C–H Activation

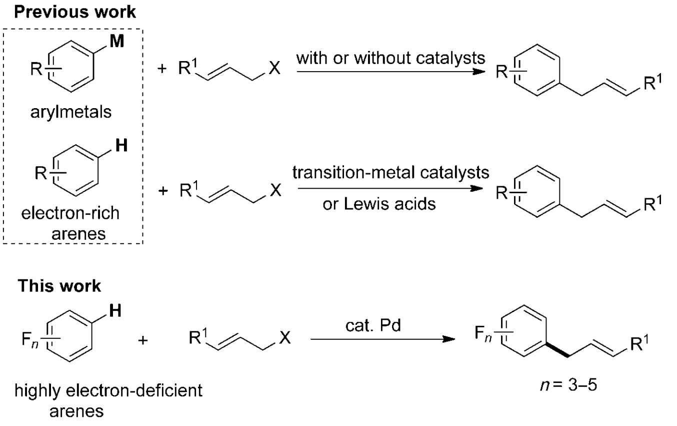
DOI: 10.1002/anie.201008174

Direct Palladium-Catalyzed Intermolecular Allylation of Highly Electron-Deficient Polyfluoroarenes**

*Shilu Fan, Fei Chen, and Xingang Zhang**

Allylated arenes are an important class of substituted aromatic compounds owing to the presence of allylic arene moieties in many biologically active compounds.[1] Moreover, the allylic substituent is synthetically useful, because the carbon–carbon double bond can lead to a variety of structures after simple manipulations.[2] The most common synthetic method used to prepare this functional group is the cross-couplings of allylic electrophiles with stoichiometric amounts of aryl metals, such as aryl copper,[3] aryl magnesium halide,[4] and aryl boron reagents.[5] However, these strategies have drawbacks in terms of the stability and availability of aryl metal reagents. Furthermore, additional transformations are required for preparation of these reagents. Therefore, for synthetic simplicity, the direct C–H allylation of aromatic rings represents an attractive alternative.[6] Although in some cases, the direct C–H allylation of electron-rich arenes catalyzed by Lewis acids[7] or transition metals[8] has been developed, the direct C–H allylation of electron-deficient arenes is an ongoing challenge owing to their poor reactivities.[9] Inspired by our recent study on the palladium-catalyzed direct olefination of polyfluoroarenes, which represents one of the rare examples of catalytic direct olefination of electron-deficient arenes,[10] we hypothesized that the direct palladium-catalyzed C–H allylation of highly electron-deficient polyfluoroarenes with allylic electrophiles may be possible, and would benefit the preparation of allylated electron-deficient arenes (Scheme 1). Although Tsuji–Trost reaction involving addition of a nucleophile to (π-allyl)palladium intermediate offers a powerful tool for preparation of allyl-substituted compounds,[11] the reaction of highly electron-deficient polyfluoroarenes through the present strategy has never been studied. Consequently, developing new direct transition-metal-catalyzed allylative cross-coupling reactions for widespread applications is still highly desirable.

It is well established that polyfluoroarenes are a key structural unit for various functional molecules, such as pharmaceuticals, agrochemicals, liquid crystals, and electronic devices.[12] Hence, it is of great synthetic interest to develop an efficient reaction for installing various fluoroaryl groups. Despite impressive progress in direct arylation of polyfluoroarenes,[13] there are few coupling methods for introducing alkyl (C_{sp^3}) substituents.[14] Herein, we report our preliminary results on direct palladium-catalyzed intermolecular allylation of highly electron-deficient polyfluoroarenes. This approach provides a highly efficient protocol for the preparation of a wide range of allyllated polyfluoroarene compounds.[15]



Scheme 1. Intermolecular allylation of aromatic rings.

Initially, the reaction of pentafluorobenzene **1** with cinnamyl methyl carbonate **2** was investigated in the presence of $Pd(OAc)_2$ (10 mol %) and PPh_3 (20 mol %) in toluene at 120 °C. This reaction provided only a trace amount of allylated pentafluorobenzene (Table 1, entry 1). However, when the **2** was switched to *tert*-butyl cinnamyl carbonate (*E*)-**3a**, 60 % yield of linear allylated product **5a** was isolated along with a trace amount of isomer **4a** (**5a**/**4a** = 68:1), thus suggesting that more-basic alkoxide is essential for the reaction to proceed efficiently (Table 1, entry 2). Notably, no branched product was observed under this catalytic system. Encouraged by this result, a variety of palladium catalysts, ligands, and solvents were examined. Other Pd^{II} catalysts, such as $[Pd(TFA)_2]$, $PdCl_2$, $[PdCl_2(CH_3CN)_2]$, and $[PdCl_2(PhCN)_2]$, were ineffective, and only Pd^0 catalysts $[Pd(PPh_3)_4]$ and $[Pd(dba)_2]$ afforded 18 % to 33 % yield based on NMR spectroscopy (see Table S1 in the Supporting Information). The reaction was also found to be sensitive to the phosphine ligands and solvents, and the readily available PPh_3 and toluene were the best choice (see Table S1).

Considering that copper complexes can function as copromoters in the palladium-catalyzed processes,[16] and 1,10-phenanthroline (phen) may stabilize the soluble copper

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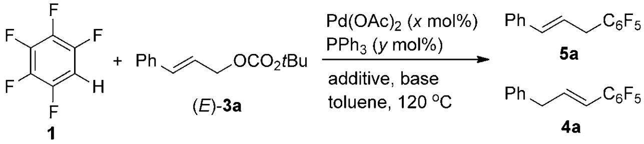
[**] This work was financially supported by the NSFC (20902100, 20832008), the Shanghai Rising-Star Program (09QA1406900), and the SIOC. We thank Prof. Wei-Liang Duan and Prof. Shu-Li You for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201008174.

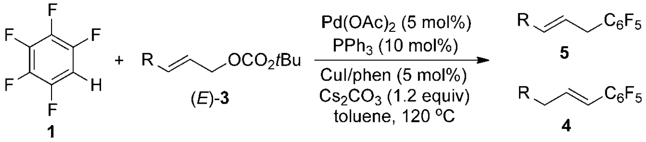
Table 1: Representative results for optimization of direct palladium-catalyzed intermolecular allylation of pentafluorobenzene **1**.[a]

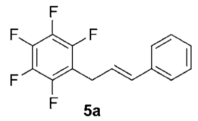
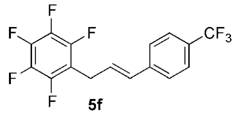
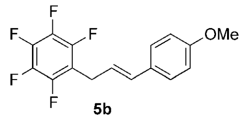
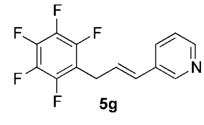
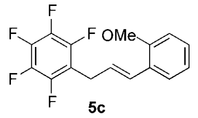
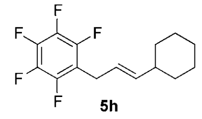
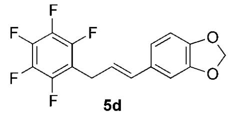
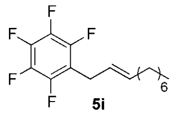
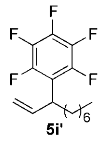
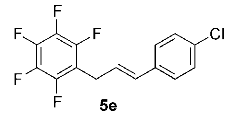


Entry	x/y [mol%]	Additive (mol%)	Base (equiv)	Yield of **5a** [%][b]
1[c]	10/20	–	–	trace
2	10/20	–	–	(60)
3	10/20	CuI (10)/phen (10)	–	67
4	10/20	CuI (10)/phen (10)	Cs_2CO_3 (1.2)	100 (87)
5[d]	10/20	CuI (10)/phen (10)	Cs_2CO_3 (1.2)	100 (86)
6[d]	10/20	CuI (10)/phen (10)	K_2CO_3 (1.2)	60
7[d]	10/20	CuI (10)/phen (10)	K_3PO_4 (1.2)	35
8[d]	10/20	CuI (10)/phen (10)	*t*BuOLi (1.2)	35
9[d]	10/20	CuCl(10)/phen(10)	Cs_2CO_3 (1.2)	66
10[d]	10/20	CuBr(10)/phen(10)	Cs_2CO_3 (1.2)	80
11[d]	10/20	$CuBr_2$(10)/phen(10)	Cs_2CO_3 (1.2)	85
12	10/20	–/phen (10)	–	63
13	10/–	–/phen (10)	–	NR
14	–/–	CuI (10)/phen (10)	Cs_2CO_3 (1.2)	NR
15	**5/10**	**CuI (5)/phen (5)**	**Cs_2CO_3 (1.2)**	**(96)**

[a] Reaction conditions (unless otherwise specified): **1** (2.0 equiv), (*E*)-**3a** (0.4 mmol), toluene (2.0 mL), 12 h, 120 °C. **5a**/**4a** = 68:1, determined by HPLC methods. [b] Yield determined by ^{19}F NMR spectroscopy using fluorobenzene as the internal standard and the yield of the isolated product is in parentheses. [c] Cinnamyl methyl carbonate **2** was used instead of (*E*)-**3a**. [d] Reaction run at 100 °C. NR = no reaction.

Table 2: Direct palladium-catalyzed allylation of pentafluorobenzene **1** with various allyl carbonates (*E*)-**3**.[a]



Entry	Product	Entry	Product
1	 96%, **5a/4a** = 68:1	6	 (**5f** + **4f**) 78%, **5f/4f** = 5:1
2	 90%, **5b/4b** = 40:1	7	 (**5g** + **4g**) 80%, **5g/4g** = 3:1
3	 84%, **5c/4c** = 67:1	8	 (**5h** + **4h**) 48%, **5h/4h** = 5.7:1
4	 90%, **5d/4d** = 34:1	9[b]	 (**5i** + **4i** + **5i'**) 52%,  **5i/4i/5i'** = 40:8:5
5	 (**5e** + **4e**) 85%, **5e/4e** = 7:1		

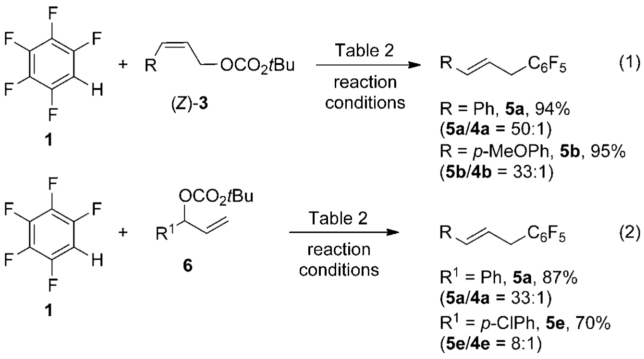
[a] Reaction conditions (unless otherwise specified): **1** (2.0 equiv), (*E*)-**3** (0.6 mmol), toluene (2.0 mL), 12 h, 120 °C. Yields are of the isolated product. [b] **1** (0.6 mmol), (*E*)-**3i** (2.0 equiv).

complexes by chelation and increase electron density at the copper center,[17] we assumed that the presence of a catalytic amount of Cu^I/phen in this $Pd(OAc)_2/PPh_3$ catalytic system may assist the reaction of **1** with the (π-allyl)palladium intermediate and improve the yield of the reaction. However, the use of CuI/phen (10 mol%) only resulted in a comparable yield (Table 1, entry 3). Introduction of Cs_2CO_3 (1.2 equiv) to this catalytic system significantly improved the reaction efficiency and gave 87% yield (Table 1, entry 4), while other bases and copper salts were less effective (Table 1, entries 6–11). In addition, $Pd(OAc)_2/PPh_3$ are essential for the reaction, because the absence of either of them failed to give any desired product, and therefore ruled out the possibility that copper catalyzes this reaction under our present reaction conditions[15] (Table 1, entries 13 and 14). Further optimization showed that the best yield of isolated product (96%) was afforded by decreasing the $Pd(OAc)_2$ loading to 5 mol% with use of Ph_3P (10 mol%) and CuI/phen (5 mol%; Table 1, entry 15).

A variety of allylated pentafluorobenzene compounds were generated by the present method and good to high yields and regioselectivities were obtained (Table 2). For the aromatic allyl carbonate, the reaction efficiency and the regioselectivity depended on the nature of the substituents on the aromatic ring (Table 2, entries 1–6). Substrates bearing an electron-donating group furnished the product smoothly in excellent yields (up to 96%) with high regioselectivity (Table 2, entries 1–4), while for electron-withdrawing substituted aromatic allyl carbonates, slightly lower yields (78–85%) and regioselectivities were observed (Table 2, entries 5 and 6). The increasing formation of isomers **4** with use of electron-deficient allyl carbonates is probably a result of the relatively easier 1,3-hydrogen shift taking place under basic conditions. Chloride is compatible with the catalytic system, and provided a good opportunity for further transformations utilizing traditional techniques (Table 2, entry 5). A pyridyl group did not interfere with the coupling reaction (Table 2, entry 7). Less-reactive aliphatic allyl carbonates are also suitable substrates, and reasonable yields with moderate regioselectivities were still afforded (Table 2, entries 8 and 9). But for linear (*E*)-*tert*-butyl dec-2-enyl carbonate (*E*)-**3i**, a small amount of branched product **5i′** was obtained (Table 2, entry 9), thus suggesting that the steric effect plays an important role in the regioselectivity.

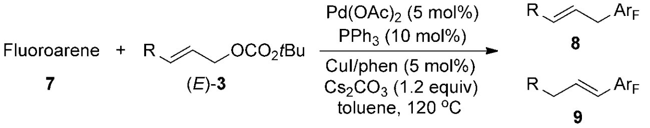
The reactions of *Z*-allyl carbonates (*Z*)-**3** and branched allyl carbonates **6** were also tested. As shown in Equations (1) and (2) of Scheme 2, the linear *E*-allylated products **5** were obtained in high stereo- and regioselectivities with no observation of Z-allylated or branched isomers, thus indicating that a (π-allyl)palladium intermediate is involved in the catalytic process.

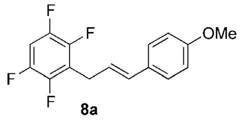
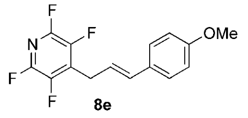
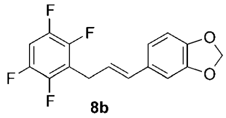
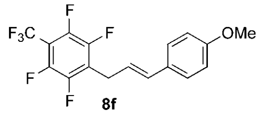
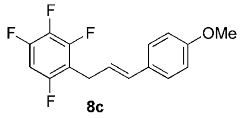
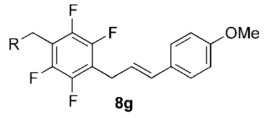
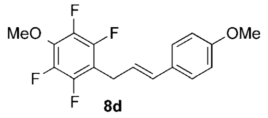
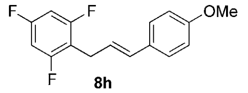
In addition to the demonstrated broad range of polyfluoroarenes, various fluoroarenes **7** containing 3 or 4 fluorines were also competent coupling partners (Table 3). For substrates bearing 3 or 4 fluorine atoms, thus containing more than one reaction site, good yields of monoallylated products were still observed with using 3.0 equivalents of fluoroarenes[18] (Table 3, entries 1–3 and 8). The low yield (43 %) of **8f** is probably a result of the highly electron-withdrawing effect of 1,2,4,5-tetrafluoro-3-(trifluoromethyl)-benzene **7f**, which could influence the catalytic cycle[19] (Table 3, entry 6). Benzylated fluoroarene **7g** was also a suitable substrate and provided allylated product in a reasonable yield with high regioselectivity (Table 3, entry 7). The X-ray crystallographic analysis of **8g** further confirmed its structure.[20] However, for 1,2,3,5-tetrafluorobenzene (**7c**), 1,2,4,5-tetrafluoro-3-methoxybenzene (**7d**), and 1,3,5-trifluorobenzene (**7h**), unsatisfactory yields were afforded under the standard conditions. The addition of PivOH[10,21] benefited the reaction (see Table S2). Further optimization revealed that the use of PivOH instead of CuI/Phen afforded the desired products in moderate to good yields (Table 3, entries 3, 4, and 8). But 1,3-difluorobenzene did not react owing to the low acidity of the C–H bond that was to be activated.[22]



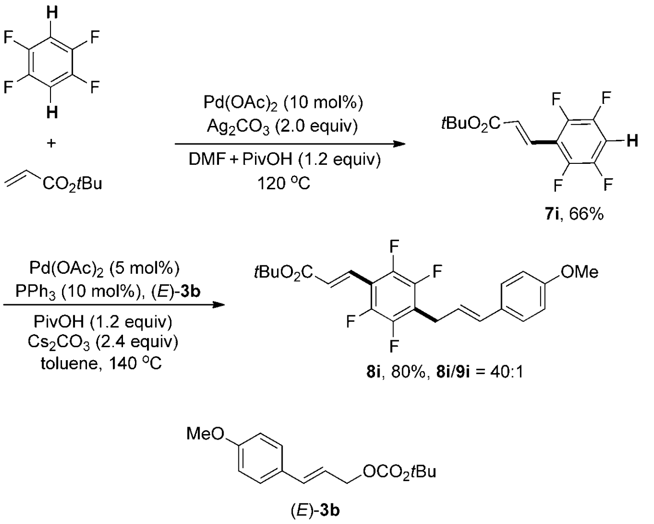
Scheme 2. Direct palladium-catalyzed allylation of pentafluorobenzene **1** with linear allyl carbonates (Z)-**3** and branched allyl carbonates **6**.

Table 3: Direct palladium-catalyzed allylation of fluoroarenes **7** with allyl carbonates (E)-**3**.[a]



Entry	Product	Entry	Product
1	 **8a** 80%, **8a**/**9a** > 20:1	5[b]	 **8e** (**8e** + **9e**) 61%, **8e**/**9e** = 5.4:1
2	 **8b** 82%, **8b**/**9b** > 20:1	6[b]	 **8f** 43%, **8f**/**9f** = 20:1
3[c]	 **8c** 65%, **8c**/**9c** = 33:1	7[e]	 **8g** 50%, **8g**/**9g** = 36:1 R = p-MeOPh
4[d]	 **8d** 70%, **8d**/**9d** = 33:1	8[c]	 **8h** 57%, **8h**/**9h** = 33:1

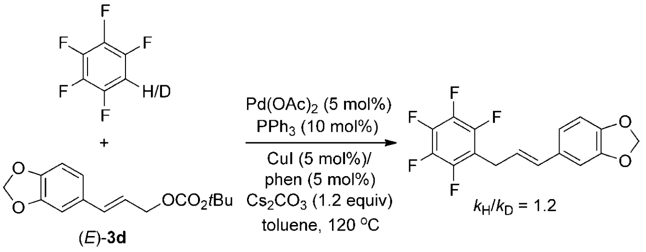
[a] Reaction conditions (unless otherwise specified): **7** (3.0 equiv), (E)-**3** (0.6 mmol), toluene (2.0 mL), 12 h, 120 °C. Yields are of the isolated product. [b] **7** (2.0 equiv), (E)-**3** (0.6 mmol), toluene (2.0 mL), 12 h, 120 °C. [c] **7** (3.0 equiv), (E)-**3** (0.6 mmol), PivOH (1.2 equiv), Cs_2CO_3 (2.4 equiv), toluene (2.5 mL), 12 h, 140 °C. [d] **7** (2.0 equiv), (E)-**3** (0.6 mmol), PivOH (1.2 equiv), Cs_2CO_3 (2.4 equiv), toluene (2.5 mL), 12 h, 140 °C. [e] Fluoroarene (1.2 equiv), (E)-**3** (1.8 mmol, 1.0 equiv).



Scheme 3. Iterative palladium-catalyzed C–H bond functionalization. DMF = N,N-dimethylformamide, Piv = pivaloyl.

It was also possible to prepare highly functionalized polyfluoroarenes from simple fluoroarenes by using the present strategy. As depicted in Scheme 3, after iterative palladium-catalyzed C–H bond functionalization of 1,2,4,5-tetrafluorobenzene, namely palladium-catalyzed oxidative olefination,[10] and direct allylation, compound **8i** was obtained in a highly efficient manner. This approach features the present method and was used to synthesize the target in fewer steps compared to traditional techniques.

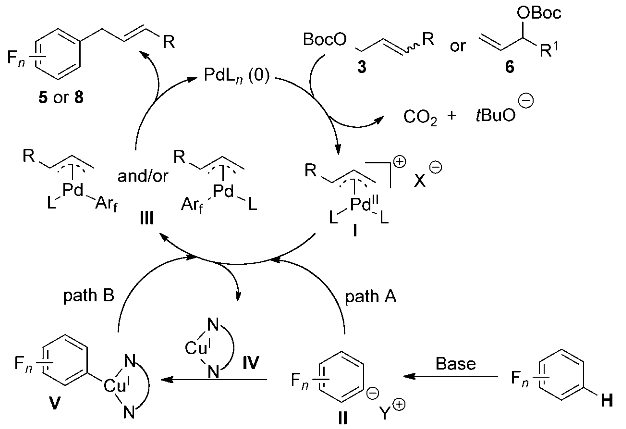
To investigate the working mode of the present catalytic systems, we looked at the kinetic isotope effect (KIE; Scheme 4). The intermolecular competition reactions between pentafluorobenzene and its deuterated derivative do not exhibit a kinetic isotope effect ($k_H/k_D = 1.2$; Scheme 4). This observation implies that cleavage of the C–H bond in polyfluoroarenes is not involved in the rate-determining step in the overall catalytic process. This finding is different from



Scheme 4. Kinetic isotope effect study.

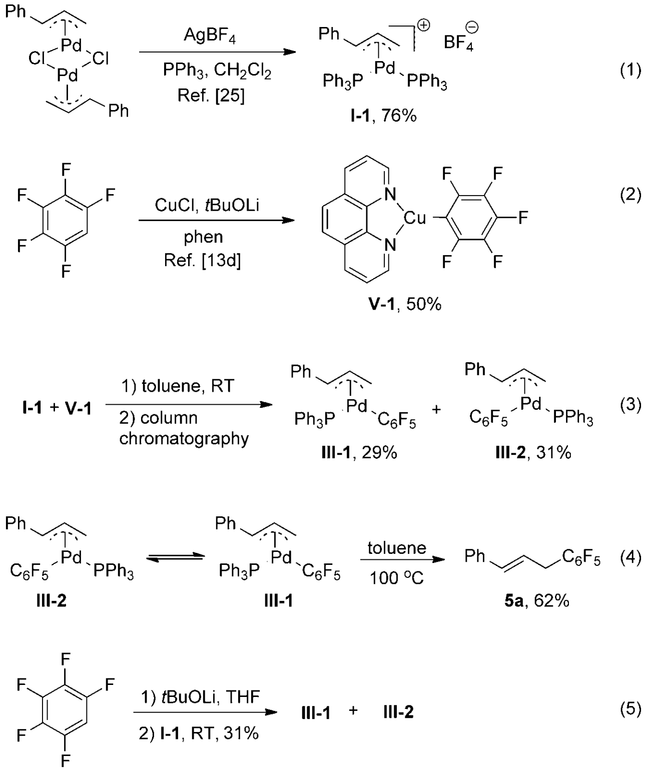
the well-known concerted metalation/deprotonation (CMD) process,[13a,23] in which C–H bond activation is a rate-determining step.

In an attempt to understand the mechanism of the present palladium-catalyzed direct allylation of polyfluoroarenes, a proposal is shown in Scheme 5 on the basis of preliminarily kinetic data and the fact that copper does not catalyze the reaction under our present conditions (Table 1, entry 14) and a (π-allyl)palladium intermediate is involved in the catalytic cycle (equation (2) in Scheme 2). The sequence begins with the formation of π-allylpalladium complexes **I** by decarboxylation of allylic carbonates **3** with Pd^0. Subsequently, base abstracts a proton from the acidified C–H bonds on the polyfluoro aromatic rings[13c,d] to generate intermediate **II**, followed by the reaction of Pd species **I** with **II**, thus providing the Pd(polyfluoroaryl)(allyl) complex **III**, which may lead to two regioisomers (path A). Finally, the reductive elimination would lead to the expected allylated compound **5** or **8**, and regenerate the Pd^0 species.[24] Alternatively, the presence of copper complex **IV** may easily produce polyfluoroarylcopper complex **V**,[13c,d] which would make the generation of key Pd species **III** relatively easier by transmetalation (path B), thus resulting in higher reaction yields in most cases.



Scheme 5. Mechanistic proposal for direct palladium-catalyzed allylation of polyfluoroarenes with allyl carbonates. Ar_f = polyfluoroaryl, Boc = *tert*-butoxycarbonyl.

To further probe the reaction mechanism illustrated in Scheme 5, several experiments were conducted (Scheme 6). Firstly, the (π-allyl)palladium complexe **I-1**[25] and pentafluorophenylcopper complex **V-1**[13d] were prepared according to the literature (Equations 1 and 2 of Scheme 6), in which the successful generation of **V-1** through the reaction of pentafluorobenzene with *t*BuOLi and CuCl/phen (Equation 2 of Scheme 6) convinced us that the copper complex **V** is involved in the catalytic cycle when the C–H allylation reaction was carried out in the presence of CuI/phen. With these two intermediates in hand, we then investigated the formation of the Pd(polyfluoroaryl)(allyl) complex **III** by the reaction of **I-1** with **V-1** (Equation 3 of Scheme 6). The reaction was monitored by NMR spectroscopy, which showed that two regioisomers (**III-1** and **III-2**) of Pd(pentafluorophenyl)(allyl) complex **III** was formed. These regioisomers are air stable and can be isolated by flash column chromatography, and their formation indicates the attack of copper complex **V-1** at the palladium center. Assignments of the spectra of **III-1** and **III-2** were mainly based on the preferential coupling of ^{31}P with allylic protons *trans* to the phosphorus atom, thus leading to the location of the phenyl in **III-2** *trans* to the phosphine group.[26] The X-ray crystallographic analysis of **III-2** further confirmed its structure (Figure 1).[20] Because **III-1** and **III-2** can easily isomerize into each other,[27] a mixture of **III-1** and **III-2** was used to investigate the final step, reductive elimination. Subjection of a solution of **III-1** and **III-2** in toluene to heating at 100 °C indeed afforded allylated product **5a** (Equation 4 of Scheme 6),[28] thus demonstrating that the generation of the final product via path B is involved in the catalytic cycle. In addition, the possibility of formation of **III** via path A was also examined. As shown in Equation 5 of Scheme 6, 31 % yield of **III** was afforded when the (π-allyl)palladium complexes **I-1**



Scheme 6. Experiments for mechanistic studies. THF = tetrahydrofuran.

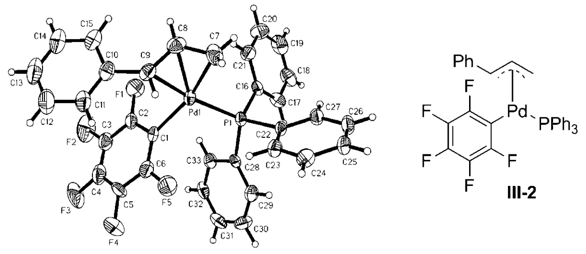


Figure 1. ORTEP plot of complex **III-2**. Thermal ellipsoids drawn at 30% probability.

was treated with intermediate **II**, which was generated in situ by treatment of pentafluorobenzene with *t*BuOLi, thus indicating that the catalytic cycle via path A is also reasonable.

In conclusion, we have developed an efficient and straightforward $Pd(OAc)_2/PPh_3$-catalyzed method for direct allylation of highly electron-deficient polyfluoroarenes, which represents a concise, operationally simple, and useful method to the preparation of polyfluoroarylated derivatives of interest in both life and materials science. Further studies to expand the substrates scope and their applications are now in progress.

Experimental Section

Representative general procedure for direct palladium-catalyzed intermolecular allylation of highly electron-deficient polyfluoroarenes: $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), Cs_2CO_3 (1.2 equiv), CuI (5 mol%), phen (5 mol%), and toluene (2 mL) were added to a sealed tube (25 mL) fitted with a septum cap under N_2, and then stirred. Polyfluoroarene (1.2 mmol, 2.0 equiv) and allyl carbonate (0.6 mmol, 1 equiv) were then added subsequently. The sealed tube was screw capped and heated to 120°C (oil bath). After stirring for 12 h, the reaction mixture was cooled to RT, diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified with column chromatography on silica gel to provide the pure product.

Received: December 24, 2010
Revised: April 4, 2011
Published online: May 17, 2011

Keywords: allylation · C–H activation · cross-coupling · palladium · polyfluoroarenes

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[27] Complexes **III-1** and **III-2** can easily isomerize into each other in CH_2Cl_2 or $CHCl_3$.

[28] As determined by monitoring the reaction by NMR spectroscopy; the reductive elimination of **III** showed that the formation of allylated product **5a** did not occur until the reaction temperature increased to 80 °C, thus indicating that the reductive elimination is the rate-determining step in the overall catalytic process. For details see Figure S1.