

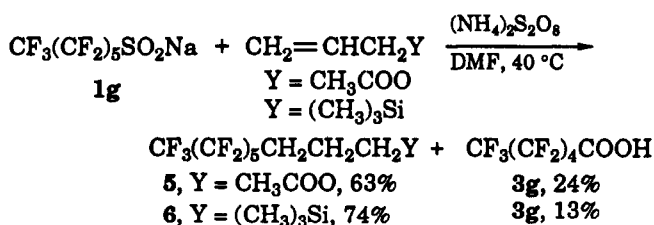
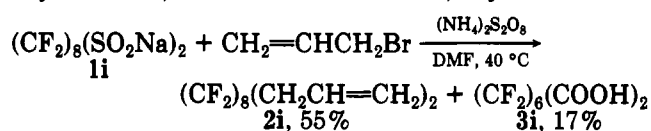
From these observations, it was hypothesized that the reaction of $\text{R}_f\text{CF}_2\text{SO}_2\text{Na}$ and an oxidant, in the presence of allyl or propargyl halides, would lead to perfluoroalkylation of the halides by way of a perfluoroalkyl radical. In fact, $\text{Cl}(\text{CF}_2)_8\text{OCF}_2\text{CF}_2\text{SO}_2\text{Na}$ (**1a**) did react readily with allyl bromides, in the presence of an oxidant, to give $\text{Cl}(\text{CF}_2)_8\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$. The results are summarized in Table I.

Because it was obvious from Table I that $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was an effective oxidant for initiating the perfluoroalkylation of allyl bromide, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was adopted as the oxidant of choice for the reaction of $\text{R}_f\text{CF}_2\text{SO}_2\text{Na}$ with allyl and propargyl halides.

Synthesis of 3-(Perfluoroalkyl)prop-1-enes. Perfluoroalkanesulfonates reacted readily with allyl halides, in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, to give 3-(perfluoroalkyl)prop-1-enes. The byproducts were perfluoroalkane-carboxylic acids **3**. Some $\text{Cl}(\text{CF}_2)_8\text{Br}$ (**4c**) was also formed in one case (Table II, entry 4). The results are summarized in Table II.

No 3-(perfluoroalkyl)prop-1-yl halide, the product of addition of perfluoroalkyl radical to the carbon-carbon double bond of the allyl halide, was formed in these reactions. Allyl bromide gave higher product yields than allyl chloride.

A perfluoroalkanedisulfinate also reacted readily with allyl bromide, to form **2i**. In contrast, allyl acetate and

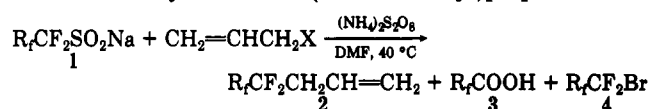


allyltrimethylsilane reacted with **1g** to yield only the addition products **5** and **6**.

Synthesis of 3-(Perfluoroalkyl)allenes. Propargyl halides reacted readily with **1**, in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, to yield the allenes **7c-h** (Table III). The main byproduct was the corresponding perfluoroalkane-carboxylic acid **3**.

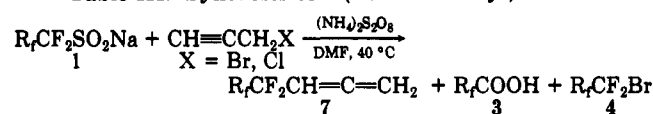
The fluorinated allenes so obtained could be isolated by distillation. Possible alkyne byproducts could not be detected. The composition of **7** was determined by mass spectrometry and elemental analysis. The ^1H NMR spectra showed the presence of olefinic protons and the absence of acetylenic protons. The infrared spectra showed strong

Table II. Synthesis of 3-(Perfluoroalkyl)prop-1-enes



entry no.	R_fCF_2	X	products (isolated yields, %)		
			2	3	4
1	$\text{Cl}(\text{CF}_2)_8\text{OCF}_2\text{CF}_2$ (1a)	Br	2a (75)	3a (10)	
2	$\text{Cl}(\text{CF}_2)_8\text{OCF}_2\text{CF}_2$ (1a)	Cl	2a (34)	3a (16)	
3	CF_3CCl_2 (1b)	Br	2b (46)	3b (33)	
4	$\text{Cl}(\text{CF}_2)_2$ (1c)	Br	2c (53)	3c (14)	4c (22)
5	$\text{Cl}(\text{CF}_2)_4$ (1d)	Br	2d (62)	3d (10)	
6	$\text{Cl}(\text{CF}_2)_4$ (1d)	Cl	2d (28)	3d (15)	
7	$\text{Cl}(\text{CF}_2)_6$ (1e)	Br	2e (65)	3e (18)	
8	$\text{Cl}(\text{CF}_2)_6$ (1e)	Cl	2e (40)	3e (16)	
9	$\text{CF}_3(\text{CF}_2)_3$ (1f)	Br	2f (72)	3f (10)	
10	$\text{CF}_3(\text{CF}_2)_5$ (1g)	Br	2g (67)	3g (12)	
11	$\text{CF}_3(\text{CF}_2)_7$ (1h)	Br	2h (74)	3h (15)	
12	$\text{CF}_3(\text{CF}_2)_7$ (1h)	Cl	2h (32)	3h (17)	

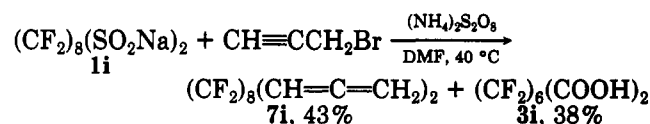
Table III. Synthesis of 3-(Perfluoroalkyl)allenes



entry no.	R_fCF_2	X	products (isolated yields, %)		
1	ClCF_2CF_2 (1c)	Br	7c (32)	3c (12)	4c (30)
2	$\text{Cl}(\text{CF}_2)_4$ (1d)	Br	7d (46)	3d (20)	
3	$\text{Cl}(\text{CF}_2)_4$ (1d)	Cl	7d (27)	3d (30)	
4	$\text{Cl}(\text{CF}_2)_6$ (1e)	Br	7e (47)	3e (15)	
5	$\text{CF}_3(\text{CF}_2)_3$ (1f)	Br	7f (42)	3f (10)	
6	$\text{CF}_3(\text{CF}_2)_5$ (1g)	Br	7g (54)	3g (17)	
7	$\text{CF}_3(\text{CF}_2)_7$ (1h)	Br	7h (50)	3h (25)	

absorptions at 1955 and 1975 cm^{-1} , characteristic of allenes.

Compound **1i** also reacted readily with propargyl bromide to yield **7i**. It was noteworthy that $\text{R}_f\text{CF}_2\text{H}$, which



could have been formed by hydrogen abstraction by the $\text{R}_f\text{CF}_2^\bullet$ radical, was not detected.

The experimental results can be explained by invoking a radical addition-elimination mechanism for the reaction (Scheme I).¹⁷ Thus, the oxidizing agent ammonium persulfate decomposes spontaneously to produce $\text{SO}_4^{\bullet-}$.¹⁸

(17) Poutsma, M. L. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, 113.

(18) Kberhardt, M. K. *J. Am. Chem. Soc.* 1981, 103, 3876.

(19) Aldrich Catalog, 1988-1989, No. 30,203-1, p 1474.

The radical anion then receives an electron from $R_fCF_2SO_2Na$ to generate the $R_fCF_2^{\cdot}$ radical. The $R_fCF_2^{\cdot}$ radical then adds to allyl or propargyl bromide to form the radical intermediate $R_fCF_2CH_2C^{\cdot}HCH_2Br$ or $R_fCH_2CH=C^{\cdot}CH_2Br$. These eliminate bromine atom Br^{\cdot} to give $R_fCF_2CH_2CH=CH_2$ or $R_fCF_2CH=C=CH_2$. Bromine atom may then combine with $R_fCF_2^{\cdot}$ to form R_fCF_2Br .

It is unlikely that the reaction proceeds by a radical S_N2 process.¹⁷ If this were the case, 3-(perfluoroalkyl)prop-1-ynes would have been formed in the reaction of **1g** with propargyl bromide. Also, the reaction of **1g** with benzyl bromide, which would be expected to show reactivity similar to that of allyl bromide toward radical displacement, should have produced $R_fCF_2CH_2C_6H_5$ or R_fCF_2Br . However, only R_fCOOH was detected in the reaction mixture by ^{19}F NMR.

In conclusion, a convenient synthesis of a variety of 3-(perfluoroalkyl)prop-1-enes and 3-(perfluoroalkyl)allenes is described. The reaction is believed to proceed by radical addition-elimination.

Experimental Section

General Comments. Boiling points and melting points are uncorrected. 1H NMR spectra were recorded with a Varian EM-60 instrument at 60 MHz, with external TMS reference. ^{19}F NMR spectra were recorded with a Varian EM-60 instrument at 56.4 MHz, with external CF_3COOH reference. Infrared (IR) spectra were recorded with a Shimadzu IR-440 instrument. Mass spectra were recorded with a Finnegan GC-MS-4021 mass spectrometer.

All chemicals were of analytical grade and were used without further purification.

Preparation of Perfluoroalkanesulfonates 1a-i. General Procedure. A mixture of 0.1 mol of R_fX ($X = I, SO_2F,$ or CCl_3), 0.12 mol of $Na_2S_2O_8$, 0.1 mol of $NaHCO_3$, 30 mL of H_2O , and 15 mL of CH_3CN was stirred at 25–70 °C for 2–6 h. Then the mixture was poured into 70 mL of ethyl acetate, and the organic layer was separated. The organic layer was washed with brine and dried (Na_2SO_4). After removal of solvent, the solid residue was crystallized (iPrOH) to give the pure perfluoroalkanesulfonate.

Sodium 3-oxa-11-chloro-1,1,2,2,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-eicosafluoroundecanesulfonate (1a):⁹ from $Cl(CF_2)_9OCF_2CF_2SO_2F$; reaction temperature 70 °C; reaction time 7 h; yield 78%; ^{19}F NMR (iPrOH) –9.0 (2 F, s, CF_2Cl), 4.7 (4 F, s, CF_2OCF_2), 42.5–47.3 (12 F, m, $6 \times CF_2$), 55.4 (2 F, s, CF_2SO_2Na).

Sodium 1,1-dichloro-2,2,2-trifluoroethanesulfonate (1b):¹¹ from CF_3CCl_3 ; reaction temperature 25 °C; reaction time 6 h; yield 60%; ^{19}F NMR (AcOEt) –4.8 (s).

Sodium 2-chloro-1,1,2,2-tetrafluoroethanesulfonate (1c):¹⁰ from $ClCF_2CF_2I$; reaction temperature 30 °C; reaction time 4 h; yield 55%; ^{19}F NMR (AcOEt) –11.0 (2 F, s, CF_2Cl), 51.5 (2 F, s, CF_2SO_2Na).

Sodium 4-chloro-1,1,2,2,3,3,4,4-octafluorobutanesulfonate (1d):¹⁰ from $Cl(CF_2)_3I$; reaction temperature 45 °C; reaction time 2 h; yield 85%; ^{19}F NMR (AcOEt) –8.6 (2 F, s, CF_2Cl), 43.2 (2 F, s, CF_2), 45.7 (2 F, s, CF_2), 54.2 (2 F, s, CF_2SO_2Na).

Sodium 6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexanesulfonate (1e):¹⁰ from $Cl(CF_2)_5I$; reaction temperature 45 °C; reaction time 2 h; yield 82%; ^{19}F NMR (AcOEt) –9.4 (2 F, s, CF_2Cl), 42.2 (2 F, s, CF_2), 44.2 (6 F, s, $3 \times CF_2$), 53.8 (2 F, s, CF_2SO_2Na).

Sodium perfluorobutanesulfonate (1f):¹⁰ from $CF_3(CF_2)_3I$; reaction temperature 45 °C; reaction time 3 h; yield 75%; ^{19}F NMR (AcOEt) 5.7 (3 F, s, CF_3), 48.0 (4 F, s, $2 \times CF_2$), 55.5 (2 F, s, CF_2SO_2Na).

Sodium perfluorohexanesulfonate (1g):¹⁰ from $CF_3(CF_2)_5I$; reaction temperature 55 °C; reaction time 4 h; yield 83%; ^{19}F

NMR (AcOEt) 4.3 (3 F, s, CF_3), 45.6 (6 F, s, $3 \times CF_2$), 49.5 (2 F, s, CF_2), 54.2 (2 F, s, CF_2SO_2Na).

Sodium perfluorooctanesulfonate (1h):¹⁰ from $CF_3(CF_2)_7I$; reaction temperature 60 °C; reaction time 5 h; yield 72%; ^{19}F NMR (AcOEt) 5.2 (3 F, s, CF_3), 45.9 (10 F, s, $5 \times CF_2$), 55.4 (2 F, s, CF_2SO_2Na).

Sodium perfluorooctane-1,8-disulfonate (1i):¹⁰ from $I(CF_2)_8I$; reaction temperature 70 °C; reaction time 5 h; yield 55%; ^{19}F NMR (AcOEt) 44.5 (12 F, s, $6 \times CF_2$), 53.2 (4 F, s, $2 \times CF_2SO_2Na$).

Synthesis of 3-(Perfluoroalkyl)prop-1-enes 2a-i. General Procedure. A mixture of sodium perfluoroalkanesulfonate (**1**) (10 mmol), allyl halide (10 mmol), $(NH_4)_2S_2O_8$ (2.7 g, 10 mmol), and 30 mL of DMF was stirred at 40 °C for 4 h. The cooled mixture was poured into 40 mL of H_2O and was extracted with ether (3×100 mL). The combined ether extracts were neutralized with aqueous $NaHCO_3$ and washed with H_2O . The water layers were combined and were evaporated to dryness. To the residue, which was mainly the sodium salt of the fluorinated carboxylic acid, was added 10 mL of concentrated H_2SO_4 . Distillation of the mixture gave the fluoro carboxylic acid **3**. The ether extracts were then dried (Na_2SO_4). After evaporation of ether, distillation under reduced pressure gave **2** and **4**.

6-Oxa-14-chloro-4,4,5,5,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-eicosafuoro-1-tetradecene (2a): bp 96–97 °C (5 mmHg); ^{19}F NMR (neat) –8.7 (2 F, s, CF_2Cl), 7.0 (2 F, s, CF_2O), 10.7 (2 F, s, CF_2O), 41.0 (2 F, t, $J = 16$ Hz, CF_2CH_2), 44.0 (2 F, s, CF_2), 45.3 (8 F, s, $4 \times CF_2$), 49.0 (2 F, s, CF_2); 1H NMR (neat) 2.90 (2 H, td, $^3J_{F,H} = 16$ Hz, $^3J_{H,H} = 6$ Hz, $CF_2CH_2CH=CH_2$), 5.10–6.20 (3 H, m, vinylic H); IR (neat) 1650 ($C=C$) cm^{-1} ; mass spectrum m/z (relative intensity) 41 (100, C_3H_5), 91 (97.96, $CF_2CH_2CH=CH_2$), 592 (1.28, M).

Anal. Calcd for $C_{13}H_5ClF_{20}O$: C, 26.32; H, 0.84; F, 64.13. Found: C, 26.37; H, 0.79; F, 63.98.

4,4-Dichloro-5,5,5-trifluoro-1-pentene (2b): bp 85–87 °C; ^{19}F NMR (neat) 2.7 (s); 1H NMR (neat) 2.65 (2 H, d, $^3J_{H,H} = 6$ Hz, $CCl_2CH_2CH=CH_2$), 5.20–6.10 (3 H, m, vinylic H); IR 1648 ($C=C$) cm^{-1} ; mass spectrum m/z (relative intensity) 41 (45.15, $CH_2CH=CH_2$), 157 (100.00, M – Cl), 192 (2.62, M).

Anal. Calcd for $C_5H_5F_3Cl_2$: C, 31.25; H, 2.60; F, 29.69. Found: C, 31.75; H, 2.85; F, 27.38.

5-Chloro-4,4,5,5-tetrafluoro-1-pentene (2c): bp 49–51 °C; ^{19}F NMR (neat) –5.7 (2 F, s, CF_2Cl), 37.3 (2 F, t, $J = 16$ Hz, CF_2CH_2); 1H NMR (neat) 2.90 (2 H, td, $^3J_{F,H} = 16$ Hz, $^3J_{H,H} = 6$ Hz, $CF_2CH_2CH=CH_2$), 5.10–6.00 (3 H, m, vinylic H); IR 1650 ($C=C$) cm^{-1} ; mass spectrum m/z (relative intensity) 41 (100.00, $CH_2CH=CH_2$), 85 (17.52, CF_2Cl), 91 (88.66, $CF_2CH_2CH=CH_2$), 176 (25.23, M).

Anal. Calcd for $C_5H_5F_4Cl$: C, 34.09; H, 2.84; F, 43.18. Found: C, 34.23; H, 2.94; F, 42.08.

1-Bromo-2-chloro-1,1,2,2-tetrafluoroethane (4c): ^{19}F NMR (neat) –11.7 (2 F, s, CF_2Br), –7.6 (2 F, s, CF_2Cl); mass spectrum m/z (relative intensity) 85 (24.15, CF_2Cl), 135 (100.00, M – Br), 179 (8.39, M – Cl), 214 (1.27, M).

7-Chloro-4,4,5,5,6,6,7,7-octafluoro-1-heptene (2d): bp 90–91 °C; ^{19}F NMR (neat) –7.3 (2 F, s, CF_2Cl), 38.3 (2 F, t, $J = 16$ Hz, CF_2CH_2), 44.6 (2 F, s, CF_2), 49.0 (2 F, s, CF_2); 1H NMR (neat) 2.90 (2 H, td, $^3J_{F,H} = 16$ Hz, $^3J_{H,H} = 6$ Hz, $CF_2CH_2CH=CH_2$), 5.10–6.20 (3 H, m, vinylic H); IR 1658 ($C=C$) cm^{-1} ; mass spectrum m/z (relative intensity) 41 (35.25, $CH_2CH=CH_2$), 85 (48.63, CF_2Cl), 91 (100.00, $CF_2CH_2CH_2=CH_2$), 276 (3.58, M).

Anal. Calcd for $C_7H_5F_8Cl$: C, 30.43; H, 1.81; F, 55.07. Found: C, 31.20; H, 1.90; F, 54.48.

9-Chloro-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-1-nonene (2e): bp 118–119 °C; ^{19}F NMR (neat) –8.0 (2 F, s, CF_2Cl), 36.7 (2 F, t, $J = 16$ Hz, CF_2CH_2), 45.3 (6 F, s, $3 \times CF_2$), 47.3 (2 F, s, CF_2); 1H NMR (neat) 2.65 (2 H, td, $^3J_{F,H} = 16$ Hz, $^3J_{H,H} = 6$ Hz, $CF_2CH_2CH=CH_2$), 5.20–5.80 (3 H, m, vinylic H); IR 1647 ($C=C$) cm^{-1} ; mass spectrum m/z (relative intensity) 41 (40.65, $CH_2CH=CH_2$), 85 (27.25, CF_2Cl), 91 (100.00, $CF_2CH_2CH=CH_2$), 376 (4.71, M).

Anal. Calcd for $C_9H_5F_{12}Cl$: C, 28.68; H, 1.32; F, 60.56. Found: C, 28.65; H, 1.29; F, 61.20.

4,4,5,5,6,6,7,7,7-Nonafluoro-1-heptene (2f): bp 82–85 °C; ^{19}F NMR (neat) 5.7 (3 F, s, CF_3), 38.4 (2 F, t, $J = 16$ Hz, CF_2CH_2), 45.3 (2 F, s, CF_2), 49.4 (2 F, s, CF_2); 1H NMR (neat) 2.95 (2 H,

(20) Swarts, F. *Bull. Soc. Chim. Fr.* 1906, 42.

(21) Chen, Q.-Y.; Qiu, Z.-M. *Acta Chim. Sin.* 1988, 46, 38.

(22) Aldrich Catalog, 1990–1991, No. 15,739-2, p 686.

(23) *Ullmanns Encyklopaedie der Technischen Chemie*, 5th ed.; Band A-11, p 371-32.

(24) Aldrich Catalog, 1990–1991, No. 17,146-8, p 1011.

td, $^3J_{\text{H,F}} = 16$ Hz, $^3J_{\text{H,H}} = 6$ Hz, $\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$), 5.05–6.15 (3 H, m, vinylic H); IR 1655 (C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 41 (45.65, $\text{CH}_2\text{CH}=\text{CH}_2$), 69 (100.00, CF_3), 91 (73.68, $\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$), 260 (10.32, M).

Anal. Calcd for $\text{C}_7\text{H}_5\text{F}_9$: C, 32.31; H, 1.92; F, 65.77. Found: C, 33.08; H, 2.05; F, 64.63.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1-nonene (2g): bp 109–112 °C; ^{19}F NMR (neat) 6.0 (3 F, s, CF_3), 38.3 (2 F, t, $J = 16$ Hz, CF_2CH_2), 48.0 (6 F, s, $3 \times \text{CF}_2$), 51.0 (2 F, s, CF_2); ^1H NMR (neat) 2.65 (2 H, td, $^3J_{\text{F,H}} = 16$ Hz, $^3J_{\text{H,H}} = 6$ Hz, $\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$), 5.20–5.80 (3 H, m, vinylic H); IR 1645 (C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 41 (100.00, $\text{CH}_2\text{CH}=\text{CH}_2$), 69 (22.35, CF_3), 91 (46.70, $\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$), 360 (35.98, M).

Anal. Calcd for $\text{C}_9\text{H}_5\text{F}_{13}$: C, 30.00; H, 1.39; F, 68.61. Found: C, 29.52; H, 1.40; F, 68.32.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-1-undecene (2h): bp 124–127 °C; ^{19}F NMR (neat) 6.0 (3 F, s, CF_3), 38.3 (2 F, t, $J = 16$ Hz, CF_2CH_2), 46.3 (10 F, s, $5 \times \text{CF}_2$), 50.6 (2 F, s, CF_2); ^1H NMR (neat) 2.75 (2 H, td, $^3J_{\text{F,H}} = 16$ Hz, $^3J_{\text{H,H}} = 6$ Hz, $\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$), 5.30–5.95 (3 H, m, vinylic H); IR 1650 (C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 41 (29.63, $\text{CH}_2\text{CH}=\text{CH}_2$), 69 (100.00, CF_3), 91 (73.46, $\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$), 460 (3.85, M).

Anal. Calcd for $\text{C}_{11}\text{H}_5\text{F}_{17}$: C, 28.69; H, 1.08; F, 70.22. Found: C, 29.08; H, 1.13; F, 68.96.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Hexadecafluoro-1,13-tetradecadiene (2i): bp 75–76 °C (2 mmHg); ^{19}F NMR (neat) 37.3 (4 F, t, $J = 16$ Hz, $2 \times \text{CF}_2\text{CH}_2$), 45.0 (8 F, s, $4 \times \text{CF}_2$), 46.7 (4 F, s, $2 \times \text{CF}_2$); ^1H NMR (neat) 2.75 (2 H, t \times d, $^3J_{\text{F,H}} = 16$ Hz, $^3J_{\text{H,H}} = 6$ Hz, $\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$), 5.30–5.95 (3 H, m, vinylic H); IR 1655 (C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 41 (87.2, $\text{CH}_2\text{CH}=\text{CH}_2$), 91 (100.00, $\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$), 482 (17.17, M).

Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{F}_{16}$: C, 34.85; H, 2.07; F, 63.07. Found: C, 34.65; H, 1.99; F, 64.17.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyl acetate (5): bp 86–88 °C (2 mmHg); ^{19}F NMR (neat) 6.0 (3 F, s, CF_3), 38.5 (2 F, t, $J = 16$ Hz, CF_2CH_2), 48.5 (6 F, s, $3 \times \text{CF}_2$), 51.5 (2 F, s, CF_2); ^1H NMR (neat) 2.17 (s, 3 H, CH_3CO), 2.22–2.85 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CF}_2$), 4.40 (t, 2 H, $J = 4$ Hz, CH_2O); IR 1750 (s, C=O) cm^{-1} ; mass spectrum m/z (relative intensity) 59 (100.00, CH_3COO), 92 (43.56, $\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 420 (5.38, M).

Anal. Calcd for $\text{C}_{11}\text{H}_5\text{F}_{13}\text{O}_2$: C, 34.43; H, 2.14; F, 58.81. Found: C, 35.01; H, 2.35; F, 59.62.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1-(trimethylsilyl)nonane (6): bp 125–128 (5 mmHg); ^{19}F NMR (neat) 5.8 (3 F, s, CF_3), 37.8 (2 F, t, $J = 16$ Hz, CF_2CH_2), 48.0 (6 F, s, $3 \times \text{CF}_2$), 51.0 (2 F, s, CF_2); ^1H NMR (neat) 0.00 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.65–0.85 (m, 2 H, CH_2Si), 1.65–2.85 (m, 4 H, $\text{CF}_2\text{CH}_2\text{CH}_2$); mass spectrum m/z (relative intensity) 161 (100, $\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$), 430 (3.42, M).

Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{F}_{13}\text{Si}$: C, 33.49; H, 3.49; F, 57.44. Found: C, 34.30; H, 3.52; F, 57.01.

Synthesis of 3-(Perfluoroalkyl)allenes. General Procedure. A mixture of sodium perfluoroalkanesulfinate (10 mmol), propargyl halide (10 mmol), and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (2.7 g, 10 mmol) in 30 mL of DMF was stirred at 40 °C for 4 h. The usual workup gave the products.

5-Chloro-4,4,5,5-tetrafluoro-1,2-pentadiene (7c): bp 58–60 °C; ^{19}F NMR (neat) –4.0 (2 F, s, CF_2Cl), 32.7 (2 F, d, $^3J_{\text{H,F}} = 11.5$ Hz, $\text{CF}_2\text{CH}=\text{CH}$); ^1H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 85 (57.00, CF_2Cl), 89 (100.00, $\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$).

Anal. Calcd for $\text{C}_5\text{H}_3\text{F}_4\text{Cl}$: C, 20.69; H, 1.72; F, 43.68. Found: C, 21.45; H, 1.80; F, 45.78.

7-Chloro-4,4,5,5,6,6,7,7-octafluoro-1,2-heptadiene (7d): bp 85–87 °C; ^{19}F NMR (neat) –7.3 (2 F, s, CF_2Cl), 32.7 (2 F, d, $^3J_{\text{H,F}} = 11.5$ Hz, $\text{CF}_2\text{CH}=\text{CH}$), 43.7 (2 F, s, CF_2), 46.3 (2 F, s, CF_2); ^1H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 85 (100.00, CF_2Cl), 89 (61.63, $\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 139 (14.94, $\text{CF}_2\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 255 (3.66, M – F).

Anal. Calcd for $\text{C}_7\text{H}_3\text{F}_8\text{Cl}$: C, 30.66; H, 1.09; F, 55.47. Found: C, 31.42; H, 1.20; F, 54.68.

4,4,5,5,6,6,7,7,7-Nonafluoro-1,2-heptadiene (7f): bp 64–67 °C; ^{19}F NMR (neat) 6.0 (3 F, s, CF_3), 33.5 (2 F, d, $^3J_{\text{H,F}} = 11.5$ Hz, $\text{CF}_2\text{CH}=\text{CH}$), 46.8 (2 F, s, CF_2), 49.6 (2 F, s, CF_2); ^1H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 69 (100.00, CF_3), 89 (63.54, $\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 139 (18.30, $\text{CF}_2\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 239 (6.48, M – F).

Anal. Calcd for $\text{C}_7\text{H}_3\text{F}_9$: C, 32.56; H, 1.66; F, 66.28. Found: C, 32.98; H, 1.28; F, 65.93.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1,2-nonadiene (7g): bp 113–114 °C; ^{19}F NMR (neat) 5.6 (3 F, s, CF_3), 33.0 (2 F, d, $^3J_{\text{H,F}} = 11.5$ Hz, $\text{CF}_2\text{CH}=\text{CH}$), 47.3 (6 F, s, $3 \times \text{CF}_2$), 50.7 (2 F, s, CF_2); ^1H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 69 (100.00, CF_3), 89 (98.76, $\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 139 (17.50, $\text{CF}_2\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 339 (26.02, M – F).

Anal. Calcd for $\text{C}_9\text{H}_3\text{F}_{13}$: C, 30.17; H, 0.84; F, 68.99. Found: C, 31.22; H, 0.98; F, 68.63.

9-Chloro-4,4,5,5,6,6,7,7,8,8,9,9,9-dodecafluoro-1,2-nonadiene (7e): bp 126–128 °C; ^{19}F NMR (neat) –7.4 (2 F, s, CF_2Cl), 32.7 (2 F, d, $^3J_{\text{H,F}} = 11.5$ Hz, $\text{CF}_2\text{CH}=\text{CH}$), 47.5 (6 F, s, $3 \times \text{CF}_2$), 50.6 (2 F, s, CF_2); ^1H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 85 (87.45, CF_2Cl), 89 (100.00, $\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 139 (11.59, $\text{CF}_2\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 355 (7.80, M – F).

Anal. Calcd for $\text{C}_9\text{H}_3\text{F}_{12}\text{Cl}$: C, 28.88; H, 0.80; F, 60.96. Found: C, 29.12; H, 0.96; F, 59.03.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-1,2-undecadiene (7h): bp 63–64 °C (3 mmHg); ^{19}F NMR (neat) 6.0 (3 F, s, CF_3), 33.3 (2 F, d, $^3J_{\text{H,F}} = 11.5$ Hz, $\text{CF}_2\text{CH}=\text{CH}$), 46.0 (10 F, s, $5 \times \text{CF}_2$), 51.0 (2 F, s, CF_2); ^1H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 69 (49.80, CF_3), 89 (100.00, $\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 139 (8.20, $\text{CF}_2\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 439 (6.45, M – F).

Anal. Calcd for $\text{C}_{11}\text{H}_3\text{F}_{17}$: C, 28.82; H, 0.66; F, 70.52. Found: C, 29.23; H, 0.78; F, 69.42.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Hexadecafluoro-1,2,12,13-tetradecatetraene (7i): bp 75–77 °C (3 mmHg); ^{19}F NMR (neat) 31.0 (4 F, d, $^3J_{\text{H,F}} = 11.5$ Hz, $2 \times \text{CF}_2\text{CH}=\text{CH}$), 45.0 (8 F, s, $4 \times \text{CF}_2$), 47.3 (4 F, s, $2 \times \text{CF}_2$); ^1H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm^{-1} ; mass spectrum m/z (relative intensity) 89 (100.00, $\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 139 (10.73, $\text{CF}_2\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$), 459 (6.58, M – F).

Anal. Calcd for $\text{C}_{14}\text{H}_6\text{F}_{16}$: C, 35.15; H, 1.26; F, 63.59. Found: C, 35.45; H, 1.31; F, 62.96.

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Supplementary Material Available: Experimental results (bp, mp, ^1H NMR, and ^{19}F NMR) for compounds 3a–i (1 page). Ordering information is given on any current masthead page.