report a novel synthesis of 4-sulfonatobenzylphosphines and their application in aqueous-phase Suzuki and Sonogashira coupling reactions.

Results and discussion

Synthesis of sulfonated benzylphosphines

Synthesis of the sulfonated benzylphosphines was originally envisioned to involve electrophilic sulfonation of readily available dialkylbenzylphosphonium salts (Scheme 1). Sulfonation of tribenzylphosphine is reported to give the trisulfonated phosphine in good yield as a mixture of *ortho* and *para* isomers, with the all *para*-isomer being the major product [28]. Small amounts of phosphine oxide byproducts were also observed. Homologous tri(ω-phenylalkyl)phosphines were less prone to competitive oxidation than tribenzylphosphine. The typical sulfonation conditions are strongly oxidizing due to the presence of SO_3. Under the highly acidic reaction conditions, the basic trialkylphosphine is protonated and protected from oxidation. During neutralization with base, it is critical to control the pH in order to consume the remaining SO_3 prior to deprotonation of the phosphorus center in order to avoid oxidation of phosphorus.

Reaction of dialkylphosphines with benzyl bromide in toluene produced the respective dialkylbenzylphosphonium bromides as

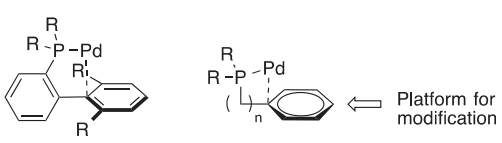
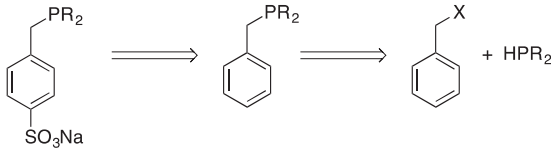
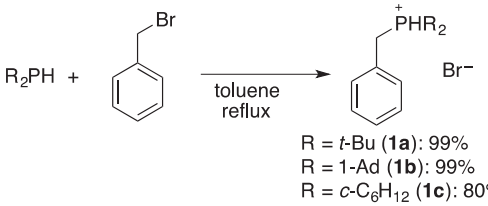


Fig. 2. Potential coordination of pendant aryl groups.

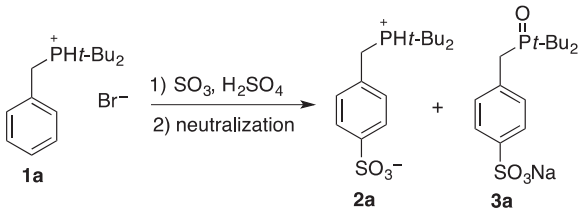


Scheme 1. Retrosynthetic plan to synthesis sulfonated benzylphosphines.

white precipitates (**1a**–**c**, Eq. (1)). Treatment of phosphonium salt **1a** with concentrated sulfuric acid gave no appreciable sulfonation. Use of 20% fuming sulfuric acid resulted in sulfonation of the aromatic ring predominately at the *para*-position to give **2a** (Eq. (2)). Neutralization of the reaction mixture afforded desired **2a** along with the corresponding oxide (**3a**) and other unknown phosphorus containing byproducts. In order to better control the pH during neutralization, 5 equivalents of KH_2PO_4 were added after completion of the sulfonation reaction followed by careful neutralization to pH 7 with 10% aqueous NaOH. The product was extracted into methanol to give **2a** with no oxide (**3a**) contamination. The product was contaminated with a significant amount of phosphate salts that could not be effectively separated, however. Use of Herrmann's [32] isolation protocol allowed sulfonated phosphine **2a** to be isolated as a pure material, but in low yield (17%). Spectroscopic characterization showed that material was exclusively the *para*-sulfonated isomer. Further attempts to improve the yields from sulfonation reactions were unsuccessful.

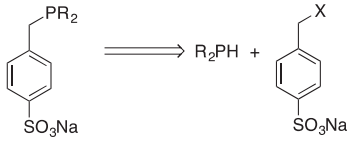


(1)



(2)

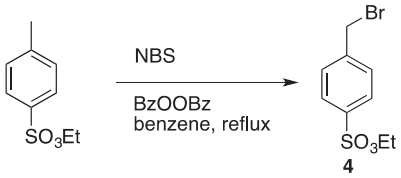
With the sulfonation reaction requiring tedious separation and providing poor yields, alternative routes to the desired sulfonated benzylphosphines were explored. Since oxidation of the phosphorus center during workup was a major challenge with **1a**, we considered an alternative synthetic strategy in which the sulfonate would be installed on the benzyl group prior to alkylation of the phosphorus center (Scheme 2). This approach would require synthesis of a 4-bromomethylbenzene sulfonic acid equivalent. The synthesis of sodium 4-bromomethylbenzenesulfonate has been previously reported in three steps starting from *N,N*-dimethylbenzylamine [33]. As an alternative, we envisioned that radical



Scheme 2. Revised approach to sulfonated benzylphosphines.

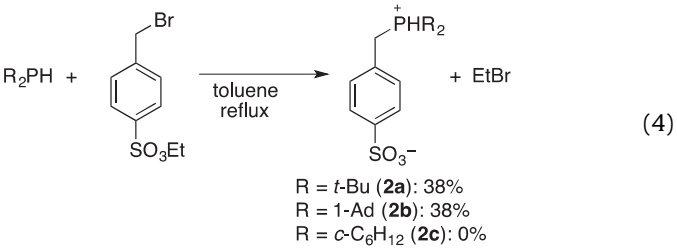
bromination of readily available *p*-toluenesulfonic acid (*p*-TSA) derivatives would be a more efficient strategy.

The direct bromination of *p*-toluenesulfonic acid (*p*-TSA) was explored initially. Treatment of *p*-TSA with NBS in the presence of either AIBN or benzoyl peroxide in refluxing chloroform gave no bromination. A small amount of brominated product (14%) was obtained by treatment of *p*-TSA with bromine in refluxing chloroform while being irradiated with a sun lamp. Although radical bromination of *p*-TSA proved difficult, tosylate esters have been reported to undergo benzylic bromination in good yields [34]. Reaction of ethyl tosylate with NBS in the presence of benzoyl peroxide in refluxing benzene gave approximately 60% conversion to ethyl 4-(bromomethyl)benzenesulfonate (**4**, Eq. (3)). Due to difficulty in separating the brominated product **4** from ethyl tosylate, the isolated yield of pure material was only 35%. Subsequently it was found that **4** containing up to 25% of ethyl tosylate could be used in the ligand synthesis without negative effects.



(3)

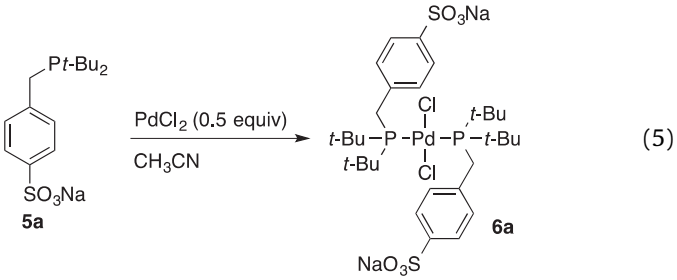
Sulfonated benzyl bromide **4** was reacted with one equivalent of either di-*tert*-butylphosphine or di-1-adamantylphosphine in toluene under nitrogen (Eq. (4)). The product precipitated from the reaction mixture and was recovered by filtration. Fortuitously, the bromide liberated during the substitution step displaced the sulfonate from the ethyl protecting group. As a result, the reaction directly afforded di-*tert*-butyl(4-sulfonatobenzyl) phosphonium (**2a**) and di-1-adamantyl(4-sulfonatobenzyl) phosphonium (**2b**), respectively. Both **2a** and **2b** were obtained in 38% yield after recrystallization from ethanol. Attempts to prepare dicyclohexyl(4-sulfonatobenzyl)phosphonium from dicyclohexylphosphine gave no conversion to the desired product (**2c**).



(4)

X-ray quality crystals of **2a** and **2b** were grown from saturated solutions in ethanol with a small amount of water. Phosphonium **2a** crystallized as a monohydrate (Fig. 3). The molecules packed as hydrogen bonded dimers with interactions between the sulfonate oxygen of one molecule with the phosphonium hydrogen of a second (see Supporting information). The steric bulk at the phosphorus center results in a large P1–C7–C4 angle (116.0(2)°). The diadamantyl analog (**2b**) crystallized without co-crystallization of water or solvent molecules (Fig. 4). The molecules organize into infinite hydrogen bonded zigzags along the *a* axis through head-to-tail P1–H···O3 hydrogen bonds (see Supporting information). The adamantyl substituents result in a larger P1–C7–C4 angle (119.6(3)°) than is seen in **2a**.

Free **5a** was prepared by deprotonation with sodium carbonate to provide a crystalline solid that slowly oxidized over a period of 2 weeks when exposed to air in the solid state. Phosphine **5a** was complexed to palladium(II) dichloride in anhydrous acetonitrile to yield a moss green precipitate with a ^{31}P NMR shift at 43 ppm (Eq. (5)). Virtual coupling of the *tert*-butyl protons in the ^{1}H NMR spectrum of **6a** indicated that the complex was a *trans*-diphosphine complex. Recrystallization from water/ethanol gave glassy yellow crystals. Attempts to obtain X-ray quality crystals were unsuccessful. The complex was analyzed by high resolution ESI-MS to confirm the structure of **6a** as Pd(**5a**)$_2$Cl$_2$.



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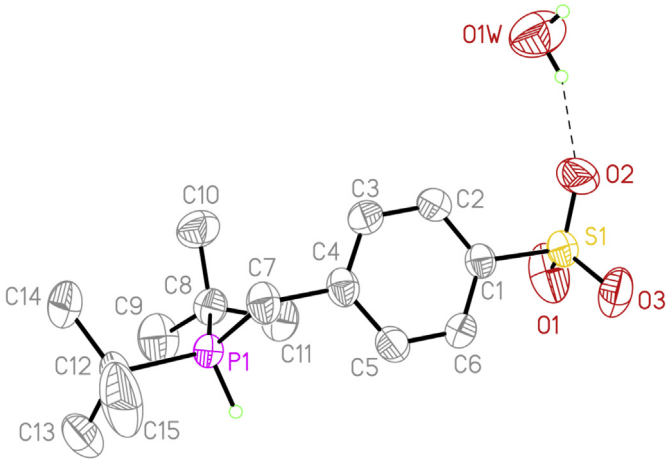


Fig. 3. Thermal ellipsoid plot of di-*tert*-butyl(4-sulfonatobenzyl)phosphonium (**2a**) at 50% probability level. Carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1–C7, 1.808(3); P1–C8, 1.844(3); P1–C12, 1.850(3); C7–P1–C8, 112.8(1); C7–P1–C12, 108.2(1); C8–P1–C12, 117.2(1); P1–C7–C4, 116.0(2); C3–C4–C7–P1, 70.3(3); H1P–P1–C7–C4, 62(1).

*Catalytic application of **2a** and **2b***

Suzuki coupling

With ligands **2a** and **2b** prepared, their application in promoting palladium-catalyzed cross-coupling in aqueous solvents was explored. The performance of ligands **2a** and **2b** was compared with the DTBPPS ligand previously reported by our group [20]. Palladium acetate (2 mol %) was chosen as the palladium source and sodium carbonate as the base. Initial studies were carried out in 1:1 water/acetonitrile. In contrast to the DTBPPS ligand, which

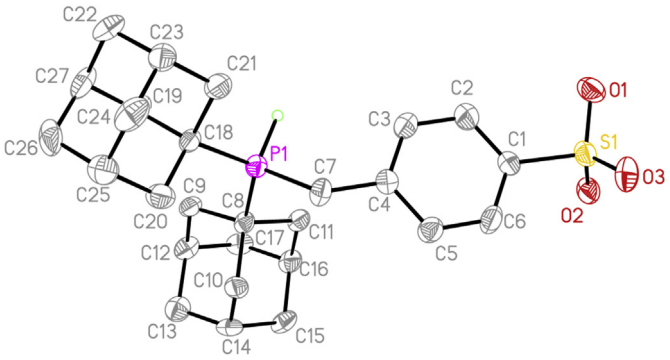


Fig. 4. Thermal ellipsoid plot of di-1-adamantyl(4-sulfonatobenzyl)phosphonium (**2b**) at 50% probability level. Carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1–C7, 1.809(4); P1–C8, 1.829(4); P1–C18, 1.827(4); C7–P1–C8, 108.8(2); C7–P1–C18, 107.5(2); C8–P1–C18, 120.3(2); P1–C7–C4, 119.6(3); C3–C4–C7–P1, 48.7(5); H1A–P1–C7–C4, 34(1).

generally gives good yields for couplings at room temperature, optimal yields with **2a** and **2b** were obtained at 50 °C in most cases.

Under these conditions, good yields were achieved for a variety of aryl bromide and arylboronic acid substrates (Table 1). Electron-deficient (entry 1) and electron-rich (entry 2) aryl bromides gave good yields when coupled with phenylboronic acid. In most cases **2b** gave somewhat higher yields than **2a** under the same conditions. Isolated yields obtained with catalysts derived from **2a** and **2b** at 50 °C were comparable to those obtained with DTBPPS at room temperature. In the case of 4-bromotoluene, a good yield was achieved at room temperature using **2a**, whereas **2b** required 50 °C for optimal yields. Lower yields were obtained with sterically demanding bromomesitylene and 2-bromotoluene substrates (entries 5 and 6). Sterically hindered 2-tolylboronic acid and 1-naphthylboronic acid gave good yields of coupled product with 4-bromoanisole, however. The challenging heterocyclic substrate 3-bromobenzothiophene gave 72% and 76% yields when coupled with 4-methoxyphenylboronic acid using ligands **2a** and **2b**, respectively (entry 9).

Aryl chlorides could not be effectively coupled using catalysts derived from **2a** or **2b**. Coupling of 4-chloroanisole with phenylboronic acid at 80 °C using 4 mol % Pd/ligand gave modest yields of coupled products. The diadamantyl ligand **2b** gave a 49% yield, whereas the *tert*-butyl ligand **2a** gave only 19% conversion to product (entry 10). The use of water/THF as the solvent gave lower yields in couplings of sterically unhindered aryl bromides (entries 1, 2, and 4). In contrast, the yields were significantly higher with *ortho*-substituted aryl bromides (entries 5 and 6).

The use of water/THF (1:1) and water alone as solvents were further explored in comparison to the water/acetonitrile solvent system at both 50 °C and room temperature (Table 2). Both water alone and water/THF proved to be effective solvents for this reaction. An interesting effect was observed as the steric hindrance of the aryl bromide substrate was altered. With unhindered aryl bromides, water/THF gave comparable (entry 3) or lower yields (entries 1 and 2) at room temperature than water/acetonitrile. In contrast, aryl bromides with one or two *ortho*-substituents gave increased yields in water/THF compared to water/acetonitrile at room temperature (entries 4–6). This effect appears to be due to steric hindrance at the reaction site rather than due to a hydrophobic effect. For example, THF/water gave lower yields than water/acetonitrile with 4-bromoanisole, but a higher yield with 2-bromoanisole. At 50 °C, the difference in performance was generally smaller. In the case of bromomesitylene, a significant improvement in yield was seen in water/THF compared to water/acetonitrile. Water alone generally gave higher yields than those obtained with the mixed solvent systems. The one exception to this trend was bromomesitylene, where the yield in water was between those obtained with water/THF and water/acetonitrile. The nature of this size dependent solvent effect is unclear.

Ligands **2a** and **2b** provide catalysts that are effective at lower temperature and with lower catalyst loading than are achieved with hydrophilic triarylphosphines, such as TPPTS [35]. The catalysts derived from **2a** and **2b** show comparable activities to those derived from DTBPPS [20] or *t*-Bu-Amphos [17] previously reported by our group for aryl bromides. The DTBPPS catalyst affords better activity towards aryl chlorides, however. The

Table 1
Suzuki coupling of aryl bromides using **2a** and **2b**[a].

Entry	ArX	$ArB(OH)_2$	Solvent[b]	% Yield[c]		
				2a	**2b**	DTBPPS
1	4-NCC_6H_4Br	$PhB(OH)_2$	MeCN/H_2O	89	96	99[d]
			THF/H_2O	74	92	
2	4-MeC_6H_4Br	$PhB(OH)_2$	MeCN/H_2O	94[e]	97	98[d]
			THF/H_2O	80[e]		92[e]
3	4-*t*-BuC_6H_4Br	$PhB(OH)_2$	MeCN/H_2O	90	91	
4	4-$MeOC_6H_4Br$	$PhB(OH)_2$	MeCN/H_2O	92	100	94[d]
			THF/H_2O	87		75[e]
5	2,4,6-$Me_3C_6H_2Br$	$PhB(OH)_2$	MeCN/H_2O	56[f]	80	70
			THF/H_2O	83		76
6	2-MeC_6H_4Br	2,4-$F_2C_6H_3B(OH)_2$	MeCN/H_2O	63[f]	77	
			THF/H_2O	79	89	
7	4-$MeOC_6H_4Br$	2-$MeC_6H_4B(OH)_2$	MeCN/H_2O	87		
8	4-$MeOC_6H_4Br$	1-naphthylB$(OH)_2$	MeCN/H_2O	100	97	
9	3-Br-benzothiophene	4-$MeOC_6H_4B(OH)_2$	MeCN/H_2O	72[f]	76	
10	4-$MeOC_6H_4Cl$	$PhB(OH)_2$	MeCN/H_2O	19[fg]	49[fg]	

[a] Reaction conditions: aryl bromide (1 equiv), arylboronic acid (1.2 equiv), $Pd(OAc)_2$ (2 mol %), ligand (2 mol %), sodium carbonate (1.1 equiv), solvent, at 50 °C for **2a** and **2b** or room temperature for DTBPPS under N_2 for 24 h. Reaction time not optimized.
[b] (1:1) solvent ratio.
[c] Isolated yield.
[d] Literature results [20].
[e] Reaction performed at room temperature.
[f] Yield determined by gas chromatography.
[g] Reaction performed with 4 mol % $Pd(OAc)_2$/ligand at 80 °C.

Table 2
Suzuki coupling of aryl bromides using **2a** aqueous media[a].

Entry	ArBr	Ligand	Yield (%) at 23 °C[b]			Yield (%) at 50 °C[b]		
			$MeCN/H_2O$	THF/H_2O	H_2O	$MeCN/H_2O$	THF/H_2O	H_2O
1	4-MeC_6H_4Br	**2a**	94	85	100	87	(88)	(95)
		DTBPPS	(95)	92	95	nd	(89)	(94)
2	4-$MeOC_6H_4Br$	**2a**	(90)	71	98	96	86	(100)
		DTBPPS	(97)	80	99	nd	(96)	(97)
3	3,5-$Me_2C_6H_3Br$	**2a**	(86)	(88)	96	(100)	(97)	97
4	2-MeC_6H_4Br	**2a**	(80)	(85)	92	96	97	98
		DTBPPS	75	80	95	91	86	94
5	2-$MeOC_6H_4Br$	**2a**	(64)	78	(90)	76	73	97
		DTBPPS	56	75	89	(91)	76	(92)
6	Br-mesitylene	**2a**	64	(75)	(62)	(57)	83	70
		DTBPPS	64	(79)	75	(88)	89	(76)

[a] Reaction conditions: aryl bromide (1 equiv), arylboronic acid (1.2 equiv), $Pd(OAc)_2$ (2 mol %), ligand (2 mol %), sodium carbonate (1.1 equiv), under N_2 for 24 h. Reaction time not optimized.
[b] Average isolated yield from at least two trials. Values in parentheses determined by GC analysis.

cataCXium FSulf water-soluble ligand developed by the Plenio group are more effective in the coupling of heteroaryl halides than **2a** and **2b** [36].

Sonogashira coupling

Conditions for the Sonogashira coupling using ligands **2a** and **2b** were optimized for the model coupling of 4-bromoanisole and phenylacetylene (Table 3). The conditions previously reported for the DTBPPS ligand, with $Pd(OAc)_2$ as the palladium source and CsOH as the base [20], were found to be ineffective in the coupling of 4-bromoanisole with phenylacetylene at 80 °C (entry 1). Using $PdCl_2(CH_3CN)_2$ as the palladium source (1 mol %) with a 2:1 L/Pd ratio and potassium carbonate as the base afforded a 65% yield of coupled products (entry 2). Increasing the L/Pd ratio to 3:1 gave a small improvement in yield to 69% (entry 3). Increasing the palladium loading to 2 mol % did not improve the yield (entry 4). Use of KOH as base gave a slightly lower yield than was achieved with potassium carbonate (entry 5). Replacing acetonitrile with dioxane in the solvent mixture decreased the yield to 57% (entry 6). Using $Pd_2(dba)_3$ gave a slight increase in yield compared to $PdCl_2(MeCN)_2$ (72%, entry 7). Given the lower cost of $PdCl_2(MeCN)_2$ compared to $Pd_2(dba)_3$, $PdCl_2(MeCN)_2$ was chosen as the preferred palladium source going forward. Unlike the Suzuki coupling, **2b** gave a significantly lower yield in the Sonogashira coupling than **2a** (entry 8). Decreasing the temperature from 80 °C resulted in lower yields of product (entries 9 and 10).

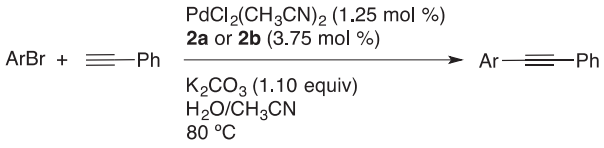
Table 3
Optimization of Sonogashira coupling with **2a**[a].

Entry	Pd	Pd/L (mol %)	Base	Yield[b] (%)
1	$Pd(OAc)_2$	2/3.75	CsOH	0
2	$PdCl_2(MeCN)_2$	1/2	K_2CO_3	64
3	$PdCl_2(MeCN)_2$	1.25/3.75	K_2CO_3	69
4	$PdCl_2(MeCN)_2$	2/6	K_2CO_3	68
5	$PdCl_2(MeCN)_2$	1.25/3.75	KOH	65
6	$PdCl_2(MeCN)_2$	1.25/3.75	K_2CO_3	57[c]
7	$Pd_2(dba)_3$	1.25/3.75	K_2CO_3	72
8	$PdCl_2(MeCN)_2$	1.25/3.75	K_2CO_3	49[d]
9	$PdCl_2(MeCN)_2$	1.25/3.75	K_2CO_3	59[e]
10	$PdCl_2(MeCN)_2$	1.25/3.75	K_2CO_3	49[f]

[a] 4-Bromoanisole (1 equiv), phenylacetylene (1.1 equiv), Pd source, **2a** base (1.1 equiv) in 1:1 water/acetonitrile at 80 °C.
[b] Yields determined by gas chromatography.
[c] Water/dioxane used as solvent.
[d] **2b** used as ligand.
[e] 50 °C.
[f] 23 °C.

Using the optimized conditions, a variety of aryl bromides were coupled with phenylacetylene to obtain moderate to excellent yields of coupled product using **2a** and **2b** as ligands (Table 4). With 4-bromoanisole, the **2a**-derived catalyst gave a higher yield than was achieved with **2b** (entry 1) as was seen in Table 3. With the more reactive 1-bromo-4-trifluoromethylbenzene, high yields (87 and 89%, respectively) were achieved with both ligands (entry 2). The moderately hindered 2-bromotoluene substrate gave good yields with both ligands, but the more hindered bromomesitylene gave lowered yields, although **2a** gave a more effective catalyst than **2b**. Excellent yields of coupled product were obtained using both ligands with 2-bromopyridine (entry 6). The more electron-rich thiophene substrates gave lower yields, however. A low yield was obtained with both ligands using 2-bromothiophene, whereas good yields were obtained with 3-bromothiophene. In

Table 4
Substrate scope for the Sonogashira coupling of aryl bromides with phenylacetylene[a].



Entry	ArBr	L	Yield (%)[b]
1	4-$MeOC_6H_4Br$	**2a**	69
		2b	43
2	4-$CF_3C_6H_4Br$	**2a**	87
		2b	89
3	2-MeC_6H_4Br	**2a**	78
		2b	73
4	2,4,6-$Me_3C_6H_2Br$	**2a**	51
		2b	33
5	1-Br-Naphth	**2a**	79
		2b	69
6	2-Br-pyridine	**2a**	86
		2b	86
7	2-Br-thiophene	**2a**	36
		2b	28
8	3-Br-thiophene	**2a**	65
		2b	73

[a] Reaction conditions: aryl bromide (1 equiv), arylboronic acid (1.2 equiv), $PdCl_2(MeCN)_2$ (1.25 mol %), ligand (3.75 mol %), potassium carbonate (1.1 equiv), under N_2 for 2 h. Reaction time not optimized.
[b] Isolated yield.

this case, **2b** gave a slightly higher yield than that obtained with **2a**. In general, the two ligands gave yields that were not significantly different, although the **2b**-derived catalyst gave lower yields in most cases. It appears that the **2b**-derived catalyst is less active towards electron-rich aryl halides than the **2a** system. The **2b** complex is also more sensitive to steric bulk than the **2a** derived catalyst. This steric sensitivity is in line with the larger steric strain at phosphorus for **2b** suggested by the X-ray structural data.

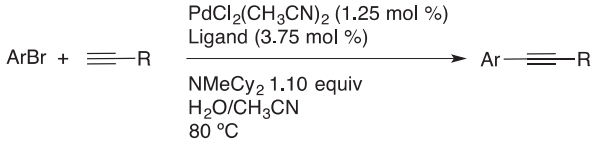
The coupling of aliphatic alkynes was also attempted (Table 5). Using the optimized conditions identified for phenylacetylene resulted in low yields with aliphatic alkynes. Switching the base to *N*-methyldicyclohexylamine afforded moderate yields for the coupling of 4-bromoanisole with 1-hexyne and 5-hexynenitrile. 2-Bromotoluene produced low yields when coupled with 1-hexyne. Modest yields of product were obtained in the coupling of 4-bromoanisole and propargyl alcohol.

The use of a water-soluble palladium source was considered as a means of more quickly generating the active catalyst species in aqueous solvents. Several different palladium sources were compared for the Sonogashira coupling of 3-bromobenzothiophene and phenylacetylene, including complex **6a** (Table 6). Sodium tetrachloropalladate gave slightly lower yields of coupled products compared to $PdCl_2(MeCN)_2$ in both water/acetonitrile and water alone (entries 1–4). Notably, the yield was higher in water alone compared with water/acetonitrile with both palladium sources. The results with palladium nitrate in water/acetonitrile were comparable to those achieved with both $PdCl_2(MeCN)_2$ and Na_2PdCl_4. In water alone, palladium nitrate was much less effective, however. The preformed Pd(II) complex **6a** was also a competent precatalyst, although it afforded a lower yield than the catalyst generated in situ from $PdCl_2(MeCN)_2$ and **2a**. In the absence of **2a**, no conversion occurred (entry 9).

The use of Na_2PdCl_4 as precatalyst with both water/acetonitrile and water alone as well as $PdCl_2(MeCN)_2$ in water was explored in the coupling of a range of aromatic and heteroaromatic aryl bromides with phenylacetylene (Table 7). The results with Na_2PdCl_4 in water/acetonitrile were similar to those obtained with $PdCl_2(MeCN)_2$ in the same solvent (Table 4). Both precatalysts gave lower yields for reactions carried out in water without a cosolvent in most cases. The lower yields are likely due to poor interaction between the hydrophobic organic substrates and the water-soluble catalyst system and base. The lone exception to this trend was 3-bromobenzothiophene, which gave a higher yield in water than in water/acetonitrile.

Buchwald has reported that propiolic acid, a challenging Sonogashira substrate, worked well in the copper-free Sonogashira coupling of aryl bromides at elevated temperatures using a sulfonated variant of X-phos (Eq. (6)) [19]. This led us to attempt the Sonogashira coupling of 4-bromoanisole with propiolic acid using the optimized conditions for $PdCl_2(CH_3CN)_2$ and **2a**. None of the expected Sonogashira product **7** could be isolated, however. A 56% yield of the decarboxylative diarylated product **8**, based on propiolic acid, was produced instead (Eq. (7)). Decarboxylative diarylation of propiolic acid has been previously reported by the Lee [37,38] and Gooßen [39] groups, including examples using aqueous solvent [40]. In these reports, the decarboxylative coupling is generally slower than the initial arylation of the terminal alkyne carbon, which allows unsymmetrical products to be generated [37]. In our case, the diarylated product was formed without any

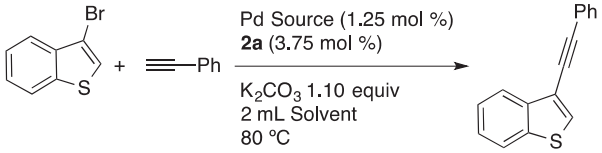
Table 5
The Sonogashira coupling of aryl bromides with aliphatic alkynes[a].



Entry	ArBr	R	L	Yield (%)
1	4-$MeOC_6H_4Br$	*n*-Bu	**2a**	57
			2b	46
2	4-$MeOC_6H_4Br$	$(CH_2)_5CN$	**2a**	78
			2b	72
3	2-MeC_6H_4Br	*n*-Bu	**2a**	25
			2b	30[a]
4	4-$MeOC_6H_4Br$	CH_2OH	**2a**	47[b,c]
			2b	30[c]

[a] Product isolated with inseparable minor impurities.
[b] CuI (1 mol %) added.
[c] 2.2 equiv of base.

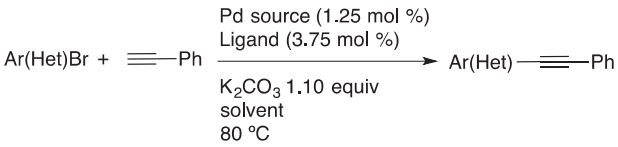
Table 6
Comparison of water-soluble palladium sources for the Sonogashira coupling of 3-bromobenzothiophene with phenylacetylene.



Entry	Pd source	Solvent	Yield (%)[a]
1	$PdCl_2(MeCN)_2$	H_2O/MeCN[b]	59
2	$PdCl_2(MeCN)_2$	H_2O	67
3	Na_2PdCl_4	H_2O/MeCN[b]	52
4	Na_2PdCl_4	H_2O	63
5	$Pd(NO_3)_2$	H_2O/MeCN[b]	54
6	$Pd(NO_3)_2$	H_2O	48
7	**6a**	H_2O/MeCN[b]	54
8	**6a**	H_2O	52
9	$PdCl_2(MeCN)_2$[c]	H_2O	0

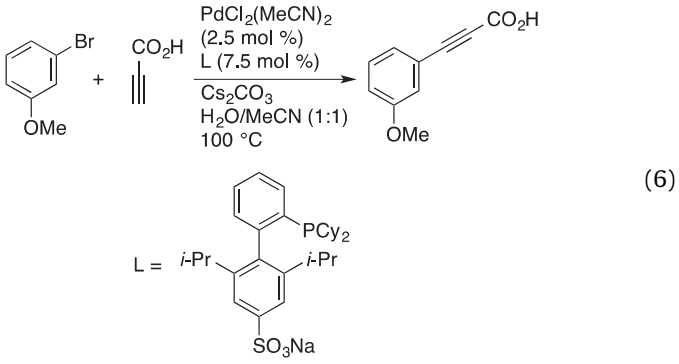
[a] Isolated yields.
[b] 1:1 water/acetonitrile.
[c] No **2a** used.

Table 7
Aqueous condition comparison for the Sonogashira coupling of aryl bromides.

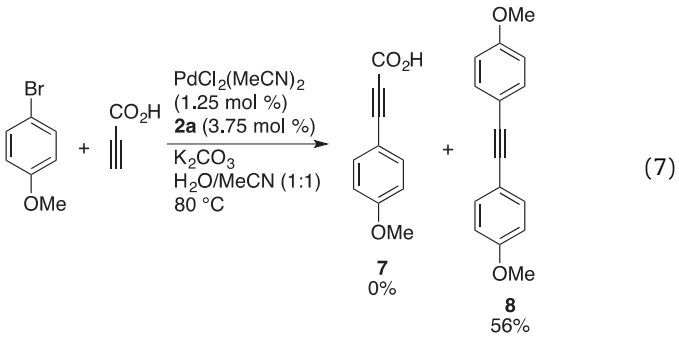


Entry	ArBr	Ligand	Isolated yield (%)		
			Na_2PdCl_4 H_2O/MeCN	Na_2PdCl_4 H_2O	$PdCl_2(MeCN)_2$ H_2O
1	4-$MeOC_6H_4Br$	**2a**	74	54	52
		2b	42	43	37
2	2-MeC_6H_4Br	**2a**	82	75	81
		2b	73	23	28
3	2-Br-pyridine	**2a**	85	56	61
		2b	81	76	76
4	2-Br-thiophene	**2a**	35	13	20
		2b	26	26	26
5	3-Br-thiophene	**2a**	70	55	54
		2b	66	56	49
6	3-Br-benzothiophene	**2a**	52	63	67
		2b	36	38	56

evidence of the propiolic acid product (**7**) being formed despite having only one equivalent of aryl bromide present.



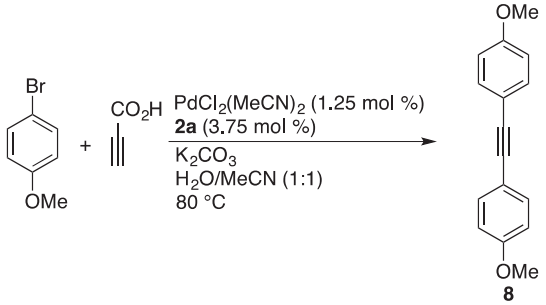
(6)



(7)

Conditions for this reaction were further explored in an effort to form either the 3-arylpropiolic acid **7** or dicarboxylated product **8** in high yield (Table 8). Use of CuI as a cocalyst with a 1:1.1 ratio of 4-bromoanisole and propiolic acid gave an improved yield (67%, based on propiolic acid) of **8** with no evidence of cross-coupled product **7** (entry 2). Using 2 equiv of aryl bromide to optimize the yield of **8** resulted in the yield decreasing to 31% (entry 4). This corresponds to approximately the same level of conversion relative to propiolic acid as entries 1 and 2, suggesting that catalyst deactivation may be limiting conversion in this reaction. Adding CuI in varying amounts did not significantly affect the yield with the higher aryl bromide to propiolic acid ratio (entries 5–6).

Table 8
Decarboxylative Sonogashira diarylation of propiolic acid with 4-bromoanisole.



Entry	ArBr:PA	CuI (mol %)	Yield (%)[a]
1	1:1	0	56
2	1:1	1	67
3	1:1	0	28[b,c]
4	2:1	0	31
5	2:1	1	32
6	2:1	2.8	38[c]

[a] Average isolated yield from two trials.
[b] Reaction performed at 50 °C.
[c] Yield determined by GC.

Conclusions

A novel approach to the synthesis of sulfonated benzylphosphine ligands is reported that involves the one pot alkylation of secondary phosphines and concomitant deprotection of a protected sulfonate ester to afford zwitterionic phosphonium sulfonate salts. This methodology overcomes the challenges of electrophilic sulfonation of oxidatively sensitive trialkylphosphines. The resulting hydrophilic ligands provide effective catalysts for the Suzuki and Sonogashira coupling of aryl bromides in water or water/organic solvent systems.

Experimental

General experimental methods

Diadamantylphosphine [41] and ethyl 4-(bromomethyl)benzenesulfonate [34] were prepared according to a literature procedure. Toluene was refluxed from molten sodium prior to use. DI water, THF, and acetonitrile were deoxygenated by sparging with N_2 for 15 min prior to use. All other compounds were obtained commercially and used as received. NMR spectral data were obtained on Brüker 360 and 500 MHz spectrometers. ^{1}H and ^{13}C NMR spectra are referenced to the NMR solvent peaks or internal TMS. ^{31}P NMR spectra were externally referenced to 85% H_3PO_4. HRMS were obtained on a Waters Autospec NT magnetic sector mass spectrometer using EI ionization and operating in the positive ion mode. ESI-HRMS on compounds **2a**, **2b**, and **6** were obtained at the LSU Mass Spectrometry Facility on an Agilent 6210 ESI-TOF instrument operating in positive ion mode. Elemental analysis was performed by Atlantic Microlab, Inc.

*General procedure for synthesis of dialkyl(4-sulfonatobenzyl) phosphonium (**2a**–**c**)*

Dialkylphosphine and ethyl 4-sulfonatobenzyl bromide (1.25 equiv) were dissolved in anhydrous toluene and left to reflux under nitrogen atmosphere overnight. The resulting cream-colored precipitate was recovered by filtration. The crude product was recrystallized from ethanol with a small amount of water to afford the desired product as white crystals.

*Di-tert-butyl(4-sulfonatobenzyl)phosphonium (**2a**)*

Di-*tert*-butylphosphine (0.75 mL, 4.00 mmol) and **4** (1.40 g, 5.00 mmol) in toluene (10 mL) were reacted according to the general procedure. The crude product was recrystallized to yield 0.50 g (38%) of **2a** contaminated with a small amount of the phosphine oxide (**3a**). ^{1}H NMR (500 MHz, MeOH-d_4): δ 7.80 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 7.9$ Hz, 2H), 4.02 (d, $J = 13.7$ Hz, 2H), 1.50 (d, $J = 16.5$ Hz, 18H). ^{13}C NMR (126 MHz, MeOH-d_4): d 145.2, 133.6 (d, $J_{P-C} = 8.7$ Hz), 129.5 (d, $J_{P-C} = 6.2$ Hz), 126.8, 33.2 (d, $J_{P-C} = 33.8$ Hz), 26.3, 20.4 (d, $J_{P-C} = 39.3$ Hz). ^{31}P NMR (203 MHz, MeOH-d_4): δ 47.3 (t, $J_{P-D} = 65.3$ Hz); (203 MHz, DMSO-d_6): δ 46.3 (d, $J_{P-H} = 458.7$ Hz). HR-ESI-MS *m/z* calcd for $C_{15}H_{26}O_3SP$, 317.1340 $[M + H]^+$; found, 317.1341.

*Di-1-adamantyl(4-sulfonatobenzyl)phosphonium (**2b**)*

Di-1-adamantylphosphine (3.89 g, 12.9 mmol) and **4** (4.49 g, 16.1 mmol) were reacted according to the general procedure in toluene (25 mL). The crude product was recrystallized to yield

2.32 g (38%) of **2b**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.61 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 7.7 Hz, 2H), 6.09 (d, J_{P-H} = 469.2 Hz, 1H), 4.00 (brs, 2H), 2.12–1.67 (m, 30H). ^{13}C NMR (126 MHz, MeOH-d_4): δ 144.9, 130.3 (d, J_{P-C} = 5.0 Hz), 129.5 (d, J_{P-C} = 6.0 Hz), 126.7, 38.0 (d, J_{P-C} = 33.2 Hz), 37.6 (d, J_{P-C} = 2.7 Hz), 36.1 (d, J_{P-C} = 20.3 Hz), 35.1, 27.7 (d, J_{P-C} = 9.2 Hz). ^{31}P NMR (203 MHz, DMSO-d_6): δ 36.9 (d, J_{P-H} = 476.0 Hz). HR-ESI-MS m/z calcd for $C_{27}H_{38}O_3SP$, 473.2279 $[M + H]^+$; found, 473.2277.

X-ray crystallography

X-ray crystallographic data collection was performed using a Brüker diffractometer using MoKα radiation with a Platform 3-circle goniometer and an Apex 2 CCD area detector. For structures obtained below ambient temperature, crystals were cooled under a cold nitrogen stream using an N-Helix cryostat. A hemisphere of data was collected for each crystal using a strategy of omega scans with 0.5° frame widths. Unit cell determination, data integration, absorption correction, and scaling were performed using the Apex2 software suite from Brüker [42]. Space group determination, structure solution, refinement, and generation of ORTEP diagrams were done using the SHELXTL software package [43].

X-ray quality crystals of **2b** were obtained by slow diffusion of ethanol into a concentrated aqueous solution of **2b**. Crystal data for **2a**: $C_{15}H_{27}O_4PS$; 334.39; 296(2) K; monoclinic; P 2(1)/c; a = 14.719(2) Å, b = 9.5904(14) Å, c = 13.9718(17) Å, b = 117.091(4)°; 20,456 reflections; 3571 independent reflections; [R_{int} = 0.0920]; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0453, $wR2$ = 0.1012; R indices (all data): R_1 = 0.0877, wR_2 = 0.1193.

X-ray quality crystals of **2b** were obtained by slow diffusion of ethanol into a concentrated aqueous solution of **2b**. Available crystals for **2b** were small and weakly scattering so extended exposure times (60 s per 0.5° frame) were used to get solvable data. Crystal data for **2b**: $C_{27}H_{37}O_3PS$; 472.59; 173(2) K; orthorhombic; P 2(1) 2(1) 2(1); a = 8.016(4) Å, b = 13.974(8) Å, c = 20.656(12) Å; 21,803 reflections; 4704 independent reflections; [R_{int} = 0.1827]; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0548, wR_2 = 0.0810; $R1$ = 0.1325, $wR2$ = 0.0999.

*Sodium di-tert-butyl(4-sulfonatobenzyl)phosphine (**5a**)*

2a (500 mg, 1.58 mmol) and sodium carbonate (850 mg, 7.91 mmol) were placed in a two-neck round bottom flask under nitrogen. Degassed methanol was added to the mixture, and the reaction was allowed to stir at room temperature for 24 h. The solution was then filtered by cannula through an air-free glass frit containing Celite into a two-neck round bottom flask, where the solvent was removed under high vacuum to yield a white solid that was modestly sensitive to oxidation in air. This material was then used directly to generate the palladium complex. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.46 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 2.83 (d, J = 2.8 Hz, 2H), 1.08 (d, J = 10.8 Hz, 18H). ^{31}P NMR (203 MHz, DMSO-d_6): δ 35.1 (s).

*Disodium [palladium bis(di-tert-butyl[4-sulfonatobenzyl] phosphine) dichloride] (**6a**)*

Ligand **5a** (500 mg, 1.48 mmol) was placed into a reflux setup under nitrogen atmosphere with palladium dichloride (133 mg, 0.74 mmol) and anhydrous acetonitrile (15 mL). The mixture was allowed to reflux overnight to yield a moss green powder (235 mg) that was precipitated using cold diethyl ether. Recrystallization by slow diffusion using ethanol and water yielded a small amount of a glassy yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.00 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 7.4 Hz, 2H), 3.67 (bs, 2H), 1.48 (brt, J = 6.0 Hz, 18H). ^{31}P NMR (203 MHz, D_2O): δ 45.5 (s). HR-ESI-MS (cation) m/z calcd for $C_{30}H_{49}P_2S_2O_6Cl_2PdNa_2$ ($[M + H]^+$) 853.0653, found 853.0646.

*General procedure for Suzuki coupling with ligands **2a** and **2b***

In a nitrogen filled glove box, $Pd(OAc)_2$ (4.5 mg, 0.020 mmol), water-soluble phosphine (**2a**, **2b**, or DTBPPS, 0.0200 mmol), sodium carbonate (116 mg, 1.10 mmol), arylboronic acid (1.10 mmol) were measured into a 1 dram vial containing a small stir bar. The vial was sealed with a screw cap and septum and removed from the glovebox before adding the aryl halide (1.00 mmol) and deoxygenated solvent (2 mL). The reaction vial was stirred at room temperature or placed in a preheated oil bath until reaction completion as determined by gas chromatography was achieved. Upon completion, the reaction mixture was taken into ethyl acetate and washed three times with brine solution, dried with anhydrous magnesium sulfate, and filtered. The excess organic solvent was removed under reduced pressure, and the crude residues were evaporated onto silica gel from methylene chloride. Once dry, the silica gel mixture was used in column chromatography to isolate the desired product.

General procedure for Sonogashira coupling of phenylacetylene

In a nitrogen filled glovebox, the $PdCl_2(CH_3CN)_2$ (3.3 mg, 0.013 mmol), **2a** (11.8 mg, 0.0375 mmol) or **2b** (17.7 mg, 0.0375 mmol), and potassium carbonate (151.8 mg, 1.10 mmol) were measured into a 1 dram vial containing a small stir bar. The vial was sealed with a screw cap and septum and removed from the glovebox before adding the aryl halide (1.00 mmol), aryl acetylene (1.10 mmol) and 1:1 water/acetonitrile (2 mL). The reaction vial was placed in a preheated oil bath at 80 °C and stirred until reaction completion was observed by gas chromatography (2–12 h). Upon completion, the reaction mixture was taken into diethyl ether, washed with brine solution, dried with anhydrous magnesium sulfate, and filtered. The excess organic solvent was removed under reduced pressure and the crude residues were taken into methylene chloride and evaporated onto silica gel under reduced pressure. Once dry, the silica gel mixture was used in column chromatography.

General procedure for Sonogashira coupling of alkylacetylenes

In a nitrogen filled glove box, $PdCl_2(CH_3CN)_2$ (3.25 mg, 0.010025 mmol) and **2a** (11.8 mg, 0.0375 mmol) or **2b** (17.7 mg, 0.0375 mmol) were measured into a 1 dram vial containing a small stir bar. The vial was sealed with a screw cap and septum and removed from the glovebox before adding Cy_2NMe (235 μL, 1.10 mmol), aryl halide (1.00 mmol), alkyl acetylene (1.10 mmol), and 1:1 water/acetonitrile (2 mL). The reaction vial was placed in a preheated oil bath at 80 °C and stirred until it reached completion as determined by gas chromatography (2–12 h). Upon completion, the reaction mixture was taken into diethyl ether, washed with brine solution, dried with anhydrous magnesium sulfate, and filtered. The excess organic solvent was removed under reduced pressure, and the crude residues were taken into methylene chloride and evaporated onto silica gel under reduced pressure. Once dry, the silica gel mixture was used in column chromatography.

Acknowledgment

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Appendix A. Supplementary material

CCDC 1023221; CCDC 1023222 for **2a** and **2b** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.11.011.

References

[1] C.-J. Li, T.H. Chan, Comprehensive Organic Reactions in Aqueous Media, second ed., John Wiley & Sons, Inc., Hoboken, NJ, 2007.
[2] K.H. Shaughnessy, Chem. Rev. 109 (2009) 643–710.
[3] M.-O. Simon, C.-J. Li, Chem. Soc. Rev. 41 (2012) 1415–1427.
[4] P.H. Dixneuf, V. Cadierno, Metal-catalyzed Reactions in Water, Wiley-VCH, Weinheim, Germany, 2013.
[5] R.N. Butler, A.G. Coyne, Chem. Rev. 110 (2010) 6302–6337.
[6] Á. Molnár, Palladium-catalyzed Coupling Reactions, Wiley-VCH, 2013.
[7] C.C.C. Johansson Seechurn, M.O. Kitching, T.J. Colacot, V. Snieckus, Angew. Chem. Int. Ed. 51 (2012) 5062–5085.
[8] C.A. Fleckenstein, H. Plenio, Chem. Soc. Rev. 39 (2010) 694–711.
[9] D.S. Surry, S.L. Buchwald, Chem. Sci. 2 (2011) 27–50.
[10] G.C. Fortman, S.P. Nolan, Chem. Soc. Rev. 40 (2011) 5151–5169.
[11] F. Barrios-Landeros, J.F. Hartwig, J. Am. Chem. Soc. 127 (2005) 6944–6945.
[12] G. Mann, Q. Shelby, A.H. Roy, J.F. Hartwig, Organometallics 22 (2003) 2775–2789.
[13] M. Yamashita, J.F. Hartwig, J. Am. Chem. Soc. 126 (2004) 5344–5345.
[14] A.L. Casalnuovo, J.C. Calabrese, J. Am. Chem. Soc. 112 (1990) 4324–4330.
[15] K.H. Shaughnessy, in: P.H. Dixneuf, V. Cadierno (Eds.), Metal-catalyzed Reactions in Water, Wiley-VCH, Weinheim, Germany, 2013, pp. 1–46.
[16] B. Cornils, E.G. Kuntz, J. Organomet. Chem. 502 (1995) 177–186.
[17] R.B. DeVasher, L.R. Moore, K.H. Shaughnessy, J. Org. Chem. 69 (2004) 7919–7927.
[18] K.H. Shaughnessy, R.S. Booth, Org. Lett. 3 (2001) 2757–2759.
[19] K.W. Anderson, S.L. Buchwald, Angew. Chem. Int. Ed. 44 (2005) 6175–6177.
[20] W.S. Brown, D.D. Boykin, M.Q. Sonnier Jr., W.D. Clark, F.V. Brown, K.H. Shaughnessy, Synthesis (2008) 1965–1970.
[21] C. Fleckenstein, H. Plenio, J. Org. Chem. 73 (2008) 3236–3244.
[22] C. Fleckenstein, H. Plenio, Chem. Eur. J. 14 (2008) 4267–4279.
[23] Y. Hirai, Y. Uozumi, Chem. Lett. 40 (2011) 934–935.
[24] H. Peng, Y.-Q. Chen, S.-L. Mao, Y.-X. Pi, Y. Chen, Z.-Y. Lian, T. Meng, S.-H. Liu, G.-A. Yu, Org. Biomol. Chem. 12 (2014) 6944–6952.
[25] C. Fleckenstein, H. Plenio, Green. Chem. 10 (2008) 563–570.
[26] C. Fleckenstein, S. Roy, S. Leuthäußer, H. Plenio, Chem. Commun. (2007) 2870–2872.
[27] S. Roy, H. Plenio, Adv. Synth. Catal. 352 (2010) 1014–1022.
[28] T. Bartik, B. Bartik, B.E. Hanson, I. Guo, I. Tóth, Organometallics 12 (1993) 164–170.
[29] H. Jansch, S. Kannenberg, G. Boche, Eur. J. Org. Chem. (2001) 2923–2926.
[30] T.E. Barder, J. Am. Chem. Soc. 128 (2006) 898–904.
[31] U. Christmann, D.A. Pantazis, J. Benet-Buchholz, J.e. McGrady, F. Maseras, R. Vilar, J. Am. Chem. Soc. 128 (2006) 6376–6390.
[32] W.A. Herrmann, G.P. Albanese, R.B. Manetsberger, P. Lappe, H. Bahrmann, Angew. Chem. Int. Ed. 34 (1995) 811–813.
[33] A. Hubbuch, R. Bindewald, J. Föhles, V.K. Naithani, H. Zahn, Angew. Chem. Int. Ed. 19 (1980) 394–396.
[34] Z. Guan, X. chai, S. Yu, H. Hu, Y. Jiang, Q. Meng, Q. Wu, Chem. Biol. Drug Des. 76 (2010) 496–504.
[35] C. Dupuis, K. Adiey, L. Charruault, V. Michelet, M. Savignac, J.-P. Genêt, Tetrahedron Lett. 42 (2001) 6523–6526.
[36] C.A. Fleckenstein, H. Plenio, Chem. Eur. J. 13 (2007) 2701–2716.
[37] K. Park, G. Bae, J. Moon, J. Choe, K.H. Song, S. Lee, J. Org. Chem. 75 (2010) 6244–6251.
[38] K. Park, T. Palani, A. Pyo, S. Lee, Tetrahedron Lett. 53 (2012) 733–737.
[39] S. Tartaggia, O. De Lucchi, L.J. Gooßen, Eur. J. Org. Chem. 2012 (2012) 1431–1438.
[40] K. Park, G. Bae, A. Park, Y. Kim, J. Choe, K.H. Song, S. Lee, Tetrahedron Lett. 52 (2011) 576–580.
[41] J.R. Goerlich, R. Schmutzler, Phosphorus, Sulfur Silicon Relat. Elem. 81 (1993) 141–148.
[42] APEX 2 AXScale and SAINT, Version 2010, Bruker AXS, Inc., Madison, WI, 2010.
[43] G.M. Sheldrick, SHELXTL, Structure Determination Software Suite, v.6.10, Bruker AXS, Madison, WI, 2001.