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NHC Nickel-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions of Arylboronate Esters with Perfluorobenzenes

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ABSTRACT

An efficient Suzuki-Miyaura cross-coupling reaction of perfluorinated arenes with aryl boronate esters using NHC nickel complexes as catalysts is described. The efficiencies of different boronate esters (*p*-tolyl-Beg, *p*-tolyl-Bneop, *p*-tolyl-Bpin, *p*-tolyl-Bcat) and the corresponding boronic acid (*p*-tolyl-B(OH)$_2$) in this type of cross-coupling reaction was evaluated (eg = ethyleneglycolato; neop = neopentylglycolato; pin = pinacolato, cat = catecholato). Aryl-Beg was shown to be the most reactive boronate ester among those studied. The use of CsF as an additive is essential for an efficient reaction of hexafluorobenzene with aryl neopentylglycolboronates.

The wide applications of pharmaceuticals, agrochemicals and materials that contain fluoroaromatics attract scientists' interest in the development of methods to introduce fluorine or fluorinated building blocks into organic molecules.[1] Transition

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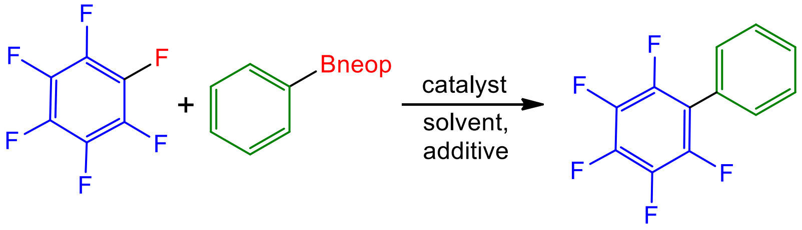
metal-catalyzed C-F bond activation has been well-developed in recent years.[2] C-C bond-forming processes in which polyfluorinated arenes are involved include Kumada,[3] Negishi,[4] Suzuki-Miyaura,[5] Songashira,[6] Stille,[5b, 5e, 7] and Hiyama cross-coupling reactions.[8] However, cross-coupling reactions of electron-deficient aryl fluorides are usually limited in turnover numbers (if they are catalytic at all) and yields and are often restricted to fluorinated substrates with directing groups (such as imine, oxazoline, pyridine, nitro, keto and hydroxo groups). Among them, Suzuki-Miyaura cross-coupling of poly- and perfluorinated arenes represents an attractive reaction due to the mild conditions employed and the compatibility with many potential functional groups. In previously reported[5g,i,l] cross-coupling reactions of poly- and perfluorinated benzenes with boronate esters, an excess of the boronate esters is required in many cases in order to obtain reasonable yields, and fluoride additives were often employed to activate the boronate ester. Over the last few years, we have investigated the use of nickel complexes stabilized by N-alkyl substituted NHCs, such as 1,3-bis(*iso*propyl)imidazolin-2-ylidene ($^{i}Pr_2Im$), in stoichiometric and catalytic C-F bond activation reactions.[9] Complexes such as $[Ni_2(^{i}Pr_2Im)_4(\mu\text{-}COD)]$ readily undergo oxidative addition of polyfluorinated arenes at ambient temperatures and are readily available catalysts for C-F bond transformations such as hydrodefluorination reactions.[9g] We have recently reported the NHC nickel-catalyzed borylation of polyfluorinated arenes via C-F bond activation.[10] Furthermore, we reported efficient Suzuki-Miyaura cross-coupling reaction of polyfluorinated arenes with boronic acids using $[Ni_2(^{i}Pr_2Im)_4(\mu\text{-}COD)]$ as a catalyst precursor.[9b] In light of the widespread use of organoboronic esters instead of organoboronic acids themselves, we decided to expand our work and we report herein preliminary results on the Suzuki-Miyaura cross-coupling of polyfluorinated arenes with aryl ethyleneglycolato (eg), neopentylglycolato (neop), pinacolato (pin), and catecholato (cat) boronic acid esters. Ohashi and Ogoshi *et al.* described briefly base-free Suzuki-Miyaura cross-coupling reactions of octafluorotoluene (C_7F_8), hexafluorobenzene (C_6F_6) and fluorobenzene (C_6H_5F) with 4-methoxyphenyl neopentylglycolboronate ester using our catalyst and demonstrated that the reactions of C_6F_6 and C_6H_5F provided low yields.[51] In the present study, we optimized the conditions for the Suzuki-Miyaura cross-coupling of C_6F_6 with phenyl neopentylglycolboronate (C_6H_5-Bneop) and compared the reactivity of different boronate esters with perfluorinated arenes. The scope of the nickel-catalyzed Suzuki-Miyaura coupling reactions of other fluorobenzenes was also explored.

Initially, a variety of nickel catalysts and additives were tested for the reaction of C_6F_6 **1a** and the boronate ester C_6H_5-Bneop **2a** to give C_6H_5-C_6F_5 **3aa** (Table 1). For an equimolar reaction (**1a**:**2a** = 1:1), the best results were obtained when 5 mol% of dimeric [$Ni_2(^iPr_2Im)_4(\mu$-COD)] (i.e. 10 mol% Ni) was used as a catalyst precursor, CsF (1 eq.) as an additive and the reaction was performed in toluene at 100 °C (Table 1, entry 1). Using these conditions, the product, C_6H_5-C_6F_5 **3aa**, was obtained in 71 % yield. Each component given in Table 1, entry 1 is necessary to obtain a high yield. Without CsF, the yield drops significantly to 17 % (Table 1, entry 2 and 3), whereas without catalyst, no conversion was detected (Table 1, entries 4 and 5). The NHC ligand $^iPr_2$Im alone is also not a catalyst for this reaction (Table 1, entry 5). Ni(II) precursors were not effective catalysts, while other Ni(0) complexes are much less effective than $[Ni_2(^iPr_2Im)_4(\mu\text{-}COD)]$. The closely related Ni(0) complex $[Ni(IMes)_2]$,[11] for example, afforded the product in only 17 % yield using the same conditions (Table 1, entry 6). Using the Ni(II) complexes $[(^iPr_2Im)_2NiBr_2]$[12] and $[(Me_2Im)_2NiI_2]$,[13] no product formation was observed (Table 1, entries 7 and 8). NHC-stabilized nickel carbonyls[14] are also ineffective for this reaction (Table 1, entries 9 and 10) as well as *in situ*-generated Ni(0) bis(phosphine) complexes[15] (Table 1, entries 11-13).

The choice of base and solvent for Suzuki–Miyaura reactions is, by and large, empirical but, in general, ethereal and aromatic hydrocarbon solvents and carbonate, phosphate, hydroxide, and fluoride bases tend to be optimal. The influence of the additives/bases were studied using the standard conditions introduced above (1 eq. C_6F_6, 1 eq. C_6H_5-Bneop, 5 mol % $[Ni_2(^iPr_2Im)_4(\mu\text{-}COD)]$, toluene as a solvent at 100 °C; Table 1, entries 14-20). All other additives, different fluorides, carbonates, alkoxides and amines gave lower yields; the second best was provided when K_3PO_4 was used as the base (61 % Table 1, entry 17). The use of CsF is crucial for efficient cross-coupling. The obvious advantage of F^- as an additive in our reactions is to avoid the consequences of direct nucleophilic attack of the base on the perfluoroarene substrate or polyfluoroarene containing reaction product.[16] F^- attack is redundant whereas many of the "non-fluoride" bases may react competitively with the perfluoroarenes. Furthermore, we found that toluene is advantageous for the reaction in comparison to THF, the use of the latter solvent gave lower yields using the standard conditions (Table 1, entries 1 and 21) as well as in the additive free case (Table 1, entries 2 and 3). The reaction can be further pushed towards the product if the fluorobenzene is used in an excess compared to the boronate ester. An increase of the amount of C_6F_6 to 2 equivalents led to formation of C_6H_5-C_6F_5 **3aa** in 80 % yield based on C_6H_5-Bneop (Table 1, entry 22).

Table 1. Optimization of conditions for the NHC nickel-catalyzed Suzuki-Miyaura cross-coupling reaction.[a]



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

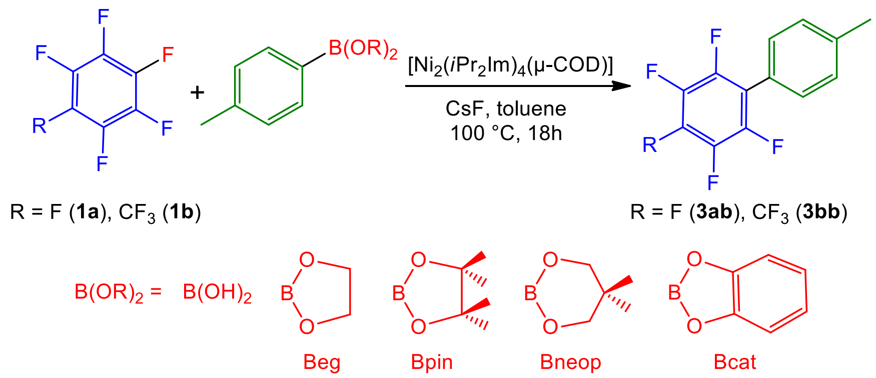
entry	catalyst	additive	solvent	yield (%) [a]
1	$Ni_2(^iPr_2Im)_4(\mu\text{-}COD)$	CsF	Toluene	71 [b]
2	$Ni_2(^iPr_2Im)_4(\mu\text{-}COD)$	-	Toluene	17 [b]
3	$Ni_2(^iPr_2Im)_4(\mu\text{-}COD)$	-	THF	6
4	-	CsF	Toluene	0
5	$^iPr_2Im$	-	Toluene	0
6	$Ni(IMes)_2$	CsF	Toluene	17
7	$(^iPr_2Im)_2NiBr_2$	CsF	Toluene	0
8	$(Me_2Im)_2NiI_2$	CsF	Toluene	0
9	$(^iPr_2Im)_2Ni(CO)_2$	CsF	Toluene	< 1

10	$(Me_2Im)_2Ni(CO)_2$	CsF	Toluene	< 1
11	(dppe)$NiCl_2$	*n*-BuLi	Toluene	0
12	(dppp)$NiCl_2$	*n*-BuLi	Toluene	0
13	(dpppf)$NiCl_2$	*n*-BuLi	Toluene	0
14	$Ni_2(^iPr_2Im)_4(\mu\text{-COD})$	KF	Toluene	43 [b]
15	$Ni_2(^iPr_2Im)_4(\mu\text{-COD})$	NMe_4F	Toluene	8 [b]
16	$Ni_2(^iPr_2Im)_4(\mu\text{-COD})$	KO^tBu	Toluene	34 [b]
17	$Ni_2(^iPr_2Im)_4(\mu\text{-COD})$	K_3PO_4	Toluene	61 [b]
18	$Ni_2(^iPr_2Im)_4(\mu\text{-COD})$	K_2CO_3	Toluene	40 [b]
19	$Ni_2(^iPr_2Im)_4(\mu\text{-COD})$	Cs_2CO_3	Toluene	8 [b]
20	$Ni_2(^iPr_2Im)_4(\mu\text{-COD})$	NEt_3	Toluene	28 [b]
21	$Ni_2(^iPr_2Im)_4(\mu\text{-COD})$	CsF	THF	38 [b]
22	$Ni_2(^iPr_2Im)_4(\mu\text{-COD})$	CsF	Toluene	80 [c]

[a] Reaction conditions, unless otherwise stated: Ni source (10 mol % Ni), C_6H_5-Bneop (0.2 mmol), C_6F_6 (0.2 mmol), additive (0.2 mmol), 5 mL solvent, 100 °C, 18 h. Yields are based on C_6H_5-Bneop; C_6H_5-C_6F_5 was determined by GC-MS using $C_{12}H_{26}$ as internal standard; [b] $[Ni_2(^iPr_2Im)_4(\mu\text{-COD})]$ (5 mol %); [c] C_6F_6 (0.4 mmol).

To compare the reactivity of different boronate esters and the analogous boronic acid the catalytic reaction of hexafluorobenzene and perfluorotoluene was conducted using *p*-tolyl boronic acid and different *p*-tolyl boronate esters. The results are presented in Table 2 and demonstrate that the neopentylglycol (*p*-tolyl-Bneop) and ethyleneglycol (*p*-tolyl-Beg) esters display a significantly higher reactivity than *p*-tolylboronic acid, the pinacol (*p*-tolyl-Bpin) and catechol (*p*-tolyl-Bcat) ester.[17] *P*-tolyl-Beg is the most efficient boronate ester being even more active than *p*-tolyl-Bneop (Table 2, entries 2, 3, 7, 8). The pinacol boronate ester displays significantly lower reactivity (Table 2, entries 4, 9). For C_6F_6, the reactivity trend is *p*-tolyl-Beg, *p*-tolyl-Bneop ≫ *p*-tolylboronic acid, *p*-tolyl-Bpin > *p*-tolyl-Bcat, whereas for CF_3-C_6F_5 a slightly modified reactivity order was observed, i.e. *p*-tolyl-Beg, *p*-tolyl-Bneop and *p*-tolylboronic acid reacted excellently, *p*-tolyl-Bpin performed less well and *p*-tolyl-Bcat revealed the lowest reactivity[18] (Table 2, entries 6-10).

Table 2. NHC nickel-catalyzed Suzuki-Miyaura cross-coupling reaction: the role of the boron component



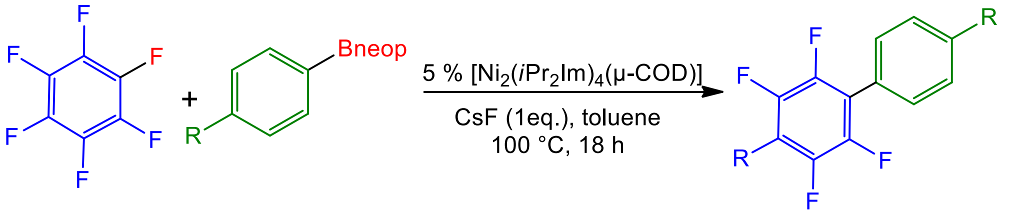
entry	Boronic esters	Ar^F-F	Yield (%)[a]
1	*p*-tolyl boronic acid	C_6F_6	10 [b]
2	*p*-tolyl-Beg	C_6F_6	95
3	*p*-tolyl-Bneop	C_6F_6	84
4	*p*-tolyl-Bpin	C_6F_6	8

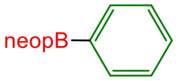
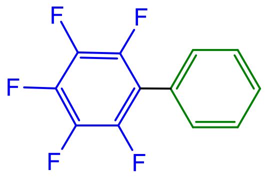
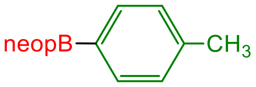
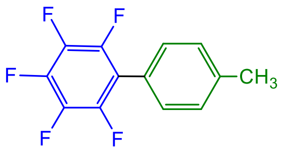
5	*p*-tolyl-Bcat	C_6F_6	6
6	*p*-tolyl boronic acid	CF_3-C_6F_5	97 [b]
7	*p*-tolyl-Beg	CF_3-C_6F_5	100
8	*p*-tolyl-Bneop	CF_3-C_6F_5	96
9	*p*-tolyl-Bpin	CF_3-C_6F_5	47
10	*p*-tolyl-Bcat	CF_3-C_6F_5	6

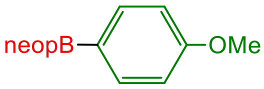
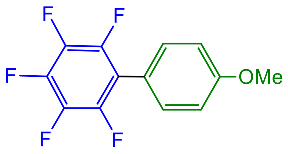
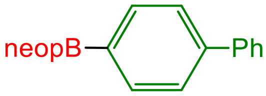
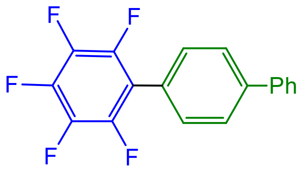
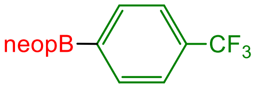
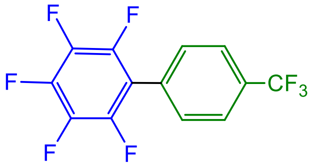
[a] Reaction conditions: $[Ni_2(^iPr_2Im)_4(\mu\text{-}COD)]$ (5 mol %), *p*-tolyl-$B(OR)_2$ (0.2 mmol), polyfluorinated arene (C_6F_6, 0.4 mmol; CF_3-C_6F_5, 0.2 mmol), CsF (0.2 mmol), 2 mL toluene, 100 °C, 18 h. GC yields based on boronic acid or boronate ester using $C_{12}H_{26}$ as internal standard. [b] K_2CO_3 (0.6 mmol) was employed as base.

Despite the fact that Ar-Beg is more reactive than Ar-Bneop, we chose the neopentylglycol boronate Ar-Bneop for all subsequent experiments, as it is usually more readily, also commercially, available for many different aryl groups.[19,20] We thus examined the use of different aryl neopentylglycol boronates for the reaction with hexafluorobenzene. Treatment of C_6F_6 (2 eq.) with 4-CH_3-C_6H_4-Bneop in toluene at 100 °C for 18 hours led to 4-CH_3-C_6H_4-C_6F_5 **3ab** in 76 % isolated yield; C_6H_5-Bneop afforded 72 % of the cross-coupling product **3aa**. (Table 3, entries 1 and 2). For 4-(MeO)-C_6H_4-Bneop, with electron-donating methoxide substituent, the yield is slightly higher (82 %, Table 3, entry 2). Furthermore, 4-Ph-C_6H_4-Bneop reacts with C_6F_6 to give **3ad** in 65 % isolated yield. (Table 3, entry 4). However, for 4-F_3C-C_6H_4-Bneop, containing the strong electron-withdrawing CF_3 substituent, only trace amounts of product were detected (Table 3, entry 5). Thus, Ar-Bneop compounds substituted with *para* electron donors perform better, and those with an electron-withdrawing substituent perform worse compared to those containing electron-neutral substituents.

Table 3. NHC nickel-catalyzed Suzuki-Miyaura cross-coupling reaction using different aryl neopentylglycol boronates



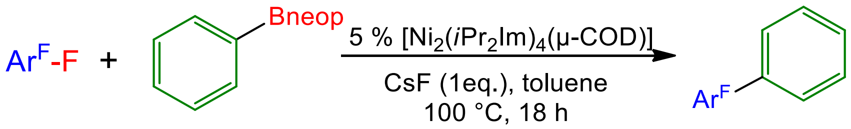
Entry	Ar-Bneop	Product	Yield (%)
1	 **2a**	 **3aa**	72
2	 **2b**	 **3ab**	76

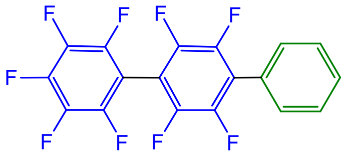
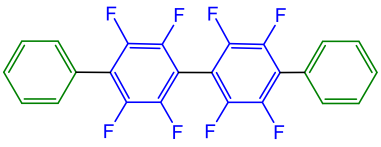
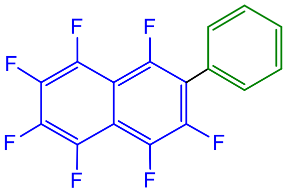
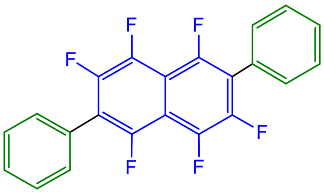
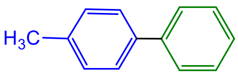
3	 **2c**	 **3ac**	82
4	 **2d**	 **3ad**	65
5	 **2e**	 **3ae**	trace

[a] Isolated yields based on Ar-Bneop, unless otherwise stated. Reaction conditions: $[\mathrm{Ni_2}(^{i}\mathrm{Pr_2Im})_4(\mu\text{-COD})]$ (5 mol %), Ar-Bneop (2 mmol), C_6F_6 (4 mmol), CsF (2 mmol), 10 mL toluene, 100 °C, 18 h.

The last step of our investigations was a test of the scope of the NHC nickel-catalyzed Suzuki-Miyaura cross-coupling reaction using different perfluoroarenes and C_6H_5-Bneop (Table 4). The results reveal that octafluorotoluene, hexafluorobenzene, perfluorobiphenyl and perfluoronaphthalene give the corresponding products in moderate to excellent yields under our optimized conditions (Table 4). For the reaction of C_6H_5-Bneop with perfluorobiphenyl and perfluoronaphthalene, small amounts of bisborylated side products **4ca** (3 %) and **4da** (4 %) were detected. For several partially fluorinated substrates such as pentafluorobenzene, 1,2,4,5-tetrafluorobenzene and 1,3,5-trifluorobenzene, and *p*-fluortoluene only trace amounts of the cross-coupling products were detected using the standard conditions (not shown in Table 4). However, this behavior changed when the fluoroarene was used as the solvent. For the neat reaction of *p*-fluorotoluene with C_6H_5-Bneop, for example, the cross-coupled product **3ea** was isolated in 50 % yield (Table 4, entry 3).

Table 4. NHC nickel-catalyzed Suzuki-Miyaura cross-coupling reaction with different fluoroarenes



Entry	Ar^F-F	Procuct and Yield
1	C_6F_5-C_6F_5 **1c**	 **3ca** (61 %)[b]  **4ca** (3 %)
2	$C_{10}F_8$ **1d**	 **3da** (48 %)[c]  **4da** (4 %)
3	4-H_3C-C_6H_4F **1e**	 **3ea** (50 %)[d]

[a] Reported are isolated yields based on C_6H_5-Bneop. [b] Reaction conditions: $Ni_2(^iPr_2Im)_4(\mu$-COD) (5 mol %), C_6H_5-Bneop (2 mmol), Ar^F-F (2 mmol), CsF (2 mmol), 10 mL toluene, 100 °C, 18 h. [c] Reaction conditions: $[Ni_2(^iPr_2Im)_4(\mu$-COD)] (5 mol %), C_6H_5-Bneop (2 mmol), Ar^F-F (4 mmol), CsF (2 mmol), 10 mL toluene, 100 °C, 18 h. [d] **1e** (2 mL), neat reaction.

In conclusion, we report that $[Ni_2(^iPr_2Im)_4(\mu$-COD)] is an effective catalyst precursor for the Suzuki-Miyaura cross-coupling reaction of perfluorinated arenes with different aryl boronate esters. Among the aryl boronates used (Ar-Beg, Ar-Bneop, Ar-Bpin and Ar-Bcat), the ethyleneglycol (aryl-Beg) and neopentylglycol (aryl-Bneop) esters are the most efficient ones. Furthermore, the use of the additive CsF is vital to this reaction.

EXPERIMENTAL SECTION

General Considerations. NMR spectra were recorded at ambient temperature (^{1}H NMR, 500 MHz; ^{13}C{^{1}H}NMR, 125 MHz; ^{19}F NMR, 470 MHz; ^{19}F{^{1}H}NMR, 188 MHz). ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas ^{13}C{^{1}H}NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm). ^{19}F{^{1}H}NMR and ^{19}F NMR spectra are reported relative to CF_3Cl. GC-MS analyses were performed using a gas chromatograph (column: 5% phenyl methyl siloxane, 30 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C min^{-1}); carrier gas: He

(1.2 mL min^{-1})) equipped with a triple-axis MSD detector operating in EI mode and an auto sampler/injector. High resolution mass spec were obtained with either an atmospheric sample analysis probe (ASAP) or heated-electrospray ionization (HESI) probe. ESI measurements were conducted using a HESI source (spray voltage 3 kV for positive mode, capillary temperature 275 °C). ASAP measurements were conducted using an APCI source (discharge current 3.5 kV, vaporizer temperature 300°C). Mass spectrometric data was acquired at a resolving power of 70,000 (full-width-at-half-maximum, at m/z 200, RFWHM), resulting in a scan rate of >1.5 scans/sec when using an automatic gain control target of 1.0×10^6 and a C-trap inject time of 100 ms.

All manipulations, unless otherwise stated, were carried out under an atmosphere of argon using conventional Schlenk, vacuum-line and glove-box techniques. All reactions were carried out in oven-dried glassware. Toluene and THF were purified by distillation from an appropriate drying agent (sodium with benzophenone as indicator). Nickel catalysts, i.e., ($[Ni_2({}^iPr_2Im)_4(\mu\text{-COD})]$,[9a] $[({}^iPr_2Im)_2Ni_2Br_2]$,[12] $[(Me_2Im)_2Ni_2I_2]$,[13] $[({}^iPr_2Im)_2Ni_2(CO)_2]$,[14] $[(Me_2Im)_2Ni_2(CO)_2]$,[14] $[(dppe)NiCl_2]$,[15] $[(dppp)NiCl_2]$[15] and $[NiIMes_2]$[11] used were prepared according to literature procedures. Boronate esters were prepared according to literature procedures.[17] All other reagents were purchased from commercial suppliers, and were checked for purity by GC-MS and/or ^1H NMR spectroscopy and used as received.

Experimental Procedures and Characterization of Products

General Procedure for the Preparation of Products

[$Ni_2(^iPr_2Im)_4$(μ-COD)] (0.1 mmol, 83 mg), CsF (2 mmol, 304 mg), Ar-Bneop (2 mmol), fluoroarene and toluene (10 mL) were added to a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was heated at 100 °C for 18 h and after that H_2O (5 mL) was added. The product was extracted with EtOAc (3 x 50 mL) and then the combined organic layers were dried over Na_2SO_4, filtered and the volatiles were removed *in vacuo*. The product was purified by column chromatography on silica-gel using hexane as the eluent. The solvent of the product containing fraction of the eluent was evaporated *in vacuo*. The yields provided are based on Ar-Bneop.

Spectroscopic Data of the Products

2,3,4,5,6-Pentafluoro-1,1'-biphenyl (3aa). Following general procedure, a white solid in 72 % yield (351 mg) was obtained from C_6F_6 (4 mmol, 462 μL) and C_6H_5-Bneop (2 mmol, 380 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.52-7.45 (m, 3 H), 7.44-7.41 (m, 2 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 144.2 (d of m, $^1J_{CF}$ = 247.3 Hz), 140.4 (d of m, $^1J_{CF}$ = 253.7 Hz), 137.8 (d of m, , $^1J_{CF}$ = 250.9 Hz), 130.1 (t, $^3J_{CF}$ = 1.5 Hz), 129.3, 128.7, 126.4, 115.9 (m); ^{19}F NMR (470 MHz, $CDCl_3$) δ = -143.26 (m, 2 F), -155.65 (t, J = 21.0 Hz, 1 F), -162.27 (m, 2 F); $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$) δ = -143.28 (dd, J = 8.1, 22.0 Hz, 2 F), -155.68 (t, J = 21.0 Hz, 1 F), -162.31 (td, J = 8.1, 22.0 Hz, 2 F). HRMS (ASAP)[$C_{12}H_5F_5$] calcd. 244.0306, found 244.0305.

Spectroscopic data for **3aa** match with those previously reported in the literature.[3k]

2,3,4,5,6-Pentafluoro-4'-methyl-1,1'-biphenyl (3ab). Following general procedure, a white solid in 76 % yield (390 mg) was obtained from C_6F_6 (4 mmol, 462 μL) and 4-CH_3-C_6H_4-Bneop (2 mmol, 408 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.31 (m, 4 H), 2.42 (s, 3 H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 144.2 (d of m, $^1J_{CF}$ = 247.7 Hz), 140.2 (d of m, $^1J_{CF}$ = 253.3 Hz), 139.4, 137.8 (d of m, $^1J_{CF}$ = 250.7 Hz), 130.0, 129.5, 123.4, 115.9 (m), 21.4; ^{19}F NMR (470 MHz, CDCl$_3$) δ = -143.37 (m, 2 F), -156.15 (t, J = 18.8 Hz, 1 F), -162.46 (m, 2 F); ^{19}F{^{1}H} NMR (188 MHz, CDCl$_3$) δ = -143.39 (dd, J = 8.1, 22.8 Hz, 2 F), -156.17 (t, J = 21.0 Hz, 1 F), -162.50 (td, J = 8.1, 22.8 Hz, 2 F); HRMS (ASAP)[$C_{13}H_7F_5$] calcd. 258.0468, found 258.0462.

Spectroscopic data for **3ab** match with those previously reported in the literature.[3k]

2,3,5,6-Tetrafluoro-4'-methyl-4-(trifluoromethyl)-1,1'-biphenyl (3bb). Following general procedure, a white solid in 90 % yield (554 mg) was obtained from octafluorotoluene (2 mmol, 284 µL) and 4-CH_3-C_6H_4-Bneop (2 mmol, 408 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.38-7.32 (m, 4 H), 2.44 (s, 3 H); ^{13}C{^{1}H}NMR (125 MHz, CDCl$_3$) δ = 144.4 (d of m, $^1J_{CF}$ = 259.5 Hz), 144.1 (d of m, $^1J_{CF}$ = 248.3 Hz), 140.3, 129.8 (t, $^3J_{CF}$ = 2.1 Hz), 129.6, 125.0 (t, $^2J_{CF}$ = 16.4 Hz), 123.1, 120.9 (d of m, $^1J_{CF}$ = 274.0 Hz), 108.2 (m), 21.4; ^{19}F NMR (470 MHz, CDCl$_3$) δ = -56.20 (t, $^3J_{\mathrm{FF}}$ = 18.8 Hz, 3 F), -140.98 (m, 2 F), -141.70 (m, 2 F); ^{19}F{^{1}H} NMR (188 MHz, CDCl$_3$) δ = -56.24 (t, $^3J_{\mathrm{FF}}$ = 21.4 Hz, 3 F), -141.03 (m, 2 F), -141.75 (m, 2 F). HRMS (ASAP)[$C_{14}H_7F_7$] calcd. 308.0430, found 308.0422.

Spectroscopic data for **3bb** match with those previously reported in the literature.[3k]

2,3,4,5,6-Pentafluoro-4'-methoxy-1,1'-biphenyl (3ac). Following general procedure, a white solid in 82 % yield (449 mg) was obtained from C_6F_6 (4 mmol, 462 µL) and *p*-OMe-C_6H_4-Bneop (2 mmol, 440 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.37-7.35 (m, 2 H), 7.03-7.01 (m, 2 H), 3.87 (s, 3 H); ^{13}C{^{1}H}NMR (125 MHz, CDCl$_3$) δ = 160.3, 144.2 (d of m, $^1J_{CF}$ = 247.0 Hz), 140.0 (d of m, $^1J_{CF}$ = 253.3 Hz), 137.8 (d of m, $^1J_{CF}$ = 250.5 Hz), 131.4 (t, $^3J_{CF}$ = 1.8 Hz), 118.4, 115.7 (m), 114.2, 55.4; ^{19}F NMR (470 MHz,

$CDCl_3$) δ = -143.62 (dd, *J* = 8.1, 22.0 Hz, 2 F), -156.51 (t, *J* = 21.1 Hz, 1 F), -162.54 (td, *J* = 8.1, 21.8 Hz, 2 F); $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$) δ = = -143.66 (dd, *J* = 8.0, 22.8 Hz, 2 F), -156.56 (t, *J* = 22.0 Hz, 1 F), -162.59 (td, *J* = 8.0, 22.0 Hz, 2 F). HRMS (ASAP)[$C_{13}H_7F_5O$] calcd. 274.0412, found 274.0409.

Spectroscopic data for **3ac** match with those previously reported in the literature.[51]

2,3,4,5,6-Pentafluoro-1,1':4',1''-terphenyl (3ad). Following general procedure, a white solid in 65 % yield (416 mg) was obtained from C_6F_6 (4 mmol, 462 μL) and PhBneop (2 mmol, 532 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.73-7.66 (m, 2 H), 7.65-7.63 (m, 2 H), 7.52-7.46 (m, 4 H), 7.41-7.38 (tt, *J* = 1.3, 7.4 Hz, 1 H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 142.2, 140.2, 130.6, 128.9, 127.8 127.4, 127.2; due to the low solubility of the compound in $CDCl_3$ the $\underline{C}$-F resonances have not been detected. ^{19}F NMR (470 MHz, $CDCl_3$) δ = -143.13 (m, 2 F), -155.50 (t, *J* = 20.9 Hz, 1 F), -162.12 (m, 2 F); $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$) δ = -143.15 (dd, *J* = 8.1, 22.8 Hz, 2 F), -155.54 (t, *J* = 21.0 Hz, 1 F), -162.12 (td, *J* = 8.1, 22.8 Hz, 2 F). HRMS (ASAP) $[C_{18}H_{10}F_5]^+$ $(M+H)^+$ calcd. 321.0697, found 321.0691.

Spectroscopic data for **3ad** match with those previously reported in the literature.[21]

2,2',3,3',4,5,5',6,6'-Nonafluoro-1,1':4',1''-terphenyl (3ca). Following general procedure, a white solid in 61 % yield (478 mg) was obtained from perfluorodiphenyl (2 mmol, 668 mg) and C_6H_5-Bneop (2 mmol, 380 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.56-7.49 (m, 5 H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 144.1 (d of m, $^1J_{CF}$ = 253.1 Hz), 144.4 (d of m, $^1J_{CF}$ = 252.6 Hz), 144.0 (d of m, $^1J_{CF}$ = 248.3 Hz), 141.0 (m), 137.9 (d of m, $^1J_{CF}$ = 253.7 Hz), 130.1 (t, $^3J_{CF}$ = 2.0 Hz), 129.6, 128.8, 126.8 (t, $^3J_{CF}$ = 2.1

Hz), 123.0 (t, $^{2}J_{CF}$ = 16.5 Hz), 103.7 (d of m, $^{1}J_{CF}$ = 301.0 Hz), 100.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ = -137.28 (m, 2 F), -138.68 (m, 2 F), -142.54 (m, 2 F), -150.37 (m, 1 F), -160.58(m, 2 F); ^{19}F{^{1}H} NMR (188 MHz, $CDCl_3$) δ = -137.28 (m, 2 F), -138.68 (m, 2 F), -142.54 (m, 2 F), -150.37 (tt, J_{FF} = 2.7, 21.0 Hz, 1 F), -160.58 (m, 2 F). HRMS (ASAP)[$C_{18}H_5F_9$] calcd. 392.0247, found 392.0235. Spectroscopic data for **3ca** match with those previously reported in the literature.[9b]

2',2'',3',3'',5',5'',6',6''-Octafluoro-1,1':4',1'':4'',1'''-quaterphenyl (**4ca**). **4ca** (25 mg, 3 %) was obtained as a side product from the reaction mixture of **3ca**. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.55-7.49 (m, 10 H, aryl-*H*); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 130.1 (t, $^{3}J_{CF}$ = 1.8 Hz), 129.6, 128.7; due to the low solubility of the compound in $CDCl_3$ the $\underline{C}$-F resonances have not been detected. ^{19}F NMR (470 MHz, $CDCl_3$) δ = -138.58 (m, 4 F), -142.85 (m, 4 F); ^{19}F{^{1}H} NMR (188 MHz, $CDCl_3$) δ = -138.60 (m, 4 F), -142.88 (m, 4 F). HRMS (ASAP)[$C_{24}H_{10}F_8H]^+(M+H)^+$ calcd. 451.0728, found 451.0711.

Spectroscopic data for **4ca** match with those previously reported in the literature.[22]

1,2,3,4,5,6,8-Heptafluoro-7-phenylnaphthalene (3da). Following general procedure, a white solid in 48 % yield (316 mg) was obtained from perfluoronaphthalene (4 mmol, 1088 mg) and C_6H_5-Bneop (2 mmol, 380 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.55-7.49 (m, 5 H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 130.3 (t, $^{3}J_{CF}$ = 1.9 Hz), 129.4, 128.7, 127.1 (d, J_{CF} = 1.9 Hz) due to the low solubility of the compound in $CDCl_3$ the $\underline{C}$-F resonances have not been detected; ^{19}F NMR (470 MHz, $CDCl_3$) δ = -121.49 (ddd, *J* = 4.0, 19.8, 74.6 Hz, 1 F), -136.90 (m, 1 F), -143.73 (m, 1 F), -146.18

(m, 1 F), -148.72 (m, 1 F), -153.52 (td, *J* = 2.7, 18.5 Hz, 1 F), -155.64 (m, 1 F); $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$) δ = -121.50 (ddd, *J* = 3.8, 18.6, 70.4 Hz, 1 F), -136.92 (m, 1 F), -143.76 (dtt, *J* = 3.4, 16.9, 70.4 Hz, 1 F), -146.19 (m, 1 F), -148.76 (dtt, *J* = 4.1, 18.2, 57.3 Hz, 1 F), -153.56 (tt, *J* = 3.4, 18.6 Hz, 1 F), -155.67 (m, 1 F). HRMS (ASAP)[$C_{16}H_5F_7$] calcd. 330.0274, found 330.0269.

Spectroscopic data for **3da** match with those previously reported in the literature.[23]

1,2,4,5,6,8-hexafluoro-3,7-diphenylnaphthalene (4da). 4da (30 mg, 4 %) was obtained as a side product from the reaction mixture of **3da**. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.57-7.48 (m, 10 H, aryl-*H*); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 130.4, 129.3, 128.6, 127.5 (d, $^3J_{CF}$ = 2.0 Hz); due to the low solubility of the compound in $CDCl_3$ the <u>*C*</u>-F resonances have not been detected. ^{19}F NMR (470 MHz, $CDCl_3$) δ = -122.65 (m, 2 F), -138.94 (m, 2 F), -147.50 (m, 2 F); $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$) δ = -122.65 (m, 2 F), -138.95 (m, 2 F), -147.51 (m, 2 F). HRMS (ASAP)$[C_{22}H_{10}F_6H]^+$ $(M+H)^+$ calcd. 389.0759, found 389.0752. Elemental analysis for $C_{22}H_{10}F_6$ (388.30 [g/mol]): C, 67.78 (68.05); H, 2.58 (2.60). Melting point (uncorrected): 203-205 °C.

4-methyl-1,1'-biphenyl (3ea). Following the general procedure, a white solid in 50 % yield (168 mg) was obtained from the reaction of *p*-fluorotoluene (2 mL) and C_6H_5-Bneop (2 mmol, 380 mg) without toluene as the solvent. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.60-7.58 (m, 2 H), 7.52-7.50 (m, 2 H), 7.45-7.42 (m, 2 H), 7.35-7.32 (m, 1 H), 7.27-7.26 (m, 2 H), 2.41 (s, 3 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$;) δ = 141.2, 138.4, 137.0, 129.5, 128.7, 127.02, 127.0, 126.99, 21.1. HRMS (ASAP) $[C_{13}H_{13}]^+$ $(M+H)^+$ calcd. 169.1012, found 169.1006.

Spectroscopic data for **3ea** match with those previously reported in the literature.[24]

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Notes

The authors declare no competing financial interest.

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Supporting information

The Supporting Information is available free of charge on the ACS Publications website. Copies of ^{1}H, ^{13}C{^{1}H}, ^{19}F NMR and ^{19}F{^{1}H}NMR spectra, and GC-MS data (PDF). Crystal data for **4da**. (CIF)

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