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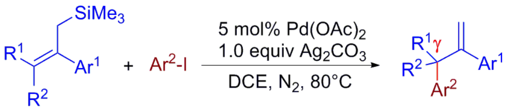

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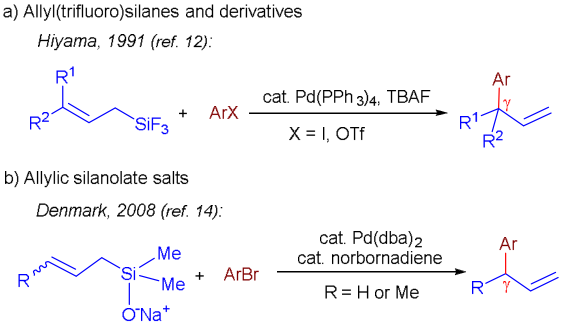
ABSTRACT

A ligand-free Pd-catalyzed cross-coupling of substituted allyl(trimethyl)silanes with aryl iodides enabled by silver salts was developed. This reaction delivered allylic arenes chemoselectively and regioselectively. The study suggested that the reaction might proceed through oxidative addition of ArI to Pd(0) followed by halide abstraction to give an electrophilic complex ArPdX, which further reacted with allyl(trimethyl)silanes via electrophilic addition/desilylation/reductive elimination to afford the allyl-aryl coupling products.

1. Introduction

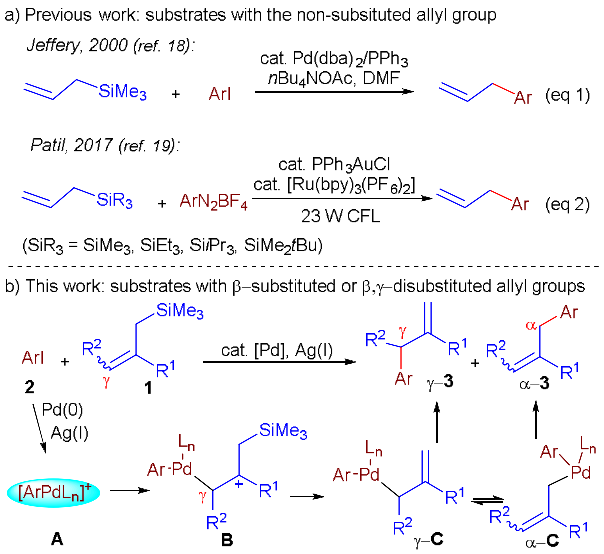
Allylic arenes represent an important structural component found in many natural products, pharmaceuticals and synthetic intermediates.[1] Existing main approaches to allylic arenes include Friedel-Crafts allylation of arenes,[2] allylic C-H arylation,[3] cross-coupling of aryl (pseudo)halides with allylmetallic compounds,[4] and cross-coupling of allylic electrophiles with arylmetallic compounds.[5] However, Friedel-Crafts allylation and allylic C-H arylation often suffered from poor regioselectivity, while the methods using organometallic compounds were often restricted to substrates with non-sensitive functional groups. As a type of mild nucleophilic allylation reagents, allylsilanes display unique properties such as high stability, good solubility and controllable reactivity. Therefore, the use of allylsilanes in the synthesis of allylic arenes seemed to be an attractive surrogate for the existing methods above.

Being activated by electrophilic addition to the allylic double-bond[6] and/or nucleophilic attack at the Si atom,[7] allylsilanes can react with various activated electrophiles[8-10] and free-radicals[11] in excellent regioselectivity and stereoselectivity. However, the reaction with unactivated electrophilic reagents such as aryl (pseudo)halides is less explored. Using allyl(trifluoro)silanes as the substrates and TBAF as the activator, Hiyama and his co-workers developed the first γ-regioselective cross-coupling of allylsilanes with aryl iodides and triflates in. 1991 (Scheme 1a).[12] They also disclosed ligand-controlled α-regioseletive cross-coupling reaction in 1994.[13] Furthermore, Denmark and his co-workers reported a γ-regioselective cross-coupling of allylic silanolate salts with aryl bromides catalyzed by $Pd(dba)_2$ in 2008 (Scheme 1b).[14] Despite high yield and excellent regioselectivity, the use of fluoro- or oxygen-substituted silanes as substrates and the need of fluoride anions for C-Si activation of some substrates limited their application.



Scheme 1. Cross-coupling reaction of activated allylsilanes with aryl halides.

Compared with other types of allylsilanes, allyl(trialkyl)silanes are more stable and therefore can be easily prepared from various starting materials.[15] Although an intramolecular arylation of ally(trimethyl)silanes to allylic arenes was successfully developed by Tietze in 1994,[16] intermolecular reactions often gave silyl-containing compounds as the major products.[17] In 2000, Jeffery reported an elegant method for the cross-coupling of allyl(trimethyl)silane with aryl iodides to give allylic arenes by a $Pd(dba)_2/PPh_3/nBu_4NOAc$ catalyst system (eq 1, Scheme 2a).[18] More recently, Patil and his co-workers developed an efficient cross-coupling of allyl(trialkyl)silanes with aryl diazonium salts to allylic arenes via merged gold/photoredox catalysis (eq 2, Scheme 2a).[19] However, the cross-coupling of substituted allyl(triakyl)silanes with aryl (pseudo)halides to give allylarenes has not been investigated so far. In this context and in connection with our interest in organosilicon chemistry, we designed a Pd/Ag catalytic system and realized the first cross-coupling of substituted allyl(trimethyl)silanes with aryl iodides to furnish allylarenes chemo-selectively (Scheme 2b). Furthermore, the reaction of β,γ-disubstituted substrates gave the γ-arylation products in high regio-selectivity.



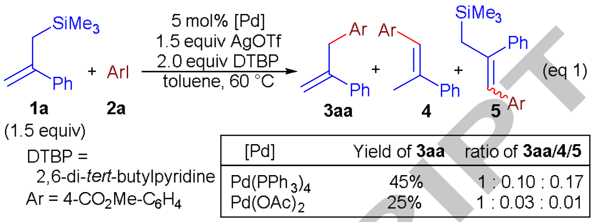
Scheme 2. Cross-coupling reaction of allyl(trialkyl)silanes with aryl (pseudo)halides.

2. Results and discussion

2.1. Reaction design and conditions optimization

The Jeffery's method realized the highly efficient and chemo-selective cross-coupling between non-substituted allyl(trimethyl)silane and aryl iodides to produce allylic arenes. However, the application of this method to the reaction of substituted allyl(trimethyl)silane **1a** with methyl 4-iodobenzoate **2a** failed to afford the desired ally-aryl coupling product **3aa**. In addition, it was mentioned in the paper published by Patil that substituted allyl(trialkyl)silanes were not compatible to the gold/photoredox catalytic conditions probably due to steric factors. In order to realize the cross-coupling of substituted allyl(trialkyl)silanes with aryl iodides, we proposed a Pd/Ag catalytic system according to the following considerations: (1) oxidative addition of ArI to Pd(0) followed by halide abstraction could generate a highly electrophilic intermediate $[ArPdL_n]^+$ **A**; (2) this intermediate might undergo electrophilic addition followed by desilylation to give an aryl-Pd-allyl complex **C**; (3) reductive elimination from **C** would furnish the allyl-aryl coupling product. In the reaction design, the high electrophilicity of the complex **A** might be crucial to the success of the investigated reaction.

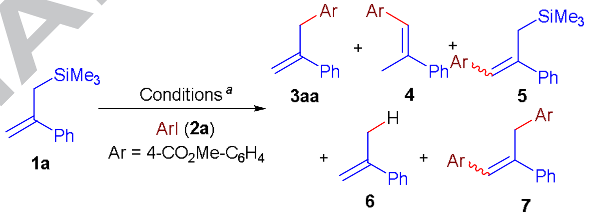
To test the feasibility of our hypothesis in the reaction design, we conducted the reaction between **1a** and **2a** with $Pd(PPh_3)_4$ as the catalyst and AgOTf as the additive. The first reaction in toluene at 60 °C under N_2 atmosphere successfully delivered the product **3aa** in 2% yield. And the yield of **3aa** was increased to 45% after a short survey of reaction parameters (Table S1). But this reaction was highly sensitive to air, moisture and even the addition sequence of reagents. Furthermore, a lot of side-products were detected by NMR. Among these side-products, the double-bond migration isomer **4** and the Heck-coupling product **5** were the major and very difficult to be separated from **3aa** by chromatography. Surprisingly, further investigation of other Pd catalysts showed that the use of $Pd(OAc)_2$ as the catalyst without a phosphine ligand led to only a trace amount of side-products, though the yield of **3aa** was also reduced (eq 1).



[Pd]	Yield of **3aa**	ratio of **3aa/4/5**
$Pd(PPh_3)_4$	45%	1 : 0.10 : 0.17
$Pd(OAc)_2$	25%	1 : 0.03 : 0.01

On the basis of the preliminary results, we continued extensive conditions optimization by screening solvents, silver salts, Pd catalysts and ligands (Table S2-S4). It was found that the reaction with 5 mol% $Pd(OAc)_2$ as the catalyst and 1.0 equiv Ag_2CO_3 as the additive in DCE at 80 °C under N_2 gave the optimal result (entry 1, Table 1). The reaction delivered **3aa** in 79% yield and a bis-arylation product **7** in 8% yield. Both of the two possible side-products **4** and **5** were not detected by NMR and the protodesilylation product **6** was detected in less than 5%

Table 1. Conditions optimization for the cross-coupling of allyl(trimethyl)silane **1a** with methyl 4-iodobenzoate **2a**.



Entry	Pd catalyst	Additive (equiv)	Yield of **3aa** [b]	Ratio of **3aa/4/5** [c]
1	$Pd(OAc)_2$	Ag_2CO_3 (1.0)	79%	10/0/1
2	$PdCl_2$	Ag_2CO_3 (1.0)	63%	12/0/1
3	$Pd(TFA)_2$	Ag_2CO_3 (1.0)	79%	10/0/1
4	$Pd(PPh_3)_4$	Ag_2CO_3 (1.0)	trace	-
5	$Pd_2(dba)_3$[d]	Ag_2CO_3 (1.0)	trace	-
6	$Pd(OTf)_2L_4$	Ag_2CO_3 (1.0)	67%	6/2/1
7	PdL_2Cl_2	Ag_2CO_3 (1.0)	57%	5/0.25/1
8[e]	$Pd(OAc)_2$	Ag_2CO_3 (1.0)	51%	5/0/1
9[f]	$Pd(OAc)_2$	Ag_2CO_3 (1.0)	trace	-
10	$Pd(OAc)_2$	AgOAc (2.0)	65%	3/0/1
11	$Pd(OAc)_2$	Ag_2O (1.0)	72%	6/0/1
12	$Pd(OAc)_2$	AgTFA (2.0)	61%	5/1/1
13	$Pd(OAc)_2$	$AgNO_3$ (2.0)	39%	-
14	$Pd(OAc)_2$	AgOTf (2.0)	trace[g]	-
15	$Pd(OAc)_2$	K_2CO_3 (1.0)	5%	-
16	$Pd(OAc)_2$	CuOAc (2.0)	12%	-

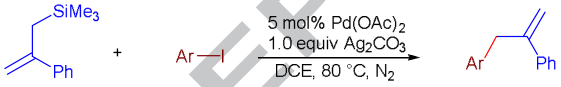
[a] Conditions: **2a** (0.2 mmol), **1a** (0.3 mmol), Pd catalyst (5 mol%), additive (1.0 equiv), DCE (4 mL), 80 °C, N_2, 12 h. [b] Isolated yield. [c] The ratios were determined by ^1H NMR. [d] 2.5 mol% $Pd_2(dba)_3$. [e] 10 mol% PPh_3, 24 h. [f] 20 mol% PPh_3, 12 h. [g] **6** was detected by GC in 99% yield. L = CH_3CN.

yield. The study also led to several key observations: (1) Pd(II) catalysts such as $PdCl_2$ and $Pd(TFA)_2$ were as effective as $Pd(OAc)_2$, while $Pd_2(dba)_3$ and $Pd(PPh_3)_4$ were not capable of catalyzing the reaction (entries 2-5, Table 1). (2) Ligands such as CH_3CN and PPh_3 were detrimental to the reaction. CH_3CN led to the formation of **4** (entries 6-7, Table 1), while PPh_3 reduced the yield and selectivity (entries 8-9, Table 1). (3) silver salts with more basic counterions than OAc^- were competent (entries 10-11, Table 1), while those with less basic counterions were not suitable for the reaction (entries 12-14, Table 1). Further study with K_2CO_3 or CuOAc replacing Ag_2CO_3 (entries 15-16, Table 1) proved that Ag_2CO_3 not only acted as a base, but also probably as an activator for aryl iodides.

2.2. Substrate scope

With the optimal conditions in hand, the substrate scope was next examined (Table 2). Firstly, aryl iodides with various substituents at *para*-, *meta*-, and *ortho*-positions were tested. Tolerated functional groups included CO_2Me (**2a**), acyl (**2b**), amido (**2c**), NO_2 (**2d**), CN (**2n**), CF_3 (**2e**), F (**2f**), Ph (**2h**), Me (**2i**), OMe (**2j**), OTf (**2k**) and OTs (**2l**). Particularly, the reaction of OTf and OTs-substituted aryl iodides delivered the OTf and OTs-containing products in 45% (**3ak**) and 73% yield (**3al**) respectively. The installation of these functional groups in the products provided opportunities for further transformations. Electronic properties and steric hindrance of substituents affected the reaction outcome strongly. Aryl iodides with electron-withdrawing substituents (**2a**-**2f**) reacted with **1a** faster and delivered the products in higher yield than aryl iodides with electron-donating substituents (**2h**-**2j**). In addition, *ortho*- and *meta*-substituted aryl iodides provided higher yield of products than *para*-substituted aryl iodides (**2d** *vs* **2m**, **2i** *vs* **2o**). Combining the two effects, the reaction of **1a** with 3-iodobenzonitrile **2n** and 2-iodobenzonitrile **2q** provided the highest yield among all examples (84% for both **3an** and **3aq**). Surprisingly, heteroaryl iodides such as 2-iodobenzofuran (**2r**) and 3-iodothiophene (**2s**) could also be coupled with **1a** to deliver the desired products **3ar** and **3as** in 30% and 36% yield. However, 3-iodopyridine failed to furnish any coupling products in the reaction with **1a**, probably due to the strong coordination between nitrogen and palladium.

Table 2. Scope of aryl iodides **2**.

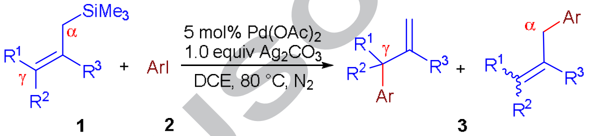


1a **2** **3**

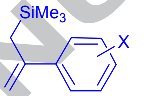
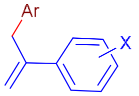
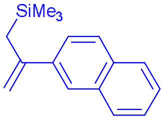
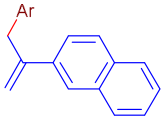
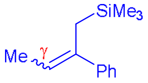
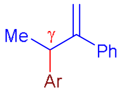
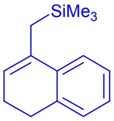
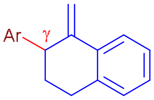
Entry	ArI (**2**)	Yield of **3**
1	**2a** (Ar = 4-$CO_2MeC_6H_4$)	**3aa**, 79%
2	**2b** (Ar = 4-AcC_6H_4)	**3ab**, 66%
3	**2c** (Ar = 4-$CONHPhC_6H_4$)	**3ac**, 73%
4	**2d** (Ar = 4-$NO_2C_6H_4$)	**3ad**, 60%
5	**2e** (Ar = 4-$CF_3C_6H_4$)	**3ae**, 60%
6	**2f** (Ar = 4-FC_6H_4)	**3af**, 57%
7	**2g** (Ar = C_6H_5)	**3ag**, 48%
8	**2h** (Ar = 4-PhC_6H_4)	**3ah**, 41%
9	**2i** (Ar = 4-MeC_6H_4)	**3ai**, 35%
10	**2j** (Ar = 4-$OMeC_6H_4$)	**3aj**, 45%
11	**2k** (Ar = 4-$OTfC_6H_4$)	**3ak**, 45%
12	**2l** (Ar = 4-$OTsC_6H_4$)	**3al**, 73%
13	**2m** (Ar = 3-$NO_2C_6H_4$)	**3am**, 80%
14	**2n** (Ar = 3-CNC_6H_4)	**3an**, 84%
15	**2o** (Ar = 3-MeC_6H_4)	**3ao**, 49%
16	**2p** (Ar = 3-$OMeC_6H_4$)	**3ap**, 35%
17	**2q** (Ar = 2-CNC_6H_4)	**3aq**, 84%
18	**2r** (Ar = benzofuran-2-yl)	**3ar**, 30%
19	**2s** (Ar = thiophen-3-yl)	**3as**, 36%
20	**2t** (Ar = pyridine-3-yl)	**3at**, 0%

Secondly, allyl(trimethyl)silanes with substituted allyl groups were investigated (Table 3). The study showed that β-aryl substitution was key to the success of the reaction. Substrates with β-aryl groups bearing either electron-withdrawing or electron-donating substituents reacted with aryl iodide **2a** well to yield the products (**3ba** to **3ia**) in 42-76% yield. Functional groups like methyl (**1b**), halogen (**1c**-**1e**, **1h**), CN (**1f**), CO_2Me (**1g**) and OMe (**1i**) were also compatible. Interestingly, the conditions could also be applicable to β,γ-disubstitued allylsilanes. The reaction of β-phenyl-γ-methyl substituted allyl(trimethyl)silane **1k** with **2a** furnished **3ka** in 34% yield and high γ-regioselectivity (γ:α>10:1). Moreover, the cyclic substrate **1l** was coupled with **2d** and **2n** regioselectively to give the γ-arylation products **3ld** and **3ln** (γ:α>20:1). However, when 10 mol% $Pd(TFA)_2$ was used as the catalyst, the two reactions of **1l** delivered the products in higher yield, but with reduced regioselectivity (γ:α = 3:1 for **3ld**, γ:α = 2.5:1 for **3ln**).

Table 3. Scope of allyl(trimethyl)silanes **1**.

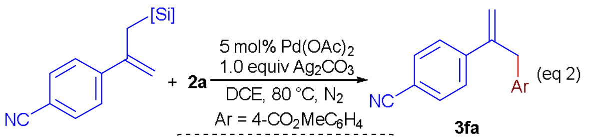


1 **2** **3**

Entry	Silane (**1**)	ArI (**2**)	Yield of **3**
			
1	**1b** (X = 4-Me)	**2a**	**3ba**, 66%
2	**1c** (X = 4-Br)	**2a**	**3ca**, 42%
3	**1d** (X = 4-Cl)	**2a**	**3da**, 66%
4	**1e** (X = 4-F)	**2a**	**3ea**, 72%
5	**1f** (X = 4-CN)	**2a**	**3fa**, 62%
6	**1g** (X = 4-CO_2Me)	**2a**	**3ga**, 60%
7	**1h** (X = 3-Cl)	**2a**	**3ha**, 76%
8	**1i** (X = 3-OMe)	**2a**	**3ia**, 52%
			
9	**1j**	**2a**	**3ja**, 58%
			
10	**1k** (*Z*:*E* = 1:3.6)	**2a**	**3ka**, 34% (γ:α >10:1)
			
11	**1l**	**2d**	**3ld**, 28% (γ:α>20:1) 43% (γ:α= 3:1)[a]
12	**1l**	**2n**	**3ln**, 32% (γ:α>20:1) 43% (γ:α= 2.5:1)[a]

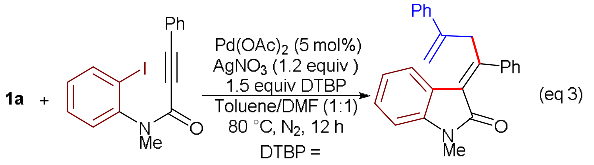
[a] $Pd(TFA)_2$ (10 mol%) instead of $Pd(OAc)_2$ (5 mol%)

After developing the allyl-aryl coupling reaction, we continued to examine other coupling partners. First, the triethyl and dimethylphenyl counterparts of **1f** were applied in the reaction with **2a**. It was found that the reaction of the triethylsilane (**1m**) delivered the desired product **3fa** in 31% yield, while the dimethylphenylsilane (**1n**) exhibited excellent reactivity (eq 2). The low reactivity of **1m** might be explained by the larger steric bulk and more electron-donating properties of the ethyl group. Although the dimethylphenylsilane **1n** gave better result, we still preferred to trimethylsilanes considering the easy accessibility and low cost. Then, we also applied the conditions to the cross-coupling of substituted allyl(trimethyl)silanes with alkenyl iodides. Unfortunately, the reaction between (*E*)-β-iodostyrene and **1a** under the above optimal conditions failed to afford the desired coupling product. In addition, a three-component reaction between **1a**, **2a** and 1,2-diphenylenthyne did not give any product. Gratifyingly, a cascade reaction between **1a** with an alkynamide **8** successfully yielded the desired cyclization-allylation product **9** in 22% yield. After modification of the reaction conditions, the yield of **9** was increased to 60% (eq 3).



3fa

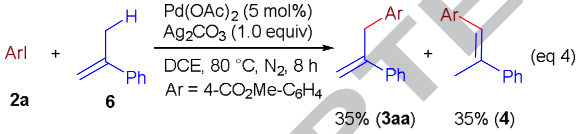
Silane ([Si])	Yield of **3fa**
1f (SiMe$_3$)	62%
1m (SiEt$_3$)	31%
1n (SiMe$_2$Ph)	86%



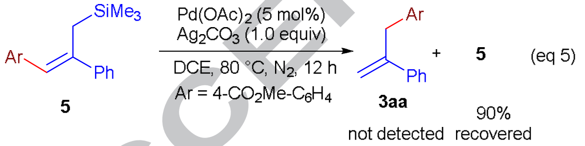
8 **9**, 60%

2.3. Mechanistic discussion

To gain more information about reaction mechanism, several control experiments were conducted and the results were summarized as below: (1) the reaction between **6** and **2a** under the optimal conditions delivered **3aa** and **4** in 70% total yield and 1:1 ratio (eq 4), while **4** was not detected in the reaction between **1a** and **2a**; (2) heating the Heck-product **5** under the optimal conditions did not give **3aa** (eq 5). The results of these experiments indicated that neither **5** nor **6** was the intermediate in the cross-coupling reaction, and further ruled out both of the protodesilylation/coupling pathway and the Heck-coupling/protodesilylation pathway as possible mechanisms.



2a **6** 35% (**3aa**) 35% (**4**)



5 **3aa** not detected 90% recovered

According to the experimental results above and literature reports,[20] a plausible mechanism involving Pd(0)/Pd(II) catalysis was proposed (Figure 1). The reaction was initiated by *in-situ* generation of Pd(0) species via reduction of Pd(OAc)$_2$. Then oxidative addition of aryl iodide to Pd(0) followed by halide abstraction by AgX (X$^-$ = OAc$^-$ or CO$_3^{2-}$) gave an arylpalladium complex **I**. This complex could undergo electrophilic addition followed by desilylation to give a η^1 γ-allyl-Pd-Ar complex **III**, from which reductive elimination furnished the γ-product.[12,18,19] In addition, due to facile interconversion between η^1 and η^3 allyl-Pd-Ar complexes, the η^1 α-allyl-Pd-Ar complex **IV** would be formed and reductive elimination from it would also give the α-arylation product.[13a] However, another pathway involving migratory insertion of the allylic double bond to **I** followed by β-silyl elimination was also possible. But this pathway might be a minor process to produce **3** as the Heck-product **5** from β-H elimination was not detected under the optimal conditions.

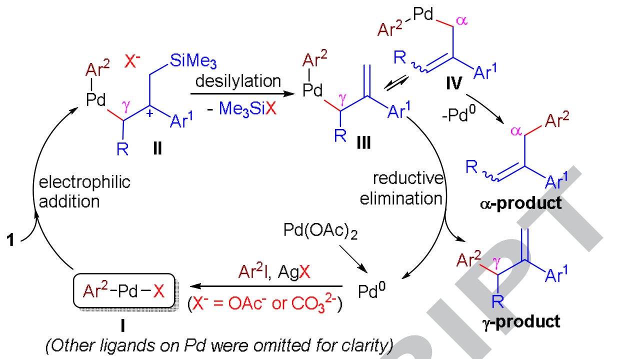


Figure 1. Plausible mechanism

3. Conclusion

In conclusion, a phosphine ligand-free Pd-catalyzed cross-coupling of substituted allyl(trimethyl)silanes with aryl iodides was developed. This reaction delivered allylarenes chemoselectively and regioselectively. The study suggested that the reaction might follow a Pd(0)/Pd(II) catalytic cycle, which included Ag(I)-mediated oxidative addition of ArI to Pd(0) to produce an electrophilic intermediate ArPdX, electrophilic addition/desilylation to give ArPd(allyl) complexes, and final reductive elimination to furnish the products **3**. The detailed mechanistic study and synthetic application in organic synthesis is underway in our lab.

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References and notes

1. (a) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 11262-11263. (b) Newton,C. G.; Drew,S. L.; Lawrence, A. L.; Willis, A. C.; Paddon-Row, M. N.; Sherburn, M. S. *Nature Chem.* **2015**, *7*, 82-86. (c) Kuttruff, C. A.; Zipse, H.; Trauner, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 1402-1405. (d) Trost, B. M.; Andersen, N. G. *J. Am. Chem. Soc.* **2002**, *124*, 14320-14321. (e) Hatanaka, Y; Ebina, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1991**, *113*, 7075-7076.
2. Kodomari, M.; Nawa, S.; Miyoshi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1895-1896.
3. Nadri, S.; Joshaghani, M.; Rafiee, E.; *Tetrahedron Lett.* **2009**, *50*, 5470–5473.
4. Doherty, S.; Knight, J. G.; Smyth, C. H.; Harrington, R. W.; Clegg, W. *Organometallics* **2007**, *26*, 6453-6461.
5. (a) Qi, L.; Ma, E.; Jia, F.; Li, Z. *Tetrahedron Lett.* **2016**, *57*, 2211-2214. (b) Dong, C.; Zhang, L.; Xue, X.; Li, H.; Yu, Z.; Tang, W.; Xu, L. *RSC Adv.* **2014**, *4*, 11152-11158.
6. (a) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200-206. (b) Fürstner, A.; Voigtländer, D. *Synthesis* **2000**, *2000*, 959-969. (c) Hosomi, A.; Miura, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 835-851.
7. (a) Hatanaka, Y.; Hiyama, T. *Synlett.* **1991**, 845-853. (b) Nakao, Y.; Hiyama, T. *Chem. Soc. Rev.* **2011**, *40*, 4893-4901. (c) Denmark, S. E.; Regens, C. S. *Acc. Chem. Res.* **2008**, *41*, 1486-1499.
8. (a) Ishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta,K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 11490-11495. (b) Gauthier, D. R.; Carreira, E. M. *Angew. Chem. Int. Ed.* **1996**, *35*, 2363-23365. (c) Braun, M.; Kotter, W. *Angew. Chem. Int. Ed.* **2004**, *43*, 514-517. (d) Mahlau, M.; Garcia-Garcia, P.; List, B. *Chem. Eur. J.* **2012**, *18*, 16283-16287.

9. (a) Saito, T; Nishimoto, Y.; Yasuda, M.; Baba, A. *J. Org. Chem.* **2007**, *72*, 8588-8590. (b) Braun, M.; Kotter, W. *Angew. Chem. Int. Ed.* **2004**, *43*, 514-517. (c) Schwier, T.; Rubin, M.; Gevorgyan, V. *Org. Lett.* **2004**, *6*, 1999-2001. (d) Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 1414-1416.
10. (a) Teare, H.; Robins, E. G.; Arstad, E.; Luthra, S. K.; Gouverneur, V. *Chem. Commun.* **2007**, 2330-2332. (b) Shimizu, R.; Egami, H.; Hamashima, Y.; Sodeoka, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 4577-4580. (c) Liu, J.; Chu, L.; Qing, F.-L. *Org. Lett.* **2013**, *15*, 894-897. (d) Arimori, S.; Takada, M.; Shibata, N. *Org. Lett.* **2015**, *17*, 1063-1065. (e) Greedy, B.; Paris, J.-M.; Vidal, T.; Gouverneur V. *Angew. Chem. Int. Ed.* **2003**, *42*, 3291-3294. (f) Mizuta, S.; Galicia-López, O.; Engle, K. M.; Verhoog, S.; Wheelhouse, K.; Rassias, G.; Gouverneur, V. *Chem. Eur. J.* **2012**, *18*, 8583-8587.
11. (a) Zhang, Y.; Raines, A. J.; Flowers, R. A., II *Org. Lett.* **2003**, *5*, 2363-2365. (b) Beeson, T. D.; Mastracchio, A.; Hong, J.-B.; Ashton, K.; MacMillan, D. W. C. *Science* **2007**, *316*, 582-585. (c) Mastracchio, A.; Warkentin, A. A.; Walji, A. M.; MacMillan, D. W. C. *Proc. Natl. Acad. Sci.* **2010**, *107*, 20648-20651. (d) Zhu, Q.; Gentry, E. C.; Knowles, R. R. *Angew. Chem. Int. Ed.* **2016**, *55*, 9969-9973.
12. See ref. 1e.
13. (a) Hatanaka, Y.; Goda, K.-I.; Hiyama, T. *Tetrahedron Lett.* **1994**, *35*, 6511-6514. (b) Hatanaka, Y.; Goda, K.-I.; Hiyama, T. *Tetrahedron Lett.* **1994**, *35*, 1279-1282.
14. Denmark, S. E.; Werner, N. S. *J. Am. Chem. Soc.* **2008**, *130*, 16382-16393.
15. Selected referenes: (a) Guo, L.; Leiendecker, M.; Hsiao, C. C.; Baumann, C.; Rueping, M. *Chem. Commun.* **2015**, *51*, 1937-1940. (b) Cai, G.; Zhou, Z.; Wu, W.; Yao, B.; Zhang, S.; Li, X. *Org. Biomol. Chem.* **2016**, *14*, 8702-8706. (c) Selander, N.; Paasch, J. R.; Szabó, K. J. *J. Am. Chem. Soc.* **2011**, *133*, 409-411. (d) McAtee, J. R.; Yap, G. P. A.; Watson, D. A. *J. Am. Chem. Soc.* **2014**, *136*, 10166-10172. (e) Wu, J. Y.; Stanzl, B. N.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 13214-13216. (f) Chai, G.; Zeng, R.; Fu, C.; Ma, S. *Eur. J. Org. Chem.* **2013**, 148-154..
16. Intramolecular arylation of allyl(trimethyl)silanes with tethered aryl iodides: (a) Tietze, L. F.; Schimpf, R. *Angew. Chem. Int. Ed.* **1994**, *33*, 1089-1091. (b) Tietze, L. F.; Raschke, T. *Synlett* **1995**, *6*, 597-598.
17. (a) Karabelas, K.; Westerlund, C.; Hallberg, A.; *J. Org. Chem.* **1985**, *50*, 3896-3900. (b) Olofsson, K.; Larhed, M.; Hallberg, A. *J. Org. Chem.* **1998**, *63*, 5076-5079. Rhodium-catalyzed reactions: (c) Omachi, H.; Itami, K. *Chem. Lett.* **2009**, *38*, 186-187.
18. Jeffery, T. *Tetrahedron Lett.* **2000**, *41*, 8445-8449.
19. Akram, M. O.; Mali, P. S.; Patil, N. T. *Org. Lett.* **2017**, *19*, 3075-3078.
20. A recent report on Pd-catalyzed oxidative cross-coupling of ally(trimethyl)silanes with aryl boronic acids to form allylarenes, see: Zhou, Z.; Hou, Z.-L.; Yang, F.; Yao, B. *Tetrahedron* **2018**, doi: https://doi.org/10.1016/j.tet.2018.10.055.

Supplementary Material

Electronic Supplementary Information (ESI) available: Experimental details, compound characterization, copies of ^{1}H NMR and ^{13}C NMR spectra. See DOI: 10.1039/x0xx00000x

Highlights

- The first cross-coupling of substituted allyl(trimethyl)silanes with aryl iodides was realized by palladium catalysis.
- The reaction of β-aryl substituted allyl(trimethyl)silanes delivered 2,3-diarylpropenes in good yield and high chemoselectivity.
- The reaction of β,γ-disubstituted allyl(trimethyl)silanes afforded the γ-arylation products in high regioselectivity.
- A cascade reaction involving the cyclization-allylation sequence was realized to synthesize substituted indolin-2-one.