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Oxidative cross-coupling of allyl(trimethyl)silanes with aryl boronic acids by palladium catalysis

Zhibing Zhou, Zhen-Lin Hou, Fan Yang, Bo Yao*

MOE Key Laboratory of Cluster Science, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, PR China

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ABSTRACT

The first oxidative cross-coupling of allylsilanes with aryl boronic acids has been developed by palladium catalysis. The reaction between β-substituted allyl(trimethyl)silanes and a wide range of aryl boronic acids afforded allylarenes in moderate to good yields and excellent selectivity. On the basis of experimental results and literature reports, it was suggested that the reaction might start from transmetalation of aryl boronic acid with AgOAc followed by transmetalation with Pd(II) to give an arylpalladium acetate complex as a key intermediate. This intermediate underwent either electrophilic addition/desilylation or transmetalation with allylsilane and subsequent reductive elimination to give the final product.

1. Introduction

As a type of mild nucleophilic allylation reagents, allylsilanes display unique properties such as high stability, good solubility in various solvents and controllable reactivity, therefore having broad application in organic synthesis [1]. Being activated by electrophilic addition to the allylic double bond [2] and/or nucleophilic attack at the Si atom [3], allylsilanes can react with various electrophiles including carbonyl compounds [4], alcohols [5], ethers [6], esters [7], and others [8] to furnish diverse allylic compounds. However, the reaction between allylsilanes and other types of nucleophiles has been far less explored. A major strategy for these reactions was the umpolung of allylsilanes by transforming them into highly reactive allylic electrophiles such as allyltelluroxides [9], allylbismuthonium [10], hypervalent allyliodine(III) reagents [11], and allylic cations [12] (Scheme 1a). Besides, the umpolung of other nucleophiles by oxidizing them to free radicals [13] and cations [14], was another strategy for the cross-coupling reaction (Scheme 1b). Many methods based on the above two strategies have been developed for the synthesis of allylic ethers [12a,12b], amines [9], azides [11], arenes [10,12c] and α-allylated carbonyl compounds [13,14]. However, the use of strong oxidants and/or moisture-sensitive Lewis acids for the umpolung and poor chemoselectivity in these reactions limited their application in organic synthesis.

Palladium is one of the most powerful transition-metals in organic synthesis [15]. Palladium catalysts have not only been widely used in traditional cross-coupling between an electrophile and a nucleophile [16], but also in recent years been extensively investigated in oxidative cross-coupling of two nucleophiles [17]. The palladium-catalyzed oxidative cross-coupling often uses a Pd(II) catalyst, which mediates the cross-coupling of two nucleophiles, and an oxidant for re-oxidation of Pd(0) to Pd(II) (Scheme 2a). When the two nucleophiles are organometallic reagents, a successful cross-coupling reaction often requires: (1) facile and selective transmetalation of Pd(II) with two nucleophiles sequentially, and (2) chemoselective oxidation of Pd(0) rather than the nucleophiles by the oxidant. In this context, the first Pd-catalyzed oxidative cross-coupling of arylsilanes with aryl boronic acids was reported by Zhang and co-workers in 2015 (Scheme 2b) [18a], although the oxidative cross-coupling of arylsilanes with arenes by gold catalysis was disclosed by Lloyd-Jones and Russell in 2012 [18b]. Furthermore, Szabó and co-workers developed the intramolecular allylation of allyl(trimethyl)silane-tethered alcohols and tosylamides in 2000 and 2001 (Scheme 2c) [19]. However, the oxidative cross-coupling of allylsilanes with other nucleophiles including organometallic reagents remains underdeveloped. In connection with our interest in development of oxidative reaction by palladium catalysis, we herein reported the first oxidative cross-

* Corresponding author.
E-mail address: yaobo@bit.edu.cn (B. Yao).

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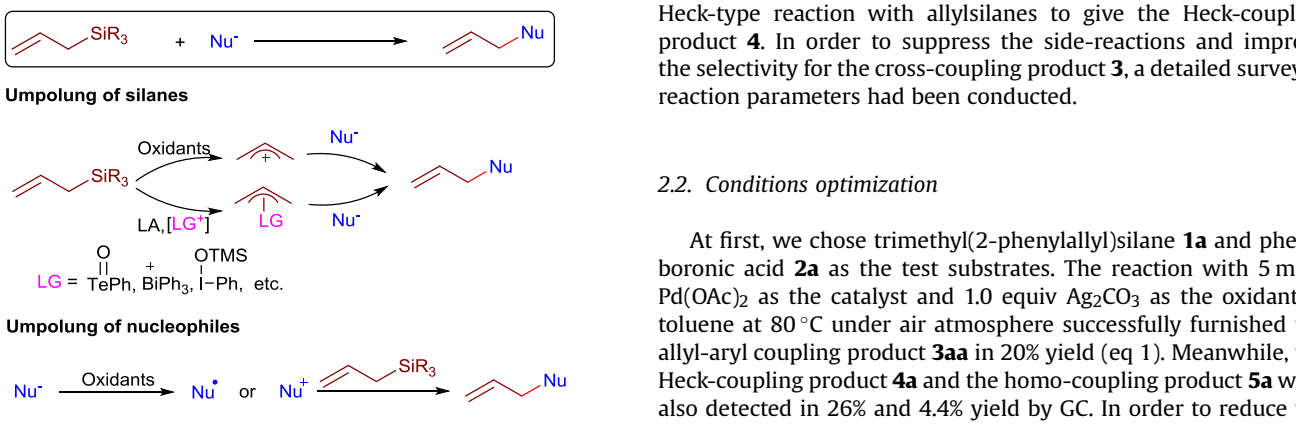


Scheme 1. The umpolung strategies for the cross-coupling of allyl(trialkyl)silanes with other nucleophiles.

coupling of allylsilanes with aryl boronic acids to give allylarenes under palladium-catalyzed aerobic conditions (Scheme 2d).

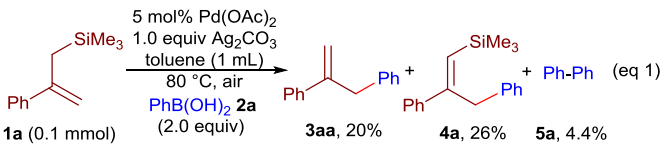
2. Results and discussion

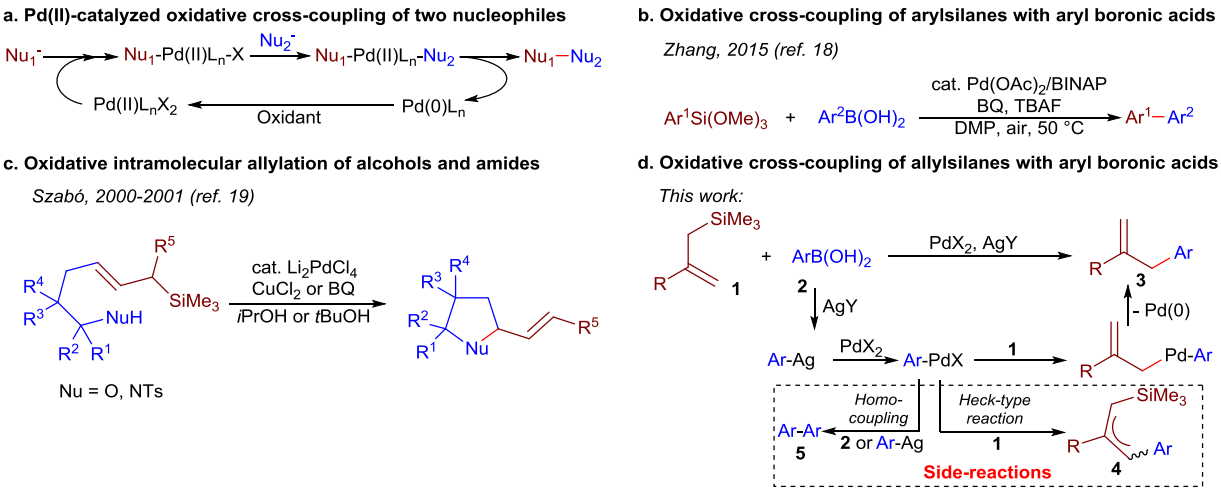
2.1. Reaction design

The challenges in palladium-catalyzed oxidative cross-coupling between allylsilanes and aryl boronic acids include: (1) slow transmetalation between allylsilanes and Pd(II) species, (2) alkene-related side-reactions such as Heck reaction and Wacker oxidation, (3) competitive homo-coupling of nucleophiles. To overcome these problems, we developed a Pd(II)/Ag(I) catalytic system, under which the facile generation of an electrophilic Ar-Pd-X complex might be crucial for the success of the cross-coupling with high efficiency and selectivity. Our reaction design is based on the considerations below (Scheme 2d): Ag(I) salts can undergo facile transmetalation with aryl boronic acid **2** to generate an Ar-Ag(I) intermediate [20,21], which reacts with PdX_2 to give an Ar-Pd(II)-X intermediate; the electrophilic Ar-Pd(II)-X can react with allylsilane **1** by electrophilic addition/desilylation or direct transmetalation [22] to afford an allyl-Pd-Ar intermediate, from which reductive elimination furnishes allylarene **3**. Meanwhile, two side-reactions via the Ar-Pd(II)-X intermediate can also take place: one is the homo-coupling reaction of **2** to deliver biaryl **5**; another is the Heck-type reaction with allylsilanes to give the Heck-coupling product **4**. In order to suppress the side-reactions and improve the selectivity for the cross-coupling product **3**, a detailed survey of reaction parameters had been conducted.

2.2. Conditions optimization

At first, we chose trimethyl(2-phenylallyl)silane **1a** and phenyl boronic acid **2a** as the test substrates. The reaction with 5 mol% $Pd(OAc)_2$ as the catalyst and 1.0 equiv Ag_2CO_3 as the oxidant in toluene at 80 °C under air atmosphere successfully furnished the allyl-aryl coupling product **3aa** in 20% yield (eq 1). Meanwhile, the Heck-coupling product **4a** and the homo-coupling product **5a** were also detected in 26% and 4.4% yield by GC. In order to reduce the yield of **4a** and increase the yield of **3aa**, an extensive survey of reaction parameters including bases, Pd catalysts, silver salts solvents, and others led to several key observations (Tables S1–S5 in ESI): (1) An extra base was not needed. The use of K_2CO_3 or Cs_2CO_3 led to the formation of biphenyl **5a** as the major product with most of the silane **1a** unreacted. (2) Pd(II) salts such as $Pd(OAc)_2$ and $PdCl_2$ were effective catalysts, while Pd(II) complexes with phosphine ligands showed very low catalytic activity. (3) Among various silver salts, AgOAc was the optimal to yield **3aa** in highest yield and selectivity. Ag_2CO_3 promoted the formation of the Heck-coupling product **4a**, while Ag_2O and AgO favored the homo-coupling of **2a** to give biphenyl **5a** in high yield. (4) DMF was the optimal solvent for the cross-coupling. Low ratio of **3aa**/**4a** was found when toluene was used as the solvent, and biphenyl **5a** became the major product when DMSO was applied. Further investigation of ligands, the loading of **2a**, temperatures and concentrations led to a set of preliminary conditions, which involved the treatment of **1a** (0.1 mmol) and **2a** (1.2 equiv) with 5 mol% $Pd(OAc)_2$, 10 mol% 1,4-benzoquinone (BQ) and 2.0 equiv AgOAc in DMF at 80 °C under air. Under these conditions, the reaction furnished **3aa** in 68% yield, the two side-products (**4a** and **5a**) in 5% total yield and unreacted **1a** in 19% yield (Table 1, entry 1).





Scheme 2. Pd(II)-catalyzed oxidative cross-coupling of organosilanes with nucleophiles.

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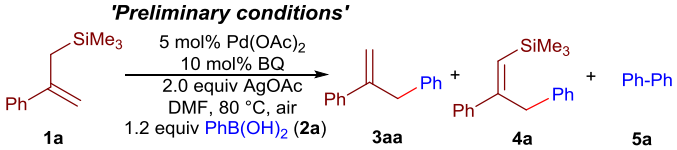
Table 1
Further conditions optimization for the reaction of allyl(trimethyl)silane **1a** with phenyl boronic acid **2a**.[a]



Entry	Variation from the preliminary conditions	Yield (%)[b]			
		3aa	**4**	**5**	**1a**
1	–	68	1.6	3.4	19
2	2.0 instead of 1.2 equiv **2a**	63	2.3	2.1	16
3	no BQ, 2.0 instead of 1.2 equiv **2a**	35	1.6	6.3	0.9
4	5 mol% instead of 10 mol% BQ	55	2.0	1.4	8.2
5	20 mol% instead of 10 mol% BQ	58	1.4	1.8	27
6	5.0 equiv H_2O	46	6.2	9.7	23
7	4 Å MS (50 mg)	25	16	11	24
8	1.0 equiv HOAc	56	1.5	2.2	28
9	1.0 equiv KOAc	4.6	1.4	1.1	82
10	0.1 equiv 2,2′-bipyridine	24	0	2.4	60
11	5.0 equiv DMSO	57	1.4	10	6.2
12[c]	1.0 equiv DMSO	77	0.8	2.4	0.4
13[c]	**1.0 equiv DMSO, 5 mol% $PdCl_2$ instead of $Pd(OAc)_2$**	**81(72)**	**0.5**	**2.2**	**0.9**
14[c]	1.0 equiv DMSO, no Pd catalyst	16	0	4.5	58
15[c]	1.0 equiv DMSO, 5 mol% $PdCl_2$ instead of $Pd(OAc)_2$, 2.0 equiv $Cu(OAc)_2$ instead of AgOAc	23	0.2	30	28

[a] The preliminary conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(OAc)_2$ (5 mol%), BQ (10 mol%), AgOAc (2.0 equiv), DMF (1 mL), 80 °C, air, 12 h.
[b] Yield was determined by GC analysis with 4-bromotoluene as the internal standard, isolated yield was provided in the parenthesis.
[c] 0.2 mmol **1a** and 1 mL DMF. BQ = Benzoquinone.

Next, further assessment of the reaction parameters of the preliminary conditions was conducted. Firstly, in the absence of BQ, the yield of **3aa** was dramatically decreased to 35% (Table 1, entry 3). And 10 mol% BQ was found to give the best result (Table 1, entry 1–5). Additionally, methylated BQs such as 2-methyl-1,4-benzoquinone and 2,3,5-trimethyl-1,4-benzoquinone were also effective and yielded **3aa** in slightly lower yields, while 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was proven to be not effective (Table S7 in ESI). These results suggested that BQ might act as a ligand in Pd complexes. Secondly, in order to further improve the conversion of **1a**, additives including H_2O, molecular sieves (4 Å MS), HOAc, KOAc, 2,2′-bipyridine and DMSO were evaluated (Table 1, entries 6–12). Among these additives, DMSO was found to be the most effective, and the reaction with 1.0 equiv DMSO under otherwise the preliminary conditions delivered **3aa** in 77% yield and a trace amount of unreacted **1a** (Table 1, entry 12) [23]. Thirdly, the use of $PdCl_2$ instead of $Pd(OAc)_2$ as the catalyst further increased the yield of **3aa** to 81% (Table 1, entry 13). Surprisingly, the reaction without Pd catalyst still furnished **3aa** in 16% yield (Table 1, entry 14). The use of 2.0 equiv $Cu(OAc)_2$ replacing AgOAc led to **3aa** in low yield and poor selectivity of cross-*versus* homo-coupling (Table 1, entry 15). These results suggested that the synergy between Pd(II) and Ag(I) salts might account for both of the efficacy and high selectivity found in the oxidative cross-coupling reaction. Finally, the optimal conditions were determined as: **1a** (0.2 mmol), **2a** (1.2 equiv), $PdCl_2$ (5 mol%), BQ (10 mol%), DMSO (1.0 equiv), AgOAc (2.0 equiv), DMF, 80 °C, air.

2.3. Substrate scope

With the optimal conditions for the reaction between **1a** and **2a**, we continued to examine the substrate scope of allyl(trimethyl)silanes and aryl boronic acids (Scheme 3). Firstly, silanes with substituted allyl groups were tested. The study showed that β-aryl substitution was crucial to the cross-coupling reaction. Allylsilanes with β-aryl groups bearing either electron-withdrawing or electron-donating substituents reacted with phenyl boronic acid **2a** well and all these reactions furnished the corresponding products (**3ba** to **3ia**) in moderate to good yield (61–71%). Functional groups such as alkyl (**1b**), halogen (**1c**-**1f**), alkoxyl (**1g**), cyano (**1h**) and COOMe groups (**1i**) were well tolerated. In addition, β-(2-naphthyl)-substituted allyl(trimethyl)silane **1j** reacted with **2a** to deliver the product **3ja** in 66%.

Secondly, a wide range of aryl boronic acids having various substituents at *para*- or *meta*-positions of the phenyl rings were tested. All these aryl boronic acids were coupled with **1a** smoothly to afford the desired products in moderate to good yields (**3ab**-**3ao**). The compatible functionalities included alkyl (**2b**-**2c**, **2n**), aryl (**2d**), halogen (**2e**-**2g**, **2m**), CF_3 (**2h**), cyano (**2i**, **2o**), COOMe (**2j**), formyl (**2k**), and methoxyl groups (**2l**). It is worth mentioning that the side-products **4** and **5** were too little to be detected by NMR in all the reactions of the scope study above. Interestingly, the conditions were also applicable to heteroaryl boronic acids. Benzofuran-2-boronic acid **2p** and 3-thiophene-boronic acid **2q** reacted with **1a** respectively to furnish the products **3ap** and **3aq**, albeit in low yield (25% for **3ap** and 27% for **3aq**) due to the facile degradation of the formed cross-coupling products.

After testing the scope of allylsilanes and aryl boronic acids, we continued to examine other organoboron reagents as the coupling partners in the reaction with allyl(trimethyl)silanes (Scheme 4). The use of phenylboroxine and various phenyl boronic esters in the reaction with **1a** under the optimal conditions above led to the formation of **3aa** in 26–61% yield and a trace amount of **4a** and **5a** (Scheme 4a). However, the reaction of **1a** with $PhBF_3K$ under the same conditions only delivered a trace product. Interestingly, methyl boronic acid was found to be a competent coupling partner, which reacted with **1j** to furnish the methylation product **6** in 51% yield. But similar reaction of cyclohexyl boronic acid failed to yield the desired product, probably due to the existence of β-hydrogen [24]. Furthermore, the pinacol methylboronate could also be

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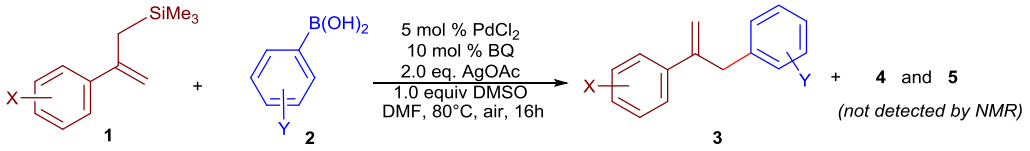
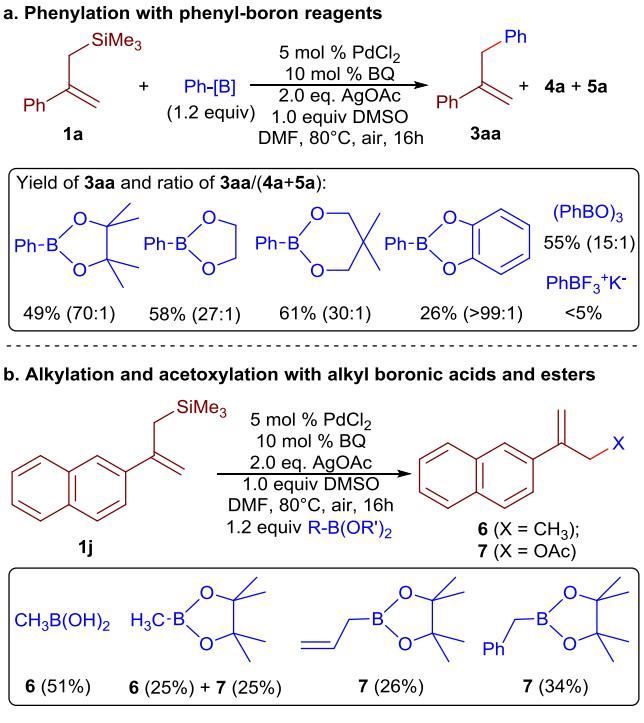


Entry	1	2	Yield of 3	Entry	1	2	Yield of 3
1	**1a** (X =H)	**2a** (Y = H)	**3aa**, 72%	14	**1a**	**2e** (Y = 4-F)	**3ae**, 73%
2	**1b** (X = 4-Me)	**2a**	**3ba**, 61%	15	**1a**	**2f** (Y = 4-Cl)	**3af**, 46%
3	**1c** (X = 4-F)	**2a**	**3ca**, 65%	16	**1a**	**2g** (Y = 4-Br)	**3ag**, 73%
4	**1d** (X = 4-Cl)	**2a**	**3da**, 69%	17	**1a**	**2h** (Y = 4-CF_3)	**3ah**, 62%
5	**1e** (X = 4-Br)	**2a**	**3ea**, 61%	18	**1a**	**2i** (Y = 4-CN)	**3ai**, 67%[c]
6	**1f** (X = 3-Cl)	**2a**	**3fa**, 69%	19	**1a**	**2j** (Y = 4-CO_2Me)	**3aj**, 51%[c]
7	**1g** (X = 3-OMe)	**2a**	**3ga**, 64%	20	**1a**	**2k** (Y = 4-CHO)	**3ak**, 60%
8	**1h** (X = 4-CN)	**2a**	**3ha**, 70%	21	**1a**	**2l** (Y = 4-OMe)	**3al**, 57%[c]
9	**1i** (X = 4-CO_2Me)	**2a**	**3ia**, 71%	22	**1a**	**2m** (Y = 3-F)	**3am**, 67%
				23	**1a**	**2n** (Y = 3-Me)	**3an**, 56%
				24	**1a**	**2o** (Y = 3-CN)	**3ao**, 51%
10	**1j**	**2a**	**3ja**, 66%	25	**1a**	**2p**	**3ap**, 25%
11	**1a**	**2b** (Y = 4-Me)	**3ab**, 66%				
12	**1a**	**2c** (Y = 4-tBu)	**3ac**, 60%				
13	**1a**	**2d** (Y = 4-Ph)	**3ad**, 50%	26	**1a**	**2q**	**3aq**, 27%

[a] Conditions: **1** (0.2 mmol), **2** (0.24 mmol), $PdCl_2$ (5 mol%), BQ (10 mol%), AgOAc (2.0 equiv), DMSO (1.0 equiv), DMF (1 mL), 80 °C, air, 16 h. [b] Isolated yield. [c] 10 mol% $PdCl_2$ and 20 mol% BQ. BQ = Benzoquinone.

Scheme 3. Substrate scope for the cross-coupling of allyl(trimethyl)silanes with aryl boronic acids[a].



Scheme 4. Reaction of other organoboron reagents with allyl(trimethyl)silanes.

coupled with **1j**. The reaction not only gave the methylation product **6**, but also an acetoxylation product **7** (Scheme 4b). Unfortunately, when the pinacol allylboronate and benzylboronate were used, only the acetoxylation product **7** was isolated in 26% and 34% yield.

2.4. Mechanism discussion

To gain more mechanistic insights, several control experiments were conducted: (1) the reaction of 2-phenylpropene **8** with **2a** under the standard conditions was found to deliver a mixture of **3aa** and its isomer **9**, which was not detected in the reaction between **1a** and **2a** (eq 1, Scheme 5); (2) heating the Heck-coupling product **4** under the standard conditions did not give **3aa** (eq 2, Scheme 5). The results of these experiments indicated that neither **8** nor **4** was the intermediate in the oxidative cross-coupling between **1a** and **2a**, and further ruled out both of the protodesilylation/coupling pathway and the Heck-coupling/protodesilylation pathway as possible mechanisms.

As found in the part of conditions optimization, AgOAc could also mediate the oxidative cross-coupling in the absence of palladium catalysts to give the product **3aa**, albeit in low yield. This reaction was totally quenched by addition of 5.0 equiv TEMPO (eq 3, Scheme 5), indicating that the silver-mediated reaction followed a radical pathway. However, the reaction under the standard conditions (with 5 mol% $PdCl_2$) in the presence of 5.0 equiv TEMPO still gave **3aa** in 19% after 16 h. The results suggested that the Pd-catalyzed oxidative reaction followed an ionic pathway.

On the basis of the results above and literature reports, a plausible mechanism for the Pd(II)-catalyzed oxidative cross-coupling of allylsilanes with aryl boronic acids was proposed as shown in

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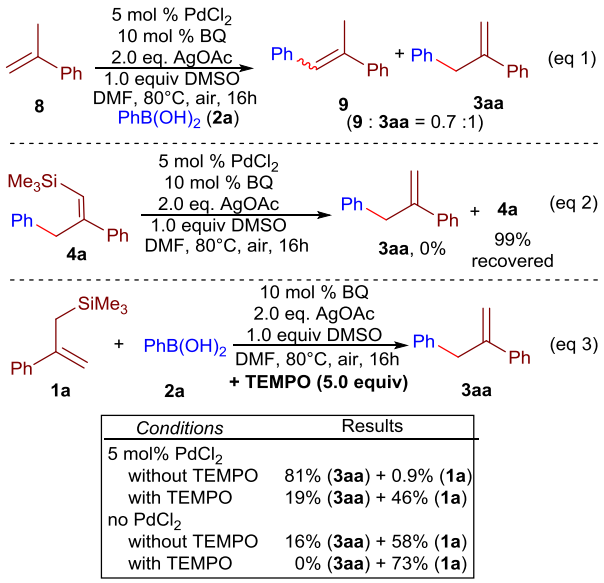

Conditions	Results
5 mol% $PdCl_2$	
without TEMPO	81% (**3aa**) + 0.9% (**1a**)
with TEMPO	19% (**3aa**) + 46% (**1a**)
no $PdCl_2$	
without TEMPO	16% (**3aa**) + 58% (**1a**)
with TEMPO	0% (**3aa**) + 73% (**1a**)

Scheme 5. Control experiments.

Fig. 1. The reaction might start from transmetalation of aryl boronic acid **2** with AgOAc to generate an aryl-Ag intermediate **IA**, which further reacted with Pd(II) in the presence of BQ to deliver an $ArPd(BQ)_nOAc$ complex **IB** [20,21]. **IB** could proceed through either electrophilic addition/desilylation or direct transmetalation to form an $ArPd(BQ)_n(allyl)$ complex **IC** [22,25]. Reductive elimination of **IC** furnished the final product **3** and $Pd^0(BQ)_n$, which could be reoxidized to $Pd(OAc)_2(BQ)_n$ by AgOAc. Although another mechanism involving silver-mediated radical addition of aryl radicals to allylsilanes was also possible, it was a minor process to produce **3**.

3. Conclusion

In conclusion, we have developed an oxidative cross-coupling of allyl(trimethyl)silanes with aryl boronic acids by Pd(II) catalysis. This reaction delivered allylic arenes in moderate to good yields and excellent selectivity from a wide range of aryl boronic acids and a series of β-aryl substituted allyl(trimethyl)silanes. The reaction was proposed to undergo silver-mediated transmetalation to form $ArPd(BQ)_nOAc$, proceed through the interaction with allylsilanes to give $ArPd(BQ)_n(allyl)$, and finally afford the final product **3** by reductive elimination.

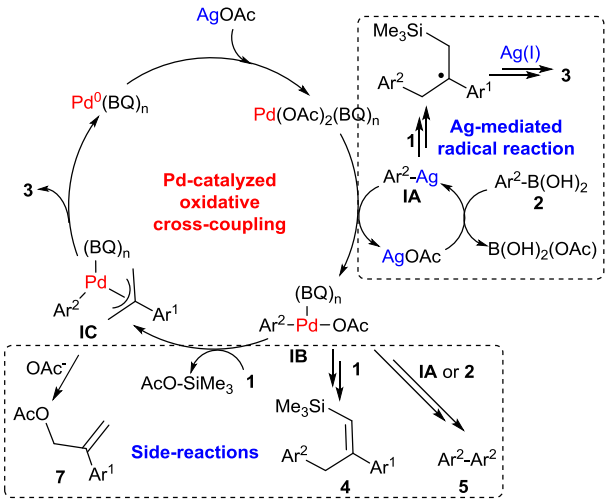

Fig. 1. Plausible mechanism.

4. Experimental section

4.1. General information

Solvents, starting materials, catalysts were purchased from Chemical companies and used without further purification. Chromatographic purification was conducted with technical grade solvents (petroleum ether, dichloromethane and ethyl acetate) and silica gel 40–63 μm. TLC was performed on silica gel 60 F_{254} TLC glass plates and visualized with UV light (254 nm). ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts were referenced relative to residual solvent signal ($CDCl_3$: 7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR). Infrared spectra were recorded on a Brucker Alpha-FTIR, which could be used to obtain FTIR transmission spectra in the range of 500–4000 cm^{-1} and were reported as cm^{-1} (w = weak, m = medium, s = strong). HRMS were performed on a mass spectrometer (APCI-MS). Melting points were measured with micro melting point apparatus.

4.2. Preparation of allyl(trimethyl)silanes

4.2.1. (2-(4-Chlorophenyl)allyl)trimethylsilane (*1d*)

1d was prepared from 4′-chloroacetophenone according to the procedure reported in the literature [26]. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 2H), 7.28–7.21 (m, 2H), 5.10 (d, J = 1.4 Hz, 1H), 4.86 (d, J = 0.9 Hz, 1H), 1.97 (s, 2H), −0.11 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 141.4, 133.1, 128.4, 127.8, 110.7, 26.2, −1.3. IR (neat) 698(w), 734(w), 767(w), 837(m), 855(s), 881(m), 942(w), 1013(m), 1094(m), 1160(w), 1251(m), 1491(m), 1615(w), 2955(w). HRMS (APCI) Calcd for $C_{12}H_{16}ClSi^-$ $[M-H]^-$ 223.0715; Found 223.0717.

4.2.2. (2-(3-Chlorophenyl)allyl)trimethylsilane (*1h*)

1h was prepared from 3′-chloroacetophenone according to the same procedure for the synthesis of **1d**. 76% yield. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.30–7.25 (m, 1H), 7.25–7.19 (m, 2H), 5.13 (d, J = 1.3 Hz, 1H), 4.90 (d, J = 0.8 Hz, 1H), 1.98 (s, 2H), −0.09 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 144.9, 134.2, 129.5, 127.3, 126.6, 124.6, 111.3, 26.2, −1.29. IR (neat) 700(w), 722(w), 788(m), 854(s), 881(m), 1084(w), 1157(w), 1250(m), 1290(w), 1562(w), 2956(w). HRMS (APCI) Calcd for $C_{12}H_{16}ClSi^-$ $[M-H]^-$ 223.0715; Found 223.0717.

4.2.3. (2-(3-Methoxyphenyl)allyl)trimethylsilane (*1i*)

1i was prepared from ethyl 3-methoxybenzoate according to the procedure reported in the literature [27]. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27–7.19 (m, 1H), 7.01 (d, J = 7.7 Hz, 1H), 6.96 (s, 1H), 6.81 (d, J = 8.1 Hz, 1H), 5.15 (s, 1H), 4.88 (s, 1H), 3.83 (s, 3H), 2.02 (s, 2H), −0.07 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 146.6, 144.5, 129.1, 119.1, 112.5, 112.5, 110.3, 55.3, 26.3, −1.3. IR (neat) 700 (w), 726 (w), 787 (w), 855 (s), 1050 (m), 1248 (m), 1300 (w), 1577(m), 1599(w), 2955(w) cm^{-1}. HRMS (APCI) Calcd for $C_{13}H_{21}OSi^+$ $[M+H]^+$ 221.1356; Found 221.1365.

4.3. General procedure for conditions screening

To an oven-dried schlenck tube with a magnetic stirring bar was added phenylboronic acid **2a**, a Pd catalyst, a base, a silver salt and additives. Then trimethyl(2-phenylallyl)silane **1a** (19.04 mg, 0.1 mmol) in a solvent (1 mL) was added to the schlenck tube by a

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syringe. After being heated and stirred under air atmosphere for 12–16 h, the reaction mixture was treated with a saturated $NaHCO_3$ aqueous solution (5 mL) and the resulting mixture was extracted by ethyl acetate (3 × 5 mL). Then the combined organic extracts were washed with brine (3 × 5 mL), dried over Na_2SO_4 and filtered. To the organic extracts was added 4-bromotoluene (8 mg) as the internal standard for gas chromatographic analysis to give GC yields.

4.4. General procedure for the scope study

A mixture of phenyl boronic acid **2a** (26.26 mg, 0.24 mmol), $PdCl_2$ (1.77 mg, 0.01 mmol), 1,4-benzoquinone (2.16 mg, 0.02 mmol), AgOAc (66.77 mg, 0.4 mmol), DMSO (14 μL, 0.2 mmol), trimethyl(2-phenylallyl)silane **1a** (38.07 mg, 0.2 mmol) in DMF (1.0 mL) was stirred at 80 °C under air for 16 h. Then the reaction mixture was treated with a saturated $NaHCO_3$ aqueous solution (10 mL) and the resulting mixture was extracted by ethyl acetate (3 × 10 mL). Then the combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and filtered. After concentration, the residue was submitted to ^1H NMR analysis with $CDCl_3$ as the solvent. The crude sample was further purified by flash chromatography on a silica gel column with petroleum ether as the eluent to give the product **3aa** as a colorless liquid.

4.4.1. Prop-2-ene-1,2-diyldibenzene (*3aa*)

28.10 mg, 72% yield. Colorless oil. ^1H NMR (400 MHz, CDCl3) δ 7.43 (d, J = 7.3 Hz, 2H), 7.34–7.12 (m, 8H), 5.49 (s, 1H), 5.01 (s, 1H), 3.83 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 141.0, 139.7, 129.1, 128.5, 128.4, 127.6, 126.3, 126.2, 114.7, 41.8. The NMR data is in good agreement with that reported in the literature [28].

4.4.2. 1-Methyl-4-(3-phenylprop-1-en-2-yl)benzene (*3ba*)

27.57 mg, 66% yield. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.7 Hz, 2H), 7.29–7.14 (m, 5H), 7.09 (d, J = 7.6 Hz, 2H), 5.46 (s, 1H), 4.97 (s, 1H), 3.82 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 139.8, 138.0, 137.3, 129.09, 129.05, 128.5, 126.2, 126.1, 113.9, 41.8, 21.2. IR (neat, cm^{-1}) 701 (s), 736 (m), 828 (s), 896 (m), 1453 (m), 1513 (m), 1624 (w), 2920 (w), 3026 (w). HRMS (APCI) Calcd for $C_{16}H_{17}^+$ $[M+H]^+$ 209.1325; Found 209.1322.

4.4.3. 1-Fluoro-4-(3-phenylprop-1-en-2-yl)benzene (*3ca*)

27.62 mg, 65% yield. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.30–7.13 (m, 5H), 6.96 (t, J = 8.3 Hz, 2H), 5.43 (s, 1H), 5.02 (s, 1H), 3.80 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, J = 246.3 Hz), 161.2, 146.0, 139.4, 136.9 (d, J = 3.3 Hz), 129.0, 128.5, 127.9 (d, J = 8.0 Hz) 126.3, 115.2 (d, J = 21.3 Hz), 114.7, 42.0. IR (neat, cm^{-1}) 478 (s), 701 (s), 748 (w), 825 (m), 899 (m), 1232 (m), 1453 (m), 1508 (m), 1624 (w), 3057 (w). HRMS (APCI) Calcd for $C_{15}H_{14}F^+$ $[M+H]^+$ 213.1074; Found 213.1072.

4.4.4. 1-Chloro-4-(3-phenylprop-1-en-2-yl)benzene (*3da*)

31.84 mg, 69% yield. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.6 Hz, 2H), 7.31–7.14 (m, 7H), 5.47 (s, 1H), 5.06 (s, 1H), 3.80 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 139.3, 139.2, 133.4, 129.0128.6, 128.5, 127.6, 126.4, 115.3, 41.7. IR (neat, cm^{-1}) 700 (m), 739 (m), 837 (s), 903 (m), 1012 (m), 1099 (m), 1493 (s), 2920 (w). HRMS (APCI) Calcd for $C_{16}H_{14}Cl^+$ $[M+H]^+$ 229.0779; Found 229.0772.

4.4.5. 1-Bromo-4-(3-phenylprop-1-en-2-yl)benzene (*3ea*)

33.50 mg, 61% yield. White solid. mp. 36.5–38.5 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.7 Hz, 2H), 7.32–7.12 (m, 7H), 5.48 (s, 1H), 5.06 (s, 1H), 3.80 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 139.8, 139.2, 131.5, 129.0, 128.6, 128.0, 126.4, 121.6, 115.3, 41.7. IR (neat, cm^{-1}) 699 (m), 735 (s), 835 (s), 903 (m), 1008 (m), 1073 (m), 1392 (m), 1490 (s), 1625 (w), 2918 (w), 3027 (w). HRMS (APCI) Calcd for $C_{16}H_{14}Br^+$ $[M+H]^+$ 273.0273; Found 273.0266.

4.4.6. 1-Chloro-3-(3-phenylprop-1-en-2-yl)benzene (*3fa*)

31.80 mg, 69% yield. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.32–7.23 (m, 3H), 7.23–7.12 (m, 5H), 5.48 (s, 1H), 5.06 (s, 1H), 3.80 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 142.8, 139.1, 134.3, 129.6, 129.0, 128.6, 127.6, 126.5, 126.4, 124.5, 115.9, 41.6. IR (neat, cm^{-1}) 700 (s), 789 (m), 905 (m), 1076 (w), 1453 (m), 1494 (m), 1562 (m), 1593 (m), 3027 (w). HRMS (APCI) Calcd for $C_{16}H_{14}Cl^+$ $[M+H]^+$ 229.0779; Found 229.0766.

4.4.7. 1-Methoxy-3-(3-phenylprop-1-en-2-yl)benzene (*3ga*)

28.70 mg, 64% yield. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.08 (m, 6H), 7.03 (d, J = 7.6 Hz, 1H), 6.96 (s, 1H), 6.78 (d, J = 8.1 Hz, 1H), 5.49 (s, 1H), 5.02 (s, 1H), 3.81 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 147.0, 142.5, 139.6, 129.3, 129.1, 128.5, 126.2, 118.9, 114.9, 112.9, 112.2, 55.3, 41.8. IR (neat, cm^{-1}) 705 (m), 785 (m), 901 (m), 1050 (m), 1237 (m), 1288 (m), 1492 (m), 1577 (s), 1600 (s), 2935 (w), 3027 (w). HRMS (APCI) Calcd for $C_{16}H_{17}O^+[M+H]^+$ 225.1274; Found 225.1272.

4.4.8. 4-(3-Phenylprop-1-en-2-yl)benzonitrile (*3ha*)

30.87 mg, 70% yield. White solid. mp. 79.0–81.0 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 7.8 Hz, 2H), 7.31–7.23 (m, 2H), 7.21–7.08 (m, 3H), 5.58 (s, 1H), 5.21 (s, 1H), 3.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 145.4, 138.6, 132.3, 128.9, 128.7, 127.0, 126.6, 119.0, 117.7, 111.1, 41.5. IR (neat, cm^{-1}) 559 (m), 704 (s), 755 (s), 847 (s), 908 (m), 1083 (m), 1492 (m), 1601 (m), 2222 (m), 2910 (w). HRMS (APCI) Calcd for $C_{16}H_{14}N^+$ $[M+H]^+$ 220.1121; Found 220.1117.

4.4.9. Methyl 4-(3-phenylprop-1-en-2-yl)benzoate (*3ia*)

35.87, 71% yield. White solid. mp. 60.1–62.5. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 7.30–7.22 (m, 2H), 7.22–7.09 (m, 3H), 5.57 (s, 1H), 5.13 (s, 1H), 3.88 (s, 3H), 3.84 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 146.4, 145.4, 139.1, 129.8, 129.2, 129.0, 128.6, 126.4, 126.3, 116.6, 52.2. 41.6. IR (neat, cm^{-1}) 697 (s), 719 (m), 783 (m), 903 (m), 1110 (m), 1181 (m), 1278 (s), 1438 (m), 1603 (m), 1714 (s), 2916 (w). HRMS (APCI) Calcd for $C_{17}H_{17}O_2^+$ $[M+H]^+$ 253.1223; Found 253.1218.

4.4.10. 2-(3-Phenylprop-1-en-2-yl)naphthalene (*3ja*)

32.24 mg, 66% yield. White solid. mp. 55.1–56.5 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.82–7.70 (m, 3H), 7.62 (d, J = 8.6 Hz, 1H), 7.50–7.38 (m, 2H), 7.32–7.08 (m, 5H), 5.64 (s, 1H), 5.13 (s, 1H), 3.96 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 139.7, 138.1, 133.5, 132.9, 129.1, 128.5, 128.4, 127.9, 127.6, 126.3, 126.2, 126.0, 125.1, 124.7, 115.3, 41.8. IR (neat, cm^{-1}) 701 (s), 749 (s), 825 (m), 864 (m), 899 (m), 947 (w), 1494 (w), 1623 (w), 2900 (w). HRMS (APCI) Calcd for $C_{19}H_{17}^+$ $[M+H]^+$ 245.1325; Found 245.1322.

4.4.11. 1-Methyl-4-(2-phenylallyl)benzene (*3ab*)

27.44 mg, 66% yield. Color oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.3 Hz, 2H), 7.33–7.19 (m, 3H), 7.15–7.02 (m, 4H), 5.47 (s, 1H), 5.01 (s, 1H), 3.79 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 141.0, 136.6, 135.7, 129.2, 128.9, 128.4, 127.5, 126.3, 114.5, 41.3, 21.2. The NMR data is in good agreement with that reported in the literature [29].

4.4.12. 1-(tert-Butyl)-4-(2-phenylallyl)benzene (*3ac*)

30.16 mg, 60% yield. White solid. mp. 39.0–40.2 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.6 Hz, 2H), 7.34–7.20 (m, 5H), 7.15 (d, J = 7.8 Hz, 2H), 5.49 (s, 1H), 5.01 (s, 1H), 3.80 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 147.1, 141.1, 136.6, 128.7, 128.4,

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127.6, 126.3, 125.4, 114.6, 41.1, 34.5, 31.5. IR (neat, cm^{-1}) 551 (s), 604 (m), 690 (m), 776 (s), 892 (m), 1267 (m), 1494 (m), 1514 (m), 1622 (m), 2962 (m). HRMS (APCI) Calcd for $C_{19}H_{23}^{+}$ $[M+H]^+$ 251.1794; Found 251.1786.

*4.4.13. 4-(2-Phenylallyl)-1,1′-biphenyl (**3ad**)*

27.03 mg, 50% yield. White solid. mp. 85.9–88.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 2H), 7.52–7.44 (m, 4H), 7.43–7.37 (m, 2H), 7.34–7.20 (m, 6H), 5.52 (s, 1H), 5.07 (s, 1H), 3.87 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 141.1, 140.9, 139.1, 138.8, 129.5, 128.8, 128.4, 127.7, 127.23, 127.19, 127.1, 126.3, 114.8, 41.4. IR (neat, cm^{-1}) 711 (s), 750 (m), 777 (m), 822 (w), 861 (w), 890 (w), 1267 (m), 1668 (m). HRMS (APCI) Calcd for $C_{21}H_{19}^{+}$ $[M+H]^+$ 271.1481; Found 271.1477.

*4.4.14. 1-Fluoro-4-(2-phenylallyl)benzene (**3ae**)*

31.25mg, 73% yield. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 2H), 7.32–7.22 (m, 3H), 7.20–7.13 (m, 2H), 6.94 (t, J = 8.2 Hz, 2H), 5.48 (s, 1H), 5.01 (s, 1H), 3.80 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (d, J = 243.9 Hz), 147.1, 140.7, 135.2 (d, J = 3.2 Hz), 130.4 (d, J = 7.8 Hz), 128.4, 127.7, 126.3, 115.3 (d, J = 21.2 Hz), 114.8, 41.0. IR (neat, cm^{-1}) 704 (m), 782 (m), 823 (m), 902 (m), 1157 (w), 1222 (m), 1508 (s), 1601 (w). HRMS (APCI) Calcd for $C_{15}H_{14}F^{+}$ $[M+H]^+$ 213.1074; Found 213.1071.

*4.4.15. 1-Chloro-4-(2-phenylallyl)benzene (**3af**)*

21.06 mg, 46% yield. White solid. mp. 41.5–43.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.4 Hz, 2H), 7.33–7.18 (m, 5H), 7.15 (d, J = 7.7 Hz, 2H), 5.49 (s, 1H), 5.02 (s, 1H), 3.80 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 140.6, 138.1, 132.0, 130.4, 128.6, 128.5, 127.7, 126.3, 115.0, 41.1. IR (neat, cm^{-1}) 706 (s), 778 (w), 853 (m), 898 (m), 1011 (m), 1069 (m), 1487 (s), 1626 (w), 2909 (w). HRMS (APCI) Calcd for $C_{15}H_{14}Cl^{+}$ $[M+H]^+$ 229.0779; Found 229.0779.

*4.4.16. 1-Bromo-4-(2-phenylallyl)benzene (**3ag**)*

40.03 mg, 73% yield. White solid. mp. 42.5–44.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, J = 8.2 Hz, 4H), 7.32–7.18 (m, 3H), 7.09 (d, J = 7.6 Hz, 2H), 5.49 (s, 1H), 5.02 (s, 1H), 3.78 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 140.5, 138.6, 131.6, 130.8, 128.5, 127.8, 126.2, 120.1, 115.0, 41.2. IR (neat, cm^{-1}) 703 (m), 778 (m), 804 (m), 902 (m), 1016 (m), 1093 (m), 1492 (s), 1627 (w), 2919 (w). HRMS (APCI) Calcd for $C_{15}H_{14}Br^{+}$ $[M+H]^+$ 273.0273; Found 273.0266.

*4.4.17. 1-(2-Phenylallyl)-4-(trifluoromethyl)benzene (**3ah**)*

32.84 mg, 60% yield. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.7 Hz, 2H), 7.41 (d, J = 7.1 Hz, 2H), 7.37–7.15 (m, 5H), 5.53 (s, 1H), 5.05 (s, 1H), 3.89 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 143.8, 140.4, 129.3, 128.5, 127.9, 126.2, 125.4 (q, J = 3.8 Hz), 115.3, 41.6. IR (neat, cm^{-1}) 705 (w), 780 (w), 820 (w), 1019 (w), 1067 (m), 1123 (m), 1163 (m), 1325 (s). HRMS (APCI) Calcd for $C_{16}H_{14}F_3^{+}$ $[M+H]^+$ 263.1042; Found 263.1038.

*4.4.18. 4-(2-Phenylallyl)benzonitrile (**3ai**)*

29.41 mg, 67% yield. White solid. mp. 58.4–60.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.7 Hz, 2H), 7.37 (d, J = 7.2 Hz, 2H), 7.35–7.20 (m, 5H), 5.54 (s, 1H), 5.06 (s, 1H), 3.89 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 145.4, 140.1, 132.3, 129.7, 128.6, 128.0, 126.2, 119.1, 115.7, 110.2, 41.9. IR (neat, cm^{-1}) 547 (m), 708 (s), 778 (s), 818 (m), 899 (m), 1411 (m), 1601 (m), 2222 (m), 2925 (w). HRMS (APCI) Calcd for $C_{16}H_{14}N^{+}$ $[M+H]^+$ 220.1121; Found 220.1120.

*4.4.19. Methyl 4-(2-phenylallyl)benzoate (**3aj**)*

25.94 mg, 51% yield. White solid. mp. 42.4–45 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.7 Hz, 2H), 7.39 (d, J = 7.3 Hz, 2H), 7.34–7.15 (m, 5H), 5.51 (s, 1H), 5.04 (s, 1H), 3.97–3.77 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 146.3, 145.2, 140.5, 129.8, 129.1, 128.5, 128.3, 127.8, 126.2, 115.2, 52.1, 41.8. IR (neat, cm^{-1}) 696 (m), 736 (w), 761 (w), 780 (w), 911 (w), 1020 (w), 1110 (m), 1183 (w), 1281 (s), 1439 (w), 1610 (w), 1722 (s), 2925 (w). HRMS (APCI) Calcd for $C_{17}H_{17}O_2^{+}$ $[M+H]^+$ 253.1223; Found 253.1219.

*4.4.20. 4-(2-Phenylallyl)benzaldehyde (**3ak**)*

26.94 mg, 60% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.39 (br, 4H), 7.31–7.13 (m, 3H), 5.54 (s, 1H), 5.07 (s, 1H), 3.92 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 147.1, 146.1, 140.3, 134.9, 130.1, 129.7, 128.5, 127.9, 126.2, 115.5, 42.0. IR (neat, cm^{-1}) 706 (m), 780 (m), 819 (m), 900 (m), 1168 (m), 1212 (m), 1605 (m), 1698 (s), 2925 (w). HRMS (APCI) Calcd for $C_{16}H_{15}O^{+}$ $[M+H]^+$ 223.1117; Found 223.1111.

*4.4.21. 1-Methoxy-4-(2-phenylallyl)benzene (**3al**)*

25.56 mg, 57% yield. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.6 Hz, 2H), 7.34–7.23 (m, 3H), 7.16 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 8.2 Hz, 2H), 5.49 (s, 1H), 5.03 (s, 1H), 4.06–3.42 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 147.5, 141.0, 131.7, 130.0, 128.4, 127.5, 126.3, 114.4, 113.9, 55.3, 40.9. IR (neat, cm^{-1}) 704 (m), 780 (m), 819 (w), 900 (w), 1036 (m), 1177 (m), 1247 (s), 1511 (s), 1611 (w), 2834 (w). HRMS (APCI) Calcd for $C_{16}H_{17}O^{+}$ $[M+H]^+$ 225.1274; Found 225.1271.

*4.4.22. 1-Fluoro-3-(2-phenylallyl)benzene (**3am**)*

28.72 mg, 67% yield. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.3 Hz, 2H), 7.33–7.14 (m, 4H), 7.00 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 10.0 Hz, 1H), 6.86 (t, J = 8.4 Hz, 1H), 5.51 (s, 1H), 5.05 (s, 1H), 3.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.09 (d, J = 245.3 Hz), 161.9, 146.4, 142.3 (d, J = 7.3 Hz), 140.5, 129.9 (d, J = 8.3 Hz), 129.8, 128.5, 127.7, 126.2, 124.7 (d, J = 2.7 Hz), 115.8, (d, J = 21.2 Hz), 115.1, 113.2 (d, J = 21.1 Hz), 41.5 (d, J = 1.5 Hz). IR (neat, cm^{-1}) 704 (m), 778 (s), 865 (w), 901 (m), 1136 (m), 1248 (s), 1486 (m), 1589 (m), 1614 (m), 2921 (w). HRMS (APCI) Calcd for $C_{15}H_{14}F^{+}$ $[M+H]^+$ 213.1074; Found 213.1071.

*4.4.23. 1-Methyl-3-(2-phenylallyl)benzene (**3an**)*

23.44 mg, 56% yield. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.7 Hz, 2H), 7.32–7.21 (m, 3H), 7.15 (t, J = 7.5 Hz, 1H), 7.07–6.96 (m, 3H), 5.49 (s, 1H), 5.01 (s, 1H), 3.79 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 141.0, 139.6, 138.0, 129.8, 128.4, 128.4, 127.6, 127.0, 126.3, 126.1, 114.7, 41.7, 21.6. IR (neat, cm^{-1}) 700 (s), 756 (m), 777 (s), 898 (m), 1028 (w), 1444 (w), 1493 (w), 1607 (w), 2917 (w). HRMS (APCI) Calcd for $C_{16}H_{17}^{+}$ $[M+H]^+$ 209.1325; Found 209.1321.

*4.4.24. 3-(2-Phenylallyl)benzonitrile (**3ao**)*

22.36 mg, 51% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.45 (d, J = 7.4 Hz, 2H), 7.37 (t, J = 9.1 Hz, 3H), 7.33–7.21 (m, 3H), 5.53 (s, 1H), 5.05 (s, 1H), 3.86 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 141.1, 140.0, 133.5, 132.5, 130.1, 129.3, 128.6, 128.0, 126.2, 119.1, 115.6, 112.5, 41.3. IR (neat, cm^{-1}) 690 (s), 704 (s), 777 (s), 813 (s), 896 (s), 1433 (w), 1493 (w), 2223 (m), 2908 (w). HRMS (APCI) Calcd for $C_{16}H_{14}N^{+}$ $[M+H]^+$ 220.1121; Found 220.1118.

*4.4.25. 2-(2-Phenylallyl)benzofuran (**3ap**)*

11.72mg, 25% yield. White solid. mp. 72.0–73.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.37 (m, 4H), 7.36–7.12 (m, 5H), 6.40 (s, 1H), 5.57 (s, 1H), 5.22 (s, 1H), 3.98 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 154.9, 143.5, 140.2, 129.0, 128.5, 127.9, 126.1, 123.5, 122.6, 120.5, 115.5, 111.0, 103.9, 34.9. IR (neat, cm^{-1}) 699.84 (s), 777.05 (s), 834.85 (m), 855.99 (m), 901.15 (m), 1445.49 (m), 1493.92 (m), 2921.79 (w). HRMS (APCI) Calcd for $C_{17}H_{15}O^{+}$ $[M+H]^+$ 235.1117; Found 235.1123.

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*4.4.26. 3-(2-Phenylallyl)thiophene (**3aq**)*

11.00 mg, 27% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.4 Hz, 2H), 7.34–7.19 (m, 4H), 7.00–6.90 (m, 2H), 5.47 (s, 1H), 5.07 (s, 1H), 3.84 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 140.9, 140.2, 128.7, 128.4, 127.7, 126.2, 125.4, 121.6, 114.3, 36.4. IR (neat, cm^{-1}) 699.84 (s), 777.05 (s), 834.85 (m), 855.99 (m), 901.15 (m), 1445.49 (m), 1493.92 (m), 2921.79 (w). HRMS (APCI) Calcd for $C_{13}H_{13}S^+$ $[M+H]^+$ 201.0732; Found 201.0722.

*4.4.27. (E)-(2,3-Diphenylprop-1-en-1-yl)trimethylsilane (**4a**)*

The reaction of **1a** with **2a** using Ag_2CO_3 gave a mixture of **3aa** and **4a**, which could not be separated from each other. The mixture of **3aa** and **4a** was treated with methyl 4-iodobenzoate, 5 mol% $Pd(OAc)_2$ and Ag_2CO_3 in DCE at 80 °C under N_2 atmosphere for 8 h. After workup and flash chromatographic purification according to the general procedure, **4a** was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 6.2 Hz, 3H), 7.24–7.14 (m, 7H), 6.14 (s, 1H), 4.02 (s, 2H), 0.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 143.3, 139.8, 130.9, 128.5, 128.4, 128.2, 127.4, 126.4, 126.0, 40.4, 0.3. IR (neat, cm^{-1}) 475.62 (m). 698.87 (m), 749.51 (m), 858.14 (s), 1249.18 (m), 1452.66 (m), 1493.84 (m), 1596.60 (w), 2962.22 (w). HRMS (APCI) Calcd for $C_{18}H_{23}Si^+$ $[M+H]^+$ 267.1564; Found 267.1573.

*4.4.28. 2-(But-1-en-2-yl)naphthalene (**6**)*

The compound **6** was obtained by the reaction of **1j** with methyl boronic acid under the standard conditions (Scheme 4b). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.78 (m, 4H), 7.60 (d, J = 8.4 Hz, 1H), 7.49–7.42 (m, 2H), 5.43 (s, 1H), 5.18 (s, 1H), 2.65 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 138.9, 133.6, 132.9, 128.3, 127.9, 127.7, 126.2, 125.9, 124.8, 124.7, 111.7, 28.3, 13.2. IR (neat, cm^{-1}) 475.44 (m), 749.91 (s), 817.36 (m), 856.72 (m), 890.75 (m), 972.93 (m), 1071.73 (m), 1624.23 (w), 2966.29 (w). HRMS (APCI) Calcd for $C_{14}H_{15}^+$ $[M+H]^+$ 183.1168; Found 183.1170.

*4.4.29. 2-(Naphthalen-2-yl)allyl acetate (**7**)*

The compound **7** was obtained by the reaction of **1j** with the pinacol methylboronate, benzylboronate or allylboronate under the standard conditions (Scheme 4b). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.76 (m, 4H), 7.60 (d, J = 8.6 Hz, 1H), 7.54–7.39 (m, 2H), 5.71 (s, 1H), 5.48 (s, 1H), 5.11 (s, 2H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 142.5, 135.4, 133.4, 133.2, 128.4, 128.3, 127.7, 126.5, 126.4, 125.0, 124.3, 115.9, 65.9, 21.2, 21.1. IR (neat, cm-1) 475.93 (m), 750.80 (s), 817.87 (m), 905.90 (m), 1027.91 (m), 1227.18 (s), 1369.63 (s), 1740.40 (s), 3055.22 (w). HRMS (APCI) Calcd for $C_{15}H_{15}O_2^+$ $[M+H]^+$ 227.1067; Found 227.1069.

4.5. Control experiments

*4.5.1. Reaction of 2-phenylpropene **8** with phenylboronic acid **2a***

The reaction of **2a** (0.24 mmol) with **8** (0.2 mmol) was conducted under the standard conditions: $PdCl_2$ (5 mol%, 0.01 mmol, 1.77 mg), BQ (10 mol%, 0.02 mmol, 2.16 mg) AgOAc (2.0 equiv, 0.4 mmol, 66.77 mg), DMSO (1.0 equiv, 0.2 mmol, 14 μL), DMF (1 mL), 80 °C, air, 16 h. This reaction gave a mixture of **3aa** and its isomer **9** in a 1:0.7 ratio by ^{1}H NMR analysis (eq 1, Scheme 3).

*4.5.2. Transformation from the Heck-coupling product **4a** to **3aa***

The mixture of **4a** (0.2 mmol), $PdCl_2$ (5 mol%, 0.01 mmol, 1.77 mg), BQ (10 mol%, 0.02 mmol, 2.16 mg) AgOAc (2.0 equiv, 0.4 mmol, 66.77 mg), DMSO (1.0 equiv, 0.2 mmol, 14 μL) and DMF (1 mL) was heated at 80 °C for 16 h. **3aa** was not detected in the reaction mixture by ^{1}H NMR analysis and **4a** was recovered in 99% yield by flash chromatography (eq 2, Scheme 3).

4.5.3. TEMPO test experiments

(1) *No palladium catalyst:* To the mixture of **1a** (0.2 mmol), **2a** (0.24 mmol), BQ (10 mol%, 0.02 mmol, 2.16 mg), AgOAc (2.0 equiv, 0.4 mmol, 66.77 mg), DMSO (1.0 equiv, 0.2 mmol, 14 μL) and DMF (1 mL) was added TEMPO (5.0 equiv, 1.0 mmol, 141.25 mg) at room temperature. The resulting mixture was heated at 80 °C under air for 16 h. After workup according to the general procedure above, GC analysis showed that **3aa** was not formed and 73% of **1a** was detected (eq 3, Scheme 3).

(2) *With palladium catalyst:* To the mixture of **1a** (0.2 mmol), **2a** (0.24 mmol), $PdCl_2$ (5 mol%, 0.01 mmol, 1.77 mg), BQ (10 mol %, 0.02 mmol, 2.16 mg), AgOAc (2.0 equiv, 0.4 mmol, 66.77 mg), DMSO (1.0 equiv, 0.2 mmol, 14 μL) and DMF (1 mL) was added TEMPO (5.0 equiv, 1.0 mmol, 141.25 mg) at room temperature. The resulting mixture was heated at 80 °C under air for 16 h. After workup according to the general procedure above, GC analysis showed that **3aa** was formed in 19% yield and 46% of **1a** was detected (eq 3, Scheme 3).

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2018.10.055.

References

[1] (a) I. Fleming, J. Dunoguès, R. Smithers, Org. React. 37 (1989) 57–575;
(b) L. Chabaud, P. James, Y. Landais, Eur. J. Org Chem. (2004) 3173–3199.
[2] (a) A. Hosomi, Acc. Chem. Res. 21 (1988) 200;
(b) A. Fürstner, D. Voigtländer, Synthesis 2000 (2000) 959–969;
(c) HosomiA, K. Miura, Bull. Chem. Soc. Jpn. 77 (2004) 835–851.
[3] (a) Y. Hatanaka, T. Hiyama, Synlett (1991) 845–853;
(b) Y. Nakao, T. Hiyama, Chem. Soc. Rev. 40 (2011) 4893–4901;
(c) S.E. Denmark, C.S. Regens, Acc. Chem. Res. 41 (2008) 1486–1499.
[4] (a) K. Ishihara, M. Mouri, Q. Gao, T. Maruyama, K. Furuta, H. Yamamoto, J. Am. Chem. Soc. 115 (1993) 11490–11495;
(b) D.R. Gauthier, E.M. Carreira, Angew. Chem. Int. Ed. 35 (1996) 2363–2365;
(c) M. Braun, W. Kotter, Angew. Chem. Int. Ed. 43 (2004) 514–517.
[5] M. Yasuda, T. Saito, M. Ueba, A. Baba, Angew. Chem. Int. Ed. 43 (2004) 1414–1416.
[6] M. Braun, W. Kotter, Angew. Chem. Int. Ed. 43 (2004) 514–517.
[7] T. Schwier, M. Rubin, V. Gevorgyan, Org. Lett. 6 (2004) 1999–2001.
[8] (a) R. Shimizu, H. Egami, Y. Hamashima, M. Sodeoka, Angew. Chem. Int. Ed. 51 (2012) 4577–4580;
(b) J. Liu, L. Chu, F.-L. Qing, Org. Lett. 15 (2013) 894–897;
(c) S. Arimori, M. Takada, N. Shibata, Org. Lett. 17 (2015) 1063–1065;
(d) B. Greedy, J.-M. Paris, T. Vidal, V. Gouverneur, Angew. Chem. Int. Ed. 42 (2003) 3291–3294.
[9] N.-X. Hu, Y. Aso, T. Otsubo, F. Ogura, Tetrahedron Lett. 29 (1988) 4949–4952.
[10] Y. Matano, M. Yoshimune, H. Suzuki, Tetrahedron Lett. 36 (1995) 7475–7478.
[11] M. Arimoto, H. Yamaguchi, E. Fujita, M. Ochiai, Y. Nagao, Tetrahedron Lett. 28 (1987) 6289–6292.
[12] (a) J. Yoshida, T. Murata, S. Isoe, Tetrahedron Lett. 27 (1986) 3373–3376;
(b) S.R. Wilson, C.E. Augelli-Safran, Tetrahedron 44 (1988) 3983–3995;
(c) T. Fuchigami, K. Yamamoto, Chem. Lett. (1996) 937–938.
[13] (a) T.D. Beeson, A. Mastracchio, J.-B. Hong, K. Ashton, D.W.C. MacMillan, Science 316 (2007) 582–585;
(b) A. Mastracchio, A.A. Warkentin, A.M. Walji, D.W.C. MacMillan, Proc. Natl. Acad. Sci. 107 (2010) 20648–20651.
[14] (a) J.R. Hwu, C.N. Chen, S.-S. Shiao, J. Org. Chem. 60 (1995) 856–862;
(b) Y. Zhang, A.J. Raines, R.A. Flowers II, Org. Lett. 5 (2003) 2363–2365.
[15] M. Beller, C. Bolm, Transition Metals for Organic Synthesis: Building Blocks

and Fine Chemicals (2nd Revised and Enlarged ed.), Wiley-VCH, Weinheim, Germany, 2004.
[16] E.-I. Negishi, A. de Meijere, Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley-Interscience, New York, 2002.
[17] (a) C. Liu, H. Zhang, W. Shi, A. Lei, Chem. Rev. 111 (2011) 1780–1824;
(b) W. Shi, C. Liu, A. Lei, Chem. Soc. Rev. 40 (2011) 2761–2776.
[18] (a) J.-X. Yu, J. Liu, G.-F. Shi, C.-D. Shao, Y.-H. Zhang, Angew. Chem. Int. Ed. 54 (2015) 4079–4082;
(b) L.T. Ball, G.C. Lloyd-Jones, C.A. Russell, Science 337 (2012) 1644–1648;
(c) T.J.A. Corrie, L.T. Ball, C.A. Russell, G.C. Lloyd-Jones, J. Am. Chem. Soc. 139 (2017) 245–254.
[19] (a) I. Macsári, K.J. Szabó, Tetrahedron Lett. 41 (2000) 1119–1122;
(b) I. Macsári, K.J. Szabó, Chem. Eur. J. 7 (2001) 4097–4106.
[20] J.M. Weibel, A. Blanc, P. Pale, Chem. Rev. 108 (2008) 3149–3173.
[21] T. Furuya, T. Ritter, Org. Lett. 11 (2009) 2860–2863.
[22] M.O. Akram, P.S. Mali, N.T. Patil, Org. Lett. 19 (2017) 3075–3078.
[23] M. Wasa, K.M. Engle, D.W. Lin, E.J. Yoo, J.-Q. Yu, J. Am. Chem. Soc. 133 (2011) 19598–19601.
[24] The reaction of cyclohexyl boronic acid with **1a** did not give any coupling product.
[25] T. Jeffery, Tetrahedron Lett. 41 (2000) 8445–8449.
[26] (a) X. Su, H. Huang, Y. Yuan, Y. Li, Angew. Chem. Int. Ed. 56 (2017) 1338–1341;
(b) R. Shimizu, H. Egami, Y. Hamashima, M. Sodeoka, Angew. Chem. Int. Ed. 51 (2012) 4577–4580.
[27] B.A. Narayanan, W.H. Bunnelle, Tetrahedron Lett. 28 (1987) 6261–6264.
[28] Y. Hayashi, T. Urushima, S. Aratake, T. Okano, K. Obi, Org. Lett. 10 (2008) 5011–5014.
[29] D.V. Moiseev, A.V. Gushchin, A.S. Shavirin, Y.A. Kursky, V.A. Dodonov, J. Organomet. Chem. 667 (2003) 176–184.

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