Ligand-free Palladium/Copper Co-catalyzed Direct Arylation of Polyfluoroarenes with Aryl Iodides

Xinyan Zhang[a], Jian Yu[b] and Guobing Yan[b]

[a] Lishui Vocational & Technical College, Lishui, 323000, P. R. China
[b] Department of Chemistry, Lishui University, Lishui 323000, P. R. China

Reprint requests to Prof. Guobing Yan. Fax: +86 578 2271250. E-mail: gbyan@lsu.edu.cn or Dr. Jian Yu. E-mail: livelyfish@lsu.edu.cn

Z. Naturforsch. **2013**, *68b*, 885 – 890 / DOI: 10.5560/ZNB.2013-3105
Received April 5, 2013

New reaction conditions for the direct arylation of polyfluoroarenes with aryl iodides have been developed. This reaction can be co-catalyzed by palladium/copper without ligands and exhibits excellent functional group compatibility.

Key words: C–H Activation, Arylation, Polyfluoroarenes

Introduction

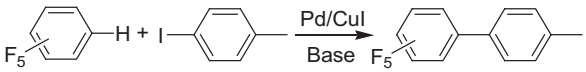
Polyfluorobiphenyl structural motifs have found wide applications in medicinal chemistry and material science [1, 2]. Hence, it is of great interest to develop efficient reactions for their synthesis. The most common method for their preparation relies on transition metal-catalyzed cross-coupling of aryl halides with aryl metals [3 – 5]. However, this "preactivation" process of coupling partners (preparations of aryl halides and organometallic reagents) suffers from intrinsic drawbacks in terms of atom and step economy. Recently, transition metal-catalyzed direct arylation of aromatic C–H bonds has emerged as a more attractive method to synthesize biaryls [6 – 8]. Despite the significant progress in this field, the substrates are mainly limited to directing group-containing arenes and electron-rich heterocycles such as azoles or indoles. In 2006, a significant breakthrough has been made in palladium-catalyzed direct arylation of electron-deficient polyfluoroarene C–H bonds with aryl halides reported by Fagnou [9, 10]. This pioneering work spurred numerous recent investigations in the transition metal-catalyzed transformation of polyfluoroarene C–H bonds, including arylation [11 – 23], alkenylation [24 – 29], alkylation [30], alkynylation [31], allylation [32, 33], trifluoromethylation [34], amination [35, 36], borylation [37], and thiolation [38].

In 2008, Daugulis developed a general method for the copper-catalyzed arylation of polyfluoroarenes with aryl halides in the presence of phenanthroline [11]. Fagnou in 2010 made further modifications to the arylation of polyfluoroarenes with aryl iodides, in which excellent yields were obtained under mild biphasic conditions at room temperature [17]. Zhang reported palladium-catalyzed direct cross-coupling of polyfluoroarenes with heteroaromatic tosylates [20]. The same group recently reported the palladium-catalyzed arylation of polyfluoroarenes with aryl iodides using pure water as reaction medium [22]. For these reactions, the ligands containing nitrogen or phosphorus have an important effect on the reaction outcome. The use of ligands was thought to improve the catalytic activity. However, the phosphine ligands are often air-/moisture-sensitive, expensive and difficult to remove from the reaction mixtures. It is desirable to find novel catalytic procedures especially without any ligand for an efficient access to such useful organic products. Herein, we report a ligand-free palladium/copper co-catalyzed direct arylation of polyfluoroarenes with aryl iodides.

Results and Discussion

On the outset of this investigation, we used pentafluorobenzene (**1a**) and 4-iodotoluene (**2a**) as model substrates to screen suitable reaction condi-

Table 1. Optimization of palladium/copper co-catalyzed arylation of pentafluorobenzene (**1a**) with 4-iodotoluene (**2a**)[a].



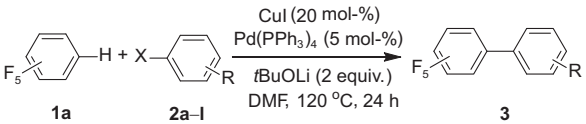
1a **2a** **3aa**

Entry	Pd	Base	Solvent	Time (h)	Yield (%)[b]
1	$Pd(PPh_3)_4$	K_2CO_3	DMF	36	48
2	$Pd(PPh_3)_4$	K_2CO_3	DMSO	36	21
3	$Pd(PPh_3)_4$	K_2CO_3	DMA	36	43
4	$Pd(PPh_3)_4$	K_3PO_4	DMF	36	56
5	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	36	55
6	$Pd(PPh_3)_4$	*t*BuOLi	DMF	24	81
7	$Pd(PPh_3)_4$	*t*BuONa	DMF	36	45
8	$Pd(PPh_3)_4$	*t*BuOK	DMF	24	67
9	$Pd(OAc)_2$	*t*BuOLi	DMF	36	43
10	$Pd_2(dba)_3$	*t*BuOLi	DMF	36	78
11	$PdCl_2(PPh_3)_2$	*t*BuOLi	DMF	36	36
12	$PdCl_2(MeCN)_2$	*t*BuOLi	DMF	36	24
13	$PdCl_2(PhCN)_2$	*t*BuOLi	DMF	36	33
14[c]	–	*t*BuOLi	DMF	48	16
15[d]	$Pd(PPh_3)_4$	*t*BuOLi	DMF	48	45
16[e]	$Pd(PPh_3)_4$	*t*BuOLi	DMF	24	72
17[f]	$Pd(PPh_3)_4$	*t*BuOLi	DMF	24	63

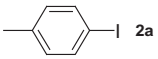
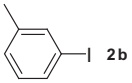
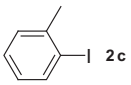
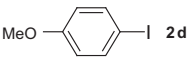
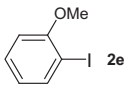
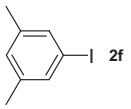
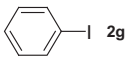
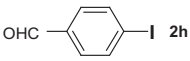
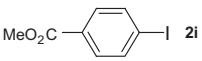
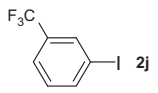
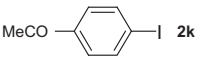
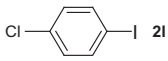
[a] Unless otherwise noted, the reaction conditions are as follows: pentafluorobenzene (**1a**) (1.5 equiv.), 4-iodotoluene (**2a**) (0.5 mmol), CuI (20 mol-%), Pd cat. (5 mol-%), base (2 equiv.), in anhydrous solvent (1.5 mL), at 120 °C, under N_2; [b] product yield; [c] the reaction was carried out in the absence of the palladium catalyst; [d] the reaction was carried out in the absence of CuI; [e] CuI (10 mol-%); [f] CuI (5 mol-%).

tions. The results are summarized in Table 1. When $Pd(PPh_3)_4$ and CuI were used as co-catalysts, and K_2CO_3 as a base, the arylation of **1a** took place in DMF at 120 °C under N_2, albeit in low yield (entry 1). The yields slightly decreased in DMSO and DMA (entries 2 – 3). Encouraged by these initial results, we proceeded to optimize the reaction conditions. Other bases, such as K_3PO_4, Cs_2CO_3, *t*BuOLi, *t*BuONa, and *t*BuOK were tested. It was found that *t*BuOLi was the most suitable base to promote the reaction with 81 % yield (entries 4 – 8). Next, various palladium sources were tested. The reactions also gave comparable yields in the presence of $Pd_2(dba)_3$, while other Pd(II) catalysts failed to improve the course of this reaction (entries 9 – 13). Finally, when for comparison the reaction was carried out in the absence of a palladium catalyst, the desired product **3aa** was obtained with only 16 % yield (entry 14). The reaction catalyzed by $Pd(PPh_3)_4$ gave only a moderate yield in the absence of CuI (entry 15), but the role of CuI is less clear.

Table 2. Palladium/copper co-catalyzed arylation of pentafluorobenzene (**1a**) with aryl iodides **2a**–**l**[a].



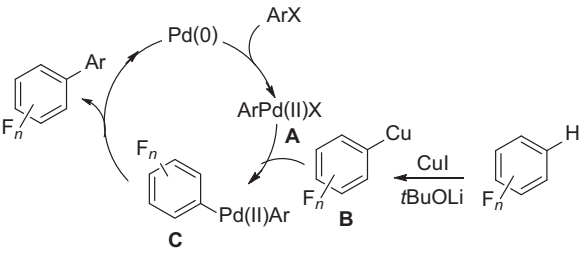
1a **2a–l** **3**

Entry	ArX (**2**)	Product (**3**)	Yield (%)[b]	Ref.
1	 **2a**	**3aa**	81	[17]
2	 **2b**	**3ab**	78	[13]
3	 **2c**	**3ac**	60	[17]
4	 **2d**	**3ad**	86	[17]
5	 **2e**	**3ae**	62	[17]
6	 **2f**	**3af**	80	[13]
7	 **2g**	**3ag**	78	[13]
8	 **2h**	**3ah**	62	[13]
9	 **2i**	**3ai**	72	[17]
10	 **2j**	**3aj**	65	[17]
11	 **2k**	**3ak**	76	[17]
12	 **2l**	**3al**	75	[13]

[a] Unless otherwise noted, the reaction conditions are as follows: pentafluorobenzene (**1a**) (1.5 equiv.), aryl iodides **2a**–**k** (0.5 mmol), CuI (20 mol-%), $Pd(PPh_3)_4$ (5 mol-%), *t*BuOLi (2 equiv.), in anhydrous DMF (1.5 mL), at 120 °C, under N_2; [b] product yield.

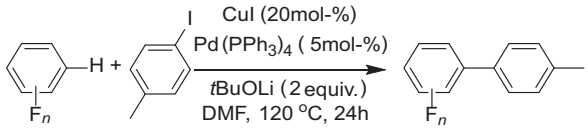
The scope of this reaction with respect to aryl iodides was investigated under the optimized conditions. The results are summarized in Table 2. A series of aryl iodides can be used as arylating reagents for the direct arylation of pentafluorobenzene, affording the desired products in moderate to good yields. The reaction was marginally affected by electronic effects of

the substituents of aryl iodides. The substituted aryl iodides bearing electron-deficient groups (entries 8 – 12) showed slightly lower reactivity than those bearing electron-rich ones (entries 1 – 6). In addition, the substantial steric hindrance of aryl iodides was obvious. Aryl iodides with electron-donating groups in *para*-position proceeded smoothly and afforded the corresponding arylation compounds in good yields (entries 1, 4), whereas the reaction with *ortho*-substituted aryl iodides only gave moderate yields (entries 3, 5). It is particularly noteworthy that the chloro substituent was tolerated in the reaction, which is advantageous for further transformations (entry 12).

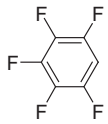
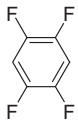
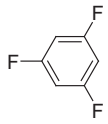
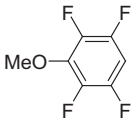
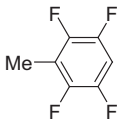
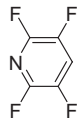


Scheme 1.

Table 3. Palladium/copper co-catalyzed arylation of polyfluoroarenes **1a–f** with 4-iodotoluene (**2a**)[a].



1a–f **2a** **3**

Entry	Polyfluoroarenes (**1**)	Product (**3**)	Yield (%)[b]	Ref.
1	 **1a**	**3aa**	81	[17]
2	 **1b**	**3ba**	83	[17]
3	 **1c**	**3ca**	72	[17]
4	 **1d**	**3da**	80	[17]
5	 **1e**	**3ea**	78	[17]
6	 **1f**	**3fa**	86	[17]

[a] Unless otherwise noted, the reaction conditions are as follows: polyfluoroarenes **1a–f** (1.5 equiv.), 4-iodotoluene (**2a**) (0.5 mmol), CuI (20 mol-%), $Pd(PPh_3)_4$ (5 mol-%), *t*BuOLi (2 equiv.), in anhydrous DMF (1.5 mL), at 120 °C, under N_2; [b] product yield.

To further ascertain the scope of this methodology, the reactions of a variety of polyfluoroarenes with 4-iodotoluene (**2a**) were investigated under the optimized conditions. The results are summarized in Table 3. Tetrafluoro- and trifluoroarenes were also found to be efficient for the coupling reaction (entries 2, 3). In addition, 2,3,5,6-tetrafluoroanisole and 2,3,5,6-tetrafluorotoluene smoothly underwent direct arylation with good yields (entries 4, 5), and fluorinated pyridines can also be arylated (entry 6).

A plausible mechanism for the arylation of polyfluoroarenes is proposed in Scheme 1. The oxidative addition between aryl iodides and palladium(0) affords ArPd(II) species **A**. It is followed by transmetalation with complex **B**, which is generated from polyfluoroarenes in the presence of CuI and *t*BuOLi. Reductive elimination occurs from intermediate **C** to give the arylation product, along with a Pd(0) species to complete the catalytic cycle.

Conclusion

In conclusion, a ligand-free palladium/copper bimetallic catalyst system for the direct arylation of polyfluoroarenes has been developed. This reaction exhibits functional group compatibility with respect to the aryl iodides and polyfluoroarenes. Further studies to expand the substrate scope is currently underway in our laboratory.

Experimental Section

Palladium and copper catalysts and aryl iodides were purchased from Accela ChemBio Co. Ltd. Polyfluoroarenes

were purchased from Alfa Aesar China (Tianjin) Co. Ltd. [D]Chloroform was purchased from Cambridge Isotope Laboratories. All solvents were distilled prior to use. For chromatography, 200 – 300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Bruker 400M spectrometers. $CDCl_3$ was used as solvent with tetramethylsilane (TMS) as internal standard.

General procedure for the arylation of polyfluoroarenes

Aryl iodides (0.5 mmol), polyfluoroarenes (1.5 equiv.), CuI (20 mol-%), $Pd(PPh_3)_4$ (5 mol-%) and *t*BuOLi (2.0 equiv.) were weighed into a 25 mL Schlenk round bottom flask under nitrogen atmosphere. The system was degassed four times by an oil pump, and then 3 mL DMF was added by a syringe. The resulting solution was stirred at 120 °C under nitrogen. The reaction progress was monitored by GC-MS. After the completion of the reaction, the solution was extracted with ethyl acetate (3×10 mL), the extract was washed with H_2O and brine, dried ($MgSO_4$), and concentrated to dryness. Purification on silica gel (petroleum ether-EtOAc, $10:1 \sim 30:1$) gave the products.

Spectral data for the products

*2,3,4,5,6-Pentafluoro-4′-methylbiphenyl (**3aa**) (Table 2, entry 1)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.30$ (s, 4 H, Ph-H), 2.42 (s, 3 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 144.2 (m), 140.3 (m), 139.4, 137.7 (m), 130.0, 129.5, 123.4, 116.0 (m), 21.4.

*2,3,4,5,6-Pentafluoro-3′-methylbiphenyl (**3ab**) (Table 2, entry 2)* [13]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.43 - 7.39$ (m, 1 H, Ph-H), 7.32 – 7.24 (m, 3 H, Ph-H), 2.45 (s, 3 H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 145.3 – 145.4 (m), 143.0 – 142.9 (m), 141.6 (m), 139.2 – 139.0 (m), 138.5, 136.7 – 136.6 (m), 130.7, 130.1, 128.6, 127.2, 126.3, 116.3 – 116.0 (m), 21.3.

*2,3,4,5,6-Pentafluoro-2′-methylbiphenyl (**3ac**) (Table 2, entry 3)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.40 - 7.33$ (m, 2H, Ph-H), 7.28 (m, 1H, Ph-H), 7.18 (d, $J = 7.6$ Hz, 1H, Ph-H), 2.18 (s, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 144.2 (m), 140.1 (m), 137.8 (m), 137.5, 130.7, 130.6, 129.8, 126.1, 126.0, 115.6 (m), 19.8.

*2,3,4,5,6-Pentafluoro-4′-methoxybiphenyl (**3ad**) (Table 2, entry 4)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.37 - 7.34$ (m, 2H, Ph-H), 7.01 (d, $J = 8.9$ Hz, 2H, 140.1 (m), 137.8 (m), 137.5, 130.7, 130.6, 129.8, 126.1, 126.0, 115.6 (m), 19.8.

Ph-H), 3.86 (s, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 160.3$, 144.2 (m), 140.2 (m), 137.7 (m), 131.4, 118.4, 115.7 (m), 114.2, 55.4.

*2,3,4,5,6-Pentafluoro-2′-methoxybiphenyl (**3ae**) (Table 2, entry 5)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.46 - 7.44$ (m, 1H, Ph-H), 7.23 (d, $J = 7.2$ Hz, 1H, Ph-H), 7.07 – 7.01 (m, 2H, Ph-H), 3.80 (s, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 157.2, 144.6 (m), 140.6 (m), 137.7 (m), 131.8, 131.3, 120.7, 115.4 (d), 113.0 (m), 111.4, 55.8.

*2,3,4,5,6-Pentafluoro-3,5′-dimethylbiphenyl (**3af**) (Table 2, entry 6)* [13]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.13$ (s, 1H, Ph-H), 7.06 (s, 2H, Ph-H), 2.41 (s, 6H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 145.5 – 145.3 (m), 143.0 – 142.9 (m), 141.5 (m), 139.2 – 138.9 (m), 138.4, 136.7 – 136.4 (m), 131.0, 123.4, 127.8, 126.1, 116.4 – 116.1 (m), 21.2.

*2,3,4,5,6-Pentafluoro-biphenyl (**3ag**) (Table 2, entry 7)* [13]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.55 – 7.53 (m, 1H, Ph-H), 7.51 – 7.49 (m, 2H, Ph-H), 7.46 – 7.44 (m, 1 H, Ph-H). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 145.5 – 145.3 (m), 143.1 – 142.8 (m), 141.8 – 141.5 (m), 139.3 – 138.9 (m), 136.8 – 136.4 (m), 130.2, 129.3, 128.7, 126.4, 116.2 – 115.8 (m).

*2,3,4,5,6-Pentafluoro-4′-formalbiphenyl (**3ah**) (Table 2, entry 8)* [13]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.08$ (s, 1H, CHO), 8.00 (d, $J = 8.3$, 2H, Ph-H), 7.61 (d, $J = 8.2$, 2H, Ph-H). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 191.5$, 145.3 (m), 142.9 – 142.3 (m), 139.7 – 139.2 (m), 136.6, 132.4, 130.9, 129.9, 114.7 (m).

*Methyl 2′,3′,4′,5′,6′-pentafluorobiphenyl-4-carboxylate (**3ai**) (Table 2, entry 9)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.96$, (s, 3H, CH_3), 7.52 (d, $J = 8.6$ Hz, 2H, Ph-H), 8.16 (d, $J = 8.6$ Hz, 2H, Ph-

H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 144.2 (m), 140.9 (m), 138.0 (m), 131.0, 130.3, 129.9, 115.0 (m), 52.4.

*2,3,4,5,6-Pentafluoro-3′-(trifluoromethyl)biphenyl (**3aj**) (Table 2, entry 10)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 – 7.69 (m, 2H, Ph-H), 7.68 – 7.59 (m, 2H, Ph-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3 (m), 141.1 (m), 138.1 (m), 133.6, 131.6 (m), 129.5, 127.4, 127.2, 126.3 (m), 123.9 (m), 114.6 (m).

*1-(2′,3′,4′,5′,6′ -Pentafluorobiphenyl-4-yl)ethanone (**3ak**) (Table 2, entry 11)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.4 Hz, 2H, Ph-H), 7.52 (d, J = 8.3 Hz, 2H, Ph-H), 2.63 (s, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 144.1 (m), 140.9 (m), 138.0 (m), 137.6, 131.1, 130.6, 128.6, 115.0 (m), 26.7.

*2,3,4,5,6-Pentafluoro-4′-chlorobiphenyl (**3al**) (Table 2, entry 12)* [13]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.5, 2H, Ph-H), 7.37 (d, J = 8.3, 2H, Ph-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4 – 145.2 (m), 142.9 – 142.8 (m), 141.9 – 141.7(m), 139.5 – 139.0 (m), 136.8 – 136.5 (m), 135.6, 131.4, 129.1, 124.7, 115.0 – 114.7 (m).

*2,3,5,6-Tetrafluoro-4′-methylbiphenyl (**3ba**) (Table 3, entry 2)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.28 (m, 4H, Ph-H), 7.03 (tt, J = 9.7, 7.3 Hz, 1H, Ph-H), 2.41 (s, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.4 (m), 143.8 (m), 139.4, 130.1, 129.5, 124.6 (m), 121.7 (m), 104.7 (m), 21.5.

*2,4,6-Trifluoro-4′-methyl-biphenyl (**3ca**) (Table 3, entry 3)* [11]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 8.1 Hz, 2H, Ph-H), 7.19 (d, J = 8.1 Hz, 2H, Ph-H), 6.60 – 6.69 (m, 2H, Ph-H), 2.33 (s, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8 (m); 160.5 (m), 138.4, 130.2, 129.3, 125.5, 115.4 – 115.0 (m), 100.7 – 100.2 (m), 21.2.

*2,3,5,6-Tetrafluoro-4-methoxy-4′-methylbiphenyl (**3da**) (Table 3, entry 4)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.4 Hz, 2H, Ph-H), 7.28 (d, J = 8.1 Hz, 2H, Ph-H), 4.10 (t, J = 1.3 Hz, 3H, CH_3), 2.41 (s, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4 (m), 141.3 (m), 139.0, 137.4 (m), 130.2 (m), 129.4, 124.4, 114.4 (m), 62.3, 21.5.

*2,3,5,6-Tetrafluoro-4,4′-dimethylbiphenyl (**3ea**) (Table 3, entry 5)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, J = 8.2 Hz, 2H, Ph-H), 7.28 (d, J = 8.0 Hz, 2H, Ph-H), 2.41 (s, 3H, CH_3), 2.30 (t, J = 2.1 Hz, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.8 (m), 143.4 (m), 139.0, 130.1 (m), 129.4, 124.9 (m), 118.1 (m), 114.9 (m), 21.5, 7.7 (m).

*2,3,5,6-Tetrafluoro-4-p-tolylpyridine (**3fa**) (Table 3, entry 6)* [17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (dt, J = 8.3, 1.6 Hz, 2H, Ph-H), 7.34 (d, J = 8.0 Hz, 2H, Ph-H), 2.43 (s, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2 (m), 141.1, 139.4 (m), 133.6 (m), 129.8, 129.7, 123.1, 21.6.

Acknowledgement

We thank the Natural Science Foundation of Zhejiang Province (no. Y4110324) for financial support.

[1] A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066 – 1096.
[2] H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119 – 2183.
[3] M.-H. Yoon, A. Facchetti, C. E. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2006**, *128*, 5792 – 5801.
[4] A. Facchetti, M.-H. Yoon, C. L. Stern, H. E. Katz, T. J. Marks, *Angew. Chem. Int. Ed.* **2003**, *42*, 3900 – 3903.
[5] L. Lin, N. Mulholland, Q. Wu, D. Beattie, S. Huang, D. Irwin, J. Clough, Y. Gu, G. Yang, *J. Agric. Food Chem.* **2012**, *60*, 4480 – 4491.
[6] D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174 – 238.
[7] O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074 – 1086.
[8] L. Ackermann, R. Vicente, A. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792 – 9826.
[9] M. Lafrance, C. N. Rowley, T. K. Woo, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 8754 – 8756.
[10] M. Lafrance, D. Shore, K. Fagnou, *Org. Lett.* **2006**, *8*, 5097 – 5100.
[11] H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 1128 – 1129.
[12] H.-Q. Do, R. M. K. Khan, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 15185 – 15192.
[13] Y. Wei, J. Kan, M. Wang, W. Su, M. Hong, *Org. Lett.* **2009**, *11*, 3346 – 3349.

[14] H.-Q. Do, O. Daugulis, *Chem. Commun.* **2009**, 6433 – 6435.
[15] C.-Y. He, S. Fan, X. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 12850 – 12852.
[16] Y. Wei, W. Su, *J. Am. Chem. Soc.* **2010**, *132*, 16377 – 16379.
[17] O. Rene, K. Fagnou, *Org. Lett.* **2010**, *12*, 2116 – 2119.
[18] H. Li, J. Liu, C.-L. Sun, B.-J. Li, Z.-J. Shi, *Org. Lett.* **2011**, *13*, 276 – 279.
[19] H. Zhao, Y. Wei, J. Xu, J. Kan, W. Su, M. Hong, *J. Org. Chem.* **2011**, *76*, 882 – 893.
[20] S. Fan, J. Yang, X. Zhang, *Org. Lett.* **2011**, *13*, 4374 – 4377.
[21] C. He, Q. Min, X. Zhang, *Organometallics* **2012**, *31*, 1335 – 1340.
[22] F. Chen, Q. Min, X. Zhang, *J. Org. Chem.* **2012**, *77*, 2992 – 2998.
[23] S. Fan, Z. Chen, X. Zhang, *Org. Lett.* **2012**, *14*, 4950 – 4953.
[24] Y. Nakao, N. Kashihara, K. S. Kanyiva, T. Hiyama, *J. Am. Chem. Soc.* **2008**, *130*, 16170 – 16171.
[25] 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.
[26] Z. Li, Y. Zhang, Z. Liu, *Org. Lett.* **2012**, *14*, 74 – 77.
[27] S. Ye, G. Liu, S. Pu, J. Wu, *Org. Lett.* **2012**, *14*, 70 – 73.
[28] S. Ye, J. Liu, J. Wu, *Chem. Commun.* **2012**, *48*, 5028 – 5030.
[29] F. Chen, Z. Feng, C. He, H. Wang, Y. Guo, X. Zhang, *Org. Lett.* **2012**, *14*, 1176 – 1179.
[30] S. Fan, C. He, X. Zhang, *Chem. Commun.* **2010**, *46*, 4926 – 4928.
[31] Y. Wei, H. Zhao, J. Kan, W. Su, M. Hong, *J. Am. Chem. Soc.* **2010**, *132*, 2522 – 2523.
[32] S. Fan, F. Chen, X. Zhang, *Angew. Chem. Int. Ed.* **2011**, *50*, 5918 – 5923.
[33] Y. Yu, S. Fan, X. Zhang, *Chem. Eur. J.* **2012**, *18*, 14643 – 14648.
[34] L. Chu, F.-L. Qing, *J. Am. Chem. Soc.* **2012**, *134*, 1298 – 1304.
[35] H. Zhao, M. Wang, W. Su, M. Hong, *Adv. Synth. Catal.* **2010**, *352*, 1301 – 1306.
[36] N. Matsuda, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2011**, *13*, 2860 – 2863.
[37] D. W. Robbins, J. F. Hartwig, *Org. Lett.* **2012**, *14*, 4266 – 4269.
[38] C. Yu, C. Zhang, X. Shi, *Eur. J. Org. Chem.* **2012**, 1953 – 1959.