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The effect of N-heterocyclic carbene ligands in the palladium-catalyzed cross-coupling reaction of $K[C_6F_5BF_3]$ with aryl iodides and aryl bromides

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ABSTRACT

The effect of *N*-heterocyclic carbene (NHC) ligands on the catalytic activity of in situ generated palladium complexes in the model cross-coupling reaction of $K[C_6F_5BF_3]$ with $4\text{-}FC_6H_4I$ was studied. Based on the obtained results, a series of pentafluorobiphenyls $C_6F_5C_6H_4X$ were prepared from $K[C_6F_5BF_3]$ and XC_6H_4I or $4\text{-}CF_3C_6H_4Br$ in high yields under aerobic conditions.

1. Introduction

Polyfluorinated biaryls like Ar–Ar_F find diverse applications in material science, molecular electronics, non-linear optics, etc.[1,2] Due to the strong π-stacking interaction between the polyfluoroaryl unit and non-fluorinated aromatic fragment,[3] such compounds tend to form molecular complexes in solutions[4] and well-controlled nanostructures in solids.[5,6] Pentafluorophenylated arenes are typical representatives of the polyfluorinated biaryls. The development of new methods for the preparation of such compounds is interesting for the synthesis of pentafluorophenylated arenes with special properties.[7] Moreover, these methods can be extended to other polyfluorinated biaryls. The unique nature of pentafluorophenyl group causes some synthetic problems. The methods for the preparation of pentafluorophenylbiaryls based on the use of pentafluorobenzenediazonium tetrafluoroborate,[8] the organoxenonium salts,[9] pentafluoro-benzenesulfonyl chloride,[10] pentafluorophenylhydrazine[11,12] and pentafluorophenyl fluoroalkanesulfonates[13] are not likely to be applicable to the synthesis of such derivatives, because of the low yields, low selectivity or requirement of excess reagents. Approaches using nucleophilic arylation of hexafluorobenzene with organolithium[14] or organomagnesium compounds[15] do not always give satisfactory yields, especially, in cases when organometallic reagents containing functional group sensitive to nucleophilic attack must be generated (for example, see Ref. 4).

The Pd-catalyzed cross-coupling reaction of organoboron compounds and organic halides (the Suzuki–Miyaura reaction) is one of the highly efficient tools for the carbon–carbon bond formation.[16] Although a very wide range of organoboron compounds were successfully involved in this process, the use of perfluoroorganoboron derivatives for the introduction of a perfluorinated moiety by this way remains an actual problem because of the strong electron withdrawing effect of many fluorine atoms. In previous papers in this field, we described the recent statement of the problem and found the convenient conditions for polyfluorophenylation of aryl halides[17,18] and arene-diazonium tetrafluoroborates.[19] All these reactions were carried out under a dry argon atmosphere. Despite the good to excellent yields of polyfluorinated biphenyls, the practical procedure can be complicated due to the sensitivity of the catalyst to oxygen and atmospheric moisture. To continue the systematic research of polyfluorinated organoboron compounds in the cross-coupling reactions, we studied the effect of *N*-heterocyclic carbene (NHC) ligands[20–23] in the palladium-catalyzed formation of pentafluorobiphenyls C_6F_5–Ar from the reaction of $K[C_6F_5BF_3]$ with aryl iodides or aryl bromides.

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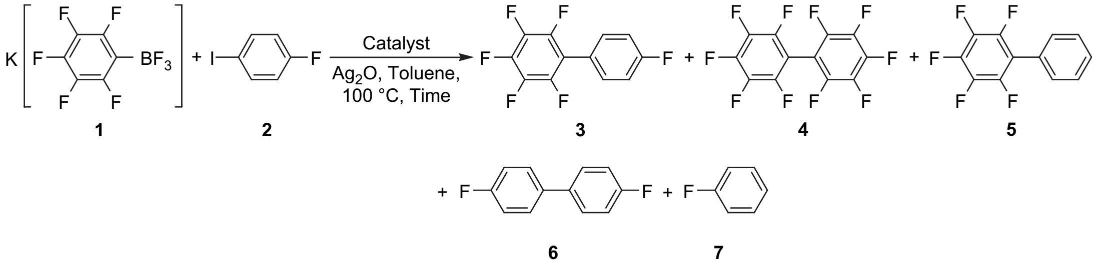


Scheme 1.

2. Results and discussion

Previously, we investigated the cross-coupling reaction of potassium pentafluorophenyltrifluoroborate $K[C_6F_5BF_3]$ (**1**) with 4-fluoroiodobenzene (**2**) in the presence of different palladium catalysts and silver oxide in toluene at 100 °C and determined the optimal conditions (Scheme 1).[17] Beside the target cross-coupling product, 2,3,4,4′,5,6-hexafluorobiphenyl (**3**), traces of decafluorobiphenyl (**4**), 2,3,4,5,6-pentafluorobiphenyl (**5**), 4,4′-difluorobiphenyl (**6**), fluorobenzene (**7**) and pentafluorobenzene were formed. For convenience, this procedure was chosen as the model for studying the effect of the NHC ligands **8**–**11**, generated in situ from the corresponding imidazolium and imidazolinium salts, **8**–**11**·HX (X=Cl, BF_4) (Fig. 1), and for the further improvement of the preparative conditions. Palladium chloride and palladium acetate in the absence of the NHC-ligand precursors were inactive under these conditions (Table 1, runs 1 and 2). A higher catalytic activity was demonstrated by $[Pd(PPh_3)_2Cl_2]$ (TOF 1.06 h^{-1}), but the selectivity of the cross-coupling reaction towards product **3** was only 59% (Table 1, run 3).

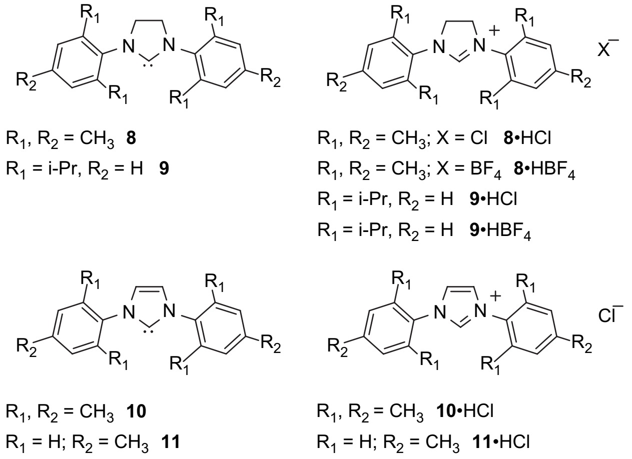


Figure 1.

A complex generated from $PdCl_2$ and the equimolar amount of salt **8**·HCl showed a lower catalytic activity than that above (TOF 0.54–0.56 h^{-1}), but the selectivity on **3** rose up to 86% (Table 1, runs 4 and 5). The similar effect was observed with $Pd(OAc)_2$ and **8**·HCl, although the contribution of the homo-coupling product **6** became significant (Table 1, run 6). An additional coordination of Pd with *n*-electron donor ligand like dialkylsulfide (Table 1, runs 7 and 8) practically did not improve the activity of the catalysts. Furthermore, the activity decreased nearly one-half (TOF 0.25–0.30 h^{-1}), when equimolar mixtures of $[Pd(MeCN)_2Cl_2]$, $[Pd(PhCN)_2Cl_2]$ and $[Pd(Ph_2S)_2Cl_2]$ with **8**·HCl were used as the catalyst precursors (Table 1, runs 9–11).

Table 1

Pd-catalyzed reaction of $K[C_6F_5BF_3]$ (**1**) with $4\text{-}FC_6H_4I$ (**2**) in the presence of *N*-heterocyclic carbene ligands

Run	Catalyst	Amount of catalyst, mol %	Time, h	Conversion of **2**, %	Product distribution, mol %					Selectivity towards **3**, %	TON[a]	TOF[b], h^{-1}
					3	**4**	**5**	**6**	**7**			
1.	$PdCl_2$	5	8	2	2	—	—	—	—	99	0.4	0.05
2.	$Pd(OAc)_2$	10	3	0	—	—	—	—	—	—	—	—
3.	$[Pd(PPh_3)_2Cl_2]$	5	8	42	25	—	3	13	1	59	8.4	1.06
4.	$PdCl_2$, **8**·HCl	5	8	22	19	—	—	1	—	86	4.4	0.54
5.	$PdCl_2$, **8**·HCl	10	9	51	44	—	—	1	1	86	5.1	0.56
6.	$Pd(OAc)_2$ **8**·HCl	5	8	36	28	—	—	12	1	78	7.2	0.91
7.	$[Pd(C_{14}H_{14}S)^{c}{}_2Cl_2]$, **8**·HCl	5	8	28	26	—	—	—	1	93	5.6	0.71
8.	$[Pd(C_{15}H_{24}S)^{d}{}_2Cl_2]$, **8**·HCl	5	8	23	22	—	—	—	—	96	4.6	0.58
9.	$[Pd(MeCN)_2Cl_2]$, **8**·HCl	5	8	12	6	—	—	—	—	50	2.4	0.30
10.	$[Pd(PhCN)_2Cl_2]$, **8**·HCl	5	8	10	8	—	—	—	—	80	2.0	0.25
11.	$[Pd(Ph_2S)_2Cl_2]$, **8**·HCl	5	8	10	9	—	—	—	—	90	2.0	0.25
12.	$Pd(dba)_2$, **8**·HCl	5	8	30	13	—	—	—	—	43	6.0	0.74
13.	$PdCl_2$, **8**·HCl, PPh_3	5	8	95	88	—	3	1	—	93	19.0	2.37
14.	$[Pd(PPh_3)_2Cl_2]$, **8**·HCl	10	3	100	94	1	3	1	1	94	>10	>3.30
15.	$[Pd(PPh_3)_2Cl_2]$, **8**·HCl	5	4	80	76	—	1	1	2	95	16	3.98
16.	$[Pd(PPh_3)_2Cl_2]$, **8**·HCl	5	8	100	95	1	2	1	1	95	>20	>1.25
17.	$[Pd(PPh_3)_2Cl_2]$, **8**·HCl	1	8	80	78	—	—	1	1	98	80	10.00
18.	$[Pd(PPh_3)_2Cl_2]$, **8**·HBF_4	5	8	48	48	—	—	—	—	100	9.6	1.20
19.	$[Pd(PPh_3)_2Cl_2]$, **9**·HCl	5	8	46	40	—	7	—	1	87	9.2	1.14
20.	$[Pd(PPh_3)_2Cl_2]$, **9**·HBF_4	10	3	47	41	2	5	—	—	87	4.7	1.57
21.	$[Pd(PPh_3)_2Cl_2]$, **10**·HCl	5	8	100	98	1	1	—	—	98	>20	>2.50
22.	$[Pd(PPh_3)_2Cl_2]$, **10**·HCl	1	8	58	58	—	—	—	—	100	58.0	7.25
23.	$[Pd(PPh_3)_2Cl_2]$, **11**·HCl	5	8	83	74	—	3	4	2	89	16.6	2.10

[a] TON (turnover number) is the ratio of moles of converted **2** to moles of the catalyst.

[b] TOF (turnover frequency) is TON divided by the time of the reaction.

[c] $C_{14}H_{14}S=(C_6H_5CH_2)_2S$.

[d] $C_{15}H_{24}S=C_8H_{17}SCH_2C_6H_5$.

The catalyst generated from $Pd(dba)_2$ and **8**·HCl showed a high catalytic activity in the cross-coupling of phenylboronic acid with aryl chlorides,[24] but a low activity (TOF 0.74 h^{-1}) and low selectivity (43%) in our case (Table 1, run 12).

In contrast, the cross-coupling of **1** with **2** successfully proceeded in the presence of $PdCl_2$, **8**·HCl and PPh_3 as well as $[Pd(PPh_3)_2Cl_2]$ and **8**·HCl to give the desirable biphenyl **3** with selectivity >94%, which was only contaminated by traces of **5** and **6** (Table 1, runs 13–17).

Thus, NHC–palladium complex generated in situ from $[Pd(PPh_3)_2Cl_2]$ or palladium chloride and triphenylphosphine and dimesitylimidazolium chloride demonstrated both high activity and selectivity in the cross-coupling reaction of **1** with **2**.

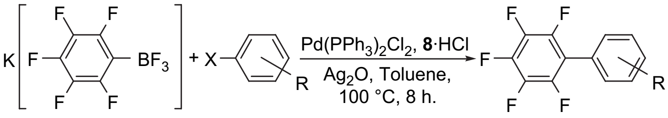
Further, we investigated the influence of the nature of the carbene (NHC) and acidic (HX) moieties of the initial imidazolium and imidazolinium salts, NHC·HX, on the catalytic activity of the resulted palladium complexes. The substitution of **8**·HCl for **8**·HBF_4 led to a decrease in catalytic activity of the catalyst (run 18). A similar effect was found in the presence of bis(diisopropylphenyl)-imidazolinium chloride, **9**·HCl (run 19). For this NHC ligand, variation in the anion of its precursor did not practically affect the catalytic activity (run 20).

The palladium complex with NHC ligand generated from dimesitylimidazolium chloride (**10**·HCl) (unsaturated back bonds) had practically the same catalytic activity as that of complex prepared with **8**·HCl (run 22) while the complex derived from ditolylimidazolium chloride (**11**·HCl) displayed a lower catalytic activity and selectivity (run 23).

The observed picture allows interpretation of the actual role of the NHC-ligand precursors in the studied reactions based on the general conceptions.[21,25] Usually imidazolinium or imidazolium salts react smoothly with silver oxide giving NHC-transferring reagents (Ag(I)–NHC).[26] Subsequent interaction of Ag(I)–NHC with Pd(II) precursor led to the formation of the corresponding NHC–palladium complexes.[26] The latter reaction provides a quite universal method for the preparation of NHC–palladium complexes, but several works demonstrated the influence of Pd(II) precursors on the NHC transfer process. For instance, Herrmann et al.[27] demonstrated the exclusive formation of $[L_2Ag]^{2+}[Pd_2Cl_6]^{2-}$ instead of the expected $[PdL_2Cl_2]$ in the reaction of LAgCl (L=dimesityltetrahydropyrimid-2-ylidene) with $[Pd(CH_3CN)_2Cl_2]$. Ag(I)–NHCs with *N*-*i*-Pr and *N*-(*S*)-1-phenylethyl substituents transferred NHC smoothly to $[Pd(allyl)Cl]_2$ but not to $[Pd(MeCN)_2Cl]_2$.[28] In our case, the low catalytic activity of the nitrile (Table 1, runs 9 and 10) and sulfide (Table 1, runs 7, 8 and 11) palladium complexes arises, probably, from the difficult transition of NHC from the silver to palladium.

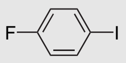
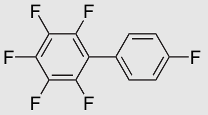
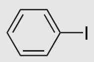
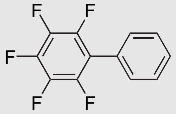
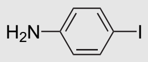
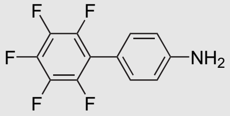
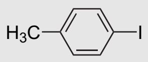
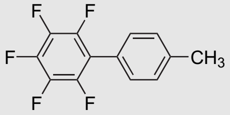
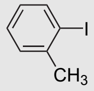
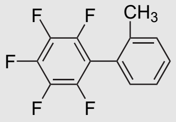
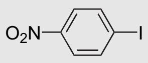
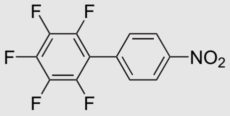
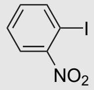
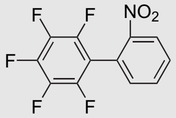
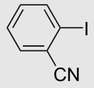
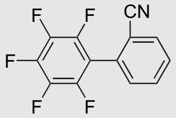
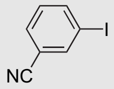
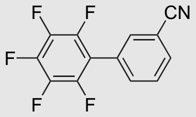
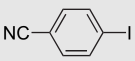
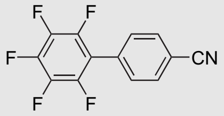
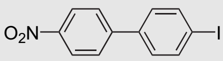
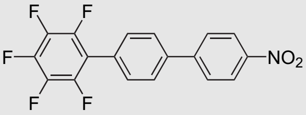
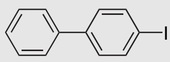
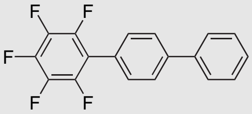
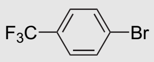
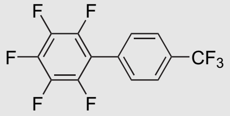
The formation of 2,3,4,5,6-pentafluorobiphenyl (**5**) can be accounted for by the palladium mediated P–Ph/Ar exchange at the bound phosphine ligand (for review, see Ref. 29). Intimate investigations of the mechanism of such reaction were reported by Novak et al.[30] and Grushin.[31] The key stage of P–Ph/Ar exchange is the reductive elimination of phosphonium salt from organopalladium complex $[ArPdL(PPh_3)X]$. Bulky ligand L stimulates the reaction. Subsequent oxidative addition of $ArPPh_3X$ to palladium(0) species L–Pd gives $[PhPdL(PArPh_2)X]$—the main intermediate of biphenyl **5** formation.

To examine the applicability of the optimal conditions (Table 1, run 16), the cross-coupling reactions of potassium pentafluorophenyltrifluoroborate were performed with other aryl iodides.



Scheme 2.

Table 2
Cross-coupling of potassium pentafluorophenyltrifluoroborate with aryl iodides and aryl bromides catalyzed by $[Pd(PPh_3)_2Cl_2]$–**8**·HCl

Run	Substrate	Product	Yield, %[a,b]
1.			**3** 96 (90)
2.			**5** 99 (93)
3.			**12** 3
4.			**13** 91 (88)
5.			**14** 49
6.			**15** 99 (91)
7.			**16** 27
8.			**17** 77
9.			**18** 96 (90)
10.			**19** 80
11.			**20** 80 (65)
12.			**21** 86 (72)
13.			**22** 80[c]

[a] Determined by ^{19}F NMR.
[b] Isolated yields are given in brackets.
[c] The reaction was carried out within 36 h.

Substrates XC_6H_4I with substituents X=H, 4-CH_3, 4-C_6H_5, 4-NO_2, 3-CN, 4-F, 4-CN and 4-(4′-$NO_2C_6H_4$) gave the corresponding biphenyls $C_6F_5C_6H_4X$ in good to excellent yield (^{19}F NMR) (Scheme 2, Table 2). Moderate yields were obtained in cross-coupling of **1** with 2-XC_6H_4I (X=CH_3, NO_2, CN). Only traces of the desired 4-$C_6F_5C_6H_4NH_2$ were detected in the reaction with 4-$NH_2C_6H_4I$.

Aryl bromides were less reactive than aryl iodides. Thus, 4′-trifluoromethyl-2,3,4,5,6-pentafluorobiphenyl was obtained in a good yield only after 36 h, while the complete consumption of aryl iodides occurred within 8 h.

3. Conclusion

The activity of different palladium catalysts prepared in situ from palladium compounds and imidazolinium or imidazolium salts was studied in the cross-coupling reaction of potassium pentafluorophenyltrifluoroborate with aryl halides. The selectivity of the reaction as well as the activity of the catalyst strongly depends on the nature of palladium containing pre-catalysts, imidazolinium or imidazolium salts and substrates. The best yields (up to 99%) of pentafluorobiphenyls were obtained when $[Pd(PPh_3)_2Cl_2]$ was applied as the source of palladium in the presence of SIMes·HCl (**8**·HCl) or IMes·HCl (**10**·HCl). The resulted catalysts are moisture and air resistant, and the reaction conditions are tolerant to a wide range of substituents in the aromatic substrate.

4. Experimental part

4.1. General

NMR spectra were recorded using a Bruker AVANCE 400 (FT 400.13 MHz, ^{1}H; 376.45 MHz, ^{19}F) spectrometer. The chemical shifts are referenced to TMS (^{1}H) and CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)). IR spectra were obtained with a Shimadzu FTIR-8300 spectrometer (KBr pellets). High resolution mass spectra were recorded on an AMD 604 spectrometer (EI mode, 70 eV).

The following salts were prepared according to the literature procedures: **8**·HCl,[32] **9**·HCl,[32] **10**·HCl[33] and **11**·HCl.[34] Salts **8**·HBF_4 and **9**·HBF_4 were prepared by metathesis of the corresponding HCl salts with $NaBF_4$ in water. Palladium chloride (Aurat), palladium acetate (Fluka) and silver oxide (Degussa) were used as supplied. Toluene was distilled over Na. Triphenylphosphine was re-crystallized from ethanol. $Pd(dba)_2$,[35] $[Pd(PPh_3)_2Cl_2]$,[35] $[Pd(CH_3CN)_2Cl_2]$,[35] $[Pd(PhCN)_2Cl_2]$[35] and $[Pd(R_2S)_2Cl_2]$ (R=C_6H_5, $C_6H_5CH_2$, C_8H_{17})[36] were prepared according to the described procedures. Aryl iodides and 4-$CF_3C_6H_4Br$ were purchased or prepared and purified by standard methods. Potassium pentafluorophenyltrifluoroborate, $K[C_6F_5BF_3]$,[37] was obtained by the modified method shown below from pentafluorophenylboronic acid, which can be prepared from the corresponding pentafluorophenylmagnesium[38] or -lithium reagents.[39] The obtained polyfluorinated biphenyls **3**,[17,19] **5**,[10,13] **12**,[13] **13**,[40] **14**,[40] **15**,[40] **16**,[10] **17**,[10] **18**,[10] **19**[10,41] and **22**[40] were authentic to earlier described compounds (^{1}H, ^{19}F NMR spectra and the high resolution mass spectra). Yields were determined by ^{19}F NMR using $C_6H_5CF_3$ as an internal quantitative standard. In some cases (see Table 2), the desired biphenyls were isolated and purified by column chromatography (silica gel (60 μM), mixtures hexane–CH_2Cl_2 4:1 to 7:1 v/v).

4.2. Potassium pentafluorophenyltrifluoroborate (1), $K[C_6F_5BF_3]$

A solution of pentafluorophenylboronic acid (4.24 g, 20 mmol) in methanol (6 mL) was added at 20 °C to KHF_2 (5.16 g, 66 mmol) dissolved in 25 mL of water. The mixture was stirred at 20 °C for 4 h. Then it was neutralized with solid K_2CO_3 to pH ∼6 to 7. A white solid product was filtered off, washed with water (2×5 mL) and dried in air. The solid was extracted with hot acetonitrile (5×5 mL) and the hot solution was filtered. After evaporation, 4.88 g (17.8 mmol, 89%) of pure $K[C_6F_5BF_3]$ was obtained.

4.3. The cross-coupling reaction of $K[C_6F_5BF_3]$ with 4-FC_6H_4I

Palladium catalyst (0.0025–0.0125 mmol), NHC-ligand precursor (0.0025–0.0125 mmol), Ag_2O (0.30 mmol), $K[C_6F_5BF_3]$ (0.30 mmol), 4-FC_6H_4I (0.25 mmol) and dry toluene (1 mL) were placed in sequence into a round-bottomed flask supplied with a magnetic stir bar. The reaction mixture was stirred at 100 °C (bath), cooled to 25 °C, charged with an internal standard $C_6H_5CF_3$ (5 μL, 0.041 mmol) and analyzed by ^{19}F NMR (Table 1).

4.4. The cross-coupling reaction of $K[C_6F_5BF_3]$ with 4-fluoroiodobenzene (a representative preparative procedure)

$[Pd(PPh_3)_2Cl_2]$ (8.8 mg, 0.0125 mmol), **1**·HCl (4.3 mg, 0.0125 mmol), Ag_2O (70 mg, 0.30 mmol), $K[C_6F_5BF_3]$ (82.5 mg, 0.30 mmol) and 4-fluoroiodobenzene (56 mg, 29 μL, 0.25 mmol) were placed into a round-bottomed flask supplied with a magnetic stir bar, and toluene (1 mL) was added. The flask was placed into an oil-bath pre-heated to 100 °C and the reaction mixture was stirred for 8 h. The reaction mixture was cooled to 20 °C, charged with an internal standard $C_6H_5CF_3$ (5 μL, 0.041 mmol) and analyzed by ^{19}F NMR (The yield determined by ^{19}F NMR was 96%). The mixture was filtered through a silica gel plug (silica gel 60 μM, 40×5 mm). The filter was washed with toluene (2 mL) and the combined toluene solution was evaporated under reduced pressure to yield biphenyl **7** (59 mg, 90%).

The cross-coupling reaction of $K[C_6F_5BF_3]$ with other aryl iodides and aryl bromides was performed similarly (Table 2).

*4.4.1. 2,3,4,5,6-Pentafluoro-4″-nitroterphenyl (**20**)*

IR (KBr) 1651, 1595, 1513, 1490, 1344, 1105, 985, 872, 854, 832, 760, 740, 698, 665, 549, 498 cm^{-1}. ^{19}F NMR ($CDCl_3$) −143.9 (dd, 2F, $^3J_{FF}$ 22.2 Hz, $^5J_{FF}$ 8.1 Hz, F-2,6), −155.7 (t, 1F, $^3J_{FF}$ 21.1 Hz, F-4), −162.6 (ddd, 2F, $^3J_{FF}$ 22.2, 21.1 Hz, $^5J_{FF}$ 8.1 Hz, F-2,5). ^{1}H NMR ($CDCl_3$) 8.27 (d, $^3J_{HH}$ 8.9 Hz, 2H), 7.72 (d, $^3J_{HH}$ 8.5 Hz, 2H), 7.69 (d, $^3J_{HH}$ 8.9 Hz, 2H), 7.50 (d, $^3J_{HH}$ 8.5 Hz, 2H). TLC (hexane–CH_2Cl_2 4:1 v/v) R_f 0.21. HRMS calcd for $C_{18}H_8F_5NO_2$: 365.2536; found: 365.2537.

*4.4.2. 2,3,4,5,6-Pentafluoroterphenyl (**21**)*

IR (KBr) 1650, 1579, 1558, 1532, 1515, 1490, 1403, 1200, 1066, 979, 863, 837, 760, 733, 697, 552, 506 cm^{-1}. ^{19}F NMR ($CDCl_3$) −144.3 (dd, 2F, $^3J_{FF}$ 22.5 Hz, $^5J_{FF}$ 8.0 Hz, F-2,6), −156.7 (t, 1F, $^3J_{FF}$ 21.1 Hz, F-4), −163.3 (ddd, 2F, $^3J_{FF}$ 22.5, 21.1 Hz, $^5J_{FF}$ 8.0 Hz, F-2,5). ^{1}H NMR ($CDCl_3$) 7.65 (d, $^3J_{HH}$ 8.5 Hz, 2H), 7.57 (d, $^3J_{HH}$ 7.5 Hz, 2H), 7.44 (d, $^3J_{HH}$ 8.5 Hz, 2H), 7.41 (dd, $^3J_{HH}$ 7.5, 7.2 Hz, 2H), 7.32 (dd, $^3J_{HH}$ 7.2 Hz, 1H). TLC (hexane–CH_2Cl_2 4:1 v/v) R_f 0.88. HRMS calcd for $C_{18}H_9F_5$: 320.2561; found: 320.2560.

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