Ring-Opening Fluorination and Ring-Expansion Fluorination of Cyclopropanemethanols with Amine/Metal Fluoride/ Poly(hydrogen fluoride)-Pyridine Complex

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Treatment of cyclopropanemethanols with pyridinium poly(hydrogen fluoride) in the presence of diisopropylamine and KHF_2 gave selectively homoallylic fluorides or fluorocyclobutanes according to the mode of substitution of the starting cyclopropanemethanols. Cyclopropanemethanols with no substitution at 1-position of the cyclopropane ring gave homoallylic fluorides in a stereoselective manner. While, 1-methylcyclopropanemethanol gave the fluorocyclobutane in high stereoselectivity. Fluorocyclobutanes containing hydroxymethyl group were also prepared from 2-(1-methylcyclopropyl)oxiranes. The amine and the metal fluoride were necessary as additives for the best results. Influencing factors involving solvents and temperature for the reactions are also described.

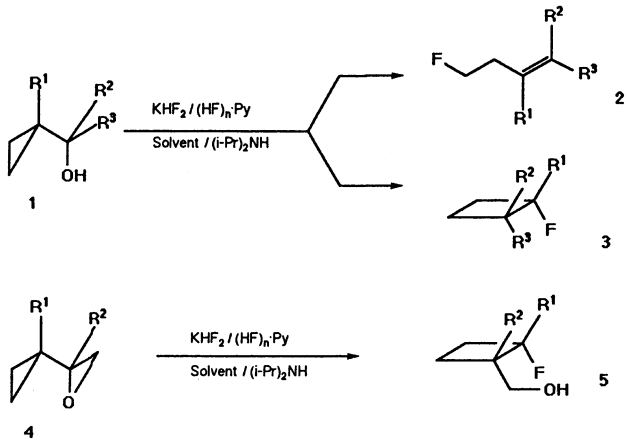
Organic synthons containing a single fluorine atom have been increasingly attracting attentions of chemists in agricultural, and pharmaceutical research areas because of their unique chemical and biological characters useful for the molecular design works.[1] For example, certain monofluorinated steroids[2] are selectively metabolized by insects to generate highly toxic fluoroacetic acid revealing potentiality as new insecticide. Some amino acids containing a fluoromethyl group have been known to be potent suicide inhibitors to enzymatic decarboxylation.[3]

There are two approaches to synthesize monofluorinated compounds. The first is an introduction of a fluorine atom onto a molecule by fluorination of alcohols or halides, and even hydrides. DAST,[4] HFP-DA,[5] quaternary ammonium fluorides,[6] or specifically modified metal fluorides[7] with crown ethers,[8] are recently developed for the nucleophilic fluorination, and F_2,[9] CF_3OF,[10] XeF_2,[11] or other modified hypofluorite reagents are for direct fluorination. The second is to make use of fluorinated building blocks or their equivalents.[12]

Among them, homoallylic fluorides are the most versatile intermediates for synthesis of a variety of monofluorinated bioactive compounds. However, there has been no pertinent method for selective fluorination leading to homoallylic fluorides. Attempts to prepare homoallylic fluorides by nucleophilic substitution of corresponding alcohols or their derivatives often results in troublesome contaminations of by-products. Particularly, fluorination of tertiary hydroxyl groups is hardly successful. For example, fluorination of 4-phenyl-3-buten-1-ol with a common fluorinating reagent such as DAST, gave only dehydrated ethers and dienes.

Thence, we attempted to use cyclopropanemethanols as better precursors to homoallylic fluorides, since a cyclopropylmethyl cation generated from a cyclopropanemethanol or its derivative with pyridinium poly(hydrogen fluoride) will be possibly rearranged to a homoallylic cation, that is promptly quenched with a fluoride anion. Here we wish to report a selective preparation of homoallylic fluorides by the ring-opening fluorination of cyclopropanemethanol derivatives. In addition, selective synthesis of monofluorocyclobutanes containing a *tertiary* fluorine atom is also described for 1-substituted cyclopropanemethanols and corresponding epoxides.[13]

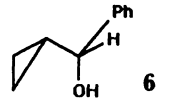
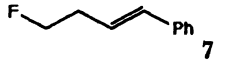
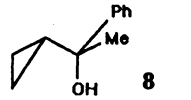
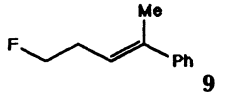
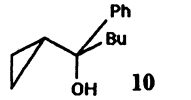
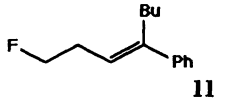
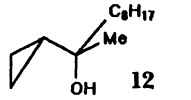
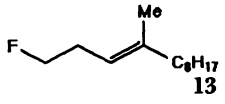
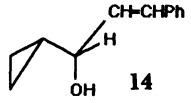
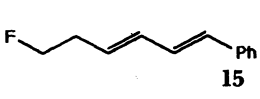
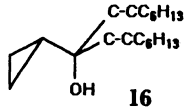
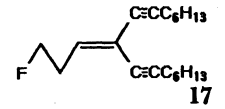
Synthesis of Homoallylic Fluorides Using Modified Pyridinium Poly(hydrogen fluoride) by Ring-Opening Fluorination. Ring opening halogenation of cyclopropanemethanols with aqueous hydrogen bromide or hydrogen chloride has been known as Julia rearrangement, that gives the corresponding homoallylic bromides or chlorides.[14] However, application of this method for fluorination of cyclopropanemethanols with aqueous hydrogen fluoride was not successful at all. Nucleophilicity of water is much stronger than that of fluoride anion, and this gave rise to only homoallylic alcohols and ethers due to self-condensation. In order to make the reaction media anhydrous, we employed the Olah's reagent[15] as fluoride anion source. Olah's reagent, or pyridinium poly(hydrogen fluoride): $(HF)_n \cdot Py$ is widely used, known to be the most useful for halo- or hydro-



Scheme 1.

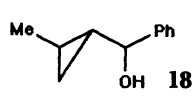
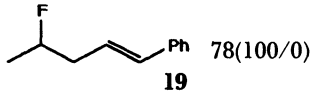
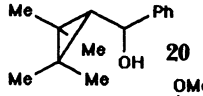
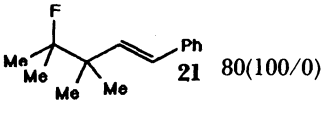
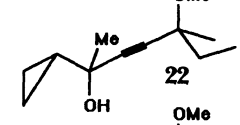
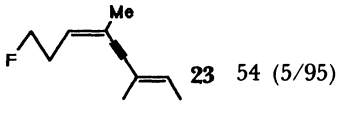
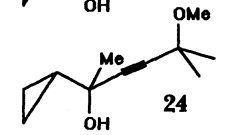
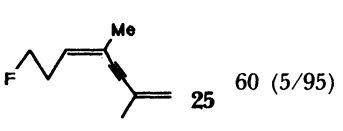
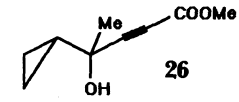
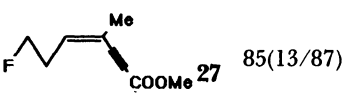
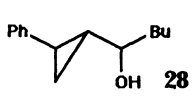
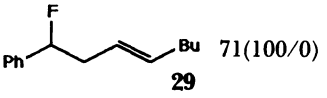
fluorination of olefins as well as fluorination of alcohols. However, the attempted fluorination of cyclopropanemethanols with the reagent afforded a homoallylic fluoride in poor yield with major contamination of homoallylic alcohols, ethers, and other by-products. It was obvious that poly(hydrogen fluoride) behaved majorly as acid catalyst for ring opening and self-condensation, and not as a reagent for nucleophilic fluorination. This result indicated that it was necessary to activate the fluoride anion more than ever. In order to control the acidity of the system and to activate fluoride anion, we tried certain additives with co-solvents. Various aromatic and aliphatic amines were employed as co-solvent together with inorganic fluorides, NaF, KF, KHF_2, CsF, and quaternary ammonium fluorides for additives. A number of combinations of an amine with a fluoride salt were screened for better result and selectivity using α-phenylcyclopropanemethanol (**6**) as a model substrate. The role of these additives may be explained as follows. These amines diminish the degree of aggregation of poly(hydrogen fluoride), and activate the fluoride anion as nucleophile giving "ammonium fluoride" type reaction species which is more reactive than fluoride anion in Olah's reagent. Second, fluoride salts increase the concentration of fluoride anion and its nucleophilicity. Among them, a combination of diisopropylamine with KHF_2 dried up in a microwave oven gave the best result. Dried KHF_2 has an additional advantage to behave as dehydrant and to avoid the attack of water which was generated from dehydration of an alcohol moiety. The choice of solvents is also essentially important. For example, ethereal solvents such as diethyl ether, or tetrahydrofuran, which are commonly used with $(HF)_n \cdot Py$, were not applicable at all for this reaction. These solvents behaved as nucleophile giving complex products.[16] Only chloroalkanes and chlorobenzene gave acceptable results. Their stability together with lipophilicity and polarity appears to be critical for the reaction. A variety of substituted cyclopropanemethanols were treated in this reaction system, and the results are summarized in Tables 1 and 2. We employed the procedure to add the $(HF)_n \cdot Py$ into a mixture of substrate, KHF_2, and diisopropylamine in dichloromethane or chlorobenzene at 0 °C. Addition of a solution of substrate into a reagent mixture always decreased the yields of the products. In the presence of a certain functional group(s) such as phenyl, vinyl, and alkynyl group which stabilize α-carbocation, the reaction generally proceeds in good yield and selectivity. On the other hand, an α,α-dialkyl-substituted substrate gave the homoallylic fluoride in poor yield (Run 4, Table 1), and majorly yielded diene products. Attack of a fluoride anion generally occurred at the more substituted carbon atom (Runs 1 and 6, Table 2). In the case of the substrate (**28**), only a ring opened and condensed product was obtained under the standard reaction conditions. Among the condi-

Table 1. Formation of Primary Homoallylic Fluorides with Modified Hydrogen Fluoride

Run	Substrate	Product	Yield(%)[a,b]
1	 **6**	 **7**	73(100/0)
2	 **8**	 **9**	65 (95/5)
3	 **10**	 **11**	55(85/15)
4	 **12**	 **13**	37(65/35)
5	 **14**	 **15**	70(100/0)
6	 **16**	 **17**	62

a) Isolated yield. b) Figures in parentheses were *E/Z* ratio of products. Major isomers are shown in the table.

Table 2. Ring-Opening Fluorination of Substituted or Functionalized Cyclopropanemethanols

Run	Substrate	Product	Yield(%)
1	 **18**	 **19**	78(100/0)
2	 **20**	 **21**	80(100/0)
3	 **22**	 **23**	54 (5/95)
4	 **24**	 **25**	60 (5/95)
5	 **26**	 **27**	85(13/87)
6	 **28**	 **29**	71(100/0)

a) Isolated yield. b) Figures in parentheses were *E/Z* ratio of products. Major isomers are shown in the table.

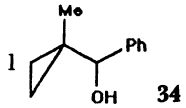
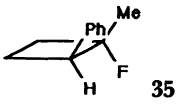
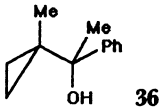
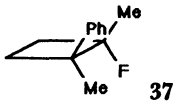
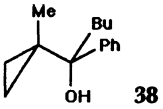
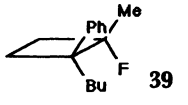
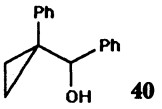
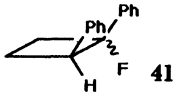
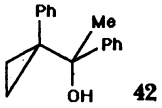
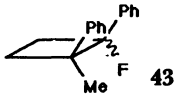
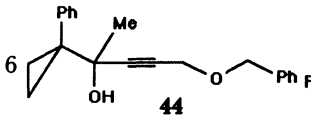
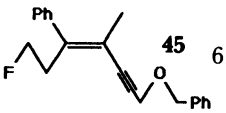
tions tried, the best result was obtained in an inverse addition mode. Dropwise addition of a THF solution of the substrate into the mixture of KHF_2, and $(HF)_n \cdot Py$ in THF with $(i\text{-}Pr)_2NH$ gave the desired fluoride (**29**) in 71% yield.

Stereochemistry of the resultant olefin was highly dependent on the steric factor of the substituent at the α-carbon, and a more bulky group is always at trans position to the 2-fluoroethyl group in the resultant olefin. The tertiary ethers (**22**, **24**), could not stand the reaction conditions. Elimination to yield the corresponding olefin was predominant. On the other hand, ester moiety was not affected (Run, 5, Table 2).

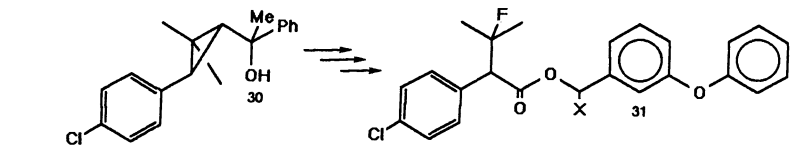
These homoallylic fluorides have wide applicability as substrate to the synthesis of monofluorinated analogues of known bioactive compounds as prototype. For example, fluorinated fenvalerate (**31**) was first prepared from α-methyl-α-phenylcyclopropanemethanol (**30**) in good overall yield, and juvenile hormone mimic (**32**) and anti-juvenile hormone mimic (**33**) have been also prepared in a few steps. These compounds showed similar activities as those of the prototypes.[17]

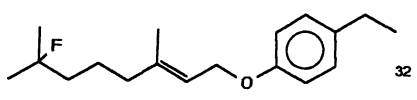
Synthesis of Fluorocyclobutanes Using 1-Substituted Cyclopropanemethanol Derivertives by Ring-Expansion Fluorination. In the course of experiments dealing with ring opening fluorination, we wish to expand it to a synthesis of fluorocyclobutanes. A cyclopropylmethyl cation can be smoothly rearranged to a homoallylic cation with release of ring strain. When a cyclopropane ring has a substituent at 1-position, generation of tertiary cyclobutyl cation by ring expantion would be preferred to rearrangement to primary homoallylic cation, although cyclobutane still has certain ring strain.[18] Then a fluoride anion would immediately attack the cyclobutyl cation to form fluorocyclobutane. Based on the hypothesis, we examined the reaction of 1-methyl-α-phenylcyclopropanemethanol (**34**) with $(i\text{-}Pr)_2NH\text{-}KHF_2\text{-}(HF)_n \cdot Py$ complex in dichloromethane at 0 °C, and it gave fluorocyclobutane in moderate yield. Ring expantion fluorination of α,1-dimethyl-α-phenylcyclopropanemethanol (**36**) gave selectively 1-fluoro-1,2-dimethyl-*trans*-2-phenylcyclobutane (**37**) in 75% yield, but the similar treatment without $(i\text{-}Pr)_2NH$ and/or KHF_2

Table 3. Ring-Expansion Fluorination of 1-Substituted Cyclopropanemethanols

Run	Substrate	Product	Yield(%)
1	 **34**	 **35**	71 (95/5)
2	 **36**	 **37**	75 (95/5)
3	 **38**	 **39**	64 (95/5)
4	 **40**	 **41**	62(45/55)[c]
5	 **42**	 **43**	68(59/41)[c]
6	 **44**	 **45**	61

a) Isolated yield. b) Figurs in parentheses are trans/cis ratio of products. Major isomers are shown unless otherwise noted. c) Phenyl-F trans/cis ratio.





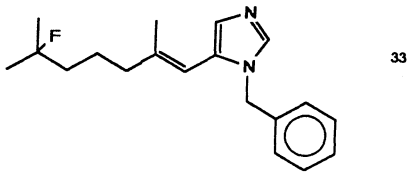


Fig. 1.

failed to give the fluorocyclobutane.

Usually poly- and perfluorocyclobutanes are synthesized via thermal,[19] photochemical,[20] or Michael type[21] [2+2] cycloaddition of polyfluoroolefins, which do not appear to be applicable to the synthesis of monofluorocyclobutanes.[22] Besides, regio- and stereochemistry would not be controlled during the cycloaddition if monofluoroolefins were available at all.

This ring expansion reaction was also sensitively affected by solvent for reaction, and we found dichloromethane or chlorobenzene to be the best solvents. The reaction temperature is also crucial to the yield of the fluorocyclobutane. For example, the substrate (**34**) gave the fluorinated cyclobutane (**35**) in 77% yield at −20 °C, whereas the yield decreased to 40% at 0 °C.

The stereoselectivity in fluorine introduction to the cyclobutane ring is highly dependent on the substituent "R^1" on the cyclopropane ring. The substrates containing methyl group for R^1 generally gave the cyclobutanes in high stereoselectivity. Fluorine was introduced in "trans" orientation to the bulkier group at the α-position of the cyclobutane in over 95% stereoselectivity (determined by HPLC, Runs 1, 2, and 3, Table 3). However, the substrates with phenyl group as R^1 gave the trans-products in the lower stereoselectivities (Runs 4 and 5). This may be explained in terms of the fixed geometry of the initially formed carbocation (**46**) due to the steric conflict between the endo hydrogen atoms and R^2, and this results in the observed high stereoselectivity (Fig. 2). When R^1 and R^2 are phenyl groups (Runs 4 and 5), each conformation (**46a**, **46b**) is equally possible and this may cause the formation of cis and trans fluorides. Another possible explanation of the low stereoselectivities observed for formation of **41** and **43** seems to be due to the cyclobutyl cation (**47**) stabilized by an extra phenyl group. The resultant plane sp^2 carbon would reduce the selectivity.[23]

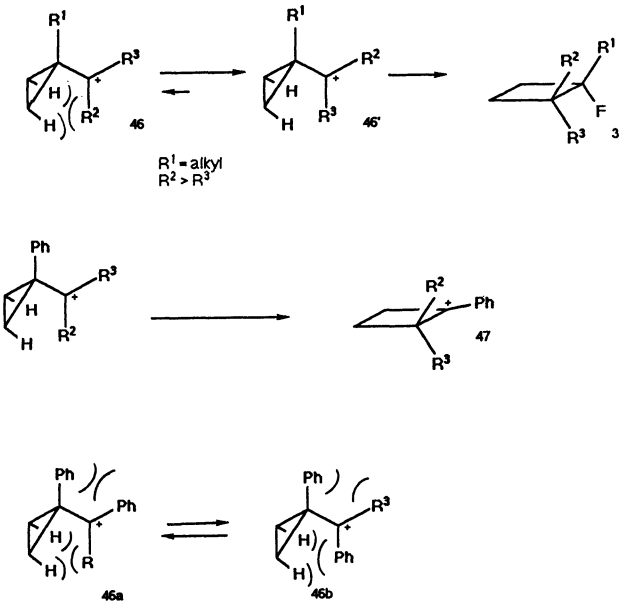


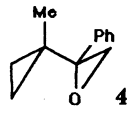
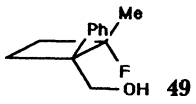
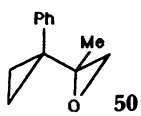
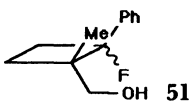
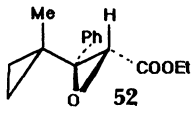
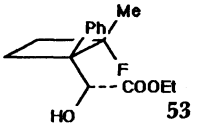
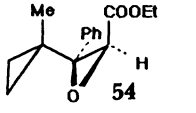
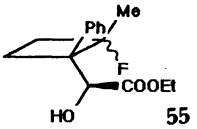
Fig. 2.

Initial formation of the carbocation is supported by the following result. Chiral (*R*)-(+)-1-methyl-α-phenylcyclopropanemethanol (**34**) as prepared from (*R*)-(+)-mandelic acid in three steps, gave the racemic fluorocyclobutane (**35**) losing perfectly its optical integrity.

The reaction pathway is controlled in accordance with the substituent R^1 on the cyclopropane and R^2 at the α-position of the hydroxyl group. No ring rearrangement occurred when substrates having an electron withdrawing group such as acyl or cyano group as R^1 on the cyclopropane ring were applied. These groups appear to prevent the formation of the rearranged carbocation.[24] As for R^2, in sharp contrast to the alkyl or phenyl substituents, the substrates containing the α-acetylenic or olefinic functions were converted exclusively to the corresponding homoallylic fluorides (Run 6, Table 3). The distinct control on the selection of these alternative pathways can be attributed to an electronic effect of acetylenic or olefinic group in the substituent R^2.

Parallel Ring Rearrangement of 2-(1-Substituted cyclopropyl)oxirane to Hydroxymethyl-Substituted Fluorocyclobutanes. It was necessary to seek a group of new substrates in order to provide fluorocyclobutanes whose substituent is variously functionalized for

Table 4. Synthesis of Hydroxymethyl-Substituted Fluorocyclobutanes Using Epoxycyclopropanes

Run	Substrate	Product	Yield(%)[a,b]
1	 **48**	 **49**	83 (5/95)
2	 **50**	 **51**	87(46/54)[c]
3	 **52**	 **53**	60 (5/95)
4	 **54**	 **55**	26(45/55)[d]

a) Isolated yield. b) Figures in parentheses are trans/cis ratio of products. Major isomers are shown unless otherwise noted. c) Hydroxymethyl-F trans/cis ratio. d) Phenyl-F trans/cis ratio.

further transformation. Cyclopropyloxirane was expected to generate fluorocyclobutanes containing hydroxymethyl group at the adjacent position of the fluorinated carbon atom upon the ring-expansion fluorination. Moreover, this parallel three-membered ring system, a cyclopropane connected with oxirane ring, has certain advantages over cyclopropanemethanols. That is, the substrate has highly strained ring system and appear to be more favored to form carbocation. Moreover, on the contrary to the cyclopropanemethanol substrates, oxiranes do not generate water that is adverse to the reaction media under the current fluorination conditions.

Under similar reaction conditions as before, the cyclopropyloxirane (**48**) was transformed stereoselectively into the fluorocyclobutane (**49**) in 83% yield (Table 4). The product has a "trans" configuration with respect to the fluorine and the phenyl groups. As it is similar to the case of the cyclopropanemethanols, the stereoselectivity decreased with the 1-phenylcyclopropyl counterpart (**50**) resulting in nearly a 1 : 1 stereoisomeric mixture (**51**) in moderate yields. Interestingly, the 2-(ethoxycarbonyl)oxirane (**52**) gave the geometrically pure fluorocyclobutane (**53**) in 60% yield (see Table 4). We assume that the oxirane (**52**) can easily take the conformation necessary for the anti-displacement of the C_1-C_2 bond of the cyclopropane when attacked by fluoride anion. In contrast, the stereoisomer (**54**) gave an isomeric mixture of fluorocyclobutane (**55**) in poor yield. Main product was an α-hydroxy-γ-lactone via intramolecular ring formation. The influencing factor over the reaction course may be ascribed for the conformation of the ethoxycarbonyl group in **54**, where the generated cyclobutyl cation and the ethoxycarbonyl group were situated closely. As result, intramolecular attack of oxygen occurred much faser than intermolecular attack of fluoride anion. These cyclobutanes containing a hydroxymethyl group may serve as useful intermediates for further functionalization. Using this ring-expansion fluorination method, we synthesized (±)-2-fluorograndisol (**57**) from the sulfonate (**56**).[25]

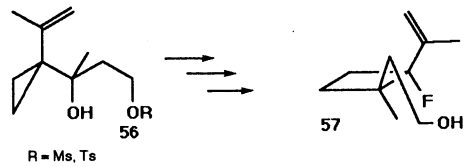


Fig. 3.

In conclusion, homoallyl fluorides or fluorocyclobutanes with multiple substituents or functional groups, which are difficult to provide by any other methods, were selectively synthesized by the current new methods we have developed. Its wide applicability is expected in the selective synthesis of functionalized homoallylic fluorides as well as fluorocyclobutanes.

Experimental

Infrared spectra of neat liquid film samples (unless otherwise noted) were determined on a Shimadzu infrared spectrophotometer IR-430, mass spectra on a Hitachi RMU-6M. and exact mass on a Hitachi M-80. ^{1}H NMR spectra were recorded on a JEOL FX-90Q or EX-90 spectrometer using TMS as an internal standard. ^{19}F NMR spectra were recorded on a JEOL EX-90 or Hitachi R-24F spectrometer using $CFCl_3$ as an internal standard. Multiplicity is designated as s, singlet; d, doublet; t, triplet; q, quartet; m, mutiplet. Preparative TLC plates were prepared with Merck Kiesel Gel PF_{254}. Column chromatography was carried out with silica gel (Wakogel C-300).

Preparation of Poly(hydrogen fluoride)-Pyridine Complex: The $(HF)_n \cdot Py$ was prepared from anhydrous hydrogen fluoride and pyridine according to the reported procedure.[15] All the reactions were carried out in polyethylene test tube as the reaction vessel and $(HF)_n \cdot Py$ was added through a polyethylene syringe.

General Procedure for the Ring-Opening Fluorination of Cyclopropanemethanol Derivertives with $(i\text{-Pr})_2NH$-KHF_2-$(HF)_n \cdot Py$ Complex: Preparation of 4-fluoro-1-phenyl-1-butene (**7**) was representative. 25 ml polyethylene test tube fitted with magnetic stirring bar inside was connected to a nitrogen line. To a suspension of KHF_2 (0.08 g, 1.0 mmol, dried in a microwave oven) in chlorobenzene (1.0 ml) was added a solution of α-phenylcyclopropanemethanol (0.15 g, 1.0 mmol) in 1.0 ml of chlorobenzene and diisopropylamine (0.6 ml), and the whole was stirred for 5 min at 25 °C. The reaction mixture was cooled with ice-water bath and $(HF)_n \cdot Py$ (2.0 ml) was added slowly to the reaction mixture. After stirring at 0 °C for 5 min, the reaction mixture was diluted with ether (5.0 ml) and aqueous KF solution (5.0 ml). The whole was poured into water (10 ml). The water layer was extracted with ether (3×30 ml) and the combined organic layers were washed with saturated aqueous sodium hydrogencarbonate and brine successively, and dried over sodium sulfate. Concentration and purification on preparative TLC (hexane) gave the title compound, 4-fluoro-1-phenyl-1-butene (**7**) (0.11 g, 76%). IR (neat) 3040, 2910, 1595, 1490, 1445, 965, 745, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.61 (ddt, 2H, J=2.40, 5.66, 5.67 Hz), 4.49 (dt, 2H, J=47.30, 5.66 Hz), 6.15 (dt, 1H, J=16.40, 5.67 Hz), 6.49 (d, 1H, J=16.40 Hz), 7.0—7.4 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−219.5; MS m/z (rel intensity in %) 91 (18), 115 (39), 117 (100), 129 (7), 150 (M^+, 63). Found: C, 80.15; H, 7.47%. Calcd for $C_{10}H_{11}F$: C, 79.97; H, 7.38%.

5-Fluoro-2-phenyl-2-pentene (9): IR (neat) 2950, 1595, 1490, 1440, 755, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.06 (d, 3H, J=1.54 Hz), 2.61 (ddt, 2H, J=22.72, 6.48, 6.48 Hz), 4.50 (dt, 3H, J=47.50, 6.48 Hz), 5.77 (tq, 1H, J=6.48, 1.54 Hz), 7.1—7.4 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−219.0; MS m/z (rel intensity in %) 78 (8), 117 (19), 118 (100), 164 (M^+, 13); exact mass spectrum m/z 164.1014. Calcd for $C_{11}H_{13}F$: M, 164.1002.

***trans*-1-Fluoro-4-phenyl-3-octene (11) (Major Isomer):** IR (neat) 2995, 1590, 1490, 1405, 750, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.86 (t, 3H, J=5.40 Hz), 1.1—1.4 (m, 4H), 2.44 (t, 2H, J=7.20 Hz), 2.73 (ddt, 2H, J=22.30, 6.83, 6.84 Hz), 4.49 (dt, 2H, J=47.50, 6.84 Hz), 5.60 (t, 1H, J=6.83 Hz), 7.1—7.4

(m, 5H); ^{19}F NMR ($CDCl_3$) δ=−219.0; MS m/z (rel intensity in %) 91 (8), 117 (18), 118 (100), 164 (26), 206 (M^+, 4); exact mass spectrum m/z 206.1468. Calcd for $C_{14}H_{19}F$: M, 206.1471.

***cis*-1-Fluoro-4-phenyl-3-octene (11) (Minor Isomer):** IR (neat) 2955, 1595, 1495, 1400, 760, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.86 (t, 3H, J=5.40 Hz), 1.1—1.4 (m, 4H), 2.3—2.6 (m, 4H), 4.38 (dt, 2H, J=46.80, 6.83 Hz), 5.54 (t, 1H, J=6.83 Hz); ^{19}F NMR ($CDCl_3$) δ=−219.0; MS m/z (rel intensity in %) 91 (7), 117 (19), 118 (100), 164 (28), 206 (M^+, 4); exact mass spectrum m/z 206.1468. Calcd for $C_{14}H_{19}F$: M, 206.1471.

1-Fluoro-4-methyl-3-dodecene (13): IR (neat) 2800, 2700, 1455, 1370, 1000, and 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87 (t, 3H, J=5.76 Hz), 1.0—1.5 (m, 12H), 1.61 (bs, 3H), 1.9—2.1 (m, 2H), 2.30 (ddt, 2H, J=22.40, 6.48, 6.80 Hz), 4.36 (dt, 2H, J=47.90, 6.48 Hz), 5.65 (t, 1H, J=6.80 Hz); ^{19}F NMR ($CDCl_3$) δ=−218.0; MS m/z (rel intensity in %) 97(29), 102(100), 112(18), 171(1), 200(M^+, 1).

***trans,trans*-6-Fluoro-1-phenyl-1,3-hexadiene (15):** IR (neat) 2910, 1670, 1485, 1445, 740, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.60 (ddt, 2H, J=24.40, 6.84, 6.84 Hz), 4.47 (dt, 2H, J=47.20, 6.84 Hz), 5.6—6.1 (m, 1H), 6.1—7.0 (m, 3H), 7.0—7.5 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−215.2; MS m/z (rel intensity in %) 91 (46), 115 (43), 128 (67), 129 (100), 141 (18), 143 (22), 176 (M^+, 30).

1-Fluoro-4-(1-octynyl)-3-dodecen-5-yne (17): IR (neat) 2900, 2850, 2250, 1715, 1460, 1380, and 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.84 (t, 3H, J=6.84 Hz), 1.0—1.7 (m, 16H), 2.1—2.4 (m, 4H), 2.70 (ddt, 2H, J=23.80, 6.84, 6.84 Hz), 4.44 (dt, 2H, J=46.80, 6.84 Hz), 6.11 (t, 1H, J=6.84 Hz), ^{19}F NMR ($CDCl_3$) δ=−219.0; MS m/z (rel intensity in %) 67 (36), 95 (28), 117 (37), 131 (42), 145 (28), 159 (24), 177 (22), 191 (23), 290 (M^+, 100); exact mass spectrum m/z 290.2431. Calcd for $C_{20}H_{31}F$: M, 290.2411.

4-Fluoro-1-phenyl-1-pentene (19): IR (neat) 3000, 2880, 1600, 1495, 1450, 1385, 1130, 965, 740, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.34 (dd, 3H, J=23.40, 6.50 Hz), 2.48 (dt, 1H, J=20.20, 6.50 Hz), 2.50 (dt, 1H, J=19.90, 6.50 Hz), 4.70 (dtq, 1H, J=48.20, 6.50, 6.50 Hz), 6.15 (dt, 1H, J=16.60, 6.50 Hz), 6.46 (d, 1H, J=16.60 Hz), 7.0—7.4 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−173.2; MS m/z (rel intensity in %) 69 (43), 83 (37), 91 (34), 115 (46), 117 (100), 129 (10), 149 (7), 164 (M^+, 22).

4-Fluoro-1-phenyl-3,3,4-trimethyl-1-pentene (21): IR ($CHCl_3$) 2950, 1600, 1490, 1380, and 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.18 (d, 6H, J=0.70 Hz), 1.35 (d, 6H, J=22.00 Hz), 6.3—6.5 (m, 2H), 7.2—7.5 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−147.7; MS m/z (rel intensity in %) 91 (35), 117 (32), 129 (17), 145 (100), 171 (25), 186 (12), 206 (M^+, 15). Found: C, 81.35; H, 9.28%. Calcd for $C_{14}H_{19}F$: C, 81.51; H, 9.31%.

9-Fluoro-3,6-dimethyl-2,6-nonadien-4-yne (23): IR (neat) 2970, 1440, 1360, and 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.6—1.9 (m, 9H), 2.67 (ddt, 2H, J=24.20, 6.84, 6.84 Hz), 4.46 (dt, 2H, J=47.90, 6.84 Hz), 5.5—5.8 (m, 2H); ^{19}F NMR ($CDCl_3$) δ=−217.5; MS m/z (rel intensity in %) 77 (17), 79 (17), 91 (51), 105 (58), 133 (77), 151 (18), 166 (M^+, 100); exact mass spectrum m/z 166.1133. Calcd for $C_{11}H_{15}F$: M, 166.1158.

8-Fluoro-2,5-dimethyl-1,5-octadien-3-yne (25): IR (neat) 2970, 1440, 1360, and 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.8—2.0 (m, 6H), 2.67 (ddt, 2H, J=23.80, 7.20, 7.20 Hz), 4.49 (dt, 2H, J=47.90, 7.20 Hz), 5.2—5.4 (m, 2H), 5.72 (tq, 1H, J=7.20, 1.10 Hz); ^{19}F NMR ($CDCl_3$) δ=−204.0; MS m/z (rel intensity in %) 77 (16), 91 (31), 104 (11), 119 (64), 137 (11), 152 (M^+, 100).

Methyl (*Z*)-7-Fluoro-4-methyl-4-hepten-2-ynoate (27) (Major Isomer): IR (neat) 2940, 2210, 1715, 1700, 1430, 1250, 1020, and 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.9—2.1 (m, 3H), 1.70 (ddt, 2H, J=25.60, 6.50, 7.20 Hz), 3.82 (s, 3H), 4.48 (dt, 2H, J=47.10, 6.50 Hz), 6.06 (tq, 1H, J=7.20, 1.40 Hz); ^{19}F NMR ($CDCl_3$) δ=−218.8; MS m/z (rel intensity in %) 79 (77), 91 (68), 109 (72), 139 (100), 149 (12), 170 (M^+, 26). Found: C, 63.67; H, 7.10%. Calcd for $C_9H_{11}O_2F$: C, 63.52; H, 6.51%.

Methyl (*E*)-7-Fluoro-4-methyl-4-hepten-2-ynoate (27) (Minor Isomer): IR (neat) 2970, 2220, 1710, 1435, 1260, 1010, and 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.8—1.9 (m, 3H), 1.54 (ddt, 2H, J=24.50, 6.50, 6.50 Hz), 3.79 (s, 3H), 4.46 (dt, 2H, J=46.80, 6.50 Hz), 6.19 (tq, 1H, J=6.50, 1.80 Hz); ^{19}F NMR ($CDCl_3$) δ=−218.4; MS m/z (rel intensity in %) 69 (100), 91 (84), 109 (58), 139 (94), 149 (39), 170 (M^+, 3). Found: C, 63.36; H, 6.53%. Calcd for $C_9H_{11}O_2F$: C, 63.52; H, 6.51%.

1-Fluoro-1-phenyl-3-octene (29): 25 ml polyethylene test tube, fitted with magnetic stirring bar inside was connected to a nitrogen line. $(HF)_n \cdot Py$ (1.0 ml), KHF_2 (0.12 g, 1.5 mmol), and diisopropylamine (0.3 ml) were mixed in THF (1.0 ml) and the mixture was stirred for 30 min at 0 °C. A solution of α-butyl-2-phenylcyclopropanemethanol (**28**) (0.10 g, 0.5 mmol) in THF (1.0 ml) was slowly added to the reaction mixture at 0 °C and the whole mixture was stirred for additional 1 h at 25 °C. After the consumption of the substrate (monitored with TLC), the reaction mixture was diluted with ether (5.0 ml) and aqueous potassium fluoride solution (5.0 ml). Extraction, and concentration gave an oil, which was purified by column chromatography to give 1-fluoro-1-phenyl-3-octene (**29**) (0.07 g, 73%). IR (neat) 3000, 2940, 2900, 2830, 1490, 1445, and 965 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.86 (t, 3H, J=6.10 Hz), 1.0—1.4 (m, 6H), 1.8—2.1 (m, 2H), 2.55 (ddd, 2H, J=26.90, 6.84, 6.84 Hz), 5.38 (dt, 1H, J=43.90, 6.50 Hz), 5.44 (dt, 2H, J=4.30, 6.50 Hz), 7.2—7.4 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−171.1; MS, m/z 91 (15), 109 (100), 129 (25), 143 (11), 186 (7), 206 (M^+, 7); exact mass spectrum m/z 206.1462. Calcd for $C_{14}H_{19}F$: M, 206.1466.

5-(4-Fluorobutyloxy)-2-phenyl-2-pentene:[16] 25 ml polyethylene test tube fitted with magnetic stirring bar inside was connected to a nitrogen line. To a suspension of KHF_2 (0.12 g, 1.5 mmol dried with microwave oven) in THF (0.5 ml) was added 1-cyclopropyl-1-phenylethanol (0.08 g, 0.5 mmol) in 0.5 ml of THF and the suspension was stirred for 10 min at 25 °C. $(HF)_n \cdot Py$ was added slowly to the suspension at 0 °C and the whole was stirred for 1 h at that temperature. The reaction mixture was diluted with ether (5.0 ml) and aqueous potassium fluoride (5.0 ml) and the entire mixture was poured into ice water. The organic layer was separated and the water layer was extracted with ethyl acetate (3×30 ml) then the combined organic layers were washed with aqueous sodium hydrogencarbonate and brine successively. The organic layer was dried over sodium sulfate and concentrated. Purification of the crude oil gave the title compound as colorless oil (0.07 g, 65%). IR (neat) 2950, 2870, 1595, 1480, 1445, 1360, 1110, 755, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.5—1.9 (m, 4H), 2.0—2.1 (m, 3H), 2.48 (dt, 2H, J=6.84, 6.84 Hz), 3.49 (t, 2H, J=4.68 Hz), 3.51 (t, 2H, J=6.84 Hz), 4.46 (dt, 2H, J=47.50, 5.94 Hz), 5.77 (tq, 1H, J=6.84, 1.81 Hz), 7.1—7.4 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−218.7; MS m/z (rel intensity in %) 55(46),

74(27), 91(13), 118(70), 131(100), 146(20), 236(M^+, 5); exact mass spectrum m/z 236.1585. Calcd for $C_{15}H_{21}OF$: M, 236.1577.

General Procedure for the Ring-Expansion Fluorination of 1-Substituted Cyclopropanemethanol Derivatives with (i-Pr)$_2$NH-KHF$_2$-(HF)$_n$·Py-Complex: Preparation of 1-fluoro-1,2-dimethyl-t-2-phenylcyclobutane (**37**) was representative. 25 ml polyethylene test tube fitted with magnetic stirring bar inside was connected to a nitrogen line. To a suspension of KHF_2 (0.12 g, 1.5 mmol dried in microwave oven) in dichloromethane (0.5 ml) was added α,1-dimethyl-α-phenylcyclopropanemethanol (**36**) (0.09 g, 0.5 mmol) in 0.5 ml of dichloromethane and diisopropylamine (0.3 ml), and the suspension was stirred for 10 min at 25 °C. The suspension was cooled to −20 °C and $(HF)_n$·Py (1.0 ml) was slowly added into the mixture with cooling. The reaction completed within 5 min and the mixture was diluted with ether (5.0 ml) and aqueous potassium fluoride solution (5.0 ml). The water layer was extracted with ether (3×30 ml), and the combined organic layers were washed with aqueous sodium hydrogencarbonate and brine successively. Drying and concentration followed by chromatographic purification gave the r-1-fluoro-1,2-dimethyl-t-2-phenylcyclobutane (**37**) (0.06 g, 62%). IR (neat) 3000, 1495, 1445, 1380, 1260, and 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.12 (d, 3H, J=22.70 Hz), 1.51 (d, 3H, J=2.20 Hz), 1.5—2.8 (m, 4H), 7.0—7.5 (m, 5H), ^{19}F NMR ($CDCl_3$) δ=−136.9; MS m/z (rel intensity in %) 78 (8), 103 (11), 117 (22), 118 (100), 150 (6), 178 (M^+, 1). Found: C, 80.72; H, 8.55%. Calcd for $C_{12}H_{15}F$: C, 80.86; H, 8.48%.

1-Fluoro-1-methyl-t-2-phenylcyclobutane (35): IR (neat) 3000, 1605, 1495, 1380, 1255, 1115, 920, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.06 (d, 3H, J=22.30 Hz), 1.0—2.6 (m, 4H), 3.80 (dt, 1H, J=20.90, 10.40 Hz), 7.0—7.4 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−116.7; MS m/z (rel intensity in %) 78 (4), 104 (100), 136 (7), 164 (M^+, 2).

2-Butyl-1-fluoro-1-methyl-t-2-phenylcyclobutane (39): IR (neat) 2950, 2850, 1605, 1450, 1380, 1175, and 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.79 (t, 3H, J=7.90 Hz), 0.7—1.4 (m, 6H), 1.09 (d, 3H, J=21.60 Hz), 1.6—2.8 (m, 4H), 7.0—7.5 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−138.7; MS m/z (rel intensity in %) 58 (57), 77 (18), 83 (22), 91 (19), 118 (100), 160 (10), 220 (M^+, 2). Found: C, 81.56; H, 9.63. Calcd for $C_{15}H_{21}F$: C, 81.77; H, 9.61%.

1-Fluoro-1,c-2-diphenylcyclobutane (41) (Major Isomer): IR ($CHCl_3$) 3050, 2970, 1605, 1500, 1450, 890, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.0—3.0 (m, 4H), 3.6—4.2 (m, 1H), 7.1—7.6 (m, 10H); ^{19}F NMR ($CDCl_3$) δ=−163.7; MS m/z (rel intensity in %) 78 (11), 91 (9), 104 (100), 122(12), 226 (M^+, 3).

1-Fluoro-1,t-2-diphenylcyclobutane (41) (Minor Isomer): IR ($CHCl_3$) 3050, 2970, 1600, 1495, 1445, 1070, 750, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.8—2.9 (m, 4H), 4.16 (ddd, 1H, 20.90, 9.00, 9.40 Hz), 6.7—7.3 (m, 10H); ^{19}F NMR ($CDCl_3$) δ=−118.2; MS m/z (rel intensity in %) 58 (73), 83 (25), 91 (15), 104 (100), 122 (13), 226 (M^+, 3).

1-Fluoro-2-methyl-1,t-2-diphenylcyclobutane (43) (Major Isomer): IR (neat) 2980, 1600, 1495, 1445, 760, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.70 (d, 3H, J=3.60 Hz), 2.0—3.2 (m, 4H), 6.8—7.5 (m, 10H); ^{19}F NMR ($CDCl_3$) δ=−144.8; MS m/z (rel intensity in %) 78 (7), 117 (36), 118 (100), 204 (13), 205 (7), 220 (4), 240 (M^+, 2). Found: C, 85.29; H, 7.11%. Calcd for $C_{17}H_{17}F$: C, 84.96; H, 7.13%.

1-Fluoro-2-methyl-1,c-2-diphenylcyclobutane (43) (Minor Isomer): IR ($CHCl_3$) 2990, 1605, 1495, 1445, 770, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.22 (s, 3H), 2.6—3.2 (m, 4H), 7.1—7.6 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−149.1; MS m/z (rel intensity in %) 78 (9), 117 (29), 118 (100), 205 (8), 220 (40), 40 (M^+, 1). Found: C, 84.86; H, 7.15%. Calcd for $C_{17}H_{17}F$: C, 84.96; H, 7.13%.

1-Fluoro-c-2-hydroxymethyl-1-methyl-2-phenylcyclobutane (49): IR (neat) 3630, 3450, 3000, 2890, 1605, 1495, 1380, 1030, 880, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20 (dd, 3H, J=23.60, 1.20 Hz), 1.2—2.8 (m, 5H), 3.97 (d, 2H, J=5.70 Hz), 7.0—7.4 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−138.6; MS m/z (rel intensity in %) 55 (100), 69 (56), 95 (31), 105 (27), 129(15), 193(M^+−1, 6). Found: C, 74.03; H, 7.87%. Calcd for $C_{12}H_{15}OF$: C, 74.20; H, 7.78%.

1-Fluoro-c-2-hydroxymethyl-1-phenylcyclobutane (51) (Major Isomer): IR (neat) 3640, 3400, 2980, 1500, 1450, 1300, 1025, 760, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.74 (s, 3H), 1.2—3.0 (m, 4H), 3.60 (bs, 1H), 3.67 (d, 1H, J=11.60 Hz), 4.03 (d, 1H, J=11.60 Hz), 7.2—7.5 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−144.8; MS m/z (rel intensity in %) 83(27), 91(20), 105(22), 115(29), 122(100), 129(41), 193 (M^+−1, 2). Found: C, 73.91; H, 7.90%. Calcd for $C_{12}H_{15}OF$: C, 74.20; H, 7.78%.

1-Fluoro-t-2-hydroxymethyl-2-methyl-1-phenylcyclobutane (51) (Minor Isomer): IR (neat) 3600, 3400, 2980, 2500, 1500, 1450, 1030, 1005, 765, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.38 (d, 3H, J=3.10 Hz), 1.40 (bs, 1H), 1.6—3.0 (m, 4H), 3.24 (bs, 2H), 7.2—7.5 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−143.7; MS m/z (rel intensity in %) 55 (100), 83 (53), 115 (37), 122 (41), 129 (40), 144 (18), 193 (M^+−1, 4). Found: C, 73.84; H, 7.86%. Calcd for $C_{12}H_{15}OF$: C, 74.20; H, 7.78%.

Ethyl (2R*)-2-(2-Fluoro-2-methyl-1-phenylcyclobutyl)-2-hydroxyacetate (53): IR (neat) 3570, 3000, 1730, 1605, 1495, 1450, and 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.11 (t, 3H, J=7.20 Hz), 3.72 (d, 3H, J=20.60 Hz), 1.8—2.2 (m, 2H), 2.4—2.8 (m, 2H), 3.00 (dd, 1H, J=5.40, 4.30 Hz), 4.01 (q, J=7.20 Hz), 4.93 (d, 1H, J=5.40 Hz), 7.1—7.4 (m, 5H); ^{19}F NMR ($CDCl_3$) δ=−132.8; MS m/z (rel intensity in %) 105 (34), 133 (100), 160 (31), 189 (35), 203 (26), 246 (M^+−20, 29). Found: C, 67.87; H, 7.23. Calcd for $C_{15}H_{19}O_2F$: C, 67.65; H, 7.19%.

Ethyl (2S*)-2-(2-Fluoro-2-methyl-1-phenylcyclobutyl)-2-hydroxyacetate (55) (Inseparable Isomeric Mixture.): IR (neat) 3570, 3000, 1725, 1600, 1490, 1450, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.84 (t, 3H, J=7.00 Hz), 1.32 (d, 3H, J=25.1 Hz), 1.8—2.3 (m, 2H), 2.4—2.8 (m, 2H), 2.9—3.0 (m, 1H), 3.6—3.9 (m, 2H), 4.7—4.8 (m, 1H), 7.0—7.5 (m, 5H), ^{19}F NMR ($CDCl_3$) δ=−135.7 and −132.8; MS m/z (rel intensity in %) 70 (34), 105 (100), 129 (71), 132 (47), 133 (47), 143 (52), 151 (44), 186 (77), 189 (73), 246 (M^+−20, 15).

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