°C); ^{1}H NMR δ 3.67 (s, 2 H), 3.83 (s, 3 H), 3.90 (m, 2 H), 4.13 (m, 2 H), 6.80–7.53 (m, 4 H).

Preparation of α-Arylalkanoic Acids from α-Haloalkyl Aryl Ketals. General Procedure. A mixture of anhydrous catalyst (amount given in Table I), α-haloalkyl aryl acetal (10 mmol), and the solvent (10 mL) was heated at reflux, under nitrogen, and kept under these conditions for the time given in Table I.

After cooling to room temperature, the reaction mixture was poured into water (100 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave the crude ester, which was dissolved in a solution of 30% aqueous sodium hydroxide (15 mL) in methanol (50 mL) and heated at reflux, under stirring, for 4 h. The reaction mixture was poured into water and extracted with diethyl ether (2 × 50 mL). The aqueous phase was acidified with concentrated hydrochloric acid and extracted with diethyl ether (3 × 80 mL). The organic extract was washed with water and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave the crude α-arylalkanoic acid. Purity, determined by GLC on the corresponding methyl ester (obtained by treatment with diazomethane), was found to be higher than 95%. The results are given in Table I.

Physical data of α-arylalkanoic acids of Table I: 2-(4-methoxyphenyl)acetic acid, mp 87–88 °C (water) (lit.[2a] mp 83–84 °C); 2-(4-methylphenyl)acetic acid, mp 94 °C (benzene) (lit.[2a] mp 91 °C); phenylacetic acid, mp 76–77 °C (hexane) (lit.[2a] mp 77 °C); 2-(4-methoxyphenyl)propionic acid, mp 57 °C (hexane) (lit.[2a] mp 56–57 °C); 2-(4-methylphenyl)propionic acid, mp 38–39 °C (hexane) (lit.[2h] mp 36–37 °C); 2-phenylpropionic acid, mp 16 °C (hexane) (lit.[2a] mp 16 °C); 2-(4-chlorophenyl)propionic acid, mp 57 °C (hexane) (lit.[10] mp 57–58 °C); 2-(6-methoxy-2-naphthyl)-propionic acid, mp 154–155 °C (acetone–hexane) (lit.[2a] mp 150–151 °C); 2-(4-isobutylphenyl)propionic acid, mp 76 °C (hexane) (lit.[2a] mp 75–77 °C).

Reaction between 2-(Bromomethyl)-2-(4-methoxyphenyl)-1,3-dioxane and Zinc Bromide. A mixture of anhydrous zinc bromide (0.67 g, 3 mmol), 2-(bromomethyl)-2-(4-methoxyphenyl)-1,3-dioxane (2.87 g, 10 mmol), and toluene (10 mL) was heated at reflux, under nitrogen, for 3 h. After cooling to room temperature, the reaction mixture was poured into water (100 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water and dried (Na_2SO_4).

Evaporation of the solvent under reduced pressure gave the 3-bromopropyl ester of 2-(4-methoxyphenyl)acetic acid (2.81 g, 9.8 mmol; yield 98%) as an oil: ^{1}H NMR δ 2.10 (m, 2 H, J = 6 Hz), 3.36 (t, 2 H, J = 6 Hz), 3.51 (s, 2 H), 3.73 (s, 3 H), 4.17 (t, 2 H, J = 6 Hz), 6.75–7.33 (m, 4 H); IR (stretching C=O) 1735 cm^{-1}.

Reaction of 2-(Bromomethyl)-2-(4-methoxyphenyl)-1,3-dioxolane with Zinc Bromide. Anhydrous zinc bromide (0.67 g, 3 mmol) and 2-(bromomethyl)-2-(4-methoxyphenyl)-1,3-dioxolane (2.73 g, 10 mmol) were reacted under the experimental conditions described above. The 2-bromoethyl ester of 2-(4-methoxyphenyl)acetic acid (2.67 g, 9.8 mmol; yield 98%) was obtained as an oil: ^{1}H NMR δ 3.47 (t, 2 H, J = 6 Hz), 3.60 (s, 2 H), 3.73 (s, 3 H), 4.37 (t, 2 H, J = 6 Hz), 6.80–7.30 (m, 4 H); IR (stretching C=O) 1735 cm^{-1}.

Reaction of 2-Bromo-1,1-dimethoxy-1-(4-methoxyphenyl)propane with a Stoichiometric Amount of Zinc Chloride: Determination of the Ratio between Methyl Chloride and Methyl Bromide. A mixture of anhydrous zinc chloride (1.36 g, 10 mmol), 2-bromo-1,1-dimethoxy-1-(4-methoxyphenyl)propane (2.88 g, 10 mmol), and toluene (10 mL) was stirred at reflux for 1 h. The gas, evolved during the reaction, was collected into cold (0 °C) chloroform. NMR analysis carried out on the chloroform solution revealed the presence of methyl bromide and methyl chloride in a 2:1 ratio. In a parallel experiment, aliquots (0.5 mL) were removed at suitable intervals and diluted with toluene. 3-Phenyl-1-bromopropane was added as internal standard. The solutions were analyzed by GLC: 2-chloro-1,1-dimethoxy-1-(4-methoxyphenyl)propane was not detected (the GLC method shows the presence of less than 0.50% of α-chloro acetal in a mixture of α-chloro and α-bromo acetals).

Competitive Experiments (Table II). A mixture of anhydrous zinc bromide (1 mmol) and of two α-halo acetals (10 mmol, molar ratio 1:1) in toluene (20 mL) was stirred, under nitrogen, at 80 °C. Aliquots (0.5 mL) were removed at suitable times and diluted with toluene (4 mL). 3-Phenyl-1-bromopropane was added as internal standard. The amount of the two methyl esters and of the unreacted α-halo acetals were determined by GLC. The results are reported in Table II.

Acknowledgment. We thank Prof. F. Minisci, Dr. L. Cassar, and Dr. A. Garbesi for helpful discussions.

Registry No. **1a**, 80336-70-5; **1b**, 84508-58-7; **1c**, 33604-54-5; **1d**, 84508-61-2; **1e**, 84508-65-6; **1f**, 87338-02-1; **1g**, 87338-03-2; **1h**, 87338-04-3; **1i**, 80336-55-6; **1j**, 84508-64-5; **1k**, 87338-05-4; **1l**, 87350-67-2; **3a**, 104-01-8; **3b**, 622-47-9; **3c**, 103-82-2; **3d**, 1878-66-6; **3e**, 942-54-1; **3f**, 938-94-3; **3g**, 492-37-5; **3h**, 938-95-4; **3i**, 23981-80-8; **3j**, 15687-27-1; $ZnBr_2$, 7699-45-8; $ZnCl_2$, 7646-85-7; $SnCl_2$, 7772-99-8; $CoCl_2$, 7646-79-9; HgCl, 7546-30-7; $PdCl_2$, 7647-10-1; CuBr, 7787-70-4; $CaBr_2$, 7789-41-5; 2-bromo-1-phenyl-1-propanone, 2114-00-3; 2-(bromomethyl)-2-(4-methoxyphenyl)-1,3-dioxane, 80336-74-9; 3-bromopropyl 2-(4-methoxyphenyl)acetate, 80336-90-9; 2-(bromomethyl)-2-(4-methoxyphenyl)-1,3-dioxolane, 4366-28-3; 2-bromoethyl (4-methoxyphenyl)acetate, 80336-89-6; 2-bromo-1-(4-methoxyphenyl)ethanone, 2632-13-5.

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Synthesis of Carbon and Phosphorus Esters of α-Fluoro Alcohols

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Carbon and phosphorus esters of α-fluoro alcohols are promising functions for the construction of suicide substrates for esterases, phosphatases, and other enzymes. A route for the synthesis of substrates incorporating these hitherto inaccessible functionalities is reported here. The acetate, diethyl phosphate, and diphenyl phosphate esters of 1,1-difluoro alcohols have been prepared in low to moderate yields from 1,1-difluoro-1-alken-3-ols by allylic transposition of the esterified hydroxyl group. A general synthetic route to the required 1,1-difluoro-1-alken-3-ols, involving ketone trimethylsilylcyanation, reduction to trimethylsilylated α-hydroxy aldehydes, and difluoromethylene Wittig reaction, has been developed. The difluorinated olefins can be reduced to the monofluoro derivatives with $LiAlH_4$. The phosphate but not the carbon esters can be prepared from the *mono*fluorovinyl alcohols by the allylic transposition approach.

The hydrolysis of carboxylic and phosphate esters, a universal biological process, is catalyzed by a broad variety of distinct enzymes that differ in mechanism, substrate specificity, and cellular location. The diversity of hydro-

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lytic enzymes and the potential pharmacological utility of enzyme-specific irreversible inhibitors make the development of appropriate specific inhibitors of substantial importance. Efforts in this area have focused recently on suicide substrates, compounds activated by the target enzymes to species that specifically and irreversibly inactivate them.[1-5] The key to suicide inactivation of an esterase is the presence of a latent reactive moiety in the substrate that is unmasked by the hydrolytic action of the enzyme and reacts with a nucleophile in its active site. Esters of 1,1-difluoro alcohols are attractive candidates for the construction of such suicide substrates because the enzymatically liberated alcohols are expected to undergo rapid conversion to acyl fluorides (eq 1).[6,7] The reactivity

$$RCF_2OC(O)R^1 \rightarrow [RCF_2OH] \rightarrow RC(O)F \quad (1)$$

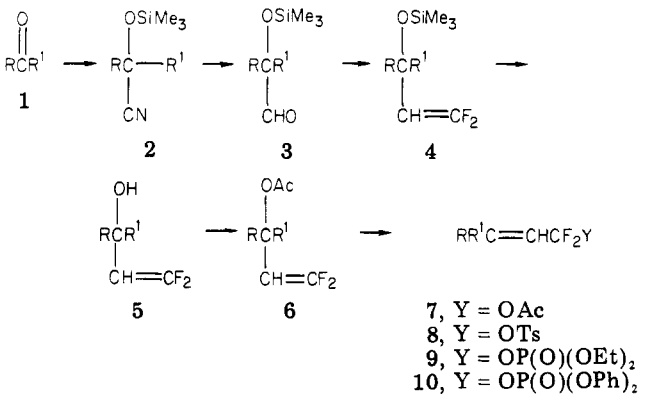
of acyl fluorides as chemical and biological acylating agents is well documented.[8] Although 1,1-dichloro alcohols are, in principle, equally suitable for the construction of suicide substrates, the close parity in size between fluorine and hydrogen makes fluorine the preferred substituent in structures subject to the steric constraints imposed by enzymic active sites. Unfortunately, general synthetic routes to carbon or phosphorus esters of 1,1-difluoro alcohols have not been mapped out, although difluoromethoxy esters are known to be formed in the reaction of acids with difluorocarbene,[9] and esters of perfluorinated, and consequently atypical, alcohols have been described.[10] We describe here a synthetic route to carbon and phosphorus esters of 1,1-difluoro alcohols[11] and its extension to the synthesis of the analogous monofluorinated esters.

The usual strategy for the synthesis of an ester, acylation of the alcohol, is ruled out for 1,1-difluoro alcohols because the very instability that makes them attractive as suicide substrates renders their direct acylation impractical. We have therefore concentrated on synthetic avenues in which the ester function, including the esterifed oxygen, is added to the fluorinated carbon. Although nucleophilic displacement of functionality from fluorinated carbons was examined in exploratory experiments,[12] rearrangement of the ester from the unfluorinated to the fluorinated end of a terminally fluorinated allylic system has yielded the best results (eq 2). The acid-catalyzed reaction of tertiary

$$RR^1C(OAc)CH{=}CF_2 \rightarrow RR^1C{=}CHCF_2OAc \quad (2)$$

allylic alcohols with acetic anhydride to give allylically transposed primary acetates[13,14] provided the point of departure for our development of this strategy. A prerequisite to our exploration of the functional group shift, however, was the development of a general synthetic route to 1,1-difluoro-1-alken-3-ols, the springboards required for the proposed rearrangement reactions.

Scheme I[a]



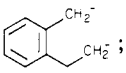
[a] a, R = CH_3, R^1 = $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH_2CH_2$; b, R,$R^1$ =  ; c, R = Me, R^1 = C_6H_5; d, R = CH_3, R^1 = $CH_3(CH_2)_8$.

Table I. Carbon Esters of 1,1-Difluoro-1-alken-3-ols[a]

starting ketone	intermediates and products (yields, %)
1a	3a (88), 5a (84), 6a (98), 7a (70)[b]
1b	3b (90),[a] 5b (72),[a] 6b (98), 7b (36) + 8b (14)
1c	3c (84), 4c (65), 7c (24)
1d	3d (64), 5d (70),[a] 7d (30)

[a] Yield of this product determined prior to preparation of the analytical sample. [b] Yield determined by NMR.

Results

1,1-Difluoro-1-alken-3-ols. Allylically fluorinated unsaturated alcohols have been constructed from ketones by a sequence of steps equivalent to addition of a 2,2-difluorovinyl moiety to the carbonyl group (Scheme I). The first step in the sequence, reaction of the ketones with trimethylsilyl cyanide (Me_3SiCN) according to the procedure of Evans et al.[15,16] yields trimethylsilylated cyanohydrins that can be isolated but are most conveniently carried through the subsequent reduction without purification. The cyanohydrins were reduced at −20 °C in tetrahydrofuran with diisopropylaluminum hydride to avoid the overreduction that occurs if $LiAlH_4$ is substituted for diisopropylaluminum hydride[15-17] or if hexane is used as the solvent. This route to α-hydroxy aldehydes is similar, except for protection of the cyanohydrin with a trimethylsilyl rather than tetrahydropyranyl group, to one developed concurrently by Schlosser and Brich.[18]

The trimethylsilylated α-hydroxy aldehydes are converted in good yield to protected 1,1-difluoro-1-alken-3-ols by reaction with the reagent generated in situ from CF_2Br_2 and *tris*(dimethylamino)phosphine.[19] Basic hydrolysis of

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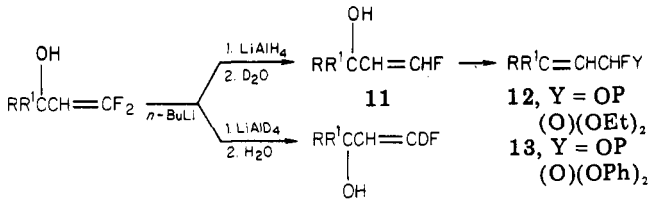
Scheme II[a]



[a] a-d as in Scheme I.

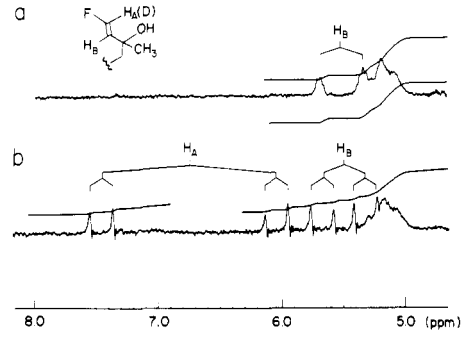


Figure 1. NMR spectra of the vinyl proton region of 1-fluoro-3,7,11-trimethyl-1,6,10-dodecatrien-3-ol (**11a**) obtained by reduction of **5a**: (a) product of reduction by $LiAlD_4$ and workup in H_2O; (b) product of reduction by $LiAlH_4$ and workup in D_2O. The latter spectrum is identical with that obtained if the reaction is carried out without labeled reagents. The protons responsible for the observed signals are labeled in the inset structure.

the trimethylsilyl protecting group provides the free alcohols (Table I) which are stable indefinitely at 0 °C in the absence of acid but rapidly decompose in its presence. Allylically fluorinated alcohols have also been prepared recently by addition of (2,2-difluorovinyl)lithium to ketones.[20]

1-Fluoro-1-alken-3-ols. Our first attempts to prepare vinylically monofluorinated alcohols involved reaction of the trimethysilylated α-hydroxy aldehydes with the reagent formed from (fluoroiodomethyl)triphenylphosphonium iodide and zinc–copper couple,[21] but the cumbersome nature of the reaction and its low and erratic yields led us to search for a better procedure.[12,22] The report that $LiAlH_4$ reduces trifluorovinyl to difluorovinyl carbinols,[23] extended during the course of our work to the dehalogenation of difluoro olefins,[24] led us to investigate the possible analogous removal of fluorine from the readily available 1,1-difluoro-1-alken-3-ols. In effect, conversion of the difluoro alcohols **5a** and **5b** to lithium alkoxides with *n*-butyllithium, followed by reaction with $LiAlH_4$, gave the monofluorovinyl derivatives **11a** and **11b** in high yield (Scheme II). The reduction provides in both instances approximately a 9:1 *Z*/*E* mixture of the monofluoro isomers.

The mechanism of the reduction was investigated by deuterium-labeling experiments. Reduction of the π bond of unhalogenated allylic alcohols with $LiAlH_4$ introduces a hydride from the reagent at the π-bond carbon farthest away from the hydroxyl group and a proton from water at the carbon closest to it.[25,26] The reaction of difluoro-

Table II. Phosphate Esters of 1-Fluoro and 1,1-Difluoro Alcohols

substrate	product (yield, %)	substrate	product (yield, %)
5a	**9a** (30)	**5d**	**10d** (75)
5a	**10a** (80)	**11a**	**12a** (15)[a]
5b	**9b** (19)	**11a**	**13a** (30)
5b	**10b** (55)	**11b**	**13b** (30)

[a] This product is highly unstable.

vinyl carbinols with $LiAlH_4$, however, results in loss of a vinylic fluoride rather than in saturation of the π bond. When the dehalogenation was carried out with $LiAlD_4$ and the reaction was worked up in H_2O, one deuterium was shown by the NMR spectra (Figure 1) and mass spectrometry to be introduced exclusively into the terminal position originally occupied by the displaced fluorine. When the reaction was carried out with $LiAlH_4$ but the workup was done in D_2O, no deuterium was incorporated into the product (Scheme II). In no instance was deuterium found at the internal vinyl position. These results require addition of the hydride to the terminal (difluorinated) carbon of the π bond. The π bond is restored when the carbanion thus generated, stabilized by the fluorine electron-withdrawing effect[27] and possibly by coordination to lithium or aluminum, eliminates one of the fluorines. Hydride addition thus occurs at opposite ends of the π bond in the reduction of unhalogenated and terminally difluorinated allylic alcohols.

Acetates of 1,1-Difluoro Alcohols. In the initial experiments, difluorovinyl carbinol **5a** was converted to the allylically rearranged 1,1-difluoroacetate **7a** by stirring in acetic anhydride with a catalytic amount of *p*-toluenesulfonic acid according to the procedure of Babler and co-workers.[13,14] The primary difluoroacetate, obtained in 35–40% isolated yield, was accompanied by approximately a 30% yield of the acyl fluoride and by small amounts of unidentified fluorohydrocarbons. On the assumption that the acyl fluoride results from rearrangement of the hydroxyl group to the difluorinated allylic terminus prior to acetylation, the acetylation and rearrangement were carried out as discrete steps. A high yield (98%) of tertiary acetate **6a** is obtained when **5a** is stirred in acetic anhydride with triethylamine and 4-(dimethylamino)pyridine, a base that catalyzes the esterification of hindered alcohols.[28] Efforts to promote allylic rearrangement of the tertiary acetate by refluxing in benzene in the presence (or absence) of KOAc and 18-crown-6 were unsuccessful, but stirring the tertiary acetate with acetic anhydride and *p*-toluenesulfonic acid afforded 1,1-difluoroacetate **7a** in 75–80% yield (by NMR analysis). The two-step procedure has consequently been employed, except in the case of **7c**, to prepare the allylically fluorinated acetates (Table I). The rearrangement of tertiary acetate **6b** does not go to completion when a catalytic amount of *p*-toluenesulfonic acid is used. Increasing the concentration of the acid leads to complete disappearance of the starting material but results not only in formation of primary acetate **7b** but also of tosylate **8b** (50% combined yield, 3:1 acetate to tosylate). If the reaction is run in dimethoxyethane with a 2-fold excess of *p*-toluenesulfonic acid, the combined yield is raised to 75%, and the tosylate becomes the dominant

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product (2:1 **8b**/**7b**). A similar ratio of tosylate **8a** to acetate **7a** is obtained if the rearrangement of **6a** is carried out under the same reaction conditions.

Phosphate Esters of 1,1-Difluoro Alcohols. The diethyl- and diphenylphosphates of 1,1-difluoro alcohols have been synthesized by allylic transposition of the phosphate ester functionalities. The lithium alkoxide of **5a** reacts with diethyl chlorophosphate in benzene, for example, to give diethyl phosphate **9a** and the primary chloride as the minor and major products, respectively (Table II). Reaction of **5a** with diphenyl phosphorochloridate, 4-(dimethylamino)pyridine, and triethylamine, on the other hand, provides a 2:1 mixture of the 2-*E* and 2-*Z* isomers of **10a** in 80% yield. The isomers of **10b** are similarly obtained from difluoro alcohol **5b** (Table II). No reaction is observed, however, if diethyl phosphorochloridate is substituted for diphenyl phosphorochloridate even when 4-pyrrolidinopyridine[29] is used to promote the reaction.

Esters of Monofluoro Alcohols. Monofluorinated phosphorus, but not carbon, esters can also be prepared by allylic transposition (Table II). The primary diphenyl phosphate esters **13a** and **13b** are readily obtained from the reactions of **11a** and **11b** with diphenyl phosphorochloridate in the presence of 4-(dimethylamino)pyridine and triethylamine. The reaction of tertiary alcohol **11a** with *n*-butyllithium and diethyl phosphorochloridate in hexane is less satisfactory as it provides diethyl phosphate **12a** in a low and erratic yield (maximum about 15%). The reaction of **11b** with diethyl phosphochloridate under similar conditions furthermore gives no detectable trace of **12b**. Attempts to prepare the diphenyl phosphate of farnesol by phosphorylation–rearrangement of nerolidol, the unfluorinated hydrocarbon analogue of **5a**, were not successful. Allylic fluorine substitution thus appears to facilitate these rearrangement reactions. Consistent with this is the fact that all attempts to prepare primary *mo*nofluoroacetates by rearrangement of the tertiary allylic acetates failed. Although the monofluorinated tertiary esters [**11a** (acetate) and **11b** (acetate): see Experimental Section] are readily prepared, only unidentified hydrocarbon products were isolated from their reaction with *p*-toluenesulfonic acid in acetic anhydride.

The fluorinated esters, reasonably stable when stored at low temperatures in the presence of anhydrous potassium carbonate, are most successfully manipulated when contact with acids is minimized or avoided. The decomposition reaction may be autocatalytic because hydrogen fluoride is liberated upon hydrolysis of the esters. The monofluorinated esters are less stable than the corresponding difluoro analogues and are particularly susceptible to decomposition by heat, silica gel chromatography, and storage.

^{19}F and ^{31}P NMR of Phosphate Esters. An unusual *F*–C–O–*P* coupling is observed in the NMR spectra of difluoro esters (**9a** and **10a,b**) but not in the NMR spectra of monofluoro esters (**12a** and **13a,b**). The fluorine–phosphorus coupling, detectable both in the ^{19}F and ^{31}P NMR spectra, is most clearly observed under proton decoupling conditions (Figure 2). Both fluorines are coupled to the phosphorus in the difluoro esters. However, although coupling is observed between the proton that replaces a fluorine in the monofluoro esters and the phosphorus (Figure 2), no coupling is observed between the fluorine and phosphorus. The reason for the difference in fluorine–phosphorus coupling in the difluoro and monofluoro phosphate esters remains obscure. One possible explanation is that a conformation is favored for the monofluoro, but not the difluoro, esters that incidentally minimizes fluorine–phosphorus coupling.

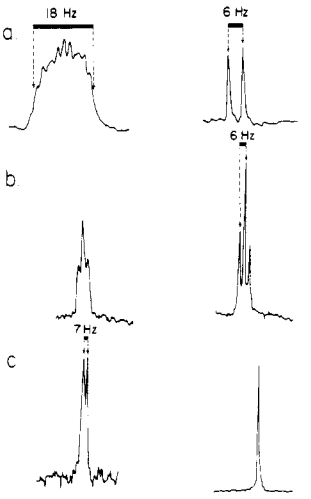

Figure 2. Long-range fluorine–phosphorus coupling in the NMR spectra of 1,1-difluorophosphate esters. (a) ^{19}F NMR spectra of the 2-*Z* isomer of diethyl phosphate **9a** before and after complete proton decoupling. (b) ^{31}P NMR spectra of the mixture of 2-*E* and 2-*Z* isomers of diphenyl phosphate **10a** before and after complete proton decoupling. (c) ^{31}P NMR spectra of the all-*trans* isomer of **13a** before and after proton decoupling.

Conclusions

The allylic rearrangement of a tertiary hydroxyl group to a fluorinated terminus subsequent to esterification provides a moderate-yield route to esters of 1,1-difluoro and 1-fluoro alcohols. This synthetic approach, albeit the first to make such structures accessible, is restricted to the preparation of vicinally unsaturated fluoro alcohol esters. The mechanisms of the rearrangement reactions, particularly those involved in translocation of the phosphate ester functionalities, remain to be defined. It is likely that the reactions involve ionization of the tertiary allylic esters to ion pairs that collapse to the sterically favored primary products. The available results suggest a reaction scheme in which a competition exists between recombination of the ion pair to the primary fluorinated ester, escape of the ion pair from the solvent cage to yield products of reaction with other nucleophiles (chloride, tosylate, hydroxyl), and proton loss from the cationic intermediate to give fluorocarbon derivatives.

Experimental Section

Materials. Gas chromatography was performed on a Varian 2100 instrument with flame-ionization detectors equipped with a 6 ft × 2 mm i.d. glass column packed with 3% OV-225 on 100–200-mesh Varaport 30 or 100–120-mesh Chromosorb W (N_2 carrier gas, 18–20 mL/min). Infrared spectra (thin film) were recorded on a Perkin-Elmer 337 grating spectrophotometer. Proton NMR spectra were determined in deuterated chloroform on a Varian A-60 or FT-80 and ^{19}F and ^{32}P NMR spectra in the same solvent on a Varian XL-100. Tetramethylsilane, trichlorofluoromethane, and trimethyl phosphate were employed as internal standards, respectively, for proton, fluorine, and phosphorus NMR. NMR chemical shifts are expressed in parts per million relative to the appropriate internal standards. Chemical-ionization mass spectra were run on an AEI MS-902 and electron-impact spectra on a Kratos MS-A25S instrument. Essentially all the reactions were run under a nitrogen atmosphere.

2,6,10-Trimethyl-2-[(trimethylsilyl)oxy]undeca-5,9-dienal (3a). A mixture of trimethylsilyl cyanide (Me_3SiCN, 155 mmol), geranyl acetone (141 mmol), and HgI_2 (approximately 100 mg)

(29) Hassner, A.; Krepski, L. R.; Alexanian, V. *Tetrahedron* **1978**, *34*, 2069–2076.

was stirred (an exothermic reaction occurs if freshly distilled Me_3SiCN is used) while the progress of the reaction was monitored by gas chromatography. The nitrile (**2a**) obtained on completion of the reaction may be isolated by distillation: 90% yield; GLC (150 °C) retention time 6.68 min; IR (film) 2950, 2910, 2850 cm^{-1}; NMR 0.25 (s, 9 H, Me_3Si), 1.58 (s, 3 H, Me), 1.63 and 1.70 (2 s, 9H, vinyl Me), 2.03 (br m, 8 H, C=CCH_2), 5.20 ppm (m, 2 H, C=CH); CIMS, *m/e* 294 (MH^+). Anal. Calcd for $C_{17}H_{31}ONSi$: C, 69.56; H, 10.65; N, 4.77. Found: C, 69.59; H, 10.54; N, 4.57. The nitrile normally was not isolated but was directly reduced after removal under vacuum of excess Me_3SiCN. Diisobutylaluminum hydride (DIBAL, 210 mmol) was added to a solution of the nitrile in 300 mL of THF with stirring under nitrogen at −78 °C. The reaction mixture was then stirred at −20 °C until the reaction was complete (gas chromatography). The cold mixture was poured into 800 mL of ice-cold 5% H_2SO_4, the reaction flask was rinsed with 100 mL of diethyl ether, the biphasic mixture was stirred at 0 °C for 30 min, and a further 200 mL of diethyl ether was added. The organic layer and three further ether extracts were combined, washed with brine, and dried ($MgSO_4$). Solvent removal on a rotary evaporator gave 39.90 g of an orange oil that, on distillation through a short-path apparatus (0.15 torr, 110–130 °C), gave **3a** in 88% yield (corrected for recovered starting material). An analytical sample was obtained by LPLC (5% ethyl acetate in hexane): GLC (150 °C) retention time 5.39 min; IR, 1740 cm^{-1} (C=O); NMR 0.17 (s, 9 H, Me_3Si), 1.30 (s, 3 H, C-3 Me), 1.62 and 1.68 (2 s, 9 H, vinyl CH_3), 2.00 (m, 8 H, C=CCH_2), 5.13 (m, 2 H, C=CH), 9.62 ppm (s, 1 H, CHO); CIMS, *m/e* 297 (MH^+), 207 ($MH^+ - Me_3SiOH$). Anal. Calcd for $C_{17}H_{31}O_2Si$: C, 68.86; H, 10.88. Found: C, 68.83; H, 10.92.

1,1-Difluoro-3,7,11-trimethyl-3-[(trimethylsilyl)oxy]-1,6,10-dodecatriene (4a). Dibromodifluoromethane (approximately 38 g, 181 mmol) was condensed into 250 mL of THF at −78 °C with the help of a dry ice condenser. *Tris*(dimethylamino)phosphine (54 g, 330 mmol) was then added, and the mixture was allowed to warm to room temperature before aldehyde **3a** (20.42 g, 68.87 mmol) was added. The aldehyde, as shown by gas chromatography, was consumed within 30 min. The reaction slurry was transferred to a separatory funnel by using 300 mL of water and 500 mL of pentane. The layers were separated, and the aqueous layer was washed with two further 200-mL aliquots of pentane. The combined organic extracts, washed with brine and dried ($MgSO_4$), yielded 23.59 g of orange oil on solvent removal. The oil, distilled through a short-path apparatus, gave 19.22 g of **4a** as a pale yellow oil: bp 85–96 °C (0.05–0.075 torr); GLC (120 °C) retention time 7.50 min. An analytical sample was prepared by LPLC (hexane): IR (film) 1740 cm^{-1} (C=CF_2); NMR 0.13 (s, 9 H, Me_3Si), 1.43 (d, J = 2.5 Hz, 2 H, C-3 Me), 1.63 and 1.72 (2 s, 9 H, vinyl Me), 2.03 (br m, 8 h, C=CCH_2), 4.38 (dd, J = 26.5, 6.5 Hz, 1 H, CH=CF_2), 5.18 ppm (m, 2 H, C=CH); ^{19}F NMR 86.8 (J = 46, 6 Hz, trans F), 84.6 ppm (J = 46, 27 Hz, cis F); CIMS, *m/e* 331 (MH^+), 241 ($MH^+ - HF - Me_3SiOH$). Anal. Calcd for $C_{18}H_{32}F_2OSi$: C, 65.40; H, 9.76. Found: C, 65.33; H, 9.54.

1,1-Difluoro-3,7,11-trimethyl-1,6,10-dodecatrien-3-ol (5a). The trimethylsilyl ether **4a** (10.00 g, 30.25 mmol) in 13 mL of 15% aqueous NaOH and 50 mL of methanol was stirred at 50 °C for 2 h, at which time the reaction was complete (gas chromatography). The reaction mixture was immediately partitioned between hexane and water. After extraction three times with hexane, the combined extracts were washed with water and dried ($MgSO_4$), and the solvent was removed to give 7.93 g (100%) of **5a** as a pale yellow oil: GLC (130 °C) retention time 8.58 min; IR (film) 3375 (OH), 1740 cm^{-1} (C=CF_2); NMR 1.43 (d, J = 2 Hz, 3 H, C-3 Me), 1.63 and 1.72 (2 s, 9 H, vinyl Me), 2.05 (br m, 8 H, C=CCH_2), 2.15 (s, 1 H, OH), 4.43 (dd, J = 26, 6 Hz, 1 H, CH=CF_2), 5.20 ppm (m, 2 H, C=CH); ^{19}F NMR 84.9 (dd, J = 46, 26 Hz, cis F), 86.3 ppm (dd, J = 46, 6 Hz, trans F); CIMS, *m/e* 241 ($MH^+ - H_2O$), 219 ($MH^+ - HF - H_2O$). Anal. Calcd for $C_{15}H_{24}F_2O$: C, 69.73; H, 9.36. Found: C, 69.63; H, 9.12.

2-Formyl-1,2,3,4-tetrahydro-2-[(trimethylsilyl)oxy]-naphthalene (3b). A mixture of HgI_2 (30 mg) and β-tetralone (15.94 g, 109 mmol) was stirred 20 min before freshly distilled Me_3SiCN was added (exothermic reaction). The mixture was heated (80 °C) for 5 h and cooled to room temperature, and the excess Me_3SiCN was removed under vacuum (water aspirator). The nitrile was reduced without isolation. THF (150 mL) was added to the residue, and the solution was cooled to −78 °C before diisobutylaluminum hydride (142 mL of a 1.0 M solution in hexane) was added dropwise. The reaction mixture was allowed to warm to room temperature while the reaction progress was monitored by gas chromatography. Upon completion of the reaction, the mixture was poured into 600 mL of ice-cold 5% H_2SO_4 with vigorous stirring. The aqueous phase was extracted with diethyl ether. The combined ether extracts were washed with brine, dried over $MgSO_4$, and concentrated under vacuum to give 24.35 g (90%) of a clear pale yellow oil. Purification by LPLC (15% ethyl acetate in hexanes) gave pure **3b**: GLC (150 °C) retention time 3.75 min; IR (film) 1740 cm^{-1} (C=O); NMR 0.06 (s, 9 H, Me_3Si), 1.57–1.96 (m, 2 H, C-3 CH_2), 2.63–3.36 (m, 4 H, C-4 and C-1 CH_2's), 7.11 (s, 4 H, aromatic H), 9.67 ppm (s, 1 H, CHO); EIMS, *m/e* 248 (M^+), 233 ($M^+ - Me$), 220 ($M^+ - CO$). Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.69; H, 8.12. Found: C, 67.33; H, 8.13.

2-(2,2-Difluoroethenyl)-2-[(trimethylsilyl)oxy]-1,2,3,4-tetrahydronaphthalene (4b). Dibromodifluoromethane (approximately 15 g, 70 mmol) was condensed into 150 mL of THF at −78 °C. *Tris*(dimethylamino)phosphine (25.5 mL, 140 mmol) was added and the mixture allowed to warm to room temperature. Aldehyde **3b** (8.69 g, 35 mmol) was added, and the reaction mixture was stirred until the reaction was complete (gas chromatography). The mixture was partitioned between water and pentane. The organic layer, washed with brine and dried over Mg_2SO_4, gave, on solvent removal, 8.38 g (85%) of **4b** as a clear orange oil. The material was usually carried on without purification but can be purified by LPLC (15% ethyl acetate in hexane), although losses are incurred due to decomposition on the column: GLC (130 °C) retention time 2.7 min; IR (film) 1740 cm^{-1} (C=CF_2); NMR 0.08 (s, 9 H, Me_3Si), 2.00 (t, J = 7 Hz, 2 H, C-3 CH_2), 2.83 (t, J = 7 Hz, 2 H, C-4 CH_2), 3.04 (s, 2 H, C-1 CH_2), 4.40 (dd, J = 27, 5 Hz, 1 H, CH=CF_2), 7.08 ppm (s, 4 H, aromatic H); ^{19}F NMR 82 (dd, J = 42, 27 Hz, *cis*-C=CF), 84.6 ppm (dd, J = 42, 5 Hz, *trans*-C=CF); EIMS, *m/e* 282 (M^+). Anal. Calcd for $C_{15}H_{20}OF_2Si$: C, 63.79; H, 7.14. Found: C, 64.00; H, 7.06.

2-(2,2-Difluoroethenyl)-1,2,3,4-tetrahydro-2-naphthalenol (5b). To a solution of **4b** (2.5 g, 8.8 mmol) in 12.5 mL of methanol was added 1.0 mL of 15% NaOH. The reaction mixture, which turned dark blue, was stirred for 12 h at room temperature. The mixture was partitioned between water and pentane, and the combined pentane extracts were washed with brine and dried over $MgSO_4$. Solvent removal gave 1.57 g of a clear yellow oil that was purified by LPLC (20% ethyl acetate in hexane): GLC (150 °C) retention time 3 min; IR (film) 3375 (OH), 1740 cm^{-1} (C=CF_2); NMR 1.80 (s, 1 H, OH), 2.03 (t, J = 7 Hz, 2 H, C-3 CH_2), 2.90 (t, J = 7 Hz, 2 H, C-4 CH_2), 3.02 (s, 2 H, C-1 CH_2), 4.48 (dd, J = 27, 5 Hz, 1 H, CH=CF_2), 7.10 ppm (s, 4 H, aromatic H); ^{19}F NMR 82.6 (dd, J = 42, 27 Hz, *cis*-C=CF), 84.6 ppm (dd, J = 42, 5 Hz, *trans*-C=CF); EIMS, *m/e* 210 (M^+), 192 ($M^+ - H_2O$). Anal. Calcd for $C_{12}H_{12}OF_2$: C, 68.56; H, 5.76. Found: C, 68.94; H, 6.16.

2-Phenyl-2-[(trimethylsilyl)oxy]propanal (3c). This compound was prepared from acetophenone as described for the preparation of **3a** in 68–84% yield: GLC (120 °C) retention time 4.69 min; IR (film) 1740 cm^{-1} (C=O); NMR 0.10 (s, 9 H, Me_3Si), 1.60 (s, 3 H, Me), 7.10–7.50 (br m, 5 H, aromatic), and 9.35 ppm (s, 1 H, CHO). CIMS, exact mass calcd for $C_{12}H_{19}SiO_2$ 223.1154, found 223.1158.

1,1-Difluoro-3-phenyl-3-[(trimethylsilyl)oxy]-1-butene (4c). Compound **4c** was obtained by the procedure used to prepare **4a** in 65% yield after purification by LPLC (5% ethyl acetate in hexane): GLC (120 °C) retention time 1.52 min; IR (film) 1740 cm^{-1} (C=CF_2); NMR 0.13 (s, 9 H, Me_3Si), 1.73 (d, J = 3 Hz, 3 H, Me), 4.63 (dd, J = 26, 6 Hz, 1 H, C=CH), 7.17–7.67 ppm (m, 5 H, aromatic); ^{19}F NMR 83.27 (d of d of q, J = 41.5, 26, 3 Hz, *cis*-F), 85.92 ppm (dd, J = 41.5, 6 Hz, *trans*-F); CIMS, *m/e* 167 ($MH^+ - Me_3SiOH$). Anal. Calcd for $C_{13}H_{18}F_2SiO$: C, 60.90; H, 7.08. Found: C, 61.13; H, 6.99.

1,1-Difluoro-3-methyl-3-[(trimethylsilyl)oxy]-1-dodecene (4d). 2-[(Trimethylsilyl)oxy]-2-methylundecanenitrile [^1H NMR 0.16 (s, 9 H, Me_3Si), 0.81 (br t, J = 4 Hz, 3 H, CH_2CH_3), 1.20 (s, 16 H, methylenes), 1.48 ppm (s, 3 H, C-2 Me)], prepared by the procedure used to synthesize **2a**, was reduced with diisopropylaluminum hydride to 2-[(trimethylsilyl)oxy]-2-methylundecanal

(**3d**) as described for **3a**: ^{1}H NMR 0.13 (s, 9 H, Me_3Si), 0.86 (br t, J = 5 Hz, 3 H, CH_2CH_3), 1.23 (s, 16 H, methylenes), 1.24 (s, 3 H, C-2 Me), 9.51 ppm (s, 1 H, CHO). The difluorovinyl derivative **4d** was prepared from **3d** as reported for **4a**: IR 1720 cm^{-1} (C=CF_2); NMR 0.10 (s, 9 H, Me_3Si), 0.88 (br t, J = 5 Hz, 3 H, CH_2CH_3), 1.26 (s, 16 H, methylenes), 1.38 (d, J = 2.5 Hz, 3 H, C-3 Me), 4.30 ppm (dd, J = 27, 6 Hz, 1 H, C=CH); ^{19}F NMR 84.75 (dd, J = 26, 35 Hz, *cis*-F), 86.96 ppm (dd, J = 8, 35 Hz, *trans*-F); EIMS, m/e 306 (M^+).

1,1-Difluoro-3-methyl-1-dodecen-3-ol (5d). Hydrolysis as described for **5a** gave the desired free alcohol: IR 3350 (OH), 1730 cm^{-1} (C=CF_2); NMR 0.87 (br t, J = 4 Hz, 3 H, CH_2CH_3), 1.26 (s, 16 H, CH_2's), 1.33 (d, J = 3 Hz, 3 H, C-3 Me), 5.46 (dd, J = 26, 6 Hz, 1 H, C=CH); ^{19}F NMR 85.96 (dd, J = 41.5, 4 Hz, *trans*-F), 82.77 ppm (dd, J = 41.5, 26, 3 Hz, *cis*-F). Anal. Calcd for $C_{13}H_{24}F_2O$: C, 66.63; H, 10.33. Found: C, 66.51; H, 10.33.

1-Fluoro-3,7,11-trimethyl-1,6,10-dodecatrien-3-ol (11a). To a solution of difluoro alcohol **5a** (1.03 g, 4.0 mmol) in 20 mL of diethyl ether at 0 °C was added *n*-butyllithium (1.39 mL of a 3.0 M hexane solution, 4.16 mmol). After the mixture was stirred 15 min at 0 °C, 228 mg (6.0 mmol) of lithium aluminum hydride was added, and the reaction mixture was warmed to room temperature and was finally refluxed for 24 h. After the mixture cooled, water (228 μL), 15% NaOH (228 μL), and additional water (684 μL) were sequentially added. Use of deuterated water in this work up does not result in incorporation of deuterium into the products. The mixture was stirred several minutes before anhydrous $MgSO_4$ was added. Filtration and solvent removal yielded 941 mg of a clear, slightly yellow, oil. LPLC (15% ethyl acetate in hexane) separated the 2-*Z* and 2-*E* isomers of **4c** (2-*Z*/2-*E* ratio 1:9, 90% combined yield). The *Z* isomer eluted first: GLC (150 °C) retention time 3.98 min; IR (film) 3400 (OH), 1670 cm^{-1} (C=CHF); NMR 1.42 (d, J = 1.5 Hz, 3 H, C-1 Me), 1.62 and 1.68 (2 s, 9 H, vinyl CH_3), 1.75 (m, 2 H, C-2 CH_2), 2.05 (m, 6 H, C=CCH_2), 5.08 (dd, J = 47, 5 Hz, 1 H, CH=CF), 5.17 (m, 2 H, C=CH), 6.13 ppm (dd, J = 85, 5 Hz, 1 H, C=CHF); ^{19}F NMR 127 ppm (dd, J = 86, 47 Hz); CIMS, m/e 223 ($MH^+ - H_2O$). Anal. Calcd for $C_{15}H_{25}OF$; C, 74.95; H, 10.48. Found: C, 75.09; H, 10.49. The *E* isomer eluted second: GLC (150 °C) retention time 5.63 min; IR (film) 3400 (HO), 1670 (C=CHF) cm^{-1}; NMR 1.32 (s, 3 H, C-1 Me), 1.63 and 1.70 (2 s, 9 H, vinyl Me), 1.73 (m, 2 H, C-2 CH_2), 2.02 (m, 6 H, C=CCH_2), 5.17 (m, 2 H, C=CH), 5.50 (dd, J = 21, 10 Hz, 1 H, CH=CF), 6.75 ppm (dd, J = 86, 10 Hz, 1 H, C=CHF); ^{19}F NMR 136 ppm (dd, J = 86, 21 Hz); CIMS, m/e 223 ($MH^+ - H_2O$), no MH^+. Anal. Calcd for $C_{15}H_{25}OF$: C, 74.95; H, 10.48. Found: C, 74.74; H, 10.36.

1-Fluoro-3,7,11-trimethyl-1,6,10-[1-^{2}H]dodecatrien-3-ol ([1-^{2}H]-11a). Difluoro alcohol **5a** was reduced as described for the preparation of unlabeled **11a** except that 2 molar equiv of lithium aluminum deuteride rather than 1.5 molar equiv of $LiAlH_4$ were used for the reduction. The 2-*Z* and 2-*E* isomers were obtained in the same 1:9 ratio as before (gas chromatography). The peak at 6.75 ppm was absent, and the signal at 5.50 ppm was a broad doublet in the NMR spectrum of the deuterated 2-*E* isomer; ^{19}F NMR 137 ppm (dt, J = 20, 13 Hz, C=C^{2}HF): CIMS, m/e 224 ($MH^+ - H_2O$). Anal. Calcd for $C_{15}H_{24}{}^2HFO$: C, 74.64; H, 10.85. Found: 74.54; H, 10.46.

2-(2-Fluoroethenyl)-1,2,3,4-tetrahydro-2-naphthalenol (11b). To a solution of difluoro alcohol **5b** (315 mg, 1.5 mmol) in 6 mL of diethyl ether at 0 °C was added 715 μL (1.7 mmol) of *n*-butyllithium as a 2.38 M solution in hexane. The reaction mixture was allowed to warm to room temperature and was stirred 15 min before it was again cooled to 0 °C and lithium aluminum hydride (85 mg, 2.25 mmol) added. After the mixture was stirred a further 24 h at room temperature, 85 μL of water, 85 μL of 15% NaOH, and 225 μL of water were sequentially added with stirring. Anhydrous $MgSO_4$ was then added, the mixture filtered, and the solvent removed under vacuum. LPLC (20% ethyl acetate in hexane) separated the 2-*E* and 2-*Z* isomers of **11b** (85% combined yield, E/Z ratio 9:1): GLC (150 °C) retention time 4.30 (2-*Z*), 5.63 min (2-*E*); IR (film) 3400 (OH), 1670 cm^{-1} (C=CF). The 2-*E* isomer: NMR 1.53 (s, 1 H, OH), 1.83–2.09 (M, 2 H, C-3 CH_2), 2.81–3.20 (m, 4 H, C-1 and C-4 CH_2's), 5.60 (dd, J = 20.5, 11 Hz, 1 H, CH=CF), 6.79 (dd, J = 84, 11 Hz, 1 H, C=CHF), 7.11 ppm (s, 4 H, aromatic H); ^{19}F NMR 135 ppm (dd, J = 84, 21 Hz); EIMS, m/e 192 (M^+), 174 ($M^+ - H_2O$). The 2-*Z* isomer: NMR 1.98–2.18 (m, 3 H, OH and C-3 CH_2), 2.82–3.14 (m, 4 H, C-1 and C-4 CH_2's), 4.97 (dd, J = 47, 5 Hz, 1 H, CH=CF), 6.42 (dd, J = 84, 5 Hz, 1 H, C=CHF), 7.11 (s, 4 H, aromatic H); ^{19}F NMR 125 ppm (dd, J = 84, 47 Hz); EIMS, m/e 192 (M^+), 174 ($M^+ - H_2O$). Anal. Calcd for $C_{12}H_{13}FO$: C, 74.98; H, 6.81. Found (for the isomer mixture): C, 74.84; H, 7.02.

1,1-Difluoro-3-acetoxy-3,7,11-trimethyl-1,6,10-dodecatriene (6a). A solution of **5a** (207 mg, 0.8 mmol), triethylamine (1.2 mmol), 4-(dimethylamino)pyridine (110 mg, 0.9 mmol), and acetic anhydride (3.2 mmol) in 5 mL of diethyl ether was stirred 2 days at room temperature until the reaction was finished (gas chromatographic analysis). The mixture, taken up in diethyl ether, was washed first with 5% NaOH and then with 0.1 N HCl. The dried organic layer on solvent removal yielded 235 mg (98%) of **6a**: GLC (140 °C) retention time 6.34 min; IR (film) 1740 cm^{-1} (br band, C=CF_2 and C=O); NMR 1.63 and 1.70 (2 s, 12 H, Me), 1.97 (m, 8 H, CH_2), 2.02 (s, 3 H, COMe), 4.67 (dd, J = 27, 5 Hz, 1 H, CH=CF_2), 5.17 ppm (m, 2 H, C=CH); ^{19}F NMR 82.63 (dd, J = 42, 27 Hz, *cis*-F), 85.72 ppm (dd, J = 42, 5 Hz, *trans*-F); CIMS, m/e 301 (MH^+), 241 (MH^+ – HOAc). Anal. Calcd for $C_{17}H_{26}F_2O_2$: C, 67.97; H, 8.73. Found: C, 68.27; H, 8.56.

1-Fluoro-3-acetoxy-3,7,11-trimethyl-1,6,10-dodecatriene (11a Acetate). Monofluoro alcohol **11a** (240 mg, 1.0 mmol), acetic anhydride (2.5 mmol), 4-(dimethylamino)pyridine (122 mg, 1.0 mmol), and triethylamine (1.5 mmol) were stirred in 5 mL of diethyl ether at room temperature for 2 days. The reaction mixture, taken up in 100 mL of diethyl ether, was washed first with 5% NaOH and then with 0.1 N HCl, dried over $MgSO_4$, and concentrated to give 280 mg of a clear yellow oil. The colorless acetate was obtained by LPLC (5% ethyl acetate in hexane): GLC (150 °C) retention time 7.5 min; IR (film) 1750 (C=O), 1680 cm^{-1} (C=CHF); NMR 1.57 (s, 3 H, C-1 Me), 1.63 and 1.70 (2 s, 9 H, vinyl Me), 1.98 (s, 3 H, COMe), 2.03 (br m, 8 H, C=CCH_2), 5.17 (m, 2 H, C=CH), 5.50 (dd, J = 21, 12 Hz, 1 H, CH=CF), 6.75 ppm (dd, J = 84, 12 Hz, 1 H, C=CHF); ^{19}F NMR 133 ppm (dd, J = 84, 21 Hz); CIMS, m/e 283 (MH^+), 263 (MH^+ – HF), 223 (MH^+ – HOAc). Anal. Calcd for $C_{17}H_{27}O_2F$: C, 72.30; H, 9.64. Found: C, 72.55; H, 9.59.

2-(2,2-Difluoroethenyl)-2-acetoxy-1,2,3,4-tetrahydronaphthalene (6b). A solution of difluoro alcohol **5b** (105 mg, 0.5 mmol), triethylamine (105 μL, 0.75 mmol), 4-(dimethylamino)pyridine (61 mg, 0.5 mmol), and acetic anhydride (118 μL, 1.25 mmol) in 3 mL of diethyl ether was stirred 24 h at room temperature. The reaction mixture was taken up in ether, was washed with 5% NaOH, 0.1 N HCl, and water, and was dried ($MgSO_4$). Solvent removal gave 123 mg of **6b** as a clear yellow oil that was further purified by LPLC (15% ethyl acetate in hexane): GLC (150 °C) retention time 2.63 min; IR (film) 1750 cm^{-1} (br, C=O and C=CF_2); NMR 1.96 (s, 3 H, COMe), 2.00–2.95 (m, 4 H, C-3 and C-4 CH_2's), 3.29 (br s, 2 H, C-1 CH_2), 4.72 (dd, J = 27, 5 Hz, 1 H, CH=CF_2), 7.10 ppm (s, 4 H, aromatic); ^{19}F NMR 80.7 (dd, J = 37, 27 Hz, *cis*-C=CF), 83.8 ppm (dd, J = 37, 5 Hz, *trans*-C=CF); EIMS, m/e 192 (M^+ – HOAc). Anal. Calcd for $C_{14}H_{14}F_2O_2$: C, 66.66; H, 5.59. Found: C, 66.51; H, 5.63.

2-(2-Fluoroethenyl)-2-acetoxy-1,2,3,4-tetrahydronaphthalene (11b Acetate). This product was obtained from **11b** as described for the preparation of the acetate of **11a** in 75% yield after LPLC: GLC (150 °C) retention time 6.75 min; IR (film) 1740 (C=O), 1670 cm^{-1} (C=CHF); NMR 1.97 (s, 3 H, COMe), 1.93–2.98 (m, 4 H, C-3 and C-4 CH_2's), 3.26 (br s, 2 H, C-1 CH_2), 5.89 (dd, J = 21, 12 Hz, 1 H, CH=CF), 6.77 (dd, J = 83, 12 Hz, 1 H, C=CHF), 7.14 ppm (s, 4 H, aromatic H); ^{19}F NMR 130 ppm (dd, J = 83, 21 Hz); EIMS, m/e 174 (M^+ – HOAc). Anal. Calcd for $C_{14}H_{15}O_2F$: C, 71.77; H, 6.45. Found: C, 72.23; H, 6.54.

1,1-Difluoro-3,7,11-trimethyl-2,6,10-dodecatrienyl Acetate (7a). To a solution of acetate **6a** (299 mg, 0.995 mmol) in 3 mL of acetic anhydride was added approximately 50 mg of *p*-toluenesulfonic acid. After 30 min (reaction monitored by gas chromatography), the mixture was taken up in pentane and washed successively with 5% NaOH and brine. The dried solution gave 301 mg of a pale yellow oil, approximately 70% of which was **7a** (NMR analysis). The material was purified by LPLC: GLC (150 °C) retention time 9.02 min; IR (film) 1790 (C=O), 1670 cm^{-1} (C=C); NMR 1.63 and 1.70 (2 s, 9 H, vinyl Me), 1.88 (m, 3 H, C-3 Me), 2.07 (br m, 8 H, C=CCH_2), 2.15 (s, 3 H, COMe), 5.17 (m, 2 H, C=CH), 5.60 ppm (t, J = 10 Hz, 1 H, C-2 vinyl H); ^{19}F

NMR 63.3 and 63.7 ppm (2 d, J = 10 Hz each); CIMS, m/e 241 (MH^+ – HOAc). Anal. Calcd for $C_{17}H_{26}F_2O_2$: C, 69.97; H, 8.73. Found: C, 68.36; H, 8.75.

2-(2-Acetoxy-2,2-difluoroethylidenyl)-1,2,3,4-tetrahydronaphthalene (7b) and 2-(2-Tosyl-2,2-difluoroethylidenyl)-1,2,3,4-tetrahydronaphthalene (8b). p-Toluenesulfonic acid (150 mg) was added to a solution of tertiary acetate **6b** (378 mg, 1.5 mmol) in 3.5 mL of acetic acid at 25 °C. The reaction mixture was stirred until gas chromatographic analysis indicated the reaction was finished. The mixture was partitioned between water and pentane, and the pentane extracts were washed with 5% NaOH and brine before being dried over $MgSO_4$. Solvent removal gave 218 mg of a clear colorless oil that was separated into two components by LPLC (20% ethyl acetate in hexane). The product (140 mg) that eluted first was **7b**: GLC (160 °C) retention times 7.12 and 8.62 min (two isomers); IR (film) 1750 cm^{-1} (C=O); NMR (isomer mixture) 2.11 and 2.13 (2 s, 3 H, COMe of the two isomers), 2.42–2.95 (m, 4 H, C-3 and C-4 CH_2's), 3.52 and 3.77 (2 d, J = 2 Hz, 2 H, each doublet is the C-1 CH_2 of one of the two isomers), 5.73 (br t, J = 10 Hz, 1 H, C=CH), 7.13 ppm (s, 4 H, aromatic H); ^{19}F NMR 63.8 and 64.2 ppm (2 d, J = 10 Hz, each doublet is due to one of the isomers); EIMS, m/e 252 (M^+), 192 (M^+ – HOAc). Anal. Calcd for $C_{14}H_{14}F_2O_2$: C, 66.66; H, 5.59. Found: C, 66.33; H, 5.59.

The second product eluted from the column (71 mg) was the primary tosylate derivative **8b**: IR (film) no C=O band; NMR (two isomers) 2.43 (s, 3 H, p-Me), 2.35–2.88 (m, 4 H, C-3 and C-4 CH_2), 3.46 and 3.60 (2 d, J = 2 Hz, 2 H, each doublet is C-1 CH_2 of one of the two isomers), 5.60 (br t, J = 10 Hz, 1 H, C=CH), 7.13 and 7.10 (2 s, 4 H total, each peak is the aromatic H of one isomer), 7.57 ppm (dd, J = 44, 8 Hz, 4 H, A_2B_2 aromatic H); ^{19}F NMR 58.6 and 58.9 ppm (2 d, J = 10 Hz, each doublet is due to one isomer); EIMS, m/e 192 (M^+ – TsOH). Anal. Calcd for $C_{19}H_{18}F_2O_3S$: C, 62.62; H, 4.98. Found: C, 62.38; H, 4.99.

1,1-Difluoro-3-phenyl-3-methyl-2-butenyl Acetate (7c). A solution of trimethylsilyl ether **4c** (126 mg, 0.50 mmol) and NaOH (30 mg, 0.75 mmol) in 10 mL of 4:1 (v/v) methanol/water was stirred at room temperature for 30 min. The mixture was partitioned between water and hexane, and the organic phase, washed with water, dried, and concentrated to about 3 mL, was directly added to 3 mL of acetic anhydride. The hexane was removed under a stream of dry nitrogen. Dry p-toluenesulfonic acid (30 mg) was then added, and the reaction mixture was stirred for 14 h at room temperature. A workup as described for **7a** gave 92 mg of a colorless oil that, on purification by LPLC (5% ethyl acetate in hexane), gave 27 mg (24%) of **7c** as a colorless oil contaminated with a trace of the acid fluoride due to decomposition of **7c**: GLC (120 °C) retention time 10.31 min; IR (film) 1790 cm^{-1} (C=O); NMR 2.17 (s, 3 H, COMe), 2.22 (m, C-3 Me), 6.08 (t, J = 10 Hz, 1 H, C=CH), 7.27 ppm (s, 5 H, aromatic); ^{19}F NMR 63.90 and 63.93 ppm (2 d, J = 10 Hz each, ratio 1:1, cis and trans isomers); CIMS, exact mass calcd for $C_{12}H_{13}F_2O_2$ m/e 227.0884, found 227.0887.

1,1-Difluoro-3-methyl-2-dodecenyl acetate (7d) was prepared by the procedure described for **7a**: IR 1760 cm^{-1} (C=O); NMR 0.87 (br t, J = 6 Hz, 3 H, CH_2CH_3), 1.26 (s, 16 H, methylenes), 1.56 (d, J = 3 Hz, 3 H, C-3 Me, 1.97 (s, 3 H, COMe), 4.56 ppm (d of d, J = 27, 5 Hz, C=$CHCF_2$); ^{19}F NMR 82.96 (d of d of q, J = 41.5, 27, 3 Hz, trans isomer), 86.07 (d of d, J = 41.5, and 5 Hz, cis isomer); EIMS, m/e 276 (M^+).

Diethyl 1,1-Difluoro-3,7,11-trimethyl-2,6,10-dodecatrienyl Phosphate (9a). To 258 mg (1.0 mmol) of difluoro alcohol **5a** in 5 mL of hexane at –78 °C was added 1.05 mmol of n-BuLi. The solution was allowed to warm to room temperature, and 1.10 mmol of diethyl phosphorochloridate was added. The solution immediately became yellow, and a precipitate began to form after about 15 min. The mixture was gravity filtered after 1.5 h, and the solvent was removed from the filtrate, yielding 258 mg of yellow oil. LPLC (30% ethyl acetate in hexane) gave 74 mg of various decomposition products and 118 mg (30% yield) of the 2-E and 2-Z isomer mixture of **9a**. The two isomers could be separated by LPLC but were not separated by our usual gas chromatographic system (retention time 3.98 min at 220 °C). 2-E isomer: NMR 1.38 (dt, J = 1, 7 Hz, 6 H, $POCH_2CH_3$), 1.63 and 1.70 (2 s, 9 H, C=CMe), 1.92 (m, 3 H, C-3 Me), 2.02 (m, 6 H, $C=CCH_2$), 2.13 (m, 2 H, C-4 CH_2), 4.25 (p, J = 7 Hz, 4 H, $POCH_2CH_3$), 5.15 (m, 2 H, C=CH), and 5.58 ppm (t, J = 10 Hz, 1 H, C-2 C=CH); ^{19}F NMR 55.06 ppm (br m). 2-Z isomer: NMR 1.37 (dt, J = 1, 7 Hz, 6 H, $POCH_2CH_3$), 1.63 and 1.70 (2 s, 9 H, C=CMe), 1.85 (m, 3 H, C-3 Me), 2.02 (m, 6 H, $C=CCH_2$), 2.28 (m, 2 H, C-4 CH_2), 4.25 (p, J = 7 Hz, 4 H, $POCH_2CH_3$), 5.18 (m, 2 H, C=CH), 5.58 ppm (t, J = 10 Hz, 1 H, C-2 C=CH); ^{19}F NMR 54.74 ppm (br m); CIMS, m/e 395 (MH^+), 375 (MH^+ – HF). Anal. Calcd for $C_{19}H_{33}F_2PO_4$ (isomer mixture): C, 57.85; H, 8.43; P, 7.85. Found: C, 58.11; H, 8.28; P, 7.76.

Diphenyl 1,1-Difluoro-3,7,11-trimethyl-2,6,10-dodecatrienyl Phosphate (10a). A solution of difluoro alcohol **5a** (256 mg, 0.991 mmol), diphenyl phosphorochloridate (2.4 mmol), p-(dimethylamino)pyridine (300 mg, 2.4 mmol), and triethylamine (2.2 mmol) in 5 mL of THF was stirred 2 days, at which time only a trace of alcohol remained (gas chromatography). The mixture was partitioned between diethyl ether and water, and the organic layer was washed sequentially with 5% NaOH, 0.1 N HCl, and brine. Drying ($MgSO_4$) and solvent removal gave 697 mg of a pale yellow oil which gave two closely spaced spots on thin-layer chromatography. The lower spot had the same R_f value as the starting alcohol. LPLC (10% ethyl acetate in hexane) separated the 2-E (R_f 0.24) and 2-Z (R_f 0.20) isomers of **10a** (80% combined yield). 2-E isomer: IR (film) 1680 cm^{-1}; NMR 1.60 and 1.70 (2 s, 9 H, C=CMe), 1.83 (m, 3 H, C-3 Me), 2.02 (br m, 6 H, $C=CCH_2$), 5.03 (m, 2 H, C=CH), 5.52 (t, J = 10 Hz, 1 H, C-2 C=CH), 7.23 ppm (s, 10 H, aromatic); ^{19}F NMR 54.67 ppm (br m). 2-Z isomer: IR 1680 cm^{-1}; NMR 1.62 and 1.70 (2 s, 9 H, C=CMe), 1.78 (m, 3 H, C-3 Me), 2.02 (br m, 6 H, $C=CCH_2$), 2.20 (m, 2 H, C-4 CH_2), 5.05 (m, 2 H, C=CH), 5.48 (t, J = 10 Hz, 1 H, C-2 C=CH), 7.22 ppm (s, 10 H, aromatic); ^{19}F NMR 54.14 ppm (br m); CIMS, m/e 491 (MH^+), 241 (MH^+ – diphenyl phosphate). The 2-Z isomer was contaminated with a trace of the parent alcohol.

2-[2-[(Diethylphosphono)oxy]-2,2-difluoroethylidenyl]-1,2,3,4-tetrahydronaphthalene (9b). To a solution of difluoro alcohol **5b** (210 mg, 1.0 mmol) in 5 mL of benzene at 0 °C was added 498 μL of a 2.38 M solution of n-butyllithium in hexane (1.2 mmol). After warming to room temperature and being stirred for 45 min, the mixture was again cooled to 0 °C, and diethyl phosphorochloridate (173 μL, 1.2 mmol) was added. The mixture was then allowed to stir for 24 h at room temperature before it was partitioned between pentane and water. The organic layer, washed with saturated $NaHCO_3$ and NaCl solutions and dried ($MgSO_4$), gave 400 mg of clear yellow oil on solvent removal. LPLC (30% ethyl acetate in hexane) gave 69 mg (19%) of a mixture of the 2-E and 2-Z isomers of **9b** (the isomers could not be separated): IR (film) 1740, 1670 cm^{-1}; NMR 1.33 (t, J = 7 Hz, 6 H, $POCH_2CH_3$), 2.47–2.90 (br m, 4 H, C-3 and C-4 CH_2), 3.51 and 3.80 (2 d, J = 2 Hz, each is C-2 CH_2 of one isomer), 4.18 (p, J = 7 Hz, 4 H, $POCH_2CH_3$), 5.72 (br t, J = 7 Hz, 1 H, C-1 C=CH), 7.12 ppm (s, 4 H, aromatic); ^{19}F NMR 55.1, 55.3 ppm (2 br m, each due to one of the isomers); EIMS, m/e 326 (M^+ – HF), 1.92 [M^+ – $HOP(O)(OEt)_2$]. Anal. Calcd for $C_{16}H_{21}F_2O_4P$; C, 55.49; H, 6.11. Found: C, 55.39; H, 6.03.

2-[2-[(Diphenylphosphono)oxy]-2,2-difluoroethylidenyl]-1,2,3,4-tetrahydronaphthalene (10b). Triethylamine (140 μL, 1.0 mmol) and 4-(dimethylamino)pyridine (153 mg, 1.25 mmol) were added to difluorovinyl alcohol **5b** (105 mg, 0.5 mmol) in 3 mL of THF at room temperature. The reaction mixture was stirred 45 min before it was cooled to 0 °C, and diphenyl phosphorochloridate (259 μL, 1.25 mmol) was added. The resulting slurry was allowed to warm to room temperature and was stirred for 24 h. The mixture was then taken up in diethyl ether and was washed sequentially with 0.1 N HCl, 5% NaOH, and brine. Drying ($MgSO_4$) and solvent removal gave 348 mg of clear yellow oil that, on purification by LPLC (15% ethyl acetate in hexane), afforded 132 mg of a mixture of the E and Z isomers of **10b** as a clear yellow oil: IR (film) 1760, 1600 cm^{-1}; NMR 2.17–2.83 (m, 4 H, C-3 and C-4 CH_2), 3.44 and 3.72 (2 d, J = 2 Hz, each d is C-1 CH_2 of one isomer), 5.69 (br t, J = 10 Hz, 1 H, C-1 C=CH), 7.10 and 7.12 (2 s, 4 H, each peak is due to aromatic protons of one isomer), 7.26 ppm (s, 10 H, phenyl); ^{19}F NMR 54.9, 55.2 ppm (2 br m, each due to one isomer); EIMS, m/e 422 (M^+ – HF), 251 [M^+ – $HOP(O)(OPh)_2$]. Anal. Calcd for $C_{24}H_{21}O_4F_2P$: C, 65.12; H, 4.79. Found: C, 64.96; H, 4.95.

Diphenyl 1,1-Difluoro-3-methyl-2-dodecenyl Phosphate (10d). Difluorophosphate ester **10d** was prepared from **5d** as

described for **10a**: 70% yield; NMR 0.87 (br t, J = 4 Hz, 3 H, CH_2CH_3), 1.25 (s, 16 H, methylenes), 1.63 (d, J = 2 Hz, 3 H, C-3 Me), 6.86 (dt, J = 7, 2 Hz, CH=C), 7.25 ppm (m, 10 H, aryl); ^{19}F NMR 54.57, 54.06 ppm (2 d, J = 7 Hz each, each due to one of the two isomers); EIMS, m/e 466 (M^+).

Diethyl 1-Fluoro-3,7,11-trimethyl-2,6,10-dodecatrienyl Phosphate (12a). Diethyl phosphate **12a** was prepared from 247 mg (1.0 mmol) of alcohol **11a**, 1.2 mmol of *n*-BuLi, and 1.2 mmol of diethyl phosphorochloridate as described for synthesis of the difluorinated analogue **9a**. The crude product was taken up in pentane and washed with water, saturated $NaHCO_3$, and brine. Drying (Na_2SO_4) and solvent removal gave 344 mg of yellow oil shown by TLC (20% ethyl acetate in hexane) to contain starting alcohol, nonpolar impurities, and two polar products (R_f 0.18 and 0.12). The lower R_f isomer comprised about 80% of the two polar products. LPLC purification (30% ethyl acetate in hexane) provided the two isomers of **12a** in low combined yield (19% maximum). 2-*E* (major) isomer: IR 2960, 1690 cm^{-1}; NMR 1.37 (t, J = 7 Hz, 6 H, OCH_2CH_3), 1.62 and 1.70 (2 s, 9 H, C=CCH_3), 1.82 (m, 3 H, C-3 Me), 2.02 (m, 6 H, allylic CH_2's), 2.08 (m, 2 H, C-4 CH_2), 4.22 (m, 4 H, OCH_2CH_3), 5.15 (m, 2 H, C=CH), 5.47 (t, J = 7 Hz, C-2 vinyl H), 6.58 ppm (dt, J = 57, 7 Hz, 1 H, CHF); ^{19}F NMR 112.09 (br d, J = 57 Hz); CIMS, m/e 377 (MH^+), 357 (MH^+ - HF). 2-*Z* (minor) isomer: ^{19}F NMR 110.66 (br d, J = 57 Hz); CIMS, m/e 377 (MH^+), 357 (MH^+ - HF). The monofluoro diethyl phosphate was much less stable than the difluoro analogue, and its synthesis proved difficult to reproduce.

Diphenyl 1-Fluoro-3,7,11-trimethyl-2,6,10-dodecatrienyl Phosphate (13a). Triethylamine (280 μL, 2.0 mmol) was added to monofluoro alcohol **11a** (240 mg, 1.0 mmol) in 5 mL of THF and the solution was stirred 10 min before 4-(dimethylamino)-pyridine (305 mg, 2.5 mmol) was added. The mixture was cooled 45 min later to 0 °C and diphenyl phosphorochloridate (518 μL, 2.5 mmol), briefly pretreated with anhydrous K_2CO_3, was slowly added. The mixture was stirred 5 days at room temperature before it was taken up in ether, washed sequentially with 0.1 N HCl, 5% NaOH, and brine, and dried ($MgSO_4$). Solvent removal and LPLC (10% ethyl acetate in hexane) provided the 2-*Z* (eluted first) and 2-*E* (eluted second) isomers of **13a** (30% combined yield, predominantly 2-*E* isomer) as colorless oils. 2-*E* isomer: IR (film) 1680 cm^{-1}; NMR 1.57 and 1.66 (2 s, 12 H, C=CMe), 2.00 (m, 8 H, C=CCH_2), 5.05 (m, 2 H, C=CH), 5.38 (br t, J = 8 Hz, 1 H, C-2 C=CH), 6.65 (dt, J = 55, 8 Hz, 1 H, C=CCHF), 7.24 and 7.26 ppm (2 s, 10 H, aromatic); ^{19}F NMR 112.5 ppm (br d, J = 55 Hz). 2-*Z* isomer: IR (film) 1680 cm^{-1}; NMR 1.59 and 1.68 (2 s, 9 H, C=CMe), 1.78 (dd, J = 4.6, 1.0 Hz, 3 H, C-3 Me), 1.99–2.27 (m, 8 H, C=CCH_2), 5.07 (m, 2 H, C=CH), 5.41 (br t, J = 8 Hz, 1 H, C-2 C=CH), 6.66 (dt, J = 55, 8 Hz, 1 H, C=CCHF), 7.28 ppm (s, 10 H, aromatic); ^{19}F NMR 111.3 ppm (br d, J = 55 Hz); EIMS (same for each isomer), m/e 452 (M^+ - HF), 250 [M^+ - $HOP(O)(OPh)_2$]. Anal. Calcd for $C_{27}H_{34}O_4FP$: C, 68.62; H, 7.25. Found (2-*E* isomer): C, 68.73; H, 7.34. Found (mixture of isomers): C, 68.93; H, 7.46.

2-(2-[(Diphenylphosphono)oxy]-2-fluoroethylidenyl)-1,2,3,4-tetrahydronaphthalene (13b). To monofluoro alcohol **11b** (163 mg, 0.85 mmol) in 5 mL of THF were added triethylamine (237 μL, 1.7 mmol) and 4-(dimethylamino)pyridine (259 mg, 2.12 mmol) at 10-min intervals. Diphenyl phosphorochloridate (439 μL, 2.12 mmol), briefly pretreated with anhydrous K_2CO_3, was slowly added 15 min later. The reaction mixture, stirred for 3 days, was partitioned between water and diethyl ether, and the organic layers were sequentially washed with 0.1 N HCl, 5% NaOH, and brine. Drying ($MgSO_4$) and solvent removal gave 278 mg of yellow oil that was purified by LPLC (15% ethyl acetate in hexane). The *E* and *Z* isomers of **13b** (109 mg) were thus obtained in 30% combined yield: NMR 2.41–2.83 (m, 4 H, C-3 and C-4 CH_2), 3.47 (br d, J = 2 Hz, 2 H, C-1 CH_2), 5.58 (br t, J = 8 Hz, 1 H, CH=C), 6.79 (dt, J = 55, 8 Hz, 1 H, C=CCHF), 7.11 (s, 4 H, aromatic), 7.26 ppm (s, 10 H, phenyls); ^{19}F NMR 113.5, 113.7 ppm (2 br t, J = 55 Hz, each due to one isomer); EIMS, m/e 404 (M^+ - HF), 250 [M^+ - HF - $HOP(O)(OPh)_2$]. Anal. Calcd for $C_{24}H_{22}O_4FP$: C, 67.91; H, 5.23. Found (isomer mixture): C, 67.64; H, 5.27.

1,1-Difluoro-1-chloro-3,7,11-trimethyl-1,6,10-dodecatriene (8a with Y = Cl Instead of OTs). To a solution of 1.56 g (6.04 mmol) of difluoro alcohol **5a**, pyridine (10 mmol), and triethylamine (10 mmol) in 15 mL of hexane was added 10 mmol of thionyl chloride, and the mixture was stirred 3 h at room temperature. The mixture, taken up in diethyl ether, was washed sequentially with 0.1 N HCl, brine, and saturated $NaHCO_3$. Drying ($MgSO_4$) and solvent removal gave 1.47 g of yellow oil (88%) that by thin-layer and gas chromatographic analysis was homogeneous. An analytical sample was obtained by LPLC (hexane): GLC (140 °C) retention time 3.28 min; NMR 1.63 and 1.70 (2 s, 9 H, C=CMe), 1.92 (m, 3 H, C-3 Me), 2.08 (br m, 8 H, C=CCH_2), 5.15 (m, 2 H, C=CH), 5.68 ppm (t, J = 12 Hz, 1 H, C=$CHCClF_2$); ^{19}F NMR 42.5, 42.8 ppm (2 d, J = 12 Hz, 1:2 ratio, each doublet due to one isomer of the product); CIMS, m/e 277 (MH^+), 241 (MH^+ - HCl). Anal. Calcd for $C_{15}H_{23}F_2Cl$: C, 65.09; H, 8.37; Cl, 12.81. Found: C, 65.35; H, 8.34; Cl, 12.25.

1,1-Difluoro-3,7,11-trimethyl-1,6,10-dodecatrienyl Tosylate (8a). Tertiary acetate **6a** (150 mg, 0.5 mmol) was stirred in 3 mL of 1,2-dimethoxyethane at 25 °C with an excess of *p*-toluenensulfonic acid (247 mg, 1.3 mmol). The reaction was taken up in diethyl ether after 24 h and was washed with saturated $NaHCO_3$, water, and brine. Drying over $MgSO_4$ and solvent removal gave 173 mg of yellow oil that was separated by low-pressure chromatography (10% ethyl acetate in hexane) into 35 mg (23%) of **7a** and 93 mg (45%) of **8a**: NMR 1.58 and 1.67 (2 s, 9 H, C=CCH_3), 1.75 (m, 3 H, C-3 Me), 1.86–2.22 (m, 8 H, C=CCH_2), 2.45 (s, 3 H, benzylic Me), 5.05 (m, 2 H, C=CH), 5.40 (br t, J = 10 Hz, 1 H, C-2 C=CH), 7.60 ppm (dd, J = 40, 8 Hz, 4 H, A_2B_2 aromatic H); ^{19}F NMR 58.4, 58.6 ppm (2 d, J = 10 Hz each); EIMS, m/e 412 (M^+), 240 (M^+ - TsoH). Anal. Calcd for $C_{22}H_{30}O_3F_2S$: C, 64.05; H, 7.33. Found: C, 63.84; H, 7.36.

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Registry No. **1a**, 3796-70-1; **1b**, 530-93-8; **1c**, 98-86-2; **1d**, 112-12-9; **2a**, 87509-03-3; **2d**, 87509-04-4; **3a**, 87509-05-5; **3b**, 87509-06-6; **3c**, 70565-65-0; **3d**, 87509-07-7; **4a**, 87509-08-8; **4b**, 87509-09-9; **4c**, 70565-67-2; **4d**, 87509-10-2; **5a**, 87509-11-3; **5b**, 87509-12-4; **5d**, 87509-13-5; **6a**, 87509-14-6; **6b**, 87509-15-7; **7a**, 87509-16-8; (*E*)-**7b**, 87509-17-9; (*Z*)-**7b**, 87509-47-5; (*E*)-**7c**, 87509-18-0; (*Z*)-**7c**, 87509-49-7; (*E*)-**7d**, 87509-19-1; (*Z*)-**7d**, 87509-50-0; (*E*)-**8a**, 87509-53-3; (*Z*)-**8a**, 87509-54-4; (*E*)-**8b**, 87509-20-4; (*Z*)-**8b**, 87509-48-6; (*E*)-**9a**, 87509-21-5; (*Z*)-**9a**, 87509-22-6; (*E*)-**9b**, 87509-23-7; (*Z*)-**9b**, 87509-24-8; (*E*)-**10a**, 87509-25-9; (*Z*)-**10a**, 87509-26-0; (*E*)-**10b**, 87509-27-1; (*Z*)-**10b**, 87509-28-2; (*E*)-**10d**, 87509-29-3; (*Z*)-**10d**, 87509-30-6; (*E*)-**11a**, 87509-31-7; (*E*)-[1-^{2}H]-**11a**, 87509-41-9; (*Z*)-**11a**, 87509-32-8; (*Z*)-[1-^{2}H]-**11a**, 87509-42-0; (*E*)-**11a** acetate, 87509-43-1; (*Z*)-**11a** acetate, 87509-44-2; (*E*)-**11b**, 87509-33-9; (*Z*)-**11b**, 87509-34-0; (*E*)-**11b** acetate, 87509-45-3; (*Z*)-**11b** acetate, 87509-46-4; (*E*)-**12a**, 87509-35-1; (*Z*)-**12a**, 87509-36-2; (*E*)-**13a**, 87509-37-3; (*Z*)-**13a**, 87509-38-4; (*E*)-**13b**, 87509-39-5; (*Z*)-**13b**, 87509-40-8; trimethylsilyl cyanide, 7774-29-0; HgI_2, 7677-24-9; diisobutylaluminum hydride, 1191-15-7; dibromodifluoromethane, 75-61-6; tris(dimethylamino)phosphine, 1608-26-0; diisopropylaluminum hydride, 18315-70-3; (*E*)-1,1-difluoro-1-chloro-3,7,11-trimethyl-1,6,10-dodecatriene, 87509-51-1; (*Z*)-1,1-difluoro-1-chloro-3,7,11-trimethyl-1,6,10-dodecatriene, 87509-52-2; diethyl phosphorochloridate, 814-49-3; diphenyl phosphorochloridate, 2524-64-3.