Application of Nickel Complexes Modified by Tridentate *O*,*N*,*O*'-Ligands as Precatalysts in Nickel-Catalyzed C(sp²)–C(sp³) Bond Formations

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1-Acetyl- [**1a**; 3,5-CF₃, 1-C(=O)CH₃] and 1-benzoyl-5-hydroxypyrazolines [**1b**; 3,5-CF₃, 1-C(=O)C₆H₅] have been synthesized and treated with Ni(OAc)₂·4H₂O in the presence of an excess of base [NH₃ or 4-(dimethylamino)pyridine (DMAP)] to form the nickel complexes **4a**–**c**. These complexes have been characterized by various techniques, which indicate a tridentate coordination mode of the ligands. X-ray crystallography determined an O_iN_iO' -coordination of the ligands, in which the ligand is planar, the oxygen donors are *trans* to each other, and the nitrogen donor is in a *cis* position. The other coordination sites on the nickel centre are occu-

Introduction

A huge number of methodologies for the formation of carbon-carbon bonds have been established.^[1] Based on the landmark coupling reactions of the groups of Heck, Suzuki and Negishi in the 1960s and 1970s, transition-metal-catalyzed reactions have been proven to be a powerful technique in organic synthesis, which is outlined by countless applications.^[2] Aside from palladium, nickel-based catalysts play an important role in these transformations.^[3] In the last few decades, various protocols have been established mainly for the coupling of sp²-carbon electrophiles with sp²-carbon nucleophiles. In contrast, the coupling of alkyl electrophiles and nucleophiles is underdeveloped because of various difficulties, e.g. β-hydride elimination, slow reductive elimination steps and high catalyst loadings, which significantly reduce the impact of the method.^[4] Therefore, the design of more active and selective catalysts and the search for suitable reaction conditions is highly desired. Recently, different protocols have been developed for the coupling of sp³-carbon atoms to sp-, sp²- and sp³-carbon atoms.^[5] The addition of suitable ligands is an important factor to influence the reaction outcome.^[6] Furthermore, low cost, availability,

pied by the added base molecules (NH₃ or DMAP). The number of NH₃ or DMAP ligands depends on the nature of the base; in the case of ammonia, one molecule is coordinated to the nickel centre to form a diamagnetic square-planar complex, whereas with DMAP, an octahedral paramagnetic complex with three additional DMAP ligands was observed. Initial catalytic experiments have been performed by applying the complexes in the nickel-catalyzed C(sp²)–C(sp³) cross-coupling of aryl halides with benzylzinc bromides or dialkylzinc reagents; excellent yields and selectivities have been achieved.

easy synthesis, high tunability, flexibility and stability of the ligands have to be considered.^[7] We have recently investigated the potential of 1-acetyl- and 1-benzoyl-5-hydroxypyrazoline ligands in coordination chemistry (Figure 1).^[8] Depending on the metal precursor and the reaction conditions, different coordination modes were feasible. In the case of nickel, 5-hydroxypyrazoline ligands were coordinated in a tridentate O,N,O'-coordination mode as reported by Joshi and co-workers (Figure 1; 4).^[9,11] Due to their high stability and the possibility for the ligand to stabilize charges by conjugation, the complexes could be suitable for catalysis.



Figure 1. Coordination modes of 5-hydroxypyrazolines 1.

On this basis, we report the synthesis and characterization of easily accessible nickel complexes modified by tridentate O,N,O'-ligands and their application in coupling

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chemistry, i.e. the selective nickel-catalyzed $C(sp^2)-C(sp^3)$ cross-coupling of aryl halides with benzylzinc bromides or dialkylzinc reagents.

Results and Discussion

Complex Synthesis and Characterization

The ligands were synthesized according to literature methods (Scheme 1).^[10] Acetohydrazide (7a) and benzohydrazide (7b) were obtained from the reaction of equimolar amounts of hydrazine monohydrate with ethyl acetate (6a) or methyl benzoate (6b), respectively, in ethanol under reflux conditions. The hydrazides 7a and 7b were obtained in good yields as colourless solids and subsequently heated to reflux with hexafluoroacetylacetone (8) in ethanol. 1-Acetyl- and 1-benzoyl-5-hydroxypyrazoline 1 were obtained as crystalline compounds in good yields (69–87%) after recrystallization from *n*-hexane.



Scheme 1. Synthesis of 1.

Having synthesized 1-acetyl- and 1-benzoyl-5-hydroxypyrazoline, the coordination of these ligands to nickel salts was investigated (Scheme 2).^[9,11] A methanol solution of the ligand and an excess of base [NH₃ (17% aqueous solution) or 4-(dimethylamino)pyridine (DMAP)] was added to a solution of Ni(OAc)₂·4H₂O in methanol at room temperature. After stirring overnight, the volatiles were removed in vacuo to obtain brown powders, which were extracted with ethanol and purified by crystallization to obtain red-brown crystals. Crystals suitable for X-ray measurements were grown from ethanol by slow evaporation of the solvent.





The solid-state structures of **4a–c** were characterized by single-crystal X-ray diffraction. Thermal-ellipsoid plots are displayed in Figure 2, and selected bond lengths and angles are listed in Table 1. In agreement with the work of Joshi and co-workers, a square-planar arrangement was observed for **4a** with similar bond lengths and angles.^[9] The tridentate ligand is coordinated in an O,N,O'-mode to create a five- and six-membered ring system, which blocks one side of the metal atom. The ammonia ligand is positioned *cis* to the oxygen donors, and the nitrogen atom of the 5-hydroxy-

pyrazoline ligand connected to the nickel centre is *trans* to the ammonia ligand. Conversely, **4b** and **4c** have octahedral structures with three DMAP molecules connected to the nickel atom. The tridentate ligand is coordinated in the same fashion as seen in **4a**. However, the bond lengths to the nickel atom are slightly elongated. A similar effect was observed for the DMAP ligands in comparison to the ammonia ligand.



Figure 2. Molecular structures of 4a (a), 4b (b) and 4c (c). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



	4 a	4b	4c
Ni–N1	1.816(3)	2.055(3)	2.0440(1)
Ni-O1	1.819(3)	2.021(3)	2.0260(1)
Ni-O2	1.829(4)	2.041(3)	2.0451(2)
Ni–N3	1.919(3)	2.118(3)	2.0950(2)
Ni–N4	—	2.132(3)	2.1648(2)
Ni–N5	—	2.164(3)	2.1383(2)
O(1)-Ni-O(2)	177.36(15)	170.16(1)	169.23(6)
N(1)–Ni–N(3)	171.87(17)	172.16(1)	175.43(8)

Complexes 4a-c were also investigated by ¹H NMR spectroscopy (Table 2). Paramagnetic 4b and 4c gave broad signals, which could not be assigned. In contrast, for diamagnetic 4a, a signal was found at $\delta = 5.93$ ppm, which was assigned to the C-H proton in the six-membered ring. This was further proven by the absence of any signal from the former CH₂ group in the ligand. In addition, a broad signal at $\delta = 1.50$ ppm was attributed to the N–H protons of the ammonia ligand. The coordination of the acetyl and benzoyl functionalities was investigated by IR spectroscopy (Table 2). The absence of signals in the $1610-1725 \text{ cm}^{-1}$ region excludes the possibility of a free or coordinated C=O functionality in the chelated ligand. In addition, strong bands were observed in the 1515–1615 cm⁻¹ region, which are attributed to the C=N functionality. Electron paramagnetic resonance (EPR) spectroscopy was applied to characterize paramagnetic 4b and 4c. Difficulties are known to arise with paramagnetic Ni^{II} complexes with an integer spin (S = 1).^[3b,12] Indeed, the EPR spectra of **4b** and **4c** are silent. Theoretically, in a pure octahedral complex, two unpaired electrons are expected. However, due to the sizeable zero-field splitting for the 3d⁸ configuration usually found for paramagnetic Ni^{II} complexes with an integer spin (S =1), octahedral 4b and 4c are silent. Nevertheless, SQUID measurements confirmed the S = 1 state for 4b and 4c. These compounds both have a constant magnetic moment (μ_{eff}) of ca. 3 μ_{B} in the temperature range of 20–300 K.

Although the reaction mechanism for the formation of 4a-c is unknown, a reasonable mechanism is described in Scheme 3. Firstly, the nickel acetate coordinates to the basic nitrogen atom of the pyrazoline and to the acetyl functionality to form the chelating intermediate **A**. Deprotonation of the hydroxy group then occurs in the presence of the base. The ring opening of the cyclic pyrazoline is initiated by the deprotonation of the acidic CH₂ functionality by

ammonia or DMAP (**B**), which has been proven by labelling studies of the ligand in $[D_4]$ methanol.^[8] The deprotonation process initiates the formation of **4a–c**.



Scheme 3. Potential reaction pathway for the synthesis of 4.

The electrochemistry of **4b** and **4c** was investigated by cyclic voltammetry, and the results are summarized in Figure 3 and Table 3. The first oxidation process is an irrevers-



Figure 3. Cyclic voltammograms of 4b and 4c.

Table 3. Cyclic voltammetric data for 4b and 4c.^[a]

	E^{Ia} [V] (q.r.) ^[b]	E^{Ic} [V] (ir.) ^[b]	E^{IIc} [V] (r.) ^[b]	E^{IIIc} [V] (ir.) ^[b]
4b	-1.05	+1.06	+1.49	+1.88
4c	-1.11	+1.11	+1.47	+1.87

[a] Electrochemical data for **4b** and **4c** at room temp., $[Bu_4N][PF_6]$ as the supporting electrolyte, scan rate = 10 mV/s, platinum disc and glassy carbon working electrode; the potentials are referenced vs. Fc⁺/Fc. Reference electrode: Ag/Ag⁺ in CH₃CN. [b] r. = reversible, ir. = irreversible, q.r. = quasireversible.

Table 2. Analytical properties of 1a, 1b, 4a, 4b, and 4c.

	1a	1b	4 a	4b	4c
¹ H NMR [ppm] ^[a] : 4-C <i>H</i> (<i>H</i>)	3.30-3.80	3.00-3.66	5.93	_	_
¹⁹ F NMR [ppm] ^[a]	-67.7	-67.4	-65.3	_	_
	-81.4	-80.5	-71.8		
IR:					
$v(C=O) [cm^{-1}]^{[b]}$	1699 (s)	1678 (s)	_	_	_
$v(C=N) [cm^{-1}]^{[b]}$	1645 (s)	1639 (s)	1615 (s)	1615 (s)	1617 (s)
	× /		1533 (s)	1533 (s)	1532 (s)

[a] Chemical shifts were measured in [D₁]chloroform at 25 °C. [b] Measured in KBr at 25 °C.

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ible wave with a peak potential at +1.06 V for **4b** and +1.11 V for **4c**. The second oxidation process is observed as a reversible wave with half-wave potentials at +1.49 V ($\delta E = 0.13$ V) for **4b** and +1.47 V ($\delta E = 0.15$ V) for **4c**. The third oxidation process is a low-intensity irreversible wave with a peak potential at +1.88 V for **4b** and +1.87 V for **4c**. Only one reduction process was observed with a peak potential at -1.05 V for **4b** and -1.11 V for **4c**, which is best described as quasireversible.

DFT calculations have been proven to give reliable predictions of the electronic structure of **4b** [B3LYP/6-31G(d) for N, C, O, F, and H; LANL2DZ for Ni].^[13] The energyminimized structure calculated by DFT is in good agreement with that obtained by X-ray diffraction. The molecular orbitals of **4b** are presented in Figure 4. The singly occupied molecular orbitals (SOMOs, -0.157 and -0.186 eV) are nearly degenerate. SOMO1 mainly originates from the tridentate O,N,O'-ligand, whereas SOMO2 comprises d-orbitals of the nickel atom with some contribution from the ligand (Figure 4a).



Figure 4. (a) Molecular orbitals of **4b**. B3LYP level 6-31G(d): basis set for N, C, O, F, and H atoms and LANL2DZ for the Ni atom. (b) Optimized model structure of **4b**' with an overlay of the computed spin density: UB3LYP level 6-31G(d) basis set for N, C, O, F, and H atoms and LANL2DZ for the Ni atom.

The one-electron reduction of **4b** was confirmed by chemical reduction using 1 equiv. of cobaltocene. Complex **4b** and cobaltocene (1:1) were dissolved in tetrahydrofuran (THF) at room temperature, transferred to an EPR tube, and the spectrum was immediately recorded at 77 K (Figure 5). The spectrum shows characteristic signals for a one-electron reduction at the nickel atom, which resulted in the formation of an Ni¹ species **4b**' ($g_x = 2.041$, $g_y = 2.115$, $g_z = 2.271$). The electronic nature of **4b**' suggested by CV and

EPR measurements was confirmed by DFT calculations [UB3LYP level 6-31G(d) basis set for N, C, O, F, and H atoms and LANL2DZ for the Ni atom]. The calculations revealed that the highest occupied molecular orbital of **4b**' is localized on the Ni atom, whereas the lowest unoccupied molecular orbital comprises the π^* -orbital of the ligand. The spin density at the nickel centre (0.9264) may be regarded as the result of a large contribution from the Ni^I species (Figure 4b).



Figure 5. EPR spectrum of the mixture of **4b** (3.0×10^{-2} mmol) and cobaltocene (3.0×10^{-2} mmol) in THF at 77 K.

Nickel-Catalyzed C(sp²)–C(sp³) Bond Formations

The catalytic abilities of 4a-c were investigated in the coupling of aryl halides and benzylzinc bromides or dialkylzinc reagents (Table 4). Initial experiments were performed to find suitable reaction conditions. As a model reaction, the coupling of 1-iodo-4-methoxybenzene (9) with benzylzinc bromide (10) was performed in the presence of 4b (Table 4, Entries 1–4). The reaction outcome was examined at different temperatures. Only at an elevated temperature (70 °C) was the desired coupling product observed in good yields (Table 4, Entry 4). The nickel complexes operated as precatalysts, and no reaction took place in their absence (Table 4, Entry 3). After initial optimization, we established that 2.0 mol-% of 4b in THF performed the $C(sp^2)-C(sp^3)$ bond formation at 70 °C in excellent yield (>99%, Table 4, Entry 4). A similar result (yield >99%) was achieved with 4c (Table 4, Entry 5). The coupling reaction was also examined by using diethylzinc to produce pethylanisole in a yield of 87% (Table 4, Entry 6). To study the effect of β -hydride elimination, the coupling reaction was investigated with α -methylbenzylzinc bromide (Table 4, Entry 7). The desired coupling product was obtained in a yield of 27%. However, nonnegligible amounts of the homocoupled products were detected by GC-MS [18% (2methylbutane-1,3-diyl)dibenzene and 29% 4,4'-dimethoxybiphenyl]. Furthermore, styrene (4%) was observed as the β -hydride elimination product.

With these conditions in hand, different aryl iodides were treated with benzylzinc bromide in the presence of **4b**. Excellent yields (> 99%) were observed for 4-iodotoluene (**12**) and iodobenzene (**13**, Table 4, Entries 9 and 10). In the case of the challenging electron-withdrawing nitro group, no

Table 4. Nickel-catalyzed C–C bond formation of benzylzinc bromide with aryl halides. $\ensuremath{^{[a]}}$

	+	ZnBr 2.0 mol9 THF, 70 °	6 cat. C, 24h	R
9 11-20		- 10		9a 11a-20a
Entry	Complex	Substrate	<i>T</i> [°C]	Yield ^[b] [%]
1	4b	MeO 9	-78	<1
2	4b	MeO 9	r.t.	<1
3	-	MeO 9	70	<1
4	4b	MeO 9	70	>99
5	4c	Meo 9	70	>99
6°	4b	MeO 9	70	87 ^[d]
7 ^e	4b	MeO 9	70	27 ^[f]
8	4b	0 ₂ N 11	70	<1
9	4b	12	70	>99
10	4b	13	70	>99
11	4b	MeO I4	70	84
12	4b	MeO Br	70	93
13	4b	Br 16	70	51
14	4b	F ₃ C Br	70	94
15	4b	N Br 18	70	>99
16	4b	F 19	70	39
17	4b		70	<1

[a] Reaction conditions: substrate (0.67 mmol), benzylzinc bromide (1.00 mmol, 0.5 M in THF), catalyst (2.0 mol-%), THF (2.0 mL), 70 °C, 24 h. [b] Yield of desired product determined by GC–MS and ¹H NMR spectroscopy. [c] Et_2Zn (1.00 mmol) in THF/*n*-hexane solution. [d] 4-Ethylanisole was observed as the product. [e] (α -Methylbenzyl)zinc bromide (1.00 mmol) in THF. [f] 1-Methoxy-4-(1-phenylethyl)benzene was observed as the product. (2-Methylbut-ane-1,3-diyl)dibenzene (18%) and 4,4'-dimethoxybiphenyl (29%) were observed as homocoupled products.

product formation was observed (Table 4, Entry 8). Moreover, some examples of aryl bromides were tested. It was found that the aryl bromides gave lower yields of the coupling products than aryl iodides (Table 4, Entries 11–13). However, 1-bromo-4-(trifluoromethyl)benzene (17), which has a strong electron-withdrawing group, was converted in excellent yield (Table 4, Entry 14). The reaction of the heteroarene 18 with benzylzinc bromide resulted in the quantitative formation of the desired coupling product (Table 4, Entry 15). On the other hand, the coupling of 1-bromo-4fluorobenzene (19) afforded 1-benzyl-4-fluorobenzene (19a) as the product in 39% yield. No activation of the C–F bond was observed. To verify the inactivity of the C–F bonds we tested the coupling reaction of fluorobenzene (20), and no coupling product was formed (Table 4, Entry 17).

In addition, we investigated the influence of the halide on the reaction outcome (Figure 6). The coupling reaction of benzylzinc bromide with substituted anisoles 9, 14 and 21 in the presence of 2 mol-% of 4c was evaluated by using GC–MS (Scheme 4). Complex 4c was highly active for the conversion of the 4-iodoanisol (9), and full conversion was reached within 15 min (turnover frequency = 375 h^{-1}). As expected for bromo- (14) and chloroanisole (21), the catalyst activity decreased compared to that with 9, e.g. t(50%yield) = 5.5 min for 9 and t(50% yield) = 160 min for 14. In particular, the reaction with chloroanisole yielded only 12% of the coupling product after 24 h.



Figure 6. Comparison of different aromatic halides. Reaction conditions: substrate (0.67 mmol), benzylzinc bromide (1.00 mmol, 0.5 M in THF), catalyst **4c** (2.0 mol-%), THF (2.0 mL), 70 °C.



Scheme 4. Coupling reaction with different haloanisoles.

Conclusions

We have synthesized and characterized new nickel complexes with the highly flexible ligands 1-acetyl- [1a; 3,5-CF₃, 1-C(=O)CH₃] and 1-benzoyl-5-hydroxypyrazoline [1b; 3,5-CF₃, 1-C(=O)C₆H₅]. The added base is coordinated to the nickel centre as a coligand. Depending on the nature of the ligand, different numbers of coligands occupy the vacancies on the nickel atom. Finally, the properties of the complexes were investigated in cross-coupling reactions. An excellent performance of the precatalysts was found for $C(sp^2)$ – $C(sp^3)$ bond formations.

Experimental Section

General: All manipulations with oxygen- and moisture-sensitive compounds were performed under dinitrogen by using standard Schlenk techniques. Methanol was used without further purification. ¹H, ¹⁹F and ¹³C NMR spectra were recorded with a Bruker AFM 200 spectrometer (1H: 200.13 MHz; 13C: 50.32 MHz; 19F: 188.31 MHz) and a Bruker AFM 400 spectrometer (¹H: 400.13 MHz; ¹³C: 100.61 MHz; ¹⁹F: 376.07 MHz) by using the proton signals of the deuterated solvents for reference. Single-crystal X-ray diffraction measurements were recorded with an Oxford Diffraction Xcalibur S Saphire spectrometer. IR spectra were recorded either with an Nicolet Series II Magna-IR-System 750 FTIR or a Perkin-Elmer Spectrum 100 FTIR instrument. UV spectra were recorded with a SPECORD® S600 instrument (Analytik Jena, Germany). Cyclic voltammetry was measured with a reference 600 system (GAMRY instruments, USA). EPR spectra were recorded at X-band with an ERS 300 spectrometer (ZWG/Magnettech Berlin/ Adlershof, Germany) equipped with a fused quartz Dewar for measurements at 77 K. The g factors were calculated with respect to a Cr^{3+}/MgO reference (g = 1.9796). Magnetic-susceptibility data were measured from powder samples of solid material in the temperature range 2-300 K with a SQUID susceptometer with a field of 1.0 T (MPMS-7, Quantum Design, calibrated with a standard palladium reference sample, error < 2%). Multiple-field variabletemperature magnetization measurements were performed at 1, 4 and 7 T in the range 2-300 K with the magnetization equidistantly sampled on a 1/T temperature scale. The experimental data were corrected for underlying diamagnetism by use of tabulated Pascal's constants^[14] as well as for temperature-independent paramagnetism. The susceptibility and magnetization data were simulated with julX for exchange-coupled systems.^[15] The simulations are based on the usual spin-Hamilton operator for mononuclear complexes with spin S = 5/2:

$$\hat{H} = g\beta \hat{\vec{S}} \cdot \vec{B} + D[\hat{S}_z^2 - 1/3S(S+1) + E/D(\hat{S}_x^2 - \hat{S}_y^2)]$$

where g is the average electronic g value and D and E/D are the axial zero-field splitting and rhombicity parameters, respectively. Diagonalization of the Hamiltonian was performed with the routine ZHEEV from the LAPACK Library,^[16] and the magnetic moments were obtained from a first-order numerical derivative dE/dB of the eigen values. The powder summations were performed by using a 16-point Lebedev grid.^[17] Intermolecular interactions were considered by using a Weiss temperature, Θ_W , as perturbation of the temperature scale, $kT' = k(T - \Theta_W)$ for the calculation.

Synthesis of 1-Acetyl-5-hydroxy-3,5-bis(trifluoromethyl)pyrazoline (1a): To a solution of 1,1,1,5,5,5-hexafluoropentane-2,4-dione (8, 55.8 mmol) in ethanol (60 mL) was added a solution of acetohydrazide (55.8 mmol) in ethanol (60 mL). After heating the mixture to reflux for 5 h, the solvent was removed in vacuo. The colourless residue was purified by recrystallization from *n*-hexane or by sublimation under high vacuum. Yield: 12.2 g (83%, colourless crystals). ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 5.98 (br. s, 1 H, OH),

3.30–3.80 (m, 2 H, CH₂), 2.29 [s, 3 H, C(=O)CH₃] ppm. ¹³C NMR (50 MHz, CDCl₃, 25 °C): δ = 173.3, 143.6 (m), 120.6 (m), 92.5 (m), 41.4 (CH₂), 22.4 (H₃CC=O) ppm. ¹⁹F NMR (188 MHz, CDCl₃, 25 °C): δ = -67.7, -81.4 ppm. IR (KBr): \tilde{v} = 3393 (br.), 1699 (s), 1645 (s), 1456 (s), 1427 (m), 1378 (m), 1338 (s), 1276 (s), 1198 (s), 1156 (s), 1116 (m), 1099 (m), 1068 (w), 1041 (w), 1026 (w), 996 (w), 924 (m), 875 (m), 760 (m), 734 (s), 658 (w), 621 (w), 581 (m), 521 (w), 501 (w), 474 (w) cm⁻¹. HRMS: calcd. for C₇H₇F₆N₂O₂ [M + H]⁺ 265.04117; found 265.04031.

1-Benzoyl-5-hydroxy-3,5-bis(trifluoromethyl)pyrazoline (1b): To a solution of 8 (55.8 mmol) in ethanol (60 mL) was added a solution of benzohydrazide (55.8 mmol) in ethanol (60 mL). After heating the mixture to reflux for 5 h, the solvent was removed in vacuo. The colourless residue was purified by recrystallization from ethanol/ *n*-hexane (9:1). Yield: 15.9 g (87%, colourless crystals). ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 7.84–7.92 (m, 2 H, Ar), 7.40–7.65 (m, 3 H, Ar), 6.40 (br. s, 1 H, OH), 3.00–3.66 (m 2 H, CH₂) ppm. ¹³C NMR (50 MHz, CDCl₃, 25 °C): δ = 171.6, 144.1, 143.7, 133.3, 131.6, 130.5, 128.3, 94.2, 93.8, 41.4 (CH₂) ppm. ¹⁹F NMR (188 MHz, CDCl₃, 25 °C): δ = -67.4, -80.5 ppm. IR (KBr): \tilde{v} = 3391 (br.), 1678 (s), 1639 (m), 1456 (m), 1439 (m), 1336 (s), 1308 (s), 1279 (s), 1175 (s), 1135 (s), 1116 (s), 1077 (s), 1027 (m), 1009 (m), 907 (w), 872 (w), 834 (w), 792 (w), 758 (w), 717 (s), 694 (m), 674 (w), 618 (w), 499 (w) cm⁻¹. HRMS: calcd. for $C_{12}H_9F_6N_2O_2$ $[M + H]^+$ 327.05627; found 327.05569.

Synthesis of 4a: To a methanol (5.0 mL) solution of Ni(OAc)₂ (1.20 mmol) was added 1b (0.92 mmol) in methanol (5.0 mL) and NH₃ (17% in water, 5.0 mL). The solution was heated to 60 °C and stirred overnight. After removal of the volatiles in vacuo, a brown solid was obtained. The residue was crystallized from ethanol. Crystals suitable for X-ray diffraction were obtained from an ethanol solution at room temperature. Yield: 0.25 g (51%, brown crystals). M.p. 192–193 °C. ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 7.83 (m, 2 H, Ar), 7.31 (m, 3 H, Ar), 5.93 (s, 1 H, CH), 1.50 (s, 3 H, NH₃) ppm. ¹³C NMR (100.61 MHz, CDCl₃, 25 °C): δ = 171.9, 157.2, 156.9, 143.4, 131.1, 128.8, 128.4, 91.5 ppm. ¹⁹F NMR (188 MHz, C₆D₆, 25 °C): δ = -65.3, -71.8 ppm. IR (KBr): \tilde{v} = 3430 (br.), 2914 (br.), 1615 (s), 1533 (s), 1444 (m), 1363 (m), 1328 (w), 1266 (s), 1228 (s), 1195 (s), 1159 (s), 1068 (m), 1007 (m), 950 (w), 880 (w), 806 (m), 758 (w), 715 (m), 701 (w), 686 (w), 614 (w), 531 (w) cm⁻¹. HRMS: calcd. for $C_{12}H_{10}F_6N_3NiO_2 [M + H]^+ 400.00307$; found 400.00305. C12H9F6N3NiO2·H2O (417.9): calcd. C 34.49, H 2.65, N 10.05; found C 34.70, H 2.55, N 9.71. UV/Vis: λ (ε) = 367.5 $(11800), 405.0 (11600 \text{ M}^{-1} \text{ cm}^{-1}) \text{ nm}.$

Synthesis of 4b: To a mixture of 1b (0.92 mmol) and DMAP (9.2 mmol) in methanol (10 mL) was added a solution of Ni(OAc)₂ (1.20 mmol) at room temperature. The solution was stirred overnight. After removal of the volatiles in vacuo, a brown solid was obtained. The residue was crystallized from ethanol. Crystals suitable for X-ray diffraction were obtained from ethanol solution at room temperature. Yield: 0.39 g (57%, first harvest, brown crystals). M.p. 191-192 °C. ¹H, ¹³C and ¹⁹F NMR were not measured because of paramagnetism. IR (KBr): $\tilde{v} = 3433$ (br.), 2921 (br.), 1615 (s), 1533 (s), 1444 (m), 1363 (m), 1328 (w), 1266 (s), 1228 (s), 1196 (s), 1159 (s), 1068 (m), 1007 (m), 950 (w), 880 (w), 806 (m), 759 (w), 715 (m), 701 (w), 685 (w), 646 (w), 613 (w), 585 (w), 531 (w) cm⁻¹. HRMS: calcd. for $C_{33}H_{36}F_6N_8NiO_2$ [M + $H - 2 \ dmap]^+$ 505.06092; found 505.05975. $C_{33}H_{36}F_6N_8NiO_2$ (749.40): calcd. C 52.89, H 4.84, N 14.95; found C 53.66, H 4.94, N 15.11. UV/Vis: λ (ε) = 360.5 (2200), 405.5 (1800 m⁻¹ cm⁻¹) nm.

Synthesis of 4c: To a mixture of 1a (0.37 mmol) and DMAP (3.70 mmol) in methanol (5 mL) was added a solution of Ni-



(OAc)₂ (0.48 mmol) at room temperature. The solution was stirred overnight. After removing the volatiles in vacuo, a brown solid was obtained. Crystals suitable for X-ray diffraction were obtained from ethanol solution at room temperature. Yield: 0.14 g (55%, brown crystals from ethanol). M.p. 205–206 °C. ¹H, ¹³C and ¹⁹F NMR were not measured because of paramagnetism. IR (KBr): $\bar{\nu}$ = 3438 (br.), 2921 (br.), 1617 (s), 1532 (s), 1446 (m), 1428 (w), 1388 (s), 1324 (m), 1265 (s), 1227 (s), 1182 (s), 1169 (s), 1159 (s), 1138 (s), 1108 (s), 1069 (w), 1054 (m), 1014 (m), 1006 (s), 982 (w), 951 (w), 906 (w), 828 (w), 807 (s), 768 (m), 759 (m), 742 (w), 683 (m), 641 (w), 607 (w), 581 (w), 531 (m), 483 (w) cm⁻¹. HRMS: calcd. for C₂₈H₃₅F₆N₈NiO₂ [M + H − 2 dmap]⁺ 443.04527; found 443.04435. C₂₈H₃₄F₆N₈NiO₂ (687.33): calcd. C 48.93, H 4.99, N 16.30; found C 49.47, H 5.01, N 16.36. UV/Vis: λ (ε) = 334.5 (5900), 368.0 (5900 M⁻¹ cm⁻¹) nm.

General Procedure for the Catalytic C–C Coupling Reaction: A Schlenk flask was charged with an appropriate amount of 4 (0.014 mmol, 2.0 mol-%) and the corresponding bromo- or iodo-arene (0.67 mmol). The flask was repeatedly flushed with nitrogen and evacuated. THF (2.0 mL) was added followed by benzylzinc bromide (1.00 mmol, 0.5 M in THF). The flask was sealed and heated at 70 °C for 24 h. The mixture was cooled in an ice bath, and dichloromethane and water were added. The aqueous layer was extracted with dichloromethane, and the collected organic layers were washed with water, brine and dried with Na₂SO₄. After filtration and removal of the solvent, the residue was dissolved in diethyl ether and purified by filtration through a short plug of silica gel. The analytical properties of the products are in agreement with literature data.

1-Benzyl-4-methoxybenzene (9a): ¹H NMR (200 MHz, CDCl₃): δ = 6.85–7.49 (m, 9 H), 4.06 (s, 2 H, CH₂), 3.86 (s, 3 H, CH₃) ppm.

¹³C NMR (50 MHz, CDCl₃): δ = 159.7, 143.1, 141.5, 129.9, 129.6, 129.0, 126.4, 121.9, 115.4, 112.0, 55.3, 42.0 ppm. MS (ESI): *m*/*z* (%) = 198 (100) [M]⁺, 183 (16), 167 (36), 153 (13), 121 (28), 91 (12).

1-Benzyl-4-methylbenzene (12a):^[18] ¹H NMR (200 MHz, CDCl₃): δ = 7.06–7.31 (m, 9 H), 3.98 (s, 2 H, CH₂), 2.36 (s, 3 H, CH₃) ppm.¹³C NMR (50 MHz, CDCl₃): δ = 141.5, 138.2, 135.6, 129.3, 129.0, 128.9, 128.8, 128.5, 128.4, 126.1, 41.6, 21.1 ppm. MS (ESI): *m*/*z* (%) = 182 (75) [M]⁺, 167 (100), 152 (14), 89 (14).

Diphenylmethane (13a):^[19] ¹H NMR (200 MHz, CDCl₃): δ = 7.10–7.37 (m, 10 H), 3.95 (s, 2 H, CH₂) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 141.1, 128.9, 128.5, 126.1, 41.6 ppm. MS (ESI): *m*/*z* (%) = 168 (100) [M]⁺, 153 (25), 91 (22), 83 (13), 65 (14).

1-Benzyl-3-Methoxybenzene (15a):^{[20] 1}H NMR (200 MHz, CDCl₃): $\delta = 6.85-7.49$ (m, 9 H), 4.06 (s, 2 H, CH₂), 3.86 (s, 3 H, CH₃) ppm.¹³C NMR (50 MHz, CDCl₃): $\delta = 159.7$, 143.1, 141.5, 129.9, 129.6, 129.0, 126.4, 121.9, 115.4, 112.0, 55.3, 42.0 ppm. MS (ESI): m/z (%) = 198 (100) [M]⁺, 183 (20), 167 (40), 152 (15), 121 (12), 91 (19).

1-Benzyl-4-(trifluoromethyl)benzene (17a):^[21] ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (d, *J* = 8.1 Hz, 2 H), 7.04–7.29 (m, 7 H), 4.07 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 145.3, 140.0, 129.2, 128.9, 128.7, 127.0, 126.5, 125.4, 41.7 ppm. ¹⁹F NMR (377 MHz, CDCl₃): δ = -62.7 ppm. MS (ESI): *m*/*z* (%) = 236 (55) [M]⁺, 217 (7), 215 (10), 168 (11), 167 (100), 166 (18), 165 (40), 152 (12).

2-Benzyl-5-methylpyridine (18a): ¹H NMR (200 MHz, CDCl₃): δ = 8.88 (s, 1 H), 7.04–7.29 (m, 7 H), 4.49 (s, 2 H), 2.33 (s, 3 H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 157.3, 147.7, 141.5, 137.2, 132.9, 129.4, 128.8, 128.4, 128.3, 42.2, 18.1 ppm. MS (ESI): *m*/*z* (%) = 182 (100) [M]⁺, 167 (15), 40 (42).

Table 5. Data collection and refinement parameters for 4a, 4b and 4c.

	4a	4b	4c	
Empirical formula	C ₁₂ H ₉ F ₆ N ₃ NiO ₂	$C_{34}H_{37}Cl_3F_6N_8NiO_2$	$C_{28}H_{34}F_6N_8NiO_2$	
Formula mass [g/mol]	399.93	868.78	687.34	
Temperature [K]	150(2)	150(2)	150(2)	
Space group	C2/c	$P2_1/c$	P3221	
Unit-cell dimensions:				
<i>a</i> [Å]	20.259(3)	17.6376(11)	18.3746(4)	
<i>b</i> [Å]	8.6098(10)	12.1712(8)	18.3746(4)	
c [Å]	16.506(2)	19.2313(11)	15.8986(4)	
	90	90	90	
β [°]	97.916(13)	110.364(7)	90	
γ [°]	90	90	120	
Volume [Å ³]	2851.6(6)	3870.4(4)	4648.63(18)	
Z	8	4	6	
$D_{\text{calcd.}} [\text{g/cm}^3]$	1.863	1.491	1.473	
<i>F</i> (000)	1600	1784	2136	
Crystal size [mm]	$0.34 \times 0.17 \times 0.04$	$0.41 \times 0.18 \times 0.17$	$0.68 \times 0.26 \times 0.20$	
θ range [°]	3.42-25.00	3.37-25.00	3.39-25.00	
Index rages	$-24 \le h \le 23$	$-20 \le h \le 20$	$-20 \le h \le 21$	
	$-9 \le k \le 10$	$-14 \le k \le 13$	$-21 \le k \le 19$	
	$-19 \le l \le 18$	$-22 \le l \le 22$	$-18 \le l \le 16$	
Reflections collected	5643	16500	32336	
Independent reflections	2509 [R(int) = 0.0808]	6805 [R(int) = 0.0601]	5436 [R(int) = 0.0391]	
Completeness to $\theta = 25.00^{\circ}$	99.8%	99.8%	99.7%	
Relative transmission factors	0.9445, 0.6395	0.8788, 0.7403	0.8722, 0.6465	
Parameters	218	530	468	
GOF	0.708	0.920	0.987	
Final <i>R</i> indices $[I > 2\sigma(I)]^{[a,b]}$	$R_1 = 0.0468, wR_2 = 0.0492$	$R_1 = 0.0520, wR_2 = 0.0915$	$R_1 = 0.0280, wR_2 = 0.0529$	
R indices (all data) ^[a,b]	$R_1 = 0.1201, wR_2 = 0.0597$	$R_1 = 0.0999, wR_2 = 0.0992$	$R_1 = 0.0343, wR_2 = 0.0540$	
$[a] R = \sum F - F /\sum F [b] w R = \sum \sum F - \sum F $				

[a] $R_1 = \Sigma ||F_o| - |F_c|| \Sigma F_o$. [b] $wR_2 = \{\Sigma [(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$.

1-Benzyl-4-fluorobenzene (19a):^{[22] 1}H NMR (400 MHz, CDCl₃): δ = 7.12–7.30 (m, 9 H), 4.69 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 161.4, 140.9, 136.7, 130.3, 128.8, 128.5, 126.2, 115.2 ppm. ¹⁹F NMR (377 MHz, CDCl₃): δ = -117.3 ppm. MS (ESI): *m*/*z* (%) = 186 (100) [M]⁺, 171 (9), 165 (28), 109 (18), 91 (14).

Single-Crystal X-ray Structure Determination:^[23] Crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N₂ flow. The data were collected by using an Oxford Diffraction Xcalibur S Sapphire at 150(2) K (Mo- K_a radiation, $\lambda =$ 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 software package. The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model (Table 5). CCDC-843194 (for 4a), -843195 (for 4b) and -843196 (for 4c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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