Cross-Coupling of Triallyl(aryl)silanes with Aryl Bromides and Chlorides: An Alternative Convenient Biaryl Synthesis

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Abstract: Cross-coupling of a diverse range of aryl bromides with triallyl(aryl)silanes is effective in the presence of $PdCl_2/PCy_3$ and tetrabutylammonium fluoride (TBAF) in DMSO–H_2O to give various biaryls in good yields. It is worthwhile to note that the all-carbon-substituted arylsilanes, stable towards moisture, acid, and base and easily accessible, serve as a highly practical alternative to their aryl(halo)silane counterparts. A catalyst system consisting of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and 2-[2,4,6-(i-Pr)$_3C_6H_2$]-$C_6H_4PCy_2$ and use of TBAF·$3H_2O$ in THF–H_2O are effective especially for the cross-coupling with aryl chlorides. Both of the catalyst systems tolerate a broad spectrum of common functional groups. The high efficiency of reactions is presumably due to the ready cleavage of the allyl groups upon treatment with TBAF·$3H_2O$ and an appropriate amount of water. Diallyl(diphenyl)silane also cross-couples with various aryl bromides and chlorides in good yields, whereas allyl(triphenyl)silane gives the cross-coupled products in only moderate yields. Through sequential cross-coupling of bromochlorobenzenes with different arylsilanes, a range of unsymmetrical terphenyls are accessible in good overall yields.

Keywords: aryl halides; biaryls; cross-coupling; palladium; terphenyls; triallyl(aryl)silanes

Introduction

Carbon-carbon bond formation is one of the most fundamental transformations in organic chemistry. In the last few decades, the cross-coupling strategy has gained considerable attention especially as a straightforward method for C(sp^2)–C(sp^2) bond formation.[1] Recently, the transition metal-catalyzed cross-coupling reaction between arylmetals and aryl halides or sulfonates has emerged as one of the most powerful tools for the synthesis of biaryl and polyaryl subunits that have been found as core structural motifs in many biologically active molecules and electronic organic materials.[2] Typical examples of arylmetals in the cross-coupling reaction are Grignard reagents (Kumada–Tamao and Corriu coupling),[3] organostannanes (Kosugi–Migita–Stille coupling),[4] organozincs and -zirconiums (Negishi coupling),[5] and organoboranes (Suzuki–Miyaura coupling).[6] Of those, the Stille and Suzuki–Miyaura reactions have been extensively used for synthetically useful transformations due to the tolerance of a vast array of functional groups. Apart from these advantages, however, inherent problems associated with toxic nature of metal residues[7] as well as the oxygen and moisture sensitivity of many organometallic reagents led to the use of organosilanes as a viable alternative organometallic reagent for the synthetic purpose owing to their easy availability, stability, and the non-toxic by-products.[8]

Over the years, we and others have pursued the possibility of the silicon-based cross-coupling reaction,[9] employing halosilanes,[10] oxysilanes,[11] silanols,[12] and polysiloxanes[13] at the beginning, whereas all-carbon-substituted silicon species were later introduced for alkenyl coupling. Phenyldimethyl,[14] pyridyl,[15] thienyl,[16] or benzyl[17] groups on the silicon in alkenylsilanes and alkenylsilacyclobutanes[18] were introduced to the cross-coupling reactions with a wide range of electrophiles. However, arylsilanes having such substituents remained to be employed as arylmetallic nucleophiles for unsymmetrical biaryl synthesis.

For aryl-aryl coupling, aryl(halo)silanes were at first employed successfully in the cross-coupling with aryl halides and triflates,[19] and were recently utilized in solid phase synthesis.[20] Later, arylsilanols,[21] trialkoxy(aryl)-silanes,[22] poly(phenylsiloxane)s,[23] aryl(halo)silacyclobutanes,[24] arylsilatranes,[25] and triethylammonium arylbis(catecholato)silicates[26] were used for the cross-coupling with aryl halides and triflates.

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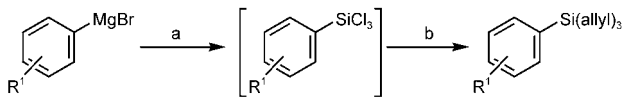
All the listed cross-coupling reactions using arylsilane reagents suggest that silanes with heteroatom substituents are mandatory for efficient reactivity and thus are generally sensitive to moisture, acid, and base. The use of all-carbon-substituted silanes would be a favorable choice that could enjoy the stability of reagent. To meet the above challenge, we envisaged that allyl(aryl)-silanes would be the reagent of choice. Above all, triallyl(aryl)silanes, readily prepared by treatment of aryltrichlorosilane with allylmagnesium bromide, have been visualized as a practical arylsilane coupling agent, because active silicate species are readily accessible by *in situ* cleavage of the allyl groups on silicon upon treatment with excess TBAF for coupling with aryl halides. Herein, we present a detailed account of our efforts in the cross-coupling of an array of triallyl(aryl)silanes with a variety of aryl bromides and chlorides.[27,28] Also described are the efficiency of the reaction depending on the number of allyl groups in the arylsilane and its application to unsymmetrical terphenyl synthesis.

Results and Discussion

Preparation of Various Triallyl(aryl)silanes

Triallyl(phenyl)silane (**1a**) and triallyl(4-methylphenyl)silane (**1b**) were prepared directly from commercially available trichlorophenylsilane and trichloro(*p*-tolyl)silanes by reaction with 3.1 equivs. of allylmagnesium bromide (Scheme 1). Other triallyl(aryl)silanes were obtained in two steps by reaction of the corresponding arylmagnesium halides with excess tetrachlorosilane ($SiCl_4$) followed by treatment of the resulting trichloroarylsilanes with 3.1 equivs. of allylmagnesium bromide. As expected, triallyl(aryl)silanes are quite stable to moisture, acids, and bases. For example, **1a** is not affected by stirring with either NaOH, KOH, or K_2CO_3 in excess; slow decomposition of **1a** was noticed when its was treated with a stoichiometric amount of aqueous HCl for 24 h, whereas a catalytic amount of HCl did not induce any change. These silanes can be stored at room temperature over months without any detectable degradation.



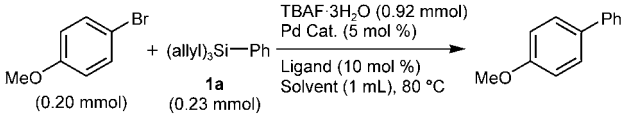
Scheme 1. Preparation of triallyl(aryl)silanes.

Cross-Coupling Reactions with Aryl Bromides

At first, the cross-coupling of **1a** with 4-bromoanisole was performed in the presence of TBAF·$3H_2O$ to find an optimal catalyst system. Because of the small electronegativity difference between carbon and silicon, the cross-coupling reaction could only be achieved by choosing an appropriate activator that polarizes a C–Si bond through the formation of activated pentacoordinate species *in situ*.[8,9] Our basic understanding on the silicon-based cross-coupling reaction suggests that an activator, mainly a fluoride source, is necessary in order to obtain this active pentacoordinate silicate species. Therefore, we considered TBAF among other fluoride sources as an activator in the cross-coupling of **1a**. Use of less than 3 equivalents of TBAF·$3H_2O$ with respect to the silane gave incomplete consumption of **1a**. However, 4 equivalents of TBAF·$3H_2O$ made it possible to achieve an efficient cross-coupling reaction. Presumably, 3 equivalents of TBAF·$3H_2O$ cleaved instantaneously the three allyl groups on silicon to form possibly phenyltrifluorosilane or its equivalent and the additional mole of TBAF·$3H_2O$ might have caused the formation of a pentacoordinate silicate species to ease the transmetalation.

The first experiment was performed using $PdCl_2/PCy_3$ in dry DMSO at 80 °C, but none of the corresponding biaryl was detected (Table 1, entry 1). To our surprise, however, the presence of water in the reaction mixture greatly assisted the formation of the coupling product. Although the formation of the desired biaryl was effectively realized by employing DMSO–H_2O (15:1) [17 equivs. of water], 4-bromoanisole was not completely consumed in 8 h (entry 2). Fortunately, complete conversion of the bromide was observed using DMSO–H_2O (10:1, 1 mL) [25 equivs. of water] without generating a noticeable amount of either the homocoupling product or the protonation product derived from 4-bromoanisole, and yield of the biaryl was estimated to be 96% by GC (entry 3). In contrast, increasing the DMSO–H_2O ratio to 2:1 [93 equivs. of water] drastically lowered the yield to 64% (GC) (entry 14) and formation of anisole was noticed; DMSO–H_2O (5:1) [46 equivs. of water] gave 88% (GC) of the biaryl (entry 15). Although Denmark and DeShong independently reported that the presence of water in the reaction mixture drastically increased product yields,[25,29] we presume that water may encompass the ready cleavage of allyl-silicon bonds to form active silicate species and/or to raise dielectric constant of the medium to accelerate transmetalation. Reactions at lower temperatures also resulted in incomplete conversion of the bromide. Of various palladium catalysts, $PdCl_2$ was found to be the best; $Pd(OAc)_2$ and $Pd_2(dba)_3$ were not effective at all; $[(\eta^3\text{-}C_3H_5)PdCl]_2$ provided the product in only 66% yield using PCy_3 in DMSO–H_2O (10:1, 1 mL) (entries 4–6). In the absence of PCy_3 (entry 7), the biaryl product was not produced at

Table 1. Optimization of catalyst/ligand/solvent systems in the cross-coupling of **1a** with 4-bromoanisole.



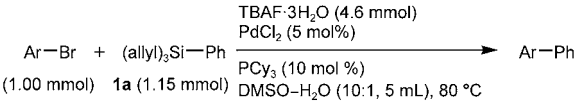
Entry	Catalyst	Ligand	Solvent	Time (h)	Yield [%][a]
1	$PdCl_2$	PCy_3	DMSO	24	0
2	$PdCl_2$	PCy_3	DMSO–H_2O (15 : 1)	8	77
3	$PdCl_2$	PCy_3	DMSO–H_2O (10 : 1)	7	96
4	$Pd(OAc)_2$	PCy_3	DMSO–H_2O (10 : 1)	24	0
5	$Pd_2(dba)_3$	PCy_3	DMSO–H_2O (10 : 1)	24	0
6	1/2[(η^3-C_3H_5)PdCl]$_2$	PCy_3	DMSO–H_2O (10 : 1)	7	66
7	$PdCl_2$	–	DMSO–H_2O (10 : 1)	24	0
8	$PdCl_2$	PPh_3	DMSO–H_2O (10 : 1)	12	54
9	$PdCl_2$	P(*o*-Tol)$_3$	DMSO–H_2O (10 : 1)	24	<5
10	$PdCl_2$	P(*t*-Bu)$_3$	DMSO–H_2O (10 : 1)	24	<5
11	$PdCl_2$	PCy_3	Dioxane–H_2O (10 : 1)	7	80
12	$PdCl_2$	PCy_3	DMF–H_2O (10 : 1)	24	63
13	$PdCl_2$	PCy_3	Toluene–H_2O (10 : 1)	24	<5
14	$PdCl_2$	PCy_3	DMSO–H_2O (2 : 1)	6	64
15	$PdCl_2$	PCy_3	DMSO–H_2O (5 : 1)	6	88

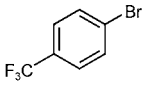
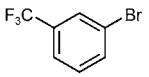
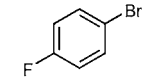
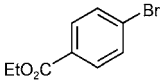
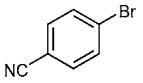
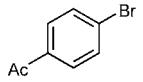
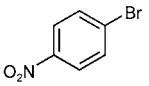
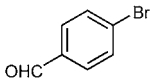
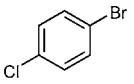
[a] The yield was determined by GC with tridecane as an internal standard.

all. Triphenylphosphine (PPh_3) was moderately effective (entry 8), whereas P(*o*-Tol)$_3$ and P(*t*-Bu)$_3$ were totally ineffective (entries 9 and 10). An extensive survey of solvents revealed that DMSO–H_2O was the best (entry 3); dioxane–H_2O was equally effective (entry 11); DMF–H_2O and toluene–H_2O were inferior (entries 12 and 13). Concerning the nucleophilic activator, metal fluorides like KF, CsF, NaF, and LiF and bases like K_3PO_4, KOH, NaOH, KO-*t*-Bu, and TASF were ineffective. In contrast, TBAF·$3H_2O$ was quite effective for the efficient cross-coupling reaction. This could be explained by many effects, such as: 1) a solubility problem that catapulted during the reaction; TBAF was soluble in the reaction media, whereas other fluoride sources and bases impart poor solubility; 2) naked cationic species like the tetrabutylammonium ion might be responsible for creating an active silicate species to attain the transmetalation successfully.

The optimized conditions [$PdCl_2$ (5 mol %), PCy_3 (10 mol %), and TBAF (4.0 equivs. with respect to arylsilanes) in DMSO–H_2O (10:1, 80 °C)] are suitable for the cross-coupling reactions of a wide array of electronically and structurally diverse aryl bromides and triallyl(aryl)silanes. Table 2 summarizes the results of the cross-coupling of various electron-poor aryl bromides with **1a**. Aryl bromides having a CF_3 or F group at the 4- and/or 3-positions gave the corresponding coupled products in excellent yields (entries 1–3). Common functional groups such as ester, cyano, keto, nitro, and formyl (entries 4–8) tolerate the reaction conditions;

Table 2. Cross-coupling reaction of **1a** with electron-poor aryl bromides.



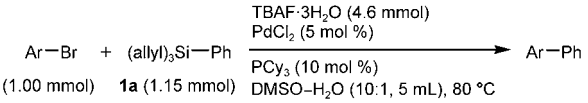
Entry	Ar—Br	Time [h]	Yield of Ar–Ph [%][a]
1		3	95
2		2	96
3		2	95
4		3 3	65 75[b]
5		3	69
6		2	81
7		4	87
8		2 2	51 54[b]
9		12	98

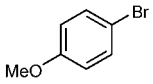
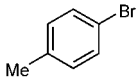
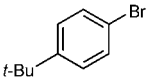
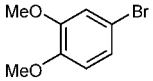
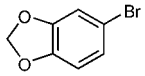
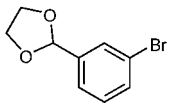
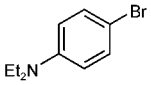
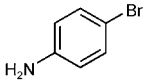
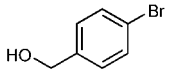
[a] Isolated yield based on ArBr.
[b] DMSO–H_2O (2:1) was used as solvent.

moderate yields are encountered with aryl bromides having an ester, cyano, or formyl group. Excess of TBAF does not lead to hydrolysis of the ester and cyano groups as evidenced by GC assays.[30] Furthermore, the phenylsilane selectively reacted with the bromide group in 4-bromochlorobenzene leaving the chloride functionality intact (entry 9).

A variety of electron-rich aryl bromides also participated in the cross-coupling with **1a** (Table 3). 4-Methoxy-, 4-methyl-, and 4-*t*-butyl-substituted aryl bromides reacted effectively to give the corresponding cross-coupled products in excellent yields (entries 1–3). The presence of two electron-donating groups did not affect the efficiency of the reaction (entries 4 and 5). Functional groups such as acetal, amino, and hydroxyl were tolerated by the catalyst system. For example, 4-bromo-*N*,*N*-diethylaniline, 4-bromoaniline, and 4-bromobenzyl alcohol cross-coupled smoothly (entries 6–

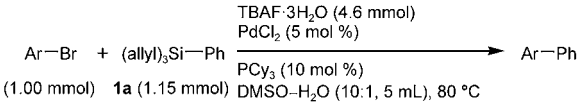
Table 3. Cross-coupling reaction of **1a** with electron-rich aryl bromides.

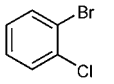
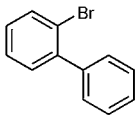
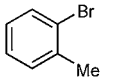
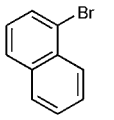
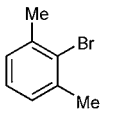
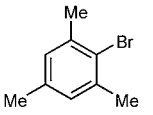
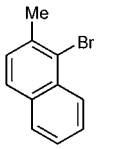


Entry	Ar−Br	Time [h]	Yield of Ar–Ph [%][a]
1		3	92
2		3	96
3		4	97
4		2	97
5		2	96
6		3	93
7		5 3	75 88[b]
8		3	83
9		4	79

[a] Isolated yield based on ArBr.
[b] DMSO–H_2O (20:1) was used as solvent.

Table 4. Cross-coupling reaction of **1a** with *o*-substituted aryl bromides.



Entry	Ar−Br	Time [h]	Yield of Ar–Ph [%][a]
1		10	87
2		3	98
3		3	91
4		3	96
5		4	95[b]
6		6	92[b]
7		18	99[b]

[a] Isolated yield based on ArBr.
[b] Accompanied with ~3–5% of the protolysis product.

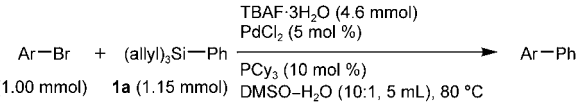
9), but 4-bromophenol completely failed to undergo the reaction.

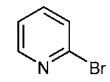
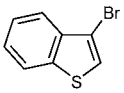
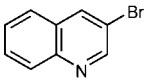
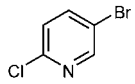
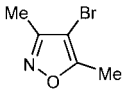
Next, the effect of *ortho*-substitution on aryl bromides was examined to assess the steric effect in the cross-coupling reaction, and the results are summarized in Table 4. The presence of either one electron-poor or -rich *o*-substituent in aryl bromides did not affect the reaction (entries 1–3). Coupling also proceeded with 1-bromonaphthalene (entry 4). It is worthwhile to mention that the cross-coupling reaction of **1a** with more sterically demanding substrates such as 2,6-dimethyl- and 2,4,6-trimethylbromobenzenes as well as 2-methyl-1-bromonaphthalene proceeded in high yields along with formation of ~3–5% of the corresponding protonation product (entries 5–7).[31]

Similarly, various heteroaryl bromides are amenable to an effective cross-coupling as depicted in Table 5. 2-Bromopyridine, 3-bromobenzothiophene, and 3-bromoquinoline also cross-coupled with **1a** smoothly to afford the corresponding biaryls in high yields (entries 1–3). 2-Chloro-5-bromopyridine selectively coupled at the bromo functionality without affecting the chloro group (entry 4). The sterically demanding 4-bromo-3,5-dimethylisoxazole also cross-coupled moderately with **1a** (entry 5).

The scope of the structure of the arylsilanes was next examined. As illustrated in Table 6, both electronically and sterically different triallyl(aryl)silanes could couple smoothly with a broad range of aryl bromides under the conditions of $PdCl_2$ (5 mol %), PCy_3 (10 mol %), and TBAF (4.0 equivs. with respect to arylsilanes) in DMSO–H_2O (10:1, 80 °C). Electron-rich arylsilanes **1b–d** reacted quite efficiently at nearly stoichiometric loading, while electron-poor arylsilane **1e** required a higher loading to attain satisfactory yields. For example, **1b** coupled with various aryl bromides, giving the corre-

Table 5. Cross-coupling reaction of **1a** with heteroaryl aryl bromides.



Entry	Ar−Br	Time [h]	Yield of Ar–Ph [%][a]
1		23	86
2		5	93
3		2	97
4		3	89
5		18	61

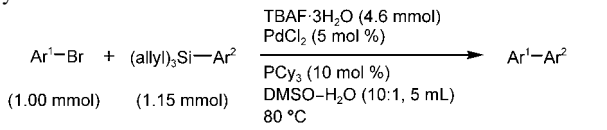
[a] Isolated yield based on ArBr.

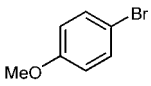
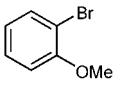
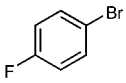
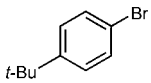
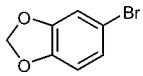
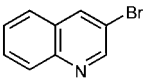
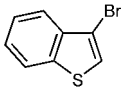
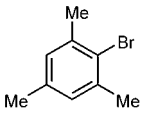
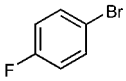
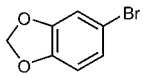
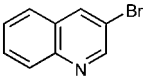
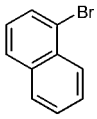
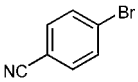
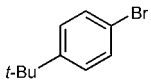
sponding biaryls in excellent yields (entries 1 and 2). Similarly, electron-poor and -rich aryl bromides resulted in efficient cross-coupling with **1c** (entries 3–5). Heteroaryl bromides such as 3-bromoquinoline and 3-bromobenzothiophene are not exceptions (entries 6 and 7). The more hindered 2,4,6-trimethylbromobenzene also coupled effectively, albeit being accompanied by ~3% of a protolysis product (entry 8).[31] Sterically hindered triallyl(2-methylphenyl)silane (**1d**) (1.3 equivs.) was next allowed to couple with electron-poor, electron-rich, and heteroaryl bromides, and the corresponding biaryls were produced in acceptable yields (entries 9–11). The hindered bromide, 1-bromonaphthalene, reacted also efficiently (entry 12). Furthermore, triallyl(4-fluorophenyl)silane (**1e**) could couple with a range of aryl bromides to give the desired biaryls in good yields when 1.8 molar equivalents of the silane reagent was used (entries 13 and 14).

Cross-Coupling Reactions with Aryl Chlorides

As cross-coupling of triallyl(aryl)silanes with various aryl bromides was successfully carried out, we next turned our attention to the cross-coupling of aryl chlorides because of the ready availability and low cost of aryl chlorides compared with other halides. To uncover the optimum conditions, we performed many experiments using triallyl(phenyl)silane (**1a**) and 4-chloroanisole in the presence of TBAF·$3H_2O$ under various cata-

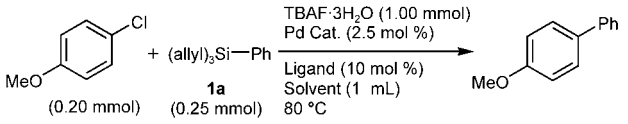
Table 6. Cross-coupling reaction of triallyl(aryl)silanes with aryl bromides.



Entry	Ar^1−Br	Ar^2−Si(allyl)$_3$	Time [h]	Yield of Ar^1–Ar^2 [%][a]
1		**1b**	6	94
2		**1b**	6	80
3		**1c**	4	98
4		**1c**	4	98
5		**1c**	3	93
6		**1c**	4	95
7		**1c**	5	87
8		**1c**	6	97[b]
9		**1d**	6	79[c]
10		**1d**	8	92[c]
11		**1d**	20	80[c]
12		**1d**	20	87[c]
13		**1e**	18	69[d]
14		**1e**	11	88[d]

[a] Isolated yield based on Ar^1Br.
[b] Accompanied with ~3% of the protolysis product.
[c] 1.3 Molar equivalents of **1d** were used.
[d] 1.8 Molar equivalents of **1e** were used.

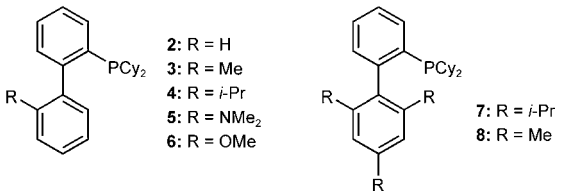
Table 7. Optimization of catalyst/ligand/solvent systems in the cross-coupling of **1a** with 4-chloroanisole.



Entry	Catalyst	Ligand	Solvent	Time [h]	Yield [%][a]
1	$PdCl_2$ (5.0 mol %)	PCy_3	DMSO–H_2O (10 : 1)	36	<10
2	$PdCl_2$ (5.0 mo l%)	**2**	DMSO–H_2O (10 : 1)	12	48
3	$Pd_2(dba)_3$	**2**	DMSO–H_2O (10 : 1)	36	0
4	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**2**	DMSO–H_2O (10 : 1)	10	57
5	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**2**	DMF–H_2O (10 : 1)	10	65
6	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**2**	Toluene–H_2O (10 : 1)	24	47
7	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**2**	THF–H_2O (10 : 1)	4	79
8	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**2**	Dioxane–H_2O (10 : 1)	5	78
9	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**2**	THF–H_2O (20 : 1)	8	82
10	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**3**	THF–H_2O (20 : 1)	16	98
11	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**4**	THF–H_2O (20 : 1)	7	84
12	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**5**	THF–H_2O (20 : 1)	36	59
13	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**6**	THF–H_2O (20 : 1)	6	85
14	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**7**	THF–H_2O (20 : 1)	8	100
15	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**8**	THF–H_2O (20 : 1)	24	58
16	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**7**	THF–H_2O (10 : 1)	8	50
17	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	**7**	THF–H_2O (30 : 1)	8	93

[a] The yield was determined by GC with tridecane as an internal standard.

Ligands **2**–**8**:



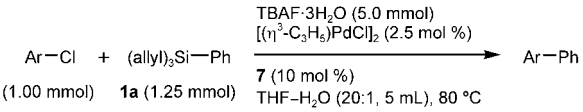
lyst/ligand/solvent systems as summarized in Table 7 and found that the optimum conditions for aryl bromides gave the coupled product at best in 10% yield (entry 1). However, the biaryl ligands introduced by Buchwald were found to be effective due possibly to their strong electron donation to palladium and the steric bulk that allow easy oxidative addition and transmetalation, respectively.[32] Thus, it is reasonable to assume that the nature of a PR_2 group in the ligand decides the efficiency of the reaction. Notably, 2-C_6H_5-C_6H_4-PCy_2 (**2**) was found to be better than its P(*t*-Bu)$_2$ analogue. Among the various palladium catalysts, $[(\eta^3\text{-}C_3H_5)PdCl]_2$ gave better results than $PdCl_2$ upon use of **2** as the ligand; $Pd_2(dba)_3$ did not provide any desired biaryl (entries 2–4). Furthermore, the solvent was also essential: DMF–H_2O (10:1, 1 mL) provided 65% of the coupled product (entry 5); toluene–H_2O (10:1, 1 mL) was moderately effective (entry 6); THF–H_2O (10:1, 1 mL) and dioxane–H_2O (10:1, 1 mL) were greatly favored over others (entries 7 and 8). Also favorable was THF–H_2O (20:1, 1 mL) (entry 9). Recent studies on catalysts with biarylphosphine ligands show that the bulk of ligands controls the catalytic activity.[33] A survey of biaryl ligands **3**–**8** (entries 10–15) led us to find that ligand **7** was the most effective to afford the desired biaryl quantitatively (entry 14).[34] The yield of the cross-coupling product was again drastically affected by the amount of water present in the reaction media (entries 16 and 17).

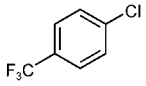
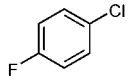
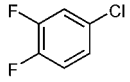
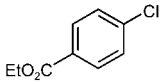
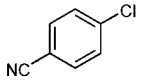
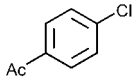
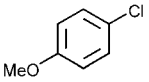
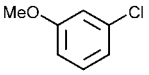
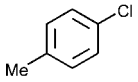
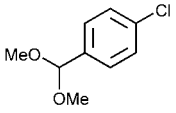
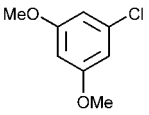
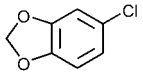
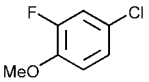
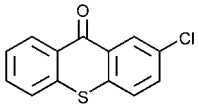
To demonstrate the generality of our reaction, we applied the optimized conditions of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2.5 mol %), **7** (10 mol %), and TBAF·3H_2O (4.0 equivs. with respect to arylsilanes) in THF–H_2O (20:1, 80 °C) for the cross-coupling reactions with **1a** and a wide array of electronically and structurally diverse aryl chlorides and summarize the results of the cross-coupling of various electron-poor and -rich aryl chlorides in Table 8. Good yields of the desired coupled products were attained with aryl chlorides having either CF_3 or F groups at the 4- and/or 3-positions (entries 1–3). Common functional groups such as ester, cyano, and keto were inert to the catalyst system: aryl chlorides with these groups afforded the corresponding cross-coupled products in moderate yields (entries 4–6).[30] The cross-coupling proceeded also with electron-rich aryl chlorides in yields over 94% (entries 7–10). The presence of two electron-donating groups did not affect the efficiency (entries 11 and 12). Aryl chlorides having both electron-donating and -withdrawing groups also reacted smoothly (entry 13). 2-Chlorothioxanthone underwent the coupling with similar satisfaction (entry 14). Our experimental results reveal that electron-rich aryl chlorides reacted quite effectively in excellent yields, while the electron-poor ones reacted rapidly but less effectively.

We next examined *o*-substitution in the aryl chlorides to evaluate the steric effect in the cross-coupling reaction with **1a** (Table 9). The reactions of *o*-trifluoromethyl and *o*-fluorophenyl chlorides proceeded in good yields (entries 1 and 2). Similarly, 2-methoxy-, 2-methyl- and 2,4-dimethylphenyl chlorides smoothly coupled in high yields (entries 3–5). An *m*-nitro group did not affect the efficiency of the reaction (entry 6). 1-Chloronaphthalene reacted efficiently (entry 7), while the more sterically demanding 2,6-dimethylchlorobenzene also coupled successfully (entry 8). Thus, variously substituted aryl chlorides are applicable to the silicon-based cross-coupling reaction. A wide array of heteroaryl chlorides also reacted smoothly: 3-chloropyridine coupled quite efficiently (entry 9); 2-chloropyridine did not provide the corresponding coupled product under the same conditions. Chlorothiophene, -quinoline, -benzoxazole, and -benzothiazole coupled successfully in good to excellent yields (entries 10–13).

We next studied the scope of the arylsilanes and the results are summarized in Table 10. Coupling of electron-rich triallyl(aryl)silanes, **1b** and **1c**, with various aryl

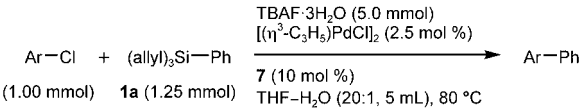
Table 8. Cross-coupling reaction of **1a** with electron-poor and -rich aryl chlorides.

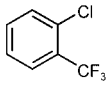
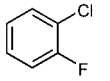
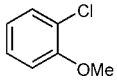
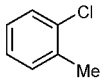
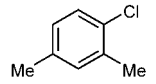
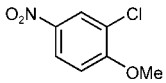
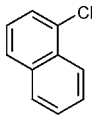
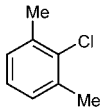
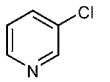
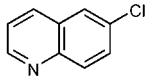
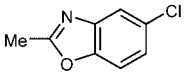
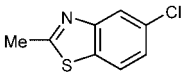


Entry	Ar−Cl	Time [h]	Yield of Ar–Ph [%][a]
1		3	95
2		3	91
3		3	89
4		4	71
5		3	77
6		4	69
7		12	97
8		14	99
9		14	98
10		12	94
11		8	94
12		14	97
13		3	95
14		12	98

[a] Isolated yield based on ArCl.

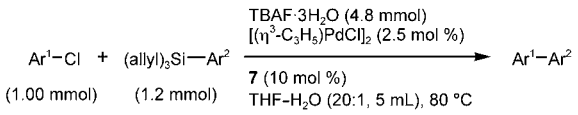
Table 9. Cross-coupling reaction of **1a** with *o*-substituted and heteroaryl chlorides.

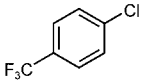
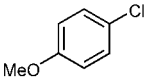
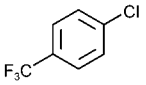
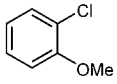
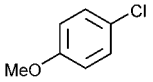
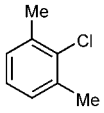
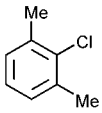
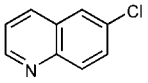
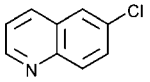
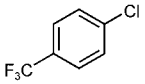
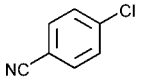
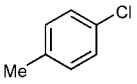
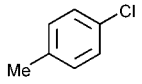
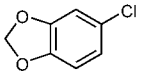
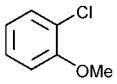
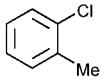
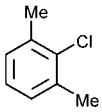
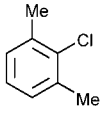
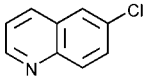


Entry	Ar−Cl	Time [h]	Yield of Ar–Ph [%][a]
1		3	86
2		3	85
3		14	94
4		16	88
5		12	87
6		3	84
7		14	94
8		12	87
9		14	98
10		12	93
11		14	99
12		14	83
13		12	84

[a] Isolated yield based on ArCl.

Table 10. Cross-coupling reaction of triallyl(aryl)silanes with aryl chlorides.

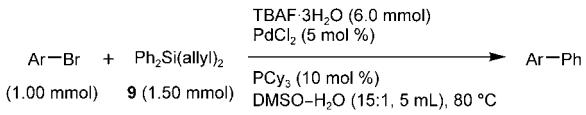


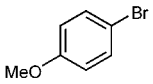
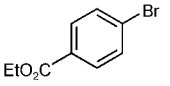
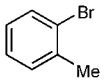
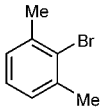
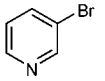
Entry	Ar^1–Cl	Ar^2–Si(allyl)$_3$	Time [h]	Yield of Ar^1-Ar^2 [%][a]	Entry	Ar^1–Cl	Ar^2–Si(allyl)$_3$	Time [h]	Yield of Ar^1-Ar^2 [%][a]
1		**1b**	3	89	11		**1c**	6	92
2		**1b**	4	93	12		**1d**	4	78[b]
3		**1b**	4	85	13		**1d**	4	92[b]
4		**1b**	9	79	14		**1d**	12	66[b]
5		**1b**	7	88	15		**1d**	7	87[b]
6		**1c**	3	89	16		**1e**	11	73[c]
7		**1c**	4	95	17		**1e**	11	99[c]
8		**1c**	4	94	18		**1e**	24	55[c,d]
9		**1c**	4	93	19		**1e**	24	46[c,d]
10		**1c**	4	87	20		**1e**	13	98[c]

[a] Isolated yield based on Ar^1Cl.
[b] 1.3 Molar equivalents of **1d** were used.
[c] 1.8 Molar equivalents of **1e** were used.
[d] Yield was determined in comparison with ^1H NMR using an internal standard.

chlorides proceeds quite efficiently using only 1.2 molar equivalents of the silanes. Both electron-poor and -rich aryl chlorides coupled with triallyl(4-methylphenyl)silane (**1b**) in excellent yields (entries 1–2). Even sterically demanding substrates such as 2-chloroanisole and 2,6-dimethylchlorobenzene as well as 6-chloroquinoline reacted smoothly with **1b** to afford the corresponding products in high yields (entries 3–5). Triallyl(4-methoxyphenyl)silane (**1c**) also were successfully coupled with various aryl chlorides in good yields by the catalyst system (entries 6–11). Furthermore, the sterically hindered arylsilane **1d** was allowed to couple with electron-poor and -rich aryl chlorides to afford the corresponding biaryls in high yields, using 1.3 molar equivalents of **1d** (entries 12 and 13). It is worthy to note that **1d** reacted with the more sterically hindered 2,6-dimethylchlorobenzene (entry 14). 6-Chloroquinoline also coupled efficiently (entry 15). The electron-deficient triallyl(4-fluorophenyl)silane (**1e**) also participated in the reaction with various aryl chlorides upon use of 1.8 molar equivalents of **1e**. Thus, electron-poor and -rich aryl chlorides successfully participated in the coupling with **1e** (en-

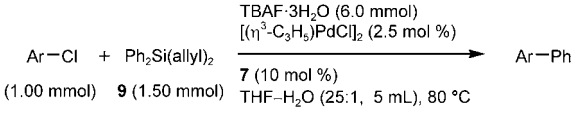
Table 11. Cross-coupling reaction of **9** with aryl bromides.

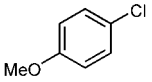
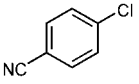
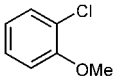
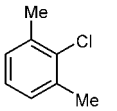


Entry	Ar−Br	Time [h]	Yield of Ar-Ph [%][a]
1		11	93
2		11	61
3		14	87
4		24	58[b]
5		12	96

[a] Isolated yield based on ArBr.
[b] Yield was determined in comparison with ^{1}H NMR using an internal standard.

Table 12. Cross-coupling reaction of **9** with aryl chlorides.



Entry	Ar−Cl	Time [h]	Yield of Ar-Ph [%][a]
1		8	93
2		5	74
3		12	79
4		7	95
5		20	57

[a] Isolated yield based on ArCl.

tries 16 and 17). However, complete conversion of *o*-substituted aryl chlorides was not achieved with **1e** (entries 18 and 19). 6-Chloroquinoline also coupled with **1e** (entry 20).

All attempts to couple triallyl(3-thienyl)silane with various aryl bromides and chlorides met with no success. The failure could be attributed due to the protonative cleavage of the Si-thienyl bond before transmetalation. A similar effect has been observed in the cross-coupling of alkenyldimethyl(2-thienyl)silanes with various aryl halides upon treatment with TBAF.[16]

Cross-Coupling Reaction of Diallyl(diphenyl)silane with Aryl Bromides and Chlorides

As described above, the Pd-catalyzed cross-couplings of triallyl(aryl)silanes with aryl halides proceeds highly efficiently by use of three robust allyl groups on silicon. We next studied the implications in the cross-coupling reaction of the number of allyl groups on silicon to invoke the merits and demerits of the present reaction conditions. Thus, we chose diallyl(diphenyl)silane (**9**) as a coupling partner, as we anticipated that the reaction would proceed with only a half molar equivalent of **9**. Additionally, it should allow us to reduce the amount of TBAF·3H$_2$O in the reaction. Unfortunately, however, cross-coupling reaction of **9** (0.6 equivs.) with 4-bromoanisole using TBAF·3H$_2$O (4 equivs. with respect to silane) provided the product in only poor yield. After many trials, 1.5 molar equivalents of **9** were found to be necessary to achieve coupling with 4-bromoanisole in DMSO–H$_2$O (15:1, 5 mL) and to isolate the desired biaryl in 93% yield (Table 11, entry 1). Electron-poor and *o*-substituted aryl bromides coupled similarly (entries 2 and 3). Coupling of sterically demanding 2,6-dimethylbromobenzene with **9** was, however, not completed and the product was produced only in a moderate yield (entry 4). A typical heterocyclic bromide, 3-bromopyridine also coupled effectively (entry 5).

Cross-coupling of **9** with 4-chloroanisole under the conditions of Table 8, except for TBAF (4.0 equivs. with respect to **9**), resulted in incomplete consumption of the chloride when 0.6 equivs. of the silane were used. Using, however, 1.5 molar equivalents of silane in THF–H$_2$O (25 : 1) afforded the biaryl in excellent yield (Table 12, entry 1). Thus, electron-poor, *o*-substituted, and heteroaryl chlorides reacted with **9** to afford the corresponding biaryls in good yields (entries 2–4). The more sterically demanding 2,6-dimethylchlorobenzene, however, reacted with a poor yield (entry 5).

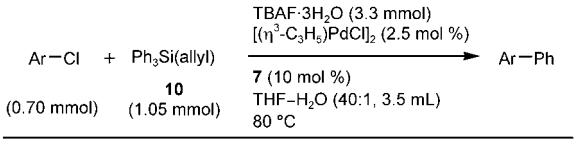
The above results suggest that only one phenyl in **9** participated in the reaction, leaving the other ineffective. This observation can be rationalized by assuming that the pentacoordinate silicate species might be formed in the first step to allow one phenyl group to transmetalate to palladium, but the second transfer of phenyl from the resulting phenylsilane may be hampered by the formation of hexacoordinate silicate, which is shown to be inert for transmetalation.[8a,9a,19b,35]

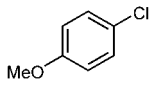
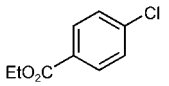
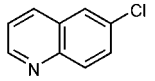
Cross-Coupling of Triphenyl(allyl)silane with Aryl Bromides and Chlorides

Additionally, triphenylallylsilane (**10**) was successfully examined for the cross-coupling with aryl chlorides. Under the conditions of Table 13, 4-chloroanisole coupled with **10** (1.5 equivs., entry 1). An ester group did not affect the efficiency in the reaction as observed previously (entry 2). The cross-coupling also proceeded with 6-chloroquinoline in excellent yield (entry 3). In contrast, aryl bromides did not undergo the coupling with **10** under the conditions used for **1** or **9**.

These results imply that a higher loading of **10** is essential in order to obtain effective cross-couplings with aryl chlorides. Thus, the efficiency of the reaction is again hampered drastically using one allyl group on silicon as evidenced with **10**.

Table 13. Cross-coupling reaction of **10** with aryl chlorides.



Entry	Ar−Cl	Time [h]	Yield of Ar-Ph [%][a]
1		12	86
2		5	87
3		7	96

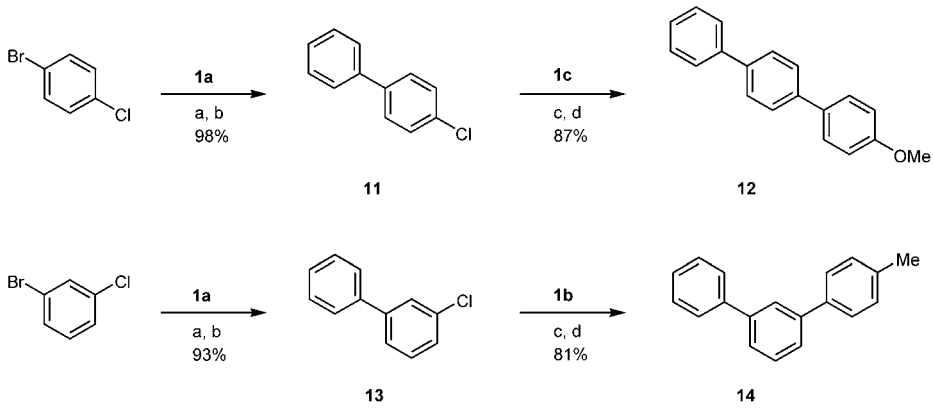
[a] Isolated yield based on ArCl.

Sequential Cross-Coupling Reactions of Bromochlorobenzenes

We applied the cross-coupling of triallyl(aryl)silanes with aryl bromides and chlorides to sequential cross-couplings with bromochlorobenzenes. In view of widespread occurrence of unsymmetrical terphenyls in many liquid crystalline compounds, application of different reaction parameters independently to bromochlorobenzene should give rise to terphenyls. The cross-coupling reaction of triallyl(phenyl)silane (**1a**) with 4-bromochlorobenzene with catalyst systems including $PdCl_2$, PCy_3, and $TBAF \cdot 3H_2O$ in DMSO–H_2O afforded the corresponding biaryls without affecting the chloro group in 98% yield.[27] Subsequent cross-coupling with triallyl(4-methoxyphenyl)silane (**1c**) gave 4-methoxy-*p*-terphenyl (**12**) in 87% yield as shown in Scheme 2. Similarly, 4-methyl-*m*-terphenyl (**14**) was prepared *via* identical reaction sequences with 3-bromochlorobenzene in good yields (Scheme 2).

Conclusion

We have demonstrated a general method for the silicon-based cross-coupling reaction that allows the easy synthesis of a wide array of unsymmetrical biaryls using allyl(aryl)silanes. The high efficiency of the reaction is attributed to the spontaneous cleavage of the allyl groups on silicon upon treatment with TBAF and an appropriate amount of water to provide possibly an active silicate species such as fluorosilanes, silanepolyols, siloxanes and/or their mixed forms that ease transmetalation.[36] The fair stability associated with triallyl(aryl)silanes allows conventional synthetic operations. Both catalyst systems described herein tolerate a broad range of functional groups.



Reagents and Conditions: a) TBAF·3H_2O (4 molar equivalents), DMSO–H_2O (10:1), rt, 1 h. b) $PdCl_2$ (5 mol %), PCy_3 (10 mol %), 80 °C, 12 h. c) TBAF·3H_2O (4 molar equivalents), THF–H_2O (20:1), rt, 1 h. d) $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2.5 mol %), **7** (10 mol %), 80 °C, 8 h.

Scheme 2. Sequential cross-coupling reactions of bromochlorobenzenes.

Our experimental results clearly reveal that the reactivity order of the allyl(phenyl)silanes depends on the number of allyl groups on silicon, i.e., $PhSi(allyl)_3 > Ph_2Si(allyl)_2 > Ph_3Si(allyl)$. Although $Ph_2Si(allyl)_2$ is also effective, a high loading of the reagent is necessary in order to obtain good yields of coupling products. Among the various arylsilanes used, those substituted by an electron-donating group show better reactivity over those having an electron-withdrawing group, due presumably to the enhanced nucleophilicity of the aryl–silicon bond to accelerate the transmetalation step that is generally considered to be the rate-determining step of the cross-coupling reaction. Considering the easy accessibility and stability of organosilane reagents as well as the non-toxic by-products associated with triallyl(aryl)silanes, the present methodology should find wide use not only in academia but also in industry.

Experimental Section

Preparation of Triallyl(phenyl)silanes (1a); General Procedure A

A flame-dried 500-mL, 3-necked, round-bottom flask equipped with a Teflon coated magnetic bar, reflux condenser, glass stopper, and a rubber septum, was purged with argon and charged with phenyltrichlorosilane (30.0 g, 0.142 mol) in Et_2O (50 mL). Allylmagnesium bromide (455 mL, 1.00 M in Et_2O, 0.455 mol) was added dropwise at 0 °C over 30 min. After an additional 1 h of stirring at 0 °C, the reaction mixture was refluxed overnight. The resulting reaction mixture was allowed to cool to room temperature, and quenched with a saturated NH_4Cl aqueous solution (80 mL) at 0 °C. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 × 70 mL). The combined extracts were washed with water (2 × 50 mL) and then with brine (50 mL) and dried over $MgSO_4$. The crude oily residue, obtained after the concentration of the filtrate under vacuum, was purified by fractional distillation (bp 81–83 °C/0.5 Torr) to afford the title compound as a colorless oil;[37] yield: 29.5 g (91%). IR (neat): ν = 3074, 2972, 1629, 1427, 1425, 1392, 1191, 1157, 1111, 1037, 991, 929, 896, 790 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.59–7.44 (m, 2H), 7.43–7.27 (m, 3H), 5.91–5.65 (m, 3H), 5.03–4.81 (m, 6H), 1.87 (dt, J = 8.0, 1.0 Hz, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 135.1, 134.1, 133.7, 129.2, 127.6, 114.2, 19.6; anal. calcd. for $C_{15}H_{20}Si$: C 78.88, H 8.83; found: C 78.91, H 9.07.

Triallyl(4-methylphenyl)silane (1b)

Following General Procedure A, the reaction of *p*-tolyltrichlorosilane (16.9 g, 75 mmol) and allylmagnesium bromide (240 mL, 1.00 M in Et_2O, 0.240 mol) gave the title compound as a colorless oil; yield: 16.6 g (91% yield); bp 120–123 °C/4 Torr). IR (neat): ν = 3076, 2972, 2918, 1629, 1417, 1393, 1190, 1157, 1107, 1038, 991, 895 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 5.91–5.67 (m, 3H), 4.99–4.83 (m, 6H), 2.35 (s, 3H), 1.84 (dt, J = 8.0, 1.4 Hz, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 139.1, 134.1, 133.8, 131.3, 128.5, 114.1, 21.4, 19.5; HRMS (FAB^+): calcd. for $C_{13}H_{17}Si$ $[M-(C_3H_5)]^+$: 201.1100; found: m/z = 201.1105.

Preparation of Triallyl(4-methoxyphenyl)silane (1c); General Procedure B

A solution of silicon tetrachloride (10.2 g, 60 mmol) in Et_2O (40 mL) was stirred in a 250-mL oven-dried, resealable Schlenk tube under an argon atmosphere at −20 °C. 4-Methoxyphenylmagnesium bromide (60 mL, 0.50 M in Et_2O, 30 mmol) was introduced dropwise over 2 h at −20 °C. After an additional 3 h of stirring at −20 °C, the reaction mixture was warmed to room temperature. The resulting bright yellow colored reaction mixture was stirred at ambient temperature overnight. The solvent along with excess $SiCl_4$ was removed under vacuum under an argon atmosphere. The resulting crude material was dissolved in Et_2O (30 mL), and allylmagnesium bromide (99 mL, 1.00 M in diethyl ether, 99 mmol) was added dropwise into the ethereal solution at −20 °C over 10 min. The resulting suspension was refluxed for 12 h and then cooled down to room temperature. The reaction mixture was quenched with a saturated NH_4Cl aqueous solution (30 mL) at 0 °C. The organic layer was separated; the aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined extracts were washed with water (2 × 30 mL) and then with brine (30 mL) and dried over $MgSO_4$. The oily residue, obtained after the concentration of the filtrate under vacuum, was purified by fractional distillation (bp 108–111 °C/0.5 Torr) to afford the title compound as a colorless oil; yield: 7.5 g (94%). IR (neat): ν = 3076, 2970, 2914, 1629, 1595, 1502, 1278, 1247, 1182, 1111, 1032, 894, 802 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 5.91–5.65 (m, 3H), 4.99–4.71 (m, 6H), 3.81 (s, 3H), 1.84 (dt, J = 8.1, 1.4 Hz, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 160.5, 135.6, 133.9, 125.8, 114.1, 113.5, 55.0, 19.9; anal. calcd. for $C_{16}H_{22}OSi$: C 74.36, H 8.58; found: C 74.08, H 8.53.

Triallyl(2-methylphenyl)silane (1d)

Following the general procedure B, the reaction of *o*-tolylmagnesium bromide (15 mL, 2.00 M in THF, 30 mmol), silicon tetrachloride (10.2 g, 60 mmol) and allylmagnesium bromide (99 mL, 1.00 M in Et_2O, 99 mmol) afforded the title compound as a colorless oil; yield: 3.5 g (48%); bp 85–87 °C/0.5 Torr. IR (neat): ν = 3059, 2972, 2916, 1629, 1591, 1418, 1153, 1034, 991, 895 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.41 (d, J = 6.9 Hz, 1H), 7.34–7.22 (m, 1H), 7.21–7.05 (m, 2H), 5.89–5.64 (m, 3H), 5.01–4.77 (m, 6H), 2.48 (s, 3H), 1.91 (dt, J = 8.0, 1.4 Hz, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 143.4, 135.2, 133.9, 133.4, 129.9, 129.5, 124.8, 114.3, 23.4, 20.1; anal. calcd. for $C_{16}H_{22}Si$: C 79.27, H, 9.15; found: C 79.32, H 9.32.

Triallyl(4-fluorophenyl)silane (1e)

General procedure B was applied to the reaction of 4-fluorophenylmagnesium bromide (30 mL, 1.00 M in Et_2O, 30 mmol), silicon tetrachloride (12.7 g, 75 mmol) and allylmagnesium bromide (99 mL, 1.00 M in Et_2O, 99 mmol) to give the title compound as a colorless oil; yield: 5.4 g (73%); bp 152–

160 °C/6 Torr. IR (neat): ν = 3078, 2974, 1629, 1589, 1501, 1389, 1234, 1163, 1105, 897, 826 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.47 (dd, *J* = 6.0, 8.6 Hz, 2H), 7.05 (dd, *J* = 8.6, 9.2 Hz, 2H), 5.91–5.64 (m, 3H), 4.97–4.85 (m, 6H), 1.86 (dt, *J* = 8.0, 1.2 Hz, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 163.8 (d, *J* = 248.8 Hz), 136.1 (d, *J* = 7.2 Hz), 133.6, 130.6 (d, *J* = 3.8 Hz), 115.0 (d, *J* = 19.5 Hz), 114.5, 19.6; MS: *m/z* (rel. intensity %) = 244 (M^+, 100), 228 (81), 202 (55), 165 (68), 152 (47), 122 (51), 91 (29), 77 (15); HRMS (EI^+): calcd. for $C_{12}H_{14}FSi$ $[M-(C_3H_5)]^+$: 205.0849; found: *m/z* = 205.0855; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −111.02 to −111.13 (m).

Diallyl(diphenyl)silane (9)

General procedure A was applied to the reaction of dichlorodiphenylsilane (25.0 g, 98.7 mmol) and allylmagnesium bromide (217 mL, 1.00 M in Et_2O, 0.217 mol) to give the title compound as a colorless oil;[38] yield: 24.8 g (95%); bp 158–161 °C/3 Torr). IR (neat): ν = 3071, 2972, 1630, 1427, 1391, 1153, 1111, 897 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.57–7.47 (m, 4H), 7.43–7.31 (m, 6H), 5.93–5.69 (m, 2H), 5.01–4.96 (m, 1H), 4.95–4.84 (m, 3H), 2.14 (dt, *J* = 8.0, 1.2 Hz, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 134.9, 134.8, 133.7, 129.4, 127.8, 114.7, 20.0; anal. calcd. for $C_{18}H_{20}Si$: C 81.76, H 7.62; found: C 81.64, H 7.62.

Triphenyl(allyl)silane (10)

Following General Procedure A, the reaction of chlorotriphenylsilane (5.0 g, 16.9 mmol) and allylmagnesium bromide (19 mL, 1.00 M in Et_2O, 18.6 mmol) gave the title compound as a colorless solid; yield: 4.7 g (93%) mp 87–88 °C (Aldrich product:[39] 88–90 °C). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.57–7.44 (m, 6H), 7.43–7.29 (m, 9H), 6.01–5.75 (m, 1H), 5.01–4.82 (m, 2H), 2.4 (dt, *J* = 7.8, 1.2 Hz, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 135.7, 134.5, 133.7, 129.5, 127.8, 115.1, 21.2.

Cross-Coupling Reaction of Triallyl(aryl)silanes with Aryl Bromides; General Procedure C

Triallyl(aryl)silane (1.15 mmol) was added to a solution of $TBAF \cdot 3H_2O$ (1.45 g, 4.6 mmol) in DMSO–H_2O (10:1, 5 mL) and the mixture was stirred in a Schlenk flask under an argon atmosphere at room temperature. Three freeze-thaw cycles were performed, and the resulting mixture was stirred in an argon atmosphere at room temperature for 1 h. The Schlenk tube was charged with $PdCl_2$ (8.9 mg, 50 μmol), PCy_3 (28 mg, 0.10 mmol) and an aryl bromide (1.00 mmol) under an argon atmosphere, and the mixture was heated in an oil bath at 80 °C. The reaction mixture was stirred for the time shown in Tables 2–6 and 11, cooled down to room temperature, diluted with dichloromethane (30 mL), and washed with water (2 × 10 mL) and brine (10 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel.

This procedure was followed in the cross-coupling reactions that represented from Tables 2–6 and 11.

Cross-Coupling Reaction of Triallyl(aryl)silanes with Aryl Chlorides; General Procedure D

To a solution of $TBAF \cdot 3H_2O$ (1.58 g, 5.00 mmol) in THF–H_2O (20:1, 5 mL) was added triallyl(aryl)silane (1.25 mmol) and the mixture was stirred in a Schlenk flask under an argon atmosphere at room temperature. Three freeze-thaw cycles were performed, and the resulting mixture was stirred under an argon atmosphere at room temperature for 1 h. The reaction mixture was transferred to a pressure tube through a cannula under argon. The pressure tube was charged with $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (9.0 mg, 25 μmol), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (**7**; 48 mg, 0.10 mmol) and an aryl chloride (1.00 mmol) under an argon atmosphere and heated in an oil bath at 80 °C. The reaction mixture was stirred for the time shown in Tables 8–10, 12, and 13, allowed to cool down to room temperature, diluted with dichloromethane (30 mL), and washed with water (2 × 10 mL) and brine (10 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude residue was purified either by flash column chromatography on silica gel or by preparative GPC.

This procedure was followed in the cross-coupling reactions that represented from Tables 8–10, 12 and 13. General remarks and characterization data for the compounds formed can be found in the Supporting Information file.

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Please note: Minor changes have been made to this article since its first publication in Wiley InterScience.

