CHEMISTRY
A EUROPEAN JOURNAL

COMMUNICATION

DOI: 10.1002/chem.201202824

Copper- and Phosphine-Ligand-Free Palladium-Catalyzed Direct Allylation of Electron-Deficient Polyfluoroarenes with Allylic Chlorides

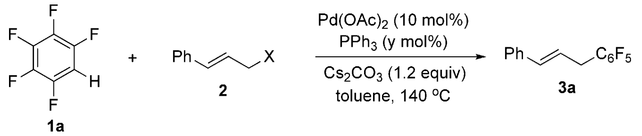
Yan-Bo Yu, Shilu Fan, and Xingang Zhang*[a]

Transition-metal-catalyzed allylation reactions of aryl metals have been used extensively in organic synthesis as a method to synthesise the allylated arene motif that is found in numerous natural products and biologically active compounds,[1] and because of the versatility of the double carbon–carbon bond for further synthetic transformations.[2] Nevertheless, this strategy is constrained by the need for multiple steps to prepare arylmetals.[3] The Friedel–Crafts-type allylation of arenes represents a complementary strategy; however, the reaction is limited by the substrate scope of π-electron-rich arenes.[4] Therefore, developing new and efficient reactions to access allylated arenes is still highly desirable. Over the past few years, impressive progress has been made towards the transition-metal-catalyzed direct functionalization of C−H bonds.[5] This strategy provides an attractive alternative to traditional techniques because the necessary preactivation of arenes is omitted. However, little attention has been given to the direct allylation of electron-deficient arenes by using this strategy. To the best of our knowledge, only isolated examples have been reported so far.[6] Although these achievements are promising, these processes are restricted by their low tolerance of important functional groups, limited substrate scope, and/or the requirement for multiple-component catalytic systems (e.g., $Pd(OAc)_2/PPh_3$ and CuI/Phen (Phen = 1,10-phenanthroline) co-catalyzed systems). Hence, the development of a new catalytic system for widespread application and that will overcome these limitations is still highly desirable.

Owing to the importance of polyfluoroarenes in materials and life sciences,[7] it is of great interest to install a fluoroaryl group on the organic molecules.[8–10] However, for less reactive fluoroarenes, such as 1,2,3,4-tetrafluorobenzene and difluorobenzene, it is difficult to obtain their corresponding allylated compounds by direct C−H bond functionalization due to the low reactivity of the C−H bond, which needs to be activated. From the new practical and academic standpoint, we herein present a highly efficient palladium-catalyzed allylation reaction of electron-deficient polyfluoroarenes with allylic chlorides. The notable features of this protocol are its simple catalytic system (copper- and phosphine-ligand free, only $[Pd_2(dba)_3]$ as the catalyst precursor), a broad substrate scope that includes difluorobenzene (an 'inert' substrate), and an excellent functional-group compatibility, which includes bromide. This protocol provides a useful and rapid access to allylated polyfluoroarenes that are of interest in both life and materials science. Mechanistic studies reveal that the reaction proceeds through the attack of a polyfluoroarene anion that is generated in situ at the (π-allyl)palladium–carboxylate complex, which is different from previous studies and is complementary to the traditional mechanism for the Pd-catalyzed allylation reaction of aryl metals.[3,11]

We began this study by examining different leaving groups on the allylated compound **2** (Table 1). However, the desired product **3a** was not obtained when *tert*-butylcinnamyl carbonate (**2a**), cinnamyl bromide (**2b**), or cinnamyl chloride (**2c**) were investigated in the reaction with pentafluorobenzene (**1**) in the presence of $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), and Cs_2CO_3 in toluene (Table 1, entries 1–3). Considering that the phosphine ligand may play an important role in the reaction efficiency, control experiments were conducted in the absence of PPh_3 to further understand the reaction. To our surprise, a 70% yield of **3a** was obtained when **2c** was used as a substrate (Table 1, entry 6).

Table 1. Effects of leaving group on the allylated compound **2** on the Pd-catalyzed allylation of pentafluorobenzene **1**.[a]



	2, X	PPh_3 [mol%]	Yield of **3a** [%]
1	**2a**, OCO_2tBu	20	trace
2	**2b**, Br	20	trace
3	**2c**, Cl	20	trace
4	**2a**, OCO_2tBu	–	56[b]
5	**2b**, Br	–	trace
6	**2c**, Cl	–	70[b]
7[c]	**2c**, Cl	–	NR

[a] Reaction conditions (unless otherwise specified): **1** (2.0 equiv), **2** (0.6 mmol), toluene (2.5 mL), 10 h. [b] Yield of isolated product. [c] Reaction conducted in the absence of Pd catalyst. NR=no reaction.

---

[a] Y.-B. Yu, S. Fan, Prof. Dr. X. Zhang
Key Laboratory of Organofluorine Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Science
345 Lingling Lu, Shanghai 200032 (P.R. China)
Fax: (+86) 21-6416-6128
E-mail: xgzhang@mail.sioc.ac.cn

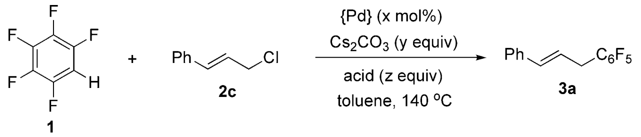
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201202824.

The reaction of compound **2a** also gave the corresponding product in 56% yield (Table 1, entry 4), whereas only a trace amount of product was formed when **2b** was examined (Table 1, entry 5). The results demonstrate that the reaction can be inhibited by PPh_3 under these reaction conditions, and that the reactivity of the leaving groups on the allylated compound **2** increase in the order: bromide < *tert*-butyl carbonate < chloride. No reaction occurred in the absence of a Pd catalyst, indicating that a palladium catalytic cycle is involved in the reaction (Table 1, entry 7).

Encouraged by these results, cinnamyl chloride (**2c**) was employed as a model substrate for further optimization of the reaction conditions (Table 2). Taking into account that a (π-allyl)palladium complex would be generated during the reaction, and that the addition of carboxylic acid may affect the reactivity of the palladium intermediate,[12] different acids were examined (Table 2, entries 1–7). We found that the nature of the acid plays an important role for the reaction efficiency. Pivalic acid (PivOH) showed a superior reactivity, providing an 82% yield of **3a** (Table 2, entry 4). The reaction was also sensitive to the solvent (see Table S1 in the Supporting Information). Reactions conducted in polar solvents, such as DMSO, DMF, DMA, and NMP, failed to give the product, and only the reaction in dioxane gave **3a** in 36% yield. Further decreasing the loading of $Pd(OAc)_2$ from 10 mol% to 5 mol% and the use of a catalytic amount of PivOH (0.1 equiv) gave **3a** in a slightly higher yield (Table 2, entry 8).[13] Given that a phosphine-ligand-free Pd^0 species must be generated to facilitate the present reaction, $[Pd_2(dba)_3]$ was investigated to further improve the reaction efficiency. To our delight, the highest product yield (96%) was obtained when the reaction was carried out with $[Pd_2(dba)_3]$ (2.5 mol%) and PivOH (0.1 equiv; Table 2, entry 10). However, the absence of PivOH in the reaction was less effective (Table 2, entry 11), indicating the important role of pivalate for the reaction efficiency. In contrast to $[Pd_2(dba)_3]$, $Pd(PPh_3)_4$ showed no catalytic activity (Table 2, entry 12). Thus, a palladium(0) complex without phosphine ligands is most favorable as the catalyst precursor for this reaction.

This method allowed the direct allylation of pentafluorobenzene **1a** with a variety of allylic chlorides (Table 3). For substrates with an electron-withdrawing group, moderate regioselectivities were observed due to the relatively easier 1,3-hydrogen shift that takes place under basic conditions. Branched allylic chloride is also a suitable substrate and a good product yield and moderate regioselectivity were obtained (Table 3, **3j**). It is noteworthy that versatile functional groups such as ester, nitrile, aldehyde, and chloride are compatible in the reaction, providing a platform for further transfor-

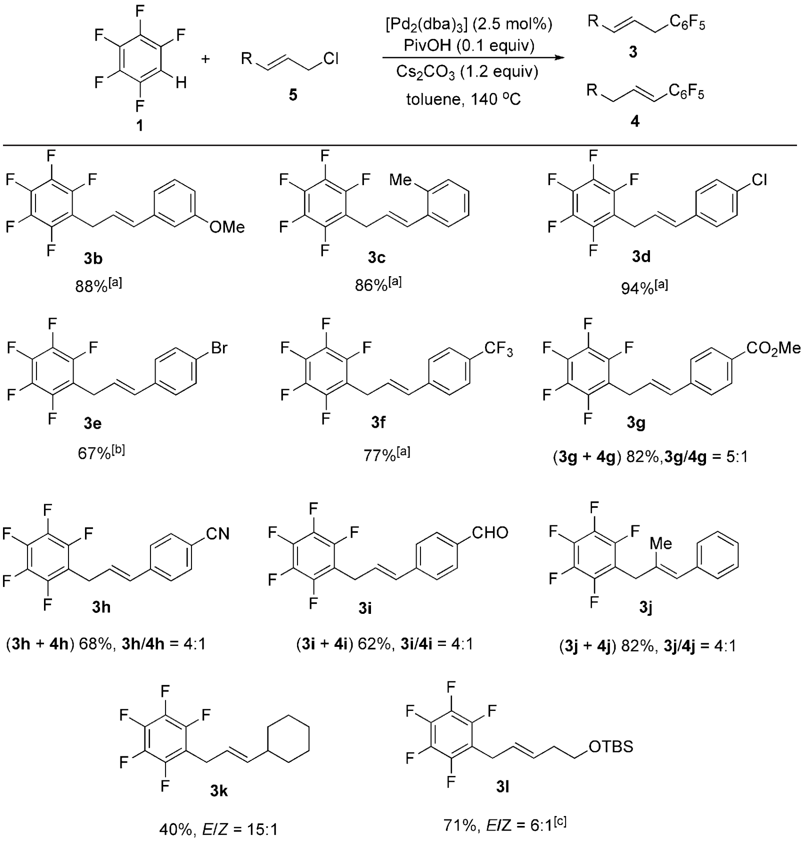
Table 2. Representative results for the optimization of the Pd-catalyzed allylation of pentafluorobenzene (**1**).[a]



	Pd catalyst, [mol%]	Cs_2CO_3 [equiv]	Acid, [equiv]	Yield [%][b]
1	$Pd(OAc)_2$, 10	2.4	CH_3COOH, 1.2	75 (62)
2	$Pd(OAc)_2$, 10	2.4	CF_3COOH, 1.2	28 (25)
3	$Pd(OAc)_2$, 10	2.4	C_2H_5COOH, 1.2	70 (53)
4	$Pd(OAc)_2$, 10	2.4	*t*BuCOOH, 1.2	87 (82)
5	$Pd(OAc)_2$, 10	2.4	AdCOOH, 1.2	79 (68)
6	$Pd(OAc)_2$, 10	2.4	PhCOOH, 1.2	78 (67)
7	$Pd(OAc)_2$, 10	2.4	TsOH, 1.2	62
8	$Pd(OAc)_2$, 5	1.2	*t*BuCOOH, 0.1	90 (85)
9	$Pd(OAc)_2$, 2.5	1.2	*t*BuCOOH, 0.1	62 (57)
10	$[Pd_2(dba)_3]$, 2.5	1.2	*t*BuCOOH, 0.1	(96)
11	$[Pd_2(dba)_3]$, 2.5	1.2	none	(79)
12	$Pd(PPh_3)_4$, 5	1.2	*t*BuCOOH, 0.1	NR

[a] Reaction conditions (unless otherwise specified): **1** (2.0 equiv), **2c** (0.6 mmol), toluene (2.5 mL), 10 h. [b] NMR yield was determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard; number in parenthesis is the isolated yield.

Table 3. Pd-catalyzed allylation of pentafluorobenzene **1** with various allylic chlorides **5**.



3b 88%[a]

3c 86%[a]

3d 94%[a]

3e 67%[b]

3f 77%[a]

3g (**3g** + **4g**) 82%, **3g**/**4g** = 5:1

3h (**3h** + **4h**) 68%, **3h**/**4h** = 4:1

3i (**3i** + **4i**) 62%, **3i**/**4i** = 4:1

3j (**3j** + **4j**) 82%, **3j**/**4j** = 4:1

3k 40%, *E*/*Z* = 15:1

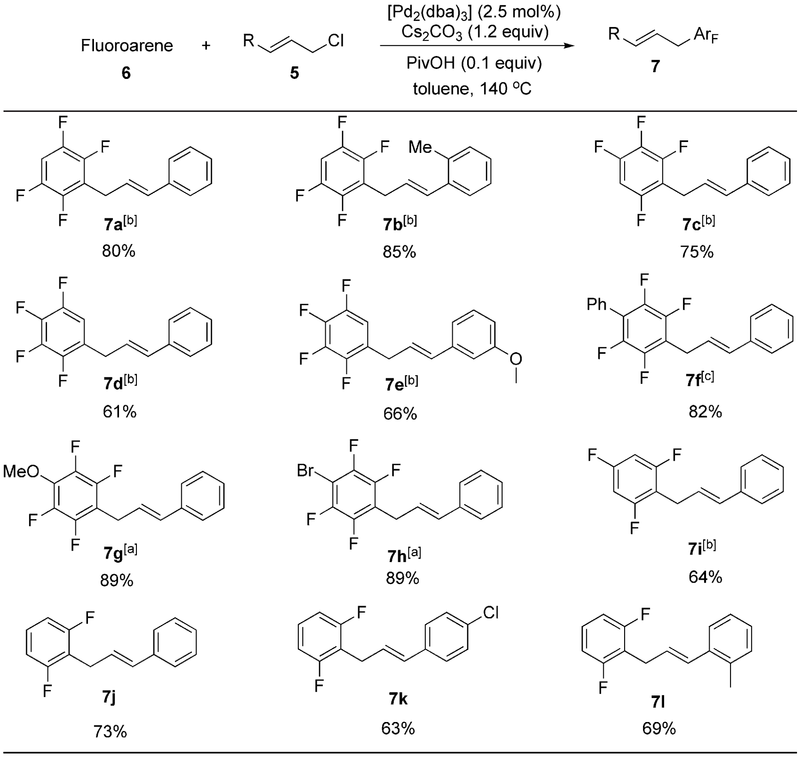
3l 71%, *E*/*Z* = 6:1[c]

Reaction conditions (unless otherwise specified): **1** (2.0 equiv), **5** (0.6 mmol), toluene (2.5 mL), 10 h. All reported reaction yields are isolated yields; all the ratios of isomers were determined by ^{19}F NMR spectroscopy before column chromatography. [a] Ratio of *E*-**3**/other isomers (Z-**3** and/or regioisomer **4**) > 20:1. [b] Ratio of *E*-**3**/other isomers (Z-**3** and/or regioisomer **4**) = 13:1. [c] A 3% yield of the branched product was obtained.

mations without the need for protection/deprotection sequences (Table 3, **3d**, **3g–i**). This is in sharp contrast to previous results[6] and highlights the advantages of the present method. Importantly, even for substrates with a bromide substituent, which is reactive in the presence of a Pd^0-catalyst, a synthetically useful yield was still obtained without the formation of the dipentafluorophenylated side product (Table 3, **3e**). In addition, less-reactive aliphatic allylic chlorides also underwent the reaction smoothly to give products in moderate yields and stereoselectivities (*E*/*Z* from 15:1 to 6:1, Table 3, **3k–l**), and for a linear aliphatic allylic chloride, only a minor branched product was formed (Table 3, **3l**). Thus, these findings suggest that a (π-allyl)-palladium complex is generated during the reaction.

The reactions of the *Z*-allylic chloride **2c′** and *Z*-allylic carbonate **2a′** were also tested. As illustrated in Scheme 1a, the linear *E*-allylated product **3a** was obtained in high stereo- and regioselectivity with no observed formation of the *Z*-allylated isomer. However, for the *Z*-allylic carbonate **2a′**, the desired product was not observed under these optimized reaction conditions. When the reaction was carried out with Pd(OAc)$_2$ (10 mol %) and Cs_2CO_3 (1.2 equiv) in toluene at 140 °C, 48 % of the *E*-allylated product **3a** was obtained with no formation of the *Z*-allylated isomer (Scheme 1b).

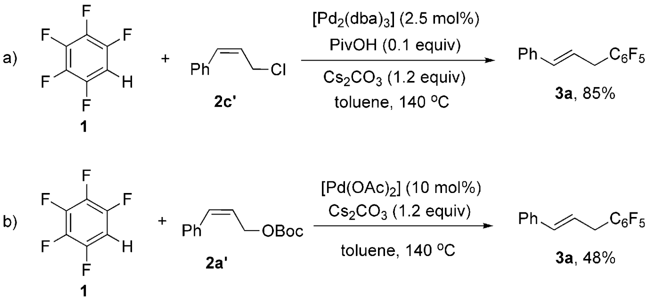
Table 4. Pd-catalyzed allylation of fluoroarene **6** with allylic chlorides **5**.



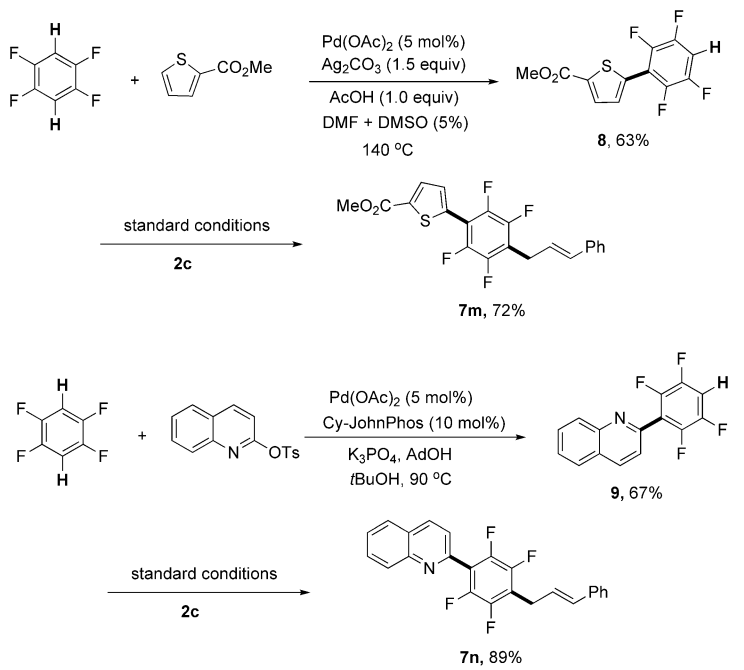
Reaction conditions (unless otherwise specified): **6** (3.0 equiv), **5** (0.6 mmol), toluene (2.0 mL), 10 h. All reported reaction yields are isolated yields; *E*-**7**/other isomers (*Z*-**7** and/or regioisomer) > 20:1, determined by ^{19}F NMR spectroscopy before column chromatography. [a] 2.0 equiv of **6** were used. [b] Minor disubstituded products were also detected by ^{19}F NMR spectroscopy (see the Supporting Information). [c] 1.2 equivalents of **6** were used.

To further ascertain the scope of this methodology, various fluoroarenes **6** containing 2–4 fluorine atoms were tested and representative results are illustrated in Table 4. Substrates containing 3–4 fluorine atoms have more than one reaction site (Table 4, **7a–e**, **7i**) and good yields of the monoallylated products were provided.[14] In particular, even reactions with an 'inert' substrate such as 1,2,3,4-tetrafluorobenzene gave the corresponding products efficiently (Table 4, **7d–e**). It is also noteworthy that 1,3-difluorobenzene, which was previously demonstrated to be an unsuitable substrate,[6] underwent smooth reactions to provide the corresponding products in good yields and high regioselectivities. In this case, the most acidic C–H bond, which is located between the two fluorine atoms, is the primary reaction site (Table 4, **7j–l**). Other useful functional groups, such as chloride and bromide, also tolerated the reaction conditions well (Table 4, **7h**, **7k**). Furthermore, for the reaction of an aryl-substituted fluoroarene, a good yield could be obtained by using only 1.2 equivalents of the fluoroarene (Table 4, **7f**), thus providing an efficient way to use this unusual substrate.

It has been demonstrated that polyfluoroarene–thiophene and -azine (e.g., pyridine, quinoline) structures constitute a distinct class of materials in electronic devices, such as organic light-emitting diodes (OLEDs) and filed-effect transistors (FETs).[7d] To demonstrate the utility of this protocol, two types of allylated polyfluoroarenes that contain a thiophene or quinoline motif were prepared. As shown in Scheme 2, after the selective Pd-catalyzed direct C–H bond heteroarylation of 1,2,4,5-tetrafluorobenzene,[9a,c] the resulting compounds **8** and **9** were directly allylated by using the present strategy to furnish the allylated polyfluoroarene–thiophene and -quinoline structures in a highly efficient manner. This provides a good opportunity for the further application of these highly functionalized structures in electronic devices.

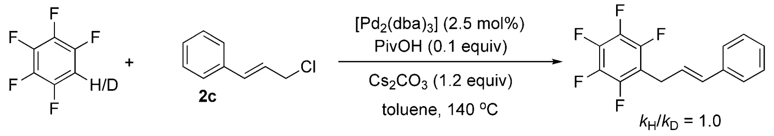


Scheme 1. Pd-catalyzed allylation of pentafluorobenzene (**1**) with linear Z-allylic chloride **2c′** and Z-allylic carbonate **2a′**.

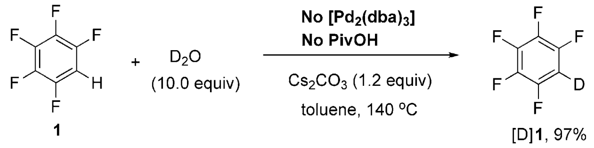


Scheme 2. Synthesis of allylated polyfluoroarene-thiophene and -quinoline structures through sequential C—H bond functionalization. Cy-JohnPhos = 2-(dicyclohexylphosphino)biphenyl, Ad = adamantanyl.

To gain some mechanistic insight into the present reaction, kinetic isotope effect (KIE) and H/D-exchange experiments were performed. The KIE experiments between pentafluorobenzene and its deuterated derivative with **2c** show a primary KIE of 1.0 (Scheme 3), which implies that the C—H bond cleavage of polyfluoroarenes does not proceed by a concerted metalation–deprotonation pathway,[15] because it is not a turnover-limiting step.[16] H/D-exchange experiments revealed that the C—H bonds of polyfluoroarenes can be directly cleaved by the sole use of Cs_2CO_3, thus implying that a polyfluoroarene anion is generated during the reaction (Scheme 4; for details, see the Supporting Information).

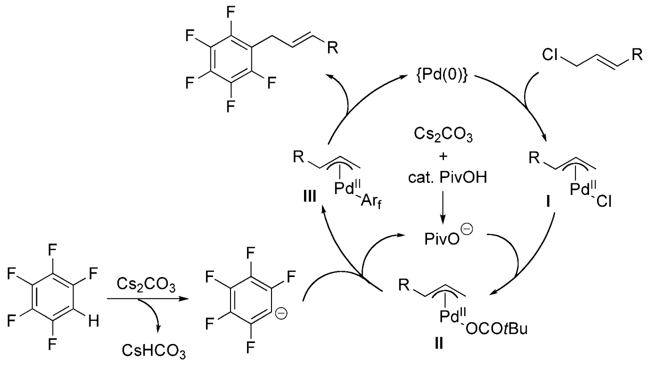


Scheme 3. Kinetic isotope effect study.



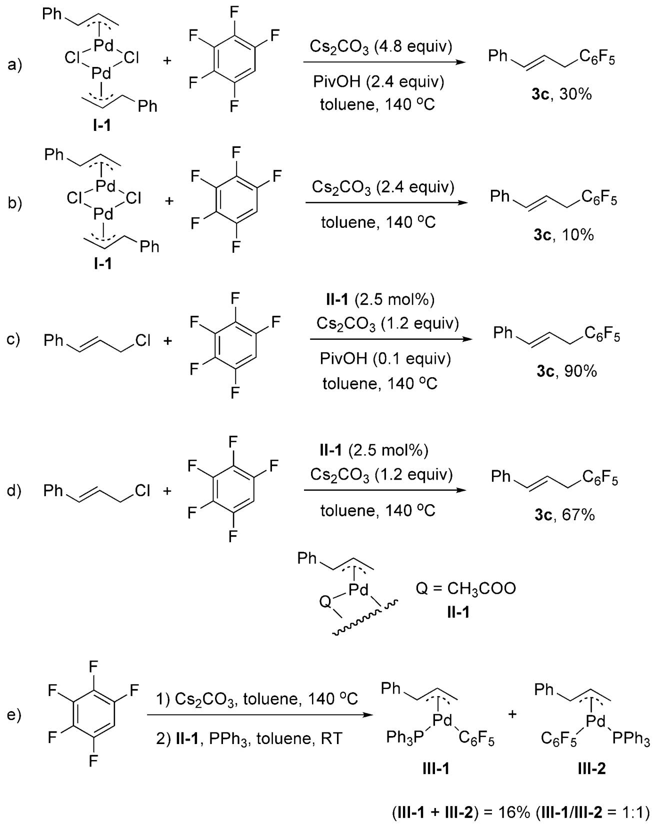
Scheme 4. H/D-exchange experiment on pentafluorobenzene (**1**).

On the basis of these results, and the fact that a phosphine-ligand-free Pd^0 species as well as PivOH is important for the reaction efficiency, we proposed the following mechanism for the Pd-catalyzed direct allylation of polyfluoroarenes with allylic chlorides (Scheme 5). The catalytic cycle begins with the oxidative addition of the allylic chloride to a Pd^0 species to produce the (π-allyl)palladium chloride **I**, which subsequently undergoes chloride and pivalate exchange to give the (π-allyl)palladium pivalate **II**. Intermediate **II** reacts with the polyfluoroarene anion that is generated in situ by the deprotonation of polyfluoroarene with Cs_2CO_3 to afford the key intermediate Pd(polyfluoroaryl)-(allyl)(π-allyl) **III**. Finally, the reductive elimination of **III** provides the allylic polyfluoroarene as the product and regenerates the active catalyst species Pd^0.



Scheme 5. Mechanistic proposal for direct Pd-catalyzed allylation of polyfluoroarenes with allylic chlorides. Ar_f = polyfluoroaryl.

To further probe the reaction mechanism shown in Scheme 5, the following experiments were conducted. Firstly, as a model complex for **I**, compound **I-1** was employed (Scheme 6). When **I-1** was treated with pentafluorobenzene **1** (4.0 equiv) and Cs_2CO_3 (4.8 equiv) in the presence of of PivOH (2.4 equiv), **3a** was produced in 30 % yield (as determined by ^{19}F NMR; Scheme 6a). However, the absence of PivOH led to a lower yield (Scheme 6b), indicating that a more active (π-allyl)palladium pivalate **II** may be generated in the reaction. Accordingly, a simplified dimer of (π-allyl)-palladium acetate **II-1**[17] was then investigated as a model complex for **II** to further understand the reaction mechanism. However, when stoichio-



Scheme 6. Experiments for mechanistic studies. Yields of **3c** were determined by ^{19}F NMR spectroscopy.

metric amounts of complex **II-1** were reacted with pentafluorobenzene in toluene at 140 °C, palladium black was formed immediately, and **3a** was only obtained in 12 and 17 % yield for the reactions with and without PivOH, respectively, as determined by ^{19}F NMR. To avoid the decomposition of the palladium complex **II-1**, a catalytic amount of **II-1** was then used, which provided **3a** in higher yields (Scheme 6c and d). The reactions in which PivOH was present was more efficient than those conducted without PivOH. Hence, on the basis of these findings, the formation of a (π-allyl)palladium pivalate in the reaction is reasonable.

We next turned our attention to the formation of the key intermediate **III**. We supposed that it may be generated by an attack of the polyfluoroarene anion at the palladium center of (π-allyl)palladium pivalate **II**. Thus, a room temperature reaction of **II-1** with the pentafluorophenyl anion that was generated in situ by the deprotonation of pentafluoroarene with Cs_2CO_3 in toluene at 140 °C was performed (Scheme 6e). However, the desired key intermediate **III** was not obtained due to its instability. Different solvents (CH_3CN, DMSO) and phosphine (PPh_3) were then used to trap the intermediate **III**. To our delight, a 16 % yield of a mixture of **III-1** and **III-2** was obtained when PPh_3 was employed. These results demonstrate that the polyfluoroarene anion can be generated by the use of Cs_2CO_3 alone under the present reaction conditions, and that the catalytic cycle illustrated in Scheme 5, which involves attack at the (π-allyl)palladium carboxylate complex by a polyfluoroarene anion that is generated in situ is reasonable. This is different from previous studies, and provides a complementary approach to the traditional techniques.

In conclusion, a copper- and phosphine-ligand-free [$Pd_2(dba)_3$]-catalyzed method for the direct allylation of electron-deficient polyfluoroarenes with allylic chlorides has been developed. The PivOH additive plays an important role in the reaction efficiency. Because of the high reaction efficiency, simple catalytic system, broad substrate scope that encompasses even 'inert' fluoroarenes, and the excellent functional group compatibility, this protocol provides a useful and facile access to allylated polyfluoroarenes that are of interest in the fields of both life and materials science. In particular, the successful synthesis of allylated polyfluoroarene–heteroarene structures by a highly efficient sequential C–H functionalization highlights the potential of this cross-coupling for further development and applications.

Experimental Section

General procedure: [$Pd_2(dba)_3$] (2.5 mol %) and Cs_2CO_3 (1.2 equiv) were added to a septum-capped sealed tube (25 mL) under N_2, followed by the addition of toluene (2.5 mL) with stirring. Polyfluoroarene (1.2 mmol, 2.0 equiv), allyl chloride (0.6 mmol, 1 equiv), and PivOH (0.06 mmol, 0.1 equiv) were then added. The sealed tube was screw-capped and heated at 140 °C in an oil bath. After stirring for 10 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography to provide the pure product.

Acknowledgements

The NSFC (No. 21172242, 20902100, and 20832008), the National Basic Research Program of China (973 Program) (No. 2012CB821600), and SIOC are greatly acknowledged for funding this work.

Keywords: allylic compounds · C–H activation · palladium · pivalic acid · polyfluoroarenes · synthetic methods

---

[1] a) *Naturally Occurring Carcinogens of Plant Origin*, (Ed.: I. Hirono), Kodansha, Tokyo, **1987**; b) T. Eicher, S. Hauptmann, *The Chemistry of Heterocycles*, Wiley-VCH, Weinheim, **2003**; for recent papers, see: c) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **2000**, *122*, 11262–11263; d) B. M. Trost, O. R. Thiel, H.-C. Tsui, *J. Am. Chem. Soc.* **2002**, *124*, 11616–11617; e) F. Del Bello, L. Mattioli, F. Ghelfi, M. Giannella, A. Piergentili, W. Quagila, C. Cardinaletti, M. Perfumin, R. J. Thomas, U. Zanelli, C. Marchioro, M. D. Cin, M. Pigini, *J. Med. Chem.* **2010**, *53*, 7825–7835; f) Z. Jin, *Nat. Prod. Rep.* **2011**, *28*, 1143.

[2] a) *Comprehensive Organic Functional Group Transformations*, (Eds.: A. R. Katritzky, O. Meth-Cohn, C. W. Rees); Elsevier, New York, **1995**; b) *Comprehensive Asymmetric Catalysis*, (Eds.: E. N. Jacobsen, A. Pfaltz, H.Yamamoto), Springer: New York, **1999**; c) *The Chemistry of Functional Groups: Supplement A3: The Chemistry of Double-Bonded Functional Groups*; (Ed.: S. Patai), , Wiley, New York, **1997**.

[3] For the allylation of aryl copper compounds, see: a) G. H. Posner, *Org. React.* **1975**, *22*, 253–400; b) N. Harrington-Frost, H. Leuser, M. I. Calaza, F. F. Kneisel, P. Knochel, *Org. Lett.* **2003**, *5*, 2111–2114; c) Y. Kiyotsuka, H. P. Acharya, Y. Katayama, T. Hyodo, Y. Kobayashi, *Org. Lett.* **2008**, *10*, 1719–1722; for the allylation of arylmagnesium halides, see: d) T. Hayashi, M. Konishi, K. Yokota, M. Kumada, *J. Chem. Soc. Chem. Commun.* **1981**, 313–314; e) T. Hayashi, M. Konishi, M. Kumada, *J. Chem. Soc. Chem. Commun.* **1984**, 107–108; for the allylation of aryl borons, see: f) F. C. Pigge, *Synthesis* **2010**, 1745–1762; g) N. Miyaura, K. Yamada, H. Suginome, A. Suzuki, *J. Am. Chem. Soc.* **1985**, *107*, 972–980; h) T. Nishikata, B. H. Lipshutz, *J. Am. Chem. Soc.* **2009**, *131*, 12103–12105; i) H. Ohmiya, Y. Makida, D. Li, M. Tanabe, M. Sawamura, *J. Am. Chem. Soc.* **2010**, *132*, 879–889.

[4] a) G. A. Olah in *Friedel–Crafts and Related Reactions, Vol. II*, Wiley, New York, **1964**; b) G. A. Olah in *Friedel–Crafts Chemistry*, Wiley, New York, **1973**; c) R. M. Roberts, A. A. Khalaf in *Friedel–Crafts Alkylation Chemistry: A Century of Discovery*, Marcel Dekker, New York, **1984**; for the Lewis acid catalyzed direct C−H allylation of electron-rich arenes, see: d) M. Kodomari, S. Nawa, T. Miyoshi, *J. Chem. Soc. Chem. Commun.* **1995**, 1895–1896; e) R. Hayashi, G. R. Cook, *Org. Lett.* **2007**, *9*, 1311–1314; only one example of Lewis acid catalyzed direct intramolecular C−H allylation of moderate electron-deficient arenes has been reported, see: f) M. Bandini, M. Tragni, A. Umani-Ronchi, *Adv. Synth. Catal.* **2009**, *351*, 2521–2524.

[5] For recent reviews related to C−H bond activation, see: a) L.-C. Campeau, K. Fagnou, *Chem. Commun.* **2006**, 1253–1264; b) O. Daugulis, V. G. Zaitzev, D. Shabashov, Q.-N. Pham, A. Lazareva, *Synlett* **2006**, 3382–3388; c) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174–238; d) R. Giri, B. F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242–3272; e) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976–10011; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792–9826; f) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655; g) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147–1169; h) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212–11222; i) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, *46*, 677–685; j) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215–1292; k) W. Han, A. R. Ofial, *Synlett* **2011**, *14*, 1951–1955.

[6] a) T. Yao, K. Hirano, T. Satoh, M. Miura, *Angew. Chem.* **2011**, *123*, 3046–3050; *Angew. Chem. Int. Ed.* **2011**, *50*, 2990–2994; b) S. Fan, F. Chen, X. Zhang, *Angew. Chem.* **2011**, *123*, 6040–6045; *Angew. Chem. Int. Ed.* **2011**, *50*, 5918–5923; c) Y. Makida, H. Ohmiya, M. Sawamura, *Angew. Chem.* **2012**, *124*, 4198–4203; *Angew. Chem. Int. Ed.* **2012**, *51*, 4122–4127.

[7] For recent reviews, see: a) E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem.* **2003**, *115*, 1244–1287; *Angew. Chem. Int. Ed.* **2003**, *42*, 1210–1250; b) K. Muller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; c) A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066–1096; d) F. Babudri, G. M. Farinola, F. Naso, R. Ragni, *Chem. Commun.* **2007**, 1003–1022; e) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330; f) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119–2183.

[8] For the transition-metal-catalyzed C−H functionalization of polyfluoroarenes, see: arylation: a) M. Lafrance, C. N. Rowley, T. K. Woo, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 8754–8756; b) H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 1128–1129; c) Y. Wei, W. Su, *J. Am. Chem. Soc.* **2010**, *132*, 16377–16379; d) H. Li, J. Liu, C.-L. Sun, B.-J. Li, Z.-J. Shi, *Org. Lett.* **2011**, *13*, 276; alkenylation and alkylation: e) Y. Nakao, N. Kashihara, K. S. Kanyiva, T. Hiyama, *J. Am. Chem. Soc.* **2008**, *130*, 16170; f) Z.-M. Sun, J. Zhang, R. S. Manan, P. Zhao, *J. Am. Chem. Soc.* **2010**, *132*, 6935; alkynylation: g) Y. Wei, H. Zhao, J. Kan, W. Su, M. Hong, *J. Am. Chem. Soc.* **2010**, *132*, 2522.

[9] For our contributions to the transition-metal-catalyzed C−H functionalization of polyfluoroarenes, see: a) C.-Y. He, S. Fan, X. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 12850–12852; b) X. Zhang, S. Fan, C.-Y. He, X. Wan, Q.-Q. Min, J. Yang, Z.-X. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 4506–4507; c) S. Fan, J. Yang, X. Zhang, *Org. Lett.* **2011**, *13*, 4374–4377; d) F. Chen, Z. Feng, C.-Y. He, H.-Y. Wang, Y.-l. Guo, X. Zhang, *Org. Lett.* **2012**, *14*, 1176–1179 and 6b.

[10] For studies related to polyfluoroarene chemistry, see: a) E. Clot, C. Mégret, O. Eisenstein, R. N. Perutz, *J. Am. Chem. Soc.* **2009**, *131*, 7817–7827; b) M. E. Evans, C. L. Burke, S. Yaibuathes, E. Clot, O. Eisenstein, W. D. Jones, *J. Am. Chem. Soc.* **2009**, *131*, 13464–13473; c) E. Clot, M. Besora, F. Maseras, C. Mégret, O. Eisenstein, B. Oelckers, R. N. Perutz, *Chem. Commun.* **2003**, 490–491.

[11] a) J. Tsuji, *Acc. Chem. Res.* **1969**, *2*, 144–152; b) B. M. Trost, *Tetrahedron* **1977**, *33*, 2615–2649; c) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395–422; d) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921–2943.

[12] M. Lafrance, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 16496–16497.

[13] The use of excess Cs_2CO_3 and PivOH does not improve the reaction efficiency, see the Supporting Information for details.

[14] Minor disubstituted allylic products were also observed, see the Supporting Information for details.

[15] For a review, see: a) D. Lapointe, K. Fagnou, *Chem. Lett.* **2010**, *39*, 1118–1126; for other examples, see: b) J. J. González, N. García, B. Gómez-Lor, A. M. Echavarren, *J. Org. Chem.* **1997**, *62*, 1286–1291; c) D. García-Cuadrado, A. A. C. Braga, F. Maseras, A. M. Echavarren, *J. Am. Chem. Soc.* **2006**, *128*, 1066–1067; d) D. García-Cuadrado, P. De Mendoza, A. A. C. Braga, F. Maseras, A. M. Echavarren, *J. Am. Chem. Soc.* **2007**, *129*, 6880–6886.

[16] E. M. Simmons, J. F. Hartwig, *Angew. Chem.* **2012**, *124*, 3120–3126; *Angew. Chem. Int. Ed.* **2012**, *51*, 3066–3072.

[17] The (π-allyl)palladium acetate **II-1** was prepared according to the literature, see: S. D. Robinson, B. L. Shaw, *J. Organomet. Chem.* **1965**, *3*, 367.

Received: August 6, 2012
Revised: September 15, 2012

Please note: Minor changes have been made to this manuscript since its publication in *Chemistry—A European Journal* Early View. The Editor.