ether was added, and the aqueous phase was separated and extracted with ether. The organic phase was dried over Na_2SO_4 and concentrated. The residue was generally chromatographed on silica gel column using hexane–ether as solvent, or crystallized when solid, to afford pure ω-hydroxy ketones (4) (Table II).

1-Hydroxynonan-3-one (4d): IR 3410, 1710, 1130, 1090, 1050; NMR 3.9 (t, 2 H, CH_2O), 3.4 (s, 1 H, OH), 2.3–2.9 (m, 4 H, $CH_2C{=}O$), 0.7–2.0 (m, 11 H, aliphatic); MS, *m/e* (relative intensity) 43 (100), 70 (45), 55 (42), 41 (31), 113 (25), 71 (18), 45 (17), 57 (16).

1-Hydroxyundecan-3-one (4e): IR 3380, 1705, 1130, 1095, 1050; NMR 3.8 (m, 4 H, $CH_2C{=}O$), 0.7–2.0 (m, 15 H, aliphatic); MS, *m/e* (relative intensity) 70 (100), 55 (60), 41 (27), 43 (25), 71 (20), 83 (18), 57 (17), 40 (16), 139 (14).

1-Hydroxy-2-methylundecan-3-one (4f): IR 3460, 1720, 1140, 1040; NMR 3.7 (m, 3 H, CH_2OH), 2.3–2.9 (m, 3 H, CH_2COCH), 0.8–1.9 (m, 18 H, aliphatic); MS, *m/e* (relative intensity) 43 (100), 41 (99), 57 (96), 159 (62), 71 (55), 72 (51), 84 (38), 55 (35), 69 (34), 59 (33), 182 ($M^+ - H_2O$), 200 (M^+).

2-Hydroxydecan-4-one (4g): IR 3460, 1720, 1130, 1060, 1050; NMR 4.2 (m, 1 H, C*H*OH), 3.8 (s, 1 H, OH), 2.3–2.8 (m, 4 H, $CH_2C{=}O$), 0.7–1.9 (m, 4 H, aliphatic); MS, *m/e* (relative intensity) 43 (100), 58 (90), 45 (50), 87 (25), 69 (23), 113 (17), 71 (15), 84 (14), 154 ($M^+ - H_2O$), 172 (M^+).

1-Hydroxytridecan-5-one (4h): IR 3250, 1705, 1150, 1070; NMR 3.7 (m, 2 H CH_2O), 2.9 (br s, 1 H, OH), 2.4 (m, 4 H, $CH_2C{=}O$), 0.8–1.8 (m, 19 H, aliphatic); MS, *m/e* relative intensity) 43 (100), 55 (81), 98 (78), 57 (77), 41 (55), 71 (47), 83 (44), 116 (35), 141 (32), 40 (32), 196 ($M^+ - H_2O$), 214 (M^+).

1-Hydroxytetradecan-6-one (4i): IR 3500, 3200, 1700, 1070, 1060; NMR 3.7 (t, 2 H, CH_2O), 2.4 (m, 4 H, $CH_2C{=}O$), 1.9 (s, 1 H, OH), 0.7–1.8 (m, 21 H, aliphatic); MS, *m/e* (relative intensity) 41 (100), 43 (96), 58 (96), 71 (95), 69 (94), 57 (90), 112 (55), 130 (53), 156 (39), 141 (38), 228 (M^+).

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Registry No. **1a**, 96-48-0; **1b**, 1679-47-6; **1c**, 108-29-2; **1d**, 57-57-8; **1e**, 1823-54-7; **1f**, 3068-88-0; **1g**, 542-28-9; **1h**, 502-44-3; **4a**, 16378-50-0; **4b**, 88703-44-0; **4c**, 7737-56-6; **4d**, 67801-46-1; **4e**, 82353-69-3; **4f**, 88703-45-1; **4g**, 88729-56-0; **4h**, 88703-46-2; **4i**, 88703-47-3; **10a**, 3112-85-4; **10b**, 16823-63-5; **10c**, 34009-05-7; **12a**, 88703-48-4; **12b**, 88703-49-5; **12c**, 88703-50-8; **12d**, 88703-51-9; **12e**, 88703-52-0; **12f**, 88703-53-1; **12g**, 88703-54-2; **12h**, 88703-55-3; **12i**, 88703-56-4; BuLi, 109-72-8.

Synthesis of ω-Tritiated and ω-Fluorinated Analogues of the Trail Pheromone of Subterranean Termites

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A series of unsaturated ω-fluoro alcohols have been prepared stereoselectively. These simple compounds are structural analogues of the trail pheromone of termites in the genus *Reticulitermes*. The toxicity of these ω-fluoro alcohols to *R. flavipes* is maximal for the C_{12} alcohols, and the attractiveness of these C_{12} analogues increases in the order saturated alkanol < (*Z*)-3-alkenol ≪ (*Z,Z*)-3,6-alkadienol. Two [12-^{3}H]-12-fluoro alcohols and a [12-^{3}H]-nonfluorinated analogue were prepared to examine the catabolism of the pheromone analogues.

The latent toxicity of fatty acids possessing an even number of carbons and bearing a single fluorine substituent in the terminal ω position is due to in vivo β-oxidation to fluoroacetate.[1] The potential utility of fluoroacetate-releasing compounds as pesticides is mitigated by their low specificity and their high toxicity for nontarget species.[2] We envisaged the use of the latent toxicity of ω-fluoro fatty acids as delayed-action toxicants in bait-block control schemes for termites[3] and as experimental probes into the nature of intermediates involved in the metabolism of acyl glycerol derivatives in insects. We have reported the toxicity and delay times for a large number of achiral and racemic synthetic ω-fluoroalkyl and ω-fluoroacyl glycerol[4] and cholesterol derivatives[5] as well as three enantiomeric pairs of alkyldiacyl glycerols[6] in feeding tests with the eastern subterranean termite, *Reticulitermes flavipes* (Kollar).

We discovered that the 16-fluoro-(*E*)-9-hexadecen-1-ol was ten-fold more toxic for *Reticulitermes* workers and had a shorter delay time than the corresponding ω-fluoro acid.[4b] We hypothesized that the efficiency of fatty alcohol catabolism in termites was related to the fact that a C_{12} alcohol, (*Z,Z,E*)-3,6,8-dodecatrien-1-ol, acts as a trail pheromone for *Reticulitermes*.[7] Laboratory choice tests using vacuum-impregnated bait blocks suggested that the long-delay time material may not be as effective as chemicals that were attractive, more toxic, and had shorter delay times.[5] We therefore prepared several pheromone analogues and their ω-fluoro derivatives, and we examined both their toxicity and their activity as trail pheromone mimics for subterranean termites (Figure 1).

Furthermore, we wished to establish the metabolic fates of the pheromone analogues in vivo and in vitro. To this end, we used intermediates already in hand to prepare [12-^{3}H]-labeled pheromone analogues in both the terminal fluoromethyl and methyl series. The identification of the metabolites of both the fluorinated and nonfluorinated

†Fellow of the Alfred P. Sloan Foundation (1981–1985) and Camille and Henry Dreyfus Teacher–Scholar (1981–1986).

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(2) Hollingworth, R. M. In "Insecticide Biochemistry and Physiology"; Wilkinson, C. F., Ed.; Plenum Press: New York, 1976; pp 431–506.

(3) (a) Beard, R. L. *Bull.–Conn. Agric. Exp. Stn., New Haven* **1974**, *No.* 748. (b) Esenther, G. R.; Beal, R. H. *J. Econ. Entomal.* **1974**, *67*, 85.

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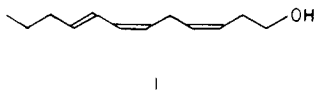
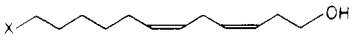


1

2, n = 7
3, n = 9

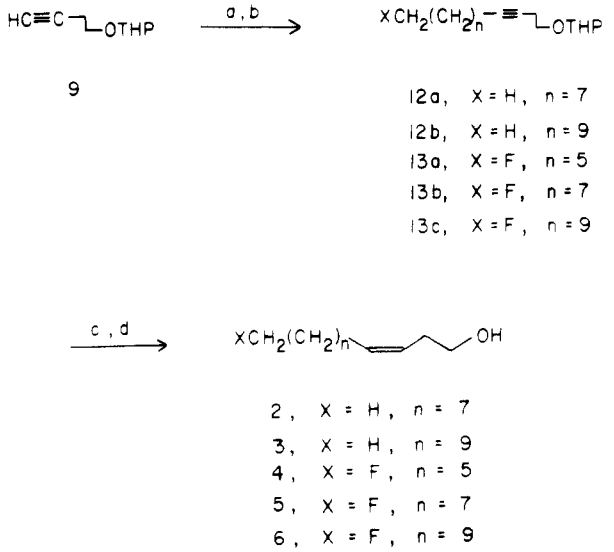
4, n = 5
5, n = 7
6, n = 9



7, X = H
8, X = F

Figure 1. Natural trail pheromone of *Reticulitermes virginicus* (1) and synthetic analogues **2–8**.

Scheme I[a]



9

12a, X = H, n = 7
12b, X = H, n = 9
13a, X = F, n = 5
13b, X = F, n = 7
13c, X = F, n = 9

2, X = H, n = 7
3, X = H, n = 9
4, X = F, n = 5
5, X = F, n = 7
6, X = F, n = 9

[a] (a) *n*-BuLi/THF; (b) $XCH_2(CH_2)_nBr$, **10a**, X = H, *n* = 7; **10b**, X = H, *n* = 9; **11a**, X = F, *n* = 5; **11b**, X = F, *n* = 7; **11c**, X = F, *n* = 9; (c) H_2, $Pd/BaSO_4$, quinoline, CH_3OH; (d) Dowex 50 X 8-50, CH_3OH.

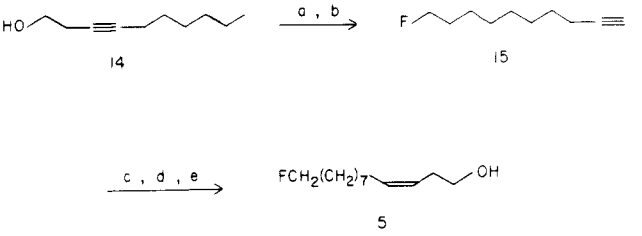
pheromone analogues in whole termites and in antennal homogenates will be presented elsewhere (G. D. Prestwich, J. J. Brown, J. F. Carvalho, and R. Yamaoka, unpublished results).

Results and Discussion

The toxic ω-fluoro alcohols containing the (*Z*)-3 double bond and their nontoxic analogues were prepared via modification of the procedures of Henrick[8a] and Rossi[8b] (Scheme I). The lithium derivative of 1-[(2-tetrahydropyranyl)oxy]but-3-yne (**9**) was coupled with either the bromide **10a** or **10b** or fluoro bromides **11a–c** to produce **12a** and **12b** or **13a–c**, respectively. Partial hydrogenation over palladium on barium sulfate followed by deprotection gave the corresponding alkenols **2–6**.

(8) (a) Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845. (b) Rossi, R. *Synthesis* **1981**, 359.

Scheme II[a]

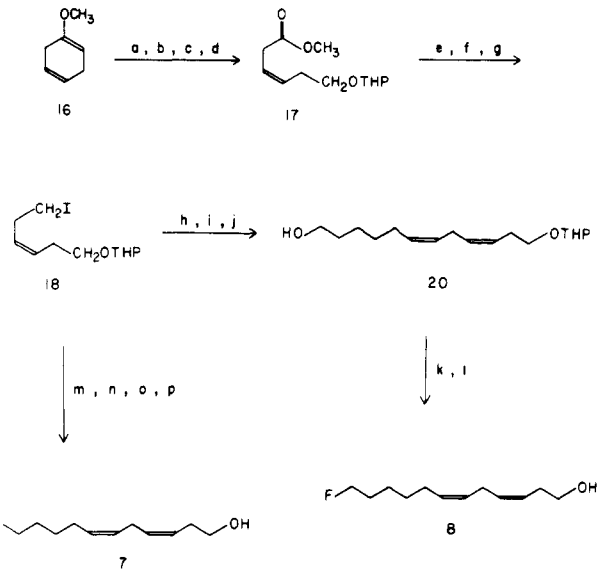


14 15

5

[a] (a) NaH, APA; (b) $DAST/CH_2Cl_2$; (c) *n*-BuLi/THF/HMPA; (d) ethylene oxide/THF; (e) H_2, $Pd/BaSO_4$, quinoline, CH_3OH.

Scheme III[a]



16 17 18 20

7 8

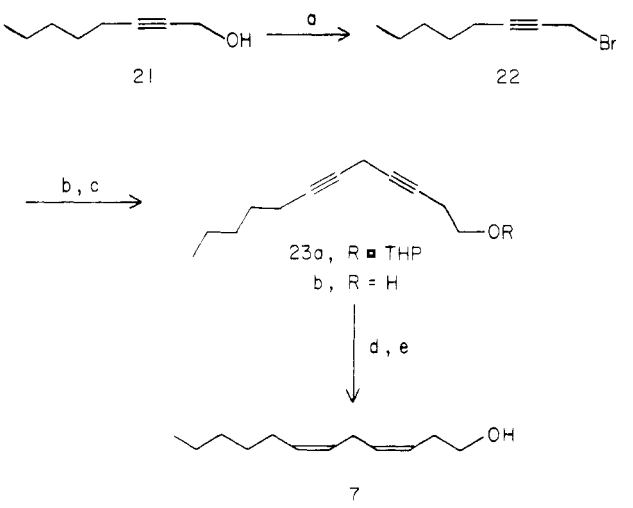
[a] (a) O_3, MeOH; (b) $(CH_3)_2S$; (c) $NaBH_4$, ethanol; (d) PPTS, DHP, CH_2Cl_2; (e) $LiAlH_4$, THF; (f) *p*-TosCl, Pyr; (g) NaI, acetone; (h) $(C_6H_5)_3P$, toluene, CH_3CN; (i) *n*-BuLi, THF; (j) $HO(CH_2)_5CHO$, THF, HMPA; (k) DAST, CH_2Cl_2; (l) PPTS, CH_3OH; (m) $(C_6H_5)_3P$, toluene, CH_3CN; (n) *n*-BuLi, THF (o) hexanal, THF, HMPA; (p) PPTS, C_2H_5OH.

For the large-scale synthesis of **5** an alternative synthesis for the fluorinated analogues was employed as outlined in Scheme II. Fluoroalkyne **15** was prepared by isomerization of the internal triple bond of 3-decyn-1-ol (**14**) to the terminal position[9] using sodium aminopropyl amide, followed by fluorination using (diethylamino)sulfur trifluoride (DAST).[10] Treatment of the lithium acetylide of **15** with ethylene oxide followed by partial hydrogenation over palladium on barium sulfate afforded **5** in 33% overall yield.

The attractive (i.e., induces orientation and following by termite workers) and toxic ω-fluoro dienol **8** and its attractive but nontoxic analogue **7** were prepared as shown in Scheme III. Treatment of 1-methoxy-1,4-cyclohexadiene (**16**) with 1 equiv of ozone in methanol–dimethyl sulfide, followed by reduction of the aldehyde with ethanolic excess sodium borohydride[11] gave an alcohol, which was subsequently protected as its THP ether **17**. The methyl ester was reduced to the corresponding alcohol, tosylated, and then converted into iodide **18**. The corre-

(9) McCaulay, S. R. *J. Org. Chem.* **1980**, *45*, 734.
(10) Middleton, J. *J. Org. Chem.* **1975**, *40*, 574.
(11) (a) Corey, E. J.; Katzenellenbogen, J. A.; Gilman, N. W.; Roman, S. A.; Erickson, B. W. *J. Am. Chem. Soc.* **1968**, *90*, 5618. (b) Pappas, J. J.; Keaveney, W. P.; Gancher, E.; Berger, M. *Tetrahedron Lett.* **1966**, 4273.

Scheme IV[a]



[a] (a) CBr_4, Ph_3P, CH_2Cl_2; (b) Cu_2Cl_2, 9/C_2H_5MgBr, THF; (c) PPTS, C_2H_5OH; (d) H_2, Pd/$BaSO_4$ quinoline, CH_3OH.

sponding phosphonium salt was treated with 1 equiv of *n*-BuLi in THF/HMPA, the ylide was condensed with hexanal at 0 °C, and the THP ether was removed to give the desired nonfluorinated (*Z,Z*)-dienol **7**. The stereochemical purity of the product was at least 86% as judged by ^1H NMR and capillary GLC analysis. Alternatively, condensation of 6-hydroxyhexanal with the ylide using 2 equiv of *n*-BuLi gave the dienol THP ether, which after fluorination and deprotection yielded the ω-fluoro dienol **8**. The stereochemical purity of the product was at least 90% as judged by ^1H NMR and GLC analysis.

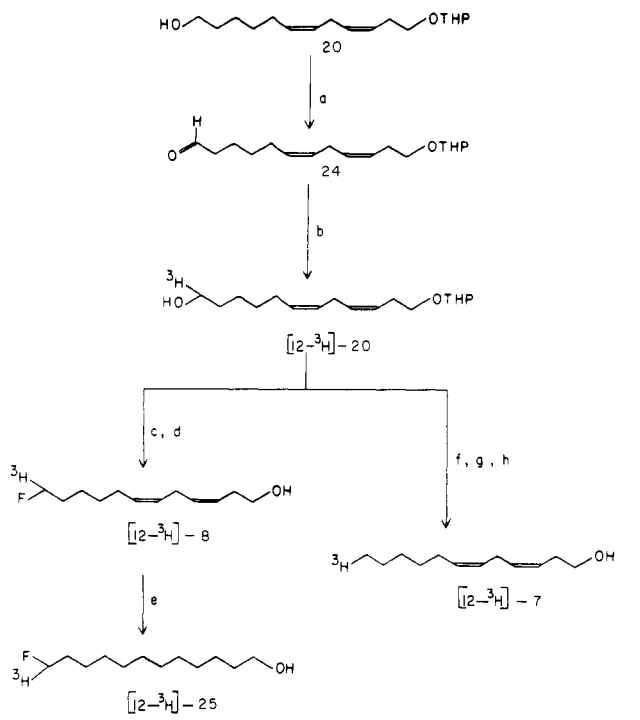
The *Z,Z* nature of the dienol **7** obtained from this route was verified by an independent synthesis via the 3,6-diyne **23** (Scheme IV). Thus, 1-bromo-2-octyne (**22**) was prepared from 2-octyn-1-ol (**21**) and coupled under Cu_2Cl_2 catalysis with the Grignard derived from THP ether **9**. The free alcohol was released with PPTS in ethanol, followed by partial hydrogenation with 5% Pd/$BaSO_4$/quinoline to give the crude dienol **7**. Purification by argentation chromatography and evaporative distillation gave material of >98% stereochemical purity, which was coincident on two capillary columns with the major dienol **7** prepared by the Wittig route.

The tritium-labeled analogues were prepared via sodium borotritide reduction of the aldehyde **24** derived from **20** by PCC oxidation (Scheme V). The [12-^3H]-dienol THP ether **20**, specific activity 1 Ci/mmol, was then converted to the [12-^3H]-fluoro dienol **8** by fluorination and deprotection as described above. The saturated [12-^3H]-12-fluorododecan-1-ol([12-^3H]-**25**)-was prepared by hydrogenation of the dienol **8**. Finally, the nonfluorinated [12-^3H]-**7** was obtained from alcohol **20** by mesylation followed by $LiAlH_4$ reduction and then deprotection.

Tai et al.[7] found that the natural trail pheromone of *R. virginicus*, (*Z,Z,E*)-3,6,8-dodecatrien-1-ol (**1**), which elicits trail-following activity at 10^{-8} μg/10-cm trail, was twice as active as the (*Z,Z*)-3,6-dodecadien-1-ol analogue (**7**) and 10^4 times as active as (*Z*)-3-dodecen-1-ol (**2**). Results from tests conducted in our laboratories showed that the trail-following activities elicited by the ω-fluoro analogues **5**, **6**, and **8** are equal to those of their nonfluorinated counterparts **2**, **3**, and **7** respectively (Table I).

The bioassays of the fluorinated compounds as termiticidal agents were performed in six replicates at each of five dosages and mortality was recorded at daily intervals (Table I). It is interesting to note that the nontrail-active 16-fluoro-(*E*)-9-hexadecen-1-ol (which is ten-fold more toxic than its acid derivative)[4b] shows comparable toxicity to the nontrail-active C-14 ω-fluoro alcohol **6**. Compounds **5** and **8**, with chain lengths the same as that of the natural pheromone, are twice as toxic as the nontrail-active compounds.

Scheme V[a]



[a] (a) PCC, CH_2Cl_2; (b) $NaBT_4$, C_2H_5OH; (c) MsCl, CH_2Cl_2, Et_3N; (d) $LiAlH_4$, THF; (e) PPTS, C_2H_5OH; (f) DAST, CH_2Cl_2; (g) H_2, Pd/C, C_2H_5OH.

Table I. Bioactivity of Synthetic Alcohols to *Reticulitermes flavipes* Workers

compound	trail-following,[a] μg/10-cm streak	toxicity[c] LC_{50} (μg/mL)
(*Z*)-dodec-3-en-1-ol (**2**)	0.05	>300
(*Z*)-tetradec-3-en-1-ol (**3**)	NR[b]	>300
10-fluoro-(*Z*)-dec-3-en-1-ol (**4**)	0.5	9.5
12-fluoro-(*Z*)-dodec-3-en-1-ol (**5**)	0.05	9.3
14-fluoro-(*Z*)-tetradec-3-en-1-ol (**6**)	5	20.4
12-fluoro-(*Z,Z*)-dodeca-3,6-dien-1-ol (**8**)	0.002	11.6
11-fluoroundecan-1-ol	NR	62.0
12-fluorododecan-1-ol	NR	7.7
dodecan-1-ol	NR	>300

[a] Threshold values (lowest quantity eliciting positive response).[7d] [b] No response at 5 μg/10 cm-trail. [c] Lethal concentration of fluoro alcohol in filter paper required to kill 50% of the test animals at the time of 3 days of incubation, as calculated by probit analysis of dose–response data.[6]

In summary, fluorinated pheromone mimics appear to be very promising as bait-block toxicants. Field tests[5] are in progress to determine how accurately the laboratory results can predict termite control properties under natural conditions.

Experimental Section

General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and used without further

purification. Tetrahydrofuran (THF, Aldrich Gold Label) was distilled from sodium benzophenone ketyl in a recirculating still, with a deep blue color maintained in the distilling pot. Hexamethylphosphoric triamide (HMPA) was distilled from BaO and stored over 3-Å molecular-sieves. Acetone was dried over potassium carbonate, distilled, and stored over 3 Å-molecular sieves. Pyridine was dried over sodium hydroxide, distilled from BaO, and stored over 3-Å molecular sieves. Hexane, ethyl acetate, and methanol were Fisher HPLC grade and used without further purification. *p*-Toluenesulfonyl chloride was recrystallized from $CHCl_3$/petroleum ether (1:5, v/v). Toluene was dried by azeotropic distillation. Acetonitrile and 1,3-diaminopropane were distilled from CaH_2. Triethylamine (Et_3N) was reagent grade and stored over NaOH. Dihydropyran (DHP) was distilled from $LiAlH_4$ and stabilized with a trace (ca. 0.1%) of 2,6-di-*tert*-butyl-4-methylphenol (BHT). Methanesulfonyl chloride was distilled before use. All reactions and distillations were performed under a N_2 atmosphere.

^1H NMR spectra were recorded at 80 MHz on a Varian HFT-80 spectrometer or at 300 MHz on an NT 300 in deuteriochloroform with tetramethylsilane as the internal standard. Data are reported in the form of values of chemical shift (peak multiplicity, coupling constant if appropriate, number of protons). When peak multiplicities are reported, the following abbreviations are used: s, singlet; d, doublet, t, triplet; q, quarter; m, multiplet; br, broadened. ^{13}C NMR spectra were recorded on a Varian CFT-20 (20 MHz) spectrometer and proton noise decoupling and shifts are reported relative to δ(TMS) = 0 ppm. Data are reported in the form of values of chemical shift (peak multiplicity, coupling constant if appropriate, intensity). Infrared spectra of neat liquids were obtained on a Perkin-Elmer 727 instrument. Data are given in reciprocal centimeters with only the important diagnostic values reported.

Thin-layer chromatography was performed by using MN Polygram Sil G/UV 254 (4 cm × 8 cm) TLC plates. R_f values are reported for either solvent system (a) hexane/ethyl acetate (7:3, v/v) or (b) hexane/ethyl acetate (1:1, v/v). Visualization was accomplished by UV light, iodine, or an ethanol–vanillin–H_2SO_4 reagent. Flash chromatography[12] was performed under N_2 pressure on Merck silica gel G (400–230 mesh) by using hexane/ethyl acetate mixtures (v/v). Analytical gas–liquid chromatography (GC) was performed on a Varian Model 3700 chromatograph (programmable temperature control) equipped with a flame ionization detector and helium carrier gas using system (a) OV-1701 vitreous silica, 50 m × 0.2 mm, 150–250 °C, 5 °C/min, (b) DX-4 fused silica, 30 m × 0.25 mm at 160 °C, or (c) Carbowax 20M, 50 m × 0.8 mm, 120–200 °C, 6 °C/min. Elemental analyses were performed by Galbraith Laboratories, Inc.

Toxicity bioassays were performed by modification of our original methods.[4] Synthetic fluoro alcohols were dissolved in HPLC-grade hexane (Fisher) to make 1 mg/mL stock solutions. Serial dilutions were prepared at 0.3 mg/mL, 0.1 mg/mL, 0.03 mg/mL, 0.01 mg/mL, and 0.003 mg/mL. A 1.0-mL portion of each solution was pipetted (Gilson Pipettman) onto each of three sterile 47-mm cellulose pads (Gelman). The solvent was allowed to evaporate (10 min); each pad was cut in half and moistened with 0.5 mL of distilled H_2O, and the six halves were placed in tight-sealing 50-mm plastic Petri dishes (Gelman). Control treatments (0.3, 0.1, 0.03, 0.01 and 0.003 mg/mL) of (*Z*)-3-dodecen-1-ol were prepared in an analogous fashion. Mortality was determined at 24-h intervals, and dead individuals were removed to reduce microbial contamination. A plot of probit mean mortality against log concentrations provides a standard method to compute the LC_{50}, or lethal concentration of fluorolipid in filter paper required to kill 50% of the test animals at a time of 4 days (72 h) of incubation. Regression lines were drawn to minimize χ^2, and approximate LC_{50} values were obtained graphically[6] (Table I).

Trial-following bioassays were performed by modifications of the methods of Howard et al.,[7b] and details of these assays are described by Prestwich et al.[7d] Results are summarized in Table I.

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1-Bromo-8-fluorooctane[1a] (11b). A solution of 8-bromooctan-1-ol[8b] (2.50 g, 11.9 mmol) in methylene chloride (3 mL) was slowly added to a stirred solution of (diethylamino)sulfur trifluoride (DAST[10]) (1.5 mL, 11.9 mmol) in methylene chloride (10 mL) cooled to −78 °C. After the addition was complete, the reaction mixture was warmed to 25 °C and saturated $NaHCO_3$ (5 mL) was added, followed by dilution with ether (200 mL). The organic layer was separated, washed with water (20 mL) and saturated $NaHCO_3$ (20 mL), and dried ($MgSO_4$). The volatiles were removed in vacuo, and the crude product was purified by flash chromatography using hexane/ethyl acetate (95:5) to afford 1.54 g (61%) of **11b** as a clear colorless liquid: R_f(a) 0.70; IR (film) 2850–3000 cm^{-1} (alkane CH); and ^1H NMR δ 1.15–2.0 (m, 12 H), 3.39 (t, J = 6 Hz, 2 H), 4.42 (dt, J = 48, 6 Hz, 2 H).

1-[(2-Tetrahydropyranyl)oxy]-12-fluorododec-3-yne (13b). To a solution of 1-[(2-tetrahydropyranyl)oxy]but-3-yne[13] (**9**, 0.482 g, 3.05 mmol) in dry THF (15 mL) was added *n*-BuLi (3.05 mmol; 2.80 mL of 1.09 M *n*-BuLi in hexane) at −78 °C. The resulting mixture was stirred for 1 h at −78 °C and warmed to −5 °C for 5 min, and then a solution of 8-bromo-1-fluorooctane (**11b**, 0.772 g, 3.65 mmol, 1.2 equiv) in HMPA (10 mL) was added dropwise over 45 min. After the addition was complete the reaction was allowed to warm to room temperature and stirred overnight. After the solution was quenched by the dropwise addition of water (10 mL), the aqueous solution was extracted with pentane (4 × 50 mL) and the combined pentane extracts were washed with saturated NaCl (50 mL) and dried ($MgSO_4$). The volatiles were removed in vacuo, and the crude product was flash chromatographed by using hexane/ethyl acetate (9:1) to give 0.526 g (60%) of fluoro ether **13b** as a clear colorless oil: R_f(a) 0.60; IR (film) 2850–3000 cm^{-1} (alkane CH); ^1H NMR δ 1.20–1.90 (m, 18 H), 2.05–2.20 (m, 2 H), 2.30–2.55 (m, 2 H), 3.30–3.95 (m, 4 H), 4.42 (dt, J = 48, 6 Hz, 2 H), 4.60 (br s, 1 H).

12-Fluoro-(*Z*)-dodec-3-en-1-ol (5). A solution of THP ether **13b** (0.526 g, 1.85 mmol) in methanol (10 mL) containing 4 drops of quinoline was hydrogenated at room temperature over 5% Pd/$BaSO_4$ (25 mg). The mixture was kept at 762 torr of hydrogen until 41.5 mL (1.85 mmol) of hydrogen had been absorbed. The catalyst was filtered off and the solvent removed in vacuo. The residue was purified by flash chromatography using hexane/ethyl acetate (9:1) to give 0.524 g (99%) of the THP ether of **5** as a clear oil: R_f(a) 0.65; IR (film) 3025 cm^{-1} (C=CH); ^1H NMR δ 1.20–1.80 (m, 18 H), 2.05 (m, 2 H), 2.35 (br q, J = 4 Hz, 2 H), 3.60 (m, 4 H), 4.41 (dt, J = 48, 6 Hz, 2 H), 4.56 (br s, 1 H), 4.51 (m, 2 H). To a solution of the THP ether of **5** (0.524 g, 1.83 mmol) in methanol (10 mL) was added Dowex (0.5 g), and the mixture was heated at 45 °C overnight. The resin was then filtered off and the solvent was removed in vacuo. The crude product was purified by flash chromatography using hexane/ethyl acetate (93:7) to give 312 mg (83%) of fluoro alcohol **5** as a clear colorless oil: R_f(a) 0.36; IR (film) 3100–3500 (OH), 3000 cm^{-1} (C=CH); ^1H NMR δ 1.25–1.75 (m, 12 H), 2.15 (m, 2 H), 2.35 (br q, J = 6 Hz, 2 H), 3.65 (t, J = 7 Hz, 2 H), 4.41 (dt, J = 48, 6 Hz, 2 H), 5.46 (m, 2 H). Anal. Calcd for $C_{12}H_{23}FO$: C, 71.31; H, 11.38%; F, 9.39. Found: C, 71.32; H, 11.39; F, 9.16.

1-Bromo-10-fluorodecane (11c) was prepared as described for compound **11b** by using 1.00 g (4.23 mmol) of 10-bromodecanol[14] and 0.529 mL (4.23 mmol) of DAST[10] in 50 mL of methylene chloride. Purification by flash chromatography using hexane/ethyl acetate (9:1) gave 826 mg (82%) of **11c** as a clear liquid: R_f(a) 0.73; IR (film) 2850–3000 cm^{-1} (alkane CH); ^1H NMR δ 1.25–1.95 (m, 16 H), 3.36 (t, J = 6 Hz, 2 H), 4.40 (dt, J = 48, 6 Hz, 2 H).

1-[(2-Tetrahydropyranyl)oxy]-14-fluorotetradec-3-yne (13c) was prepared as described for THP ether **13b** by using 1.106 g (7.0 mmol) of THP ether **9**, 6.42 mL (7.0 mmol) of 1.09 M *n*-BuLi in hexane, and 1.396 g (5.84 mmol, 1.2 eq) of alkyl bromide **11c**. Purification by flash chromatography using hexane/ethyl acetate (9:1) gave 361 mg (20%) of fluoro ether **13c** as a clear yellowish oil: R_f(a) 0.75; IR (film) 2900 cm^{-1} (alkane CH); ^1H NMR δ 1.20–1.85 (m, 22 H), 2.15 (m, 2 H), 2.47 (m, 2 H), 3.65 (m, 4 H), 4.41 (dt, J = 48, 6 Hz, 2 H), 4.65 (br s, 1 H).

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14-Fluoro-(*Z*)-tetradec-3-en-1-ol (6) was prepared as described for **5** by hydrogenating 361 mg (1.16 mmol) of fluoro ether **13c** by using 15 mg of 5% palladium on barium sulfate and 2 drops of quinoline in 10 mL of methanol. The reaction was stopped after 25.9 mL (1.16 mmol) of hydrogen had been absorbed. Purification by flash chromatography using hexane/ethyl acetate (9:1) gave 354 mg (97%) of the THP ether of **6** as a clear colorless oil: R_f(a) 0.65; IR (film) 3025 (C=CH), 2850–2950 cm^{-1} (alkane CH); ^1H NMR δ 1.20–1.80 (m, 22 H), 2.15 (m, 2 H), 2.35 (br q, J = 5 Hz, 2 H), 3.60 (m, 4 H), 4.41 (dt, J = 48, 6 Hz, 2 H), 4.65 (br s, 1 H), 5.41 (m, 2 H). The THP group was removed as described for alcohol **5** by using 354 mg (1.26 mmol) of the THP ether of **6** and 350 mg of Dowex in 10 mL of methanol. Purification by flash chromatography using hexane/ethyl acetate (9:1) afforded 212 mg (73%) of fluoro alcohol **6** as a clear colorless oil: R_f(a) 0.27; IR (film) 3200–3500 (OH), 3025 cm^{-1} (alkane CH); ^1H NMR δ 1.20–1.70 (m, 16 H), 2.10 (m, 2 H), 2.37 (br q, J = 5 Hz, 2 H), 3.65 (t, J = 6 Hz, 2 H), 4.41 (dt, J = 48, 6 Hz, 2 H), 5.45 (m, 2 H). Anal. Calcd for $C_{14}H_{27}FO$: C 73.07; H, 11.73; F, 8.25. Found: C, 72.77; H, 11.76; F, 8.04.

1-Fluoro-6-bromohexane[1a] (11a) was prepared as described for compound **11b** by using 2.078 g (11.48 mmol) of 6-bromo-1-hexanol[15] and 1.435 mL (11.48 mmol) of DAST.[10] Purification by evaporative distillation yielded 1.112 g (52.9%) of fluoroalkane **11a**: ^1H NMR δ 1.25–2.05 (m, 8 H), 3.41 (t, J = 6 Hz, 2 H), 4.11 (dt, J = 48, 6 Hz, 2 H).

1-[(2-Tetrahydropyranyl)oxy]-10-fluorodec-3-yne (13a) was prepared as described for fluoro ether **13b** by using 0.799 g (5.06 mmol) of THP ether **9**, 3.6 mL (5.06 mmol) of 1.39 M *n*-BuLi in hexane, and 1.112 g (6.07 mmol, 1.2 eqiv) of alkyl bromide **11a**. Purification by flash chromatography using hexane/ethyl acetate (9:1) afforded 570 mg (44%) of fluoro ether **13a** as a clear colorless oil; R_f(a) 0.58; IR (film) 2850–2950 cm^{-1} (alkane CH); ^1H NMR δ 1.20–1.95 (m, 14 H), 2.15 (m, 2 H), 2.45 (m, 2 H), 3.65 (m, 4 H), 4.42 (dt, J = 48, 6 Hz, 2 H), 4.65 (br s, 1 H).

10-Fluoro-(*Z*)-dec-3-en-1-ol (4) was prepared as described for **5** by hydrogenation of 568 mg (2.22 mmol) of **13a** using 24 mg of 5% palladium on barium sulfate and 2 drops of quinoline in 10 mL of methanol. The reaction was stopped when 49.7 mL (2.22 mmol) of hydrogen had been absorbed. Purification by flash chromatography using hexane/ethyl acetate (9:1) gave 563 mg (99%) of the THP ether of **4** as a clear colorless oil: R_f(a) 0.68; IR (film) 3025 (C=CH), 2850–2950 cm^{-1} (alkane CH); ^1H NMR δ 1.20–1.80 (m, 16 H), 2.05 (m, 2 H), 2.33 (br q, J = 5 Hz, 2 H), 3.57 (m, 4 H), 4.40 (dt, J = 48, 6 Hz, 2 H), 4.55 (br s, 1 H), 5.40 (m, 2 H).

The THP groups was removed as described for fluoro alcohol **5** by using 500 mg of Dowex in 20 mL of methanol. Purification by flash chromatography using hexane/ethyl acetate (9:1) gave 344 mg (90%) of **4** as a clear colorless liquid: R_f(a) 0.39; IR (film) 3100–3600 (OH), 3000 (C=CH), 2850–2950 cm^{-1} (alkane CH); ^1H NMR δ 1.20–1.65 (m, 8 H), 2.05 (m, 2 H), 2.79 (br q, J = 5 Hz, 2 H), 3.60 (t, J = 6 Hz, 2 H), 4.37 (dt, J = 48, 6 Hz, 2H), 5.42 (m, 2 H). Anal. Calcd for $C_{10}H_{19}FO$: C, 68.99; H, 10.91; F, 10.91. Found: C, 68.72; H, 10.88; F, 10.73.

Large-Scale Preparation of 12-Fluoro-(*Z*)-dodec-3-en-1-ol (5). 10-Fluoro-1-decyne (15). To NaH (Ventron Corp., 57% in mineral oil, 20.05 g, 0.473 mol, washed free of oil three times with hexane) at ice-bath temperature was added 1,3-diaminopropane (DAP) (170 mL) with vigorous stirring to minimize foaming. The mixture was heated gradually to 80 °C, and stirring was continued until hydrogen evolution had ceased (2 h). The brown mixture was then cooled to 10 °C, and 3-decyn-1-ol **14** (Farchan Labs, 21.0 g, 0.136 mol) was added gradually over a period of 5 min. The ice bath was removed and the mixture was gradually heated to 100 °C over a period of 40 min. When TLC showed that the reaction was complete, the mixture was cooled to 10 °C and cautiously poured into 150 g of crushed ice. The flask was rinsed with cold water (2 × 200 mL), and the aqueous mixture was extracted with hexane (3 × 200 mL). The combined hexane solution was washed with water (4 × 75 mL), saturated aqueous $NaHCO_3$ (50 mL), and saturated NaCl (50 mL) and dried ($MgSO_4$). After filtration and evaporation of solvent, the crude residue was distilled to give 14.52 g of 9-decyn-1-ol[16] (70%) [bp 66–69 °C (0.38 mm Hg)] as a clear colorless liquid: R_f(a) 0.42; IR (film) 3500–3150 (OH, C≡CH), 2850–2950 (alkane CH), 2110 cm^{-1} (C≡C); ^1H NMR δ 1.35 (s, 10 H), 1.95 (t, J = 3 Hz, 1 H), 2.17 (m, 2 H), 3.60 (t, J = 6 Hz, 2 H).

This material was fluorinated as described for compound **11b** by using 3.00 g (19.5 mmol) of 9-decyn-1-ol and 2.44 mL (19.5 mmol) of DAST[10] in 50 mL of methylene chloride. Purification by flash chromatography using hexane/ethyl acetate (8:2) gave 2.46 g (81.8%) of **15** as a clear yellow liquid: R_f(a) 0.81; IR (film) 3325 (C≡CH), 2875, 2950 (alkane CH), 2120 cm^{-1} (C≡C); ^1H NMR δ 1.35 (br s, 12 H), 1.92 (t, J = 3 Hz, 1 H), 2.15 (m, 2 H), 4.40 (dt, J = 48, 6 Hz, 2 H).

12-Fluoro-(*Z*)-dodec-3-en-1-ol (5). To a solution of fluoroalkyne **15** (2.5 g, 16.1 mmol) in 30 mL of THF/HMPA (1:3) at 0 °C was added *n*-BuLi (19.2 mmol; 8.7 mL of 2.2 M *n*-BuLi in hexane). The resulting orange solution was allowed to warm to room temperature, and after recooling to 0 °C, ethylene oxide (32 mmol; 8.0 mL of 4 M ethylene oxide in THF) was added dropwise. After being stirred for 1 h at 0 °C, the reaction mixture was diluted with either (200 mL) and washed successively with 15% H_2SO_4 (25 mL), H_2O (25 mL), and saturated NaCl (25 mL) and dried ($MgSO_4$). The volatiles were removed in vacuo, and the crude product was flash chromatographed by using hexane/ethyl acetate (85:15) to give 2.05 g (64%) of 12-fluorododec-3-yn-1-ol as a clear yellow oil: R_f(a) 0.55; IR (film) 3225–3575 (OH), 2850–2975 cm^{-1} (alkane CH); ^1H NMR δ 1.40 (s, 12 H), 2.15 (m, 2 H), 2.45 (m, 2 H), 3.65 (t, J = 6 Hz, 2 H), 4.41 (dt, J = 48, 6 Hz, 2 H).

This material was hydrogenated as described for the original preparation of **5** using 124 mg of 5% $Pd/BaSO_4$, 6 drops of quinoline, and 80 mL of methanol. The reaction was stopped when 224 mL of hydrogen had been absorbed. Distillation of the product afforded 1.84 g (91%) of **5** [bp 155 °C (15 mm Hg)] as a clear colorless liquid.

Methyl 6-[(2-Tetrahydropyranyl)oxy]-(*Z*)-hex-3-enoate (17). A solution of technical-grade 1-methoxy-1,4-cyclohexadiene (**16**, 2.0 g, 18.16 mmol, 2.13 mL) in 20 mL of methanol was cooled to −78 °C and treated with 1 equiv of ozonized oxygen gas with efficient stirring. While still at −78 °C, the solution was flushed with nitrogen, and dimethyl sulfide (1.5 mL, 20 mmol) was added. The solution was stirred at −10 °C for 1 h, then at ice-bath temperature for 1 h, and finally at room temperature for 1 h. Methanol and excess dimethyl sulfide were removed in vacuo, and to the residue was added anhydrous ethanol (25 mL) followed by sodium borohydride (0.22 g, 6.8 mmol, 1.5 equiv). The mixture was stirred for 1 h at room temperature and the ethanol was removed in vacuo. The residue was diluted with ether (150 mL), and the ether layer was washed with 10% HCl (75 mL). The water layer was extracted with ether (4 × 50 mL), and the combined organics were washed with saturated $NaHCO_3$ (25 mL) and dried ($MgSO_4$). Purification by flash chromatography using hexane/ethyl acetate (70:30, v/v) afforded 1.24 g (54.7%) of the unprotected ester of **17** as a clear yellowish liquid: R_f(b) 0.26; IR (film) 3200–3600 (OH), 2850–3000 (C=CH, alkane CH), 1730 cm^{-1} (C=O); ^1H NMR δ 2.30 (m, 2 H), 3.15 (br d, J = 6 Hz, 2 H), 3.62 (t, J = 6 Hz, 2 H), 3.66 (s, 3 H), 5.62 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.96 (108), 32.62 (118), 51.48 (76), 61.21 (125), 123.13 (103), 129.62 (109), 171.64 (26).

A solution of 0.768 g of this hydroxy ester (5.3 mmol), 3,4-dihydropyran (0.72 mL, 7.9 mmol, 1.5 equiv), and pyridinium *p*-toluenesulfonate[17] (PPTS, 125 mg, 0.5 mmol) in methylene chloride (25 mL) was stirred for 4 h at room temperature. The solution was then diluted with ether (150 mL), and the ether layer was washed with half-saturated NaCl (50 mL) to remove the catalyst and dried ($MgSO_4$). Purification by flash chromatography using hexane/ethyl acetate (90:10) afforded 1.1963 g (99%) of THP methyl ester **17** as a clear colorless oil: R_f(a) 0.38; IR (film) 2850–3000 (C=CH, alkane CH), 1740 cm^{-1} (C=O); ^1H NMR δ 1.45–1.65 (m, 6 H), 2.35 (m, 2 H), 3.10 (d, J = 6 Hz, 2 H), 3.30–3.70

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(m, 4 H), 3.58 (s, 3 H), 4.55 (br s, 1 H), 5.65 (br t, J = 6 Hz, 2 H).

1-Iodo-6-[(2-tetrahydropyranyl)oxy]-(*Z*)-hex-3-ene (18). To a mixture of lithium aluminum hydride (0.336 g, 8.85 mmol, 1.2 eq.) in THF (100 mL) at 0 °C was added THP methyl ester **17** (3.130 g, 14.75 mmol) in THF (10 mL) dropwise. The mixture was refluxed for 0.5 h, cooled to room temperature, and quenched by successive dropwise addition of H_2O (3 drops), saturated $NaHCO_3$ (3 drops), and H_2O (6 drops). The solvent was removed in vacuo, the residue was diluted with ether (150 mL), and the ether layer was washed successively with 5% HCl (25 mL), saturated $NaHCO_3$ (25 mL), and brine (25 mL) and dried ($MgSO_4$). Purification by flash chromatography using hexane/ethyl acetate (4:1 v/v) gave 2.116 g (73%) of THP alcohol of **17** as a clear colorless liquid: R_f(a) 0.26; IR (film) 3200–3550 (OH), 2825–3000 cm^{-1} (C=CH, alkane CH); ^{1}H NMR δ 1.40–1.70 (m, 6 H), 2.30 (m, 4 H), 3.55 (t, J = 6 Hz, 2 H), 3.40–3.80 (m, 4 H), 4.51 (br s, 1 H), 5.54 (m, 2 H).

To a solution of 1.882 g (10.2 mmol) of this alcohol in dry pyridine (15 mL) at 0 °C was added *p*-toluenesulfonyl chloride (2.931 g, 15.3 mmol, 1.5 equiv) in one portion. The mixture was stirred at 0 °C for 1 h and then stored in the refrigerator (5 °C) overnight. The reaction mixture was cooled to 0 °C, and most of the pyridine was removed in vacuo and ether (200 mL) was added. The ether layer was washed with 5% HCl (25 mL), saturated $NaHCO_3$ (25 mL), and saturated NaCl (25 mL) and dried ($MgSO_4$). After filtering and removing the ether, the crude product was diluted with dry acetone (20 mL) and dry NaI (12.22 g, 82 mmol, 10 equiv) was added. The mixture was stirred at room temperature for 3 h, and the volatiles were removed in vacuo. The residue was diluted with hexanes (200 mL), and this solution was extracted with aqueous sodium thiosulfate followed by brine. The organic layer was dried ($MgSO_4$), and the volatiles were removed in vacuo. Purification by flash chromatography using hexane/ethyl acetate (4:1) afforded 2.504 g (83%) of the THP iodide **18** as a clear yellowish oil: R_f(a) 0.76; IR (film) 2850–3050 cm^{-1} (C=CH, alkane CH); and ^{1}H NMR δ 1.45–1.70 (m, 6 H), 2.35 (br q, J = 6 Hz, 2 H), 2.71 (br t, J = 6 Hz, 2 H), 3.15 (t, 2 H), 3.30–3.85 (m, 4 H), 4.57 (br s, 1 H), 5.57 (m, 2 H).

6-Hydroxyhexanal[18] (19). To a solution of 6-hexanolactone (4.0 g, 35 mmol) in toluene (100 mL) at −78 °C was added Dibal-H[19] (52.5 mmol, 1.5 equiv, 52.5 mL of 1 M Dibal-H in toluene). The mixture was stirred for 1 h at −78 °C after which time the reaction was quenched by dropwise addition of HOAc/H_2O (1:2). The mixture was diluted with $CHCl_3$ (200 mL), and the organic layer was washed with H_2O (30 mL), saturated $NaHCO_3$ (30 mL), and brine (30 mL) and dried ($MgSO_4$). The organic layer was removed in vacuo to yield 3.12 g (78%) of the hydroxy aldehyde **19** as a clear colorless liquid: R_f(b) 0.19; IR (film) 3175–3550 (OH), 2850–2950 (alkane CH), 1720 cm^{-1} (C=O); ^{1}H NMR δ 1.50–1.68 (m, 6 H), 2.47 (dt, J = 6, 2.5 Hz, 2 H), 3.65 (t, J = 6 Hz, 2 H), 9.77 (t, J = 2.5 Hz, 1 H).

1-[(2-Tetrahydropyranyl)oxy]-12-hydroxy-(*Z*,*Z*)-dodeca-3,6-diene (20). To a solution of THP iodide **18** (4.44 g, 14.3 mmol) in toluene/CH_3CN (40 mL, 3/1) was added reagent-grade triphenylphosphine (4.50 g, 17.19 mmol, 1.2 equiv) in one portion. The solution was stirred for 48 h at 60 °C. The mixture was cooled, and the solvents were removed in vacuo to give an oily solid. This residue was washed with anhydrous ether until a white crystalline solid (7.38 g, 80%) was obtained: ^{1}H NMR δ 1.45–1.70 (m, 6 H), 2.10–2.75 (m, 4 H), 3.20–3.80 (m, 6 H), 4.57 (br s, 1 H), 5.45–5.75 (m, 2 H), 7.70–7.85 (m, 15 H).

An aliquot of the Wittig salt of **18** in acetonitrile was transferred to a preweighed round-bottomed flask, and the acetonitrile was removed in vacuo. Dry benzene (10 mL) was added, and the benzene was removed in vacuo to leave 1.118 g (1.96 mmol) of the phosphonium salt of **18**. The salt was dissolved in THF (20 mL) and *n*-BuLi (1.96 mmol, 1.45 mL of 1.35 M *n*-BuLi in hexane) was added at 0 °C. The bright orange solution of the ylide was stirred for 30 min at 0 °C followed by the rapid addition of hydroxy aldehyde **19** (227.4 mg, 1.96 mmol) dissolved in THF/HMPA (9 mL, 1:2, v/v). The mixture was stirred for 2 h at 0 °C and then quenched by the dropwise addition H_2O. The THF was removed in vacuo, the residue was taken up in hexane (200 mL), and the hexane layer was washed with H_2O (2 × 50 mL) and brine (30 mL) and dried ($MgSO_4$). Purification by flash chromatography using hexane/ethyl acetate (80:20) afforded 253.0 mg (46%) of the THP dienol **20** as a clear slightly yellow oil: R_f(b) 0.42; IR (film) 3250–3550 (OH), 2850–3050 cm^{-1} (C=CH, alkane CH); ^{1}H NMR δ 1.30–1.80 (m, 12 H), 2.15 (br d, J = 6 Hz, 2 H), 2.35 (br q, J = 6 Hz, 2 H), 2.78 (br t, J = 6 Hz, 2 H), 3.30–3.85 (m, 4 H), 3.65 (t, J = 6 Hz, 2 H), 4.56 (br s, 1 H), 5.40 (br q, J = 6 Hz, 4 H).

12-Fluoro-(*Z*,*Z*)-dodeca-3,6-dien-1-ol (8). A solution of (dimethylamino)trimethylsilane (166.1 mg, 1.42 mmol, 1.41 eq) in CCl_3F (6 mL) was cooled to −78 °C and (dimethylamino)sulfur trifluoride[10] (DAST, 0.215 mL, 1.71 mmol, 1.91 equiv) was added. The solution was stirred for 10 min at −78 °C, allowed to warm to room temperature, and cooled back to −78 °C, and dienol **20** (253.0 mg, 0.897 mmol, 1 equiv) in CCl_3F (1 mL) was added dropwise. The solution was stirred for 45 min at −78 °C, let warm to room temperature, and then stirred an additional 1 h. A few crystals of sodium carbonate were added followed by the addition of ether (200 mL), and the ether layer was washed with saturated $NaHCO_3$ (30 mL) and brine (25 mL) and dried ($MgSO_4$). Purification by flash chromatography using hexane/ethyl acetate (9:1) afforded 152 mg (59%) of the THP ether of **8** as a clear yellowish oil: R_f(b) 0.75; IR (film) 2850–3050 cm^{-1} (C=CH, alkane); ^{1}H NMR δ 1.20–1.70 (m, 2 H), 2.05 (m, 2 H), 2.35 (br q, J = 6 Hz, 2 H) 2.75 (br t, J = 6 Hz, 2 H), 3.30–3.75 (m, 4 H), 4.38 (dt, J = 48, 6 Hz, 2 H), 4.55 (br s, 1 H), 5.37 (br q, J = 6 Hz, 4 H).

This material was dissolved in methanol (10 mL) and treated with pyridinium *p*-toluenesulfonate[17] (PPTS, 14.32 mg, 0.056 mm) for 3 h at 55 °C. The solvent was evaporated, the residue was diluted with ether (150 mL), and the ether layer was washed with half-saturated NaCl (50 mL) and dried ($MgSO_4$). Purification by flash chromatography using hexane/ethyl acetate (9:1) gave 88 mg (82%) of the fluoro dienol **8** as a clear colorless liquid: R_f(b) 0.56; IR (film) 3150–3500 (OH) 2825–2910 cm^{-1} (C=CH, alkane CH); ^{1}H NMR δ 1.35–1.55 (m, 6 H), 2.10 (m, 2 H), 2.35 (br q, J = 6 Hz, 2 H), 2.80 (br t, J = 6 Hz, 2 H), 3.64 (t, J = 6 Hz, 2 H), 4.41 (dt, J = 48, 6 Hz, 2 H), 5.41 (m, 4 H); ^{13}C NMR δ 24.71 (56), 24.98 (58), 25.78 (97), 27.12 (95), 29.21 (93), 29.84 (52), 30.83 (125), 62.22 (92), 84.14 (d, J = 164 Hz, 51, 41), 125.54 (93), 127.87 (91), 130.10 (96), 131.25 (85).

1-[(2-Tetrahydropyranyl)oxy]dodec-3-yne (12a) was prepared as described previously for the THP ether **13b** by using 600 mg (3.8 mmol) of THP ether **9**, 1.53 mL (3.8 mmol) of 2.48 M *n*-BuLi, and 0.73 g (3.8 mmol, 1.2 equiv of 1-bromooctane in HMPA (10 mL). Purification by flash chromatography gave 294 mg (30%) of **12a** as a colorless oil: R_f(a) 0.70 hexane/ethyl acetate (7:3, v/v); GC (OV-101 capillary, 25 m, 70-250 °C, 8 °C/min, 97%) t_R = 14.34 min; IR (film) 2160 (C=C) cm^{-1}; ^{1}H NMR δ 0.85 (t, J = 4 Hz, 3 H), 1.20–1.70 (m, 18 H), 2.10 (br t, J = 3 Hz, 2 H), 2.42 (m, 2 H), 3.60 (m, 4 H), 4.56 (br s, 1 H).

(*Z*)-Dodec-3-en-1-ol (2) was prepared as described for compound **5** by hydrogenation of 294 mg (1.16 mmol) of THP ether **12a** using 14.7 mg of 5% palladium on barium sulfate, 1 drop of quinoline, and 10 mL of methanol. The reaction was stopped when 25.9 mL of hydrogen had been absorbed. Purification by flash chromatography afforded 281 mg (91%) of dodec-3-yn-1-ol as a colorless oil: R_f(a) 0.66, hexane/ethyl acetate (7:3, v/v); GC (OV-101 capillary, 25 m, 70–250 °C, 8 °C/min, 94%) t_R = 14.99 min; IR (film) 3025 (C=CH) cm^{-1}; ^{1}H NMR δ 0.90 (br t, J = 6 Hz, 3 H), 1.20–1.75 (m, 18 H), 2.10 (m, 2 H), 2.35 (br q, J = 4 Hz, 2 H), 3.60 (m, 4 H), 4.56 (br s, 1 H), 5.42 (m, 2 H).

Deprotection as described for **5** using 0.5 g of Dowex in 10 mL of methanol followed by flash chromatography gave 174 mg (89%) of **2** as a clear colorless oil: R_f(a) 0.42; IR (film) 3100–3500 (OH), 3025 cm^{-1} (C=CH); ^{1}H NMR δ 0.85 (br t, J = 6 Hz, 3 H), 1.15–1.65 (m, 12 H), 2.15 (m, 2 H), 2.30 (br q, J = 6 Hz, 2 H), 3.60 (t, J = 6 Hz, 2 H), 5.45 (m, 2 H).

1-[(2-Tetrahydropyranyl)oxy]tetradec-3-yne (12b) was prepared as described for compound **13b** by using 1.00g (6.33 mmol) of THP ether **9**, 2.55 mL (6.33 mmol) of 2.48 M *n*-BuLi in hexane, and 1.68 g (7.5 mmol, 1.2 equiv) of 1-bromodecane. Purification by flash chromatography afforded 0.566 g (30%) of

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12b as a clear colorless oil: R_f(a) 0.76; IR (film) 2900 cm^{-1} (alkane CH); ^1H NMR δ 0.84 (br t, J = 6 Hz, 3 H), 1.20–1.80 (m, 22 H), 2.05 (m, 2 H), 2.35 (m, 2 H), 3.45 (m, 4 H), 4.55 (br s, 1 H).

(*Z*)-Tetradec-3-en-1-ol (3) was prepared as described for compound **5** by hydrogenation of 500 mg (1.70 mmol) of THP ether **12b** in a solution of methanol (20 mL) containing 21 mg of 5% $Pd/BaSO_4$ and 2 drops of quinoline. The reaction was stopped when 38.1 mL (1.70 mmol) of hydrogen had been absorbed. Purification by flash chromatography gave 444 mg (88.2%) of tetradec-3-yn-1-ol as a clear oil: R_f(a) 0.76; IR (film) 3010 (C=CH), 2900 cm^{-1} (alkane CH); ^1H NMR δ 0.85 (br t, J = 6 Hz, 3 H), 1.20–1.70 (m, 22 H), 2.05 (m, 2 H), 2.35 (br q, J = 5 Hz, 2 H), 3.50 (m, 4 H), 4.55 (br s, 1 H), 5.35 (m, 2 H).

Deprotection as described for **5** using 500 mg of Dowex in 25 mL of methanol followed by flash chromatography afforded 163.2 mg (84%) of **3** as a clear colorless oil: R_f(a) 0.47; IR (film) 3200–3500 (OH), 3010 (C=CH), 2850–2950 cm^{-1} (alkane CH); ^1H NMR δ 0.85 (br t, J = 6 Hz, 3 H), 1.25–1.60 (m, 16 H), 2.05 (m, 2 H), 2.35 (br q, J = 5 Hz, 2 H), 3.62 (t, J = 6 Hz, 2 H), 5.45 (m, 2 H). Anal. Calcd for $C_{14}H_{28}O$: C, 79.26; H, 13.20. Found: C, 79.27; H, 13.08.

(*Z*,*Z*)-Dodeca-3,6-dien-1-ol[7] (7). An aliquot of Wittig salt **18** in acetonitrile was transferred to a preweighed 50-mL flask and the acetonitrile was removed in vacuo. Dry benzene (10 mL) was added, and the benzene was removed in vacuo to leave 0.6454 g (1.13 mmol) of dry Wittig salt **18**. The salt was dissolved in THF (20 mL), and *n*-BuLi (1.13 mmol, 1.03 mL of 1.09 M *n*-BuLi in hexane) was added at 0 °C. The bright orange-red solution was stirred for 0.5 h at 0 °C followed by the rapid addition of hexanal (112.98 mg, 1.13 mmol) dissolved in HMPA (5 mL). The mixture was stirred for 3 h at 0 °C and then quenched by the dropwise addition of H_2O. The THF was removed in vacuo, the residue was taken up in hexane (200 mL), and the hexane was washed with H_2O (4 × 50 mL) and dried ($MgSO_4$). The hexane was removed in vacuo, and to the crude product was added anhydrous ethanol (20 mL), and pyridinium *p*-toluenesulfonate[17] (28.2 mg, 0.113 mmol); the mixture was heated under reflux for 1 h. After cooling, the solvent was evaporated and the residue dissolved in ether (200 mL), and the ether solution was washed with half-saturated NaCl and dried ($MgSO_4$). Purification by flash chromatography using hexane/ethyl acetate (70:30, v/v) afforded 93.4 mg (45%) of dienol **7** as a clear yellowish liquid: R_f(b) 0.57; IR (film) 2950–3450 (OH), 2850–3050 cm^{-1} (C=CH, alkane CH); ^1H NMR δ 0.89 (br t, J = 6 Hz, 3 H), 1.20–1.50 (m, 6 H), 2.15 (m, 2 H), 2.34 (br q, J = 6 Hz, 2 H), 2.81 (br t, J = 6 Hz, 2 H), 3.65 (t, J = 6 Hz, 2 H), 5.39 (m, 4 H); ^{13}C NMR δ 14.09 (112), 22.62 (125), 25.8 (113), 27.29 (121), 29.36 (119), 30.89 (102), 31.57 (117), 62.29 (102), 125.44 (102), 127.48 (97), 130.69 (106), 131.50 (100).

1-Bromo-2-octyne (22). To a magnetically stirred solution of 2-octyn-1-ol (**21**) (Farchan Labs, 2.50 g, 19.8 mmol) and carbon tetrabromide (8.21 g, 24.8 mmol, 1.25 equiv) in 100 mL of CH_2Cl_2 was added portionwise with ice-bath cooling triphenylphosphine (7.81 g, 29.8 mmol, 1.5 equiv). After addition was complete, the mixture was stirred for an additional 10 min at ice-bath temperature and then at room temperature for 5 min. The solvent was removed in vacuo, hexane (100 mL) was added, and the mixture was filtered. The filter cake was washed with hexane (3 × 25 mL), and the combined filtrate and washings were concentrated in vacuo and filtered through a short column of silica gel to yield 3.55 g (95%) of 1-bromo-2-octyne as a clear liquid: R_f(a) 0.75; IR (film) 2875, 2950 (alkane CH), 2160 cm^{-1} (C≡C); ^1H NMR δ 1.90 (t, 3 H), 1.20–1.55 (m, 6 H), 2.20 (br t, J = 6 Hz, 2 H), 3.91 (t, J = 3 Hz, 2 H).

Dodeca-3,6-diyn-1-ol (23b). A solution of 1-[(2-tetrahydropyranyl)oxy]but-3-yne (100 mg, 0.63 mmol) in tetrahydrofuran (5 mL) was added to a solution of ethylmagnesium bromide in tetrahydrofuran (0.84 mL, 0.74 M, 0.63 mmol) at 25 °C. After complete addition, the reaction mixture was heated at 60 °C for 25 min and cooled to room temperature, and anhydrous cuprous chloride (10 mg, 0.1 eq) was added rapidly and then stirred a further 10 min. A solution of 1-bromo-2-octyne (113.4 mg, 0.60 mmol) in tetrahydrofuran (5 mL) was then added to this mixture over 20 min. After complete addition the reaction mixture was heated at 60 °C for 45 min, cooled to room temperature, and then poured into a saturated ammonium chloride solution (5 mL). The organic materials were extracted into hexane/ethyl acetate (95:5), and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to yield 142.5 mg of crude 1-[(2-tetrahydropyranyl)oxy]dodeca-3,6-diyne (**23a**). The protected coupling product was taken up in 25 mL of ethanol and hydrolyzed by stirring at 55 °C for 3 h with 10 mg of pyridinium *p*-toluenesulfonate. The solvent was evaporated, the residue was diluted with ether (75 mL), and the ether layer was washed with saturated $NaHCO_3$ (25 mL) and dried ($MgSO_4$). Purification by flash chromatography using hexane/ethyl acetate (8:2) gave 84.3 mg (78%) of the diynol **23b** as a yellow liquid: R_f(a) 0.37; IR (film) 3150–3500 cm^{-1} (OH), 2850–2900 (alkane CH); ^1H NMR δ 0.90 (t, 5 Hz, 3 H), 1.25–1.40 (m, 6 H), 2.10 (m, 2 H), 2.40 (m, 2 H), 3.10 (t, 3 Hz, 2 H), 3.67 (t, 6 Hz, 2 H).

(*Z*,*Z*)-Dodeca-3,6-dien-1-ol (7). A mixture of dodeca-3,6-diyn-1-ol (**23b**, 35 mg, 0.20 mmol), 9.0 mg of 5% $Pd/BaSO_4$, 10 μL of quinoline, and 10 mL of hexane was stirred in an atmosphere of H_2. When gas chromatographic analysis (DX-4 fused silica, 30 m × 0.25 mm, 180–225 °C, 10 °C/min; under these conditions, the diene product shows a retention time of 2.63 min, the starting diyne, 4.99 min) showed the reaction to be complete, the catalyst was filtered off, and the solvent was removed in vacuo. The resulting product was purified by column chromatography over 20% $AgNO_3$–silica gel, starting with hexane/ethyl acetate, 85:15, and then 75:25, to give 33.5 mg (92.3%) of dienol **7** as a clear colorless liquid. Other products identified by GC/MS consisted of monoenes and isomeric dienes. GLC on DX-4 (150 °C isothermal) indicated the stereochemical purity of the product to be at least 98% and indistinguishable from the dienol synthesized via the Wittig coupling method.

1-[(2-Tetrahydropyranyl)oxy]-(*Z*,*Z*)-dodeca-3,6-dien-12-al (24). Pyridinium chlorochromate (76.5 mg, 0.36 mmol, 2 equiv) and sodium acetate (5.8 mg, 0.07 mmol) were suspended in 4 mL of anhydrous CH_2Cl_2, and dienol **20** (50 mg, 0.18 mmol) in 2 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution. After 10 min, TLC showed complete disappearance of starting material. Dry ether (50 mL) was added and the supernatant decanted form the black gum. The insoluble residue was washed thoroughly with dry ether (3 × 10 mL), and the organics were combined. After removal of solvents, the crude residue was purified by flash chromatography using hexane/ethyl acetate (9:1) to afford 47.3 mg (95%) of the THP dienal as a clear oil: R_f(b) 0.73; IR (film), 2850–3050 cm^{-1} (C=CH, alkane CH), 2725 (CHO), 1740 (C=O); ^1H NMR δ 1.30–1.80 (m, 12 H), 2.17 (br t, 6 Hz, 2 H), 2.25 (br t, 6 Hz, 2 H), 2.35 (br q, 6 Hz, 2 H), 2.78 (br t, 6 Hz, 2 H), 3.30–3.85 (m, 4 H), 4.56 (br s, 1 H), 5.40 (br q, 6 Hz, 4 H), 9.76 (t, 2 Hz, 1 H).

[12-^{3}H]-1-[(2-Tetrahydropyranyl)oxy]-12-hydroxy-(*Z*,*Z*)-dodeca-3,6-diene ([12-^{3}H]-20). A solution of 30.0 mg (0.107 mmol, 1.5 equiv) of THP dienal **24** in absolute ethanol (1 mL) was added to an ampule containing a stirring bar and 100 mCi (0.0182 mmol, 1 equiv) of [^{3}H]-$NaBH_4$ (specific activity, 5.5 Ci/mmol). The flask was washed with absolute ethanol (2 × 1 mL), the washings were added to the ampule, and the solution was stirred for 45 min. Cold $NaBH_4$ (2.0 mg, 2.8 equiv) was then added, and after stirring for 25 min, 2 drops of 1 M CH_3COOH was added and the reaction mixture was transferred to a 25-mL round-bottomed flask, washing the ampule several times with anhydrous ether (1 mL) and adding the washings to the flask. The solvents were removed and 8 mL of anhydrous ether was added, and this ether solution was washed with 2 mL of a saturated $NaHCO_3$ solution by stirring. The ether layer was transferred to a test tube, dried over $MgSO_4$, passed through $MgSO_4$, and the solvent was removed to yield 32.1 mg of crude material. Pipet flash chromatography of this material using hexane/ethyl acetate (80:20) afforded 29.3 mg (97.2%) of tritiated THP dienol **20** (specific activity 1.29 Ci/mmol).

[12-^{3}H]-1-[(2-Tetrahydropyranyl)oxy]-12-fluoro-(*Z*,*Z*)-dodeca-3,6-diene. To a solution of [12-^{3}H] THP dienol **20** (14 mg, 0.050 mmol, 1.29 Ci/mmol) in methylene chloride (3 mL) cooled to −78 °C was added 75 μL of a 0.8 M solution of (diethylamino)sulfur trifluoride (DAST, 0.06 mmol) in methylene chloride. After the addition was complete, the reaction mixture was warmed to 25 °C and stirred an additional 20 min. A few crystals of Na_2CO_3 were added, then saturated $NaHCO_3$ (1 mL), followed by dilution with ether (5 mL), and the mixture was stirred

for 10 min. The ether layer was transferred to a 25-mL round-bottomed flask, and the water layer was extracted with ether (3 × 5 mL) by stirring. The combined ether extracts were dried over $MgSO_4$ and then passed through $MgSO_4$. The solvents were removed, and the crude residue was purified by pipet flash chromatography using hexane/ethyl acetate (90:10) to give 13.5 mg, (95.8%, 44.8 mCi) of tritiated fluoro diene **8b** (specific activity = 0.94 Ci/mmol).

[12-^{3}H]-12-Fluoro-(*Z*,*Z*)-dodeca-3,6-dien-1-ol ([12-^{3}H]-8). To a solution of tritiated THP fluoro diene **8b** (13.5 mg, 0.048 mmol, 0.943 Ci/mmol) in dry ethanol (3 mL) was added pyridium *p*-toluenesulfonate (PPTS, 2 mg, 0.008 mmol), and the mixture was gently refluxed overnight. After cooling to room temperature, the ethanol was removed, the residue was diluted with ether (5 mL), and the ether solution was washed with saturated $NaHCO_3$ (1 mL) by stirring. The ether layer was then transferred to a 25-mL round-bottomed flask, the water layer was extracted with ether (3 × 5 mL), and the combined extracts were dried over $MgSO_4$. The solution was then passed through $MgSO_4$, the solvent was removed, and the crude product was purified by pipet flash chromatography using hexane/ethyl acetate (80:20) to yield 6.9 mg (71.8%, 34.2 mCi) of the tritiated fluoro dienol 8, (specific activity 0.99 Ci/mmol).

[12-^{3}H]-12-Fluorododecanol (25). A solution of the tritiated fluoro dienol 8 (2.0 mg, 0.01 mmol) in absolute ethanol (1 mL) was placed in a 10-mL round-bottomed flask containing 1 mg of 10% Pd/C and a stir bar. The flask was connected to a three-way stopcock adaptor equipped with a ballon. The system was evacuated and filled with hydrogen (1 L), and the mixture was stirred overnight. GC analysis (DB-5 fused silica, 30 m × 0.25 mm, 100–200 °C, 2 °C/min) indicated the reaction to be complete. The reaction mixture was filtered through silica gel, and the solvent was removed to give the saturated dienol **25** (99%, 10 mCi) (specific activity = 1.0 Ci/mmol).

[12-^{3}H]-(*Z*,*Z*)-Dodeca-3,6-dien-1-ol ([12-^{3}H]-7). To a solution of tritiated THP dienol **20** (14.0 mg, 0.050 mmol, 1 equiv) and triethylamine (100 μL of a 96.2 μL/mL solution, 0.070 mmol, 1.4 equiv) in methylene chloride (2 mL) cooled to 0 °C was added methanesulfonyl chloride (100 μL of a 50.0 μL/mL solution, 0.065 mmol, 1.3 equiv). The mixture was stirred at ice-bath temperature for 4 h, diluted with ether (10 mL), and washed with water (2 mL) by stirring. The organic layer was transferred to a round-bottomed flask, the water layer was extracted with ether (3 × 5 mL), and the combined organics were dried over $MgSO_4$. The solution was then passed through $MgSO_4$, and the volatiles were removed. The residue was diluted with dry ether (3 mL), and lithium aluminum hydride (2 mg, 0.050 mmol, 4 equiv) was added. The mixture was stirred for 1 h at room temperature, and then 2 N sodium hydroxide (4 drops) was added. After being stirred for 5 min, the mixture was further diluted with ether (3 mL) and 2 N NaOH (1 mL), the ether layer was removed, and the water layer was extracted with ether (3 × 3 mL). The combined organics were dried over $MgSO_4$, and the solvent was removed. The crude material was purified by pipet flash chromatography using hexane/ethyl acetate (95:5) to give 11.9 mg (90.0%, 55.3 mCi) of the tritiated THP ether (specific activity = 1.24 Ci/mmol).

Deprotection with PPTS as described above gave the crude dienol, which was purified by pipet flash chromatography using hexane/ethyl acetate (83:17) to give 5.2 mg (63.3%, 28.9 mCi) of the tritiated dienol **7** (specific activity = 1.20 Ci/mmol).

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Registry No. **2**, 32451-95-9; **2**-yne, 55182-73-5; **3**, 68892-27-3; **3**-yne, 55182-74-6; **4**, 88730-45-4; **4** (THP ether), 88730-46-5; **5**, 88730-47-6; **5** (THP ether), 88730-48-7; **5**-yne, 88730-68-1; **6**, 88730-49-8; **6** (THP ether), 88730-50-1; **7**, 29125-78-8; [12-^{3}H]-**7**, 88730-51-2; [12-^{3}H]-**7** (THP ether), 88730-52-3; **8**, 88730-53-4; **8** (THP ether), 88730-54-5; [12-^{3}H]-**8**, 88746-43-4; **8b**, 88730-55-6; **9**, 40365-61-5; **10a**, 111-83-1; **10b**, 112-29-8; **11a**, 373-28-4; **11b**, 593-12-4; **11c**, 334-61-2; **12a**, 87641-52-9; **12b**, 88730-56-7; **13a**, 88746-44-5; **13b**, 88730-57-8; **13c**, 88730-58-9; **14**, 51721-39-2; **15**, 1549-82-2; **16**, 2886-59-1; **17**, 88730-59-0; **17** (methyl ester alcohol), 38341-83-2; **17** (THP ether alcohol), 88730-60-3; **18**, 88730-61-4; **18**·PPh_3, 88730-62-5; **19**, 34067-76-0; **20**, 88730-63-6; [12-^{3}H]-**20**, 88730-64-7; **21**, 20739-58-6; **22**, 18495-27-7; **23a**, 88730-65-8; **23b**, 65090-68-8; **24**, 88730-66-9; [12-^{3}H]-**25**, 88730-67-0; $Br(CH_2)_8OH$, 50816-19-8; $Br(CH_2)_{10}OH$, 53463-68-6; $Br(CH_2)_6OH$, 4286-55-9; $HC{\equiv}C(CH_2)_8OH$, 17643-36-6; $CH_3(CH_2)_4CHO$, 66-25-1; 6-hexanolactone, 502-44-3.

Electrophilic Cleavage of 1-Allyl-1,2,5-trimethyl-1-silacyclopentane. Stereochemistry at Silicon

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The preparation of mixtures of the isomers of 1-allyl-1,2,5-trimethyl-1-silacyclopentane and some of their reactions with electrophiles are described. Individual isomers and reaction products have not been isolated but have been characterized by ^{1}H and ^{13}C NMR spectroscopy. Cleavage of the allyl group may proceed with retention, inversion, or loss of configuration at silicon according to the reagent employed.

We have previously described the synthesis, separation and characterization of the stereoisomers of 1,2,5-trimethyl-1-silacyclopentane and have illustrated the use of substrates derived from this system in stereochemical studies.[1,2] These results suggest that the system might be well suited to the examination of the stereochemical consequences at silicon of the electrophilic cleavage of allyl groups and provide definitive information on the mechanism of this reaction.

Allylic silanes are of considerable synthetic importance by virtue of their reactivity towards a variety of electrophiles and the regioselectivity of the processes.[3] Allylic

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