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Palladium-Catalyzed Aerobic Dehydrogenative Cross-Coupling of Polyfluoroarenes with Thiophenes: Facile Access to Polyfluoroarene−Thiophene Structure

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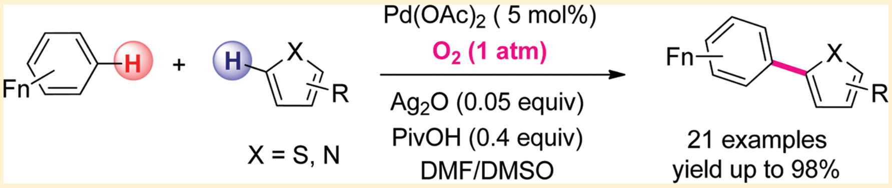
S *Supporting Information*



ABSTRACT: We report a Pd-catalyzed aerobic dehydrogenative cross-coupling of polyfluoroarenes with thiophenes via 2-fold C−H functionalization. The advantages of this reaction are its high reaction efficiency, excellent functional group compatibility, and use of molecular O_2 as terminal oxidant. This reaction provides a useful and facile protocol for the preparation of polyfluoroarene−thiophene structure of interest in functional materials. Mechanistic studies revealed that the reaction is initiated by the C−H bond cleavage of polyfluoroarenes.

■ INTRODUCTION

The formation of aryl−aryl bonds is an important and fundamental transformation in organic synthesis since the biaryl structural motif is found in many natural products, pharmaceuticals, agrochemicals, and functional materials.[1] The most common method used to prepare biaryls relies on transition-metal-catalyzed cross-coupling of aryl halides with aryl metals.[2] These reactions are extremely useful and are one of the most reliable synthetic methods. However, this "prefunctionalization" process suffers from an intrinsic limitation in terms of atom and step economy. In recent years, the direct C−H arylation in which the C−H bond is used as a functional group has attracted considerable attention.[3] In particular, the carbon−carbon bond formation obtained via 2-fold C−H bond functionalization (i.e., the dehydrogenative cross-coupling approach) is the ideal strategy from the point of view of synthetic simplicity.[4−8] But such methods face great challenges, including the difficulties in controlling the selectivity of the two C−H activation steps and in suppressing undesired homocoupling of the substrates and identification of an atom-economical oxidant for the reaction. In view of the fact that the majority of Pd-catalyzed methods for dehydrogenative cross-coupling between two different arenes require stoichiometric transition-metal oxidants, such as Cu(II) salt or Ag(I) salt,[6] which decrease their atom economy, new catalytic systems to overcome this intrinsic limitation for widespread synthetic application are highly desirable.

On the other hand, molecules containing polyfluoroarene−thiophene structure play a primary role as active materials in electronic devices, such as organic light-emitting diodes (OLEDs) and field-effect transistors (FETs).[9,10] Hence, it is of great synthetic interest to develop efficient reactions to access them. Very recently, we successfully developed an efficient method for the synthesis of polyfluoroarene−thiophene structure through Pd-catalyzed dehydrogenative cross-coupling of polyfluoroarenes with thiophenes.[11a] One drawback of this reaction is the use of excess Ag_2CO_3 as oxidant. In view of the importance of polyfluoroarene−thiophene structure in the functional materials, the use of molecular O_2 as oxidant is appealing,[12] because only water is produced as a byproduct in this Pd-catalyzed overall process. However, replacement of stoichiometric transition-metal oxidants with O_2 represents a significant fundamental challenge that has important implications for practical applications of these methods.[12] To the best of our knowledge, only limited success has been achieved thus far.[7] Herein, we describe a convenient method for the Pd-catalyzed aerobic dehydrogenative cross-coupling of polyfluoroarenes with thiophenes,[13] which provides a concise and useful protocol for the preparation of polyfluoroarene−thiophene structures of interest in functional materials (Scheme 1).

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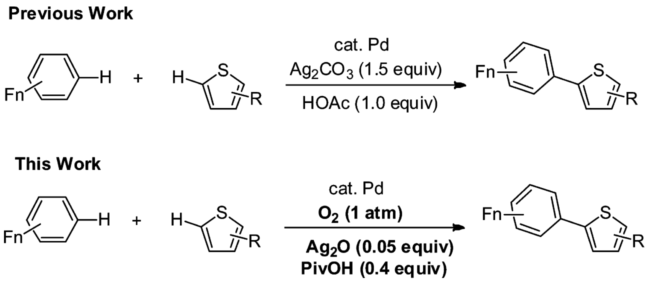
Scheme 1. Pd-Catalyzed Dehydrogenative Cross-Coupling of Polyfluoroarenes with Thiophenes

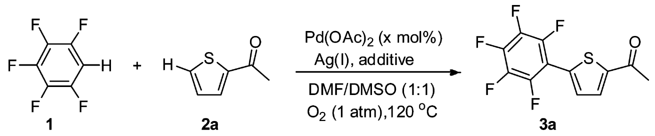


RESULTS AND DISCUSSION

Initially, the dehydrogenative cross-coupling of pentafluorobenzene (**1**) with 1-(thiophen-2-yl)ethanone (**2a**) was investigated in the presence of $Pd(OAc)_2$ (10 mol %) and a catalytic amount of Ag_2CO_3 (0.1 equiv) in anhydrous DMSO[14] under 1 atm O_2 at 120 °C (Table 1, entry 1). Fortunately, this reaction provided 56% NMR yield of **3a** without observation of decomposed thiophene substrate. Further switching DMSO with a mixed solvent system of DMSO/DMF (1:1) was found to benefit the reaction (Table 1, entry 2). Encouraged by this result, a survey of silver salts and additive was conducted (Table 1, entries 3−12). We found that Ag_2O is the best choice, and 0.4 equiv of pivalic acid (PivOH)[15] is also beneficial to the reaction, while the absence of either Ag_2O or O_2 failed to provide the desried product (Table 1, entries 15, 16), thus demonstrating that silver salt and O_2 play pivotal roles in the catalytic cycle. However, the possibility that silver salt could also serve as a base cannot be ruled out. The replacement of Ag_2O with other bases, such as K_2CO_3 and K_3PO_4, could also furnish **2a**, albeit in low yields (Table 1, entries 17, 18). The absence of Pd-catalyst did not give any desired product (Table 1, entry 14), thus indicating that Pd-catalyst was involved in the catalytic cycle. The reaction concentration also had a critical impact on the reaction efficiency. The best yield of isolated product (81%) can be obtained by increasing the reaction concentration with utilization of only 5 mol % of $Pd(OAc)_2$, 0.05 equiv of Ag_2O, and 0.4 equiv of pivalic acid (PivOH) (Table 1, entry 13).

A variety of pentafluorophenyl-substituted thiophenes were generated by the present method, and good to high yields were obtained (Table 2). Importantly, substrates bearing functional groups, such as ester, amide, methyl ketone, aldehyde, chloride, and nitro, all showed good tolerance to the reaction conditions. Although for chloride-substituted thiophene **3e**, a slightly lower yield (60%) was obtained compared to previous work (65% yield),[11a] the homocoupling of 2-chlorothiophene was suppressed, thus making the purification process easier (Table 2, **3e**). It should be pointed out that the access to **3g** is more efficient and can afford 10% higher yield through the present strategy than using excessive silver salts as oxidant, thus providing a facile protocol to prepare symmetrical bis-pentafluorophenyl-substituted thiophene structures[10,16] (Table 2, **3g**). 2-Aryl-substituted thiophenes are also suitable substrates for the reaction, and the nature of the substituents on the aromatic ring does not influence the reaction efficiency (Table 2, **3h**−**3j**). In addition, benzo[*b*]thiophene and indole are also suitable substrates for the reaction (Table 2, **3k** and **3l**). However, for the benzofuran, a complex was obtained (Table 2,

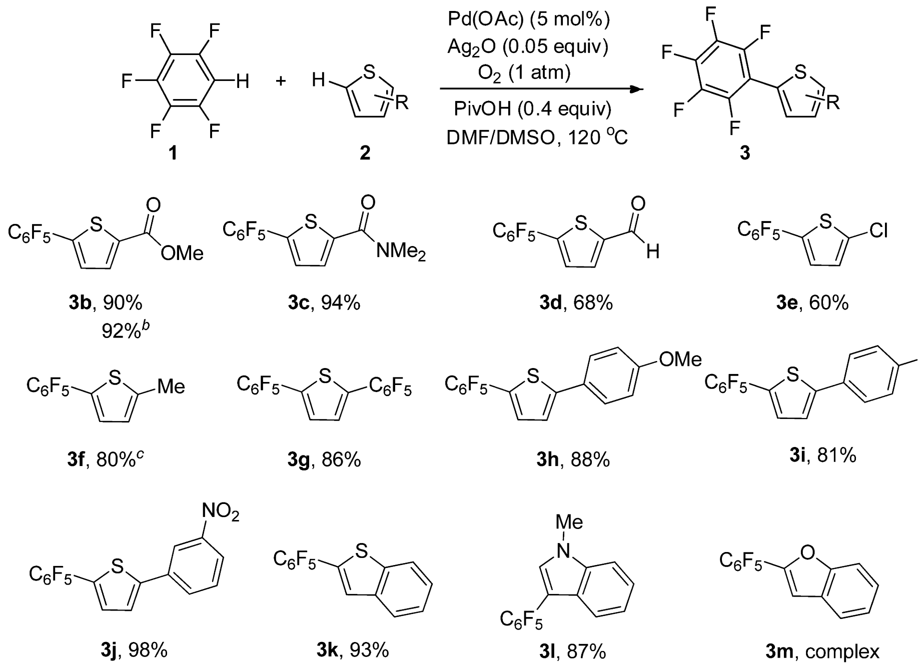
Table 1. Optimization of Aerobic Dehydrogenative Cross-Coupling of Pentafluorobenzene (1) with 1-(Thiophen-2-yl)ethanone (2a)[a]



entry	*x* (mol %)	Ag(I) (equiv)	additive (equiv)	yield (%)[b]
1[c]	10	Ag_2CO_3 (0.1)		56
2	10	Ag_2CO_3 (0.1)		67
3	10	AgOAc (0.2)		69
4	10	AgF (0.2)		61
5	10	Ag_2O (0.1)		80 (72)
6	10	Ag_2O (0.1)	PivOH (0.1)	80
7	10	Ag_2O (0.1)	AdOH (0.1)	71
8	10	Ag_2O (0.1)	PivOH (0.2)	81
9	10	Ag_2O (0.1)	PivOH (0.4)	85 (76)
10	10	Ag_2O (0.1)	PivOH (0.6)	80
11	5	Ag_2O (0.1)	PivOH (0.4)	70 (67)
12	5	Ag_2O (0.05)	PivOH (0.4)	74 (69)
13[d]	**5**	**Ag_2O (0.05)**	**PivOH (0.4)**	**88 (81)**
14[d]		Ag_2O (0.05)	PivOH (0.4)	N.D.
15[d]	5		PivOH (0.4)	trace
16[d,e]	5	Ag_2O (0.05)	PivOH (0.4)	trace
17[d]	5	Cs_2CO_3 (0.05)	PivOH (0.4)	29
18[d]	5	K_3PO_4 (0.05)	PivOH (0.4)	29

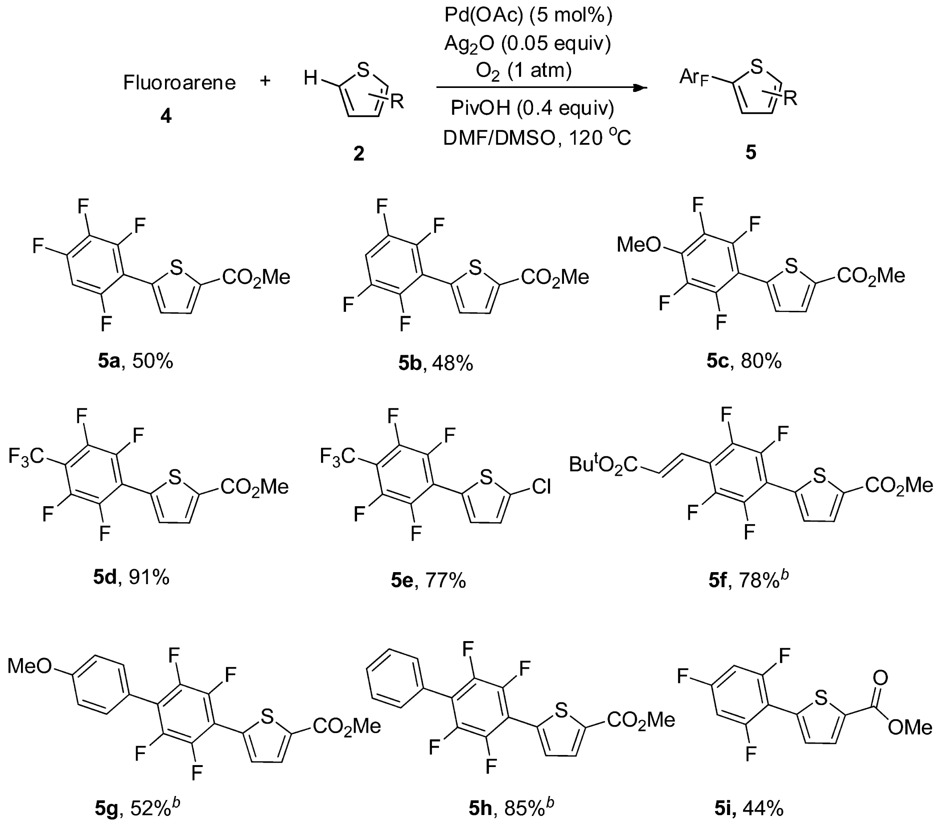
[a] Reaction conditions (unless otherwise specified): **1** (3.0 equiv), **2a** (0.3 mmol), DMF/DMSO (v/v = 1:1, 2 mL, DMSO must be stored with the powder of 4 Å molecular sieves), O_2 (1 atm), 120 °C, 9 h. [b] Yield determined by ^{19}F NMR spectroscopy using fluorobenzene as the internal standard, and the yield of the isolated product is in parentheses. [c] DMSO (2 mL) was used as solvent. [d] DMF/DMSO (v/v = 1:1, 1 mL) were used as solvent. [e] Reaction run in the absence of O_2.

Table 2. Aerobic Dehydrogenative Cross-Coupling of Pentafluorobenzene (1) with Heteroarenes 2[a]



[a]Reaction conditions (unless otherwise specified): **1** (3.0 equiv), **2** (0.3 mmol), DMF/DMSO (v/v = 1:1, 1 mL), 120 °C, 9 h. All reported yields are isolated yields. [b]Reaction run in 2 mmol scale. [c]Reaction run at 140 °C.

Table 3. Aerobic Dehydrogenative Cross-Coupling of Fluoroarenes 4 with Thiophenes 2[a]

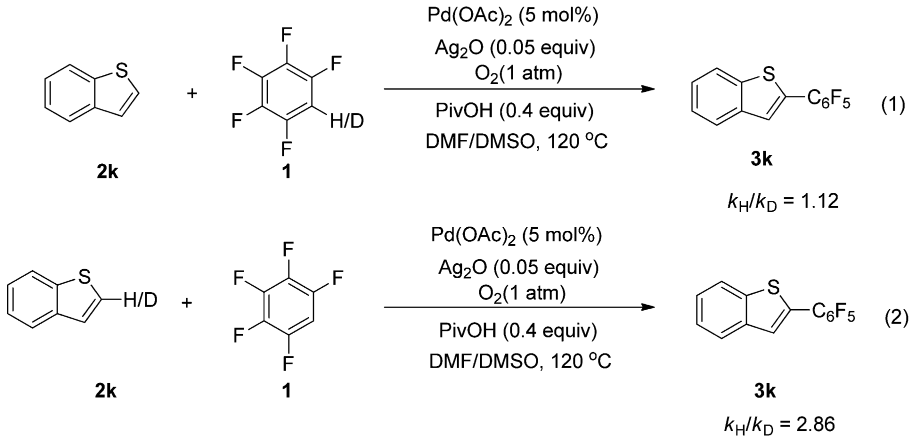


[a]Reaction conditions (unless otherwise specified): **4** (3.0 equiv), **2** (0.3 mmol), DMF/DMSO (v/v = 1:1, 1 mL), 120 °C, 9 h. All reported yields are isolated yields. [b]**4** (0.3 mmol, 1.0 equiv) and **2** (2.0 equiv).

3m). The usefulness of this method can also be featured by rapid access of **3b** (92%) in a 2 mmol scale synthesis, thus indicating the good reliability of the process (Table 2, **3b**).

To further probe the applicability of this catalytic system, couplings of various fluoroarenes **4** bearing three or four fluorines with thiophenes were also tested (Table 3). To our

Scheme 2. Kinetic Isotope Effect Studies



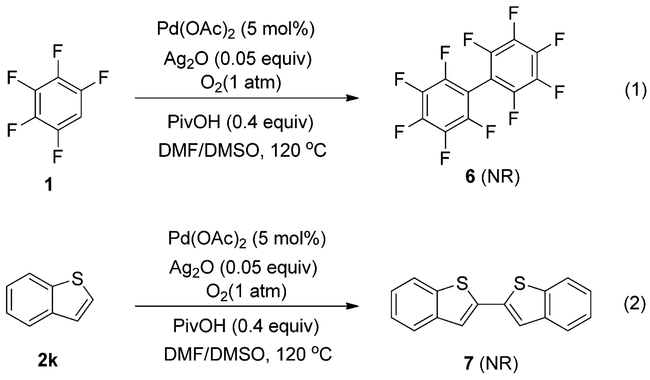
delight, comparable yields of compounds **5a** and **5b** were provided at 120 °C with use of 3.0 equiv of fluoroarenes, while 140 °C and 5.0 equiv of fluoroarenes were required under our previous reaction conditions (Pd(OAc)$_2$ (5 mol %), Ag$_2$CO$_3$ (1.5 equiv), and HOAc (1.0 equiv) in DMF + DMSO (5%))[11a] (Table 3, **5a** and **5b**). Furthermore, higher yields of **5c** and **5i** could also be obtained (Table 3, **5c** and **5i**), which demonstrated high reaction efficiency of this catalytic system, by using an inexpensive and environmentally benign oxidant (O$_2$). Another fluoroarene, 1,2,4,5-tetrafluoro-3-(trifluoromethyl)benzene, is also a good coupling partner under the present reaction conditions; thus good yields are obtained as well (Table 3, **5d** and **5e**). It should be mentioned that for the vinyl- and aryl-substituted fluoroarenes (Table 3, **5f**−**5h**), the use of 1.0 equiv of fluoroarene still can provide moderate to good yields, thus providing an efficient way for using these unusual substrates.[17]

To investigate the working mode of the present catalytic system, kinetic isotope effect (KIE) experiments for both coupling partners were conducted (Scheme 2). An intermolecular competition reaction between pentafluorobenzene and its deuterated derivative does not exhibit a kinetic isotope effect (k_H/k_D = 1.12) (Scheme 2, eq 1), which implies that the C−H bond cleavage of polyfluoroarenes is not involved in a rate-determining step. However, a primary KIE of 2.86 was observed by coupling of pentafluorobenzene (**1**) with **2k**/*d*-**2k**, indicating that the C−H bond cleavage of benzo[*b*]thiophene (**2k**) is the rate-determining step in the overall catalytic process. This finding further implied that the C−H bond cleavage of thiophenes may proceed via a concerted metalation−deprotonation pathway,[18] as the typical electrophilic aromatic substitution pathway does not involve C−H cleavage in the rate-determining step.[19]

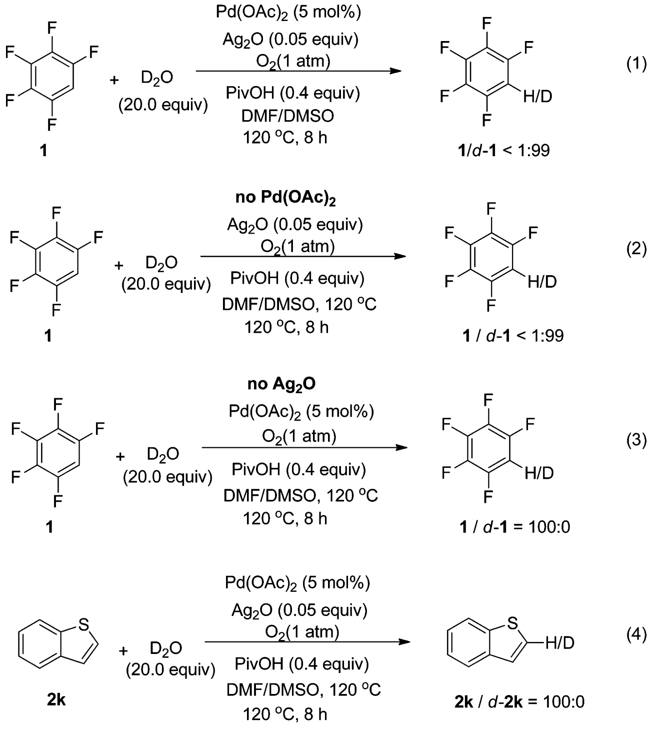
Further experiments by comparison of the homocoupling reactions of **1** and **2k** revealed that both pentafluorobenzene (**1**) and benzo[*b*]thiophene (**2k**) failed to afford homocouplings (Scheme 3). These findings indicate that the formation of homocouplings can be suppressed under the optimized reaction conditions; thus only desired cross-couplings were obtained.

To further understand the selectivity of the cross-coupling, the following H/D exchange experiments were conducted (Scheme 4). When pentafluorobenzene (**1**) was treated with D$_2$O under optimized conditions, almost a quantitative yield of deuterated *d*-**1** was observed (determined by ^{19}F NMR, Scheme

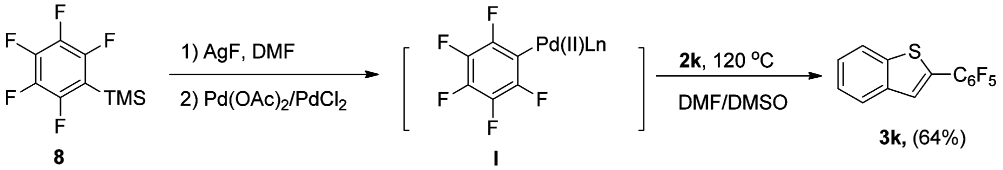
Scheme 3. Homocouplings of Pentafluorobenzene (1) and Benzo[*b*]thiophene (2k)



Scheme 4. H/D Exchange Experiments of Pentafluorobenzene (1) and Benzo[*b*]thiophene (2k)



Scheme 5. Experiment for Mechanistic Study

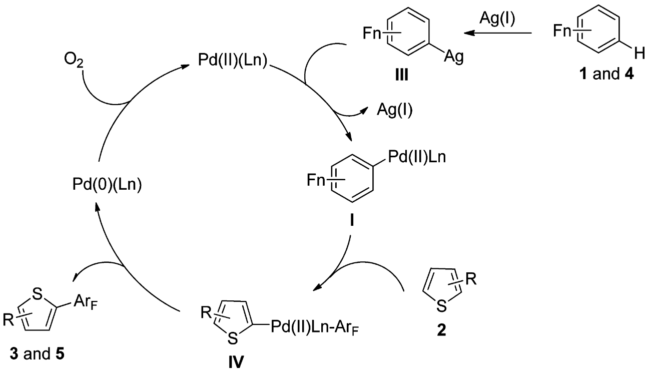


4, eq 1). The absence of $Pd(OAc)_2$ led to a comparable yield as well (determined by ^{19}F NMR, Scheme 4, eq 2). However, no deuterated *d*-**1** was detected, when the reaction was performed without Ag_2O (Scheme 4, eq 3). These results indicated that the present cross-coupling initiated from polyfluoroarene is reasonable, and the silver salt may serve as a base for deprotonation of highly acidic polyfluoroarene, which is consistent with our previous results (Table 1, entries 15, 17, 18). The H/D exchange experiment of **2k** did not afford deuterated *d*-**2k** (Scheme 4, eq 4); thus the possibility that the reaction starts from thiophenes can be ruled out. This finding further indicated that an electrophilic attack of Pd(II) on the thiophenes is not involved in the reaction.

To further confirm that the reaction is initiated from polyfluoroarene, a reaction of Pd(pentafluorophenyl) complex **I** with **2k** was conducted, providing **3k** in 64% yield (Scheme 4 eq 1). Hence, the present cross-coupling that starts from polyfluoroarene is reasonable. Intermediate **I** was prepared in two steps by desilylation of compound **8** with AgF in DMF,[20] followed by metal exchange with Pd(II). The formation of intermediate **I** was further confirmed by ESI-MS analysis.[21]

On the basis of the preliminary studies, we proposed the following mechanism for the dehydrogenative cross-coupling of polyfluoroarenes with thiophenes (Scheme 6). The reaction is initiated by the deprotonation of polyfluoroarene with silver salts to give intermediate **III**, which then reacts with Pd(II)Ln by metal exchange to generate Pd(polyfluoroaryl) complex **I**. **I** subsequently goes through the concerted metalation−deprotonation to form **IV**. Finally, reductive elimination and reoxidation by O_2 regenerates Pd(II)Ln.[12]

Scheme 6. Mechanistic Proposal for Pd-Catalyzed Aerobic Dehydrogenative Cross-Coupling of Polyfluoroarenes with Thiophenes



CONCLUSIONS

In conclusion, we have developed a straightforward method for Pd-catalyzed aerobic dehydrogenative cross-coupling of polyfluoroarenes with thiophenes via 2-fold C−H functionalization. The reaction makes use of molecular O_2 as terminal oxidant and affords high yields and excellent functional group compatibillity. Hence, it is a useful and facile protocol for the preparation of polyfluoroarene−thiophene structure. The mechanistic studies revealed that this tandem oxidation of C−H bonds is initiated by the C−H cleavage of polyfluoroarenes.

EXPERIMENTAL SECTION

General Procedure for Pd-Catalyzed Aerobic Dehydrogenative Cross-Coupling of Polyfluoroarenes with Thiophenes 2. To a septum-capped 25 mL sealed tube were added $Pd(OAc)_2$ (5 mol %) and Ag_2O (3.5 mg, 0.015 mmol, 0.05 equiv). After the sealed tube was refilled with O_2 three times, DMSO (0.5 mL), DMF (0.5 mL), and PivOH (15 μL, 0.12 mmol, 0.4 equiv) were added with stirring. Polyfluoroarene (0.9 mmol, 3.0 equiv) and thiophene **2** (0.3 mmol 1.0 equiv) were then added. The sealed tube was screw capped and heated to 120 °C (oil bath). After stirring for 9 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified with silica gel chromatography to provide pure product.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) DMSO must be stored with the powder of 4 Å molecular sieves.

(15) There might be two roles for the PivOH in the reaction. One is to function as a pivalato ligand and assist deprotonation at a transition state; see: Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315. The other is to suppress undesired homocoupling in Pd-catalyzed oxidative cross-coupling reactions; for details, see: Yang, S.; Sun, C.; Fang, Z.; Li, B.; Li, Y.; Shi, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 1473, and references therein.

(16) For preparation of **3g** using traditional techniques, see: (a) Takimiya, K.; Niihara, N.; Otsubo, T. *Synthesis* **2005**, 1589. (b) Crouch, D. J.; Skabara, P. J.; Heeney, M.; McCulloch, I.; Coles, S. J.; Hursthouse, M. B. *Chem. Commun.* **2005**, 1465. (c) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900.

(17) For the preparation of vinyl group substituted fluoroarene (Table 3, **5f**), see ref 11b; for the preparation of aryl group substituted fluoroarene (Table 3, **5g**, **5h**), see: Rene, O.; Fagnou, K. *Org. Lett.* **2010**, *12*, 2116.

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(21) For the ESI-MS analysis of intermediate I, see the Supporting Information.