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Halofluorination of alkenes mediated by 1,1,3,3,3-pentafluoropropene-diethylamine adduct

Justyna Walkowiak *, Bartosz Marciniak, Henryk Koroniak

Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznań, Poland

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ABSTRACT

1,1,3,3,3-Pentafluoropropene-diethylamine complex (PFPDEA) has been found useful as a fluoride source in halofluorination reactions of various olefins. Reactions proceeded with PFPDEA and *N*-halosuccinimide (NXS, X = Br, I) or 1,3-dibromo-5,5-dimethylhydantoin (DBH), as sources of electrophilic halogens, in a regioselective manner.

1. Introduction

Fluoroorganic compounds show unique chemical and physical properties in the field of biological and material science [1]. Preparation of fluoroorganic derivatives has risen considerable interest in development of selective and convenient methods of introducing fluorine atom(s) into molecules. One of the most straightforward ways is halofluorination of unsaturated hydrocarbons, allowing introduction of fluoride ion under conditions much milder than direct hydrofluorination. Halofluoroalkanes, *i.e.* the resultant products, are useful synthetic intermediates of numerous fluoroorganic compounds [2].

In general, halofluorination of the carbon-carbon double bond is performed by formal addition of halogen fluorides (ClF, BrF, IF), generated *in situ*. It can be achieved in reaction of positive halogen sources and appropriate fluorination reagent. A 70% HF·pyridine complex (Olah's reagent) [3] or $Et_3N{\cdot}HF$ [4] are most commonly used as fluoride sources, and *N*-halosuccinimide (NXS) [3,4], *N*-halosaccharin (NXSac) [5] or trihaloisocyanuric acids (TXCA) [6] as sources of electrophilic halogen. Likewise, tetrabutylammonium bifluoride (TBABF) [7], ionic liquid, 1-ethyl-3-methylimidazolium oligo hydrogen fluoride ($EMIMF(HF)_{2.3}$) [8] or hexafluoropropene–diethylamine complex (Ishikawa reagent) [9], combined with *N*-halosuccinamides, has been successfully used to prepare halofluorinated derivatives.

In our previous studies, aimed at synthesis of a new selective nucleophilic reagent suitable for introduction of fluorine atom(s) into organic molecules, we developed a convenient route of obtaining an adduct of 1,1,3,3,3-pentafluoropropene with diethylamine (PFPDEA) [10]. Now we have found that use of PFPDEA and positive halogen sources (NXS, DBH) supports efficient conversion of various olefins into corresponding halofluorides under mild conditions.

2. Results and discussion

2.1. 1,1,3,3,3-Pentafluoropropene-diethylamine adduct (PFPDEA)

1,1,3,3,3-Pentafluoropropene-diethylamine adduct (PFPDEA) was synthesized by formal nucleophilic substitution of fluoride with diethylamine (DEA) at the double bond of pentafluoropropene (PFP), similarly to the procedure described previously by Ishikawa [11]. This reaction gave a mixture of two products, namely 1-diethylamino-1,3,3,3-tetrafluoropropene (**1**) and only traces of the desired *N*,*N*-diethyl-1,1,3,3,3-pentafluoropropylamine (**2**) (Fig. 1). The presented fluorinating mixture readily hydrolyzes when exposed to moist air, and vigorously reacts with

* Corresponding author. Tel.: +48 61 8291225; fax: +48 61 8291505.
E-mail address: Justyna.A.Walkowiak@amu.edu.pl (J. Walkowiak).

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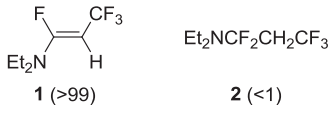


Fig. 1. PFPDEA.

water, forming the *N*,*N*-diethyl-3,3,3-trifluoropropionamide and hydrogen fluoride [10a].

2.2. Halofluorination of alkenes with PFPDEA

Our initial survey focused on optimizing conditions for halofluorination of styrene with PFPDEA as a hydrogen fluoride source (Table 1). Applying the same literature protocol as the one used in halofluorination of olefins with Ishikawa reagent (HFP-DA) [9] led to formation of the desired product but these transformations were very low-yielding. Increasing the amount of PFPDEA added did not influence significantly the yields of 1-fluoro-2-haloethylbenzenes. However, changing the reagents addition sequence led to successful halofluorination of styrene and considerably improved the yields of the formed products. As shown in Table 1, the best results were achieved when the reactions were carried out with PFPDEA (5.0 equiv.), H_2O (5.0 equiv.), *N*-iodosuccinimide (NIS, 2.5 equiv.) or 1,3-dibromo-5,5-dimethylohydantoin (DBH, 2.5 equiv.) and hexamethylphosphoric triamide (HMPA, 2.0 equiv.) in CH_2Cl_2 at −30 °C to room temperature for 24 h.

In further works we decided to test various olefins that could be suitable for halofluorination. It should give us a range of halofluorinated derivatives. The procedure we developed for forming the products, was applied in reactions of aromatic, aliphatic and alicyclic unsaturated hydrocarbons. In the optimized reaction conditions, various olefins were converted into corresponding halofluorides in good to very good yields, as shown in Table 2.

The present halofluorination reaction most probably proceeds *via* controlled generation of limited amounts of hydrogen fluoride from PFPDEA and H_2O, followed by *in situ* formation of iodine fluoride or bromine fluoride species with NIS or DBH, respectively. The formal electrophilic addition of "XF" to the double bond proceeds stereospecifically in an *anti*-sense, as evidenced by the formation, in good yield, of *trans*-1-bromo-2-fluorocyclohexane **6a**, or *trans*-1-iodo-2-fluorocyclohexane **6b** from *cis*-cyclohexene (Table 2, Entry 7–8). These results prove that halofluorinations of olefins proceed *via* an intermediate halonium ion. However, the bromofluorination of *trans*-stilbene yield a mixture of *erythro*- and *threo*-1-bromo-2-fluoro-1,2-diphenylethane in 95:5 ratio, respectively. These observations indicate that both bridged (bromonium ion) and nonbridged (benzylic cation) intermediates can be involved in the reaction mechanism.

In an unsaturated hydrocarbon system such as 2,5-norbornadiene, where transannular π-participations is possible, halofluorination did occur and led to forming a mixture of halofluorides **7** and **8** (Table 2, Entry 9–10).

The addition is regioselective and the regiochemistry is in line with the Markovnikov rule. For example, the bromo- and iodofluorinations of styrene give the 2-bromo-1-fluoro-1-phenylethane with complete regioselectivity (Table 1), and not even traces of the regioisomeric adduct were detected by ^{19}F NMR spectroscopy of the crude reaction mixtures. Similarly, in the case of 2-vinylpyridine, fluorine atom was introduced in more substituted carbon, forming only one bromofluorinated product **9** (Table 2, Entry 11). In halofluorinations of other simple unsymmetrical olefins such as 1-alkenes (Table 2, entry 1–6), the Markovnikov products **4a**–**f** also predominate (9:1) over the corresponding anti-Markovnikov **5a**–**f** compounds.

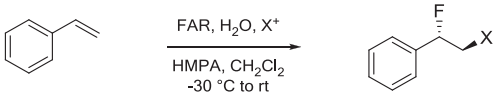
Concluding, we demonstrated that 1,1,3,3,3-pentafluoropropene-diethylamine adduct PFPDEA can be a good source of hydrogen fluoride in halofluorination reactions. The reactions provide a ready procedure for introducing fluorine into alkenes under mild conditions with high regioselectivity and stereospecifity. Our competitive studies revealed that in halofluorination reactions PFPDEA is an efficient fluorinating agent, comparable to the Ishikawa reagent.

3. Experimental

3.1. General methods

NMR spectra were recorded in deuterated solvents at 300 MHz (^1H), 75 MHz (^{13}C) and at 282 MHz (^{19}F), calibrated using an

Table 1
Halofluorination of styrene.[a]



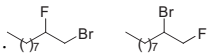
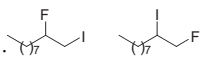
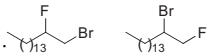
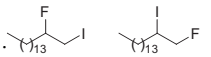
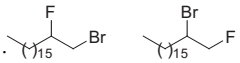
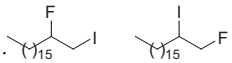
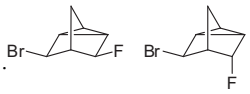
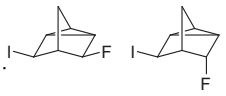
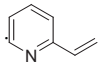
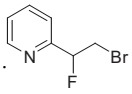
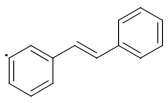
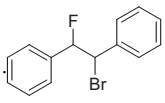
FAR = HFP-DA, PFP-DA
X^+ = Br^+ (NBS, DBH), I^+ (NIS)

3a (X = Br)
3b (X = I)

Entry	F^- source (equiv.)	X^+ source (equiv.)	H_2O (equiv.)	Yield[b]
1	HFP-DA (2.5)	NIS (2.5)	2.5	81%
2	PFPDEA (2.5)	NIS (2.5)	2.5	19%
3	PFPDEA (5.0)	NIS (2.5)	5.0	47%
4[c]	PFPDEA (5.0)	NIS (2.5)	5.0	74%
5	HFP-DA (2.5)	NBS (2.5)	2.5	46%
6	PFPDEA (2.5)	NBS (2.5)	2.5	10%
7	PFPDEA (5.0)	NBS (2.5)	5.0	18%
8[c]	PFPDEA (5.0)	NBS (2.5)	5.0	50%
9	HFP-DA (2.5)	DBH (2.5)	2.5	71%
10	PFPDEA (2.5)	DBH (2.5)	2.5	17%
11	PFPDEA (5.0)	DBH (2.5)	5.0	38%
12[c]	PFPDEA (5.0)	DBH (2.5)	5.0	77%

[a] Literature protocol: HFP-DA or PFPDEA, NXS or DBH, H_2O and HMPA [9].
[b] Yields determined by ^{19}F NMR analysis, using *m*-fluorotoluene as an internal standard (^{19}F NMR (282 MHz, $CDCl_3$) $\delta = -114.1$ (m, 1 F)).
[c] Alternative addition sequence: PFPDEA + H_2O, NXS or DBH and HMPA.

Table 2
Products distribution in halofluorination of various olefins with PFPDEA.

Entry	Olefin	X^+ source	Products	Yields[a]
1		DBH	 **4a** **5a**	68% (**4a:5a**, 90:10)
2		NIS	 **4b** **5b**	76% (**4b:5b**, 86:14)
3		DHB	 **4c** **5c**	52% (**4c:5c**, 87:13)
4		NIS	 **4d** **5d**	74% (**4d:5d**, 88:12)
5		DBH	 **4e** **5e**	64% (**4e:5e**, 88:12)
6		NIS	 **4f** **5f**	64% (**4f:5f**, 88:12)
7		DBH	 **6a**	59%
8		NIS	 **6b**	46%
9		DBH	 **7a** **8a**	39% (**7a:8a**, 44:56)
10		NIS	 **7b** **8a**	32% (**7b:8b**, 42:58)
11		DBH	 **9**	51%
12		DBH	 **10**	59% (**erythro:threo**, 95:5)

[a] Yields determined by ^{19}F NMR analysis using *m*-fluorotoluene as an internal standard (^{19}F NMR (282 MHz, $CDCl_3$) $\delta = -114.1$ (m, 1F)).

internal reference: TMS (^1H), $CDCl_3$ (^{13}C) or $CFCl_3$ (^{19}F). Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (J) are measured in Hertz (Hz). The following abbreviations are used to describe multiplicities s = singlet, d = doublet, t = triplet, q = quartet, b = broad, m = multiplet. Mass spectra were recorded by GC/MS coupling (EI, 70 eV). HRMS (EI) were recorded using a AMD-402 spectrometer. Thin-layer chromatography (TLC) was performed on coated silica gel plate Merck 60 F_{254}. Visualization of the reaction components was achieved using U.V. fluorescence (254 nm) and cerium(IV) ammonium nitrate or $KMnO_4$ solution stain. For purification of products column chromatography was carried out over Merck silica gel

60 (0.063–0.2 mm). All reagents purchased from suppliers were used without further purification. CH_2Cl_2 was dried and distilled over CaH_2. Solvents for chromatography were distilled prior to use.

3.2. General procedures

3.2.1. Halofluorination of alkenes; general procedure

In an ordinary glassware round-bottom flask to a solution of PFP-DA (5 equiv.) in dry CH_2Cl_2 (1.5 mL) at room temperature, water (5 equiv.) was added. Forthwith the hydrolysis occurred, the resulting mixture was placed in cooling bath (acetonitrile/dry ice). To the cooled reaction mixture (−30 °C) NXS or DBH (2.5 equiv.) and HMPA (2.0 equiv.) were added, and the whole was stirred at the temperature for next 30 min. A solution of alkene (1 equiv.) in CH_2Cl_2 (1.5 mL) was added dropwise, cooling bath was removed and the reaction mixture was allowed to stand at room temperature for 24 h. When the reaction was complete the appropriate amount of NMR internal standard, *m*-fluorotoluene (1 equiv.), was added and a sample analyzed by NMR.

3.2.1.1. Bromofluorination of styrene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), DBH (0.715 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and styrene (0.104 g, 0.115 mL, 1.0 mmol) in dry CH_2Cl_2 **3a** was obtained. The NMR data were in a good agreement with those already reported [7–9].

3.2.1.2. Iodofluorination of styrene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), NIS (0.563 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and styrene (0.104 g, 0.115 mL, 1.0 mmol) in dry CH_2Cl_2 **3b** was obtained. The NMR data were in a good agreement with those already reported [3d,6–9].

3.2.1.3. Bromofluorination of 1-decene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), DBH (0.715 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and 1-decene (0.140 g, 0.189 mL, 1.0 mmol) in dry CH_2Cl_2 a mixture of **4a** and **5a** was obtained. The NMR data were in a good agreement with those already reported [12].

*3.2.1.4. Iodofluorination of 1-decene (**4b**).* According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), NIS (0.563 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and 1-decene (0.140 g, 0.189 mL, 1.0 mmol) in dry CH_2Cl_2 a mixture of **4b** and **5b** was obtained.

4b: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.45 (dddt, 1H, *J* = 47.2, 11.0, 5.8, 5.0 Hz, C*H*F), 3.33 (ddd, 1H, *J* = 19.9, 10.9, 5.0 Hz, CH_aH$_b$I), 3.29 (ddd, 1H, *J* = 19.9, 10.9, 5.8 Hz, CH$_a$$H_b$I), 1.86–1.61 (m, 2H), 1.52–1.14 (m, 12H), 0,88 (t, 3H *J* = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 97.1 (d, *J* = 174.6 Hz), 34.8 (d, *J* = 20.5 Hz), 31.8, 29.3, 29.2, 29.1, 24.7 (d, *J* = 4.2 Hz), 22.6, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −171.5 (m, 1F, CH*F*). HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{10}H_{20}FI$: 286.0594; found: 286.0602.

5b: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.62 (ddd, 1H, *J* = 47.2, 9.5, 5.3 Hz, CH$_a$$H_b$F), 4.48 (ddd, 1H, *J* = 47.2, 9.5, 8.1 Hz, CH_aH$_b$F), 4.18 (dddt, 1H, *J* = 13.7, 8.1, 5.3, 5.3 Hz, C*H*I), 1.94–1.67 (m, 2H), 1.46–1.16 (m, 12H), 0.88 (t, 3H *J* = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.6 (d, *J* = 177.5 Hz), 31.8, 31.2 (d, *J* = 19.6 Hz), 29.3, 29.2, 29.1, 22.6, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −198.5 (td, 1F, *J* = 47.2, 13.7 Hz, CH_2F). HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{10}H_{20}FI$: 286.0594; found: 286.0602.

3.2.1.5. Bromofluorination of 1-hexadecene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), DBH (0.715 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and 1-hexadecene (0.224 g, 0.289 mL, 1.0 mmol) in dry CH_2Cl_2 a mixture of **4c** and **5c** was obtained. The NMR data were in a good agreement with those already reported [12].

3.2.1.6. Iodofluorination of 1-hexadecene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), NIS (0.563 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and 1-hexadecene (0.224 g, 0.289 mL, 1.0 mmol) in dry CH_2Cl_2 a mixture of **4d** and **5d** was obtained.

4d: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.48 (dddt, 1H, *J* = 48.0, 11.1, 5.8, 5.0 Hz, C*H*F), 3.33 (ddd, 1H, *J* = 19.5, 11.1, 5.0 Hz, CH_aH$_b$I), 3.28 (ddd, 1H, *J* = 19.5, 11.1, 5.8 Hz, CH$_a$$H_b$I), 1.91–1.56 (m, 2H), 1.46–1.15 (m, 24H), 0.88 (t, 3H *J* = 6.7, Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 92.2 (d, *J* = 174.5 Hz), 34.8 (d, *J* = 20.5 Hz), 31.9, 29.69, 29.67, 29.65, 29.6, 29.4, 29.3, 29.2, 24.7 (d, *J* = 4.2 Hz), 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −171.4 (m, 1F, CH*F*). HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{32}FI$: 370.1533; found: 370.1537.

5d: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.65 (ddd, 1H, *J* = 48.2, 9.5, 5.3 Hz, CH$_a$$H_b$F), 4.49 (ddd, 1H, *J* = 48.2, 9.5, 8.1 Hz, CH_aH$_b$F), 4.21 (dddt, 1H, *J* = 13.3, 8.1, 5.3, 5.3, Hz, C*H*I), 1.96–1.65 (m, 2H), 1.48–1.14 (m, 24H), 0.88 (t, 3H *J* = 6.7, Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.6 (d, *J* = 177.4 Hz), 31.9, 31.2 (d, *J* = 19.2 Hz), 29.68, 29.67, 29.65, 29.6, 29.5, 29.4, 29.3, 29.1, 28.7, 24.1, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −198.5 (td, 1F, *J* = 48.2, 13.3 Hz, CH_2F). HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{32}FI$: 370.1533; found: 370.1537.

3.2.1.7. Bromofluorination of 1-octadecene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), DBH (0.715 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and 1-octadecene (0.253 g, 0.320 mL, 1.0 mmol) in dry CH_2Cl_2 a mixture of **4e** and **5e** was obtained.

4e: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.62 (dddt, 1H, *J* = 47.0, 11.1, 6.2, 5.7 Hz, C*H*F), 3.48 (ddd, 1H, *J* = 19.7, 10.8, 5.7 Hz, CH_aH$_b$Br), 3.42 (ddd, 1H, *J* = 19.7, 10.8, 6.2 Hz, CH$_a$$H_b$Br), 1.87–1.55 (m, 2H), 1.52–1.13 (m, 28H), 0.88 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 91.1 (d, *J* = 174.7 Hz), 32.7 (d, *J* = 25.5 Hz), 32.4 (d, *J* = 20.5 Hz), 30.9 (s, C-6), 28.7–28.6 (7C), 28.6, 28.5, 28.4, 28.3 (d, *J* = 6.5 Hz), 23.7 (d, *J* = 4.3 Hz), 21.7, 13.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −178.3 (m, 1F, CH*F*). HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{36}BrF$: 350.1954; found: 350.1963.

5e: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.61 (ddd, 1H, *J* = 47.1, 9.3, 5.4 Hz, CH$_a$$H_b$F), 4.45 (ddd, 1H, *J* = 47.1, 9.3, 8.1 Hz, CH_aH$_b$F), 4.19 (dddt, 1H, *J* = 13.8, 8.1, 5.4, 5.4, Hz, C*H*Br), 1.93–1.66 (m, 2H), 1.47–1.15 (m, 28H), 0.88 (t, 3H *J* = 6.8, Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 85.2 (d, *J* = 176.4 Hz), 56.0 (d, *J* = 51.9 Hz), 36.2 (d, *J* = 34.0 Hz), 31.9, 29.7–29.6 (7C), 29.6, 29.5, 29.4 (d, *J* = 2.1 Hz), 28.8, 26.8, 22.7, 14.13. ^{19}F NMR (282 MHz, $CDCl_3$): δ −210.33 (td, 1F, *J* = 47.1, 13.8 Hz, CH_2F). HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{36}BrF$: 350.1954; found: 350.1963.

3.2.1.8. Iodofluorination of 1-octadecene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), NIS (0.563 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and 1-hexadecene (0.253 g, 0.320 mL, 1.0 mmol) in dry CH_2Cl_2 a mixture of **4f** and **5f** was obtained.

4f: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.45 (dddt, 1H, *J* = 47.6, 11.0, 5.8, 5.1 Hz, C*H*F), 3.33 (ddd, 1H, *J* = 19.5, 10.9, 5.1 Hz, CH_aH$_b$I), 3.29 (ddd, 1H, *J* = 19.5, 10.9, 5.8 Hz, CH$_a$$H_b$I), 1.84–1.64 (m, 2H), 1.49–1.13 (m, 28H), 0.87 (t, 3H *J* = 6.7, Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ

90.2 (d, J = 172.6 Hz), 32.5 (d, J = 26.4 Hz), 32.2 (d, J = 20.3 Hz), 30.7, 28.8-28.7 (7 C), 28.6, 28.5, 28.4, 28.3 (d, J = 6.6 Hz), 23.7 (d, J = 4.5 Hz), 21.5, 13.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ −171.35 (m, 1F, CH*F*). HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{36}FI$: 398.1846; found: 398.1851.

5f: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.61 (ddd, 1H, *J* = 47.8, 9.2, 5.4 Hz, CH_aH_bF), 4.46 (ddd, 1H, *J* = 47.28, 9.2, 8.3 Hz, CH_aH_bF), 4.13 (dddt, 1H, *J* = 13.8, 8.3, 5.4, 5.4, Hz, C*H*I), 1.92–1.65 (m, 2H), 1.42–1.11 (m, 28H), 0.87 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 83.1 (d, J = 175.8 Hz), 55.4 (d, J = 50.7 Hz), 36.0 (d, J = 32.9 Hz), 31.8, 29.7-29.6 (7 C), 29.5, 29.4, 29.3 (d, J = 2.1 Hz), 28.8, 26.8, 22.7, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ −198.54 (td, 1F, *J* = 47.8, 13.8 Hz, CH_2F). HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{36}FI$: 398.1846; found: 398.1851.

3.2.1.9. Bromofluorination of cyclohexene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), DBH (0.715 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and cyclohexene (0.082 g, 0.101 mL, 1.0 mmol) in dry CH_2Cl_2 **6a** was obtained. The NMR data were in a good agreement with those already reported [8].

3.2.1.10. Iodofluorination of cyclohexene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), NIS (0.563 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and styrene (0.082 g, 0.101 mL, 1.0 mmol) in dry CH_2Cl_2 **6b** was obtained. The NMR data were in a good agreement with those already reported [8].

3.2.1.11. Bromofluorination of 2,5-norbornadiene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g. 9.0 μL, 5.0 mmol), DBH (0.715 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and 2,5-norbornadiene (0.092 g, 0.320 mL, 1.0 mmol) in dry CH_2Cl_2 a mixture of 3-*exo*-bromo-5-*exo*-fluoronortricyclane **7a** and 3-*exo*-bromo-5-*endo*-fluoronortricyclane **8a** was obtained. The ^{1}H, ^{13}C NMR data were in a good agreement with those already reported [13a,b].

7a: ^{19}F NMR (282 MHz, $CDCl_3$): δ −191.60 (d, 1F, *J* = 58.3 Hz, CH*F*).

8a: ^{19}F NMR (282 MHz, $CDCl_3$): δ −197.07 (d, 1F, *J* = 58.7 Hz, CH*F*).

3.2.1.12. Iodofluorination of 2,5-norbornadiene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), NIS (0.563 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and 2,5-norbornadiene (0.092 g, 0.320 mL, 1.0 mmol) in dry CH_2Cl_2 a mixture of 5-*exo*-fluoro-3-*exo*-iodonortricyclane **7b** and 5-*endo*-fluoro-3-*exo*-iodonortricyclane **8b** was obtained. The ^{1}H, ^{13}C NMR data were in a good agreement with those already reported [13c].

7b: ^{19}F NMR (282 MHz, $CDCl_3$): δ −191.83 (d, 1F, *J* = 58.5 Hz, CH*F*).

8b: ^{19}F NMR (282 MHz, $CDCl_3$): δ −197.16 (d, 1F, *J* = 58.8 Hz, CH*F*).

3.2.1.13. Bromofluorination of 2-vinylpyridine. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), DBH (0.715 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and 2-vinylpyridine (0.105 g, 0.108 mL, 1.0 mmol) in dry CH_2Cl_2 **9** was obtained.

9: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (m, 1H, *Ar*), 7.71 (td, 1H, *J* = 7.7, 1.8 Hz, *Ar*), 7.44 (m, 1H, *Ar*),7.22 (m, 1H, *Ar*), 5.68 (ddd, 1H, *J* = 46.2, 6.4, 3.5 Hz, C*H*F), 3.90 (ddd, 1H, *J* = 23.6, 11.4, 3.5 Hz, CH_aH_bBr), 3.73 (ddd, 1H, *J* = 22.6, 11.4, 6.4 Hz, CH_aH_bBr); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5 (d, *J* = 24.5 Hz), 149.2 (d, *J* = 2.3 Hz), 136.9, 123.5, 120.5 (d, *J* = 6.6 Hz), 92.2 (d, *J* = 179.4 Hz), 33.7 (d, *J* = 23.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −189.43 (ddd, 1F, *J* = 46.2, 23.6, 22.6 Hz CH*F*). HRMS (EI): *m*/*z* [M^+] calcd for C_7H_7BrFN: 202.9746; found: 202.9752.

3.2.1.14. Bromofluorination of trans-stilbene. According to the general procedure, in the reaction of fluorinating agent PFPDEA (0.926 g, 5.0 mmol), H_2O (0.009 g, 9.0 μL, 5.0 mmol), DBH (0.715 g, 2.5 mmol), HMPA (0.358 g, 0.35 mL, 2.0 mmol) and *trans*-stilbene (0.180 g, 1.0 mmol) in dry CH_2Cl_2 a mixture of *erythro*-1-bromo-2-fluoro-1,2-diphenylethane **erythro-10** and *threo*-1-bromo-2-fluoro-1,2-diphenylethane **threo-10** was obtained. The NMR data were in a good agreement with those already reported [14].

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