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Noncatalytic Pyridyl-Directed Alkylation and Arylation Carbon–Fluorine Bond of Polyfluoroarenes with Grignard Reagents

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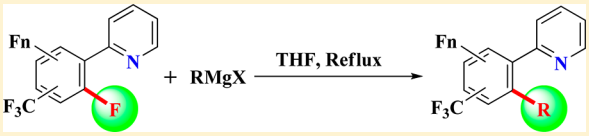
Supporting Information

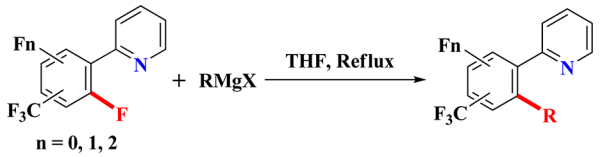
ABSTRACT: Cross-coupling reaction of polyfluoroarenes with Grignard reagents via pyridine-directed cleavage of C–F bond in the absence of metal catalysts was developed. A possible mechanism was suggested.



The cleavage of unactivated of carbon–fluorine bonds is a great challenge in organic synthesis.[1] Until now, many efforts have been made in the development of novel methods for the cleavage of carbon–fluorine bonds. Catalytic conversion of the C–F bond to the C–C bond has received increasing attention in recent years.[2] These transformations include Kumada,[3] Negishi,[4] Suzuki,[5] and Sonogashira[6] reactions. One of the facile methods for activation of the C–F bond is to introduce a directing group (such as hydroxyl, hydroxymethyl, amino, imino, pyridinyl, pyrazolyl, and oxazolinyl) at the position *ortho* to the C–F bond of fluoroarenes, followed by coupling of this activated C–F bond with a functionalized starting material such as RMgX, $RB(OH)_2$, or R_2Zn in the presence of metal catalyst.[7]

The metal-catalyzed cross-coupling reactions of alkyl, vinyl, or aryl halides or aryl triflates with Grignard reagents are powerful synthetic methods for the construction of C–C bonds.[8] The most common electrophiles used in these kinds of coupling reactions are aryl (alkyl) chlorides, bromides, iodides, and tosylates. However, the use of aryl fluorides as coupling partner remains limited due to the exceptional stability of the C–F bonds. Although a few excellent examples of metal-catalyzed cross-coupling reactions involving C–F bond cleavage have been reported, expensive metal complex catalysts or very complicated ligands are required in most of these reaction systems.[9] Until now, there were very few examples of coupling reactions of Grignard reagents with aryl fluorides using a directing group strategy. In 1978, Meyers reported the first directing group-promoted coupling reactions between Grignard reagent and fluorobenzene bearing an oxazoline moiety as activating group in the *ortho*-position to the C–F bond.[10] In 1999, Cahiez et al. described the cross-coupling reaction of Grignard reagents with an aryl fluoride bearing imino group in the *ortho*-position in the presence of $MnCl_2$ (10 mol %). They also indicated that in the absence of $MnCl_2$ the yield of coupling product decreased obviously (40%, GC, 24 h).[7g] In 2008, Manabe et al. developed the first examples of *ortho*-selective cross-coupling of fluorobenzene derivatives bearing electron-donating groups (OH, CH_2OH, NH_2) with Grignard reagents in the presence of Pd-based catalysts.[7h] As far as we know, until now, there has been no report available on the reaction of fluoroarenes with Grignard reagents via pyridine-directed C–F bond cleavage with or without metal catalysts. In continuation of our research on the functionalization of C–F bond,[11] in this paper we report a new method for the alkylation and arylation of polyfluoroarenes with Grignard reagents via pyridine-directed regioselective cleavage of carbon–fluorine bond in the absence of transition metal (Scheme 1).

Scheme 1. Alkylation and Arylation of Polyfluoroarenes with Grignard Reagents via Pyridine-Directed Cleavage of C–F Bond



Encouraged by the recent exciting progress in the field of pyridine-directed C–H bond activation[12] and also inspired by the Meyers reaction involving the displacement of an oxazoline-activated aromatic fluorine atom,[13] we envisaged that the metal-catalyzed coupling reaction of Grignard reagents with aryl fluorides could take place using pyridine as activating group in aromatic substitution. We began our investigation by using the cross-coupling reaction of *n*-butylmagnesium chloride **2a** with 2-(2-fluorophenyl)pyridine **1a** as the model reaction in the presence of various metal catalysts or in the absence of metal catalyst (Table 1). Screening of the suitable conditions for the

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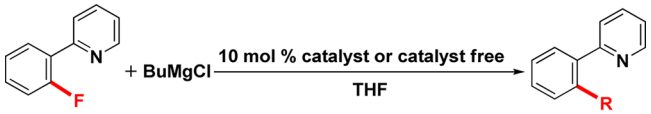
Table 1. Reaction of 2-(2-Fluorophenyl)pyridine 1a with *n*-Butylmagnesium Chloride 2a in the Presence or Absence of Metal Catalyst[a]



1a 2a 3a

entry	cat. (10 mol %)	temp (°C)	time (h)	yield[b] (%)
1	$NiCl_2$	reflux	12	51
2	$AlCl_3$	reflux	24	21
3	$ZnCl_2$	reflux	24	44
4	$CeCl_3$	reflux	24	13
5	$RhCl_2$	reflux	24	21
6	$BiCl_3$	reflux	24	16
7	$ZrCl_4$	reflux	24	0
8	$PdCl_2$	reflux	24	8
9	$FeCl_3$	reflux	24	5
10	$NiBr_2$	reflux	12	20
11	$CuCl_2$	reflux	24	3
12	CuCl	reflux	24	5
13	$LaCl_3$	reflux	24	4
14	$NbCl_5$	reflux	24	3
15	$CoCl_2$	reflux	24	18
16	$Co(acac)_3$	reflux	24	16
18	$NiCl_2$(dppp)	reflux	24	19
19	$MnCl_2$	reflux	2	94
20	none	20	12	76
21	none	40	12	87
22	none	reflux	12	93

[a]THF was used as solvent. BuMgCl (2.5 equiv). [b]Yields were based on GC analysis.

reaction revealed that the manganese chloride ($MnCl_2$) was the best catalyst among the tested metal catalysts and provided the corresponding alkylation product **3a** in 94% yield within 2 h (entry 19). Much to our delight, the reaction also proceeded well in the absence of metal catalyst. Further optimization of reaction conditions indicated that when the reaction was performed at reflux of THF with prolonged reaction time (12 h), the desired product **3a** was obtained in high yield (entry 22). In addition, a decrease in the amount of BuMgCl to less than 2.5 equiv led to lower conversion of the C−F bonds to C−C bonds.

Today, the transition-metal-free protocols appear particularly attractive and have found tremendous importance in the pharmaceutical industry due to the strict demand for the absence of any transition-metal impurity in final product.[14] From a green chemistry point of view, we carried out this coupling reaction without any additional metal catalyst in the following studies.

The partially fluorinated aromatic compounds have always been used as intermediates for the synthesis of pharmaceuticals and agrochemicals.[2,15] Although these functionalized polyfluoroarenes could be prepared by cross coupling of the corresponding fluorinated aryl chloride, bromide, or iodide, the mixed aryl halides which used as starting materials are very expensive and not readily available. Therefore, the selective activation and functionalization of C−F bonds in the commercially available polyfluoroarenes or perfluoroarenes have become a subject of great interest for fluorine chemistry. Thus, we used a range of structurally diverse 2-polyfluorophenyl pyridines as substrates to examine the scope of this reaction under the optimized reaction conditions.

The yields of the reaction of 2-polyfluorophenyl pyridines (**1a**−**f**) with Grignard reagents are summarized in Table 2. Most 2-polyfluorophenylpyridines could undergo the coupling reaction efficiently in the absence of metal catalyst. Both aliphatic Grignard reagents and aromatic Grignard reagent could react smoothly and provided the coupling products in high isolated yields (Table 2, entries 1−10); however, the reaction of PhMgBr needed a longer reaction time (24 h, entries 4 and 6). In most cases, 2-polyfluorophenylpyridines gave alkylated or phenylated 2-phenylpyridines as the main products, and no dialkylated or diphenylated products were observed. In the case of 2-(2-chlorophenyl)pyridine **1g**, the monoalkylated product **3b** was isolated in slightly lower yield than was obtained with **1a** (Table 2, entries 11 and 1, respectively). When 4-(2-fluorophenyl)pyridine **1h**, 2-(4-fluorophenyl)pyridine **1i**, and 2-(3-fluorophenyl)pyridine **1j** were used as substrates, no alkylated products **3k**, **3l**, and **3m** were detected, and the starting materials were recovered completely (entries 12−14).

The results revealed that the distance between the nitrogen atom and the fluorine atom in fluorophenylpyridine derivatives played an important role in the formation of alkylated product. Finally, the reaction of 2-phenylpyridine **1k** with ethylmagnesium chloride **2b** was performed under the same reaction conditions. As expected, the C−H bond *ortho* to the pyridyl nitrogen could not be activated without metal catalyst and no reaction has occurred. It is suggested that the C−F bond in the benzene ring are activated by the pyridine directing group in preference to C−H bond in the absence of metal catalyst.

Based on these experimental results and literatures,[13,16] a plausible mechanism for the noncatalyzed reaction of 2-(2-fluorophenyl)pyridine derivatives with Grignard reagent was suggested in Scheme 2. In the first step, the magnesium ion in Grignard reagent (RMgX) coordinated to the lone-pair electrons at the nitrogen atom of pyridine to form a magnesium complex (**I**). The C−F bond was slightly activated by both pyridine-directing group and magnesium ion. Subsequently, the addition of alkyl or aryl to benzene ring led to the formation of C−C bond via a six-membered ring transition state (**II**). Finally, cleavage of C−F bond of analogue of Meisenheimer complex (**III**) afforded the cross-coupling product.

In summary, we have developed *ortho*-selective cross-coupling of polyfluoroarenes with Grignard reagents via pyridinyl-directed C−F bond cleavage in the absence of metal catalyst. We also suggested a possible pyridyl mediated C−F bond cleavage mechanism. Although pyridinyl is not strongly electron-withdrawing group in the S_NAr reaction, it can serve as coordinating ligand and activating moiety in the *ortho*-position to the C−F bond. The suitable distance between the pyridyl nitrogen and the fluorine atom in 2-fluorophenylpyridine derivatives ensure the transformation of C−F bond to C−C bond to proceed smoothly.

EXPERIMENTAL SECTION

General Comments. All reagents were of analytical grade and obtained from commercial suppliers and used without further purification. THF was dried by standard methods prior to use and degassed. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) using TMS as internal standard, The ^{19}F NMR spectra were obtained using a 400 spectrometer (376 MHz). $CDCl_3$ was used as the NMR solvent in all

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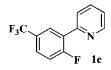
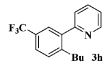
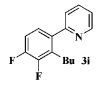
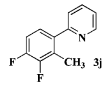
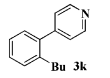
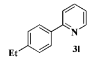
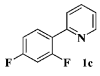
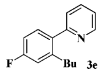
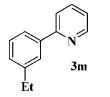
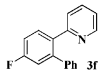
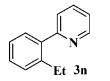
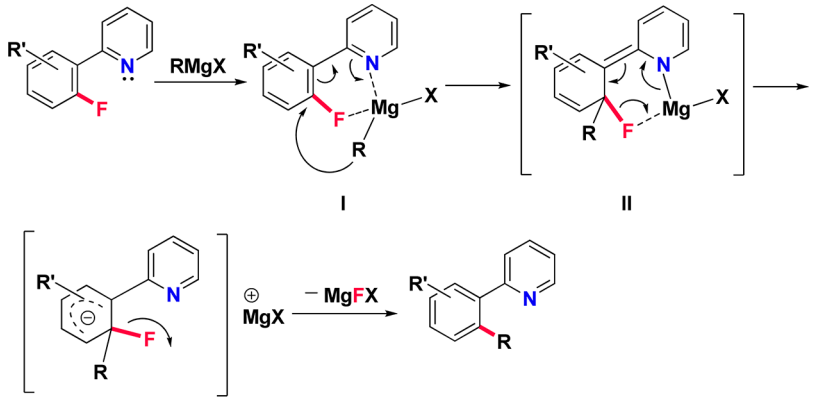
Table 2. Noncatalyzed *Ortho*-Alkylation or Phenylation of 2-(2-Fluorophenyl)pyridine Derivatives with Grignard Reagents[a]

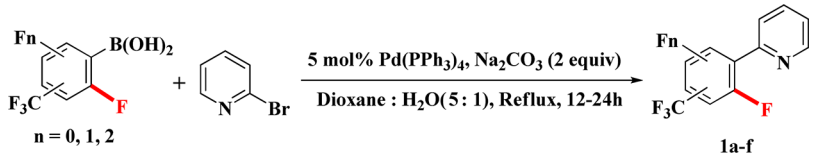
Entry	Substract	RMgX	Product	Yield (%) [b]	Entry	Substract	RMgX	Product	Yield (%) [b]
1	 1a	BuMgCl **2a**	 3a	89	8	 1e	**2a**	 3h	82
					9	 1f	**2a**	 3i	83
2	**1a**	EtMgCl **2b**	 3b	90	10	**1f**	CH_3MgCl **2d**	 3j	85
3	 1b	**2a**	 3c	88	11	 1g	**2b**	**3b**	80
4	**1b**	PhMgBr **2c**	 3d	83	12	 1h	**2a**	 3k	0
					13	 1i	**2b**	 3l	0
5	 1c	**2a**	 3e	87	14	 1j	**2b**	 3m	0
6	**1c**	**2c**	 3f	80					
7	 1d	**2b**	 3g	89	15	 1k	**2b**	 3n	0

[a]Reaction condition: RMgX (2.5 equiv), THF, reflux, 6−24 h. [b]Isolated yields.

Scheme 2. Possible Mechanism for the Noncatalyzed Reaction of 2-(2-Fluorophenyl)pyridine Derivatives with RMgX



Scheme 3. Synthesis of 2-(2-Fluorophenyl)pyridine Derivatives via Suzuki−Miyaura Coupling Reaction



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cases. The GC and GC−MS were calibrated by authentic standards. High-resolution mass spectra (HRMS) were acquired in the electron-impact mode (EI) using a TOF mass analyzer.

Preparation of 2-(2-Fluorophenyl)pyridine derivatives (1a−f). 2-(2-Fluorophenyl)pyridine derivatives **1a−f** were prepared by $Pd(PPh_3)_4$-catalyzed Suzuki−Miyaura coupling of the corresponding polyfluoroarylboronic acid and the 2-bromopyridine (**1g−k** was prepared by the same procedure) (Scheme 3).

To a stirred solution of 2-bromopyridine (0.79 g, 5 mmol), Na_2CO_3 (1.06 g, 10 mmol), and $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol) in 6 mL of dioxane/H_2O (5:1) was added fluorophenylboronic acid (6 mmol) in 6 mL of dioxane/H_2O (5:1) was added dropwise via syringe, and the mixture was heated to 120 °C and then stirred for 12−24 h (monitored by TLC) in a Schlenk tube. The reaction mixture was allowed to cool to room temperature, filtered, and extracted with H_2O (20 mL) and CH_2Cl_2 (3 × 10 mL). The organic layer was separated and dried over $MgSO_4$, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate (10:1) mixture as eluent to afford the pure target compounds (light orange oil or white solid, 83−91%).

General Procedure for Compounds 3a−n. To a stirred solution of aryl fluorides (**1a−f**, **h−j**), **1g**, and **1k** (2 mmol) in 5 mL of THF at room temperature was added a THF solution of RMgX (5 mmol, 2.5 mL, 2.00 M) dropwise via syringe, and the mixture was heated to 70 °C and then stirred for 6−24 h (monitored by TLC) in a Schlenk tube. The reaction mixture was quenched by the addition of saturated aqueous solution of NH_4Cl (5 mL) and extracted with H_2O (20 mL) and ethyl acetate (3 × 10 mL). The organic layer was separated and dried over $MgSO_4$, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate (20:1) mixture as eluent to afford the pure target compounds.

*2-(2-Butylphenyl)pyridine (**3a**, CAS: 914253-98-8):*[17] yield 89% (188.2 mg), light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 2.8 Hz, 1H), 7.76−7.72 (m, 1H), 7.41−7.25 (m, 6H), 2.75 (t, J = 7.8 Hz, 2H), 1.52−1.44 (m, 2H), 1.28−1.22 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).

*2-(2-Ethylphenyl)pyridine (**3b**, CAS: 914253-97-7):*[17] yield 90% (171.1 mg), light yellow liquid; ^{1}H NMR δ 8.68 (d, J = 4.0 Hz, 1H), 7.87−7.83 (m, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.36−7.33 (m, 4H), 7.30−7.26 (m, 1H), 2.76 (q, J = 7.5 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H).

*2-(2-Butyl-3-fluorophenyl)pyridine (**3c**):* yield 88% (202.4 mg), light yellow liquid; ^{1}H NMR δ 8.71 (d, J = 4.0 Hz, 1H), 7.79−7.75 (m, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.30−7.27 (m, 1H), 7.24−7.21 (m, 1H), 7.15 (d, J = 6.8 Hz, 1H), 7.11−7.06 (m, 1H), 2.75−2.71 (m, 2H), 1.50−1.43 (m, 2H), 1.26−1.21 (m, 2H), 0.80 (t, J = 7.6 Hz, 3H); ^{13}C NMR δ 161.6 (d, $^1J_{CF}$ = 242.8 Hz), 159.1 (d, $^4J_{CF}$ = 2.7 Hz), 149.2, 142.6 (d, $^3J_{CF}$ = 4.7 Hz), 136.2, 128.4 (d, $^2J_{CF}$ = 16.5 Hz), 126.8 (d, $^3J_{CF}$ = 9.0 Hz), 125.3 (d, $^4J_{CF}$ = 3.1 Hz), 124.1, 122.0, 115.1 (d, $^2J_{CF}$ = 23.3 Hz), 32.4, 29.7, 22.6, 13.7; ^{19}F NMR δ −117.5 (s, 1F); HRMS (EI) calcd for $C_{15}H_{16}FN$ $[M]^+$ 229.1267, found 229.1264.

*2-(6-Fluorobiphenyl-2-yl)pyridine (**3d**, CAS: 1174895-61-4):*[18] yield 83% (206.2 mg), white solid; mp 91.8−92.9 °C; ^{1}H NMR δ 8.62 (d, J = 4.0 Hz, 1H), 7.56−7.54 (m, 1H), 7.49−7.43 (m, 1H), 7.40−7.36 (m, 1H), 7.29−7.16 (m, 6H), 7.12−7.09 (m, 1H), 6.86 (d, J = 7.6 Hz, 1H); ^{13}C NMR δ 159.8 (d, $^1J_{CF}$ = 243.5 Hz), 157.9 (d, $^4J_{CF}$ = 3.1 Hz), 149.3, 142.1 (d, $^3J_{CF}$ = 2.7 Hz), 135.2, 134.1, 130.7, 128.9 (d, $^3J_{CF}$ = 8.9 Hz), 128.2 (d, $^2J_{CF}$ = 16.3 Hz), 127.9, 127.3, 126.0 (d, $^4J_{CF}$ = 3.1 Hz), 125.2, 121.6, 115.6 (d, $^2J_{CF}$ = 23.3 Hz); ^{19}F NMR δ −115.6 (s, 1F).

*2-(2-Butyl-4-fluorophenyl)pyridine (**3e**):* yield 87% (200.2 mg), light yellow liquid; ^{1}H NMR δ 8.68 (d, J = 4.0 Hz, 1H), 7.74−7.70 (m, 1H), 7.38−7.30 (m, 2H), 7.25−7.22 (m, 1H), 7.02 (dd, J = 10.4 Hz, J = 2.8 Hz, 1H), 6.97−6.92 (m, 1H), 2.71 (t, J = 7.6 Hz, 2H), 1.49−1.42 (m, 2H), 1.23 (q, J = 7.6 Hz, 2H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 162.7 (d, $^1J_{CF}$ = 245.0 Hz), 159.4, 149.2, 143.4 (d, $^3J_{CF}$ = 7.5 Hz), 136.4 (d, $^4J_{CF}$ = 3.0 Hz), 136.2, 131.4 (d, $^3J_{CF}$ = 8.4 Hz), 124.2, 121.7, 116.1 (d, $^2J_{CF}$ = 20.9 Hz), 112.6 (d, $^2J_{CF}$ = 21.0 Hz), 33.1, 32.6, 22.4, 13.8; ^{19}F NMR δ −114.4 (dd, J_1 = 15.8 Hz, J_2 = 9.0 Hz, 1F); HRMS (EI) calcd for $C_{15}H_{16}FN$ $[M]^+$ 229.1267, found 229.1268.

*2-(5-Fluorobiphenyl-2-yl)pyridine (**3f**, CAS: 1024586-00-2):*[19] yield 80% (198.2 mg), white solid; mp 92.5−93.8 °C; ^{1}H NMR δ 8.64 (d, J = 4.4 Hz, 1H), 7.73−7.69 (m, 1H), 7.41−7.37 (m, 1H), 7.27−7.26 (m, 3H), 7.18−7.10 (m, 5H), 6.86 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 162.6 (d, $^1J_{CF}$ = 246.3 Hz), 158.3, 149.4, 142.7 (d, $^3J_{CF}$ = 7.9 Hz), 140.3, 135.7 (d, $^4J_{CF}$ = 3.0 Hz), 135.3, 132.4 (d, $^3J_{CF}$ = 8.4 Hz), 129.5, 128.2, 127.2, 125.3, 121.4, 117.0 (d, $^2J_{CF}$ = 21.7 Hz), 114.4 (d, $^2J_{CF}$ = 20.9 Hz); ^{19}F NMR δ −113.8 (dd, J_1 = 14.7 Hz, J_2 = 7.9 Hz, 1F).

*2-(2-Ethyl-3-(trifluoromethyl)phenyl)pyridine (**3g**):* yield 89% (222.6 mg), light yellow liquid; ^{1}H NMR δ 8.72 (d, J = 4.4 Hz, 1H), 7.82−7.78 (m, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.40−7.29 (m, 3H), 2.94 (q, J = 7.6 Hz, 2H), 0.93 (t, J = 7.6 Hz, 3H); ^{13}C NMR δ 157.9, 151.9, 150.0, 136.6, 135.1, 129.0, 127.5 (q, $^3J_{CF}$ = 10.1 Hz), 124.8, 124.3, 123.1, 122.7 (q, $^1J_{CF}$ = 273.7 Hz), 119.0 (q, $^2J_{CF}$ = 22.0 Hz), 26.1, 15.6; ^{19}F NMR δ −59.1 (s, 3F); HRMS (ESI) calcd for $C_{14}H_{13}F_3N$ $[M + H]^+$ 252.1000, found 252.1001.

*2-(2-Butyl-5-(trifluoromethyl)phenyl)pyridine (**3h**):* yield 82% (227.7 mg), light yellow liquid; ^{1}H NMR δ 8.72 (d, J = 4.0 Hz, 1H), 7.80−7.76 (m, 1H), 7.63 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H) 7.42 (dd, J = 11.2 Hz, J = 8.0 Hz, 2H), 7.30 (dd, J = 7.2 Hz, J = 4.8 Hz, 1H), 2.77 (t, J = 8.0 Hz, 2H), 1.49−1.45 (m, 2H), 1.24 (q, J = 7.6 Hz, 2H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 158.2, 148.7, 144.8, 140.6, 135.8, 129.8, 127.3 (q, $^2J_{CF}$ = 32.4 Hz), 126.0 (q, $^3J_{CF}$ = 3.8 Hz), 124.0 (q, $^3J_{CF}$ = 3.6 Hz), 123.9 (q, $^1J_{CF}$ = 272.7 Hz), 123.4, 121.6, 32.6, 32.0, 21.7, 12.6; ^{19}F NMR δ −62.3 (s, 3F); HRMS (EI) calcd for $C_{16}H_{16}F_3N$ $[M]^+$ 279.1235, found 279.1236.

*2-(2-Butyl-3,4-difluorophenyl)pyridine (**3i**):* yield 87% (215.9 mg), light yellow liquid; ^{1}H NMR δ 8.71 (d, J = 3.2 Hz, 1H), 7.81−7.77 (m, 1H), 7.38−7.36 (m, 1H), 7.32−7.30 (m, 1H), 7.14−7.05 (m, 2H), 2.78−2.61 (m, 2H), 1.46−1.44 (m, 2H), 1.26−1.23 (m, 2H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 158.4, 150.4 (dd, $^1J_{CF}$ = 268.4 Hz, $^2J_{CF}$ = 15.5 Hz), 149.2, 149.2 (dd, $^1J_{CF}$ = 243.4 Hz, $^2J_{CF}$ = 11.6 Hz), 137.4, 136.4, 126.8 (d, $^3J_{CF}$ = 8.3 Hz), 125.4−125.2 (m), 124.1, 122.1, 114.1 (d, $^2J_{CF}$ = 16.9 Hz), 32.2, 25.6, 22.5, 13.6; ^{19}F NMR δ −138.3 to −138.4 (m, 1F), −142.1 to −142.2 (m, 1F); HRMS (EI) calcd for $C_{15}H_{15}F_2N$ $[M]^+$ 247.1173, found 247.1174.

*2-(3,4-Difluoro-2-methylphenyl)pyridine (**3j**):* yield 85% (174.7 mg), white solid; mp 61.9−63.4 °C; ^{1}H NMR δ 8.71 (d, J = 4.0 Hz, 1H), 7.80−7.76 (m, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.32−7.29 (m, 1H), 7.19−7.15 (m, 1H), 7.12−7.05 (m, 1H), 2.32 (d, J = 4.0 Hz, 3H); ^{13}C NMR δ 158.0, 150.5 (dd, $^1J_{CF}$ = 247.3 Hz, $^2J_{CF}$ = 13.7 Hz), 149.4, 149.2 (dd, $^1J_{CF}$ = 243.4 Hz, $^2J_{CF}$ = 12.4 Hz), 137.6, 136.4, 125.9 (d, $^2J_{CF}$ = 13.6 Hz), 125.0 (dd, $^3J_{CF}$ = 6.6 Hz, $^4J_{CF}$ = 4.1 Hz), 124.2, 122.2, 114.6 (d, $^2J_{CF}$ = 17.0 Hz), 12.1 (d, $^3J_{CF}$ = 3.3 Hz); ^{19}F NMR δ −138.4 to −138.4 (m, 1F), −140.4 (d, J = 15.0 Hz, 1F); HRMS (EI) calcd for $C_{12}H_9F_2N$ $[M]^+$ 205.0703, found 205.0699.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR spectra for compounds **3a−b** and ^{1}H, ^{19}F and ^{13}C NMR spectra for compounds **3c−j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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