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Nickel(0)-Catalyzed Fluoroalkylation of Alkenes, Alkynes, and Aromatics with Perfluoroalkyl Chlorides

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Treatment of perfluoroalkyl chlorides (R_FCl) with alkenes, alkynes, or aromatics in the presence of 0.1 equiv of nickel dichloride, 1.5 equiv of zinc powder, and 0.4 equiv of triphenylphosphine in DMF at 95−100 °C for 6−8 h give the corresponding perfluoroalkylated products in good yields. A single electron-transfer mechanism is suggested.

Introduction

The addition reaction of perfluoroalkyl iodides (R_FI) and bromides (R_FBr) to olefins, alkynes, or aromatics is one of the most important methods for introducing perfluoroalkyl group to organic compounds.[1] Such a process is traditionally accomplished with photochemical,[2−5] thermal,[6] electrolytic,[7] and free radical initiations.[8] Recently, however, some reductive systems were found to be more effective. For example: metals, transition metals,[9,10] and inorganic reductants[11] as well as redox systems[12] such as Cu,[13,14] Zn,[15] Mg,[16] Ni,[17] Fe,[18] Pd,[19,20] Pt,[21] $Fe(CO)_4$,[22] $Na_2S_2O_4$,[23] thiourea dioxide,[24] $(NH_4)_2S_2O_8/HCO_2Na$,[25] $CrCl_3/Fe$,[26] Co(II)/Zn,[27] etc. were successfully applied to this reaction. Uniquely, it was found that oxidant such as $Pb(OAc)_4$, PbO_2,[28] $Ce(SO_2)_4{\bullet}4H_2O$, $(NH_4)_2Ce(NO_3)_6$, $Na_2S_2O_8$, $(NH_4)_2S_2O_8$, or $KMnO_4$[29] can also initiate the same addition reaction even to fluorinated olefins.[30] The results obtained by using these initiators can be rationalized in terms of single electron-transfer (SET) mechanism.[9,10] Unfortunately, all these initiation systems cannot be applied to perfluoroalkyl chlorides (R_FCl) because of their stronger carbon−chlorine bonds. In fact, α-, ω-chloroperfluoroalkyl iodides [$Cl(CF_2)_nI$, $n \geq 2$] have been used as substrates in the reaction: the iodine being attacked, while the chlorine inert.[9−12] It was not until very recently that this problem has been partially solved: using dimethyl sulfoxide (DMSO) as a solvent instead of CH_3CN/H_2O in $Na_2S_2O_4/NaHCO_3$ initiation system (so-called sulfinatodehalogenation reaction),[11] perfluoroalkyl chlorides, ethyl chlorofluoro-, chlorodifluoroacetates, even nonfluorinated compounds, such as ethyl dichloro-, chloroacetates and chloroform, can either be converted to the corresponding sulfinate salts or alkylate alkenes, alkynes,[31] and aromatics.[32] The tremendous role of solvent encouraged us to further reexamine the perfluoroalkylation of organic compounds with perfluoroalkyl chlorides by means of varous metals in different solvents. We, herein, present the results of nickel(0)-catalyzed perfluoroalkylation of alkenes, alkynes, and aromatics with perfluoroalkyl chlorides.

Results and Discussion

In 1986 we carried out the addition reaction of α-, ω-chloroperfluoroalkyl iodides [$Cl(CF_2)_nI$, $n = 4, 6$] to

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Table 1. Reaction of R_FCl with Electron-Rich Alkenes (2) Induced by Ni(0) in the Presence or Absence of Ph_3P in DMF[a]

entry	R_FCl[b]	alkenes	*T* °C	time (h)	**3** yield % (no PPh_3)[c]
1	**1a**	**2a**	95	8	72 (29)
2		**2b**	100	7	75 (31)
3		**2c**	100	6	70 (*cis*/*trans* = 70:30) (25)[d]
4		**2f**	95	7	63 (15)
5	**1b**	**2a**	95	8	70 (31)
6		**2b**	100	7	73 (27)
7		**2c**	95	6	70 (*cis*/*trans* = 70:30) (25)[d]
8		**2d**	100	6	71 (30)
9		**2f**	95	7	62 (15)
10	**1c**	**2a**	95	7	74 (30)
11		**2b**	100	7	75 (28)
12		**2c**	95	6	70 (*cis*/*trans* = 70:30) (24)[d]
13		**2e**	100	6	78 (27)
14		**2f**	95	8	62 (14)

[a] **1**/**2**/Zn/$NiCl_2$/PPh_3 = 1:1.5:1.5:0.1:0.4. [b] The conversion of R_FCl was 100% (determined by ^{19}F NMR). [c] The isolated yields were based on R_FCl and a trace of R_FH was also obtained; the yields in the bracket were obtained in HMPA in the absence of PPh_3, R_FH (≥40%) being the major products. [d] The ratio of *cis*/*trans* based on ^1H NMR.

Table 2. Reaction of R_FCl with Electron-Poor Alkenes (4) Induced by Ni(0) in the Presence or Absence of Ph_3P in DMF[a]

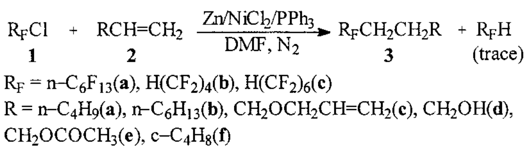
entry	R_FCl[b]	alkenes	*T* °C	time (h)	**5** yields % (no PPh_3)[c]
1	**1a**	**4a**	95	8	67 (30)
2		**4b**	100	8	71 (27)
3	**1b**	**4a**	95	7	64 (25)
4		**4b**	100	8	70 (30)
5	**1c**	**4a**	95	8	65 (28)
6		**4b**	100	7	68 (28)

[a] **1**/**2**/Zn/$NiCl_2$/PPh_3 = 1:1.5:1.5:0.1:0.4. [b] The conversion of R_FCl was 100% (determined by ^{19}F NMR). [c] The isolated yields were based on R_FCl and a trace of R_FH was also obtained; the yields in the bracket were obtained in HMPA in the absence of PPh_3, R_FH (≥40%) being the major products.

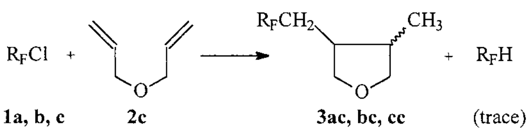
olefins in the presence of Raney nickel in EtOH at 80 °C to give the iodine adducts in high yields.[17] Later, Zhou and Huang showed that the ω-chloro perfluoroalkylation of amines,[33] anilines,[34] furan, thiophene and pyrrole[35] with the same iodides can occur in the presence of tetrakis(triphenylphosphine) nickel. Besides the easy hydrogenation with Zn/$NiCl_2$ in DMF at 80−120 °C, perfluoroalkyl chloride is hardly functionalized by other groups.[31,36] Surprisingly, in HMPA, the addition reaction of R_FCl to alkenes did take place in the presence of Zn/$NiCl_2$ at 100 °C for 8 h despite of the low yields of the adducts (15−30%), R_FH being the major products (≥ 40%). The results are listed in Table 1 and Table 2. After many attempts, it was found that the undesired R_FH could be suppressed significantly, subsequently raising the yields of the adducts if 0.4 equiv of PPh_3 was added to the reaction mixture. Additionally, DMF can be used instead of carcinogenic HMPA in the reaction.

1. Perfluoroalkylation of Electron-Rich Alkenes with Perfluoroalkyl Chlorides. It was found that perfluoroalkyl chlorides (**1**) can smoothly react with electron-rich alkenes (**2**) in DMF in the presence of zinc powder and catalytic amount of nickel dichloride and triphenylphosphine under nitrogen (**1**:**2**:Zn:$NiCl_2$:PPh_3 = 1:1.5:1.5:0.1:0.4) at 95−100 °C for 6−8 h to give the corresponding chlorine-free adducts (**3**) in good yields (see Scheme 1).

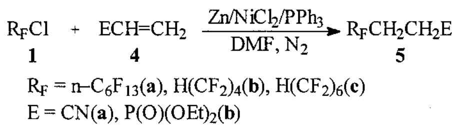
Scheme 1



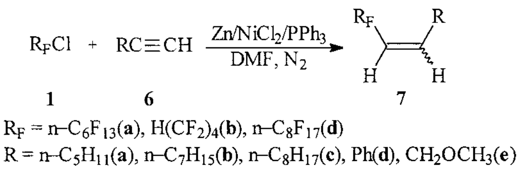
Scheme 2



Scheme 3



Scheme 4



The addition products **3ac**, **3bc**, and **3cc**, from the perfluoroalkyl chlorides and **2c**, are the tetrahydrofuran derivatives, indicative of a free radical intermediate.[10,13] The *cis*- and *trans*-configuration of **3ac**, **3bc**, and **3cc** can be assigned by comparing ^1H NMR chemical shift of $-CH_3$ (*cis* < *trans*) (see Scheme 2). All the results are listed in Table 1.

2. Perfluoroalkylation of Electron-Poor Alkenes with Perfluoroalkyl Chlorides. Different from the previous DMSO-induced sulfinatodehalogenation method,[31] we found that perfluoroalkyl chlorides can react not only with electron-rich alkenes but also with electron-poor ones under the similar conditions. Thus, when perfluoroalkyl chlorides (**1**) were treated with electron-deficient alkenes (**4**) in DMF in the presence of zinc powder, catalytic amounts of nickel dichloride and triphenylphosphine under nitrogen, hydrofluoroalkylated adducts (**5**) were obtained in good yields (see Scheme 3). The results are listed in Table 2.

3. Perfluoroalkylation of Alkynes with Perfluoroalkyl Chlorides. Similarly, treatment of alkynes with perfluoroalkyl chlorides in the presence of Zn/$NiCl_2$/PPh_3 (1.5:0.1:0.4) in DMF at 95−100 °C under nitrogen for 7−8 h gave the corresponding of *E*/*Z* mixture of alkenes in 50−75% yields (see Scheme 4). The *E*- and *Z*-isomers were determined by comparing the chemical shifts of the $R_F'\mathbf{CF_2}CH{=}CHR$ in their respective ^{19}F NMR spectra, the downfield signal being assigned to the *Z*-isomer and the upfield signal being assigned to the *E*-isomer.[31,37] The results are listed in Table 3.

4. Perfluoroalkylation of Aromatics with Perfluoroalkyl Chlorides. Perfluoroalkylation of electron-rich aromatic compounds (**8**) could be accomplished with

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Table 3. Reaction of R_FCl with Alkynes (6) Induced by Ni(0) in DMF[a]

entry	R_FCl[b]	alkynes	T °C	time (h)	**7** *Z*/*E*[c]	**7** yield %[d]
1	**1a**	**6a**	100	7	34/66	73
2		**6c**	100	7	33/67	72
3		**6d**	95	8	40/60	65
4		**6e**	95	7	0/100	56
5	**1b**	**6a**	95	8	34/66	72
6		**6b**	100	7	34/66	74
7		**6d**	95	7	50/50	63
8	**1d**	**6a**	100	8	33/67	75
9		**6e**	95	7	0/100	51

[a] **1**/**2**/Zn/$NiCl_2$/PPh_3 = 1:1.5:1.5:0.1:0.4. [b] The conversion of R_FCl was 100% (determined by ^{19}F NMR). [c] The ratio of *Z*/*E* was determined by ^{19}F NMR. [d] The isolated yields were based on R_FCl and a trace of R_FH was also obtained.

Scheme 5

R_F = n-C_6F_{13}(**a**), $H(CF_2)_4$(**b**), n-C_8F_{17}(**d**)
ArH = anisole(**a**), *N, N*–dimethyl aniline(**b**), *p*–aminoanisole(**c**), pyrrole(**d**), 2, 5-dimethyl pyrrole(**e**)

Table 4. Reaction of R_FCl with Aromatics (8) Induced by Ni(0) in DMF[a]

entry	R_FCl[b]	ArH (**8**)	*T* °C	time (h)	products (**9**)[c]	yield %[d]
1	**1a**	**8a**	100	8	**9aa** (*o*/*p*/*m* = 44:38:18)	62
2		**8b**	100	7	**9ab**	65
3		**8c**	95	8	**9ac**	56
4		**8d**	95	6	**9ad**	78
5		**8e**	95	7	**9ae**	70
6	**1b**	**8d**	95	6	**9bd**	75
7		**8e**	95	8	**9be**	68
8	**1d**	**8a**	100	8	**9da** (*o*/*p*/*m* = 48:32:20)	71
9		**8b**	100	8	**9db**	60
10		**8c**	95	7	**9dc**	58
11		**8d**	95	6	**9dd**	76
12		**8e**	95	7	**9de**	70

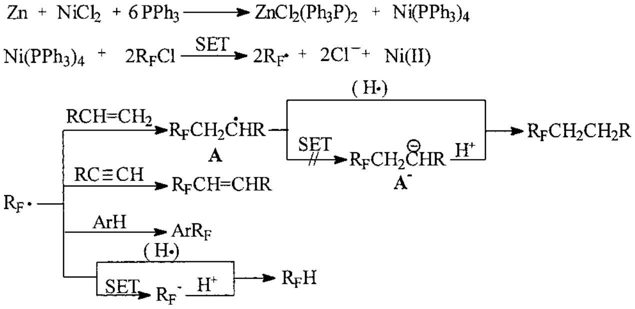
[a] **1**/**2**/Zn/$NiCl_2$/PPh_3 = 1:1.5:1.5:0.1:0.4. [b] The conversion of R_FCl was 100% (determined by ^{19}F NMR). [c] The position of perfluoroalkyl group located was determined by ^{19}F NMR. [d] The isolated yields were based on R_FCl and a trace of R_FH was also obtained.

moderate to good yields in similar fashion with perfluoroalkyl chlorides in DMF in the presence of Zn/$NiCl_2$/PPh_3 (1.5:0.1:0.4) under nitrogen at 95−100 °C (see Scheme 5). The results are listed in Table 4.

The results in Table 4 are consistent with the electrophilic property of perfluoroalkyl radical. The yields and regioselectivity of the products were depended on the structures of the starting aromatics. For example, with anisole (**8a**), a mixture of *o*-, *p*-, and *m*- was obtained, while with *N*,*N*-dimethyl aniline (**8b**) only *p*-perfluoroalkylated products were isolated. The perfluoroalkyl group was located on the *o*-position relative to $-NH_2$ in the reaction with *p*-aminoanisole (**8c**). When pyrrole (**8d**) was used as substrate, only *2*-perfluoroalkylated products were obtained in good yields.

5. Inhibitor and Mechanism Consideration. Before the mechanism consideration, some inhibition experiments were carried out. Addition of ET scavenger, i.e., *p*-dinitrobenzene (DBN) (20mol %), or free radical inhibitor, i.e., hydroquinone (HQ) (20mol %), to the reaction mixture of **1a** and **2b** decreased the conversion of **1a** significantly (from 90% without DNB to 0% and from 61% without HQ to 35%) at the same reaction temperature and time.

Scheme 6



Both the inhibition experiments and the formation of tetrahydrofuran derivatives from the reaction with diallyl ether indicated that the perfluoroalkyl radical might be involved in the reaction mechanism. The most likely explanation of generation of R_F• is that R_FCl, quite similar to R_FI,[9−12] accepts one electron from Ni(0) complex, produced by reaction of nickel dichloride with zinc and triphenylphosphine, then dissociated to give R_F• and Cl^-. The R_F• adds to alkene to form intermediate **A**. The intermediate, **A**, does not abstract chlorine from R_FCl due to the strong carbon−chlorine bond but easily picks a hydrogen from the solvents to afford the adduct. Along with the H-abstraction from the solvent to give R_FH,[38] R_F• can be reduced by SET to form R_F^-, which is then protonated to yield the same hydride. The one-electron reduction of intermediate **A** to produce carbanion $\mathbf{A}^-$, then the adduct, after protonation, seemingly, is less important because the electron-accepting ability of **A** should be much weaker than that of R_F•. Similarly, the R_F• undergoes the addition reactions to alkynes and aromatic compounds to afford perfluoroalkylated alkenes and substituted aromatic compounds, respectively (see Scheme 6).

The reason the formation of R_FH can be suppressed by adding Ph_3P is not very clear yet. Some interaction among protons Ph_3P and R_F• is expected to evaluate in this system. However, it is known that the big ligand (Ph_3P) role is played in the formation of highly active teriary phosphine complexes of Ni(0) and the proper environment for both C−Cl bond activation and further functionalization.[39]

In conclusion, we have developed a new practical perfluoroalkylation method of alkenes, alkynes, and aromatics with available perfluooroalkyl chlorides in the presence of Ni(0).

Experimental Section

^1H NMR spectra were recorded at 300 or 400 MHz on a machine using TMS as an internal standard (positive for upfield). ^{19}F NMR spectra were recorded at 282 or 376 MHz using CF_3COOH as an external standard (positive for upfield). The solvent for NMR measurement was $CDCl_3$ or CD_3COCD_3.

1. Typical Procedure for the Reaction of 1 with 2. A 25 mL three-necked flask, equipped with a water condenser

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(38) We thank the Referee for reminding us of the possibility of the formation of R_FH from the reduction of R_F• to R_F^- followed by the protonation along with the H-abstraction from the solvent. Indeed, a previous report showed that both processes are of comparable importance for the CF_3• radicals produced upon electrochemical reduction of CF_3Br in DMSO: Andreux, C. P.; Gelis, L.; Medebielle, M.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 3509.

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and a magnetic stirring bar, was charged with zinc powder (488 mg, 7.5 mmol), nickel dichloride (65 mg, 0.5 mmol), and triphenylphosphine (530 mg, 2.0 mmol). The flask was filled with nitrogen and the nitrogen purged solvent DMF (10 mL) was then added. The mixture was heated to about 95 °C to form a brown catalyst. A mixture of **1a** (1.77 g, 5 mmol) and **2a** (630 mg, 7.5 mmol) was added and stirred at this temperature for 8 h. The conversion of **1a** was 100%, determined by ^{19}F NMR. After cooled, the precipitate was filtered off and the product was extracted with ether. The combined extracts were washed with water and dried over Na_2SO_4. After removing ether, the residue was subjected to flash chromatography on silica gel to give **3aa** as a colorless oil (1.45 g, yield 72%).

3aa: colorless oil; ^{1}H NMR δ 0.90 (t, $J = 6.6$ Hz, 3H), 1.28−1.42 (m, 6H), 1.54−1.64 (m, 2H), 1.96−2.14 (m, 2H); ^{19}F NMR δ 4.0 (t, $J = 10$ Hz, 3F), 37.6 (m, $J = 15$ Hz, 2F), 45.1 (s, 2F), 46.1 (s, 2F), 46.8 (s, 2F), 49.4 (s, 2F); MS *m/z* (relative intensity) 403 ($M^+ - 1$, 0.89), 389 (1.68), 85 (47.10), 71 (26.52), 69 (16.63), 57 (70.46), 43 (100.00); HRMS calcd for $C_{12}H_{13}F_{13}$: 404.0809, Found: 404.0768.

3ab: colorless oil; ^{1}H NMR δ 0.89 (t, $J = 5.8$ Hz, 3H), 1.28−1.64 (m, 12H), 2.02−2.13 (m, 2H); ^{19}F NMR δ 3.98 (t, $J = 10$ Hz, 3F), 37.6 (m, $J = 15$ Hz, 2F), 45.1 (s, 2F), 46.1 (s, 2F), 46.8 (s, 2F), 49.4 (s, 2F); MS *m/z* (relative intensity) 431 ($M^+ - 1$, 0.91), 389 (14.48), 85 (12.80), 71 (44.32), 69 (18.03), 57 (95.06), 43 (100.00); HRMS calcd for $C_{14}H_{17}F_{13}$: 432.1122, Found: 432.1104.

3ac: colorless oil; ^{1}H NMR δ 1.01 (d, $J = 6.6$ Hz, 0.7×3H, *cis*-CH_3), 1.09 (d, $J = 6.6$ Hz, 0.3×3H, *trans*-CH_3), 1.95−2.46 (m, 4H), 3.35−3.56 (m, 2H), 3.94−4.13 (m, 2H); ^{19}F NMR δ 3.90 (t, $J = 10$ Hz, 3F), 36.7 (m, 2F), 45.0 (s, 2F), 46.1 (s, 2F), 46.7 (d, $J = 9$ Hz, 2F), 49.4 (d, $J = 9$ Hz, 2F); MS *m/z* (relative intensity) 418 (M^+, 0.85), 388 (52.77), 69 (100.00), 55 (74.16), 41 (34.19); Anal. Calcd for $C_{12}H_{11}F_{13}O$: C, 34.45; H, 2.63. Found: C, 34.59; H, 2.66.

3af: colorless oil; ^{1}H NMR δ 1.15−2.16 (m, 11H); ^{19}F NMR δ 4.0 (t, $J = 9.4$ Hz, 3F), 41.3 (d, $J = 10.2$ Hz, 2F), 43.8 (s, 2F), 45.3 (s, 2F), 46.0 (d, 2F), 49.4 (d, $J = 12.7$ Hz, 2F); MS *m/z* (relative intensity) 402 (M^+, 10.77), 401 (75.42), 381 (48.91), 81 (100.00), 69 (25.01), 41 (53.26). Anal. Calcd for $C_{12}H_{11}F_{13}$: C, 35.82; H, 2.74; F, 61.44. Found: C, 35.87; H, 2.93; F, 61.30.

3ba:[31] colorless oil; ^{1}H NMR δ 0.91 (t, $J = 6.7$ Hz, 3H), 1.31−1.66 (m, 8H), 1.98−2.16 (m, 2H), 6.06 (tt, $J = 52$, 5.6 Hz, 1H); ^{19}F NMR δ 37.4 (t, $J = 12$ Hz, 2F), 48.7 (s, 2F), 53.3 (m, $J = 5$ Hz, 2F), 60.4 (d, $J = 45$ Hz, 2F); MS *m/z* (relative intensity) 286 (M^+, 1.25), 285 ($M^+ - 1$, 10.70), 284 (12.83), 271 (20.41), 85 (100.00), 71 (36.63), 57 (60.83), 43 (24.73).

3bb:[31] colorless oil; ^{1}H NMR δ 0.9 (t, $J = 6.6$ Hz, 3H), 1.55−1.65 (m, 2H),1.29−1.44 (m, 10H), 1.97−2.15 (m, 2H), 6.04 (tt, $J = 52$, 5.6 Hz, 1H); ^{19}F NMR δ 36.7 (s, 2F), 48.3 (s, 2F), 52.8 (s, 2F), 59.9 (d, 2F); MS *m/z* (relative intensity) 314 (M^+, 0.82), 313 ($M^+ - 1$, 5.28), 271 (34.97), 85 (6.46), 71 (19.86), 57 (100.00), 43 (59.78).

3bc:[31] colorless oil; ^{1}H NMR δ 0.98 (d, $J = 7.0$ Hz, 0.7×3H, *cis*-CH_3), 1.09 (d, $J = 6.6$ Hz, 0.3×3H, *trans*-CH_3), 1.95−2.64 (m, 4H), 3.35−3.55 (m, 2H), 3.94−4.13 (m, 2H), 6.05 (tt, $J = 52$, 5.5 Hz, 1H); ^{19}F NMR δ 34.9−38.2 (m, 2F), 48.6 (s, 2F), 52.9 (s, 2F), 60.3 (d, $J = 51.5$ Hz, 2F); MS *m/z* (relative intensity) 301 ($M^+ + 1$, 62.44), 299 (31.75), 283 (38.97), 270 (46.68), 69 (100.00), 55 (82.65), 51 (20.49), 41 (52.19).

3bd: colorless oil; ^{1}H NMR δ 1.81−2.30 (m, 5H), 3.73 (t, $J = 6.2$ Hz, 2H), 6.05 (tt, $J = 52$, 5.5 Hz, 1H);^{19}F NMR δ 32.7 (m, 2F), 44.1 (d, $J = 6.8$ Hz, 2F), 48.7 (t, $J = 5$ Hz, 2F), 57.0 (d, $J = 50$ Hz, 2F); MS *m/z* (relative intensity) 260 (M^+, 1.89), 259 ($M^+ - 1$, 13.07), 243 (9.77), 223 (100.00), 177 (59.78), 151 (39.61), 109 (83.25), 101 (35.85), 91 (73.07), 77 (52.57), 59 (65.46), 51 (96.57), 47 (57.14). Anal. Calcd for $C_7H_8F_8O$: C, 32.31; H, 3.08; F, 58.46. Found: C, 32.00; H, 3.28; F, 58.48.

3bf:[31] colorless oil; ^{1}H NMR δ 1.17−2.17 (m, 11H), 6.02 (tt, $J = 52$, 5.6 Hz, 1H); ^{19}F NMR δ 41.1 (t, $J = 4.2$ Hz, 2F), 46.0 (d, $J = 6.6$ Hz, 2F), 50.7 (m, $J = 6$ Hz), 60.6 (d, $J = 52$ Hz, 2F); MS *m/z* (relative intensity) 284 (M^+, 0.63), 283 ($M^+ - 1$, 5.65), 263 (4.05), 245 (7.90), 113 (9.53), 83 (100.00), 56 (12.02), 55 (59.71), 51 (22.12), 41 (36.18).

3ca:[31] colorless oil; ^{1}H NMR δ 0.88 (t, $J = 6.5$ Hz, 3H), 1.29−1.65 (m, 8H), 1.96−2.13 (m, 2H), 6.02 (tt, $J = 52$, 5.2 Hz, 1H); ^{19}F NMR δ 37.8 (t, $J = 15$ Hz, 2F), 45.2 (s, 2F), 46.9 (s, 4F), 53.1 (s, 2F), 60.5 (d, $J = 52$ Hz, 2F); MS *m/z* (relative intensity) 386 (M^+, 0.24), 385 ($M^+ - 1$, 1.63), 371 (3.95), 85 (30.98), 71 (20.60), 57 (68.75), 43 (100.00).

3cb:[31] colorless oil; ^{1}H NMR δ 0.89 (t, $J = 6$ Hz, 3H), 1.29−1.65 (m, 12H), 1.95−2.13 (m, 2H), 6.03 (tt, $J = 52$, 5.2 Hz, 1H);^{19}F NMR δ 38.3 (t, 2F), 45.5 (s, 2F), 47.5 (s, 4F), 53.8 (s, 2F), 61.3 (d, 2F); MS *m/z* (relative intensity) 413 ($M^+ - 1$), 385 (3.42), 371 (2.52), 101 (2.46), 85 (7.19), 71 (31.45), 57 (59.11), 43 (100.00).

3cc:[31] colorless oil; ^{1}H NMR δ 0.97 (d, $J = 7.0$ Hz, 0.7×3H, *cis*-CH_3), 1.07 (d, $J = 6.5$ Hz, 0.3×3H, *trans*-CH_3), 1.93−2.63 (m, 4H), 3.34−3.54 (m, 2H), 3.92−4.12 (m, 2H) 6.05 (tt, $J = 52$, 5.2 Hz, 1H); ^{19}F NMR δ 35.1−38.3 (m, 2F), 45.0 (s, 2F), 46.7 (s, 4F), 52.7 (s, 2F), 60.2 (d, $J = 52$ Hz, 2F); MS *m/z* (relative intensity) 401 ($M^+ + 1$, 18.31), 400 (M^+, 2.38), 399 ($M^+ - 1$, 11.22), 383 (18.03), 370 (13.70), 69 (100.00), 55 (74.65), 41 (47.32).

3ce: colorless oil; ^{1}H NMR δ 1.72−2.10 (m, 5H), 2,24−2.44 (m, 2H), 4.17 (t, $J = 6.3$ Hz, 2H), 6.84 (tt, $J = 51$, 5.3 Hz, 1H);^{19}F NMR δ 38.2 (s, 2F), 45.5 (s, 2F), 47.4 (s, 4F), 53.6 (s, 2F), 61.4 (d, 2F); MS *m/z* (relative intensity) 403 ($M^+ + 1$, 29.50), 91 (7.34), 73 (4.29), 61 (23.67), 51 (10.91), 43 (100.00). Anal. Calcd for $C_{11}H_{10}F_{12}O_2$: C, 32.84; H, 2.49. Found: C, 32.76; H: 2.29.

3cf:[31] colorless oil; ^{1}H NMR δ 1.18−2.14 (m, 11H), 6.04 (tt, $J = 52$, 5.2 Hz, 1H);^{19}F NMR δ 41.3 (dd, $J = 7.2$, 3.6 Hz, 2F), 43.8 (s, 2F), 45.3 (s, 2F), 46.7 (s, 2F), 52.9 (s, 2F), 60.3 (d, $J = 52$ Hz, 2F); MS *m/z* (relative intensity) 383 ($M^+ - 1$, 1.62), 382 (3.68), 363 (3.67), 345 (10.83), 83 (100.00), 55 (48.80), 51 (35.77), 41 (29.89).

2. General Procedure for the Reaction of 1 with 4. A 25 mL three-necked flask, equipped with a water condenser and a magnetic stirring bar, was charged with zinc powder (488 mg, 7.5 mmol), nickel dichloride (65 mg, 0.5 mmol), and triphenylphosphine (530 mg, 2.0 mmol). The flask was filled with nitrogen and the nitrogen purged solvent DMF (10 mL) was then added. The mixture was heated to about 95 °C to form a brown catalyst. A mixture of **1a** (1.77 g, 5 mmol) and **4a** (398 mg, 7.5 mmol) was added and stirred at this temperature for 8 h. The conversion of **1a** was 100%, determined by ^{19}F NMR. After it was cooled, the precipitate was filtered off and the product was extracted with ether. The combined extracts were washed with water and dried over Na_2SO_4. After removal of ether, the residue was subjected to flash chromatography on silica gel to give **5aa** as a colorless oil (1.25 g, yield 67%).

5aa: colorless oil; ^{1}H NMR δ 2.43−2.73 (m, 4H); ^{19}F NMR δ 4.1 (t, $J = 10$ Hz, 3F), 38.6 (m, 2F), 45.1 (s, 2F), 46.1 (s, 2F), 46.7 (s, 2F), 49.5 (s, 2F); MS *m/z* (relative intensity) 373 (M^+, 0.76), 343 (10.54), 149 (15.42), 104 (47.63), 69 (37.31), 54 (100.00); Anal. Calcd for $C_9H_4F_{13}N$: C, 28.95; H, 1.07; N, 3.75; F, 66.22. Found: C, 28.94; H, 0.97; N, 3.77; F, 66.13.

5ab: colorless oil; ^{1}H NMR δ 1.35 (t, $J = 7.0$ Hz, 6H), 1.93−2.49 (m, 4H), 4.15 (m, 4H); ^{19}F NMR δ 4.0 (t, $J = 9.5$ Hz, 3F), 38.6 (t, $J = 5$ Hz, 2F), 45.1 (s, 2F), 46.1 (s, 2F), 46.6 (s, 2F), 49.4 (s, 2F); MS *m/z* (relative intensity) 484 (M^+, 1.34), 429 (38.17), 169 (45.04), 97 (31.02), 70 (100.00), 69 (73.81); Anal. Calcd for $C_{12}H_{14}F_{13}O_3P$: C, 29.75; H, 2.89. Found: C, 29.77; H, 3.00.

5ba: colorless oil; ^{1}H NMR δ 2.62−2.99 (m, 4H), 6.73 (tt, $J = 51$, 5.6 Hz, 1H);^{19}F NMR δ 33.7 (m, 2F), 44.0 (s, 2F), 48.4 (d, $J = 4$ Hz, 2F), 57.0 (d, $J = 49.5$ Hz, 2F); MS *m/z* (relative intensity) 256($M^+ + 1$, 1.68), 166 (15.28), 104 (100.00), 69 (26.62), 55 (22.38), 54 (93.74), 51 (71.48), 41 (37.17). Anal. Calcd for $C_7H_5F_8N$: C, 32.94; H, 1.96. Found: C, 33.01; H, 2.02.

5bb: colorless oil; ^{1}H NMR δ 1.32 (m, 6H), 1.98−2.50 (m, 4H), 4.14 (m, 4H), 6.77 (tt, $J = 51$, 5.5 Hz, 1H);^{19}F NMR δ 33.6 (m, 2F), 43.8 (s, 2F), 48.5 (d, $J = 4$ Hz, 2F), 57.0 (d, $J = 52$ Hz, 2F); MS *m/z* (relative intensity) 367 ($M^+ + 1$, 13.57), 339 (7.08), 311 (8.75), 293 (2.18), 165 (6.15), 109 (2.81), 51

(4.51); Anal. Calcd for $C_{10}H_{15}F_8O_3P$: C, 32.79; H, 4.10. Found: C, 32.76; H, 4.40.

5ca: colorless oil; ^{1}H NMR δ 2.43−2.72 (m, 4H), 6.06 (tt, J = 51.8, 5.1 Hz, 1H); ^{19}F NMR δ 38.7 (q, J = 15 Hz, 2F), 45.2 (d, J = 10.7 Hz, 2F), 46.8 (s, 4F), 52.8 (s, 2F), 60.5 (d, J = 52 Hz, 2F); MS *m/z* (relative intensity) 356 ($M^+ + 1$, 2.86), 286 (10.85), 104 (96.11), 69 (18.33), 54 (100.00), 51 (44.40); Anal. Calcd for $C_9H_5F_{12}N$: C, 30.42; H, 1.41; N, 3.94; F, 64.22. Found: C, 30.43; H, 1.49; N, 3.96; F, 64.80.

5cb: colorless oil; ^{1}H NMR δ 1.32 (m, 6H), 1.97−2.47 (m, 4H), 4.15 (m, 4H), 6.88 (tt, J = 50.8, 5.3 Hz, 1H); ^{19}F NMR δ 37.6 (s, 2F), 44.6 (s, 2F), 46.1 (s, 4F), 52.2 (s, 2F), 61.1 (d, 2F); MS *m/z* (relative intensity) 467 ($M^+ + 1$, 83.46), 439 (33.33), 411 (100.00), 393 (25.34), 353 (15.08), 165 (41.80), 138 (23.35), 109 (43.74), 81 (26.98), 65 (28.31), 51 (34.83); Anal. Calcd for $C_{12}H_{15}F_{12}O_3P$: C, 30.90; H, 3.22. Found: C, 30.89; H, 3.33.

3. General Procedure for the Reaction of 1 with 6. A 25 mL three-necked flask, equipped with a water condenser and a magnetic stirring bar, was charged with zinc powder (488 mg, 7.5 mmol), nickel dichloride (65 mg, 0.5 mmol), and triphenylphosphine (530 mg, 2.0 mmol). The flask was filled with nitrogen and the nitrogen purged solvent DMF (10 mL) was then added. The mixture was heated to about 100 °C to form a brown catalyst. A mixture of **1a** (1.77 g, 5 mmol) and **6a** (720 mg, 7.5 mmol) was added and stirred at this temperature for 7 h. The conversion of **1a** was 100%, determined by ^{19}F NMR. After cooled, the precipitate was filtered off and the product was extracted with ether. The combined extracts were washed with water and dried over Na_2SO_4. After removing ether, the residue was subjected to flash chromatography on silica gel to give **7aa** as a colorless oil (1.52 g, yield 73%).

7aa: colorless oil; ^{1}H NMR δ 0.85 (t, J = 6.5 Hz, 3H), 1.23−1.57 (m, 6H), 2.10−2.28 (m, 2H), 5.40−6.41 (m, 2H); ^{19}F NMR δ 4.24 (t, J = 9.6 Hz, 3F), 30.0 (d, J = 12.7 Hz, 0.34 × 2F, *Z*), 34.6 (d, J = 11.7 Hz, 0.66 × 2F, *E*), 45.0 (s, 0.66 × 2F), 45.2 (s, 0.34 × 2F), 46.2 (s, 2F), 47.0 (m, 2F), 49.6 (s, 2F); MS *m/z* (relative intensity) 416 (M^+, 58.99), 415 (70.70), 347 (35.03), 83 (23.34), 69 (38.77), 56 (100.00), 55 (72.04), 41 (57.19); HRMS calcd for $C_{13}H_{13}F_{13}$: 416.0809, Found: 416.0821.

7ac: colorless oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H), 1.28−1.86 (m, 12H), 2.19−2.33 (m, 2H), 5.41−6.46 (m, 2H); ^{19}F NMR δ 3.87 (t, J = 10 Hz, 3F), 29.7 (d, J = 12.4 Hz, 0.33 × 2F, *Z*), 34.3 (d, J = 11.6 Hz, 0.67 × 2F, *E*), 44.8 (s, 2F), 46.0 (s, 2F), 46.7 (d, J = 9.1 Hz, 0.67 × 2F), 46.9 (d, J = 14.3 Hz, 0.33 × 2F), 49.3 (s, 2F); MS *m/z* (relative intensity) 457 ($M^+ - 1$, 3.87), 414 (22.69), 83 (38.89), 70 (72.69), 69 (67.71), 57 (100.00), 56 (94.03), 55 (83.32), 43 (83.88), 41 (68.85); HRMS calcd for $C_{16}H_{19}F_{13}$: 458.1279, Found: 458.1290.

7ad: colorless oil; ^{1}H NMR δ 5.42−6.50 (m, 2H), 7.25 (m, 5H); ^{19}F NMR δ 3.96 (t, J = 9.8 Hz, 3F), 29.8 (d, J = 13.0 Hz, 0.40 × 2F, *Z*), 34.4 (d, J = 11.2 Hz, 0.60 × 2F, *E*), 44.8 (s, 2F), 46.0 (s, 2F), 46.6 (s, 2F), 49.3 (s, 2F); MS *m/z* (relative intensity) 422 (M^+, 1.62), 339 (42.01), 220 (28.59), 205 (100.00), 145 (19.23), 57 (34.45), 43 (34.32); HRMS calcd for $C_{14}H_7 F_{13}$: 422.0340, Found: 422.0383.

7ae: colorless oil; ^{1}H NMR δ 3.41 (s, 3H), 4.08 (m, 2H), 5.92−6.49 (m, 2H); ^{19}F NMR δ 3.87 (t, J = 10 Hz, 3F), 34.9 (d, J = 11.5 Hz, 2F), 44.8 (s, 2F), 46.0 (s, 2F), 46.6 (s, 2F), 49.4 (s, 2F); MS *m/z* (relative intensity) 390 (M^+, 5.92), 127 (99.40), 69 (28.99), 57 (53.61), 56 (100.00), 55 (47.30), 43 (53.43), 41 (51.05); HRMS calcd for $C_{10}H_7F_{13}O$: 390.0289, Found: 390.0251.

7ba: colorless oil; ^{1}H NMR δ 0.90 (t, J = 6.2 Hz, 3H), 1.27−1.64 (m, 6H), 2.16−2.32 (m, 2H), 5.46−6.44 (m, 3H); ^{19}F NMR δ 29.7 (d, J = 9.5 Hz, 0.34 × 2F, *Z*), 34.4 (d, J = 9.4 Hz, 0.66 × 2F, *E*), 48.7 (t, J = 7.6 Hz, 0.66 × 2F), 48.9 (d, J = 7.1 Hz, 0.34 × 2F), 53.1 (d, J = 4.8 Hz, 0.66 × 2F), 53.4 (d, J = 5.5 Hz, 0.34 × 2F), 60.6 (d, J = 48.6 Hz, 2F); MS *m/z* (relative intensity) 298 (M^+, 15.79), 270 (18.42), 70 (71.80), 57 (51.13), 56 (100.00), 55 (81.39), 44 (77.44), 43 (53.20), 41 (74.25); HRMS calcd for $C_{11}H_{14}F_8$: 298.0967, Found: 298.0931.

7bb: colorless oil; ^{1}H NMR δ 0.88 (t, J = 6.8 Hz, 3H), 1.17−1.68 (m, 10H), 2.15−2.32 (m, 2H), 5.46−6.43 (m, 3H); ^{19}F NMR δ 29.6 (d, J = 9.4 Hz, 0.34 × 2F, *Z*), 34.3 (d, J = 9.5 Hz, 0.66 × 2F, *E*), 48.6 (t, J = 7.8 Hz, 0.66 × 2F), 48.8 (d, J = 6.7 Hz, 0.34 × 2F), 53.0 (d, J = 5.9 Hz, 2F), 60.5 (d, J = 50.3 Hz, 2F); MS *m/z* (relative intensity) 326 (M^+, 4.27), 297 (25.65), 70 (50.12), 69 (48.68), 56 (77.91), 55 (52.22), 43 (100.00), 41 (45.91); HRMS calcd for $C_{13}H_{18}F_8$: 326.1280, Found: 326.1287.

7bd:[31] colorless oil; ^{1}H NMR δ 5.72−6.23 (m, 3H), 7.09−7.48 (m, 5H); ^{19}F NMR δ 28.35 (d, J = 8.4 Hz, 0.5 × 2F, *Z*), 34.2 (d, J = 10.3 Hz, 0.5 × 2F, *E*), 48.2 (s, 2F), 58.9 (s, 2F), 60.4 (d, J = 52 Hz, 2F); MS *m/z* (relative intensity) 304 (M^+, 15.74), 153 (100.00), 133 (76.81), 51 (15.14).

7da: colorless oil; ^{1}H NMR δ 0.91 (t, J = 6.7 Hz, 3H), 1.29−2.31 (m, 8H), 5.52−6.48 (m, 2H); ^{19}F NMR δ 3.92 (t, J = 9.8 Hz, 3F), 29.8 (d, J = 13 Hz, 0.33 × 2F, *Z*), 34.4 (d, J = 11.2 Hz, 0.67 × 2F, *E*), 44.6 (s, 2F), 45.1 (s, 4F), 45.9 (s, 2F), 46.7 (s, 2F), 49.3 (s, 2F); MS *m/z* (relative intensity) 516 (M^+, 8.39), 440 (49.66), 169 (7.81), 121 (98.86), 82 (71.90), 70 (79.83), 69 (70.86), 56 (100.00), 55 (89.21), 41 (89.21); HRMS calcd for $C_{15}H_{13}F_{17}$: 516.0745, Found: 516.0752.

7de: colorless oil; ^{1}H NMR δ 3.42 (s, 3H), 4.09 (m, 2H), 5.93 (m, 1H), 6.46 (m, 1H); ^{19}F NMR δ 3.90 (t, J = 10 Hz, 3F), 34.9 (d, J = 11.5 Hz, 2F), 44.6 (d, J = 7.4 Hz, 2F), 45.1 (d, J = 6.7 Hz, 4F), 45.9 (s, 2F), 46.6 (s, 2F), 49.3 (d, J = 10.5 Hz, 2F); MS *m/z* (relative intensity) 490 (M^+, 20.60), 471 (55.36), 121 (18.42), 71 (100.00), 69 (21.79); HRMS calcd for $C_{12}H_7F_{17}O$: 490.0225, Found: 490.0224.

4. General Procedure for the Reaction of 1 with 8. A 25 mL three-necked flask, equipped with a water condenser and a magnetic stirring bar, was charged with zinc powder (488 mg, 7.5 mmol), nickel dichloride (65 mg, 0.5 mmol), and triphenylphosphine (530 mg, 2.0 mmol). The flask was filled with nitrogen and the nitrogen purged solvent DMF (10 mL) was then added. The mixture was heated to about 100 °C to form a brown catalyst. A mixture of **1a** (1.77 g, 5 mmol) and **8a** (810 mg, 7.5 mmol) was added and stirred at this temperature for 8 h. The conversion of **1a** was 100%, determined by ^{19}F NMR. After cooled, the precipitate was filtered off and the product was extracted with ether. The combined extracts were washed with water and dried over Na_2SO_4. After removing ether, the residue was subjected to flash chromatography on silica gel to give **9aa** as a colorless oil (1.32 g, yield 62%).

9aa (*o*/*p*/*m* = 44:38:18): colorless oil; ^{1}H NMR δ 3.85 (s, 3H), 6.98−7.53 (m, 4H); ^{19}F NMR δ 4.04 (t, J = 8.5 Hz, 3F), 30.9 (t, J = 15 Hz, 0.44 × 2F, *o*), 32.9 (t, J = 15 Hz, 0.38 × 2F, *p*), 33.8 (t, J = 15 Hz, 0.18 × 2F, *m*), 44.6 (m, 2F), 45.2 (m, 2F), 46.0 (d, J = 8 Hz, 2F), 49.4 (s, 2F); MS *m/z* (relative intensity) 426 (M^+, 100.00), 407 (18.60), 219 (8.11), 157 (66.19), 109 (18.21), 69 (3.35); HRMS calcd for $C_{13}H_7F_{13}O$: 426.0289, Found: 426.0245.

9ab: colorless oil; ^{1}H NMR δ 3.01 (s, 6H), 6.70 (d, J = 8.9 Hz, 2H), 7.40 (d, J = 8.9 Hz, 2H); ^{19}F NMR δ 4.08 (t, J = 10 Hz, 3F), 32.4 (t, J = 14 Hz, 2F), 44.8 (s, 2F), 45.2 (m, 2F), 46.5 (d, J = 6 Hz, 2F), 49.4 (m, 2F); MS *m/z* (relative intensity) 439 (M^+, 64.21), 420 (15.31), 170 (100.00), 154 (15.42), 69 (6.34); Anal. Calcd for $C_{14}H_{10}F_{13}N$: C, 38.28; H, 2.29; N, 3.19. Found: C, 38.23; H, 2.36; N, 3.46.

9ac: colorless oil; ^{1}H NMR δ 3.78 (s, 3H), 3.84 (br, 2H), 6.72 (d, J = 8.8 Hz, 1H), 6.88−6.98 (m, 2H); ^{19}F NMR δ 4.10 (t, J = 10 Hz, 3F), 31.8 (t, J = 14 Hz, 2F), 45.0 (s, 4F), 45.6 (s, 2F), 49.5 (s, 2F); MS *m/z* (relative intensity) 441 (M^+, 100.00), 426 (22.38), 172 (37.82), 157 (3.35), 129 (7.90), 69 (1.45); Anal. Calcd for $C_{13}H_8F_{13}NO$: C, 35.39; H, 1.83; N, 3.17; F, 55.98. Found: C, 35.44; H, 1.88; N, 3.35; F, 56.02.

9ad: colorless oil; bp 88−90 °C/20 mmHg; ^{1}H NMR *d* 6.31 (d, J = 1.0 Hz, 1H), 6.63 (s, 1H), 6.95 (s, 1H), 8.53 (br, 1H); ^{19}F NMR *d* 4.02 (t, J = 9.5 Hz, 3F), 30.42 (t, J = 13.0 Hz, 2F), 45.0 (s, 2F), 45.8 (d, J = 13 Hz, 2F), 46.1 (s, 2F), 49.4 (s, 2F). MS *m/z* (relative intensity) 386 ($M^+ + 1$, 4.85), 385 (M^+, 30.67), 366 (10.16), 347 (14.49), 178 (25.82), 147 (13.19), 116 (100.00), 69 (18.24). Anal. Calcd for $C_{10}H_4F_{13}N$: C, 31.17; H, 1.04; N, 3.64; F, 64.16. Found: C, 31.23; H, 1.26; N, 3.85; F, 64.54.

9ae:[40] colorless oil; ^{1}H NMR *d* 1.44 (s, 3H), 2.25 (s, 3H), 6.60 (d, J = 4.8 Hz, 1H), 7.43 (d, J = 5.2 Hz, 1H); ^{19}F NMR *d* 5.16 (t, J = 10 Hz, 3F), 37.1 (m, 2F), 43.4 (m, 2F), 45.8 (s, 2F), 46.7

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(40) Huang, W.-Y.; Ma, W.-P. *Chin. Chem. Lett.* **1991**, *2*, 755.

(s, 2F), 50.2 (s, 2F). MS *m*/*z* (relative intensity) 414 (M$^+$ + 1, 100.00), 412 (M$^+$ − 1, 30.55), 394 (3.34), 95 (12.98), 94 (21.88), 69 (2.05).

9bd: colorless oil; ^{1}H NMR *d* 5.99 (tt, *J* = 52, 5.5 Hz, 1H), 6.31 (m, 1H), 6.63 (s, 1H), 6.96 (d, *J* = 1.1 Hz, 1H), 8.50 (br, 1H); ^{19}F NMR *d* 24.7 (s, 2F), 42.8 (s, 2F), 48.5 (t, *J* = 5 Hz, 2F), 56.9 (d, *J* = 51.8 Hz, 2F); MS *m*/*z* (relative intensity) 267 (M$^+$, 16.23), 248 (3.87), 210 (21.65), 144 (100.00), 116 (75.20), 94 (23.55), 51 (21.42); Anal. Calcd for $C_8H_5F_8N$: C, 35.97; H, 1.89; N, 5.24; F, 56.90. Found: C, 36.16; H, 1.72; N, 5.50; F, 56.73.

9be: colorless oil; ^{1}H NMR *d*1.43 (s, 3H), 2.23 (s, 3H), 6.60 (d, *J* = 4.8 Hz, 1H), 6.67 (tt, *J* = 51.2, 5.8 Hz, 1H), 7.44 (d, *J* = 4.8 Hz, 1H); ^{19}F NMR *d* 31.9 (m, 2F), 40.1 (m, 2F), 48.8 (m, 2F), 57.0 (d, *J* = 51 Hz, 2F); MS *m*/*z* (relative intensity) 295 (M$^+$, 11.74), 294 (18.41), 269 (17.73), 144 (100.00), 118 (78.68), 95 (67.24), 51 (21.02); HRMS calcd for $C_{10}H_9F_8N$: 295.0607, Found: 295.0616.

9da (*o*/*p*/*m* = 48:32:20): colorless oil; ^{1}H NMR δ 3.86 (s, 3H), 6.98−7.54 (m, 4H); ^{19}F NMR δ 4.10 (t, *J* = 10 Hz, 3F), 30.9 (t, *J* = 13 Hz, 0.48 × 2F, *o*), 32.9 (t, *J* = 15 Hz, 0.32 × 2F, *p*), 33.8 (t, *J* = 15 Hz, 0.20 × 2F, *m*), 44.5 (m, 2F), 45.1 (m, 6F), 46.0 (s, 2F), 49.4 (t, *J* = 11 Hz, 2F); MS *m*/*z* (relative intensity) 526 (M$^+$, 67.28), 507 (26.43), 219 (7.74), 157 (100.00), 109 (15.71), 69 (4.26); Anal. Calcd for $C_{15}H_7F_{17}O$: C, 34.24; H, 1.34; F, 61.38. Found: C, 34.29; H, 1.31; F, 61.25.

9db: white solid; ^{1}H NMR δ 3.03 (s, 6H), 6.72 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H); ^{19}F NMR δ 3.98 (t, *J* = 10 Hz, 3F), 32.4 (t, *J* = 15 Hz, 2F), 44.5 (s, 2F), 45.2 (s, 6F), 45.9 (s, 2F), 49.3 (t, *J* = 14 Hz, 2F); MS *m*/*z* (relative intensity) 539 (M$^+$, 52.21), 520 (16.87), 170 (100.00), 154 (12.82), 119 (2.91), 69 (6.13); Anal. Calcd for $C_{16}H_{10}F_{17}N$: C, 35.64; H, 1.87; N, 2.60; F, 59.89. Found: C, 35.46; H, 1.98; N, 3.08; F, 59.40.

9dc: white solid; ^{1}H NMR δ 3.68 (s, 2H), 3.76 (br, 3H), 6.70 (d, *J* = 8.8 Hz, 1H), 6.85 (d, *J* = 2.9 Hz, 1H), 6.93 (dd, *J* = 8.8, 2.9 Hz, 1H); ^{19}F NMR δ 4.04 (t, *J* = 10 Hz, 3F), 31.8 (t, *J* = 15 Hz, 2F), 44.7 (s, 2F), 45.0 (s, 4F), 45.2 (s, 2F), 46.0 (s, 2F), 49.4 (m, 2F); MS *m*/*z* (relative intensity) 542 (M$^+$ + 1, 40.41), 541 (M$^+$, 100.00), 526 (13.11), 172 (21.07), 129 (5.91), 69 (2.42); Anal. Calcd for $C_{15}H_8F_{17}NO$: C, 33.29; H, 1.49; N, 2.59; F, 59.68. Found: C, 33.46; H, 1.59; N, 2.55; F, 59.92.

9dd: Colorless oil; bp 112−114 °C/20 mmHg; ^{1}H NMR *d* 6.36 (s, 1H), 6.65 (s, 1H), 6.97 (s, 1H), 8.50 (br, 1H). ^{19}F NMR *d* 0.26 (t, *J* = 9.6 Hz, 3F), 24.84 (t, *J* = 13.5 Hz, 2F), 40.1 (s, 2F), 40.43 (s, 4F), 40.82 (s, 2F), 41.27 (s, 2F), 44.78 (t, *J* = 14 Hz, 2F); MS *m*/*z* (relative intensity) 485 (M$^+$, 94.03), 466 (43.83), 447 (17.26), 409 (56.1), 178 (22.04), 116 (100.00), 69 (12.43); Anal. Calcd for $C_{12}H_4F_{17}N$: C, 29.69; H, 0.82; N, 2.87; F, 66.60. Found: C, 29.52; H, 1.00; N, 2.93; F, 66.41.

9de: colorless oil; ^{1}H NMR *d* 1.44 (s, 3H), 2.26 (s, 3H), 6.63 (d, *J* = 4.8 Hz, 1H), 7.46 (d, *J* = 4.8 Hz, 1H); ^{19}F NMR *d* −0.47 (t, *J* = 9.8 Hz, 3F), 31.6 (m, 2F), 38.0 (m, 2F), 40.4 (s, 2F), 40.4 (s, 4F), 41.3 (s, 2F), 44.8 (s, 2F); MS *m*/*z* (relative intensity) 513 (M$^+$, 100.00), 494 (44.46), 444 (7.01), 325 (3.51), 144 (21.52); Anal. Calcd for $C_{14}H_8F_{17}N$: C, 32.77; H, 1.57; N, 2.73; F, 62.93. Found: C, 32.70; H, 1.78; N, 2.75; F, 62.60.

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Supporting Information Available: ^{1}H NMR and ^{19}F NMR spectra of **3aa**, **3ac**, **3ca**, **5ab**, **5bb**, **5ca**, **7ac**, **7de**, **9aa**, **9ad**, **9ae**, **9db**, and **9dc**. This material is available free of charge via the Internet at http://pubs.acs.org.

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