Practical, Stereocontrolled Synthesis of Polyfluorinated Artificial Pyrethroids

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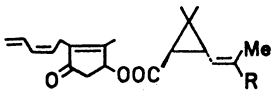
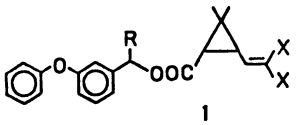
Practical and stereocontrolled approaches to polyfluorinated synthetic pyrethroids based on aldehyde addition of CF_3CCl_2ZnCl are described. The zinc reagent was allowed to react with 3-formyl-2,2-dimethylcyclopropanecarboxylates (**6**) to give the corresponding adducts. These were acetylated and then reduced again with zinc to afford (1*R**, 3*S**)-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylates (**12**). The (1R*, 3R*)-isomer was derived from 2,2-dichloro-1,1,1-trifluoro-5-methyl-4-hexen-3-ol by diazoacetylation, Cu(II)-catalyzed intramolecular carbene addition, and finally by the zinc reduction. An alternative access to **12** and its halogen homologues of the (*Z*)-pyrethroids involves addition of 1-halo-2,2-difluoroethenyl group across the CHO group of **6** and subsequent regio- and stereoselective halogenation.

In spite of high insecticidal activity and low mammalian toxicity, use of such natural pyrethroids as pyrethrin I and pyrethrin II has been limited owing to rapid biological degradation and poor photo-oxidative stability.[1] Since the discovery of a photo-stable and more potent analogue permethrin (**1a**), a great deal of effort has been made in search for new highly potent artificial pyrethroids, and a number of derivatives including cypermethrin (**1b**) and deltamethrin (**1c**) have been developed and used currently.



R = Me : Pyrethrin I

R = COOMe : Pyrethrin II



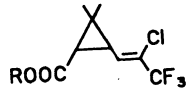
1

a : X = Cl, R = H (permethrin)

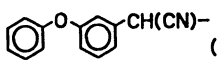
b : X = Cl, R = CN (cypermethrin)

c : X = Br, R = CN (deltamethrin)

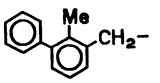
New fluorinated analogues having a $CH=C(Cl)CF_3$ group commonly in place of $CH=CCl_2$ moiety are found recently to exhibit remarkably enhanced activity: Typical examples are cyhalothrin (**2a**)[2] and bifenthrin (**2b**),[3] which show, in addition to intensified insecticidal activity, 50 to 100 fold acaricidal activity as compared to **1**. Although several synthetic methods for **2** are reported to date,[2-4] the stereochemical control yet remained unsettled. Described herein is practical and stereocontrolled synthesis of **2** based on aldehyde-addition of CF_3CCl_2ZnCl reagent.[5]



2

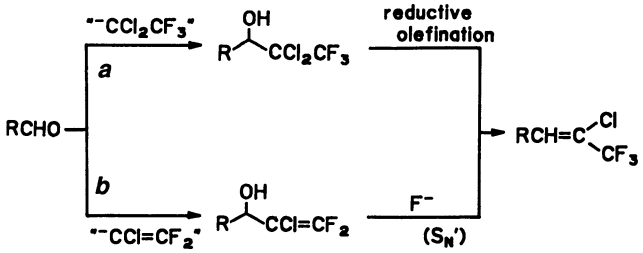
a: R = 

(cyhalothrin)

b: R = 

(bifenthrin)

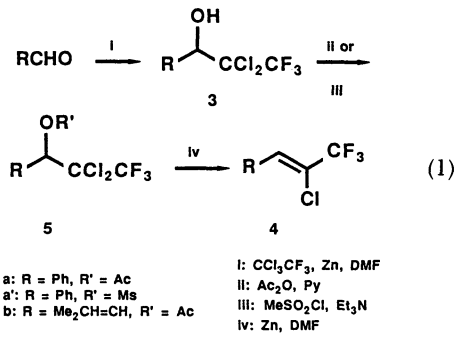
Retrosynthetic analysis of **2** led us to a new strategy (Scheme 1) which is characterized by a new transformation of CHO group to $CH=C(Cl)CF_3$ moiety through two routes as summarized in Scheme 1. The one involves the addition of $^-CCl_2CF_3$ to an aldehyde carbonyl and subsequent reductive β-elimination (route *a*). The other will be realized by the addition of $^-CCl=CF_2$ followed by S_N'-type fluorination (route *b*).



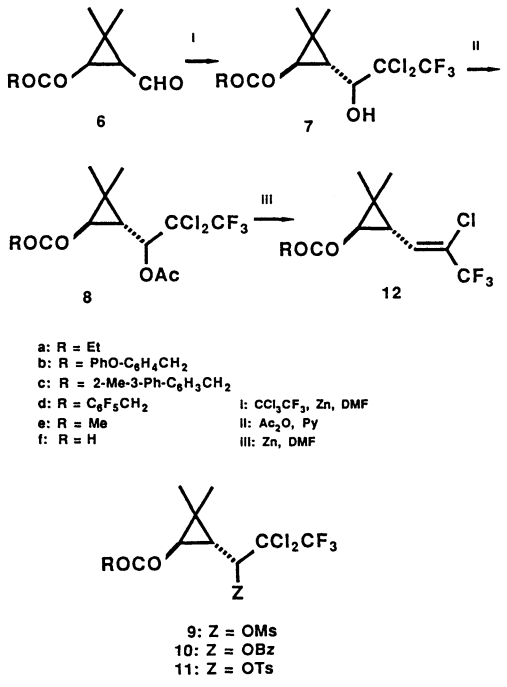
Scheme 1.

Results and Discussion

Stereocontrolled Synthesis of 2. The first step of the route *a* is now readily achieved by the recently found zinc carbenoid reagent CF_3CCl_2ZnCl.[6] The second step was studied benzaldehyde-CCl_2CF_3 adduct **3a** as the model. Reduction of **3a** under the standard conditions (zinc in acetic acid) gave the desired olefin **4a** in only 33% yield in contrast to the related reduction in permethrin synthesis.[1] The yield of **4a** was improved to 84% by the reduction of the acetate **5a** in *N*,*N*-dimethylformamide (DMF). The mesylate **5a'** equally underwent the reductive olefination to give **4a** in 65% yield. Similarly, the acetate **5b** derived from 3-methyl-2-butenal was reduced to a diene **4b**, another precursor of our target compound **2**.



These findings were successfully applied to 3-formyl-2,2-dimethylcyclopropanecarboxylates **6**[7] which were readily prepared by ozonolysis[8] of the corresponding chrysanthemates (81—89% yield). The addition of CF_3CCl_2ZnCl to **6** took place in good yields (Scheme 2 and Table 1). The adducts **7** were acetylated, and the resulting acetates **8** were transformed to **12** whose stereochemistry was proved to be uniform (1R*, 3S*) with the Z/E ratio of 86 : 14 to 93 : 7. As the alcohols **7** consisted of ca. 1 : 1 mixture of two diastereomers, each isomer was separated by column chromatography. To check the stereochemical course of the reductive olefination, each diastereomer was converted into **12**, whose Z/E ratios were almost the same and thus totally independent of the configuration of the OH group in **7**. The mesylate (**9**), benzoate (**10**), and tosylate (**11**) of **7** also are potential precursors of **12**. Results are summarized in Table 1.



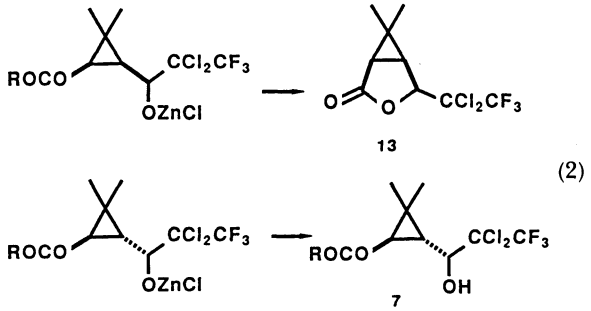
Scheme 2.

Table 1. Transformation of **6** to **12**

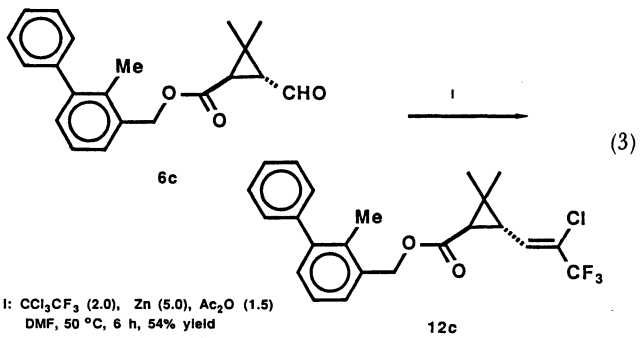
Aldehyde	**7** (yield/%)	**8** (yield/%)	**12** (yield/%)
6a[a]	58	93	86[d]
6b[b]	74	98	74[d]
6c[b]	86	100	95[e]
6d[b]	71	—	—
6e[c]	75	—	—

a) Trans/cis=4 : 1. b) Trans/cis=6 : 1. c) Trans/cis=100 : 0. d) Z/E=6 : 1. e) Z/E=8 : 1.

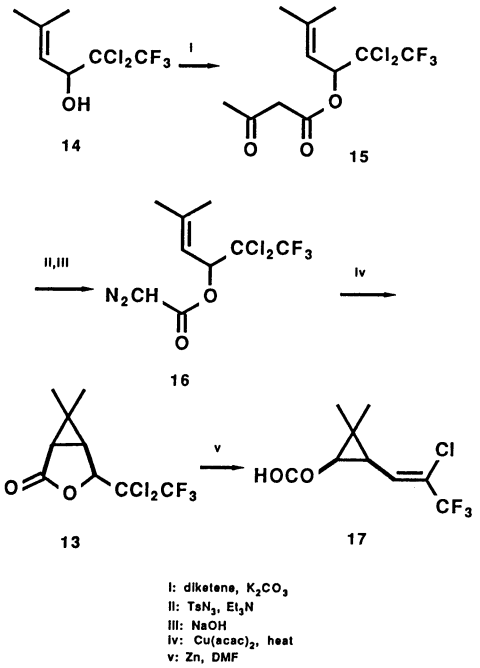
It should be noted that, though trans/cis isomeric mixture (4 to 6 : 1) of **6** was employed, only *trans*-**6** gave the adduct **7**. The CF_3CCl_2 adducts of the *cis*-**6** apparently underwent lactonization under the reaction conditions to give a bicyclic lactone **13** (<10% yield) which was isolated in some cases. The lactone **13** was not produced from pure *trans*-**6e**. Thus, the correlation of *trans*-**6**→**7** and *cis*-**6**→**13** is disclosed. Since *cis*-**6** is easily epimerized to the trans-isomer under the basic conditions,[9] a method is now established for control of the trans-configuration on the cyclopropane ring.



A one-step transformation of **6c** to **12c** (*trans*-bifenthrin) was effected with the $CF_3CCl_3/Zn/Ac_2O$ reagent (Eq. 3)[10] Although the same transformation was previously carried out by the Wittig type olefination using 1,1,1-trichloro-2,2,2-trifluoroethane, triphenylphosphine (2 mol), and zinc,[4c] the method disclosed herein is apparently more practical in view of low cost of reagents and much simpler separation technique.



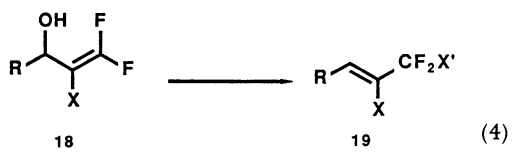
The (1R*,3R*)-isomer of **2** was synthesized stereospecifically according to Scheme 3.[11] The alcohol **14**[6] was treated with diketene in the presence of potassium carbonate to give the acetylacetate **15** (88% yield), which was converted into the diazoacetate **16** by treatment with a slight excess of *p*-toluenesulfonyl (tosyl) azide and triethylamine followed by alkaline hydrolysis (82% yield from **15**). Intramolecular cyclopropanation of **16** was successfully performed with copper(II) acetylacetonate catalyst to give the lactone **13** in 75%



Scheme 3.

yield. Finally, reduction with zinc afforded the cis-acid **17** in 84% yield.

Regio- and Stereocontrolled Halogenation of 1-Substituted 2-Chloro-3,3-difluoro-2-propen-1-ols. In order to effect the transformation of route *b* in Scheme 1, we studied fluorination of the adducts **18** which are readily accessible by the reaction of aldehydes with $CCl_3CF_3/Zn/AlCl_3$ (cat) reagent[10] or by polyfluoroethenylsilane/F^- (catalyst) reagent.[12] Although several reagents for fluorinating alcohols have been developed,[13] the reaction applied to allylic alcohols is problematic due to side reactions like dehydration and lack of regioselectivity.[13a,14] In contrast, polyfluoroallylic alcohols **18** are found to be fluorinated with diethylaminosulfur trifluoride (DAST) under high regio- and stereocontrol (Eq. 4). When 1,1,2-trifluoro-1-tridecen-3-ol (**18a**) was treated with DAST, quantitative formation of 1,1,1,2-tetrafluoro-2-tridecene (**19a**) free of any stereo- or regioisomers was demonstrated by ^{19}F NMR. The configuration of **19a** was confirmed to be Z as judged by $^3J_{H\text{-}F}$ value (33 Hz).[15] The fluoride attack at the difluoromethylene carbon is particularly facilitated by highly electronegative fluorine substituent, and thus smooth and regioselective nucleophilic attack by fluoride ion is achieved under concomitant



(4)

a: R = n-$C_{10}H_{21}$, X = F
b: R = n-$C_{10}H_{21}$, X = Cl
c: R = c-C_6H_{11}, X = Cl
d: R = Ph, X = Cl

no superscript : X' = F
': X' = Cl
'': X' = Br

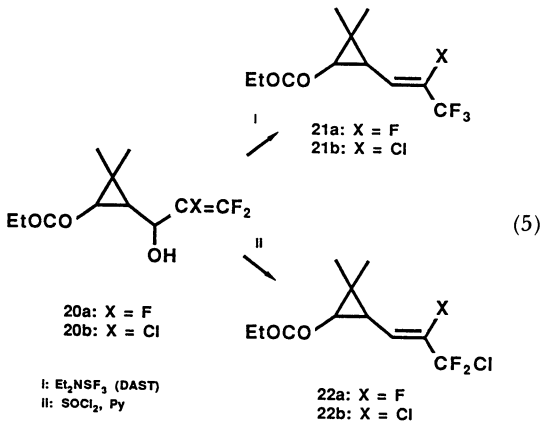
Table 2. Halogenation of **18**

Alcohol	Reagent[a] Solvent	Condition	Product[b] (yield/%)[c]
18a	DAST (1.0)/CH_2Cl_2	−78 °C—r.t., 0.2 h	**19a** (90)
18a	$SOCl_2$ (1.0)/Et_2O[e]	r.t., 3 h	**19a'** (85)
18b	DAST (1.0)/CH_2Cl_2	−78 °C—r.t., 0.3 h	**19b** (70)
18b	$SOCl_2$ (1.4)/Et_2O	50 °C, 13 h[d]	**19b'** (90)
18b	$SOBr_2$ (1.2)/Et_2O	50 °C, 4 h[d]	**19b''** (84)
18b	PBr_3 (1.05)/Et_2O	r.t., 1.5 h; 35 °C, 13 h	**19b''** (67)
18c	$SOCl_2$ (1.0)/Et_2O	50 °C, 18 h[d]	**19c'** (75)
18d	$SOCl_2$ (1.1)/Et_2O	50 °C, 12 h[d]	**19d'** (79)

a) Values in the parentheses refer to molar ratio to **18**. b) Only (Z)-isomers were isolated. c) Isolated yields. d) Carried out in a sealed tube. e) Pyridine (2.0 mol) was added.

deoxygenation.[16] Chlorination and bromination of the allylic alcohols **18** also proceeded with high regio- and stereoselectivity to allord (Z)-2-alkenes **19'** and **19''**, which should have been yielded by a cyclic S_Ni'-mechanism. The stereochemistry was determined again by ^1H and/or ^{13}C NMR spectrometry.[17] Results are summarized in Table 2. Thus, halogen analogues of **3** grew readily accessible by the two-step strategy which involves the aldehyde addition of $^-CCl{=}CF_2$ group and subsequent regio- and stereoselective halogenation.

Halogen analogues of **2** such as **21** and **22** were also shown to have high insecticidal activity.[2a,4f] The regio- and stereocontrolled halogenation disclosed above was applied successfully to the synthesis of these halogen analogues as well. The $CX{=}CF_2$ adducts **20** were prepared from **6** by the addition of trifluoroethenyllithium[18] or by the fluoride ion mediated addition of polyfluoroethenylsilanes[12] followed by acid hydrolysis. Fluorination or chlorination of **20** afforded respectively **21** or **22** under high regiocontrol (Eq. 5).



(5)

In summary, the method reported in this paper provides facile ways to polyfluorinated artificial pyrethroids under high stereocontrol. Practicability of these processes deserves particular emphasis: Most of reagents are commercially available, and the reaction conditions of each step are mild enough.

Experimental

Experimental apparatus and instrumental facilities are the same as those of the preceding paper.

2,2-Dichloro-3,3,3-trifluoro-1-phenylpropyl Methanesulfonate (5a'). Triethylamine (0.42 ml, 3 mmol) and methanesulfonyl chloride (0.155 ml, 2.0 mmol) were successively added to an ethereal solution (10 ml) of 2,2-dichloro-3,3,3-trifluoro-1-phenyl-1-propanol (**3a**, 0.26 g, 1.0 mmol) at 0 °C, and the resulting mixture was stirred for 2 h at 0 °C and for 1 h at room temperature. Workup and purification by preparative TLC (CH_2Cl_2-hexane 1 : 1) gave **5a'** (0.29 g, 85% yield) as a viscous colorless oil. ^1H NMR ($CDCl_3$) δ=2.65 (s, 3 H), 6.00 (s, 1 H), 7.2—7.9 (m, 5 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.0 (s); IR 1369, 1191, 962, 900, 819, 740, 701 cm^{-1}; MS *m/z* (rel intensity) 338 (M^++2, trace), 336 (M^+, 4), 185 (51), 107 (100), 79 (26), 77 (22), 51 (13).

Found: C, 35.56; H, 2.70%. Calcd for $C_{10}H_9Cl_2F_3O_3S$: C, 35.63; H, 2.69%.

4-Acetoxy-5,5-dichloro-6,6,6-trifluoro-2-methyl-2-hexene (5b). A mixture of 5,5-dichloro-6,6,6-trifluoro-2-methyl-2-hexen-4-ol (**3b**, 0.116 g, 0.49 mmol), acetic anhydride (0.2 ml), and pyridine (0.2 ml) was stirred for 8 h at room temperature. Concentration in vacuo followed by preparative TLC (CH_2Cl_2-hexane 1 : 1) gave **5b** (0.131 g, 96% yield) as a colorless oil. ^1H NMR ($CDCl_3$) δ=1.83 (s, 6 H), 2.10 (s, 3 H), 5.28 (d, *J*=9.3 Hz, 1 H), 6.08 (d, *J*=9.3 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.1 (s); IR 1767, 1254, 1208, 1190, 1024 cm^{-1}; MS *m/z* (rel intensity) 280 (M^++2, trace), 278 (M^+, trace), 183 (10), 85 (100), 43 (88), 41 (10).

Found: C, 38.73; H, 3.94%. Calcd for $C_9H_{11}Cl_2F_3O_2$: C, 38.73; H, 3.97%.

2-Chloro-1,1,1-trifluoro-5-methyl-2,4-hexadiene (4b). Zinc powder (36 mg, 0.55 mmol) and copper(I) chloride (1 mg) were added to a solution of **5b** (0.142 g, 0.51 mmol), and the whole was stirred for 6 h at 50 °C before quenching with water (2 ml) and 3 drops of conc hydrochloric acid. Extraction with pentane (4×3 ml), drying over magnesium sulfate, followed by careful concentration at 0 °C under reduced pressure gave **4b** (77 mg, 82% yield) as a colorless oil which consisted of (Z)- and (E)-isomers in a ratio of 85 : 15. ^1H NMR ($CDCl_3$) δ=1.87 (s, 3 H), 1.96 (s, 3 H), 6.13 (d, *J*=11.1 Hz, 1 H), 7.01 (d, *J*=11.1 Hz, 1 H) for the (Z)-isomer, δ=6.83 (d, *J*=11.1 Hz, 1 H) for the (E)-isomer, ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−69.0 (s) for the (Z)-isomer and −62.1 (s) for the (E)-isomer.

A Typical Procedure for the Preparation of 2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylates. To an ethereal solution (10 ml) of 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarbonyl chloride[8] (2.80 g, 15.0 mmol) was added (2-methyl-3-phenylphenyl)methanol (2.97 g, 15.0 mmol) dissolved in pyridine (1.5 ml) and diethyl ether (10 ml), and the whole was stirred for 3 h at room temperature. Workup and purification by column chromatography (CH_2Cl_2-hexane 1 : 2) gave (2-methyl-3-phenylphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate (0.29 g, 85% yield) as a colorless viscous oil. ^1H NMR ($CDCl_3$) δ=1.14 (s, 3 H), 1.29 (s, 3 H), 1.54 (d, *J*=5 Hz, 1 H), 1.71 (s, 6 H), 2.17 (dd, *J*=5 and 8 Hz, 1 H), 2.22 (s, 3 H), 4.94 (d, *J*=8 Hz, 1 H), 5.20 (s, 3 H); IR 1733, 1160, 764, 707 cm^{-1}; MS *m/z* (rel intensity) 348 (trace, M^+), 182 (21), 181 (94), 166 (35), 165 (28), 123 (100), 81 (23).

Found: C, 82.52; H, 8.14%. Calcd for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10%.

According to the similar procedure, following esters were prepared and characterized spectrometrically.

(3-Phenoxyphenyl)methyl 2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate: 98% yield as a trans/cis mixture. ^1H NMR ($CDCl_3$) δ=1.12 (s, 3 H), 1.24 (s, 3 H), 1.42 (d, *J*=5 Hz, 1 H), 1.69 (s, 6 H), 2.04 (dd, *J*=5 and 8 Hz, 1 H), 4.85 (d, *J*=8 Hz, 1H), 5.04 (s, 2 H), 6.8—7.4 (m, 9 H) for the trans isomer, δ=1.18 (s, 3 H), 1.23 (s, 3 H), 1.69 (s, 6 H), 5.03 (s, 2 H), 5.33 (d, *J*=8 Hz, 1 H), 6.8—7.4 (m, 9 H) for the cis isomer. IR 1732, 1591, 1492, 1260, 1219, 1160, 694 cm^{-1}.

(Pentafluorophenyl)methyl 2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate: 85% yield. ^1H NMR ($CDCl_3$) δ=1.13, 1.19, 1.25, 1.26 (s, totally 6 H), 1.37 (d, *J*=5 Hz, 1 H), 2.05 (dd, *J*=5 and 8 Hz, 1 H), 4.85 and 5.27 (br d, *J*=8 Hz, totally 1 H), 6.32 and 6.33 (s, totally 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−142 (m, 2 F), −153 (m, 1 F), −162 (m, 2 F); IR 1736, 1527, 1509, 1153, 1133 cm^{-1}.

A Typical Procedure for the Preparation of 3-Formyl-2,2-dimethylcyclopropanecarboxylates. Ozone was bubbled into an ethyl acetate (10 ml) solution of (2-methyl-3-phenylphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropanecarboxylate (0.70 g, 2.0 mmol) at −78 °C until the solution became pale blue. Excess ozone and the ozonide were reduced by addition of dimethyl sulfide (1 ml), and the reaction mixture was allowed to warm to room temperature. Concentration under reduced pressure followed by purification by column chromatography (CH_2Cl_2-hexane 1 : 1) afforded (2-methyl-3-phenylphenyl)methyl 3-formyl-2,2-dimethylcyclopropanecarboxylate **6c** (0.59 g, 92% yield) as a colorless viscous oil. The trans/cis ratio was estimated to be 6 : 1 by ^1H NMR analysis. ^1H NMR (400 MHz, $CDCl_3$) δ=1.31 (s, 3 H), 1.36 (s, 3 H), 2.22 (s, 3 H), 2.53 (d, *J*=1.5 Hz, 1 H), 2.53 (s, 1 H), 5.23 (s, 2 H), 7.23—7.44 (m, 8 H), 9.59 (dd, *J*=1.1 and 2.5 Hz, 1 H) for the trans-isomer. δ=1.27 (s, 3 H), 1.58 (s, 3 H), 1.88 (dd, *J*=6.5 and 8.6 Hz, 1 H), 2.20 (d, *J*=8.6 Hz, 1 H), 2.23 (s, 3 H), 5.28 (s, 3 H), 7.23—7.44 (m, 8 H), 9.79 (d, *J*=6.5 Hz, 1 H) for the cis-isomer. IR 1730, 1710, 1233, 1164, 1112, 763, 704 cm^{-1}; MS *m/z* (rel intensity) 322 (M^+, trace), 182 (18), 181 (100), 180 (74), 179 (16), 178 (12), 167 (11), 166 (56), 165 (67), 152 (10), 97 (61), 43 (12), 41 (36).

Found: C, 77.97; H,6.92%. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88%.

By the similar procedure, **6b** and **6d** were prepared.

(3-Phenoxyphenyl)methyl 3-Formyl-2,2-dimethylcyclopropanecarboxylate (6b): 82% yield. ^1H NMR ($CDCl_3$) δ=1.29 (s, 3 H), 1.32 (s, 3 H), 2.46 (ABq, 2 H), 5.06 (s, 2 H), 6.8—7.5 (m, 9 H), 9.56 (dd, *J*=1.8 and 1.8 Hz, 1 H) for the trans isomer, δ=1.8—2.3 (m, 2H), 9.73 (d, *J*=6.7 Hz, 1 H) for the cis isomer. IR 1732, 1711, 1588, 1492, 1258, 1215, 1167, 693 cm^{-1}; MS *m/z* (rel intensity) 325 (M^++1, 2), 324 (M^+, 21), 184 (20), 183 (100), 97 (40), 77 (10), 41 (10).

Found: C, 74.08; H, 6.31%. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21%.

(Pentafluorophenyl)methyl 3-Formyl-2,2-dimethylcyclopropanecarboxylate (6d): 89% yield. ^1H NMR ($CDCl_3$) δ=1.30 (s, 3 H), 1.36 (s, 3 H), 2.4—2.6 (m, 2 H), 5.15—5.25 (m, 2 H), 9.58 (d, *J*=3.0 Hz, 1 H) for the trans isomer, δ=1.55 (s, 3 H), 1.86 (dd, *J*=6.0 and 8.5 Hz, 1 H), 2.11 (d, *J*=8.5 Hz, 1H), 9.72 (d, *J*=6.0 Hz, 1 H) for the cis isomer. ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−141.8 (m, 2 F), −152.2 (m, 1 F), −161.3 (m, 2 F); IR 1740, 1712, 1528, 1512, 1160, 1133, 1056, 946 cm^{-1}; MS *m/z* (rel intensity) 294 (M^++1, 2), 293 (M^+, 11), 181

(100), 113 (11), 97 (90), 69 (10), 67 (14), 43 (17), 41 (37).

Ethyl (1*R,3*S**)-3-(2,2-Dichloro-3,3,3-trifluoro-1-hydroxypropyl)-2,2-dimethylcyclopropanecarboxylate (7a). A Typical Procedure for the Reaction of 6 with a CCl_3CF_3/Zn Reagent.** To a DMF (1 ml) solution of **6a** (trans/cis 4 : 1 mixture, 0.174 g, 1.0 mmol) were added zinc powder (96 mg, 1.47 mmol) and 1,1,1-trichloro-2,2,2-trifluoroethane (0.36 ml, 3.0 mmol) at 0 °C. The solution was stirred for 2 h at 0 °C and for 10 h at 50 °C, then treated with sat ammonium chloride aq solution (2 ml), and extracted with diethyl ether (3×2 ml). The combined ethereal extract was dried over magnesium sulfate and concentrated under reduced pressure to give a crude product. Purification by preparative TLC (CH_2Cl_2-hexane 1 : 1) afforded **7a** (54: 46 diastereomeric mixture, 0.188 g, 58% yield) as a viscous colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ=1.22 (s, 3 H), 1.25 (s, 3 H), 1.29 (t, J=7.2 Hz, 3 H), 1.69 (d, J=5.8 Hz, 1 H), 1.94 (dd, J=5.8 and 8.9 Hz, 1H), 2.63 (br s, 1 H), 3.82 (br d, J=8.9 Hz, 1 H), 4.10—4.20 (m, 2 H) for the major isomer, δ=1.26 (t, J=7.2 Hz, 3 H), 1.30 (s, 3 H), 1.33 (s, 3 H), 1.70 (d, J=5.4 Hz, 1 H), 1.82 (dd, J=5.4 and 9.6 Hz, 1 H), 2.43 (br d, 1 H), 3.82 (br d, J=9.6 Hz, 1 H), 4.10—4.20 (m, 2 H) for the minor isomer; ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.3 (s) for the major isomer, −74.7 (s) for the minor isomer. IR 3465, 1710, 1260, 1200 cm^{-1}; MS m/z (rel intensity) 277 (11), 197 (13), 142 (11), 141 (100), 125 (16), 113 (59), 98 (20), 97 (18), 95 (30), 69 (18), 67 (22), 59 (29), 55 (41), 53 (10), 43 (30).

Found: C, 41.02; H, 4.67%. Calcd for $C_{11}H_{15}Cl_2F_3O_3$: C, 40.89; H, 4.68%.

Adducts **7b—e** were prepared similarly.

(3-Phenoxyphenyl)methyl 3-(2,2-Dichloro-3,3,3-trifluoro-1-hydroxypropyl)-2,2-dimethylcyclopropanecarboxylate (7b): A colorless viscous oil. The two diastereomers were separated by preparative TLC (CH_2Cl_2). The less polar isomer (R_f 0.70) showed ^1H NMR ($CDCl_3$) δ=1.21 (s, 3 H) 1.24 (s, 3 H), 1.73 (d, J=5.8 Hz, 1 H), 1.94 (dd, J=5.8 and 9.0 Hz, 1 H), 2.44 (d, J=9.6 Hz, 1 H), 3.79 (dd, J=8.7 and 9.0 Hz, 1 H), 5.07 (s, 2 H), 6.8—7.4 (m, 8 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.0 (s); IR 3480, 1713, 1588, 1490, 1255, 1180, 870 cm^{-1}; MS m/z (rel intensity) 478 (M^++2, 3), 476 (M^+, 4), 200 (5), 184 (16), 183 (100), 77 (6).

Found: C, 55.39; H, 4.53%. Calcd for $C_{22}H_{21}Cl_2F_3O_4$: C, 55.36; H, 4.43%.

The more polar one: R_f 0.55 (CH_2Cl_2), ^1H NMR ($CDCl_3$) δ=1.28 (s, 3 H), 1.32 (s, 3 H), 1.7—1.9 (m, 2 H), 2.35 (d, J=8.4 Hz, 1 H), 3.78 (dd, J=8.4 and 8.0 Hz, 1 H), 5.06 (s, 2 H), 6.8—7.4 (m, 8 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.6 (s); IR 3470, 1728, 1713, 1583, 1491, 1254, 1200, 870, 692 cm^{-1}; MS m/z (rel intensity) 478 (M^++2), 476 (M^+, 2), 184 (16), 183 (100), 89 (6), 77 (9), 55 (10), 51 (6), 41 (6).

Found: C, 55.43; H, 4.52%. Calcd for $C_{22}H_{21}Cl_2F_3O_4$: C, 55.36; H, 4.43%.

(2-Methyl-3-phenylphenyl)methyl 3-(2,2-Dichloro-3,3,3-trifluoro-1-hydroxypropyl)-2,2-dimethylcyclopropanecarboxylate (7c): The two diastereomers were separated by preparative TLC (CH_2Cl_2). The less polar isomer, R_f 0.45: colorless solid, mp 155—156 °C. ^1H NMR ($CDCl_3$) δ=1.26 (s, 6 H), 1.76 (d, J=6.0 Hz, 1 H), 1.97 (dd, J=6.0 and 8.7 Hz, 1 H), 2.19 (s, 3 H), 2.59 (d, J=9.0 Hz, 1H), 3.81 (dd, J=8.7 and 9.0 Hz, 1 H), 5.18 (s, 2 H), 7.15—7.50 (m, 8 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.6 (s); IR (KBr) 3460 (br), 1728, 1711, 1257, 1220, 1200, 1180, 1113, 873, 760, 702 cm^{-1}; MS m/z (rel intensity) 476 (M^++2, trace), 474 (M^+, trace), 182 (16), 181 (100), 180 (91), 179 (10), 166 (38), 165 (40).

Found: C, 57.99; H, 5.04%. Calcd for $C_{23}H_{23}Cl_2F_3O_3$: C, 58.12; H, 4.88%.

The more polar isomer (R_f 0.33) was a colorless oil, ^1H NMR ($CDCl_3$) δ=1.31 (s, 3 H), 1.32 (s, 3 H), 1.79 (d, J=5 Hz, 1 H), 1.93 (dd, J=5 and 8 Hz, 1 H), 2.19 (s, 3 H), 2.35 (d, J=8 Hz, 1 H), 3.82 (t, J=8 Hz, 1 H), 5.20 (s, 2 H), 7.2—7.4 (m, 8 H): ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.3 (s); IR 3425, 1711, 1260, 1227, 1200, 1184, 706 cm^{-1}; MS m/z (rel intensity) 277 (trace), 198 (14), 182 (15), 181 (100), 180 (90), 179 (17), 167 (10), 166 (40), 165 (63), 152 (10), 151 (10), 57 (22), 56 (11), 43 (17).

Found: C, 58.40; H, 4.96%. Calcd for $C_{23}H_{23}Cl_2F_3O_3$: C, 58.12; H, 4.88%.

(Pentafluorophenyl)methyl 3-(2,2-Dichloro-3,3,3-trifluoro-1-hydroxypropyl)-2,2-dimethylcyclopropanecarboxylate (7d): The two isomers were separated by preparative TLC (CH_2Cl_2). The less polar isomer showed R_f 0.65, mp 75 °C, and ^1H NMR ($CDCl_3$) δ=1.22 (s, 3 H), 1.24 (s, 3 H), 1.67 (d, 1 H), 1.95 (dd, 1 H), 2.43 (d, 1 H), 3.80 (dd, 1 H), 5.19 (t, 2 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.0 (s); IR (KBr) 1727, 1529, 1510, 1253, 1190, 1168, 1134, 1053, 940, 932, 868 cm^{-1}; MS m/z (rel intensity) 476 (M^++2, trace), 474 (M^+, trace), 293 (35), 181 (100), 59 (11), 55 (13).

Found: C, 40.60; H, 2.61%. Calcd for $C_{16}H_{12}Cl_2F_8O_3$: C, 40.44; H, 2.55%.

The more polar isomer (R_f 0.53, mp 103—104 °C): ^1H NMR ($CDCl_3$) δ=1.31 (s, 3 H), 1.33 (s, 3 H), 1.69 (d, 1 H), 1.81 (dd, 3 H), 2.33 (d, 1 H), 3.77 (dd, 1 H), 5.17 (t, 2 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.6 (s); IR (KBr) 3440, 1721, 1526, 1509, 1260, 1223, 1220, 1188, 1178 cm^{-1}; MS m/z (rel intensity) 293 (29), 181 (100), 55 (13).

Found: C, 40.55; H, 2.64%. Calcd for $C_{16}H_{12}Cl_2F_8O_3$: C, 40.44; H, 2.55%.

Methyl 3-(2,2-Dichloro-3,3,3-trifluoro-1-hydroxypropyl)-2,2-dimethylcyclopropanecarboxylate (7e): A colorless oil consisted of two diastereomers. ^1H NMR (400 MHz, $CDCl_3$) δ=1.23 (s, 3 H), 1.25 (s, 3 H), 1.71 (d, J=5.8 Hz, 1 H), 1.95 (dd, J=5.8 and 9.0 Hz, 1 H), 2.75 (d, J=9.0 Hz, 1 H), 3.71 (s, 3 H), 3.83 (t, J=5.8 Hz, 1 H) for the major isomer δ=1.29 (s, 3 H), 1.33 (s, 3 H), 1.72 (d, J=5.5 Hz, 1 H), 1.83 (dd, J=5.5 and 9.7 Hz, 1 H), 2.48 (d, J=7.8 Hz, 1 H), 3.70 (s, 3 H), 3.83 (dd, J=7.8 and 9.7 Hz, 1 H), 3.70 (s, 3 H), 3.83 (dd, J=7.8 and 9.7 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.1 (s) for the major isomer, −75.5 (s) for the minor isomer. IR 3465, 1716, 1260, 1200, 1180, 872 cm^{-1}; MS m/z (rel intensity) 277 (5), 128 (11), 127 (100), 125 (15), 98 (14), 97 (16), 96 (10), 95 (49), 73 (18), 69 (15), 67 (27), 59 (24), 55 (30), 43 (20), 41 (32).

Found: C, 39.11; H, 4.30%. Calcd for $C_{10}H_{13}Cl_2F_3O_3$: C, 38.86; H, 4.24%.

Acetylation of 7a. A mixture of **7a** (0.31 g, 0.94 mmol), pyridine (1 ml) and acetic anhydride (1 ml) was stirred for 5 h at room temperature. Concentration in vacuo followed by purification by column chromatography (CH_2Cl_2-hexane 1 : 1) gave ethyl 3-(1-acetoxy-2,2-dichloro-3,3,3-trifluoropropyl)-2,2-dimethylcyclopropanecarboxylate (**8a**) as a mixture of two diastereomers in a ratio of 55 : 45 (0.32 g, 93% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ=1.24 (s, 3 H), 1.26 (t, J=7.1 Hz, 3 H), 1.32 (s, 3 H), 1.59 (d, J=5.7 Hz, 1 H), 2.06 (dd, J=5.7 and 9.8 Hz, 1 H), 2.13 (s, 3 H), 4.09—4.22 (m, 2 H), 5.35 (d, J=9.8 Hz, 1H) for the major isomer, δ=1.17 (s, 3 H), 1.26 (s, 3 H), 1.26 (t, J=7.1 Hz, 3 H), 1.77 (d, J=5.6 Hz, 1 H), 2.01 (dd, J=5.7 and 10.1 Hz, 1 H),

2.15 (s, 3 H), 4.09—4.22 (m, 2 H), 5.28 (d, J=10.1 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.5 (s) for the major isomer, −74.6 (s) for the minor isomer; IR 1769, 1732, 1374, 1262, 1250, 1208, 1188, 1030 cm^{-1}; MS m/z (rel intensity) 331 (trace), 329 (3), 197 (11), 141 (37), 113 (18), 43 (100).

Found: C, 42.75; H, 4.59%. Calcd for $C_{13}H_{17}Cl_2F_3O_4$: C, 42.76; H, 4.69%.

(3-Phenoxyphenyl)methyl 3-(1-Acetoxy-2,2-dichloro-3,3,3-trifluoro-propyl)-2,2-dimethylcyclopropanecarboxylate (8b): A colorless oil composed of two diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.22 (s, 3 H), 1.31 (s, 3 H), 1.66 (d, J=5.7 Hz, 1 H), 2.07 (s, 3 H), 2.08 (dd, J=5.7 and 9.9 Hz, 1 H), 5.11 (s, 2 H), 5.35 (d, J=9.9 Hz, 1 H), 6.90—7.15 (m, 5 H), 7.25—7.40 (m, 4 H) for the major isomer, δ=1.16 (s, 3 H), 1.24 (s, 3 H), 1.84 (d, J=5.6 Hz, 1 H), 2.03 (dd, J=5.6 and 10.1 Hz, 1 H), 2.13 (s, 3 H), 5.05—5.15 (m, 1 H), 5.12 (d, J=10.1 Hz, 1 H), 5.28 (d, 1 H), 6.09—7.15 (m, 5 H), 7.25—7.40 (m, 4 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−76.0 (s) for the major isomer, −75.2 (s) for the minor isomer; IR 1767, 1732, 1588, 1492, 1446, 1374, 1255, 1205, 1168, 1028, 692 cm^{-1}; MS m/z (rel intensity) 521 (M^++3, trace), 520 (M^++2, 2), 519 (M^++1, 1), 518 (M^+, 4), 184 (16), 183 (100), 43 (55).

Found: C, 55.52; H, 4.67%. Calcd for $C_{24}H_{23}Cl_2F_3O_5$: C, 55.51; H, 4.46%.

(2-Methyl-3-phenylphenyl)methyl 3-(1-Acetoxy-2,2-dichloro-3,3,3-trifluoropropyl)-2,2-dimethylcyclopropanecarboxylate (8c) Derived from the Less Polar Isomer of 7c: 98% yield, a colorless oil, R_f 0.46 (CH_2Cl_2-hexane 1 : 1). ^{1}H NMR ($CDCl_3$) δ=1.27 (s, 3 H), 1.33 (s, 3 H), 1.70 (d, J=6 Hz, 1 H), 2.09 (s, 3 H), 2.13 (dd, J=6 and 10 Hz, 1 H), 2.22 (s, 3 H), 5.25 (s, 2 H), 5.40 (d, J=10 Hz, 1 H), 7.2—7.5 (m, 8 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.5 (s); IR 1754, 1749, 1730, 1256, 1228, 1204, 1188, 1160, 1028, 758, 702 cm^{-1}; MS m/z (rel intensity) 518 (M^++2, trace), 516, (M^+, trace), 182 (15), 181 (100), 180 (86), 166 (28), 165 (30), 43 (38).

Found: C, 58.31; H, 4.91%. Calcd for $C_{25}H_{25}Cl_2F_3O_4$: C, 58.04; H, 4.87%.

The Diastereomeric Acetate Derived from the More Polar Isomer of 7c. This compound was obtained in 100% yield as a colorless oil, R_f 0.39 (CH_2Cl_2-hexane 1 : 1). ^{1}H NMR ($CDCl_3$) δ=1.18 (s, 3 H), 1.30 (s, 3 H), 1.85 (d, J=6 Hz, 1 H), 2.05 (dd, J=6 and 10 Hz, 1 H), 2.14 (s, 3 H), 2.20 (s, 3 H), 5.19 (s, 2 H), 5.24 (d, J=10 Hz, 1 H), 7.1—7.5 (m, 8 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.8 (s); IR 1770, 1730, 1260, 1230—1160 (br), 1031, 842, 762, 704 cm^{-1}; MS m/z (rel intensity) 518 (M^++2, trace), 516 (M^+, trace), 182 (15), 181 (100), 180 (74), 166 (24), 165 (25), 43 (31).

Found: C, 58.13; H, 4.90%. Calcd for $C_{25}H_{25}Cl_2F_3O_4$: C, 58.04; H, 4.87%.

Ethyl 3-[2,2-Dichloro-3,3,3-trifluoro-1-(methylsulfonyloxy)propyl]-2,2-dimethylcyclopropanecarboxylate (9a). Methanesulfonyl chloride (0.073 ml, 0.94 mmol) and triethylamine (0.133 ml, 0.95 mmol) were added to an ethereal solution (2 ml) of **7a** (0.135 g, 0.79 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature. Workup and TLC purification (CH_2Cl_2-hexane 1 : 1) gave **9a** (0.157 g, 80% yield) as a colorless oily diastereomeric mixture. ^{1}H NMR ($CDCl_3$) δ=1.2—1.4 (m, 9 H), 1.8—2.2 (m, 2 H), 3.12 and 3.16 (s, totally 3 H), 4.14 (q, J=7.2 Hz, 2 H), 4.89 and 4.90 (d, J=10 Hz, totally 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.8 (s) and −73.8 (s); IR 1730, 1368, 1257, 1232, 1180, 932, 896, 809 cm^{-1}; MS m/z (rel intensity) 357 (5), 355 (7), 269 (12), 233 (18), 232 (10), 231 (24), 199 (33), 198 (11), 197 (100), 195 (19), 175 (11), 161 (32), 159 (20), 141 (69), 137 (15), 113 (28), 97 (12), 95 (14), 80 (10), 79 (26), 69 (10), 67 (13), 59 (17), 43 (14), 41 (28).

Found: C, 35.86; H, 4.27%. Calcd for $C_{12}H_{17}Cl_2F_3O_5S$: C,35.92; H, 4.27%.

(2-Methyl-3-phenylphenyl)methyl 3-[2,2-Dichloro-3,3,3-trifluoro-1-(methylsulfonyloxy)propyl]-2,2-dimethylcyclopropanecarboxylate (9c): 97% yield a colorless oil of a 1 : 1 diastereomeric mixture. ^{1}H NMR ($CDCl_3$) δ=1.26, 1.31, 1.38 (s, totally 6 H), 1.9—2.3 (2 H), 2.18, 2.20 (s, totally 3 H), 3.03, 3.13 (s, totally 3 H), 4.88, 4.99 (d, J=10 Hz, totally 1 H), 5.19 (s, 2 H), and 7.1—7.5 (m, 8 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−73.7 (s), −74.8 (s); IR 1729, 1360, 1252, 1230—1160 (br), 928, 808, 761, 704 cm^{-1}; MS m/z (rel intensity) 554 (M^++2, trace), 552 (M^+, trace), 182 (17), 181 (100), 180 (45), 179 (11), 166 (32), 165 (33).

Found: C, 52.02; H, 4.68%. Calcd for $C_{24}H_{25}Cl_2F_3O_5S$: C, 52.09; H, 4.55%.

(2-Methyl-3-phenylphenyl)methyl 3-(1-Benzoyloxy-2,2-dichloro-3,3,3-trifluoropropyl)-2,2-dimethylcyclopropanecarboxylate (10c). Benzoyl chloride (0.114 ml, 0.98 mmol) and triethylamine (0.137 ml, 0.98 mmol) were added to an ethereal solution (2 ml) of **7c** (0.39 g, 0.82 mmol) at 0 °C, and the mixture was stirred for 12 h at room temperature. As TLC assay showed slow consumption of **7c**, benzoyl chloride (0.23 ml, 2.0 mmol) and triethylamine (0.28 ml, 2.0 mmol) were further added, and stirring was continued for 10 h at room temperature. Workup and preparative TLC (CH_2Cl_2-hexane 1 : 1) gave **10c** (0.175 g, 37% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.32 (s, 3 H), 1.40 (s, 3 H), 1.81 (d, J=5 Hz, 1 H), 1.96 (s, 3 H), 2.21 (dd, J=5 and 10 Hz, 1 H), 5.07 (s, 2 H), 5.58 (d, J=10 Hz, 1 H), 7.0—7.6 (m, 11 H), 7.9—8.1 (m, 2 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.5 (s); IR 1732, 1450, 1068, 1028, 889, 836, 830, 799, 762, 706 cm^{-1}; MS m/z (rel intensity) 580 (M^++2, trace), 578 (M^+, trace), 182 (16), 181 (100), 180 (94), 179 (10), 166 (35), 165 (36), 105 (35), 77 (10).

Found: C, 62.26; H, 4.78%. Calcd for $C_{30}H_{27}Cl_2F_3O_4$: C, 62.19; H, 4.70%.

(2-Methyl-3-phenylphenyl)methyl 3-[2,2-Dichloro-3,3,3-trifluoro-1-(*p*-tolylsulfonyloxy)propyl]-2,2-dimethylcyclopropanecarboxylate (11c). Sodium hydride (50% in oil, 12 mg, 0.25 mmol) and *p*-toluenesulfonyl chloride (39 mg, 0.20 mmol) were added to **7c** (97 mg, 0.20 mmol) dissolved in diethyl ether (0.5 ml) and DMF (0.5 ml), and the mixture was stirred for 12 h at room temperature. Workup and purification by preparative TLC (CH_2Cl_2-hexane 1 : 1) gave **11c** (83 mg, 65% yield) as a viscous oil. ^{1}H NMR ($CDCl_3$) δ=1.23, 1.33, 1.37 (s, totally 3 H), 1.9—2.3 (m, 2 H), 2.19, 2.21 (s, totally 3 H), 2.37, 2.43 (s, totally 3 H), 4.85—5.05 (m, 1 H), 5.15, 5.16 (s, totally 2 H), 7.1—7.4 (m, 10 H), 7.6—7.9 (m, 2 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.6 (s) and −73.3 (s); IR 1730, 1600, 1360, 1387, 1114, 1096, 560 cm^{-1}; MS m/z (rel intensity) 630 (M^++2, trace), 628 (M^+, trace), 182 (15), 181 (100), 180 (74), 166 (30), 165 (28).

Found: C, 57.23; H, 4.70%. Calcd for $C_{30}H_{29}Cl_2F_3O_5S$: C, 57.24; H, 4.64%.

Reduction of 8a with Zinc. Zinc powder (35 mg, 0.54 mmol) was added to a DMF (0.5 ml) solution of **8a** (0.183 g, 0.50 mmol) and the mixture was stirred for 4 h at 50 °C before quenching by addition of sat ammonium chloride aq solution (1 ml). Extraction with diethyl ether (5×1 ml), drying the ethereal extract over magnesium sulfate, concentration in vacuo, followed by preparative TLC (CH_2Cl_2-hexane

1 : 1) gave ethyl (1*R**,3*S**)-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (**12a**) as a Z/E=6 : 1 mixture (0.116 g, 86% yield, a colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.24 (s, 3 H), 1.28 (t, J=7.1 Hz, 3 H), 1.33 (s, 3 H), 1.77 (d, J=5.3 Hz, 1 H), 2.40 (ddq, J=5.3, 9.3, and 1.0 Hz, 1 H), 4.10—4.22 (m, 2 H), 6.15 (dq, J=9.3 and 1.0 Hz, 1 H) for the (Z)-isomer, δ=1.21 (s, 3 H), 1.27 (t, J=7.1 Hz, 3 H), 1.28 (s, 3 H), 1.69 (d, J=5.4 Hz, 1 H), 2.38—2.44 (m, 2 H), 4.10—4.22 (m, 2 H), 5.89 (d, J=9.4 Hz, 1 H) for the (E)-isomer; ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−68.9 (s) for the (Z)-isomer, −62.5 (d, J=3.2 Hz) for the (E)-isomer; IR 1731, 1286, 1229, 1176, 1142 cm^{-1}.

(3-Phenoxyphenyl)methyl 3-(2-Chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (12b): A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.21 (s, 3 H), 1.30 (s, 3 H), 1.76 (d, J=5.4 Hz, 1 H), 2.37 (dd, J=5.4 and 9.0 Hz, 1 H), 5.06 (s, 2 H), 6.08 (d, J=9.0 Hz, 1 H), 6.8—7.4 (m, 8 H) for the (Z)-isomer, δ=1.22 (s, 3 H), 1.70 (d, J=5.4 Hz, 1 H), 5.82 (d, J=9.0 Hz, 1 H) for the (E)-isomer; ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−69.2 (s), −62.9 (s) for the (E)-isomer; IR 1732, 1588, 1492, 1283, 1256, 1221, 1167, 1140, 1113, 693 cm^{-1}.

When **8b** (49 mg, 0.094 mmol) was treated with zinc (9 mg, 0.13 mmol) in THF (0.2 ml) for 23 h at 50 °C, **12b** was obtained in 88% isolation yield. Z/E=77 : 23.

(2-Methyl-3-phenylphenyl)methyl 3-(2-Chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (12c): A colorless oil, Z/E=89 : 11 from the less polar isomer of **8c**. ^{1}H NMR ($CDCl_3$) δ=1.23 (s, 3 H), 1.35 (s, 3 H), 1.82 (d, J=5 Hz, 1 H), 2.22 (s, 3 H), 2.42 (dd, J=5 and 9 Hz, 1 H), 5.20 (s, 2 H), 6.10 (dq, J=10 and 1 Hz, 1 H), 7.15—7.5 (m, 8 H) for the (Z)-isomer, δ=1.23 (s, 3 H), 1.29 (s, 3 H), 5.85 (d, J=9.1 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−68.7 (s) for the (Z)-isomer, −62.5 (s) for the (E)-isomer.

The more polar isomer of **8c** gave **12c** of Z/E=93 : 7 in a similar yield.

One-Pot Conversion of 6c into 12c. To a DMF (1 ml) solution of **6c** (0.28 g, 0.87 mmol) were added 1,1,1-trichloro-2,2,2-trifluoroethane (0.21 ml, 1.7 mmol), zinc powder (0.29 g, 4.4 mmol) and acetic anhydride (0.12 ml), and the mixture was stirred for 6 h at 50 °C. After quenching with water (2 ml) and 2 drops of conc hydrochloric acid, the reaction mixture was extracted with diethyl ether (3×3 ml). The ethereal extract was dried over anhydrous magnesium sulfate and concentrated in vacuo. Purification by column chromatography (dichloromethane-hexane 1 : 3 to 1 : 2) gave **12c** (0.20 g, 54% yield) as a colorless oil which consisted of 6 : 1 (Z)- and (E)-isomers.

By applying **9c** and **10c** to the reduction with zinc, we obtained **12c** in 95% (Z/E=88 : 12) and 98% (Z/E=86 : 14) yield respectively.

4-(2,4-Dioxobutoxy)-5,5-dichloro-6,6,6-trifluoro-2-methyl-2-hexene (15). A mixture of **14** (0.95 g, 4.0 mmol), sodium acetate (50 ml), and diketene (0.5 ml) was heated at 80 °C for 4 h under stirring and then charged on a silica-gel column. Elution with dichloromethane-hexane 1 : 1 gave **15** (1.13 g, 88% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.83 (s, 6 H), 2.26 (s, 3 H), 3.46 (s, 2 H), 5.28 (d, J=9.6 Hz, 1 H), 6.08 (d, J=9.6 Hz, 1 H) for the keto form, δ=1.97 (s, 3 H), 5.03 (s, 1 H), 6.17 (d, J=9.6 Hz, 1 H) for the enol tautomer; ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.0 (s); IR 3480, 1756, 1728, 1255, 1210, 1188, 1149 cm^{-1}; MS m/z (rel intensity) 285 (2), 183 (9), 127 (5), 86 (6), 85 (100), 84 (5), 83 (5), 69 (6), 67 (7), 58 (5), 55 (9), 44 (12), 43 (48), 41 (24).

Found: C, 40.89; H, 3.96%. Calcd for $C_{11}H_{13}Cl_2F_3O_3$: C, 41.14; H, 4.08%.

4-Diazoacetoxy-5,5-dichloro-6,6,6-trifluoro-2-methyl-2-hexene (16). Triethylamine (0.060 ml, 0.43 mmol) and *p*-toluenesulfonyl azide (80 mg, 0.41 mmol) were added to an acetonitrile (1 ml) solution of **15** (0.128 g, 0.40 mmol), and the mixture was stirred for 0.5 h at room temperature. At this point, all of **15** was converted into the diazo compound as assayed by TLC. Sodium hydroxide (1,2 M† aq solution, 1 ml) was added, and stirring was continued for 1 h at room temperature. Extraction with diethyl ether (3×2 ml) and then with dichloromethane (2 ml), drying the combined organic extract over magnesium sulfate, concentration in vacuo, and finally purification by column chromatography (CH_2Cl_2-hexane 1 : 1) gave **16** (0.100 g, 82% yield) as a pale yellow oil. ^{1}H NMR ($CDCl_3$) δ=1.85 (s, 6 H), 4.77 (s, 1 H), 5.03 (d, J=9.6 Hz, 1 H), 6.13 (d. J=9.6 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.0 (s); IR 2120, 1710, 1376, 1210, 1188, 1163 cm^{-1}; MS m/z (rel intensity) 278 (11), 221 (20), 219 (33), 213 (47), 185 (25), 184 (20), 183 (64), 147 (30), 143 (44), 127 (49), 125 (54), 97 (25), 79 (21), 77 (24), 70 (69), 53 (26), 51 (20), 43 (31), 42 (69), 41 (100).

Found: C, 35.45; H, 2.86; N, 9.21%. Calcd for $C_9H_9Cl_2F_3N_2O_2$: C, 35.43; H, 2.97; N, 9.18%.

4-(1,1-Dichloro-2,2,2-trifluoroethyl)-6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (13). An dioxane (0.5 ml) solution of **12** (38 mg, 0.12 mmol) was added over 0.5 h to a refluxing suspension of copper(II) acetylacetonate (1 mg) in dioxane (3 ml), and the heating and stirring were continued for additional 2.5 h. The reaction mixture was treated with water (5 ml) and extracted with diethyl ether (2×10 ml). The extract was dried over magnesium sulfate and concentrated under reduced pressure to afford a crude product which was purified by column chromatography (CH_2Cl_2-hexane 1 : 2) to give **13** (26 mg, 75% yield) as colorless crystals, mp 49—60 °C. ^{1}H NMR ($CDCl_3$) δ=1.25 (s, 6 H), 2.11 (d, J=5.7 Hz, 1 H), 2.36 (d, J=5.7 Hz, 1 H), 4.61 (s, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.2 (s); IR (KBr) 1802, 1260, 1212, 1194, 1070, 1012, 908 cm^{-1}. MS m/z (rel intensity) 278 (M^++2, 2), 276 (M^+, 3), 243 (32), 241 (92), 205 (10), 199 (23), 197 (64), 161 (34), 159 (11), 141 (47), 126 (11), 125 (100), 97 (86), 96 (16), 95 (12), 91 (14), 81 (63), 79 (35), 77 (12), 69 (31), 67 (39), 65 (14), 63 (11), 55 (12), 53 (48), 51 (16), 43 (51), 42 (13).

Found: C, 38.98; H, 3.20%. Calcd for $C_9H_9Cl_2F_3O_2$: C, 39.02; H, 3.27%.

(1*R,3*R**)-3-(2-Chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylic Acid (17).** Zinc powder (6 mg, 0.09 mmol) was added to a DMF (0.1 ml) solution of **13** (23 mg, 0.083 mmol), and the resulting mixture was stirred for 3 h at 60 °C before quenching by addition of water (1 ml) and conc hydrochloric acid (0.5 ml). Extraction with diethyl ether (4×3 ml), drying the ethereal extract over magensium suflate, and concentration in vacuo gave rise to **17** (17 mg, 84% yield, Z/E=93 : 7) as colorless crystals, mp 103—105 °C (sublime).[19] ^{1}H NMR ($CDCl_3$) δ=1.33 (s, 6 H), 1.96 (d, J=8 Hz, 1 H), 2.22 (dd, J=8 and 9 Hz, 1 H), 6.81 (d, J=9 Hz, 1 H) for the (Z)-isomer, 6.52 (d, J=9 Hz, 1 H) attributed to the (E)-isomer. ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−68.8 (s) for the (Z)-isomer, −62.0 (s) for the (E)-isomer; IR 1708, 1437, 1293, 1272, 1194, 1146, 1128 cm^{-1}.

Ethyl 3-(2,3,3-Trifluoro-1-hydroxy-2-propenyl)-2,2-di-

† 1 M=1 mol dm^{-3}.

methylcyclopropanecarboxylate (20a). Gaseous chlorotrifluoroethene (240 ml at room temperature, 10 mmol) was dissolved in a mixture of THF (10 ml), hexane (1 ml), and diethyl ether (1 ml) at −78 °C. The solution was cooled at −130 °C. Butyllithium (1.67 M hexane solution, 6.0 ml, 10 mmol) was added dropwise to the solution, and the mixture was stirred for 1 h at −130 °C. To this solution was added **6a** (2.0 g, 12 mmol) dissolved in the trap solvent mixture composed of THF (10 ml), hexane (1 ml) and diethyl ether (1 ml) at −130 °C drop by drop over a period of 5 min. The reaction mixture was allowed to warm gradually to −40 °C over 7 h. Workup and purification by column chromatography (CH_2Cl_2-AcOEt 1 : 0 to 1 : 1) gave **20a** (0.63 g, 25% yield) as a colorless viscous oil. ^1H NMR ($CDCl_3$) δ=1.1—1.4 (m, 9 H), 1.65 (d, J=6 Hz, 1 H), 1.84 (dd, J=6 and 10 Hz, 1 H), 3.76—4.1 (m, 2 H), 4.10 (q, J=7 Hz, 2 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−102 (ddd, J=6, 33, and 81 Hz, 1 F), −120 (ddd, J=1, 37, and 47 Hz, 1 F), −188 (m, 1 F); IR 3440, 2970, 1791, 1730, 1709, 1306, 1256, 1213, 1175, 1114, 1100, 1072, 1032, 1018 cm^{-1}; MS m/z (rel intensity) 207 (6), 142 (17), 141 (100), 114 (12), 113 (78), 111 (27), 109 (12), 96 (11), 95 (55), 69 (17), 67 (36), 59 (39), 55 (19), 53 (11), 43 (31), 41 (38).

Found: m/z 207.0673. Calcd for $C_{11}H_{15}F_3O_3$: M, 207.0632.

The adduct **20a** was alternatively prepared by the reaction of **6a** with triethyl(trifluoroethenyl)silane. A THF solution of tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF) (1.0 M solution 0.1 ml, 0.1 mmol) was added to a mixture of **6a** (0.175 g, 1.0 mmol), triethyl(trifluoroethenyl)-silane (0.24 g, 1.2 mmol) and THF (2 ml) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and for 10 h at room temperature. Workup followed preparative TLC (hexane-dichloromethane 1 : 1) afforded ethyl (1*R**,3*R**)-3-(1-triethylsiloxy-2,3,3-trifluoro-2-propenyl)-2,2-dimethylcyclopropanecarboxylate (22 mg) and its (1R*,3R*)-isomer (75 mg). Total yield was 39%. The (1R*,3R*)-isomer exhibited ^1H NMR consistent to the structure (J=8.7 Hz for the coupling constant of the ring proton, 2.58: 1 diastereomeric mixture); IR 1795, 1730 cm^{-1}; Found: m/z 337.1415. Calcd for $C_{15}H_{24}F_3O_3Si$: M−Et, 337.1444. The (1R*,3R*)-isomer exhibited J=5.52 Hz for the coupling constant of the ring proton (ca. 1 : 1 diastereomeric mixture); IR 1790, 1735 cm^{-1}; Found: m/z 337.1431. Calcd for $C_{15}H_{24}F_3O_3Si$: M−Et, 337.1445.

Desilylation was effected by treating the silyl ether with 0.2 M hydrochloric acid (0.5 ml) and THF (0.5 ml) at room temperature for 0.5 h. Workup and TLC purification gave **20a** quantitatively.

Ethyl 3-(2-Chloro-3,3-difluoro-1-hydroxy-2-propenyl)-2,2-dimethylcyclopropanecarboxylate (20b). A THF solution (1.0 M, 0.1 ml) of TASF (0.1 mmol) was added to a mixture of **6a** (0.34 g, 2.0 mmol), (1-chloro-2,2-difluoroethenyl)-triethylsilane (0.21 g, 1.0 mmol) and THF (2 ml) at room temperature. The reaction mixture was stirred for 16 h, and then worked up. Preparative TLC (dichloromethane-hexane 1 : 1) afforded **20b** (27 mg), its triethylsilyl ether (49 mg) and the recovered **6a** (101 mg). The silyl ether (39 mg out of the 49 mg sample) was dissolved in 0.2 M hydrochloric acid-THF 1 : 1 mixture (1 ml), and the solution was stirred for 1 h at room temperature. Work-up and preparative TLC afforded **21b** (27 mg, 99% yield) as a colorless oil. ^1H NMR ($CDCl_3$) δ=1.1—1.4 (m, 9 H), 1.67 (d, J=5 Hz, 1 H). 1.87 (d, J=5 and 10 Hz, 1 H), 2.29 (br s, 1 H), 3.95—4.3 (m, 3 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−87 (dd, J=4 and 40 Hz, 1 F), −91 (dd, J=9 and 40 Hz, 1 F); MS m/z (rel intensity) 223 (5), 142 (24), 141 (100), 127 (32), 125 (12), 114 (19), 113 (92), 96 (14), 95 (53), 69 (19), 67 (38), 61 (14), 59 (37), 55 (14), 53 (13), 43 (33), 41 (39).

Found: m/z 223.0349. Calcd for $C_9H_{10}ClF_2O_2$: M−OEt, 223.0336.

2-Chloro-1,1-difluoro-1-tridecen-3-ol (18b). The silyl ether of **18b** was prepared by the similar procedure as above, starting from undecanal (0.93 ml, 4.5 mmol), 1-chloro-2,2-difluoroethenyltriethylsilane (0.53 g, 3.0 mmol), THF (6 ml), and TASF (0.3 mmol). TLC purification using dichloromethane-hexane 1 : 2 gave 2-chloro-1,1-difluoro-3-triethylsilyloxy-1-tridecene (0.33 g, 39% yield) as a colorless oil. ^1H NMR ($CDCl_3$) δ=0.45—0.8 (m, 6 H), 0.8—1.15 (m, 12 H), 1.30 (s, 16 H), 1.45—1.85 (m, 2 H), 4.35—4.65 (m, 1 H), ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−88 (d, J=44 Hz, 1 F), −92 (d, J=44 Hz, 1 F); IR 2950, 1747, 1470, 1286, 1100, 1002, 750, 730 cm^{-1}; MS m/z (rel intensity) 355 (38), 354 (25), 353 (M^+−Et, 96), 241 (27), 115 (36), 109 (16), 105 (72), 104 (11), 103 (100), 97 (35), 95 (37), 91 (15), 89 (35), 87 (38), 83 (42), 81 (33), 77 (63), 75 (85), 71 (15), 69 (43), 67 (28), 59 (27), 57 (32), 55 (58), 47 (26), 43 (59), 41 (35).

Found: C, 60.02; H, 9.44%. Calcd for $C_{19}H_{37}ClF_2OSi$: C, 59.58; H, 9.74%.

Acid-catalyzed desilylation was effected in 0.2 M hydrochloric acid and THF in 83% yield to give **18b** as a colorless oil. ^1H NMR ($CDCl_3$) δ=0.7—1.0 (m, 3 H), 1.25 (s, 16 H), 1.45—1.9 (m, 2 H), 1.77 (br s, 1 H), 4.35—4.6 (m, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−87 (dd, J=39 and 2 Hz, 1 F), −91 (dd, J=39 and 3 Hz, 1F); IR 3380, 2945, 2875, 1747, 1288 cm^{-1}; MS m/z (rel intensity) 250 (M^+−H_2O, trace), 129 (34), 127 (100), 57 (2), 55 (14), 43 (39), 41 (25).

Found: m/z 250.1326. Calcd for $C_{13}H_{21}ClF_2$: M−H_2O, 250.1299.

Fluorination of 18a. A Typical Fluorination Procedure. To a solution of DAST (82 mg, 0.50 mmol) dissolved in dichloromethane (5 ml) was added dropwise 1,1,2-trifluoro-1-tridecen-3-ol (**18a**, 0.123 g, 0.49 mmol) at −78 °C, and the solution was allowed to warm to room temperature over 10 min. The solution was concentrated under reduced pressure, and the residue was subjected to column chromatography (dichloromethane-haxane 1 : 9) to afford 1,1,1,2-tetrafluoro-2-tridecene (**19a**, 0.112 g, 90% yield) as a colorless oil. ^1H NMR ($CDCl_3$) δ=0.8—1.0 (m, 3 H), 1.1—1.6 (m, 16 H), 2.1—2.4 (m, 2 H), 5.53 (dt J=33 and 7.8 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−72 (d, J=12 Hz, 3 F), −137 (dq, J=33 and 12 Hz, 1F); IR 2940, 2870, 1833, 1470, 1362, 1194, 1148, 1050 cm^{-1}; MS m/z (rel intensity) 254 (M^+, trace), 97 (12), 85 (12), 84 (16), 83 (15), 71 (23), 70 (31), 69 (30), 57 (54), 56 (47), 55 (34), 43 (100), 42 (16), 41 (46).

Found: m/z 254.1647. Calcd for $C_{13}H_{22}F_4$: M, 254.1659.

2-Chloro-1,1,1-trifluoro-2-tridecene (19b): ^1H NMR ($CDCl_3$) δ=0.7—1.0 (m, 3 H), 2.27 (s, 16 H), 2.1—2.4 (m, 2 H), 6.43 (tq, J=7 and 1 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−69 (m), IR 2940, 2865, 1307, 1186, 1148 cm^{-1}; MS m/z (rel intensity) 270 (M^+, trace), 111 (10), 98 (12), 97 (18), 85 (14), 84 (28), 83 (25), 71 (32), 70 (64), 69 (56), 57 (77), 56 (97), 55(55), 43 (100), 42 (25), 41 (66).

Found: C, 57.95; H, 8.17%. Calcd for $C_{13}H_{22}ClF_3$: C, 57.67; H, 8.19%.

Ethyl 3-(2,3,3,3-Tetrafluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (21a): A colorless oil. ^1H NMR ($CDCl_3$) δ=1.21 (s, 3 H), 1.27 (t, J=7.1 Hz, 3 H), 1.30 (s, 3 H),

1.67 (d, J=5.3 Hz, 1 H), 2.32 (dd, J=5.3 and 9.8 Hz, 1 H), 4.15 (q, J=7.1 Hz, 1 H), 5.30 (dd, J=9.8 and 31.5 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−72.8 (d, J=11.8 Hz, 3 F), −136.9 (dq, J=31.5 and 11.8 Hz, 1 F); MS m/z (rel intensity) 254 (M^+, 3), 209 (24), 182 (10), 181 (92), 141 (18), 115 (11), 97 (12), 77 (11), 59 (10), 47 (21), 41 (21).

Found: m/z 254.0936. Calcd for $C_{11}H_{14}F_4O_2$: M, 254.0929.

Ethyl 3-(2-Chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (21b): A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.22 (s, 3 H), 1.27 (t, J=7 Hz, 3 H), 1.33 (s, 3 H), 1.74 (d, J=5.1 Hz, 1 H), 2.37 (dd, J=5 and 10 Hz, 1 H), 4.13 (m, 2 H), 6.13 (d, J=10 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−69 (s); IR 1733, 1724, 1304, 1286, 1228, 1176, 1144 cm^{-1}; MS m/z (rel intensity) 270 (M^+, 1), 225 (18), 119 (24), 197 (68), 161 (20), 141 (27), 41 (18).

Chlorination of 18a. A Typical Chlorination Procedure. Pyridine (0.081 ml, 1.0 mmol) and thionyl chloride (0.038 ml, 0.50 mmol) were added to an ethereal solution (1 ml) of **18a** (0.126 g, 0.50 mmol) at 0 °C, and the mixture was stirred for 3 h at room temperature. The precipitated material was filtered off, and the filtrate was concentrated under reduced pressure. Preparative TLC (dichloromethane-hexane 1 : 5) afforded 1-chloro-1,1,2-trifluoro-2-tridecene (**19a'**, 0.115 g, 85% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.7—1.0 (m, 3 H), 1.1—1.6 (m, 16 H), 2.0—2.4 (m, 2 H), 5.47 (dt, J=33 and 8 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−59 (dt, J=17 and 3 Hz, 2 F), −131 (ddt, J=33, 17, and 4 Hz, 1 F); IR 2940, 2870, 1470, 1146, 1052, 928 cm^{-1}; MS m/z (rel intensity) 243 (trace), 97 (14), 85 (12), 84 (18), 83 (20), 71 (24), 70 (36), 69 (34), 57 (57), 56 (52), 55 (38), 43 (100), 42 (16).

Found: C, 57.85; H, 8.06%. Calcd for $C_{13}H_{22}ClF_3$: C, 57.67; H, 8.19%.

1,2-Dichloro-1,1-difluoro-2-tridecene (19b'). Thionyl chloride (0.020 ml, 0.27 mmol) was added to **18b** (54 mg, 0.20 mmol) dissolved in diethyl ether (0.4 ml), and the solution was stirred for 2 h at room temperature and for 15 h at 50 °C. Workup and purification by preparative TLC (dichloromethane-hexane 1 : 10) afforded **19b'** (52 mg, 90% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.7—1.0 (m, 3 H), 1.26 (s, 16 H), 2.1—2.4 (m, 2 H), 6.40 (t, J=7 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−54.1 (s): IR 2950, 2880, 1244, 1142, 1128, 1008, 825 cm^{-1}; MS m/z (rel intensity) 288 (M^++2, 3), 286 (M^+, 4) 124 (12), 111 (11), 98 (13), 97 (20), 85 (14), 84 (28), 83 (26), 71 (28), 70 (55), 69 (50), 57 (66), 56 (72), 55 (49), 43 (100), 42 (18), 41 (64).

Found: C, 54.37; H, 7.82%. Calcd for $C_{13}H_{22}Cl_2F_2$: C, 54.36; H, 7.72%.

1-Cyclohexyl-2,3-dichloro-3,3-difluoropropene (19c'). This was prepared by the procedure applied to the synthesis of **19b'** and obtained as a colorless oil, bp 75—80 °C (bath temp)/12 Torr (1 Torr=133.322 Pa). ^{1}H NMR ($CDCl_3$) δ=0.8—2.0 (m, 10 H), 2.2—2.8 (m, 1 H), 6.26 (d, J=9.3 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−54.0 (s); IR 2945, 2870, 1449, 1246, 1212, 1129, 1096, 996, 828 cm^{-1}; MS m/z (rel intensity) 228 (M^+, 1), 137 (13), 115 (5), 101 (5), 83 (8), 82 (100), 81 (21), 69 (9), 68 (5), 67 (69), 55 (10), 54 (16), 41 (25).

Found: C, 47.00; H, 5.36%. Calcd for $C_9H_{12}Cl_2F_2$: C, 47.19; H, 5.28%.

Ethyl 3-(3-Chloro-2,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (22a). This was obtained as a colorless oil which consisted of ca. 1 : 1 stereoisomers. ^{1}H NMR ($CDCl_3$) δ=1.21 (s, 3 H), 1.27 (t, J=7.2 Hz, 3 H), 1.31 (s, 3 H), 1.67 (d, J=5.5 Hz, 1 H), 2.30 (ddd, J=5.5, 9.7, and 0.9 Hz, 1 H), 4.18 (m, 2 H), 5.26 (dd, J=9.7 and 31 Hz, 1 H) for the (1R*,3R*)-isomer, δ=1.27 (s, 3 H), 1.27 (t, J=7.2 Hz, 3 H), 1.89 (d, J=8.6 Hz, 1 H), 2.11 (dd, J=8.6 and 9.8 Hz, 1 H), 4.18 (m, 2 H), 6.10 (dd, J=9.8 and 33 Hz, 1H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−58.5 (d, J=17 Hz, 2 F), −58.8 (d, J=17 Hz, 2 F), −131 (dt, J=31 and 17 Hz, 1 F); IR 1733, 1221, 1190, 1152, 1136, 1091, 1062, 1050, 934 cm^{-1}; MS m/z (rel intensity) 270 (M^+, 3), 225 (17), 199 (19), 197 (58), 162 (11), 161 (14), 141 (20), 97 (11), 65 (15), 59 (10), 41 (19).

Found: m/z 270.0643. Calcd for $C_{11}H_{14}F_3ClO_2$: M, 270.0633.

Ethyl 3-(2,3-Dichloro-3,3-difluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (22b): A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.23 (s, 3 H), 1.28 (t, J=7.2 Hz, 3 H), 1.33 (s, 3 H), 1.75 (d, J=5.3 Hz, 1 H), 2.39 (dd, J=5.3 and 9.2 Hz, 1 H), 4.14 (q, J=7.2 Hz, 1 H), 6.23 (d, J=9.2 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−54 (s); MS m/z (rel intensity) 286 (M^+, trace), 241 (10), 215 (25), 213 (37), 177 (12), 141 (17), 77 (10), 61 (15), 41 (17).

Found: m/z 286.0358. Calcd for $C_{11}H_{14}Cl_2F_2O$: M, 286.0338.

1-Bromo-2-chloro-1,1-difluoro-2-tridecene (19b"). Thionyl bromide (33 mg, 0.16 mmol) was added to **18b** (24 mg, 0.13 mmol) dissolved in diethyl ether (0.5 ml), and the mixture was stirred for 4 h at 40 °C in a sealed tube. Workup and preparative TLC (dichloromethane-hexane 1 : 10) afforded **19b"** (36 mg, 84% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.8—1.0 (m, 3 H), 1.1—1.7 (m, 16 H), 2.1—2.4 (m, 2 H), 6.40 (t, J=7.2 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−48.8 (s); IR 2945, 2875, 1824, 1470, 1233, 1141, 1128, 990, 802 cm^{-1}; MS m/z (rel intensity) 330 (M^+, trace), 124 (11), 97 (7), 85 (11), 84 (6), 83 (10), 71 (21), 70 (11), 69 (15), 57 (53), 56 (16), 55 (27), 43 (100), 42 (11), 41 (57).

Found: m/z 330.0554. Calcd for $C_{13}H_{22}BrClF_2$: M, 330.0560.

The compound **19b"** was alternatively prepared in 67% yield by treatment of **18b** with an equimolar amount of phosphorus tribromide at 0 °C in ether and stirring the reaction mixture at room temperature for 1.5 h and at 35 °C for 13 h.

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19) Although the cis-acid has been claimed in Ref 4f, its mp is not noted. Pure trans-acid **12f** has been reported to have mp 97—103 °C (Ref. 4f); cis/trans 1 : 1 mixture, mp 64—74 °C or oil.