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Preparation and Regioselective S_N2' Reaction of Novel *gem*-Difluorinated Vinyloxiranes with RLi

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A series of hitherto unknown 3,4-epoxy-1,1-difluorobutenes were prepared from the readily accessible α,β-epoxy ketones and these compounds were found to undergo regioselective S_N2' reactions with hard RLi nucleophiles occurring at the highly positively charged terminal fluorine-possessing sp^2 carbon atom in quite sharp contrast to the cases of the corresponding nonfluorinated vinyloxiranes which only attained a low level of regioselectivity. Addition of HMPA substantially improved the products' olefinic stereoselectivity. Theoretical calculations were used to qualitatively explore the nature of selectivity in these reactions.

Introduction

Introduction of fluorine into organic compounds sometimes brings about a quite significant change toward their chemical and physical properties due to the unique effect of this atom,[1] which is why fluorine-containing compounds have drawn profound interest in fine chemical and pharmaceutical fields. Despite such characteristics, utilization of fluorinated organic materials is not always easy because they are rare in nature[2] and such remarkable changes in properties enormously affect their reactivity, which does not often allow application of various synthetic methods developed for nonfluorinated prototypes. For instance, fluorinated carbon atoms in *gem*-difluorinated olefins have appeared to possess extraordinarily high electrophilicity due to the strong electronic repulsion between lone pairs around fluorine atoms and π-electrons while the corresponding nonfluorinated counterparts usually show nucleophilicity.[3] Therefore, independent synthetic pathways should be developed, and accordingly, various methods as well as building units with fluorine have been synthesized and reported thus far.[1b,4]

Recently, we have established the preparation of compounds **1**,[5] the terminally fluorine-substituted analogues of vinyloxiranes, from easily obtained α,β-epoxy ketones by way of the difluoro Wittig reaction,[4b,6] which, as far as we know, have not been reported thus far except for perfluorinated 3,4-epoxybutene (Chart 1).[7] Moreover, considering the synthetic utility of vinyloxiranes as intermediates[8] for a wide variety of molecules, compounds **1** are regarded as highly potent and versatile building blocks possessing a $CF_2{=}C$ moiety, which, by reaction with appropriate nucleophiles, could be readily converted to the sp^3-hybridized CF_2 groups known to be isosteric and isopolar to an oxygen atom[9] especially in

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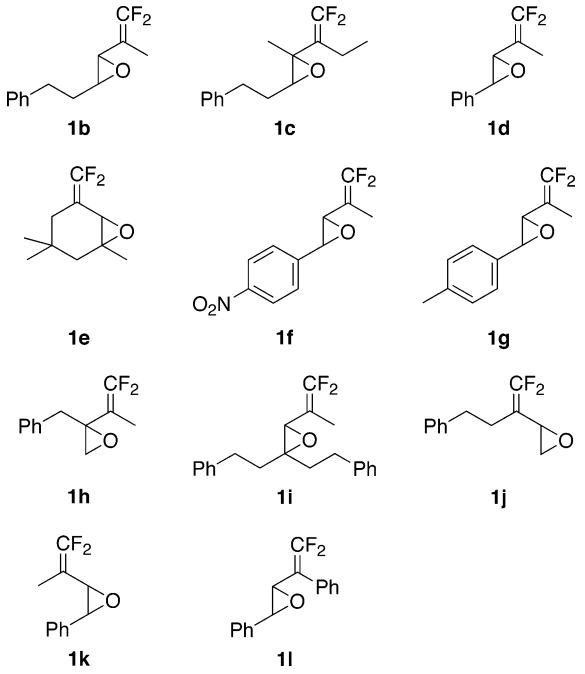
CHART 1. *gem*-Difluorinated Vinyloxiranes Prepared in the Present Work



the field of medicinal chemistry and thus utilized as enzyme inhibitors.[4f,10] On the basis of the ab initio calculation[11] of **1a** and the corresponding nonfluorinated counterpart **2a** (Figure 1), introduction of fluorine atoms has unambiguously demonstrated that the charge on the fluorine-possessing carbon atom was unusually altered from −0.425 to +0.805 (NBO (natural bond orbital) charges). This result led to the expectation that hard nucleophiles such as RLi would realize the smooth addition to **1** at this specific site in a highly regioselective manner. This was actually the case, and we have already reported in the previous communication[5] that the regioselective S_N2' reactions of RLi toward **1** in THF afforded a wide range of difluorinated allylic alcohols, while the nonfluorinated species was known to attain only a low level of regioselectivity to yield a mixture of products.[12] In this article, we would like to describe the full details of the preparation of hitherto not synthesized *gem*-difluorinated vinyloxiranes and their reactions with RLi which will be discussed from the standpoint of semiempirical or ab initio computation.

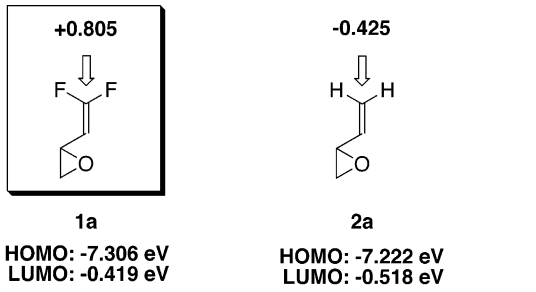


FIGURE 1. Ab initio calculation of *gem*-difluorinated vinyloxirane **1a** and its prototype **2a**.

Results and Discussion

Taking relatively high reactivity of a terminally difluorinated olefin part reported into account, difluoromethylenation was planned to be carried out at the last step of the preparation of **1**, which led to the formation of various types of starting materials **1** from a wide variety of α,β-epoxy ketones easily obtained by many protocols including their enantioselective pathways. For the clarification of the scope and limitation of **1** as building blocks, α,β-epoxy ketones **3b**−**i** were prepared from the corresponding ketones basically by such a routine method as NaOH-mediated H_2O_2 epoxidation, while **3j** and **3k** were obtained from epoxy alcohols by way of oxidation with Jones reagent and pyridinium dichromate (PDC), respectively, and *trans*-2,3-epoxy-1,3-diphenyl-1-propanone **3*l*** was purchased from a commercial supplier. At the final stage, their carbonyl moieties were difluoromethylenated with CF_2Br_2-hexamethylphosphorus triamide (HMPT)[4b,6] in the presence of MS 4A due to moisture sensitivity of the reaction intermediates.[13] All epoxy ketones **3b**−***l*** were smoothly converted into the corresponding *gem*-difluoro vinyloxiranes **1b**−***l*** in excellent yields (Table 1), and a slightly decreased yield of **1e** might stem from its inherent volatility.

On standing at ambient temperature after chromatographic purification, **1b** was found to be partially decomposed within a few days and, from the residual mixture, acid fluoride **4b** and CF_3-containing allylic alcohol **5b** were isolated as the sole isomeric product in both cases whose stereochemistry was not clarified yet (Scheme 1). **1b** probably reacted with air moisture in an S_N2' fashion under concentrated conditions and the subsequent HF elimination[14] produced **4b**, and moreover, HF thus generated was added to **1b** to form **5b**. Because of this inherent

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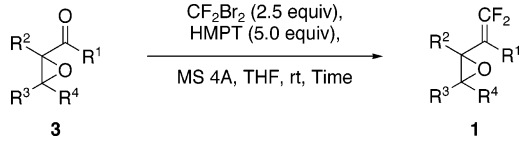
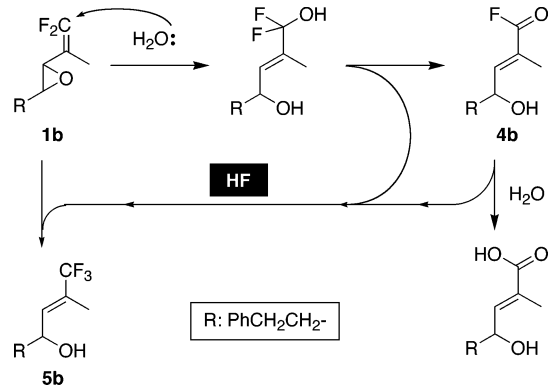
TABLE 1. Preparation of *gem*-difluorinated Vinyloxiranes 1[a]



entry	product	time (h)	yield of **1** (%)
1	**1b**	1	94
2	**1c**	6	(85)
3	**1d**	1	88
4	**1e**	1	75 (>99)
5	**1f**	1	94
6	**1g**	1	>99
7	**1h**	2	93
8	**1i**	2	96
9	**1j**	1	99
10	**1k**	1	91
11	**1*l***	1	97

[a] Yields in parentheses were determined by ^{19}F NMR.

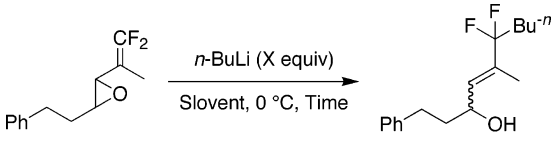
SCHEME 1



instability, compounds **1** are highly recommended to be kept as a hexane solution under an argon atmosphere in a refrigerator for a couple of days, except for **1h** and **1i** which are stable enough even at ambient temperature.

1b was selected as the representative substrate for finding out suitable reaction conditions with *n*-BuLi. At first, an excess amount of *n*-BuLi (5 equiv) was employed for treatment of **1b** in several solvents at 0 °C. In hexanes, the anticipated S_N2' product **6b** was obtained only in 38% yield as an inseparable *E*/*Z* mixture along with 23% recovery of the starting material **1b**, which did not compete at all with the possible S_N2 type direct epoxide opening pathway (Table 2, entry 1). Acceleration of this process and increase of the chemical yields were observed for such ethereal solvents as Et_2O, THF, and 1,4-dioxane. The reaction in 1,4-dioxane recorded the best yield among solvents employed, but this solvent brought about no olefinic stereoselectivity and rate retardation (entry 4). THF and Et_2O gave comparable yields, but the former attained the better product *E*/*Z* ratio (entries 2 and 3), which was improved by lowering the temperature but with longer reaction time necessary for completion (entry 5). Then, we fixed THF as a solvent, and tried to decrease the amount of *n*-BuLi (entries 6∼8). Usage of 2 equiv was eventually found to be effective for suppression of unfavorable defluorination with an increase in the chemical yields at the same *E*/*Z* ratio, but 1 equiv of *n*-BuLi led to the partial recovery of **1b**. This defluorination is considered to be the major reason we could not obtain good material balance in all experiments examined.

TABLE 2. Solvent Effect for the S_N2' Reaction of 1b with *n*-BuLi



entry	*X* (equiv)	solvent	time (h)	yield[a] (%)	*E*/*Z* ratio[a]	recovery[a] (%)
1	5.0	*n*-hexane	24	38	66/34	23
2	5.0	Et_2O	2	52	60/40	1
3	5.0	THF	2	52	72/28	0
4	5.0	1,4-dioxane	24	66	53/47	15
5[b]	5.0	THF	24	42	81/19	10
6	3.0	THF	2	59	73/27	0
7	2.0	THF	2	63	73/27	0
8	1.0	THF	2	36	74/26	41

[a] Determined by ^{19}F NMR. [b] The reaction was conducted at −78 °C.

It is well-known that reactivities of RLi and selectivities of the products change in the presence of hexamethylphosphoric triamide (HMPA) possessing the strongly chelating ability to metals.[15,16] In our instance, the *E*/*Z* ratio of the product was proved to be dramatically improved to 95/5 by the addition of an excess amount of HMPA (Table 3, entry 5). Further study clarified that only 0.5 equiv of HMPA was suffice to achieve the same level of *E*/*Z* ratio, while still 2.0 equiv of RLi was required for complete consumption of **1b** (entries 2−5). When the reaction was conducted at −78 °C, the stereoisomeric ratio was further increased (entries 3 and 9) with thorough consumption of **1b**, which was in quite sharp contrast to the fact that only low conversion was realized in the absence of HMPA (see Table 2, entry 5). Addition of *n*-BuLi to a mixed solution of **1b** and HMPA turned out to be the method of choice, one reason being that HMPA itself can react with RLi.[17] Next, we checked the effect of additives. Safe substitutes for HMPA like tetramethylethylenediamine (TMEDA), 12-crown-4, 1,3-dimethyl-2-imidazolidinone (DMI), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) attained only slight to moderate improvement on the chemical yields as well as the *E*/*Z* ratio of the products (entries 6−10).[18]

Since the difluoro Wittig reagent from CF_2Br_2 and HMPT furnishes HMPA as a byproduct, we tried to make

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(16) 300 times stronger interaction with Li was observed for HMPA than THF. See: Reich, H. J.; Kulicke, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 273.

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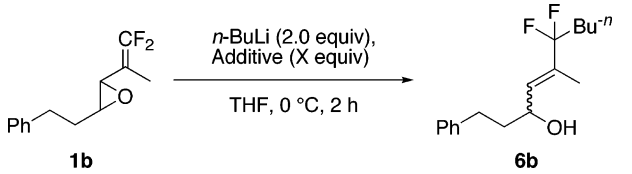
TABLE 3. Effect of HMPA toward the Stereoselectivity of the Products



1b **6b**

entry	additive	*X* (equiv)	yield[a] (%)	*E*/*Z* ratio[a]	recovery (%)
1	HMPA	0	63	73/27	0
2		0.5	76	95/5	0
3[b]		0.5	78	>99/<1	0
4		1.0	66	95/5	0
5		2.0	62	95/5	0
6	TMEDA	0.5	62	74/26	0
7	12-crown-4	0.5	52	76/24	14
8	DMI	0.5	66	80/20	11
9[b]		0.5	49	90/10	44
10	DMPU	0.5	44	81/19	28

[a] Determined by ^{19}F NMR. [b] The reaction was conducted at −78 °C.

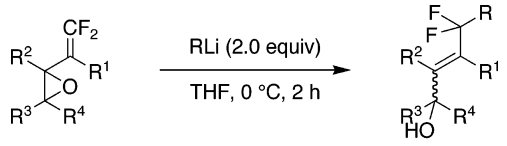
use of it and found out that, by application of the standard amount of *n*-BuLi (2.0 equiv) at 0 °C, the reaction mixture of **1b** without any further purification afforded the desired S_N2' product in good yield (51%) with the *E*/*Z* selectivity (86/14) between the cases with (95/5, entry 2) and without HMPA (73/27, entry 1).

These results in hand, various kinds of RLi were subjected to the above conditions in the presence or absence of HMPA (Table 4). Without HMPA, almost all RLi exclusively afforded the regioselective S_N2' products with moderate to excellent *E* preference, and bulkier organolithium reagents seemed to provide higher olefinic *E* selectivity. On the other hand, addition of 0.5 equiv of HMPA usually attained the excellent product *E* stereoselection and better chemical yields with the exception that 5.0 equiv was required for the apparent change in the case of MeLi (entry 1). When the well-known formyl anion equivalent 1,3-dithiane was used, the HF-eliminated product **7** was obtained possibly by way of the initial formation of the S_N2' product (Scheme 2). On the other hand, **1b** was recovered by treatment with the enolates derived from *N*,*N*-dimethylacetamide and acetophenone as well as the carbanions from phenylacetylene and 1-octyne which gave the important information that an appropriately higher pK_a value was requisite for nucleophilic reagents to smoothly construct new carbon−carbon bonds.

Entry 7 described 36% recovery of **1c** when reacted with MeLi, while still 26% of **1c** remained intact even with the double amount (4 equiv) of MeLi along with the formation of 72% of **6ca** observed by ^{19}F NMR. This trisubstituted material afforded the S_N2' products in moderate yields (entries 7−10) along with the formation

(18) It is reported that the product regioselectivity by the reaction between RLi and vinyloxiranes was affected by Lewis acidic additives, but in our case, only sluggish results were obtained, possibly due to the ready decomposition of **1b** under such circumstance even in the absence of RLi. See: (a) Alexakis, A.; Vrancken, E.; Mangeney, P.; Chemla, F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3352. (b) Alexakis, A.; Vrancken, E.; Mangeney, P. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3354. (c) Mukerji, I.; Wayda, A.; Dabbagh, G.; Bertz, S. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 760.

TABLE 4. Reaction of *1* with Various RLi[a]

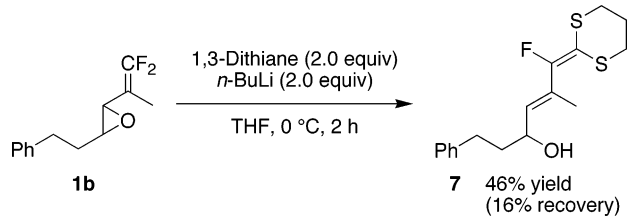


1 **6**

entry	**1**	R	yield[b] (%)	*E*/*Z* ratio[c]	recovery[c] (%)
1	**1b**	Me	84 (67):[d] **6ba**	60/40 (93/7)[d]	0 (0)
2		*n*-Bu	51 (65): **6bb**	73/27 (>99/<1)	0 (0)
3		*sec*-Bu	33:[e] **6bc**	87/13[f]	0
4		*t*-Bu	52 (68): **6bd**	94/6 (>99/<1)	0 (0)
5		Ph	58 (60): **6be**	73/27 (98/2)	0 (0)
6		furyl-	19: **6bf**	>99/<1	35
7	**1c**	Me	52: **6ca**	63/37	36
8		*n*-Bu	31 (27): **6cb**	95/5 (65/35)	0 (17)
9		*t*-Bu	16: **6cd**	>99/<1	9
10		Ph	31: **6ce**	86/14	0
11	**1d**	Me	69: **6da**	63/37	0
12		*n*-Bu	52 (62): **6db**	83/17 (>99/<1)	0 (0)
13		*t*-Bu	49: **6dd**	97/3	0
14		Ph	50: **6de**	77/23	0
15	**1e**	Me	65: **6ea**		0
16		*n*-Bu	63 (70): **6eb**		0 (0)
17		*t*-Bu	69: **6ed**		0
18		Ph	81: **6ee**		0
19	**1f**	*n*-Bu			20 (7)
20	**1g**	*n*-Bu	54 (61): **6gb**	78/22 (>99/<1)	0 (0)
21	**1h**	*n*-Bu			9 (19)
22	**1i**	*n*-Bu	4[c] (12):[c] **6ib**	>99/<1 (>99/<1)	80 (42)
23	**1j**	*n*-Bu	45 (64): **6jb**	67/33 (97/3)	0 (0)
24	**1k**	Ph	16:[c] **6de**	99/1	8
25	**1*l***	*n*-Bu	79 (51): **6lb**	64/36 (83/17)	0 (0)

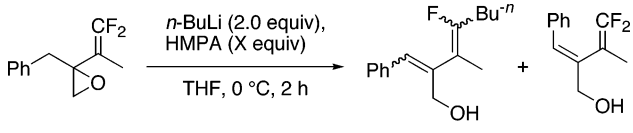
[a] In the parentheses are shown the results in the presence of HMPA (0.5 equiv) at −78 °C. [b] Isolated yield. [c] Determined by ^{19}F NMR of a crude reaction mixture. [d] The reaction was carried out with 5 equiv of HMPA at 0 °C. [e] Diastereomeric ratio of 52/48. [f] Combined *E*/*Z* ratio.

SCHEME 2



1b **7** 46% yield (16% recovery)

SCHEME 3



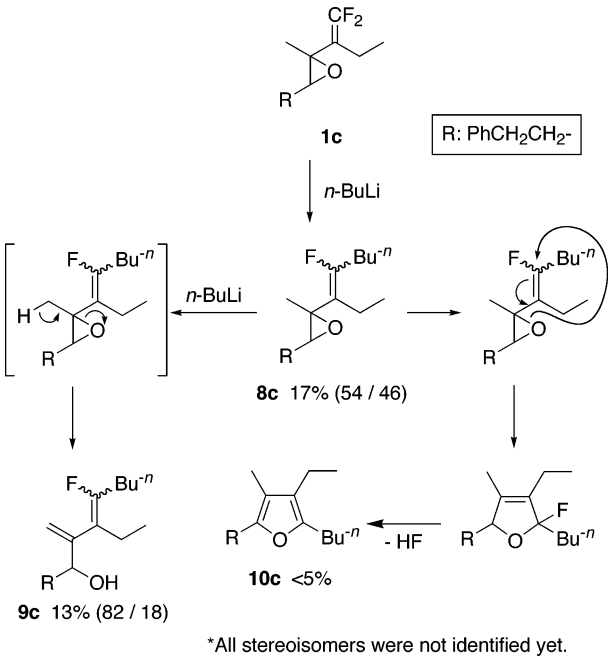
1h **9h** **11h**

X (equiv)	**9h**#	**11h**
0	35% (74 / 26)	20%
0.5	48% (65 / 35)	16%

In the parenthesis was shown the stereoisomeric ratio which was not determined yet.

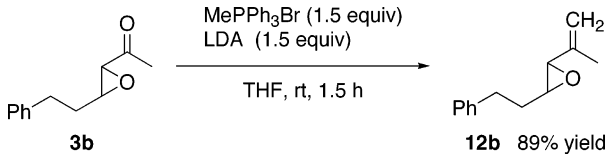
of the oxirane-opened diene **9c** and the tetrasubstituted furan **10c** by way of 5-*endo*-*trig* cyclization as the side products (Scheme 3). Usually the 5-*endo*-*trig* mode is disfavored on the basis of Baldwin's rule;[19] however, some exceptional examples have been reported[20] for *gem*-

SCHEME 4



difluorinated olefins presumably because, as was already shown in Figure 1, the highly polarized sp^2 carbon would facilitate the reaction.[21] A similar type of compounds **9h** and **11h** (the stereochemistry of the latter was determined from the NOESY peak correlation between vinyl H and allylic CH_2 moieties but the former has not been assigned yet) were also isolated when **1h** was used as a substrate. They were formed by the proton abstraction from the benzylic position, followed by the oxirane ring-opening sequence with and without the addition−elimination procedure of *n*-BuLi, respectively (Scheme 4). Poor conversion was recorded for the different type of trisubstituted substrate **1i** (entry 22). Stereoisomeric **1d** and **1k** exhibited remarkable a difference on the product preference (entries 14 and 24): **1d** with the *E* oxirane structure underwent the selective S_N2' reaction showing the apparent effect of HMPA, while only sluggish results were obtained from the latter *Z* isomer and the desired products were formed and isolated only in the case of PhLi. Investigation of **1f** and **1g** containing electron-withdrawing and -donating moieties, respectively, showed their sharp contrast in reactivity and only the latter gave satisfactory results (entries 19 and 20). Cyclic **1e**, mono-substituted epoxide **1j**, and **1*l*** followed the desired regioselective S_N2' process and the effect of HMPA was similarly noticed (entries 15−18, 23, and 25), while improvement of the *E*/*Z* ratio with a decrease of the product yield was observed by the addition of HMPA to **1*l***.

SCHEME 5



Olefinic stereochemistry of the products was determined by NOE experiments of **6bd** and **6de** as the representative examples. In the former case, the peak correlation was observed between vinylic hydrogen (R^2) and *t*-Bu (R) as well as allylic hydrogen (R^4) and Me (R^1), and between Me (R^1) and allylic hydrogen (R^4) or vinylic hydrogen (R^2) for the latter major or minor isomers, respectively. These facts unambiguously indicated the *E* stereochemistry at the newly formed carbon−carbon double bonds for the major isomers.

For the clarification of the inherent high reactivity of the difluorinated materials **1**, the corresponding non-fluorinated prototype **12b** was prepared and treated with MeLi and *n*-BuLi under similar conditions (Scheme 5), but 88% of **12b** was recovered by the action of MeLi in the absence of HMPA. On the other hand, although addition of HMPA led to total disappearance of **12b**, unidentified products were obtained presumably as a result of MeLi working as a base to abstract allylic hydrogen; this assumption was based on the fact that this Me peak was not observed by ^1H NMR spectroscopy. If such a reaction really occurred, the *E*/*Z* ratios of difluorinated **6** might be determined not at the ring-opening S_N2' step but by the protonation of the above type of allylic anion generated by an excess amount of alkyllithiums. The fact that **6bb** was completely recovered without any change of its original olefinic stereochemical proportion in the presence of *n*-BuLi and HMPA led to the conclusion that the product *E*/*Z* ratio was kinetically determined at the stage of the epoxide-ring opening. As shown above, we have unambiguously clarified the significant effect of two fluorine atoms at the terminal carbon of **1** toward the regioselective reactions with a wide range of RLi.

On the basis of the previous literature on nonfluorinated vinyloxiranes,[22] it has been suggested that *E* and *Z* isomers might be afforded from *s-trans* and *s-cis* conformers of **1**, respectively. On the other hand, Table 4 demonstrated a tendency that *E* preference of the products was dependent on the employed RLi and increased in the order of MeLi < PhLi < *n*-BuLi < *sec*-BuLi < *t*-BuLi, which was totally opposite to the order of their inherent aggregation state in the same solvent employed here.[23] Thus, the lower aggregation state of RLi was considered to be responsible for the production of *E* isomers with higher selectivity and this might be one of the reasons why a larger amount of HMPA was required when MeLi was employed because this species is known to constitute a tetrameric form in THF, the highest aggregation state of all RLi tested in this study.

(19) (a) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734. (b) Baldwin, J. E.; Cutting, J.; Dupont, W.; Kruse, L.; Silberman, L.; Thomas, R. C. *J. Chem. Soc., Chem. Commun.* **1976**, 736.

(20) (a) Ichikawa, J.; Wada, Y.; Fujiwara, M.; Sakoda, K. *Synthesis* **2002**, 1917. (b) Ichikawa, J.; Fujiwara, M.; Wada, Y.; Okauchi, T.; Minami, T. *Chem. Commun.* **2000**, 1887. (c) Coe, P. L.; Burdon, J.; Haslock, I. B. *J. Fluorine Chem.* **2000**, *102*, 43. (d) Wang, Z.-G.; Hammond, G. B. *J. Org. Chem.* **2000**, *65*, 6547. (e) Volle, J.-N.; Schlosser, M. *Eur. J. Org. Chem.* **2000**, 823. (f) Ichikawa, J.; Wada, Y.; Okauchi, T.; Minami, T. *Chem. Commun.* **1997**, 1537.

(21) Yamazaki, T.; Hiraoka, S.; Sakamoto, J.; Kitazume, T. *J. Phys. Chem. A* **1999**, *103*, 6820.

(22) (a) Zaidlewich, M.; Uzarewich, A.; Sarnowski, R. *Synthesis* **1979**, 62. (b) Lenox, R. S.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 957.

(23) (a) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (b) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371.

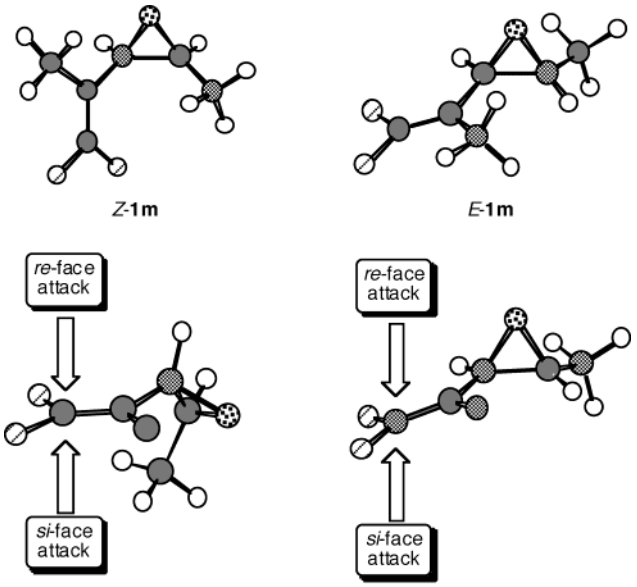


FIGURE 2. The ground-state models of *E* and *Z* isomers.

The above discussion could be summarized that the success of the present reactions would be governed by the steric circumstance around the oxirane ring and then we have calculated the ground state of the more realistic stereoisomeric models *Z*- and *E*-**1m** (Figure 2) rather than **1a**.[11] Although the most stable conformation of the *E*-form was proved to be the *s-trans* type conformation (with the $C-C-C=CF_2$ dihedral angle of 152.5°) similar to **1a**, the perpendicular relationship between epoxy C−C and C=C bonds (−67°) was observed for the *Z* isomer. Our initial assumption was that the RLi attack would occur for the most stable conformation of the *E* isomer from the sterically unbiased *re*-face possibly with formation of chelation with the epoxy oxygen atom. On the other hand, if the corresponding *Z* isomer also followed a similar pattern, the reaction might not proceed readily because the *si*-face attack was encumbered by the proximate methyl moiety, and moreover, the transition state (TS) should increase the steric congestion due to partial pyramidalization when RLi was approached from the opposite *re*-face. Table 4 clearly indicated that this was actually the case for **1h** and **1j**, the acyclic substrates with the *Z*-epoxide structure leading only to sluggish results. Then, we have started the detailed computation for obtaining more explicit information on the present reaction mechanism using the semiempirical computational methods.[24]

We selected the simplest *gem*-difluorinated vinyloxirane **1a** as was already shown in Figure 1 and monomeric MeLi as the representative nucleophile. Me_2O molecules as the smallest ethereal solvent were added to the lithium atom so as to fulfill its tetracoordinated circumstance. The result is summarized in Scheme 6 and

(24) Semiempirical molecular orbital calculation was performed by MOPAC v 6.10 (PM3) implemented in CAChe Worksystem (Fujitsu) for all the conformers obtained by CONFLEX with the threshold value of 25 kcal, followed by their full optimization by the eigenvector following the minimization (EF) method with the extra keyword "PRECISE", final gradient norm being less than 0.01 kcal/Å.

SCHEME 6

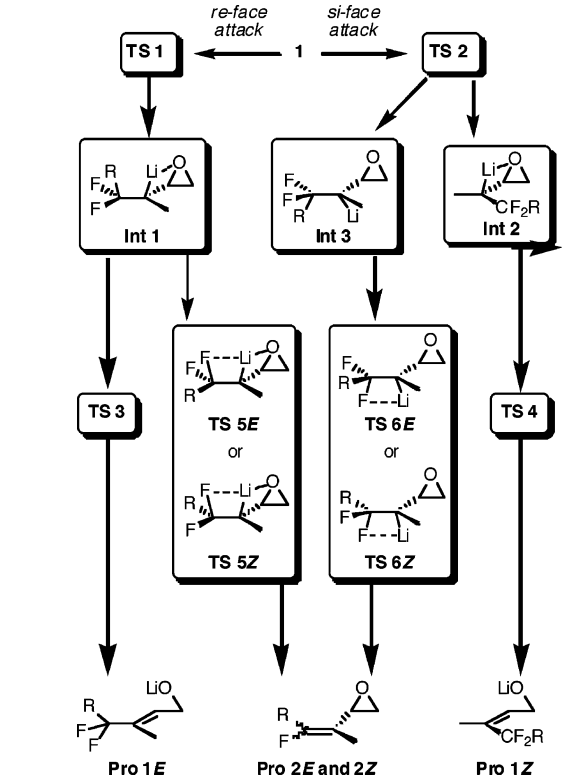


TABLE 5. Relative Energies of the Reactants, Products, and Transition States

species	Δ*G* (kcal/mol)	species	Δ*G* (kcal/mol)
1a	0.00	**1a**	0.00
TS 1	17.12	**TS 2**	27.74
Int 1	−25.43	**Int 2**	−23.02
TS 3	−24.07	**TS 4**	−20.41
Pro 1*E*	−61.89	**Pro 1*Z***	−59.94
TS 5*E*	−7.07	**TS 6*E***	−7.61
TS 5*Z*	−7.49	**TS 6*Z***	−7.93
Pro 2*E*	−52.95	**Pro 2*E***	−52.95
Pro 2*Z*	−52.94	**Pro 2*Z***	−52.94

Table 5. The transition state **TS 1** with the expected *s-trans* structure accepted the MeLi attack from the *re*-face of **1a** with chelation to the epoxy oxygen to produce the intermediary **Int 1**, whose activation energy Δ*G* at 0 °C was calculated to be 17.12 kcal/mol as the rate determining step of the whole process. On the other hand, the corresponding TS leading to the *Z* isomer, **TS 2**, possessed the perpendicular relationship between the olefin and epoxide parts (the dihedral angle $F_2C=C-C-C$: −100.8°) where RLi approached from the opposite *si*-face. The relatively large activation energy difference of 10.6 kcal/mol between **TS 1** and **TS 2** allowed us to qualitatively anticipate exclusive *E* olefin formation and this is totally consistent with the experimental results (Table 4). First intermediates **Int 1** and **2** would then experience either the epoxide opening via **TS 3** and **TS 4** to the final product **Pro 1*E*** and **1*Z***, respectively, or the LiF elimination (**TS 5** and **6**) to the monofluorinated butadiene monooxide, **Pro 2*E*** or **2*Z***. Table 5 points out the ready formation of **Pro 1*E*** and **1*Z*** with a quite low energy barrier of 1−3 kcal/mol rather than the other elimination pathways (15−18 kcal/mol activation energy

was required), which supported **Pro 2*E*** and/or **2*Z*** produced only as minor byproducts. As the size of the R moiety in RLi increases, the higher rotational energy was likely to be required for the formation of the more sterically constrained **Int 2** compared with **Int 1** and **Int 3**, which supported the *E* preference of the stereochemical outcome in the current reaction. Taking these results into account, we estimated the effect of HMPA. As was already pointed out, the *re*-face attack of RLi to the *s-trans* conformer gave rise to intermediate **Int 1** to eventually afford the difluorinated **Pro 1*E***, or **Pro 2*E*** or **2*Z*** with one fluorine atom after RF_2C-C bond rotation.[25] Addition of HMPA promoted the coordination to lithium to lower the Li−C bond strength and develop more anionic character on the lithium-bound carbon atom. **Int 2** was the energetically preferred intermediate over **Int 3** by 12.7 kcal/mol, but HMPA would diminish the effect of the intramolecular chelation to increase the population of **Int 3** from which **Pro 1*E*** was obtained through the epoxy ring opening by the S_N2 type mechanism of the carbanionic species, leading to increase of the **Pro 1*E*** proportion as was actually observed from the experimental results.

Conclusions

In summary, we have successfully established the novel synthetic route to the hitherto unprecedented *gem*-difluorinated vinyloxiranes which would be regarded as highly potential synthetic intermediates for the construction of a wide variety of fluorine-possessing compounds starting from various kinds of α,β-epoxy ketones by way of the difluoro Wittig reaction. Their reactions with RLi enabled the highly regioselective S_N2' type oxirane-opening process due to the extraordinary electrophilic sp^2 carbon atom by the significant p−π electronic repulsive effect of fluorine to furnish difluorinated allylic alcohols with good to excellent *E* stereoselectivity, which was greatly improved by the addition of only 0.5 equiv of HMPA. At present, reactions of these *gem*-difluorinated vinyloxiranes with other nucleophilic species are underway in this laboratory.

Experimental Section

General Procedure for Difluorinated Vinyloxiranes 1. To a flask containing ca. 200 mg of MS 4 Å were added 10 mL of dry THF and dibromodifluoromethane (0.46 mL, 5.0 mmol) at −78 °C under argon. After formation of a white precipitate by further addition of hexamethylphosphorus triamide (1.82 mL, 10.0 mmol), the mixture was allowed to warm to room temperature. Then, a starting epoxy ketone (2.0 mmol) was added with 4 mL of dry THF and the mixture was, after 1 h, filtered under reduced pressure with the aid of *n*-hexane. Saturated sodium hydrogen carbonate was added to the filtrate, the organic layer was extracted with *n*-hexane three times, and the combined organic layer was dried over anhydrous $MgSO_4$. After evaporation of the solvents, purification by short-path Florisil column chromatography (*n*-hexane:AcOEt = 60:1) afforded the desired terminally difluorinated vinyloxirane **1** in excellent yield as shown in Table 1.

(*E*)-3,4-Epoxy-1,1-difluoro-2-methyl-6-phenylhex-1-ene (1b): ^{1}H NMR δ 1.39 (3 H, m), 1.88−1.93 (2 H, m), 2.72−2.86 (2 H, m), 2.98 (1 H, td, *J* = 5.86, 2.45 Hz), 3.34 (1 H, q, *J* = 1.38 Hz), 7.17−7.31 (5 H, m). ^{19}F NMR δ 68.2 (1 F, dd, *J* = 45.8, 7.10 Hz), 74.8 (1 F, dd, *J* = 42.4, 3.05 Hz). ^{13}C NMR δ 6.60 (t, *J* = 1.15 Hz), 32.1, 33.6, 54.0 (dd, *J* = 6.53, 2.52 Hz), 55.4 (t, *J* = 1.72 Hz), 83.3 (dd, *J* = 20.1, 13.7 Hz), 125.9, 128.1, 128.3, 140.1, 154.8 (t, *J* = 287.5 Hz). IR (neat) ν 699, 744, 790, 880, 948, 1058, 1134, 1210, 1257, 1303, 1451, 1496, 1603, 1750, 2366, 2861, 2931, 2997, 3025, 3062, 3585, 3629, 3655, 3751 cm^{-1}.

(*E*)-3,4-Epoxy-2-ethyl-1,1-difluoro-3-methyl-6-phenylhex-1-ene (1c): ^{1}H NMR δ 1.07 (3 H, dd, *J* = 7.57, 7.44 Hz), 1.38 (3 H, s), 1.85−1.96 (2 H, m), 2.02−2.10 (2 H, m), 2.77 (1 H, m), 2.83 (1 H, m), 2.96 (1 H, t, *J* = 6.35 Hz), 7.18−7.32 (5 H, m). ^{19}F NMR δ 67.5 (1 F, d, *J* = 51.4 Hz), 73.3 (1 F, d, *J* = 50.4 Hz). ^{13}C NMR δ 13.5 (dd, *J* = 2.87, 2.58 Hz), 17.9 (dd, *J* = 2.87, 1.43 Hz), 18.0 (d, *J* = 2.30 Hz), 30.5, 32.4, 58.0 (dd, *J* = 6.02, 1.58 Hz), 63.1 (dd, *J* = 2.58, 0.86 Hz), 93.8 (dd, *J* = 18.2, 13.6 Hz), 126.0, 128.2, 128.3, 141.0 153.4 (dd, *J* = 287.4, 287.2 Hz). IR (neat) ν 699, 746, 793, 826, 865, 904, 960, 995, 1066, 1091, 1137, 1237, 1263, 1311, 1380, 1456, 1496, 1604, 1743, 2874, 2935, 2972, 3028, 3063 cm^{-1}.

(*E*)-3,4-Epoxy-1,1-difluoro-2-methyl-4-phenylbut-1-ene (1d): ^{1}H NMR δ 1.55 (3 H, dd, *J* = 3.29, 3.03 Hz), 3.63 (1 H, q, *J* = 1.65 Hz), 3.88 (1 H, d, *J* = 1.92 Hz), 7.25−7.40 (5 H, m). ^{19}F NMR δ 68.9 (1 F, dqd, *J* = 44.8, 3.45, 1.72 Hz), 75.5 (1 F, m). ^{13}C NMR δ 6.35 (dd, *J* = 1.43, 1.14 Hz), 55.8 (t, *J* = 1.72 Hz), 57.9 (dd, *J* = 6.30, 2.58 Hz), 83.4 (dd, *J* = 20.5, 13.9 Hz), 125.3, 128.1, 128.3, 136.4, 155.1 (dd, *J* = 288.4, 287.6 Hz). IR (neat) ν 696, 741, 802, 846, 873, 1086, 1125, 1187, 1226, 1254, 1300, 1458, 1499, 1750, 2338,2361, 2932, 3001 cm^{-1}.

2,3-Epoxy-1-difluoromethylidene-3,5,5-trimethylcyclohexane (1e): ^{1}H NMR δ 0.85 (3 H, s), 0.95 (3 H, s), 1.37 (3 H, s), 1.54 (1 H, d, *J* = 15.1 Hz), 1.75 (1 H, dd, *J* = 15.0, 0.69 Hz), 1.81 (2 H, m), 3.52 (1 H, t, *J* = 1.51 Hz). ^{19}F NMR δ 66.9 (1 F, dd, *J* = 48.0, 2.75 Hz), 73.6 (1 F, dq, *J* = 48.0, 2.58 Hz). ^{13}C NMR δ 24.8, 26.9, 29.8 (dd, *J* = 2.01, 0.86 Hz), 30.1 (d, *J* = 0.86 Hz), 31.4 (d, *J* = 0.86 Hz), 43.2, 55.3 (dd, *J* = 7.16, 2.00 Hz), 58.2 (dd, *J* = 1.72, 0.86 Hz), 84.9 (dd, *J* = 20.9, 13.5 Hz), 155.2 (dd, *J* = 288.6, 286.3 Hz). IR (neat) ν 815, 907, 933, 1000, 1055, 1098, 1173, 1226, 1297, 1373, 1415, 1457, 1751, 1798, 2872, 2958 cm^{-1}.

(*E*)-3,4-Epoxy-1,1-difluoro-2-methyl-4-(4-nitrophenyl)-but-1-ene (1f): ^{1}H NMR δ 1.57 (3 H, dd, *J* = 3.29, 3.04 Hz), 3.62 (1 H, q, *J* = 1.65 Hz), 4.00 (1 H, d, *J* = 1.92 Hz), 7.44−7.53 (2 H, m), 8.19−8.27 (2 H, m). ^{19}F NMR δ 69.9 (1 F, dqd, *J* = 43.5, 3.44, 1.71 Hz), 76.7 (1 F, m). ^{13}C NMR δ 6.58 (dd, *J* = 1.72, 1.15 Hz), 55.1 (m), 58.8 (dd, *J* = 6.58, 2.29 Hz), 83.0 (dd, *J* = 21.3, 13.6 Hz), 123.7, 126.2, 143.9, 147.8, 155.5 (t, *J* = 288.9 Hz). IR (KBr) ν 528, 586, 607, 690, 741, 771, 806, 830, 848, 864, 891, 976, 1012, 1085, 1121, 1183, 1224, 1253, 1302, 1345, 1458, 1522, 1602, 1686, 1749, 1937, 3116 cm^{-1}. Anal. Calcd for $C_{11}H_9F_2NO_3$: C, 54.78; H, 3.76; N, 5.81. Found: C, 54.75; H, 4.16; N, 5.55. Mp 69 °C.

(*E*)-3,4-Epoxy-1,1-difluoro-2-methyl-4-(4-methylphenyl)-but-1-ene (1g): ^{1}H NMR δ 1.53 (3 H, dd, *J* = 3.29, 3.02 Hz), 2.34 (3 H, s), 3.61 (1 H, dd, *J* = 3.29, 1.93 Hz), 3.84 (1 H, d, *J* = 1.92 Hz), 7.17 (4 H, bs). ^{19}F NMR δ 68.8 (1 F, ddd, *J* = 45.0, 8.39, 3.05 Hz), 75.3 (1 F, dq, *J* = 45.0, 3.05 Hz). ^{13}C NMR δ 6.63 (dd, *J* = 1.15, 1.14 Hz), 21.3, 55.9 (dd, *J* = 1.72, 1.71 Hz), 58.0 (dd, *J* = 6.30, 2.57 Hz), 83.4 (dd, *J* = 20.3, 14.0 Hz), 125.4, 129.1, 133.4, 138.1, 155.2 (t, *J* = 288.0 Hz). IR (KBr) ν 351, 382, 409, 501, 536, 563, 586, 609, 752, 795, 822, 872, 972, 1088, 1103, 1130, 1184, 1227, 1258, 1300, 1346, 1381, 1447, 1520, 1616, 1748, 1913, 2099, 2257, 2874, 2928, 3036 cm^{-1}. Mp 37 °C.

2-Benzyl-3,4-epoxy-1,1-difluoro-2-methylbut-1-ene (1h): ^{1}H NMR δ 1.54 (3 H, dd, *J* = 3.30, 3.02 Hz), 2.82 (1 H, d, *J* = 4.94 Hz), 2.85 (1 H, ddd, *J* = 4.94, 1.64, 0.54 Hz), 2.91 (1 H, d, *J* = 14.3 Hz), 3.04 (1 H, d, *J* = 14.3 Hz), 7.17−7.34 (5 H, m). ^{19}F NMR δ 68.6 (1 F, dq, *J* = 47.0, 3.01 Hz), 74.4 (1 F, ddq, *J* = 47.0, 5.17, 3.01 Hz). ^{13}C NMR δ 9.59 (dd, *J* = 2.00, 0.86 Hz), 40.8 (dd, *J* = 2.86, 1.43 Hz), 53.3 (dd, *J* = 3.14, 0.57 Hz), 57.5 (dd, *J* = 7.16, 2.58 Hz), 85.5 (dd, *J* = 20.6, 16.9 Hz),

(25) Lee, J.; Tsukazaki, M.; Snieckus, V. *Tetrahedron Lett.* **1993**, *34*, 415.

126.8, 128.2, 129.5, 135.7, 153.6 (dd, J = 287.2, 285.7 Hz). IR (neat) ν 673, 701, 752, 780, 825, 859, 898, 941, 976, 1031, 1091, 1137, 1186, 1249, 1284, 1388, 1455, 1496, 1605, 1751, 1949, 2346, 2365, 2929, 2996, 3031, 3064, 3087 cm^{-1}. Anal. Calcd for $C_{12}H_{12}F_2O$: C, 68.56; H, 5.75. Found: C, 68.10; H, 6.10.

3,4-Epoxy-1,1-difluoro-2-methyl-6-phenyl-4-(2-phenylethyl)hex-1-ene (1i): ^{1}H NMR δ 1.53 (3 H, td, J = 4.30, 0.82 Hz), 1.57−1.99 (3 H, m), 2.16 (1 H, ddd, J = 14.0, 9.62, 6.32 Hz), 2.65−2.86 (4 H, m), 3.30 (1 H, m), 7.13−7.35 (10 H, m). ^{19}F NMR δ 70.9 (1 F, dddd, J = 48.3, 8.18, 6.46, 3.45 Hz), 73.4 (1 F, dquint, J = 48.3, 3.45 Hz). ^{13}C NMR δ 9.87 (dd, J = 2.29, 0.86 Hz), 31.2, 31.2, 32.7, 36.3, 59.3 (d, J = 5.44 Hz), 63.8 (dd, J = 1.43, 1.43 Hz), 81.9 (dd, J = 20.6, 15.5 Hz), 125.9, 125.9, 128.0, 128.1, 128.1, 128.3, 140.9, 141.4, 153.2 (t, J = 286.6 Hz). IR (neat) ν 669, 698, 747, 925, 1030, 1136, 1221, 1276, 1419, 1457, 1473, 1496, 1507, 1734, 1752, 1772, 2346, 2365, 2931, 3026 cm^{-1}. Anal. Calcd for $C_{21}H_{22}F_2O$: C, 76.81; H, 6.75. Found: C, 76.66; H, 7.07.

3,4-Epoxy-1,1-difluoro-2-(2-phenylethyl)but-1-ene (1j): ^{1}H NMR δ 2.06−2.13 (2 H, m), 2.59−2.82 (3 H, m), 2.90 (1 H, t, J = 4.40 Hz), 3.58 (1 H, ddd, J = 4.40, 2.75, 1.92 Hz), 7.14−7.33 (5 H, m). ^{19}F NMR δ 69.9 (1 F, dq, J = 42.7, 2.15 Hz), 76.0 (1 F, dt, J = 42.7, 2.15 Hz). ^{13}C NMR δ 24.1 (d, J = 1.43 Hz), 35.1 (dd, J = 3.34, 2.48 Hz), 45.6 (t, J = 2.00 Hz), 47.5 (dd, J = 7.16, 2.29 Hz), 87.0 (dd, J = 20.3, 11.5 Hz), 126.1, 128.3, 128.3, 140.8, 155.8 (dd, J = 291.2, 288.6 Hz). IR (neat) ν 669, 699, 736, 751, 789, 835, 870, 951, 998, 1030, 1055, 1085, 1133, 1176, 1211, 1270, 1297, 1350, 1405, 1454, 1497, 1604, 1741, 2346, 2363, 2866, 2931, 3028, 3063 cm^{-1}.

(*Z*)-3,4-Epoxy-1,1-difluoro-2-methyl-4-phenylbut-1-ene (1k): ^{1}H NMR δ 1.34 (3 H, td, J = 2.38, 0.86 Hz), 3.75 (1 H, m), 4.15 (1 H, d, J = 4.16 Hz), 7.25−7.35 (5 H, m). ^{19}F NMR δ 71.2 (1 F, ddt, J = 45.8, 6.84, 3.05 Hz), 73.3 (1 F, dquint, J = 45.8, 3.05 Hz). ^{13}C NMR δ 9.51 (m), 55.3 (d, J = 6.30 Hz), 57.6 (t, J = 1.58 Hz), 81.0 (dd, J = 22.0, 15.5 Hz), 126.0, 127.6, 127.8, 134.7, 153.8 (dd, J = 287.6, 286.5 Hz). IR (neat) ν 605, 649, 668, 699, 728, 753, 825, 843, 894, 918, 971, 1027, 1057, 1076, 1142, 1186, 1215, 1255, 1369, 1387, 1415, 1457, 1496, 1757, 2342, 2360, 2960, 3033, 3065 cm^{-1}.

(*E*)-3,4-Epoxy-1,1-difluoro-2,4-diphenylbut-1-ene (1l): ^{1}H NMR δ 3.61 (1 H, d, J = 2.20 Hz), 3.83 (1 H, dd, J = 1.92, 1.92 Hz), 7.23−7.45 (10 H, m). ^{19}F NMR δ 72.3 (1 F, dd, J = 31.0, 1.72 Hz), 79.5 (1 F, d, J = 31.0 Hz). ^{13}C NMR δ 56.9 (dd, J = 1.72, 1.25 Hz), 57.9 (dd, J = 5.16, 1.15 Hz), 90.9 (dd, J = 18.0, 16.3 Hz), 125.4, 128.2, 128.3, 128.3, 128.4, 128.8 (dd, J = 3.54, 2.39 Hz), 129.5 (dd, J = 2.86, 2.86 Hz), 136.1, 155.9 (dd, J = 294.6, 293.2 Hz). IR (neat) ν 696, 725, 759, 844, 875, 918, 981, 1032, 1202, 1261, 1309, 1448, 1458, 1496, 1696, 1700, 1718, 1734, 2346, 2364, 3061 cm^{-1}.

4-Hydoroxy-2-methyl-6-phenylhex-2-enoyl fluoride (4b): ^{1}H NMR δ 1.80−1.90 (1 H, m), 1.84 (3 H, s), 2.00 (1 H, dtd, J = 14.0, 8.24, 5.77 Hz), 2.71 (1 H, ddd, J = 14.1, 8.24, 7.42 Hz), 2.79 (1 H, ddd, J = 14.0, 9.04, 5.77 Hz), 4.50 (1 H, td, J = 8.24, 4.95 Hz), 6.86 (1 H, ddd, J = 8.24, 3.02, 1.65 Hz), 7.16−7.35 (5 H, m). ^{19}F NMR δ 177.3 (s). ^{13}C NMR δ 12.9 (d, J = 1.14 Hz), 31.2, 37.6, 67.8, 123.8 (d, J = 52.4 Hz), 126.1, 128.2, 128.4, 140.6, 149.8, 158.0 (d, J = 347.8 Hz). IR (neat) ν 698, 729, 795, 930, 957, 1030, 1069, 1169, 1215, 1315, 1389, 1454, 1497, 1605, 1651, 1802, 2342, 2365, 2862, 2932, 3028, 3063, 3372, 3530 cm^{-1}. Anal. Calcd for $C_{13}H_{15}FO_2$: C, 70.25; H, 6.80. Found: C, 70.28; H, 7.12.

6,6,6-Trifluoro-5-methyl-1-phenylhex-4-en-3-ol (5b): ^{1}H NMR δ 1.75 (3 H, d, J = 1.10 Hz), 1.82 (1 H, dddd, J = 14.5, 9.07, 6.87, 5.22 Hz), 1.98 (1 H, dddd, J = 14.0, 8.79, 7.68, 6.32 Hz), 2.68 (1 H, ddd, J = 14.0, 8.79, 6.87 Hz), 2.75 (1 H, ddd, J = 14.0, 9.07, 6.32 Hz), 4.42 (1 H, m), 6.07 (1 H, dddd, J = 8.52, 3.02, 3.02, 1.37 Hz), 7.16−7.34 (5 H, m). ^{19}F NMR δ 91.7 (s). ^{13}C NMR δ 11.0 (dd, J = 2.57, 1.43 Hz), 31.3, 38.1 (dd, J = 4.01, 2.86 Hz), 67.0, 123.7 (q, J = 272.9 Hz), 126.0, 126.4 (q, J = 24.5 Hz), 128.2, 128.3, 134.7 (dd, J = 11.0, 5.44 Hz), 140.9. IR (neat) ν 670, 747, 892, 1030, 1118, 1177, 1335, 1455, 1496, 2863, 2933, 3029, 3064, 3375 cm^{-1}. Anal. Calcd for $C_{13}H_{15}F_3O$: C, 63.93; H, 6.19. Found: C, 63.97; H, 6.05.

General Procedure for the Reactions with RLi and F_2-Vinyloxiranes. The reaction of (*E*)-3,4-epoxy-1,1-difluoro-2-methyl-6-phenylhex-1-ene (**1b**) and MeLi is described as the representative example. To a flask containing **1b** (0.10 g, 0.45 mmol) and 5 mL of dry THF was added 2.0 equiv of MeLi at 0 °C under an argon atmosphere. After 2 h of stirring and an addition of NH_4Cl aq, the reaction mixture was extracted with ether three times, and dried over anhydrous $MgSO_4$. After removal of solvents, purification by silica gel column chromatography (*n*-hexane:AcOEt = 4:1) furnished the product **6ba** in 84% yield. When HMPA is employed as an additive, 0.5 or 5.0 equiv of HMPA is introduced before the addition of MeLi. Then, similar treatment gave the same product in 78% or 67% yields (*E*:*Z* = 68:32 or 93:7, respectively).

6,6-Difluoro-5-methyl-1-phenylhept-4-en-3-ol (6ba): IR (neat) ν 699, 746, 922, 1051, 1139, 1172, 1384, 1450, 1496, 1603, 1721, 2862, 2930, 3026, 3360 cm^{-1}. Anal. Calcd for $C_{14}H_{18}F_2O$: C, 69.98; H, 7.55. Found: C, 70.39; H, 7.43. ***E* isomer:** ^{1}H NMR δ 1.67 (3 H, t, J = 18.3 Hz), 1.69 (3 H, d, J = 1.47 Hz), 1.80 (1 H, m), 1.96 (1 H, dddd, J = 13.6, 8.40, 6.57, 6.11 Hz), 2.67 (1 H, ddd, J = 13.8, 9.28, 6.57 Hz), 2.74 (1 H, ddd, J = 14.0, 9.53, 5.99 Hz), 4.38 (1 H, m), 5.78 (1 H, m), 6.97−7.16 (5 H, m). ^{19}F NMR δ 69.1 (1 F, dq, J = 247.2, 18.3 Hz), 69.6 (1 F, dq, J = 248.7, 18.3 Hz). ^{13}C NMR δ 19.7 (t, J = 5.01 Hz), 22.9 (t, J = 29.4 Hz), 31.5, 38.5, 67.3, 121.8 (t, J = 237.5 Hz), 125.8, 128.2, 130.8 (t, J = 8.16 Hz), 133.6 (t, J = 24.6 Hz), 141.3. ***Z* isomer:** ^{1}H NMR δ 1.64 (3 H, t, J = 18.6 Hz), 1.78 (3 H, d, J = 1.22 Hz), 1.65−1.85 (2 H, m), 2.59−2.78 (2 H, m), 4.56 (1 H, m), 5.44 (1 H, dd, J = 9.82, 1.47 Hz), 6.97−7.16 (5 H, m). ^{19}F NMR δ 75.7 (1 F, dq, J = 244.1, 18.3 Hz), 76.6 (1 F, dq, J = 245.7, 18.3 Hz). ^{13}C NMR δ 11.7 (t, J = 3.15 Hz), 24.6 (t, J = 29.4 Hz), 31.7, 38.9, 67.3, 122.6 (t, J = 237.5 Hz), 125.7, 128.2, 133.5 (t, J = 24.3 Hz), 134.0 (t, J = 3.43 Hz), 141.5.

6,6-Difluoro-5-methyl-1-phenyldec-4-en-3-ol (6bb): IR (neat) ν 699, 740, 913, 1024, 1118, 1170, 1266, 1331, 1380, 1454, 1721, 2338, 2362, 2869, 2933, 2958, 3399 cm^{-1}. Anal. Calcd for $C_{17}H_{24}F_2O$: C, 72.31; H, 8.57. Found: C, 72.48; H, 8.64. ***E* isomer:** ^{1}H NMR δ 0.91 (3 H, t, J = 7.14 Hz), 1.20−1.48 (6 H, m), 1.69 (3 H, d, J = 0.47 Hz), 1.70−2.12 (2 H, m), 2.68 (1 H, ddd, J = 13.9, 9.15, 6.59 Hz), 2.74 (1 H, ddd, J = 13.7, 9.40, 5.98 Hz), 4.42 (1 H, m), 5.80 (1 H, dq, J = 8.55, 1.58 Hz), 7.16−7.32 (5 H, m). ^{19}F NMR δ 61.2 (1 F, dt, J = 231.1, 16.8 Hz), 61.8 (1 F, dt, J = 239.6, 16.8 Hz). ^{13}C NMR δ 12.1 (dd, J = 3.43, 2.86 Hz), 14.0, 22.5, 24.5 (dd, J = 4.29, 4.01 Hz), 31.5, 35.3 (dd, J = 26.9, 26.6 Hz), 38.6 (t, J = 1.15 Hz), 67.5, 122.9 (dd, J = 241.3, 241.1 Hz), 125.8, 128.2, 128.3, 131.2 (dd, J = 8.59, 8.30 Hz), 132.7 (t, J = 23.8 Hz), 141.3. ***Z* isomer:** ^{1}H NMR δ 0.91 (3 H, t, J = 7.14 Hz), 1.20−1.48 (6 H, m), 1.79 (3 H, d, J = 1.34 Hz), 1.70−2.12 (2 H, m), 2.60−2.82 (2 H, m), 4.53 (1 H, ddt, J = 15.6, 7.42, 2.20 Hz), 5.54 (1 H, dq, J = 9.15, 1.58 Hz), 7.16−7.32 (5 H, m). ^{19}F NMR δ 61.2 (1 F, dt, J = 244.1, 16.8 Hz), 61.8 (1 F, dt, J = 244.1, 16.8 Hz). ^{13}C NMR δ 12.1 (dd, J = 3.43, 2.86 Hz), 20.2 (t, J = 5.15 Hz), 22.5, 24.1 (dd, J = 4.01, 3.72 Hz), 31.7, 37.1 (dd, J = 26.9, 26.6 Hz), 39.0 (m), 67.5, 123.9 (t, J = 242.2 Hz), 125.8, 128.2, 128.3, 133.2 (t, J = 24.9 Hz), 134.4 (t, J = 3.44 Hz), 141.6.

6,6-Difluoro-5,7-dimethyl-1-phenylnon-4-en-3-ol (6bc): IR (neat) ν 698, 735, 911, 1018, 1072, 1197, 1383, 1457, 2878, 2933, 2967, 3380 cm^{-1}. Anal. Calcd for $C_{17}H_{24}F_2O$: C, 72.31; H, 8.57. Found: C, 72.73; H, 8.98. **(*E*1 isomer + *E*2 isomer):(*Z*1 isomer + *Z*2 isomer) = 89:11. *E*1 isomer:*E*2 isomer = 50:50.** ^{13}C NMR δ 11.8, 11.9, 11.9 (dd, J = 5.15, 4.01 Hz), 12.2 (dd, J = 4.58, 4.58 Hz), 12.5 (t, J = 3.15 Hz), 22.3 (dd, J = 4.72, 4.01 Hz), 22.5 (dd, J = 4.72, 3.00 Hz), 31.6, 38.7, 38.7, 39.5 (t, J = 25.3 Hz), 39.5 (t, J = 25.3 Hz), 67.5, 124.2 (t, J = 245.1 Hz), 124.2 (t, J = 245.1 Hz), 124.2 (t, J = 246.3 Hz), 125.8, 128.2, 128.3, 131.8 (t, J = 8.87 Hz), 131.8 (t, J = 8.87 Hz), 132.1 (t, J = 22.6 Hz), 132.1 (t, J = 22.6 Hz), 141.4, 141.4. ***E*1 isomer:** ^{1}H NMR δ 0.93 (3 H, t, J = 7.63

Hz), 0.96 (3 H, d, J = 6.91 Hz), 1.09−2.06 (5 H, m), 1.67 (3 H, s), 2.66 (1 H, ddd, J = 13.7, 9.21, 6.60 Hz), 2.75 (1 H, ddd, J = 13.7, 9.34, 6.59 Hz), 4.43 (1 H, qt, J = 7.19, 1.35 Hz), 5.80 (1 H, dq, J = 8.52, 1.65 Hz), 7.15−7.32 (5 H, m). ^{19}F NMR δ 52.6 (1 F, dd, J = 236.5, 15.3 Hz), 53.4 (1 F, dd, J = 236.5, 15.3 Hz). ***E*2 isomer:** ^{1}H NMR δ 0.93 (3 H, t, J = 7.36 Hz), 0.98 (3 H, d, J = 6.83 Hz), 1.09−2.06 (5 H, m), 1.67 (3 H, s), 2.66 (1 H, ddd, J = 13.7, 9.21, 6.60 Hz), 2.75 (1 H, ddd, J = 13.7, 9.34, 6.59 Hz), 4.43 (1 H, qt, J = 7.19, 1.35 Hz), 5.80 (1 H, dq, J = 8.52, 1.65 Hz), 7.15−7.32 (5 H, m). ^{19}F NMR δ 52.2 (1 F, dd, J = 238.0, 15.3 Hz), 54.3 (1 F, dd, J = 236.5, 15.3 Hz). ***Z*1 isomer:*Z*2 isomer = 54:46. *Z*1 isomer:** ^{1}H NMR δ 0.90 (3 H, t, J = 7.23 Hz), 0.91−1.00 (3 H, m), 1.09−2.06 (5 H, m), 1.79 (3 H, s), 2.60−2.80 (2 H, m), 4.52 (1 H, m), 5.53 (1 H, dd, J = 8.28, 0.22 Hz), 7.15−7.32 (5 H, m). ^{19}F NMR δ 59.7 (1 F, dd, J = 245.7, 16.8 Hz), 61.5 (1 F, dd, J = 245.7, 15.3 Hz). ***Z*2 isomer:** ^{1}H NMR δ 0.90 (3 H, t, J = 7.23 Hz), 0.91−1.00 (3 H, m), 1.09−2.06 (5 H, m), 1.79 (3 H, s), 2.60−2.80 (2 H, m), 4.52 (1 H, m), 5.53 (1 H, dd, J = 8.28, 0.22 Hz), 7.15−7.32 (5 H, m). ^{19}F NMR δ 60.2 (1 F, dd, J = 245.7, 15.3 Hz), 60.9 (1 F, dd, J = 245.7, 15.3 Hz).

6,6-Difluoro-5,7,7-trimethyl-1-phenyloct-4-en-3-ol (6bd): IR (neat) ν 699, 749, 825, 885, 916, 1004, 1031, 1068, 1095, 1163, 1203, 1250, 1368, 1397, 1454, 1486, 1496, 2344, 2352, 2879, 2979, 3027, 3063, 3374 cm^{-1}. Anal. Calcd for $C_{17}H_{24}F_2O$: C, 72.31; H, 8.57. Found: C, 72.47; H, 8.87. ***E* isomer:** ^{1}H NMR δ 1.04 (9 H, s), 1.73 (3 H, d, J = 1.22 Hz), 1.80 (1 H, dddd, J = 13.6, 9.89, 6.35, 5.62 Hz), 1.97 (1 H, dddd, J = 13.6, 9.64, 7.45, 5.98 Hz), 2.68 (1 H, ddd, J = 13.8, 9.62, 6.35 Hz), 2.75 (1 H, ddd, J = 13.9, 9.89, 5.99 Hz), 4.44 (1 H, m), 5.71 (1 H, dsex, J = 10.5, 1.34 Hz), 7.16−7.30 (5 H, m). ^{19}F NMR δ 53.6 (1 F, d, J = 235.0 Hz), 54.9 (1 F, d, J = 235.0 Hz). ^{13}C NMR δ 13.9 (t, J = 4.58 Hz), 24.5 (t, J = 4.01 Hz), 31.6, 38.6, 39.1 (dd, J = 26.1, 25.8 Hz), 67.7, 125.1 (t, J = 249.1 Hz), 125.8, 128.2, 128.3, 132.0 (t, J = 25.5 Hz), 134.5 (t, J = 8.31 Hz), 141.4. ***Z* isomer:** ^{19}F NMR δ 59.8 (1 F, d, J = 244.3 Hz), 62.2 (1 F, d, J = 244.3 Hz).

6,6-Difluoro-5-methyl-1,6-diphenylhex-4-en-3-ol (6be): IR (neat) ν 653, 669, 698, 749, 766, 817, 877, 920, 989, 1051, 1161, 1182, 1257, 1319, 1388, 1452, 1496, 1603, 1955, 2345, 2360, 2861, 2927, 3027, 3063, 3356, 3553 cm^{-1}. Anal. Calcd for $C_{19}H_{20}F_2O$: C, 75.47; H, 6.67. Found: C, 75.18; H, 6.40. ***E* isomer:** ^{1}H NMR δ 1.66 (3 H, d, J = 1.35 Hz), 1.70−1.86 (1 H, m), 1.95 (1 H, dddd, J = 13.7, 9.53, 7.57, 6.11 Hz), 2.64 (1 H, ddd, J = 13.9, 9.40, 6.59 Hz), 2.73 (1 H, ddd, J = 13.8, 9.52, 5.98 Hz), 4.41 (1 H, m), 5.82 (1 H, dddd, J = 8.67, 4.99, 3.52, 1.47 Hz), 7.13−7.48 (10 H, m). ^{19}F NMR δ 64.6 (1 F, d, J = 251.8 Hz), 65.2 (1 F, d, J = 251.8 Hz). ^{13}C NMR δ 12.0 (dd, J = 2.58, 2.29 Hz), 31.5, 38.5 (t, J = 1.15 Hz), 67.5, 120.8 (t, J = 241.3 Hz), 125.5 (t, J = 5.73 Hz), 125.8, 128.2, 128.2, 128.3, 129.7 (dd, J = 2.00, 1.72 Hz), 132.6 (t, J = 7.73 Hz), 133.5 (t, J = 16.1 Hz), 135.8 (dd, J = 27.7, 27.1 Hz), 141.3. ***Z* isomer:** ^{1}H NMR δ 1.70−1.89 (2 H, m), 1.84 (3 H, d, J = 1.34 Hz), 2.58 (1 H, ddd, J = 13.9, 10.0, 6.60 Hz), 2.62−2.76 (1 H, m), 4.52 (1 H, m), 5.63 (1 H, dddd, J = 9.28, 3.18, 1.59, 0.73 Hz), 7.13−7.48 (10 H, m). ^{19}F NMR δ 73.8 (1 F, d, J = 259.4 Hz), 76.1 (1 F, d, J = 259.4 Hz). ^{13}C NMR δ 20.2 (t, J = 4.58 Hz), 31.6, 38.7, 67.4 (dd, J = 3.72, 3.44 Hz), 121.1 (dd, J = 241.5, 241.3 Hz), 125.1 (dd, J = 5.44, 5.15 Hz), 125.7, 128.2, 128.2, 128.4, 130.0 (dd, J = 2.01, 1.71 Hz), 135.4 (t, J = 27.1 Hz), 135.6 (dd, J = 3.73, 3.43 Hz), 136.5 (t, J = 27.1 Hz), 141.5.

6,6-Difluoro-6-furyl-5-methyl-1-phenylhex-4-en-3-ol (6bf), *E* isomer: ^{1}H NMR δ 1.73 (3 H, d, J = 1.22 Hz), 1.82 (1 H, dddd, J = 13.7, 9.52, 6.71, 5.73 Hz), 1.98 (1 H, dddd, J = 13.7, 9.28, 7.45, 6.11 Hz), 2.69 (1 H, ddd, J = 13.8, 9.28, 6.59 Hz), 2.75 (1 H, ddd, J = 13.8, 9.64, 6.10 Hz), 4.46 (1 H, m), 5.87 (1 H, ddt, J = 8.55, 3.81, 1.71 Hz), 6.42 (1 H, m), 6.59 (1 H, dd, J = 3.18, 0.86 Hz), 7.15−7.35 (5 H, m), 7.46 (1 H, m). ^{19}F NMR δ 64.7 (1 F, d, J = 265.5 Hz), 65.3 (1 F, d, J = 265.5 Hz). ^{13}C NMR δ 11.9 (td, J = 2.29, 0.86 Hz), 31.5, 38.4 (dd, J = 1.44, 1.14 Hz), 67.5, 110.1 (td, J = 3.29, 1.15 Hz), 110.3, 116.2 (dd, J = 237.3, 237.0 Hz), 125.9, 128.3, 128.3, 131.5 (dd, J = 25.2, 24.9 Hz), 133.6 (dd, J = 7.73, 7.44 Hz), 141.3, 143.7, 147.6 (dd, J = 37.2, 36.1 Hz). IR (neat) ν 700, 737, 823, 884, 910, 1007, 1066, 1161, 1234, 1268, 1387, 1454, 1496, 1603, 2344, 2360, 2861, 2929, 3027, 3063, 3386, 3587 cm^{-1}.

5-Ethyl-6,6-difluoro-4-methyl-1-phenylhept-4-en-3-ol (6ca): IR (neat) ν 700, 738, 918, 1052, 1106, 1162, 1208, 1251, 1303, 1382, 1453, 1495, 1603, 1647, 1724, 2078, 2874, 2939, 2968, 3025, 3062, 3409, 3584 cm^{-1}. Anal. Calcd for $C_{16}H_{22}F_2O$: C, 71.61; H, 8.26. Found: C, 71.36; H, 7.98. ***E* isomer:** ^{1}H NMR δ 0.94 (3 H, t, J = 7.45 Hz), 1.70 (3 H, t, J = 18.1 Hz), 1.80 (3 H, t, J = 3.18 Hz), 1.65−2.15 (4 H, m), 2.63 (1 H, ddd, J = 13.6, 9.34, 7.02 Hz), 2.80 (1 H, ddd, J = 13.8, 10.3, 5.13 Hz), 4.58 (1 H, dd, J = 8.78, 4.64 Hz), 7.16−7.32 (5 H, m). ^{19}F NMR δ 77.0 (1 F, q, J = 18.3 Hz). ^{13}C NMR δ 12.6 (t, J = 4.01 Hz), 15.1, 21.1 (t, J = 5.15 Hz), 24.9 (dd, J = 30.1, 29.9 Hz), 32.3, 36.8, 70.3, 123.1 (t, J = 242.0 Hz), 125.8, 128.3, 134.3 (dd, J = 22.6, 22.3 Hz), 137.5 (dd, J = 4.86, 4.58 Hz), 141.4. ***Z* isomer:** ^{1}H NMR δ 1.03 (3 H, t, J = 7.57 Hz), 1.61 (3 H, t, J = 18.2 Hz), 1.75 (3 H, t, J = 2.45 Hz), 1.65−2.15 (4 H, m), 2.54−2.65 (1 H, m), 2.77−2.83 (1 H, m), 4.72 (1 H, m), 7.16−7.32 (5 H, m). ^{19}F NMR δ 79.8 (1 F, dq, J = 245.7, 18.3 Hz), 82.1 (1 F, dq, J = 244.2, 18.3 Hz). ^{13}C NMR δ 12.3, 15.3, 22.2 (dd, J = 5.44, 5.15 Hz), 26.2 (t, J = 30.1 Hz), 32.4, 36.8, 70.3, 123.4 (t, J = 240.1 Hz), 125.8, 128.3, 134.6 (dd, J = 22.9, 22.6 Hz), 138.3 (dd, J = 4.58, 4.01 Hz), 141.7.

5-Ethyl-6,6-difluoro-4-methyl-1-phenyldec-4-en-3-ol (6cb): IR (neat) ν 700, 749, 806, 910, 1001, 1040, 1116, 1161, 1265, 1319, 1381, 1455, 1496, 1604, 1653, 1943, 2844, 2381, 2874, 2960, 3027, 3064, 3096, 3383, 3587 cm^{-1}. Anal. Calcd for $C_{19}H_{28}F_2O$: C, 73.51; H, 9.09. Found: C, 73.56; H, 9.44. ***E* isomer:** ^{1}H NMR δ 0.91 (3 H, t, J = 7.21 Hz), 0.94 (3 H, t, J = 7.21 Hz), 1.30−1.38 (2 H, m), 1.42−1.52 (2 H, m), 1.66−2.18 (6 H, m), 1.79 (3 H, t, J = 2.93 Hz), 2.62 (1 H, ddd, J = 13.7, 9.52, 6.84 Hz), 2.81 (1 H, ddd, J = 13.7, 10.0, 5.37 Hz), 4.59 (1 H, dd, J = 8.79, 4.76 Hz), 7.18−7.32 (5 H, m). ^{19}F NMR δ 67.6 (1 F, dt, J = 241.1, 16.8 Hz), 68.4 (1 F, dt, J = 239.6, 16.8 Hz). ^{13}C NMR δ 12.6 (t, J = 4.01 Hz), 14.0, 15.2, 21.4 (t, J = 5.16 Hz), 22.5, 24.1 (t, J = 3.44 Hz), 32.3, 36.8, 37.4 (dd, J = 27.5, 27.2 Hz), 70.4, 124.6 (t, J = 243.6 Hz), 125.8, 128.3, 128.3, 134.0 (dd, J = 22.6, 22.3 Hz), 137.7 (dd, J = 4.87, 4.58 Hz), 141.4. ***Z* isomer:** ^{19}F NMR δ 70.8 (1 F, dt, J = 247.2, 16.8 Hz), 72.2 (1 F, dt, J = 242.6, 16.8 Hz).

5-Ethyl-6,6-difluoro-4,7,7-trimethyl-1-phenyloct-4-en-3-ol (6cd), *E* isomer: ^{1}H NMR δ 0.96 (3 H, t, J = 7.42 Hz), 1.04 (9 H, s), 1.72 (1 H, dddd, J = 14.0, 9.89, 6.87, 4.67 Hz), 1.83 (3 H, t, J = 3.03 Hz), 1.90−2.20 (3 H, m), 2.65 (1 H, ddd, J = 13.5, 8.62, 6.87 Hz), 2.83 (1 H, ddd, J = 13.7, 9.89, 5.22 Hz), 4.65 (1 H, dd, J = 8.79, 4.67 Hz), 7.14−7.38 (5 H, m). ^{19}F NMR δ 58.4 (1 F, d, J = 241.3 Hz), 60.8 (1 F, d, J = 241.3 Hz). ^{13}C NMR δ 13.7 (t, J = 5.44 Hz), 16.3, 23.1 (dd, J = 5.72, 5.44 Hz), 25.0 (t, J = 3.73 Hz), 32.5, 37.0, 41.0 (t, J = 26.1 Hz), 70.8, 125.9, 127.5 (dd, J = 250.2, 249.9 Hz), 128.3, 128.3, 131.8 (t, J = 22.6 Hz), 140.3 (t, J = 4.30 Hz), 141.5. IR (neat) ν 700, 746, 921, 1006, 1059, 1073, 1090, 1118, 1161, 1252, 1366, 1397, 1454, 1487, 1748, 2877, 2965, 3027, 3063, 3397, 3587 cm^{-1}. Anal. Calcd for $C_{19}H_{28}F_2O$: C, 73.51; H, 9.09. Found: C, 73.38; H, 9.38.

5-Ethyl-6,6-difluoro-4-methyl-1,6-diphenylhex-4-en-3-ol (6ce): IR (neat) ν 699, 735, 770, 911, 982, 1022, 1065, 1092, 1117, 1176, 1236, 1255, 1302, 1321, 1380, 1452, 1495, 1604, 1719, 1735, 1812, 1959, 2875, 2936, 3027, 3064, 3406, 3583 cm^{-1}. Anal. Calcd for $C_{21}H_{24}F_2O$: C, 76.34; H, 7.32. Found: C, 75.91; H, 7.67. ***E* isomer:** ^{1}H NMR δ 1.00 (3 H, t, J = 7.45 Hz), 1.61 (3 H, t, J = 2.87 Hz), 1.74 (1 H, dddd, J = 14.4, 10.0, 6.84, 4.52 Hz), 2.02 (1 H, dtd, J = 14.2, 9.64, 5.24 Hz), 2.06−2.25 (2 H, m), 2.65 (1 H, ddd, J = 13.6, 9.65, 6.84 Hz), 2.83 (1 H, ddd, J = 13.6, 10.0, 5.25 Hz), 4.69 (1 H, dd, J = 8.79, 4.39 Hz), 7.03−7.56 (10 H, m). ^{19}F NMR δ 77.8 (1 F, d, J = 265.5 Hz), 78.8 (1 F, d, J = 265.6 Hz). ^{13}C NMR δ 13.3 (t, J = 2.58 Hz), 15.0, 21.7 (t, J = 4.58 Hz), 32.3, 36.9 (dd, J = 1.43, 1.14 Hz), 70.4, 121.8 (dd, J = 241.3, 241.1 Hz), 125.5 (t, J = 4.87

Hz), 125.9, 128.3, 128.3, 129.8 (t, J = 2.01 Hz), 133.1 (dd, J = 23.5, 23.2 Hz), 137.5 (t, J = 28.2 Hz), 140.3 (dd, J = 5.44, 5.16 Hz), 141.4. ***Z* isomer:** ^{1}H NMR δ 1.11 (3 H, t, J = 7.33 Hz), 1.67−1.85 (1 H, m), 1.83 (3 H, dd, J = 2.81, 2.56 Hz), 1.70−2.07 (1 H, m), 2.06−2.38 (2 H, m), 2.58 (1 H, ddd, J = 15.6, 11.0, 4.64 Hz), 2.80−2.87 (1 H, m), 4.40 (1 H, dt, J = 9.51, 3.60 Hz), 7.03−7.56 (5 H, m). ^{19}F NMR δ 80.8 (1 F, d, J = 265.5 Hz), 83.8 (1 F, d, J = 267.0 Hz). ^{13}C NMR δ 13.6, 15.0, 22.7 (t, J = 4.72 Hz), 32.3, 36.1, 70.4, 121.6 (t, J = 239.3 Hz), 125.5 (t, J = 4.87 Hz), 125.9, 128.2, 128.2, 129.9 (t, J = 1.71 Hz), 133.7 (t, J = 22.9 Hz), 138.4 (t, J = 28.1 Hz), 140.7 (dd, J = 5.44, 6.01, 5.44 Hz), 141.6.

4,4-Difluoro-3-methyl-1-phenylpent-2-en-1-ol (6da): IR (neat) ν 699, 759, 921, 1007, 1075, 1136, 1178, 1226, 1299, 1385, 1450, 1493, 1604, 1674, 1716, 1812, 1887, 1956, 2929, 3003, 3032, 3063, 3311, 3584 cm^{-1}. Anal. Calcd for C_{12}-$H_{14}F_2O$: C, 67.91; H, 6.65. Found: C, 68.00; H, 6.70. ***E* isomer:** cm^{-1}**:** ^{1}H NMR δ 1.71 (3 H, dd, J = 18.4, 18.1 Hz), 1.86 (3 H, d, J = 1.10 Hz), 5.48 (1 H, dt, J = 8.52, 1.38 Hz), 6.02 (1 H, dddd, J = 8.52, 5.22, 3.57, 1.65 Hz), 7.25−7.41 (5 H, m). ^{19}F NMR δ 69.1 (qt, J = 18.1, 3.01 Hz). ^{13}C NMR δ 11.8 (dd, J = 3.15, 2.86 Hz), 22.8 (t, J = 29.2 Hz), 70.0, 121.8 (t, J = 237.0 Hz), 125.9, 127.7, 128.5, 130.4 (dd, J = 8.59, 8.30 Hz), 133.6 (dd, J = 24.9, 24.7 Hz), 142.4 (t, J = 1.15 Hz). ***Z* isomer:** ^{1}H NMR δ 1.77 (3 H, t, J = 18.4 Hz), 1.82 (3 H, s), 5.64 (1 H, dt, J = 9.90, 1.38 Hz), 5.69 (1 H, d, J = 9.89 Hz), 7.25−7.41 (5 H, m). ^{19}F NMR δ 75.4 (1 F, dq, J = 244.7, 18.1 Hz), 77.4 (1 F, dq, J = 245.6, 18.1 Hz). ^{13}C NMR δ 19.8 (dd, J = 5.17, 4.87 Hz), 24.7 (t, J = 29.2 Hz), 69.6 (t, J = 4.58 Hz), 122.6 (t, J = 241.1 Hz), 125.9, 127.5, 128.4, 133.0 (m), 133.6 (m), 142.8.

4,4-Difluoro-3-methyl-1-phenyloct-2-en-1-ol (6db): IR (neat) ν 698, 735, 910, 1007, 1116, 1171, 1327, 1382, 1454, 1601, 1674, 2871, 2934, 2960, 3031, 3359, 3584 cm^{-1}. Anal. Calcd for $C_{15}H_{20}F_2O$: C, 70.84; H, 7.93. Found: C, 70.90; H, 8.35. ***E* isomer:** ^{1}H NMR δ 0.89 (3 H, t, J = 7.10 Hz), 1.20−1.40 (3 H, m), 1.83 (3 H, d, J = 1.73, Hz), 1.80−2.00 (3 H, m), 5.50 (1 H, d, J = 8.52 Hz), 6.02 (1 H, dsex, J = 8.52, 1.65 Hz), 7.26−7.40 (5 H, m). ^{19}F NMR δ 61.1 (1 F, dt, J = 240.0, 16.8 Hz), 61.7 (1 F, dt, J = 241.0, 16.8 Hz). ^{13}C NMR δ 12.2 (t, J = 3.15 Hz), 13.9, 22.4, 24.4 (dd, J = 4.31, 4.01 Hz), 35.3 (dd, J = 27.9, 27.6 Hz), 70.1, 122.9 (dd, J = 241.3, 240.5 Hz), 125.9, 127.6, 128.5, 130.9 (t, J = 8.59 Hz), 132.4 (t, J = 24.1 Hz), 142.5. ***Z* isomer:** ^{19}F NMR δ 67.7 (1 F, dt, J = 244.9, 16.8 Hz), 69.7 (1 F, dt, J = 244.1, 16.8 Hz).

4,4-Difluoro-3,5,5-trimethyl-1-phenylhex-2-en-1-ol (6dd): IR (neat) ν 567, 668, 699, 736, 763, 825, 892, 912, 942, 1004, 1031, 1063, 1077, 1096, 1196, 1259, 1368, 1385, 1398, 1455, 1465, 1485, 1950, 2248, 2350, 2364, 2879, 2979, 3031, 3064, 3087, 3346 cm^{-1}. Anal. Calcd for $C_{15}H_{20}F_2O$: C, 70.84; H, 7.93. Found: C, 71.19; H, 7.85. ***E* isomer:** ^{1}H NMR δ 1.01 (9 H, s), 1.86 (3 H, d, J = 1.34 Hz), 5.48 (1 H, d, J = 8.30 Hz), 5.95 (1 H, dsex, J = 8.49, 1.34 Hz), 7.27−7.45 (5 H, m). ^{19}F NMR δ 53.6 (1 F, d, J = 235.0 Hz), 54.4 (1 F, d, J = 235.0 Hz). ^{13}C NMR δ 14.1 (dd, J = 4.58, 4.30 Hz), 24.5 (dd, J = 4.01, 3.72 Hz), 39.3 (t, J = 25.8 Hz), 70.5, 125.1 (t, J = 249.3 Hz), 125.9, 127.7, 128.6, 132.0 (dd, J = 25.8, 25.5 Hz), 134.1 (t, J = 8.59 Hz), 142.5. ***Z* isomer:** ^{19}F NMR δ 59.6 (1 F, d, J = 244.1 Hz), 63.6 (1 F, d, J = 245.7 Hz).

4,4-Difluoro-3-methyl-1,4-diphenylbut-2-en-1-ol (6de): IR (neat) ν 632, 659, 698, 746, 766, 845, 890, 919, 990, 1072, 1159, 1206, 1257, 1319, 1385, 1452, 1493, 1540, 1604, 1811, 1890, 1957, 2346, 2927, 2957, 3033, 3064, 3087, 3347 cm^{-1}. Anal. Calcd for $C_{17}H_{16}F_2O$: C, 74.44; H, 5.88. Found: C, 74.44; H, 6.27. ***E* isomer:** ^{1}H NMR δ 1.79 (3 H, d, J = 1.46 Hz), 5.48 (1 H, d, J = 8.42 Hz), 6.07 (1 H, dd, J = 8.42, 1.37 Hz), 7.25−7.55 (10 H, m). ^{19}F NMR δ 64.5 (1 F, d, J = 251.8 Hz), 65.3 (1 F, d, J = 251.8 Hz). ^{13}C NMR δ 12.2 (t, J = 2.29 Hz), 70.3, 120.8 (t, J = 241.5 Hz), 125.5 (t, J = 5.73 Hz), 125.9, 127.8, 128.2, 128.6, 129.7 (t, J = 1.83 Hz), 132.1 (t, J = 8.02 Hz), 133.3 (t, J = 26.1 Hz), 135.7 (t, J = 27.9 Hz), 142.8. ***Z* isomer:** ^{1}H NMR δ 1.85 (3 H, t, J = 1.46 Hz), 5.63 (1 H, d, J = 9.15 Hz), 5.83 (1 H, dd, J = 9.76, 0.85 Hz), 7.25−7.55 (10 H, m). ^{19}F NMR δ 74.1 (1 F, d, J = 260.9 Hz), 77.3 (1 F, d, J = 260.9 Hz). ^{13}C NMR δ 20.3 (t, J = 4.43 Hz), 69.8 (t, J = 4.01 Hz), 121.2 (t, J = 241.8 Hz), 125.4 (t, J = 5.30 Hz), 125.9, 127.8, 128.4, 128.5, 130.2 (t, J = 1.83 Hz), 132.3 (t, J = 26.1 Hz), 134.7 (t, J = 3.44 Hz), 136.4 (t, J = 27.9 Hz), 142.6.

3-(1,1-Difluoroethyl)-1,5,5-trimethylcyclohex-2-en-1-ol (6ea): ^{1}H NMR δ 1.02 (3 H, s), 1.05 (3 H, s), 1.32 (3 H, s), 1.56 (1 H, d, J = 14.3 Hz), 1.69 (1 H, ddd, J = 14.3, 1.38, 1.10 Hz), 1.70 (3 H, t, J = 18.3 Hz), 1.84 (1 H, dq, J = 17.0, 1.92 Hz), 1.95 (1 H, dquint, J = 17.0, 1.24 Hz), 5.92 (1 H, brs). ^{19}F NMR δ 68.0 (1 F, dq, J = 248.7, 18.3 Hz), 68.8 (1 F, dq, J = 250.4, 18.3 Hz). ^{13}C NMR δ 22.8 (dd, J = 29.2, 28.9 Hz), 27.3, 30.0, 30.6, 30.9 (dd, J = 1.14, 0.86 Hz), 36.9 (dd, J = 2.29, 2.00 Hz), 49.9, 68.7, 121.5 (t, J = 236.5 Hz), 129.6 (t, J = 8.01 Hz), 134.3 (t, J = 24.9 Hz). IR (neat) ν 809, 876, 910, 1061, 1137, 1174, 1277, 1379, 1458, 1678, 1720, 2338, 2363, 2874, 2956, 3379, 3590 cm^{-1}. Anal. Calcd for $C_{11}H_{18}F_2O$: C, 64.68; H, 8.88. Found: C, 64.57; H, 8.57.

3-(1,1-Difluoropentyl)-1,5,5-trimethylcyclohex-2-en-1-ol (6eb): ^{1}H NMR δ 0.92 (3 H, dd, J = 7.42, 6.86 Hz), 1.01 (3 H, s), 1.05 (3 H, s), 1.31 (3 H, s), 1.24−1.48 (6 H, m), 1.55 (1 H, d, J = 14.3 Hz), 1.69 (1 H, dt, J = 14.3, 1.37 Hz), 1.81−1.92 (2 H, m), 5.91 (1 H, brs). ^{19}F NMR δ 60.5 (1 F, dt, J = 242.1, 16.4 Hz), 61.7 (1 F, dt, J = 242.1, 16.4 Hz). ^{13}C NMR δ 13.9, 22.4, 24.3 (dd, J = 4.29, 4.01 Hz), 27.3, 30.0, 30.7, 31.0 (dd, J = 1.15, 0.86 Hz), 35.2 (t, J = 26.6 Hz), 37.3 (dd, J = 2.58, 2.29 Hz), 49.8, 68.7, 122.6 (dd, J = 240.5, 240.2 Hz), 130.0 (t, J = 8.31 Hz), 133.4 (t, J = 24.3 Hz). IR (neat) ν 810, 837, 879, 907, 1004, 1060, 1112, 1172, 1270, 1314, 1345, 1370, 1462, 1677, 1723, 2339, 2364, 2872, 2958, 3376, 3593 cm^{-1}. Anal. Calcd for $C_{14}H_{24}F_2O$: C, 68.26; H, 9.82. Found: C, 68.44; H, 9.44.

3-(1,1-Difluoro-2,2-dimethylpropyl)-1,5,5-trimethylcyclohex-2-en-1-ol (6ed): ^{1}H NMR δ 1.00 (3 H, s), 1.05 (9 H, s), 1.07 (3 H, s), 1.32 (3 H, s), 1.55 (1 H, d, J = 13.9 Hz), 1.69 (1 H, dt, J = 14.2, 1.34 Hz), 1.87 (1 H, brd, J = 17.1 Hz), 2.20 (1 H, dd, J = 17.3, 1.16 Hz), 5.84 (1 H, dt, J = 2.32, 1.10 Hz). ^{19}F NMR δ 52.4 (1 F, d, J = 238.1 Hz), 55.5 (1 F, d, J = 236.5 Hz). ^{13}C NMR δ 24.5 (t, J = 4.01 Hz), 27.2, 30.4, 30.9, 31.2, 39.0 (t, J = 3.44 Hz), 39.3 (t, J = 25.8 Hz), 49.9, 68.8, 124.8 (dd, J = 248.8, 247.6 Hz), 133.1 (dd, J = 26.1, 23.2 Hz), 133.3 (dd, J = 8.87, 7.73 Hz). IR (KBr) ν 517, 562, 579, 743, 795, 824, 840, 884, 894, 906, 937, 990, 1013, 1032, 1078, 1110, 1166, 1189, 1249, 1349, 1370, 1486, 1495, 1542, 1560, 2346, 2979, 3316 cm^{-1}. Anal. Calcd for $C_{14}H_{24}F_2O$: C, 68.26; H, 9.82. Found: C, 68.32; H, 9.61. Mp 65 °C.

3-(1,1-Difluoro-1-phenylmethyl)-1,5,5-trimethylcyclohex-2-en-1-ol (6ee): ^{1}H NMR δ 0.95 (3 H, s), 0.97 (3 H, s), 1.31 (3 H, s), 1.55 (1 H, d, J = 14.3 Hz), 1.68 (1 H, brd, J = 14.3 Hz), 1.77 (1 H, ddd, J = 17.0, 3.57, 1.92 Hz), 1.87 (1 H, brd, J = 17.0 Hz), 5.95 (1 H, m), 7.38−7.52 (5 H, m). ^{19}F NMR δ 62.3 (1 F, d, J = 252.5 Hz), 65.2 (1 F, d, J = 251.6 Hz). ^{13}C NMR δ 27.2, 30.1, 30.6, 31.0, 36.9, 49.9, 68.7, 120.5 (t, J = 240.8 Hz), 125.5 (dd, J = 6.01, 5.72 Hz), 128.2, 129.7, 131.2 (t, J = 7.73 Hz), 134.2 (t, J = 26.3 Hz), 135.7 (t, J = 27.8 Hz). IR (neat) ν 668, 699, 754, 768, 804, 832, 880, 905, 978, 1025, 1051, 1111, 1163, 1187, 1220, 1262, 1369, 1388, 1452, 2350, 2368, 2926, 2956, 3404 cm^{-1}. Anal. Calcd for $C_{16}H_{20}F_2O$: C, 72.16; H, 7.57. Found: C, 72.05; H, 7.94.

4,4-Difluro-3-methyl-1-(4-methylphenyl)oct-2-en-1-ol (6gb): IR (neat) ν 669, 721, 762, 818, 894, 912, 943, 1009, 1087, 1117, 1170, 1263, 1327, 1382, 1457, 1513, 2873, 2933, 2960, 3344. Anal. Calcd for $C_{16}H_{22}F_2O$: C, 71.61; H, 8.26. Found: C, 71.27; H, 8.31. ***E* isomer:** ^{1}H NMR δ 0.89 (3 H, t, J = 7.20 Hz), 1.29−1.42 (4 H, m), 1.81 (3 H, d, J = 1.35 Hz), 1.86−1.96 (2 H, m), 2.35 (3H, s), 5.46 (1 H, m), 6.02 (1 H, ddq, J = 8.42, 3.05, 1.35 Hz), 7.23−7.27 (4 H, m). ^{19}F NMR δ 61.4 (2 F, td, J = 16.8, 4.58 Hz). ^{13}C NMR δ 12.2 (t, J = 3.15 Hz), 13.9, 21.2, 22.4, 24.4 (t, J = 4.15 Hz), 35.3 (t, J = 26.4 Hz), 70.1, 122.9 (t, J = 241.3 Hz), 125.9, 129.2, 132.0 (t, J = 23.9 Hz), 132.3 (t, J = 23.9 Hz), 137.4, 139.6. ***Z* isomer:** ^{1}H NMR δ 0.92 (3 H, t, J = 7.20 Hz), 1.42−1.52 (4 H, m), 1.81 (3 H, m),

1.86−2.02 (2 H, m), 2.34 (3 H, s), 5.62 (1 H, m), 5.68 (1 H, dqd, J = 9.53, 1.47, 0.74 Hz), 7.23−7.27 (4 H, m). ^{19}F NMR δ 67.7 (1 F, dt, J = 244.1, 16.8 Hz), 69.5 (1 F, dt, J = 244.1, 16.8 Hz). ^{13}C NMR δ 13.9, 20.1 (t, J = 5.15 Hz), 21.2, 22.5, 24.0 (t, J = 3.87 Hz), 35.3 (t, J = 26.8 Hz), 70.1 (t, J = 4.58 Hz), 123.9 (t, J = 278.1 Hz), 125.8, 129.1, 132.4 (dd, J = 25.3, 24.5 Hz), 133.7 (t, J = 3.34 Hz), 137.2, 140.0.

6,6-Difluoro-5-methyl-1-phenyl-3-(2-phenylethyl)dec-4-en-3-ol (6ib), *E* isomer: ^{1}H NMR δ 0.86−0.96 (3 H, m), 1.20−1.50 (6 H, m), 1.84−2.08 (7 H, m), 2.62−2.84 (4 H, m), 5.80 (1 H, sex, J = 1.65 Hz), 7.10−7.36 (10 H, m). ^{19}F NMR δ 62.4 (td, J = 16.4, 2.15 Hz). ^{13}C NMR δ 12.5 (t, J = 2.86 Hz), 14.0, 22.5, 24.9 (t, J = 4.30 Hz), 30.3, 35.5 (t, J = 27.2 Hz), 44.2, 76.3, 123.5 (t, J = 242.2 Hz), 125.9, 128.2, 128.4, 132.4 (t, J = 8.88 Hz), 132.9 (t, J = 22.9 Hz), 141.9. IR (neat) ν 669, 699, 748, 910, 1030, 1117, 1170, 1266, 1318, 1380, 1454, 1491, 1507, 1603, 1617, 1624, 1636, 1648, 1654, 1675, 1685, 1696, 1700, 1718, 1734, 1869, 1943, 2344, 2362, 2871, 2957, 3026, 3062, 3085, 3447 cm^{-1}.

4,4-Difluoro-3-(2-phenylethyl)oct-2-en-1-ol (6jb): IR (neat) ν 700, 751, 833, 909, 999, 1065, 1083, 1115, 1171, 1224, 1267, 1325, 1382, 1455, 1496, 1604, 1696, 1869, 1943, 2345, 2362, 2873, 2934, 2959, 3027, 3063, 3086, 3345 cm^{-1}. Anal. Calcd for $C_{16}H_{22}F_2O$: C, 71.61; H, 8.26. Found: C, 71.97; H, 7.91. ***E* isomer:** ^{1}H NMR δ 0.92 (3 H, t, J = 7.14 Hz), 1.28−1.50 (4 H, m), 1.88−2.06 (2 H, m), 2.39−2.46 (2 H, m), 2.73 (2 H, m), 3.93 (2 H, dt, J = 6.60, 2.48 Hz), 5.93 (1 H, tt, J = 6.59, 2.20 Hz), 7.17−7.37 (5 H, m). ^{19}F NMR δ 64.6 (tq, J = 16.6, 2.58 Hz). ^{13}C NMR δ 13.9, 22.5, 24.5 (t, J = 4.15 Hz), 28.9 (t, J = 2.29 Hz), 35.6, 36.1 (t, J = 27.6 Hz), 58.7, 123.6 (dd, J = 242.1, 241.3 Hz), 126.1, 128.3, 128.7, 130.0 (t, J = 8.88 Hz), 135.8 (t, J = 23.5 Hz), 141.1. ***Z* isomer:** ^{1}H NMR δ 0.91 (3 H, dd, J = 7.41, 6.87 Hz), 1.28−1.50 (4 H, m), 1.83−2.05 (2 H, m), 2.32−2.44 (2 H, m), 2.74−2.82 (2 H, m), 4.29 (2 H, m), 5.61 (1 H, brt, J = 6.31 Hz), 7.15−7.35 (5 H, m). ^{19}F NMR δ 67.7 (tt, J = 17.2, 3.02 Hz). ^{13}C NMR δ 13.9, 22.5, 24.1 (t, J = 3.47 Hz), 34.5 (t, J = 4.30 Hz), 35.4, 37.3 (t, J = 27.1 Hz), 59.3 (t, J = 5.44 Hz), 124.2 (dd, J = 242.8, 243.1 Hz), 125.9, 128.2, 128.3, 131.6 (t, J = 4.15 Hz), 136.0 (t, J = 24.2 Hz), 141.1.

4,4-Difluoro-1,3-diphenyloct-2-en-1-ol (6*l*b): IR (neat) ν 700, 725, 760, 777, 822, 908, 1011, 1074, 1116, 1147, 1179, 1264, 1317, 1382, 1456, 1494, 1762, 1811, 1890, 1953, 2873, 2933, 2960, 3031, 3061, 3085, 3341, 3584 cm^{-1}. Anal. Calcd for $C_{20}H_{22}F_2O$: C, 75.92; H, 7.01. Found: C, 76.09; H, 7.04. ***E* isomer:** ^{1}H NMR δ 0.84 (3 H, dd, J = 7.41, 7.14 Hz), 1.19−1.34 (2 H, m), 1.35−1.48 (2 H, m), 1.75−2.14 (2 H, m), 5.03 (1 H, d, J = 9.07 Hz), 6.35 (1 H, dt, J = 9.34, 1.92 Hz), 7.20−7.38 (10 H, m). ^{19}F NMR δ 69.7 (1 F, dt, J = 241.7, 16.8 Hz), 64.2 (1 F, dt, J = 241.7, 16.4 Hz). ^{13}C NMR δ 13.4, 22.3, 24.2 (t, J = 4.01 Hz), 35.6 (dd, J = 26.3, 26.1 Hz), 70.8, 122.1 (t, J = 243.1 Hz), 126.0, 127.8, 128.1, 128.2, 128.5, 129.5, 132.8 (dd, J = 8.59, 8.30 Hz), 138.1 (dd, J = 23.5, 23.2 Hz), 138.3 (dd, J = 2.87, 2.57 Hz), 142.3. ***Z* isomer:** ^{1}H NMR δ 0.83 (3 H, dd, J = 7.42, 7.14 Hz), 1.19−1.34 (2 H, m), 1.35−1.48 (2 H, m), 1.75−2.14 (2 H, m), 5.87 (1 H, brd, J = 9.34 Hz), 5.93 (1 H, dd, J = 9.34, 0.82 Hz), 7.20−7.38 (10 H, m). ^{19}F NMR δ 70.9 (1 F, dt, J = 249.0, 16.4 Hz), 72.0 (1 F, dt, J = 249.0, 16.4 Hz). ^{13}C NMR δ 13.4, 22.3, 23.4 (t, J = 3.72 Hz), 37.7 (dd, J = 26.3, 26.1 Hz), 69.9 (dd, J = 6.01, 5.44 Hz), 123.6 (t, J = 243.9 Hz), 126.1, 127.7, 127.7, 128.1, 128.7 (dd, J = 1.43, 1.15 Hz), 134.1 (t, J = 2.00 Hz), 137.4 (dd, J = 24.6, 24.3 Hz), 142.7.

6-(1,3-Dithian-2-ylidene)-6-fluoro-5-methyl-1-phenylhex-4-en-3-ol (7), *E* isomer: ^{1}H NMR δ 1.83 (3 H, d, J = 1.37 Hz), 1.84 (1 H, dddd, J = 13.5, 9.07, 6.87, 6.04 Hz), 1.99 (1 H, m), 2.13 (2 H, quint, J = 6.04 Hz), 2.73 (1 H, d, J = 7.97 Hz), 2.75 (1 H, dd, J = 7.14, 1.65 Hz), 2.81 (1 H, dt, J = 5.49, 1.92 Hz), 2.83 (1 H, ddd, J = 6.05, 2.75, 1.65 Hz), 2.94 (2 H, m), 4.48 (1 H, m), 5.72 (1 H, ddt, J = 8.51, 3.02, 1.37 Hz), 7.15−7.35 (5 H, m). ^{19}F NMR δ 70.3 (m). ^{13}C NMR δ 14.3 (d, J = 1.44 Hz), 24.7, 28.7 (d, J = 2.00 Hz), 29.9 (d, J = 0.68 Hz), 31.5, 38.6, 67.7 (m), 109.3 (d, J = 29.5 Hz), 125.7, 127.6 (d, J = 27.8 Hz), 128.2, 137.4 (d, J = 6.88 Hz), 141.5, 156.0 (d, J = 249.4 Hz). IR (neat) ν 668, 700, 734, 826, 911, 951, 1004, 1030, 1051, 1176, 1243, 1275, 1301, 1380, 1419, 1454, 1495, 1603, 2342, 2361, 2860, 2926, 3026, 3061, 3385, 3568 cm^{-1}. Anal. Calcd for $C_{17}H_{21}F_2OS_2$: C, 62.93; H, 6.52. Found: C, 61.86; H, 6.56.

3,4-Epoxy-5-ethyl-6-fluoro-4-methyl-1-phenyldec-5-ene (8c): IR (neat) ν 698, 821, 861, 906, 1078, 1135, 1191, 1223, 1255, 1379, 1457, 1496, 1696, 1701, 2871, 2962 cm^{-1}. **Major isomer:** ^{1}H NMR δ 0.91 (3 H, t, J = 7.33 Hz), 1.04 (3 H, t, J = 7.56 Hz), 1.32 (2 H, sex, J = 7.74 Hz), 1.37 (3 H, s), 1.47 (2 H, quint, J = 7.70 Hz), 1.82−2.30 (6 H, m), 2.74−2.92 (3 H, m), 7.16−7.32 (5 H, m). ^{19}F NMR δ 49.8 (t, J = 22.9 Hz). ^{13}C NMR δ 14.0 (d, J = 4.01 Hz), 14.0 (d, J = 4.01 Hz), 18.6 (d, J = 1.14 Hz), 19.7 (d, J = 6.58 Hz), 22.5, 28.5, 29.4 (d, J = 27.1 Hz), 30.7, 32.7, 60.6 (d, J = 11.0 Hz), 63.7 (d, J = 0.86 Hz), 119.3 (d, J = 16.9 Hz), 126.0, 128.2, 128.4, 140.9, 157.1 (d, J = 251.4 Hz). **Minor isomer:** ^{1}H NMR δ 0.92 (3 H, t, J = 7.33 Hz), 1.06 (3 H, td, J = 7.56, 0.86 Hz), 1.27−1.39 (2 H, m), 1.40 (3 H, s), 1.47−1.55 (2 H, m), 1.82−2.30 (6 H, m), 2.74−2.92 (3 H, m), 7.16−7.32 (5 H, m). ^{19}F NMR δ 55.2 (t, J = 22.9 Hz). ^{13}C NMR δ 14.5 (d, J = 3.15 Hz), 14.5 (d, J = 3.15 Hz), 18.9 (d, J = 3.15 Hz), 20.4 (d, J = 5.73 Hz), 22.2, 28.2 (d, J = 28.3 Hz), 28.7, 30.9, 32.4, 59.6 (d, J = 6.59 Hz), 64.0 (d, J = 1.58 Hz), 119.5 (d, J = 13.6 Hz), 125.8, 128.1, 128.2, 141.4, 155.6 (d, J = 247.9 Hz).

5-Ethyl-6-fluoro-4-methylene-1-phenyldec-5-en-3-ol (9c): IR (neat) ν 699, 749, 785, 808, 910, 942, 972, 1067, 1120, 1191, 1222, 1254, 1322, 1379, 1430, 1454, 1497, 1604, 1636, 1685, 1943, 2345, 2362, 2873, 2932, 2964, 3027, 3063, 3096, 3361 cm^{-1}. Anal. Calcd for $C_{19}H_{27}FO$: C, 78.58; H, 9.37. Found: C, 78.27; H, 9.33. **Major isomer:** ^{1}H NMR δ 0.87 (3 H, t, J = 7.33 Hz), 0.91 (3 H, t, J = 7.44 Hz), 1.22−1.56 (4 H, m), 1.70 (1 H, dtd, J = 14.0, 9.89, 4.95 Hz), 1.95 (1 H, dddd, J = 13.9, 10.2, 6.87, 3.30 Hz), 2.15−2.37 (4 H, m), 2.70 (1 H, ddd, J = 13.7, 9.89, 6.84 Hz), 2.85 (1 H, ddd, J = 13.8, 10.1, 4.95 Hz), 4.16 (1 H, dd, J = 9.28, 2.69 Hz), 4.91 (1 H, m), 5.33 (1 H, d, J = 1.47 Hz), 7.16−7.31 (5 H, m). ^{19}F NMR δ 51.5 (dd, J = 24.4, 22.9 Hz). ^{13}C NMR δ 13.0 (d, J = 1.71 Hz), 14.0, 20.4 (d, J = 7.45 Hz), 22.5, 29.3 (d, J = 28.1 Hz), 29.4, 32.2, 37.3, 71.9 (d, J = 3.43 Hz), 113.3 (d, J = 2.01 Hz), 119.1 (d, J = 18.9 Hz), 125.8, 128.3, 128.3, 141.6, 148.6 (d, J = 8.01 Hz) 157.1 (d, J = 251.9 Hz). **Minor isomer:** ^{19}F NMR δ 57,2 (dd, J = 24.9, 22.9 Hz).

2-Benzylidene-4-fluoro-3-methyloct-3-en-1-ol (9h): IR (neat) ν 669, 700, 759, 827, 875, 922, 1038, 1121, 1169, 1219, 1379, 1458, 1466, 1491, 1647, 1653, 1685, 1700, 2345, 2363, 2872, 2930, 2958, 3023, 3057, 3392, 3587 cm^{-1}. Anal. Calcd for $C_{16}H_{21}FO$: C, 77.38; H, 8.52. Found: C, 76.90; H, 8.67. **Major isomer:** ^{1}H NMR δ 0.95 (3 H, t, J = 7.14 Hz), 1.25−1.47 (2 H, m), 1.48−1.64 (2 H, m), 1.87 (3 H, d, J = 2.75 Hz), 2.30−2.38 (1 H, m), 2.38−2.48 (1 H, m), 4.39 (2 H, d, J = 5.77 Hz), 6.61 (1 H, s), 7.23−7.40 (5 H, m). ^{19}F NMR δ 57.6 (brt, J = 24.1 Hz). ^{13}C NMR δ 14.0, 16.6 (d, J = 5.72 Hz), 22.2, 28.9 (d, J = 1.14 Hz), 29.3 (d, J = 29.5 Hz), 60.8 (d, J = 4.58 Hz), 112.2 (d, J = 14.3 Hz), 127.0, 128.1, 128.9, 131.1 (d, J = 2.57 Hz), 136.5, 138.4, 156.6 (d, J = 249.1 Hz). **Minor isomer:** ^{1}H NMR δ 0.90 (3 H, t, J = 7.14 Hz), 1.25−1.47 (2 H, m), 1.48−1.64 (2 H, m), 1.84 (3 H, m), 2.30−2.38 (1 H, m), 2.38−2.48 (1 H, m), 4.34 (2 H, d, J = 4.94 Hz), 6.48 (1 H, s), 7.23−7.40 (5 H, m). ^{19}F NMR δ 54.7 (brt, J = 24.1 Hz). ^{13}C NMR δ 13.6 (d, J = 8.30 Hz), 14.0, 22.5, 29.2 (d, J = 28.1 Hz), 29.4 (d, J = 0.86 Hz), 59.5 (d, J = 2.86 Hz), 113.9 (d, J = 19.5 Hz), 127.1, 128.2, 128.6, 130.7 (d, J = 2.29 Hz), 136.2, 139.2 (d, J = 8.30 Hz), 157.9 (d, J = 252.8 Hz).

5-Butyl-4-ethyl-3-methyl-2-(2-phenylethyl)furan (10c): ^{1}H NMR δ 0.93 (3 H, t, J = 7.33 Hz), 1.04 (3 H, t, J = 7.57 Hz), 1.34 (2 H, sex, J = 7.32 Hz), 1.57 (2 H, quint, J = 7.45 Hz), 1.71 (3 H, s), 2.26 (2 H, q, J = 7.57 Hz), 2.51 (2 H, t, J = 7.45 Hz), 2.78 (2 H, m), 2.86 (2 H, m), 7.10−7.28 (5 H, m). ^{13}C NMR δ 8.23, 14.1, 15.5, 17.0, 22.5, 25.9, 28.4, 31.4, 35.1, 114.5, 120.1, 125.7, 128.1, 128.4, 141.6, 147.1, 148.3. IR (neat) ν 698, 749, 957, 1056, 1121, 1139, 1253, 1379, 1454, 1496, 1595,

1604, 2344, 2360, 2860, 2870, 2930, 2960, 3027, 3062 cm^{-1}. Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.11; H, 9.38.

(*E*)-2-benzylidene-4,4-difluoro-3-methylbut-3-en-1-ol (11h): ^1H NMR δ 1.71 (3 H, dd, $J = 3.30, 3.02$ Hz), 4.28 (2 H, brs), 6.63 (1 H, dd, $J = 3.03, 1.38$ Hz), 7.20−7.32 (5 H, m). ^{19}F NMR δ 69.7 (1 F, dddd, $J = 43.9, 4.74, 3.01, 1.73$ Hz), 72.7 (1 F, ddd, $J = 43.9, 7.46, 3.44$ Hz). ^{13}C NMR δ 12.5 (dd, $J = 2.29, 0.86$ Hz), 65.9 (dd, $J = 3.44, 2.29$ Hz), 83.9 (dd, $J = 22.1, 19.5$ Hz), 127.4, 128.1, 128.3, 128.7 (dd, $J = 2.86, 1.43$ Hz), 134.2 (dd, $J = 3.87, 2.72$ Hz), 136.1, 152.0 (dd, $J = 287.6, 284.9$ Hz). IR (neat) ν 669, 695, 755, 872, 924, 1014, 1074, 1093, 1125, 1198, 1260, 1448, 1491, 1648, 1740, 2345, 2364, 2929, 3026, 3339. Anal. Calcd for $C_{12}H_{12}F_2O$: C, 68.56; H, 5.75. Found: C, 68.80; H, 5.71.

Supporting Information Available: Preparation of α,*β*-unsaturated ketones (Table 6 and Scheme 7) and α,*β*-epoxy ketones (Table 7 and Scheme 8) and some of their physical properties, as well as MOPAC computational details (Figures 3 and 5: energetic preference of the reaction of **1** with monomeric MeLi from both *re*- and *si*-face attack; Figure 4: transition states of the reaction of **1** with monomeric MeLi, followed by the Cartesian coordinates for the obtained stationary points). This material is available free of charge via the Internet at http://pubs.acs.org.

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