A comprehensive study of the effects of spectator ligands, transition metals and lithium halide additives on the efficiency of iron, nickel and palladium-catalyzed cross-coupling reactions of cyclohexyl magnesium bromide with fluorinated bromobenzenes

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Abstract

Thirteen mono-, bis- and trifluorinated bromobenzene derivatives have been coupled with cyclohexyl magnesium bromide or the corresponding lithiumchloride or lithiumbromide adducts. Iron, nickel and palladium complexes of the general formula [MCl_2(dppx)] (x = $(CH_2)_n$, n = 1, 2, 3) have been used as the precatalysts. Palladium based catalysts give high yields of the coupling product with the Grignard reagent itself whereas lithium halides are needed as additives to achieve comparable efficiencies if nickel and iron catalysts are used. Yields also depend on the chain length of the bridging units and on the fact whether fluorine substituents are present in *ortho* position with respect to bromine.

Keywords: Iron, nickel, palladium, cross-coupling reactions, Grignard reagents

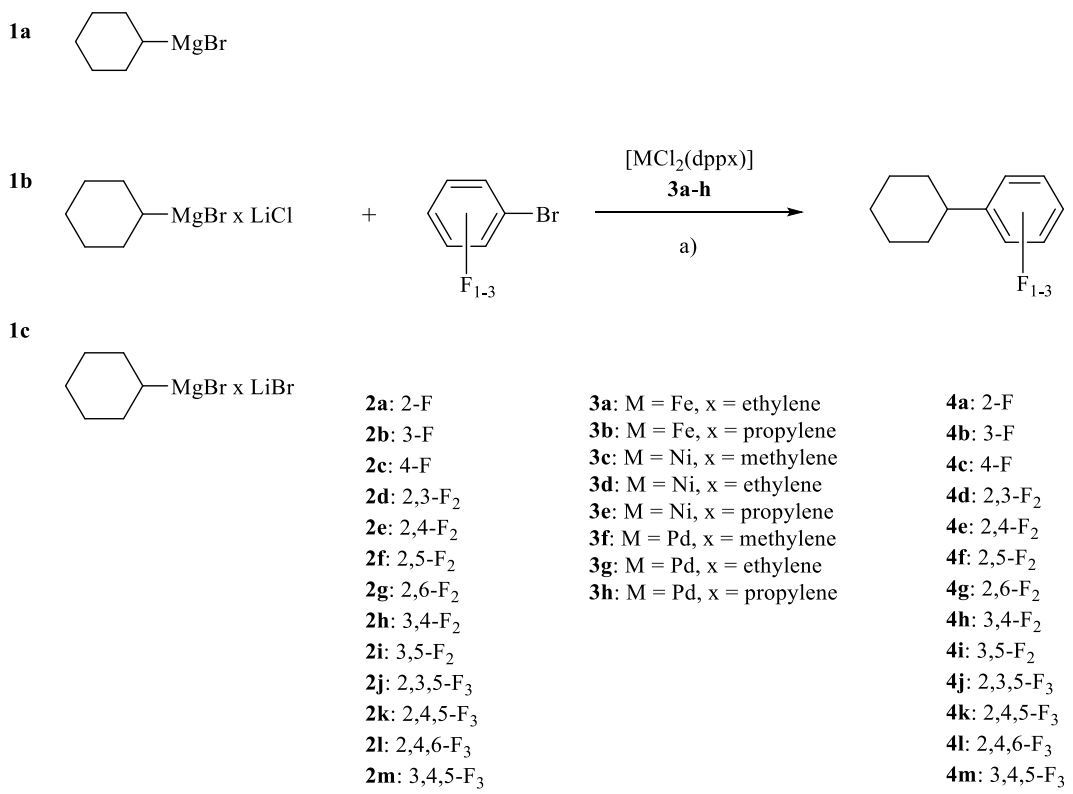
Introduction

Transition metal-catalyzed cross-coupling reactions have been shown to be an invaluable tool in terms of C-C bond formations. Most commonly organic halides are coupled with various nucleophiles like boronic acid derivatives, tin or zinc or lithium organic compounds or Grignard reagents.[1,2] Besides to the use of palladium and nickel a number of iron and even vanadium catalyzed variations of these reactions have been reported.[3-43] To the best of our knowledge all reported iron catalyzed cross coupling reactions related to our work describe the coupling of an aryl Grignard reagent with an alkyl halide. We became interested in this field in connection with

the search for efficient synthetic protocols for the cross coupling of cyclohexyl magnesium bromide with various fluorinated bromo benzene derivatives as electrophiles. The resulting cyclohexylbenzene derivatives and related compounds are widely used as liquid crystalline materials or as precursors in the synthesis of those.[44-50] Up to now they are mainly produced by cross-coupling reactions of the Suzuki type.[51-53] Nevertheless, this reaction protocol exhibits some major intrinsic disadvantages. First of all, the corresponding boronic acid esters have to be purchased or synthesized. Moreover, stoichiometric amounts of a base have to be applied and there are quite substantial amounts of waste. On the other hand, cross-coupling reactions involving Grignard reagents have to be performed under inert conditions and ideally concentrations of Grignard solutions have to be determined by titration before the coupling reaction itself. Of course solutions of Grignard reagents also have to be purchased or synthesized. Nevertheless, in most cases they will be cheaper compared to boronic acid esters. If Grignard reagents are to be used as nucleophiles in coupling reactions with aryl bromides or chlorides it has been shown that lithium halide adducts of the Grignard reagents show an enhanced reactivity.[54-58] The aim of this research therefore was to gain an understanding of the mutual effects of various transition metals, different spectator ligands, lithium halide additives and the substitution pattern of the respective bromobenzene derivative on the efficiency of the cross-coupling reaction. Moreover, we were highly interested to find a synthetic protocol that allows for the use of iron catalysts with yields that should be comparable to the very well working palladium catalysts.

Results and Discussion

Scheme 1 shows the coupling reactions that have been performed during the investigation described herein. Grignard reagents and the corresponding LiCl or LiBr adducts as well as the precatalysts [$FeCl_2$(dppe)], **3a**, [$FeCl_2$(dppp)], **3b**, [$NiCl_2$(dppm)], **3c**, [$NiCl_2$(dppe)], **3d**, [$NiCl_2$(dppp)], **3e**, [$PdCl_2$(dppm)], **3f**, [$PdCl_2$(dppe)], **3g**, and [$PdCl_2$(dppp)], **3h**, have been produced following literature procedures.[59-61] All fluorinated bromobenzene derivatives **2a-m** have been obtained from commercial sources. The resulting coupling products **4a-m** have been purified by column chromatography. Table 1 summarizes the isolated yields of **4a-m** for each of the catalytic reactions. **4a-c** as well as **4d** and **4i** have been synthesized by catalytic cross coupling reactions before.[3-43] Nevertheless, in those cases always the coupling of an aryl Grignard reagent with an alkyl halide has been investigated.



Scheme 1. Cross-coupling reactions of cyclohexyl magnesium bromide or the corresponding LiCl or LiBr adducts with various fluorinated bromobenzene derivatives employing nine different Fe, Ni and Pd precatalysts. a) 3 mol% **3a-h**, THF, r.t., 24 h.

From Table 1 some general trends get obvious. In all combinations that have been investigated precatalysts with dppm ligands give lower yields than those with dppe ligands with the best yields being achieved using dppp ligands. This behaviour has been explained before by the acceleration of migration reactions leading to increased yields of catalytic reactions at palladium complexes with large P-M-P angles.[62-64] In addition, it can be concluded that Ni and Fe in most cases give very similar results whereas Pd is the most effective transition metal for the precatalysts. With regard to the used nucleophiles simple Grignard reagents show the lowest reactivity whereas the LiCl and LiBr adducts give rise to higher yields of **4a-m** if all other parameters are identical. In most cases the LiBr adduct works best although there are some examples where LiCl and LiBr give very similar or identical results. It can also be seen from the results that the use of the LiCl or LiBr adducts leads to significantly increased yields for nickel and iron containing precatalysts, which are then getting acceptable to excellent. The effect of lithium halides has been rationalized by the fact that by these additives the formation of polymeric aggregates of the Grignard compounds is hampered. Moreover, highly nucleophilic complexes with magnesiate character $[RMgCl_2]Li$ are responsible for an enhanced reactivity toward electrophiles.[65-67]

Table 1. Yields of **4a-m** depending on the used nucleophiles, electrophiles and precatalysts **3a-h**. The highest yield for each transition metal is presented with an italic number, the highest yield for each product is shown as a bold number

		nucleophile: CyMgBr							
		[$FeCl_2$(dppx)]			[$NiCl_2$(dppx)]			[$PdCl_2$(dppx)]	
product	substitution	**3a** (dppe)	**3b** (dppp)	**3c** (dppm)	**3d** (dppe)	**3e** (dppp)	**3f** (dppm)	**3g** (dppe)	**3h** (dppp)
4a	2-F	35	*50*	10	40	*60*	30	53	***55***
4b	3-F	40	*65*	30	53	***80***	50	65	*75*
4c	4-F	55	*65*	45	52	*60*	55	70	***85***
4d	2,3-F_2	30	*35*	15	30	*40*	25	45	***55***
4e	2,4-F_2	25	*45*	27	35	*50*	50	55	***60***
4f	2,5-F_2	30	*55*	40	50	*60*	40	66	***75***
4g	2,6-F_2	20	*30*	10	30	*35*	20	35	***40***
4h	3,4-F_2	55	*60*	55	60	*70*	60	75	***80***
4i	3,5-F_2	75	*85*	70	78	*89*	91	94	***97***
4j	2,3,5-F_3	50	*65*	20	55	*73*	40	60	***75***
4k	2,4,5-F_3	40	*63*	25	50	*68*	35	50	***75***
4l	2,4,6-F_3	35	***45***	15	30	*40*	25	30	***45***
4m	3,4,5-F_3	70	***80***	50	66	*65*	48	75	***80***

		nucleophile: CyMgBr × LiCl							
		[$FeCl_2$(dppx)]			[$NiCl_2$(dppx)]			[$PdCl_2$(dppx)]	
product	substitution	**3a** (dppe)	**3b** (dppp)	**3c** (dppm)	**3d** (dppe)	**3e** (dppp)	**3f** (dppm)	**3g** (dppe)	**3h** (dppp)
4a	2-F	40	*55*	35	45	*60*	55	57	***65***
4b	3-F	65	*80*	40	65	***85***	55	76	***85***
4c	4-F	75	*85*	67	71	*85*	80	85	***90***
4d	2,3-F_2	50	***60***	27	45	*55*	40	55	***60***
4e	2,4-F_2	40	*65*	30	45	*67*	65	70	***80***
4f	2,5-F_2	50	*70*	45	50	*65*	50	70	***85***
4g	2,6-F_2	45	*50*	15	40	*50*	30	43	***55***
4h	3,4-F_2	70	*80*	60	67	*75*	70	78	***85***
4i	3,5-F_2	80	*90*	88	93	*96*	95	98	***99***
4j	2,3,5-F_3	55	*70*	30	60	*75*	50	65	***80***
4k	2,4,5-F_3	40	*60*	35	55	*75*	45	60	***80***
4l	2,4,6-F_3	50	***55***	20	40	*45*	35	45	***55***
4m	3,4,5-F_3	75	*85*	60	65	*73*	65	80	***90***

Table 1 (continued)

		nucleophile: CyMgBr × LiBr							
		[$FeCl_2$(dppx)]		[$NiCl_2$(dppx)]			[$PdCl_2$(dppx)]		
product	substitution	**3a** (dppe)	**3b** (dppp)	**3c** (dppm)	**3d** (dppe)	**3e** (dppp)	**3f** (dppm)	**3g** (dppe)	**3h** (dppp)
4a	2-F	45	*60*	40	52	*70*	65	70	***73***
4b	3-F	80	*90*	55	75	*88*	70	90	***95***
4c	4-F	90	*95*	89	94	*98*	88	95	***100***
4d	2,3-F_2	55	*65*	40	60	*75*	50	66	***80***
4e	2,4-F_2	70	*75*	40	65	*75*	70	77	***85***
4f	2,5-F_2	75	*85*	50	75	*90*	60	80	***95***
4g	2,6-F_2	50	*70*	30	45	*65*	45	65	***75***
4h	3,4-F_2	75	*85*	65	75	*80*	75	88	***97***
4i	3,5-F_2	90	*95*	90	97	***100***	95	99	***100***
4j	2,3,5-F_3	60	*70*	50	65	*75*	60	85	***95***
4k	2,4,5-F_3	65	*75*	45	58	*80*	50	80	***90***
4l	2,4,6-F_3	50	***66***	30	40	*50*	35	50	*65*
4m	3,4,5-F_3	80	*90*	65	80	*88*	70	90	***98***

There also is a profound effect of the electrophile used in terms of the substitution positions being highly influential on the yield of coupling products **4a**-**m**. All bromobenzene derivatives with fluorine substituents in *ortho* positions show lower yields than the corresponding electrophiles that are only substituted in *meta* or *para* position with respect to the bromine function. If *ortho* fluorinated bromobenzenes are used, the amount of the homo-coupling product dicyclohexyl, which is observed in GC-MS measurements of the crude reaction mixtures, increases. In addition, nucleophiles **2d**, **2f** and **2j** with fluorine atoms in 2,3 and 2,5 position show side reactions in which obviously also C-F bonds were activated if Grignard compounds without lithium halide additives are used. The corresponding fluorine NMR spectra of crude reaction mixtures are depicted in Figure 1. If **2d** is employed in the reaction the main product is the expected cross coupled compound **4d**. Nevertheless, fluorine NMR also shows the formation of **4a** and **4b** in significant amounts besides traces of other compounds that also give rise to singlets in the ^{19}F NMR spectrum which means that also only one fluorine atom is present Figure 1, upper spectrum). The formation of **4a** and **4b** means that formally one fluorine substituent in **2d** is replaced by a hydrogen atom. This might happen by a C-F bond cleavage in terms of an oxidative addition and subsequent hydrolysis of the organometallic species without an intermediate C-C coupling with the Grignard compound. The reaction mixture from the reaction of **2f** also demonstrates the formation of the cross-coupling product **4f** as well as the formation of **4a** and **4b** (Figure 1, middle spectrum). Moreover, there is another singlet of high intensity at δ -118.5 ppm which might be attributed to a cross-coupling compound in which C-C bond formation also occurred at the position of the former fluorine substituent producing either 1,2-

dicyclohexyl-5-fluorobenzene or 1,3-dicyclohexyl-6-fluorbenzene. The situation gets even more complicated if the trifluorinated substrate **2j** is reacted with CyMgBr in the presence of a suitable catalyst. The ^{19}F NMR spectrum of a crude reaction mixture is depicted in Figure 1 as the lower spectrum. Besides one doublet of doublets and two additional doublets representing the expected product **4j** it gets obvious that significant amounts of **4f** have also been formed whereas only very small traces of **4d** are visible (not marked in Figure 1). In addition, also the formation of **4a** and **4b** as well as of the unknown compound from the reaction of **2f** is detectable. But there are at least two more compounds exhibiting two fluorine substituents as shown by doublets at δ -132.5, -116.1 and -115.2 ppm and three products with only one fluorine left as verified by singlets at δ -131.1, -124.6 and -111.4 ppm. In summary, there seems to be a mutual activating effect triggering an additional C-F activation reaction if two fluorine substituents are either in *ortho* or *para* position (or both) relative to each other and one of the fluorine atoms is *ortho* with respect to the bromine substituent. Nevertheless, these side reactions are almost completely supressed by the addition of lithium halides (Table 1). The activation of C-F bonds in Suzuki-Miyaura reactions using nickel precatalysts has recently been described.[68] Nevertheless, metal fluorides as ZrF_4 or TiF_4 had to be added to achieve the reaction in the case of the presence of additional electron-withdrawing substituents. In addition, the formation of side products has also been shown in a highly related study on the cross coupling of CyMgBr with bromobenzene catalyzed by palladium NHC complexes.[69]

Conclusions

Thirteen bromobenzene derivatives with one, two or three additional fluorine substituents have been reacted with cyclohexyl magnesium bromide or the corresponding lithium chloride or lithium bromide adducts to produce the respective cross coupling products. In the survey precatalysts of the general formula $[MCl_2(dppx)]$ ($x = (CH_2)_n$, n = 1, 2, 3) have been used with Fe, Ni and Pd as the transition metals. For all substitution positions of fluorine the dppp complexes produce the highest yield of coupling products for each of the transition metals. In addition, palladium based catalysts in almost all reactions give the highest yields of the coupling products. If not the pure Grignard reagents themselves but their lithium halide adducts are introduced to the reactions nickel and iron catalysts achieve comparable efficiencies. In terms of a cost-benefit analysis the preferred protocol therefore should be the use of the use of the lithium bromide adduct of the Grignard reagent together with $[FeCl_2(dppp)]$ as the precatalyst. The effect of fluorine substituents in *ortho* positions with respect to bromine is also addressed. In these cases the additional acitivation of C-F bonds is observed by ^{19}F NMR spectra of the crude reaction mixtures leading to undesirable multiple aryl alkyl coupling reactions.

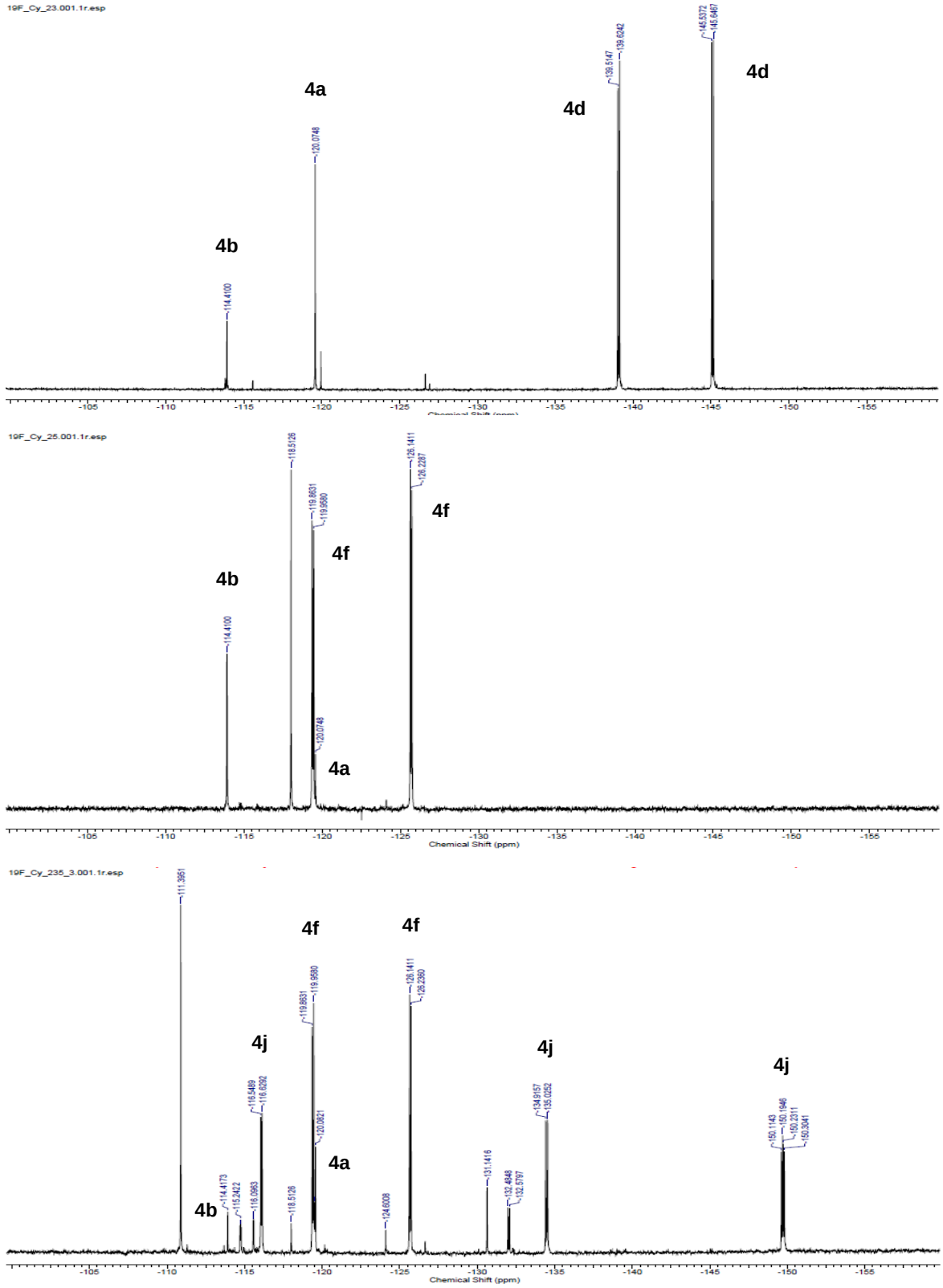


Figure 1. ^{19}F NMR spectra of crude reaction mixtures from the reaction of CyMgBr with **2d** (above), **2f** (middle) and **2j** (below).

Experimental Section

General. Bromobenzene derivatives **2a** and **2b** were purchased from Sigma Aldrich, **2c**-**m** were purchased from Fluorochem Ltd. All compounds were used without further purification but were checked for purity by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy. Grignard reagents and the corresponding LiCl or LiBr adducts as well as the precatalysts [$FeCl_2$(dppe)], **3a**, [$FeCl_2$(dppp)], **3b**, [$NiCl_2$(dppm)], **3c**, [$NiCl_2$(dppe)], **3d**, [$NiCl_2$(dppp)], **3e**, [$PdCl_2$(dppm)], **3f**, [$PdCl_2$(dppe)], **3g**, and [$PdCl_2$(dppp)], **3h**, have been produced following literature procedures.[59-61] Anhydrous $FeCl_2$ was purchased in 99.998% purity from Sigma Aldrich. This purity was verified by ICP-MS-AES-AAS analysis on the content of 69 other elements that was performed by Mikroanalytisches Labor Pascher, An der Pulvermühle 1, 53424 Remagen-Bandorf, Germany. This analysis e.g. shows 5 ppm Ni, <2 ppm Ru, <1 ppm Rh and <5 ppm Pd. Determination of the concentration of Grignard solutions has been performed by titraton.[70] All catalytical reaction procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvents.[71] Relative yields of the coupling products **4a**-**m** with respect to bicyclohexyl and biphenyl by-products were determined by GC. NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H: 200 MHz, ^{13}C: 50.32 MHz, ^{19}F: 188.29 MHz), a Bruker DRX 400 spectrometer (^{1}H: 400.13 MHz; ^{13}C: 100.62 MHz; ^{19}F: 376.58). The respective deuterated solvents are used as an internal standard for ^{1}H and ^{13}C NMR spectroscopy, fluorobenzene has been used as an external standard for ^{19}F NMR spectroscopic investigations. Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. High-resolution mass spectra were recorded on a Finnigan MAT 95 XL using EI techniques. Elemental analyses were performed on a Leco CHNS-932 at the laboratory of the Institute of Organic Chemistry and Macromolecular Chemistry of Friedrich-Schiller-University Jena. Due to the high volatility of the products deviations from calculated values even for NMR pure compounds in some cases are higher than expected.

General procedure for cross-coupling reactions. In a typical experiment a dry and argon-flushed 50-mL Schlenk tube, equipped with a magnetic stirring bar, was charged with the respective fluorinated bromobenzene derivative (0.5 mmol, 88 mg for monosubstituted, 97 mg for disubstituted and 105 mg for trisubstituted derivatives) and 3 mol% of the respective catalyst dissolved in 15 ml of THF ([$FeCl_2$(dppe)]: 7.9 mg, [FeCl2(dppp)]: 8.1 mg, [$NiCl_2$(dppm)]: 7.7 mg, [$NiCl_2$(dppe)]: 7.9 mg, [$NiCl_2$(dppp)]: 8.1 mg, [$PdCl_2$(dppm)]: 8.4 mg, [$PdCl_2$(dppe)]: 8.6 mg, [$PdCl_2$(dppp)]: 8.8 mg). The solution was stirred for 5 min, then cyclohexyl magnesium bromide or the respective LiCl or LiBr adduct (0.8 mmol, 4 ml of a 0.2M Grignard reagent) was quickly added to the reaction mixture and vigorous stirring at room temperature was continued for 24 hours. After hydrolysis with diluted hydrochloric acid, the organic layer and ether extracts from the aqueous layer were combined, washed with water and saturated NaCl solution, dried over MgSO4 and filtrated through a pad of silica. Concentration under reduced pressure followed by column chromatography (hexane : diethyl ether, *v/v* 100 : 1) afforded the respective coupling

products as light yellow oily compounds. Analytical data for **4a-c**, **4d** and **4i** were identical to those reported in the literature.[44-50,72,73]

1-Cyclohexyl-2-fluorobenzene (4a). MS (EI) [(*m/z*, %)]: 178 (3) [M^+], 160 (100) [MH^+-F], 131 (12) [$C_{10}H_{11}^+$], 128 (13) [$C_{10}H_8^+$], 117 (69) [$C_9H_9^+$], 104 (99) [$C_8H_8^+$], 91 (60) [$C_7H_7^+$], 83 (6) [$C_6H_{11}^+$], 77 (19) [$C_6H_5^+$], 65 (9) [$C_5H_5^+$], 55 (5) [$C_4H_7^+$], 41 (23) [$C_3H_5^+$] . HRMS $C_{12}H_{15}F$ (178.11578): 178.11551, Δ = 0.27 mmu. ^{1}H NMR (200.13 MHz, 298 K, $CDCl_3$): δ 0.83 – 1.88 (m, 10H, CH_2), 2.39 – 2.50 (m, 1H, CH), 7.04 – 7.39 (m, 4H, CH_{ar}). ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$) [ppm]: δ 26.2 (CH_2), 26.9 (CH_2), 34.5 (CH_2) , 44.6 (CH), 115.2 (C_{ar}H, d, *J* 22 Hz), 123.9 (C_{ar}H, d, *J* 4 Hz), 127.0 (C_{ar}H, d, *J* 8 Hz), 127.6 (C_{ar}H, d, *J* 6 Hz), 134.5 (C_{ar}, d, *J* 15 Hz), 160.6 (C_{ar}, d, *J* 244 Hz). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -120.1. Elemental analysis ($C_{12}H_{15}F$, M = 178.25 g mol^{-1}) [%]: Calcd: C 80.86, H 8.48; Found: C 79.12, H 9.12.

1-Cyclohexyl-3-fluoro-benzene (4b) MS (EI) [(*m/z*, %)]: 178 (100) [M^+], 160 (21) [MH^+-F], 135 (52) [$C_{10}H_{15}^+$], 122 (98) [$C_9H_{14}^+$], 109 (52) [$C_8H_{13}^+$], 104 (13) [$C_8H_8^+$], 96 (12) [$C_7H_{12}^+$], 83 (16) [$C_6H_{11}^+$], 65 (9) [$C_5H_9^+$], 55 (5) [$C_4H_7^+$], 41 (13) [$C_3H_5^+$]. HRMS $C_{12}H_{15}F$ (178.11578): 178.11577, Δ = 0.01 mmu. ^{1}H NMR (200.13 MHz, 298 K, $CDCl_3$) [ppm]: δ 1.08 – 1.96 (m, 10 H, CH_2), 2.38 – 2.59 (m, 1H, CH), 6.80 – 7.04 (m, 3H, CH_{ar}), 7.17 – 7.28 (m, 1H, CH_{ar}). ^{13}C NMR (50.32 MHz, $CDCl_3$) [ppm] : δ 26.1 (CH_2), 26.8 (CH_2), 34.3 (CH_2) , 44.3(CH), 112.5 (C_{ar}H, d, *J* 21 Hz), 113.6 (C_{ar}H, d, *J* 21 Hz), 122.5 (C_{ar}H, d, *J* 3 Hz), 129.6 (C_{ar}H, d, *J* 9 Hz), 150.74 (C_{ar}, d, *J* 7 Hz), 163.0 (C_{ar}, d, *J* 245 Hz), ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -114.4. Elemental analysis ($C_{12}H_{15}F$, M = 178.25 g mol^{-1}) [%]: Calcd: C 80.86, H 8.48; Found: C 79.27, H 8.52.

1-Cyclohexyl-4-fluoro-benzene (4c). MS (EI) [(*m/z*, %)]: 178 (19) [M^+], 159 (10) [M^+-F], 154(18) [$C_{10}H_{15}F^+$], 136 (56) [$C_{10}H_{16}^+$], 121 (60) [$C_9H_{13}^+$], 107 (64) [$C_8H_{11}^+$], 96 (68) [$C_7H_{12}^+$], 82 (100) [$C_6H_{10}^+$], 67 (95) [$C_5H_7^+$], 55 (55) [$C_4H_7^+$], 41 (52) [$C_3H_5^+$]. HRMS $C_{12}H_{15}F$ (178.11578): 178.11577, Δ = 0.01 mmu. ^{1}H NMR (200.13 MHz, 298 K, d^8-THF) [ppm]: δ 0.91 – 1.84 (m, 10 H, CH_2), 2.42 – 2.49 (m, 1H, CH), 6.91 – 7.00 (m, 2H, CH_{ar}), 7.10 – 7.22 (m, 2H, CH_{ar}). ^{13}C NMR (50.32 MHz, d^8-THF) [ppm] : δ 26.8 (CH_2), 27.6 (CH_2), 35.4 (CH_2) , 44.7(CH), 115.4 (C_{ar}H, d, *J* 21 Hz), 128.8 (C_{ar}H, d, *J* 8 Hz), 162.1 (C_{ar}, d, *J* 242 Hz), ^{19}F NMR (188.29 MHz, 298 K, d^8-THF) [ppm]: δ -121.5. Elemental analysis ($C_{12}H_{15}F$, M = 178.25 g mol^{-1}) [%]: Calcd: C 80.86, H 8.48; Found: C 79.60, H 8.75.

1-Cyclohexyl-2,3-difluorobenzene (4d). MS (EI) [(*m/z*, %)]: 196 (68) [M^+], 178 (56) [MH^+ - F], 160 (100) [MH_2^+ - 2 F], 140 (98) [$C_{11}H_8^+$], 127 (44) [$C_{10}H_8^+$], 122 (39) [$C_9H_{14}^+$], 117 (60) [$C_9H_9^+$], 109 (26) [$C_8H_{13}^+$], 104 (84) [$C_8H_8^+$], 91 (44) [$C_7H_7^+$], 83 (14) [$C_6H_{11}^+$], 77 (12) [$C_6H_5^+$], 67 (16) [$C_5H_7^+$], 55 (11) [$C_4H_7^+$], 41 (40) [$C_3H_5^+$]. HRMS $C_{12}H_{14}F_2$ (196.10636): 196.10644, Δ = 0.06 mmu. ^{1}H NMR (200.13 MHz, 298 K, $CDCl_3$) [ppm]: δ 0.83 – 1.51 (m, 10 H, CH_2), 1.71 – 1.85 (m, 1H, CH), 6.87 – 7.32 (m, 3H, CH_{ar}). ^{13}C NMR (100.61 MHz, 298 K, $CDCl_3$) [ppm] : δ 26.0 (CH_2), 26.7 (CH_2), 33.0 (CH_2), 37.2 (CH), 114.2 (C_{ar}H, d, *J* 18 Hz), 122.3 (C_{ar}H, t, *J* 4 Hz), 123.7 (C_{ar}H, dd, *J* 9 Hz, *J* 5 Hz), 137.0 (C_{ar}, d, *J* 11 Hz), 148.5 (C_{ar}, dd, *J* 245 Hz, *J* 11 Hz), 150.6

(C_{ar}, dd, *J* 245 Hz, *J* 13 Hz). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -139.6 (d, *J* 20.7 Hz), -145.6 (d, *J* 20.7 Hz). Elemental analysis ($C_{12}H_{14}F_2$, M = 196.24 g mol^{-1}) [%]: Calcd: C 73.45, H 7.19; Found: C 73.98, H 8.15.

1-Cyclohexyl-2,4-difluorobenzene (4e). MS (EI) [(*m/z*, %)]: 196 (99) [M^+], 178 (18) [M^+ - F], 165 (10) [$C_{11}H_{12}F^+$], 153 (91) [$C_{12}H_9^+$], 140 (100) [$C_{11}H_8^+$], 127 (95) [$C_{10}H_7^+$], 122 (23) [$C_8H_7F^+$], 109 (17) [$C_7H_6F^+$], 101 (18) [$C_8H_5^+$], 83 (19) [$C_6H_{11}^+$], 69 (18) [$C_5H_9^+$], 55 (13) [$C_4H_7^+$], 41 (36) [$C_3H_5^+$]. HRMS $C_{12}H_{14}F_2$ (196.10636): 196.10475, Δ = 1.61 mmu. ^{1}H NMR (200.13 MHz, 298 K, $CDCl_3$) [ppm]: δ 1.05 – 1.93 (m, 10H, CH_2), 2.67 – 2.92 (m, 1H, CH), 6.63 – 6.88 (m, 2H, CH_{ar}), 7.05 – 7.23 (m, 1H, CH_{ar}). ^{13}C NMR (50.32 MHz, 298 K, $CDCl_3$) [ppm] : δ 26.1 (CH_2), 26.8 (CH_2), 33.1 (CH_2), 36.8 (CH), 103.5 (dd, *J* 27 Hz, *J* 25 Hz, $C_{ar}H$), 110.8 (dd, *J* 21 Hz, *J* 4 Hz, $C_{ar}H$), 128.2 (dd, *J* 10 Hz, *J* 7 Hz, $C_{ar}H$), 130.1 (dd, *J* 45 Hz, *J* 4 Hz, C_{ar}), 155.4 (dd, *J* 251 Hz, *J* 12 Hz, C_{ar}), 160.7 (dd, *J* 205 Hz, *J* 12 Hz, C_{ar}). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -116.1 (d, *J* 7 Hz), -115.2 (d, *J* 7 Hz). Elemental analysis ($C_{12}H_{14}F_2$, M = 196.24 g mol^{-1}) [%]: Calcd: C 73.45, H 7.19; Found: C 74.46, H 7.58.

1-Cyclohexyl-2,5-difluorobenzene (4f). MS (EI) [(*m/z*, %)]: 196 (100) [M^+], 178 (77) [M^+ - F], 153 (36) [$C_{12}H_9^+$], 140 (100) [$C_{11}H_8^+$], 135 (40) [$C_9H_8F^+$], 127 (33) [$C_{10}H_7^+$], 122 (36) [$C_9H_{14}^+$], 109 (16) [$C_8H_{13}^+$]. HRMS $C_{12}H_{14}F_2$ (196.10636): 196.10213, Δ = 4.23 mmu. ^{1}H NMR (400.13 MHz, 298 K, $CDCl_3$) [ppm]: δ 0.86 – 1.95 (m, 10H, CH_2), 2.35 – 2.59 (m, 0.5H, CH), 2.73 – 2.94 (m, 0.5H, CH), 6.75 – 7.02 (m, 2H, CH_{ar}), 7.12 – 7.18 (m, 1H, CH_{ar}). ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$) [ppm]: δ 25.9 (CH_2), 26.6 (CH_2), 32.8 (CH_2), 40.0 (CH), 113.0 (dd, *J* 9 Hz, *J* 24 Hz, $C_{ar}H$), 114.0 (dd, *J* 5 Hz, *J* 24 Hz, $C_{ar}H$), 115.9 (dd, *J* 9 Hz, *J* 25 Hz, $C_{ar}H$), 136.2 (dd, *J* 8 Hz, *J* 17 Hz, C_{ar}), 156.4 (d, *J* 245 Hz, C_{ar}), 158.8 (d, *J* 247 Hz, C_{ar}). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -126.2 (d, *J* 9 Hz), -119.9 (d, *J* 9 Hz). Elemental analysis ($C_{12}H_{14}F_2$, M = 196.24 g mol^{-1}) [%]: Calcd: C 73.45, H 7.19; Found: C 75.00, H 7.41.

1-Cyclohexyl-2,6-difluorobenzene (4g). MS (EI) [(*m/z*, %)]: 196 (71) [M^+], 153 (28) [$C_{12}H_9^+$], 140 (100) [$C_{11}H_8^+$], 127 (43) [$C_{10}H_7^+$], 97 (21) [$C_7H_{13}^+$], 81 (21) [$C_6H_9^+$], 69 (18) [$C_5H_9^+$], 67 (19) [$C_5H_7^+$], 55 (25) [$C_5H_7^+$]. HRMS $C_{12}H_{14}F_2$ (196.10636): 196.10529, Δ = 1.07 mmu. ^{1}H NMR (400.13 MHz, 298 K, $CDCl_3$) [ppm]: δ 0.79 – 1.75 (m, 11H, CH_2, CH), 6.85 – 7.50 (m, 3H, CH_{ar}). ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$) [ppm]: δ 26.9 (CH_2), 30.2 (CH_2), 43.5 (CH), 111.4 (dd, *J* 6 Hz, *J* 20 Hz, $C_{ar}H$), 127.2 (t, *J* 7 Hz, C_{ar}), 130.8 (t, *J* 10 Hz, $C_{ar}H$), 160.6 (d, *J* 249 Hz, br). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -111.0 (s). Elemental analysis ($C_{12}H_{14}F_2$, M = 196.24 g mol^{-1}) [%]: Calcd : C 73.45, H 7.19; Found: C 74.67, H 7.53.

1-Cyclohexyl-3,4-difluorobenzene (4h). MS (EI) [(*m/z*, %)]: 196 (100) [M^+], 178 (9) [MH^+ - F], 166 (64) [$C_{11}H_{15}F^+$], 153 (84) [$C_{12}H_9^+$], 140 (100) [$C_{11}H_8^+$], 127 (72) [$C_{10}H_7^+$], 83 (56) [$C_6H_{11}^+$], 82 (84) [$C_6H_{10}^+$], 67 (60) [$C_5H_7^+$], 55 (44) [$C_4H_8^+$], 41 (34) [$C_3H_5^+$]. HRMS $C_{12}H_{14}F_2$ (196.10636): 196.10575, Δ = 0.61 mmu. ^{1}H NMR (400.13 MHz, 298 K, CD_2Cl_2) [ppm]: δ 0.87 – 1.91 (m, 10H, CH_2), 2.43 – 2.55 (m, 1H, CH), 6.92 – 7.13 (m, 3H, CH_{ar}). ^{13}C NMR (50.32 MHz, 298 K, CD_2Cl_2) [ppm][74]: δ 26.4 (CH_2), 27.1 (CH_2), 27.3* (CH_2), 30.6* (CH_2), 34.8 (CH_2), 43.9* (CH), 44.2 (CH), 115.7 ($C_{ar}H$, d, *J* 16 Hz), 117.0 ($C_{ar}H$, d, *J* 17 Hz), 119.0* ($C_{ar}H$, d, *J* 18 Hz), 121.3* ($C_{ar}H$, d, *J* 20 Hz), 123.1 ($C_{ar}H$, dd, *J* 6 Hz, *J* 4 Hz), 128.3* ($C_{ar}H$, d, *J* 6 Hz), 145.8 (C_{ar},

t, *J* 4 Hz), 148.8 (C_{ar}, dd, *J* 244 Hz, *J* 13 Hz), 150.5 (C_{ar}, dd, *J* 246 Hz, *J* 13 Hz). ^{19}F NMR (188.29 MHz, 298 K, CD_2Cl_2) [ppm][60]: δ -144.1 (d, *J* 21 Hz), -140.5* (d, *J* 21 Hz), -140.2 (d, *J* 21 Hz), -135.9* (d, *J* 21 Hz). Elemental analysis ($C_{12}H_{14}F_2$, M = 196.24 g mol^{-1}) [%]: Calcd: C 73.45, H 7.19; Found: C 73.49, H 7.65.

1-Cyclohexyl-3,5-difluorobenzene (4i). MS (EI) [(*m/z*, %)]: 196 (100) [M^+], 178 (5) [MH^+ - F], 164 (40) [$C_{11}H_{13}F^+$], 153 (60) [$C_{12}H_9^+$], 140 (92) [$C_{11}H_8^+$], 128 (73) [$C_{10}H_8^+$], 114 (22) [$C_9H_6^+$], 101 (20), [$C_8H_5^+$], 83 (16) [$C_6H_{11}^+$], 81 (24) [$C_6H_9^+$], 69 (36) [$C_5H_9^+$], 55 (22) [$C_4H_7^+$], 41 (45) [$C_3H_5^+$]. HRMS $C_{12}H_{14}F$ (196.10636): 196.10604, Δ = 0.32 mmu. ^{1}H NMR (200.13 MHz, 298 K, $CDCl_3$) [ppm]: δ 0.82 – 1.96 (m, 10H, CH_2), 2.41 – 2.58 (m, 1H, CH), 6.48 – 6.78 (m, 3H, CH_{ar}). ^{13}C NMR (50.32 MHz, 298 K, $CDCl_3$) [ppm]: δ 26.0 (CH_2), 26.6 (CH_2), 34.1 (CH_2), 44.4 (CH), 101.1 (C_{ar}H, t, *J* 26 Hz), 109.5 (C_{ar}H, d, *J* 24 Hz), 152.1 (C_{ar}, t, *J* 9 Hz), 163.0 (C_{ar}, dd, *J* 248 Hz, *J* 13 Hz). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -109.3 (s). Elemental analysis ($C_{12}H_{14}F_2$, M = 196.24 g mol^{-1}) [%]: Calcd: C 73.45, H 7.19; Found: C 74.49, H 7.64.

1-Cyclohexyl-2,3,5-trifluorobenzene (4j). MS (EI) [(*m/z*, %)]: 214 (16) [M^+], 196 (41) [$C_{12}H_{14}F_2^+$], 178 (100) [$C_{12}H_{15}F^+$], 160 (31) [$C_{12}H_{16}^+$], 158 (38) [$C_{11}H_7F^+$], 153 (21) [$C_{12}H_9^+$], 147 (34) [$C_{10}H_8F^+$], 140 (68) [$C_{11}H_8^+$], 135 (89) [$C_9H_8F^+$], 127 (43) [$C_{10}H_7^+$], 122 (100) [$C_9H_{14}^+$], 116 (32) [$C_9H_8^+$], 109 (82) [$C_8H_{13}^+$], 104 (23) [$C_8H_{10}^+$], 101 (20) [$C_8H_5^+$], 96 (19) [$C_6H_5F^+$], 91 (20) [$C_7H_7^+$], 83 (16) [$C_6H_{11}^+$], 67 (18) [$C_5H_7^+$], 55 (14) [$C_4H_7^+$], 41 (34) [$C_3H_5^+$]. HRMS $C_{12}H_{13}F_3$ (214.09694): 214.09692, Δ = 0.02 mmu. ^{1}H NMR (298 K, $CDCl_3$) [ppm]: δ 0.83 – 2.49 (m, 11H, CH_2, CH), 6.66 – 7,26 (m, 2H, CH_{ar}). ^{13}C NMR (150.9 MHz, 298 K, $CDCl_3$) [ppm]: δ 26.2 (CH_2), 26.9 (CH_2), 34.5 (CH_2), 44.6 (CH), 112.5 (dd, *J* 5 Hz, *J* 17 Hz, C_{ar}H), 123.2 (ddd, *J* 6 Hz, *J* 8 Hz, *J* 9 Hz, C_{ar}H), 140.1 (dt, *J* 15 Hz, *J* 252 Hz, C_{ar}), 148.0 (s, C_{ar}), 151.6 (dd, *J* 3 Hz, *J* 249 Hz, C_{ar}), 151.5 (dd, *J* 6 Hz, *J* 250 Hz). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -150.2 (dd, *J* 15 Hz, *J* 21 Hz), -134.9 (d, *J* 21 Hz), -116.6 (dd, *J* 15 Hz). Elemental analysis ($C_{12}H_{13}F_3$, M = 214.23 g mol^{-1}) [%]: Calcd: C 67.28, H 6.12; Found: C 67.34, H 6.30.

1-Cyclohexyl-2,4,5-trifluoro-benzene (4k). MS (EI) [(*m/z*, %)]: 214 (66) [M^+], 196 (40) [$C_{12}H_{14}F_2^+$], 178 (9) [$C_{12}H_{15}F^+$], 171 (34) [$C_{12}H_8F^+$], 166 (48) [$C_{13}H_{10}^+$], 158 (70) [$C_{11}H_7F^+$], 145 (48) [$C_{10}H_6F^+$], 140 (40) [$C_{11}H_8^+$], 127 (22) [$C_{10}H_7^+$], 109 (15) [$C_8H_{13}^+$], 96 (12) [$C_6H_5F^+$], 82 (100) [$C_6H_{10}^+$], 67 (62) [$C_5H_7^+$], 55 (57) [$C_4H_7^+$], 41 (55) [$C_3H_5^+$]. HRMS $C_{12}H_{13}F_3$ (214.09694): 214.09697, Δ = 0.03 mmu. ^{1}H NMR (200 MHz, 298 K, $CDCl_3$) [ppm]: δ 0.79 – 2.10 (m, 10H, CH_2), 2.68 – 2.97 (m, 1H, CH), 6.73 – 7.13 (m, 2H, CH_{ar}). ^{13}C NMR (150.9 MHz, 298 K, $CDCl_3$) [ppm]: δ 26.2 (CH_2), 26.9 (CH_2), 34.5 (CH_2), 44.6 (CH), 103.4 (ddd, *J* 5 Hz, *J* 9 Hz, *J* 20 Hz, C_{ar}H), 114.8 (dd, *J* 3 Hz, *J* 23 Hz, C_{ar}H), 140.1 (ddd, *J* 2 Hz, *J* 12 Hz, *J* 255 Hz, C_{ar}), 141.3 (ddd, *J* 5 Hz, *J* 17 Hz, *J* 257 Hz, C_{ar}), 144.8 (dd, *J* 5 Hz, *J* 11 Hz, C_{ar}), 147.2 (ddd, *J* 5 Hz, *J* 12 Hz, *J* 257 Hz, C_{ar}). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -144.0 (dd, *J* 15 Hz, *J* 21 Hz), -138.7 (d, *J* 23 Hz), -121.9 (d, *J* 15 Hz). Elemental analysis ($C_{12}H_{13}F_3$, M = 214.23 g mol^{-1}) [%]: Calcd: C 67.28, H 6.12; Found: C 67.44, H 7.02.

1-Cyclohexyl-2,4,6-trifluorobenzene (4l). MS (EI) [(*m/z*, %)]: 214 (45) [M^+], 196 (28) [$C_{12}H_{14}F_2^+$], 178 (22) [$C_{12}H_{15}F^+$], 171 (23) [$C_{12}H_8F^+$], 158 (100) [$C_{11}H_7F^+$], 145 (35) [$C_{10}H_6F^+$],

140 (41) [$C_{11}H_8^+$], 135 (14) [$C_9H_8F^+$], 127 (19) [$C_{10}H_7^+$], 122 (20) [$C_9H_{14}^+$], 109 (13) [$C_8H_{13}^+$], 91 (7) [$C_7H_7^+$], 81 (10) [$C_6H_9^+$], 69 (9) [$C_5H_9^+$], 55 (6) [$C_4H_7^+$], 41 (14) [$C_3H_5^+$]. HRMS $C_{12}H_{13}F_3$ (214.09694): 214.09681, Δ = 0.13 mmu. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) [ppm]: δ 1.15 – 1.92 (m, 10H, CH_2), 2.37 – 2.50 (m, 1H; CH), 6.70 (d, 2H, *J* 12 Hz, CH_{ar}). ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$) [ppm]: δ 26.3 (CH_2), 27.0 (CH_2), 34.6 (CH_2), 44.8 (CH), 110.8 (d, *J* 21 Hz, $C_{ar}H$), 121.2 (d, *J* 2 Hz, C_{ar}), 150.3 (d, *J* 7 Hz, C_{ar}), 161.5 (dd, *J* 3 Hz, *J* 241 Hz, C_{ar}), 163.0 (d, *J* 245 Hz, C_{ar}). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -107.8 (dd, *J* 2 Hz, *J* 7 Hz), -106.5 (t, *J* 7 Hz). Elemental analysis ($C_{12}H_{13}F_3$, M = 214.23 g mol^{-1}) [%]: Calcd: C 67.28, H 6.12; Found: C 66.77, H 6.80.

1-Cyclohexyl-3,4,5-trifluorobenzene (4m). MS (EI) [(*m/z*, %)]: 214 (68) [M^+], 196 (35) [MH^+ - F], 178 (20) [MH_2^+ - 2F], 158 (100) [$C_{12}H_{14}^+$], 140 (53) [$C_{11}H_8^+$], 127 (25) [$C_{10}H_9^+$], 123 (23) [$C_9H_{15}^+$], 109 (11) [$C_8H_{13}^+$], 91 (6) [$C_7H_7^+$], 82 (8) [$C_6H_{10}^+$], 69 (17) [$C_5H_9^+$], 55 (5) [$C_4H_7^+$], 41 (16) [$C_3H_5^+$]. HRMS $C_{12}H_{13}F_3$ (214.09694): 214.09717, Δ = 0.23 mmu. ^{1}H NMR (200.13 MHz, 298 K, $CDCl_3$) [ppm]: δ 1.15 – 1.89 (m, 10H, CH_2), 2.37 – 2.45 (m, 1H, CH), 6.78 (dd, *J* 10 Hz, *J* 8 Hz, 2H, CH_{ar}). ^{13}C NMR (50.32 MHz, 298 K, $CDCl_3$) [ppm] : δ 25.9 (CH_2), 26.5 (CH_2), 34.2 (CH_2) , 43.9 (CH), 110.51 (dd, *J* 20 Hz, *J* 6 Hz, $C_{ar}H$), 137.8 (dd, *J* 264 Hz, *J* 16 Hz, C_{ar}), 144.2 (dt, *J* 5 Hz, *J* 4 Hz, C_{ar}), 151.0 (ddd, *J* 248 Hz, *J* 10 Hz, *J* 4 Hz, C_{ar}). ^{19}F NMR (188.29 MHz, 298 K, $CDCl_3$) [ppm]: δ -165.4 (t, *J* 21 Hz), -135.9 (d, *J* 21 Hz). Elemental analysis ($C_{12}H_{13}F_3$, M = 214.23 g mol^{-1}) [%]: Calcd: C 67.28, H 6.12; Found: C 68.16, H 6.73.

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