Generation and Carbonyl Addition Reactions of Dibromofluoromethyllithium Derived from Tribromofluoromethane as Applied to the Stereoselective Synthesis of Fluoro Olefins and 2-Bromo-2-fluoro-1,3-alkanediols

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The treatment of tribromofluoromethane with BuLi in THF–Et_2O (2 : 1) at −130 °C generated dibromofluoromethyllithium, which was allowed to react smoothly with a coexisting aldehyde or ketone ($RR'C{=}O$) to give fluorinated alcohol $RR'C(OH)CFBr_2$ (**3**) in good yield. Alcohol **3** was converted stereoselectively to (*E*)-1-bromo-1,2-difluoro olefin **5** via fluorination with Et_2NSF_3, followed by dehydrobromination with lithium 2,2,6,6-tetramethylpiperidide, while (*E*)-1-bromo-1-fluoro olefin was obtained with high selectivity by acetylation of **3**, followed by reductive elimination using EtMgBr/$(i\text{-}Pr)_2NH$. Difluoro olefin **5** underwent a cross-coupling reaction with an aryl, alkenyl, or alkynylmetal reagent to afford the corresponding fluoro olefin with retention of configuration. On the other hand, the treatment of $RCH[OCH_2O(CH_2)_2OCH_3]CFBr_2$ with BuLi at −130 °C in the presence of 4-heptanone gave the corresponding adduct diastereoselectively. The stereochemical outcome is explained in terms of chelation between lithium and oxygen atoms of the (2-methoxyethoxy)methyl group. Starting with 2-phenylpropanal, a product is obtained highly selectively containing three contiguous stereocenters including a –CFBr– moiety.

Carbenoids are highly versatile and widely used reagents in organic synthesis[1] and are defined by Köbrich as compounds that have a metal atom and a leaving group on the same carbon. Fluorine-containing carbenoids are among the most reliable reagents[2] and, indeed, a variety of them are prepared and applied for the synthesis of organofluorine compounds, which have recently been attracting much attention in view of pharmaceutical, agrochemical, or material science.[3] Among the fluorine-containing carbenoids, fluorohalomethylmetals have a high potential as a C1 synthetic unit, because the carbon–halogen bond(s) of the initial products can be converted into carbon–carbon bond(s) and/or various carbon–heteroatom bond(s). In general, however, fluorohalomethylmetals are thermally labile[4] and decompose readily to give electrophilic carbenes.[5] Thus, the carbenoids substituted by fluorine rarely undergo nucleophilic reactions.[6]

We describe here that dibromofluoromethyllithium is generated by a bromine–lithium exchange of tribromofluoromethane with butyllithium at −130 °C, and reacts smoothly with a variety of aldehydes and ketones to give fluorinated alcohols, which are converted into fluoro olefins and fluorine-containing 1,3-diols stereoselectively.[7]

Results and Discussion

Generation and Carbonyl Addition of Dibromofluoromethyllithium. We have envisaged whether tribromofluoromethane (**1**) would be a versatile precursor of monofluorinated carbenoid, because **1** has a polyhalogenated functionality and is commercially available. Indeed, **1** was reported to be a useful starting material for the synthesis of monofluoro compounds.[8]

Using naphthalene-1-carbaldehyde as a typical electrophile, we first studied the generation and aldehyde addition of lithium carbenoid **2**. In fact, carbenoid **2** was successfully generated by treatment of **1** with an equimolar amount of butyllithium at −130 °C (Eq. 1). However, the carbenoid reagent proved to be extremely labile thermally, as demonstrated by the treatment of **2** with the aldehyde *after* carbenoid generation, giving adduct **3a** in only 10% yield. When carbenoid generation was carried out *in the presence of* the aldehyde, **3a** was isolated in 85% yield. The same reaction carried out at −78 °C or 0 °C gave **3a** in 30% or 0% yield. Therefore, we concluded that the procedure involving

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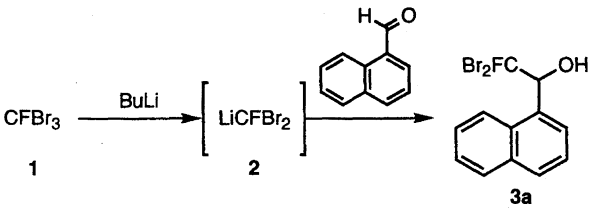
carbenoid generation in the presence of an electrophile was essential particularly, for carbenoid **2**.



(1)

The above-mentioned procedure was applied to various aldehydes and ketones; the results are summarized in Table 1. Both aromatic and aliphatic aldehydes gave **3** in good yields. Noteworthy is that ketones are also good substrates (Entries 12—15). α,β-Unsaturated carbonyl compounds gave the corresponding 1,2-adducts (Entries 11, 15) exclusively. No butyl adduct *n*-BuC(OH)RR′ was detected in all cases. Accordingly, at −130 °C the bromine–lithium exchange appears to be faster than the carbonyl addition of butyllithium.

Another characteristic feature is that the Darzen-type reaction does not take place, in contrast to $LiCH_2Br$ or $LiCHBr_2$, which, upon warming a reaction mixture to room temperature, generally gives epoxides.[9] The lithium alkoxide of **3** did not cyclize, even upon heating at the refluxing temperature of THF. These observations are in accord with the fact that the fluorine-substituted carbon of **3** is reluctant to undergo a nucleophilic substitution reaction, probably due to a shielding effect of a fluorine atom.[10]

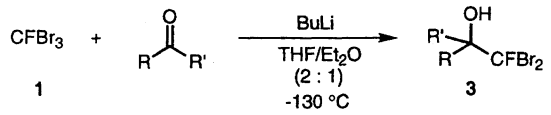


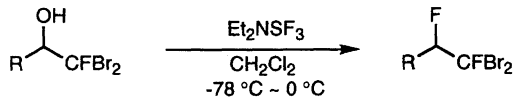
Table 1. Reaction of **1** with Carbonyl Compounds[a]

Entry	Carbonyl compound		Product	Yield/%[b]
	R	R′		
1	1-Naphthyl-	H	**3a**	85
2	4-NC–C_6H_4–	H	**3b**	85
3	4-O_2N–C_6H_4–	H	**3c**	77
4	4-MeO–C_6H_4–	H	**3d**	87
5	3,4-(OCH_2O)–C_6H_3–	H	**3e**	90
6	Ph	H	**3f**	78
7	Ph(CH_2)$_2$–	H	**3g**	81
8	*c*-Hex	H	**3h**	71
9	*i*-Pr	H	**3i**	56
10	*n*-$C_{11}H_{23}$–	H	**3j**	60[c]
11	*trans*-PhCH=CH–	H	**3k**	82
12	Ph	Ph	**3l**	64
13	Ph	Me	**3m**	96
14	–(CH_2)$_5$–		**3n**	72
15	Me_2C=CH–	Me	**3o**	86

a) Butyllithium (1.0 mmol) was added into a solution of $CFBr_3$ (1.2 mmol) and a carbonyl compound (1 mmol) in THF–Et_2O (6 ml/3 ml) at −130 °C. b) Isolated yields. c) Dodecanal (1 mmol) and $CFBr_3$ (1.2 mmol) were dissolved in THF–Et_2O (10 ml/5 ml).

Stereoselective Synthesis of Bromofluoro Olefins. Fluoro olefins have received growing interest recently as liquid crystalline materials[11] as well as peptide isosteres[12] and enzyme inhibitors.[13] Since the physical properties and biological activities greatly depend on the configuration of fluoro olefins, their stereocontrolled synthesis is desired. In the meantime, stereodefined bromo olefins are valuable precursors for the stereoselective synthesis of di-, tri-, and tetrasubstituted ethenes, because many types of cross-coupling reactions or sequential metalation-substitution reactions of bromo olefins proceed with the retention of configuration.[14] Accordingly, the development of an efficient and stereoselective synthesis of bromofluoro olefins[15] can lead to a new powerful method for stereodefined fluoro olefins.

For the synthesis of 1-bromo-1,2-difluoro-1-alkenes **5**, dehydrobromination of 1,1-dibromo-1,2-difluoroalkanes **4** would be an approach of choice (Scheme 1). In turn, **4** can be readily prepared from **3**. Indeed, dibromodifluoro compounds **4** were easily derived from **3** by fluorination with Et_2NSF_3 (1 equimol) at −78 °C (Eq. 2).[16]

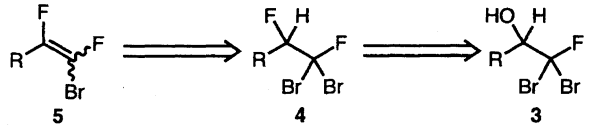


3a : R = 1-C_8H_7- **4a** (76%)
3d : R = 4-MeO-C_6H_4- **4d** (59%)
3p : R = 3,4-$(MeO)_2C_6H_3$- **4p** (49%)
3q : R = 4-Me-C_6H_4- **4q** (57%)

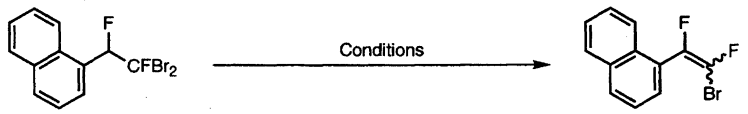
(2)

With **4a** as a model substrate, various types of bases were tested for dehydrobromination; the results are summarized in Table 2. The stereochemistry of the resulting olefin **5a** was assigned on the basis of ^{19}F NMR spectroscopy: $^3J_{F-F} = 7.4$ Hz for (*E*)-isomer and 140.6 Hz for (*Z*)-isomer. When **4a** was treated with KO*t*-Bu, $KN(SiMe_3)_2$, $LiN(SiMe_3)_2$, or LiN(*i*-Pr)$_2$ (Entries 1—5), **5a** was produced in good yields, but with varying selectivities. The best (*E*)-selectivity was observed with lithium 2,2,6,6-tetramethylpiperidide in THF at −98 °C (Entry 6). In lieu of the metal amides or alkoxides, a base without a metal cation gave (*Z*)-**5a** preferentially. In particular, the treatment of **4a** with (n-Bu)$_4$NOH (Entry 8) and 2-*t*-butylimino-2-diethylamino-1,3-dimethyl-1,3,2λ^5-diazaphosphorinane (BEMP) (Entry 11) resulted in the formation of **5a** with 87% and 77% (*Z*)-selectivity, respectively. Thus, the stereoselectivity of the dehydrobromination was found to depend on the nature of the base used.

The best conditions for the (*E*)-olefin synthesis using lithium 2,2,6,6-tetramethylpiperidide were applied to dibromodifluoroalkanes **4d**, **4p**, and **4q**. The results, summarized in Table 3, demonstrate that good yields and (*E*)-selectivities were observed in all cases. The configurations of **5d**,



Scheme 1. Retrosynthesis of difluoro olefin **5**.

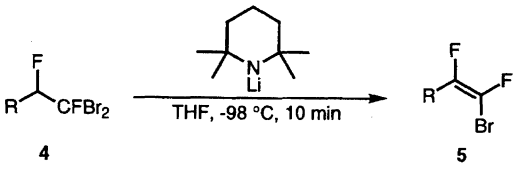


4a 5a

Table 2. Stereoselective Synthesis of Difluoro Olefin **5a** via Dehydrobromination of **4a**

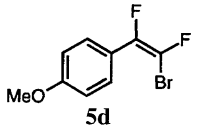
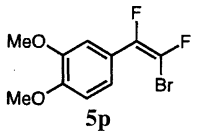
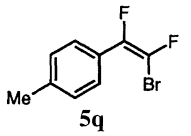
Entry	Base (1.5 mol amount)	Conditions	Yield/%[a]	(*E*)-**5a** : (*Z*)-**5a**[b]
1	KO-*t*-Bu	THF, r.t., 1 h	85	48 : 52
2		THF, −78 °C, 30 min	91	36 : 64
3	$KN(SiMe_3)_2$	THF/Toluene, −78 °C, 10 min	97	48 : 52
4		THF/Et_2O/Toluene, −130 °C, 20 min	97	74 : 26
5	LiN-(*i*-Pr)$_2$	THF, −98 °C, 12 min	87	85 : 15
6	$LiN[(CMe_2CH_2)_2CH_2]$	THF, −98 °C, 10 min	82	> 99 : < 1
7	(*n*-Bu)$_4$NOH	CH_2Cl_2/H_2O, r.t., 15 min	98	26 : 74
8		CH_2Cl_2/H_2O, −78 °C, 1 h	42[c]	13 : 87
9	DBU	CH_2Cl_2, r.t., 1 h	95	40 : 60
10		CH_2Cl_2, −78 °C—0 °C, 6h	84	40 : 60
11	BEMP	CH_2Cl_2, r.t., 12 h	93	23 : 77

a) Isolated yield. b) *E*/*Z* ratio was determined by capillary gas chromatography. Stereochemistry was assigned on the basis of ^{19}F NMR spectroscopy: $^3J_{F-F}$ = 7.4 Hz for (*E*)-isomer and 140.6 Hz for (*Z*)-isomer. c) Substrate **4a** was recovered (40%).

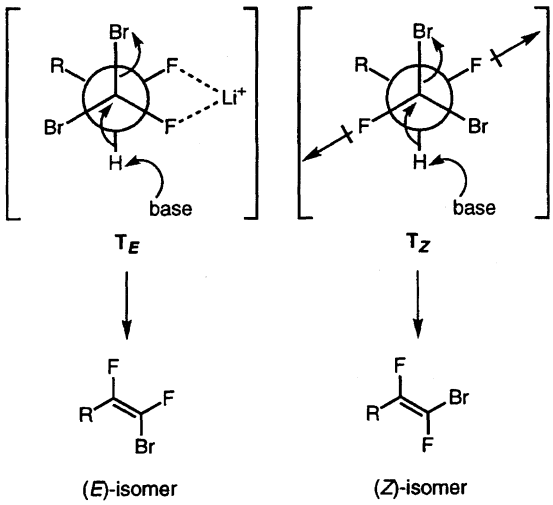


4 5

Table 3. Synthesis of (*E*)-2-Substituted 1-Bromo-1,2-difluoroethene **5**[a]

Entry	Product	Yield/%[b]	(*E*)-**5** : (*Z*)-**5**[c]
1	 **5d**	87	92 : 8
2	 **5p**	90	91 : 9
3	 **5q**	78	91 : 9

a) The reaction was carried out in THF at −98 °C using lithium 2,2,6,6-tetramethylpiperidide (1—3 mol amount). b) Isolated yield. c) *E*/*Z* ratio was determined by capillary chromatography. Stereochemistry was assigned on the basis of ^{19}F NMR spectroscopy: $^3J_{F-F}$ = 10—11 Hz for (*E*)-isomers and 133—134 Hz for (*Z*)-isomers.

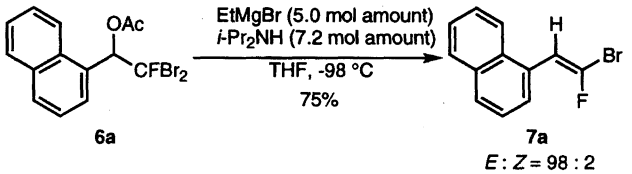


Scheme 2. Plausible transition states of dehydrobromination.

5p, and **5q** were assigned on the basis of the $^3J_{F-F}$ coupling constants: 10—11 Hz for (*E*)-isomers and 133—134 Hz for (*Z*)-isomers.[17]

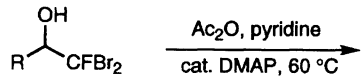
To explain the stereoselectivity of the base-dependent elimination reaction, we propose transition states $\mathbf{T}_E$ and $\mathbf{T}_Z$, as depicted in Scheme 2. With a lithium amide base, dehydrobromination proceeded via $\mathbf{T}_E$, in which two fluorine atoms were arranged in a synclinal manner due to Li–F chelation[18] to produce the (*E*)-isomer. On the other hand, the elimination of HBr occurred with (*n*-Bu)$_4$NOH by way of $\mathbf{T}_Z$, wherein a dipole–dipole repulsion of C–F bonds played an important role, giving rise to the (*Z*)-isomer.

During the course of the difluoro olefin synthesis, we treated **6a** with a reagent prepared from EtMgBr (5 mol amount) and (*i*-Pr)$_2$NH (7.2 mol amount), and found that fluoro ethene **7a** was produced in 75% yield with 98% (*E*)-selectivity (Eq. 3). For the reductive olefination reaction, acetates **6** were found to be good substrates, which were easily prepared by the acetylation of **3** (Eq. 4). These results stimulated us to study the stereoselective synthesis of fluoro olefins **7** in more detail.



6a **7a**

E : *Z* = 98 : 2 (3)

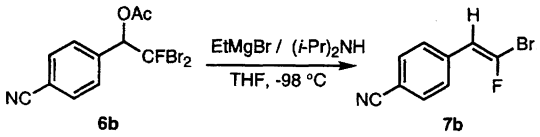


3a : R = 1-C_8H_7- **6a** (85%)
3b : R = 4-NC-C_6H_4- **6b** (78%)
3d : R = 4-MeO-C_6H_4- **6d** (86%)
3e : R = 3,4-(OCH_2O)-C_6H_3- **6e** (76%)
3g : R = $Ph(CH_2)_2$- **6g** (78%) (4)

Using **6b** as a model substrate, we scrutinized the amount and mol ratio of the reagents. The results, summarized in Table 4, clearly show that the highest selectivitiy (*E*/*Z* = > 99 : < 1) was achieved using EtMgBr (15 mol amount) and (*i*-Pr)$_2$NH (5 mol amount), respectively (Entry 1). The treatment of **6b** with EtMgBr (7.2 mol amount) and (*i*-Pr)$_2$NH (5 mol amount) also gave **7b** with high selectivity (95% *E*) (Entry 2), while the reductive olefination using other equivalence of EtMgBr and (*i*-Pr)$_2$NH resulted in moderate selectivity (Entries 3—7).

The optimum reagent system was quite effective for the transformation of **6** (R = aryl; see Entries 1, 2, 4, and 5) to (*E*)-**7** as shown in Table 5. Diethylmagnesium in THF–1,4-dioxane could also effect the same transformation (Entry 3). Although zinc or magnesium metal promoted the reductive elimination of **6a** and gave **7a** as well, the stereoselectivity was lower: Zn, 50 °C, DMF, 80% yield, *E*/*Z* = 58 : 42; Mg, room temperature, THF, 42% yield, *E*/*Z* = 45 : 55.

On the other hand, the reduction of **6g** (R = aliphatic) gave (*Z*)-**7g** as the major product (Entry 6). The *E*/*Z* ratio of **7g** was improved up to 6 : 94 when tosylate **8g** was reacted with Et_2Mg (1.5 mol amount) at −98 °C, as illustrated in Scheme 3.

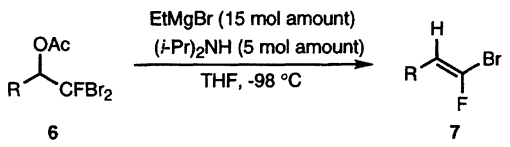


6b **7b**

Table 4. Equivalence of Reagents

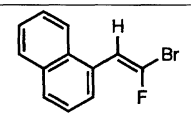
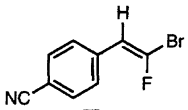
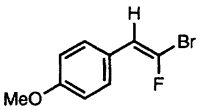
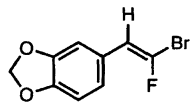
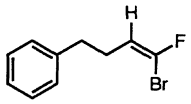
Entry	EtMgBr	(*i*-Pr)$_2$NH	Yield[a]	(*E*)-**7b** : (*Z*)-**7b**[b]
	mol amount	mol amount	%	
1	15.0	5.0	89	> 99 : < 1
2	7.2	5.0	89	95 : 5
3	5.0	5.0	48	75 : 25
4	4.5	1.5	84	80 : 20
5	3.0	1.0	88	75 : 25
6	1.5	0.5	30	75 : 25
7	5.0	0	93	75 : 25

a) Isolated yield. b) *E*/*Z* ratio was determined by capillary gas chromatography. Stereochemistry was assigned on the basis of ^{1}H NMR and ^{19}F NMR spectroscopy: $^3J_{H-F}$ = 31.8 Hz for (*E*)-isomer and 14.5 Hz for (*Z*)-isomer.

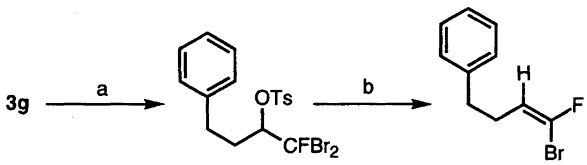


6 **7**

Table 5. Synthesis of (*E*)-2-Substituted 1-Bromo-1-fluoroethene **7**

Entry	Product	Yield/%[a]	(*E*)-**7** : (*Z*)-**7**[b]
1	 **7a**	81	> 99 : < 1
2	 **7b**	89	> 99 : < 1
3[c]		93	96 : 4
4	 **7d**	84	> 99 : < 1
5	 **7e**	88	> 99 : < 1
6	 **7g**	80	33 : 67

a) Isolated yield. b) *E*/*Z* ratio was determined by capillary gas chromatography. Stereochemistry was assigned on the basis of ^{1}H NMR and ^{19}F NMR spectroscopy: $^3J_{H-F}$ = 30—32 Hz for (*E*)-isomer and 12—15 Hz for (*Z*)-isomer. c) The reaction was carried out in THF-1,4-dioxane at −98 °C using Et_2Mg (7.5 mol amount).



8g **7g** (*E* : *Z* = 6 : 94)

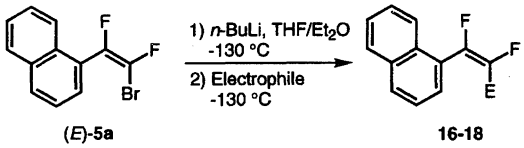
a) TsCl (1 mol amount), NaH, THF, 0 °C (72%)
b) Et_2Mg (1.5 mol amount), THF-1,4-dioxane, -98 °C (87%)

Scheme 3. Preparation of (*Z*)-1-bromo-1-fluoro-2-phenethylethene (**7g**).

Although the real active species derived from EtMgBr and (*i*-Pr)$_2$NH and the reason why the olefinic stereochemistry resulting from the reductive elimination reversed by changing substituent R from aryl to aliphatic is not clear at present, the reagent system involving EtMgBr (15 mol amount) and (*i*-Pr)$_2$NH (5 mol amount) undoubtedly provides a method for the highly stereoselective synthesis of fluoro olefin **7**.

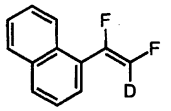
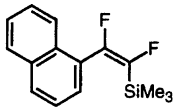
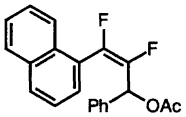
Cross-Coupling Reaction of Bromofluoro Olefins. With bromo(di)fluoro olefins **5** and **7** in hand, we studied the carbon–carbon bond extension of **5** and **7** in order to synthesize various types of (di)fluoro olefins.[19] The results of the cross-coupling reaction of **5** are summarized in Table 6. Coupling reactions between **5** and various arylmetal reagents (metal = Si, Sn, B, or Zn) proceeded in the presence of a palladium catalyst in good-to-excellent yields with a complete retention of the olefin geometry (Entries 1—8). An alkenylborane reagent also underwent a palladium-catalyzed cross-coupling reaction of **5a** to give (*Z*, *E*)-**13a** in 42% yield while retaining the configurations of both **5a** and the alkenylborane reagent (Entry 9). The yield of **13a** increased up to 55% when (*E*)-PhCH=CHSiMeF$_2$ was used as the alkenylmetal reagent with a slight loss of stereochemistry ((*Z*, *E*) : (*E*, *E*) = 92 : 8, Entry 10).[20] Furthermore, stereospecific coupling between **5a** and 1-alkyne occurred in the presence of PdCl$_2$(PPh$_3$)$_2$ together with a catalytic amount of CuI (Entries 11 and 12).

Sequential Lithiation-Substitution Reaction of Bromo Fluoro Olefins. In addition to the cross-coupling approach, a two-step procedure involving a sequential metalation-substitution of bromo(di)fluoro olefins is also effective for the one-pot elaboration of a carbon framework.[21] Indeed, bromine–lithium exchanges of both difluoroethene (*E*)-**5a** and monofluoroethene **7a** with butyllithium at −130 °C followed by a reaction with electrophiles gave the corresponding products **16a—18a** and **19a**, respectively,[22] with retention of the configuration (Table 7 and Eq. 5).

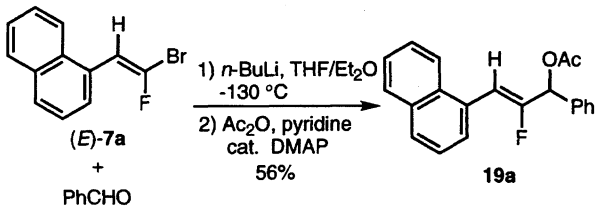


(*E*)-**5a** **16-18**

Table 7. Generation of 1,2-Difluorovinyllithium from (*E*)-**5a** and the Reaction with Electrophiles

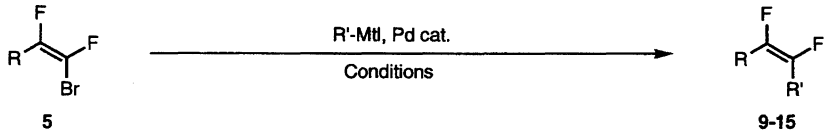
Entry	Electrophile	Product	Yield/%[a]
1	CD_3OD	 **16a**	96
2	Me_3SiCl	 **17a**	97
3[b]	1) PhCHO 2) Ac_2O	 **18a**	66

a) Isolated yield. b) The product **18a** was isolated after acetylation of the corresponding crude alcohol.



(*E*)-**7a** + PhCHO **19a**

(5)



5 **9-15**

Table 6. Cross-Coupling Reaction of (*E*)-1,2-Difluoroethene **5** with Organometallic Reagents

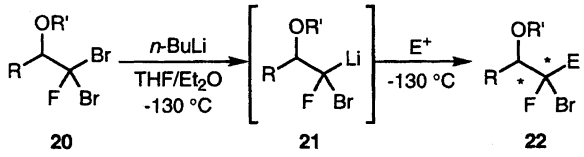
Entry	Olefin[a]	R′-Mtl	Pd cat. (mot amount/10^{-2} mol)	Conditions	Product[b]	Yield/%[c]
1	**5a**	$PhSiEtF_2$	[PdCl(η^3-C_3H_5)]$_2$ (2.5)	TBAF, DMF, 80 °C, 64 h	**9a**	50
2	**5a**	$PhSnBu_3$	PdCl$_2$(PPh$_3$)$_2$ (2.0)	DMF, 90 °C, 2 h	**9a**	88
3	**5a**	PhB(OH)$_2$	Pd(PPh$_3$)$_4$ (3.0)	Na_2CO_3 aq, benzene, 100 °C, 2 h	**9a**	99
4	**5a**	4-MeO–C_6H_4–ZnCl	Pd(PPh$_3$)$_4$ (5.0)	THF, 80 °C, 1 h	**10a**	80
5	**5a**	4-MeO–C_6H_4–B(OH)$_2$	Pd(PPh$_3$)$_4$ (3.0)	Na_2CO_3 aq, benzene, 100 °C, 2 h	**10a**	97
6	**5a**[d]	PhB(OH)$_2$	Pd(PPh$_3$)$_4$ (3.0)	Na_2CO_3 aq, benzene, 100 °C, 2 h	**9a**[e]	97
7	**5d**[f]	PhB(OH)$_2$	Pd(PPh$_3$)$_4$ (3.0)	Na_2CO_3 aq, benzene, 100 °C, 2 h	**11d**[g]	88
8	**5p**[h]	PhB(OH)$_2$	Pd(PPh$_3$)$_4$ (3.0)	Na_2CO_3 aq, benzene, 100 °C, 2 h	**12p**[i]	87
9	**5a**	(*E*)-PhCH=CHB($O_2C_6H_4$)	Pd(PPh$_3$)$_4$ (3.0)	NaOEt, benzene, 80 °C, 15 h	**13a**[j]	42
10	**5a**	(*E*)-PhCH=CHSiMeF$_2$	[PdCl(η^3-C_3H_5)]$_2$ (2.5)	TBAF, THF, 55 °C, 64 h	**13a**[k]	55
11	**5a**	PhC≡CH/CuI	PdCl$_2$(PPh$_3$)$_2$ (2.0)	Et_3N, r.t., 8 h	**14a**	30[l]
12	**5a**	HO[$(CH_2)_2$]$_2$C≡CH/CuI	PdCl$_2$(PPh$_3$)$_2$ (2.0)	Et_3N, r.t., 16 h	**15a**	64[m]

a) Ratio of *E*/*Z* **5** used was > 99 : < 1 unless otherwise noted. b) Ratio of the *E*/*Z* product was > 99 : < 1 unless otherwise noted. c) Isolated yield. d) *E*/*Z* = 14 : 86. e) *E*/*Z* = 83 : 17. f) *E*/*Z* = 89 : 11. g) *E*/*Z* = 12 : 88. h) *E*/*Z* = 91 : 9. i) *E*/*Z* = 11 : 89. j) (*Z*, *E*) product only. k) (*Z*, *E*) : (*E*, *E*) = 92 : 8. l) Substrate **5a** (68%) was recovered. m) Recovery of **5a** was 30%.

Diastereoselective Generation of RCH(OMEM)-CFBrLi and Their Reactions with Electrophiles. For extending the carbon framework of **3**, the remaining carbon–bromine bonds behave as a useful functionality. We envisaged that a bromine–lithium exchange of **3** and a subsequent reaction with an electrophile would be appropriate to this end, and that novel organofluorine compounds would be accessible bearing a –CFBr– group. To realize this idea, we first protected the hydroxy group of **3** and obtained the corresponding silyl, methyl, methoxymethyl (MOM), and (2-methoxyethoxy)methyl (MEM) ethers **20**. Since the bromine–lithium exchange of 1,1-dibromoalkanes with a 3-alkoxy[23] or 2-silyloxy group[24] is known to occur diastereoselectively, we studied the diastereoselective generation of the lithium carbenoid **21** from **20** and its reaction with electrophiles, as summarized in Scheme 4.

A solution of **20** and 4-heptanone in THF–Et_2O (2 : 1) was treated with butyllithium at −130 °C. The resulting mixture was stirred for 1 h at −130 °C and allowed to warm up to −78 °C before being quenched with sat. NH_4Cl aq solution. A workup and purification gave the corresponding alcohol **22** as a mixture of diastereomers. The results are given in Table 8.

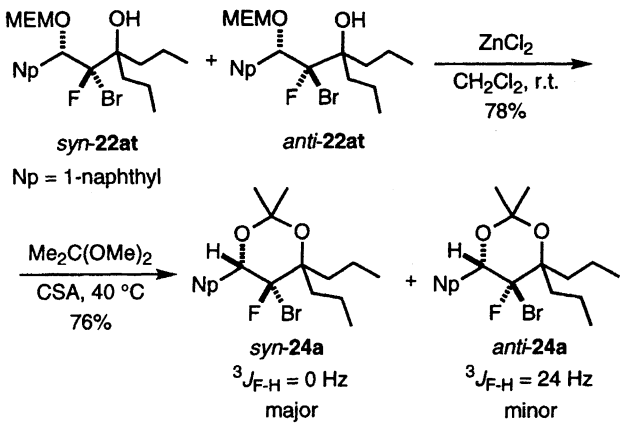
Silyl and methyl ethers **20ap**—**20ar** were allowed to react with 4-heptanone to give **22ap**—**22ar** with 57—67% *syn*-selectivity. It is particularly worthy of noting that silyl ethers **20ap** and **20aq** afforded oxiranes **23p** and **23q**, respectively.



Scheme 4. Diastereoselective generation of **21** and reactions with electrophiles.

These were apparently produced from *anti*-**22ap** and **22aq**, respectively, via intramolecular cyclization. On the other hand, MOM ether **20as** and MEM ether **20at**, having one or two ethereal oxygen(s), afforded *syn*-**22as** and **22at**, respectively, with relatively high diastereoselectivity. These results show that the protecting group plays an important role in the diastereoselective generation of the lithium carbenoid **21**.[25,26] The diastereoselectivity is also affected by the substituent R. Substrate **20ft** or **20gt** exhibited moderate selectivities, whereas high *syn*-selectivities were observed with **20ht** or **20it**. Thus, with bulkier substituent R, higher *syn*-diastereoselectivity resulted. The yields were generally moderate, probably because fluorine-containing carbenoid **21** was thermally labile, even at −130 °C, and possibly underwent proton abstraction from 4-heptanone.

The stereochemistry of **22at** was assigned on the basis of ^1H and ^{19}F NMR spectroscopy of acetonide **24a** prepared through deprotection followed by acetalization, as shown in Scheme 5. Thus, one vicinal coupling constant, $^3J_{F-H}$, of the major isomer of **24a** was smaller than that of the minor



Scheme 5. Stereochemical assignment of **22at**.

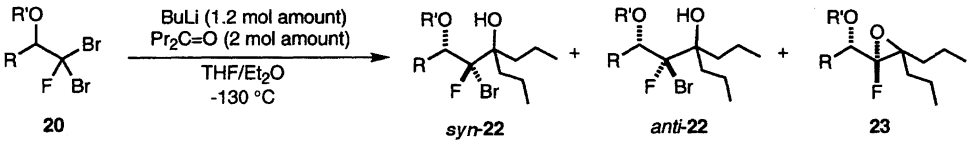
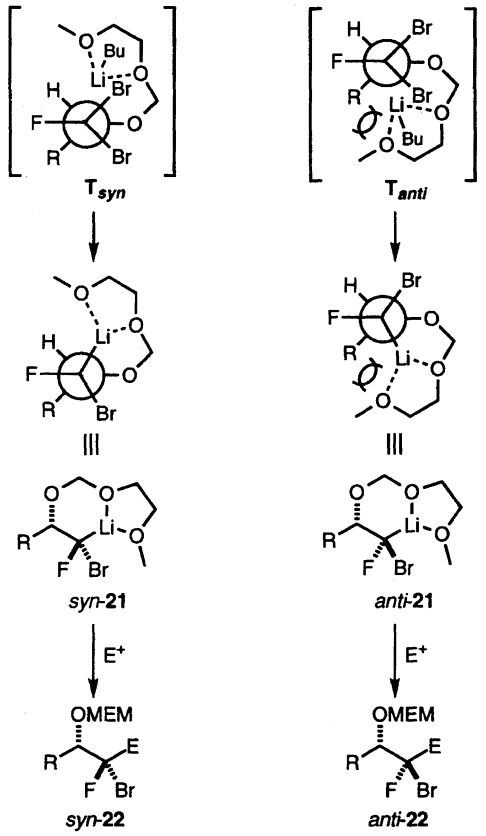


Table 8. Diastereoselectivity in the Bromine–Lithium Exchange of RCH(OR′)$CFBr_2$ (**20**) Followed by the Reaction with 4-Heptanone[a)]

Entry	Substrate			Yield[b)]	Product ratio[c)]				
		R	R′	%	*syn*-**22**	:	*anti*-**22**	:	**23**
1	**20ap**	1-Naphthyl-	$SiEt_3$	38	57	:	25	:	18
2	**20aq**	1-Naphthyl-	$SiMe_2t$-Bu	47	67	:	0	:	33
3	**20ar**	1-Naphthyl-	Me	49	60	:	40	:	0
4	**20as**	1-Naphthyl-	MOM	55	85	:	15	:	0
5	**20at**	1-Naphthyl-	MEM	55	83	:	17	:	0
6	**20ft**	Ph-	MEM	58	50	:	50	:	0
7	**20gt**	$Ph(CH_2)_2$-	MEM	62	62	:	38	:	0
8	**20ht**	*c*-Hex-	MEM	51	92	:	8	:	0
9	**20it**	*i*-Pr-	MEM	46	92	:	8	:	0

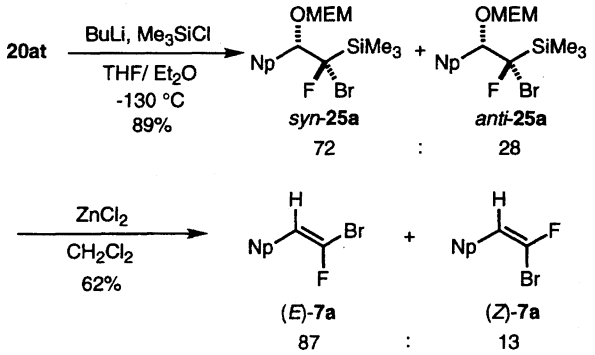
a) Butyllithium was added into a solution of **20** and 4-heptanone in THF–Et_2O (2 : 1) at −130 °C. b) Isolated yield. c) The diastereomeric ratio was determined by ^{19}F NMR.



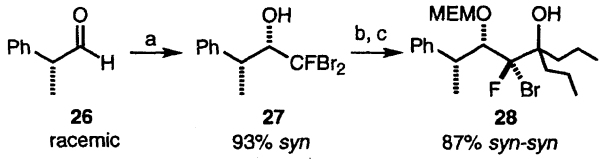
Scheme 6. Transition states in the diastereoselective bromine–lithium exchange of **20**.

isomer; this observation shows that fluorine and hydrogen atoms of the minor isomer are positioned *anti*. Accordingly, the stereochemistry of the major diastereomer of **22at** was assigned *syn*.

The stereochemical outcome is tentatively attributed to the chelation effect, as illustrated in Scheme 6.[27] We assume



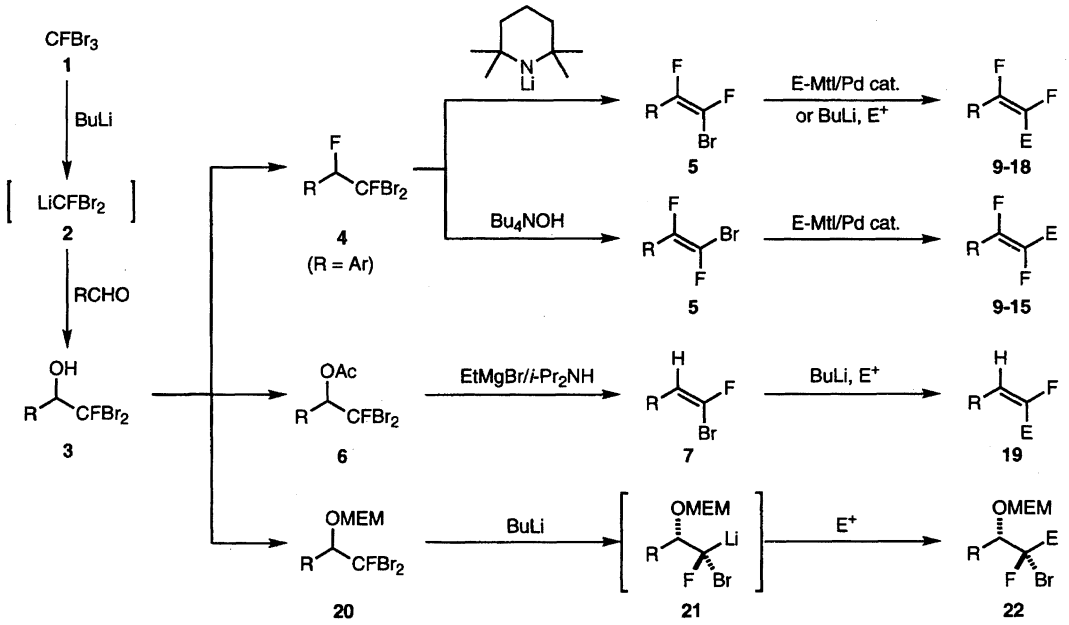
Scheme 7. Silylation of **20at** and olefination via deprotection of MEM group followed by Peterson reaction.



a) $CFBr_3$, BuLi, THF/Et_2O, -130 °C (69%)
b) MEMCl, (i-Pr)$_2$NEt, $(CH_2Cl)_2$, 60 °C (60%)
c) Pr_2CO, BuLi, THF/Et_2O, -130 °C (35%)

Scheme 8. Diastereocontrol of three contiguous stereocenters.

that the conformations in which the carbon–fluorine bond and carbon–oxygen bond are oriented *anti* are favorable due to the dipole–dipole repulsion between these bonds.[28] Thus, two transition states ($\mathbf{T}_{syn}$ and $\mathbf{T}_{anti}$) are possible.[29] While $\mathbf{T}_{anti}$ involves a steric interaction between the substituent R and the lithium chelating with the MEM group, such interaction is absent in $\mathbf{T}_{syn}$. Accordingly, exchange of *pro*-(*R*)-bromine–lithium with retention of configuration proceeds preferentially via $\mathbf{T}_{syn}$, and the resulting carbenoid *syn*-**21** undergoes carbonyl addition with retention of the configuration to give rise to *syn*-**22**. Based on the transition-state



Scheme 9.

model $\mathbf{T}_{syn}$, it can reasonably be explained that the sense of diastereoselectivity should be *syn* and that the degree of the selectivity should depend on the size of substituent R.

Silylation of **20at** with chlorotrimethylsilane also occurred stereoselectively to give *syn*-**25a** as the major diastereomer in a good yield (Scheme 7). The stereochemistry of **25a** was determined by the conversion of **25a** into **7a** with zinc chloride through deprotection of the MEM group, and the Peterson elimination in one-pot, followed by a ^{1}H NMR analysis of $^3J_{H-F}$ of **7a**.

Finally, we explored the stereocontrol of three contiguous chiral centers, starting with (±)-2-phenylpropanal (**26**) as the starting substrate (Scheme 8). Thus, the treatment of $CFBr_3$ with butyllithium at −130 °C in the presence of **26** gave **27** with 93% *syn*-selectivity.[30] Alcohol **27** was protected with an MEM group and treated with butyllithium in the presence of 4-heptanone to give **28** with 87% selectivity, whose stereochemistry was deduced to be *syn–syn* based on the results of the reaction of **20**.

In summary, we have demonstrated that dibromofluoromethyllithium (**2**) can be successfully generated from tribromofluoromethane (**1**) at −130 °C and reacted with aldehydes or ketones to give 2-substituted 1,1-dibromo-1-fluoro-2-alkanols (**3**) in good yields (Scheme 9). The alcohols **3** are transformed to difluoro olefins **9**—**18** through fluorination, dehydrobromination, and cross-coupling reactions. Monofluoro olefins of type **19** are available via acetylation, reductive elimination, and sequential lithiation-substitution. In addition, the protection of **3** with an MEM group followed by a bromine–lithium exchange of the resulting MEM ether **20** and the subsequent reactions with various electrophiles are found to proceed diastereoselectively. The sequence of transformations using tribromofluoromethane (**1**) as a fluorine source allows us to obtain stereoselectively a wide variety of organofluorine compounds, which have been receiving growing interest in a broad area of medicinal, agricultural, and material sciences.

Experimental

General. Not all of the temperatures were corrected. The melting points were determined using an Olympus polarization microscope (BH-2) equipped with a Mettler hot stage (FP-90, FP-82). ^{1}H NMR spectra were measured on a Bruker AC 200 (200 MHz), a JEOL JNM-GX 270 (270 MHz), or a JNM-FX 100 (100 MHz) spectrometer. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. ^{13}C NMR spectra were measured on a Bruker AC 200 (50 MHz) spectrometer with tetramethylsilane as an internal standard (δ = 0 ppm). ^{19}F NMR spectra were measured on a Bruker AC 200 (188 MHz), or a JEOL JNM-FX 100 (94 MHz) spectrometer with trichlorofluoromethane as an internal standard (δ = 0 ppm). The chemical-shift values are given in parts per million downfield relative to the internal standard. Infrared spectra (IR) were recorded on a Hitachi 260-10 or Shimadzu FTIR-8100A spectrometer. GC-MS analyses were performed with a Shimadzu GC-MS QP-5000 or a Hitachi M-80 spectrometer by electron ionization at 70 eV, unless otherwise noted. High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer. Elemental analyses were carried out with a Yanako MT2 CHN CORDER machine. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} and column chromatography was carried out using Merck Kieselgel 60 (230—400 mesh). Capillary gas chromatography was performed with a Shimadzu GC-17A chromatograph equipped with a DB-1 column (0.25 mm×30 m). Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using a JAIGEL-1H and -2H GPC columns. THF, diethyl ether, 1,4-dioxane, and hexane were distilled from benzophenone and sodium before use under a nitrogen atmosphere. Dichloromethane and DMF were distilled from calcium hydride prior to use under a nitrogen atmosphere. Tribromofluoromethane was purchased from PCR or Aldrich Chemical Company, Inc. and used without further purification. Butyllithium was purchased from Kanto Chemical Co., Inc. and titrated with anhydrous 2-butanol in the presence of 1,10-phenanthroline as an indicator before use. Chlorotrimethylsilane and *t*-butylchlorodimethylsilane were kindly donated by Shin-Etsu Chemical Co., Ltd., Japan. All reactions were carried out under an argon atmosphere. Cooling a reaction vessel at −130 °C was effected using a mixture of liquid nitrogen and pentane.

General Procedure for the Generation and Carbonyl Addition of Dibromofluoromethyllithium. To a solution of tribromofluoromethane (**1**) (59 µl, 0.60 mmol) and an aldehyde or ketone (0.50 mmol) in THF (3 ml)–Et_2O (1.5 ml) was added a 1.60 M (1 M = 1 mol dm^{-3}) hexane solution of butyllithium (3.1 ml, 0.50 mmol) at −130 °C via syringe over a period of 10 min. The resulting mixture was stirred for 0.5 h at −130 °C before quenching with a sat. NH_4Cl aq solution. The aq layer was extracted with diethyl ether (20 ml×5). The combined extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by silica-gel column chromatography to afford fluorinated alcohol **3**.

2,2-Dibromo-2-fluoro-1-(1-naphthyl)ethanol (3a): 85% yield, a yellow oil, R_f 0.30 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.19 (d, J = 3.4 Hz, 1H), 6.02 (dd, J = 2.7, 8.1 Hz, 1H), 7.42—7.66 (m, 3H), 7.85—8.13 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 78.5 (d, J = 22.6 Hz), 103.0 (d, J = 326.3 Hz), 123.5 (d, J = 3.1 Hz), 125.1, 125.8, 126.7, 127.0, 129.1, 130.3, 131.2, 131.6, 133.7; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −60.3 (d, J = 8.1 Hz); IR (neat) 3425, 3050, 1510, 1395, 1350, 1260, 1230, 1205, 1170, 1095, 1080, 1030, 1010, 980, 920, 865, 815 cm^{-1}; MS *m/z* (rel intensity) 351 (M^++5; 0.5), 350 (M^++4; 4), 349 (M^++3; 1), 348 (M^++2; 8), 347 (M^++1; 0.6), 346 (M^+; 4), 157 (100), 129 (64). Found: C, 41.61; H, 2.78%. Calcd for $C_{12}H_9Br_2FO$: C, 41.42; H, 2.61%.

2,2-Dibromo-1-(4-cyanophenyl)-2-fluoroethanol (3b): 85% yield, colorless plates, mp 122—126 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.60 (brs, 1H), 5.18 (d, J = 8.3 Hz, 1H), 7.68 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 82.0 (d, J = 22.5 Hz), 101.5 (d, J = 323.6 Hz), 113.1, 118.4, 129.5, 131.9, 140.0; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −62.8 (d, J = 8.3 Hz); IR (CH_2Cl_2) 3390, 9050, 2220, 1400, 1290, 1230, 1190, 1080, 1005, 995, 870, 850, 835, 798, 780 cm^{-1}; MS *m/z* (rel intensity) 325 (M^++4; 0.1), 323 (M^++2; 0.2), 321 (M^+; 0.1), 132 (100), 104 (28). Found: C, 33.56; H, 1.90; N, 4.34%. Calcd for $C_9H_6Br_2FNO$: C, 33.47; H, 1.87; N, 4.34%.

2,2-Dibromo-2-fluoro-1-(4-nitrophenyl)ethanol (3c): 77% yield, a white powder, mp 122—123 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.43 (brs, 1H), 5.25 (d, J = 8.2 Hz, 1H), 7.76 (ddd, J = 0.5, 1.3, 9.0 Hz, 2H), 8.22—8.27 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 81.9 (d, J = 22.6 Hz), 101.4 (d, J = 323.4 Hz), 123.2,

129.7 (d, J = 1.9 Hz), 141.6, 148.5; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −63.0 (d, J = 8.2 Hz); IR (KBr) 3380, 1510, 1340, 1075, 1255, 790, 690 cm^{-1}; MS m/z (rel intensity) 343 (M^++2; 30), 342 (M^++1; 14), 341 (M^+; 34), 278 (28), 259 (59), 256 (70), 233 (29), 219 (15), 172 (38), 152 (48), 140 (34), 91 (60), 69 (100). Found: C, 28.35; H, 1.68%. Calcd for $C_8H_6Br_2FNO_3$: C, 28.02; H, 1.76%.

2,2-Dibromo-2-fluoro-1-(4-methoxyphenyl)ethanol (3d): 87% yield, a colorless oil, R_f 0.40 (hexane–dichloromethane = 1 : 2). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.18 (brs, 1H), 3.82 (s, 3H), 5.00 (d, J = 9.4 Hz, 1H), 6.88—6.95 (m, 2H), 7.44—7.49 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 55.4, 82.7 (d, J = 22.2 Hz), 103.4 (d, J = 324.0 Hz), 113.6, 127.1, 129.9, 160.4; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −62.1 (d, J = 9.4 Hz); IR (neat) 3440, 1605, 1580, 1510, 1460, 1440, 1305, 1250, 1175, 1115, 1075, 1025, 990, 860, 830, 790, 705 cm^{-1}; MS m/z (rel intensity) 331 (M^++5; 0.2), 330 (M^++4; 1), 329 (M^++3; 0.3), 328 (M^++2; 3), 327 (M^++1; 0.2), 326 (M^+; 1), 137 (10), 109 (25). Found: C, 32.68; H, 2.45%. Calcd for $C_9H_9Br_2FO_2$: C, 32.95; H, 2.76%.

2,2-Dibromo-2-fluoro-1-(3,4-methylenedioxyphenyl)ethanol (3e): 90% yield, a colorless oil, R_f 0.50 (dichloromethane). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.24 (brs, 1H), 5.02 (d, J = 9.4 Hz, 1H), 5.98 (s, 2H), 6.81 (d, J = 8.0 Hz, 1H), 6.97—7.05 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 82.7 (d, J = 22.2 Hz), 101.4, 102.9 (d, J = 323.9 Hz), 107.9, 108.8, 122.9, 128.7, 147.5, 148.5; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −62.1 (d, J = 9.4 Hz); IR (neat) 3475, 2880, 1495, 1480, 1440, 1380, 1360, 1240, 1090, 1070, 1030, 990, 920, 895, 860, 825, 795, 735, 700 cm^{-1}; MS m/z (rel intensity) 345 (M^++5; 0.7), 344 (M^++4; 6), 343 (M^++3; 1.2), 342 (M^++2; 12), 341 (M^++1; 0.7), 340 (M^+; 7), 182 (21), 151 (100). Found: C, 31.57; H, 2.01%. Calcd for $C_9H_7Br_2FO_3$: C, 31.61; H, 2.06%.

2,2-Dibromo-2-fluoro-1-phenylethanol (3f): 78% yield, a colorless oil, R_f 0.61 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.11 (brs, 1H), 5.12 (d, J = 9.4 Hz, 1H), 7.30—7.65 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 82.7 (d, J = 22.0 Hz), 102.4 (d, J = 321.8 Hz), 128.0, 128.5 (d, J = 1.9 Hz), 129.3, 134.8; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −62.3 (d, J = 9.4 Hz); IR (neat) 3450, 3070, 3034, 1700, 1495, 1455, 1380, 1090, 1067, 1030, 994, 851, 804, 777, 733 cm^{-1}. Found: C, 32.01; H, 2.50%. Calcd for $C_8H_7Br_2FO$: C, 32.25; H, 2.37%.

1,1-Dibromo-1-fluoro-4-phenyl-2-butanol (3g): 81% yield, a colorless oil, R_f 0.45 (hexane–dichloromethane = 1 : 3). ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.87—2.01 (m, 1H), 2.20—2.32 (m, 1H), 2.56 (d, J = 5.3 Hz, 1H), 2.77 (ddd, J = 8.4, 8.4, 13.8 Hz, 1H), 2.98 (ddd, J = 4.8, 9.1, 14.0 Hz, 1H), 3.86 (dddd, J = 2.3, 5.6, 7.7, 12.8 Hz, 1H), 7.19—7.36 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 31.6, 33.7, 80.5 (d, J = 21.1 Hz), 104.2 (d, J = 322.4 Hz), 126.5, 128.7, 128.8, 140.8; ^{19}F NMR (94 MHz, $CDCl_3$) δ = −60.1 (d, J = 7.7 Hz); IR (neat) 3415, 3025, 2935, 1505, 1460, 1105, 1085, 1055, 1020, 985, 830, 800, 750, 705 cm^{-1}; MS m/z (rel intensity) 328 (M^++4; 2), 327 (M^++3; 3, 13), 326 (M^++2; 4), 325 (M^++1; 26), 324 (M^+; 2), 323 (M^+−1; 13), 243 (10), 245 (10), 165 (100). Found: C, 36.70; H, 3.55%. Calcd for $C_{10}H_{11}Br_2FO$: C, 36.84; H, 3.40%.

2,2-Dibromo-2-fluoro-1-cyclohexylethanol (3h): 71% yield, a colorless oil, R_f 0.40 (hexane–ethyl acetate = 8 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.88—1.43 (m, 5H), 1.60—2.02 (m, 6H), 2.58 (brs, 1H), 3.70 (dd, J = 4.2, 11.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 25.9, 26.1, 26.2, 27.4, 30.8 (d, J = 2.8 Hz), 40.6, 84.6 (d, J = 20.1 Hz), 104.8 (d, J = 327.7 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −57.4 (d, J = 11.2 Hz); IR (neat) 3420, 2930, 2850, 1455, 1105, 1095, 1065, 1015, 900, 803, 745 cm^{-1}; MS m/z (rel intensity) 207 (0.2), 205 (0.2), 142 (2), 141 (13), 95 (100), 55 (5). Found: C, 31.79; H, 4.36%. Calcd for $C_8H_{13}Br_2FO$: C, 31.61; H, 4.31%.

1,1-Dibromo-1-fluoro-3-methyl-2-butanol (3i): 56% yield, a colorless oil, R_f 0.29 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.07 (d, J = 2.5 Hz, 3H), 1.10 (d, J = 2.5 Hz, 3H), 2.32 (m, 1H), 2.53 (d, J = 6.2 Hz, 1H), 3.72 (ddd, J = 4.7, 6.2, 11.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 17.2 (d, J = 2.3 Hz), 20.8 (d, J = 3.8 Hz), 30.9, 85.0 (d, J = 20.1 Hz), 104.6 (d, J = 326.0 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −58.1 (d, J = 11.7 Hz); IR (neat) 3450, 2969, 2878, 2361, 2342, 1472, 1395, 1372, 1294, 1240, 1177, 1148, 1096, 1067, 1026, 968, 905, 851, 820, 799, 743 cm^{-1}; MS m/z (rel intensity) 266 (M^++4; 0.3), 264 (M^++2; 0.7), 262 (M^+; 0.2), 219 (6), 211 (3), 183 (3), 167 (12), 140 (39), 73 (100). HRMS Found: m/z 261.8984. Calcd for $C_5H_9Br_2FO$: M, 261.9004.

1,1-Dibromo-1-fluoro-2-tridecanol (3j): 60% yield, a colorless oil, R_f 0.45 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (270 MHz, $CDCl_3$) δ = 0.88 (t, J = 6.8 Hz, 3H), 1.27—1.37 (m, 17H), 1.52—1.64 (m, 2H), 1.86—1.94 (m, 1H), 2.46 (dt, J = 1.8, 7.4 Hz, 1H), 3.83—3.92 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.1, 22.7, 25.6, 29.3, 29.4, 29.5, 29.57, 29.64, 31.9, 32.1 (d, J = 0.9 Hz), 81.4 (d, J = 21.1 Hz), 104.5 (d, J = 322.7 Hz); ^{19}F NMR (94 MHz, $CDCl_3$) δ = −59.7 (d, J = 7.3 Hz); IR (neat) 3390, 2930, 2860, 1475, 1385, 1315, 1100, 1035, 800, 770 cm^{-1}; MS m/z (rel intensity) 185 (36), 121 (10), 69 (60), 43 (100). Found: C, 41.28; H, 6.43%. Calcd for: $C_{13}H_{25}Br_2FO$: C, 41.51; H, 6.69%.

(*E*)-1,1-Dibromo-1-fluoro-4-phenyl-3-buten-2-ol (3k): 82% yield, a colorless oil, R_f 0.40 (dichloromethane). ^{1}H NMR (100 MHz, $CDCl_3$) δ = 2.95 (brs, 1H), 4.66 (dd, J = 6.0, 6.6 Hz, 1H), 6.25 (dd, J = 6.0, 15.9 Hz, 1H), 6.89 (d, J = 15.9 Hz, 1H), 7.28—7.48 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 81.8 (d, J = 22.5 Hz), 102.6 (d, J = 323.0 Hz), 122.9, 127.0, 128.75, 128.82, 135.7, 136.5; ^{19}F NMR (94 MHz, $CDCl_3$) δ = −61.0 (d, J = 6.6 Hz); IR (neat) 3380, 1605, 1490, 1445, 1120, 1080, 990, 960, 830, 785, 735 cm^{-1}; MS m/z (rel intensity) 327 (M^++5; 0.2), 326 (M^++4; 1), 325 (M^++3; 0.3), 324 (M^++2; 2), 323 (M^++1; 0.1), 322 (M^+; 1), 191 (3.6), 133 (100), 115 (41). Found: C, 37.45; H, 2.73%. Calcd for $C_{10}H_9Br_2FO$: C, 37.07; H, 2.80%.

2,2-Dibromo-2-fluoro-1,1-diphenylethanol (3l): 64% yield, colorless needles, mp 111—113 °C. ^{1}H NMR (100 MHz, $CDCl_3$) δ = 3.42 (s, 1H), 7.22—7.34 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 85.0 (d, J = 18.4 Hz), 108.6 (d, J = 334.5 Hz), 127.7 (d, J = 3.4 Hz), 128.0, 128.3, 140.3 (d, J = 1.7 Hz); ^{19}F NMR (94 MHz, $CDCl_3$) δ = −57.0; IR (KBr) 3545, 3057, 2361, 1541, 1491, 1448, 1327, 1300, 1190, 1153, 1089, 1057, 1034, 1010, 997, 933, 902, 756, 733, 700, 694, 655, 623, 617 cm^{-1}; MS m/z (rel intensity) 376 (M^++4; 0.1), 374 (M^++2; 0.2), 372 (M^+; 0.1), 183 (100), 165 (12), 105 (73). Found: C, 44.99; H, 2.83%. Calcd for $C_{14}H_{11}Br_2FO$: C, 44.96; H, 2.96%.

1,1-Dibromo-1-fluoro-2-phenyl-2-propanol (3m): 96% yield, a colorless oil, R_f 0.40 (hexane–dichloromethane = 1 : 2). ^{1}H NMR (100 MHz, $CDCl_3$) δ = 1.94 (d, J = 1.2 Hz, 3H), 2.82 (brs, 1H), 7.33—7.44 (m, 3H), 7.58—7.69 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 26.0, 81.9 (d, J = 19.5 Hz), 109.2 (d, J = 329.7 Hz), 127.4, 127.9, 128.5, 138.9; ^{19}F NMR (94 MHz, $CDCl_3$) δ = −59.6 (d, J = 1.2 Hz); IR (neat) 3550, 1450, 1380, 1180, 1140, 1110, 1060, 1030, 950, 915, 805, 790, 730, 700 cm^{-1}; MS m/z (rel intensity) 314 (M^++4; 0.2), 312 (M^++2; 0.3), 310 (M^+; 0.2), 191 (15), 121 (100). Found: C, 34.36; H, 3.03%. Calcd for $C_9H_9Br_2FO$: C, 34.64; H, 2.91%.

1-(Dibromofluoromethyl)cyclohexanol (3n): 72% yield, colorless needles, mp 47—49 °C. ^{1}H NMR (100 MHz, $CDCl_3$) δ = 1.26—2.01 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 21.7,

25.1, 31.7 (d, J = 1.1 Hz), 80.0 (d, J = 18.8 Hz), 111.8 (d, J = 328.3 Hz); ^{19}F NMR (94 MHz, $CDCl_3$) δ = −62.9; IR (KBr) 3480, 2941, 2858, 1450, 1160, 1140, 1107, 1041, 995, 956, 931, 810, 750 cm^{-1}; MS m/z (rel intensity) 193 (M^++2−$C_6H_{11}O$; 1), 191 (M^+−$C_6H_{11}O$; 3), 99 (M^+−$CFBr_2$; 100). Found: C, 28.91; H, 3.76%. Calcd for $C_7H_{11}Br_2FO$: C, 29.00; H, 3.82%.

1,1-Dibromo-1-fluoro-2,4-dimethyl-3-penten-2-ol (3o): 86% yield, a colorless oil, R_f 0.25 (hexane–ethyl acetate = 15 : 1). ^{1}H NMR (100 MHz, $CDCl_3$) δ = 1.64 (d, J = 1.0 Hz, 3H), 1.79 (d, J = 1.2 Hz, 3H), 1.93 (d, J = 1.5 Hz, 3H), 2.41 (s, 1H), 5.54 (d, J = 0.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 19.2 (d, J = 0.6 Hz), 23.8 (d, J = 1.4 Hz), 27.6, 81.6 (d, J = 19.0 Hz), 110.1 (d, J = 330.2 Hz), 123.2 (d, J = 1.3 Hz); ^{19}F NMR (94 MHz, $CDCl_3$) δ = −62.9; IR (neat) 3560, 3460, 2980, 2930, 1670, 1450, 1385, 1330, 1225, 1130, 1070, 948, 851, 808, 770, 730 cm^{-1}; MS (10 eV) 274 (0.4), 272 (0.3), 192 (2.7), 190 (5.2), 188 (2.9), 129 (4), 99 (100), 43 (98). Found: C, 29.15; H, 3.90%. Calcd for $C_7H_{11}Br_2FO$: C, 29.00; H, 3.82%.

General Procedure for the Preparation of 1,1-Dibromo-1,2-difluoroethane 4. To a solution of (diethylaminato)trifluorosulfur (0.92 ml, 7.0 mmol) in dichloromethane (6 ml) was added alcohol **3** (6.0 mmol) in dichloromethane (6 ml) at −78 °C. The reaction mixture was allowed to warm up to 0 °C over a period of 1.5 h, and was quenched with sat. $NaHCO_3$ aq solution. The aq layer was extracted with dichloromethane (30 ml×5). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give 1,1-dibromo-1,2-difluoroethane **4**.

1,1-Dibromo-1,2-difluoro-2-(1-naphthyl)ethane (4a): 76% yield, a colorless oil, R_f 0.60 (hexane–dichloromethane = 7 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.55 (dd, J = 9.9, 42.9 Hz, 1H), 7.53—7.61 (m, 3H), 7.90—8.05 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 94.1 (dd, J = 25.0, 193.0 Hz), 96.5 (dd, J = 35.7, 323.4 Hz), 123.5 (d, J = 2.63 Hz), 125.0, 126.2, 127.1, 127.8 (d, J = 8.6 Hz), 127.9 (d, J = 19.5 Hz), 129.2, 131.3, 131.6, 133.7; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −167.4 (dd, J = 29.5, 42.9 Hz), −65.5 (dd, J = 11.1, 29.5 Hz); IR (neat) 3050, 1520, 1250, 1175, 1120, 1095, 1085, 1045, 1025, 980, 940, 820, 800, 790, 775, 725, 710 cm^{-1}; MS m/z (rel intensity) 353 (M^++5; 0.8), 352 (M^++4; 6), 351 (M^++3; 1.4), 350 (M^++2; 12), 349 (M^++1; 0.8), 348 (M^+; 6), 190 (7), 189 (19), 188 (9), 160 (20), 159 (100). Found: C, 41.40; H, 2.16%. Calcd for $C_{12}H_8Br_2F_2$: C, 41.18; H, 2.30%.

1,1-Dibromo-1,2-difluoro-2-(4-methoxyphenyl)ethane (4d): 59% yield, a colorless oil, R_f 0.58 (hexane–dichloromethane = 2 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.84 (s, 3H), 5.63 (dd, J = 10.7, 43.5 Hz, 1H), 6.94 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 55.4, 96.8 (dd, J = 34.4, 322.6 Hz), 97.2 (dd, J = 23.7, 193.4 Hz), 113.8, 123.8 (d, J = 21.6 Hz), 129.9 (dd, J = 1.2, 6.1 Hz), 161.2; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −167.1 (dd, J = 28.2, 43.5 Hz), −67.0 (dd, J = 10.7, 28.2 Hz); IR (neat) 1605, 1580, 1510, 1460, 1300, 1290, 1250, 1180, 1120, 1090, 1065, 1025, 1000, 940, 825, 795, 735 cm^{-1}; MS m/z (rel intensity) 332 (M^++4; 1), 331 (M^++3; 14), 330 (M^++2; 3), 329 (M^++1; 29), 328 (M^+; 2), 327 (M^+−1; 15), 250 (18), 248 (18), 170 (68), 139 (100). Found: C, 32.88; H, 2.46%. Calcd for $C_9H_8Br_2F_2O$: C, 32.76; H, 2.44%.

1,1-Dibromo-1,2-difluoro-2-(3,4-dimethoxyphenyl)ethane (4p): 49% yield, a colorless oil, R_f 0.55 (hexane–dichloromethane = 1 : 2). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.90 (s, 6H), 5.62 (dd, J = 10.7, 43.4 Hz, 1H), 6.94 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 56.1, 96.5 (dd, J = 34.4, 322.9 Hz), 97.2 (dd, J = 23.8, 193.8 Hz), 110.5, 111.1 (d, J = 5.6 Hz), 121.8 (d, J = 6.6 Hz), 124.0 (d, J = 21.7 Hz), 148.8, 150.7; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −166.7 (dd, J = 28.3, 43.4 Hz), −67.0 (dd, J = 10.7, 28.3 Hz); IR (neat) 1525, 1470, 1425, 1275, 1245, 1170, 1150, 1030, 805, 715 cm^{-1}; MS m/z (rel intensity) 363 (M^++5; 0.5), 362 (M^++4; 5), 361 (M^++3; 1.2), 360 (M^++2; 10), 359 (M^++1; 0.7), 358 (M^+; 5), 169 (100). Found: C, 33.63; H, 2.91% Calcd for $C_{10}H_{10}Br_2F_2O_2$: C, 33.36; H, 2.80%.

1,1-Dibromo-1,2-difluoro-2-(4-methylphenyl)ethane (4q): 57%, a colorless oil, R_f 0.61 (hexane–dichloromethane = 8 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.40 (s, 3H), 5.66 (dd, J = 10.2, 43.6 Hz, 1H), 7.25 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.1, 21.4, 96.4 (dd, J = 33.8, 322.3 Hz), 97.3 (dd, J = 23.9, 193.8 Hz), 128.4 (d, J = 6.1 Hz), 128.9 (d, J = 20.0 Hz), 129.0; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −168.5 (dd, J = 27.8, 43.6 Hz), −66.94 (dd, J = 10.2, 27.8 Hz); IR (neat) 2930, 1615, 1520, 1205, 1190, 1130, 1095, 1075, 1030, 1010, 945, 870, 855, 805, 735, 705 cm^{-1}; MS m/z (rel intensity) 316 (M^++5; 2), 315 (M^++4; 18), 314 (M^++3; 4), 313 (M^++2; 37), 312 (M^++1; 2), 311 (M^+; 19), 235 (16), 233 (17), 191 (6), 123 (100). HRMS Found: m/z 311.8966. Calcd for $C_9H_8Br_2F_2$: M, 311.8962.

General Procedure for the Stereoselective Dehydrobromination of 4 with Lithium 2,2,6,6-Tetramethylpiperidide. To a solution of 2,2,6,6-tetramethylpiperidine (5.2 ml, 31 mmol) in THF (30 ml) was added a 1.6 M hexane solution of butyllithium (15.5 ml, 25 mmol) at −78 °C; the resulting solution was stirred for 30 min at 0 °C. The mixture was cooled to −98 °C, and a solution of **4** (17 mmol) in THF (30 ml) was added dropwise. After 10 min, the reaction mixture was quenched with 0.1 M hydrochloric acid, and the aq layer was extracted with diethyl ether (50 ml×5). The organic extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica-gel using hexane to give 1-bromo-1,2-difluoroethene **5** as a mixture of olefinic stereoisomers.

(*E*)-1-Bromo-1,2-difluoro-2-(1-naphthyl)ethene (5a): Colorless needles, mp 36—40 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.45—7.68 (m, 4H), 7.86—8.00 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 124.8 (d, J = 1.0 Hz), 124.9 (d, J = 1.9 Hz), 125.5 (d, J = 21.0 Hz), 126.6, 127.3 (d, J = 1.0 Hz), 128.3 (dd, J = 39.4, 319.7 Hz), 130.0 (dd, J = 2.9, 2.9 Hz), 131.3 (d, J = 4.0 Hz), 131.5 (d, J = 2.8 Hz), 133.5 (d, J = 1.7 Hz), 143.3 (dd, J = 14.4, 256.4 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −111.0 (dd, J = 1.0, 7.4 Hz), −101.6 (d, J = 7.4 Hz); IR (neat) 1300, 1255, 1195, 1150, 1125, 1065, 1025, 1005, 951, 800, 780 cm^{-1}; MS m/z (rel intensity) 270 (M^++2; 10), 268 (M^+; 10), 190 (12), 189 (100), 188 (72), 170 (16), 169 (15), 168 (9), 94 (19). Found: C, 53.51; H, 2.31%. Calcd for $C_{12}H_7BrF_2$: C, 53.56; H, 2.62%.

(*Z*)-5a: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.41—7.65 (m, 4H), 7.84—7.99 (m, 3H); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −125.8 (d, J = 140.6 Hz), −117.0 (d, J = 140.6 Hz).

1-Bromo-1,2-difluoro-2-(4-methoxyphenyl)ethene (5d): 87% yield, a colorless oil, R_f 0.34 (hexane–dichloromethane = 10 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.84 (s, 3H), 5.63 (dd, J = 10.7, 43.5 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.93 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 55.3, 113.9, 120.2 (dd, J = 0.9, 24.2 Hz), 125.5 (dd, J = 40.6, 315.6 Hz), 129.5 (dd, J = 3.3, 4.4 Hz), 144.7 (dd, J = 15.2, 144.7 Hz), 160.9 (d, J = 1.2 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) (*E*)-isomer: δ = −120.8 (d, J = 10.1 Hz), −102.7 (d, J = 10.1 Hz); (*Z*)-isomer: δ = −141.5 (d, J = 133.4 Hz), −119.9 (d, J = 133.4 Hz); IR (neat) 1605, 1575, 1510, 1460, 1440, 1305, 1290, 1255, 1180, 1165, 1140, 1115, 1060, 1025, 900, 830 cm^{-1}; MS m/z (rel intensity) 252 (M^++4; 1), 251 (M^++3; 12), 250 (M^++2; 83), 249 (M^++1; 14), 248 (M^+; 82), 236

(3), 235 (31), 234 (5), 233 (31), 220 (1), 219 (2), 218 (1), 217 (4), 208 (2), 207 (19), 206 (3), 205 (20), 138 (15), 137 (5), 136 (10), 107 (24), 92 (17), 79 (11). Found: C, 43.68; H, 3.09%. Calcd for $C_9H_7BrF_2O$: C, 43.40; H, 2.83%.

1-Bromo-1,2-difluoro-2-(3,4-dimethoxyphenyl)ethene (5p): 90% yield, a colorless oil, R_f 0.38 (hexane–dichloromethane = 1 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.89 (s, 3H), 3.89 (s, 3H), 6.90 (m, 1H), 7.23 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 55.9, 56.0, 110.8, 120.3 (d, J = 24.1 Hz), 121.3, 125.6 (dd, J = 40.6, 316.0 Hz), 144.6 (dd, J = 15.2, 249.8 Hz), 148.8, 150.5; ^{19}F NMR (188 MHz, $CDCl_3$) (*E*)-isomer: δ = −120.7 (d, J = 10.2 Hz), −102.2 (d, J = 10.2 Hz); (*Z*)-isomer: δ = −141.0 (d, J = 133.1 Hz), −119.1 (d, J = 133.1 Hz); IR (neat) 1600, 1520, 1465, 1415, 1342, 1315, 1275, 1260, 1223, 1180, 1145, 1075, 1025, 810 cm^{-1}; MS *m/z* (rel intensity) 281 (M^++3; 16), 280 (M^++2; 84), 279 (M^++1; 14), 278 (M^+; 100), 235 (23), 220 (14), 156 (81), 113 (46). HRMS Found: *m/z* 277.9737. Calcd for $C_{15}H_{12}F_2O$: M, 277.9754.

1-Bromo-1,2-difluoro-2-(4-methylphenyl)ethene (5q): 78% yield, a colorless oil, R_f 0.56 (hexane–ethyl acetate = 200 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.40 (s, 3H), 7.20 (d, J = 8.2 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 21.4, 125.2 (d, J = 23.5 Hz), 126.0 (dd, J = 40.6, 316.2 Hz), 127.8 (dd, J = 3.4, 4.5 Hz), 129.2, 140.4, 144.9 (dd, J = 15.2, 250.0 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) (*E*)-isomer: δ = −121.7 (d, J = 10.5 Hz), −101.6 (d, J = 10.5 Hz); (*Z*)-isomer: δ = −142.1 (d, J = 133.1 Hz), −117.9 (d, J = 133.1 Hz); IR (neat) 1515, 1300, 1275, 1160, 1140, 1120, 1055, 1015, 900, 810 cm^{-1}; MS *m/z* (rel intensity) 235 (M^++3; 8), 234 (M^++2; 75), 233 (M^++1; 15), 232 (M^+; 78), 231 (M^+−1; 8), 153 (26), 152 (14), 151 (47), 133 (100). HRMS Found: *m/z* 231.9709. Calcd for $C_9H_7BrF_2$: M, 231.9699.

A General Procedure for the Preparation of Acetate 6. After acetic anhydride (1.9 ml, 20 mmol) and a catalytic amount of 4-(dimethylamino)pyridine (10 mg) were added to a mixture of crude alcohol **3** (10 mmol) and pyridine (3.2 ml, 40 mmol), the resulting mixture was heated at 60 °C for 1 h. To remove excess pyridine and acetic anhydride via azeotropic distillation, toluene was added and the mixture was concentrated in vacuo. Purification of the residue by silica-gel column chromatography afforded acetate **6**.

2,2-Dibromo-2-fluoro-1-(1-naphthyl)ethyl Acetate (6a): 85% yield, a colorless oil, R_f 0.40 (hexane–dichloromethane = 3 : 2). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.52 (s, 3H), 7.26 (d, J = 12.9 Hz, 1H), 7.51—7.65 (m, 3H), 7.87—7.98 (m, 3H), 8.30 (d, J = 8.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 20.9, 77.2 (d, J = 22.8 Hz), 96.9 (d, J = 324.4 Hz), 123.6, 125.0, 126.0, 127.0, 127.8, 129.0, 129.3, 130.7, 131.9, 133.7, 168.7; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −62.2 (d, J = 12.4 Hz); IR (neat) 1760, 1375, 1220, 1175, 1080, 1055, 1035, 928, 818, 795, 778, 725 cm^{-1}; MS *m/z* (rel intensity) 393 (M^++5; 0.6), 392 (M^++4; 3), 391 (M^++3; 1.2), 390 (M^++2; 6), 389 (M^++1; 0.6), 388 (M^+; 3), 199 (17), 157 (100), 43 (41). Found: C, 42.94; H, 2.85%. Calcd for $C_{14}H_{11}Br_2FO_2$: C, 43.11; H, 2.84%.

2,2-Dibromo-2-fluoro-1-(4-cyanophenyl)ethyl Acetate (6b): 78% yield, colorless plates, mp 82—86 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.23 (s, 3H), 6.31 (d, J = 12.1 Hz, 1H), 7.60—7.68 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 20.7, 80.5 (d, J = 23.0 Hz), 95.4 (d, J = 322.1 Hz), 113.8, 118.1, 129.9, 132.0, 137.8, 168.3; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −64.4 (d, J = 12.1 Hz); IR (CH_2Cl_2) 2210, 1750, 1560, 1410, 1200, 1105, 1075, 1035, 1010, 920, 860, 830, 780 cm^{-1}; MS *m/z* (rel intensity) 365 (M^++2; 0.07), 363 (M^+; 0.04), 174 (38), 145 (31), 102 (11), 43 (100). Found: C, 36.10; H, 2.22; N, 3.73%. Calcd for $C_{11}H_8Br_2FNO_2$: C, 36.20; H, 2.21; N, 3.84%.

2,2-Dibromo-2-fluoro-1-(4-methoxyphenyl)ethyl Acetate (6d): 86% yield, a pale yellow oil, R_f 0.50 (hexane–dichloromethane = 1 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.20 (s, 3H), 3.81 (s, 3H), 6.24 (d, J = 13.0 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 7.46 (d, J = 8.9 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 20.8, 55.3, 81.2 (d, J = 22.3 Hz), 97.4 (d, J = 323.1 Hz), 113.7, 124.9, 130.6, 160.7, 168.6; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −63.5 (d, J = 13.0 Hz); IR (neat) 1755, 1610, 1515, 1465, 1375, 1310, 1290, 1255, 1210, 1180, 1120, 1030, 949, 929, 869, 834, 799, 766 cm^{-1}; MS *m/z* (rel intensity) 373 (M^++5; 0.2), 372 (M^++4; 1.3), 371 (M^++3; 0.4), 370 (M^++2; 2.7), 369 (M^++1; 0.2), 368 (M^+; 1.3), 230 (5), 179 (18), 137 (100), 108 (10), 43 (45). Found: C, 35.82; H, 2.75%. Calcd for $C_{11}H_{11}Br_2FO_3$: C, 35.71; H, 3.00%.

2,2-Dibromo-2-fluoro-1-(3,4-methylenedioxyphenyl)ethyl Acetate (6e): 76% yield, a pale yellow powder, mp 82—84 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.20 (s, 3H), 5.99 (s, 2H), 6.19 (d, J = 13.0 Hz, 1H), 6.80 (d, J = 8.5 Hz, 1H), 6.99—7.03 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 20.8, 81.2 (d, J = 22.4 Hz), 97.0 (d, J = 323.1 Hz), 101.5, 108.0, 109.1, 123.8, 126.4, 147.7, 148.8, 168.5; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −63.6 (d, J = 13.0 Hz); IR (CH_2Cl_2) 1745, 1490, 1480, 1440, 1360, 1205, 1090, 1025, 920 cm^{-1}; MS *m/z* (rel intensity) 387 (M^++5; 0.4), 386 (M^++4; 3), 385 (M^++3; 0.8), 384 (M^++2; 6), 383 (M^++1; 0.4), 382 (M^+; 3), 193 (12), 151 (100), 93 (11), 43 (39). Found: C, 34.33; H, 2.24%. Calcd for $C_{11}H_9Br_2FO_4$: C, 34.40; H, 2.36%.

1-(Dibromofluoromethyl)-3-phenylpropyl Acetate (6g): 78% yield, a colorless oil, R_f 0.45 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (100 MHz, $CDCl_3$) δ = 2.05—2.40 (m, 2H), 2.15 (s, 3H), 2.51—2.78 (m, 2H), 5.43 (dt, J = 2.7, 9.3 Hz, 1H), 7.23—7.34 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 20.7, 31.5, 32.4, 79.0 (d, J = 21.9 Hz), 97.6 (d, J = 322.0 Hz), 126.5, 128.5, 128.7, 140.2, 169.5; ^{19}F NMR (94 MHz, $CDCl_3$) δ = −60.6 (d, J = 9.3 Hz); IR (neat) 2935, 1760, 1455, 1375, 1215, 1120, 1080, 1050, 984, 781, 747, 699 cm^{-1}; MS (10 eV, *m/z* (rel intensity) 369 (M^++3; 5), 367 (M^++1; 10), 365 (M^+−1; 5), 307 (14), 229 (40), 147 (100), 43 (12). Found: C, 39.36; H, 3.82%. Calcd for $C_{12}H_{13}Br_2FO_2$: C, 39.16; H, 3.56%.

A Typical Procedure for the Preparation of 1-Bromo-1-fluoroethene 7. A THF solution of EtMgBr (1.8 M, 25 ml, 45 mmol) was added to a solution of diisopropylamine (2.1 ml, 15 mmol) in THF (8 ml) at 0 °C. After 5 min, a white solid precipitated. The resulting suspension was stirred for 30 min at 0 °C. To the suspension cooled at −98 °C was added a THF (6 ml) solution of acetate **6** (3 mmol) dropwise via a syringe over a period of 30 min. After 10 min, a 0.1 M solution of hydrochloric acid was added to the reaction mixture, and the aq layer was extracted with diethyl ether (60 ml×5). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo to provide a crude product, which was purified by silica-gel column chromatography to give **7**.

1-Bromo-1-fluoro-2-(1-naphthyl)ethene (7a): 81% yield, a white powder, mp 39—43 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.65 (d, J = 30.6 Hz, 1H), 7.44—7.59 (m, 3H), 7.68—7.72 (m, 1H), 7.81—8.01 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 110.2 (d, J = 7.8 Hz), 123.7, 125.5, 126.1, 126.6, 127.1, 127.2, 128.6, 128.8, 130.8, 133.7, 134.6 (d, J = 329.8 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) (*E*)-isomer: δ = −69.5 (d, J = 30.6 Hz); (*Z*)-isomer: δ = −65.8 (d, J = 12.9 Hz); IR (CH_2Cl_2) 3045, 1640, 1585, 1345, 1035, 1005, 835, 800, 770, 705 cm^{-1}; MS *m/z* (rel intensity) 252 (M^++2; 19), 250 (M^+; 20), 171 (100), 85 (20). Found: C, 57.03; H, 3.21%. Calcd for $C_{12}H_8BrF$: C, 57.40; H, 3.21%.

1-Bromo-2-(4-cyanophenyl)-1-fluoroethene (7b): 89% yield,

colorless needles, mp 114—117 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.03 (d, J = 31.8 Hz, 1H), 7.46—7.50 (m, 2H), 7.60—7.65 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 111.3 (d, J = 2.4 Hz), 112.0 (d, J = 6.0 Hz), 118.6, 128.5 (d, J = 7.7 Hz), 132.5, 136.81 (d, J = 334.1 Hz), 136.83 (d, J = 4.9 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) (*E*)-isomer: δ = −63.2 (d, J = 31.8 Hz); (*Z*)-isomer: δ = −60.5 (d, J = 14.5 Hz); IR (KBr) 2926, 2855, 2224, 1925, 1734, 1684, 1649, 1605, 1558, 1541, 1504, 1412, 1329, 1307, 1277, 1205, 1178, 1124, 1066, 1043, 1014, 860, 839, 819, 808 cm^{-1}; MS *m/z* (rel intensity) 257 (M^++2; 100), 225 (M^+; 100), 126 (17), 99 (38). Found: C, 48.17; H, 2.07; N, 5.96%. Calcd for C_9H_5BrFN: C, 47.82; H, 2.22; N, 6.19%.

1-Bromo-1-fluoro-2-(4-methoxyphenyl)ethene (7d): 84% yield, colorless needles, mp 34—37 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.81 (s, 3H), 5.91 (d, J = 33.1 Hz, 1H), 6.85—6.90 (m, 2H), 7.30—7.37 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 55.3, 112.6 (d, J = 6.5 Hz), 114.1, 125.4 (d, J = 4.5 Hz), 129.4 (d, J = 7.1 Hz), 132.3 (d, J = 328.9 Hz), 159.2 (d, J = 2.9 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) (*E*)-isomer: δ = −71.55 (d, J = 33.1 Hz); (*Z*)-isomer: δ = −68.3 (d, J = 15.3 Hz); IR (neat) 2980, 2960, 1670, 1625, 1535, 1485, 1355, 1330, 1315, 1275, 1205, 1060, 875 cm^{-1}; MS *m/z* (rel intensity) 233 (M^++3; 10), 232 (M^++2; 97), 231 (M^++1; 8), 230 (M^+; 100), 108 (73), 107 (37). Found: C, 47.02; H, 3.63%. Calcd for C_9H_8BrFO: C, 46.78; H, 3.49%.

1-Bromo-1-fluoro-2-(3,4-methylenedioxyphenyl)ethene (7e): 88% yield, colorless needles, mp 52—55 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 5.87 (d, J = 32.6 Hz, 1H), 5.96 (s, 2H), 6.73—6.83 (m, 2H), 6.98 (d, J = 1.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 101.3, 108.1 (d, J = 6.5 Hz), 108.4, 112.8 (d, J = 6.1 Hz), 122.4 (d, J = 6.0 Hz), 126.7 (d, J = 4.7 Hz), 132.6 (d, J = 329.5 Hz), 147.3 (d, J = 3.0 Hz), 148.0; ^{19}F NMR (188 MHz, $CDCl_3$) (*E*)-isomer: δ = −70.7 (d, J = 32.5 Hz); (*Z*)-isomer: δ = −67.8 (d, J = 15.3 Hz); IR (CH_2Cl_2) 2920, 1525, 1505, 1465, 1280, 1220, 1055, 880, 860, 850, 830 cm^{-1}; MS *m/z* (rel intensity) 247 (M^++3; 8), 246 (M^++2; 80), 245 (M^++1; 42), 244 (M^+; 77), 123 (7), 107 (100). HRMS Found: *m/z* 243.9522. Calcd for $C_9H_6BrFO_2$: M, 243.9535.

1-Bromo-1-fluoro-4-phenyl-1-butene (7g): 80% yield, a colorless oil, R_f 0.60 (hexane–dichloromethane = 20 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.29—2.42 (m, 2H), 2.73 (t, J = 7.6 Hz, 2H), 5.52 (dt, J = 7.6, 13.0 Hz, 1H), 7.16—7.37 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 29.5 (d, J = 2.6 Hz), 34.9 (d, J = 1.9 Hz), 109.2 (d, J = 15.3 Hz), 126.4, 128.6 (d, J = 316.6 Hz), 135.8 (d, J = 314.6 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) (*Z*)-isomer: δ = −71.93 (dt, J = 0.6, 13.0 Hz); (*E*)-isomer: δ = −75.57 (dt, J = 2.5, 31.1 Hz); IR (neat) 3040, 1680, 1505, 1470, 1130, 1010, 760, 715 cm^{-1}; MS *m/z* (rel intensity) 230 (M^++2; 0.1), 228 (M^+; 0.1), 149 (28), 91 (100). Found: C, 52.58; H, 4.44%. Calcd for $C_{10}H_{10}BrF$: C, 52.43; H, 4.40%.

1-(Dibromofluoromethyl)-3-phenylpropyl *p*-Toluenesulfonate (8g). To a solution of 60% NaH (0.172 g, 4.3 mmol) in THF was added **3g** (1.41 g, 4.3 mmol) in THF (5 ml) at 0 °C. After stirring for 10 min at 0 °C, *p*-toluenesulfonyl chloride (0.82 g, 4.3 mmol) in THF (5 ml) was added at 0 °C. The resulting solution was stirred for 10 min before quenching with 0.1 M hydrochloric acid. The aq layer was extracted with diethyl ether (20 ml×5), and the combined extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography on silica-gel to give tosylate **8g** (1.49 g, 72% yield) as a white powder. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.19—2.46 (m, 1H), 2.46 (m, 3H), 2.78—2.92 (m, 3H), 5.00 (ddd, J = 2.7, 6.6, 8.9 Hz, 1H), 7.19—7.40 (m, 7H), 7.81—7.88 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 21.8, 31.1, 86.0 (d, J = 20.0 Hz), 96.4 (d, J = 323.3 Hz), 126.6, 128.0, 128.6, 128.7, 129.9, 133.9, 139.9, 145.6; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −56.7 (d, J = 6.6 Hz); IR (KBr) 1615, 1465, 1390, 1205, 1195, 1135, 1110, 1035, 945, 875, 855, 825, 780, 745, 715 cm^{-1}; MS *m/z* (rel intensity) 482 (M^++4; 0.1), 481 (M^++3; 0.3), 480 (M^++2; 0.1), 479 (M^++1; 0.6), 478 (M^+; 0.1), 477 (M^+−1; 0.3), 229 (50), 227 (50), 147 (100), 91 (98). HRMS Found: *m/z* 477.9270. Calcd for $C_{17}H_{17}Br_2FO_3S$: M, 477.9250.

General Procedure for the Cross-coupling Reaction of 1-Bromo-1,2-difluoroethenes. With an Organosilicon Reagent: To a flame-dried test tube were added **5a** (87.5 mg, 0.3 mmol), an organosilicon reagent (0.6 mmol), 1 M solution of TBAF in THF (0.6 ml, 0.6 mmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2.8 mg, 7.5×10^{-3} mmol), and DMF (2 ml), and the resulting mixture was heated at 80 °C for 64 h. The reaction mixture was passed through a short silica-gel column to remove the catalyst, and the crude product was purified by preparative TLC.

With an Organotin Reagent: To a flame-dried test tube were added **5a** (87.2 mg, 0.3 mmol), tributylphenyltin (140 µl, 0.45 mmol), $PdCl_2(PPh_3)_2$ (4.2 mg, 6.0×10^{-3} mmol), and DMF (2 ml); the resulting mixture was heated at 90 °C for 2 h before quenching with aq KF solution. The aq layer was extracted with hexane. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Short silica-gel column chromatography followed by preparative TLC gave **9a** in 88% yield.

(*Z*)-1,2-Difluoro-1-(1-naphthyl)-2-phenylethene (9a): A colorless oil, R_f 0.54 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.10—8.21 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 125.3 (d, J = 1.2 Hz), 125.5 (d, J = 2.3 Hz), 126.7 (d, J = 3.1 Hz), 126.8 (t, J = 2.7 Hz), 127.56 (dd, J = 1.5, 21.4 Hz), 127.56 (d, J = 1.2 Hz), 128.4 (d, J = 1.1 Hz), 128.8, 129.0 (t, J = 1.1 Hz), 129.9 (d, J = 23.7 Hz), 130.2 (dd, J = 2.7, 3.4 Hz), 131.3 (d, J = 3.1 Hz), 132.0 (dd, J = 0.76, 3.1 Hz), 133.9 (d, J = 1.9 Hz), 144.8 (dd, J = 20.8, 251.2 Hz), 147.1 (dd, J = 21.0, 246.4 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) (*Z*)-isomer: δ = −117.6 (dd, J = 2.4, 17.5 Hz), −133.8 (d, J = 17.4 Hz); (*E*)-isomer: δ = −134.9 (d, J = 132.9 Hz), −151.5 (d, J = 132.9 Hz); IR (neat) 3061, 1578, 1508, 1495, 1446, 1398, 1277, 1248, 1186, 1128, 1091, 1072, 1057, 1020, 985, 902, 798, 777, 763 cm^{-1}; MS *m/z* (rel intensity) 267 (M^++1; 18), 266 (M^+; 95), 265 (M^+−1; 41), 264 (M^+−2; 14), 246 (100), 215 (49), 188 (29), 122 (19), 107 (29). Found: C, 81.41; H, 4.33%. Calcd for $C_{18}H_{12}F_2$: C, 81.19; H, 4.54%.

With an Organoboron Reagent: To a flame-dried test tube were added **5a** (0.138 g, 0.51 mmol), organoboron reagent (0.75 mmol), 2.0 M Na_2CO_3 aq (0.5 ml, 1.0 mmol), $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol), and benzene (4 ml) and the resulting mixture was heated at 100 °C for 2 h. The reaction mixture was passed through a column containing anhydrous sodium sulfate and short silica-gel to remove the catalyst. The crude product was purified by preparative TLC.

With an Organozinc Reagent: To a solution of 4-bromoanisole (100 µl, 0.80 mmol) in THF (2 ml) was added, 1.6 M hexane solution of butyllithium (0.50 ml, 0.80 mmol) at −78 °C. After 10 min, zinc chloride (0.80 mmol) dissolved in diethyl ether (0.8 ml) was added at −78 °C to the solution and the resulting solution was warmed up to 0 °C over a period of 2 h. The zinc reagent obtained was added via cannula to a solution of **5a** (98 mg, 0.40 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.020 mmol) in THF (2 ml). The resulting mixture was heated at 80 °C for 1 h before quenching with sat. aq NH_4Cl solution. The aq layer was extracted with diethyl ether, and the combined organic extracts were dried over anhydrous sodium

sulfate and concentrated in vacuo. The residue was purified by preparative TLC to afford **10a** (87 mg, 80%) as a white powder.

(*Z*)-1,2-Difluoro-1-(4-methoxyphenyl)-2-(1-naphthyl)ethene (10a): ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.71 (s, 3H), 6.64 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 7.76 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 55.2, 113.7 (d, J = 0.8 Hz), 122.1 (d, J = 25.2 Hz), 125.3 (d, J = 1.1 Hz), 125.5 (d, J = 1.9 Hz), 126.7, 127.4 (d, J = 1.2 Hz), 127.7 (dd, J = 1.7, 21.5 Hz), 128.3 (dd, J = 3.4, 5.3 Hz), 128.7, 130.1 (t, J = 2.9 Hz), 131.0 (d, J = 3.1 Hz), 132.0 (d, J = 3.3 Hz), 133.9 (d, J = 1.9 Hz), 143.6 (dd, J = 21.4, 248.7 Hz), 147.0 (dd, J = 20.9, 246.1 Hz), 160.0 (d, J = 1.2 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −120.4 (dd, J = 1.7, 18.2 Hz), −132.3 (d, J = 18.2 Hz); IR (KBr) 1689, 1605, 1576, 1514, 1466, 1417, 1302, 1279, 1250, 1180, 1128, 1082, 1062, 1032, 1020, 987, 902, 868, 839, 804, 777 cm^{-1}; MS *m/z* (rel intensity) 298 (M^++2; 0.65), 297 (M^++1; 5), 296 (M^+; 22), 295 (M^+−1; 4), 233 (12). HRMS Found: *m/z* 296.1042. Calcd for $C_{19}H_{14}F_2O$: M, 296.1013.

(*Z*)-1,2-Difluoro-1-(4-methoxyphenyl)-2-phenylethene (11d): A colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$) (*Z*)-isomer: δ = 3.82 (s, 3H), 6.84 (m, 2H), 7.31 (m, 7H); (*E*)-isomer: δ = 3.87 (s, 3H); ^{19}F NMR (188 MHz, $CDCl_3$) (*Z*)-isomer: δ = −126.2 (d, J = 14.8 Hz), −131.5 (d, J = 14.9 Hz); (*E*)-isomer: δ = −151.3 (d, J = 120.4 Hz), −154.8 (d, J = 120.4 Hz); IR (neat) 2960, 2940, 2840, 1608, 1576, 1514, 1462, 1444, 1298, 1253, 1176, 1122, 1101, 1074, 1020, 1007, 902, 835, 765 cm^{-1}; MS *m/z* (rel intensity) 248 (M^++2; 2), 247 (M^++1; 19), 246 (M^+; 100), 231 (23), 215 (6), 196 (46), 123 (8), 119 (11), 89 (22), 77 (9). HRMS Found: *m/z* 246.0834. Calcd for $C_{15}H_{12}F_2O$: M, 246.0856.

(*Z*)-1,2-Difluoro-1-(3,4-dimethoxyphenyl)-2-phenylethene (12p): A colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.67 (s, 3H), 3.87 (s, 3H), 6.76—6.80 (m, 2H), 6.93—6.97 (m, 1H), 7.26—7.48 (m, 5H); ^{19}F NMR (188 MHz, $CDCl_3$) (*Z*)-isomer: δ = −127.2 (d, J = 14.5 Hz), −130.6 (d, J = 14.5 Hz); (*E*)-isomer: δ = −154.0 (d, J = 120.5 Hz), −153.9 (d, J = 120.0 Hz); IR (neat) 3003, 2937, 2839, 1603, 1583, 1518, 1464, 1446, 1269, 1221, 1174, 1143, 1115, 1074, 1053, 1026, 941, 920, 860, 831, 812, 765, 733, 696 cm^{-1}; MS *m/z* (rel intensity) 277 (M^++1; 45), 276 (M^+; 100), 260 (54), 245 (5), 202 (20), 171 (12), 170 (31), 151 (15), 137 (12), 108 (7), 100 (16), 77 (2). HRMS Found: *m/z* 276.0964. Calcd for $C_{16}H_{14}F_2O_2$: M, 276.0962.

(1*Z*, 3*E*)-1,2-Difluoro-1-(1-naphthyl)-4-phenyl-1,3-butadiene (13a): A pale yellow oil, R_f 0.29 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.41 (ddd, J = 1.8, 16.1, 25.1 Hz, 1H), 7.03 (d, J = 16.1 Hz, 1H), 7.20—7.29 (m, 5H), 7.50—7.66 (m, 4H), 7.92—8.13 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 115.7 (d, J = 1.9 Hz), 116.1 (d, J = 1.9 Hz), 125.2 (d, J = 1.5 Hz), 125.6 (d, J = 2.3 Hz), 126.8, 126.9 (d, J = 1.2 Hz), 127.5 (d, J = 1.5 Hz), 128.4 (d, J = 1.2 Hz), 128.7, 128.8, 129.8 (dd, J = 4.2, 12.6 Hz), 130.2 (dd, J = 2.3, 3.4 Hz), 131.5 (d, J = 2.7 Hz), 132.2 (d, J = 1.5 Hz), 133.9 (d, J = 1.9 Hz), 145.9 (dd, J = 18.7, 255.6 Hz), 146.7 (dd, J = 20.0, 248.3 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −118.8 (d, J = 16.1 Hz), −145.4 (dd, J = 16.1, 25.1 Hz); IR (neat) 3059, 3026, 1948, 1800, 1668, 1622, 1595, 1578, 1508, 1496, 1448, 1398, 1373, 1338, 1277, 1250, 1205, 1188, 1126, 1061, 1041, 958, 933, 864, 817, 802, 777, 752, 740 cm^{-1}; MS *m/z* (rel intensity) 293 (M^++1; 22), 292 (M^+; 100), 291 (M^+−1; 20), 272 (64), 214 (57), 201 (49), 183 (37), 128 (42). HRMS Found: *m/z* 292.1075. Calcd for $C_{20}H_{14}F_2$: M, 292.1064.

(*Z*)-1,2-Difluoro-1-(1-naphthyl)-4-phenyl-1-buten-3-yne (14a). To a flame-dried test tube were added **5a** (0.120 g, 0.45 mmol), phenylacetylene (0.70 mmol), CuI (1.9 mg, 0.01 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol), and triethylamine (1.5 ml, 10 mmol). The resulting mixture was stirred at room temperature for 8 h before a treatment with 0.1 M hydrochloric acid. The aq layer was extracted three times with benzene. The combined organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by preparative TLC to yield **14a** (39 mg, 30% yield) as a yellow oil.

R_f 0.45 (hexane–ethyl acetate = 24 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.14—8.34 (m, 12H); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −133.8 (d, J = 22.3 Hz), −109.9 (d, J = 22.3 Hz); IR (neat) 3061, 2210, 1672, 1578, 1510, 1489, 1442, 1398, 1334, 1296, 1252, 1192, 1180, 1159, 1128, 1064, 1049, 933, 827, 775, 754 cm^{-1}; MS *m/z* (rel intensity) 291 (M^++1; 14), 289 (M^+−1; 100), 271 (24), 252 (5), 239 (10), 144 (26), 131 (22). Found: C, 83.02; H, 4.10%. Calcd for $C_{20}H_{12}F_2$: C, 82.75; H, 4.17%.

(*Z*)-5,6-Difluoro-6-(1-naphthyl)-5-hexen-3-yn-1-ol (15a): A yellow oil, R_f 0.18 (hexane–dichloromethane = 1 : 3). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.41 (ddt, J = 1.8, 4.8, 6.3 Hz, 2H), 3.42 (s, 1H), 3.47 (t, J = 6.3 Hz, 2H), 7.34—8.26 (m, 7H); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −133.1 (dd, J = 4.8, 22.3 Hz), −111.4 (d, J = 22.3 Hz); IR (neat) 3350, 2900, 2230, 1684, 1508, 1338, 1271, 1248, 1190, 1134, 1076, 1060, 993, 976, 931, 898, 860, 804, 775 cm^{-1}; MS *m/z* (rel intensity) 258 (M^+; 17), 238 (19), 227 (58), 207 (100), 201 (27). HRMS Found: *m/z* 258.0853. Calcd for $C_{16}H_{12}F_2O$: M, 258.0856.

A Typical Procedure for the Lithiation and Substitution of Fluoroethene 5a. To a solution of **5a** (0.27 g, 1 mmol) in THF (3 ml) and diethyl ether (1.5 ml) was added a 1.64 M hexane solution of butyllithium (0.61 ml, 1.0 mmol) at −130 °C. After stirring for 20 min at −130 °C, an electrophile (1—5 mmol) was added to the solution. The resulting solution was stirred for an additional 30 min at −130 °C and allowed to warm up to −78 °C over a period of 30 min. After the reaction mixture was quenched with sat. NH_4Cl aq solution, the aq layer was extracted with diethyl ether (20 ml×5). The organic layer was concentrated in vacuo, and the residue was purified by silica-gel column chromatography to give fluoroethene **16a** or **17a**.

(*Z*)-(1-^{2}H)-1,2-Difluoro-2-(1-naphthyl)ethene (16a): 96% yield, a colorless oil, R_f 0.55 (hexane). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.42—7.65 (m, 4H), 7.88—7.97 (m, 2H), 8.13—8.19 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 125.2 (d, J = 3.6 Hz), 125.8 (dd, J = 1.4, 20.9 Hz), 126.6, 127.3 (d, J = 1.1 Hz), 128.2 (dd, J = 2.7, 4.0 Hz), 128.6, 131.2 (d, J = 1.7 Hz), 131.7 (dd, J = 1.4, 3.1 Hz), 133.5 (ddt, J = 16.6, 31.6, 258.7 Hz), 133.7 (d, J = 1.1 Hz), 148.6 (ddt, J = 3.5, 6.8, 251.9 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −158.5 (dt, J = 11.4, 18.4 Hz), −125.2 (d, J = 18.4 Hz); IR (neat) 1700, 1525, 1320, 1270, 1210, 1170, 1125, 1075, 1010, 850, 820, 790, 780 cm^{-1}; MS (30 eV) *m/z* (rel intensity) 191 (M^+; 100), 190 (66), 189 (35), 171 (68). HRMS Found: *m/z* 191.0640. Calcd for $C_{12}H_7DF_2$: M, 191.0655.

(*E*)-1,2-Difluoro-2-(1-naphthyl)-1-trimethylsilylethene (17a): 97% yield, a colorless oil, R_f 0.35 (hexane). ^{1}H NMR (200 MHz, $CDCl_3$) δ = −0.11 (s, 9H), 7.43—7.63 (m, 4H), 7.87—7.99 (m, 2H), 8.06—8.12 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = −2.06 (dd, J = 1.6, 1.6 Hz), 124.7 (d, J = 2.2 Hz), 125.4, 126.6, 127.29 (dd, J = 2.6, 22.8 Hz), 127.32 (d, J = 0.9 Hz), 128.4, 130.5 (dd, J = 3.0, 3.0 Hz), 131.5 (d, J = 3.0 Hz), 132.8 (d, J = 2.9 Hz), 133.5 (d, J = 1.9 Hz), 152.2 (dd, J = 3.0, 275.2 Hz), 154.1 (dd, J = 14.6, 269.8 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −149.17 (d, J = 25.7 Hz), −101.8 (dd, J = 1.4, 25.7 Hz); IR (neat) 2975, 1670, 1305, 1260, 1195, 1130, 1105, 910, 850, 810, 805, 795, 785, 765 cm^{-1}; MS (30 eV) *m/z* (rel intensity) 263 (M^+; 13), 262 (M^+−1; 62), 188 (13), 170 (100), 151 (44), 77 (54). Found: C, 68.58; H, 6.14%.

Calcd for $C_{15}H_{16}F_2Si$: C, 68.67; H, 6.15%.

(*Z*)-2,3-Difluoro-3-(1-naphthyl)-1-phenyl-2-propenyl Acetate (18a). A crude sample obtained from **5a** and benzaldehyde was dissolved in pyridine (0.97 ml, 12 mmol), acetic anhydride (0.57 ml, 6.0 mmol) and a catalytic amount of 4-dimethylaminopyridine (10 mg). The resulting mixture was stirred at room temperature for 3.5 h and then diluted with toluene. Concentration under reduced pressure followed by purification by silica-gel column chromatography afforded acetate **18a** (0.45 g, 66% yield). R_f 0.25 (hexane–ethyl acetate = 16 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.09 (s, 3H), 6.18 (dd, J = 2.2, 26.2 Hz, 1H), 7.28—7.35 (m, 5H), 7.56—7.62 (m, 4H), 7.90—8.03 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 20.8, 70.8 (dd, J = 2.2, 21.0 Hz), 125.2 (d, J = 1.0 Hz), 125.5 (d, J = 21.0 Hz), 126.9, 127.1, 127.5, 128.7, 128.8, 128.9, 129.9 (dd, J = 2.9, 2.9 Hz), 131.9 (d, J = 2.9 Hz), 132.2 (d, J = 2.3 Hz), 133.8 (d, J = 2.1 Hz), 135.8 (d, J = 1.0 Hz), 144.8 (dd, J = 18.8, 259.1 Hz), 146.3 (dd, J = 16.3, 255.8 Hz), 169.3; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −148.5 (dd, J = 15.3, 26.2), −117.5 (d, J = 15.3 Hz); IR (neat) 3051, 3034, 2974, 1795, 1720, 1605, 1579, 1508, 1496, 1464, 1454, 1398, 1367, 1342, 1290, 1257, 1186, 1143, 1122, 1082, 1061, 1035, 1020, 974, 929, 916, 866, 848, 831, 808, 792, 779, 727, 696, 659, 642, 623 cm^{-1}; MS *m/z* (rel intensity) 276 (51), 229 (13), 228 (13), 127 (100), 109 (21). Found: C, 74.85; H, 4.76%. Calcd for $C_{21}H_{16}F_2O_2$: C, 74.55; H, 4.76%.

(*Z*)-2-Fluoro-3-(1-naphthyl)-1-phenyl-2-propenyl Acetate (19a): A colorless oil, R_f 0.23 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.23 (s, 3H), 6.51 (d, J = 35.5 Hz, 1H), 6.60 (d, J = 14.1 Hz, 1H), 7.30—7.94 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 21.2, 73.9 (d, J = 30.5 Hz), 106.4 (d, J = 8.3 Hz), 124.0, 125.4, 125.8, 126.3, 127.4, 127.6, 128.3, 128.4, 128.7, 128.8, 128.9, 131.4, 133.7, 136.0, 156.9 (d, J = 268.4 Hz), 169.7; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −116.3 (dd, J = 14.1, 35.5 Hz); IR (neat) 3040, 1730, 1675, 1440, 1360, 1270, 1210, 1150, 1005, 960, 775, 760, 730, 685 cm^{-1}; MS *m/z* (rel intensity) 322 (M$^+$+2; 1), 321 (M$^+$+1; 4), 320 (M$^+$; 25), 277 (2), 261 (10), 184 (26), 183 (100), 171 (32), 152 (12), 149 (15), 133 (35), 127 (6). HRMS Found: *m/z* 320.1232. Calcd for $C_{15}H_{12}F_2O$: M, 320.1213.

1,1-Dibromo-1-fluoro-2-(1-naphthyl)-2-(triethylsiloxy)ethane (20ap). A 50-ml two-necked round-bottomed flask was charged with **3a** (0.31 g, 0.89 mmol), imidazole (0.136 g, 2.0 mmol), 4-dimethylaminopyridine (ca. 10 mg), and DMF (5 ml) under an argon atmosphere. Chlorotriethylsilane (0.34 ml, 2.0 mmol) was added to the solution. The reaction mixture was heated for 1 h at 60 °C and then poured into water. The organic layer was separated, and the aq layer was extracted with hexane. The combined organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give **20ap** (0.36 g, 96% yield) as a pale yellow viscous oil. R_f 0.78 (hexane–dichloromethane = 1 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.52—0.76 (m, 6H), 0.89—1.03 (m, 9H), 6.04 (brs, 1H), 7.48—7.62 (m, 3H), 7.85—8.13 (m, 4H); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −58.9; IR (neat) 2957, 2912, 2878, 1599, 1512, 1458, 1412, 1379, 1334, 1280, 1234, 1174, 1134, 1082, 1041, 1022, 1005, 931, 873, 844, 812, 790, 771, 731 cm^{-1}; MS *m/z* (rel intensity) 464 (M$^+$+4; 0.8), 462 (M$^+$+2; 1), 460 (M$^+$; 0.8), 302 (25), 271 (100), 167 (69), 140 (55), 127 (31), 77 (86). HRMS Found: *m/z* 459.9877. Calcd for $C_{18}H_{23}Br_2FOSi$: M, 459.9869.

1,1-Dibromo-2-*t*-butyldimethylsilyloxy-1-fluoro-2-(1-naphthyl)ethane (20aq). A 50-ml two-necked round-bottomed flask was charged with **3a** (0.97 g, 2.8 mmol) and dichloromethane (10 ml) under an argon atmosphere and cooled at 0 °C. To the flask were added 2,6-lutidine (7.0 ml, 6.0 mmol) and *t*-butyldimethylsilyl trifluoromethanesulfonate (1.05 ml, 9.0 mmol) at 0 °C. The reaction mixture was stirred for 5 h at room temperature and then neutralized with sat. Na_2CO_3 aq solution (5 ml). The organic layer was separated, and the aq layer was extracted with dichloromethane. The combined organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give **20aq** (1.06 g, 82%) as a pale yellow oil. R_f 0.79 (hexane–dichloromethane = 1 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = −0.18 (s, 3H), 0.23 (s, 3H), 0.98 (s, 9H), 6.0 (d, J = 4.8 Hz, 1H), 7.5 (m, 3H), 7.90 (m, 2H), 8.10 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = −4.8, −4.4, 18.4, 25.9, 78.3 (d, J = 24.4 Hz), 103.8 (d, J = 326.0 Hz), 123.1, 125.1, 125.7, 126.7, 128.0, 129.2, 130.0, 131.7, 133.1, 133.6; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −18.8 (d, J = 4.8 Hz); IR (neat) 2955, 2930, 2858, 1599, 1512, 1471, 1462, 1399, 1361, 1334, 1280, 1253, 1172, 1132, 1041, 1024, 1005, 933, 877, 839, 777, 717 cm^{-1}; MS *m/z* (rel intensity) 466 (M$^+$+6; 0.03), 465 (M$^+$+5; 0.1), 464 (M$^+$+4; 0.4), 463 (M$^+$+3; 0.2), 462 (M$^+$+2; 0.8), 461 (M$^+$+1; 0.09), 460 (M$^+$; 0.3), 302 (0.5), 271 (29), 245 (16), 167 (100), 140 (19), 127 (10), 77 (24). Found: C, 46.89; H, 4.89%. Calcd for $C_{18}H_{23}Br_2FOSi$: C, 46.77; H, 5.02%.

1, 1- Dibromo- 1- fluoro- 2- methoxy- 2- (1- naphthyl)ethane (20ar). A 50 ml two-necked round-bottomed flask was charged with NaH (60% in oil, 0.080 g, 2.0 mmol) and THF (4 ml), filled with argon and cooled to 0 °C. To the flask were added a solution of **3a** (0.52 g, 1.5 mmol) in THF (4 ml) and methyl iodide (0.19 ml, 3.0 mmol) at 0 °C. The reaction mixture was stirred for 3 h at 0 °C and for 1 h at room temperature and then treated with sat. NH_4Cl aq solution (5 ml). The organic layer was separated and the aq layer was extracted with diethyl ether. The combined organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give **20ar** (0.26 g, 47% yield) as a brown oil. R_f 0.59 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.49 (s, 3H), 5.52 (d, J = 7.6 Hz, 1H), 7.56 (m, 3H), 7.91 (m, 3H), 8.13 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 58.5, 87.1 (d, J = 23.6 Hz), 99.8 (d, J = 321.9 Hz), 123.6 (d, J = 3.8 Hz), 125.3, 125.9, 126.8, 127.7, 129.2, 129.8, 130.4, 132.7, 133.9; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −59.7 (d, J = 6.8 Hz); IR (neat) 3070, 2932, 2829, 1597, 1512, 1450, 1396, 1333, 1286, 1230, 1199, 1167, 1120, 1101, 1051, 1026, 997, 974, 931, 875, 819, 796, 773, 721 cm^{-1}; MS *m/z* (rel intensity) 365 (M$^+$+5; 0.5), 364 (M$^+$+4; 3), 363 (M$^+$+3; 0.9), 362 (M$^+$+2; 6), 361 (M$^+$+1; 0.5), 360 (M$^+$; 3), 282 (0.2), 202 (12), 171 (100), 127 (32). Found: C, 43.22; H, 3.10%. Calcd for $C_{13}H_{11}Br_2FO$: C, 43.13; H, 3.06%.

1,1-Dibromo-1-fluoro-2-(methoxy)methoxy-2-(1-naphthyl)-ethane (20as). A 50-ml two-necked round-bottomed flask was charged with NaH (60% in oil, 0.072 g, 1.8 mmol) and THF (3 ml) under an argon atmosphere and cooled to 0 °C. To the flask were added a solution of **3a** (0.42 g, 1.2 mmol) in THF (3 ml) and chloromethyl methyl ether (140 µl, 1.8 mmol). The reaction mixture was stirred for 1 h at 0 °C and for 0.5 h at room temperature. A workup followed by purification by column chromatography gave **20as** (0.33 g, 70% yield). R_f 0.65 (hexane–dichloromethane = 1 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.44 (s, 3H), 4.61 (d, J = 6.9 Hz, 1H), 4.80 (d, J = 6.9 Hz, 1H), 6.00 (d, J = 9.2 Hz, 1H), 7.53 (m, 3H), 7.90 (m, 3H), 8.14 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 56.8, 80.0, 95.2, 99.6 (J = 323 Hz), 123.5, 124.9, 125.7, 126.6, 127.8, 130.0, 130.2, 132.4, 133.5; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −59.42 (d, J = 6.8 Hz); IR (neat) 3053, 2957, 2895, 2843, 2826, 1952, 1597, 1512, 1464, 1441, 1396, 1340, 1288, 1265, 1232, 1215, 1153, 1107, 1050, 922, 873, 821, 773, 735 cm^{-1}; MS

m/z (rel intensity) 394 (M^++4; 3), 392 (M^++2; 6), 390 (M^+; 3), 314 (1), 312 (1), 232 (15), 201 (95), 170 (100), 159 (79), 141 (98), 127 (92), 85 (90), 63 (57). Found: C, 42.82; H, 3.31%. Calcd for $C_{14}H_{13}Br_2FO_2$: C, 42.89; H, 3.34%.

1,1-Dibromo-1-fluoro-2-(2-methoxyethoxy)methoxy-2-(1-naphthyl)ethane (20at). A solution of **3a** (1.01 g, 2.9 mmol) in THF (5 ml) and successively chloromethyl 2-methoxyethyl ether (0.41 ml, 3.6 mmol) were added to NaH (60% in oil, 0.14 g, 3.6 mmol) in THF (5 ml) at 0 °C under an argon atmosphere. A workup and purification by column chromatography gave **20at** (1.09 g, 86% yield) as a pale yellow oil. R_f 0.29 (hexane–dichloromethane = 1 : 4). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.27 (s, 3H), 3.29—3.60 (m, 3H), 3.92—4.01 (m, 1H), 4.70 (d, J = 7.0 Hz, 1H), 4.95 (d, J = 7.0 Hz, 1H), 6.03 (d, J = 9.4 Hz, 1H), 7.36 (m, 3H), 7.89 (m, 3H), 8.15 (d, J = 8.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 58.9, 67.9, 71.4, 85.4 (d, J = 21.5 Hz), 94.2, 99.6 (d, J = 322.7 Hz), 123.6, 124.9, 125.8, 126.6, 127.9, 128.4, 128.9, 130.2, 132.3, 133.6; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −59.4 (d, J = 7.8 Hz); IR (neat) 3053, 2926, 2893, 1597, 1512, 1452, 1396, 1367, 1288, 1240, 1199, 1176, 1116, 1055, 987, 931, 852, 821, 798, 775, 723 cm^{-1}; MS *m/z* (rel intensity) 436 (M^++2; 0.6), 252 (4), 250 (15), 170 (63), 127 (31), 89 (100). Found: C, 43.78; H, 3.94%. Calcd for $C_{16}H_{17}Br_2FO_3$: C, 44.07; H, 3.93%.

1,1-Dibromo-1-fluoro-2-(2-methoxyethoxy)methoxy-2-phenylethane (20ft): 78% yield, a pale yellow oil, R_f 0.28 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.33 (s, 3H), 3.36—3.64 (m, 3H), 3.80—3.98 (m, 1H), 4.73 (d, J = 7.0 Hz, 1H), 4.91 (d, J = 7.0 Hz, 1H), 5.13 (d, J = 10.3 Hz, 1H), 7.31—7.55 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 59.0, 67.9, 71.5, 85.5 (d, J = 22.1 Hz), 94.2, 99.4 (d, J = 321.6 Hz), 128.2, 129.5, 129.6 (d, J = 1.5 Hz), 134.0 (d, J = 0.76 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −61.3 (d, J = 10.2 Hz); IR (neat) 3065, 3034, 2926, 2893, 2818, 1495, 1454, 1405, 1367, 1279, 1242, 1199, 1172, 1118, 1057, 974, 937, 790, 758, 735, 700 cm^{-1}; MS *m/z* (rel intensity) 388 (M^++4; 3), 386 (M^++2; 9), 384 (M^+; 3), 307 (13), 226 (15), 155 (15), 105 (22), 89 (51), 82 (100). HRMS Found: *m/z* 383.9400. Calcd for $C_{12}H_{15}Br_2FO_3$: M, 383.9372.

1,1-Dibromo-1-fluoro-2-(2-methoxyethoxy)methoxy-4-phenylbutane (20gt): 81% yield, a pale yellow oil, R_f 0.32 (hexane–dichloromethane = 1 : 5). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.94—2.36 (m, 2H), 2.67—3.03 (m, 2H), 3.84 (s, 3H), 3.55—3.59 (m, 2H), 3.70—3.87 (m, 1H), 3.90—3.98 (m, 2H), 4.90 (d, J = 7.0 Hz, 1H), 4.98 (d, J = 7.0 Hz, 1H), 7.18—7.34 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 31.6, 34.5 (d, J = 1.5 Hz), 59.2, 68.4, 71.7, 85.9 (d, J = 17.9 Hz), 97.3 (d, J = 3.4 Hz), 102.3 (d, J = 321.6 Hz), 126.4, 128.6, 128.7, 141.0; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −56.5 (d, J = 6.8 Hz); IR (neat) 3063, 3028, 2930, 2818, 1603, 1496, 1454, 1365, 1286, 1244, 1197, 1116, 1012, 935, 850, 785, 752, 700 cm^{-1}; MS *m/z* (rel intensity) 340 (3), 338 (5), 336 (3), 229 (2), 227 (2), 147 (91), 129 (18), 89 (100), 77 (22). Found: C, 40.48; H, 4.48%. Calcd for $C_{14}H_{19}Br_2FO_3$: C, 40.61; H, 4.62%.

1,1-Dibromo-2-cyclohexyl-1-fluoro-2-(2-methoxyethoxy)-methoxyethane (20ht): 71% yield, a pale yellow oil, R_f 0.30 (hexane–dichloromethane = 1 : 5). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.11—2.04 (m, 11H), 3.39 (s, 3H), 3.57 (t, J=4.7 Hz, 2H), 3.70—3.80 (m, 2H), 3.89 (dt, J = 4.7, 11.0 Hz, 1H), 4.93 (s 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 26.4, 26.8, 27.7 (d, J = 1.5 Hz), 32.6 (d, J = 1.1 Hz), 40.8 (d, J = 0.77 Hz), 59.3, 68.6 (d, J = 0.76 Hz), 71.8, 90.3 (d, J = 17.5 Hz), 98.1 (d, J = 1.9 Hz), 101.9 (d, J = 325.0 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −54.8 (d, J = 10.2 Hz); IR (neat) 2928, 2855, 1450, 1242, 1199, 1172, 1120, 1099, 1020, 976, 846, 781, 748 cm^{-1}; MS *m/z* (rel intensity) 289 (0.3), 287 (0.7), 285 (0.5), 207 (10), 205 (10), 125 (22), 105 (47), 83 (45), 60 (100). Found: C, 36.79; H, 5.60%. Calcd for $C_{12}H_{21}Br_2FO_3$: C, 36.76; H, 5.40%.

1,1-Dibromo-1-fluoro-2-(2-methoxyethoxy)methoxy-3-methylbutane (20it): 56% yield, a pale yellow oil, R_f 0.37 (hexane-ethyl acetate = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.09 (t, J = 7.4 Hz, 6H), 2.37 (d, J = 2.3 Hz, 1H), 3.39 (s, 3H), 3.39—3.59 (m, 2H), 3.69—3.94 (m, 3H), 4.96 (dd, J = 7.0, 10.7 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 17.1 (d, J = 1.9 Hz), 22.1, 30.6, 59.1, 68.4, 71.7, 90.3 (d, J = 17.9 Hz), 98.0, 101.7 (d, J = 325.4 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −55.3 (d, J = 11.5 Hz); IR (neat) 2968, 2880, 2818, 1469, 1388, 1367, 1280, 1242, 1199, 1176, 1035, 980, 906, 852, 783, 744 cm^{-1}; MS *m/z* (rel intensity) 279 (0.9), 277 (2), 275 (0.7), 249 (3), 247 (6), 245 (3), 167 (18), 165 (16), 105 (41), 89 (63), 87 (37), 61 (100). Found: C, 30.83; H, 5.02%. Calcd for $C_9H_{17}Br_2FO_3$: C, 30.71; H, 4.87%.

A General Procedure for the Diastereoselective Generation and Carbonyl Addition of RCH(OR′)CFBrLi. A hexane solution of butyllithium (1.62 M, 0.30 ml, 0.48 mmol) was added to a solution of **20** (0.40 mmol) and 4-heptanone (120 µl, 0.80 mmol) in THF (3 ml) and diethyl ether (1.5 ml) at −130 °C via a syringe over a period of 10 min. The resulting mixture was stirred for 1 h at −130 °C and warmed up to −78 °C before quenching with sat. aq NH_4Cl solution. The aq layer was extracted with diethyl ether (20 ml×5). The combined extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by silica-gel column chromatography to afford the adduct.

2-Bromo-2-fluoro-1-(1-naphthyl)-3-propyl-1-triethylsiloxy-3-hexanol (22ap): 31% yield as a mixture of diastereomers. A colorless oil, R_f 0.26 (hexane–dichloromethane = 2 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) *syn*-isomer: δ = 0.23—0.55 (m, 6H), 0.72—0.89 (m, 9H), 0.91—1.08 (m, 6H), 1.42—1.65 (m, 4H), 1.76—2.13 (m, 4H), 3.28 (s, 1H), 6.23 (s, 1H), 7.42—7.58 (m, 3H), 7.85—8.13 (m, 4H); *anti*-isomer: δ = 6.34 (d, J = 23.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 5.2, 6.8, 14.9 (d, J = 0.76 Hz), 15.1, 17.2 (d, J = 3.1 Hz), 17.7 (d, J = 2.6 Hz), 38.1, 38.5, 70.8 (d, J = 33.2 Hz), 80.4 (d, J = 20.9 Hz), 122.6 (d, J = 4.2 Hz), 123.1 (d, J = 260.7 Hz), 124.5, 125.3, 126.4, 129.05, 129.11, 129.5, 131.9 (d, J = 1.9 Hz), 133.4, 134.7; ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −113.2; *anti*-isomer: δ = −132.0 (d, J = 23.7 Hz); IR (neat) 3497, 3053, 2961, 2876, 1599, 1512, 1458, 1412, 1379, 1299, 1236, 1172, 1118, 1072, 1003, 970, 879, 858, 808, 775, 744 cm^{-1}; MS *m/z* (rel intensity) 323 (2), 321 (2), 302 (3), 271 (85), 227 (3), 225 (2), 213 (4), 141 (11), 127 (4), 115 (24), 43 (100). Found: C, 59.56; H, 7.62%. Calcd for $C_{25}H_{38}BrFO_2Si$: C, 60.35; H, 7.70%.

(1*R, 2*S**)-(±)-2,3-Epoxy-2-fluoro-1-(1-naphthyl)-3-propyl-1-triethylsilyloxyhexane (23ap):** 7% yield, a coloress oil, R_f 0.43 (hexane–dichloromethane = 2 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.54—0.67 (m, 6H), 0.76—0.94 (m, 15H), 1.23—1.41 (m, 4H), 1.45—1.62 (m, 3H), 1.69—1.85 (m, 1H), 5.79 (d, J = 17.2 Hz, 1H), 7.41—7.57 (m, 3H), 7.71—7.87 (m, 3H), 8.16 (d, J = 7.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 4.9, 6.8, 14.1, 14.4, 18.2 (d, J = 1.5 Hz), 18.2, 32.0 (d, J = 1.1 Hz), 32.3 (d, J = 2.6 Hz), 70.8 (d, J = 19.1 Hz), 72.6 (d, J = 35.5 Hz), 102.5 (d, J = 270.5 Hz), 124.2 (d, J = 2.7 Hz), 125.2, 125.6 (d, J = 2.7 Hz), 125.7, 126.0, 128.87, 128.94, 131.2; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −138.1 (d, J = 16.9 Hz); IR (neat) 3053, 2961, 2876, 1599, 1512, 1466, 1414, 1379, 1238, 1169, 1113, 1005, 951, 848, 790, 744 cm^{-1}; MS *m/z* (rel intensity) 271 (100), 213 (7), 141 (28), 127 (6), 115 (35). Found: C, 71.99; H, 9.03%. Calcd for $C_{25}H_{37}FO_2Si$: C, 72.07; H, 8.95%.

(1*R, 2*S**)-(±)-2-Bromo-1-*t*-butyldimethylsilyloxy-2-fluoro-1-(1-naphthyl)-3-propyl-3-hexanol (22aq):** 34% yield, a colorless oil, R_f 0.35 (hexane–dichloromethane = 2 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = −0.51 (s, 3H), 0.12 (s, 3H), 0.86—1.06 (m, 6H), 0.96 (s, 9H), 1.39—1.62 (m, 4H), 1.79—2.07 (m, 4H), 3.09 (s, 1H), 6.20 (s, 1H), 7.43—7.58 (m, 3H), 7.84—7.98 (m, 2H), 8.01—8.09 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = −4.4, −3.6, 15.0 (d, J = 1.1 Hz), 15.1 (d, J = 0.76 Hz), 17.2 (d, J = 4.1 Hz), 17.7 (d, J = 2.7 Hz), 18.2, 26.1, 38.1, 38.7, 70.0 (d, J = 32.8 Hz), 80.5 (d, J = 21.4 Hz), 122.6 (d, J = 3.8 Hz), 123.22 (d, J = 262.1 Hz), 124.6, 125.3, 126.5, 129.2, 129.4, 132.0, 133.4, 134.0, 134.7; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −113.1; IR (neat) 3510, 3053, 2961, 2859, 1599, 1512, 1464, 1390, 1361, 1336, 1286, 1255, 1232, 1170, 1120, 1070, 1005, 968, 839, 777, 735 cm^{-1}; MS *m/z* (rel intensity) 498 (M^++2; 11), 496 (M^+; 8), 477 (18), 350 (10), 300 (16), 271 (10), 156 (10), 115 (26), 81 (81), 79 (30), 69 (100). Found: C, 60.63; H, 7.69%. Calcd for $C_{25}H_{38}FBrO_2Si$: C, 60.35; H, 7.70%.

(1*R, 2*S**)-(±)-2,3-Epoxy-1-*t*-butyldimethylsilyloxy-2-fluoro-1-(1-naphthyl)-3-propylhexane (23aq):** 13% yield, a colorless oil, R_f 0.56 (hexane–dichloromethane = 2 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = −0.02 (s, 3H), 0.15 (s, 3H), 0.75—0.92 (m, 6H), 0.92 (s, 9H), 1.18—1.43 (m, 4H), 1.46—1.82 (m, 4H), 5.79 (d, J = 21.0 Hz, 1H), 7.42—7.57 (m, 3H), 7.71—7.88 (m, 3H), 8.13—8.17 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = −4.8, −4.6 (d, J = 0.7 Hz), 14.1, 14.3, 18.1 (d, J = 1.5 Hz), 18.3, 18.5, 26.0, 32.1 (d, J = 0.76 Hz), 32.3 (d, J = 2.7 Hz), 70.7 (d, J = 18.7 Hz), 73.1 (d, J = 34.7 Hz), 102.6 (d, J = 296.0 Hz), 124.3 (d, J = 2.6 Hz), 125.1, 125.5 (d, J = 2.6 Hz), 125.7, 126.0, 128.9 (d, J = 3.4 Hz), 131.2, 133.9, 135.3, 135.4; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −137.8 (d, J = 21.0 Hz); IR (neat) 3053, 2961, 2932, 2858, 1599, 1512, 1460, 1361, 1253, 1169, 1113, 1005, 951, 868, 839, 779 cm^{-1}; MS *m/z* (rel intensity) 416 (M^+; 0.1), 359 (2), 339 (5), 271 (52), 233 (99), 213 (9), 155 (20), 141 (18), 127 (8), 77 (76), 73 (100). HRMS Found: *m/z* 416.2571. Calcd for $C_{25}H_{37}FO_2Si$: M, 416.2547.

2-Bromo-2-fluoro-1-methoxy-1-(1-naphthyl)-3-propyl-3-hexanol (22ar): 49% yield as a mixture of diastereomers, a pale yellow oil, R_f 0.22 (hexane–diethyl ether = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.89—1.09 (m, 6H), 1.26—2.05 (m, 8H), 3.31 (s, 3H), 5.68 (s, 1H), 7.43—7.68 (m, 3H), 7.87—7.90 (m, 4H); ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −113.8; *anti*-isomer: δ = −131.8 (d, J = 23.7 Hz); IR (neat) 3491, 3051, 2963, 2934, 2874, 2361, 1597, 1512, 1466, 1398, 1294, 1232, 1197, 1169, 1099, 1072, 1032, 1001, 964, 910, 798, 777, 735 cm^{-1}; MS *m/z* (rel intensity) 398 (M^++2; 0.4), 396 (M^+; 0.5), 252 (3), 250 (3), 243 (1), 241 (1), 202 (1), 171 (100), 128 (9), 115 (4). HRMS Found: *m/z* 396.1072. Calcd for $C_{20}H_{26}BrFO_2$: M, 396.1101.

2-Bromo-2-fluoro-1-methoxymethoxy-1-(1-naphthyl)-3-propyl-3-hexanol (22as): 55% yield as a mixture of diastereomers, a pale yellow oil, R_f 0.25 (hexane–diethyl ether = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) *syn*-isomer: δ = 0.90—1.10 (m, 6H), 1.25—1.68 (m, 4H), 1.90—2.12 (m, 4H), 3.30 (s, 1H), 3.46 (s, 3H), 4.58 (d, J = 6.7 Hz, 1H), 4.66 (dd, J = 1.8, 6.7 Hz, 1H), 6.26 (s, 1H), 7.44—7.62 (m, 3H), 7.86—8.01 (m, 4H); *anti*-isomer: δ = 6.38 (d, J = 22.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 15.0 (d, J = 0.76 Hz), 15.1, 17.2 (d, J = 3.4 Hz), 17.7 (d, J = 2.3 Hz), 37.4, 38.7, 57.7, 73.6 (d, J = 32.1 Hz), 80.5 (d, J = 20.9 Hz), 95.0, 121.5 (d, J = 261.7 Hz), 123.1 (d, J = 4.6 Hz), 124.9, 125.6, 126.5, 128.3, 129.0, 129.7, 131.3, 133.0, 133.6; ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −113.0; *anti*-isomer: δ = −130.6 (d, J = 22.0 Hz); IR (neat) 3503, 3053, 2963, 2874, 2828, 1597, 1512, 1466, 1379, 1292, 1265, 1234, 1213, 1157, 1045, 922, 856, 798, 777, 738 cm^{-1}; MS *m/z* (rel intensity) 428 (M^++2; 2), 426 (M^+; 2), 252 (16), 250 (16), 201 (100), 171 (17), 169 (41), 141 (44). HRMS Found: *m/z* 426.1191. Calcd for $C_{21}H_{28}BrFO_3$: M, 426.1205.

2-Bromo-2-fluoro-1-(2-methoxyethoxy)methoxy-1-(1-naphthyl)-3-propyl-3-hexanol (22at): 55% yield as a mixture of diastereomers, a pale yellow oil, R_f 0.12 (hexane–diethyl ether = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) *syn*-isomer: δ = 0.88—1.07 (m, 6H), 1.42—1.61 (m, 4H), 1.92—2.06 (m, 4H), 3.32 (s, 3H), 3.35—3.65 (m, 3H), 3.76—3.94 (m, 1H), 4.62 (d, J = 6.9 Hz, 1H), 4.79 (dd, J = 1.8, 6.9 Hz, 1H), 6.27 (s, 1H), 7.41—7.59 (m, 3H), 7.84—8.18 (m, 4H); *anti*-isomer: δ = 3.30 (s, 3H), 4.39 (d, J = 6.8 Hz, 1H), 4.67 (d, J = 6.8 Hz, 1H), 6.37 (d, J = 23.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.9, 15.0, 17.0 (d, J = 3.1 Hz), 17.6 (d, J = 2.3 Hz), 37.4, 38.6, 58.9, 69.0, 71.6, 73.2 (d, J = 32.4 Hz), 80.3 (d, J = 21.0 Hz), 93.6, 121.4 (d, J = 261.7 Hz), 123.2 (d, J = 4.2 Hz), 124.7, 125.4, 126.3, 128.1, 128.8, 129.4, 131.4, 132.9, 133.4; ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −112.7; *anti*-isomer: δ = −130.0 (d, J = 23.7 Hz); IR (neat) 3497, 3053, 2963, 2874, 1597, 1512, 1456, 1396, 1294, 1234, 1199, 1174, 1045, 925, 912, 854, 798, 777, 738 cm^{-1}; MS *m/z* (rel intensity) 472 (M^++2; 0.4), 470 (M^+; 0.4), 351 (0.3), 250 (13), 245 (15), 225 (2), 199 (1), 183 (3), 171 (12), 156 (8), 128 (6), 115 (10), 89 (100), 71 (16). HRMS Found: *m/z* 470.1469. Calcd for $C_{23}H_{32}BrFO_4$: M, 470.1468.

2-Bromo-2-fluoro-1-(2-methoxyethoxy)methoxy-1-phenyl-3-propyl-3-hexanol (22ft): 58% yield as a mixture of diastereomers, a pale yellow oil, R_f 0.15 (hexane–diethyl ether = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) *syn*-isomer: δ = 0.87—1.02 (m, 6H), 1.42—1.78 (m, 4H), 1.80—1.97 (m, 4H), 3.34 (s, 3H), 3.38—3.68 (m, 4H), 3.77—3.96 (m, 1H), 4.52 (d, J = 7.0 Hz, 1H), 4.69 (d, J = 7.0 Hz, 1H), 5.26 (s, 1H), 7.34—7.54 (m, 5H); *anti*-isomer: δ = 3.35 (s, 3H), 4.69 (d, J = 7.0 Hz, 1H), 4.81 (dd, J = 1.9, 7.0 Hz, 1H), 5.29 (d, J = 23.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) one isomer: δ = 14.9 (d, J = 0.77 Hz), 14.6 (d, J = 0.76 Hz), 16.7 (d, J = 2.6 Hz), 17.2 (d, J = 2.6 Hz), 37.5, 38.2, 59.1, 68.9, 71.7, 79.5 (d, J = 31.5 Hz), 79.9 (d, J = 21.4 Hz), 93.7, 120.2 (d, J = 261.7 Hz), 128.0, 129.1, 130.7 (d, J = 1.3 Hz), 135.2; the other isomer: δ = 15.06, 15.09, 17.3, 17.7 (d, J = 3.1 Hz), 59.1, 69.2, 71.8, 80.5 (d, J = 19.1 Hz), 82.7 (d, J = 20.6 Hz), 93.9, 127.8, 129.0, 129.7 (d, J = 1.9 Hz), 135.0 (d, J = 1.5 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −113.9 (s); *anti*-isomer: δ = −127.5 (d, J = 23.7 Hz); IR (neat) 3500, 2963, 2874, 1506, 1456, 1400, 1300, 1242, 1201, 1172, 1113, 1070, 1024, 850, 736, 702 cm^{-1}; MS *m/z* (rel intensity) 423 (M^++2; 0.5), 421 (M^+; 0.6), 342 (0.6), 307 (1), 305 (0.8), 200 (16), 195 (6), 164 (3), 105 (7), 89 (100). HRMS Found: *m/z* 421.1375. Calcd for $C_{19}H_{31}BrFO_4$: M, 421.1390.

4-Bromo-4-fluoro-3-(2-methoxyethoxy)methoxy-1-phenyl-5-propyl-5-octanol (22gt): 62% yield as a mixture of diastereomers, a pale yellow oil, R_f 0.14 (hexane–diethyl ether = 4 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) *syn*-isomer: δ = 0.84—0.97 (m, 6H), 1.21—1.46 (m, 4H), 1.59—1.87 (m, 4H), 2.11—2.40 (m, 1H), 2.73—2.83 (m, 3H), 2.87 (s, 1H), 3.38 (s, 3H), 3.53—3.58 (m, 2H), 3.74—3.79 (m, 2H), 4.02—4.09 (m, 1H), 4.86 (d, J = 6.9 Hz, 1H), 4.90 (d, J = 8.2 Hz, 1H), 7.19—7.34 (m, 5H); *anti*-isomer: δ = 0.73 (t, J = 6.8 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H), 3.40 (s, 3H), 4.91 (s, 2H); ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −112.3 (s); *anti*-isomer: δ = −107.1 (d, J = 6.8 Hz); IR (neat) 3460, 3026, 2963, 2874, 2249, 1948, 1603, 1496, 1456, 1363, 1294, 1199, 1157, 1033, 910, 860 cm^{-1}; MS *m/z* (rel intensity) 450 (M^++2; 0.1), 448 (M^+; 0.1), 275 (8), 223 (1), 210 (5), 208 (5), 147 (39), 115 (45), 91 (79), 89 (100). HRMS Found: *m/z* 448.1610. Calcd for $C_{21}H_{34}BrFO_4$: M, 448.1624.

2-Bromo-1-cyclohexyl-2-fluoro-1-(2-methoxyethoxy)methoxy-3-propyl-3-hexanol (22ht): 51% yield as a mixture of

diastereomers, a colorless oil, R_f 0.20 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.89—0.98 (m, 6H), 1.10—1.48 (m, 10H), 1.60—1.89 (m, 8H), 2.03—2.89 (m, 2H), 3.08 (s, 1H), 3.38 (s, 3H), 3.39—3.67 (m, 2H), 3.70—3.86 (m, 3H), 4.86 (d, J = 6.4 Hz, 1H), 4.90 (dd, J = 1.4, 6.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.8 (d, J = 0.76 Hz), 15.0 (d, J = 0.76 Hz), 16.7 (d, J = 3.1 Hz), 17.5 (d, J = 3.4 Hz), 26.5, 26.6, 26.9, 29.0 (d, J = 1.2 Hz), 33.9 (d, J = 3.1 Hz), 37.3, 38.4, 41.4 (d, J = 1.5 Hz), 59.1, 68.7, 71.8, 79.6 (d, J = 22.1 Hz), 84.7 (d, J = 27.5 Hz), 97.5, 123.5 (d, J = 266.6 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −113.7 (s); *anti*-isomer: δ = −110.9 (d, J = 16.9 Hz); IR (neat) 3235, 2961, 2928, 1450, 1379, 1346, 1296, 1242, 1170, 1120, 1026, 981, 855, 750 cm^{-1}; MS *m/z* (rel intensity) 428 (M^++2; 0.04), 426 (M^+; 0.04), 208 (11), 185 (2), 146 (4), 127 (29), 115 (100). HRMS Found: *m/z* 426.1775. Calcd for $C_{19}H_{36}BrFO_4$: M, 426.1781.

5-Bromo-5-fluoro-6-(2-methoxyethoxy)methoxy-7-methyl-3-propyl-4-octanol (22it): 46% yield as a mixture of diastereomers, a colorless oil, R_f 0.24 (hexane–ethyl acetate = 4 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.93 (t, J = 7.1 Hz, 6H), 1.08 (dt, J = 1.4, 7.0 Hz, 6H), 1.26—1.49 (m, 4H), 1.66—1.93 (m, 4H), 2.27—2.43 (m, 1H), 3.03 (s, 1H), 3.38 (s, 3H), 3.52—3.58 (m, 2H), 3.69—3.88 (m, 3H), 4.85 (d, J = 6.7 Hz, 1H), 4.92 (dd, J = 1.2, 6.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.8 (d, J = 0.76 Hz), 15.0 (d, J = 1.1 Hz), 16.8 (d, J = 3.1 Hz), 17.5 (d, J = 3.4 Hz), 18.5 (d, J = 1.5 Hz), 22.9 (d, J = 3.4 Hz), 31.2 (d, J = 1.9 Hz), 37.3, 38.5 (d, J = 0.77 Hz), 59.1, 68.7, 71.8, 79.6 (d, J = 22.5 Hz), 85.0 (d, J = 27.1 Hz), 97.6, 123.7 (d, J = 267.0 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −113.4 (s); *anti*-isomer: δ = −110.6 (d, J = 17.0 Hz); IR (neat) 3240, 2963, 2934, 2876, 1468, 1367, 1294, 1242, 1199, 1174, 1130, 1041, 987, 864, 746 cm^{-1}; MS *m/z* (rel intensity) 388 (M^++2; 0.1), 386 (M^+; 0.1), 281 (0.2), 267 (1), 210 (4), 208 (4), 115 (28), 89 (100). HRMS Found: *m/z* 386.1453. Calcd for $C_{16}H_{32}BrFO_4$: M, 386.1468.

5-Bromo-5-fluoro-2,2-dimethyl-4-(1-naphthyl)-6,6-dipropyl-1,3-dioxane (24a): 76% yield as a mixture of diastereomers, a pale yellow oil, R_f 0.72 (hexane–ethyl acetate = 1 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) *syn*-isomer: δ = 0.87—1.43 (m, 6H), 1.54—1.67 (m, 6H), 1.54—2.29 (m, 8H), 6.04 (s, 1H), 7.42—7.60 (m, 3H), 7.85—7.98 (m, 4H); *anti*-isomer: δ = 6.20 (d, J = 23.8 Hz, 1H); ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −117.5 (s); *anti*-isomer: δ = −128.1 (d, J = 23.7 Hz); IR (neat) 3053, 2960, 2874, 2733, 1944, 1724, 1626, 1599, 1512, 1468, 1398, 1360, 1288, 1200, 1090, 1020, 985, 900, 773, 731 cm^{-1}; MS *m/z* (rel intensity) 424 (M^++2; 1.0), 422 (M^+; 1.6), 173 (3), 171 (11), 156 (100), 127 (10), 111 (2), 79 (13), 71 (56). HRMS Found: *m/z* 422.1248. Calcd for $C_{22}H_{28}BrFO_2$: M, 422.1257.

1-Bromo-1-fluoro-2-(2-methoxyethoxy)methoxy-2-(1-naphthyl)-1-trimethylsilylethane (25a): 89% yield as a mixture of diastereomers, a pale yellow oil, R_f 0.57 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) *syn*-isomer: δ = 0.10 (s, 9H), 3.29 (s, 3H), 3.30—3.60 (m, 4H), 4.64 (d, J = 6.9 Hz, 1H), 4.84 (d, J = 6.9 Hz, 1H), 7.45—7.96 (m, 7H); *anti*-isomer: δ = 0.27 (s, 9H), 3.27 (s, 3H), 4.56 (d, J = 6.6 Hz, 1H), 4.75 (d, J = 6.6 Hz, 1H); ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −141.1; *anti*-isomer: δ = −141.7; IR (neat) 3051, 2955, 2891, 2818, 1950, 1597, 1512, 1452, 1410, 1396, 1365, 1252, 1199, 1174, 1110, 1030, 927, 887, 847, 775, 702 cm^{-1}; MS *m/z* (rel intensity) 430 (M^++2; 1), 428 (M^+; 1), 245 (6), 244 (12), 209 (11), 170 (6), 165 (9), 153 (13), 152 (94), 140 (2), 127 (1). HRMS Found: *m/z* 428.0813. Calcd for $C_{19}H_{26}BrFO_3Si$: M, 428.0819.

1,1-Dibromo-1-fluoro-3-phenyl-2-butanol (27): 69% yield as a mixture of diastereomers, a pale yellow oil, R_f 0.44 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) *syn*-isomer: δ = 1.43 (dd, J = 1.2, 7.0 Hz, 3H), 2.73 (d, J = 5.8 Hz, 1H), 3.47 (dq, J = 4.3, 7.0 Hz, 1H), 4.14 (ddd, J = 4.3, 5.9, 12.2 Hz, 1H), 7.22—7.32 (m, 5H); *anti*-isomer: δ = 4.03 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) *syn*-isomer: δ = 16.2 (d, J = 2.3 Hz), 41.6, 84.6 (d, J = 19.1 Hz), 104.0 (d, J = 329.6 Hz), 127.0, 127.8, 128.8, 144.2 (d, J = 1.2 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) *syn*-isomer: δ = −58.7; *anti*-isomer: δ = −57.2; IR (neat) 3464, 3086, 3063, 3028, 2984, 2937, 1603, 1495, 1454, 1385, 1325, 1271, 1234, 1122, 1084, 1024, 1005, 991, 939, 850, 789, 765, 700 cm^{-1}; MS *m/z* (rel intensity) 328 (M^++4; 4), 326 (M^++2; 7), 324 (M^+; 4), 246 (5), 244 (5), 166 (14), 135 (27), 117 (22), 105 (100), 78 (89). Found: C, 36.66; H, 3.37%. Calcd for $C_{10}H_{11}Br_2FO$: C, 36.84; H, 3.40 %.

5-Bromo-5-fluoro-6-(2-methoxyethoxy)methoxy-7-phenyl-4-propyl-4-octanol (28): 35% yield, a pale yellow oil, R_f 0.21 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.83—0.96 (m, 6H), 1.17—1.39 (m, 4H), 1.44 (d, J = 7.2 Hz, 3H), 1.61—1.86 (m, 4H), 3.08 (s, 1H), 3.35 (s, 3H), 3.46—3.84 (m, 5H), 4.30 (dd, J = 3.2, 4.6 Hz, 1H), 4.72 (d, J = 6.5 Hz, 1H), 4.87 (dd, J = 1.6, 6.5 Hz, 1H), 7.16—7.35 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.8, 14.9, 16.7 (d, J = 3.1 Hz), 17.0, 17.4 (d, J = 3.8 Hz), 37.7, 38.4, 42.3 (d, J = 2.7 Hz), 59.1, 68.8, 71.8, 79.7 (d, J = 22.5 Hz), 84.4 (d, J = 26.7 Hz), 97.6, 124.1 (d, J = 267.3 Hz), 126.5, 127.7 (d, J = 1.5 Hz), 128.7, 145.9; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −110.7; IR (neat) 3450, 2963, 2931, 2876, 1603, 1495, 1454, 1379, 1294, 1242, 1199, 1039, 1026, 912, 856, 762, 733, 702 cm^{-1}. Found: C, 56.17; H, 7.72%. Calcd for $C_{21}H_{34}BrFO_4$: C, 56.23; H, 7.65%.

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30) The stereochemistry of **27** was assigned by comparison of the ^{1}H NMR chemical shift with 1,1,1-trichloro-3-phenyl-2-butanol: M. Fujita, M. Obayashi, and T. Hiyama, *Tetrahedron*, **44**, 4135 (1988). ^{1}H NMR ($CDCl_3$) $\delta = 4.14$ (ddd, $J = 4.3$, 5.9, 12.2 Hz, 1H) for *syn*-**27** (lit, 4.23 (dd, $J = 2.5$, 7.0 Hz), 4.03 (m, 1H) for *anti*-**27** (lit, 4.10 (brs, 1H).